
**Inorganic Reactions
and Methods**

Volume 13

Inorganic Reactions and Methods

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Inorganic Reactions and Methods

Volume 13

**The Formation of Bonds to Group-I, -II,
and -IIIB Elements**

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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

for $\text{Ti}(\text{SO}_4)_2$ is	$\text{O}_8\text{S}_2\text{Ti}$
$\text{BH}_3 \cdot \text{NH}_3$	BH_6N
Be_2CO_3	CBe_2O_3
CsHBr_2	Br_2CsH
$\text{Al}(\text{HCO}_3)_3$	$\text{C}_3\text{H}_3\text{AlO}_9$

The formulas themselves are ordered alphanumerically without exception; that is, the formulas listed above follow each other in the sequence BH_6N , Br_2CsH , CBe_2O_3 , $\text{C}_3\text{H}_3\text{AlO}_9$, $\text{O}_8\text{S}_2\text{Ti}$.

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

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

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

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

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

2.7. Subject Index

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

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

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

2.8. Periodic Table (Back Endpaper)

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

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

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

Preface to the Series

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

A.P. HAGEN
Norman, Oklahoma
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6. Formation of the Bonds to Group-IIIB (B, Al, Ga, In, Tl) Elements

6.1. Introduction

This chapter describes formation of bonds between B, Al, Ga, In and Tl atoms and formation of bonds of these elements with metals and group 0 gases.

(A. P. HAGEN)

6.2. Formation of the Group-IIIB–Group-IIIB Element (B, Al, Ga, In, Tl) Bond

6.2.1. Introduction

Diboron tetrahydride is obtained by matrix isolation methods from diborane and F atoms¹. The staggered H_2BBH_2 structure with a two-electron $\text{B}—\text{B}$ bond is² more stable than a nonplanar, doubly bridged form $\text{HB}(\mu\text{-H})_2\text{BH}$, but only by 6 kJ mol^{-1} . Electron-pair base adducts of B_2H_4 result from the action of excess base on $\text{B}_3\text{H}_7 \cdot \text{THF}$, B_5H_9 or B_4H_{10} to give $\text{B}_2\text{H}_4\text{L}_2$, where L is trimethylamine³, PMe_3 , PPh_3 or other phosphines⁴. Attempts to convert B_2Cl_4 to B_2H_4 using LiBH_4 give instead B_4H_{10} with the structure $\text{H}_2\text{B}(\mu\text{-BH}_3)_2\text{BH}_2$. Stable tetrahedral structures are predicted for the as yet unknown B_4H_4 , B_4F_4 and B_4Me_4 molecules^{5,6}.

The higher polyboranes, which include many compounds with structures based on B_n clusters with $\text{B}—\text{B}$ bonds bridged by hydrogen, are treated in §1.7.

Synthesis depends on gas-phase pyrolysis techniques^{7,8}, and interconversion is by electrochemical oxidation⁹. Understanding of the mechanisms by which the boranes interconvert and build up into larger clusters is growing¹⁰.

Direct $\text{B}—\text{B}$ σ bonds occur in some of the higher polyboranes that have linked multicage structures, e.g., $(\text{B}_4\text{H}_9)_2$, $(\text{B}_5\text{H}_8)_2$, $(\text{B}_{10}\text{H}_{13})_2$, $[(\text{B}_{10}\text{H}_9)_2]^{4-}$. In these¹¹, and in a few carboranes in which there are σ linkages¹², the $\text{B}—\text{B}$ bond arises during redox reactions involving polyborane species. Attempts to produce straight-chain polymeric $\text{B}—\text{B}$ compounds have been largely unsuccessful¹³.

The remainder of this chapter covers reactions by which homonuclear bonds between the group-IIIB elements¹⁴ are formed and includes a few examples of heteronuclear bonds, e.g., $\text{B}—\text{Al}$ and $\text{Ga}—\text{In}$ in compounds of these elements.

(M. J. TAYLOR)

1. B. Ruščio, M. Schwarz, J. Berkowitz, *J. Chem. Phys.*, **91**, 4576 (1989).
2. R. R. Mohr, W. N. Lipscomb, *Inorg. Chem.*, **25**, 1053 (1986).
3. R. E. DePoy, G. Kodama, *Inorg. Chem.*, **24**, 2871 (1985).
4. R. K. Hertz, M. L. Denniston, S. G. Shore, *Inorg. Chem.*, **17**, 2673 (1978).
5. M. L. McKee, W. N. Lipscomb, *Inorg. Chem.*, **20**, 4148 (1981).
6. M. A. Vincent, H. F. Schaefer III, *J. Am. Chem. Soc.*, **103**, 5677 (1981).
7. R. J. Astheimer, L. G. Sneddon, *Inorg. Chem.*, **22**, 1928 (1983).
8. M. A. Toft, J. B. Leach, F. L. Himpsl, S. G. Shore, *Inorg. Chem.*, **21**, 1952 (1982).
9. P. J. Dolan, J. H. Kindsvater, D. G. Peters, *Inorg. Chem.*, **15**, 2170 (1976).
10. N. N. Greenwood, R. Greatrex, *Pure Appl. Chem.*, **59**, 857 (1987); recommended reading.
11. R. P. Micciche, J. S. Plotkin, L. G. Sneddon, *Inorg. Chem.*, **22**, 1765 (1983).
12. R. J. Astheimer, L. G. Sneddon, *Inorg. Chem.*, **22**, 1928 (1983).

6.2. Formation of the Group-IIIB–Group-IIIB Element Bond
 6.2.2. from Group-IIIB Halides
 6.2.2.1. by Comproportionation with the Group-IIIB Element

13. R. J. Brotherton, in *Progress in Boron Chemistry*, Vol. 1, H. Steinberg, E. L. McCloskey, eds., Pergamon Press, Oxford, 1964, p. 1; comprehensive account of the early work on B—B compounds.
14. M. J. Taylor, *Metal-to-Metal Bonded States of the Main Group Elements*, Academic Press, London, 1975, Ch. 3. Describes M—M bonded compounds of Al, Ga, In and Tl.

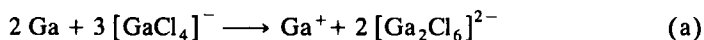
6.2.2. from Group-IIIB Halides

6.2.2.1. by Comproportionation with the Group-IIIB Element or Its Univalent State

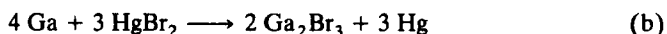
Reaction of BF_3 with solid B at 1850°C and low pressure forms BF, which upon condensation with BF_3 yields¹ B_2F_4 . At -196°C this procedure also yields $(\text{BF}_2)_2\text{BF}$, which is unstable and disproportionates above -50°C to B_2F_4 and the dimer of $(\text{BF}_2)_3\text{B}$. Stable crystalline adducts $(\text{BF}_2)_3\text{B} \cdot \text{L}$ result² from condensation of BF with $\text{L} = \text{PF}_3, \text{PCl}_3, \text{PH}_3, \text{AsH}_3, \text{SMe}_2, \text{CO}$. For BX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) reaction with BX generated in the gas phase by discharge methods gives B_2X_4 and $(\text{BX})_n$ polymers^{3,4} (§6.2.2.2).

Anhydrous AlCl_3 or AlBr_3 is partially reduced to the dihalide when heated with Al powder at 120°C in an autoclave⁵, the product being either $(\text{AlX}_2)_2$ or a higher oligomer with Al—Al bonding. In the gas phase⁶ the reaction of AlCl_3 with Al favors monomeric AlCl .

Comproportionation to form $[\text{Cl}_3\text{GaGaCl}_3]^{2-}$ to the extent of ca. 5% occurs when GaCl_2 , which has structure $\text{Ga}^+[\text{GaCl}_4]^-$, is melted with Ga at 180°C :



but the reverse reaction occurs on cooling⁷. The process goes to completion in bromide or iodide systems, giving the $[\text{Ga}_2\text{X}_6]^{2-}$ species in the halides Ga_2X_3 , or $[\text{Ga}]^+[\text{Ga}_2\text{X}_6]^{2-}$, which are prepared by heating GaBr_3 or GaI_3 with a small excess of Ga in a sealed glass ampule^{8,9}. Alternatively, Ga_2Br_3 can be made directly from Ga and Br_2 in stoichiometric amounts, or from Ga and HgBr_2 by fusion¹⁰:



The Li salt $\text{Li}_2[\text{Ga}_2\text{Br}_6]$ can be obtained¹¹ from LiBr and GaBr_2 at 250°C .

The Ga—Ga bonded compounds $\text{Ga}_2\text{X}_4\text{L}_2$ where L is a nitrogen, oxygen or sulfur ligand of low basicity are obtained from the mixed-valence dihalides $\text{Ga}[\text{GaX}_4]$ ($\text{X} = \text{Cl}, \text{Br}$) by treatment with the base $\text{L} = \text{morpholine, THF, THP, 1,4-dioxane, dimethylsulfide, THT or 1,4-thioxan}$. Typically, dry dioxane(diox) is condensed on to GaX_2 in vacuo and after several days at 0°C removal of the excess leaves $\text{Ga}_2\text{X}_4(\text{diox})_2$ as a white powder¹². Complexes with more basic ligands, $\text{Ga}_2\text{X}_4\text{L}_2$ ($\text{L} = \text{py, 3-Mepy or 4-Mepy}$; $\text{X} = \text{Cl, Br}$), are prepared from $\text{Ga}_2\text{X}_4(\text{diox})_2$ by ligand displacement¹³. Use of $\text{In}[\text{GaX}_4]$ ($\text{X} = \text{Cl, Br}$) in this process leads to GaInX_4L_2 , in which the covalent Ga—In bond has been formed¹⁴, and these products are converted to $[\text{n-Bu}_4\text{N}]_2[\text{X}_3\text{GaInX}_3]$ by addition of the halide salt. Treatment with $\text{LiCH}(\text{SiMe}_3)_2$ in n-pentane at -60°C converts¹⁵ $\text{Ga}_2\text{Br}_4(\text{diox})_2$ into Ga—Ga-bonded $\text{Ga}_2[\text{CH}(\text{SiMe}_3)_2]_4$.

6.2. Formation of the Group-IIIB–Group-IIIB Element Bond**6.2.2. from Group-IIIB Halides****6.2.2.1. by Comproportionation with the Group-IIIB Element**

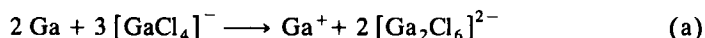
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6.2.2. from Group-IIIB Halides**6.2.2.1. by Comproportionation with the Group-IIIB Element or Its Univalent State**

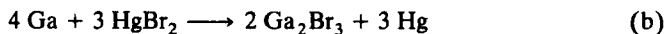
Reaction of BF_3 with solid B at 1850°C and low pressure forms BF, which upon condensation with BF_3 yields¹ B_2F_4 . At -196°C this procedure also yields $(\text{BF}_2)_2\text{BF}$, which is unstable and disproportionates above -50°C to B_2F_4 and the dimer of $(\text{BF}_2)_3\text{B}$. Stable crystalline adducts $(\text{BF}_2)_3\text{B} \cdot \text{L}$ result² from condensation of BF with $\text{L} = \text{PF}_3, \text{PCl}_3, \text{PH}_3, \text{AsH}_3, \text{SMe}_2, \text{CO}$. For BX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) reaction with BX generated in the gas phase by discharge methods gives B_2X_4 and $(\text{BX})_n$ polymers^{3,4} (§6.2.2.2).

Anhydrous AlCl_3 or AlBr_3 is partially reduced to the dihalide when heated with Al powder at 120°C in an autoclave⁵, the product being either $(\text{AlX}_2)_2$ or a higher oligomer with Al—Al bonding. In the gas phase⁶ the reaction of AlCl_3 with Al favors monomeric AlCl .

Comproportionation to form $[\text{Cl}_3\text{GaGaCl}_3]^{2-}$ to the extent of ca. 5% occurs when GaCl_2 , which has structure $\text{Ga}^+[\text{GaCl}_4]^-$, is melted with Ga at 180°C :



but the reverse reaction occurs on cooling⁷. The process goes to completion in bromide or iodide systems, giving the $[\text{Ga}_2\text{X}_6]^{2-}$ species in the halides Ga_2X_3 , or $[\text{Ga}]_2^+[\text{Ga}_2\text{X}_6]^{2-}$, which are prepared by heating GaBr_3 or GaI_3 with a small excess of Ga in a sealed glass ampule^{8,9}. Alternatively, Ga_2Br_3 can be made directly from Ga and Br₂ in stoichiometric amounts, or from Ga and HgBr_2 by fusion¹⁰:



The Li salt $\text{Li}_2[\text{Ga}_2\text{Br}_6]$ can be obtained¹¹ from LiBr and GaBr_2 at 250°C .

The Ga—Ga bonded compounds $\text{Ga}_2\text{X}_4\text{L}_2$ where L is a nitrogen, oxygen or sulfur ligand of low basicity are obtained from the mixed-valence dihalides $\text{Ga}[\text{GaX}_4]$ ($\text{X} = \text{Cl}, \text{Br}$) by treatment with the base $\text{L} = \text{morpholine, THF, THP, 1,4-dioxane, dimethylsulfide, THT, or 1,4-thioxan}$. Typically, dry dioxane(diox) is condensed on to GaX_2 in vacuo and after several days at 0°C removal of the excess leaves $\text{Ga}_2\text{X}_4(\text{diox})_2$ as a white powder¹². Complexes with more basic ligands, $\text{Ga}_2\text{X}_4\text{L}_2$ ($\text{L} = \text{py, 3-Mepy or 4-Mepy; X} = \text{Cl, Br}$), are prepared from $\text{Ga}_2\text{X}_4(\text{diox})_2$ by ligand displacement¹³. Use of $\text{In}[\text{GaX}_4]$ ($\text{X} = \text{Cl, Br}$) in this process leads to GaInX_4L_2 , in which the covalent Ga—In bond has been formed¹⁴, and these products are converted to $[\text{n-Bu}_4\text{N}]_2[\text{X}_3\text{GaInX}_3]$ by addition of the halide salt. Treatment with $\text{LiCH}(\text{SiMe}_3)_2$ in n-pentane at -60°C converts¹⁵ $\text{Ga}_2\text{Br}_4(\text{diox})_2$ into Ga—Ga-bonded $\text{Ga}_2[\text{CH}(\text{SiMe}_3)_2]_4$.

Low-valent indium halides are prepared by reducing the trihalide with In metal, and spectroscopic evidence points to In—In bonds in InCl_3 –In melts¹⁶. The chlorides¹⁷ InCl , In_3Cl_4 , In_2Cl_3 and In_5Cl_9 and bromides^{18,19} InBr , In_4Br_7 and InBr_2 contain In^+ and $[\text{InX}_6]^{3-}$ complex ions. Another phase^{20,21}, In_5Br_7 , contains the In—In bonded $[\text{In}_2\text{Br}_6]^{2-}$ complex. For this material, anhyd InBr_3 and In shot in 1:1 mole ratio are sealed under argon and heated to 340°C for 1 d, then vacuum sublimed at 220°C to yield pale yellow plates²¹. Less is known of the indium iodide system: InI_2 has the $[\text{InI}_4]$ structure²².

The $[\text{In}_2\text{X}_6]^{2-}$ ions ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are obtained as $[\text{n-Bu}_4\text{N}]^+$ salts by treating a suspension of InX_2 in xylene with $[\text{n-Bu}_4\text{N}]\text{X}$, initially at RT, then under reflux²³. Reaction of InX_2 ($\text{X} = \text{Br}, \text{I}$) with tetramethylethylenediamine or Et_3P in benzene at 10°C gives the molecular adducts $\text{In}_2\text{X}_4\text{L}_2$ ($\text{L} = \text{TMED}$ or Et_3P)²⁴. Other In—In-bonded compounds $\text{In}_2\text{X}_4\text{L}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{THF}, \text{THP}, \text{THT}$) and $\text{In}_2\text{X}_4\text{L}_4$ ($\text{L} = \text{pip}, \text{piperazine}, \text{morpholine}$) can be made²⁵ by condensing excess ligand on to InX_2 . The bromide or iodide complexes $\text{In}_2\text{X}_4(\text{Me}_2\text{S})_2$, $\text{In}_2\text{X}_4(\text{py})_4$ and $\text{In}_2\text{X}_4(\text{DMSO})_4$ are prepared similarly²⁶, but the reaction of these ligands with InCl_2 yields the indium(III) complex InCl_3L , and InCl , without comproportionation. The In—In bond is retained when $\text{In}_2\text{Br}_4(\text{TMED})_2$ is converted to the organometallic derivative $\text{In}_2[\text{CH}(\text{SiMe}_3)_2]_4$ using $\text{LiCH}(\text{SiMe}_3)_2$ as the alkylating agent²⁶.

(M. J. TAYLOR)

1. P. L. Timms, *Acc. Chem. Res.*, **6**, 118 (1973).
2. R. W. Kirk, D. L. Smith, W. Airey, P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 1392 (1972).
3. P. L. Timms, *J. Am. Chem. Soc.*, **89**, 1629 (1967).
4. A. G. Massey, *Adv. Inorg. Chem. Radiochem.*, **26**, 1 (1983).
5. G. A. Olah, O. Farooq, S. M. F. Farnia, M. R. Bruce, F. L. Clouet, P. R. Morton, G. K. S. Prakash, R. C. Stevens, R. Bau, K. Lammertsma, S. Suzer, L. Andrews, *J. Am. Chem. Soc.*, **110**, 3231 (1988).
6. M. Tacke, H. Schnöckel, *Inorg. Chem.*, **28**, 2895 (1989).
7. M. J. Taylor, *J. Chem. Soc., A*, 2812 (1970).
8. L. G. Waterworth, I. J. Worrall, *J. Inorg. Nucl. Chem.*, **35**, 1535 (1973).
9. W. Hönlé, G. Gerlach, W. Weppner, A. Simon, *J. Solid State Chem.*, **61**, 171 (1986).
10. G. Gerlach, W. Hönlé, A. Simon, *Z. Anorg. Allg. Chem.*, **486**, 7 (1982).
11. W. Hönlé, A. Simon, *Z. Naturforsch., Teil B*, **41**, 1391 (1986).
12. J. C. Beamish, R. W. H. Small, I. J. Worrall, *Inorg. Chem.*, **18**, 220 (1979).
13. J. C. Beamish, A. Boardman, R. W. H. Small, I. J. Worrall, *Polyhedron*, **4**, 983 (1985).
14. I. Sinclair, I. J. Worrall, *Inorg. Nucl. Chem. Lett.*, **17**, 279 (1981).
15. W. Uhl, M. Layh, T. Hildebrand, *J. Organomet. Chem.*, **364**, 289 (1989).
16. J. H. R. Clarke, R. E. Hester, *Inorg. Chem.*, **8**, 1113 (1969).
17. G. Meyer, R. Blachnik, *Z. Anorg. Allg. Chem.*, **503**, 126 (1983).
18. P. H. L. Walter, J. Kleinberg, E. Griswold, *J. Inorg. Nucl. Chem.*, **19**, 223 (1961).
19. W. Morawietz, H. Morawietz, G. Brauer, *Z. Anorg. Allg. Chem.*, **316**, 220 (1962).
20. J. E. Davies, L. G. Waterworth, I. J. Worrall, *J. Inorg. Nucl. Chem.*, **36**, 805 (1974).
21. T. Staffel, G. Meyer, *Z. Anorg. Allg. Chem.*, **552**, 113 (1987).
22. M. A. Khan, D. G. Tuck, *Inorg. Chim. Acta*, **97**, 73 (1985).
23. B. H. Freeland, J. L. Hencher, D. G. Tuck, J. G. Contreras, *Inorg. Chem.*, **15**, 2144 (1976).
24. M. J. Taylor, D. G. Tuck, L. Victoriano, *Can. J. Chem.*, **60**, 691 (1982).
25. I. Sinclair, I. J. Worrall, *Can. J. Chem.*, **60**, 695 (1982).
26. W. Uhl, M. Layh, W. Hiller, *J. Organomet. Chem.*, **368**, 139 (1989).

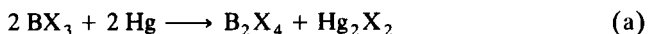
6.2. Formation of the Group-IIIB–Group-IIIB Element Bond

6.2.2. from Group-IIIB Halides

6.2.2.2. by Reduction with Metals

6.2.2.2. by Reduction with Metals

Reductive methods form B—B bonds from B—X bonds. For B_2X_4 (X = Cl, Br, I) from BX_3 , an electric discharge is supplemented by the presence of a metal, or metal atoms, as halide scavenger. The passage of BX_3 at low pressure through a rf discharge in the presence of Hg produces^{1–3} the diboron tetrahalides B_2X_4 at 300 mg h^{–1}:



where (X = Cl, Br, I). Copper can replace Hg, and the Cu atom method is recommended⁴ for larger scale synthesis of B_2Cl_4 . Convenient routes from B_2Cl_4 give B_2F_4 using CCl_3F as the fluoridizing agent⁵ and B_2Br_4 or B_2I_4 using⁶ BBr_3 (or BI_3).

A modification of the rf discharge method⁷, in which the BCl_3 source is held at $-78^\circ C$, yields B_4Cl_4 containing a tetrahedron of linked B atoms. Reaction of B_4Cl_4 with diborane leads to chlorohexaborane and chlorodecaborane clusters⁸.

Diboron compounds with alkylamino or alkyloxy substituents are prepared from the appropriate halogenoborane derivative using active metals^{9,10}:



where X = Cl, Br; M = Na, Na–K, Na–Hg, Mg. Mixed products, e.g., $(Me_2N)_2B_2(OMe)_2$, can be made^{11,12} and transamination or transesterification provides routes to higher alkyl members¹³. Dialkylaminopolyboranes with B—B links, $B_n(NR_2)_{2n+2}$ (R = Me, Et; n = 3–6), can be attained from $Cl(R_2N)_2B_2(NR_2)Cl$ and $(R_2N)_2BCl$ or $(R_2N)_2B_2(NR_2)Cl$ using Na in pentane¹⁴. Dehalogenation of a z-bis(dialkylaminochloroboryl)alkene with Na–K yields a diboraheterocycle with a B—B bond¹⁵. Reactions of $B_2(NMe_2)_2$ with diols, using HCl in ether to eliminate dimethylamine, give products having the B—B bond within or between heterocyclic components¹⁶.

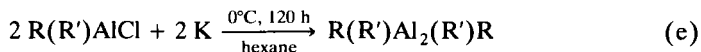
Ligand exchange extends the range of diboron compounds¹⁷ conveniently accessible from $B_2(NMe_2)_4$ or $B_2(OMe)_4$. Treatment of $B_2(NMe_2)_4$ with BX_3 gives¹⁸ $B_2(NMe_2)_nX_{4-n}$ (X = Cl, Br; n = 1, 2). The methyloxy group is more easily displaced from boron than is the —NMe₂ group and the action of BBr_3 on $B_2(OMe)_4$ is a practical route¹⁹ to B_2Br_4 . Careful acidic hydrolysis of $B_2(NMe_2)_4$ or $B_2(OMe)_4$ in ether yields¹⁰ $B_2(OH)_4$ as the chief product.

Organodiborons, B_2R_4 , are obtained only in poor yields by reacting R_2BX halides with metallic reducing agents. Reactions of $R(Me_2N)BX$ with Na to give alkyl- or aryl(amino)diborons are more successful²⁰. Tetramethyldiboron has been obtained as the trimethylamine adduct by reducing Me_2BBr in Na–NMe₃ medium²¹:



Tetraalkyldiborons, $t-Bu_2B_2(t-Bu)R$ (R = Me²² or neopentyl²³), can be prepared from $B_2(OMe)_4$ using lithium alkyl reagents. Reductive coupling of $(t-Bu)_2BCl$ with Na–K in THF produces $[B_2(t-Bu)_4]^-$ with a bond order of 1.5, a radical anion of limited stability²⁴. Treating $trans(t-Bu)_2B_2Cl_2$ with Na–K gives the tetrameric radical anion $[(t-Bu)_4B_4]^-$ apparently via the $(t-Bu)_4B_4$ molecule²⁵.

Organoaluminum(II) compounds with the Al—Al bond form by:



High yields and stable products result when $\text{R} = \text{i-Bu}$ and $\text{R}' = \text{Me}_2\text{N}$, i-BuO or i-Bu ²⁶, or if R and R' are $(\text{Me}_3\text{Si})_2\text{CH}$ ²⁷. If substituents with lower electron-releasing capacity are used, the method fails because of disproportionation into $\text{AlR}_3 + \text{Al}$. Addition of γ -picoline (γ -pic) to $\text{Al}_2(\text{i-Bu})_4$ gives²⁸ $\text{Al}_2(\text{i-Bu})_4(\gamma\text{-pic})_2$ with enhanced stability of the metal–metal bond. The action of B_2H_6 on $\text{Al}_2(\text{i-Bu})_4$ produces $\text{Al}_2(\text{BH}_2)_4$ in which both Al—Al and Al—B bonds occur²⁹.

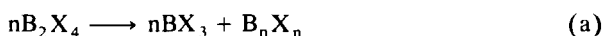
Reduction of Me_2GaCl by Na in liq NH_3 yields³⁰ Ga_2Me_4 as the adduct $\text{Ga}_2\text{Me}_4(\text{NH}_3)_2$, which easily decomposes with Me_2GaNH_2 as the main product.

(M. J. TAYLOR)

1. A. G. Briggs, A. G. Massey, M. S. Reason, P. J. Portal, *Polyhedron*, **3**, 369 (1984).
2. T. Davan, J. A. Morrison, *Inorg. Chem.*, **25**, 2366 (1986).
3. N. A. Kutz, J. A. Morrison, *Inorg. Chem.*, **19**, 3295 (1980).
4. P. L. Timms, *Inorg. Synth.*, **19**, 74 (1979).
5. D. A. Saulys, J. Castillo, J. A. Morrisson, *Inorg. Chem.*, **28**, 1619 (1989).
6. W. Haubold, P. Jacob, *Z. Anorg. Allg. Chem.*, **507**, 231 (1983).
7. T. Davan, J. A. Morrison, *Inorg. Chem.*, **18**, 3194 (1979).
8. S. L. Emery, J. A. Morrison, *Inorg. Chem.*, **24**, 1612 (1985).
9. R. J. Brotherton, A. L. McCloskey, L. L. Peterson, H. Steinberg, *J. Am. Chem. Soc.*, **82**, 6242 (1960).
10. H. Noth, W. Meister, *Chem. Ber.*, **94**, 509 (1961).
11. R. J. Brotherton, in *Progress in Boron Chemistry*, Vol. 1, H. Steinberg, A. L. McCloskey, eds., Pergamon Press, Oxford, 1964, p. 1.
12. C. N. Welch, S. G. Shore, *Inorg. Chem.*, **7**, 225 (1968).
13. M. P. Brown, A. E. Dunn, D. W. Hunt, H. B. Silver, *J. Chem. Soc.*, 4648 (1962).
14. K. H. Hermansdörfer, Dissertation, University of Munich (1966).
15. W. Siebert, in *Boron Chemistry: Proceedings of the 6th International Meeting on Boron Chemistry*, S. Heřmánek, ed., World Scientific, Singapore, 1987, p. 476.
16. H. Nöth, *Z. Naturforsch., Teil B*, **39**, 1463 (1984).
17. R. J. Brotherton, A. L. McCloskey, J. L. Boone, H. M. Manasevit, *J. Am. Chem. Soc.*, **82**, 6245 (1960).
18. H. Nöth, H. Schick, W. Meister, *J. Organomet. Chem.*, **1**, 401 (1964).
19. H. Nöth, H. Pommerening, *Chem. Ber.*, **114**, 398 (1981).
20. H. Nöth, P. Fritz, *Z. Anorg. Allg. Chem.*, **324**, 129 (1963).
21. R. J. Brotherton, H. M. Manasevit, A. L. McCloskey, *Inorg. Chem.*, **1**, 749 (1962).
22. W. Biffar, H. Nöth, H. Pommerening, *Angew. Chem., Int. Ed. Engl.*, **19**, 56 (1980).
23. K. Schlüter, A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **19**, 56 (1980).
24. H. Klusik, A. Berndt, *J. Organomet. Chem.*, **232**, C21 (1982).
25. H. Klusik, A. Berndt, *J. Organomet. Chem.*, **234**, C17 (1982).
26. H. Hoberg, S. Krause, *Angew. Chem., Int. Ed. Engl.*, **15**, 694 (1976).
27. W. Ulm, *Z. Naturforsch., Teil B*, **43**, 1113 (1988).
28. E. P. Schram, M. A. Miller, *Inorg. Chim. Acta*, **113**, 131 (1986).
29. M. A. Miller, E. P. Schram, *Organometallics*, **4**, 1362 (1985).
30. C. A. Kraus, F. E. Toonder, *J. Am. Chem. Soc.*, **55**, 3547 (1933).

6.2.2.3. by Disproportionation of Dinuclear Compounds

Thermal decomposition of B_2X_4 yields various halogenopolyboranes^{1–3}:



6.2. Formation of the Group-IIIB–Group-IIIB Element Bond

7

6.2.2. from Group-IIIB Halides

6.2.2.3. by Disproportionation of Dinuclear Compounds

Organoaluminum(II) compounds with the Al—Al bond form by:



High yields and stable products result when $\text{R} = \text{i-Bu}$ and $\text{R}' = \text{Me}_2\text{N}$, i-BuO or i-Bu ²⁶, or if R and R' are $(\text{Me}_3\text{Si})_2\text{CH}$ ²⁷. If substituents with lower electron-releasing capacity are used, the method fails because of disproportionation into $\text{AlR}_3 + \text{Al}$. Addition of γ -picoline (γ -pic) to $\text{Al}_2(\text{i-Bu})_4$ gives²⁸ $\text{Al}_2(\text{i-Bu})_4(\gamma\text{-pic})_2$ with enhanced stability of the metal–metal bond. The action of B_2H_6 on $\text{Al}_2(\text{i-Bu})_4$ produces $\text{Al}_2(\text{BH}_2)_4$ in which both Al—Al and Al—B bonds occur²⁹.

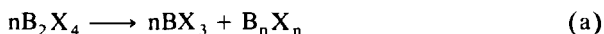
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3. N. A. Kutz, J. A. Morrison, *Inorg. Chem.*, **19**, 3295 (1980).
4. P. L. Timms, *Inorg. Synth.*, **19**, 74 (1979).
5. D. A. Saulys, J. Castillo, J. A. Morrisson, *Inorg. Chem.*, **28**, 1619 (1989).
6. W. Haubold, P. Jacob, *Z. Anorg. Allg. Chem.*, **507**, 231 (1983).
7. T. Davan, J. A. Morrison, *Inorg. Chem.*, **18**, 3194 (1979).
8. S. L. Emery, J. A. Morrison, *Inorg. Chem.*, **24**, 1612 (1985).
9. R. J. Brotherton, A. L. McCloskey, L. L. Peterson, H. Steinberg, *J. Am. Chem. Soc.*, **82**, 6242 (1960).
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12. C. N. Welch, S. G. Shore, *Inorg. Chem.*, **7**, 225 (1968).
13. M. P. Brown, A. E. Dunn, D. W. Hunt, H. B. Silver, *J. Chem. Soc.*, 4648 (1962).
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16. H. Nöth, *Z. Naturforsch., Teil B*, **39**, 1463 (1984).
17. R. J. Brotherton, A. L. McCloskey, J. L. Boone, H. M. Manasevit, *J. Am. Chem. Soc.*, **82**, 6245 (1960).
18. H. Nöth, H. Schick, W. Meister, *J. Organomet. Chem.*, **1**, 401 (1964).
19. H. Nöth, H. Pommerening, *Chem. Ber.*, **114**, 398 (1981).
20. H. Nöth, P. Fritz, *Z. Anorg. Allg. Chem.*, **324**, 129 (1963).
21. R. J. Brotherton, H. M. Manasevit, A. L. McCloskey, *Inorg. Chem.*, **1**, 749 (1962).
22. W. Biffar, H. Nöth, H. Pommerening, *Angew. Chem., Int. Ed. Engl.*, **19**, 56 (1980).
23. K. Schlüter, A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **19**, 56 (1980).
24. H. Klusik, A. Berndt, *J. Organomet. Chem.*, **232**, C21 (1982).
25. H. Klusik, A. Berndt, *J. Organomet. Chem.*, **234**, C17 (1982).
26. H. Hoberg, S. Krause, *Angew. Chem., Int. Ed. Engl.*, **15**, 694 (1976).
27. W. Ulm, *Z. Naturforsch., Teil B*, **43**, 1113 (1988).
28. E. P. Schram, M. A. Miller, *Inorg. Chim. Acta*, **113**, 131 (1986).
29. M. A. Miller, E. P. Schram, *Organometallics*, **4**, 1362 (1985).
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6.2.2.3. by Disproportionation of Dinuclear Compounds

Thermal decomposition of B_2X_4 yields various halogenopolyboranes^{1–3}:



where if $X = \text{Cl}$, $n = 8-12$; if $X = \text{Br}$, $n = 7-10$; if $X = \text{I}$, $n = 8$ or 9 . Dodecahedral B_8Cl_8 is produced⁴ from B_2Cl_4 in CCl_4 at 100°C ; whereas tricapped trigonal-pyramidal B_9Cl_9 is obtained at 450°C without solvent⁵. At 200°C B_9Br_9 is recovered⁶ from the disproportionation products of B_2Br_4 . An alternative route to halogenopolyboranes depends on treating hydridopolyboranes (B_nH_n) or such polyborates as $[\text{B}_6\text{H}_6]^{2-}$, $[\text{B}_9\text{H}_9]^{2-}$ or $[\text{B}_{10}\text{H}_{10}]^{2-}$ with Cl_2 , Br_2 or I_2 , or with N-halosuccinimide followed, in the anions, by oxidation to the particular B_nX_n cluster⁷⁻¹⁰.

(M. J. TAYLOR)

1. A. G. Massey, *Adv. Inorg. Chem. Radiochem.*, **26**, 1 (1983); comprehensive account.
2. A. K. Holliday, A. G. Massey, *Chem. Rev.*, **62**, 303 (1962).
3. A. J. Markwell, A. G. Massey, P. J. Portal, *Polyhedron*, **1**, 134 (1982).
4. S. L. Emery, J. A. Morrison, *J. Am. Chem. Soc.*, **104**, 6790 (1982).
5. T. Davan, J. A. Morrison, *Inorg. Chem.*, **25**, 2366 (1986).
6. N. A. Kutz, J. A. Morrison, *Inorg. Chem.*, **19**, 3295 (1980).
7. D. A. Saulys, N. A. Kutz, J. A. Morrison, *Inorg. Chem.*, **22**, 1821 (1983).
8. E. H. Wong, *Inorg. Chem.*, **20**, 1300 (1981).
9. W. Preetz, J. Fritze, *Z. Naturforsch., Teil B*, **42**, 282 (1987).
10. P. R. LeBreton, S. Urano, M. Shahbaz, S. L. Emery, J. A. Morrison, *J. Am. Chem. Soc.*, **108**, 3937 (1986).

6.2.2.4. by Metal Atom and Related Reactions

The B—B bond can be formed from BCl_3 by the codeposition of Cu atoms with BCl_3 . This serves as a convenient synthetic method for B_2Cl_4 formation¹⁻³:

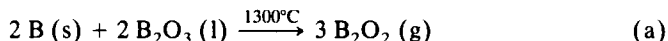


(K. J. KLABUNDE)

1. P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 1525 (1968).
2. P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 830 (1972).
3. P. L. Timms, *Inorg. Synth.*, **19**, 74 (1979).

6.2.3. in Combination with Group-VIB Elements

The reactive species $\text{O}=\text{B}-\text{B}=\text{O}$ is generated from B and B_2O_3 in the gas phase¹:



If B_2O_2 is condensed with BCl_3 at -196°C , B_2Cl_4 is obtained²; with SF_4 , B_2O_2 yields B_2F_4 . Polymeric solid boron monoxide can be prepared by heating B_2O_3 with B at 1050°C , or by the action of H_2O vapor on B_2Cl_4 followed by dehydration at 270°C ³.

Group-IIIB–group-IIIB bonds feature in the low-valent chalcogenides of Al, Ga and In shown in Table 1. These involve $[\text{Al}-\text{Al}]^{4+}$, $[\text{Ga}-\text{Ga}]^{4+}$, $[\text{In}-\text{In}]^{4+}$ or $[\text{In}-\text{In}-\text{In}]^{5+}$ in the solid state. The discrete compounds are synthesized by heating stoichiometric mixtures of the metal and S, Se or Te, typically in evacuated quartz

6.2. Formation of the Group-IIIB–Group-IIIB Element Bond**6.2.2. from Group-IIIB Halides****6.2.2.4. by Metal Atom and Related Reactions**

where if $X = \text{Cl}$, $n = 8\text{--}12$; if $X = \text{Br}$, $n = 7\text{--}10$; if $X = \text{I}$, $n = 8$ or 9 . Dodecahedral B_8Cl_8 is produced⁴ from B_2Cl_4 in CCl_4 at 100° ; whereas tricapped trigonal-pyramidal B_9Cl_9 is obtained at 450°C without solvent⁵. At 200°C B_9Br_9 is recovered⁶ from the disproportionation products of B_2Br_4 . An alternative route to halogenopolyboranes depends on treating hydridopolyboranes (B_nH_n) or such polyborates as $[\text{B}_6\text{H}_6]^{2-}$, $[\text{B}_9\text{H}_9]^{2-}$ or $[\text{B}_{10}\text{H}_{10}]^{2-}$ with Cl_2 , Br_2 or I_2 , or with N-halosuccinimide followed, in the anions, by oxidation to the particular B_nX_n cluster^{7–10}.

(M. J. TAYLOR)

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2. A. K. Holliday, A. G. Massey, *Chem. Rev.*, **62**, 303 (1962).
3. A. J. Markwell, A. G. Massey, P. J. Portal, *Polyhedron*, **1**, 134 (1982).
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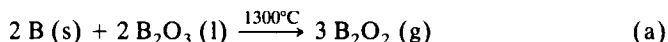


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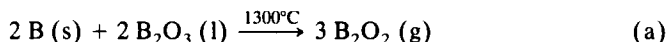


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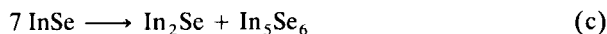
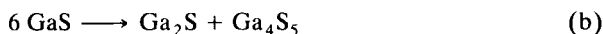
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TABLE 1. GROUP-IIIB–GROUP-VIB COMPOUNDS WITH Al—Al,
Ga—Ga OR In—In BONDS

Element	Compounds	Species	Refs.
Al	Al ₇ Te ₁₀	Al ₂ ⁴⁺	4
Ga	GaY (Y = S, Se, Te)	Ga ₂ ⁴⁺	5–7
	GaS _x Se _{1-x} (x = 0.2–0.8)	Ga ₂ ⁴⁺	8
	Ga ₄ S ₅	Ga ₂ ⁴⁺	9
	Ga ₃ Se ₂	Ga ₂ ⁴⁺	10
	InY (Y = S, Se, Te)	In ₂ ⁴⁺	6, 11
In	In ₆ Y ₇ (Y = S, Se)	In ₂ ⁴⁺	12
	In ₅ S ₄	In ₂ ⁴⁺ , In ₅ ⁶⁺	13
	In ₄ Y ₃ (Y = Se, Te)	In ₃ ⁵⁺	14

tubes for 24 h. They can be obtained as single crystals for semiconductor purposes by zone refining¹⁵. Some of the low-valent phases are best made by disproportionation induced at high T^{9,16}:



A convenient synthesis of In₅S₄ from In and S uses molten Sn as solvent¹⁷. Other In–S phases, InS (red crystals) and In₆S₇ (black), are obtained from the melt when In₂S₃ is reduced with In in a sealed tube¹⁸. To prepare In₆Se₇, the In₂Se₃ phase is heated to 1000°C in an argon flow, resulting in the loss of Se as the more volatile component¹².

The Ga(II) complex Na₂Ga₂Se₃, in which (Ga—Ga)⁴⁺ is coordinated by linked Se²⁻ ions, is made by combining¹⁹ the elements in stoichiometric proportions at 990°C. Crystalline In₆La₁₀O₆S₁₇, containing the In₂⁴⁺ dimer, is synthesized²⁰ from In₂S₃ and La₂O₂S at high T; Na₂₄In₅O₁₅ (containing In₅⁶⁺ tetrahedral clusters) is made by reducing In₂O₃ with sodium²¹, and In₁₁Mo₄₀O₆₂ (containing In₅⁷⁺ and In₆⁸⁺ chains) by heating a stoichiometric mixture of MnO₂, Mo and In at 1100°C²².

The compounds discussed in §6.2.3 are significant as examples of metal–metal bonding in group IIIB, but their value for chemical utilization is restricted by their insolubility and their tendency to disproportionate to E(0) or E(I) and E(III) states.

(M. J. TAYLOR)

1. P. L. Timms, *Acc. Chem. Res.*, **6**, 118 (1973).
2. P. S. Maddren, Ph.D. Thesis, University of Bristol, 1975.
3. A. L. McCloskey, R. J. Brotherton, J. L. Boone, *J. Am. Chem. Soc.*, **83**, 4750 (1961).
4. R. Nesper, J. Curda, *Z. Naturforsch., Teil B*, **42**, 557 (1987).
5. H. Hahn, *Angew. Chem.*, **65**, 538 (1953).
6. P. Fielding, G. Fischer, E. Mooser, *Phys. Chem. Solids*, **8**, 434 (1959).
7. A. Kuhn, A. Chevy, R. Chevalier, *Acta Crystallogr., Sect. B*, **32**, 983 (1976).
8. A. Kuhn, R. Chevalier, C. Desnoyers, J. C. J. M. Terhell, *Acta Crystallogr., Sect. B*, **32**, 1910 (1976).
9. H. Spandau, F. Klanberg, *Z. Anorg. Allg. Chem.*, **295**, 300 (1958).

10. J. Terhell, J. Lieth, *Phys. Status Solidi*, **10**, 529 (1972).
11. J. Rigault, A. Rimski, A. Kuhn, *Acta Crystallogr.*, *Sect. B*, **36**, 916 (1980).
12. J. H. C. Hogg, *Acta Crystallogr.*, *Sect. B*, **27**, 1630 (1971).
13. T. Wadsten, L. Arnberg, J. E. Berg, *Acta Crystallogr.*, *Sect. B*, **36**, 2220 (1980).
14. J. H. C. Hogg, H. H. Sutherland, *Acta Crystallogr.*, *Sect. B*, **29**, 2483 (1973).
15. J. M. Thomas, I. Adams, R. H. Williams, M. Barber, *J. Chem. Soc., Faraday Trans. 2*, **68**, 755 (1972).
16. B. Čelustka, S. Popvić, *J. Phys. Chem. Solids*, **35**, 287 (1974).
17. T. Wadsten, *Chem. Scripta*, **8**, 63 (1975).
18. W. J. Duffin, J. H. C. Hogg, *Acta Crystallogr.*, **20**, 566 (1966).
19. J. Weiss, H. Schäfer, *Z. Naturforsch., Teil B*, **31**, 1341 (1976).
20. L. Gastaldi, D. Carré, M. P. Cardo, *Acta Crystallogr.*, *Sect. B*, **38**, 2365 (1982).
21. G. Wagner, R. Hoppe, *J. Less-Common Met.*, **116**, 129 (1986).
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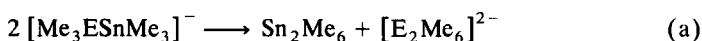
6.2.4. from Group-IIIB–Group-IVB Bonds

Organometallic compounds of group-IIIB elements in the M(II) state are unstable even when they incorporate electron-releasing groups, and few have been prepared.

Reacting AlMe_3 with $\text{B}_2(\text{NMe}_2)_4$ gives materials that seem to have Al—Al and Al—B bonds^{1–3}. The products include $\text{Me}_3\text{Al}_3(\text{NMe}_2)_2$, $\text{Me}_6\text{Al}_4\text{B}(\text{NMe}_2)_3$ and $\text{Me}_{12}\text{Al}_6\text{B}_6(\text{NMe}_2)_6$, apparently a boron cluster compound. Action of alkali metals on trialkylaluminum compounds usually leads to the formation of $\text{M}[\text{AlR}_4]$; however, $(i\text{-Bu})_3\text{Al}$ reacts with K in hexane to give $\text{K}_2[(i\text{-Bu})_6\text{Al}_2]$ in 60% yield⁴. Treating with Me_3SiCl in THF converts this salt to the adduct $(i\text{-Bu})_4\text{Al}_2(\text{THF})_2$ with retention of the Al—Al bond. Further treatment of $(i\text{-Bu})_4\text{Al}_2$ with K in cyclopentane affords⁵ $\text{K}_3[(i\text{-Bu})_{10}\text{Al}_5]$. Reactions of AlEt_3 and $(i\text{-Bu})_2\text{AlH}$ with K proceed without initial disproportionation to give unstable Al—Al-bonded substances^{6,7}. Products of reacting GaR_3 or InR_3 ($\text{R} = \text{CH}_2\text{SiMe}_3$) with KH in benzene⁸ are not low valent but are the E(III) compounds $\text{K}[\text{ER}_3\text{H}]$, arising by addition of the hydride ligand to the metal alkyl.

Although in neither case is the E(II) product well characterized, GaMe_3 is reduced by Na in liq NH_3 to $\text{Na}_2[\text{Ga}_2\text{Me}_6]$ ^{9,10}, and TlMe_3 by K-NH_3 to $\text{K}_2[\text{Tl}_2\text{Me}_6]$ ¹¹. Attempts to obtain Tl—Tl-bonded compounds, e.g., Tl_2Ph_4 , by electrochemical reduction of diorganothallium(III) derivatives do not succeed^{12,13}.

Compounds $\text{Li}[\text{R}_3\text{EE}'\text{R}_3]$, with group-IIIB–group-IVB bonds are accessible from ER_3 ($\text{E} = \text{Al, Ga, In, Tl}$; $\text{R} = \text{Me, Ph}$) combined with $\text{LiE}'\text{R}_3$ ($\text{E}' = \text{Si, Ge, Sn}$); polysubstituted forms, e.g., $\text{Li}[\text{Me}_n\text{Tl}(\text{SnMe}_3)_{4-n}]$ ($n = 0–3$), can also be obtained¹⁴. Side reactions yield Sn_2Me_6 , ascribed to disproportionation:



The process generates E—E-bonded complex anions of the type considered here.

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4. H. Hoberg, S. Krause, *Angew. Chem., Int. Ed. Engl.*, **17**, 950 (1978).

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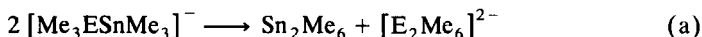
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7. E. P. Schram, *Inorg. Chim. Acta*, **141**, 69 (1988).
8. R. B. Hallock, O. T. Beachley Jr., L. Yong-Ji, W. M. Sanders, M. R. Churchill, W. E. Hunter, J. L. Atwood, *Inorg. Chem.*, **22**, 3683 (1983).
9. C. A. Krauss, F. E. Toonder, *J. Am. Chem. Soc.*, **55**, 3547 (1933).
10. C. A. Krauss, *J. Chem. Ed.*, **29**, 549 (1952).
11. G. E. Coates, K. Wade, *Organometallic Compounds*, Vol. 1, Methuen, London, 1967, p. 372.
12. K. Isslieb, S. Naumann, H. Matschiner, B. Walther, *Z. Anorg. Allg. Chem.*, **381**, 226 (1971).
13. S. Zecchin, G. Pilloni, *J. Electroanal. Chem.*, **36**, 117 (1972).
14. A. T. Weibel, J. P. Oliver, *J. Organomet. Chem.*, **74**, 155 (1974).

6.2.5. from Gallium in Halogen Acid Media

Gallium(II) halide complexes with Ga—Ga bonds are prepared from Ga metal by oxidation in acidic halide media. Dissolution of powdered Ga in cold conc HCl, HBr or HI (or in HX–diethyl ether mixtures) yields solutions containing the $[X_3GaGaX_3]^{2-}$ and $[GaX_4]^-$ complex anions. Salts $[Me_4N]_2Ga_2X_6$ (X = Cl, Br, I) can be precipitated and separated from $[Me_4N]GaX_4$ by recrystallization and are stable in the solid state or in CH_3CN soln¹. A better preparative method is to make Ga the anode of a cell with aq HCl or HBr as electrolyte and a Pt cathode; $[Ga_2X_6]^{2-}$ species are the principal product¹. The halogen acids furnish $[Ga_2X_6]^{2-}$ quantitatively on anodic oxidation of Ga in an electrolyte of HX in acetonitrile. This procedure enables² single-stage high-yield preparation of crystalline $[Ph_3PH]_2[Ga_2X_6]$ (X = Cl, Br, I) from Ga.

Attempts to prepare In(II) halide complexes by this method are unsuccessful. Anodic oxidation of In metal produces In^+ , which disproportionates to the element and In(II) halide complexes³.

(M. J. TAYLOR)

1. C. A. Evans, K. H. Tan, S. P. Tapper, M. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 988 (1973).
2. M. J. Taylor, D. G. Tuck, *Inorg. Synth.*, **22**, 135 (1983).
3. M. J. Taylor, unpublished observations.

6.2. Formation of the Group-IIIB–Group-IIIB Element Bond

6.2.5. from Gallium in Halogen Acid Media

11

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11. G. E. Coates, K. Wade, *Organometallic Compounds*, Vol. 1, Methuen, London, 1967, p. 372.
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14. A. T. Weibel, J. P. Oliver, *J. Organomet. Chem.*, **74**, 155 (1974).

6.2.5. from Gallium in Halogen Acid Media

Gallium(II) halide complexes with Ga—Ga bonds are prepared from Ga metal by oxidation in acidic halide media. Dissolution of powdered Ga in cold conc HCl, HBr or HI (or in HX–diethyl ether mixtures) yields solutions containing the $[X_3GaGaX_3]^{2-}$ and $[GaX_4]^-$ complex anions. Salts $[Me_4N]_2Ga_2X_6$ (X = Cl, Br, I) can be precipitated and separated from $[Me_4N]GaX_4$ by recrystallization and are stable in the solid state or in CH_3CN soln¹. A better preparative method is to make Ga the anode of a cell with aq HCl or HBr as electrolyte and a Pt cathode; $[Ga_2X_6]^{2-}$ species are the principal product¹. The halogen acids furnish $[Ga_2X_6]^{2-}$ quantitatively on anodic oxidation of Ga in an electrolyte of HX in acetonitrile. This procedure enables² single-stage high-yield preparation of crystalline $[Ph_3PH]_2[Ga_2X_6]$ (X = Cl, Br, I) from Ga.

Attempts to prepare In(II) halide complexes by this method are unsuccessful. Anodic oxidation of In metal produces In^+ , which disproportionates to the element and In(II) halide complexes³.

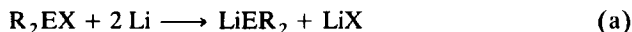
(M. J. TAYLOR)

1. C. A. Evans, K. H. Tan, S. P. Tapper, M. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 988 (1973).
2. M. J. Taylor, D. G. Tuck, *Inorg. Synth.*, **22**, 135 (1983).
3. M. J. Taylor, unpublished observations.

6.3. Formation of Group-IIIB–Group-IA or Group-IIA Bonds

Direct combination of group-IIIB and group-IA elements occurs in intermetallic compounds, e.g., KGa_3 , RbGa_7 , $\text{Na}_7\text{Ga}_{13}$, $\text{Li}_3\text{Ga}_{14}$, $\text{Na}_{23}\text{Ga}_{39}$ and $\text{Na}_3\text{Ga}_8\text{Sn}_3$ phases^{1–4}. Particular stability attaches to the Ga_8^{2-} , Ga_{11}^{2-} and Ga_{12}^{2-} clusters in association with the group IA metals⁵.

Compounds of the type $\text{E(I)}[\text{E(III)}\text{R}_2]$ that are analogous to the group-IA–group-IVB compounds, e.g., LiSnPh_3 , should be given by dehalogenation of diorganometal halides:



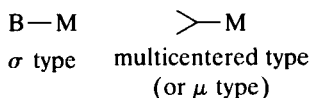
Alternatively, group-IIIB–group-IIIB bond cleavage by a group-IA or -IIA element may be employed. Success by either route is influenced by the choice of substituent on the group IIIB element, since the coordinatively unsaturated and electron-deficient product is always highly reactive. Reactions of group IIIB trialkyl compounds ER_3 , which with a group-IA metal may give E'ER_2 and E'R , generally lead to ionic compounds E'ER_4 with separation of the metal E (Al, Ga, In, Tl). In exceptional cases $\text{E}_2[\text{E}_2\text{R}_6]$ complex salts result (§6.2.4). Reaction of AlEt_3 with K in hexane produces unstable radical $\text{K[AlEt}_3]$ and the dimer $\text{K}_2[\text{Et}_3\text{AlAlEt}_3]$, which disproportionate to $\text{K[AlEt}_4]$ and Al metal⁶.

(M. J. TAYLOR)

1. R. G. Ling, C. Belin, *Acta Crystallogr., Sect. B*, **38**, 1101 (1982).
2. C. Belin, R. G. Ling, *J. Solid State Chem.*, **48**, 40 (1983).
3. U. Frank-Cordier, G. Cordier, H. Schafer, *Z. Naturforsch., Teil B*, **37**, 119 (1982).
4. W. Blase, G. Cordier, *Z. Naturforsch., Teil B*, **44**, 1011 (1989).
5. R. B. King, *Inorg. Chem.*, **28**, 2796 (1989).
6. H. Hoberg, S. Krause, E. Kiegler, *J. Organomet. Chem.*, **184**, 1 (1980).

6.4. Formation of Group III-B–Group-IB or Group-IIB Bonds

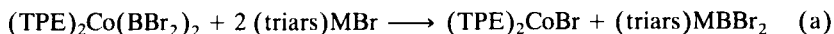
Formation of group-IIIB–group-IB and -IIB element bonds is limited almost exclusively to the element B and is observed predominantly in metalloboranes and metallocarboranes. The boron–IB and boron–group-IIB bonding interactions either are of the σ type or can be described as multicenter bonds:



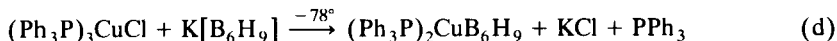
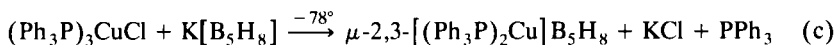
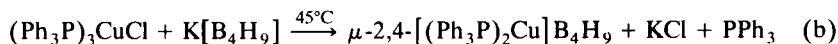
Some group-IB and -IIB boranes or carboranes, especially of Cu, possess $\text{M} - \text{H} - \text{B}$ structure units and are not discussed here because no direct metal–boron bond exists.

The formation of boron–group IB bonds succeeds in two ways: by transfer of a boryl group from metal–boron compounds to other metals, and by reaction of anionic boranes or carboranes with transition-metal halides.

The transfer of the BBr_2 group to Cu and Ag is accomplished using¹ $(\text{dppe})_2\text{Co}(\text{BBr}_2)_2$:

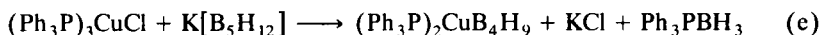


where $\text{M} = \text{Cu}, \text{Ag}$. Reactions are carried out in hot benzene excluding O_2 and H_2O ; the dibromoboryl copper and silver complexes $(\text{triars})\text{M} - \text{BBr}_2$ form in 78–79% yield. Copper-containing boranes with a direct B–Cu interaction result from the reaction of potassium borates with $(\text{Ph}_3\text{P})_2\text{CuCl}$, e.g.^{2–4}:



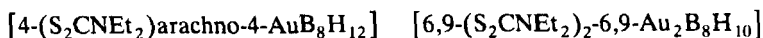
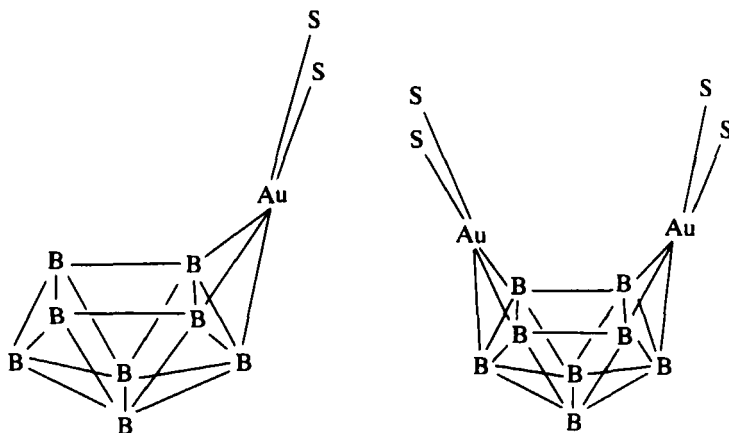
Low reaction T are preferred and THF– CH_2Cl_2 solvent mixtures are used.

Using the dodecahydropentaborate(1–) ion in reaction with $(\text{Ph}_3\text{P})_3\text{CuCl}$ results in a change in the borane shape, leading to a tetraborane derivative²:



In these examples the metal atom is connected to the borane frame via multicentered bonds.

Arachno-type auranoboranes are prepared when $\text{AuBr}_2(\text{S}_2\text{CNEt}_2)$ reacts with the arachno $[\text{B}_9\text{H}_{14}]^-$ anion⁵. The very pale nine-vertex 4- $(\text{S}_2\text{CNEt}_2)_2$ -4- $\text{AuB}_8\text{H}_{12}$ and the bright yellow 10-vertex 6,9- $(\text{S}_2\text{CNEt}_2)_2$ -6,9- $\text{Au}_2\text{B}_8\text{H}_{10}$ are formed in low yields. The gold atoms are linked with three boron atoms each:

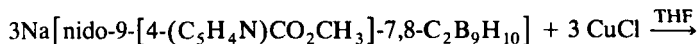


In ethereal solution LiB_5H_8 and $\text{Ph}_3\text{PAuNO}_3$ yield pale red crystals of $\text{Ph}_3\text{PAu-2.3-B}_5\text{H}_8$ (38%)⁶.

Copper and gold carborane complexes are discussed with the metalloboranes (§6.5.3.4.).

Metallocarboranes containing Cu-B or Au-B bonds can be prepared using the undecahydro-1,2(or-1,7)-dicarba-nido-undecaborate(2) anion as its ammonium or alkali-metal salt. The copper anion $[3,3'\text{-Cu}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^{2-}$ forms from $[\text{C}_2\text{B}_9\text{H}_{12}]^{2-}$ and CuSO_4 in sodium hydroxide solution (40%) at 0°C and is isolated as the $[\text{Et}_4\text{N}]^+$ salt in 60% yield after $[\text{Et}_4\text{N}]\text{Br}$ addition. Oxidation by air leads^{7,8} to the Cu(III) complex $[3,3'\text{-Cu}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$.

$[\text{Closio-3-(PPh}_3\text{)}\text{-3,1,2-CuC}_2\text{B}_9\text{H}_{11}]^-$ contains three direct Cu-B bonds and is synthesized in 84% yield⁹ by reacting $\text{Ti}_2[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]$ with Ph_3PCuCl . Several derivatives, e.g., $\text{closio-3-(PPh}_3\text{)}\text{-4-[4-(C}_5\text{H}_4\text{N)CO}_2\text{CH}_3\text{]}\text{-3,1,2-CuC}_2\text{B}_9\text{H}_{10}$ or the trinuclear complex¹⁰, can be prepared similarly:

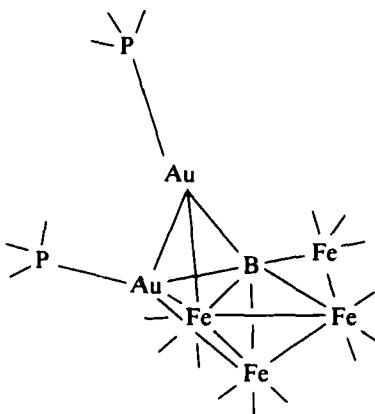


Both $3\text{-Ph}_3\text{P-4-py-3,1,2-Cu}_2\text{B}_9\text{H}_{10}$ and $3\text{-Ph}_3\text{P-4-py-3,1,2-Au}_2\text{B}_9\text{H}_{10}$ are analogs formed from $(\text{Ph}_3\text{PCuCl})_4$ or Ph_3PAuCl and $[\text{7,8-C}_2\text{B}_9\text{H}_{11}\text{py}]^{2-}$ in THF at RT in 91 and 48% yields, respectively¹¹. The $\text{Ti}_2[\text{7,8-C}_2\text{B}_9\text{H}_{11}]$ salt and $(\text{Et}_2\text{NCS}_2)\text{AuBr}_2$ react in diethylether at 25°C to give¹² $3\text{-(Et}_2\text{NCS}_2\text{)}\text{-3,1,2-Au}_2\text{B}_9\text{H}_{11}$ (12%) and $[\text{Et}_2\text{NCS}_2)_2\text{Au}]^+[\text{Au}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ (21%).

In the presence of $[\text{Et}_4\text{N}]\text{Br}$ or $[\text{Ph}_3\text{PMe}]\text{Br}$ and H_2O_2 $[1,2\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$ also reacts⁸ with AuCl_3 to form the corresponding ammonium or phosphonium salts of $[3,3\text{-Au}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$.

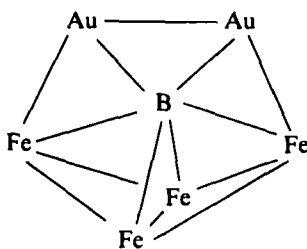
The Au—B compound $\mu\text{-4,5-(Ph}_3\text{PAu)-(2,3-C}_2\text{B}_4\text{H}_7\text{)}$ can be isolated in 60% yield by reacting Ph_3PAuCl with $[\text{2,3-C}_2\text{B}_4\text{H}_7]$ in THF¹³.

Novel boron-gold bonds containing complexes are realized in two borido clusters. Addition of $[\text{HFe}_4(\text{CO})_{12}\text{BH}]$ ppn to xs $(\text{PPh}_3)\text{AuCl}$ in CH_2Cl_2 forms^{14,15} the green-brown, air-sensitive $\text{Fe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2\text{BH}$:



Some other derivatives can be prepared similarly¹⁶: $\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)\text{BH}$, $\text{Fe}_4(\text{CO})_{12}(\text{AuPEt}_3)(\text{AuPPh}_3)\text{BH}$, $\text{Fe}_4(\text{CO})_{12}(\text{AuPEt}_3)_2\text{BH}$.

A structural variation shows the borido cluster¹⁷ $\text{HFe}_4(\text{CO})_{12}(\text{Et}_3\text{PAu})_2\text{B}$, where the B atom is within bonding contact of all six metal atoms and the two Au atoms symmetrically bridge the wingtips of the butterfly-shaped complex:



The first example with concrete short Tl—Au bonds¹⁸ is $\text{AuTl}[\text{Ph}_2\text{P}(\text{CH}_2)\text{S}]_2$. The complex is formed by reacting Tl^+ with $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{AuPh}_2\text{P}(\text{CH}_2)\text{S}]^-$. It forms a one-dimensional polymer along the unique crystallographic b-axis of the lattice:

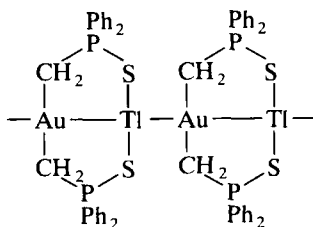


TABLE 1. ZINC AND CADMIUM DECARBORANE COMPLEXES

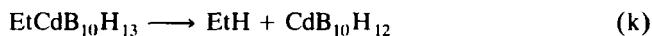
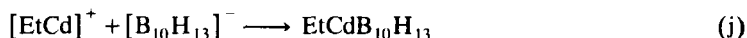
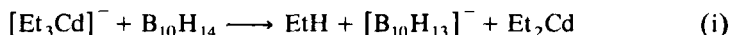
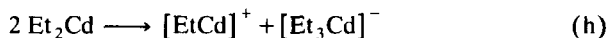
R ₂ M	Solvent	Product	Yield (%)	Refs.
Me ₂ Zn	Et ₂ O	ZnB ₁₀ H ₁₂ · 1.4 Et ₂ O	6	19
Me ₂ Zn	THF	ZnB ₁₀ H ₁₂ · 1.7 THF	5	19
Et ₂ Zn	Et ₂ O	ZnB ₁₀ H ₁₂ · 1.3 Et ₂ O	63	19
Et ₂ Zn	C ₆ H ₆ Et ₂ O	ZnB ₁₀ H ₁₂ · 1.4 Et ₂ O	48	19
Ph ₂ Zn	Et ₂ O	ZnB ₁₀ H ₁₂ · 1.5 Et ₂ O	83	19
Ph ₂ Zn	THF	ZnB ₁₀ H ₁₂ · 1.8 THF	83	19
Et ₂ Cd	Et ₂ O	CdB ₁₀ H ₁₂ · 2 Et ₂ O	77	20, 21
Et ₂ Cd	THF	CdB ₁₀ H ₁₂ · 2 THF	85	20

The synthesis of compounds containing boron-group IIB bonds also occurs by two pathways. The most convenient method is using anionic borane or carborane species, as in the group-IB case, to react with Zn, Cd, or Hg halides. Moreover, reactions between organometallic compounds (Zn, Cd) with unchanged boranes are also realized, so Zn and Cd decaboranes, e.g., MB₁₀H₁₂ · n solvent (M = Zn, Cd), result^{19,20} from reactions of decaborane(14) with MR₂:

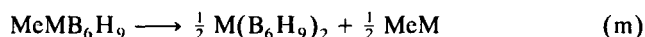
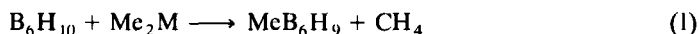


Examples are given in Table 1.

The Cd—B interaction on CdB₁₀H₁₂ · 2 Et₂O is multicentered as shown by x-ray²¹; the compound is a dimer. Whether other Zn and Cd decaboranes are monomeric or dimeric is still unknown. Formation of the CdB₁₀H₁₂ framework can be described via intermediates²⁰:



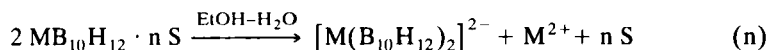
Besides B₁₀H₁₄, the hexaborane(10) B₆H₁₀ also reacts with Me₂Zn and Me₂Cd forming²² metalloboranes of the type M(B₆H₉)₂:



where M = Zn, Cd. The reactivity of Me₂Zn is higher than that of Me₂Cd, whereas Me₂Hg shows no reaction. The Zn compound is isolated as a 1:2 THF adduct of Me₂Zn and B₆H₁₀ cocondenses on THF in vacuo. After warming to 0°C unreacted

B_6H_{10} and Me_2Zn are pumped off and a chloroform solution of the residue precipitates $Zn(B_6H_9)_2 \cdot 2 THF$ in 50% yield on Et_2O addition. In a similar manner the synthesis of $Cd(B_6H_9)_2$ may be performed in 35% yield at $65^\circ C$. Air and light must be excluded. In the latter case only a small amount of THF remains coordinated.

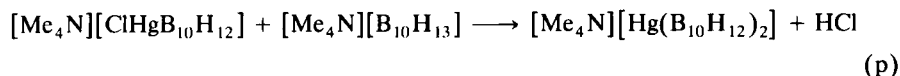
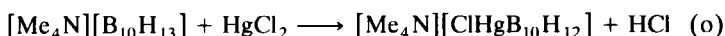
The anionic species $[M(B_{10}H_{12})_2]^{2-}$ ($M = Zn, Cd$) is prepared by decomposing the neutral metalloboranes, $MB_{10}H_{12} \cdot n S$, in $EtOH$ or H_2O . The products are isolated as the corresponding $[Me_4N]^+{}^{20,21}$ or $[Ph_3PMe]^+{}^{23}$ salts:



where $M = Zn, Cd$.

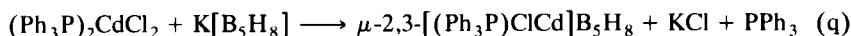
The magnesium halide derivative $B_{10}H_{13}MgX$ ($X = Br, I$) reacts with $RHgX$ ($R = Me, X = Cl, Br, I; R = Et, n-Pr, X = Cl$) yielding complex intermediates that decompose in H_2O to give $[Hg(B_{10}H_{12})_2]^{2-}$ ^{24,25}.

Reaction of $[Me_4N][B_{10}H_{13}]$ with $HgCl_2$ proceeds in boiling THF²⁶:



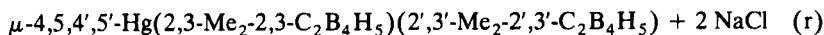
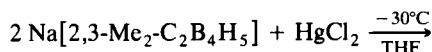
In contrast to the reaction^{24,25} of $B_{10}H_{13}MgX$ with $RHgX$ $MeHgCl$ and $[Me_2Ti][B_{10}H_{12}TiMe]$ react at RT in THF with retention of the $Me-Hg$ bond to give $[MeHgB_{10}H_{12}]^-$, which can be isolated as the $[Ph_3PMe]^+$ salt in 98% yield²⁷.

The lower borates, e.g., μ -2,3-[(Ph_3P)ClCd] B_5H_8 and μ -2,3-[(Ph_3P)ClCd]- B_5H_7Br , also form metalloboranes with group-II B elements²⁸:

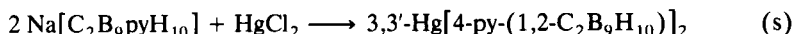


The Cd-borane interaction is assumed to be two electron, three centered. The only pentaborane derivative of mercury is represented²⁹ as $Hg(B_5H_8)_2$.

Metallacarboranes containing group-II B elements are limited to mercury^{30,31}:

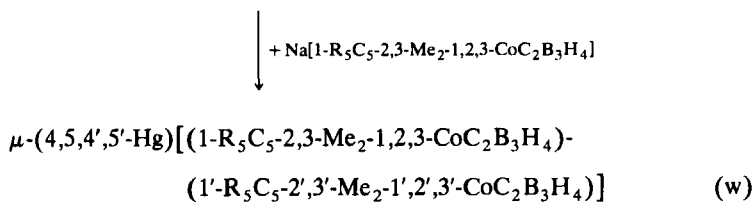
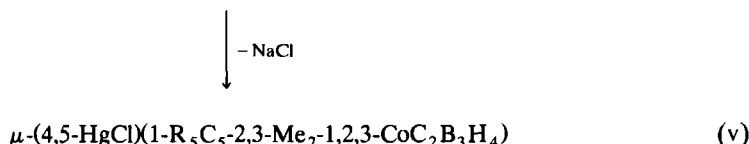
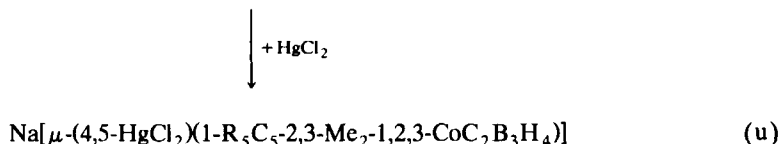
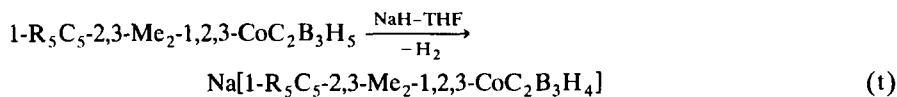


Temperatures up to RT are possible, e.g.¹¹:



Linearly coordinated Hg atoms with σ -type $B-Hg-B$ or $B-Hg-P$ bonds are characteristic of $Hg(C_2B_9pyH_{10})_2$ and the related 8- $(Ph_3PHg)(1,2-C_2B_9H_{11})$. Of more complexity are $[\mu(4,5-HgCl_2)(1-R_5C_5-2,3-Me_2-1,2,3-CoC_2B_7H_4)]^-$, μ -(4,5- $HgCl$)(1- $R_5C_5-2,3-Me_2-1,2,3-CoC_2B_3H_4$) and μ -(4,5,4',5'- Hg)-(1- $R_5C_5-2,3-Me_2-1,2,8-CoC_2B_3H_4$)(1'- $R_5C_5-2',3'\text{-}Me_2-1',2',3'\text{-}CoC_2B_3H_4$)]³² ($R = H, Me$), which consist of cobaltocarboran moieties interacting with linearly coordinated mercury atoms. The

reaction scheme for the complexation of cobaltocarborane anion with HgCl_2 is:



The carborane $\text{Hg}(\text{C}_2\text{H}_2\text{B}_{10}\text{H}_9)_2$ is reported^{33,34} reactive toward Se and Te and to give³⁵ $(\text{C}_2\text{H}_2\text{B}_{10}\text{H}_9)\text{Hg-Y-B}_{10}\text{H}_9\text{C}_2\text{H}_2$ ($\text{Y} = \text{Se}, \text{Te}$).

With SnCl_2 and MCl_3 ($\text{M} = \text{As}, \text{Sb}$), the derivatives $(\text{C}_2\text{H}_2\text{B}_{10}\text{H}_9)\text{SnCl}_2$ and $(\text{C}_2\text{H}_2\text{B}_{10}\text{H}_9)\text{MCl}_2$ are formed³³ besides $(\text{C}_2\text{H}_2\text{B}_{10}\text{H}_9)\text{HgCl}$.

(G. SCHMID)

1. G. Schmid, *Chem. Ber.*, **102**, 191 (1969).
2. K. E. Inkrott, S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 866 (1978).
3. V. T. Brice, S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 1312 (1970).
4. V. T. Brice, S. G. Shore, *J. Chem. Soc., Dalton Trans.*, 334 (1975).
5. M. A. Beckett, J. E. Crook, N. N. Greenwood, J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1427 (1984).
6. N. W. Alcock, L. Parkhill, M. G. H. Wallbridge, *Acta Crystallogr., Sect. C*, **41**, 716 (1985).
7. M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren Jr., P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968).
8. L. F. Warren Jr., M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 4823 (1968).
9. Y. Do, H. C. Kang, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.*, **26**, 2348 (1987).
10. H. C. Kang, Y. Do, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.*, **27**, 1716 (1988).
11. H. M. Colquhoun, T. J. Greenhough, M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 619 (1979).
12. H. M. Colquhoun, T. J. Greenhough, M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 1019 (1976).
13. C. P. Magee, L. G. Sneddon, D. C. Beer, R. N. Grimes, *J. Organomet. Chem.*, **86**, 159 (1975).
14. C. E. Housecroft, A. L. Rheingold, *J. Am. Chem. Soc.*, **108**, 6420 (1986).
15. C. E. Housecroft, A. L. Rheingold, *Organometallics*, **6**, 1332 (1987).
16. K. S. Harpp, C. E. Housecroft, *J. Organomet. Chem.*, **340**, 389 (1988).
17. C. E. Housecroft, M. S. Shoungwe, A. L. Rheingold, *Organometallics*, **7**, 1885 (1988).

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18. S. Wang, J. P. Fackler Jr., C. King, J. C. Wang, *J. Am. Chem. Soc.*, **110**, 3308 (1988).
 19. N. N. Greenwood, M. F. Travers, *J. Chem. Soc., A*, 15 (1968).
 20. N. N. Greenwood, M. F. Travers, *J. Chem. Soc., A*, 880 (1967).
 21. N. N. Greenwood, J. A. McGinnety, J. D. Owen, *J. Chem. Soc., Dalton Trans.*, 989 (1972).
 22. D. L. Denton, W. R. Clayton, M. Mangion, S. G. Shore, E. A. Meyers, *Inorg. Chem.*, **15**, 541 (1976).
 23. N. N. Greenwood, J. A. McGinnety, J. D. Owen, *J. Chem. Soc., A*, 809 (1971).
 24. N. N. Greenwood, N. F. Travers, *J. Chem. Soc., Chem. Commun.*, 216 (1967).
 25. N. N. Greenwood, N. F. Travers, *J. Chem. Soc., A*, 3257 (1971).
 26. N. N. Greenwood, D. N. Sharrocks, *J. Chem. Soc., A*, 2334 (1969).
 27. N. N. Greenwood, B. S. Thomas, D. W. Waite, *J. Chem. Soc., Dalton Trans.*, 299 (1975).
 28. N. N. Greenwood, J. Staves, *J. Chem. Soc., Dalton Trans.*, 1786 (1977).
 29. A. Nelson, G. Kodama, *Inorg. Chem.*, **20**, 3579 (1981).
 30. N. S. Hosmane, R. N. Grimes, *Inorg. Chem.*, **18**, 2886 (1979).
 31. H. M. Colquhoun, T. J. Greenhough, M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 737 (1977).
 32. D. C. Finster, R. N. Grimes, *Inorg. Chem.*, **20**, 863 (1981).
 33. V. I. Bregadze, V. Ts. Kampel, N. N. Godovikov, *J. Organomet. Chem.*, **157**, C1 (1978).
 34. V. I. Bregadze, A. Y. Usyatinskii, N. N. Godovikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **8**, 1903 (1983); *Chem. Abstr.*, **100**, 6730 (1984).
 35. V. I. Bregadze, V. Ts. Kampel, A. Y. Usiatinsky, O. B. Ponomareva, N. N. Godovikov, *J. Organomet. Chem.*, **233**, C33 (1982).

6.5. Formation of Group-IIIB–Transition- or –Inner Transition-Metal Bonds

6.5.1. Introduction

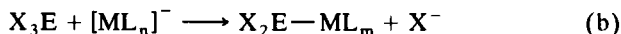
Sections 6.5.2–6.5.4 describe the most convenient synthetic pathways for preparing group IIIB–transition-element bonds, excluding the IB and IIB metals (§6.4). Three main methods can be distinguished.

1. Group-IIIB halides (§6.5.2), through interaction with neutral metal bases, lead to acid–base adducts in which the group-IIIB elements possess higher coordination numbers than before (§6.5.2.1):

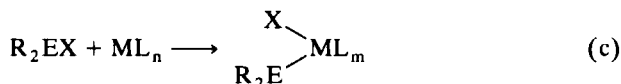


where $n \geq m$.

2. Anionic metal bases react with group-IIIB halides by eliminating halide anions, forming neutral, σ -bonded IIIB–metal compounds (§6.5.2.2):



3. Group-IIIB halides sometimes act as oxidizing agents (§6.5.2.2):



where $n \geq m$.

Interactions between non-halogen-containing IIIB compounds and transition-metal complexes are found in §6.5.3. Most of these IIIB compounds are boron-containing heterocycles. A series of interesting sandwich compounds, including triple- and tetradecapped complexes, are synthesized by methods in §6.5.2.1–6.5.3.

Metallocarboranes and metalloboranes, discussed in §6.5.4, may be prepared from metal halides and carborane anions. Selected examples of complexes formed by thermal—or otherwise—induced polyhedral rearrangements of existing metallocarboranes are given in a few equations, and some other individual compounds are listed in tables.

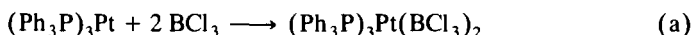
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6.5.2. Formation from Group-IIIB Halides

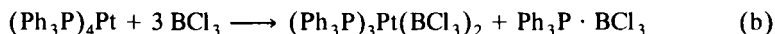
6.5.2.1. by Reaction with Neutral Metal Bases

Neutral transition-metal complexes that are not fully coordinatively saturated possess nucleophile metal centers capable of coordinating to electrophiles. On the other hand, group-IIIB halides serve as typical electron-pair acceptors and are, therefore, able to interact coordinatively with basic metal complexes.

Solid $(\text{Ph}_3\text{P})_3\text{Pt}$, e.g., reacts¹ with BCl_3 gas at 26664 N m^{-2} (200 torr):

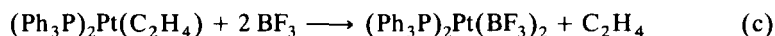


and $(\text{Ph}_3\text{P})_4\text{Pt}$ is able to dissociate one Ph_3P ligand¹:

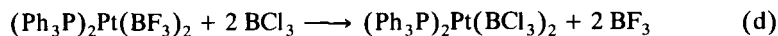


Even SiF_4 in $(\text{Ph}_3\text{P})_2\text{PtSiF}_4$ can be substituted by BCl_3 to form $(\text{Ph}_3\text{P})_2\text{PtBCl}_3$. Tensimetric titrations in benzene show¹ the same ratio of Pt complex and absorbed BCl_3 .

The use of $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$ allows easy displacement of the ethylene by two BF_3 molecules²:

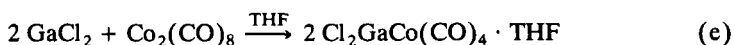


The stronger electron-pair acceptor activity of BCl_3 compared with BF_3 is demonstrated² by the quantitative displacement of BF_3 :



Reaction between $(\text{TiCl}_4)_2\text{Pt}(\text{TiCl}_4 \cdot \text{PPh}_3)_2$ and BCl_3 is similar³; BCl_3 is condensed onto the complex at -196°C . After warming to 0°C for 24 h and pumping off unreacted BCl_3 , the Pt—B compound remains.

Group-IIIB halides react with $\text{Co}_2(\text{CO})_8$ to form Ga— and In—Co bonds:



Gallium(II) chloride, “ GaCl_2 ” ($\text{Ga}[\text{GaCl}_4]$), reacts with $\text{Co}_2(\text{CO})_8$ in THF at RT to give $\text{Cl}_2\text{GaCo}(\text{CO})_4 \cdot \text{THF}$ in 60% yield⁴. Similar reactions lead to $\text{Br}_2\text{GaCo}(\text{CO})_4 \cdot \text{THF}$ and $\text{I}_2\text{GaCo}(\text{CO})_4 \cdot \text{THF}$. Since “ GaCl_2 ” probably exists as $\text{ClGa}(\text{THF})_3$ and $\text{Cl}_3\text{Ga}(\text{THF})$ in THF, the reaction sequence with $\text{Co}_2(\text{CO})_8$ is:

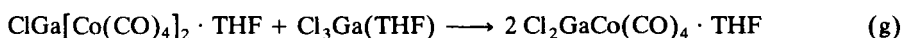
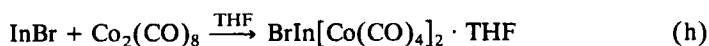


TABLE 1. BASIC SITES IN RHODIUM COMPLEXES

Complex	BF ₃	BCl ₃
[(dppe) ₂ Rh]BPh ₄	Rh	Rh
(Ph ₃ P) ₂ RhCl	Cl	Cl or Rh
(Ph ₃ P)(COD)RhCl	Rh?	PPh ₃
(Ph ₃ P) ₂ (CO)RhCl	Cl	Rh

Cobalt carbonyl complexes involving InBr form^{4,5} when InBr inserts into the Co—Co bond in Co₂(CO)₈:



In vacuum, THF can be pumped off to give the solvate-free compound. In benzene InBr and Co₂(CO)₈ form the heteronuclear cluster^{6,7}, Br₃In₃[Co(CO)₄]₄, consisting of an apical tricarbonylcobalt group interacting with the three In atoms. Each of these binds a terminal Co(CO)₄ group, whereas the Br atoms bridge the In atoms. If the insertion reaction between InBr and Co₂(CO)₈ is carried out in the presence of [Et₄N]Cl, [Br₂Co₂(CO)₈In][−] with a μ-InBr₂ group between the Co(CO)₄ units is formed⁸.

A series of Rh and Ir complexes is also basic enough to add boron halides, although the metal–boron bonds are weak, e.g., dppe and PPh₃–Rh complexes serve as electron-pair bases when they react with BF₃ and BCl₃⁹. Table 1 summarizes the results.

Both phosphine and chloride may act as basic sites in the Rh complexes. The reactions are carried out as tensimetric titrations in CH₂Br₂, CH₂Cl₂ or CHCl₃. The [(dppe)₂Rh(BCl₃)₂]BPh₄ complex is stable enough to be isolated. The BCl₃ molecules are axial in the octahedral environment of Rh. Whereas BF₃ interacts with (Ph₃P)₂(CO)RhCl via the chloride ligand, in benzene solution BCl₃ and BBr₃ use the metal site for coordination in L₂(CO)RhX(BX₃)₂ (L = PPh₃, AsPh₃; X = Cl, Br) complexes. These Rh—B bond-containing adducts are isolated in 60–95% yield¹⁰. The corresponding Ir complexes behave similarly; (Ph₃P)₂(CO)IrCl adds 1 or 2 mol of BF₃^{11,12}. The reaction is carried out as a tensimetric titration in benzene solution at 5.5°C, which leads to a break in the pressure–composition curve at BF₃:Ir = 2:1. The formation of the 1:1 complex in solution is indicated by titrations. Insertion of InCl into the Fe—Fe bond in boiling dioxane yields [η⁵-Cp(CO)₂Fe]₂InCl in 55% yield¹³. The only group-VIIA compound that forms an addition compound with a group-IIIB halide, namely with BF₃, is [(η⁵-Cp)₂ReH]¹⁴. The formation of (η⁵-Cp)₂ReH · BF₃ is established when (η⁵-Cp)₂ReH is titrated tensimetrically in toluene with BF₃ at 0°C.

Examples of BX₃–group-VIA element adducts include (η⁵-Cp)₂MoH₂, which adds BF₃, and (η⁵-Cp)₂WH₂, which adds BF₃ as well as BCl₃^{14,15}. A tensimetric titration of BF₃ with (η⁵-Cp)₂MoH₂ in toluene indicates a 1:1 adduct, and (η⁵-Cp)₂WH₂ reacts with BF₃ gas both in the solid state (33.6°C, 3 d) and in toluene solution, whereby (η⁵-Cp)₂WH₂ · BF₃ precipitates immediately. Similarly, if a (η⁵-

$(\text{Cp})_2\text{WH}_2$ solution in toluene is allowed to react with BCl_3 at 0°C , the 1:1 adduct forms immediately.

The ylide complexes $\text{Ph}_3\text{PC}_5\text{H}_4\text{M}(\text{CO})_3$ ($\text{M} = \text{Mo}, \text{W}$) are also able¹⁶ to add BF_3 . Solutions of these complexes in CH_2Cl_2 can be titrated tensimetrically with BF_3 at 0°C and -78°C . The titration curves suggest that the reactions between the metal complexes and BF_3 are reversible. The red adducts are air stable.

Vinyldimethylaminobromborane acts as a butadiene-analogous 4π -electron donor in $[\text{H}_2\text{C}=\text{CH}-\text{B}(\text{Br})-\text{NMe}_2]\text{Fe}(\text{CO})_3$ and is formed from the neutral ligand and $\text{Fe}_2(\text{CO})_9$ in diethylether¹⁷.

(G. SCHMID)

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6.5.2.2. by Reaction with Anionic Metal Bases

This reaction is a principal method of forming IIIB–transition-metal σ bonds. The formation of thermodynamically favored alkali-metal halides or related salts and acids HX enhances the easy formation of those bonds. A second possible interaction between anionic metal bases and group-IIIB halides is a simple acid–base relationship without elimination of halide anions. However examples of this are rare, and they have been described often for group-IIIB compounds without halogen ligands (§6.5.3.2).

Carbonyl chemistry provides the most common anionic transition-metal compounds.

Cobalt is one of the favored transition metals to form bonds with group-IIIB elements. Besides B, the heavier elements give especially stable bonds to Co.

The well-known complex, bis(dimethylglyoximate)triphenylphosphinecobalt(III)chloride¹ reacts with metallic potassium to give $\text{K}[\text{Ph}_3\text{P}(\text{DMG})_2\text{Co}]^2$. This complex reacts with Ph_2BCl to substitute the hydrogen in the $\text{O}-\text{H}-\text{O}$ bridges by Ph_2B groups and form $(\text{Ph}_3\text{P}(\text{DMG}-\text{BPh}_2)_2\text{Co})$. Repeated reaction with K fol-

6.5. Group-IIIB–Transition- or –Inner Transition-Metal Bonds

23

6.5.2. Formation from Group-IIIB Halides

6.5.2.2. by Reaction with Anionic Metal Bases

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6.5.2.2. by Reaction with Anionic Metal Bases

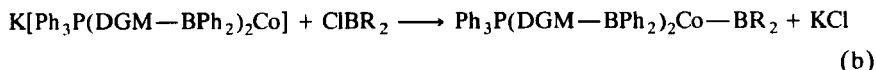
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lowed by addition of further boron halide leads to the corresponding Co—B compounds³:

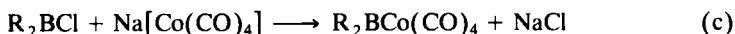


where R_2BCl may be Ph_2BCl ; 9-Cl-9-borafluorene; $(\text{Me}_2\text{N})_2\text{BCl}$ or BCl_3 itself. The reactions are best done in THF and give the complexes in 60–90% yield.

Replacement of the bridging hydrogens in the cobalt glyoximate complex also occurs^{3,4} on reaction with Bu_3B in boiling THF. The $\text{Ph}_3\text{P}(\text{DGM}-\text{BBu}_2)_2\text{CoCl}$ product reacts like the analogous BPh_2 compound with K in THF to form $\text{K}[\text{Ph}_3\text{P}(\text{DGM}-\text{BBu}_2)_2\text{Co}]$. Elimination of KCl occurs when Ph_2BCl is added and $\text{Ph}_3\text{P}(\text{DGM}-\text{BBu}_2)\text{CoBPh}_2$ is isolated in 85% yield³.

Use of Ph_3As as ligand instead of PPh_3 results in formation of $(\text{Ph}_3\text{As})(\text{DGM}-\text{BPh}_2)_2\text{CoBPh}_2$ in 30% yield; py complexes are not suitable for preparing the related Co—B compounds³.

The $[(\text{CO})_4\text{Co}]^-$ anion reacts with halides of group-IIIB elements, e.g.:



where $\text{R} = \text{Ph}, \text{Me}_2\text{N}, \text{Cl}$.

Phosphine-substituted carbonylates lead to a stabilization of the very sensitive B—Co bond⁵.

The transiently stable $2-[\text{Co}(\text{CO})_4]\text{B}_5\text{H}_8$ is given⁶ from $\text{Na}[(\text{CO})_4\text{Co}]$ and $2-\text{XB}_5\text{H}_8$ ($\text{X} = \text{Cl}, \text{Br}$).

A boron-containing Co cluster is formed by reacting Et_3NBBR_3 with $\text{Ti}[(\text{CO})_4\text{Co}]$ in benzene at RT ⁷:

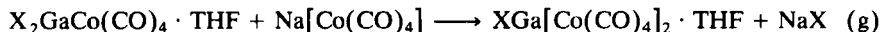
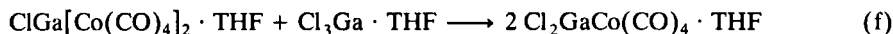


The B atom becomes part of a tetrahedral cluster.

The In—Co compound $\text{In}[\text{Co}(\text{CO})_4]_3$ can be prepared by reacting $\text{Ti}[(\text{CO})_4\text{Co}]$ ⁸ or $\text{Na}[(\text{CO})_4\text{Co}]$ ⁹ with InCl_3 in THF. The covalently bonded $\text{Co}(\text{CO})_4$ groups coordinate the central In atom in a trigonal-planar manner¹⁰. The homolog Ti complex $\text{Ti}[(\text{CO})_4\text{Co}]_3$ is prepared the same way⁹. An additional CO—In and Co—Ti bond results when the neutral compounds $\text{M}[\text{Co}(\text{CO})_4]_3$ ($\text{M} = \text{In}, \text{Ti}$) react with $[\text{Ph}_4\text{As}][\text{Co}(\text{CO})_4]$ in CH_2Cl_2 -heptane; $\text{In}[\text{Co}(\text{CO})_4]_3$ is used in 10% and $\text{Ti}[(\text{CO})_4\text{Co}]_3$ in 100% xs¹¹, e.g.⁹:



where $\text{M} = \text{Ga}, \text{In}$;



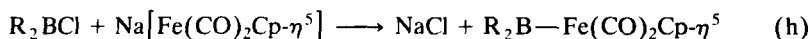
where $\text{X} = \text{Cl}, \text{Br}$. In a few examples the interaction of anionic cobalt species with group-IIIB halides does not involve chloride abstraction and only addition occurs; e.g., $[(\text{Ph}_3\text{P})_2\text{N}]^+[(\text{CO})_4\text{Co}]^-$ adds GaBr_3 and InBr_3 to form the complex ions

6.5.2. Formation from Group-IIIB Halides

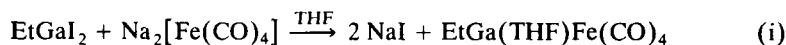
6.5.2.2. by Reaction with Anionic Metal Bases

$[(\text{CO})_4\text{CoGaBr}_3]^-$ and $[(\text{CO})_4\text{CoInBr}_3]^-$, respectively, by reaction of the components in CH_2Cl_2 of 30 min¹².

Iron–group-IIIB bonds are formed from anionic Fe compounds and group-IIIB halides; e.g., $\text{R}_2\text{BFe}(\text{CO})_2\text{Cp-}\eta^5$ can be prepared from R_2BCl and $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp-}\eta^5]$ ¹³.



where $\text{R} = \text{Cl}, \text{Ph}, \text{NMe}_2$. The Ga—Fe σ bonds are obtained^{14,15} by reacting $[\text{Fe}(\text{CO})_4]^{2-}$ with EtGaI_2 in THF:

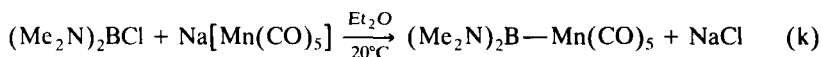


2,2-Bipyridine or pyridine may also coordinate the Ga instead of THF. The reaction between $[\text{Fe}(\text{CO})_4]^{2-}$ and the group-IIIB bromides proceeds readily in THF. The anion is generated as the Na salt [from Na amalgam and $\text{Fe}_3(\text{CO})_{12}$] or, alternatively, from $[\text{HFe}(\text{CO})_4]^-$ in CH_2Cl_2 . The best yields of $[\text{Fe}(\text{CO})_4\text{GaBr}_3]^{2-}$ and $[\text{Fe}(\text{CO})_4\text{InBr}_3]^{2-}$ are obtained¹² with a twofold xs of $[\text{HFe}(\text{CO})_4]^-$:



where $\text{E} = \text{Ga}, \text{In}$.

The first boron–metal σ bond to be discovered is in $(\text{Me}_2\text{N})_2\text{BMn}(\text{CO})_5$ ¹³:



This reaction is used with different boron halides and manganese carbonyl derivatives in Et_2O at RT to yield B—Mn compounds (Table 1).

The heavy group-IIIB elements Ga, In and Tl also form covalent bonds to Mn via halide abstraction from corresponding MX_3 derivatives, e.g., $[\mu\text{-GaMn}(\text{CO})_5]_2\text{-Mn}_2(\text{CO})_8$ ¹⁸, $\text{In}[\text{Mn}(\text{CO})_5]_3$ ¹⁹, $\text{XIn}[\text{Mn}(\text{CO})_5]_2$ ¹⁹, $\text{X}_2\text{InMn}(\text{CO})_5$ ¹⁹, $\text{Ph}_2\text{TlMn}(\text{CO})_5$ ²⁰, $\text{ClTl}[\text{Mn}(\text{CO})_5]_2$ ²⁰ and $\text{Tl}[\text{Mn}(\text{CO})_5]_3$ ^{21,22}. The B—Re compound $(\text{Me}_2\text{N})_2\text{BRe}(\text{CO})_5$ is synthesized by metathesis of $\text{Na}[\text{Re}(\text{CO})_5]$ and $(\text{Me}_2\text{N})_2\text{BCl}$ ²³.

TABLE 1. BORON–MANGANESE COMPOUNDS OF THE TYPE $\text{R}_2\text{BMn}(\text{CO})_4\text{L}$ AND $\text{RB}[\text{Mn}(\text{CO})_4\text{L}]_2$

$\text{R}_2\text{BX}, \text{RBX}_2$	$[\text{Mn}(\text{CO})_4\text{L}]^-$	Product	Yield (%)	Refs.
$(\text{Me}_2\text{N})_2\text{BCl}$	$[\text{Mn}(\text{CO})_5]^-$	$(\text{Me}_2\text{N})_2\text{BMn}(\text{CO})_5$	75	13, 16
$(\text{Me}_2\text{N})_2\text{BCl}$	$[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$	$(\text{Me}_2\text{N})_2\text{BMn}(\text{CO})_4\text{PPh}_3$	70–80	16
Ph_2BCl	$[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$	$\text{Ph}_2\text{BMn}(\text{CO})_4\text{PPh}_3$	60	17
$\text{C}_{12}\text{H}_8\text{BCl}^a$	$[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$	$\text{C}_{12}\text{H}_8\text{BMn}(\text{CO})_4\text{PPh}_3$	52	17
$n\text{-Bu}_2\text{BCl}$	$[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$	$\text{Bu}_2\text{BMn}(\text{CO})_4\text{PPh}_3$	33	17
BCl_3	$[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$	$\text{Cl}_2\text{BMn}(\text{CO})_4\text{PPh}_3$	60	17
Et_2NBCl_2	$[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$	$\text{ClB}[\text{Mn}(\text{CO})_4\text{PPh}_3]_2$	66	17

^a 9-Chlorine-9-borafluorene.

The conjugate acid of $[\text{Mn}(\text{CO})_5]^-$; $\text{HMn}(\text{CO})_5$, protonates B_5H_9 to give 2,2,2-(CO)₃-2-MnB₅H₁₀ that contains two Mn—H—B bonds as well as a direct Mn—B bond between the apical boron atom and manganese²⁴.

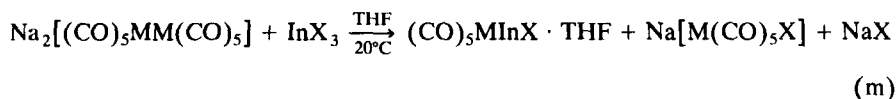
If an aqueous solution of $\text{InCl}_3 \cdot 3 \text{H}_2\text{O}$ is reacted with 1 equiv of solid $\text{Na}[(\text{CO})_5\text{Re}]$ in an atmosphere of CO, $[(\text{CO})_5\text{Re}]_3\text{In}$ precipitates in 86% yield²⁵.

Group-VIA and -IIIB bonds are limited to a few examples; e.g., $\text{R}_2\text{BM}(\text{CO})_3\text{Cp-}\eta^5$ compounds are prepared²⁶:



where R = Ph, Cl; M = Mo, W. Either Et₂O or THF serves as solvent and the yields are not higher than 30%.

A Cr—B bond is not realized by that pathway; however, a Cr—In bond forms when $\text{Na}_2[(\text{CO})_5\text{CrCr}(\text{CO})_5]$ reacts with InX_3 and analogous reactions are also known for the Mo and W derivatives²⁷:



where M = Cr, Mo; X = Cl, Br, I. The structure of the Cr complex (X = Br) has the THF coordinated to In, the latter occupying an octahedral position in the metal-coordination sphere to give a coordination polymer as the In atom is additionally interacting with two bromide ligands of neighboring molecules.

Metathesis between $\text{Na}[\eta^5\text{-Cp}(\text{CO})_3\text{Mo}]$ and InCl_3 in THF in a 3:1 molar ratio affords $[\eta^5\text{-Cp}(\text{CO})_3\text{Mo}]_3\text{In}$ in 94% yield²⁵. When the ratio is changed to 2:1 and InBr_3 used instead of InCl_3 , $[\eta^5\text{-Cp}(\text{CO})_3\text{Mo}]_2\text{InBr}$ is isolated²⁵ in 80% yield. Similarly, the 1:1 molar mixture of InCl_3 and $\text{Na}[\eta^5\text{-Cp}(\text{CO})_3\text{M}]$ yields²⁵ $\eta^5\text{-Cp}(\text{CO})_3\text{MoInCl}_2$.

Finally, in some In and Tl complexes the group-IIIB element is coordinated to very special ligands. $(\text{TPP})\text{InCo}(\text{CO})_4$ and $(\text{TPP})\text{InMn}(\text{CO})_5$ may be prepared from $(\text{TPP})\text{InCl}$ and $\text{Na}[\text{Co}(\text{CO})_4]$ and $\text{Na}[\text{Mn}(\text{CO})_5]$, respectively²⁸; $(\text{oep})\text{InCo}(\text{CO})_4$, $(\text{oep})\text{InMn}(\text{CO})_5$ and $(\text{oep})\text{InM}(\text{CO})_3\text{Cp-}\eta^5$ (M = Cr, Mo, W; oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato) are prepared similarly from $(\text{oep})\text{InCl}$ and the metalates²⁹. The corresponding $(\text{oep})\text{Tl}$ complexes are also known³⁰.

(G. SCHMID)

1. L. Tschugaeff, *Ber. Dtsch. Chem. Ges.*, **40**, 3498 (1907).
2. G. N. Schrauzer, J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964).
3. G. Schmid, P. Powell, H. Nöth, *Chem. Ber.*, **101**, 1205 (1968).
4. G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962).
5. G. Schmid, *Angew. Chem., Int. Ed. Engl.*, **9**, 819 (1970).
6. M. B. Fischer, D. F. Gaines, J. A. Ulman, *J. Organomet. Chem.*, **231**, 55 (1982).
7. G. Schmid, V. Bätzel, G. Etzrodt, R. Pfeil, *J. Organomet. Chem.*, **86**, 257 (1975).
8. S. E. Pedersen, W. R. Robinson, D. P. Schussler, *J. Organomet. Chem.*, **4**, C44 (1972).
9. D. J. Patmore, W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966).
10. W. R. Robinson, D. P. Schussler, *Inorg. Chem.*, **12**, 848 (1973).
11. W. R. Robinson, D. P. Schussler, *J. Organomet. Chem.*, **30**, C5 (1971).
12. J. K. Ruff, *Inorg. Chem.*, **7**, 1499 (1968).
13. H. Nöth, G. Schmid, *Angew. Chem.*, **75**, 861 (1963).
14. T. H. Cymbaluk, R. D. Ernst, *Inorg. Chem.*, **19**, 2381 (1980).

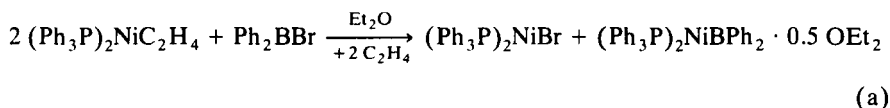
6.5.2. Formation from Group-IIIB Halides

6.5.2.3. by Oxidative-Addition Reactions

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17. H. Nöth, G. Schmid, *Z. Anorg. Allg. Chem.*, **345**, 69 (1966).
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21. H. J. Haupt, F. Neumann, *J. Organomet. Chem.*, **33**, C56 (1971).
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27. H. Behrens, M. Moll, E. Sixtus, G. Thiele, *Z. Naturforsch., Teil B*, **32**, 1109 (1977).
28. S. Onaka, Y. Kondo, M. Yamashita, Y. Tatematsu, Y. Kato, M. Goto, T. Ito, *Inorg. Chem.*, **24**, 1070 (1985).
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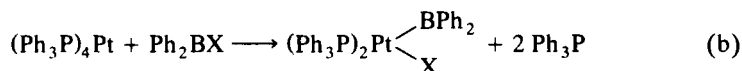
6.5.2.3. by Oxidative-Addition Reactions

Oxidative additions occur of complexes when metals in low oxidation states (0, 1 +) are used to add AB compounds with rupture of the A—B bond. The addition of the new ligands A and B can take place to one or in some cases two metal centers, e.g.:



The stoichiometry product does not agree with that used in the experiment, as Ni and B compounds are mixed in diethylether in a 1 : 1 mole ratio. The $(\text{Ph}_3\text{P})_2\text{NiBPh}_2 \cdot 0.5 \text{OEt}_2$ product is a dimer with a Ni—B—Ni multicentered bond¹.

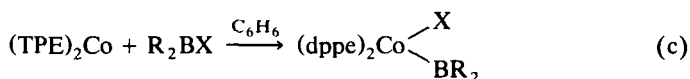
In §6.5.2.1 it is shown that BF_3 and BCl_3 add to phosphine Pt complexes without cleaving the B—X bond. In contrast, aryl and alkyl boron halides are added oxidatively with phosphine Pt complexes^{2,3}:



where X = Cl, Br. Tetrakis(triphenylphosphine)platinum(0) is dissolved in cyclohexane at 70°C and the diphenylboron halides are added.

Reaction between $(\text{Ph}_3\text{P})_4\text{Pt}$ and Me_2BBr follows a different path since a 1 : 2 stoichiometry is observed. The 6-coordinate Pt(IV) derivative $(\text{Ph}_3\text{P})_2\text{Pt}(\text{BMe}_2)_2\text{Br}$ is formed².

Classical oxidative addition is observed³ when $(\text{dppe})_2\text{Co}$ reacts with R_2BX :



6.5. Group-III B–Transition- or –Inner Transition-Metal Bonds

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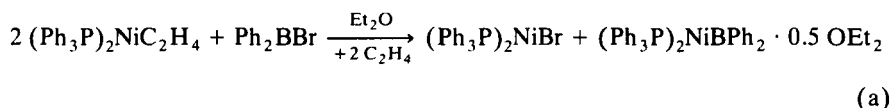
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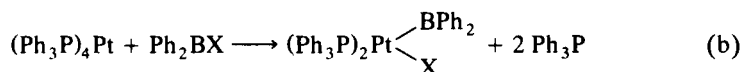
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Classical oxidative addition is observed³ when $(\text{dppe})_2\text{Co}$ reacts with R_2BX :

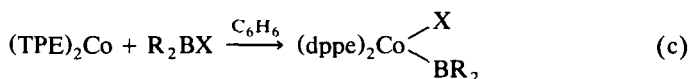
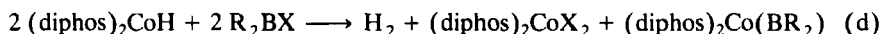


TABLE 1. BORON-COBALT COMPOUNDS BY OXIDATIVE ADDITION REACTIONS

(diphos) ₂ CoH	R ₂ BX	Product	Yield (%)	Refs.
(dppe) ₂ CoH	Ph ₂ BCl	(dppe) ₂ Co(BPh ₂) ₂	94	4,5
(dppe) ₂ CoH	C ₁₂ H ₈ BCl	(dppe) ₂ Co(BC ₁₂ H ₈) ₂	79	5
(dppe) ₂ CoH	PhBCl ₂	(dppe) ₂ Co(BPhCl) ₂	90-100	5
(dppe) ₂ CoH	BBr ₃	(dppe) ₂ Co(BBr ₂) ₂	85	6
(dppe) ₂ CoH	BI ₃	(dppe) ₂ Co(BI ₂) ₂	90	6
(dmpb) ₂ CoH	Ph ₂ BCl	(dmpb) ₂ Co(BPh) ₂	89	5
(dmpb) ₂ CoH	C ₁₂ H ₈ BCl	(dmpb) ₂ Co(BC ₁₂ H ₈) ₂	100	5

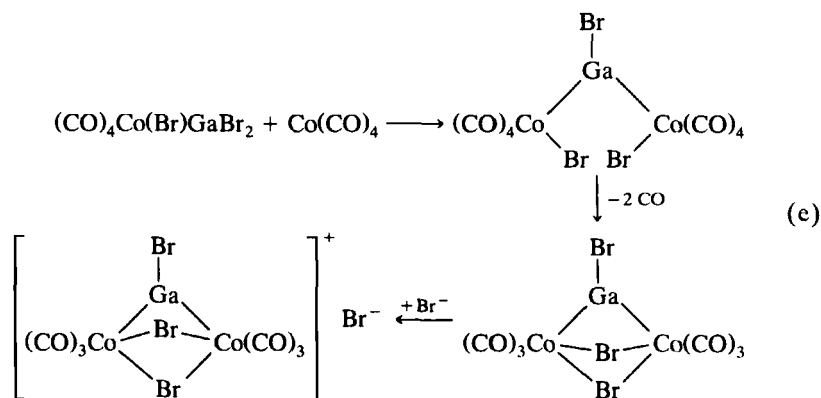
where R = Ph, Cl, Br. The 4-coordinated Co(0) in (dppe)₂Co turns to 6-coordinated Co(II) having a Co—B σ bond.

A special kind of oxidative addition occurs between phosphine cobalt hydride complexes and boron halides⁴⁻⁶:



The five-coordinated Co(I) in (diphos)₂CoH is additively oxidized to 6-coordinated Co(II) with loss of hydrogen. These reactions, normally carried out in aromatic solvents, yield the compounds listed in Table 1.

Boron and aluminum halides react with Co₂(CO)₈ by addition of the electron pair acceptor to the oxygen atom of a bridging CO group⁷⁻⁹. Another kind of behavior is observed with GaBr₃ and InBr₃; reactions with Co₂(CO)₈ in benzene at RT lead to the light green complexes GaCo₂Br₄(CO)₆ and InCo₂Br₄(CO)₆¹⁰:

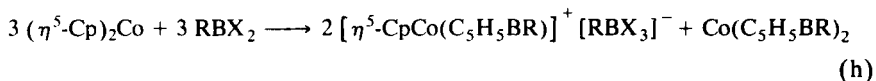
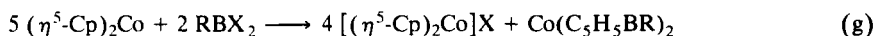
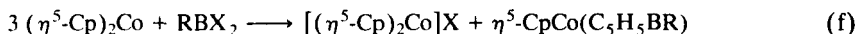


A special type of oxidative addition takes place between cobaltocene and boron halides (MeBBr₂, PhBCl₂, BCl₃, BBr₃)¹¹⁻¹⁴. Treatment of cobaltocene in hexane or

6.5.3. Formation from Other Group-IIIB Compounds

6.5.3.1. by Reaction with Neutral Metal Bases

toluene with organoboron dihalides at -80 to -20°C leads to:



Cobaltocene is partially oxidized and in part undergoes insertion of a borylene group, RB. The borinato ligands derive from the unknown borabenzene (§6.5.3.4). Some porphyrinatoindium and thallium complexes (§6.5.2.2) can also be synthesized via oxidative addition reactions; (TPP)InCl is added oxidatively to $\text{Co}_2(\text{CO})_8$ and $\text{Mn}_2(\text{CO})_{10}$ to give (TPP)In—Co(CO)₄ and (TPP)In—Mn(CO)₅, respectively^{14,15}, and (oep)InCl is added to $\text{Co}_2(\text{CO})_8$ to yield (oep)In—Co(CO)₄.

(G. SCHMID)

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3. G. Schmid, W. Petz, W. Arloth, H. Nöth, *Angew. Chem., Int. Ed. Engl.*, **6**, 696 (1967).
4. G. Schmid, H. Nöth, *Z. Naturforsch., Teil B.*, **20**, 1008 (1965).
5. G. Schmid, H. Nöth, *Chem. Ber.*, **100**, 2899 (1967).
6. G. Schmid, *Chem. Ber.*, **102**, 191 (1969).
7. G. Schmid, V. Bätzel, *J. Organomet. Chem.*, **46**, 149 (1972).
8. J. S. Kristoff, N. J. Nelson, D. F. Shriver, *J. Organomet. Chem.*, **49**, C82 (1973).
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11. G. E. Herberich, G. Greiss, H. F. Heil, *Angew. Chem., Int. Ed. Engl.*, **9**, 805 (1970).
12. G. E. Herberich, G. Griess, H. F. Heil, *J. Chem. Soc., Chem. Commun.*, 1328 (1971).
13. G. E. Herberich, G. Greiss, *Chem. Ber.*, **105**, 3413 (1972).
14. S. Onaka, Y. Kondo, M. Yamashita, Y. Tatematsu, Y. Kato, M. Goto, T. Ito, *Inorg. Chem.*, **24**, 1070 (1985).
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6.5.3. Formation from Other Group-IIIB Compounds

Compounds with trivalent group-IIIB elements are electron-pair acceptors from the electron deficiency of the group-IIIB element. In many cases the substituents of the group-IIIB element have backbonding character and give rise to further decrease of the electron deficiency. Even if the ligands possess typical donor capacities, e.g., R_2N , OR, SR, there remains a significant acceptor power on the group-IIIB element. For that reason many group-IIIB compounds may interact with basic metal centers in transition-metal moieties. Noncyclic compounds as well as numerous heterocycles, especially with boron, lead to group-IIIB–transition-metal complexes.

(G. SCHMID)

6.5.3.1. by Reaction with Neutral Metal Bases

The B atoms in the mono- and diaminoboranes $(\text{R}_2\text{N})_2\text{BR}'$ and $\text{R}_2\text{NBR}'_2$ show only moderate functions. Therefore, boron–metal interactions are relatively weak.

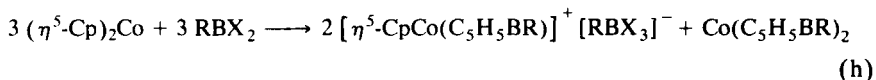
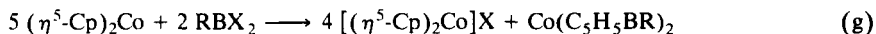
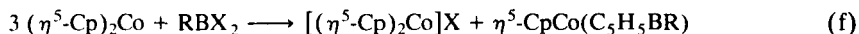
6.5. Group-IIIB–Transition- or –Inner Transition-Metal Bonds

29

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8. J. S. Kristoff, N. J. Nelson, D. F. Shriver, *J. Organomet. Chem.*, **49**, C82 (1973).
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10. G. Schmid, V. Bätzel, *J. Organomet. Chem.*, **81**, 321 (1974).
11. G. E. Herberich, G. Greiss, H. F. Heil, *Angew. Chem., Int. Ed. Engl.*, **9**, 805 (1970).
12. G. E. Herberich, G. Griess, H. F. Heil, *J. Chem. Soc., Chem. Commun.*, 1328 (1971).
13. G. E. Herberich, G. Greiss, *Chem. Ber.*, **105**, 3413 (1972).
14. S. Onaka, Y. Kondo, M. Yamashita, Y. Tatematsu, Y. Kato, M. Goto, T. Ito, *Inorg. Chem.*, **24**, 1070 (1985).
15. R. Guillard, P. Mitaine, C. Moise, C. Lecomte, A. Boukhris, C. Swistak, A. Tabard, D. Lacombe, J.-L. Cornillon, K. M. Kadish, *Inorg. Chem.*, **26**, 2467 (1987).

6.5.3. Formation from Other Group-IIIB Compounds

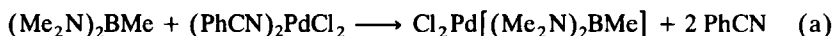
Compounds with trivalent group-IIIB elements are electron-pair acceptors from the electron deficiency of the group-IIIB element. In many cases the substituents of the group-IIIB element have backbonding character and give rise to further decrease of the electron deficiency. Even if the ligands possess typical donor capacities, e.g., R_2N , OR, SR, there remains a significant acceptor power on the group-IIIB element. For that reason many group-IIIB compounds may interact with basic metal centers in transition-metal moieties. Noncyclic compounds as well as numerous heterocycles, especially with boron, lead to group-IIIB–transition-metal complexes.

(G. SCHMID)

6.5.3.1. by Reaction with Neutral Metal Bases

The B atoms in the mono- and diaminoboranes $(\text{R}_2\text{N})_2\text{BR}'$ and $\text{R}_2\text{NBR}'_2$ show only moderate functions. Therefore, boron–metal interactions are relatively weak.

The complete interactions are based on the donor and acceptor qualities of the B—N compounds. In solution $(\text{PhCN})_2\text{PdCl}_2$ enables¹ addition of $(\text{Me}_2\text{N})_2\text{BMe}$:



The reaction takes place in an excess of the liquid aminoborane as solvent.

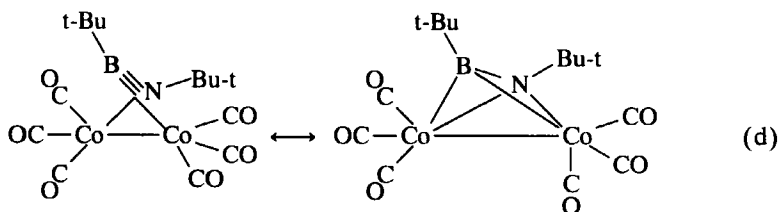
A corresponding reaction is observed² when $\text{bis}(\eta^3\text{-allyl})\text{Ni}$ reacts with the monoaminoborane $\text{Me}_2\text{N—BMe}_2$. The $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$ compound, dissolved in the liquid aminoborane, slowly decomposes at RT with loss of one allyl group which is then substituted by two Me_2NBMe_2 ligands: the red, liquid and air-sensitive product is volatile and is isolated in less than 1% yield.

In one compound² iron carbonyl moieties serve as electron donors to the B of a simple aminoborane, whereas the N atoms have donor functions to Fe:

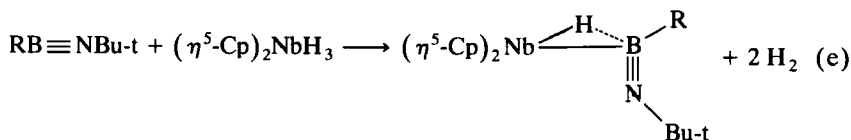


Bis(dimethylamino)methylborane thus acts as a four-electron donor. The reaction takes place in dioxane at RT and the red, crystalline complex is sublimable at 10^{-4} torr/20°C in 2–4% yield.

The finding of preparatively available iminoboranes $\text{RB}\equiv\text{NR}'$ some years ago opened exciting new possibilities not only in B—N chemistry, but also in coordination chemistry. The first examples of iminoborane–transition-metal complexes have now been published. The structurally completely characterized³ $\text{t-BuB}\equiv\text{NBu-t}$ adds, like its alkyne analog, to the $\text{Co}_2(\text{CO})_6$ fragment as a bridging ligand⁴. When $\text{Co}_2(\text{CO})_8$ and $\text{t-BuB}\equiv\text{NBu-t}$ are dissolved in pentane at 0°C, warming to RT and evaporation of unreacted iminoborane yields $(\text{t-BuBNBu-t})\text{Co}_2(\text{CO})_6$ (86%) as a black solid, which can be recrystallized from ether–nitromethane (1 : 3):



Niobium and zirconium are also appropriate transition metals to coordinate iminoboranes side on; $(\eta^5\text{-Cp})_2\text{NbH}_3$ and $\text{RB}\equiv\text{NBu-t}$ [$\text{R} = \text{t-Bu}, \text{Me}_3\text{Si}(\text{t-Bu})\text{N}$] react with the loss of two hydrogen atoms. The remaining H atom probably interacts additionally with the boron atom⁵:



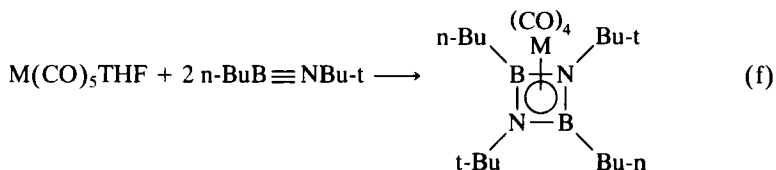
The complexes are formed with 68% ($\text{R} = \text{t-Bu}$) and 73% [$\text{R} = \text{Me}_3\text{Si}(\text{t-Bu})\text{N}$] yield in warm (85°C) toluene in the course of 90 min. Surprisingly, the B—N distance is extended only a little ($\sim 0.03 \text{ \AA}$), compared with the free iminoborane. In contrast to this side-on coordinated iminoborane, the zirconium complex $(\eta^5\text{-Cp})_2\text{ZrCl}(\text{H})$

6.5.3. Formation from Other Group-III B Compounds

6.5.3.1. by Reaction with Neutral Metal Bases

[*t*-BuN≡B(TMP)] shows the iminoborane only interacting via the N atom and is therefore better described as a N-metallated aminoborane⁶.

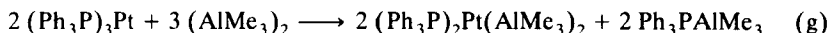
Some iminoboranes dimerize during reaction with a transition-metal complex to diazadiboretidines. These four-membered rings then act as four-electron donors in different complexes⁷:



where M = Cr, W. The M(CO)₅(THF) [from M(CO)₆ in THF by UV irradiation] and the iminoborane react in THF solution to the crystalline complexes in 72% (Cr) and 64% (W) yield. The same complexes are available if the diazadiboretidine rings, formed by dimerization of the iminoboranes under the catalytic influence of *t*-BuNC, are reacted with the carbonyl compounds.

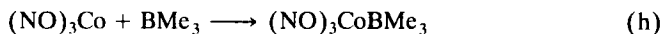
A 1 : 1 complex also forms with TiCl₄ and with diazadiboretidine [PrBNBU-*t*]₂ in pentane⁸. The lack of Ti—B bonds is shown by the x-ray analysis, they are weak but important B ⋯ Cl interactions.

Trimethylaluminum is an adequate enough electron-pair acceptor to react⁹ with (Ph₃P)₃Pt if the latter is exposed to (Me₃Al)₂ (g or l) over 6 d:



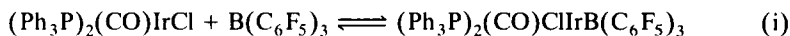
During the reaction the color of the platinum complex changes from yellow to pale orange. Excess (AlMe₃)₂ can be removed under reduced pressure.

Trinitrosyl cobalt behaves as a base when it reacts¹⁰ with BMe₃:



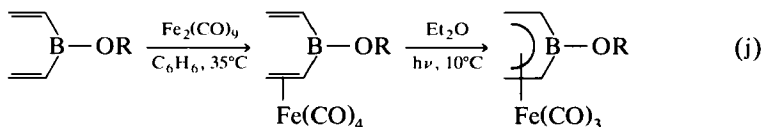
The adduct is formed exothermically in benzene. The relative stabilities show (NO)₃Co to be a stronger base than NH₃ or Me₃N.

Spectroscopic titration of (Ph₃P)₂(CO)IrCl with B(C₆F₅)₃ shows a weak affinity between the two compounds leading to an equilibrium¹⁰:



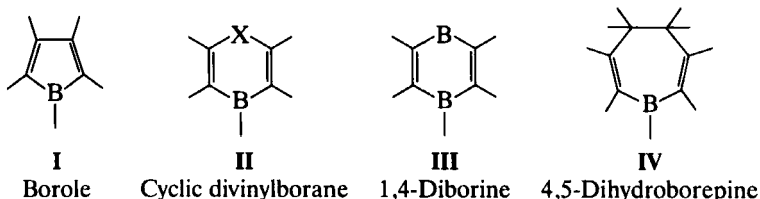
The analogous PEt₂Ph derivative may also be used, but (AlMe₃)₂ and Me₃Ga are unable to form donor-acceptor complexes with iridium.

Divinyl boranes (CH₂=CH)₂BR react with metal carbonyls, e.g.^{11,12}:

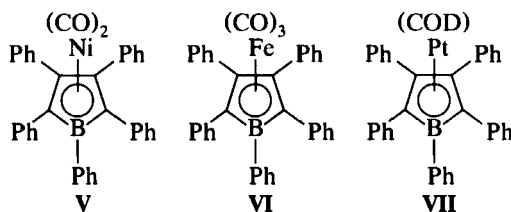


Further examples are¹³ (CO)₃Ru[η⁵-(C₂H₃)₂BCl], (η⁵-Me₅C₅)Rh[η⁵-(C₂H₃)₂-BOMe], [(η⁵-Me₅C₅)Rh]₂(C₂H₃B—O—BC₂H₃) and (η⁵-Me₅C₅)Rh[(C₂H₃-η⁵)₂BR] (R = Me, Ph).

Boron in heterocycles is an electron acceptor, and the following neutral carbocycles form transition-metal complexes via basic metal centers:



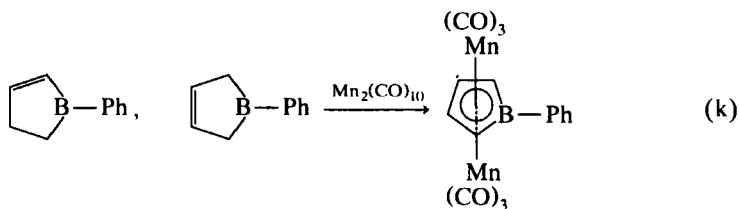
Pentaphenylborole reacts with $\text{Pt}(\text{COD})_2$, $\text{Ni}(\text{CO})_4$ and $\text{Fe}_2(\text{CO})_9$ to form stable pentaphenylborole-transition-metal complexes^{14,15}:



Pentaphenylborole-tricarbonyliron, e.g., is prepared from $\text{Fe}_2(\text{CO})_9$ and the borole in toluene at 45–50°C. Chromatography on Al_2O_3 yields the complex as yellow light- and air-sensitive crystals¹⁴.

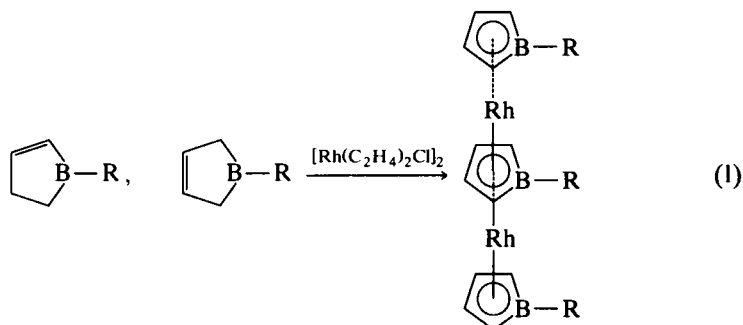
The triple-decked $\eta^5\text{-CpFe}(\text{PhBC}_4\text{H}_3\text{Et})\text{FeCp-}\eta^5$ complex is formed from 1-phenyl-4,5-dihydroborepine and $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ by thermal reaction; the borabenzene derivative $\eta^5\text{-CpFe}(\text{PhBC}_5\text{H}_4\text{Me})$ also forms¹⁶. With $\text{Mn}_2(\text{CO})_{10}$ 1-phenyl-4,5-dihydroborepine yields the triple-decker complex¹⁶ $(\text{CO})_3\text{Mn}(\text{PhBC}_4\text{H}_3\text{Et})\text{Mn}(\text{CO})_3$. The borole complexes described so far are available using stable boroles as reactants. But borole molecules can also be generated from precursors in the course of complexation.

The reaction of 2- and 3-borolenes $\text{C}_4\text{H}_6\text{BR}$ ($\text{R} = \text{Ph}, \text{Me}, \text{C}_6\text{H}_{11}, \text{OMe}$) with Co, Fe and Mn carbonyls leads, under dehydrogenation of the borolenes, to η^5 -borole complexes¹⁷. 2-Borolene and 3-borolene also react with $\text{Mn}_2(\text{CO})_{10}$ at 160°C to a red-brown triple-decked complex:

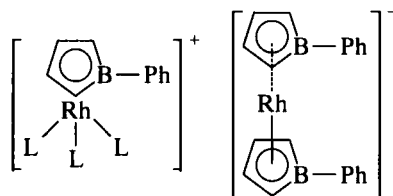


The mononuclear complex $(\text{CO})_3\text{Mn}(\text{PhC}_5\text{H}_4\text{-}\eta^5)$ is found as a by-product. When heated, $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$ react with the two phenylborolenes to give $(\text{CO})_3\text{Fe}(\text{C}_4\text{H}_4\text{BPh-}\eta^5)$. Using $\text{Fe}(\text{CO})_5$, the different substituted borolenes all form the corresponding $(\text{CO})_3\text{Fe}(\text{C}_4\text{H}_4\text{BR})$ complex under photolysis. Moreover, $\text{Co}_2(\text{CO})_8$, $2\text{-C}_4\text{H}_6\text{BPh}$, $2\text{-C}_4\text{H}_6\text{BMe}$ and $3\text{-C}_4\text{H}_6\text{BPh}$ form the dinuclear system $(\text{C}_4\text{H}_4\text{BR})_2\text{Co}_2(\text{CO})_4$ with two bridging Co groups.

A dehydrogenating complexation of the 2- and 3-borolenes C_4H_6BR ($R = Me, Ph$) also occurs¹⁸ with $[Rh(\eta^2-C_2H_4)_2Cl]_2$, forming a triple-decked complex:

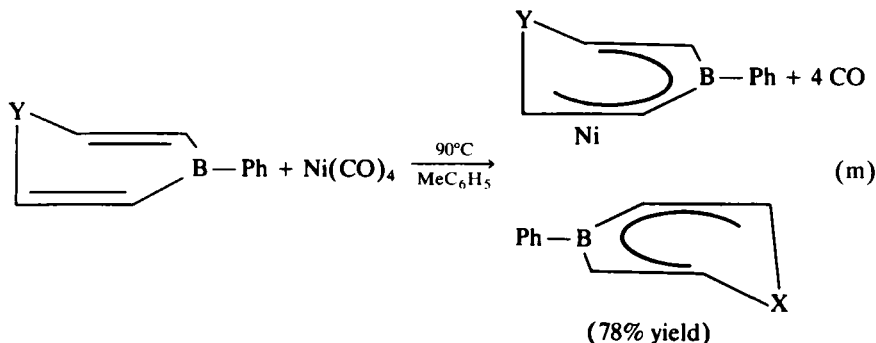


Cyclopentadienide degrades the triple-decked system, giving the uncharged η^5 -CpRh(C_4H_4BR) complexes the water-soluble $Na[Rh(C_4H_4BR-\eta^5)_2]$ salts. Phosphoric acid transforms this ionic complexes into the hydrides $HRh(C_4H_4BR)_2$. Different ligand systems, e.g., $L = PMe_3, P(OMe)_3$, and $CNBu-t$, react with the triple-decked compound ($R = Ph$) under degradation to the ion-pair complex:



Cyanide degradation (KCN) in MeCN yields $K_2[(C_4H_4BPh)Rh(CN)_3]$, also available as the $[PPh_4]^+$ salt. The anion $[C_4H_4B(CN)Ph]^-$, isolated as the $[Co(Cp-\eta^5)_2]^+$ salt, results from further degradation in aqueous solution.

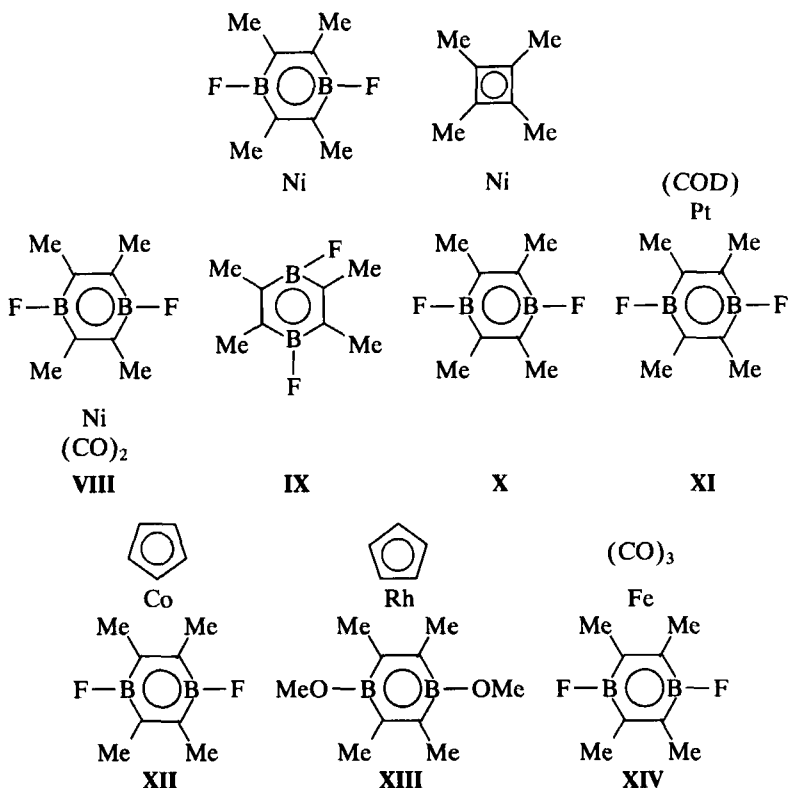
Cyclic divinyl boranes (bora-2,5-cyclohexadienes) also act as good complex ligands and are available from the corresponding stannacyclohexadienes by treatment with $PhBCl_2$. They react photochemically or thermally with transition-metal complexes, e.g.^{12,19-21}:



$$\begin{array}{c} \text{Y} \\ \diagdown \\ \text{---} \\ \diagup \\ \text{---} \end{array} \text{B-Ph} + \text{Fe(CO)}_5 \xrightarrow[\text{Et}_2\text{O}]{h\nu, 12^\circ\text{C}} \begin{array}{c} \text{Y} \\ \diagdown \\ \text{---} \\ \diagup \\ \text{---} \end{array} \text{B-Ph} + 2 \text{CO}$$

Fe(CO)_3
(n)

The six-membered 1,4-diborines (1,4-diaboracyclohexadienes) are prepared by cocondensing alkynes with monomeric BF_3 ²²⁻²⁴ or by the tin route^{25,26}. They form a series of transition-metal complexes **VIII-XIV** by reaction with various complex moieties, e.g.^{26,27}:



Complex I is formed if 1,4-difluoro-2,3,5,6-tetramethyl-1,4-diboracyclohexa-2,5-diene and $\text{Ni}(\text{CO})_4$ are condensed with dry, degassed toluene into a tube on a vacuum line. When the tube is allowed to warm to RT for 30 min, the complex can be trapped as yellow crystals at -30°C when all volatile material is pumped off. The sandwich

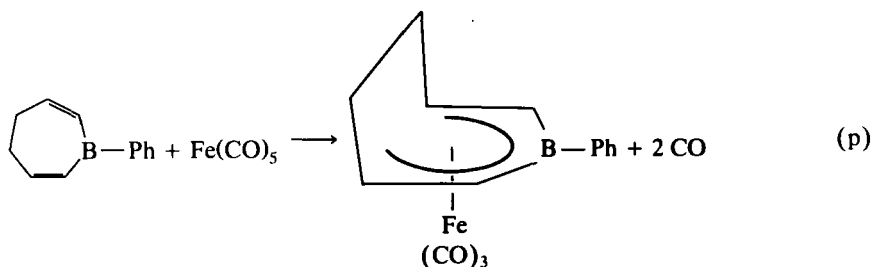
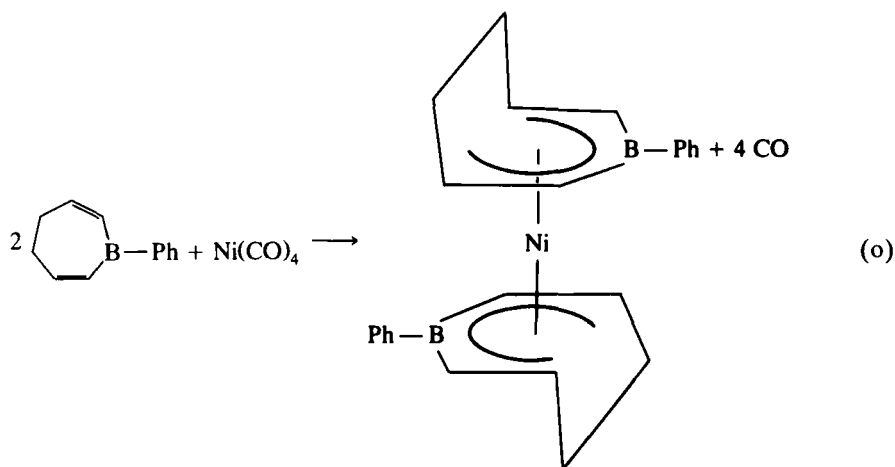
complex **IX** is prepared by photolysis of the reactants in a sealed tube during 12 h in 75% yield.

Complex **X** is formed from $\text{NiCl}_2(\text{Me}_4\text{C}_4)$ and $\text{Pt}(\text{COD})_2$ reacts to give²⁸ **XI**.

Solutions of $\eta^5\text{-CpCo}(\text{CO})_2$, and $(\eta^5\text{-Me}_5\text{C}_5)\text{RhCl}_2$ together with $(\eta^5\text{-Cp})_2\text{Co}$ as reductant in CH_2Cl_2 , are employed²³ as starting materials for the diborine complexes **XII** and **XIII**. Complex **XIV** results from the reaction of $\text{Fe}(\text{CO})_5$ and the diborine in toluene by irradiation²⁷.

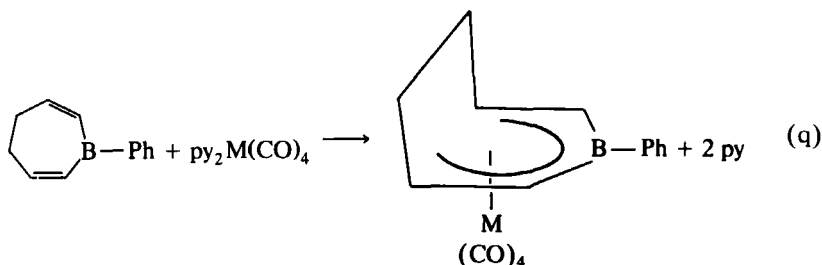
1,4-Diferrocenyl-1,4-dibora-2,5-cyclohexadiene reacts with $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$ or $(\text{COD})\text{Mo}(\text{W})(\text{CO})_4$ to give the corresponding tetracarbonyl metal complexes²⁹. The tricarbonyl metal complexes $(\text{CO})_3\text{M}(\text{RBC}_4\text{H}_4\text{BR})$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$)³⁰ form from $\text{Fe}_2(\text{CO})_9$ and $\text{Ru}_3(\text{CO})_{12}$ as well as $\text{Os}_3(\text{CO})_{12}$. The diboracyclohexadienes $\text{RBC}_4\text{H}_4\text{BR}$ ($\text{R} = \text{OMe}, \text{Me}, \text{Ph}, \text{ferrocenyl}$) and $\text{Ni}(\text{CO})_4$ form the sandwich complexes $(\text{RBC}_4\text{H}_4\text{BR})_2\text{Ni}$; $\eta^5\text{-CpCo}(\text{CO})_2$ and $(\text{Me}_5\text{C}_5)\text{Ru}(\text{CO})_2$ give $\eta^5\text{-CpCo}(\text{RBC}_4\text{H}_4\text{Br})$ and $(\text{Me}_5\text{C}_5)\text{Co}(\text{RBC}_4\text{H}_4\text{BR})$, respectively ($\text{R} = \text{Cl}, \text{OMe}, \text{NMe}_2, \text{H}$ for Co , $\text{R} = \text{OMe}, \text{H}, \text{Me}, \text{Ph}, \text{ferrocenyl}$ for RH)³¹.

The series of neutral B-containing carbocycles as complex ligands within the theme of metal-boron donor-acceptor relationships concludes with the 4,5-dihydroborepines. 1-Phenyl-4,5-dihydroborepine is able to substitute pyridine, acetonitrile or CO ¹⁹:



1-Phenyl-4,5-dihydroborepine and $\text{Fe}(\text{CO})_5$ are irradiated in ether, and the product is

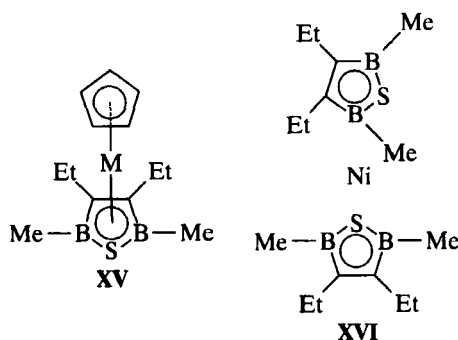
separated by chromatography on silica gel to give the iron complex in 58% yield¹²:



where $M = \text{Cr, Mo, W}$, and $(\text{CH}_3\text{CN})_3\text{M}(\text{CO})_3$ or $\text{M}(\text{CO})_6$ can also be used as starting material.

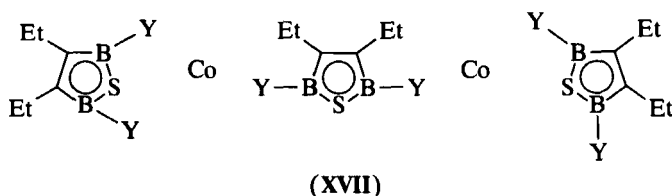
2,5-Dihydro-1,2,5-thiadiboroles ($\text{Et}_2\text{C}_2\text{B}_2\text{R}_2\text{S}$) have remarkable acceptor properties toward metal-ligand moieties. Dihydrothiadiborole-derived complexes can be achieved thermally or photochemically, e.g., Co and Fe sandwich, triple-decked and even tetradecked complexes are known, all having direct metal-boron bonds.

The five-membered heterocycle $\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S}$ reacts with $\eta^5\text{-CpM}$ fragments ($M = \text{Ni, Co}$) from $[\eta^5\text{-CpNi}(\text{CO})_2]_2$ and $\eta^5\text{-CpCo}(\text{CO})_2$ to form mixed sandwich complexes of the type $\eta^5\text{-CpM}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})$ ^{32,33}, whereas $\text{Ni}(\text{CO})_4$ yields the bis(dihydrothiadiborol) complex³⁴. The $(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})\text{Ni}(\text{CO})_2$ is formed in the first step.



where $M = \text{Ni, Co}$.

The $(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})_2\text{Co}_2(\text{CO})_4$ complex is formed if the dihydrothiadiborole is treated with $\text{Co}_2(\text{CO})_8$ in toluene as an isolable intermediate^{32,35}, leading to the triple-decked complex:

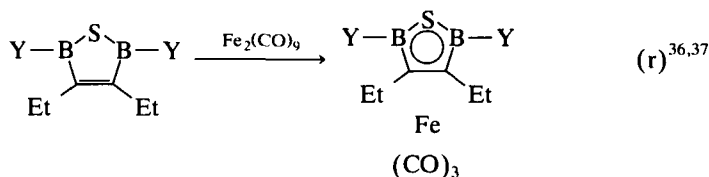


6.5.3. Formation from Other Group-IIIB Compounds

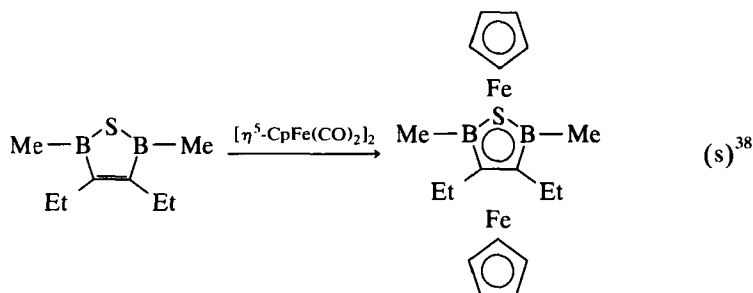
6.5.3.1. by Reaction with Neutral Metal Bases

where $Y = \text{Me, Cl, Br, I}$, which is isolated in 71% yield after 90 min refluxing of the materials in toluene^{32,35}.

Dihydrothiadiborole iron complexes can be prepared thermally or photochemically:



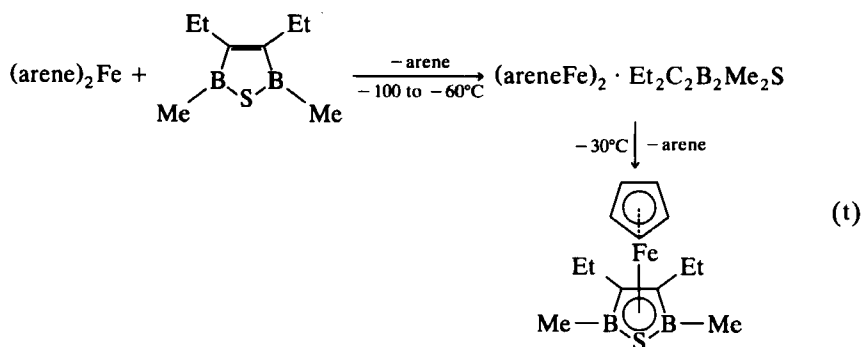
where $Y = \text{H, Cl, Br, I, Me, Ph, SMe, OEt, NMe}_2$;



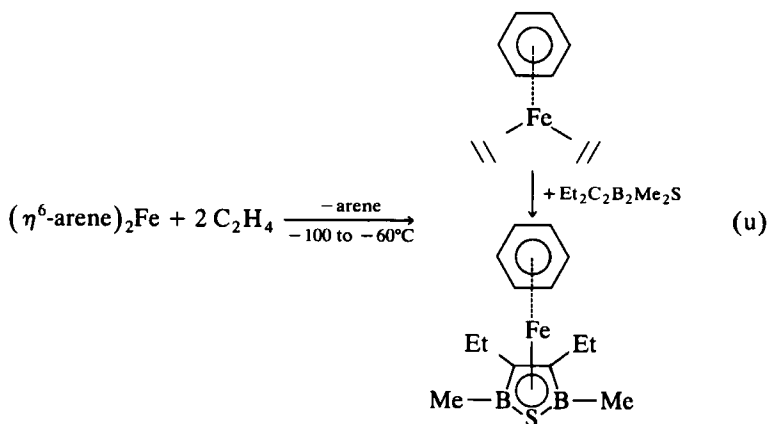
The triple-decked complex is formed in 11% yield from $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ and the dihydrothiadiborole in mesitylene at 160–170°C. It is isolated through chromatography on silica gel with pentane followed by vacuum sublimation³⁸. If the reaction between $\text{Fe}(\text{CO})_5$ and $\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S}$ is carried out in a 1:2 molar ratio in hexane, the dark violet monocarbonyl complex $(\text{CO})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})_2$ (68%) and $(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})\text{Fe}(\text{CO})_3$ (25%) form³⁹. The first complex is also available if the $\text{Fe}(\text{CO})_3$ complex is reacted with free ligand under irradiation. The above-mentioned triple-decked complex $\eta^5\text{-CpFe}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})\text{FeCp-}\eta^5$ can also be prepared³⁹ if $(\text{CO})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})_2$ reacts with $[\eta^5\text{-CpFe}(\text{CO})_2]_2$, together with $(\text{CO})_3\text{Fe}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})$. If the monocarbonyl complex reacts with $\eta^5\text{-CpCo}(\text{CO})_2$ and $[\eta^5\text{-CpNi}(\text{CO})]_2$, respectively³⁹, $\eta^5\text{-CpCo}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})$ as well as $\eta^5\text{-CpNi}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})$ and $(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})_2\text{Ni}$ are obtained; $\text{Mn}_2(\text{CO})_{10}$ gives the triple-decked complex $(\text{CO})_3\text{Mn-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})\text{Mn}(\text{CO})_3$, which is also available from the dihydrothiadiborole and $\text{Mn}_2(\text{CO})_{10}$ [see Eq. (v)].

Mixed arene-2,5-dihydro-1,2,5-thiadiborole-iron complexes have been synthesized by a novel route: thermally unstable bis(arene)iron sandwich complexes, prepared by cocondensation of iron atoms with arene, react in the temperature range of –100 to –60°C with free $\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S}$ to form reactive intermediates that decom-

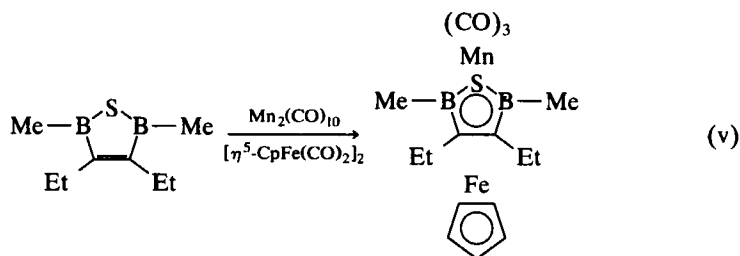
pose at -30°C to give⁴⁰ $(\eta^6\text{-arene})(\eta^5\text{-Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})\text{Fe}$:



where arene = p-xylene, toluene, benzene, 1,4-difluorobenzene. Another route uses $(\eta^6\text{-arene})\text{Fe}(\text{C}_2\text{H}_4)_2$ as reactive intermediate⁴⁰:



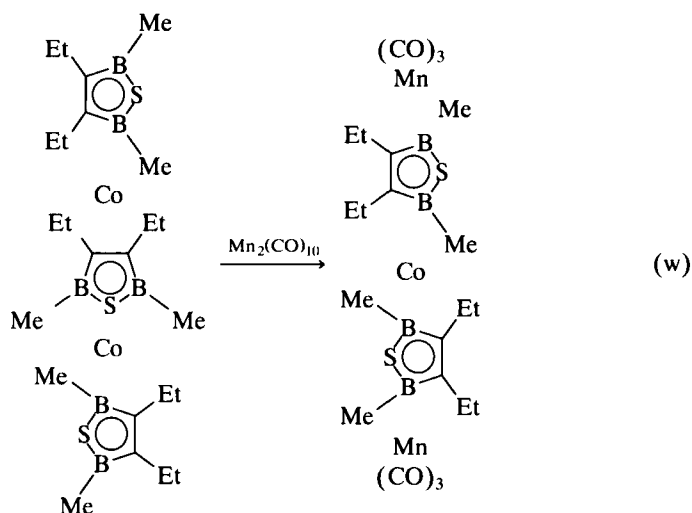
where arene = p-xylene, toluene, benzene. The dihydrothiadiborole reacts with $\text{Mn}_2(\text{CO})_{10}$ and $[\eta^5\text{-CpFe}(\text{CO})_2]_2$ in mesitylene at 165°C giving a green air-stable complex with Mn—B and Fe—B bonds in 37% yield⁴¹:



6.5.3. Formation from Other Group-IIIB Compounds

6.5.3.1. by Reaction with Neutral Metal Bases

A similar mixed complex with Mn and Co is obtained by reacting the triple-decked cobalt compound **XVII** with $\text{Mn}_2(\text{CO})_{10}$:

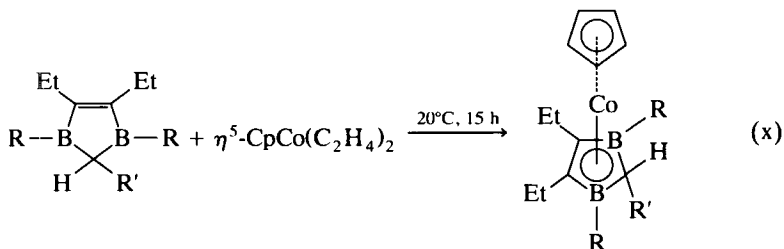


Reacting $\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S}$ and $\text{Mn}_2(\text{CO})_{10}$ in boiling mesitylene for 5 h gives $(\text{CO})_3\text{Mn}-\mu-(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})\text{Mn}(\text{CO})_3$ in 21% yield⁴².

Like the $\text{Ni}(\text{CO})_2$ and $\text{Fe}(\text{CO})_3$ fragments, $\text{M}(\text{CO})_4$ ($\text{M} = \text{Cr}, \text{Mo}$) acts as a two-electron donor⁴³. Thermal reaction of $\text{Cr}(\text{CO})_6$ and $\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S}$ leads to $(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})\text{Cr}(\text{CO})_4$, whereas photolysis yields $(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})_2\text{Cr}(\text{CO})_2$ (11%) and the tetracarbonyl complex (21%).

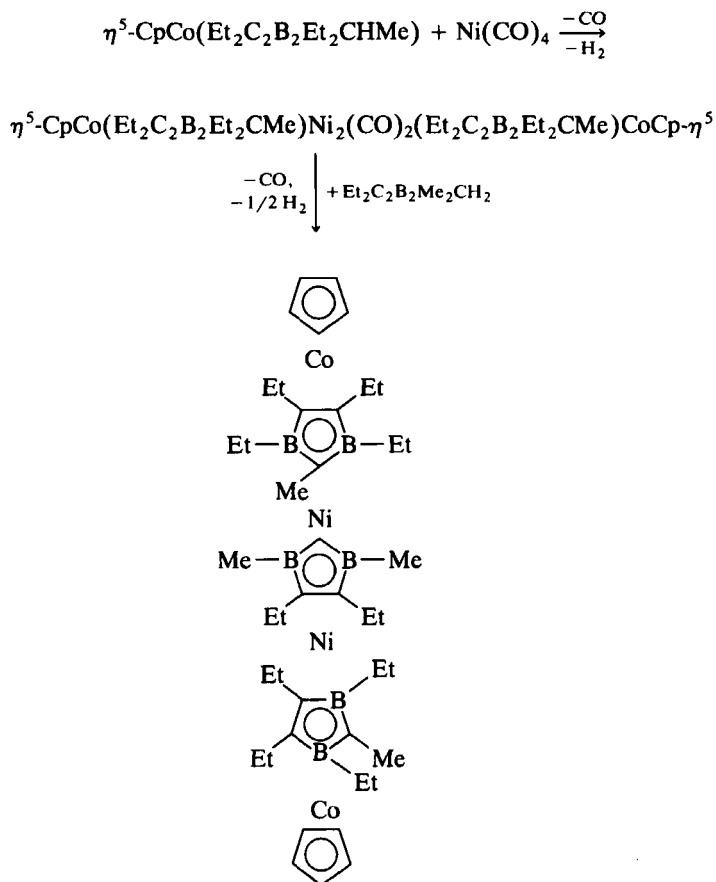
Neutral 2,3-dihydro-1,3-diboroles can act as two-electron donor ligands, but many more examples are known where the neutral diborole loses one H atom to give the 2,3-dihydro-1,3-diborolyl radical (§6.5.3.3); e.g., $\text{R}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2$ ($\text{R} = \text{Me}, \text{Et}$) reacts with $\text{Ni}(\text{C}_2\text{H}_4)_3$ or $\text{Ni}(\text{C}_3\text{H}_5)_2$ to form⁴⁴ $(\text{R}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2)_2\text{Ni}$, and the first route to $(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CHMe})_2\text{Ni}$ is by generating Ni atoms from NiBr_2 and NaHBEt_3 in the presence of the ligand⁴⁴. The homologous Pt sandwich complex is obtained⁴⁴ from $\text{Pt}(\text{C}_2\text{H}_4)_3$ and $\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CHMe}$.

Neutral 2,3-dihydro-1,3-diboroles is also present in the sandwich complex $\eta^5\text{-CpCo}(\text{Et}_2\text{C}_2\text{B}_2\text{R}_2\text{CHR}')^{45}$:

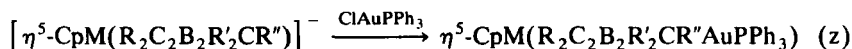


This route is used for the synthesis of the first pentadecked-sandwich complex by

reaction with $\text{Ni}(\text{CO})_4$ ⁴⁶:



Both $\eta^5\text{-CpCo}(\text{Me}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2)$ ^{44,47} and $\eta^5\text{-CpRh}(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CHMe})$ ⁴⁷ have been used to synthesize special 2,3-dihydro-1,3-diborole sandwich compounds. Via the anions $[\eta^5\text{-CpM}(\text{R}_2\text{C}_2\text{B}_2\text{R}'_2\text{CR}'')^-]$, available by reduction with K, the AuPPh_3 derivatives are obtained ⁴⁷:



where if $\text{M} = \text{Co}$, $\text{R} = \text{R}' = \text{Me}$, $\text{R}'' = \text{H}$; if $\text{M} = \text{Rh}$, $\text{R} = \text{R}' = \text{Et}$, $\text{R}'' = \text{Me}$. The orange-red Co compound is formed in 52% yield, the yellow Rh complex in 40% yield.

Further dihydrodiborole rhodium complexes are prepared by reacting free ligand with appropriate Rh complexes: e.g., $[(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CHMe})\text{Rh}(\mu\text{-Cl})_2]$ from $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ and the ligand ⁴⁸. Reduction of this dinuclear complex with K in THF in the presence of free ligand yields the mixed (2,3-dihydro-1,3-diborole)(2,3-dihydro-

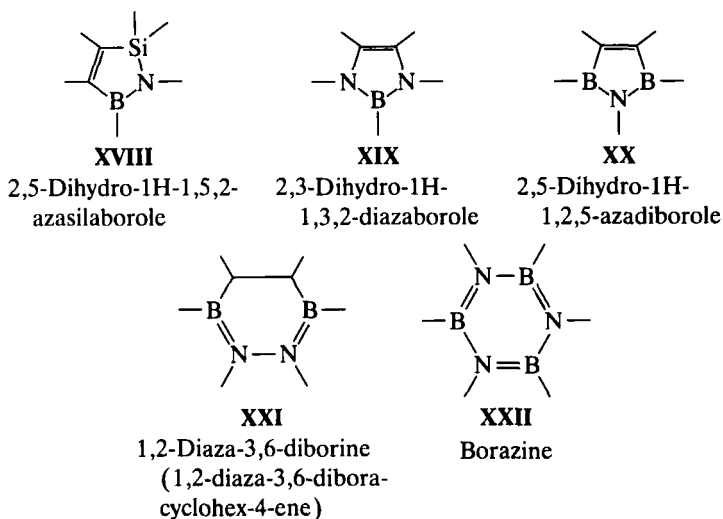
6.5.3. Formation from Other Group-III B Compounds

6.5.3.1. by Reaction with Neutral Metal Bases

1,3-diborolyl)Rh sandwich compound; $\text{NaCp-}\eta^5$ transforms the dinuclear compound to $\eta^5\text{-CpRh}(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CHMe})$ ⁴⁸.

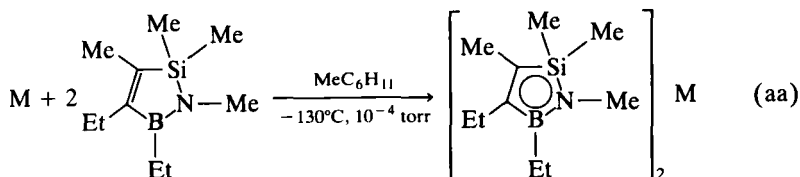
In (cis-cyclooctene)₂Fe(CO)₃Et₂C₂B₂Et₂CHMe can substitute the cyclooctene ligand to give (Et₂C₂B₂Et₂CHMe)Fe(CO)₃, whereas Et₂C₂B₂Me₂CH₂ forms the paramagnetic tetradecadek diborol-2-yl complex (CO)₃Fe-μ-(Et₂C₂B₂Me₂CH)Fe-μ-(Et₂C₂B₂Me₂CH₂)Fe(CO)₃⁴⁹. (Toluene)Fe(Et₂C₂B₂Et₂CHMe) and Fe(CO)₅ also react to give the corresponding tetradecadek complex⁴⁹.

Boron- and nitrogen-containing five- and six-membered rings behave similarly with open-chained aminoboranes through interaction of electron-pair acceptor B atoms and donor N atoms. In spite of good electron compensation in the free BN system, coordination to metal complex fragments having an adequate number of electrons is still possible. The following neutral N—B heterocycles form stable transition-metal complexes:



2,5-Dihydro-1H-1,5,2-azasilaboroles derive from the 2,5-dihydro-1H-1,2-azaboroles (§6.5.3.3) by substitution of the carbon neighboring N by a silicon atom. They may act as four-electron donors using electron density from the C=C double bond and the N atom. The B atom behaves as an acceptor center. Two pathways are known for complex synthesis: reaction with a generated transition-metal complex fragment and reaction with metal atoms by the metal-vapor synthesis method.

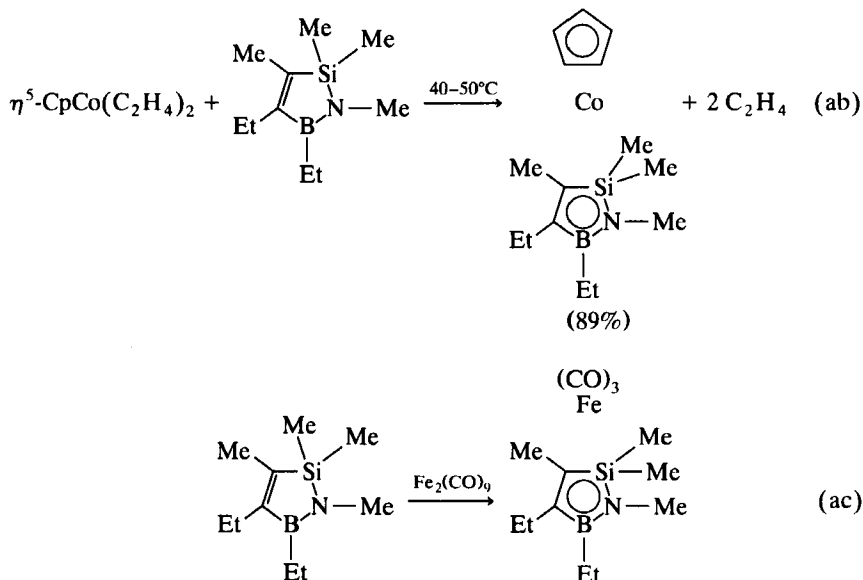
In methylcyclohexane 2,3-diethyl-1,4,5,5-tetramethyl-1H-1,5,2-azasilaborole reacts with Ni or Fe atoms at -130°C in an apparatus for metal vaporization to give sandwich complexes⁵⁰:



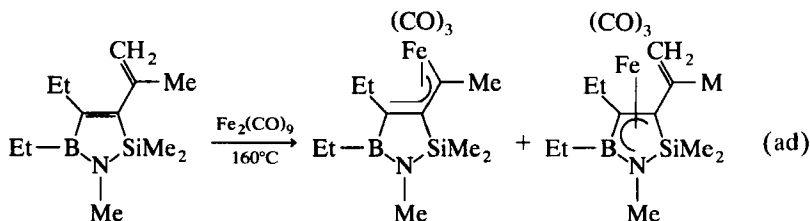
where M = Ni (69%), Fe (61%).

The Ni sandwich is also obtained when excess ligand is treated with Ni(CDT) (CDT = all-trans-cyclododecatriene) at 70–80°C. The yield of the orange-red sandwich is 78%.

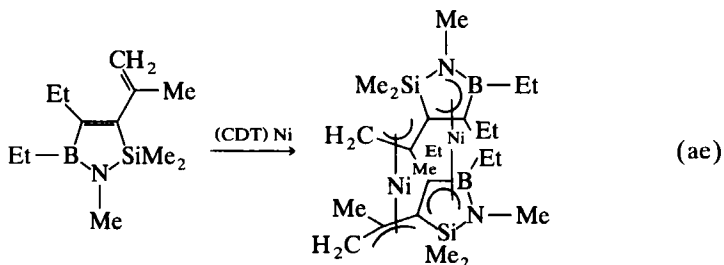
The η^5 -CpCo and Fe(CO)₃ fragments from η^5 -CpCo(C₂H₄)₂ and Fe₂(CO)₉, respectively, give dihydroazasilaborole complexes, too:



The compounds may be purified by sublimation in vacuum. Dihydroazasilaboroles with vinyl substituents possess different coordination centers and consequently form different kinds of complexes when they react with neutral metal complexes⁵¹:



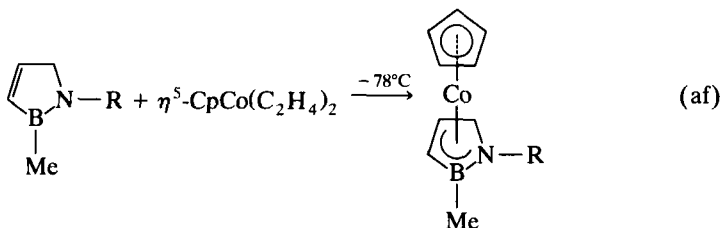
With ttt-1,5,9-cyclododecatriene-nickel a novel bimetallic nickel sandwich is formed⁵¹:



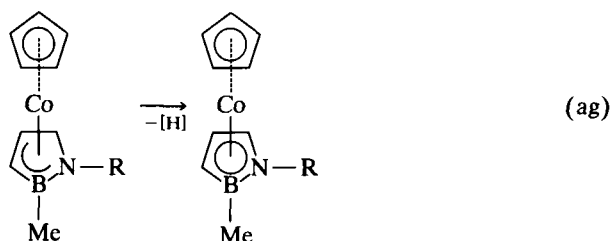
6.5.3. Formation from Other Group-III B Compounds

6.5.3.1. by Reaction with Neutral Metal Bases

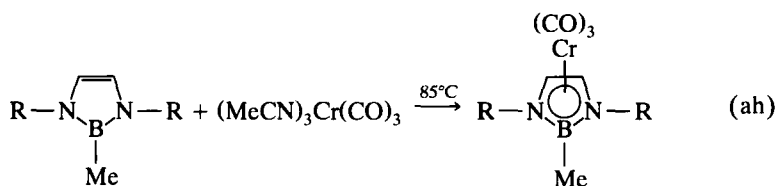
2,5-Dihydro-1H-1,2-azaboroles react with $\eta^5\text{-CpCo}(\text{C}_2\text{H}_4)_2$ at -78°C giving mixed $\eta^5\text{-cyclopentadienyl-}\eta^4\text{-dihydroazaborole}$ complexes with an 18-electron configuration⁵²:



where $\text{R} = \text{CMe}_3$, SiMe_3 . Even at RT they lose hydrogen and convert into the 19-electron systems with dihydro-1H-1,2-azaborolyl rings⁵²:



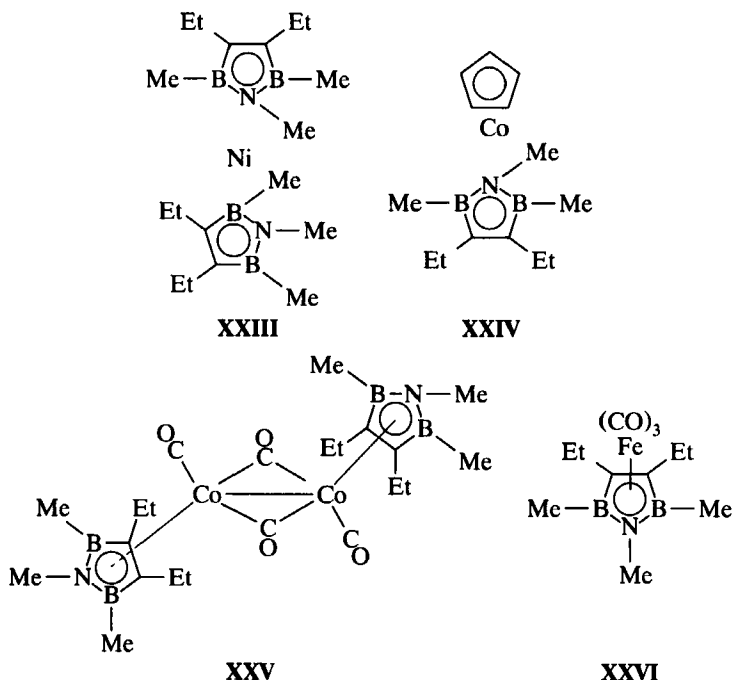
Neutral 2,3-dihydro-1H-1,3,2-diazaboroles are isoelectronic with the cyclopentadienyl anion and, therefore, prefer to react with neutral transition-metal fragments having 12 electrons^{53,54}:



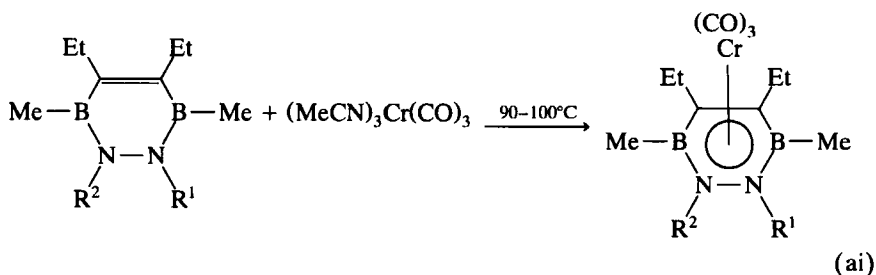
where $\text{R} = \text{t-Bu}$, SiMe_3 . The reactions are carried out in dioxane at 85°C to give the yellow complexes in high yields. Photochemically activated $\text{Cr}(\text{CO})_6$ also yields the complexes, but in lower yields. The corresponding Mo and W complexes cannot be prepared by this method.

2,5-Dihydro-1,2,5-azaadiboroles are comparable to the 2,5-dihydro-1,2,5-thiadiboroles, but compared with boroles and thiadiboroles they are weaker ligands³². Their transition-metal complexes are accessible photochemically or thermally in

moderate yields from $\text{Ni}(\text{CO})_4$, $\eta^5\text{-CpCo}(\text{CO})_2$, $\text{Co}_2(\text{CO})_8$, and $\text{Fe}(\text{CO})_5$ precursors⁵⁵:



1,2-Diaza-3,6-diborines have an intermediate position between arenes and borazines and act as six-electron donors like the 2,3-dihydro-1,3,2-diazaboroles. Therefore, they react with $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$ at 80°C to afford orange-red diazadiborine-tricarbonylchromium complexes^{56,57}:

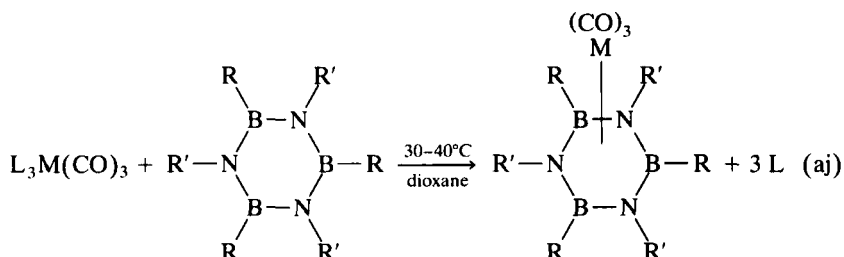


The reactions are carried out without solvent and under reduced pressure (1467 N m^{-2} , 11 torr) to remove dissociated acetonitrile. Sublimation or recrystallization from hexane yields the compounds in ca. 50% yields.

Borazine is isoelectronic and isostructural with benzene and may act as a six-electron donor in complex chemistry. In contrast to arene ligands of arene-transition-metal complexes, coordinated borazines lose their planarity and are slightly puckered^{58,59}. Nevertheless, the B atoms show interactions with metal atoms.

Though borazine itself gives no stable complexes, alkyl substituted derivatives are formed by the reaction of borazines with $\text{L}_3\text{M}(\text{CO})_3$ (L = nitrile) (Table 1,

method I):



where M = Cr, Mo, or the reaction between photochemically activated hexacarbonyl and the appropriate borazine (Table 1, method II)^{60–64}.

TABLE 1. BORAZINE COMPLEXES $(CO)_3M(RBNR')_3$ (M = Cr, Mo, R; R' = alkyl)

M	R, R'	Method	Refs.
Cr	R = R' = Me	I	60, 61
Cr	R = Et, R' = Me	I, II	61, 62
Cr	R = Me, R' = Et	I, II	62
Cr	R = Et, R' = Et	I, II	63
Cr	R = n-Pr, R' = Me	I	63
Cr	R = Me, R' = n-Pr	I	63
Cr	R = i-Pr, R' = Me	I	63
Cr	R = Me, R' = i-Pr	I	63
Mo	R = Me, R' = Et	I, II	64
Mo	R = Et, R' = Me	I, II	64

Equation (aj) also allows the synthesis of unsymmetrically substituted borazines, e.g., $(EtBMe_2B_2N_3Me_3)Cr(CO)_3$ or $(PhBMe_2B_2N_3Me_3)Cr(CO)_3$ ⁶⁵. The reactions take place in dioxane at 30–40°C with reduced pressure to pump off eliminated nitrile. The dioxane complexes $(C_4H_8O_2)_2M_2(CO)_6$ are intermediates. If liquid borazines are used additional solvent becomes unnecessary.

Neutral carboranes and boranes react with transition-metal complexes forming metallocarboranes or metalloboranes, respectively. However, most metallocarboranes and metalloboranes are prepared from transition-metal halides and anionic carborane and borane species (§6.5.3.4) or by reacting metal atoms and neutral boranes and carboranes. These reactions are oxidative addition reactions (§6.5.3.3).

The Pt, Pd and Ni complexes $(Et_3P)_3Pt$, $(trans\text{-stilbene})(Et_3P)_2Pt$, $(PhMe_2P)_4Pt$, $(COD)_2Ni$, $(COD)(Et_3P)_2Ni$ and $(t\text{-BuNC})_2Pd$ react with closo-2,3-Me-2,3- $C_2B_9H_9$ to give closo-metallocarboranes 1,1- L_2 -2,4-Me-2,1,2,3-MC₂B₉H₉ (M = Pt, L = PEt_3 , PMe_3 , PMe_2Ph ; M = Ni, L_2 = COD, PEt_3 ; M = Pd, L = $t\text{-BuNC}$)⁶⁶. The $Pt_2(COD)(PEt_3)_4$ complex loses COD when it reacts with closo-2,4-R₂-2,4-C₂B₅H₅ (R = H, Me) to give⁶⁷ 4,4-(Et_3P)₂-1,7-R₂-4,1,7-PtC₂B₅H₅ and 1,1-(Et_3P)₂-6,6-(Et_3P)₂-4,5-Me-2,1,6,4,5-Pt₂C₂B₂H₅.

Reaction of $(COD)(t\text{-BuNC})_2Ni$, $(t\text{-BuNC})_2Pd$ and $(trans\text{-stilbene})(Et_3P)_2Pt$ with either $[closo\text{-CB}_9H_{11}]^-$ or closo-2-NMe₃-2-CB₁₀H₁₀ affords either the metallocarbo-

rane anion, $[1,1\text{-L}_2\text{-}1,2\text{-MCB}_{10}\text{H}_{11}]^-$, or $1,2\text{-L}_2\text{-}2\text{-NMe}_3\text{-}1,2\text{-MCB}_{10}\text{H}_{10}$ ($\text{M} = \text{Ni, Pd}$, $\text{L} = \text{t-BuNC}$; $\text{M} = \text{Pt}$, $\text{L} = \text{PEt}_3$), respectively⁶⁸; $3,3\text{-(Et}_3\text{P)}_2\text{-}3,1,2\text{-PtC}_2\text{B}_8\text{H}_{11}$ can be prepared similarly⁶⁹.

Reaction of closo- $1,6\text{-Me}_2\text{-}1,6\text{-C}_2\text{B}_7\text{H}_7$ with $(\text{Et}_3\text{P})_3\text{Pt}$ affords⁷⁰ $10,10\text{-(Et}_3\text{P)}_2\text{-}2,8\text{-Me}_2\text{-}10,2,8\text{-PtC}_2\text{B}_7\text{H}_7$.

Vapor-phase reaction of $2,4\text{-C}_2\text{B}_5\text{H}_7$ with $\eta^5\text{-CpCo(CO)}_2$ yields⁷¹ $1,8\text{-(}\eta^5\text{-Cp)}_2\text{-}1,8,5,6\text{-Co}_2\text{B}_5\text{H}_7$ and $1,7\text{-(}\eta^5\text{-Cp)}_2\text{-}1,7,5,6\text{-Co}_2\text{C}_2\text{B}_5\text{H}_7$.

Reaction of $(\text{Et}_3\text{P})_4\text{Co}$ with closo- $1,7\text{-C}_2\text{B}_6\text{H}_6$ or closo- $1,5\text{-C}_2\text{B}_3\text{H}_5$ gives the complexes $2\text{-H-}2,2\text{-(Et}_3\text{P)}_2\text{-}2,1,8\text{-CoC}_2\text{B}_6\text{H}_8$ and $2,2\text{-(Et}_3\text{P)}_2\text{-}2,1,6\text{-CoC}_2\text{B}_3\text{H}_5$ in 63% and 45% yields, respectively⁷².

$\text{FeH}_2(2,3\text{-Me}_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4)_2$ reacts with $\text{Co(PEt}_3)_4$, $\text{Pt}_2(\text{COD})(\text{PEt}_3)_4$ and $(\text{COD})\text{FeCp-}\eta^5$ to afford the bimetallic species $\text{CoFe(Me}_4\text{C}_4\text{B}_8\text{H}_8)(\text{PEt}_3)_2$, $\text{FePt(Me}_4\text{C}_4\text{B}_8\text{H}_8)(\text{PEt}_3)_2$ and $\text{Fe}_2(\text{Me}_4\text{C}_4\text{B}_8\text{H}_8)\text{Cp-}\eta^5$, respectively⁷³. Likewise, $2,4\text{-Me}_2\text{-}2,4\text{-C}_2\text{B}_5\text{H}_5$ and $\text{Co(PEt}_3)_4$ react to give $4\text{-(Et}_3\text{P)}_2\text{-}1,7\text{-Me}_2\text{-}\mu\text{-}4,8\text{-[Co(H)-(PEt}_3)_2\text{-}\mu\text{-H-}\mu\text{-(PEt}_3)_2]\text{-}4,1,7\text{-CoC}_2\text{B}_5\text{H}_4$, whereas Fe(CNBu-t)_5 affords formation of $4,4,4\text{-t-BuNC)}_3\text{-}1,7\text{-Me}_2\text{-}4,1,7\text{-FeC}_2\text{B}_5\text{H}_5$ ⁷⁴.

Reaction of $1\text{-}\eta^5\text{-Cp-}2,2\text{-Me}_2\text{-}1,2,3\text{-CoC}_2\text{B}_4\text{H}_4$ with Fe(CO)_5 produces $1,1,1\text{-(CO)-}4,4,4\text{-(CO)-}3\text{-}9\text{-}\eta^5\text{-Cp-}2,8\text{-Me}_2\text{-}1,4,9\text{-Fe}_2\text{CoC}_2\text{B}_4\text{H}_4$, a nine-vertex polyhedral cage system⁷⁵.

Two cobaltoboranes are produced using the hot-cold reaction technique. Starting with $\eta^5\text{-CpCo(CO)}_2$ and B_5H_9 , $1\text{-}\eta^5\text{-Cp-}1\text{-CoB}_5\text{H}_9$ (3.9%) and $2\text{-}\eta^5\text{-Cp-}2\text{-CoB}_9\text{H}_{13}$ (2.5%) can be isolated in addition to a number of uncharacterized products.⁷⁶

(G. SCHMID)

1. G. Schmid, L. Weber, *Z. Naturforsch. Teil B*, **25**, 1083 (1970).
2. G. Schmid, *Chem. Ber.*, **103**, 528 (1970).
3. P. Paetzold, Ch. v. Plötho, G. Schmid, R. Boese, B. Schrader, D. Bougeard, U. Pfeiffer, R. Gleiter, W. Schäfer, *Chem. Ber.*, **117**, 1089 (1984).
4. P. Paetzold, K. Delpy, *Chem. Ber.*, **118**, 2552 (1985).
5. E. Bulak, G. E. Herberich, I. Manners, H. Mayer, P. Paetzold, *Angew. Chem., Int. Ed. Engl.*, **27**, 958 (1988).
6. D. Männig, H. Nöth, M. Schwarz, S. Weber, U. Wietelmann, *Angew. Chem., Int. Ed. Engl.*, **24**, 998 (1985).
7. K. Delpy, D. Schmitz, P. Paetzold, *Chem. Ber.*, **116**, 2994 (1983).
8. G. Schmid, D. Kampmann, W. Meyer, R. Boese, P. Paetzold, K. Delpy, *Chem. Ber.*, **118**, 2418 (1985).
9. T. R. Durkin, E. P. Schram, *Inorg. Chem.*, **11**, 1054 (1972).
10. R. N. Scott, D. F. Shriver, D. D. Lehmann, *Inorg. Chim. Acta*, **4**, 73 (1970).
11. G. E. Herberich, H. Müller, *Angew. Chem., Int. Ed. Engl.*, **10**, 937 (1971).
12. G. E. Herberich, E. Bauer, J. Hengesbach, U. Kölle, G. Huttner, H. Lorenz, *Chem. Ber.*, **110**, 760 (1977).
13. G. E. Herberich, G. Pampaloni, *J. Organomet. Chem.*, **240**, 121 (1982).
14. G. E. Herberich, J. Hengesbach, U. Kölle, W. Oschmann, *Angew. Chem., Int. Ed. Engl.*, **16**, 42 (1977).
15. G. E. Herberich, B. Buller, B. Hessner, W. Oschmann, *J. Organomet. Chem.*, **195**, 253 (1980).
16. G. E. Herberich, J. Hengesbach, G. Huttner, A. Frank, U. Schubert, *J. Organomet. Chem.*, **246**, 141 (1983).
17. G. E. Herberich, W. Boveleth, B. Hessner, D. P. J. Köffer, M. Negele, R. Saive, *J. Organomet. Chem.*, **308**, 153 (1986).
18. G. E. Herberich, U. Büschges, B. Hessner, H. Lütke, *J. Organomet. Chem.*, **312**, 13 (1986).
19. U. Kölle, W.-D. H. Beiersdorf, G. E. Herberich, *J. Organomet. Chem.*, **152**, 7 (1978).

6.5.3. Formation from Other Group-IIIB Compounds

6.5.3.1. by Reaction with Neutral Metal Bases

20. G. E. Herberich, M. Tönnessen, D. Schmitz, *J. Organomet. Chem.*, **191**, 27 (1980).
21. G. E. Herberich, E. Raabe, *J. Organomet. Chem.*, **309**, 143 (1986).
22. P. L. Timms, *J. Am. Chem. Soc.*, **90**, 4585 (1968).
23. P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, **14**, 121 (1972).
24. P. L. Timms, *Acc. Chem. Res.*, **6**, 118 (1973).
25. J. Y. Corey, *Adv. Organomet. Chem.*, **13**, 139 (1975).
26. G. E. Herberich, B. Hessner, *J. Organomet. Chem.*, **161**, C36 (1978).
27. P. S. Maddren, A. Modinos, P. L. Timms, P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1272 (1975).
28. G. E. Herberich, in *Comprehensive Organometallic Chemistry*, Vol. 1, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, 1982, pp. 381–410.
29. G. E. Herberich, B. Hessner, S. Beswetherick, J. A. K. Howard, P. Woodward, *J. Organomet. Chem.*, **192**, 421 (1980).
30. G. E. Herberich, M. M. Kucharska-Jansen, *J. Organomet. Chem.*, **243**, 45 (1983).
31. G. E. Herberich, B. Hessner, *Chem. Ber.*, **115**, 3115 (1982).
32. W. Siebert, in *Advances Organomet. Chem.*, Vol. 18, F. G. A. Stone, R. West, eds., Academic Press, New York, 1980, p. 301.
33. W. Siebert, M. E.-D. M. El-Essawi, R. Full, J. Heck, *Z. Naturforsch., Teil B*, **40**, 458 (1985).
34. W. Siebert, R. Full, C. Krüger, Y.-H. Tsay, *Z. Naturforsch., Teil B*, **31**, 203 (1976).
35. W. Siebert, W. Rothermel, *Angew. Chem., Int. Ed. Engl.*, **16**, 333 (1977).
36. W. Siebert, G. Augustin, R. Full, C. Krüger, Y.-H. Tsay, *Angew. Chem., Int. Ed. Engl.*, **14**, 262 (1975).
37. W. Siebert, R. Full, J. Edwin, K. Kinberger, C. Krüger, *J. Organomet. Chem.*, **131**, 1 (1977).
38. W. Siebert, T. Renk, K. Kinberger, M. Bochmann, C. Krüger, *Angew. Chem., Int. Ed. Engl.*, **15**, 779 (1976).
39. J. Edwin, W. Siebert, C. Krüger, *J. Organomet. Chem.*, **282**, 297 (1985).
40. U. Zenneck, L. Suber, H. Pritzkow, W. Siebert, *Chem. Ber.*, **119**, 971 (1986).
41. W. Siebert, C. Böhle, C. Krüger, Y.-H. Tsay, *Angew. Chem., Int. Ed. Engl.*, **17**, 527 (1978).
42. W. Siebert, K. Kinberger, *Angew. Chem., Int. Ed. Engl.*, **15**, 434 (1976).
43. K. Kinberger, W. Siebert, *Chem. Ber.*, **111**, 356 (1978).
44. W. Siebert, *Angew. Chem., Int. Ed. Engl.*, **24**, 943 (1985).
45. W. Siebert, J. Edwin, H. Pritzkow, *Angew. Chem., Int. Ed. Engl.*, **21**, 148 (1982).
46. M. W. Whiteley, H. Pritzkow, U. Zenneck, W. Siebert, *Angew. Chem., Int. Ed. Engl.*, **21**, 453 (1982).
47. K. Geilich, K. Stumpf, H. Pritzkow, W. Siebert, *Chem. Ber.*, **120**, 911 (1987).
48. K. Geilich, W. Siebert, *Z. Naturforsch., Teil B*, **41**, 671 (1986).
49. W. Siebert, D. Büchner, H. Pritzkow, H. Wadeppohl, F.-W. Grevels, *Chem. Ber.*, **120**, 1511 (1987).
50. R. Köster, G. Seidel, S. Amirkhalili, R. Boese, G. Schmid, *Chem. Ber.*, **115**, 738 (1982).
51. R. Köster, G. Seidel, *Angew. Chem., Int. Ed. Engl.*, **21**, 207 (1982).
52. G. Schmid, U. Höhner, D. Kampmann, *Z. Naturforsch., Teil B*, **38**, 1094 (1983).
53. G. Schmid, J. Schulze, *Angew. Chem., Int. Ed. Engl.*, **16**, 249 (1977).
54. J. Schulze, G. Schmid, *Chem. Ber.*, **114**, 495 (1981).
55. W. Siebert, H. Schmidt, R. Full, *Z. Naturforsch., Teil B*, **35**, 873 (1980).
56. W. Siebert, R. Full, *Angew. Chem., Int. Ed. Engl.*, **15**, 45 (1976).
57. W. Siebert, R. Full, H. Schmidt, J. von Seyerl, M. Halstenberg, G. Huttner, *J. Organomet. Chem.*, **191**, 15 (1980).
58. G. Huttner, B. Krieg, *Angew. Chem., Int. Ed. Engl.*, **10**, 512 (1971).
59. G. Huttner, B. Krieg, *Chem. Ber.*, **105**, 3437 (1972).
60. R. Prinz, H. Werner, *Angew. Chem., Int. Ed. Engl.*, **6**, 91 (1967).
61. H. Werner, R. Prinz, E. Deckelmann, *Chem. Ber.*, **102**, 95 (1969).
62. K. Deckelmann, H. Werner, *Helv. Chim. Acta*, **53**, 139 (1979).
63. M. Scotti, H. Werner, *Helv. Chim. Acta*, **57**, 1234 (1974).
64. K. Deckelmann, H. Werner, *Helv. Chim. Acta*, **54**, 2189 (1971).
65. J. L. Adcock, J. J. Lagowski, *Inorg. Chem.*, **12**, 2533 (1973).
66. M. Green, J. L. Spencer, F. G. A. Stone, A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 179 (1975).
67. G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 46 (1982).

68. W. E. Carroll, M. Green, F. G. A. Stone, A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2263 (1975).
69. D. M. P. Mingos, M. I. Forsyth, A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1363 (1978).
70. M. Green, J. L. Spencer, F. G. A. Stone, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 571 (1974).
71. V. R. Miller, L. G. Sneddon, D. C. Beer, R. N. Grimes, *J. Am. Chem. Soc.*, 96, 3090 (1974).
72. G. K. Barker, M. Green, M. P. Garcia, F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1266 (1980).
73. G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone, A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1679 (1982).
74. G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone, H. E. Parge, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 688 (1982).
75. W. M. Maxwell, R. N. Grimes, *J. Chem. Soc., Chem. Commun.*, 943 (1975).
76. R. Wilczynski, L. G. Sneddon, *Inorg. Chem.*, 18, 864 (1979).

6.5.3.2. by Reaction with Anionic Metal Bases

Group-IIIB element-transition-metal compounds have been synthesized by means of anionic metal bases and halide-free group-IIIB compounds. The carbonylate anions of Mn and Re interact with BH_3 to give $[\text{H}_3\text{BM}(\text{CO})_5]^-$, which are best isolated as the tetraalkylammonium or phosphonium salts¹:



where $\text{M} = \text{Mn, Re}$. $[\text{Mn}(\text{CO})_5]^-$ is less nucleophilic toward BH_3 than is $[\text{Re}(\text{CO})_5]^-$, but $[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$ gives a more stable borane complex. The higher nucleophilicity of $[\text{Re}(\text{CO})_5]^-$ compared with $[\text{Mn}(\text{CO})_5]^-$ is also demonstrated by isolation of $[\text{Et}_4\text{N}][(\text{H}_3\text{B})_2\text{Re}(\text{CO})_5]$, whereas the manganese analog is unobtainable.

Complexes of Ph_3E ($\text{E} = \text{Al, Ga, In}$) with the metal carbonyl anions $[\text{Co}(\text{CO})_4]^-$, $[\eta^5\text{-CpFe}(\text{CO})_2]^-$, $[\text{Mn}(\text{CO})_5]^-$ and $[\eta^5\text{-CpW}(\text{CO})_3]^-$ can be prepared by combining the donor salt with the acceptor in CH_2Cl_2 or, for $[\eta^5\text{-CpFe}(\text{CO})_2]^-$, in THF ². The cobalt compounds $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ph}_3\text{ECo}(\text{CO})_4]$ ($\text{E} = \text{Al, Ga, In}$) are formed when $[(\text{Ph}_3\text{P})_2\text{N}][\text{Co}(\text{CO})_4]$ and Ph_3E are dissolved in CH_2Cl_2 at -78°C ($\text{E} = \text{Ga}$) and RT ($\text{E} = \text{In}$).

A stable complex of $[\text{Mn}(\text{CO})_5]^-$ is given only with Ph_3In , while reactions with Ph_3Ga and Ph_3Al lead to unstable products.

Solutions of Ph_3In and $[\eta^5\text{-CpW}(\text{CO})_3]^-$ interact in CH_2Cl_2 to form an $\text{In}-\text{W}$ bond. Use of Ph_3Al leads to a complex in which the oxygen atom of a carbonyl ligand is the site of electron pair basicity in a $\text{WC}\equiv\text{OAl}$ link. Solutions of $[\text{n-Bu}_4\text{N}][\text{Ph}_3\text{GaCpW}(\text{CO})_3]$ in CH_2Cl_2 contain, in addition to free $[\text{CpW}(\text{CO})_3]^-$, two isomeric complexes: a metal-metal-bonded species and a C- and O-bonded adduct of the type found in the Ph_3Al case.

The ions $[\eta^5\text{-CpMo}(\text{CO})_3]^-$, $[\eta^5\text{-CpW}(\text{CO})_3]^-$, $[\text{Co}(\text{CO})_4]^-$, and $[\text{Mn}(\text{CO})_5]^-$ serve as electron-pair bases toward TiR_3 to give complexes of the type $[\text{R}_3\text{Ti}(\text{M})]^-$ ($\text{R} = \text{C}_6\text{F}_5\text{H}_2, \text{C}_6\text{F}_5$; $\text{M} = \text{metal complex anion}$)³.

The iron complexes $[\text{Et}_4\text{N}][\text{Ph}_3\text{EFe}(\text{CO})_2\text{Cp-}\eta^5]$ ($\text{E} = \text{Al, Ga, In}$) result in 55–63% yield when the components are added together in THF .

(G. SCHMID)

1. G. W. Parshall, *J. Am. Chem. Soc.*, 86, 361 (1964).

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6.5. Group-IIIB–Transition- or –Inner Transition-Metal Bonds

6.5.3. Formation from Other Group-IIIB Compounds

6.5.3.2. by Reaction with Anionic Metal Bases

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69. D. M. P. Mingos, M. I. Forsyth, A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1363 (1978).
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The iron complexes $[\text{Et}_4\text{N}][\text{Ph}_3\text{EFe}(\text{CO})_2\text{Cp-}\eta^5]$ ($\text{E} = \text{Al}, \text{Ga}, \text{In}$) result in 55–63% yield when the components are added together in THF.

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6.5. Group-III B–Transition- or –Inner Transition-Metal Bonds

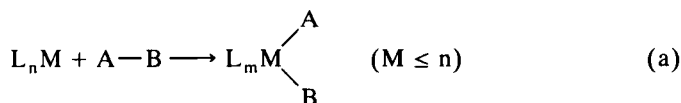
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6.5.3. Formation from Other Group-III B Compounds

6.5.3.3. by Oxidative Addition Reactions

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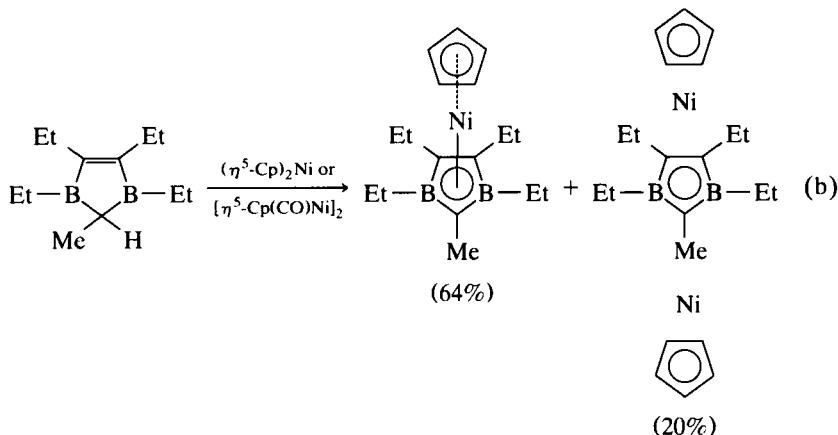
As mentioned in §6.5.2.3, classical oxidative additions can be denoted:



The oxidation state of M is increased by two.

The reactions discussed here, however, disobey this strong definition as oxidation of the metal is often accompanied by an elimination of hydrogen or of organic substituents. Nevertheless, these reactions are best described in this section.

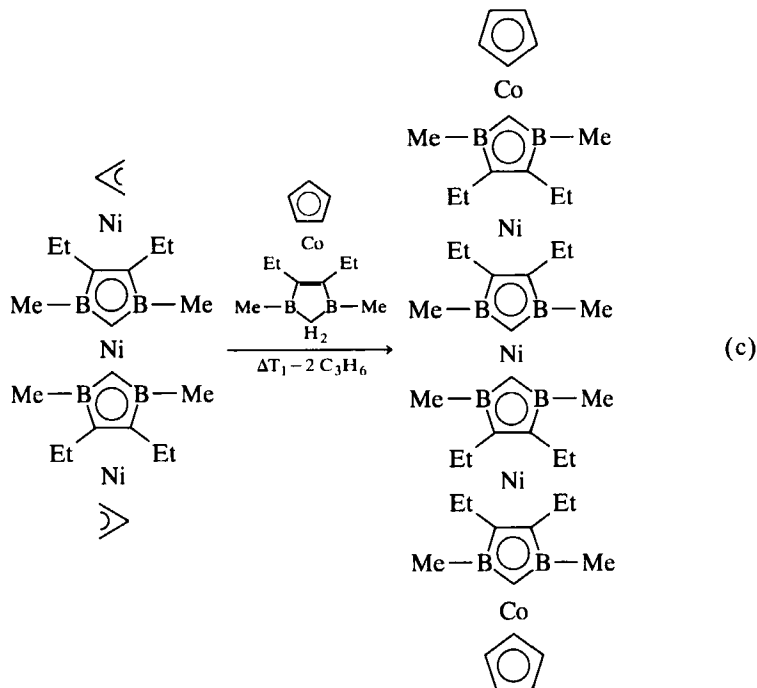
2,3-Dihydro-1,3-diborolenes are accessible as pentaorgano derivatives^{1–3} and serve as ideal precursors of the diborolyl radical. The formation of the radical and its interaction with a metal center is formally described as a metal oxidation. The resulting 2,3-dihydro-1,3-diborolyl ligand is either a three-electron donor or an anionic four-electron donor. 1,3,4,5-Tetraethyl-2-methyl-2,3-dihydro-1,3-diborole reacts with $[\eta^5\text{-CpNi}(\text{CO})_2]$ or $(\eta^5\text{-Cp})_2\text{Ni}$ in hot mesitylene to yield a sandwich complex and a triple-decked complex^{2,3}:



The derivative $\eta^5\text{-CpNi}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH})$ may be prepared in an analogous manner together with small amounts of the corresponding triple-decked sandwich⁴. If $\eta^5\text{-CpNi}(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe})$ (§6.5.3.3) reacts with $[\eta^5\text{-CpNi}(\text{CO})_2]$ in mesitylene at 150°C the original sandwich is piled up by the $\eta^5\text{-CpNi}$ fragment to give the triple-decked complex $\eta^5\text{-CpNi}(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe})\text{NiCp-}\eta^5$ in 54% yield⁴. The derivative $\eta^5\text{-CpNi}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH})\text{NiCp-}\eta^5$ is formed under corresponding conditions in 85% yield⁴. Using $\eta^5\text{-CpCo}(\text{CO})_2$ instead of $[\eta^5\text{-CpNi}(\text{CO})_2]$ the cobalt-containing triple-decked complex $\eta^5\text{-CpNi}(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe})\text{CoCp-}\eta^5$ and $\eta^5\text{-CpNi}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH})\text{CoCp-}\eta^5$ can be prepared in high yields⁴.

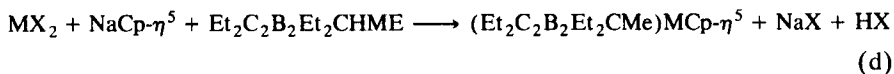
Both $\eta^5\text{-CpNi}(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CH})$ and $\eta^5\text{-CpNi-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe})\text{NiCp-}\eta^5$ are also obtained when $(\eta^3\text{-C}_3\text{H}_5)_2\text{NiCp-}\eta^5$ reacts with the neutral dihydrodiborole⁵. The diborole-system and $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$ combine in boiling toluene to a tetra-decked complex, having two dihydrodiborolyl rings as μ ligands: $\eta^3\text{-C}_3\text{H}_5\text{Ni-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{R}_2\text{CMe})\text{Ni-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{R}_2\text{CMe})\text{NiC}_3\text{H}_5\text{-}\eta^3$ (R = Me, Et)⁵. Using the thermally more stable $(\eta^3\text{-}\beta\text{-C}_3\text{H}_4\text{Me})_2\text{Ni}$ for the reaction with $\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2$ in

refluxing toluene, small amounts of the triple-decked complex $(\eta^3\text{-}\beta\text{-C}_3\text{H}_4\text{Me})\text{Ni-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH})\text{Ni}(\beta\text{-C}_3\text{H}_4\text{Me-}\eta^3)$ are found⁵. The tetradecaded sandwich compound (R = Me) is the starting material for a hexadecked complex, as it can be stacked with $\eta^5\text{-CpCo(Et}_2\text{C}_2\text{B}_2\text{Me}_4\text{CH}_2)$ ⁶.



As by-products triple- and tetradecaded complexes are obtained: $\eta^5\text{-CpCo-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH})\text{CoCp-}\eta^5$, $\eta^5\text{-CpCo-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH})\text{M-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH})\text{-CoCp-}\eta^5$ (M = Co, Ni). A second route to the hexadecked complex uses⁵ $\eta^3\text{-C}_3\text{H}_5\text{Ni-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH})\text{CoCp-}\eta^5$ and $(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2)_2\text{Ni}$.

Changing R in the 2,3-dihydro-1,3-diborole from Me to Et the pentadecked system $\eta^5\text{-CpCo-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe})\text{Ni-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe})\text{Ni-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe})\text{CoCp-}\eta^5$ is formed⁶. The first polydecked sandwich system results⁷ from the reaction of $\text{Me}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2$ with excessive $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$. At low T, the dinuclear complex $\eta^3\text{-C}_3\text{H}_5\text{Ni-}\mu\text{-(Me}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH})\text{Ni(C}_3\text{H}_5\text{-}\eta^1)_2$ is formed first. Thin layers of this compound, if heated in a vacuum, change to the black polymer. 2,3-Dihydro-1,3-diborolyl complexes of Pd and Pt as mixed $\eta^5\text{-Cp}$ sandwiches are available by the reaction of $\text{NaCp-}\eta^5$, the neutral 2,3-dihydro-1,3-diborole and MX_2 (M = Pd, Pt)⁸:

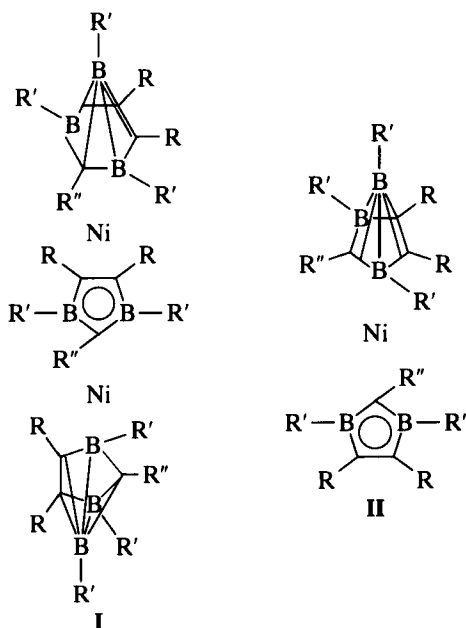


Alternatively 2 mol $\text{NaCp-}\eta^5$ can be used, and consequently 2 NaX and C_5H_6 are eliminated. Dehalogenation of PtCl_2 by means of $\text{Na[HB(Et)}_3]$ in the presence of $\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CHMe}$ forms $(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe})_2\text{Pt}$; $[(\text{C}_2\text{H}_4)_2\text{PtCl}_2]_2$ can be used also, as dehalogenation occurs at 70–80°C in benzene and $\text{Na[HB(Et)}_3]$ is not neces-

sary. The yields are very low. Better for preparative aims⁸ is the thermolysis of $(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CHMe})_2\text{Pt}$. The dihydrodiborolyl complex is obtained as dark red needles in 80% yield. Potassium reduces the sandwich complex to the dianion⁸. Triple- and tetradecadecked mixed complexes are prepared by reaction of $(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe})_2\text{Pt}$ with $\eta^5\text{-CpFe}(\text{C}_8\text{H}_{12})$ ($\text{C}_8\text{H}_{12} = 1,5\text{-COD}$), $\eta^5\text{-CpCo}(\text{C}_2\text{H}_4)_2$ or $[\eta^5\text{-CpNi}(\text{CO})]_2$: $\eta^5\text{-CpM-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)Pt(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)}$ ($\text{M} = \text{Co, Ni}$) and $\eta^5\text{-CpM-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)Pt-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)MCp-}\eta^5$ ($\text{M} = \text{Fe, Ni}$)⁹.

In refluxing toluene $\eta^5\text{-CpNi-}\mu\text{-(Et}_2\text{CB}_2\text{Et}_2\text{CMe)CoCp-}\eta^5$ reacts with $\text{Fe}_2(\text{CO})_9$ to give⁴ $\eta^5\text{-Cp(CO)Fe(}\mu\text{-CO)}_2\text{Ni(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{Me)CoCp-}\eta^5$; $\eta^5\text{-CpNi-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{CH)NiCp-}\eta^5$ and $\text{Fe}_2(\text{CO})_9$ interact to give different products: $\eta^5\text{-CpNi-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH)Fe(CO)}_3$, $\eta^5\text{-Cp(CO)Fe(}\mu\text{-CO)}_2\text{Ni-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH)Fe(CO)}_3$, $\eta^5\text{-CpFe-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH)Fe(CO)}_3$ ⁴.

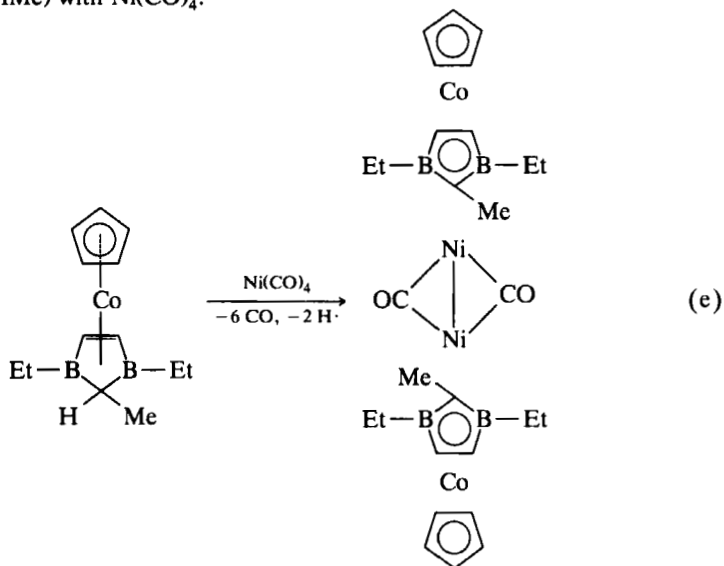
A very surprising route follows the reaction between $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$ and different 2,3-dihydro-1,3-diboroles $\text{R}_2\text{C}_2\text{B}_2\text{R}'_2\text{CHR}''$ ($\text{R} = \text{R}' = \text{Et}$, $\text{R}'' = \text{Me}$; $\text{R} = \text{Et}$, $\text{R}' = \text{Me}$, $\text{R}'' = \text{H}$; $\text{R} = \text{Me}$, $\text{R}' = \text{Me}$, $\text{R}'' = \text{H}$) in refluxing toluene. After evaporation of the solvent the sublimation of the residue gives the first $(\eta^5\text{-2,3,5-tricarbahexaboranyl})\text{nickel complexes}$ ¹⁰:



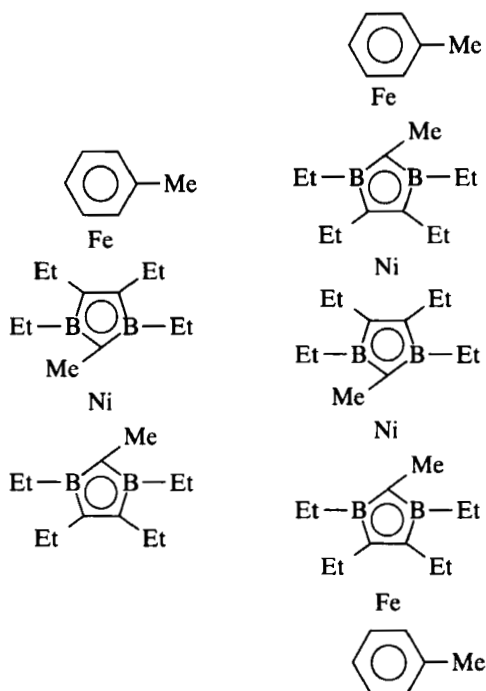
A tetradecadecked complex with the novel tricarbahexaboranyl ligand is obtained, if $(\text{Me}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2)_2\text{Ni}$ is recrystallized from CH_2Cl_2 : $[(\text{MeB})\text{Me}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}]\text{Ni-}\mu\text{-(Me}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH)Ni-}\mu\text{-(Me}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH)Ni}[(\text{MeB})\text{Me}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}]$ is isolated by sublimation as a deep-green solid¹⁰.

The first bis($\eta^5\text{-2,3,5-tricarbahexaboranyl})\text{nickel sandwich}$ is generated¹¹ by the reaction of $\text{Ni}(\text{C}_2\text{H}_4)_3$ and the 2,3-dihydro-1,3-diborole $\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2$. Besides $[(\text{MeB})\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}]\text{Ni}$ (12%) the tricarbahexaboranyl(allyl)nickel complex $[(\text{MeB})\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}]\text{Ni}(\text{MeCHCHCHEt})$ can be isolated by distillation.

A mixed Co-Ni oligodecked complex is available¹² by reacting η^5 -CpCo-(Et₂C₂B₂Et₂CHMe) with Ni(CO)₄:



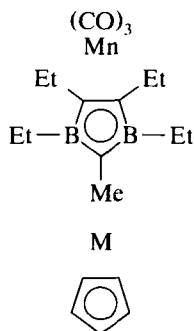
The above-mentioned η^3 -C₃H₅Ni- μ -(Et₂C₂B₂Et₂CMe)Ni- μ -(Et₂C₂B₂Et₂-CMe)NiC₃H₅- η^3 can be used to produce novel triple- and pentadecked sandwiches together with (toluene)Fe(Et₂C₂B₂Et₂CHMe), having toluene ligands at the ends of the stack¹³.



The mixed triple-decked complex $\eta^5\text{-CpCo-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)NiCp-}\eta^5$ results¹⁴ if $\eta^5\text{-CpNi(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)}$ is treated with $\eta^5\text{-CpCo(CO)}_2$. The neutral dihydridoborole $\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMeH}$ reacts with $\eta^5\text{-CpCo(CO)}_2$ in mesitylene under reflux to give^{4,14} the triple-decked sandwich $\eta^5\text{-CpCo-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)CoCp-}\eta^5$, whereas the corresponding $\eta^5\text{-CpCo(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH)CoCp-}\eta^5$ complex is obtained if $\eta^5\text{-CpCo(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2)$ (§6.5.3.1) is warmed together with $\eta^5\text{-CpCo(C}_2\text{H}_4)_2$ in petroleum ether (40–50°C) as olive-green crystals in 54% yield. Using $[\eta^5\text{-CpFe(CO)}_2]_2$ instead of $\eta^5\text{-CpCo(C}_2\text{H}_4)_2$ the heterometallic triple-decked sandwich $\eta^5\text{-CpFe(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH)CoCp-}\eta^5$ results (24%)⁴. It is also formed if $\eta^5\text{-CpFe(C}_8\text{H}_{12})$ is used instead of $[\eta^5\text{-CpFe(CO)}_2]_2$.

The reaction of the 2,3-dihydro-1,3-diborole with $[\eta^5\text{-CpFe(CO)}_2]_2$ and $\eta^5\text{-CpCo(CO)}_2$ at 180–200°C affords the green, triple-decked $\eta^5\text{-CpFe-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)CoCp-}\eta^5$ in 10% yield¹⁵.

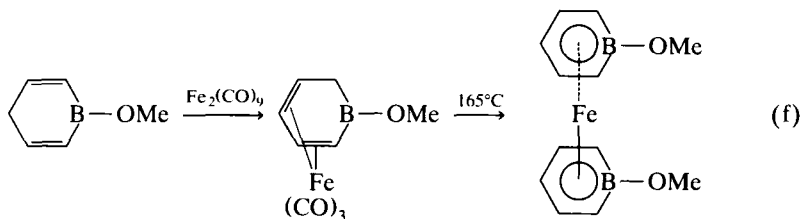
Boron–manganese bonds are produced^{12,16} if $\eta^5\text{-CpNi-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)NiCp-}\eta^5$, $\eta^5\text{-CpNi-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)CoCp-}\eta^5$ or $\eta^5\text{-CpCo(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2)$ react with $\text{Mn}_2(\text{CO})_{10}$:



where M = Ni, Co.

One Rh complex with a 2,3-dihydro-1,3-diborolyl ligand is prepared by dehalogenation of $[(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)RhCl}]_2$ with K in the presence of free 2,3-dihydro-1,3-diborole: $(\text{Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CHMe)Rh(Et}_2\text{C}_2\text{B}_2\text{Et}_2\text{CMe)}$ possesses one borole and one borolyl ring ligand¹².

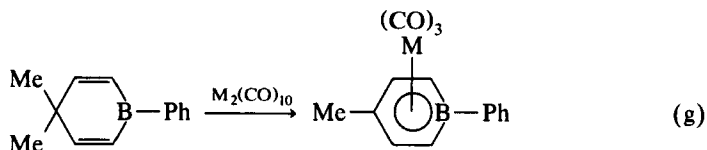
Comparable reactions between cyclic divinyl boranes and metal carbonyls lead to borinato (borabenzene) complexes^{17,18}:



During the reaction, the diene ring loses an H atom or an R radical and is now to be considered as a neutral five-electron donor or an anionic six-electron system.

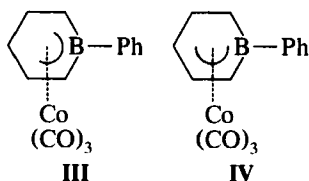
The intermediate $(\text{MeOBC}_5\text{H}_6)\text{Fe(CO)}_3$ shows no boron–metal bonding. The borinato sandwich is formed if boradiene tricarbonyliron is heated to 165°C for 12 h.

Methyl groups can be eliminated instead of H:

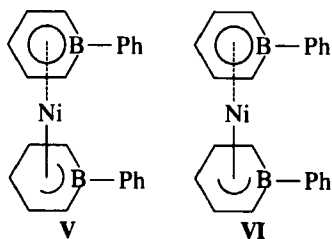


If the borinato ligand is a six-electron donor, the metals possess oxidation states of 2 + (Fe) and 1 + (Mn, Re), respectively.

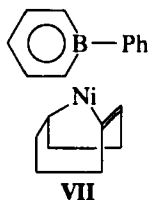
As described (§6.5.3.1) 1-phenylbora-2,5-cyclohexadiene (cyclic divinylborane) reacts with $\text{Fe}(\text{CO})_5$ under irradiation to the $\text{Fe}(\text{CO})_3$ complex. The dinuclear borabenzene complex $[(\text{C}_5\text{H}_5\text{BPh})\text{Fe}(\text{CO})_2]_2$ is found¹ as a by-product. It is to be compared with the well-known $[\eta^5\text{-CpFe}(\text{CO})_2]_2$. $\text{C}_5\text{H}_6\text{BPh}$ reacts spontaneously with $\text{Co}_2(\text{CO})_8$ to form three products. Above 60°C $(\text{C}_5\text{H}_5\text{BPh})\text{Co}(\text{CO})_2$ is the only product²⁰. At 30°C yellow isomers **III** and **IV** having partially hydrogenated borabenzene ligands form¹⁹; above 40°C **III** isomerizes to **IV**.



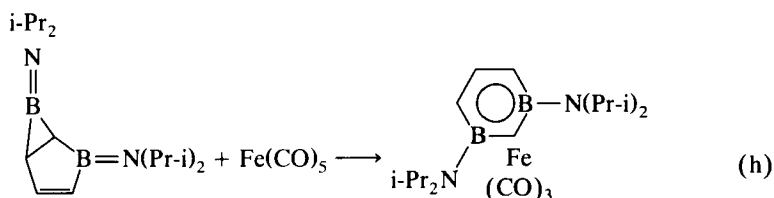
Whereas $4,4\text{-Me}_2\text{C}_5\text{H}_4\text{BPh}$ and $\text{Ni}(\text{CO})_4$ react²¹ to give $(4,4\text{-Me}_2\text{C}_5\text{H}_4\text{BPh})_2\text{Ni}$, $\text{C}_5\text{H}_6\text{BPh}$ and $\text{Ni}(\text{CO})_4$ form two isomers:



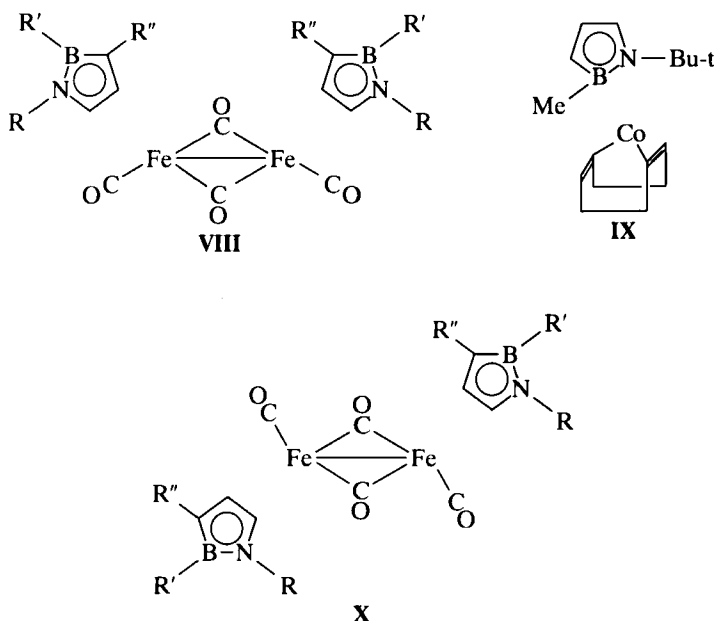
$\text{Ni}(\eta^4\text{-1,5-COD})_2$ behaves differently from $\text{Ni}(\text{CO})_4$ and yields²¹:



The first examples with a 1,3-diborabenzene skeleton have been described²². This ligand is generated during the reaction:

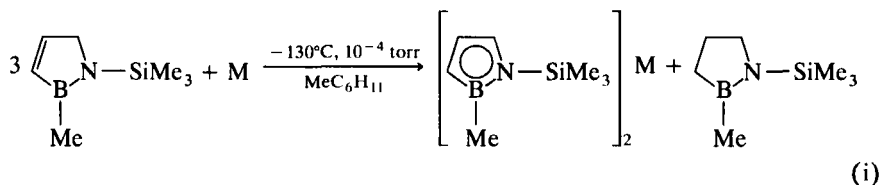


Dihydro-1H-1,2-azaboroles derive from cyclopentadiene by the isoelectronic replacement of a $\text{C}=\text{C}$ group by a BN moiety^{23–26}. The neutral rings react in xs boiling $\text{Fe}(\text{CO})_5$ without any other solvent to form red-brown iron–dihydro-1,2-azaborolyldicarbonyl dimers as their cis and trans isomers in 56% yield, or with $\text{Co}_2(\text{CO})_8$ in petroleum ether at 60–80°C to the half-sandwich complex (dihydro-1,2-azaborolyl) $\text{Co}(\text{CO})_2$ (40%)²⁷. The CO group can easily be substituted by olefins:



where $\text{R} = \text{t-Bu}$, $\text{R}' = \text{Ph}$, $\text{R}'' = \text{Me}$; $\text{R} = \text{t-Bu}$, $\text{R}' = \text{Me}$, $\text{R}'' = \text{H}$; $\text{R} = \text{SiMe}_3$, $\text{R}' = \text{Me}$, $\text{R}'' = \text{H}$; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$, $\text{R}'' = \text{H}$. During the reaction the neutral dihydroazaboroles are transformed to the anionic azaboroly systems, which act as six-electron ligands, while Fe is concurrently oxidized to the 1+ state. The hydrogen eliminated during the reaction hydrogenates equivalent amounts of free dihydroazaborole to form the saturated 1,2-azaborolidine.

1,2-Azaborolyl sandwich complexes can be prepared by metal-vapor synthesis (§6.5.3.1):



where M = Co, Fe.

One-third of the 2,5-dihydroazaborole used is hydrogenated to saturated 1,2-azaborolidine. The Co and Fe sandwich complexes each exist in a “clockwise” and a “counterclockwise” form^{28–32} (§6.5.3.4). A methylcyclohexane solution of the 2,5-dihydro-1,3-azaborole at -130°C is reacted with metal vapor. The colorless solutions become green (Co) and red (Fe) in the course of 15–30 min. Sublimation of the metal is continued until an excess of unreacted black metal is observed. The reactions are quantitative in azaborole. Isolation of the complexes is accomplished by pumping off the solvent and 1,2-azaborolidine in vacuum and subliming at $50\text{--}60^\circ\text{C}$ (0.0133 N m^{-2} , 10^{-4} torr) of the remaining red-black oils. Partial decomposition during sublimation decreases the yield to 30%. (For a second method of preparing these sandwich complexes see §6.5.4.3.)

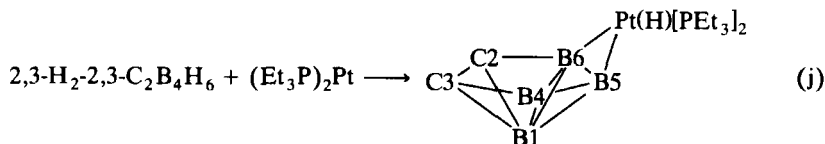
A series of boranes and carboranes react with metal complexes with loss of hydrogen, indicating a formal oxidation of the metal, which then makes bonds with B and/or C atoms. In some cases the borane frame changes its structure. These reactions are considered with the oxidative reactions in this section. Nido-5,6- $\text{C}_2\text{B}_8\text{H}_{12}$ and $(\eta^5\text{-Cp})_2\text{Ni}$ react to wine-red crystals of nido-[9- $\eta^5\text{-Cp}$ -7,8,9- $\text{C}_2\text{NiB}_8\text{H}_{11}$ with the Ni atom occupying one vertex in the open $\text{C}_2\text{B}_2\text{Ni}$ five-membered ring³³. A gold derivative is obtained if the Ni complex is treated with MeAuPPh_3 , whereas the dichromium complex $\text{closo-[1,3-(}\eta^5\text{-Cp)}_2\text{-1,2,3,4-CrCCrCB}_8\text{H}_{10}]$ is formed with $(\eta^5\text{-Cp})_2\text{Cr}$.

Reaction³⁴ of $(\text{COD})(\text{Et}_3\text{P})_2\text{Ni}$ with 5,9- Me_2 -5,9- $\text{C}_2\text{B}_7\text{H}_{11}$ leads to evolution of H_2 and formation of 6,6-(Et_3P)₂-5,9- Me_2 -6,5,9- $\text{NiC}_2\text{B}_7\text{H}_9$; $(\text{PPh}_3)_4\text{Pt}$ and arachno-4- CB_8H_{14} form³⁵ 9,6-(PPh_3)₂ $\text{PtCB}_8\text{H}_{12}$.

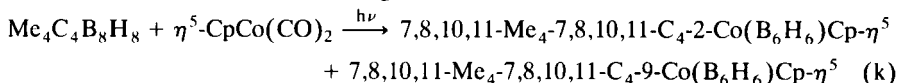
An Et_2O solution of $[\mu\text{-(COD)(PEt}_3)_4]\text{Pt}_2$ reacts^{36,37} at RT with nido-5,6- $\text{C}_2\text{B}_8\text{H}_{12}$ to form 9-H-9,9-(Et_3P)₂- μ -(10,11-H)-9,7,8- $\text{PtC}_2\text{B}_8\text{H}_{10}$.

With nido-2,3- $\text{C}_2\text{B}_6\text{H}_8$, nido-2,3- Me_2 -2,3- $\text{C}_2\text{B}_6\text{H}_8$ and nido- CB_6H_9 the binuclear Pt complex affords μ -4,5-[trans-(Et_3P)₂ PtH]- μ -(5,6-H)-2,3- CB_5H_6 , μ -4,5-[trans-(Et_3P)₂ PtH]- μ -(5,6-H)-2,3- Me_2 -2,3- $\text{C}_2\text{B}_4\text{H}_4$ and μ -4,5-[trans-(Et_3P)₂ PtH]- μ -(3,4-H)- μ -(5,6-H)-2- CB_5H_6 , respectively³⁸.

A hexane solution of $(\text{Et}_3\text{P})_2\text{Pt}$ reacts at RT with 2,3- $\text{C}_2\text{B}_4\text{H}_8$ or 2,3- Me_2 -2,3- $\text{C}_2\text{B}_4\text{H}_6$ to form the corresponding, crystalline μ -4,5-[trans-(Et_3P)₂ Pt(H)]- μ -(5,6-H)-2,3- $\text{C}_2\text{B}_4\text{H}_6$ and μ -4,5-[trans-(Et_3P)₂ Pt(H)]- μ -(5,6-H)-2,3- Me_2 -2,3- $\text{C}_2\text{B}_4\text{H}_4$ complexes³⁹:



Two isomeric 11-vertex nido cages can be formed⁴⁰:



The yields are only 6% each. A third complex is found (10% yield) having the formula $\eta^5\text{-CpCoMe}_4\text{C}_4\text{B}_7\text{H}_7$. From *closo*-1-Me-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ with 2 equiv of $(\text{PEt}_3)_4\text{Co}$ 1-Me-4-Et₃P- μ -4,6(7)-[Co(PEt₃)₂- μ -(H)₂]-4,1,2-CoC₂B₁₀H₁₀ can be synthesized⁴¹.

Two cobaltaborane isomers form when arachno-B₁₀H₈(SEt₂)₂ reacts with Co₂(CO)₈ and Co₄(CO)₁₂, respectively⁴²: *closo*-1,1,2,2-(CO)₄-1,2- μ -(CO)-4,11-(SEt₂)₂1,2-Co₂B₁₀H₈ and *closo*-1,1,2,2-(CO)₄-1,2- μ -(CO)-4,7-(SEt₂)₂1,2-Co₂B₁₀H₈; 9-(Me₂S)7-[(Me₃Si)₂CH]CB₁₀H₁₁ and Co atoms in toluene afford⁴³ 2-(toluene)-1-[(Me₃Si)₂CH]-2,1-CoB₁₀H₁₀. Using [$\eta^5\text{-CpNi(CO)}_2$]₂ as the complex reactand⁴³ 2- $\eta^5\text{-Cp-1-[(Me}_3\text{Si)}_2\text{CH]-2,1-NiCB}_{10}\text{H}_{10}$ is available. Metal-rich cobaltaboranes have been synthesized: $\mu_3\text{-(H)}_2\text{-(}\eta^5\text{-CpCo)}_4\text{B}_2\text{H}_2$ is afforded⁴⁴ by BH₃ · THF and $\eta^5\text{-CpCo(PPh}_3\text{)(C}_2\text{Et}_2\text{)}$. The Co₄B₂ unit forms an icosahedron with *cis*-standing B atoms. The same authors synthesized⁴⁵ 2-Ph-1,3,6,7,2-($\eta^5\text{-CpCo)}_4\text{PB}_2\text{H}_2$ from BH₃ · THF and $\eta^5\text{-CpCo(PPh}_3\text{)}_2$.

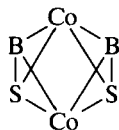
Heating a mixture of C₂B₄H₈ and *xs* Fe(CO)₅ to 240°C in a borosilicate glass tube with its lower end maintained at 25°C gives two products⁴⁶, namely 7,7,7-(CO)₃-7,2,3-FeC₂B₄H₆ and 6,6,6-(CO)₃-6,1,2-FeC₂B₃H₇. Both are nonvolatile at that temperature, but each can be separated from the other by repeated fractionation through a trap at -23°C⁴⁶. With Fe₂(CO)₉, B₂H₆Fe₂(CO)₆ reacts to yield the butterfly cluster HFe₄(BH₂)(CO)₁₂ with a BH₂ fragment bridging the wing tips^{47,48}. At -78°C Fe(CO)₅, Li[BHET₃] and BH₄ · THF combine to yield⁴⁹ B₂H₆Fe₂(CO)₆.

Hexaborane(10) and Fe₂(CO)₉ form μ -[3,4-Fe(CO)₄]B₆H₁₀. The Fe(CO)₄ moiety is coordinated to the unique basal B—B bond of B₆H₁₀^{50,51}. If Os₃(CO)₁₂ reacts with either *closo*-(Me₃Si)₂SnC₂B₄H₄ or *nido*-(Me₃Si)₂C₂B₄H₆, the product is *closo*-1-Os(CO)₃-2,3-(Me₂Si)₂C₂B₄H₄, a pentagonal bipyramid having Os as one vertex⁵².

Chromocene and *nido*-5,6-B₂B₈H₁₂ form the bimetallic chromium complex³⁵ 1,3-($\eta^5\text{-Cp}$)₂-1,3,2,4-Cr₂C₂B₈H₁₀.

The complexes W(≡CR)(CO)₂L (L = $\eta^5\text{-Cp}$, R = Me, C₆H₄Me-4, Ph; L = $\eta^5\text{-Me}_5\text{C}_5$, R = $\eta^6\text{-C}_6\text{H}_4\text{Me-4}$) react with BH₃ · THF to afford W₂- μ -[RCB(H)-CH₂R](CO)₄L₂ with a W₂BC tetrahedron as the molecular skeleton⁵³.

Metal-vapor synthesis also prepares metallaboranes and metallacarboranes with oxidation of the metal. Thermally generated Ni, Co and Fe atoms react with the *nido*-carborane 2,6-C₂B₇H₁₁ and either cyclopentadiene, toluene, mesitylene, or 2-butyne to give metallacarborane clusters⁵⁴: 5,7,8-Me₂-11,7,8,10-[$\eta^3\text{-C}_4\text{Me}_4\text{H}$]NiC₃-B₇H₇, 2-($\eta^5\text{-CpCo}$)-1,4-C₂B₇H₉, 4-($\eta^5\text{-CpCo}$)-2,3-C₂B₇H₁₃, 2-($\eta^6\text{-C}_6\text{H}_5\text{Me}$)Fe-1,6-C₂B₇H₉ and 6-($\eta^6\text{-C}_6\text{H}_3\text{Me}_3$)Fe-9,10-C₂B₇H₁₁ have been characterized. The same reaction principle leads⁵⁵ to the triple-decked metallaborane complex 4,6-[($\eta^5\text{-Cp}$)₂Co₂]-3,5-S₂B₂H₂, using Co atoms, C₅H₆, B₅H₉ and either COS or H₂S. ($\mu_3\text{-CO})(\eta^5\text{-Cp})_3\text{Co}_3\text{S}$, 2,3-($\eta^5\text{-Cp}$)₂Co₂-6-SB₅H₇ and 6,8-[($\eta^5\text{-Cp}$)₂Co₂]-7,9-S₂B₅H₅ are formed additionally. Frame of the Co₂S₂B₂ cluster:



The reaction of thermally generated Co atoms with B_6H_{10} , $Me_3SiC \equiv CSiMe_3$ and C_5H_6 yields⁵⁶ as major products 5:1',2'-[(1- η^5 -Cp)Co-2,3-(Me_3Si) $_2$ C $_2$ B $_4$ H $_3$][B $_2$ H $_5$], 1-(η^5 -CpCo)-4,6-(Me_3Si) $_2$ C $_2$ B $_6$ H $_6$ and 1-(η^5 -CpCo)-4,5-(Me_3Si) $_2$ C $_2$ B $_6$ H $_6$ together with smaller amounts of 5-(η^5 -CpCo)-1,8-(Me_3Si) $_2$ C $_2$ B $_5$ H $_5$ and 1-(η^5 -CpCo)-2,3-(Me_3Si) $_2$ C $_2$ B $_4$ H $_4$. The new cobaltaborane compound iso-8- η^5 -CpCoB $_{17}$ H $_{21}$ is given, in very low yield⁵⁷, by n-B $_{18}$ H $_{22}$ and Co atoms.

Reaction of thermally produced Fe atoms with B $_{10}$ H $_{14}$ and mesitylene or toluene leads to the first (η^6 -arene)ferraboranes: 5-LFeB $_9$ H $_{13}$, 1-LFeB $_9$ H $_9$, 1-LFeB $_{10}$ H $_{10}$ and traces of 2-LFe-6-OB $_8$ H $_{10}$ (L = mesitylene, toluene)⁵⁸. In the presence of toluene nido-7-SB $_{10}$ H $_{12}$ or nido-6-SB $_9$ H $_{11}$ reacts with Fe atoms to give⁵⁹ closo-2-(η^6 -C $_6$ H $_5$ Me)-2,1-FeSB $_{10}$ H $_{10}$ as well as nido-8-(η^6 -C $_6$ H $_5$ Me)-8,7-FeSB $_9$ H $_{11}$.

In the presence of toluene and 2-butyne B $_5$ H $_9$ reacts with Fe atoms to give⁶⁰ the (arene)ferracarborane sandwich complex 1-(C $_6$ Me $_6$)Fe-2,3-Me $_2$ C $_2$ B $_4$ H $_4$ along with smaller amounts of 1-(C $_6$ Me $_6$)Fe-4,5,7,8-Me $_4$ C $_4$ B $_3$ H $_3$, 1-(C $_6$ H $_5$ Me)Fe-4,5,7,8-Me $_4$ C $_4$ B $_3$ H $_3$ and 2-(C $_6$ H $_5$ Me)Fe-6,7,9,10-Me $_4$ C $_4$ B $_3$ H $_5$.

Iron atoms react with toluene and the carborane 2,3-Et $_2$ C $_2$ B $_4$ H $_6$ under low T to yield⁶¹ 1-(η^6 -MeC $_6$ H $_5$)-Fe-2,3-Et $_2$ C $_2$ B $_4$ H $_4$.

(G. SCHMID)

1. P. Binger, *Angew. Chem., Int. Ed. Engl.*, **7**, 286 (1968).
2. W. Siebert, M. Bochmann, *Angew. Chem., Int. Ed. Engl.*, **16**, 468 (1977).
3. W. Siebert, J. Edwin, M. Bochmann, C. Krüger, Y.-H. Tsay, *Z. Naturforsch., Teil B*, **33**, 1410 (1978).
4. J. Edwin, M. Bochmann, M. C. Böhm, D. E. Brennan, W. E. Geiger, C. Krüger, J. Pebler, H. Pritzkow, W. Siebert, W. Swiridoff, H. Wadepohl, J. Weiss, U. Zennek, *J. Am. Chem. Soc.*, **105**, 2582 (1983).
5. Th. Kuhlmann, W. Siebert, *Z. Naturforsch., Teil B*, **39**, 1046 (1984).
6. Th. Kuhlmann, W. Siebert, *Z. Naturforsch., Teil B*, **40**, 167 (1985).
7. Th. Kuhlmann, S. Roth, J. Rozière, W. Siebert, *Angew. Chem., Int. Ed. Engl.*, **25**, 105 (1986).
8. H. Wadepohl, W. Siebert, *Z. Naturforsch., Teil B*, **39**, 50 (1984).
9. H. Wadepohl, H. Pritzkow, W. Siebert, *Chem. Ber.*, **118**, 729 (1985).
10. Th. Kuhlmann, H. Pritzkow, U. Zennek, W. Siebert, *Angew. Chem., Int. Ed. Engl.*, **23**, 965 (1984).
11. J. Zwecker, H. Pritzkow, U. Zennek, W. Siebert, *Angew. Chem., Int. Ed. Engl.*, **25**, 1099 (1986).
12. J. Edwin, M. C. Böhm, N. Chester, D. M. Hoffman, R. Hoffmann, H. Pritzkow, W. Siebert, K. Stumpf, H. Wadepohl, *Organometallics*, **2**, 1666 (1983).
13. W. Siebert, *Angew. Chem., Int. Ed. Engl.*, **24**, 943 (1985).
14. W. Siebert, J. Edwin, M. Bochmann, *Angew. Chem., Int. Ed. Engl.*, **17**, 868 (1978).
15. W. Siebert, M. Bochmann, *Angew. Chem., Int. Ed. Engl.*, **16**, 857 (1977).
16. W. Siebert, in *Advances in Organometallic Chemistry*, Vol. 18, F. G. A. Stone, R. West, eds., Academic Press, New York, 1980, p. 301.
17. A. J. Ashe III, W. Butler, H. F. Sandford, *J. Am. Chem. Soc.*, **101**, 7066 (1979).
18. G. E. Herberich, E. Bauer, *Chem. Ber.*, **110**, 1167 (1977).
19. G. E. Herberich, E. Raabe, *J. Organomet. Chem.*, **309**, 143 (1986).
20. G. E. Herberich, H. J. Becker, *Z. Naturforsch., Teil B*, **29**, 439 (1974).
21. G. E. Herberich, M. Tönnessen, D. Schmitz, *J. Organomet. Chem.*, **191**, 27 (1980).
22. G. E. Herberich, H. Ohst, *J. Organomet. Chem.*, **307**, C16 (1986).
23. J. Schulze, G. Schmid, *Angew. Chem.*, **92**, 61 (1980).
24. J. Schulze, R. Boese, G. Schmid, *Chem. Ber.*, **113**, 2348 (1980).
25. J. Schulze, G. Schmid, *J. Organomet. Chem.*, **193**, 83 (1980).
26. J. Schulze, R. Boese, G. Schmid, *Chem. Ber.*, **114**, 1297 (1980).
27. G. Schmid, F. Schmidt, *Chem. Ber.*, **119**, 1766 (1986).

6.5.3. Formation from Other Group-IIIB Compounds

6.5.3.4. by Reaction with Metal Halides

28. S. Amirkhalili, U. Höhner, G. Schmid, *Angew. Chem., Int. Ed. Engl.*, **21**, 68 (1982); *Angew. Chem. Suppl.* 1982, 49.
29. S. Amirkhalili, R. Boese, U. Höhner, D. Kampmann, G. Schmid, P. Rademacher, *Chem. Ber.*, **115**, 732 (1982).
30. G. Schmid, S. Amirkhalili, U. Höhner, D. Kampmann, R. Boese, *Chem. Ber.*, **115**, 3830 (1982).
31. G. Schmid, U. Höhner, D. Kampmann, D. Zaika, R. Boese, *Chem. Ber.*, **116**, 951 (1983).
32. G. Schmid, R. Boese, *Z. Naturforsch., Teil B*, **38**, 485 (1983).
33. G. K. Barker, N. R. Godfrey, M. Green, H. E. Parge, F. G. A. Stone, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 277 (1983).
34. M. Green, J. A. K. Howard, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 2274 (1975).
35. G. A. Kukina, I. A. Zakharova, M. A. Porai-Koshits, B. Stibr, V. S. Sergienko, K. Base, J. Dolanski, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1978, 1228; *Chem. Abstr.*, **93**, 239,615 (1980).
36. G. K. Barker, M. Green, F. G. A. Stone, A. J. Welch, W. C. Wolsey, *J. Chem. Soc., Chem. Commun.*, 627 (1980).
37. G. K. Barker, M. Green, F. G. A. Stone, W. C. Wolsey, *J. Chem. Soc., Dalton Trans.*, 2063 (1983).
38. G. K. Barker, M. Green, F. G. A. Stone, A. J. Welch, T. P. Onak, G. Siwapanoyos, *J. Chem. Soc., Dalton Trans.*, 1687 (1979).
39. G. K. Barker, M. Green, T. P. Onak, F. G. A. Stone, C. B. Ungermann, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 169 (1978).
40. R. B. Maynard, E. Sinn, R. N. Grimes, *Inorg. Chem.*, **20**, 3858 (1981).
41. G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 137 (1983).
42. D. M. Schubert, C. B. Knobler, P. A. Wegner, M. F. Hawthorne, *J. Am. Chem. Soc.*, **110**, 5219 (1988).
43. W. Quintana, R. L. Ernest, P. J. Carroll, L. G. Sneddon, *Organometallics*, **7**, 166 (1988).
44. J. Feilong, Th. P. Fehlner, A. L. Rheingold, *J. Am. Chem. Soc.*, **109**, 1860 (1987).
45. J. Feilong, Th. P. Fehlner, A. L. Rheingold, *J. Chem. Soc., Chem. Commun.*, 1395 (1987).
46. R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 261 (1971).
47. K. S. Wong, W. R. Scheidt, T. P. Fehlner, *J. Am. Chem. Soc.*, **104**, 1111 (1982).
48. T. P. Fehlner, C. E. Housecroft, W. R. Scheidt, K. S. Wong, *Organometallics*, **2**, 825 (1983).
49. G. B. Jacobsen, E. L. Andersen, C. E. Housecroft, F.-E. Hong, M. L. Buhl, G. J. Long, T. T. Tchluer, *Inorg. Chem.*, **26**, 4040 (1987).
50. A. Davison, D. D. Traficante, S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, 1155 (1972).
51. M. Mangion, W. R. Clayton, O. Hollander, S. G. Shore, *Inorg. Chem.*, **16**, 2110 (1977).
52. N. S. Hosmane, N. N. Sirmokadam, *Organometallics*, **3**, 1119 (1984).
53. D. Barratt, S. J. Davies, G. P. Elliott, J. A. K. Howard, D. B. Lewis, F. G. A. Stone, *J. Organomet. Chem.*, **325**, 185 (1987).
54. J. J. Briguglio, L. G. Sneddon, *Organometallics*, **5**, 327 (1986).
55. R. P. Micciche, P. J. Carroll, L. G. Sneddon, *Organometallics*, **4**, 1619 (1985).
56. J. J. Briguglio, L. G. Sneddon, *Organometallics*, **4**, 721 (1985).
57. S. O. Wang, L. G. Sneddon, *Inorg. Chem.*, **27**, 587 (1988).
58. R. P. Micciche, J. J. Briguglio, L. G. Sneddon, *Inorg. Chem.*, **23**, 3992 (1984).
59. S. O. Wang, P. J. Carroll, L. G. Sneddon, *Organometallics*, **7**, 772 (1988).
60. R. P. Micciche, J. J. Briguglio, L. G. Sneddon, *Organometallics*, **3**, 1396 (1984).
61. R. P. Micciche, L. G. Sneddon, *Organometallics*, **2**, 674 (1983).

6.5.3.4. by Reaction with Metal Halides

Reactions between anionic species containing one or more group-IIIB elements (particularly boron) and complexes of transition-metal halides are used to produce an immense number of ionic boron-containing compounds. For this reason a strong selection factor must be made.

6.5. Group-IIIB–Transition- or –Inner Transition-Metal Bonds

59

6.5.3. Formation from Other Group-IIIB Compounds

6.5.3.4. by Reaction with Metal Halides

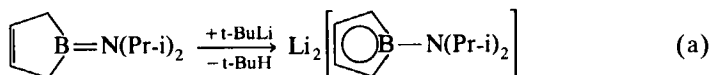
28. S. Amirkhalili, U. Höhner, G. Schmid, *Angew. Chem., Int. Ed. Engl.*, **21**, 68 (1982); *Angew. Chem. Suppl.* 1982, 49.
29. S. Amirkhalili, R. Boese, U. Höhner, D. Kampmann, G. Schmid, P. Rademacher, *Chem. Ber.*, **115**, 732 (1982).
30. G. Schmid, S. Amirkhalili, U. Höhner, D. Kampmann, R. Boese, *Chem. Ber.*, **115**, 3830 (1982).
31. G. Schmid, U. Höhner, D. Kampmann, D. Zaika, R. Boese, *Chem. Ber.*, **116**, 951 (1983).
32. G. Schmid, R. Boese, *Z. Naturforsch., Teil B*, **38**, 485 (1983).
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34. M. Green, J. A. K. Howard, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 2274 (1975).
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40. R. B. Maynard, E. Sinn, R. N. Grimes, *Inorg. Chem.*, **20**, 3858 (1981).
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45. J. Feilong, Th. P. Fehlner, A. L. Rheingold, *J. Chem. Soc., Chem. Commun.*, 1395 (1987).
46. R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 261 (1971).
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52. N. S. Hosmane, N. N. Sirmokadam, *Organometallics*, **3**, 1119 (1984).
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54. J. J. Briguglio, L. G. Sneddon, *Organometallics*, **5**, 327 (1986).
55. R. P. Micciche, P. J. Carroll, L. G. Sneddon, *Organometallics*, **4**, 1619 (1985).
56. J. J. Briguglio, L. G. Sneddon, *Organometallics*, **4**, 721 (1985).
57. S. O. Wang, L. G. Sneddon, *Inorg. Chem.*, **27**, 587 (1988).
58. R. P. Micciche, J. J. Briguglio, L. G. Sneddon, *Inorg. Chem.*, **23**, 3992 (1984).
59. S. O. Wang, P. J. Carroll, L. G. Sneddon, *Organometallics*, **7**, 772 (1988).
60. R. P. Micciche, J. J. Briguglio, L. G. Sneddon, *Organometallics*, **3**, 1396 (1984).
61. R. P. Micciche, L. G. Sneddon, *Organometallics*, **2**, 674 (1983).

6.5.3.4. by Reaction with Metal Halides

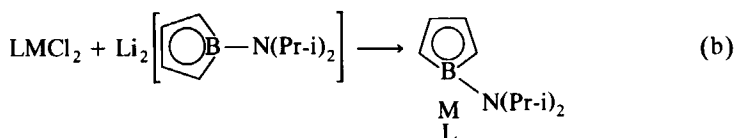
Reactions between anionic species containing one or more group-IIIB elements (particularly boron) and complexes of transition-metal halides are used to produce an immense number of ionic boron-containing compounds. For this reason a strong selection factor must be made.

Three kinds of B containing species may be used to react with metal halides: cyclic compounds, carboranes and borane anions. The carboranes especially form an enormous number of complexes.

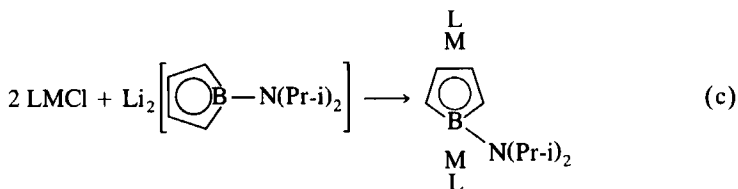
Borole complexes (§6.5.3), normally prepared from dihydroboroles by loss of hydrogen during the complexation process, are also available using a borole dianion via lithiation of dihydroboroles^{1,2}.



Metal halides react with this dianion to form the corresponding complexes²:



where LM = Me₅C₅Rh, η⁶-C₆Me₆Ru;

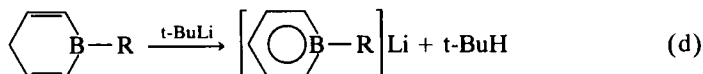


where LM = (C₂H₄)₂Rh, (COD)Rh, [C₄H₄BN(Pr-i)₂]Rh.

Using [(CO)₂RhCl]₂ a different reaction path occurs because cis-C₄H₄BN(i-Pr)₂Rh(CO)-μ-(CO)₂-Rh(CO)C₄H₄BN(Pr-i)₂ is formed. The 34-electron triple-decked complex η⁵-CpNi-μ-[C₄H₄BN(Pr-i)₂]₂NiCp-η⁵ is given by [η⁵-CpNi(COD)]BF₄. As expected, NiBr₂ yields [C₄H₄BN(i-Pr)₂]₂Ni (63%), whereas CoBr₂ produces the triple-decked sandwich [C₄H₄BN(i-Pr)₂]₂Co-μ-[C₄H₄BN(i-Pr)₂]₂Co (30%).

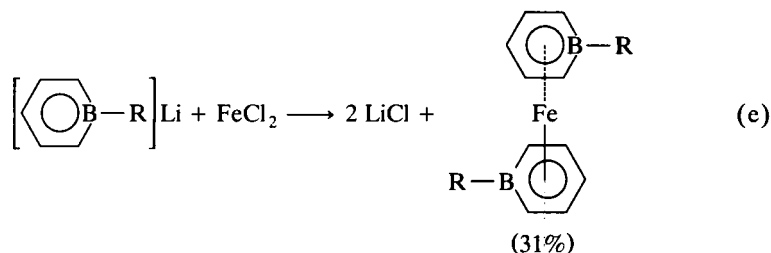
The reaction between the dianion and metal halides in the presence of additional ligands such as CO ends in a row of carbonylborole complexes of Fe, Co, Mn, and Cr². In a CO atmosphere FeBr₂ · dimethoxyethane gives [C₄H₄BN(i-Pr)₂]Fe(CO)₃ and [C₄H₄BN(i-Pr)₂]Fe(CO) simultaneously, with 11 and 16% yields, respectively, whereas CoBr₂ · dimethoxyethane, under corresponding conditions, results in [C₄H₄BN(i-Pr)₂]Co(CO)-μ-(CO)₂-Co(CO)C₄H₄BN(Pr-i)₂. A mixed(arene) Ru(borole) systems arises¹ if Li₂[C₄H₄BN(Pr-i)₂] reacts with [(Me₆C₆)RuCl₂]₂ in THF, yielding the yellow complex (Me₆C₆)Ru[C₄H₄BN(Pr-i)₂]. Both [C₄H₄BN(i-Pr)₂]₂Mn(CO) and [C₄H₄BN(i-Pr)₂]₂Cr(CO)₂ are isolated if the dianion is allowed to react with MnBr₂ and CrCl₃, respectively, in a CO atmosphere.

A broad synthetic approach to borinato complexes (§6.5.3.3) via alkali-metal borinates has been developed³⁻⁵. Treatment of 1-boracyclohexadiene with t-BuLi leads to the anionic borinato ligand:

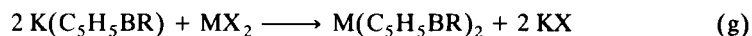


where R = Ph, Me, t-Bu, Br.

Ferrous chloride reacts with the borinato anion to give sandwich complexes:

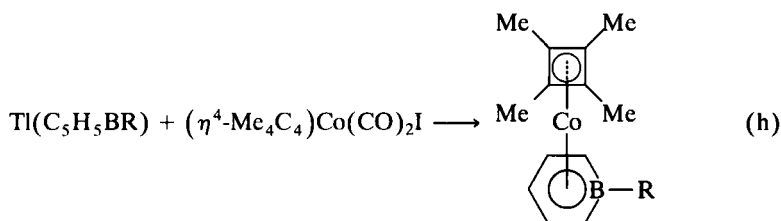


Another elegant synthesis route to borinato ligands and sandwich complexes uses cyanide degradation of otherwise prepared borinato complexes (§6.5.3.3). The reactions proceed quantitatively to yield borinato ligands^{6,7} and insoluble metal cyanides:

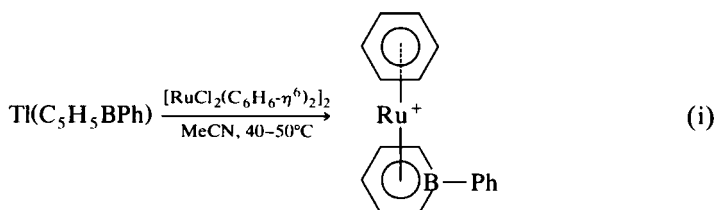


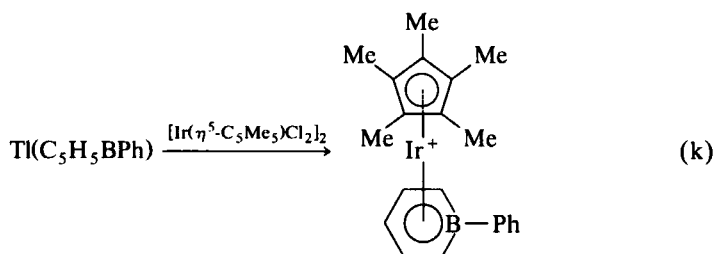
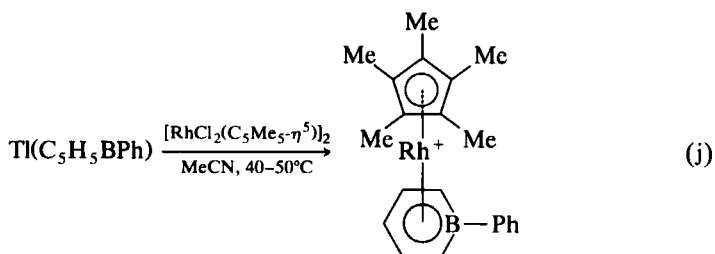
The filtered solutions of the borinato salts are used directly to synthesize such different complexes as $\text{Fe}(\text{C}_5\text{H}_5\text{BR})_2$, $\text{Ru}(\text{C}_5\text{H}_5\text{BR})_2$, $\text{Os}(\text{C}_5\text{H}_5\text{BR})_2$, $(\text{COD})\text{Rh}(\text{C}_5\text{H}_5\text{BR})$, $\text{Me}_3\text{Pt}(\text{C}_5\text{H}_5\text{BR})_2$ or $\text{Cr}(\text{C}_5\text{H}_5\text{BR})_2$ ($\text{R} = \text{Me}, \text{Ph}$)⁸.

Thallium borinates, $\text{Tl}(\text{C}_5\text{H}_5\text{BR})$ ($\text{R} = \text{Me}, \text{Ph}$) are also used to synthesize transition-metal complexes^{9–11}. Alkali-metal borinates react with TlCl in MeCN to give $\text{Tl}(\text{C}_5\text{H}_5\text{BR})$. In contrast to the alkali salts, thallium borinates are isolatable compounds, e.g.:



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





where $[\text{PF}_6]^-$ is the anion.

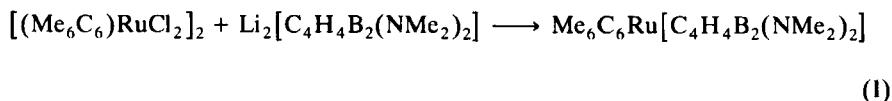
When $\eta^4\text{-C}_4\text{H}_4\text{Co}(\text{CO})_2\text{I}$ is reacted with $\text{Ti}[\text{C}_5\text{H}_5\text{BR}]$ ($\text{R} = \text{Me}, \text{Rh}$) the cyclobutadiene ligand as well as the CO groups may be substituted to give $(\text{RBC}_5\text{H}_5)\text{Co}(\text{CO})_2$ or $(\text{RBC}_5\text{H}_5)\text{Co}(\text{C}_4\text{H}_4\text{-}\eta^4)$, respectively¹².

As a derivative of the borabenzene, 2-boronaphthalene can also be used for complex formation via its anion. From solutions of the lithium-2-boranaphthalenes $\text{Li}[\text{RBC}_9\text{H}_7]$ [$\text{R} = \text{Ph}, (\text{i-Pr})_2\text{N}$] and corresponding metal halides, the crystalline complexes $\text{Fe}(\text{RBC}_9\text{H}_7)_2$ and $\text{L}_2\text{Rh}(\text{RBC}_9\text{H}_7)$ ($\text{L} = \text{C}_2\text{H}_4, 2 \text{ L} = \text{C}_8\text{H}_{12}$) can be isolated. Iron and Rh atoms are η^6 bonded to the B-containing moiety of the naphthalene system¹³.

In dioxane $\text{Na}[\text{MeBC}_5\text{H}_5]$ reacts with $(\text{CO})_3\text{Cr}(\text{NH}_3)_3$ to give $\text{Na}[(\text{MeBC}_5\text{H}_5)\text{-Cr}(\text{CO})_3] \cdot 2 \text{ dioxane}$. The sodium cation can be substituted¹⁴ by $[\text{Ph}_4\text{P}]^+$ or Hg^+ .

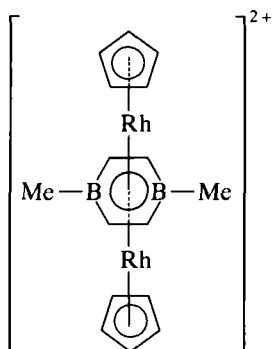
The paramagnetic sandwich complexes $(\text{RBC}_5\text{H}_5)_2\text{V}$ can be prepared if $[\text{RBC}_5\text{H}_5]^-$ ($\text{R} = \text{Me}, \text{Ph}$) reacts with VCl_3 . The tetracarbonyl complex $(\text{CO})_4\text{V}(\text{C}_5\text{H}_5\text{BR})$ is yielded via $[\text{V}(\text{CO})_6]^-$. In hot cycloheptatriene it can be transformed into $(\text{C}_7\text{H}_7)\text{V}(\text{C}_5\text{H}_5\text{BR})$ sandwich-type compounds¹⁵.

Transition-metal chlorides react with the anion $[\text{C}_4\text{H}_4\text{B}_2(\text{NMe}_2)_2]^{2-}$ to produce novel 1,2-diborabenzene complexes¹⁶.

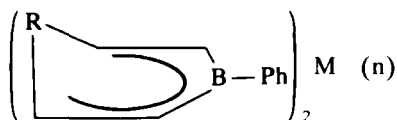
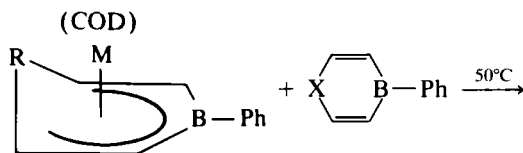
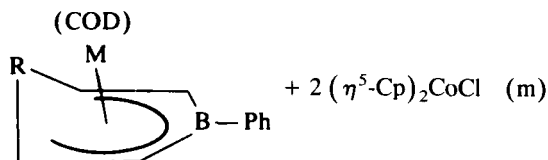
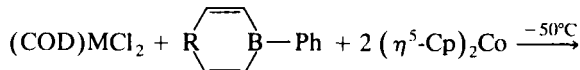


The dark red 30-electron triple-decked complex $(\text{C}_8\text{H}_{12})\text{Rh-}\mu\text{-}[\text{C}_4\text{H}_4\text{B}_2(\text{NMe}_2)_2]\text{Rh}(\text{C}_8\text{H}_{12})$ can be made from $[(1,5\text{-C}_8\text{H}_{12})\text{RhCl}]_2$. 1,4-Diborabenzene acts

as a bridging ligand in the triple-decked cation¹⁷:

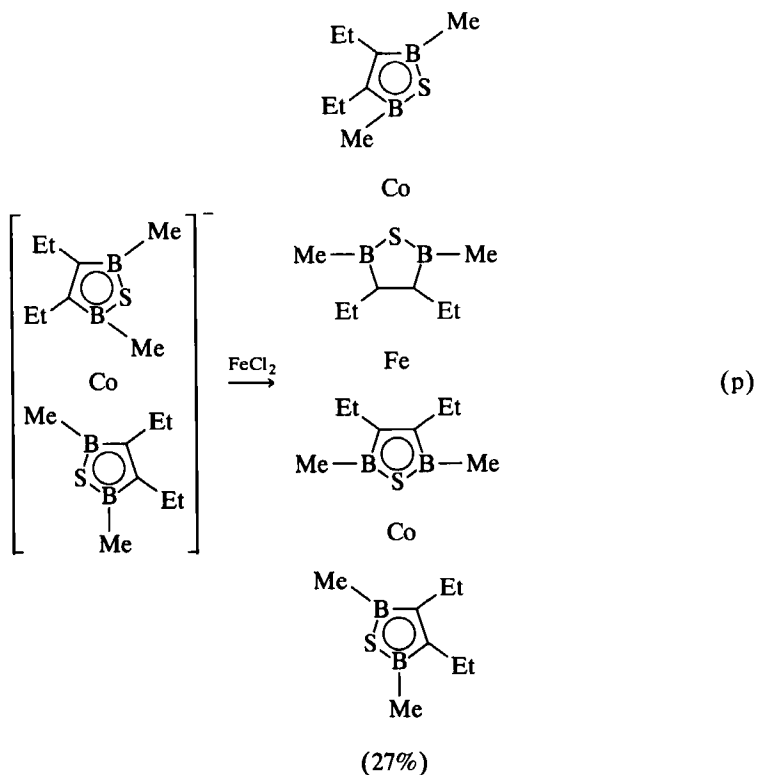
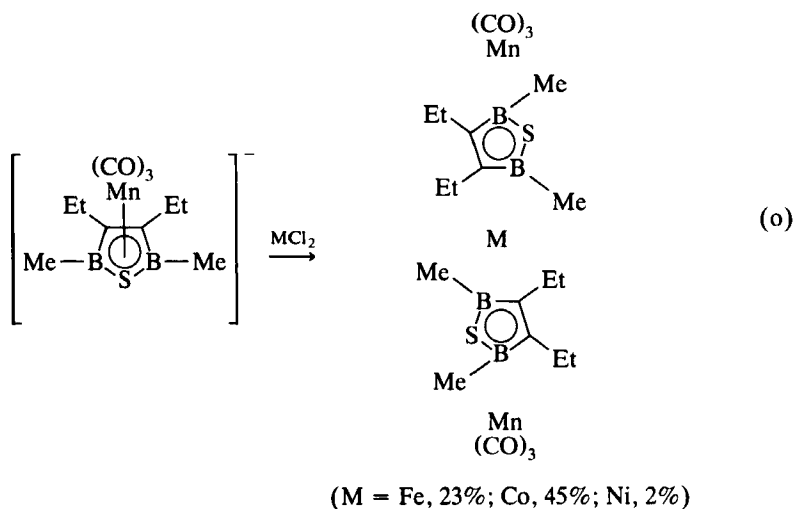


Divinylborane-transition-metal complexes (§6.5.3.1) are accessible from metal halides and divinylboranes with simultaneous reduction by $(\eta^5\text{-Cp})_2\text{Co}$, e.g.¹⁸:

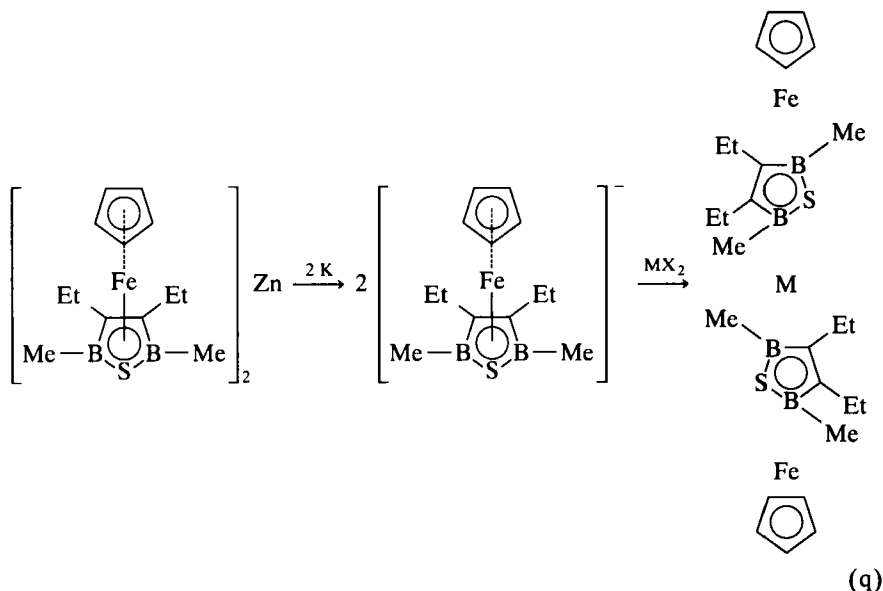


where $\text{M} = \text{Pd}, \text{Pt}$; $\text{R} = \text{Me}_2\text{C}, \text{Me}_2\text{Si}, (\text{CH}_2)_2$. The reactions are carried out in CH_2Cl_2 . Water or alcohol must be avoided as divinyl boranes are strong electron-pair acceptors and are degraded by those basic solvents. Yields are between 70 and 80%.

The existence of complex anions, e.g., $[(\text{CO})_3\text{Mn}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})]^-$ or $[(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})_2\text{Co}]^-$, allows the preparation of triple-decked and tetradecked

sandwich complexes, e.g.^{19,20}:


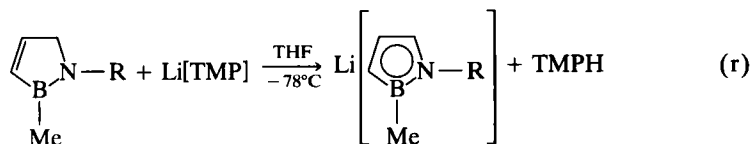
Mixed cyclopentadienyl-thiadiborolene tetradecked sandwich compounds are available using a novel zinc complex, e.g.²⁰:



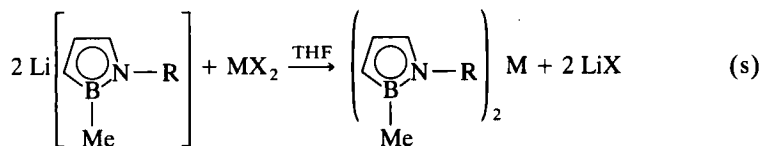
Reaction of the Zn complex itself with CoCl_2 yields different compounds by ligand transfer²⁰, e.g., $\eta^5\text{-CpCo}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})$ (83%), $(\eta^5\text{-Cp})_2\text{Fe}$ (70%) and traces of the triple-decked complex $\eta^5\text{-CpFe-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{S})\text{FeCp-}\eta^5$.

Using a potassium mirror $\eta^5\text{-CpCo}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2)$ can be reduced to the monoanion, which then may react with $\eta^5\text{-CpFe}(\text{CO})_2\text{I}$ to give a mixture²¹ of $\eta^5\text{-CpFe}(\text{Et}_2\text{C}_2\text{B}_2\text{Ne}_2\text{CH})\text{CoCp-}\eta^5$ (< 5%), $\eta^5\text{-CpCo}(\text{Et}_2\text{C}_2\text{B}_2\text{Ne}_2\text{CH})\text{CoCp-}\eta^5$ (15%), $\eta^5\text{-CpCo-}\mu\text{-(Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH}_2)$ (50%) and $[\eta^5\text{-CpFe}(\text{CO})_2]_2$. With Fe^{2+} and Co^{2+} , and Mn^{2+} the tetradecked sandwiches of the type $[\eta^5\text{-CpCo}(\text{Et}_2\text{C}_2\text{B}_2\text{Me}_2\text{CH})]_2\text{M}$ ($\text{M} = \text{Fe}, \text{Co}$) are formed^{22,23}.

Dihydro-1,2-azaborolyl sandwich complexes, available by metal-vapor synthesis (§6.5.3.3), can be prepared in a greater variety by reaction of metal halides with azaborolyl anions, e.g.²⁴⁻³⁰:



where $\text{R} = \text{t-Bu}, \text{SiMe}_3$;

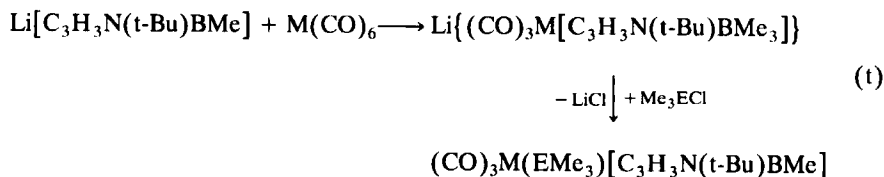


where $\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Ru}$.

Each of the sandwich compounds forms two isomers, described as "clockwise" and "counterclockwise," respectively. "Clockwise" means that the atomic sequence in both rings is the same, "counterclockwise" that the atomic sequence is opposite. The syntheses occur best in THF at -78°C . After warming, the solvent is removed. Purification can be carried out by crystallization from petroleum, ether or better by sublimation at $60\text{--}70^{\circ}\text{C}$ and 10^{-4} torr. The yields vary between 25 and 85%. The 17- and 18-electron complexes with V and Fe atoms show the metal atoms to be fixed above and below the ring centers. In contrast, the 19- and 20-electron complexes of Co and Ni possess slipped rings.

Both TiBr_4 and $\text{Li}[\text{C}_3\text{H}_3\text{N}(\text{t-Bu}_3)\text{BMe}]$ react to the red bis(1-Bu-2-methyl-dihydro-1,2-azaborolyl)titanium dibromide²⁴. The chlorine derivative bis(2-methyl-1-trimethylsilyldihydro-1,2-azaborolyl)titaniumdichloride³¹ as well as the V complex bis(2-methyl-1-trimethylsilyldihydro-1,2-azaborolyl)vanadium chloride³¹ shows metal-chlorine interactions, additionally to metal-ring bonds proved by x-ray analysis. This demonstrates the great electron deficiency on the boron atom. Both compounds are made from the Li salt of the azaborol rings with TiCl_4 and VCl_3 , respectively. 1-t-Butyl-2-methyldihydro-1,2-azaborolyl lithium reacts with $[(\text{CH}_3\text{CN})_3\text{Mn}(\text{CO})_3]\text{PF}_6$ to give³² $[\text{C}_3\text{H}_3\text{N}(\text{t-Bu}_3)\text{BMe}]\text{Mn}(\text{CO})_3$.

Some half-sandwich complexes with dihydro-1,2-azaborolyl ring ligands have been described, too³³:



where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$.

Mixed (arene)(dihydroazaborolyl) Fe complexes are available³⁴:

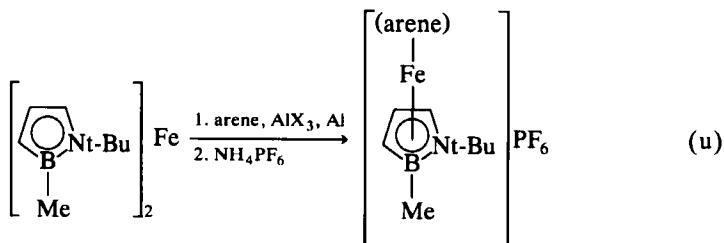


TABLE 1. METALLACARBORANES WITH THREE BORON ATOMS

Compound	Refs.
$1-\eta^5\text{-Cp-1,2,3-CoC}_2\text{B}_3\text{H}_7$	47
$1,7-(\eta^5\text{-Cp})_2\text{-1,7,2,3-CoC}_2\text{B}_3\text{H}_5$	47, 48
$1,7-(\eta^5\text{-Cp})_2\text{-1,7,2,4-CoC}_2\text{B}_3\text{H}_5$	47, 48
$1,7-(\eta^5\text{-Cp})_2\text{-}\mu\text{-(2,3-C}_3\text{H}_4\text{)-1,7,2,3-CoC}_2\text{B}_3\text{H}_5$	49
$1,7-(\eta^5\text{-Me}_5\text{C}_5)_2\text{-2,3-Me}_2\text{-1,7,2,3-CoC}_2\text{B}_3\text{H}_3$	50
$(2,3\text{-Et}_2\text{C}_2\text{B}_3\text{H}_5)\text{-5-CoB}_9\text{H}_{12}\text{-1-O(CH}_2)_4$	51, 52
$1,1,1\text{-(CO)}_3\text{-2-Me-1,2,3,4-MnC}_3\text{B}_3\text{H}_5$	53

TABLE 2. METALLACARBORANES WITH FOUR BORON ATOMS

Compound	Refs.
1-(dppe) ₂ -1,2,3-NiC ₂ B ₄ H ₆	47
6:4,5'-(1-η ⁵ -Cp-1-Co-2,3-Me ₂ -2,3-C ₂ B ₄ H ₃)X(2',3'-Me ₂ -2',3'-C ₂ B ₄ H ₅)	54
(2,3-Et ₂ -2,3-C ₂ B ₄ H ₄)-2-CoB ₅ H ₁₀	51
(2,3-Et ₂ -2,3-C ₂ B ₄ H ₄)-5-CoB ₉ H ₁₂ -1-O(CH ₂) ₄	51, 52
1-η ⁵ -Cp-1,2,4-CoC ₂ B ₄ H ₆	47, 55
1-η ⁵ -Cp-2,3-Me ₂ -1,2,3-CoC ₂ B ₄ H ₄	56, 57
1-(η ⁵ -Me ₅ C ₅)-2,3-Me ₂ -1,2,3-CoC ₂ B ₄ H ₄	50
3,4-(η ⁵ -Cp) ₂ -3,4,1,7-Co ₂ C ₂ B ₄ H ₆	55
1,1'-Co-(2,3-Me ₂ -2,3-C ₂ B ₄ H ₄)-(2,3-Me ₂ -2,3-C ₂ B ₇ H ₇)	56
1,1'-Co(H)-(2,3-Me ₂ -2,3-C ₂ B ₄ H ₄) ₂	56, 58
1-PPh ₃ -1,2,3-RhC ₃ B ₄ H ₇	59
1,1,2-(CO) ₃ -1-(PPh ₃)-2,2,3,5-(Ph ₂ PC ₆ H ₄) ₂ -1,2-Ir ₂ B ₄ H ₂	60
1-η ⁵ -Cp-1,2,4-FeC ₂ B ₄ H ₆	61
μ-4,5-[Fe(CO) ₂ Cp-η ⁵]-2,3-C ₂ B ₅ H ₇	61, 62
1-η ⁵ -Cp-6-(2,4-C ₂ B ₅ H ₆)-1,2,4-FeC ₂ B ₄ H ₅	61
1-(C ₈ H ₁₀)-2,3-Me ₂ -1,2,3-FeC ₂ B ₄ H ₄	63
1,1'-(FeH ₂)-(2,3-Me ₂ -2,3-C ₂ B ₄ H ₄)-(2,3-Me ₂ -2,3-C ₂ B ₅ H ₅)	56, 64
H ₂ Fe(R ₂ C ₂ B ₄ H ₄) ₂ (R = alkyl)	65
1-(C ₈ H ₈)-2,3-Et ₂ -1,2,3-VC ₂ B ₄ H ₄	66

TABLE 3. METALLACARBORANES WITH FIVE BORON ATOMS

Compound	Refs.
1,2-(η ⁵ -Cp) ₂ -1,2,7,8-Ni ₂ C ₂ B ₅ H ₇	47
4-η ⁵ -Cp-4,1,8-CoC ₂ B ₅ H ₇	55, 67
3,8-(η ⁵ -Cp) ₂ -3,8,1,9-Co ₂ C ₂ B ₅ H ₇	55
3':2-(2',4'-C ₂ B ₅ H ₆)-1,8-(η ⁵ -Cp) ₂ -1,8,5,6-Co ₂ C ₂ B ₅ H ₆	67
2-η ⁵ -Cp-2,2-(CO) ₂ -2-FeB ₅ H ₈	68
2-η ⁵ -CpFe(CO) ₂ -B ₅ H ₈	69

TABLE 4. METALLACARBORANES WITH SIX BORON ATOMS

Compound	Refs.
1-η ⁵ -Cp-1,4,5-CoC ₂ B ₆ H ₈	70
2,9-(η ⁵ -Cp) ₂ -2,9,1,10-Co ₂ C ₂ B ₆ H ₈	70
7,9-(η ⁵ -Cp) ₂ -7,9,1,6-Co ₂ C ₂ B ₆ H ₈	55
2,7-(η ⁵ -Cp) ₂ -2,7,1,10-Co ₂ C ₂ B ₆ H ₈	71
1,12-(η ⁵ -Cp) ₂ -1,12,2,3,7,8-Co ₂ C ₄ B ₆ H ₁₀ (3 isomers)	72
4-η ⁵ -Cp-4,1,8-FeC ₂ B ₆ H ₈	70
1,6-(η ⁵ -Cp) ₂ -1,6,1,2-Fe ₂ C ₂ B ₆ H ₈	73
[9,9,9-(CO) ₃ -9,5,6-MnC ₂ B ₆ H ₈] ⁻	74–76

TABLE 5. METALLACARBORANES WITH SEVEN BORON ATOMS

Compound	Refs.
$2,3-(\eta^5\text{-Cp})_2\text{-}2,3,10\text{-NiCoCB}_7\text{H}_8$	77-79
$3,5-(\eta^5\text{-Cp})_2\text{-}3,5,10\text{-NiCoCB}_7\text{H}_8$	77, 78
$2\text{-}\eta^5\text{-Cp-}2,3,10\text{-CoC}_2\text{B}_7\text{H}_9$	70
$2\text{-}\eta^5\text{-Cp-}2,1,6\text{-CoC}_2\text{B}_7\text{H}_9$	75, 80
$2\text{-}\eta^5\text{-Cp-}2,1,10\text{-CoC}_2\text{B}_7\text{H}_9$	80
$1\text{-}\eta^5\text{-Cp-}2,3,7,8\text{-Me}_4\text{-}12\text{-OEt}_2\text{-}1,2,3,7,8\text{-CoC}_4\text{B}_7\text{H}_6$	64
$1\text{-}\eta^5\text{-Cp-}2,3,7,8\text{-Me}_4\text{-}1,2,3,7,8\text{-CoC}_4\text{B}_7\text{H}_7$	81
$[2,2'\text{-Co}(6,7\text{-C}_2\text{B}_7\text{H}_9)_2]^-$	80
$[2,2'\text{-Co}(1,10\text{-C}_2\text{B}_7\text{H}_9)_2]^-$	80
$[2,2'\text{-Co}(1,6\text{-C}_2\text{B}_7\text{H}_9)_2]^-$	80
$1,10-(\eta^5\text{-Cp})_2\text{-}1,10,2,3\text{-Co}_2\text{C}_2\text{B}_7\text{H}_9$	82
$1,8-(\eta^5\text{-Cp})_2\text{-}1,8,2,3\text{-Co}_2\text{C}_2\text{B}_7\text{H}_9$	83
$2,3,5-(\eta^5\text{-Cp})_3\text{-}2,3,5,1,7\text{-Co}_3\text{C}_2\text{B}_7\text{H}_9$	82
$1,2,8-(\eta^5\text{-Cp})_3\text{-}1,2,8,3,6\text{-Co}_3\text{C}_2\text{B}_7\text{H}_9$	83
$(1,2\text{-Et}_2\text{C}_2\text{B}_7\text{H}_7)\text{-}6\text{-CoC}_9\text{H}_{12}\text{-}2\text{-O}(\text{CH}_2)_4$	51, 52
$6,6\text{-(Et}_3\text{P)}_2\text{-}6,1,2\text{-CoC}_2\text{B}_7\text{H}_9$	84
$2\text{-H-}2,2\text{-(Et}_3\text{P)}_2\text{-}2,1,6\text{-CoC}_2\text{B}_7\text{H}_9$	85
$2\text{-H-}2,2\text{-(Et}_3\text{P)}_2\text{-}2,1,6\text{-RhC}_2\text{B}_7\text{H}_9$	85
$6,6\text{-(Ph}_3\text{P)}_2\text{-}6\text{-H-}6,2,3\text{-RhC}_2\text{B}_7\text{H}_9$	86
$1,8-(\eta^5\text{-Cp})_2\text{-}1,8,2,3\text{-FeCoC}_2\text{B}_7\text{H}_9$	87
$6,6\text{-(Ph}_3\text{P)}_2\text{-}6,2,3\text{-RuC}_2\text{B}_7\text{H}_9$	86
$2\text{-}\eta^5\text{-Cp-}7,8,10,12\text{-Et}_4\text{-}2,7,8,10,12\text{-CrC}_4\text{B}_7\text{H}_7$	88

TABLE 6. METALLACARBORANES WITH EIGHT BORON ATOMS

Compound	Refs.
$10\text{-}\eta^5\text{-Cp-}10,1\text{-NiCB}_8\text{H}_9$	89
$1\text{-}\eta^5\text{-Cp-}1,2,3\text{-CoC}_2\text{B}_8\text{H}_{10}$	70, 90
$1\text{-}\eta^5\text{-Cp-}2,3,7,8\text{-Me}_4\text{-}1,2,3,7,8\text{-CoC}_4\text{B}_8\text{H}_8$	81
$1\text{-}\eta^5\text{-Cp-}2\text{-C}_2\text{B}_8\text{H}_9\text{-}1,2,3\text{-CoC}_2\text{B}_8\text{H}_9$	70
$1,2-(\eta^5\text{-Cp})_2\text{-}1,2,3,6\text{-Co}_2\text{C}_2\text{B}_8\text{H}_{10}$	70
$1,2-(\eta^5\text{-Cp})_2\text{-}1,2,5,7\text{-Co}_2\text{C}_2\text{B}_8\text{H}_{10}$	70
$2,3-(\eta^5\text{-Cp})_2\text{-}2,3,1,7\text{-Co}_2\text{C}_2\text{B}_8\text{H}_{10}$	82
$3,6-(\eta^5\text{-Cp})_2\text{-}3,6,8,10\text{-Co}_2\text{C}_2\text{B}_8\text{H}_{10}$	91
$3,6-(\eta^5\text{-Cp})_2\text{-}3,6,1,2\text{-Co}_2\text{C}_2\text{B}_8\text{H}_{10}$	92, 93
$1,1\text{-(Et}_3\text{P)}_2\text{-}1,2,4\text{-CoC}_2\text{B}_8\text{H}_{10}$	84
$7,7'-(\eta^5\text{-Me}_5\text{C}_5)_2\text{-}1,1',2,2'\text{-Me}_4\text{-}7,7',1,1',2,2'\text{-Co}_3\text{C}_4\text{B}_8\text{H}_7$	50
$1,1\text{-(Ph}_3\text{P)}_2\text{-}1\text{-H-}1,2,4\text{-IrC}_2\text{B}_8\text{H}_{10}$	94
$1\text{-(Ph}_3\text{P)}\text{-}2\text{-H-}2,2\text{-(Ph}_3\text{P)}_2\text{-}2,10\text{-IrCB}_8\text{H}_8$	95
$1\text{-}\eta^5\text{-Cp-}1,2,3\text{-FeC}_2\text{B}_8\text{H}_{10}$	73
$7,8(\eta^5\text{-Cp})_2\text{-}4,11,12,14\text{-Me}_4\text{-}7,8,4,11,12,14\text{-Fe}_2\text{C}_4\text{B}_8\text{H}_8$	96-98
$9,9,9\text{-(CO}(\text{PPh}_3)_2\text{-}9,6\text{-MCB}_8\text{H}_{10}\text{-}5\text{-(PPh}_3)_2\text{)}\text{ (M = Ru, Os)}$	99
$4\text{-}\eta^5\text{-Cp-}1,2,8,9\text{-Et}_4\text{-}4,1,2,8,9\text{-CrC}_4\text{B}_8\text{H}_8$	88

TABLE 7. METALLACARBORANES WITH NINE BORON ATOMS

Compound	Refs.
$[3-\eta^5\text{-Cp-3,1,2-NiC}_2\text{B}_9\text{H}_{11}]^{0,1-,1+}$	100
$3,3'\text{-Ni(7-Me-1,7-CPB}_9\text{H}_{10})_2$	47
$[3,3'\text{-Ni}^{n+}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^{n-4}$ ($n = 2, 3, 4$)	101
$[3,3'\text{-Ni}^{n+}(1,2\text{-Me}_2\text{-1,2-C}_2\text{B}_9\text{H}_{11})_2]^{n-4}$ ($n = 2, 3, 4$)	101
$[3,3'\text{-Ni}^{n+}(1,7\text{-C}_2\text{B}_9\text{H}_{11})_2]^{n-4}$ ($n = 2, 3, 4$)	100, 102–105
$[3-\mu\text{-(CO)-8-PPh}_3\text{-3,1,2-NiC}_2\text{B}_9\text{H}_{10}]_2$	106
$[3,3'\text{-Pd}^{n+}(1,2\text{-Me}_2\text{-1,2-C}_2\text{B}_9\text{H}_{11})_2]^{n-4}$ ($n = 2, 3, 4$)	101
$[3,3'\text{-Pd}^{n+}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^{n-4}$ ($n = 2, 3, 4$)	101
$3\text{[Me}_2\text{N(CH}_2)_2\text{NMe}_2\text{-3,1,2-PdC}_2\text{B}_9\text{H}_{11}]$	107
$3\text{-(}\eta^2\text{,}\eta^2\text{-C}_8\text{H}_{12}\text{)-3,1,2-PdC}_2\text{B}_9\text{H}_{11}$	108
$3,3'\text{-(C}_4\text{Ph}_4\text{)-3,1,2-PdC}_2\text{B}_9\text{H}_{11}$	102
$3\text{-(COD)-3,1,2-PtC}_2\text{B}_9\text{H}_{11}$	101
$(\text{Ph}_2\text{P-CH}_2\text{CH}_2\text{-PPh}_2)\text{PtC}_2\text{B}_9\text{H}_{11}$	109
$2\text{-}\eta^5\text{-Cp-2,1,12-CoC}_2\text{B}_9\text{H}_{11}$	110
$2\text{-}\eta^5\text{-Cp-3,1,2-CoC}_2\text{B}_9\text{H}_{11}$	102
$3\text{-(}\eta^5\text{-C}_9\text{H}_7\text{)-3,1,2-CoC}_2\text{B}_9\text{H}_{11}$	110
$3,3'\text{-Co(1,7-C}_2\text{B}_9\text{H}_{11})_2$	102
$[3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$	102, 103, 105, 111–116
$[3,3'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{11})_2]^{2-}$	102, 103, 105, 111–116
$[3,3'\text{-Co(1,2-Me}_2\text{-1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$	102
$3,3'\text{-Co(7-Me-1,7-CPB}_9\text{H}_{10})_2$	117
$3,3'\text{-Co(2-Me-1,2-CPB}_9\text{H}_{10})_2$	117
$[3,3'\text{-Co(1,7-CPB}_9\text{H}_{10})_2]^-$	117
$[3,3'\text{-Co(1,2-CPB}_9\text{H}_{10})_2]^-$	117
$4,5\text{-(}\eta^5\text{-Cp)}_2\text{-4,5,1,13-Co}_2\text{C}_2\text{B}_9\text{H}_{11}$	118
$1,1\text{-(Ph}_3\text{P)}_2\text{-1-Cl-1,2,3-RhC}_2\text{B}_9\text{H}_{11}$	119
$1\text{-Ph}_3\text{P-1-C}_6\text{H}_5\text{-1,2,3-RhC}_2\text{B}_9\text{H}_{11}$	119
$1\text{-Ph}_3\text{P-1-H-1,2,3-RhC}_2\text{B}_9\text{H}_{11}$	119
$3,3\text{-(Ph}_3\text{P)}_2\text{-3-H-3,1,2-RhC}_2\text{B}_9\text{H}_{11}$	120
$2,2\text{-(Ph}_3\text{P)}_2\text{-2-H-2,1,7-RhC}_2\text{B}_9\text{H}_{11}$	120
$2,2\text{-(Ph}_3\text{P)}_2\text{-2-H-2,1,12-RhC}_2\text{B}_9\text{H}_{11}$	110
$3,3\text{-(Ph}_3\text{P)}_2\text{-3-(CO)-4-py-3,1,2-RhC}_2\text{B}_9\text{H}_{10}$	121
$3\text{-H-3,3-(Ph}_3\text{P)}_2\text{-3,1,2-RhC}_2\text{B}_9\text{H}_{11}$	122
$3\text{-H-3,3-(Et}_3\text{P)}_2\text{-3,1,2-RhC}_2\text{B}_9\text{H}_{11}$	122
$[3\text{-(Et}_3\text{P)-3-H-3,1,2-RhC}_2\text{B}_9\text{H}_{10}]_2$	123
$[3\text{-(Ph}_3\text{P)-3-H-3,1,2-RhC}_2\text{B}_9\text{H}_{11}]_2$	124
$[3\text{-(Ph}_3\text{P)-3-H-2-Ph-3,1,2-RhC}_2\text{B}_9\text{H}_{10}]_2$	124
$1,2\text{-}\mu\text{-(1',2'-CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{)-3,3-(PPh}_3\text{)}_2\text{-3-H-3,1,2-Rh-C}_2\text{B}_9\text{H}_9$	125
$6,10\text{-[(PPh}_3\text{)(PChx}_3\text{)Rh]-6,10-}\mu\text{-(H)}_2\text{-7,8-}\mu\text{-(1',2'-CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{)-10,11-}\mu\text{-(H)-7,8-C}_2\text{B}_9\text{H}_7$	125
$4,9\text{-[(PPh}_3\text{)}_2\text{Rh]-4,9-}\mu\text{-(H)}_2\text{-7-Me-8-Ph-7,8-C}_2\text{B}_9\text{H}_8$	125
$2,2\text{-(PPh}_3\text{)}_2\text{-2-H-1-Me-7-Ph-2,1,7-RhC}_2\text{B}_9\text{H}_9$	126
$[(\text{Ph}_3\text{P)}_3\text{Rh}]^+[7\text{-(1'(1',2'-C}_2\text{B}_{10}\text{H}_{11}))\text{-7,8-C}_2\text{B}_9\text{H}_{11}]^-$	127
$1\text{-R-2-R'-3,3-(PPh}_3\text{)}_2\text{-3-H-3,1,2-RhC}_2\text{B}_9\text{H}_9$ ($\text{R} = \text{R}' = \text{H}$; $\text{R} = \text{R}' = \text{D}$; $\text{R} = \text{H}$, $\text{R}' = \text{Ph, Me, n-Bu}$)	128

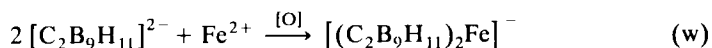
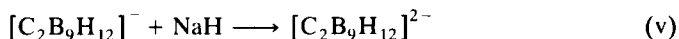
(continued)

TABLE 7. (continued)

Compound	Refs.
1-R-2,2-(PPh ₃) ₂ -2-H-2,1,7-RhC ₂ B ₉ H ₁₀ (R = H, Ph, Me)	128
2,2-(PPh ₃) ₂ -2-H-2,1,12-RhC ₂ B ₉ H ₁₁	128
3'-(CODH)-3'-H-3',1',2'-RhC ₂ B ₉ H ₁₀ -3,3-(Et ₃ P) ₂ -μ-7-(H)- 3-H-3,1,8-RhC ₂ B ₉ H ₁₀	124
1,3-μ-(3,4-CH ₂ =CH-CH ₂ -CH ₂)-3-H-3- PPh ₃ -3,1,2-RhC ₂ B ₉ H ₁₀	129
3-η ⁵ -Cp-3,1,2-FeC ₂ B ₉ H ₁₁	102
[3-η ⁵ -Cp-3,1,2-FeC ₂ B ₉ H ₁₁] ⁻	103, 113
[3,3'-Fe(1,2-C ₂ B ₉ H ₁₁) ₂] ⁻	102
[3,3'-Fe(1,2-C ₂ B ₉ H ₁₁) ₂] ²⁻	102, 103, 130
[3,3'-Fe(1,2-Me ₂ -1,2-C ₂ B ₉ H ₁₁) ₂] ^{1-, 2-}	102, 130-132
1-PhMe-2,4-Me ₂ -1,2,4-FeC ₂ B ₉ H ₉	133
η ⁵ -Cp-Fe(7-Me-1,7-CPB ₉ H ₁₀)	117
[3,3'-Fe(1,7-CPB ₉ H ₁₀) ₂] ⁻	117
3,3'-Fe(7-Me-1,7-CPB ₉ H ₁₀) ₂	117
3,3'-Fe(2-Me-1,2-CPB ₉ H ₁₀) ₂	117
[3,3'-Fe(1,7-CPB ₉ H ₁₀) ₂] ²⁻	117
[3,3'-Fe(1,2-CPB ₉ H ₁₀) ₂] ²⁻	117
4,5-(η ⁵ -Cp) ₂ -4,5,1,8-CoFeC ₂ B ₉ H ₁₁	118
4,5-(η ⁵ -Cp) ₂ -4,5,2,3-Fe ₂ C ₂ B ₉ H ₁₁	134
4-η ⁵ -Cp-5-(1,2-C ₂ B ₉ H ₁₁)-4,5,2,3-Fe ₂ C ₂ B ₉ H ₁₁	134
1-η ⁵ -Cp-2-CH(OEt) ₂ -1,2,3-FeC ₂ B ₉ H ₁₀	135
3-(η ³ -MePh)-3,1,2-FeC ₂ B ₉ H ₁₁	136
3-(η ⁶ -1,4-Me ₂ C ₆ H ₄)-3,1,2-FeC ₂ B ₉ H ₁₁	136
3,3,3-(CO) ₃ -3,1,2-RuC ₂ B ₉ H ₁₁ · 0.5 C ₆ H ₆	119, 137
3-(η ⁶ -C ₆ H ₆)-3,1,2-RuC ₂ B ₉ H ₁₁	138
2,2-(Ph ₃ P) ₂ -2,2-(H) ₂ -2,1,7-RuC ₂ B ₉ H ₁₁	134
3,3-(Ph ₃ P) ₂ -3,3-(H) ₂ -3,1,2-RuC ₂ B ₉ H ₁₁	134
2,2-(Ph ₃ P) ₂ -2,2-(H) ₂ -2,1,7-RuC ₂ B ₉ H ₁₁	139
3,3-(Ph ₃ P) ₂ -3,3-(H) ₂ -3,1,2-RuC ₂ B ₉ H ₁₁	139
[3,3,3-(CO) ₃ -3,1,2-MnC ₂ B ₉ H ₁₁] ⁻	102
[3,3,3-(CO) ₃ -3,1,7-MnCPB ₉ H ₁₀] ⁻	117
3,3,3-(CO) ₃ -7-Me-3,1,7-MnCPB ₉ H ₁₀	117
[3,3,3-(CO) ₃ -3,1,2-ReC ₂ B ₉ H ₁₁] ⁻	102, 140
[3,3'-Cr(1,2-C ₂ B ₉ H ₁₁) ₂] ⁻	141
[3,3'-Cr(1-Me-1,2-C ₂ B ₉ H ₁₁) ₂] ⁻	141
[3,3'-Cr(1,2-Me ₂ -1,2-C ₂ B ₉ H ₁₁) ₂] ⁻	141
3-η ⁵ -Cp-3,1,2-CrC ₂ B ₉ H ₁₁	141
3-η ⁵ -Cp-1-Me-3,1,2-CrC ₂ B ₉ H ₁₁	141
3-η ⁵ -Cp-1,2-Me ₂ -3,1,2-CrC ₂ B ₉ H ₁₁	141
[(Ph ₃ P) ₂ N][3,3,3-(CO) ₃ -3-Tl-3,1,2-MC ₂ B ₉ H ₁₁] (M = Mo, W)	142
[(Ph ₃ P) ₂ N] ₂ [Mo ₂ Cu ₂ (μ-CO) ₄ (CO) ₂ (μ-H)C ₂ B ₉ H ₁₀] ₂	142
[(Ph ₃ P) ₂ N][4-MeC ₆ H ₄ C≡W(CO) ₂ (7,8-C ₂ B ₉ H ₉ Me ₂)]	143, 144
[(Ph ₃ P) ₂ N][4-MeC ₆ H ₄ C≡W(CO) ₂ (7,8-C ₂ B ₉ H ₁₁)]	144
[Et ₄ N][MeC≡W(CO) ₂ -7,8-C ₂ B ₉ H ₉ Me ₂]	144
[3-C ₈ H ₈ -3,1,2-TiC ₂ B ₉ H ₁₁] ⁻	145, 146
L ₄ SmC ₂ B ₉ H ₁₁ (L = THF, CH ₃ CH, DMF)	147
L ₄ YbC ₂ B ₉ H ₁₁ (L = THF, CH ₃ CN, DMF)	147
[(Ph ₃ P) ₂ N][3,3-(THF) ₂ -3,3'-Sm(3,1,2-SmC ₂ B ₉ H ₁₁) ₂]	147

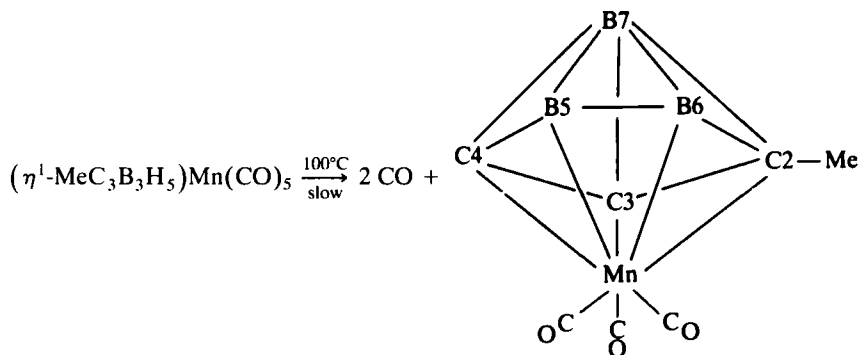
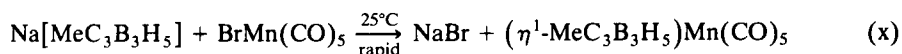
where arene = benzene, toluene, o- or p-xylene, mesitylene. The p-xylene ligand in $[(C_3H_3N(t-Bu)BMe)FeC_6H_4Me_2-\eta^6]PF_6$ can be replaced to make other half-sandwich complexes³⁵: $[(C_3H_3N(t-Bu)BMe)Fe[P(OMe)_3]_3PF_6$, $[(C_3H_3N(t-Bu)BMe)Fe(PMe_3)_3]PF_6$, $[(C_3H_3N(t-Bu)BMe)Fe(CH_3CN)(PMe_3)_2]PF_6$ and $[(C_3H_3N(t-Bu)BMe)Fe(CO)(PMe_3)_2]PF_6$ are some examples.

The original synthesis of metallacarboranes is effected by deprotonation of nido-carborane anions in a manner like that employed to prepare ferrocene, e.g.³⁶:

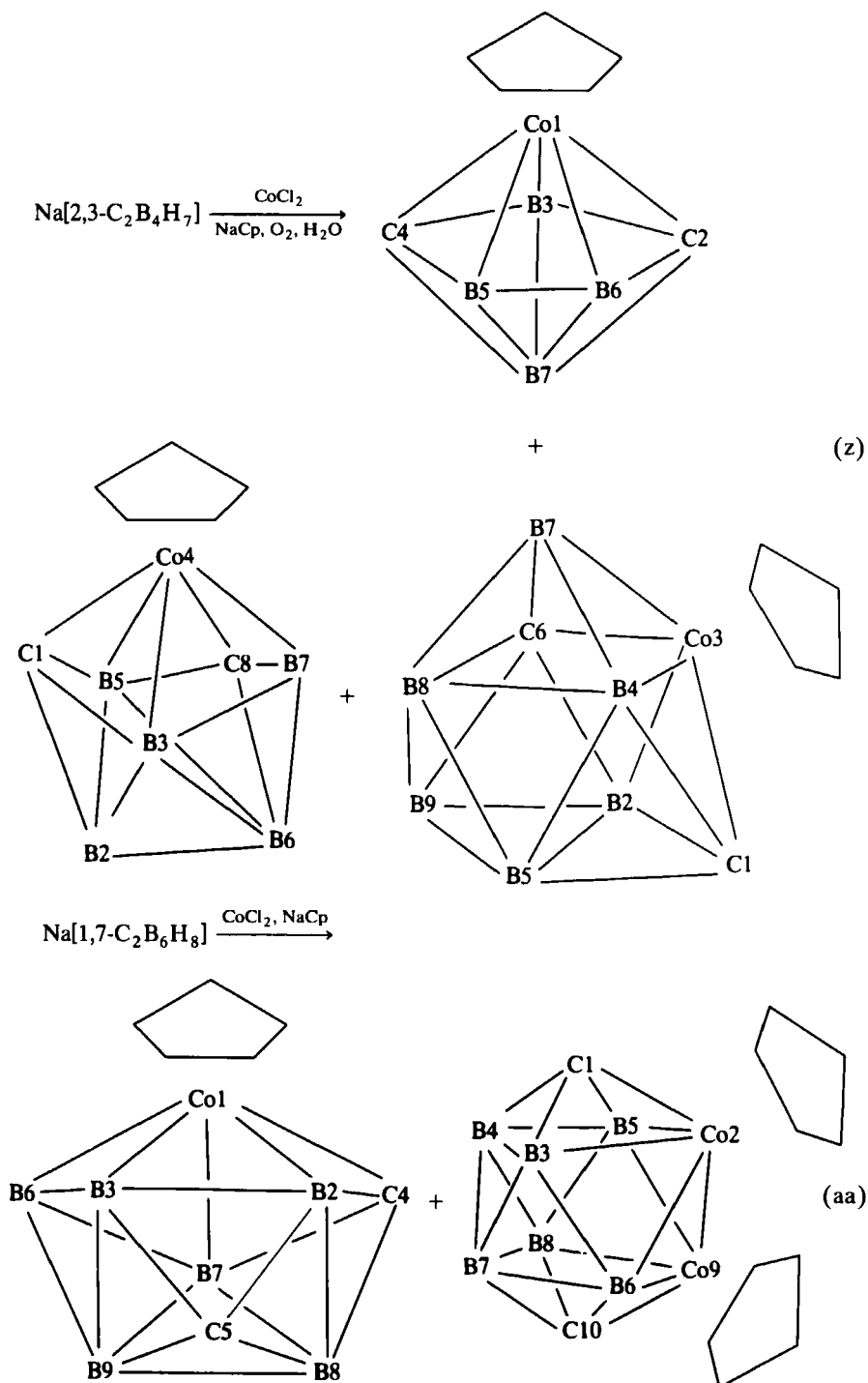


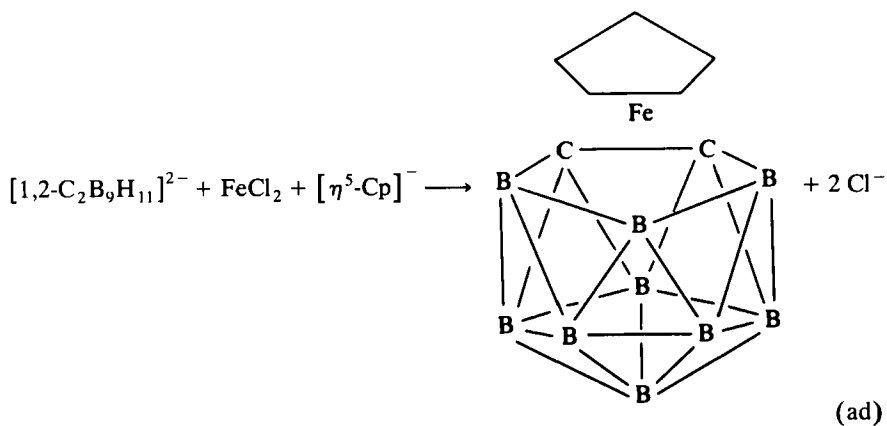
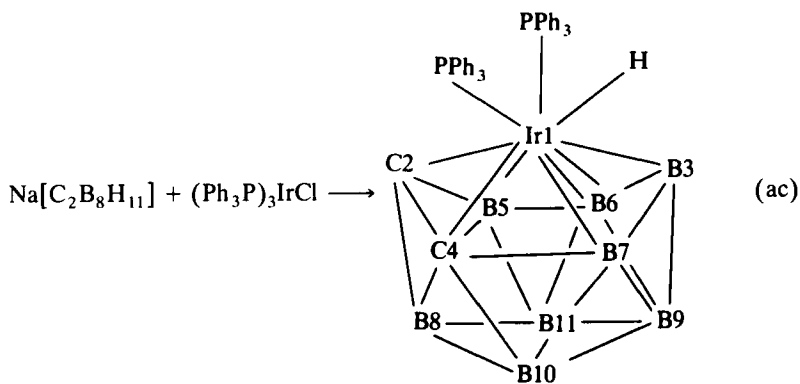
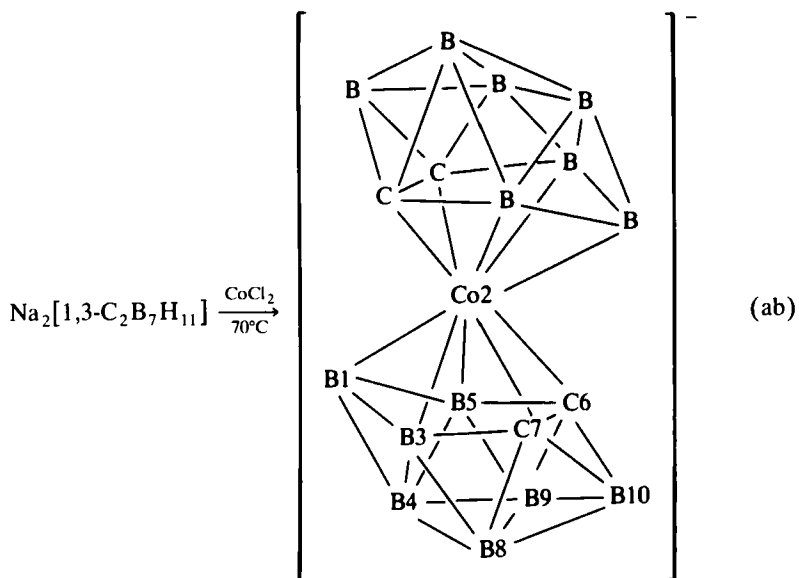
The chemistry of metallaboranes and metallacarboranes is a large field in boron-metal chemistry with a confusing variety of compounds³⁷⁻⁴⁶. The most convenient synthesis methods using carborane anions and metal halides leading to boron-metal bonds are described here and most of the known metallacarboranes are summarized. To simplify the highly complicated structure and bonding relationships, the material is arranged by increasing number of skeletal boron atoms in the species, independent of structural features. Reactions giving derivatives of existing metallaboranes or metallacarboranes such as substitution reactions, oxidation and reduction processes or isomerization are not regarded here.

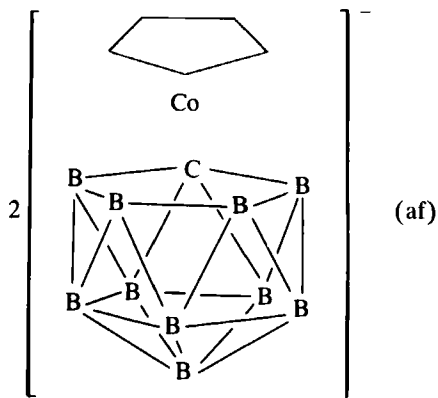
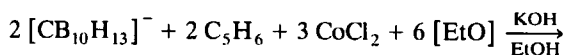
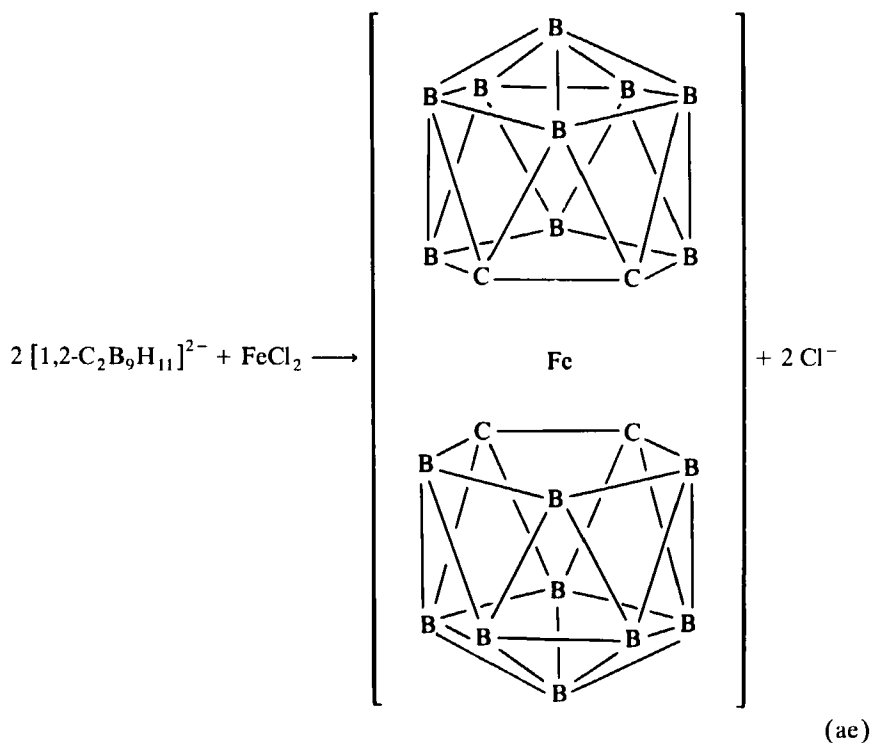
Because the complexes listed in Tables 1-8 are all prepared with metal halides and carborane anions, only one example for each type of metallocarborane (number of B atoms) is given in the following representative equations for clarity, the skeletal framework in the equations have numbered positions and H atoms are omitted:



(y)







Systems containing boron hydrides and transition metals are called metallaboranes and are related to the metallocarboranes. Tables 9–12 contain a series of the

TABLE 8. METALLACARBORANES WITH TEN BORON ATOMS

Compound	Refs.
$2-\eta^5\text{-Cp-2,7-NiCB}_{10}\text{H}_{11}$	148
$10-\eta^5\text{-Cp-10,1-NiCB}_{10}\text{H}_{11}$	149
$[2,2'\text{-Ni}(7\text{-CB}_{10}\text{H}_{11})_2]^{2-}$	150
$2,2'\text{-Ni}(7\text{-CB}_{10}\text{H}_{11})_2$	151
$[13,13'\text{-Ni}(7,9\text{-C}_2\text{B}_{10}\text{H}_{12})(7',11'\text{-C}_2\text{B}_9\text{H}_{12})]^{2-}$	152
$(\text{Ph}_2\text{P-CH}_2\text{CH}_2\text{-PPh}_2)\text{PdC}_2\text{B}_{10}\text{H}_{12}$	109
$[2-\eta^5\text{-Cp-2,7-CoCB}_{10}\text{H}_{11}]^-$	148
$[2,2'\text{-Co}(7\text{-CB}_{10}\text{H}_{11})_2]^{3-}$	150
$[2,2'\text{-Co}(7\text{-CB}_{10}\text{H}_{11})_2]^{2-}$	151
$13-\eta^5\text{-Cp-13,7,9-CoC}_2\text{B}_{10}\text{H}_{12}$	152, 153
$[13,13'\text{-Co}(7,9\text{-C}_2\text{B}_{10}\text{H}_{12})(7',11'\text{-C}_2\text{B}_9\text{H}_{12})]^-$	157
$1,14-(\eta^5\text{-Cp})_2\text{-1,14,2,10-Co}_2\text{C}_2\text{B}_{10}\text{H}_{12}$	154
$12-\eta^5\text{-Cp-7-R-12,7-CoPB}_{10}\text{H}_{10}$ (R = Me, Et, n-Pr, Ph)	118
$1,1-(\text{Ph}_3\text{P})_2\text{-1-H-1,2,4-RhC}_2\text{B}_{10}\text{H}_{12}$	155
$(\text{Ph}_3\text{P})_2\text{HfC}_2\text{B}_{10}\text{H}_{11}(\text{OMe})$	109
$[2,2-(\text{PPh}_3)_2\text{-2-H-1-(NH}_2\text{)-2,1-RhCB}_{10}\text{H}_{10}]^-$	156
$[2,2'\text{-Fe}(7\text{-CB}_{10}\text{H}_{11})_2]^{3-}$	150
$[13,13'\text{-Fe}(7,9\text{-C}_2\text{B}_{10}\text{H}_{12})(7',11'\text{-C}_2\text{B}_9\text{H}_{12})]^{2-}$	157
$[2,2'\text{-Mn}(7\text{-CB}_{10}\text{H}_{11})_2]^{2-}$	151
$[4,4'\text{-Mn}(1,6\text{-C}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$	146
$[4,4'\text{-Cr}(1,6\text{-C}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$	146
$[4,4'\text{-V}(1,6\text{-C}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$	146
$[4,4'\text{-V}(1,6\text{-Me}_2\text{-1,6-C}_2\text{B}_{10}\text{H}_{10})_2]^{2-}$	146
$[3-\eta^5\text{-Cp-3,1,2-TiC}_2\text{B}_{10}\text{H}_{12}]^-$	145
$[3-(\text{C}_8\text{H}_8)\text{-3,1,2-TiC}_2\text{B}_{10}\text{H}_{12}]^-$	145
$[4,4'\text{-Ti}(1,6\text{-Me}_2\text{-1,6-C}_2\text{B}_{10}\text{H}_{10})_2]^{2-}$	146
$[4,4'\text{-Ti}(1,6\text{-C}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$	146
$[4,4'\text{-Zr}(1,6\text{-Me}_2\text{-1,6-C}_2\text{B}_{10}\text{H}_{10})_2]^{2-}$	146
$[4,4'\text{-Hf}(1,6\text{-Me}_2\text{-1,6-C}_2\text{B}_{10}\text{H}_{10})_2]^{2-}$	146

TABLE 9. METALLABORANES WITH THREE BORON ATOMS

Compound	Refs.
$[\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2]\text{PdB}_3\text{H}_7$	157, 158
$(\text{Et}_3\text{P})_2\text{PtB}_3\text{H}_7$	157, 158
$(\text{Ph}_2\text{EtP})_2\text{PtB}_3\text{H}_7$	157, 158
$(\text{Ph}_3\text{P})_2\text{PtB}_3\text{H}_7$	157, 158
$(\text{PhMe}_2\text{P})_2\text{PtB}_3\text{H}_7$	157, 158
$[(p\text{-MeC}_6\text{H}_4)_3\text{P}]_2\text{PtB}_3\text{H}_7$	157, 158
$1,2,3-(\eta^5\text{-Cp})_3\text{-1,2,3-Co}_3\text{B}_3\text{H}_5$	159, 160
$1,1-(\text{Ph}_3\text{P})_2\text{-1-H-1-(CO)-1-IrB}_3\text{H}_7$	161, 162

TABLE 10. METALLABORANES WITH FOUR, FIVE AND SIX BORON ATOMS

Compound	Refs.
μ -(2,3)-([Ph ₂ P(CH ₂) ₂ PPh ₂] χ Ni)B ₅ H ₈ (X = Cl, Br, I)	163
7,7'-(PhMe ₂ P) ₂ -7,7'-Pt ₂ (B ₆ H ₉) ₂	164
2- η^5 -Cp-2-CoB ₄ H ₈	159, 160
2-(Me ₅ C ₅) ₂ -2-CoB ₄ H ₈	165
1-(Me ₅ C ₅) ₂ -1-CoB ₄ H ₈	165
1,2-(η^5 -Cp) ₂ -1,2-Co ₂ B ₄ H ₆	159, 160
1,2-(η^5 -Me ₅ C ₅) ₂ -1,2-Co ₂ B ₄ H ₆	165
1,2,3-(η^5 -Me ₅ C ₅) ₃ -1,2,3-Co ₃ B ₄ H ₄	166
1,2,4,7-(η^5 -Cp) ₄ -1,2,4,7-Co ₄ B ₄ H ₄	160
Cu(η^2 - B ₅ H ₈)(PPh ₃) ₂	167-171
1,2-(η^5 -Me ₅ C ₅) ₂ -1,2-Co ₂ B ₅ H ₇	165
1,2-(η^5 -Me ₅ C ₅) ₂ -1,2-Co ₂ B ₅ H ₅	165
2,3-(η^5 -Cp) ₂ -2,3,6-Co ₂ SB ₅ H ₇	172
7- η^5 -Cp-7,6,8-CoS ₂ B ₆ H ₈	172
6,8-(η^5 -Cp) ₂ -6,8,7,9-Co ₂ S ₂ B ₅ H ₅	172
1-(CO)-1,1-(PMe ₃) ₂ -1-IrB ₄ H ₉	173
2,2-(Ph ₃ P) ₂ -2-CO-2-Cl-2-IrB ₅ H ₈	174
2,2-(Ph ₃ P) ₂ -2-CO-2-IrB ₅ H ₈	162, 174
1- η^5 -Cp-1-FeB ₅ H ₁₀	175, 176
2- η^5 -Cp-2-FeB ₅ H ₁₀	175, 176
2-[(η^5 -Cp)(CO) ₂ Fe]-B ₅ H ₈	177
2,2-(Ph ₃ P) ₂ -2-CO-2-OsB ₄ H ₈	162
4,4-(Ph ₃ P) ₂ -4-CO-4-OsB ₅ H ₉	162
2,2,2-(COXPPH ₃) ₂ -7,7-(Cl)PMe ₂ Ph- μ -2,7-H-2,7-OsPtB ₅ H ₇	178

TABLE 11. METALLABORANES WITH EIGHT AND NINE BORON ATOMS

Compound	Refs.
1,6 Cu(η^2 - B ₅ H ₈)(PPh ₃) ₂ - η^5 -Cp) ₂ -1,6-Ni ₂ B ₈ H ₈	179
11,11'-Ni(6-SB ₉ H ₁₁) ₂	180
11,11'-Pd(6-SB ₉ H ₁₁) ₂	180
11-H-11,11-(Ph ₃ P) ₂ -11,6-PtSB ₉ H ₁₀	180
11-H-11,11-(Et ₃ P) ₂ -11,6-PtSB ₉ H ₁₀	181
(Et ₃ P) ₂ PtB ₉ H ₁₁ · L (L = NR ₃ , PR ₃ , R ₂ S, etc.)	182
6,6,9,9-(PMe ₂ Ph) ₄ -6,9-Pt ₂ B ₈ H ₁₀	183
4,4-(PMe ₂ Ph) ₂ -4-PtB ₈ H ₁₂	183
(Me ₂ PhP) ₂ PtB ₈ H ₁₁ OMe	184
5- η^5 -Cp-5-CoB ₉ H ₁₃	159
6-(η^5 -Me ₅ C ₅) ₂ -6-CoB ₈ H ₁₈	165
6,9-(η^5 -Me ₅ C ₅) ₂ -6,9-Co ₂ B ₈ H ₁₂	165, 185
5,7-(η^5 -Me ₅ C ₅) ₂ -5,7-Co ₂ B ₈ H ₁₂	165, 185
6-Cl-5,7-(η^5 -Me ₅ C ₅) ₂ -5,7-Co ₂ B ₈ H ₁₁	165, 185
5,9-(η^5 -Me ₅ C ₅) ₂ -5,9-Co ₂ B ₈ H ₁₂	165
6-(η^5 -Me ₅ C ₅) ₂ -6-CoB ₉ H ₁₃	185

(continued)

6.5.3. Formation from Other Group-III B Compounds

6.5.3.4. by Reaction with Metal Halides

TABLE 11. (continued)

Compound	Refs.
6-COD-6-Cl-6-RhB ₉ H ₁₃	186
[(η^5 -Me ₅ C ₅)Rh] ₂ (SB ₉ H ₈ Cl)	187
7-PPh ₃ -7,8-PPh ₂ C ₆ H ₄ -3-OMe-10-OH-7,10-IrCB ₈ H ₆	188
7,7-(PMe ₃) ₂ -9-PPh ₃ -9,4-Ph ₂ PC ₆ H ₄ -9-H-7,9-PtIrB ₉ H ₁₀	189
μ -1,2-CH ₃ CO ₂ -2-H-2,10-(PPh ₃) ₂ -2,1-IrCB ₈ H ₇	190
1-(PPh ₃) ₂ -1-H-1,2-Ph ₂ PC ₆ H ₄ -1-IrB ₉ H ₈	191
6-H-6,6-(PPh ₃) ₂ -6-IrB ₉ H ₁₃	192
6-H-6,6-(PMe ₃) ₂ -6-IrB ₉ H ₁₃	192
6-COD-6-Cl-6-IrB ₉ H ₁₃	192
6,6,6-(CO) ₃ -2-THF-6-MnB ₉ H ₁₂	182, 193
[6,6,6-(CO) ₃ -6-MnB ₉ H ₁₂] ⁻	182, 193
[6,6,6-(CO) ₃ -6-ReB ₉ H ₁₂] ⁻	193
6,6,6,6-(CO) ₂ (PPh ₃) ₂ -6-MoB ₉ H ₁₃	194
5-Cl-6,6,6,6-(CO) ₂ (PMe ₃ Ph) ₂ -6-MoB ₉ H ₁₂	194
6,6,6,6-(CO) ₃ (PMe ₂ Ph)-6-WB ₉ H ₁₃	194

TABLE 12. METALLABORANES WITH TEN AND MORE BORON ATOMS

Compound	Refs.
[7,7'-Ni(B ₁₀ H ₁₂) ₂] ⁻	195, 196
[Ni(B ₁₀ H ₁₂) ₂] ₂ ²⁻	197
1,7-(η^5 -Cp) ₂ -1,6-Ni ₂ B ₁₀ H ₁₀	179
[7,7'-Pd(B ₁₀ H ₁₂) ₂] ⁻	195, 196
7,7-[Ph ₂ P(CH ₂) ₂ PPh ₂]-7-PdB ₁₀ H ₁₂	195
7,7-(Ph ₃ P) ₂ -7-PdB ₁₀ H ₁₂	195
7,7-[Ph ₂ P(CH ₂) ₂ PPh ₂]-7-PtB ₁₀ H ₁₂	198
7,7-(PPh ₃) ₂ -7-PtB ₁₀ H ₁₂	198
[7,7'-Pt(B ₁₀ H ₁₂) ₂] ⁻	195, 196, 199
(PtB ₁₀ H ₁₁) ₂ ⁴⁻	199
(PtB ₂₀ H ₂₄) ₂ ²⁻	199
7,7-(Bu ₃ P) ₂ -7-PtB ₁₀ H ₁₂	195
7,7-(Et ₃ P) ₂ -7-PtB ₁₀ H ₁₂	195
7,7-(Ph ₃ P) ₂ -7-PtB ₁₀ H ₁₂	195
7-PMe ₂ Ph-7-PtB ₁₆ H ₁₈ -9'-PMe ₂ Ph	200
(PhMe ₂ P) ₂ PtB ₁₈ H ₂₀ (three isomers)	201
(PhMe ₂ P) ₂ Pt ₂ B ₁₈ H ₁₆	201
(PhMe ₂ P) ₂ Pt ₂ B ₁₂ H ₁₈	186
(PhMe ₂ PX)7-PtB ₁₆ H ₁₈)PMe ₂ Ph	186
[7,7'-Co(B ₁₀ H ₁₂) ₂] ⁻	195, 196
[Co(B ₁₀ H ₁₂) ₂] ₂ ²⁻	197
[7,7,7-(CO) ₃ -7-CoB ₁₀ H ₁₂] ⁻	195
[7,7-(Ph ₃ P) ₂ -7-(CO)-7-RhB ₁₀ H ₁₂] ⁻	195
2,2-(Ph ₃ P) ₂ -2-H-2,1-RhSB ₁₀ H ₁₀	202
2-[(Ph ₃ P) ₂ (H)ClIr]-1-SB ₉ H ₈	202
[7,7-(Ph ₃ P) ₂ -7-(CO)-7-IrB ₁₀ H ₁₂] ⁻	195
2- η^5 -Cp-2-FeB ₁₀ H ₁₅	176

most typical metalloboranes synthesized from boranes and their derivatives and transition-metal halides. The compounds are again arranged by increasing number of skeletal boron atoms. Complexes where the transition metal is connected to the borane framework only by hydrogen bridges are not included here.

(G. SCHMID)

1. G. E. Herberich, H. Ohst, *Z. Naturforsch., Teil B*, **38**, 1388 (1983).
2. G. E. Herberich, H. Ohst, *Chem. Ber.*, **118**, 4303 (1985).
3. A. J. Ashe III, P. Shu, *J. Am. Chem. Soc.*, **93**, 1804 (1971).
4. A. J. Ashe III, E. Meyers, P. Shu, T. von Lehmann, J. Bustide, *J. Am. Chem. Soc.*, **97**, 6865 (1975).
5. A. J. Ashe III, W. Butler, H. F. Sandford, *J. Am. Chem. Soc.*, **101**, 7066 (1979).
6. G. E. Herberich, H. J. Becker, *Angew. Chem., Int. Ed. Engl.*, **14**, 184 (1975).
7. G. E. Herberich, H. J. Becker, K. Carsten, C. Engelke, W. Koch, *Chem. Ber.*, **109**, 2382 (1976).
8. G. E. Herberich, W. Koch, *Chem. Ber.*, **110**, 816 (1977).
9. G. E. Herberich, A. K. Naithani, *J. Organomet. Chem.*, **241**, 1 (1983).
10. G. E. Herberich, H. J. Becker, C. Engelke, *J. Organomet. Chem.*, **153**, 265 (1978).
11. G. E. Herberich, C. Engelke, W. Pohlmann, *Chem. Ber.*, **112**, 607 (1979).
12. G. E. Herberich, H. J. Becker, B. Hessner, L. Zelenka, *J. Organomet. Chem.*, **280**, 147 (1985).
13. G. E. Herberich, N. Finke, P. Wennek, G. Schmid, R. Boese, *Z. Naturforsch., Teil B*, **41**, 167 (1986).
14. G. E. Herberich, D. Söhnen, *J. Organomet. Chem.*, **254**, 143 (1983).
15. G. E. Herberich, W. Boveleth, B. Hessner, W. Koch, E. Raabe, D. Schmitz, *J. Organomet. Chem.*, **265**, 225 (1984).
16. G. E. Herberich, B. Hessner, M. Hostalek, *Angew. Chem., Int. Ed. Engl.*, **25**, 642 (1986).
17. G. E. Herberich, B. Hessner, G. Huttner, L. Zsolnai, *Angew. Chem., Int. Ed. Engl.*, **20**, 472 (1981).
18. G. E. Herberich, M. Thönessen, D. Schmitz, *J. Organomet. Chem.*, **191**, 27 (1980).
19. W. Siebert, W. Rothermel, C. Böhle, C. Krüger, D. J. Brauer, *Angew. Chem., Int. Ed. Engl.*, **18**, 949 (1979).
20. W. Siebert, C. Böhle, C. Krüger, *Angew. Chem., Int. Ed. Engl.*, **19**, 746 (1980).
21. J. Edwin, M. Bochmann, M. C. Böhm, D. E. Brennan, W. E. Geiger, C. Krüger, J. Pebler, H. Pritzkow, W. Siebert, W. Swiridoff, H. Wadepohl, J. Weiss, U. Zennek, *J. Am. Chem. Soc.*, **105**, 2582 (1983).
22. W. Siebert, J. Edwin, H. Wadepohl, H. Pritzkow, *Angew. Chem., Int. Ed. Engl.*, **21**, 149 (1982).
23. J. Edwin, M. C. Böhm, N. Chester, D. M. Hoffman, R. Hoffmann, H. Pritzkow, W. Siebert, K. Stumpf, H. Wadepohl, *Organometallics*, **2**, 1666 (1983).
24. G. Schmid, S. Amirkhalili, U. Höhner, D. Kampmann, R. Boese, *Chem. Ber.*, **115**, 3830 (1982).
25. S. Amirkhalili, R. Boese, U. Höhner, D. Kampmann, G. Schmid, P. Rademacher, *Chem. Ber.*, **115**, 732 (1982).
26. G. Schmid, U. Höhner, D. Kampmann, D. Zaika, R. Boese, *Chem. Ber.*, **116**, 951 (1983).
27. G. Schmid, R. Boese, *Z. Naturforsch., Teil B*, **38**, 485 (1983).
28. G. Schmid, D. Kampmann, U. Höhner, D. Bläser, R. Boese, *Chem. Ber.*, **117**, 1052 (1984).
29. G. Schmid, *Comments Inorg. Chem.*, **4**, 17 (1985).
30. G. Schmid, O. Boltsch, D. Bläser, R. Boese, *Z. Naturforsch., Teil B*, **39**, 1082 (1984).
31. G. Schmid, D. Kampmann, W. Meyer, R. Boese, P. Paetzold, K. Delpy, *Chem. Ber.*, **118**, 2418 (1985).
32. G. Schmid, U. Höhner, D. Kampmann, F. Schmidt, D. Bläser, R. Boese, *Chem. Ber.*, **117**, 672 (1984).
33. G. Schmid, F. Schmidt, R. Boese, *Chem. Ber.*, **118**, 1949 (1985).
34. G. Schmid, G. Barbenheim, R. Boese, *Z. Naturforsch., Teil B*, **40**, 787 (1985).
35. G. Schmid, G. Barbenheim, *Chem. Ber.*, **120**, 400 (1987).
36. M. F. Hawthorne, D. C. Young, P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

6.5.3. Formation from Other Group-IIIB Compounds

6.5.3.4. by Reaction with Metal Halides

-
37. M. F. Hawthorne, *Endeavour*, 25, 146 (1966).
 38. M. F. Hawthorne, *Acc. Chem. Res.*, 1, 281 (1968).
 39. L. J. Todd, in *Advances in Organometallic Chemistry*, Vol. 8, F. G. A. Stone, R. West, eds., Academic Press, New York, 1970, p. 87.
 40. M. F. Hawthorne, *J. Organomet. Chem.*, 100, 97 (1975).
 41. K. P. Callahan, M. F. Hawthorne, *Advances in Organometallic Chemistry*, Vol. 14, F. G. A. Stone, R. West, eds., Academic Press, New York, 1976, p. 145.
 42. G. B. Dunks, M. F. Hawthorne, in *Boron Hydride Chemistry*, E. L. Muetterties, ed., Academic Press, New York, 1975.
 43. *Gmelin's Handbook of Inorganic Chemistry, Boron Compounds*, 1st Suppl., Vol. 3, 8th Ed., Springer Verlag, Berlin, 1981.
 44. *Gmelin's Handbook of Inorganic Chemistry, Boron Compounds*, 1st Suppl., Vol. 15, Part 2, 8th Ed., Springer Verlag, Berlin, 1974.
 45. C. E. Housecroft, *Polyhedron*, 6, 1935 (1987).
 46. C. E. Housecroft, Th. P. Fehlner, in *Advances in Organometallic Chemistry*, Vol. 21, F. G. A. Stone, R. West, eds., Academic Press, New York, 1982, p. 57.
 47. R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, R. Reiss, *Inorg. Chem.*, 13, 1138 (1974).
 48. D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, G. J. Palenik, *J. Am. Chem. Soc.*, 95, 3046 (1973).
 49. V. R. Miller, R. Weiss, R. N. Grimes, *J. Am. Chem. Soc.*, 99, 5646 (1977).
 50. D. C. Finster, E. Sinn, R. N. Grimes, *J. Am. Chem. Soc.*, 103, 1399 (1981).
 51. L. Borodinsky, R. N. Grimes, *Inorg. Chem.*, 21, 1921 (1982).
 52. L. Borodinsky, E. Sinn, R. N. Grimes, *Inorg. Chem.*, 21, 1928 (1982).
 53. J. W. Howard, R. N. Grimes, *Inorg. Chem.*, 11, 263 (1972).
 54. A. J. Borelli, Jr., J. S. Plotkin, L. G. Sneddon, *Inorg. Chem.*, 21, 1328 (1982).
 55. V. R. Miller, R. N. Grimes, *J. Am. Chem. Soc.*, 95, 2830 (1973).
 56. N. S. Hosmane, R. N. Grimes, *Inorg. Chem.*, 19, 3482 (1980).
 57. J. S. Plotkin, L. G. Sneddon, *Inorg. Chem.*, 18, 2165 (1979).
 58. W. M. Maxwell, V. R. Miller, R. N. Grimes, *J. Am. Chem. Soc.*, 98, 4818 (1976).
 59. C. P. Magee, L. G. Sneddon, D. C. Beer, R. N. Grimes, *J. Organomet. Chem.*, 86, 159 (1975).
 60. J. E. Crook, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 383 (1982).
 61. L. G. Sneddon, D. C. Beer, R. N. Grimes, *J. Am. Chem. Soc.*, 95, 6623 (1973).
 62. L. G. Sneddon, R. N. Grimes, *J. Am. Chem. Soc.*, 94, 7161 (1972).
 63. R. B. Maynard, R. G. Swisher, R. N. Grimes, *Organometallics*, 2, 500 (1983).
 64. W. M. Maxwell, K.-S. Wong, R. N. Grimes, *Inorg. Chem.*, 16, 3094 (1977).
 65. R. B. Maynard, R. N. Grimes, *J. Am. Chem. Soc.*, 104, 5983 (1982).
 66. R. G. Swisher, E. Sinn, G. A. Brewer, R. N. Grimes, *J. Am. Chem. Soc.*, 105, 2079 (1983).
 67. R. P. Micciche, J. S. Plotkin, L. G. Sneddon, *Inorg. Chem.*, 22, 1765 (1983).
 68. N. N. Greenwood, J. D. Kennedy, C. G. Savory, J. Staves, K. R. Trigwell, *J. Chem. Soc., Dalton Trans.*, 237 (1978).
 69. M. B. Fischer, D. F. Gaines, J. A. Ulman, *J. Organomet. Chem.*, 231, 55 (1982).
 70. W. J. Evans, G. B. Dunks, M. F. Hawthorne, *J. Am. Chem. Soc.*, 95, 4565 (1973).
 71. G. B. Dunks, M. F. Hawthorne, *J. Am. Chem. Soc.*, 92, 7213 (1970).
 72. K.-S. Wong, J. R. Bowser, J. R. Pipal, R. N. Grimes, *J. Am. Chem. Soc.*, 100, 5045 (1978).
 73. K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, M. F. Hawthorne, *J. Am. Chem. Soc.*, 97, 296 (1975).
 74. A. D. George, M. F. Hawthorne, *Inorg. Chem.*, 8, 1801 (1969).
 75. M. F. Hawthorne, A. D. Pitts, *J. Am. Chem. Soc.*, 89, 7115 (1967).
 76. M. F. Hawthorne, G. B. Dunks, *Science*, 178, 462 (1972).
 77. C. G. Salentine, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 560 (1973).
 78. C. G. Salentine, M. F. Hawthorne, *J. Am. Chem. Soc.*, 97, 6382 (1975).
 79. G. E. Hardy, K. P. Callahan, M. F. Hawthorne, *Inorg. Chem.*, 17, 1662 (1978).
 80. T. A. George, M. F. Hawthorne, *J. Am. Chem. Soc.*, 91, 5475 (1969).
 81. W. M. Maxwell, R. N. Grimes, *Inorg. Chem.*, 18, 2174 (1979).
 82. W. J. Evans, M. F. Hawthorne, *Inorg. Chem.*, 13, 869 (1974).

-
83. W. J. Evans, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 706 (1973).
 84. G. K. Barker, M. P. Garcia, M. Green, G. N. Pain, F. G. A. Stone, S. K. R. Jones, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 652 (1981).
 85. G. K. Barker, M. P. Garcia, M. Green, F. G. A. Stone, J.-M. Basset, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 653 (1981).
 86. C.-W. Jung, R. T. Baker, M. F. Hawthorne, *J. Am. Chem. Soc.*, 103, 810 (1981).
 87. D. F. Dustin, W. J. Evans, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 805 (1973).
 88. R. B. Maynard, Z.-T. Wang, E. Sinn, R. N. Grimes, *Inorg. Chem.*, 22, 873 (1983).
 89. C. G. Salentine, R. R. Rietz, M. F. Hawthorne, *Inorg., Chem.*, 13, 3025 (1974).
 90. W. J. Evans, M. F. Hawthorne, *J. Am. Chem. Soc.*, 93, 3063 (1971).
 91. W. J. Evans, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 611 (1972).
 92. C. J. Jones, M. F. Hawthorne, *Inorg. Chem.*, 12, 608 (1973).
 93. J. Plešek, B. Stibr, S. Herrmánek, *Synth. Inorg. Met.-Org. Chem.*, 3, 291 (1973).
 94. C.-W. Jung, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 499 (1976).
 95. N. W. Alcock, J. G. Taylor, M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 1168 (1983).
 96. W. M. Maxwell, E. Sinn, R. N. Grimes, *Chem. Soc., Chem. Commun.*, 389 (1976).
 97. W. M. Maxwell, R. F. Bryan, R. N. Grimes, *J. Am. Chem. Soc.*, 99, 4008 (1977).
 98. W. M. Maxwell, R. Weiss, E. Sinn, R. N. Grimes, *J. Am. Chem. Soc.*, 99, 4016 (1977).
 99. N. W. Alcock, M. J. Jaszal, M. G. H. Wallbridge, *J. Chem. Soc. Dalton Trans.*, 2793 (1987).
 100. R. J. Wilson, L. F. Warren, M. F. Hawthorne, *J. Am. Chem. Soc.*, 91, 758 (1969).
 101. L. F. Warren, M. F. Hawthorne, *J. Am. Chem. Soc.*, 92, 1157 (1970).
 102. M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren Jr., P. A. Wegner, *J. Am. Chem. Soc.*, 90, 879 (1968).
 103. L. F. Warren, M. F. Hawthorne, *J. Am. Chem. Soc.*, 89, 470 (1967).
 104. L. F. Warren, M. F. Hawthorne, *J. Am. Chem. Soc.*, 90, 4823 (1968).
 105. R. M. Wing, *J. Am. Chem. Soc.*, 90, 4828 (1968).
 106. R. E. King III, St. B. Miller, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.*, 22, 3548 (1983).
 107. H. M. Colquhoun, T. J. Greenhough, M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 761 (1985).
 108. D. E. Smith, A. J. Welch, *Acta Crystallogr., Sect. C*, 42, 1717 (1986).
 109. N. W. Alcock, J. G. Taylor, M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1805 (1987).
 110. D. C. Busby, M. F. Hawthorne, *Inorg. Chem.*, 21, 4101 (1982).
 111. M. F. Hawthorne, T. D. Andrews, *J. Chem. Soc., Chem. Commun.*, 443 (1965).
 112. W. E. Geiger, D. E. Smith, *J. Chem. Soc., Chem. Commun.*, 8 (1971).
 113. M. F. Hawthorne, R. L. Pilling, *J. Am. Chem. Soc.*, 87, 3987 (1965).
 114. A. Zalkin, T. E. Hopkins, D. H. Templeton, *Inorg. Chem.*, 6, 1911 (1967).
 115. C. B. Harris, *Inorg. Chem.*, 7, 1517 (1968).
 116. A. R. Siedle, G. M. Bodner, L. J. Todd, *J. Organomet. Chem.*, 33, 137 (1971).
 117. J. L. Little, P. S. Welcker, N. J. Loy, L. J. Todd, *Inorg. Chem.*, 9, 63 (1970).
 118. D. F. Dustin, M. F. Hawthorne, *J. Am. Chem. Soc.*, 96, 3462 (1974).
 119. A. R. Siedle, *J. Organomet. Chem.*, 90, 249 (1975).
 120. T. E. Paxon, M. F. Hawthorne, *J. Am. Chem. Soc.*, 96, 4674 (1974).
 121. R. G. Teller, J. J. Wilczynski, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 472 (1979).
 122. W. C. Kalb, C. W. Kreimendahl, D. C. Busby, M. F. Hawthorne, *Inorg. Chem.*, 19, 1590 (1980).
 123. P. E. Behnken, C. B. Knobler, M. F. Hawthorne, *Angew. Chem., Int. Ed. Engl.*, 22, 722 (1983).
 124. P. E. Behnken, T. B. Marder, R. Th. Baker, C. B. Knobler, M. R. Thompson, M. F. Hawthorne, *J. Am. Chem. Soc.*, 107, 932 (1985).
 125. C. B. Knobler, T. B. Marder, E. A. Mizusawa, R. G. Teller, J. A. Long, P. E. Behnken, M. F. Hawthorne, *J. Am. Chem. Soc.*, 106, 2990 (1984).
 126. J. D. Hewes, M. Thompson, M. F. Hawthorne, *Organometallics*, 4, 13 (1985).
 127. J. A. Long, T. B. Marder, P. E. Behnken, M. F. Hawthorne, *J. Am. Chem. Soc.*, 106, 2979 (1984).

6.5.3. Formation from Other Group-III B Compounds

6.5.3.4. by Reaction with Metal Halides

128. R. Th. Baker, M. S. Delaney, R. E. King III, C. B. Knobler, J. A. Long, T. B. Marder, T. E. Paxson, R. G. Teller, M. F. Hawthorne, *J. Am. Chem. Soc.*, **106**, 2965 (1984).
129. M. S. Delaney, C. B. Knobler, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 849 (1980).
130. M. F. Hawthorne, D. C. Young, P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).
131. E. D. Germann, M. E. Dyatkina, *J. Struct. Chem.*, **7**, 803 (1966).
132. A. H. Maki, Th. E. Barry, *J. Am. Chem. Soc.*, **87**, 4437 (1965).
133. M. P. Garcia, M. Green, F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 871 (1981).
134. E. H. S. Wong, M. F. Hawthorne, *Inorg. Chem.*, **17**, 2863 (1978).
135. L. I. Zakharkin, V. V. Kobak, A. I. Yanovsky, Y. Struchkov, T. Struchkov, *J. Organomet. Chem.*, **228**, 119 (1982).
136. H. C. Kang, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.*, **26**, 3409 (1987).
137. P. E. Behnken, M. F. Hawthorne, *Inorg. Chem.*, **23**, 3420 (1984).
138. M. P. Garcia, M. Green, F. G. A. Stone, C. E. Briant, D. N. Cox, D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 2343 (1985).
139. E. H. S. Wong, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 257 (1976).
140. M. F. Hawthorne, T. D. Andrews, *J. Am. Chem. Soc.*, **87**, 2496 (1965).
141. H. W. Rühle, M. F. Hawthorne, *Inorg. Chem.*, **7**, 2279 (1968).
142. Y. Do, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.*, **109**, 1853 (1987).
143. M. Green, J. A. K. Howard, A. P. James, C. M. Nunn, F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1113 (1984).
144. M. Green, J. A. K. Howard, A. P. James, Ch. M. Nunn, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 61 (1987).
145. C. G. Salentine, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 848 (1975).
146. C. G. Salentine, M. F. Hawthorne, *Inorg. Chem.*, **15**, 2872 (1976).
147. M. J. Manning, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.*, **110**, 4458 (1988).
148. R. R. Rietz, D. F. Dustin, M. F. Hawthorne, *Inorg. Chem.*, **13**, 1580 (1974).
149. C. G. Salentine, R. R. Rietz, M. F. Hawthorne, *Inorg. Chem.*, **13**, 3025 (1974).
150. D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, L. J. Todd, *J. Am. Chem. Soc.*, **89**, 3342 (1967).
151. W. H. Knoth, *J. Am. Chem. Soc.*, **89**, 3342 (1967).
152. D. F. Dustin, G. B. Dunks, M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 1109 (1973).
153. G. B. Dunks, M. M. McKnown, M. F. Hawthorne, *J. Am. Chem. Soc.*, **93**, 2541 (1971).
154. J. W. Evans, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 38 (1974).
155. J. D. Hewes, C. B. Knobler, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 206 (1981).
156. J. A. Walker, C. A. O'Con, L. Zheng, C. B. Knobler, M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 803 (1983).
157. A. R. Kane, E. L. Muetterties, *J. Am. Chem. Soc.*, **93**, 1041 (1971).
158. L. J. Guggenberger, A. R. Kane, E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 5665 (1972).
159. V. R. Miller, R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973).
160. V. R. Miller, R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 1600 (1976).
161. N. N. Greenwood, J. D. Kennedy, D. Reed, *J. Chem. Soc., Dalton Trans.*, 1 (1980).
162. J. Bould, N. N. Greenwood, J. D. Kennedy, *J. Organomet. Chem.*, **249**, 11 (1983).
163. N. N. Greenwood, J. Staves, *J. Chem. Soc., Dalton Trans.*, 1788 (1977).
164. N. N. Greenwood, M. J. Hails, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 37 (1980).
165. T. L. Venable, R. N. Grimes, *Inorg. Chem.*, **21**, 887 (1982).
166. T. L. Venable, E. Sinn, R. N. Grimes, *Inorg. Chem.*, **21**, 904 (1982).
167. H. D. Johnson, R. A. Greenangel, S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).
168. V. T. Brice, S. G. Shore, *Chem. Commun.*, 1312 (1970).
169. V. T. Brice, S. G. Shore, *J. Chem. Soc., Dalton Trans.*, 334 (1975).
170. G. G. Outtonson, Jr., V. T. Brice, S. G. Shore, *Inorg. Chem.*, **15**, 1456 (1976).
171. N. N. Greenwood, J. A. K. Howard, W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 37 (1977).
172. G. J. Zimmermann, L. G. Sneddon, *J. Am. Chem. Soc.*, **103**, 1102 (1981).
173. J. Bould, N. N. Greenwood, J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 481 (1982).
174. N. N. Greenwood, J. D. Kennedy, W. S. McDonald, D. Reed, J. Staves, *J. Chem. Soc., Dalton Trans.*, 117 (1979).

-
175. R. Weiss, R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 8087 (1977).
 176. R. Weiss, R. N. Grimes, *Inorg. Chem.*, **18**, 3291 (1979).
 177. N. N. Greenwood, J. D. Kennedy, C. G. Savory, J. Staves, K. R. Trigwell, *J. Chem. Soc., Dalton Trans.*, 237 (1978).
 178. J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 951 (1983).
 179. J. R. Bowser, A. Bonny, J. R. Pipal, R. N. Grimes, *J. Am. Chem. Soc.*, **101**, 1979.
 180. A. R. Siedle, D. McDowell, L. J. Todd, *Inorg. Chem.*, **13**, 2735 (1974).
 181. A. R. Kane, L. J. Guggenberger, E. L. Muetterties, *J. Am. Chem. Soc.*, **92**, 2571 (1970).
 182. J. W. Lott, D. F. Gaines, H. Shenhav, R. Schaeffer, *J. Am. Chem. Soc.*, **95**, 3042 (1973).
 183. S. K. Boocock, N. N. Greenwood, M. J. Hails, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1415 (1981).
 184. R. Ahmad, J. E. Crook, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1019 (1982).
 185. T. L. Venable, E. Sinn, R. N. Grimes, *Inorg. Chem.*, **21**, 895 (1982).
 186. N. N. Greenwood, *Pure Appl. Chem.*, **55**, 77 (1983).
 187. G. Ferguson, M. F. Hawthorne, B. Kaitner, F. J. Calor, *Acta Crystallogr., Sect. C*, **40**, 1707 (1984).
 188. J. E. Crook, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 933 (1981).
 189. J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 949 (1983).
 190. J. E. Crook, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 83 (1983).
 191. J. Bould, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 465 (1982).
 192. S. K. Boocock, J. Bould, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 713 (1982).
 193. J. W. Lott, D. F. Gaines, *Inorg. Chem.*, **13**, 2261 (1974).
 194. N. N. Greenwood, J. D. Kennedy, I. Macpherson, M. Thornton-Pett, *Z. Anorg. Allg. Chem.*, **540 / 541**, 45 (1986).
 195. F. Klanberg, P. A. Wegner, G. W. Parshall, E. L. Muetterties, *Inorg. Chem.*, **7**, 2072 (1968).
 196. A. R. Siedle, T. A. Hill, *J. Inorg. Nucl. Chem.*, **31**, 3874 (1969).
 197. D. F. Gaines, G. A. Steehler, *J. Chem. Soc., Chem. Commun.*, 122 (1982).
 198. T. E. Paxson, M. F. Hawthorne, *Inorg. Chem.*, **14**, 1604 (1975).
 199. S. K. Boocock, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, J. Staves, *J. Chem. Soc., Dalton Trans.*, 2573 (1981).
 200. M. A. Beckett, J. E. Crook, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 552 (1982).
 201. Y. M. Cheek, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 80 (1982).
 202. D. A. Thompson, R. W. Rudolph, *J. Chem. Soc., Chem. Commun.*, 770 (1976).

6.6. The Formation of the Group IIIB–Group 0 Element Bond

Bonding between a noble-gas element and another element generally requires electron transfer from the former to the latter (see §2.10). The group-IIIB element most likely to form bonds to any of the noble gases is therefore B, but even with this least electropositive of the group-IIIB elements, electronegative ligands are necessary. The symmetrical rotor ArBF_3 has been detected by microwave spectroscopy in $\text{Ar}-\text{BF}_3$ gas mixtures, cooled by supersonic expansion.¹ The Ar atom evidently acts as an electron-pair donor toward the BF_3 in the ArBF_3 molecule. The compound XeBF_3 (decomp. > 243 K), derived² from the interaction of Xe with $\text{O}_2[\text{BF}_4]$, at ca. 173 K, could be similar to ArBF_3 (perhaps with BF_3 in a pyramidal excited state and, consequently, with superior electron-acceptor properties to that of the planar form). Alternatively, the compound could be $\text{F}-\text{Xe}-\text{BF}_2$.

(N. BARTLETT)

1. K. C. Janda, L. S. Bernstein, J. M. Steed, S. E. Novick, W. Klemperer, *J. Am. Chem. Soc.*, **100**, 8074 (1978).
2. C. T. Goetschel, K. R. Loos, *J. Am. Chem. Soc.*, **94**, 3018 (1972).

6.7. Formation of Borides

6.7.1. Introduction

Borides of the transition and inner transition metals have important practical applications. Diborides MB_2 ($M = Ti, Zr, Hf, Nb, Ta$) are refractory materials with high hardness and strength and are excellent electrical conductors. Moreover, some resist oxidation to a much larger extent than the corresponding carbides. Among the rare-earth hexaborides, LaB_6 , e.g., has good chemical stability, a mp $\sim 2500^\circ C$ and a high electrical conductivity and is one of the best thermionic materials for high-electron-density cathodes. Finally, all boron-rich borides (e.g., MB_6 , MB_{12} , MB_{66}) are among the solids that exhibit the highest hardness known.

Borides, in contrast to carbides and nitrides, are characterized by an unusual structural complexity for both metal-rich and B-rich compositions. This complexity has its origin in the tendency of B atoms to form one-, two-, or three-dimensional covalent arrangements and to show uncommon coordination numbers because of their large size ($r_B = 0.88 \cdot 10^2$ pm) and their electronic structure (deficiency in valence electrons). The structures of the transition-element borides are well established¹⁻⁸.

The bonding is known from theoretical considerations and crystallographic and physical data for the most important structure types. The agreement between theory and experiment is not always satisfactory.

A systematic approach to the crystal chemistry of borides is possible on the simple basis of atom size considerations, as well as the tendency of B to form covalent skeletons.

In contrast to the carbides and nitrides, there are a large variety of formulas and structure types for borides (from M_4B to MB_{66}). Although it is possible to establish a comparison between metal-rich borides and carbides, B-rich borides have no counterpart in the carbides.

It is helpful to divide the boride structures into four partially overlapping groups based primarily on the arrangement of B atoms:

1. Borides with isolated B atoms, which includes borides from M_4B to M_2B : As the B content increases there is a tendency for B atoms to form isolated pairs, e.g., in M_3B_2 and M_5B_3 .
2. Borides with boron chains (single chains in MB and double chains in M_3B_4).
3. Borides with two-dimensional nets of B atoms (MB_2 and M_2B_5).
4. Borides with three-dimensional boron frameworks (MB_4 , MB_6 , MB_{12} , $MgAlB_{14}$, Mg_2B_{14} , $Na_xB_{0.8}B_{14}$ and MB_{66}).

The crystal chemistry of the borides is discussed in §6.7.2 according to this scheme. General methods of preparation, single-crystal growth and sintering of borides is considered, respectively, in §6.7.3, 6.7.4 and 6.7.5.

(J. R. ETourneau)

1. R. Kiessling, *Acta Chem. Scand.*, **4**, 209 (1950).
2. B. Post, in *Boron, Metallo-boron Compounds and Boranes*, R. M. Adams, ed., Interscience, New York, 1964, p. 301.
3. B. Aronsson, T. Lundström, S. Rundqvist, *Borides, Silicides and Phosphides*, Methuen, London, 1965.
4. J. L. Hoard, R. E. Hughes, in *The Chemistry of Boron and Its Compounds*, E. L. Muetterties, ed., John Wiley and Sons, New York, 1967, p. 25.
5. T. Lundström, *Ark. Kemi*, **31**, 227 (1969); *Chem. Abstr.*, **71**, 34,034 (1969).
6. G. V. Samsonov, T. I. Serebryakova, V. A. Neronov, *Borides*, Atomizdat, Moscow, 1975.
7. T. Lundström, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 351.
8. H. Nowotny, P. Rogl, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 413.

6.7.2. Existence and Crystal Chemistry of Borides

Ranking metal borides as refractory compounds results from the formation of covalent B—B bonds by the electron-deficient B atoms¹⁻⁴. As a result the metal lattice may be changed drastically, even for low B contents.

The stabilizing influence of small amounts of B ($M/B > 0.25$) in the voids of the metal host lattice varies with the mode of filling (partial or complete) of the interstitial, mostly O_h , sites and whether the compounds develop from the binary-intermetallic host lattice. The structures of B-rich compounds ($M/B < 4$) are mainly determined by the formation of regular, covalent B polyhedra (O_h , icosahedron) and the connections between them (B frame structures). Typical metal (M) borides therefore are found within a characteristic ratio of metal to boron: $0.125 \leq M/B \leq 4$.

The crystal chemistry of borides is described¹ using three structural units: (a) trigona prism, M_6B ; (b) M_8B antiprism, and (c) octahedron, M_6B . For example, the binary and ternary borides are reduced to the modes of linking these few structural units⁵. Considering the size and form of the B—B aggregation as a function of the M/B atomic ratio, a classification scheme is derived¹⁻³. The classification (Table 1) is not unambiguous, and overlaps occur; owing to B defects (particularly in group-VIIIA metals) some compounds are listed in strange groups, whereas full occupancy would result in a correct classification with respect to B—B aggregation.

Figure 1 presents a scheme for the formation of B—B bonds in binary metal borides, i.e., the occurrence of one-, two- and three-dimensional B aggregates as a function of the periodic group of the metal constituent.

The present status of information about phase equilibria and the formation of borides is summarized in Table 2 (binary borides) and in Figure 2a,b (ternary systems)⁶⁻²⁰⁹.

The crystal structures of the borides of the rare earth metals (M_{RE}) are described^{174,209}, and phase equilibria in ternary and higher order systems containing rare earths and B, including information on structures, magnetic and electrical properties as well as low-T phase equilibria, are available¹⁷⁵. Phase equilibria and crystal structure in binary and ternary systems containing an actinide metal and B are reviewed^{17,203}.

6.7. Formation of Borides

85

6.7.2. Existence and Crystal Chemistry of Borides

1. R. Kiessling, *Acta Chem. Scand.*, **4**, 209 (1950).
2. B. Post, in *Boron, Metallo-boron Compounds and Boranes*, R. M. Adams, ed., Interscience, New York, 1964, p. 301.
3. B. Aronsson, T. Lundström, S. Rundqvist, *Borides, Silicides and Phosphides*, Methuen, London, 1965.
4. J. L. Hoard, R. E. Hughes, in *The Chemistry of Boron and Its Compounds*, E. L. Muetterties, ed., John Wiley and Sons, New York, 1967, p. 25.
5. T. Lundström, *Ark. Kemi*, **31**, 227 (1969); *Chem. Abstr.*, **71**, 34,034 (1969).
6. G. V. Samsonov, T. I. Serebryakova, V. A. Neronov, *Borides*, Atomizdat, Moscow, 1975.
7. T. Lundström, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 351.
8. H. Nowotny, P. Rogl, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 413.

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The stabilizing influence of small amounts of B ($M/B > 0.25$) in the voids of the metal host lattice varies with the mode of filling (partial or complete) of the interstitial, mostly O_h , sites and whether the compounds develop from the binary-intermetallic host lattice. The structures of B-rich compounds ($M/B < 4$) are mainly determined by the formation of regular, covalent B polyhedra (O_h , icosahedron) and the connections between them (B frame structures). Typical metal (M) borides therefore are found within a characteristic ratio of metal to boron: $0.125 \leq M/B \leq 4$.

The crystal chemistry of borides is described¹ using three structural units: (a) trigona prism, M_6B ; (b) M_8B antiprism, and (c) octahedron, M_6B . For example, the binary and ternary borides are reduced to the modes of linking these few structural units⁵. Considering the size and form of the B—B aggregation as a function of the M/B atomic ratio, a classification scheme is derived¹⁻³. The classification (Table 1) is not unambiguous, and overlaps occur; owing to B defects (particularly in group-VIIIA metals) some compounds are listed in strange groups, whereas full occupancy would result in a correct classification with respect to B—B aggregation.

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The present status of information about phase equilibria and the formation of borides is summarized in Table 2 (binary borides) and in Figure 2a,b (ternary systems)⁶⁻²⁰⁹.

The crystal structures of the borides of the rare earth metals (M_{RE}) are described^{174,209}, and phase equilibria in ternary and higher order systems containing rare earths and B, including information on structures, magnetic and electrical properties as well as low-T phase equilibria, are available¹⁷⁵. Phase equilibria and crystal structure in binary and ternary systems containing an actinide metal and B are reviewed^{17,203}.

TABLE 1. CLASSIFICATION OF METAL BORIDES

Metal-boron ratio	Metal borides and structure types	Boron aggregation
A. Metal frame structures and metal borides with isolated B atoms		
> 8	β -Mn-borides κ -borides η -(Ti ₂ Ni type) borides Filled up Mn ₅ Si ₃ borides Perovskite borides Nd ₂ Fe ₂₃ B ₃ type Nd ₂ Fe ₁₄ B type	Isolated borons
8.0	Nd ₃ Ni ₁₃ B ₂ type	
5.0	Dy ₃ Ni ₇ B ₂ type Ca ₅ Ni ₁₅ B ₄ type CeCo ₄ B type Fe ₅ P ₂ B (W ₅ Si ₃ type) Pt _{~4} B type	
4.0	ScRh ₃ B (filled perovskite) La ₅ Ni ₁₉ B ₆ type LiPt ₃ B type Ti ₃ Co ₅ B ₂ type	
3.83	Cr ₂₃ C ₆ (τ) borides	
3.5	Ce ₂ Co ₅ B ₂ type Ce ₃ Co ₁₁ B ₄ type	
3.3	Sc ₄ Ni ₂₉ B ₁₀ type	Isolated borons + B pairs
3.0	Ce ₂ Co ₇ B ₃ type Re ₃ B type [Mo, Fe] ₃ B (Ti ₃ P type) [Ir, Fe] ₃ B (Fe ₃ C type) TaCo ₂ B type	Isolated borons
2.83	Ho ₂ Ni ₁₅ B ₆ type	Isolated borons + B pairs
2.9	PrRh _{4,8} B ₂ type	Isolated borons
2.5	Pd ₄ B ₂ (Mn ₅ C ₂ type)	
2.4	Na ₃ Pt ₉ B ₅ type Li _{~3} Ni _{~16} B _{~8}	
2.33	Ru ₇ B ₃ (Th ₇ Fe ₃ type)	
2.2	Ho ₃ Ni ₁₉ B ₁₀ type	'Isolated boron + boron pairs
2.17	SrNi ₁₂ B ₆ type	Isolated borons
2.0	t-Mn ₂ B (CuAl ₂ type) o-Mn ₂ B (Mg ₂ Cu type) Pd ₂ B (anti-CaCl ₂ type) NbFeB (Fe ₂ P type) NbCoB type MoCoB (anti-PbCl ₂ type) CeCo ₃ B ₂ (CaCu ₅ type) ErIr ₃ B ₂ type URu ₃ B ₂ type (Nd, Rh)Rh ₃ B ₂ type La _{1-0.19} Rh ₃ B ₂ type HfCo ₃ B ₂ type Li _{1.2} Ni _{2.5} B ₂₃ type	Boron pair formation Boron pair formation

Metal-boron ratio	Metal borides and structure types	Boron aggregation
1.93	$\text{Ca}_7\text{Rh}_{20}\text{B}_{14}$ type	Isolated borons
1.90	$\text{Sr}_5\text{Rh}_{14}\text{B}_{10}$ type	Isolated borons
1.89	$\text{Ho}_3\text{Ni}_{15}\text{B}_9$ type	Isolated borons + B pairs
1.83	$\text{Ba}_2\text{Ni}_9\text{B}_6$ type	Boron pair formation
	$\text{Ba}_2\text{Pt}_9\text{B}_6$ type	Structure needs confirmation
	$\text{Ca}_3\text{Rh}_8\text{B}_6$ type	Isolated borons
1.75	$[\text{Re}, \text{Co}]_7\text{B}_4$ type	
	$\text{Ca}_2\text{Rh}_5\text{B}_4$ type	Isolated borons
	$\text{Sc}_2\text{Ru}_5\text{B}_4$ type	Isolated B atoms + B pairs
	$\text{Nd}_2\text{Ni}_5\text{B}_4$ type	B_4 chain fragments
	$\text{Pr}_8\text{Re}_{13-x}\text{B}_{12}$ type	
1.7	Cr_5B_3 type	Isolated B atoms + B pairs
1.64	$\text{Mg}_5\text{Ru}_{13}\text{B}_{11}$ type	Isolated B atoms + B pairs
1.58	$\text{Ba}_7\text{Ir}_{12}\text{B}_{12}$ type	Isolated B atoms + B pairs
1.5	REFe_2B_2 (ThCr_2Si_2 type)	Isolated B atoms
	CaRh_2B_2 type	
B. Metal borides with B pairs, B chain fragments, and chains incompletely developed owing to B defects		
1.5	$[\text{W}, \text{Fe}]_3\text{B}_2$ (U_3Si_2 type)	Boron pairs
	W_2CoB_2 type	
	$\text{Mg}_2\text{IrB}_{2-x}$ type	Boron pairs + isolated borons
1.33	W_3CoB_3 type	B_3 groups (chain fragments)
1.28–	CeCo_4B_4 type	Boron pairs
1.25	NdCo_4B_4 type	
	LuRu_4B_4 type	
	$\text{LuRh}_{4+x}\text{B}_4$ type	
	$\text{Ce}_{1+x}\text{Fe}_4\text{B}_4$ type	
	YOs_4B_4 type	
C. Metal borides with B chains		
1.17	$\text{Pr}_5\text{Co}_2\text{B}_6$ type	Boron net
1.37	Ru_{11}B_8 type	Branched chains
1.33	$\text{o-Ni}_4\text{B}_{3-x}$ type	Chains + isolated borons
	$\text{m-Ni}_4\text{B}_{3-x}$ type	Boron chains
	$\text{ZrIr}_3\text{B}_{4-x}$ type	Linear chains + isolated borons
1.0	NaIr_5B_4 type	Boron pairs + B_6 -net fragments
1.0	LuRuB_2 type	Boron chains dissolved into B pairs
	$\text{Ca}_2\text{Os}_5\text{B}_5$ type	Chain fragments, B_4
	FeB type	Boron chains
	CrB type	
	$\alpha\text{-MoB}$ type	
	NbCoB_2 type	Chains + B pairs
	$\text{W}_2\text{Ir}_3\text{B}_6$ type	
	$\text{Nb}_3\text{Co}_4\text{B}_7$ type	Boron pairs + B_5 rings
	PtB (anti-NiAs type)	Linear B chains
	YBC type	Boron chains

(continued)

TABLE 1. (continued)

Metal-boron ratio	Metal borides and structure types	Boron aggregation
	ThBC type	Branched with C atoms
	UBC type	
	Th ₃ B ₂ C ₃ type	
	Mo ₂ BC type	
0.83	Pr ₂ Re ₃ B ₆ type	Branched chain
	Lu ₂ Ni ₃ B ₆ type	Chain net formation
0.81	V ₅ B ₆ type	Chains and double chains
0.75	Ta ₃ B ₄ type	Double chains
	IrB _{1.35} type	Isolated B + B net
	Ru ₂ R _{3-x} type	Isolated B + B net
0.70	La ₂ Re ₃ B ₇ type	Chain net fragments
	V ₂ B ₃ type	Triple chains
0.57	Er ₃ CrB ₇ type	Chain net structure
D. Metal borides with two-dimensional B networks		
0.5	AlB ₂ type	Two-dimensional B net
	ReB ₂ type	Puckered B net
	RuB ₂ type	Folded B net
	YCrB ₄ type	5-, 7-membered B rings
	ThMoB ₄ type	5-, 7-membered B rings
	ErNiB ₄ type	Eight-member B rings linked by B pairs
	Y ₂ ReB ₆ type	5-, 6-, 7-membered B rings
	CeCr ₂ B ₆ type	Net fragments
	LaB ₂ C ₂ type	Boron-carbon net
	ScB ₂ C ₂ type	Boron-carbon net
	YB ₂ C type	Boron-carbon net
0.384	Er ₄ ViB ₁₃ type	Four-, seven-membered B rings
0.4	W ₂ B _{5-x} type	Branched nets
	Mo ₂ B _{5-x} type	
	Sm ₂ B ₅ type	
		B ₆ units
E. Three-dimensional B frameworks		
	UB ₄ type	
	ThB ₆ type	
	Mg ₂ B ₁₄ type, LiAlB ₁₄ type	
	UB ₁₂ type	
	MB _{>20} : solid solutions of M atoms in β -rh. B	
	MB ₆₆₋₁₀₀ hectoborides, various modifications of B and impurity phases	

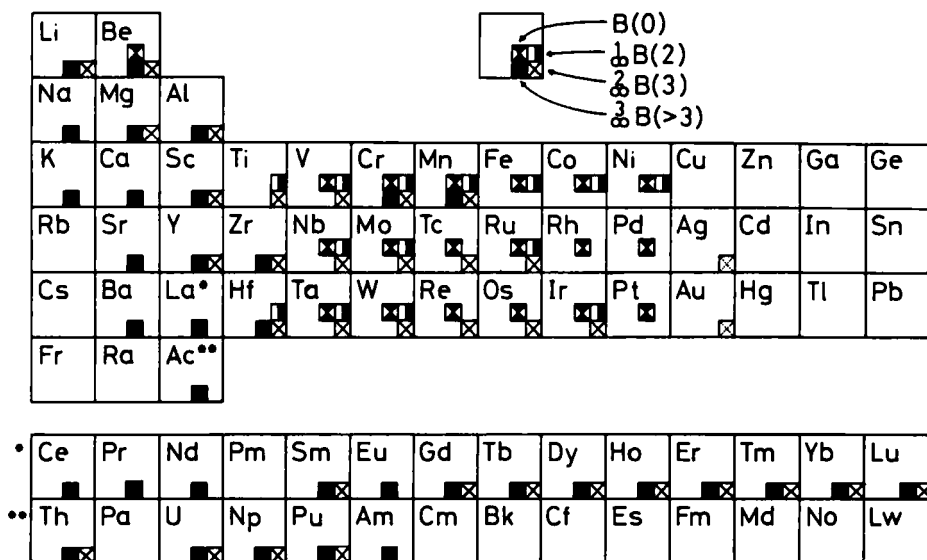


Figure 1. Scheme of the formation of B—B bonds in binary metal borides: B(0), borides with isolated B atoms; $\frac{1}{\infty}$ B(2), borides with one-dimensional infinite B chains, each B atom having two nearest-B-neighbor atoms; $\frac{2}{\infty}$ B(3), borides with infinite two-dimensional B nets (three B neighbors for each B atom); $\frac{3}{\infty}$ B, formation of a three-dimensional B network (more than three nearest-neighbor B atoms for each B atom).

A different approach to the structures of binary borides is based on an analysis of the commensurability of the spatial correlation of the valence electrons¹⁵².

Critical assessment of phase-diagram data employing the thermodynamics of the phase equilibria in the form of phase-diagram modeling provides consistent thermochemical data (including also the liquid solution) for binary metal–boron systems such as: V—B¹⁵³; Cr—B, Mn—B, Fe—B, Co—B, Ni—B^{154,175}; Mo—B^{155,171}; and Nb—B, W—B, Al—B¹⁷¹. Despite these efforts, reinvestigation of binary systems is necessary, in particular Fe—B (existence of FeB₂?), Zr—B (reaction isotherms involving ZrB₁₂), Th—B (metal-rich region), most of the platinum metal–B systems, and all systems containing alkalis and alkaline earths. Few phase equilibria are known in transition metal element–boron systems. Similarly, for the ternary systems M_T–M_T–B (M_T = transition metal), phase equilibria are established from isothermal sections, whereas information about thermodynamic equilibria within M_T–M_B–B (M_B = group-B element) systems is scarce and no ternary borides are known for combinations M_B–M_B–B. However, the geometrical, electrochemical and energy band factors responsible for crystal structure stability of a given composition help to form complete or extended-solid solutions between isotopic binary borides of the same or neighboring group numbers.

Uncharacterized ternary and binary metal borides, lacking precise composition or crystal chemistry data (see Fig. 2, Table 2), are not covered in this context. Further-

TABLE 2

Li		Be	Al	phase diagram established phase diagram partly investigated phase diagram proposed compound metastable compound predicted to form high-flow-t temperature compound hP compound forms under high pressure																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														
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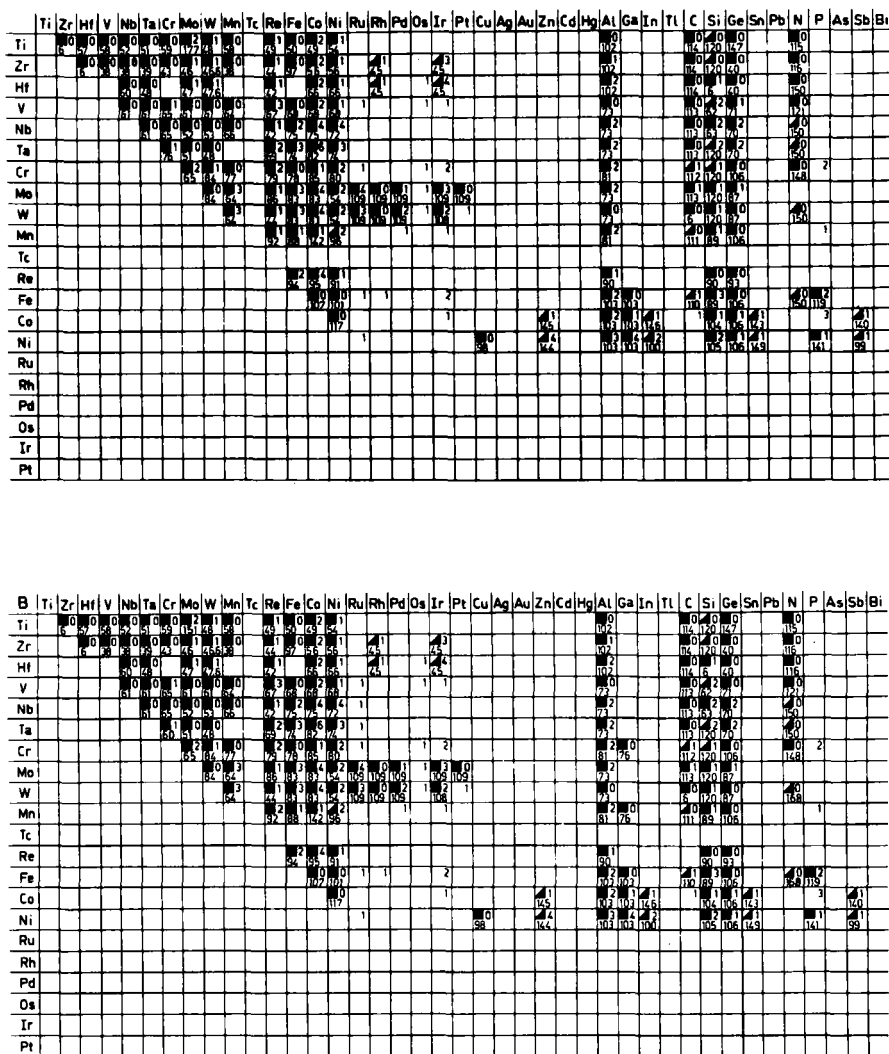


Figure 2. Formation of ternary borides and phase equilibria within ternary boride systems of the type M-M-B or M-Y-B (M = metal, Y = nonmetal). ■, complete isothermal section established; ◼, part of a diagram only. Numbers in the lower part of each square correspond to the refs. to the ternary section. The number of ternary compounds observed is indicated in the right upper corner of each square.

more, most preparations are performed to obtain well-defined samples for laboratory investigations and are far from being optimized for large-scale technical production at low energy.

(P. ROGL)

1. H. Nowotny, P. Rogl, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 411; *J. Less-Common Met.*, 61, 39 (1979).
2. T. Lundström, in *Boron and Refractory Borides*, Vol. I, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 351.
3. P. Rogl, *J. Less-Common Met.*, 11, 283 (1985).
4. T. Serebryakova, *J. Less-Common Met.*, 67, 499 (1979).
5. R. Kiessling, *Acta Chem. Scand.*, 4, 209 (1950).
6. E. Rudy, Compendium of Phase Diagram Data, AFML-TR-65-2-5, 1969; *Chem. Abstr.*, 72, 25,616 (1970).
7. K. E. Spear, in *Boron and Refractory Borides*, Vol. I, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 439.
8. M. L. Borlera, G. Pradelli, *Met. Ital.*, 2, 61 (1971); see also S. Okada, T. Atoda, *J. Solid State Chem.*, 68, 61 (1987).
9. K. I. Portnoi, V. M. Romashov, *Sov. Powder Metall. Met. Ceram.*, 5, 48 (1972).
10. G. Pradelli, C. Gianoglio, *Met. Ital.*, 12, 659 (1974).
11. L. Ya. Markovskij, E. T. Bezruk, *Vys. Neorg. Soedin Akad. Nauk Ukr. SSR, Inst. Probl. Materialoved.*, 433 (1965).
12. U. Herold, U. Köster, *Z. Metallkd.*, 69, 326 (1978).
13. J. D. Schöbel, H. H. Stadelmaier, *Z. Metallkd.*, 56, 856 (1965).
14. K. E. Spear, in *Applications of Phase Diagrams in Metallurgy and Ceramics*, Vol. 2, NBS Spec. Publ. 496, 1978; *Chem. Abstr.*, 89, 31,531 (1978).
15. H. Ipsier, P. Rogl, *J. Less-Common Met.*, 82, 363 (1981).
16. F. Wald, A. J. Rosenberg, *Trans. A.I.M.E.*, 233 796 (1965); in *Boron—Preparation and Properties*, Vol. 3, PWN, Warsaw, 1970, p. 103.
17. P. E. Potter, in *Handbook on the Physics and Chemistry of the Actinides*, Vol. 6, C. Keller, ed., North Holland Publishers, Amsterdam, 1990.
18. J. Stecher, F. Aldinger, *Z. Metallkd.*, 10, 684 (1973).
19. V. N. Gurin, M. M. Korsukova, in *Boron and Refractory Compounds*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 293.
20. Yu. B. Kuz'ma, N. S. Bilonizhko, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 7, 542 (1971); *Chem. Abstr.*, 74, 147,080 (1971).
21. N. S. Bilonizhko, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 10, 227 (1974); *Chem. Abstr.*, 81, 7050 (1974).
22. N. S. Bilonizhko, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 8, 163 (1972); for CeFeB_3 , see also *Vestn. L'vov Un-ta: Ser. Khim.*, (19), 37 (1977); *Chem. Abstr.*, 76, 104,398 (1972). *Chem. Abstr.*, 88, 201,447 (1978).
23. N. F. Chaban, Yu. B. Kuz'ma, *Dopov. Akad. Nauk, Ukr. RSR, Ser. A*, 33, 1048 (1971); *Chem. Abstr.*, 76, 51,060 (1972).
24. Yu. B. Kuz'ma, S. N. Svarichevskaya, V. I. Fomenko, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 9, 1372 (1973); *Chem. Abstr.*, 79, 150,265 (1973).
25. S. I. Mikhaleiko, Yu. B. Kuz'ma, *Dopov. Akad. Nauk, Ukr. RSR, Ser. A*, 951 (1977); *Chem. Abstr.*, 88, 30,613 (1978).
26. N. F. Chaban, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 13, 757 (1977); *Chem. Abstr.*, 87, 29,793 (1977).
27. H. H. Stadelmaier, H. J. Lee, *Z. Metallkd.*, 69, 685 (1978); see also ref. 26.
28. I. P. Vol'ovka, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 14, 469 (1978); *Chem. Abstr.*, 88, 177,892 (1978).
29. N. S. Bilonizhko, N. F. Chaban, Yu. B. Kuz'ma, M. D. Ugrin, *Dopov. Akad. Nauk, Ukr. RSR, Ser. B*, 6, 26 (1983).
30. Yu. B. Kuz'ma, N. S. Bilonizhko, S. I. Svarichevskaya, in *Tugoplavkie Boridy i. Silicidy*, Naukova Dumka, Kiev, 1977, pp. 67–74; *Chem. Abstr.*, 88, 111,278 (1978).
31. Yu. B. Kuz'ma, A. S. Sobolev, M. P. Furtak, *Inorg. Mater. (USSR)*, 6, 1936 (1970).

32. H. C. Ku, D. C. Johnston, B. T. Matthias, H. Barz, G. Burri, L. Rinderer, *Mater. Res. Bull.*, **14**, 1591 (1979).
33. J. Bauer, H. Nowotny, *Monatsh. Chem.*, **102**, 1129 (1971).
34. P. K. Smith, P. W. Gilles, *J. Inorg. Nucl. Chem.*, **29**, 375 (1967).
35. P. Rogl, J. Bauer, J. Debuique, *J. Nucl. Mater.*, **165**, 74 (1989).
36. N. S. Bilonizhko, *Vestn. L'vovsk. Un-ta: Ser. Khim.*, **19**, 56 (1977).
37. N. F. Chaban, *Vestn. L'vovsk. Un-ta: Ser. Khim.*, **21**, 44 (1979); *Chem. Abstr.*, **91**, 163,755 (1979).
38. Yu. V. Voroshilov, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, **57**, 49 (1967); *Chem. Abstr.*, **68**, 81,752 (1968).
39. Yu. V. Voroshilov, Yu. B. Kuz'ma, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, **10**, 145 (1967); *Chem. Abstr.*, **68**, 24,919 (1968).
40. M. A. Marko, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **13**, 759 (1977); *Chem. Abstr.*,
41. H. Holleck, *J. Nucl. Mater.*, **21**, 14 (1967).
42. Yu. B. Kuz'ma, V. I. Lakh, B. I. Stadnyk, D. A. Kovalyk, *Poroshk. Metall. (Kiev)*, **10**, 59 (1970); *Chem. Abstr.*, **74**, 146,837 (1971).
43. Yu. V. Voroshilov, V. I. Lakh, B. I. Stadnyk, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **3**, 1390 (1967); *Chem. Abstr.*, **69**, 5716 (1968).
44. Yu. B. Kuz'ma, V. I. Lakh, B. I. Stadnyk, Yu. V. Voroshilov, *Poroshk. Metall. (Kiev)*, **8**, 462 (1968).
45. P. Rogl, H. Nowotny, *J. Less-Common Met.*, **67**, 41 (1979).
46. P. Rogl, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **104**, 182 (1973).
47. P. Rogl, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **102**, 971 (1971).
48. Yu. B. Kuz'ma, S. N. Svarichevskaya, V. S. Telegus, *Poroshk. Metall. (Kiev)*, **102**, 61 (1969).
49. Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **7**, 452 (1971); *Chem. Abstr.*, **75**, 25,992 (1971).
50. T. F. Fedorov, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **3**, 1307 (1967); *Chem. Abstr.*, **68**, 63,278 (1968).
51. A. S. Sobolev, Yu. B. Kuz'ma, T. E. Soboleva, T. F. Fedorov, *Poroshk. Metall. (Kiev)*, **8**, 62 (1968); *Chem. Abstr.*, **68**, 71,633 (1968).
52. Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, **11**, 54 (1971); *Chem. Abstr.*, **75**, 41,421 (1971).
53. Yu. B. Kuz'ma, V. I. Lakh, B. I. Stadnyk, Yu. V. Voroshilov, *Sov. Powder Metall. Met. Ceram.*, **42**, 73 (1966).
54. Yu. B. Kuz'ma, M. V. Chepiga, *Poroshk. Metall. (Kiev)*, **9**, 71 (1968); *Chem. Abstr.*, **72**, 16,370 (1970); for Mo-Ni-B see also ref. 55.
55. H. Haschke, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **97**, 1459 (1966).
56. Yu. V. Voroshilov, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, **9**, 94 (1969); *Chem. Abstr.*, **72**, 48,208 (1970).
57. Y. A. Chang, Air Force Materials Laboratory, Tech. Rept., AFML-TR-65-2, II, V (1966).
58. Yu. B. Kuz'ma, T. P. Paitash, S. I. Baidala, *Visn. L'viv. Derzh. Univ., Ser. Khim.*, No. 11, 18 (1969); *Chem. Abstr.*, **74**, 25,545 (1971).
59. T. F. Fedorov, *Sov. Powder Metall. Met. Ceram.*, **6**, 42 (1962).
60. Yu. B. Kuz'ma, V. S. Telegus, M. A. Marko, *Poroshk. Metall. (Kiev)*, No. 12, 66 (1972); *Chem. Abstr.*, **77**, 10,306 (1972).
61. Yu. B. Kuz'ma, M. A. Marko, M. V. Petrovskaya, *Visn. L'viv. Derzh. Univ., Ser. Khim.*, **13**, 3 (1972).
62. H. Kudielka, H. Nowotny, G. Findeisen, *Monatsh. Chem.*, **88**, 1048 (1957).
63. H. Nowotny, *Bull. Soc. Chim. Fr.*, 1881 (1960).
64. V. S. Telegus, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, **11**, 67 (1971); *Chem. Abstr.*, **74**, 131,054 (1971).
65. Yu. B. Kuz'ma, V. S. Telegus, D. A. Kovalyk, *Poroshk. Metall. (Kiev)*, **9**, 79 (1969); *Chem. Abstr.*, **71**, 74,691 (1969).
66. Yu. B. Kuz'ma, *Visn. L'viv. Univ., Ser. Khim.*, No. 13, 20 (1972); *Chem. Abstr.*, **81**, 42,175 (1974).
67. Yu. B. Kuz'ma, D. A. Kovalyk, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **5**, 1428 (1969); *Chem. Abstr.*, **72**, 71,708 (1970).

68. Yu. B. Kuz'ma, P. K. Starodub, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 9, 337 (1973); *Chem. Abstr.*, 79, 10,889 (1973).
69. Yu. B. Kuz'ma, V. I. Lakh, B. I. Stadnyk, N. F. Chaban, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, No. 9, 849 (1971); *Chem. Abstr.*, 75, 144,697 (1971).
70. M. A. Marko, Yu. B. Kuz'ma, E. I. Gladyshevsky, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, No. 6, 555 (1976); *Chem. Abstr.*, 86, 46,295 (1977).
71. M. A. Marko, *Visn. L'viv. Derzh. Univ., Ser. Khim.*, 17, 28 (1975).
72. A. S. Sobolev, Yu. B. Kuz'ma, T. F. Fedorov, *Izv. Akad. Nauk SSSR, Met.*, 3, 638 (1967); *Chem. Abstr.*, 67, 68,032 (1967).
73. W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, 96, 844 (1965).
74. Yu. B. Kuz'ma, A. S. Sobolev, T. F. Fedorov, *Poroshk. Metall. (Kiev)*, 11, 81 (1971); *Chem. Abstr.*, 75, 92,091 (1971).
75. Yu. B. Kuz'ma, T. N. Ts'olkovskii, O. P. Babyrova, *Inorg. Mater. (USSR)*, 4, 950 (1968); *Chem. Abstr.*, 69, 70,738 (1968).
76. N. F. Chaban, *Vestn. L'vovsk. Un-ta, Ser. Khim.*, No. 19, 57 (1977); *Chem. Abstr.*, 88, 159,308 (1978).
77. G. Pradelli, C. Gianoglio, *Metall. Ital.*, 4, 191 (1976).
78. C. Gianoglio, G. Pradelli, M. Vallino, *Metall. Sci. Technol.*, 1, 53 (1983).
79. V. S. Telegus, Yu. B. Kuz'ma, C. K. Stefanishina, *Poroshk. Metall. (Kiev)*, 11, 64 (1969); *Chem. Abstr.*, 71, 7101 (1969).
80. E. Lugscheider, O. Knotek, H. Reimann, *Monatsh. Chem.*, 105, 80 (1974).
81. N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 9, 1696 (1973).
82. W. Steurer, Thesis, Univ. Vienna, 1979.
83. H. Haschke, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, 97, 5 (1966); for Mo-Co-B see also Yu. B. Kuz'ma, O. V. Nych, R. V. Skolozdra, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 2, 1709 (1966); *Chem. Abstr.*, 66, 69,353 (1967); for Mo-Fe-B see also E. I. Gladyshevskij, *Sov. Powder Metall. Met. Ceram.*, 4, 55 (1966).
84. V. S. Telegus, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, 8, 68 (1968); *Chem. Abstr.*, 69, 110,405 (1968); for Mo-W-B see also V. I. Kharitonov, F. I. Shamrai, *Sov. Powder Metall. Met. Ceram.*, 79, 60 (1969).
85. Yu. B. Kuz'ma, M. V. Chepiga, A. M. Plakhina, *Inorg. Mater. (USSR)*, 2, 1038 (1966).
86. Yu. B. Kuz'ma, B. I. Stadnyk, V. I. Lakh, V. S. Telegus, N. N. Borbulevich, *Izv. Vyssh. Ucheb. Zaved., Tsvet. Met.*, 13, 160 (1970); *Chem. Abstr.*, 73, 81,228 (1970).
87. M. A. Marko, P. S. Saakyai, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 12, 1087 (1976); *Chem. Abstr.*, 85, 152,170 (1976).
88. G. Pradelli, C. Gianoglio, *Metall. Ital.*, 1, 19 (1976).
89. N. F. Chaban, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 6, 883 (1970); *Chem. Abstr.*, 73, 59,645 (1970).
90. N. F. Chaban, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 8, 933 (1972); *Chem. Abstr.*, 77, 67,160 (1972).
91. M. V. Chepiga, *Vestn. L'vovsk. Un-ta, Ser. Khim.*, No. 14, 27 (1972); *Chem. Abstr.*, 81, 159,651 (1974).
92. V. S. Telegus, Yu. B. Kuz'ma, *Dopov. Akad. Nauk Ukr. RSR. Ser. A*, No. 10, 945 (1969).
93. M. A. Marko, *Visn. L'viv. Derzh. Univ., Ser. Khim.*, 16, 31 (1974).
94. E. Ganglberger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, 97, 718 (1966).
95. M. V. Chepiga, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 9, 1505 (1973); *Chem. Abstr.*, 80, 31,242 (1974).
96. H. H. Stadelmaier, *Metall.*, 23, 11 (1969).
97. Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 7, 514 (1971); *Chem. Abstr.*, 75, 25,992 (1971).
98. E. Lugscheider, H. Reimann, *Monatsh. Chem.*, 108, 1005 (1977).
99. G. Hofer, H. H. Stadelmaier, *Metall.*, 9, 963 (1964).
100. J. D. Schöbel, H. H. Stadelmaier, *Z. Metallkd.*, 55, 378 (1964).
101. Yu. B. Kuz'ma, V. I. Koval, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 4, 381 (1968); *Chem. Abstr.*, 69, 70,384 (1968).
102. W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, 95, 1417 (1964).

103. N. F. Chaban, Yu. B. Kuz'ma, *Str. Svoistva Primen, Metallid. (2nd Mater. Simp., 1972)*, T. I. Kornilov, N. M. Mateveeva, eds., Nauka, Moscow, 1972, p. 102; *Chem. Abstr.*, 82, 178,302 (1975).
104. N. F. Chaban, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 9, 1886 (1973); *Chem. Abstr.*, 80, 125,393 (1974).
105. E. Lugscheider, H. Reimann, O. Knotek, *Monatsh. Chem.*, 106, 1155 (1975).
106. M. A. Marko, Yu. B. Kuz'ma, E. I. Gladyshevskii, *Strukt. Faz. Fazovyi Prevrashch. Diag. Sostoyania Met. Syst.*, O. S. Ivanov, Z. M. Alekseeva, eds., Nauka, Moscow, 1974, p. 25; *Chem. Abstr.*, 82, 103,851 (1975).
107. P. Rogl, J. C. Schuster, H. Nowotny, in *Boron Steel, Proc. Int. Symp., 1980*, p. 33; see also G. Pradelli, *Metall. Ital.*, 7, 351 (1981).
108. P. Rogl, F. Benesovsky, H. Nowotny, *Monatsh. Chem.*, 103, 965 (1972).
109. H. Haschke, Thesis, Univ. Vienna, 1965.
110. M. L. Borlera, G. Pradelli, *Metall. Ital.*, 59, 907 (1967).
111. M. L. Borlera, G. Pradelli, *Atti Accad. Naz. Lincei, Mem., Cl. Sci. Fis., Mat. Nat., Sez. 2a*, 10, 69 (1971); *Chem. Abstr.*, 76, 157,350 (1972).
112. G. Pradelli, *Metall. Ital.*, 66, 551 (1974); 5, 223 (1978).
113. E. Rudy, F. Benesovsky, L. Toth, *Z. Metallkd.*, 54, 345 (1963).
114. E. Rudy, St. Windisch, *AFML-TR-2*, 11, 13 (1966).
115. H. Nowotny, F. Benesovsky, C. Brukl, O. Schob, *Monatsh. Chem.*, 92, 404 (1961); see also T. J. Yurick, K. E. Spear, IAEA-SM-236/53, *Thermodynamics of Nucl. Mater.*, 1979, Vol. 1, 73, 1979; *Chem. Abstr.*, 94, 163,585 (1981).
116. H. Nowotny, E. Rudy, F. Benesovsky, *Monatsh. Chem.*, 91, 964 (1960).
117. I. I. Kornilov, P. T. Kolomytsev, *Dokl. Akad. Nauk, SSSR*, 125, 325 (1959).
118. H. Nowotny, E. Rudy, F. Benesovsky, *Monatsh. Chem.*, 92, 383 (1961).
119. S. Rundqvist, *Acta Chem Scand.*, 16, 1 (1962).
120. H. Nowotny, R. Kieffer, F. Benesovsky, *Planseeber. Pulvermetall.*, 5, 86 (1957).
121. K. E. Spear, H. Schäfer, P. W. Gilles, *J. Less-Common Met.*, 14, 449 (1968).
122. G. F. Stepanchikova, Yu. B. Kuz'ma, *Visn. L'viv. Un-tu. Ser. Khim.*, No. 18, 16 (1976); *Chem. Abstr.*, 85, 182,954 (1976).
123. S. I. Mikhaleenko, O. I. Bilén, *Visn. L'viv. Un-tu. Ser. Khim.*, No. 21, 42 (1979); *Chem. Abstr.*, 91, 113,196 (1979).
124. Yu. B. Kuz'ma, V. E. Romashov, *Visn. L'viv. Derzh. Univ., Ser. Khim.*, 17, 26 (1975).
125. M. A. Marko, M. S. Nalyvayko, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 14, 1055 (1978); *Chem. Abstr.*, 89, 95797 (1978).
126. N. F. Chaban, Yu. B. Kuz'ma, I. D. Gerasim, *Poroshk. Metall. (Kiev)*, No. 8, 24 (1978); *Chem. Abstr.*, 89, 186704 (1978).
127. M. L. Fiedler, H. H. Stadelmaier, I. K. Simonson, *Z. Metallkd.*, 68, 356 (1977).
128. Yu. B. Kuz'ma, *Visn. L'viv. Derzh., Ser. Khim.*, 16, 57 (1974).
129. K. A. Schwetz, M. Hoerle, J. Bauer, *Ceramurg. Intern.*, 5, 105 (1979).
130. N. F. Chaban, Yu. B. Kuz'ma, N. S. Bilonizhko, O. O. Kachmar, N. V. Petriv, *Dopov. Akad. Nauk RSR, Ser. A*, 875 (1980).
131. M. A. Marko, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 15, 2070 (1979); *Chem. Abstr.*, 92, 65,446 (1980).
132. S. I. Mikhaleenko, Yu. B. Kuz'ma, *Poroshk. Metall.*, No. 2, 56 (1976); *Chem. Abstr.*, 84, 141,331 (1976).
133. G. F. Stepanchikova, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 10, 44 (1980); *Chem. Abstr.*, 94, 21,153 (1981).
134. N. S. Bilonizhko, Yu. B. Kuz'ma, L. D. Polyanskaya, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 16, 575 (1980); *Chem. Abstr.*, 93, 81,335 (1980).
135. Yu. B. Kuz'ma, M. P. Khaburskaya, *Inorg. Mater. (USSR)*, 11, 1893 (1973).
136. S. I. Mikhaleenko, Yu. B. Kuz'ma, A. S. Sobolev, *Poroshk. Metall. (Kiev)*, No. 1, 48 (1977); *Chem. Abstr.*, 86, 128,127 (1977).
137. D. T. Pitman, D. K. Das, *J. Electrochem. Soc.*, 107, 763 (1960).
138. Yu. B. Kuz'ma, G. F. Stepanchikova, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 10, 1905 (1974); *Chem. Abstr.*, 82, 132,183 (1975).
139. Yu. B. Kuz'ma, N. S. Bilonizhko, E. M. Nimkovich, *Dopov. Akad. Nauk Ukr. RSR., Ser. A*, 10, 939 (1973); *Chem. Abstr.*, 80, 20,383 (1974).

140. G. Hofer, H. H. Stadelmaier, *Metall.*, **19**, 1257 (1965).
141. R. I. Stearns, P. E. Greene, *J. Electrochem. Soc.*, **112**, 1239 (1965).
142. Yu. B. Kuz'ma, M. V. Chepiga, A. M. Plakhina, *Inorg. Mater. (USSR)* **2**, 1038 (1966); for liquidus projection see also G. Pradelli, *Atti Acad. Sci. Torino, Cl. Sci. Fiz., Mat. Nat.* **113**, 425 (1979); *Chem. Abstr.*, **94**, 215,285 (1981).
143. H. H. Stadelmaier, R. B. Fitts, *Metallwiss., Technik*, **16**, 773 (1962).
144. H. H. Stadelmaier, J. D. Schöbel, L. T. Jordan, *Metallwiss., Technik*, **16**, 752 (1962).
145. H. H. Stadelmaier, J. D. Schöbel, R. E. Burgess, *Metallwiss., Technik*, **17**, 781 (1963).
146. J. D. Schöbel, H. H. Stadelmaier, R. T. Smith, *Metallwiss., Technik*, **25**, 10 (1971).
147. M. A. Marko, *Visn. L'viv. Un-tu, Ser. Khim.*, No. 19, 59 (1977); *Chem. Abstr.*, **88**, 159,307 (1978).
148. T. Kato, S. Hirano, M. Yoshimura, S. Somiya, *Yogyo Kyokai Shi*, **88**, 346 (1980).
149. H. H. Stadelmaier, L. T. Jordan, *Z. Metallkd.*, **53**, 719 (1962).
150. P. Rogl, H. Klesnar, P. Fischer, B. Chevalier, B. Buffat, G. Demareau, J. Etourneau, *J. Mater. Sci. Lett.*, **7**, 1229 (1988).
151. A. Wittmann, H. Nowotny, H. Boller, *Monatsh. Chem.* **91**, 608 (1960).
152. K. Schubert, *Chem. Scr.*, **12**, 109 (1977).
153. K. E. Spear, P. K. Liao, J. F. Smith, *Bull. Alloy. Phase Diagr.*, **8**, 447 (1987).
154. K. Hack, T. Chart, paper presented at the IX CALPHAD Meeting Montreal, Canada, May 1980.
155. K. E. Spear, J. H. Blanks, M. S. Wang, *J. Less-Common Met.*, **82**, 237 (1981).
156. L. R. Bidwell, *J. Less-Common Met.*, **20**, 19 (1970).
157. P. Rogl, H. Haines, P. E. Potter, *Bull. Alloy Phase Diagr.*, In press (1990).
158. Y. Khan, E. Kneller, M. Sostarich, *Z. Metallkd.*, **73**, 625 (1982).
159. E. Storms, B. Müller, *J. Phys. Chem.*, **81**, 318 (1977).
160. V. I. Bakarinova, E. M. Savitskii, B. G. Arabei, S. E. Salibekov, *Inorg. Mater. (USSR)*, **6**, 2071 (1970).
161. N. F. Chaban, *Sov. Powder Metall. Met. Ceram.*, **229**, 61 (1982); *Chem. Abstr.*, **96**, 130,566 (1982).
162. Yu. B. Kuz'ma, N. S. Bilonizhko, N. F. Chaban, S. V. Chernjak, *J. Less-Common Met.*, **90**, 217 (1983).
163. N. S. Bilonizhko, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **19**, 487 (1983); *Chem. Abstr.*, **99**, 28,714 (1983).
164. N. S. Bilonizhko, B. I. Krik, Yu. B. Kuz'ma, *Dopov. Akad. Nauk, Ukr. RSR, Ser. B*, **4**, 21 (1982); *Chem. Abstr.*, **97**, 45,146 (1982).
165. G. F. Stepanchikova, *Visn. L'viv. Politekh. Inst.*, **130**, 58 (1979); *Chem. Abstr.*, **92**, 100,176 (1980).
166. G. F. Stepanchikova, Yu. B. Kuz'ma, *Vestn., L'viv., Ser. Khim.*, No. 23, 48 (1981); *Chem. Abstr.*, **95**, 68,813 (1981).
167. S. I. Mikhaleiko, Yu. B. Kuz'ma, O. K. Tschir, *Poroshk. Metall. (Kiev)*, No. 9, 50 (1982); *Chem. Abstr.*, **98**, 112,030 (1983).
168. P. Rogl, *Proc. 11th Plansee Seminar, Reuilt/Tigne*, Vol. 2, 1985, p. 1029.
169. T. Endo, O. Fukunga, M. Iwata, *J. Mater. Sci.*, **14**, 1676 (1979).
170. T. Endo, O. Fukunga, M. Iwata, *J. Mater. Sci.*, **16**, 2227 (1981).
171. L. Kaufman, B. Uhrenius, D. Birnie, K. Taylor, paper presented at the XII CALPHAD Meeting, Liege, Belgium, 29 Aug.–2 Sept., 1983.
172. Private Communication.
173. Private Communication.
174. E. Parthé, B. Chabot, in *Handbook on the Physics and Chemistry of the Rare Earths*, Vol. 6, Ch. 48, K. A. Gschneidner Jr., L. Eyring, eds., North Holland, Amsterdam, 1983, p. 113.
175. P. Rogl, in *Handbook on the Physics and Chemistry of the Rare Earths*, Vol. 6, Ch. 49, K. A. Gschneidner Jr., L. Eyring, eds., North Holland, Amsterdam, 1983, p. 335–523.
176. Yu. B. Kuz'ma, N. F. Chaban, O. S. Vityuk, *Poroshk. Metall. (Kiev)*, No. 9, 101 (1979); *Chem. Abstr.*, **91**, 199,675 (1979).
177. H. Klesnar, Thesis, University of Vienna, 1989.
178. I. Smid, P. Rogl, F. Weitzer, *Proceedings, 12th Plansee Seminar*, Vol. 2, H. Bildstein, H. Ortner eds., Tyrolia, Innsbruck, 1989, p. 577.
179. C. Horvath, P. Rogl, research at the University of Vienna, to be published.

180. O. N. Il'yut'skaya, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 4, 64 (1986); *Chem. Abstr.*, 104, 214,059 (1986).
181. O. N. Il'yut'skaya, *Vestn. Univ. Lvov., Ser. Khim.*, 25, 37 (1984).
182. Yu. B. Kuz'ma, I. P. Zhaharyuk, L. T. Maksymova, *Poroshk. Metall. (Kiev)*, No. 9, 70 (1988); *Chem. Abstr.*, 109, 238,170 (1988).
183. S. I. Mikhaleenko, L. P. Gymenna, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 12, 73 (1983); *Chem. Abstr.*, 100, 55,690 (1984).
184. Y. C. Chuang, C. H. Wu, F. H. Wang, *J. Less-Commons Met.*, 135, 5 (1987); see also N. S. Bilonizhko, L. V. Leshko, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 21, 1568 (1985).
185. N. S. Bilonizhko, M. F. Fedyna, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 21, 130 (1985).
186. O. M. Dub, N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 7, 994 (1985).
187. O. M. Dub, Yu. B. Kuz'ma, M. I. David, *Poroshk. Metall. (Kiev)*, No. 7, 56 (1987); *Chem. Abstr.*, 107, 184,586 (1987).
188. O. M. Dub, N. F. Chaban, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 10, 82 (1988); *Chem. Abstr.*, 110, 64,534 (1989).
189. G. V. Chernyak, N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 19, 1554 (1983).
190. G. V. Chernyak, N. F. Chaban, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 6, 65 (1983); *Chem. Abstr.*, 99, 94,462 (1983).
191. N. F. Chaban, V. I. Datsina, *Poroshk. Metall. (Kiev)*, No. 1, 62 (1986).
192. O. M. Dub, Ya. M. Shostak, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 24, 1270 (1988).
193. K. Remschnig, P. Rogl, *Proceedings, 12th Int. Plansee Seminar*, Vol. 2, H. Bildstein, H. Ortner, eds., Tyrolia, Innsbruck, 1989, p. 599.
194. P. Rogl, P. E. Potter, H. Haines, to be published.
195. H. Klesnar, P. Rogl, to be published, see also H. Klesnar, thesis, University of Vienna 1989.
196. I. P. Valyovka, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 5, 98 (1984); *Chem. Abstr.*, 101, 95,875 (1984).
197. I. P. Valyovka, Yu. B. Kuz'ma, *Sov. Powder Metall. Met. Ceram.*, 288(12), 986 (1981).
198. I. P. Valyovka, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 8, 71 (1981); *Chem. Abstr.*, 97, 116,152 (1982).
199. I. P. Valyovka, Yu. B. Kuz'ma, *Sov. Powder Metall. Met. Ceram.*, 288(12), 186 (1986).
200. P. Rogl, C. Horvath, *J. Solid State Chem.*, to be published.
201. P. Rogl, *Proceedings of a NATO-workshop*, Manchester, U.K., Sept. 1989.
202. P. Rogl, *J. Less-Common Met.*, 110, 283 (1985).
203. P. Rogl, in *Handbook on the Physics and Chemistry of the Actinides*, Vol. 6, C. Keller, ed., North Holland, Amsterdam, 1990.
204. B. Rupp, A. Resnik, D. Shaltiel, P. Rogl, *J. Mater. Sci.*, 23, 2133 (1988).
205. J. Bauer, *Proc. 8th Int. Conf. Solid Compounds of Transition Elements*, Extended Abstracts P2A1, Vienna, April 1985.
206. J. Bauer, B. Vennegués, J. L. Vergneau, *J. Less-Common Met.*, 110, 295 (1985).
207. F. Bonhomme, P. Gosselin, D. Ansel, J. Bauer, *Etude Crystallochimique du Systeme Cerium-Bore-Carbure* (in French), Projet de fin d'études 5^{ém}, G.P. INSA, Rennes, June 1988.
208. Yu. B. Kuz'ma, N. S. Bilonizhko, S. I. Mikhaleenko, G. F. Stepanchikova, N. F. Chaban, *J. Less-Common Met.*, 67, 51 (1979).
209. Yu. B. Kuz'ma, *Crystal Chemistry of Borides*, Nysha Schola, L'viv, 1983.

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180. O. N. Iljutskaya, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 4, 64 (1986); *Chem. Abstr.*, 104, 214,059 (1986).
181. O. N. Iljutskaya, *Vestn. Univ. Lvov., Ser. Khim.*, 25, 37 (1984).
182. Yu. B. Kuz'ma, I. P. Zhaharyuk, L. T. Maksymova, *Poroshk. Metall. (Kiev)*, No. 9, 70 (1988); *Chem. Abstr.*, 109, 238,170 (1988).
183. S. I. Mikhaleenko, L. P. Gymenna, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 12, 73 (1983); *Chem. Abstr.*, 100, 55,690 (1984).
184. Y. C. Chuang, C. H. Wu, F. H. Wang, *J. Less-Commons Met.*, 135, 5 (1987); see also N. S. Bilonizhko, L. V. Leshko, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 21, 1568 (1985).
185. N. S. Bilonizhko, M. F. Fedyna, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 21, 130 (1985).
186. O. M. Dub, N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 7, 994 (1985).
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189. G. V. Chernyak, N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 19, 1554 (1983).
190. G. V. Chernyak, N. F. Chaban, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 6, 65 (1983); *Chem. Abstr.*, 99, 94,462 (1983).
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194. P. Rogl, P. E. Potter, H. Haines, to be published.
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197. I. P. Valyovka, Yu. B. Kuz'ma, *Sov. Powder Metall. Met. Ceram.*, 288(12), 986 (1981).
198. I. P. Valyovka, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 8, 71 (1981); *Chem. Abstr.*, 97, 116,152 (1982).
199. I. P. Valyovka, Yu. B. Kuz'ma, *Sov. Powder Metall. Met. Ceram.*, 288(12), 186 (1986).
200. P. Rogl, C. Horvath, *J. Solid State Chem.*, to be published.
201. P. Rogl, Proceedings of a NATO-workshop, Manchester, U.K., Sept. 1989.
202. P. Rogl, *J. Less-Common Met.*, 110, 283 (1985).
203. P. Rogl, in *Handbook on the Physics and Chemistry of the Actinides*, Vol. 6, C. Keller, ed., North Holland, Amsterdam, 1990.
204. B. Rupp, A. Resnik, D. Shaltiel, P. Rogl, *J. Mater. Sci.*, 23, 2133 (1988).
205. J. Bauer, *Proc. 8th Int. Conf. Solid Compounds of Transition Elements*, Extended Abstracts P2A1, Vienna, April 1985.
206. J. Bauer, B. Vennegués, J. L. Vergneau, *J. Less-Common Met.*, 110, 295 (1985).
207. F. Bonhomme, P. Gosselin, D. Ansel, J. Bauer, *Etude Crystallochimique du Systeme Cerium-Bore-Carbure* (in French), Projet de fin d'études 5^{ém}, G.P. INSA, Rennes, June 1988.
208. Yu. B. Kuz'ma, N. S. Bilonizhko, S. I. Mikhaleenko, G. F. Stepanchikova, N. F. Chaban, *J. Less-Common Met.*, 67, 51 (1979).
209. Yu. B. Kuz'ma, *Crystal Chemistry of Borides*, Nysha Schola, L'viv, 1983.

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TABLE 1. MODE OF FILLING THE VOIDS IN κ PHASES

Phase	Trigonal prismatic void in 2c ^a	Metal host lattice atoms in 12k + 6h(1) + 6h(2)	Icosahedral center in 2a	Octahedral void in 6g ^a
Mn ₃ Al ₁₀	□	Mn ₃ Al ₉	Al	□
Co ₂ Al ₅ (Co ₄ Al ₁₀)	Co	Co ₃ Al ₉	Al	□
W ₁₀ Co ₃ C _{3,4}	C _{0,42}	Co ₃ W ₉	W	C ₃
W _{9,6} Fe _{3,4} C _{3,5}	C _{0,54}	Fe _{3,12} W _{8,88}	Fe _{0,45} W _{0,55}	C ₃
(Mo, Al) ₉ (Cu, Al) ₄ C ₃	□	(Cu, Al) ₃ (Mo, Al) ₉	Al	C ₃
Ti ₉ Fe ₃ (Ti _{0,7} Fe _{0,3})O ₃	□	Fe ₃ Ti ₉	Ti _{0,7} + Fe _{0,3}	O ₃
Hf ₉ Mo ₄ B	B	Mo ₃ Hf ₉	Mo	□
Hf _{9,29} Mo _{3,71} P	P	Mo _{2,79} Hf _{9,21}	Mo _{0,92} Hf _{0,08}	□
Hf ₉ Mo ₄ Ni	Ni	Mo ₃ Hf ₉	Mo	□ ^b
Hf ₉ Mo ₄ O ₃	□	Mo ₃ Hf ₉	Mo	O ₃

^a □ = Unoccupied void, the space group is P6₃/mmc-No. 194; for representatives among borides see also §6.7.2.1.1, Table 2.

^b Contains oxygen impurities up to occ. = 0.2.

W_{6,7}Re_{13,3}B³, a β -Mn-type structure forms; in both cases a statistical distribution of metal atoms is described with an incomplete filling of the O_h interstices as compared to the ideal formula (T, Re)₅B₁.

Compounds isotypic with the κ phases are found among intermetallics, borides, carbides and oxides and also with silicides, germanides, arsenides, sulfides and selenides; no nitrides, however, are found. The mode of filling the various voids in the metal host lattice of the κ phases follows the scheme⁴ in Ref. 4 and is presented in Table 1 for all those compounds for which the atom distribution is well known from x-ray or neutron diffraction. Accordingly, B atoms in κ -borides⁴, Zr₉(Mo, W, Re)₄B and Hf₉(Mo, W, Re, Os)₄B⁴, occupy the trigonal prismatic interstices within the parent metal framework of a Mn₃Al₁₀-type structure (see Table 1; see also ref. 48). Extended solid solutions are found for (Hf, Al)₉(Mo, Al)₄B.

The Cr₂₃C₆ structure is widespread among metal-rich borides. Although numerous ternary borides form with this cubic structure⁵, no binary τ -Cr₂₃C₆ boride exists in thermodynamic equilibrium. As seen in directions [100], [010], [001], the crystal structure is an alternating sequence of metal clusters of cuboctahedra [M_{T13}] or [M_{T12}M_{T'}₁] (formed by metal atoms in sites 48h plus 4a) and cubes [M_{T8}] (atoms in site 32f), thus forming a superstructure related to Cu₃Au, [M_{T13}][M_{T8}][M_{T2}B₆] or [M_{T12}M_{T'}₁][M_{T8}][M_{T2}B₆]. Cluster formation as well as the high coordination number of the center points of the polyhedra (sites 8c, CN = 16) favors the larger M_{T'} metal atoms to occupy this site; the resulting formula is then M_{T21}M_{T2}B₆. For higher M_{T'} metal concentration M_{T20}M_{B3}B₆ the M_{T'} atoms additionally may occupy the center points of the cuboctahedra (site 4a, CN = 12).

The B atoms fill the center points (site 24e) of an antiprism formed by four metal atoms of site 32f and four metal atoms of site 48h. Usually no boron defects occur, but a still unsolved problem is where xs B would be accommodated in the structure

TABLE 2. STRUCTURE TYPES, BORON COORDINATION AND REPRESENTATIVES OF METAL BORIDES WITH ISOLATED B ATOMS (FILLED METAL HOST LATTICE COMPOUNDS)

Structure type space group	Boron coordination	Binary representatives	Ternary representatives	Refs.
Filled up β -Mn type ($\text{Mo}_3\text{Al}_2\text{C}$) P4_132 W_6Fe_7 (μ -phase) $\text{R}\bar{3}\text{m}$	Octahedron	—	$\text{Mo}_{\sim 4.5}\text{Re}_{\sim 15.5}\text{B}_{\sim 2.2}$ $\text{W}_{6,7}\text{Re}_{13,3}\text{B}$	20 3
$\text{Hf}_9\text{Mo}_4\text{B}$ $\text{P6}_3/\text{mmc}$	Complex	—	$\text{Hf}_{0.45}\text{Al}_{10.5}\text{B}_{0.05}$	1
	Trigonal prism Hf_6	—	$\text{Zr}_9\text{M}_{\text{Td}}\text{B}$: $\text{M}_{\text{T}} = \text{Mo}, \text{W}, \text{Re}$ $\text{Hf}_6\text{M}_{\text{Td}}\text{B}$: $\text{M}_{\text{T}} = \text{Mo}, \text{W}, \text{Re}, \text{Os}$ $\text{Hf}_{9-x}\text{Zr}_x\text{Mo}_4\text{B}$, $0 \leq x \leq 1$ (Hf, Al) $_9(\text{Mo}, \text{Al})_4\text{B}$ A. Ordered structure variants $\text{M}_{21}\text{M}'_2\text{B}_6$ or $\text{M}_{20}\text{M}'_3\text{B}_6$ (For details in composition see Fig. 1) $\text{M} = \text{Co}$: $\text{M}' = \text{Sc}, \text{U}, \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}^8, \text{Ta}^{51}, \text{Cr}, \text{Mo},$ $\text{W}, \text{Mg}, \text{Al}, \text{Ga}, \text{In}, \text{Ge}, \text{Sn}, \text{Sb}$ $\text{M} = \text{Ni}$: $\text{M}' = \text{Sc}, \text{Ce}^{22}, \text{Er}^5, \text{Tm}^5, \text{Yb}^5, \text{Lu}^5, \text{U}, \text{Ti}, \text{Zr},$ $\text{Hf}, \text{V}, \text{Nb}, \text{Ta}, \text{Li}^6, \text{Mg}, \text{Ca}^5,$ $\text{Zn}, \text{Al}, \text{Ga}, \text{In}, \text{Ge}, \text{Sn}, \text{Sb}$ B. Structure variants with an extended statistical distribution or with partial ordering $\text{M}_{23-x}\text{M}'_xB_6$: $\text{M}' = \text{Mn}, \text{M} = \text{Co}$ $x = 3-11.5, 800^\circ\text{C}$; $x = 2-11, 850^\circ\text{C}$	2, 4 2, 4 2 2 5, 7
Cr_{23}C_6 $\text{Fm}\bar{3}\text{m}$	Antiprism	$\text{Fe}_{23}\text{B}_6, \text{Co}_{23}\text{B}_6$ (metastable, Ref. 17)		21 12

Ni ($x = 2-8$, 800°C, Fig. 1)	5
Fe ($x = 5.6-13.8$, 850°C)	15
M' = Re, M = Mn ($x = 4.5-14.6$, 800°C)	40
Fe ($x = 7-20$, 1100°C)	23
Co ($x = 11.5-17.4$, 1300°C)	41
x = 1.5-17.4, 1000°C)	42
Ni ($x = 11.5-13$, 800°C)	5
M' = Fe, M = Ni ($x = 2.9$, metastable)	7
M' = Ir, M = Cr, Mn, Co (M:M' ratio ≈ 2), Fe ($x = 7.6-13$, 950°C)	8
M' = Ru, M = Nb, Ta ($x = 19-21$, 1100°C, part of M atoms preferentially in site 4a)	12
Co ₂₁ (M _{1-x} M' _x) ₂ B ₆ ; M = Mn, M' = Mo ($x = 0-1$, 900°C)	48
Ni ₂₁ (M _{1-x} M' _x) ₂ B ₆ ; M = Ti, M' = Al ($x = 0-1$, 800°C)	48
M = Zr, M' = Sn ($x = 0-1$, 800°C)	48
M = V, M' = Nb ($x = 0-1$, 800°C)	48
M = V, M' = Ta ($x = 0-1$, 800°C)	45
Ni _{20.7-x} Cr _x Ta _{2.3} B ₆ ; $x = 0-0.6$, 850°C	48
Ni _{20.4-x} Co _x V _{2.6} B ₆ ; $x = 0-20.4$, 800°C	49
Ni _{20-x} Fe _x Al ₃ B ₆ ; $x = 0 \sim 4$, 800°C	49
Ni _{20-x} Co _x Al ₃ B ₆ ; $x = 0-20$, 800°C	50
Ni _{21.2-x} Co _x Sn _{1.8} B ₆ ; $x = 0-21.2$, 800-900°C	49
Co _{20-x} Fe _x Al ₃ B ₆ ; $x = 0 \sim 8$, 800°C	
M ₂₃ (B _{1-y} C _y) ₆ ; M = Cr ($y = 1-0.7$, 1450°C)	
M = Mn ($y = 1-0.31$, 850°C; y = 0.9-0.6, 1000°C)	

(continued)

TABLE 2. (continued)

Structure type space group	Boron coordination	Binary representatives	Ternary representatives	Refs.
			$M = Fe$ [$y = 0.4-0.73$, $700^{\circ}C$; $y = 0.38-0.77$, $800^{\circ}C$; $965^{\circ}C: Fe_{23}B_3C_3 \rightarrow Fe_3(B, C) + \gamma-Fe$] $M = Co$ ($y = 0.33$, $1300^{\circ}C$) $(M_{1-x}M')_{23}(B_{1-y}C_y)_6$: $M = Cr, M' = Fe, x = 0-1$: $y = 0.75$, $800^{\circ}C$ $x = 0.76-1$; $y = 0.5$, $800^{\circ}C$ $x = 0.83-1$; $y = 0.4$, $800^{\circ}C$ $M' = Co, y = 0.6$: $x = 0.1-0.35$; $y = 0.7$: $x = 0-0.35$; $y = 0.8$: $x = 0-0.33$; $y = 0.9$: $x = 0-0.27$; $x = 0.1$: $y = 1-0.6$; $x = 0.2$: $y = 1-0.58$; $x = 0.3$: $y = 0.85-0.58$; all data at $1000^{\circ}C$ $M = Mn, M' = Fe, x = 0.75$; $y = 0-0.37$ $x = 0.50$; $y = 0-0.95$ $x = 0.25$; $y = 0-1$ $y = 0.0$; $x = 0.2-0.6$ $y = 0.4$; $x = 0-1$ $y = 0.75$; $x = 0-1$ $y = 1.0$; $x = 0-0.30$ all data at $850^{\circ}C$ $M = Mn, M' = Co$, $y = 0.1$: $x = 0.4-0.9$; $y = 0.2$: $x = 0.2-0.85$;	9, 10-15 25 12 46 43

Cu_3Au , filled $\text{Pm}\bar{3}\text{m}$	O_h			
			$y = 0.35$; $x = 0-0.08$; $y = 0.5$; $x = 0-0.7$; $y = 0.7$; $x = 0-0.5$; $y = 0.9$; $x = 0-0.2$; at 850°C	12
			$x = 0.2$; $y = 0.2-0.9$; $x = 0.4$; $y = 0.1-0.8$ $x = 0.6$; $y = 0-0.6$; $x = 0.8$; $y = 0-0.3$; at 850°C	12
			$\text{M} = \text{Fe}$, $\text{M}' = \text{Co}$ isothermal section at 1027°C of the double-pseudobinary section $\text{Fe}_3\text{C}-\text{Fe}_3\text{B}-\text{Co}_3\text{B}-\text{Co}_3\text{C}$	44
			$(\text{M}, \text{M}', \text{M}'')_{23}(\text{B}_{1-y}\text{C})_6$; $\text{M}, \text{M}', \text{M}'' = \text{Cr}, \text{Mn}, \text{Fe}$ (partial pseudoternary section at 1000°C , $y = 0.5$)	9 5 18
			$\text{Ni}_3\text{InB}_{0.5}$ $\text{Sc}_3\text{MB}_{1-x}$; $\text{M} = \text{In}, \text{Ti}, \text{Sn}, \text{Pb}$ $\text{AnRu}_3\text{B}_{1-x}$; $\text{An} = \text{Th}$ ($x = 0.1$), U ($x = \sim 0.25$) (at 1300°C)	27
			$\text{M}_{\text{RE}}\text{Rh}_3\text{B}_{1-x}$; Sc ($x = 0-1$, 1300°C), Y ($x = 0-0.55$, 1400°C), La (0.2), Ce (0.45), Pr (0.25), Nd (0.1), Sm (0.2), Eu (0.1), Gd (0.15), Tb (0.1), Dy (0.1), Ho (0.05), Er (0.02), Tm (0.02), Yb (0.15), Lu (0.2) (values in parentheses indicate size of x at 1300°C ; see also Fig. 2a), $\text{CeRh}_{2.86}\text{B}_{0.90}$ ⁵⁴ ; see also ref. 56	17, 19
			$\text{ErRh}_{3-x}\text{M}_{\text{Tx}}\text{B}_{1-y}$; $\text{M}_{\text{T}} = \text{Pd}$ ($x = 1.2, 1.8, 2.4, \text{d11}$) $\text{M}_{\text{T}} = \text{Pt}$ ($x = 0, 0.6, 1.2, 1.8, 2.4, 1$) To each value of x a value of y was determined via the lattice parameters	57 57
			$\text{M}_{\text{T}}\text{Rh}_3\text{B}_{1-x}$; $\text{M}_{\text{T}} = \text{Zr}$ ($x = 0-1.0$), Hf ($x = 0.22-1.0$) (at 1100°C) Th ($x = 0$) ⁵⁴	17

(continued)

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Structure type space group	Boron coordination	Binary representatives	Ternary representatives	Refs.
Mn_5Si_3 $P6_3/mcm$	O_h	—	$M_{RE}Pd_3B_{1-x}$: La, Ce, Pr, Nd, Sm, Eu ⁴¹ , Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu (for details of boron filling see text and Fig. 2b)	38
			$M_TIr_3B_{1-x}$: $M_T = Sc$	18
			$M_T = Zr$ ($x = 0.5-1.0$), Hf ($x = 0.55-1.0$) (at 1100°C)	17
			$V_5Si_3B_{\sim 0.45}$, Nb_5Si_3B , Ta_5Si_3B , Cr_5Si_3B , $V_5Ge_3B^a$, Nb_5Ge_3B , Ta_5Ge_3B ,	28 37
			Zr_5Al_3B , Hf_5Al_3B , Ta_5Al_3B , Ng , Ga_3B , Ta_5Ga_3B	26, 29
W_5Si_3 $I4/mcm$	Icosahedron	—	$M_{RE}Si_3B_x$, $M_{RE}^b = Nd, Gd, Tb, Dy$	30
			$M_{RE}Si_3B_x$, $M_{RE}^b = La, Gd, Tb, Dy$	30
			$Fe_{\sim 4.8}Si_2B$, $Co_{\sim 4.6}Si_2B$	
			$Ni_{4.29}Si_2B_{1.43}$	29, 31, 34
			$Cr_{\sim 4.5}P_2B$	35

^a V_5Ge_3B is the end member of a homogeneous solid solution³⁸ $V_5Ge_3B_x$ ($0 \leq x \leq 1$, 700°C) starting from binary V_5Ge_3 .
^b In some cases values of $x \approx 2$ have been reported; however, additional $Si(Ge)-B$ substitution may account for the higher B content with respect to a filled-up composition of $RE_5Si_3B_1$.

Co _{23-x} T _x B ₆										Mg	Al			
Sc	Ti 25-35	V 19-30	Cr 2	Mn 29-116							Ga 2	Ge 1.45		
	Zr 203	Nb 175-255	Mo 125-145								In 0.75	Sn 1.9-203	Sb 1.16-16	
	Hf 13-175	Ta 175-19	W 13-145	Re 15-174					Ir 15					
U														

Ni _{23-x} T _x B ₆										Mg	Al			
Li 3	Sc	Ti 25-30	V 23-276		Mn 2-81	Fe* 2.9				Zn 2.9-3.78	Ga 1.9-3.48	Ge* 1.45		
Ca* 203		Zr 203-276	Nb 218-26								In 1.3-2.3	Sn 1.74-197	Sb 1.9-203	
	RE	Hf 218-276	Ta 218-232		Re ~115-13									
U														

RE = Ce, Ho, Er, Tm, Yb, Lu
* = metastable

Figure 1. Formation of borides $\text{Co}_{23-x}\text{M}_x\text{B}_6$ and $\text{Ni}_{23-x}\text{M}_x\text{B}_6$; the numbers given reveal the homogeneous range and M_T -metal content in at% at $\sim 800^\circ\text{C}$ ^{5,48,50}.

for those combinations with higher boron contents. One of these examples is the stabilization of a $\text{Ni}-\tau$ boride by traces of Ca; B may substitute for Ni atoms⁵⁰, but B may also fill the centers of the 32f metal cubes⁵, thereby accounting for a formula of $\text{M}_{\text{T}23}\text{B}_7$.

As seen from Table 2 and Fig. 1, many M'_T main-group elements act as stabilizers, e.g., Li, Mg, Al, Zn, Ga, Ge, with a constantly decreasing M'_T content, when the M'_T group number is increased^{49,50}. A rather similar behavior applies for the electropositive M'_T transition metals. The similarity is demonstrated by exchange of comparable main-group and transition-element M_T stabilizers (Table 2)^{49,50}.

With decreasing differences in electronegativity and size, the M_T and M'_T metals tend toward a statistical distribution in a formula $(\text{M}_T, \text{M}'_T)_{23}\text{B}_6$. Thus a second group of τ -borides is formed with a ratio $\text{M}_T/\text{M}'_T \approx 1-2$, displaying extended homogeneous regions such as $(\text{Re}, \text{M}_T)_{23}\text{B}_6$ ($\text{M}_T = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) and $(\text{Ir}, \text{M}_T)_{23}\text{B}_6$ ($\text{M}_T = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$); occasionally, a partial ordering may occur, as in $\text{Re}_7\text{Fe}_{16}\text{B}_6$ (Re atoms preferentially⁵ in 8c), and $\text{Nb}_3\text{Ru}_{20}\text{B}_6$ (Nb atoms preferentially⁸ in 4a).

Solution behavior and phase equilibria are published for ternary and higher order τ phases and for the mixed interstitial τ -carbaborides (borocarbides) with extended substitution on both the metal and nonmetal sublattices: $\text{M}_{\text{T}23-x}\text{M}'_{\text{T}x}\text{B}_6$, $(\text{M}_{\text{T}21-x}\text{M}'_{\text{T}x})\text{M}''_{\text{T}2}\text{B}_6$, $\text{M}_{\text{T}21}(\text{M}_{\text{T}1-x}\text{M}'_{\text{T}x})_2\text{B}_6$, $\text{M}_{\text{T}23}(\text{B}_{1-y}\text{C}_y)_6$, $(\text{M}_{\text{T}1-x}\text{M}'_{\text{T}x})_{23}(\text{B}_{1-y}\text{C}_y)_6$ and the quinary section $(\text{Cr}, \text{Mn}, \text{Fe})_{23}(\text{B}, \text{C})_6$; for details in composition see Table 2 and references therein.

From the occurrence of minima or a change of the slope in the lattice parameters of some of the borocarbide solid solutions, metal atom ordering can be suggested^{12,13,44,47} e.g., for $(\text{Fe}_{1-x}\text{Cr}_x)_{23}(\text{B}_{0.25}\text{C}_{0.75})_6$, $(\text{Fe}_{1-x}\text{Mn}_x)_{23}(\text{B}_{0.25}\text{C}_{0.75})_6$ and $(\text{Co}_{1-x}\text{Mn}_x)_{23}(\text{B}_{0.8}\text{C}_{0.2})_6$. Based on the phase equilibria and lattice parameter variations of the extended homogeneous solutions, the lattice parameters of each of the hypothetical binary borides $\text{M}_{\text{T}23}\text{B}_6$ with $\text{M}_T = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$, as well as their thermodynamic free energies of formation can be derived⁹. For Fe_{23}B_6 , instability by an amount as low as 2500 Jg-at^{-1} metal⁹ with respect to neighboring equilibrium

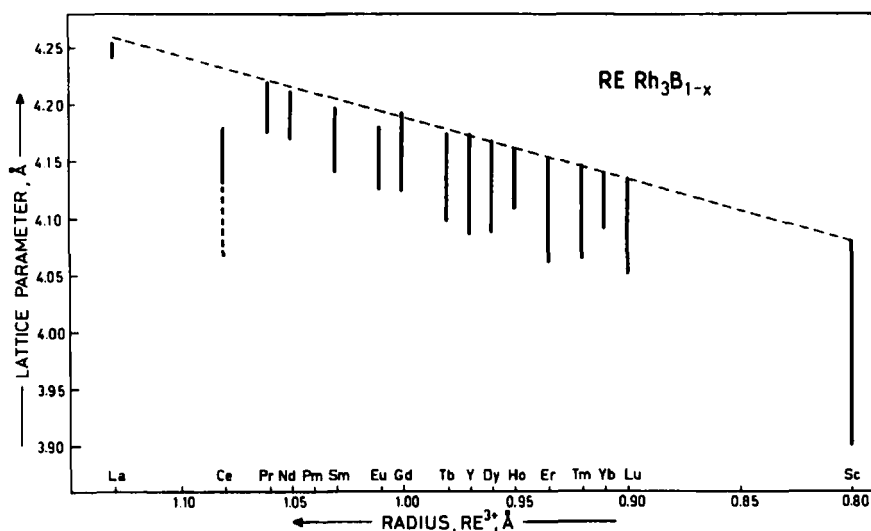


Figure 2. (a) Formation and lattice parameters of perovskite borides $M_{RE}Rh_3B_x$ versus rare-earth radius; values at $1300^\circ C$ ^{19,29}.

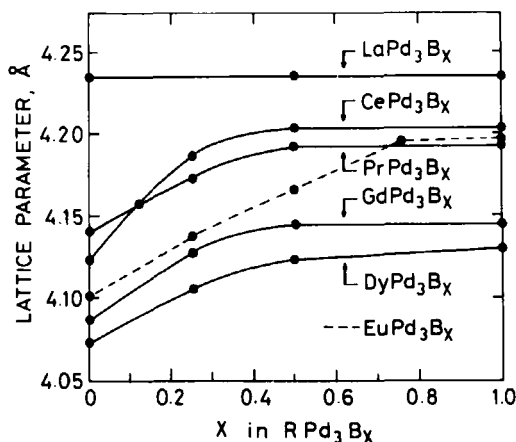


Figure 2. (b) Formation and lattice parameters of perovskite borides $M_{RE}Pd_3B_x$. B content; from as-cast alloys^{40,41}, $M_{RE} = La, Ce, Pr, Eu, Gd, Dy$.

phases explains why $Fe_{23}B_6$ is easily obtained from nonequilibrium, splat-cooled surfaces¹⁶. The combined properties of high mechanical hardness and magnetically soft behavior of some complex τ phases, such as $Fe_4Co_{16}Al_3B_6$ or $(Co, Fe, Al, Ti)_{23}B_6$, led to their application as magnetic-head assemblies (Borocube⁵⁰).

The τ - and perovskite borides resemble each other (Cu_3Au parent lattice) (see above). The boron environment in the latter is O_h , whereas most interstitial borides

prefer the trigonal prismatic metal surrounding⁸. Nevertheless, two branches of perovskite borides exist, $M_{T_3}M'_TB$ and $M_TM'_T_3B$, such as $Ni_3InB_{0.5}$, $Sc_3(Pb, Sn)B_{1-x}$ or $Zr(Rh, Ir)_3B$; the latter is derived by simply filling the voids of the binary metal host lattice^{5,17,18}, whereas for $YRh_3B_{0.45-1.0}$ no binary $YRh_3(Cu_3Au \text{ type})$ phase exists¹⁹. Small boron deficiencies are observed from alloys $M_{RE}Rh_3B_{1-x}$ and $M_{RE}Pd_3B_{1-x}$ (M_{RE} = rare earth element) as is seen from the lattice parameter variation vs. boron content in Fig. 2a, b.

From a detailed analysis of the stability regions in the alloy series $M_{RE}Rh_3B_{1-y}$ and $Er(Rh_{1-x}M_x)_3B_{1-y}$ the formation of the perovskite structure was discussed^{57,58} in terms of a stabilizing charge transfer (B as electron donor) and a corresponding characteristic VEC, $31 \leq VEC \leq 34$.

The stabilizing influence of B atoms in O_h sites is well known from $M_{T_5}M'_T_3B_x$ borides (Mn_5Si_3 type), e.g., in the formation of boride interstitials by filling metal host lattices that develop from $M_{T_5}M'_T_3$ binaries. Boron occupancy (octahedral metal coordination) is incomplete ($x < 1$), but some alloys $M_{RE5}Ge(Si)_3B_x$ have higher boron contents³⁰ up to $x \sim 2$ (Table 1). In these cases, however, the boron solubility may also be accompanied by a simultaneous substitution of $Ge(Si)/B$, which also explains the irregular variation of the lattice parameters.

Silico- and phosphorus borides crystallizing with ordered W_5Si_3 -type structures, such as $Ni_{4.6}Si_2B$ and $Cr_{\sim 4.5}P_2B$, are closely related structurally³¹⁻³⁵.

Because of the tendency to form B—B bonds, further substitution in the direction of a higher B : P ratio results in boron-pair formation, even if the total boron content is as low as in Cr_5PB_2 (ordered Cr_5B_3 -type structure; see also §6.7.2.2).

(P. ROGL)

1. W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **95**, 1417 (1964).
2. Yu. B. Kuz'ma, B. I. Stadnyk, V. I. Lach, V. S. Telegus, N. N. Borbulevich, *Izv. Vyssh. Ucheb. Zaved. Tsvet. Met.*, **13**, 160, (1970); *Chem. Abstr.*, **73**, 81,228 (1970).
3. Yu. B. Kuz'ma, V. I. Lach, B. I. Stadnyk, Yu. V. Voroshilov, *Porosh. Met.*, No. 8, 462 (1968); *Chem. Abstr.*, **69**, 70,401 (1968).
4. P. Rogl, H. Nowotny, *Monatsh. Chem.*, **104**, 1497 (1973).
5. H. H. Stadelmaier, in *Developments in the Structural Chemistry of Alloy Phases*, B. C. Giessen, ed., Plenum Press, New York, 1969, p. 141; see also L. T. Jordan, R. K. Mathur, K. R. Brose, H. H. Stadelmaier, *Z. Metallkd.*, **72**, 782 (1981).
6. N. F. Chaban, Yu. B. Kuz'ma, P. V. Kotovska, *Dopov. Akad. Nauk. Ukr. RSR, Ser. A*, **6**, 88 (1980); *Chem. Abstr.*, **93**, 142,120 (1980).
7. W. Jung, *Naturwissenschaften*, **63**, 246 (1976).
8. H. Nowotny, P. Rogl, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 411; see also *Monatsh. Chem.*, **104**, 1325 (1973).
9. W. Steurer, P. Rogl, H. Nowotny, *Monatsh. Chem.*, **110**, 791 (1979).
10. P. Rogl, J. C. Schuster, H. Nowotny, in *Boron Steel, Proceedings of Int. Symp.*, 1980, p. 33.
11. M. L. Borlera, G. Pradelli, *Metall. Ital.*, **59**, 907 (1967).
12. M. L. Borlera, G. Pradelli, *Atti Accad. Naz. Lincei, Mem., Classe Sci. Fis., Mat. Nat.*, Sez. **2a**, **10**, 68 (1971).
13. G. Pradelli, C. Gianoglio, E. Quadrini, *Metall. Ital.*, **69**, 64, 487 (1977); *Atti Accad. Sci. Torino, Classe Sci. Fis., Mat. Nat.*, **113**, 293 (1979).
14. M. L. Borlera, G. Pradelli, *Metall. Ital.*, **63**, 107 (1971).
15. G. Pradelli, C. Gianoglio, *Metall. Ital.*, **1**, 21 (1975).
16. G. Pradelli, C. Gianoglio, *Metall. Ital.*, **1**, 19 (1976).
17. U. Herold, U. Köster, *Z. Metallkd.*, **69**, 326 (1978).
18. P. Rogl, H. Nowotny, *J. Less-Common Met.*, **67**, 41 (1979).
19. H. Holleck, *J. Less-Common Met.*, **52**, 167 (1977).
20. P. Rogl, L. Delong, *J. Less-Common Met.*, **91**, 97 (1983).

21. P. Rogl, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **104**, 182 (1973); **102**, 971 (1971).
22. Yu. B. Kuz'ma, M. V. Chepiga, A. M. Plakhina, *Inorg. Mater. (USSR)*, **2**, 1038 (1966).
23. Yu. B. Kuz'ma, N. S. Bilonishko, *Izv. Akad. Nauk. SSSR, Neorg. Mater.*, **7**, 542 (1971); *Chem. Abstr.*, **74**, 147,080 (1971).
24. E. Ganglbberger, H. Nowotny, *Monatsh. Chem.*, **96**, 1144 (1965); **97**, 101, 718 (1966).
25. P. Rogl, H. Nowotny, *Monatsh. Chem.*, **108**, 1167 (1977).
26. L. Ya. Markovskii, E. T. Bezruk, G. E. Berlova, *Inorg. Mater. (USSR)*, **7**, 50 (1971).
27. H. Holleck, W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **95**, 552 (1964).
28. H. Holleck, *AED-Conf. 73-128-015*, Zentralst. f. Atomkern-energie-Dokumentation, Eggstein, Ludwigshafen, 1973.
29. B. Aronsson, *Acta Chem. Scand.*, **14**, 1403, 1414 (1960); **13**, 433 (1959).
30. W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **96**, 844 (1965).
31. I. Mayer, I. Felner, *J. Less Common Met.*, **37**, 171 (1974).
32. N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **6**, 883 (1970); *Chem. Abstr.*, **73**, 59,645 (1970).
33. N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **8**, 933 (1972); *Chem. Abstr.*, **77**, 67,160 (1972).
34. N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **9**, 1886 (1973); *Chem. Abstr.*, **80**, 125,393 (1974).
35. E. Lugscheider, H. Reimann, O. Knotek, *Monatsh. Chem.*, **106**, 1155 (1975).
36. H. E. Baurecht, H. Boller, H. Nowotny, *Monatsh. Chem.*, **102**, 373 (1971).
37. M. A. Marko, *Visn. L'viv. Derzh. Univ., Ser. Khim.*, No. 17, 26 (1975); *Chem. Abstr.*, **87**, 27,177 (1977).
38. M. A. Marko, Yu. B. Kuz'ma, E. I. Gladyshevskij, *Dopov. Akad. Nauk, RSR, Ser. A*, **6**, 555 (1976); *Chem. Abstr.*, **86**, 46,295 (1977).
39. S. K. Dhar, S. K. Malik, R. Vijayaraghavan, *Mater. Res. Bull.* **16**, 1557 (1981).
40. S. K. Dhar, S. K. Malik, D. Rambabu, R. Vijayaraghavan, *J. Appl. Phys.* **53**, 8077 (1982).
41. V. S. Telegus, Yu. B. Kuz'ma, *Dopov. Akad. Nauk. Ukr. RSR, Ser. A*, **31**, 945 (1969); *Chem. Abstr.*, **72**, 26,053 (1970).
42. M. V. Chepiga, Yu. B. Kuz'ma, *Isv. Akad. Nauk SSSR Neorg. Mater.*, **9**, 1688 (1973); *Chem. Abstr.*, **80**, 31,242 (1974).
43. M. V. Chepiga, *Vestn. L'vov. Un-ta, Ser. Khim.*, **14**, 27 (1972).
44. G. Pradelli, C. Gianoglio, *Atti Accad. Naz. Lincei, Rend. Classe Sci. Fis., Mat. Nat., Ser. VIII*, **57**, 655 (1974).
45. C. Gianoglio, G. Pradelli, *Metall. Ital.*, **75**, 282 (1983).
46. E. Lugscheider, H. Reimann, R. Pankert, *Z. Metallkd.*, **71**, 654 (1980).
47. G. Pradelli, C. Gianoglio, E. Quadrini, *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat.*, **113**, 293 (1979).
48. A. Hårsta, E. Wennebo, *Acta Chem. Scand., Ser. A*, **35**, 227 (1981); **36**, 547 (1982); **35**, 43 (1981); **36**, 535 (1982).
49. H. H. Stadelmaier, J. B. Ballance, *Z. Metallkd.*, **58**, 449 (1967).
50. H. Hirota, *J. Phys. Soc. Jpn.*, **23**, 512 (1967); see also H. Hirota, Y. Tawara, Y. Kamatzu, *Jpn. J. Appl. Phys.*, **8**, 962 (1969).
51. L. T. Jordan, R. K. Mathur, K. R. Brose, H. H. Stadelmaier, *Z. Metallkd.*, **72**, 782 (1981).
52. H. H. Stadelmaier, H. H. Davis, H. K. Manaktala, E. T. Henig, *Z. Metallkd.*, **80**, 371 (1989).
53. I. S. Yvich, N. F. Chaban, *Abstracts, Conference on the Crystal Chemistry of Intermetallic Compounds, Tersizy. Dokl., L'vov, October 1989*, p. 46.
54. Z. Zolnievek, D. Kacrorowski, *J. Magn. Magn. Mater.*, **63-64**, 178 (1987).
55. T. Higashi, T. Lundström, *J. Less-Common Met.*, **120**, L7 (1986).
56. H. Takeya, T. Shishido, H. Takai, *J. Less-Common Met.*, **134**, 263 (1987).
57. H. Takai, T. Shishido, *J. Less-Common Met.*, **97**, 223 (1984).

6.7.2.1.2. Substitutional Metal Borides.

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6.7.2. Existence and Crystal Chemistry of Borides

6.7.2.1. Borides with Isolated Boron Atoms

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21. P. Rogl, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **104**, 182 (1973); **102**, 971 (1971).
22. Yu. B. Kuz'ma, M. V. Chepiga, A. M. Plakhina, *Inorg. Mater. (USSR)*, **2**, 1038 (1966).
23. Yu. B. Kuz'ma, N. S. Bilonishko, *Izv. Akad. Nauk. SSSR, Neorg. Mater.*, **7**, 542 (1971); *Chem. Abstr.*, **74**, 147,080 (1971).
24. E. Ganglberger, H. Nowotny, *Monatsh. Chem.*, **96**, 1144 (1965); **97**, 101, 718 (1966).
25. P. Rogl, H. Nowotny, *Monatsh. Chem.*, **108**, 1167 (1977).
26. L. Ya. Markovskii, E. T. Bezruk, G. E. Berlova, *Inorg. Mater. (USSR)*, **7**, 50 (1971).
27. H. Holleck, W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **95**, 552 (1964).
28. H. Holleck, *AED-Conf. 73-128-015*, Zentralst. f. Atomkern-energie-Dokumentation, Eggstein, Ludwigshafen, 1973.
29. B. Aronsson, *Acta Chem. Scand.*, **14**, 1403, 1414 (1960); **13**, 433 (1959).
30. W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **96**, 844 (1965).
31. I. Mayer, I. Felner, *J. Less Common Met.*, **37**, 171 (1974).
32. N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **6**, 883 (1970); *Chem. Abstr.*, **73**, 59,645 (1970).
33. N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **8**, 933 (1972); *Chem. Abstr.*, **77**, 67,160 (1972).
34. N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **9**, 1886 (1973); *Chem. Abstr.*, **80**, 125,393 (1974).
35. E. Lugscheider, H. Reimann, O. Knotek, *Monatsh. Chem.*, **106**, 1155 (1975).
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37. M. A. Marko, *Visn. L'viv. Derzh. Univ., Ser. Khim.*, No. 17, 26 (1975); *Chem. Abstr.*, **87**, 27,177 (1977).
38. M. A. Marko, Yu. B. Kuz'ma, E. I. Gladyshevskij, *Dopov. Akad. Nauk, RSR, Ser. A*, **6**, 555 (1976); *Chem. Abstr.*, **86**, 46,295 (1977).
39. S. K. Dhar, S. K. Malik, R. Vijayaraghavan, *Mater. Res. Bull.* **16**, 1557 (1981).
40. S. K. Dhar, S. K. Malik, D. Rambabu, R. Vijayaraghavan, *J. Appl. Phys.* **53**, 8077 (1982).
41. V. S. Telegus, Yu. B. Kuz'ma, *Dopov. Akad. Nauk. Ukr. RSR, Ser. A*, **31**, 945 (1969); *Chem. Abstr.*, **72**, 26,053 (1970).
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43. M. V. Chepiga, *Vestn. L'viv. Un-ta, Ser. Khim.*, **14**, 27 (1972).
44. G. Pradelli, C. Gianoglio, *Atti Accad. Naz. Lincei, Rend. Classe Sci. Fis., Mat. Nat., Ser. VIII*, **57**, 655 (1974).
45. C. Gianoglio, G. Pradelli, *Metall. Ital.*, **75**, 282 (1983).
46. E. Lugscheider, H. Reimann, R. Pankert, *Z. Metallkd.*, **71**, 654 (1980).
47. G. Pradelli, C. Gianoglio, E. Quadrini, *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat.*, **113**, 293 (1979).
48. A. Hårsta, E. Wennebo, *Acta Chem. Scand., Ser. A*, **35**, 227 (1981); **36**, 547 (1982); **35**, 43 (1981); **36**, 535 (1982).
49. H. H. Stadelmaier, J. B. Ballance, *Z. Metallkd.*, **58**, 449 (1967).
50. H. Hirota, *J. Phys. Soc. Jpn.*, **23**, 512 (1967); see also H. Hirota, Y. Tawara, Y. Kamatzu, *Jpn. J. Appl. Phys.*, **8**, 962 (1969).
51. L. T. Jordan, R. K. Mathur, K. R. Brose, H. H. Stadelmaier, *Z. Metallkd.*, **72**, 782 (1981).
52. H. H. Stadelmaier, H. H. Davis, H. K. Manaktala, E. T. Henig, *Z. Metallkd.*, **80**, 371 (1989).
53. I. S. Yvich, N. F. Chaban, *Abstracts, Conference on the Crystal Chemistry of Intermetallic Compounds, Tersizy. Dokl., L'viv, October 1989*, p. 46.
54. Z. Zolnievek, D. Kacrorowski, *J. Magn. Magn. Mater.*, **63-64**, 178 (1987).
55. T. Higashi, T. Lundström, *J. Less-Common Met.*, **120**, L7 (1986).
56. H. Takeya, T. Shishido, H. Takai, *J. Less-Common Met.*, **134**, 263 (1987).
57. H. Takai, T. Shishido, *J. Less-Common Met.*, **97**, 223 (1984).

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TABLE 1. MODE OF FILLING THE VOIDS IN η -PHASES

Phase	Octahedral void I in 16c ^a	Octahedral void II in 8a ^a	Icosahedral center in 16d ^a	Metal host lattice atoms in 48f + 32e
Nb ₃ Fe ₂	□	□	□	Nb ₃ Fe ₂
Nb _{5±x} Ni	□	□	Ni	Nb ₃ Nb ₂
Zr ₄ Fe ₂	□	□	Zr	Zr ₃ Fe ₂
Hf ₃ Mn ₃	□	□	Mn	Hf ₃ Mn ₂
Hf ₄ (Ni _{2/3} Ru _{1/3}) ₂	□	□	Hf	Hf ₃ (Ni _{2/3} Ru _{1/3}) ₂
Hf ₃ Au ₂ Al	□	□	Al	Hf ₃ Au ₂
Mn ₃ Ni ₂ Si	□	□	Si	Mn ₃ Ni ₂
Zn ₃ Ni ₂ Si	□	□	Si	Zn ₃ Ni ₂
Re ₃ Al ₂ B	□	□	B	Re ₃ Al ₂
Hf ₄ Os ₂ O _{0.75}	O	□	Hf	Hf ₃ Os ₂
Zr ₃ Zn ₃ O	O	□	Zn	Zr ₃ Zn ₃
Nb ₃ Zn ₃ N	N	□	Zn	Nb ₃ Zn ₂
Nb ₄ Zn ₂ N	N	□	Nb	Nb ₃ Zn ₂
W ₃ Fe ₃ O _{0.5}	□	O _{0.5}	Fe	W ₃ Fe ₂
W ₄ Fe ₂ C	C	□	W	W ₃ Fe ₂
W ₃ Fe ₃ C _{0.5}	□	C _{0.5}	Fe	W ₃ Fe ₂
Mo ₄ Ni ₂ C _{1+x}	C	C _{0.5}	Mo	Mo ₃ Ni ₂
Ta ₃ Cr ₂ AlC	C	□	Cr	Ta ₃ CrAl
Ta ₃ CrAl ₂ C	C	□	Cr	Ta ₃ Al ₂
Nb ₃ Ni ₃ AlC	C	□	Ni	Nb ₃ Al ₂
Nb ₃ NiAl ₂ C	C	□	Al	Nb ₃ Ni ₂
Nb ₄ Zn ₂ C _{1.5}	C	C _{0.5}	Nb	Nb ₃ Zn ₂

^a □ = unoccupied void; the space group is Fd3m, origin in $\bar{4}3m$.

atoms or Si; two additional O_h voids remain unoccupied (Table 1). Traces of boron²⁷ are responsible for the existence of a metastable, superconducting Ti₂Ni-type phase in arc-melted and quenched alloys Sc_{2.15}Cr_{0.85}B_{0.01}; although the atomic site distribution is not known precisely, a partial ordering with Sc atoms in 48f of Fdm is likely.

Similarly, boron stabilizes a ternary phase (Ni_{0.63}Be_{0.37}(Be_{0.7}B_{0.3})₂), a MgCu₂-type structure, by substitution of small metal atoms on a typical metal site³.

The metallic character of boron is revealed by the existence of two groups (structural series) of ternary metal-rich borides, which at least in a formal way are generated by substitution of the small metal atoms by B atoms. Both structural series $M_{REm+n}M_{T5m+3n}B_{2n}$ and $M_{REn+1}^B M_{T3n+1}B_{2n-2}$ are based upon intermetallic structure types (CaCu₅ and MgZn₂) and terminate in the same end member⁴: CeCo₃B₂. The structure of CeCo₃B₂ (m = 0) corresponds to a CaCu₅-type superstructure, owing to the ordered distribution of B and Co atoms, the borons being located at the center of trigonal Co prisms with tetrakaidecahedral metal coordination, Ce₃Co₆B. Representatives are listed in Table 2 (and refs. therein) and are numerous among M_T metals such as M_T = Co, Ni, Ru and the larger M_{RE} members in combination with Rh, Os and Ir. The same structure type is derived¹⁰ for Zr(Hf)Co₃B₂; however, a

TABLE 2. STRUCTURE TYPES, BORON COORDINATION AND REPRESENTATIVES OF METAL BORIDES (SUBSTITUTIONAL TYPES AND CaCu_2 STRUCTURE FAMILY)

Structure type	Boron coordination	Binary representative	Ternary representatives	Refs.
Ti_2Ni	Icosahedron	—	$\text{Re}_3\text{Al}_2\text{B}$	2
$\text{Fd}\bar{3}m$	Complex	—	$\text{Sc}_{2.15}\text{Cr}_{0.85}\text{B}_{0.01}$ (metastable)	26
MgCu_2	Complex	—	$(\text{Ni}_{0.63}\text{Be}_{0.37})\text{Be}_{0.7}\text{B}_{0.3}^2$	3
$\text{Fd}\bar{3}m$	Trigonal prism	—	$\text{M}_{\text{RE}}\text{Ni}_{13}\text{B}_2$: $\text{M}_{\text{RE}} = \text{Y, La, Ce, Pr, Nd, Sm, Eu}^{57}, \text{Gd, Tb, Dy, Ho, Er, Tm}$	26, 33
$\text{P6}/\text{mmm}$	Trigonal prism	—	$\text{La}_3\text{Ni}_{13}\text{B}_2\text{H}_{4.6}$	35
CeCo_4B	Trigonal prism	—	$\text{M}_{\text{RE}}\text{Fe}_4\text{B}$: $\text{M}_{\text{RE}} = \text{Er, Tm, Lu}$	31
$\text{P6}/\text{mmm}$	Trigonal prism	—	$\text{M}_{\text{RE}}\text{Co}_4\text{B}$: $\text{M}_{\text{RE}} = \text{Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb}^{34}, \text{Lu}$	4
			$\text{M}_{\text{RE}}\text{Co}_{4-x}\text{Fe}_x\text{B}$: $\text{M}_{\text{RE}} = \text{Pr, Nd, Sm, Gd}^{55}, \text{Dy}^5$	51
			$\text{UM}_{\text{T}}\text{B}$: $\text{M}_{\text{T}} = \text{Ni}^5$	32
			$\text{M}_{\text{RE}}\text{Ni}_4\text{B}$: $\text{M}_{\text{RE}} = \text{La}^{26}, \text{Pr}^{26}, \text{Nd}^{26}, \text{Sm}^{48}, \text{Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$ (for $\text{M}_{\text{RE}} = \text{Y, Ce}$ see text), Ca^{90}	4
$\text{Ce}_3\text{Co}_{11}\text{B}_4$	Trigonal prism	—	$\text{M}_{\text{RE}}\text{Co}_{11}\text{B}_4$: $\text{M}_{\text{RE}} = \text{Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu}$	4
$\text{P6}/\text{mmm}$	Trigonal prism	—	$\text{M}_{\text{RE}}\text{Co}_7\text{B}_3$: $\text{M}_{\text{RE}} = \text{Y, Ce, Pr, Nd, Sm}^{36}, \text{Gd, Tb, Dy, Ho, Er, Tm}$	4
$\text{Ce}_2\text{Co}_7\text{B}_3$	Trigonal prism	—	$\text{M}_{\text{RE}}\text{Co}_{7-x}\text{Fe}_x\text{B}_3$: $\text{M}_{\text{RE}} = \text{Pr, Nd, Sm}$	53
CeCo_3B_2	Trigonal prism	—	$\text{M}_{\text{RE}}\text{Co}_3\text{B}_2$: $\text{M}_{\text{RE}} = \text{Sc, Y, Ce, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$	4, 20
$\text{P6}/\text{mmm}$	Trigonal prism	—	$\text{M}_{\text{RE}}\text{Ru}_3\text{B}_2$: $\text{M}_{\text{RE}} = \text{Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$ and $\text{La}_{0.9}\text{Ru}_3\text{B}_2$ 8a $\text{Y}_{0.5}\text{Th}_{0.5}\text{Ru}_3\text{B}_2$ 8	7, 8
			$\text{M}_{\text{RE}}\text{Rh}_3\text{B}_2$: $\text{M}_{\text{RE}} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd}$	8, 28
			$\text{Y}_{0.5}\text{La}_{0.5}\text{Rh}_3\text{B}_2$, $\text{Sr}_{0.67}\text{Rh}_3\text{B}_2$ 61 , $\text{Ba}_{0.67}\text{Rh}_3\text{B}_2$ 61	
			$\text{YRh}_3\text{Si}_{2-x}\text{B}_x$, $x \leq 1.5$ 29 , $\text{SmRh}_{3-x}\text{Fe}_x\text{B}_2$ 55 ; $\text{Ce}_{1-x}\text{La}_x\text{Rh}_3\text{B}_2$ 58	
			$\text{M}_{\text{RE}}\text{Os}_3\text{B}_2$: $\text{M}_{\text{RE}} = \text{Er, Lu}$; and $\text{Lu}_{0.5}\text{Th}_{0.5}\text{Os}_3\text{B}_2$ (see also text)	8
			$\text{M}_{\text{RE}}\text{Ir}_3\text{B}_2$: $\text{M}_{\text{RE}} = \text{La}^8, \text{Pr}^9$	
			$\text{UM}_{\text{T}}\text{B}_2$: $\text{M}_{\text{T}} = \text{Fe}^5, \text{Co}^5, \text{Ir}^8$	
			$\text{ThM}_{\text{T}}\text{B}_2$: $\text{M}_{\text{T}} = \text{Ir}^8, \text{Ru}^{7,8}$	
URu_3B_2	Trigonal prism	—	$\text{UM}_{\text{T}}\text{B}_2$: $\text{M}_{\text{T}} = \text{Ru, Os}$	12
$\text{P}\bar{3}$	Trigonal prism	—	$\text{PuM}_{\text{T}}\text{B}_2$: $\text{M}_{\text{T}} = \text{Ru, Os}$	30
$\text{Nd}_{0.71}\text{Rh}_{3.29}\text{B}_2$	Trigonal prism	—	$\text{Nd}_{1-x}\text{Rh}_x\text{Rh}_3\text{B}_2$, $0.29 \leq x \leq 0.52$,	37
$\text{P6}2m$	Trigonal prism	—	$\text{M}_{\text{RE}1-x}\text{Rh}_x\text{Rh}_3\text{B}_2$, $x = 0.43$, $\text{M}_{\text{RE}} = \text{Y, La, Sm, Gd, Tb, Dy, Ho, Er}$	47

$\text{La}_{1-x}\text{Rh}_x\text{B}_2$ P6/mmm x 0.5	—	Trigonal prism	$\text{RE}_{1-x}\text{Rh}_x\text{B}_2$, RE = La, Ce, Pr, Nd RE = Y, Eu, Lu, (?)	62, 63
$\text{PrRh}_{4.8}\text{B}_2$ Immm	—	Trigonal prism	EuRh_6B_4 , EuPd_6B_4 (?) $\text{PrRh}_{4.8}\text{B}_2$	45
HfCo_3B_2 R3	—	Trigonal prism	TCO_3B_2 , T = Zr, Hf	45
ErIr_3B_2 C2/m	—	Trigonal prism	$\text{M}_{\text{RE}}\text{Rh}_3\text{B}_2$, $\text{M}_{\text{RE}} = \text{Y, Tb, Dy, Ho, Er, Tm, Yb, Lu}$ $\text{M}_{\text{RE}}\text{Ir}_3\text{B}_2$, $\text{M}_{\text{RE}} = \text{Sc, Y, Ce, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$ PuTl_3B_2 , T = Rh, Ir $\text{Lu}_5\text{Ni}_{19}\text{B}_6$	10, 11
$\text{Lu}_5\text{Ni}_{19}\text{B}_6$ P6/mmm	—	Trigonal prism		9
LiPt_3B P62m	—	Trigonal prism	LiPt_3B shift variant of CeCo_3B_2	9
$\text{NaPt}_3\text{B}_{2-x}$ P6/mmm	—	Trigonal prism	$\text{NaPt}_3\text{B}_{2-x}$ defect variant of CeCo_3B_2	30
$\text{Na}_3\text{Pt}_9\text{B}_5$ Cmcm	—	Polyhedron $\text{BPt}_{4+4}\text{Na}_2$	$\text{Na}_3\text{Pt}_9\text{B}_5$	68
$\text{Li}_{1.2}\text{Ni}_{2.5}\text{B}_2$ P622	—	Distorted trigonal prism, boron-pair formation	$\text{Li}_{1.2}\text{Ni}_{2.5}\text{B}_2$	60
$\text{Sc}_2\text{Ru}_5\text{B}_4$ P2/m	—	Trigonal prism, isolated borons and boron pairs	$\text{MgNi}_{2.5}\text{B}_2$ $\text{Sc}_2\text{Tl}_5\text{B}_4$; T = Ru, Os $\text{Mg}_2\text{Ru}_5\text{B}_4$ (PGam)	60
$\text{Mg}_5\text{Ru}_{13}\text{B}_{11}$ Pbam	—	Trigonal prism isolated borons, and boron pairs	$\text{Mg}_5\text{Rh}_{13}\text{B}_{11}$	13
$\text{Ba}_2\text{Ni}_9\text{B}_6$ R3c	—	Trigonal prisms, boron-pair	$\text{Ba}_2\text{Ni}_9\text{B}_6$	13
$\text{Ba}_2\text{Pt}_9\text{B}_6$ (?) P63/mmc	—	Needs confirmation	$\text{M}_2\text{Pt}_9\text{B}_6$, M = Ca, Sr, Ba	40

(continued)

TABLE 2. (continued)

Structure type	Boron coordination	Binary representative	Ternary representatives	Refs.
CaIr_2B_2 Fddd	Distorted trigonal prism BRh_4Ca_2	—	MRh_2B_2 , $\text{M} = \text{Ca}, \text{Sr}^{66}$ Mlr_2B_2 , $\text{M} = \text{Ca}, \text{Sr}^{66}$ $\text{M}_{\text{RE}}\text{Ru}_2\text{B}_2$, $\text{M}_{\text{RE}} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}$ ThRu_2B_2 $\text{M}_{\text{RE}}\text{Os}_2\text{B}_2$, $\text{M}_{\text{RE}} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Ga}$ ThOs_2B_2 $\text{Ca}_7\text{Rh}_{20}\text{B}_{14}$	15 15 69 69 69 69 61
$\text{Ce}_7\text{Rh}_{20}\text{B}_{14}$ Fmmm	Trigonal prism	—	$\text{Sr}_5\text{Rh}_{14}\text{B}_{10}$	61
$\text{Sr}_5\text{Rh}_{14}\text{B}_{10}$ Fmmm	Trigonal prism	—	$\text{Ca}_3\text{Rh}_8\text{B}_6$, $\text{Sr}_3\text{Rh}_8\text{B}_6$	61
$\text{Ca}_3\text{Rh}_8\text{B}_6$ Fmmm	Trigonal prism	—	$\text{Ca}_2\text{Rh}_5\text{B}_4$, $\text{Sr}_2\text{Rh}_5\text{B}_4$	61
$\text{Ti}_3\text{Co}_3\text{B}_2$ P4/mbm	Trigonal prism	—	$\text{Ti}_3\text{Co}_5\text{B}_2$ $\text{Ta}_3\text{Co}_5\text{B}_3$ $\text{Hf}_3\text{Ir}_5\text{B}_2$ $\text{Li}_{\sim 3}\text{Ni}_{16}\text{B}_{\sim 8}$	17 18 19 24
$\text{Li}_{\sim 3}\text{Ni}_{16}\text{B}_{\sim 8}$ P4/mbm	Trigonal prism archimedean antiprism	—	$\text{U}_3\text{Co}_7\text{B}_2$ $\text{M}_{\text{RE}}\text{Ni}_7\text{B}_2$: $\text{M}_{\text{RE}} = \text{Y}, \text{Nd}, \text{Sm} (?)$ Gd, Tb, Dy, Ho, Er, Tm, Lu (see also text)	23 48 38, 39, 48
$\text{U}_3\text{Co}_7\text{B}_2$ P6 ₃ /mmc	Trigonal prism $\text{BCo}_6\text{M}_{\text{RE}3}$	—		

6.7.2.1. Borides with Isolated Boron Atoms

6.7.2.1.2. Substitutional Metal Borides.

$\text{Eu}_3\text{Ni}_7\text{B}_2$ CeCo ₄ B type variant P6/mmm	Trigonal prism, structure needs confirmation	—	$\text{M}_{\text{RE}3}\text{Ni}_7\text{B}_2$; $\text{M}_{\text{RE}} = \text{Sm, Eu, Yb}$ (see also U ₃ Co ₇ B ₂ type and text)	39
$\text{Ce}_2\text{Co}_3\text{B}_2$ P6 ₃ /mmc	Trigonal prism BCo ₆ M _{RE3}	—	$\text{M}_{\text{RE}}\text{Co}_3\text{B}_2$; $\text{M}_{\text{RE}} = \text{Ce}^{22}, \text{Pr, Nd, Sm}^{54}$	26
$\text{Nd}_2\text{Fe}_{14}\text{B}$ P4 ₂ /mmm	Trigonal prism BFe ₆ Nd ₃	—	$\text{RE}_2\text{Fe}_{14}\text{B}$; $\text{RE} = \text{Y, La, Ce, Pr, Nd}^{76,84}$, Sm, Gd, Tb, Dy, Ho, Er, Tm	70, 71 88 72 74
			$\text{Th}_2\text{Fe}_{14}\text{B}$ $\text{Pr}_{2-x-y}(\text{Tb, Dy})_x\text{Nd}_y\text{Fe}_{11.6}\text{Co}_2\text{Al}_{0.4}\text{B}$ $\text{RE}_2\text{Fe}_{14-x}\text{Ni}_x\text{B}$, $\text{RE} = \text{Nd, Gd}$ $\text{RE}_2\text{Fe}_{14-x}\text{M}_x\text{B}$, $\text{RE} = \text{Pr, Nd, Dy}^{79}$, Er ⁷⁹ Y ⁸³ , Gd ⁸³ M = Cr, Mn, Co	78, 80–82, 87 75 77 85 86
			$\text{Nd}_2\text{Fe}_{14}\text{BH}_x$, $0 < x < 5$ $\text{Nd}_{2-x}\text{M}_x\text{Fe}_{14}\text{B}$, M = Tb, Dy $\text{Nd}_2\text{Fe}_{14-x}\text{Ru}_x\text{B}$ $\text{Er}_{2-x}\text{Dy}_x\text{Fe}_{14}\text{B}$	

^a Crystallizes also with the YO₃B₂ type (unknown structure type, observed with all lanthanides, La: LaRu₂B₂⁴¹).

superstructure according to $a_0 \cdot \sqrt{3}$ and $3c_0$ is more appropriate¹¹; coordination numbers are still high but significantly reduced, depending on the smaller radius R_{Zr}/R_{Co} as compared to R_{RE}/R_{Co} . Therefore, the B atoms are shifted from the $CaCu_5$ positions because of their tendency for B—B bond formation, and with respect to crystal chemistry $(Zr, Hf)Co_3B_2$ should be listed among boron-pair borides.

Among the $CeCo_3B_2$ -derivative structures the actinide metal combinations^{12,30} $M_{AN}M_{T3}B_2$ ($M_{AN} = U, Pu$; $M_T = Ru, Os$) adopt a simple superstructure ($a = 2a_0$,

	Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt
Sc	r	a	r	r			r	h	
Y	r	a	l	b	uht		k	h	
La	r	r	r	c	sgt			c	
Ce	r	a	r	b	sg			h	
Pr				b	sg			h	
Nd	r	r	r	b	sgt			h	
Pm									
Sm	r	a		b	gt		k	h	
Eu					ug	u			
Gd	r	a	m	b	gt		k	h	
Tb		a		b	ht		k	h	
Dy		a		b	ht		k	h	
Ho		a		b	ht		k	h	
Er		a		b	ht		c	k	h
Tm		a		b	h		k	h	
Yb		a		b	h		k	h	
Lu		a		b	uh		c	h	
Th				b			k	c	
Pa									
U	f	f	r	d			d	c	
Np									
Pu				e	e		e	e	

$La_{0.81}Rh_3B_2$
 $CeCo_3B_2$
 $ErIr_3B_2$
 URu_3B_2
 $Nd_{0.71}Rh_{3.29}B_2$
 $'YOs_3B_2'$
 type unknown

Figure 1. Formation of ternary borides $M_{RE}M_{T3}B_2$ and different structure types (M_{RE} = rare-earth element, M_T = transition-metal element). $CeCo_3B_2$ type; $ErIr_3B_2$ type; URu_3B_2 type; $Nd_{0.71}Rh_{3.29}B_2$ type; YOs_3B_2 type; $La_{0.81}Rh_3B_2$ type; compound formation observed, but structure type unknown. Refs: a^{4,23}, b^{7,8}, c⁸, d¹², e³⁰, f⁵, g^{6,28}, h⁹, i³⁷, j⁴⁰, k⁴¹, l⁴², m⁴³, r⁴⁴, s⁶²⁻⁶⁴, t⁴⁷, u = 45; see also ref. 62.

6.7.2.1. Borides with Isolated Boron Atoms

6.7.2.1.2. Substitutional Metal Borides.

$c = 2c_0$) accommodating isolated B atoms in a distorted tetrakaidecahedral metal coordination. Most of the smaller rare earth members $M_{RE}(Rh, Ir)_3B_2$ crystallize with a monoclinically distorted orthohexagonal $CeCo_3B_2$ cell⁹, and for the Os series $M_{RE}Os_3B_2$, an orthorhombic superstructure related to $CeCo_3B_2$ ($a = a_0$, $b = a_0 \cdot \sqrt{3}$, $c = 6c_0$) is found; a precise structure determination, however, is still lacking. Similarly a series of $M_{RE}M_{T6}B_4$ compounds has been claimed⁴⁵ ($M_T = Ru, Rh, Pd$) with a sixfold superstructure of a $CeCo_3B_2$ -type subcell as seen along the c axis; determination of the structure as $La_{0.81}Rh_3B_2$, however, revealed a threefold superstructure of a $CeCo_3B_2$ ($a = a_0$, $c = 2c_0$)⁶²⁻⁶³ (see also below).

The phase relations in the Nd-Rh-B system in the range $Nd_{1-x}Rh_xRh_3B_2$ for values of $0 < x < 0.52$ are complicated. A multiphase region is observed between $NdRh_3B_2$ ($CeCo_3B_2$ type) and a new phase $Nd_{1-x}Rh_xRh_3B_2$, revealing a homogeneous region for $0.29 < x < 0.52$. Thus $Nd_{0.71}Rh_{3.29}B_2$ constitutes another $CeCo_3B_2$ derivative type of lower symmetry ($P\bar{6}2m$) with a statistical distribution of Nd and Rh atoms on the M_{RE} sites³⁷. The earlier described $M_{RE}Rh_6B_4$ borides are claimed³⁷ to crystallize with the $Nd_{0.71}Rh_{3.29}B_2$ structure ($M_{RE} = Y, La, Nd, Sm, Gd, Tb, Dy, Ho$ and Er). A complete listing of the $M_{RE}M_{T3}B_2$ types appears in Fig. 1.

Derivative structures belonging to the series $M_{REm+n}M_{T5m+3n}B_{2n}$ are formed by Co/B substitution in terms of alternating slabs of $CaCu_5$ and $CeCo_3B_2$ units according to a ratio: $B/(B + Co) = 2/15$ ($M_{RE3}Ni_{13}B_2$; $m = 2$, $n = 1$), $3/15$ ($M_{RE}Co_4B$; $m = 1$, $n = 1$), $4/15$ ($M_{RE}Co_{11}B_4$; $m = 1$, $n = 2$), $4.5/15$ ($M_{RE2}Co_7B_3$; $m = 1$, $n = 3$) and $6/25$ ($M_{RE5}Ni_{19}B_6$; $m = 2$, $n = 3$). The B atoms in all cases are isolated and have tetrakaidecahedral metal coordination. Representatives mainly occur within the systems^{4,6,25,68} M_{RE} -Co-B and M_{RE} -Ni-B (see Table 2) but no compounds or derivatives are yet observed with noble metals. Owing to the similar alloying behavior, isotypism is found for Co-, Fe- and Ni-containing phases (see Table 2); YNi_4B ⁴² and $CeNi_4B$ ⁴⁶, however, are said to exhibit a threefold ($a = 3a_0$) and an eightfold ($a = 8a_0$) superstructure of a $CeCo_4B$ -type subcell, respectively; structures are not available for these two compounds.

The combination of structural units of $CeCo_3B_2$ and $MgZn_2$ -type phases generates the second structural series of the substitution-type metal-rich borides: $M_{REn+1}M_{T3n+1}B_{2n-2}$. In both crystal structures of $U_3Co_7B_2$ ($n = 2$)³⁸ and $Ce_2Co_5B_2$ ($n = 3$)²², isolated B atoms are found in tetrakaidecahedral metal coordination Ni_6RE_3 . Derived structures, obtained by combining layer-stacking sequences of the $CaCu_5$ type with those of the Laves phase type, are already known from a series of intermetallics, such as the $CeNi_3$ or the Er_2Co_7 family of structures²⁴. A representation of the two structural series based on slabs of the $CeCo_3B_2$ -, $CaCu_5$ - and $MgZn_2$ -type structures appears in Fig. 2.

The structural and magnetochemistry of $RE_3Ni_7B_2$ phases³⁹ confirms an earlier structure³⁸ for $M_{RE} = Gd, Tb, Dy, Ho, Er, Tm, Lu$ ($U_3Co_7B_2$ type, $P6_3/mmc$). For $M_{RE} = Sm, Eu, Yb$, however, a symmetry reduction is claimed ($P6/mmm$) corresponding to a different site occupation, which actually represents an occupation variant of the $CeCo_4B$ type insofar as Eu + Ni statistically occupy the $2c$ sites³⁹.

Another $CeCo_3B_2$ -type variant with B atoms in triangular prismatic metal coordination⁶⁵ is $PrRh_{4.8}B_2$. Further $CaCu_5$ derivatives are characterized in the systems M_{AE} -Ni-B ($M_{AE} =$ alkali or alkaline-earth metal); e.g., $Li_{1.2}Ni_{2.5}B_2$ and isotypic $MgNi_{2.5}B_2$ show a simple superstructure¹³ (a , $3c$) with puckered layers of Ni and Li (Mg) atoms in a statistical distribution, revealing unusually short Ni(Li) distances of ~ 204 pm, favoring boron-pair formation. Isolated B atoms are common

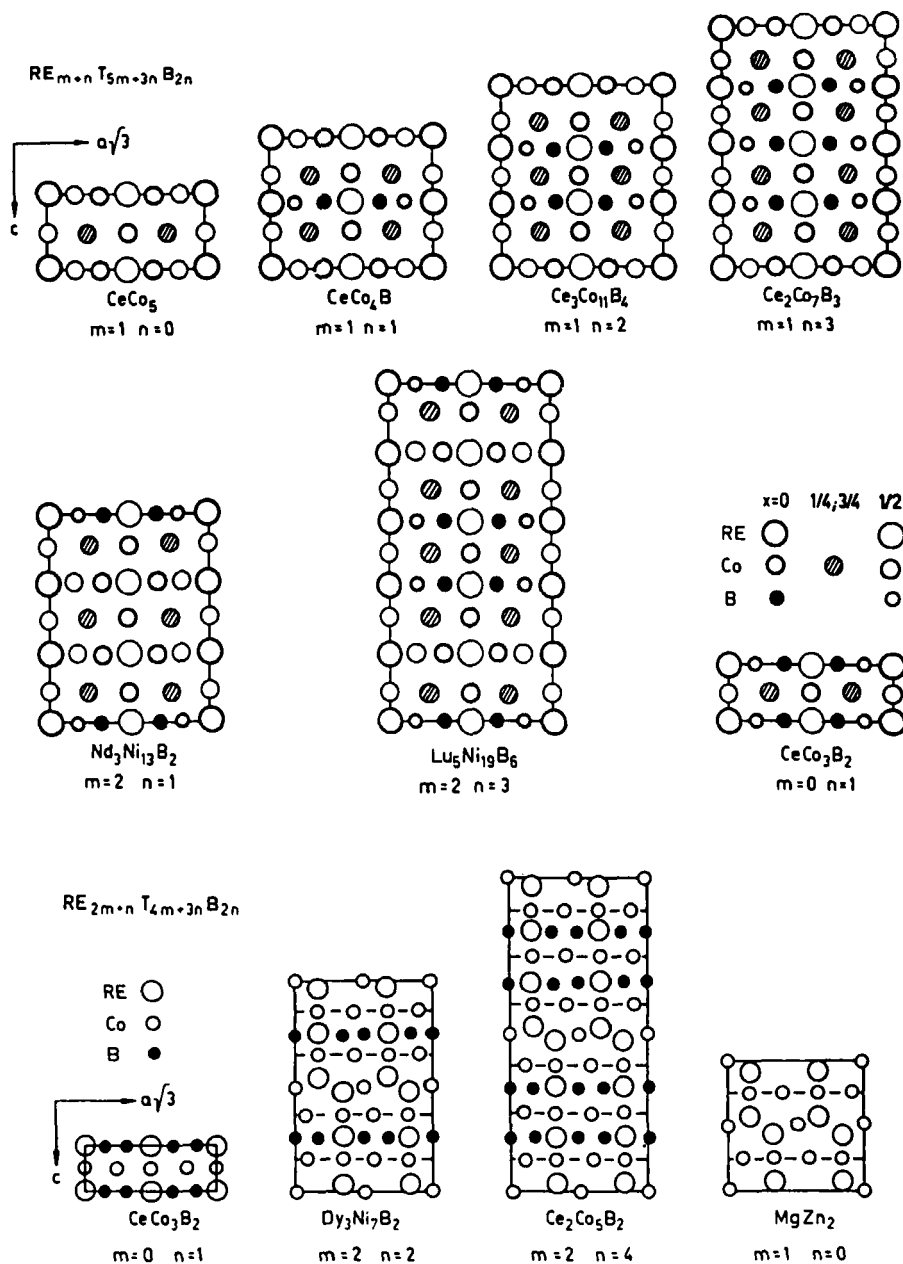


Figure 2. Comparison of the various structure types belonging to two homologous structure series based on the $CeCo_3B_2$, $CaCu_5$ and $MgZn_2$ structure types.

to three structure types deriving from CeCo_3B_2 ; i.e., LiPt_3B , which is a shift variant of CeCo_3B_2 , can accommodate only half the amount of B atoms because of the formation of small Pt polyhedra⁶⁰. Likewise, $\text{NaPt}_3\text{B}_{1+x}$ ($x < 0.45$), a defect variant of CeCo_3B_2 , exhibits⁶⁰ a homogeneous range with unit cell dimensions varying smoothly between $0 \leq x \leq 2$ and $0.3 \leq x \leq 0.45$ and a discontinuous transition around $x \approx 0.25$. The crystal structure of $\text{Na}_3\text{Pt}_9\text{B}_5$ can be derived from CeCo_3B_2 by periodic unit cell twinning, resulting in densely packed Pt_4 tetrahedra⁶⁰. Further representatives consisting of CaCu_5 -, CeCo_3B_2 - and Laves-type subunits are⁹⁰ $\text{Ca}_5\text{Ni}_{12}\text{B}_4$ and $\text{Ca}_3\text{Ni}_7\text{B}_2$.

Nickel atoms in $\text{Ba}_2\text{Ni}_9\text{B}_6$ form distorted, puckered 3.6.3.6-kagomé nets stacked in six layers perpendicular to the c axis. The densely packed framework of trigonal-Ni prisms again result in boron-pair formation, although Ba atoms are too large to be sandwiched between two Ni layers, and only four Ba can be accommodated within six Ni layers¹⁴. Superconductivity is found for $(\text{Ca}, \text{Sr}, \text{Ba})_2\text{Pt}_9\text{B}_6$ borides¹⁶ with a structure related to $\text{Ba}_2\text{Ni}_9\text{B}_6$ and CeCo_3B_2 ; however, with respect to crystal chemistry and boron coordination, only the subcell is derived so far.

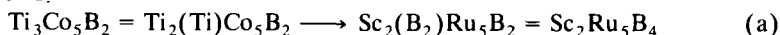
For $(\text{Ca}, \text{Sr})(\text{Rh}, \text{Ir})_2\text{B}_2$ borides the problem of accommodating the large alkaline-earth atoms is solved by creating defects within the puckered $\text{Rh}(\text{Ir})$ 3.6.3.6 layer, thus forming Rh chains that introduce a high degree of anisotropy (orthorhombic structure type with $b/c = 1.575$) strongly deviating from the ideal value of $\sqrt{3}$ as well as truncated coordination polyhedra; isolated B atoms are coordinated by four Rh plus five remote Ca atoms¹⁵. Combining structural units of the types CeCo_3B_2 and CaRh_2B_2 , a series of homologous structures is obtained⁶¹ with the general formula $\text{A}_n\text{Rh}_{3n-1}\text{B}_{2n}$, e.g., $\text{Ca}_2\text{Rh}_5\text{B}_4$, $\text{Ca}_3\text{Rh}_8\text{B}_6$, $\text{Sr}_5\text{Rh}_{14}\text{B}_{10}$, $\text{Ca}_7\text{Rh}_{20}\text{B}_{14}$ (Table 2).

Few of the possible ternary combinations $\text{M}_{\text{AE}}\text{-M}_{\text{T}}\text{-B}$ are investigated, and a larger variety of structure types is to be expected. The crystal chemistry of the CaCu_5 -type derivative structures in combination with alkaline-earth or rare-earth metals reveals some characteristic features (as seen from interatomic distances):

1. Weak boron- $\text{M}_{\text{AE}}(\text{M}_{\text{RE}})$ -metal bonding.
2. Strong boron-transition metal interaction; interatomic distances are shorter by 5–10%, as compared to the sum of the metal radii.
3. Increasing content of the large $\text{M}_{\text{AE}}(\text{M}_{\text{RE}})$ -metals as well as increasing electronegativity differences $\epsilon_{\text{M}_{\text{AE}}\text{-M}_{\text{T}}}$ reduce the formation of boron-boron aggregates, with respect to the values simply derived from the metal-boron ratio (see Table 2, §6.7.2).

According to the classification scheme in Table 1 of §6.7.2, a boron-metal ratio $\text{B}/\text{M}_{\text{T}} = 1.5$ represents the borderline between borides with isolated B atoms and the formation of higher B aggregates, i.e., boron pairs. It is natural to find a combination of both when $\text{B}/\text{M}_{\text{T}}$ approaches 1.5, which particularly is true for the crystal structures, such as $\text{Ba}_2\text{Ni}_9\text{B}_6$, $\text{Ba}_2\text{Pt}_9\text{B}_6(?)$, $\text{Li}_{1.2}\text{Ni}_{2.5}\text{B}_2$, $\text{MgNi}_{2.5}\text{B}_2$, $\text{Mg}_5\text{Ru}_{13}\text{B}_{11}$ and $\text{Sc}_2\text{Ru}_5\text{B}_4$ ($\text{Mg}_2\text{Ru}_5\text{B}_4$). The latter is a variation of the CeCo_3B_2 type with respect to the reduced coordination number of the much smaller Sc atoms located in nonregular pentagonal columns of edge-connected trigonal prisms. Owing to the decrease in the CN of Sc, some of the trigonal prisms are face connected and thereby provide the formation of a B pair⁴⁰.

A formal substitution of this boron pair by a metal atom generates the structure type $\text{Ti}_3\text{Co}_5\text{B}_2$:



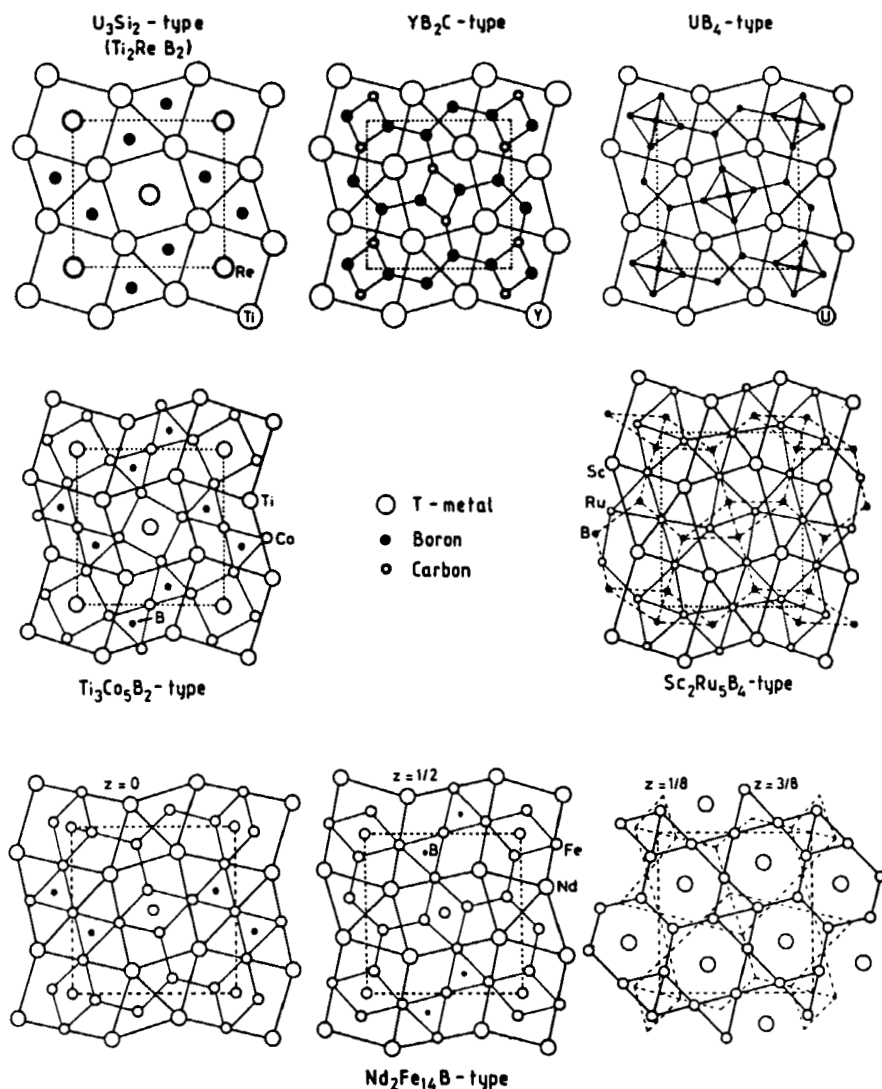
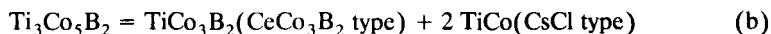


Figure 3. Common 4.3³.4.3 metal layers and crystallographic relation between the structure types of (a) U₃Si₂, YB₂C and ThB₄ (upper row), (b) Ti₃Co₅B₂ and Sc₂Ru₅B₄ (middle rows), (c) Nd₂Fe₁₄B (lower part); all structures are seen in projection along [001].

Consequently, $\text{Ti}_3\text{Co}_5\text{B}_2$ is a topochemical combination of CeCo_3B_2 -type units with intermetallic clusters:



Boron atoms are isolated with tetrakaidecahedral metal surrounding BCo_6Ti_3 ; representatives are $\text{Ta}_3\text{Co}_5\text{B}_2$ ¹⁸ and $\text{Hf}_3\text{Ir}_5\text{B}_2$ ¹⁹, the former decomposing above 1000°C ²⁰.

Combining structural units of $\tau(\text{Cr}_{23}\text{C}_6)$ and $\text{Ti}_3\text{Co}_5\text{B}_2$ an array of edge-connected cuboctahedra and trigonal prisms²¹ is formed in the structure of $\text{Li}_{\sim 3}\text{Ni}_{16}\text{B}_{\sim 8}$. The isolated B atoms are accommodated in (a) BNi_8 antiprismatic, in (b) BNi_{6+1} trigonal prismatic and (c) BNi_{6+2} trigonal prismatic coordination with a Ni atom centering one lateral face and one additional Ni atom centering one of the trigonal base planes.

Both $\text{Nd}_2\text{Fe}_{14}\text{B}$ and alloys derived from it by various modes of substitution have superb hard magnetic properties^{71,76-89}. The crystal structure of $\text{Nd}_2\text{Fe}_{14}\text{B}$ contains isolated B atoms in triangular metal coordination but also combines the characteristics of topologically densely packed structures. Thus it is not surprising to see a close correspondence with the σ -phase or Mn_5LiC -type structures. Its $4.3^2.4.3$ Kagomé metal layer, furthermore, resembles that in $\text{Ti}_3\text{Co}_5\text{B}_2$ and $\text{Sc}_2\text{Ru}_5\text{B}_4$ (Fig. 3). Structural and magnetochemical properties of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ family of compounds are known⁸⁹.

(P. ROGL)

1. P. Rogl, H. Nowotny, *Monatsh. Chem.*, **108**, 1167 (1977).
2. N. F. Chaban, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **8**, 933 (1972); *Chem. Abstr.*, **77**, 67,160 (1972).
3. H. J. Becher, H. Neidhard, *Z. Anorg. Allg. Chem.*, **344**, 125 (1966).
4. Yu. B. Kuz'ma, N. S. Bilonizhko, *Sov. Phys. Crystallogr. (Engl. Transl.)*, **18**, 447 (1974).
5. I. P. Vol'ovka, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **14**, 356 (1978); *Chem. Abstr.*, **88**, 177,892 (1978).
6. Yu. B. Kuz'ma, M. P. Khaburskaya, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **11**, 1625 (1975); *Chem. Abstr.*, **84**, 50,397 (1976).
7. K. Hiebl, P. Rogl, E. Uhl, M. J. Sienko, *Inorg. Chem.*, **19**, 3316 (1980).
8. H. C. Ku, G. P. Meisner, F. Acker, D. Johnston, *Solid-State Commun.*, **35**, 91 (1980).
9. H. C. Ku, G. P. Meisner, *J. Less-Common Met.*, **78**, 99 (1981).
10. H. H. Stadelmaier, J. Schöbel, *Monatsh. Chem.*, **100**, 224 (1969).
11. Yu. V. Voroshilov, P. I. Krypyakevich, Yu. B. Kuz'ma, *Kristallografiya*, **15**, 934 (1970); *Chem. Abstr.*, **74**, 16,681 (1971).
12. P. Rogl, *J. Nucl. Mater.*, **92**, 292 (1980).
13. W. Jung, *Z. Naturforsch., Teil B*, **32**, 1371 (1977).
14. W. Jung, D. Quentmeier, *Z. Kristallogr.*, **151**, 172 (1980).
15. B. Schmidt, W. Jung, *Z. Naturforsch., Teil B*, **33**, 1430 (1978).
16. R. N. Shelton, *J. Less-Common Met.*, **62**, 191 (1978).
17. Yu. B. Kuz'ma, Yu. P. Yarmolyuk, *Zh. Strukt. Khim.*, **12**, 458 (1971); *Chem. Abstr.*, **75**, 92,087 (1971).
18. Yu. B. Kuz'ma, N. F. Chaban, O. S. Vityuk, *Poroshk. Metall. (Kiev)*, No. 9, 101 (1979); *Chem. Abstr.*, **91**, 199,675 (1979).
19. P. Rogl, H. Nowotny, *J. Less-Common Met.*, **67**, 41 (1979).
20. W. Steurer, Thesis, University of Vienna, 1979.
21. W. Jung, *Z. Kristallogr.*, **151**, 113 (1980).
22. Yu. B. Kuz'ma, *Dopo. Akad. Nauk Ukr. RSR, Ser. A*, 147 (1979).

23. Yu. B. Kuz'ma, I. P. Val'ovka, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **16**, 1421 (1980); *Chem. Abstr.*, **94**, 23,262 (1981).
24. W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley-Interscience, New York, 1972.
25. P. Rogl, *Monatsh. Chem.*, **104**, 1623 (1973).
26. Yu. B. Kuz'ma, N. S. Bilonizhko, N. F. Chaban, G. V. Chernjak, *J. Less-Common Met.* **90**, 217 (1983); **82**, 364 (1981).
27. J. M. Vandenberg, B. T. Matthias, E. Corenzwit, H. Barz, *J. Solid-State Chem.*, **18**, 395 (1976).
28. S. K. Malik, S. K. Dhar, R. Vijayaraghavan, W. E. Wallace, *J. Appl. Phys.*, **53**, 8074 (1982); *J. Magn. Mater.*, **37**, 303 (1981).
29. B. Chevalier, A. Cole, P. Lejay, J. Etourneau, *Mater. Res. Bull.*, **16**, 1067 (1981).
30. P. Rogl, H. Haines, P. E. Potter, *J. Less-Common Met.*, **121**, 431 (1986).
31. G. V. Chernjak, *Inorg. Mater. (USSR)*, **19**, 436 (1983).
32. G. V. Chernjak, N. F. Chaban, *Inorg. Mater. (USSR)*, **18**, 590 (1982).
33. Yu. B. Kuz'ma, N. S. Bilonizhko, *Dopov. Akad. Nauk. Ukr. RSR, Ser. A*, No. 10, 878 (1981); *Chem. Abstr.*, **96**, 61,117 (1982).
34. N. F. Chaban, *Vestn. L'vov. Gos. Univ., Ser. Khim.*, **23**, 43 (1981).
35. F. Spada, H. Oesterreicher, *J. Less-Common Met.*, **90**, L1 (1983).
36. N. S. Bilonizhko, Yu. B. Kuz'ma, L. D. Polanskaya, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **16**, 575 (1980); *Chem. Abstr.*, **93**, 81,335 (1980).
37. M. Vlasse, T. Ohtani, B. Chevalier, J. Etourneau, *J. Solid-State Chem.*, **46**, 188 (1983).
38. Yu. B. Kuz'ma, N. F. Chaban, *Dopov. Akad. Nauk. URSR, Ser. A*, **86** (1980); *Chem. Abstr.*, **92**, 139,064 (1980).
39. I. Felner, *J. Phys. Chem. Solids* **4(1)**, 43 (1983).
40. P. Rogl, *J. Solid-State Chem.*, **55**, 262 (1984).
41. H. C. Ku, Thesis, Univ. California, San Diego, 1980.
42. Yu. B. Kuz'ma, M. P. Khaburskaya, *Inorg. Mater. (USSR)*, **11**, 1893 (1973).
43. Yu. B. Kuz'ma, N. S. Bilonizhko, N. F. Chaban, G. V. Chernjak, *J. Less-Common Met.*, **90**, 217 (1983).
44. No compound formation observed; see isothermal section from Fig. 1, §6.7.2.
45. I. Felner, I. Nowik, *Phys. Rev.*, **45**, 2128 (1980).
46. Yu. B. Kuz'ma, N. S. Bilonizhko, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **7**, 542 (1971); *Chem. Abstr.*, **74**, 147,080 (1971).
47. T. Ohtani, B. Chevalier, P. Lejay, J. Etourneau, M. Vlasse, P. Hagenmuller, *J. Appl. Phys.*, **54(10)**, 5928 (1983).
48. N. S. Bilonizhko, N. F. Chaban, Yu. B. Kuz'ma, M. D. Grin, *Dokl. Akad. Nauk, Ukr. RSR, Ser. B*, No. 6, 26 (1983); *Chem. Abstr.*, **99**, 94,463 (1983).
49. G. V. Chernjak, N. F. Chaban, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 6, 65 (1983); *Chem. Abstr.*, **99**, 94,462 (1983).
50. A. C. Lawson, A. Williams, J. G. Huber, *J. Less-Common Met.*, **136**, 87 (1987).
51. Y. Gros, F. Hartmann-Boutron, C. Meyer, M. A. Fremy, P. Tenaud, P. Auric, *J. Phys.*, Ser. C, **8(12)**, 49, 547 (1988); *J. Magn. Magn. Mater.*, **74**, 319 (1988).
52. N. M. Hong, J. J. M. Franse, N. P. Thuy, T. D. Hien, *J. Phys. C8, Supp. 12*, Tome 49, 545 (1988).
53. S. Aly, E. Singleton, G. C. Hadjipanayis, *J. Magn. Magn. Mater.*, **75**, 88 (1988).
54. N. S. Bilonizhko, L. V. Leshko, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **21**, 1568 (1985).
55. S. N. Mishra, S. H. Devare, H. G. Devare, *Hyperfine Interact.*, **28**, 467 (1986).
56. Z. Dozazga, A. Winiarska, F. Stein, *J. Less-Common Met.*, **153**, L21 (1989).
57. O. M. Dub, N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **7**, 994 (1985).
58. S. K. Malik, A. M. Umarji, G. K. Shenoy, T. A. Aldred, D. G. Niarchos, *J. Appl. Phys.*, **57(1)**, 3043 (1985).
59. K. Schweitzer, W. Jung, *Z. Anorg. Allg. Chem.*, **530**, 127 (1985).
60. R. Mirgel, W. Jung, *J. Less-Common Met.*, **144**, 87 (1982).
61. W. Jung, *J. Less-Common Met.*, **97**, 253 (1984).
62. H. C. Ku, L. J. Ma, M. F. Tai, Y. Wang, H. E. Horng, *J. Less-Common Met.*, **109**, 219 (1985).

63. H. C. Ku, Y. B. You, L. J. Ma, H. Y. Chao, Y. D. Yav, *J. Magn. Magn. Mater.*, **4748**, 573 (1985).
64. J. S. Schilling, R. N. Shelton, P. Klavins, S. A. Shaheen, *Phys. Rev. Ser. B*, **28**(10), 6548 (1983).
65. I. Higashi, T. Shishido, H. Takei, T. Kobayashi, *Kidorui*, **12**, 54 (1988).
66. W. Jung, *Z. Naturforsch., Teil B*, **34**, 1221 (1979).
67. V. F. Bashev, I. S. Miroshnichenko, G. A. Sergeev, *Inorg. Mater. (USSR)*, **17**, 892 (1981).
68. Yu. B. Kuz'ma, O. M. Dub, N. F. Chaban, *Dokl. Akad. Nauk Ukr. SSR., Ser. B*, **7**, 36 (1985).
69. C. Horvath, P. Rogl, K. Hiebl, *J. Solid-State Chem.*, **67**, 70 (1987).
70. O. M. Dub, Yu. B. Kuz'ma, *Porosh. Met.*, No. 7, 49 (1986).
71. M. Sagawa, S. Fujimura, H. Yamamoto, Y. Matsuura, H. Hiraga, *IEEE Trans. on Magnetics*, Vol. Mag-20, 1584 (1984).
72. F. Pourarian, S. G. Shankar, W. E. Wallace, *J. Magn. Magn. Mater.*, **74**, 177 (1988).
73. K. H. J. Buschow, *J. Less-Common Met.*, **144**, 65 (1988).
74. A. Kowalczyk, P. Stefanski, A. Wrzeciono, A. Szlaferek, *Phys. Status Solidi*, **144a**, 355 (1989).
75. P. Heritier, P. Chaudouet, R. Madar, A. Ronault, J. P. Senateur, R. Fruchart, *C.R. Hebd. Seances Acad. Sci.*, t299, Ser. II, 299(13) 849 (1984).
76. J. F. Herbst, J. J. Croat, F. E. Pinkerton, W. B. Yelon, *Phys. Rev. Ser. B*, **29**, 4176 (1984).
77. B. Grieb, G. Schneider, E. Th. He, G. Petzow, *Z. Metallkde.*, **80**, 515 (1989).
78. Y. C. Chuang, C. H. Wu, J. Q. Xie, *J. Less-Common Met.*,
79. A. T. Pedziwiatr, W. E. Wallace, *J. Magn. Magn. Mater.*, **66**, 63 (1987).
80. F. Bolzoni, J. M. D. Coey, J. Gravigan, D. Givord, O. Moze, L. Pareti, T. Viadieu, *J. Magn. Magn. Mater.*, **65**, 123 (1987).
81. C. D. Fürst, G. P. Meisner, F. E. Pinkerton, W. B. Yelon, *J. Less-Common Met.*, **133**, 255 (1987).
82. M. Q. Huang, E. B. Boltich, W. E. Wallace, E. Oswald, *J. Less-Common Met.*, **124**, 55 (1986); *J. Magn. Magn. Mater.*, **60**, 276 (1986).
83. A. Szytula, J. Drąjewicz, *Solid-State Commun.*, **57**, 809 (1986).
84. D. Givord, H. S. Li, J. M. Moreau, *Solid-State Commun.*, **50**, 497 (1984).
85. A. T. Pedziwiatr, W. E. Wallace, E. Burzo, *J. Magn. Magn. Mater.*, **61**, 173 (1986).
86. D. Niarchos, A. Simopoulos, *Solid-State Commun.*, **59**, 669 (1986).
87. M. Jurczyk, W. E. Wallace, *J. Less-Common Met.*, **124**, 149 (1986).
88. K. H. J. Buschow, H. M. van Noort, D. B. de Mooij, *J. Less-Common Met.*, **109**, 79 (1985).
89. K. H. J. Buschow, in *Ferromagnetic Materials—A Handbook on the Properties of Magnetically Ordered Substances*, Vol. 4, E. P. Wohlfahrt, K. H. J. Buschow, eds., North Holland, Amsterdam, 1988, pp. 1–129.
90. W. Jung, W. Weltzer, *Z. Kristallogr.*, **185**, 177 (1988).

6.7.2.1.3. Metal Boride Structures (Isolated Boron Atoms).

Binary and ternary structure types with isolated B atoms are listed in Table 1. In the metal borides of the formula $(M_T, M'_T)_3B$ or $T_3(B, E)$ (M_T, M'_T = transition metals, E = nonmetal), the influence of the radius ratio $R_B : R_{M_T}$, as well as the number of outer electrons per atom is decisive^{1,2}. These borides crystallize in competing structure types, namely Fe_3P , Ti_3P , Fe_3C and Re_3B . Therefore, among the types with typical trigonal-prismatic boron coordination, Fe_3C , Ti_3P , a higher electron per atom ratio in combination with a smaller radius ratio, $R_B : R_{M_T}$, favors the formation of ternary Fe_3C -type structures. At even lower electron/atom ratios, the structure types of Re_3B ⁹, $TaCo_2B$ (Re_3B -type supercell: 2a, 2c)¹⁰ and Mo_2IrB_2 (B_4 groups)¹¹ are observed, i.e., combinations of trigonal-prismatic and O_h metal units the centers of which act as preferential sites for nonmetal occupation. Neutron diffraction of the filled Re_3B -type $Cr_3(B_{0.44}C_{0.56})C_{0.85}$ shows that the larger nonmetal atoms (B) prefer a trigonal-prismatic metal coordination, whereas the smaller C

6.7.2. Existence and Crystal Chemistry of Borides

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6.7.2.1. Borides with Isolated Boron Atoms

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63. H. C. Ku, Y. B. You, L. J. Ma, H. Y. Chao, Y. D. Yav, *J. Magn. Magn. Mater.*, **4748**, 573 (1985).
64. J. S. Schilling, R. N. Shelton, P. Klavins, S. A. Shaheen, *Phys. Rev. Ser. B*, **28**(10), 6548 (1983).
65. I. Higashi, T. Shishido, H. Takei, T. Kobayashi, *Kidorui*, **12**, 54 (1988).
66. W. Jung, Z. *Naturforsch., Teil B*, **34**, 1221 (1979).
67. V. F. Bashev, I. S. Miroshnichenko, G. A. Sergeev, *Inorg. Mater. (USSR)*, **17**, 892 (1981).
68. Yu. B. Kuz'ma, O. M. Dub, N. F. Chaban, *Dokl. Akad. Nauk Ukr. SSR., Ser. B*, **7**, 36 (1985).
69. C. Horvath, P. Rogl, K. Hiebl, *J. Solid-State Chem.*, **67**, 70 (1987).
70. O. M. Dub, Yu. B. Kuz'ma, *Porosh. Met.*, No. 7, 49 (1986).
71. M. Sagawa, S. Fujimura, H. Yamamoto, Y. Matsuura, H. Hiraga, *IEEE Trans. on Magnetics*, Vol. Mag-20, 1584 (1984).
72. F. Pourarian, S. G. Shankar, W. E. Wallace, *J. Magn. Magn. Mater.*, **74**, 177 (1988).
73. K. H. J. Buschow, *J. Less-Common Met.*, **144**, 65 (1988).
74. A. Kowalczyk, P. Stefanski, A. Wrzeciono, A. Szlaferek, *Phys. Status Solidi*, **144a**, 355 (1989).
75. P. Heritier, P. Chaudouet, R. Madar, A. Ronault, J. P. Senateur, R. Fruchart, *C.R. Hebd. Seances Acad. Sci.*, t299, Ser. II, 299(13) 849 (1984).
76. J. F. Herbst, J. J. Croat, F. E. Pinkerton, W. B. Yelon, *Phys. Rev. Ser. B*, **29**, 4176 (1984).
77. B. Grieb, G. Schneider, E. Th. He, G. Petzow, *Z. Metallkde.*, **80**, 515 (1989).
78. Y. C. Chuang, C. H. Wu, J. Q. Xie, *J. Less-Common Met.*, **66**, 63 (1987).
79. A. T. Pedziwiatr, W. E. Wallace, *J. Magn. Magn. Mater.*, **66**, 63 (1987).
80. F. Bolzoni, J. M. D. Coey, J. Gravigan, D. Givord, O. Moze, L. Pareti, T. Viadieu, *J. Magn. Magn. Mater.*, **65**, 123 (1987).
81. C. D. Fürst, G. P. Meisner, F. E. Pinkerton, W. B. Yelon, *J. Less-Common Met.*, **133**, 255 (1987).
82. M. Q. Huang, E. B. Boltich, W. E. Wallace, E. Oswald, *J. Less-Common Met.*, **124**, 55 (1986); *J. Magn. Magn. Mater.*, **60**, 276 (1986).
83. A. Szytula, J. Drajewicz, *Solid-State Commun.*, **57**, 809 (1986).
84. D. Givord, H. S. Li, J. M. Moreau, *Solid-State Commun.*, **50**, 497 (1984).
85. A. T. Pedziwiatr, W. E. Wallace, E. Burzo, *J. Magn. Magn. Mater.*, **61**, 173 (1986).
86. D. Niarchos, A. Simopoulos, *Solid-State Commun.*, **59**, 669 (1986).
87. M. Jurczyk, W. E. Wallace, *J. Less-Common Met.*, **124**, 149 (1986).
88. K. H. J. Buschow, H. M. van Noort, D. B. de Mooij, *J. Less-Common Met.*, **109**, 79 (1985).
89. K. H. J. Buschow, in *Ferromagnetic Materials—A Handbook on the Properties of Magnetically Ordered Substances*, Vol. 4, E. P. Wohlfahrt, K. H. J. Buschow, eds., North Holland, Amsterdam, 1988, pp. 1–129.
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TABLE 1. STRUCTURE TYPES, BORON COORDINATION AND REPRESENTATIVES OF METAL BORIDE STRUCTURES CONTAINING ISOLATED B ATOMS ($B-B > 200$ pm)

Structure type	Boron coordination	Binary representatives	Ternary representatives	Refs.
Fe_3C	Trigonal prism	Co_3B , Ni_3B , Pd_3B ³⁹	$Fe_{2.2}Rh_{0.8}B^{40}$, $Fe_{2.2}Ir_{0.8}B^{41}$	
$Pbmm$	BM_{6+3}			
Ti_3P	Trigonal prism	—	$Fe_{2.6}Mo_{0.4}B^{42}$, $Fe_{2.6}Re_{0.4}B^{40}$, $Fe_{2.8}W_{0.2}B^{59}$, $Fe_{2.6}Ru_{0.4}B^{41}$, $(Re_{0.48}Co_{0.52})_3B^{43}$, $Fe_3(P_{0.52-0.06}B_{0.48-0.94})^{44}$	
$P4_2/n$	BM_{6+3}		$Cr_3(B_{0.44}C_{0.56})C_{0.85}^{45,56}$	
Re_3B	Trigonal prism	Tc_3B^{46} , Re_3B^9		
$Cmcm$	BM_{6+3}		$TaCo_2B$, $NbCo_2B$; $TaCo_{2-x}Ni_xB$	10
$TaCo_2B$	Trigonal prism	—		
$C2mm$	BM_{6+3}			
Mn_5C_2	Trigonal prism	$Pd_5B_2^{47}$	—	
$C2/c$	BM_{6+3}			
Th_7Fe_3	Trigonal prism	$Tc_7B_3^{46}$, $m = Re_7B_3^{48}$, Ru_7B_3 , Rh_7B_3		
$P6_3mc$	BM_{6+3}	—		
$SrNi_{12}B_6$	Distorted trigonal prism BNi_{6+1}		$CaNi_{12}B_6^{61}$, $SrNi_{12}B_6^{13}$, $BaNi_{12}B_6^{13}$ $M_{RE}Co_{12}B_6$; $M_{RE} = Y, La, Ce, Pr, Nd, Sm,$ Eu, Gd, Tb, Dy, Ho, Er $M_{RE}Ni_{12}B_6$; $M_{RE} = Y, Eu, Gd, Tb, Dy$ $M_{RE}Ni_{12}B_6$; $M_{RE} = Y, La, Ce, Pr,$ Nd, Sm, Tb, Dy $ThNi_{12}B_6^{64}$	57 57 62, 63 64
$R\bar{3}m$				
$CaNi_{12}B_6$	Isolated trigonal prism BNi_{6+1}			
$Cmc2_1$				

CuAl ₂ I4/mcm	Archimedean anti-prism BM ₈	Mn ₂ B, Fe ₂ B, Co ₂ B, Ni ₂ B, Ta ₂ B _{0.83} , Mo ₂ B, W ₂ B (see Ref. 48)	V _{0.95-0.63} Re _{1.05-1.37} B ³⁸ V _{0.15-0.20} Cr _{1.85-1.80} B ²³ Mo _{0.24-0.39} Cr _{1.76-1.61} B ²³	
Mg ₂ Cu (Mn ₄ B) Fddd	Distorted BM ₈	Cr ₂ B ²⁰ , o-Mn ₂ B ^{53,37}	V _{0.51-0.36} Re _{1.49-1.64} B ³⁸ Mn _{0.5} Re _{1.5} B ²⁵ Mo _{1.7} Ge _{0.3} B ²⁶ Re _{5.0-3.5} Co _{2.0-3.5} B ₄ ⁴³	
(Re, Co) ₇ B ₄ P4/mbm	Trigonal prism BM ₆₊₂ , archimedean antiprism BM ₈ , B—B contacts 194 pm	—		
Fe ₂ P or ZrNiAl P62m	Trigonal prism BM ₆₊₃	—	NbFeB ⁵⁰ , TaFeB ⁵⁰ , h-NbCoB ³¹ , h-TaCoB ³¹ , Ni ₆ Si ₂ B ⁵¹	
Anti-PbCl ₂ Pnma	Trigonal prism BM ₆₊₃	—	MoCoB ³⁵ , WCoB ³⁵ , WFeB ³⁵ , ReCoB ⁴³	
NbCoB Pmmn	Trigonal prism	—	NbCoB ³⁰ , TaCoB ⁴⁹	
AlRu ₄ B ₂ P4/mmm	Trigonal prism BRu ₆	—	Al ₃ Ru ₄ B ₂	65
BaAl ₄ (ThCr ₂ Si ₂) I4/mmm	Antiprism BM ₈	—	BaRh ₂ B ₂ ²⁹ , BaIr ₂ B ₂ ²⁹ M _{RE} Fe ₂ B ₂ , M _{RE} = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu M _{RE} Co ₂ B ₂ , M _{RE} = Sc, Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er ⁶⁰	52
Rh ₅ B ₄ P6 ₃ /mmc	Octahedron BM ₆	Rh ₅ B ₄ ⁵⁴	—	28

atoms predominantly occupy the O_h sites. The existence of $Cr_3(BC)C$ is restricted to a limited region¹², $1550^\circ C < T < 1710^\circ C$, and no isotypic ternary borocarbides exist.

Although Fe_3B with the Fe_3C type is never found in stable thermodynamic equilibrium, it is obtained from quenched alloys under metastable conditions. This is also true for $Fe_{23}B_6$ ($Cr_{23}C_6$ type), and a metastable Fe-B phase diagram is derived³. The small thermodynamic instability of Fe_3B (~ 1.5 kJ g-at⁻¹ metal)⁴ explains the easy stabilization of $(M_T, Fe)_3(B, E)$ compounds by alloying with transition metals or by boron-nonmetal substitution ($E = C, Si, P$)²⁻⁶. Depending on the quenching rates and the condition of heat treatment of rapidly quenched amorphous Fe-B alloys, crystalline phases $Fe_{\sim 3}B$ with different structure types (Fe_3C , Fe_3P , Ti_3P and Fe_4B)^{3,7,55,57} are obtained. Although these phases are metastable (see below)⁵⁸, above $1150^\circ C$ Fe_3B an equilibrium phase is suspected, crystallizing in two different modifications, the Fe_3P type as the high-T and the Ti_3P type as the low-T form. Orthorhombic Fe_3B cementite, usually obtained from amorphous alloys in cooling rates too slow for glass formation³ is metastable. A small deviation from $Fe : B = 3 : 1$ stoichiometry toward more Fe-rich compositions is claimed⁵⁸. A disordered Fe_3P -type phase is the first crystallization product^{3,7,58} on heating amorphous alloys $Fe_{20-25}B_{80-75}$. On further annealing at higher T a transformation of the Fe_3P type in the Ti_3P type occurs^{55,58}, and the sequence of phases obtained⁵⁸ by liquid quenching with decreasing cooling rates is the same as that found in the crystallization during heating from low T: amorphous state $\rightarrow Fe_3B$ (Fe_3P type) $\rightarrow Fe_3B$ (Ti_3P type) $\rightarrow Fe_2B + \alpha$ -Fe. Electron diffraction and microscopy of amorphous metallic $Fe_{83}B_{17}$ and $Fe_{80}B_{20}$ alloys⁵⁵ aged at 380, 400, 450, $550^\circ C$, 5 min to 5 h reveal the beginning of crystallization with the formation of fine grains of a metastable, ordered crystalline phase Fe_4B , indexable as a deformed bcc lattice ($a = 291$, $b = 293$ pm). Structure models are derived for a bcc cell ($a = 291$ pm, $Im\bar{3}$, O_h coordination of B atoms). The tendency to achieve regular coordination around the B atoms and the formation of an ordered solid solution with lower lattice energy have a predominant effect on the desymmetrization of the cubic phase to tetragonal or lower symmetry⁵⁵. After prolonged aging a transformation to metastable, tetragonal Fe_3B (Ti_3P type?) takes place⁵⁶.

A complex arrangement of trigonal prisms is found in the structure of $SrNi_{12}B_6$. Here deformed Ni prisms are connected along the edges of their triangular faces forming an array of six- and three-membered rings around the large alkaline-earth atoms¹³. As seen from Table 1, Ba and the rare earths form representatives of the $SrNi_{12}B_6$ type; trigonal lattice $CaNi_{12}B_6$, earlier described with a $(a' = a \cdot \sqrt{3})$ ¹⁶ is isotopic⁶¹. Besides the $SrNi_{12}B_6$ type, the light rare earth members La through Ho adopt an orthorhombic $CeNi_{12}B_6$ structure, claimed to exist at somewhat higher B concentrations than the $SrNi_{12}B_6$ type whenever both types occur in the same ternary⁶².

Among metal borides of the formula $M_T M_T' B$ or $(M_T, M_T')_2 B$, the competing structural units are (a) the antiprism and (b) the trigonal metal prism. In many cases the $CuAl_2$ structure with BM_8 -antiprismatic B coordination is adopted in close resemblance to transition-metal silicides, but no boron-carbon substitution is observed^{6,17-19}.

For Cr_2B , the only stable modification crystallizes with the Mg_2Cu structure; Cr_2B with a $CuAl_2$ structure is questionable and is impurity stabilized^{18,20,21}. The degree of instability is low, as judged from the existence of a $CuAl_2$ solid solution $(W_{1-x}Cr_x)_2B$, which at $1500^\circ C$ extends²² to 90 mol% Cr_2B . A similar argument

is found from the ternary Cr-rich CuAl_2 borides²³, e.g., $\text{V}_{0.15-0.2}\text{Cr}_{1.85-1.8}\text{B}$ and $\text{Mo}_{0.24-0.39}\text{Cr}_{1.76-1.61}\text{B}$.

A single-crystal study⁵³ of o- Mn_2B (Mg_2Cu type) reveals complete occupancy (98.2%, $R = 2.9\%$) of the B positions. The single crystal was obtained from a homogenized (1000°C) sample in equilibrium with α -(Mn, B) in contradiction to earlier studies³⁷ concerning the B deficiency and nonstoichiometry of Mg_2Cu -type $\text{Mn}_2\text{B}_{1-x}$ ($x < 0.5$). Concerning the existence of the tetragonal and stoichiometric CuAl_2 -type compound, t- Mn_2B (polymorph?), a reinvestigation of the phase equilibria within the Mn-rich region of the Mn-B system is necessary. The same is true for the ternary solid solution $(\text{Mn}_{1-x}\text{Cr}_x)_2\text{B}_{1-y}$, where Cr/Mn substitution²⁴ is accompanied by considerably boron defect formation at the metal-rich phase boundary. No deviations from the ideal stoichiometry $\text{M}:\text{B} = 2$ are observed²⁵ with the isotypic ternary boride $\text{Re}_{1.5}\text{Mn}_{0.5}\text{B}$ (Mg_2Cu type); Mo_2B is not stable with the Mg_2Cu type, but small amounts of B metals (Ge) stabilize²⁶ a ternary Mg_2Cu -type boride $\text{Mo}_{1.7}\text{Ge}_{0.3}\text{B}$.

Different stacking modes of planar 3².4.3.4 metal layers generate the CuAl_2 , (Re, Co)₇B₄, Cr₅B₃ and U₃Si₂ borides structures, thus forming²⁷ a series $\text{M}_{\text{T}2\text{m}+3\text{n}}\text{B}_{\text{m}+2\text{n}}$. The corresponding increase in the boron-metal ratio increases the tendency to form B—B bonds (see also Table 1, §6.7.2 for B aggregation). However, complete boron-metal substitution is found in Ta(Co, B)₂ alloys (CuAl_2 type) at high T¹², bridging the gap between interstitial and substitutional metal borides.

Many ternary borides crystallize with the ordered BaAl₄ or ThCr₂Si₂ structure: $\text{M}_{\text{RE}}\text{Fe}_2\text{B}_2$ ⁵², $\text{M}_{\text{RE}}\text{Co}_2\text{B}_2$ and $\text{Ba}(\text{Rh}, \text{Ir})_2\text{B}_2$ ²⁹. The large rare-earth or alkaline-earth atoms reduce B—B aggregation and the antisquare $\text{M}_{\text{RE}4}\text{Co}_4$ coordination around the isolated borons still dominates²⁸. There is a similarity to the Mo_2CoB_2 type, in which boron pairs are formed according to a much smaller $R_{\text{Mo}}:R_{\text{B}}$ ratio (R = radius).

Trigonal-prismatic boron coordination predominates in borides, $(\text{M}_{\text{T}}, \text{M}_{\text{T}}')_2\text{B}$ with such structures as Fe_2P , anti-PbCl₂ and NbCoB, which all are closely related; NbCoB can be derived as the topochemical sum of the former two³⁰, and at higher T Nb(Ta)CoB transforms into the Fe_2P type³¹.

The close resemblance of the crystal symmetry (Fig. 1) of ZrNiAl (or ordered Fe_2P) borides and $\text{ZrIr}_3\text{B}_{\sim 4}$ is expressed by a common crystallographic supergroup³², the metal sublattice of which corresponds to the structure of anti-NiAs and boron atoms may enter either the O_{h} or the trigonal prismatic voids³³. Occupation of the O_{h} interstices in the NiAs-type metal sublattice occurs with noble-metal monoborides, such as RhB and $\text{PtB}_{0.7}$ ³⁴. Similarly, a group-subgroup relationship exists between the structures of NiAs and WC (RuB, OsB and IrB high-T modification), the borons now filling the trigonal prismatic voids. Finally, in the low-T modification of $\text{IrB}_{0.7}$, both lattice sites of NiAs are occupied by Ir metal atoms, leaving two different interstices for B accommodation: (1) trigonal prismatic voids corresponding to the structure of Ni₂In, and (2) a smaller distorted trigonal-prismatic void, which owing to short B—B distances is only partially occupied in $\text{IrB}_{0.7}$. Considering crystal symmetry, the structure of $\text{IrB}_{0.7}$ forms the missing link of the group-subgroup relationship NiAs-MnP: symmetry reduction of the $\text{IrB}_{0.7}$ metal sublattice leads to filled MnP or anti-PbCl₂ (MoCoB). Now owing to the presence of the smaller Co atoms, however, the metal sublattice in MoCoB³⁵ is not able to accommodate additional B atoms within the small trigonal-prismatic voids of type (2).

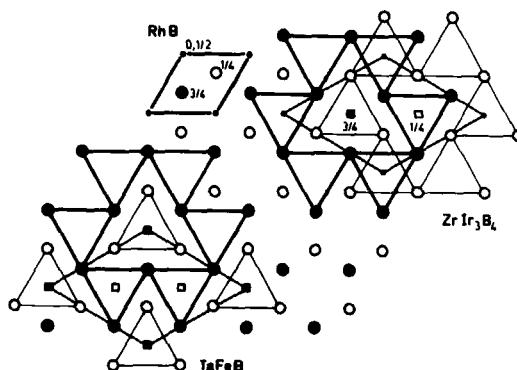


Figure 1. Crystallographic relation (schematic) between the structure types of RhB (anti-NiAs type), TaFeB (ordered Fe₂P type) and ZrIr₃B₄ type. Numbers given indicate heights in projection along [001]. Large circles are metal atoms, small circles are B atoms. Metal sublattice of RhB and different modes of filling the voids (squares) generate the different structure types (see text).

A new structure type with B atoms in O_h metal coordination is found within the Rh-B system: the structure of Rh₅B₄ is characterized by a (chhhc)₂ stacking (BABABCACAC) of 10 closely packed Rh layers⁵⁴. In this case all O_h holes between the layers are fully occupied by isolated B atoms, arranged in linear B₄ groups (B—B ~ 222 pm).

The formation of higher transition-metal borides depends on the competition and the statistical weight of the d⁵ and d¹⁰ states of the metal atoms³⁶. Consequently, the acceptor metals Ni, Pd and Pt are expected to form metal-rich borides only: i.e., besides the known PtB_{0.7} (anti-NiAs), Pt forms two borides, Pt_{~2}B and Pt_{~4}B, which

TABLE 2. CRYSTAL STRUCTURES AND BORON COORDINATION OF PLATINUM METAL BORIDES WITH ISOLATED B ATOMS (OWING TO DEFECT BORON SUBLATTICE)

Structure type	Binary representatives	Ternary representatives	Boron coordination	Type of boron defects
Pt _{~4} B	Pt _{~4} B	No	Trigonal prism	Defect B pairs
Anti-MoS ₂	Pt _{~2} B	No	Trigonal prism	Defect planar net
Anti-CaCl ₂	Pd ₂ B	No	Octahedron	Ordered B sublattice, isolated B atoms
IrB	IrB _{0.7}	No	Trigonal prism	Defect zigzag chains
Anti-NiAs	RhB, PtB _{0.7}	No	Octahedron	Defect linear "chains" (B—B ~ 203 pm)
AlB ₂ (WC)	RuB, OsB, IrB	No	Trigonal prism	Defect planar net
ThSi ₂ (NbP)	IrB	No	Trigonal prism	Defect three-dimensional network

both exhibit extended boron defects owing to short B—B distances³⁴. In this context the nonstoichiometric behavior of metal-rich Pt metal borides (owing to B defects on the boron sublattice; see also Table 2) becomes more understandable. There are, however, few compounds for which the boron sublattice is well established, i.e., from neutron diffraction data. The defects may represent a more complicated B sublattice structure with ordered boron/vacancy arrangements, as in Pd₂B (anti-CaCl₂-type³⁴; NiAs derivative structure with B atoms in every second of the O_h voids).

(P. ROGL)

1. H. Nowotny, P. Rogl, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 411.
2. S. Rundqvist, *Ark. Kem.*, **20**, 67 (1962).
3. U. Herold, U. Köster, *Z. Metallkd.*, **69**, 326 (1978).
4. P. Rogl, J. C. Schuster, H. Nowotny, in *Boron Steel, Proc. Int. Symp.*, 1980, p. 33.
5. N. F. Chaban, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **8**, 933 (1972); *Chem. Abstr.*, **77**, 67,160 (1972).
6. M. L. Borlera, G. Pradelli, *Metall. Ital.*, **59**, 907 (1967).
7. O. T. Inal, L. Keller, F. G. Yost, *J. Mater. Sci.*, **15**, 1947 (1980).
8. W. K. Choo, R. Kaplow, *Met. Trans.*, **8A**, 417 (1977).
9. B. Aronsson, M. Bäckman, S. Rundqvist, *Acta Chem. Scand.*, **14**, 1001 (1960).
10. W. Steurer, P. Rogl, H. Nowotny, paper presented at the VIth International Conference on Solid Compounds of Transition Elements, Stuttgart, June 12–16, 1979.
11. P. Rogl, E. Rudy, *J. Solid-State Chem.*, **24**, 175 (1978).
12. W. Steurer, Thesis, University of Vienna, 1979.
13. W. Jung, D. Quentmeier, *Z. Kristallogr.*, **151**, 121 (1980).
14. K. Niihara, S. Yajima, *Chem. Lett.*, 875 (1972).
15. H. H. Stadelmaier, H. J. Lee, *Z. Metallkd.*, **69**, 685 (1978).
16. M. L. Fiedler, H. H. Stadelmaier, I. K. Simonson, *Z. Metallkd.*, **68**, 356 (1977).
17. E. Rudy, Compendium of Phase Diagram Data, AFML-TR-65-2-5, 1969; *Chem. Abstr.*, **72**, 25,616 (1970).
18. M. L. Borlera, G. Pradelli, *Metall. Ital.*, **7**, 421 (1973); see also *Met. Sci. Technol.*, **1**, 51 (1983).
19. M. L. Borlera, G. Pradelli, *Atti Accad. Naz. Lincei, Mem., Cl. Sci. Fis., Mat. Nat., Sez. 2a*, **10**, 69 (1971); *Chem. Abstr.*, **76**, 157,350 (1972).
20. M. L. Borlera, G. Pradelli, *Metall. Ital.*, **2**, 61 (1971).
21. K. I. Portnoi, V. M. Romashov, *Porosh. Met.*, **12**, 48 (1972); *Chem. Abstr.*, **77**, 98,417 (1972).
22. V. S. Telegus, Yu. B. Kuz'ma, *Porosh. Met.*, **8**, 68 (1968); *Chem. Abstr.*, **69**, 110,405 (1968).
23. Yu. B. Kuz'ma, V. S. Telegus, D. A. Kovalyk, *Porosh. Met.*, **9**, 79 (1969); *Chem. Abstr.*, **71**, 74,691 (1969).
24. G. Pradelli, C. Gianoglio, *Metall. Ital.*, **4**, 191 (1976).
25. V. S. Telegus, Yu. B. Kuz'ma, *Dopov. Akad. Nauk. Ukr. RSR, Ser. A*, **31**, 945 (1969); *Chem. Abstr.*, **72**, 26,053 (1970).
26. M. A. Marko, P. S. Saakyan, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **12**, 1087 (1976); *Chem. Abstr.*, **85**, 152,170 (1976).
27. P. I. Krypyakevich, Yu. B. Kuz'ma, M. V. Chepiga, *Dopov. Akad. Nauk. Ukr. RSR, Ser. A*, **9**, 856 (1972); *Chem. Abstr.*, **78**, 34,811 (1973).
28. P. Rogl, *Monatsh. Chem.*, **104**, 1623 (1973).
29. W. Jung, *Z. Naturforsch., Teil B*, **34**, 1221 (1979).
30. P. I. Krypyakevich, Yu. B. Kuz'ma, Yu. V. Voroshilov, Cl. B. Shoemaker, D. B. Shoemaker, *Acta Crystallogr., Ser. B*, **27**, 257 (1971).
31. P. Rogl, W. Steurer, H. Nowotny, to be published.
32. P. Rogl, H. Nowotny, *J. Less-Common Met.*, **67**, 41 (1979).
33. P. I. Krypyakevich, *Dokl. Akad. Nauk. SSSR*, **79**, 439 (1951).
34. E. Hassler, T. Lundström, L. E. Tergenius, *J. Less-Common Met.*, **67**, 567 (1979).
35. W. Jeitschko, *Acta Crystallogr., Ser. B*, **24**, 930 (1968).

36. G. V. Samsonov, B. A. Kovenskaya, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p.5.
37. G. Pradelli, C. Gianoglio, *Metall. Ital.*, **12**, 659 (1974).
38. Yu. B. Kuz'ma, D. A. Kovalyk, *Inorg. Mater. (USSR)*, **5**, 1428 (1969); *Chem. Abstr.*, **72**, 71,708 (1970).
39. S. Rundqvist, *Acta Chem. Scand.*, **12**, 658 (1958).
40. E. Ganglberger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **97**, 718 (1966).
41. P. Rogl, H. Nowotny, *Monatsh. Chem.*, **104**, 943 (1973).
42. H. Haschke, Thesis, University of Vienna, 1965.
43. M. V. Chepiga, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **9**, 1505 (1973); *Chem. Abstr.*, **80**, 31,242 (1974).
44. S. Rundqvist, *Acta Chem. Scand.*, **16**, 1 (1962).
45. Yu. D. Kondrashev, *Sov. Phys. Crystallogr. (Engl. Transl.)*, **11**, 492 (1967).
46. W. Trzebiatowski, J. Rudzinski, *J. Less-Common Met.*, **6**, 244 (1964).
47. E. Stenberg, *Acta Chem. Scand.*, **15**, 861 (1961).
48. T. Lundström, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 351–376.
49. Yu. B. Kuz'ma, O. M. Rudakevich, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, 164 (1972).
50. Yu. B. Kuz'ma, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, **10**, 939 (1967).
51. S. Rundqvist, F. Jellinek, *Acta Chem. Scand.*, **13**, 425 (1959).
52. G. F. Stepanchikova, Yu. B. Kuz'ma, B. I. Chernjak, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, p. 950 (1978).
53. L. E. Tergenius, *J. Less-Common Met.*, **82**, 335 (1981).
54. B. I. Nöläng, L. E. Tergenius, I. Westman, *J. Less-Common Met.*, **82**, 303 (1981).
55. P. Duhaj, F. Hanic, *Phys. Status Solidi, A*, **62**, 719 (1980).
56. P. Rogl, B. Kunsch, P. Ettmayer, H. Nowotny, W. Steurer, *Z. Kristallogr.*, **160**, 275 (1982).
57. Yu. B. Kuz'ma, G. V. Chernjak, N. F. Chaban, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, (12), **80** (1981); **75**, 699 (1984).
58. Y. Khan, E. Kneller, M. Sostarich, *Z. Metallkd.* **73**, 624 (1982); *Chem. Abstr.*, **96**, 95,318 (1982).
59. H. Klesnar, P. Rogl, research at University of Vienna, to be published.
60. B. Rupp, P. Rogl, F. Hulliger, *J. Less-Common Met.*, **135**, 113 (1987).
61. L. V. Leshko, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **23**, 923 (1987).
62. O. M. Dub, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **23**, 42 (1987).
63. L. G. Akselrud, Yu. B. Kuz'ma, V. A. Byskov, *Dokl. Akad. Nauk Ukr. SSR, Ser. B*, **3**, 33 (1985).
64. K. Remschnig, P. Rogl, research at University of Vienna, to be published.
65. W. Jung, K. Schweitzer, *Z. Kristallogr.*, **174**, 109 (1986).

6.7.2.2. Borides with Boron Chains

6.7.2.2.1. Structure Types with Chain Fragments (B₂, B₃, B₄ Groups).

With increasing B content, the covalent component of the bonding in boride lattices increases owing to the appearance of direct B—B bonds and a decrease in the metallic bond character, e.g., in the structural series of the CuAl₂ family¹: CuAl₂ → (Re, Co)₇B₄ → Cr₅B₃ → U₃Si₂ (for representatives see Table 1). Boron-pair formation is rarely encountered from two B atoms both in antiprismatic coordination; therefore the characteristic structural unit accommodating a B pair is a double prism, sharing a common rectangular face (i.e., Cr₅B₃, U₃Si₂, W₂CoB₂ types). For the compound W₂FeB₂ a low-T form of a W₂CoB₂ type and a partially ordered high-T form with the U₃Si₂-type structure is observed², demonstrating the resemblance of these structure types. The Ce₃B₂N₄ structure is an occupation variant of the W₂CoB₆ type and the structural correspondence may be seen¹⁰⁶ from the

6.7.2. Existence and Crystal Chemistry of Borides

6.7.2.2. Borides with Boron Chains

6.7.2.2.1. Structure Types with Chain Fragments.

36. G. V. Samsonov, B. A. Kovenskaya, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p.5.
37. G. Pradelli, C. Gianoglio, *Metall. Ital.*, **12**, 659 (1974).
38. Yu. B. Kuz'ma, D. A. Kovalyk, *Inorg. Mater. (USSR)*, **5**, 1428 (1969); *Chem. Abstr.*, **72**, 71,708 (1970).
39. S. Rundqvist, *Acta Chem. Scand.*, **12**, 658 (1958).
40. E. Ganglberger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **97**, 718 (1966).
41. P. Rogl, H. Nowotny, *Monatsh. Chem.*, **104**, 943 (1973).
42. H. Haschke, Thesis, University of Vienna, 1965.
43. M. V. Chepiga, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **9**, 1505 (1973); *Chem. Abstr.*, **80**, 31,242 (1974).
44. S. Rundqvist, *Acta Chem. Scand.*, **16**, 1 (1962).
45. Yu. D. Kondrashev, *Sov. Phys. Crystallogr. (Engl. Transl.)*, **11**, 492 (1967).
46. W. Trzebiatowsky, J. Rudzinski, *J. Less-Common Met.*, **6**, 244 (1964).
47. E. Stenberg, *Acta Chem. Scand.*, **15**, 861 (1961).
48. T. Lundström, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 351–376.
49. Yu. B. Kuz'ma, O. M. Rudakevich, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, 164 (1972).
50. Yu. B. Kuz'ma, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, **10**, 939 (1967).
51. S. Rundqvist, F. Jellinek, *Acta Chem. Scand.*, **13**, 425 (1959).
52. G. F. Stepanchikova, Yu. B. Kuz'ma, B. I. Chernjak, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, p. 950 (1978).
53. L. E. Tergenius, *J. Less-Common Met.*, **82**, 335 (1981).
54. B. I. Nöläng, L. E. Tergenius, I. Westman, *J. Less-Common Met.*, **82**, 303 (1981).
55. P. Duhaj, F. Hanic, *Phys. Status Solidi, A*, **62**, 719 (1980).
56. P. Rogl, B. Kunsch, P. Ettmayer, H. Nowotny, W. Steurer, *Z. Kristallogr.*, **160**, 275 (1982).
57. Yu. B. Kuz'ma, G. V. Chernjak, N. F. Chaban, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, (12), **80** (1981); **75**, 699 (1984).
58. Y. Khan, E. Kneller, M. Sostarich, *Z. Metallkd.* **73**, 624 (1982); *Chem. Abstr.*, **96**, 95,318 (1982).
59. H. Klesnar, P. Rogl, research at University of Vienna, to be published.
60. B. Rupp, P. Rogl, F. Hulliger, *J. Less-Common Met.*, **135**, 113 (1987).
61. L. V. Leshko, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **23**, 923 (1987).
62. O. M. Dub, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **23**, 42 (1987).
63. L. G. Akselrud, Yu. B. Kuz'ma, V. A. Byskov, *Dokl. Akad. Nauk Ukr. SSR, Ser. B*, **3**, 33 (1985).
64. K. Remschnig, P. Rogl, research at University of Vienna, to be published.
65. W. Jung, K. Schweitzer, *Z. Kristallogr.*, **174**, 109 (1986).

6.7.2.2. Borides with Boron Chains

6.7.2.2.1. Structure Types with Chain Fragments (B_2 , B_3 , B_4 Groups).

With increasing B content, the covalent component of the bonding in boride lattices increases owing to the appearance of direct B—B bonds and a decrease in the metallic bond character, e.g., in the structural series of the $CuAl_2$ family¹: $CuAl_2 \longrightarrow (Re, Co)_7B_4 \longrightarrow Cr_5B_3 \longrightarrow U_3Si_2$ (for representatives see Table 1). Boron-pair formation is rarely encountered from two B atoms both in antiprismatic coordination; therefore the characteristic structural unit accommodating a B pair is a double prism, sharing a common rectangular face (i.e., Cr_5B_3 , U_3Si_2 , W_2CoB_2 types). For the compound W_2FeB_2 a low-T form of a W_2CoB_2 type and a partially ordered high-T form with the U_3Si_2 -type structure is observed², demonstrating the resemblance of these structure types. The $Ce_3B_2N_4$ structure is an occupation variant of the W_2CoB_6 type and the structural correspondence may be seen¹⁰⁶ from the

TABLE 1. METAL BORIDES: STRUCTURE TYPES AND REPRESENTATIVES WITH BORON PAIRS

Structure type	Boron coordination	Binary representatives	Ternary representatives	Refs.
Cr_5B_3 I4/mcm	B(1) isolated: archimedian antiprism BCr_8 B(2) trigonal prismatic BCr_{6+2} B(2)-B(2) pair formation Trigonal prism BM_{6+2}	Cr_5B_3 ¹⁹	Cr_5PB_2 Mn_5PB_2 ²¹ , Fe_5PB_2 ²¹ , Co_5PB_2 ²¹ , Mo_5SiB_2 ^{22,49} , $\text{W}_5\text{Si}_{1.5}\text{B}_{1.5}$ ²² , Mn_5SiB_2 ²³ , Fe_5SiB_2 ²³ , V_5SiB_2 ²⁴ $\text{Nb}_5\text{Si}_{3-x}\text{B}_x^*$ ($x \leq 2$, 1600°C) $\text{Nb}_5\text{Ge}_2\text{B}$, $\text{Ta}_5\text{Ge}_2\text{B}$ $\text{Cr}_{1.8}\text{W}_{3.2}\text{B}_3$ $\text{Ti}_{2.5-2.0}\text{Re}_{0.5-1.0}\text{B}_2$ (1400°C) $\text{Nb}_{1.5}\text{Re}_{1.5}\text{B}_2$ $\text{Ta}_{1.5}\text{Re}_{1.5}\text{B}_2$ $\text{Mo}_{2-1.5}\text{Cr}_{1-1.5}\text{B}_2$, (1400°C) $\text{Mo}_{1.8-2.0}\text{Mn}_{1.2-1.0}\text{B}_2$ (800°C) $\text{W}_{1.8-2.0}\text{Mn}_{1.2-1.0}\text{B}_2$ (800°C) Mo_2FeB_2 $\text{W}_{1.75-1.8}\text{Fe}_{1.25-1.2}\text{B}_2$ (1500°C) high-T phase > 1300°C $\text{Ba}_7\text{Ir}_{12}\text{B}_{12}$	20 51 15 25 27 28 29 30 31 31 32, 33 34, 35 2
U_3Si_2 P4/mbm		V_3B_2 , Nb_3B_2 , $\text{Ta}_3\text{B}_{1.87}$		
$\text{Ba}_7\text{Ir}_{12}\text{B}_{12}$ $\text{R}\bar{3}\text{m}$	Trigonal prism $\text{BIr}_4\text{Ba}_{2+2}$, isolated boron plus boron pairs	—	Mo_2CoB_2 , Mo_2NiB_2 W_2FeB_2 (low-temperature phase < 1300°C) W_2CoB_2 , W_2NiB_2 $\text{V}_{1.8-2.0}\text{Ir}_{1.2-1.0}\text{B}_2$ (1400°C) Cr_2IrB_2 , Mo_2IrB_2 , $\text{Mo}_{1.75}\text{Ru}_{1.25}\text{B}_2$, $\text{W}_{1.75}\text{Ru}_{1.25}\text{B}_2$, $\text{V}_{1.8}\text{Os}_{1.2}\text{B}_2$, Mo_2OsB_2 , $\text{W}_{1.85-2}\text{Os}_{1.15-1}\text{B}_2$, at 1600°C ($\text{M}_{\text{T}2}\text{M}_{\text{T}}\text{B}_2$ phases)	2, 32, 36
Mo_2CoB_2 Immm	Trigonal prism BM_{6+2}	—		
Mo_2IrB_2 Pnnm	Trigonal prism $\text{BIr}_2\text{Mo}_{4+2}$, BIr_4Mo_2 , formation of B_4 groups	—		

(continued)

TABLE 1. (continued)

Structure type	Boron coordination	Binary representatives	Ternary representatives	Refs.
W_3CoB_3 Cmcm	Trigonal prism BW_{6+1} , BCo_2W_{4+1} , formation of B_3 groups	—	Mo_3CoB_3 , Mo_3NiB_3 , W_3CoB_3 , W_3NiB_3	5, 32
$Nd_2Fe_{23}B_3$ I43d	Trigonal prism, BF_6 B pairs	—	$Nd_2Fe_{23}B_3$	107
$Sc_4Ni_{29}B_{10}$ $I4_1/amd$	Cubeoctahedron, antiprism, isolated borons + B pairs	—	$M_{RE4}Ni_{29}B_{10}$; $M_{RE} = Sc, Er, Tm, Yb, Lu$	108
$Ho_2Ni_{15}B_6$ $P2_1/c$	Tetragonal prism, isolated borons + B pairs	—	$M_{RE2}Ni_{15}B_6$; $M_{RE} = Y, Tb, Dy, Ho, Er, Tm, Yb, Lu$	111
$Ho_3Ni_{19}B_{10}$ $A2/m$	Antiprism, trigonal prism, isolated borons + B pairs	—	$Ho_3Ni_{19}B_{10}$	112
$Ho_2Ni_{15}B_9$ Cmca	Antiprism, trigonal prism, isolated borons + B pairs	—	$M_{RE2}Ni_{15}B_9$; $M_{RE} = Y, Tb, Dy, Ho, Er, Tm, Yb, Lu$	111
$Nd_2Ni_3B_4$ $C2/m$	Trigonal prism, BNd_2Ni_4 , formation of B_4 groups	—	$M_{RE2}Ni_5B_4$; $M_{RE} = La (?), Nd$	109
$Pr_8Re_{13-x}B_{12}$ $R\bar{3}m$	Trigonal prism, Pr_4Re_2 , antiprism, Pr_4Re_4	—	$Pr_8Re_{13-x}B_{12}$	110

$\text{Mg}_2\text{IrB}_{2-x}$ C2/m	Trigonal prism, $\text{BIr}_2\text{Mg}_{4+}$, B pairs	—	$\text{Mg}_2\text{IrB}_{2-x}$	98
$\text{Ce}_3\text{B}_2\text{N}_4$ Immm	Trigonal prism, BCe_6 , B pairs	—	$\text{M}_{\text{RE}3}\text{B}_2\text{N}_4$; $\text{M}_{\text{RE}} = \text{La, Ce, Pr, Nd}$	106
$\text{Ca}_2\text{Os}_3\text{B}_5$ C2	Boron-osmium layer with the formation of B_4 groups	—	$\text{Ca}_2\text{Os}_3\text{B}_5$, $\text{Eu}_2\text{Os}_3\text{B}_5$	100
$\text{Al}_5\text{Ru}_9\text{B}_6$ P4/m	Trigonal prism, BRu_6 formation of B_4 groups	—	$\text{Al}_5\text{Ru}_9\text{B}_6$, $\text{Zn}_5\text{Ru}_8\text{B}_8$	99
CeCo_4B_4 P4 ₂ /nmc	Trigonal prism $\text{BCe}_2\text{Co}_{4+1}$	—	A. Ternary systems $\text{M}_{\text{RE}}\text{Co}_4\text{B}_4$: $\text{M}_{\text{RE}} = \text{Sc}^{48}, \text{Y, Ce, Gd, Tb, Dy, Ho, Er, Tm, Yb}^{52}, \text{Lu}$ UCo_4B_4 $\text{M}_{\text{RE}}\text{Rh}_4\text{B}_4$: $\text{M}_{\text{RE}} = \text{Y}^{14}, \text{Ce (hp), Pr (hp), Nd (hp)}$ (see refs. 101, 104, 105) Sm^{14} , Gd, Tb, Dy, Ho, Er ¹⁰² , Tm, Lu $\text{M}_{\text{AN}}\text{Rh}_4\text{B}_4$; $\text{M}_{\text{AN}} = \text{Th}$ $\text{M}_{\text{RE}}\text{Ir}_4\text{B}_4$: $\text{M}_{\text{RE}} = \text{Ho, Er, Tm (all metastable)}$	7 38 38 14, 36 60
			B. Quaternary and higher order systems $\text{Ca}_{0.7}\text{Sc}_{0.3}\text{Rh}_4\text{B}_4$ $\text{M}_{\text{RE}}\text{Sc}_{1-x}\text{Rh}_4\text{B}_4$ [high-T phase for $x = 0.7$; $\text{M}_{\text{RE}} = \text{Ce, Pr, Nd, Sm, Tb, Dy, Ho (x = 0.6), Er, Tm}$	37 37

(continued)

TABLE 1. (continued)

Structure type	Boron coordination	Binary representatives	Ternary representatives	Refs.
NdCo ₄ B ₄ P4 ₂ /n	Trigonal prism BNd ₂ Co ₄	—	Dy(Rh _{1-x} Ir _x) ₄ B ₄ ($x < 0.9$)	55
			Gd _x Er _{1-x} Rh ₄ B ₄	57
			Gd _x Ho _{1-x} Rh ₄ B ₄	114
			ErCo _x Rh _{1-x} B ₄ ($0.7 \leq x \leq 1$)	58
			Er _{1-x} Ho _x Rh ₄ B ₄	59, 72
			Er(Ir _x Rh _{1-x}) ₄ B ₄	60
			Er _x Sm _{1-x} Rh ₄ B ₄	62
			Er _x Tm _{1-x} Rh ₄ B ₄	63, 71
			Er _x Y _{1-x} Rh ₄ B ₄	64
			Gd _x Y _{1-x} Rh ₄ B ₄	65
			Ho(Rh _x Ir _{1-x}) ₄ B ₄ ($x \geq 0.15$)	55, 66, 73
			Lu _{1-x} Y _x Ir ₄ B ₄ (metastable for 0.1 < $x < 0.7$)	60
			Lu _x Th _{1-x} Rh ₄ B ₄	36, 69
			Ho _x La _{1-x} Rh ₄ B ₄	115
			Lu _x Y _{1-x} Rh ₄ B ₄	69
			Sc _x Th _{1-x} Rh ₄ B ₄ ($x \leq 0.8$)	36, 37
			(Sc _x Y _{1-x})(Ir _{0.9} Rh _{0.1}) ₄ B ₄ ($x = 0.1, 0.2,$ 0.25, 0.3, 0.5)	60
			Y _x Th _{1-x} Rh ₄ B ₄	70
			Lu _x Y _{1-x} Rh ₄ B ₄	69
			A. Ternary systems	
			M _{RE} Co ₄ B ₄ : M _{RE} = La, Pr, Nd, Sm	9
			M _{RE} Ru ₄ B ₄ : M _{RE} = La	12
			M _{RE} Os ₄ B ₄ : M _{RE} = La, Ce, Pr, Nd, Sm, Eu ⁵³	39, 40, 53
			M _{AN} Os ₄ B ₄ : M _{AN} = Th	13
			M _{RE} Ir ₄ B ₄ : M _{RE} = Y, La ¹³ , Ce, Pr, Nd, Sm, Eu ⁵³ , Gd, Tb; Dy (metastable)	39, 40, 53
			M _{AN} Ir ₄ B ₄ : M _{AN} = Th, Pu	13 97

LuRh ₄ B ₄ Ccca	Unusually short B—B distances (145 pm); boron defect? Triagonal prism BLu ₂ Ru ₄₊₁	—	B. Quaternary and higher order systems	
			LaIr _{4-x} Os _x B ₄ (x = 1, 2, 3)	40
LuRu ₄ B ₄ I4 ₁ /acd		—	PrIr _{4-x} Os _x B ₄ (x = 2)	40
			CeIr _{4-x} Os _x B ₄ (x = 1, 1.52, 2, 2.2, 2.5, 2.7, 3)	53
			SmIr _{4-x} Os _x B ₄ (x = 1, 2, 3)	53
			M _{RE} Rh _{4+x} B ₄ : M _{RE} = Er, Tm, Yb, Lu (x ≤ 0.05, low-T modifications?)	46
			A. Ternary systems	
			M _{RE} Ru ₄ B ₄ : M _{RE} = Sc ⁴² , Y ^{9,15} , Ce, Pr (metastable), Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	8
			M _{AN} Ru ₄ B ₄ : M _{AN} = Th, U, Pu	4, 13, 97
			M _{RE} Rh ₄ B ₄ : M _{RE} = Y, all Ln (except La, Ce) claimed to exist under metastable conditions, no lattice parameters available yet; ErRh ₄ B _{4-x} ¹⁰³	3
			M _{AN} Os ₄ B ₄ : M _{AN} = U	13
			B. Quaternary and higher order systems	
			M _{REx} Sc _{1-x} Rh ₄ B ₄ (low-T phase for x = 0.7; M _{RE} = Sm, Gd, Ho)	37
			M _{RE} (Rh _{0.85} Ru _{0.15}) ₄ B ₄ (M _{RE} = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)	8
			Dy(Ru _x Rh _{1-x}) ₄ B ₄ (0.1 < x ≤ 1)	56
			Er(Co _x Rh _{1-x}) ₄ B ₄ (0 ≤ x ≤ 0.3)	58
			Er(Rh _{1-x} Ru _x) ₄ B ₄	61

(continued)

TABLE 1. (continued)

Structure type	Boron coordination	Binary representatives	Ternary representatives	Refs.
YOs ₄ B ₄ NdCo ₄ B ₄ -type derivative	Trigonal prism	—	La _{1-x} Lu _x (Rh _{0.88} Ru _{0.15}) ₄ B ₄ (x > 0.3)	67
			Lu _x Sc _{1-x} Ru ₄ B ₄ (x = 0.1, 0.3, 0.5, 0.7, 0.9)	41
			Ca _{0.7} Sc _{0.3} Rh ₄ B ₄ (?) Y(Ru _{1-x} Rh _x) ₄ B ₄ (x = 0.3, 0.5, 0.6, 0.8) M _{RE} Os ₄ B ₄ : M _{RE} = Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	37 8, 14, 116
Ce _{1+x} Fe ₄ B ₄ NdCo ₄ B ₄ -type derivative P4 ₂ /n (or Pccn ¹¹³) LuRuB ₂ Pnma	Trigonal prism	—	M _{AN} Os ₄ B ₄ : M _{AN} = Pu M _{RE1+x} Fe ₄ B ₄ : M _{RE} = Ce, Pr, Nd, Sm, Gd, Tb (see also Table 2) M _{RE} Fe ₄ B ₄ (?): M _{RE} = Y ⁴⁴ , Ce ⁴⁴ , Nd ⁴³ (P4/ncc?) Sm ⁴³ , Gd ⁴³ , Dy ⁹⁴ , Er ⁹⁴ A. Ternary systems M _{RE} RuB ₂ : M _{RE} = Y, Ce ⁹⁶ , Gd ⁹⁶ , Tb, Dy, Ho, Er, Tm, Lu M _{RE} OsB ₂ : M _{RE} = Sc, Y, Gd ⁹⁶ , Tb, Dy, Ho, Er, Tm, Lu, Yb ⁹⁶ PuM _T B ₂ : M _T = Tc, Re, Ru, Os B. Quaternary systems (M _{RE1-x} Lu _x)RuB ₂ (x = 0.8, 0.9, M _{RE} = Gd, Tb, Dy, Ho, Er, Tm) Lu _x Tm _{1-x} RuB ₂ Y _x Sc _{1-x} RuB ₂ (x = 0.8)	42 97 54, 113

*A high-T modification of Nb₅Si₃ crystallizes with the Cr₂B₃ type, Si—B substitution stabilizes the high-T form to lower T reaching far into the ternary system. The stabilization of the homologous Ta₅(Si, B)₃, however, is far less pronounced.

structural chemical identity $\text{Ce}_3\text{B}_2\text{N}_4 \equiv (\text{W}_2\text{Co})\text{B}_2 \square_4$. The structure of $\text{Ce}_3\text{B}_2\text{N}_4$ is also isopointal with the structure type of $\text{CeCr}_2\text{B}_6 \equiv (\text{CeCr}_2)\text{B}_2\text{B}_4$ (see §6.7.2.3).

A larger ratio ($R_{\text{Ba}} : R_{\text{Ir}} > R_{\text{W}} : R_{\text{Co}}$) explains the formation of distorted trigonalprismatic (BIr_4Ba_2) coordination for B pairs as well as the existence of isolated B atoms² in $\text{Ba}_7\text{Ir}_{12}\text{B}_{12}$. Similarly, $\text{Mg}_2\text{IrB}_{2-x}$, as a monoclinic derivative of the W_2CoB_2 type, contains boron pairs and/or B atoms on a prism edge⁹⁸; NaIr_3B_4 is closely related. From interatomic distances in ternary borides of the type $\text{M}_{\text{RE}}(\text{M}_{\text{AE}})\text{—M}_{\text{T}}\text{—B}$ (M_{RE} = rare earth, M_{AE} = alkaline earth, M_{T} = transition metal), a tendency toward stronger $\text{M}_{\text{RE}}(\text{M}_{\text{AE}})\text{—B}$ interaction is derived, whereas $\text{M}_{\text{RE}}(\text{M}_{\text{AE}})\text{—B}$ bonding is weak. As a consequence the large atoms reduce B—B aggregation. Similarly, isolated B atoms are found in CeCo_3B_2 -type borides, but B pair formation occurs in ZrCo_3B_2 (CeCo_3B_2 superstructure; see also §6.7.2.1) for a more favorable ratio of radii $R_{\text{Zr}} : R_{\text{Co}}$.

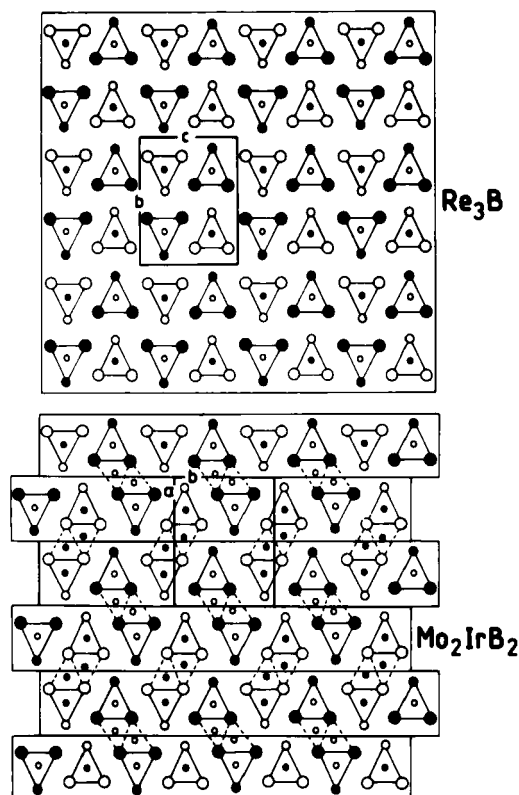


Figure 1. Relationship among the crystal structures of Re_3B and Mo_2IrB_2 . Full circles are atoms in $1/2$; open circles are atoms in 0 ; the two metal sites in Re_3B (8f and 4b) are differentiated by larger and smaller circles; smallest circles are B atoms. The structure of Mo_2IrB_2 is generated by a shift of every second prism row of Re_3B (vector $c/4$).

Boron pairs in distorted double prisms or distorted antiprisms of rare-earth nonmetal atoms are also encountered from the structure types of $\text{Sc}_4\text{Ni}_{29}\text{B}_{10}$ (earlier denoted ScNi_4B_4)¹⁰⁸, $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ ¹⁰⁷, $\text{Ho}_2\text{Ni}_{15}\text{B}_6$ ¹¹¹, $\text{Ho}_3\text{Ni}_{19}\text{B}_{10}$ ¹¹², $\text{Ho}_2\text{Ni}_{15}\text{B}_9$ ¹¹¹ and $\text{Pr}_8\text{Re}_{13-x}\text{B}_{12}$ ¹¹⁰. The LuRuB_2 structure³ is formed from alternating, antisymmetric planar 4.3.4.3² layers of Lu and Ru atoms in $y = 1/4, 3/4$. Although the metal atom parameters correspond to those of the anti- PbCl_2 type—as encountered, e.g., in the boride structure of MoCoB^4 —the architecture of both structures is different. Rows of face-connected trigonal prisms Lu_3Ru_3 run parallel [010] and accommodate B—B pairs at a bonding distance of 174 pm. Owing to the high $R_{\text{RE}}:R_{\text{Ru}}$ ratio, B pairs remain separated from each other by only ~ 196 pm, revealing the strong tendency toward B chain formation as expected from the ratio $M:B = 1$. Indeed a closer relation is found to typical chain borides, such as FeB or m-, o- Ni_3B_4 : a shift operation transforms the FeB-type cell into the unit cell of LuRuB_2 .

Linking of more than two boron-centered trigonal prisms along common rectangular faces leads to the formation of B_3 groups (W_3CoB_3 type)⁵ and B_4 groups (Mo_2IrB_2 type)⁶, which may be regarded as chain fragments. The ordered metal sublattice of the Mo_2IrB_2 type corresponds to the Re_3B metal sublattice by a simple transposition (Fig. 1) of each second prism row by a vector $c/4$ (Re_3B). No representatives are known among binary borides, but the formation of ternary Mo_2IrB_2 compounds is regulated by a constant electron-atom ratio, $e:a = 5.2$; i.e., the combination of two different transition metals is adjusted so as to form a group-VIIA

TABLE 2. LATTICE PARAMETERS AND REPEAT UNITS OF THE IRON AND RARE-EARTH SUBLATTICES (IN Å) $M_{\text{RE}1+m}\text{Fe}_4\text{B}_4$ COMPOUNDS $[M_{\text{RE}1+m}(\text{Fe}_4\text{B}_4)_n]_n$, AS OBTAINED FROM SINGLE-CRYSTAL X-RAY DATA^a

RE	Ce	Pr	Nd	Sm	Gd	Tb
a	7.090(1)	7.158(1)	7.141(3)	7.098(1)	7.073(3)	7.049(1)
c_{Fe}	3.9102(3)	3.9042(5)	3.9073(7)	3.9124(5)	3.9217(4)	3.919(1)
c_{R}	3.4889(4)	3.5301(2)	3.5241(7)	3.4574(2)	3.442(1)	3.4109(4)
$c_{\text{Fe}}/c_{\text{R}}$	1.1208(5)	1.1060(5)	1.1087(11)	1.1316(6)	1.1394(12)	1.1490(12)
$m = 1, n =$	8	10	9	8	7	7
$(n + m)/n$	1.1250	1.1000	1.1111	1.1250	1.1429	1.1429
$m = 2, n =$	17	19	19	15	15	13
$(n + m)/n$	1.1176	<u>1.1053</u>	1.1053	<u>1.1333</u>	1.1333	1.1538
$m = 3, n =$	25	28	28	23	22	20
$(n + m)/n$	1.1200	1.1071	1.1071	1.1304	1.1364	1.1500
$m = 4, n =$	33	39	37	31	29	27
$(n + m)/n$	<u>1.1212</u>	1.1026	<u>1.1081</u>	1.1290	<u>1.1379</u>	1.1481
c	129.04	74.18	144.57	58.69	113.73	105.81

^a The numbers in parentheses correspond to 1 estimated standard deviation (esd), except those for the $c_{\text{Fe}}:c_{\text{R}}$ ratio, which correspond to 3 esd. The values of n and m shown are the smallest integers for which the ratio $(n + m)/n$ lies within the experimental error limits of the measured axial ratio $c_{\text{Fe}}:c_{\text{R}} \approx 1 + \epsilon$. The c parameters in the bottom line refer to the supercells corresponding to the underlined $(n + m)/n$ values⁵⁵

6.7.2.2. Borides with Boron Chains

6.7.2.2.1. Structure Types with Chain Fragments.

pseudoelement⁶. Four-membered boron-pair zigzag chain fragments are also encountered among the structure types $\text{Nd}_2\text{Ni}_5\text{B}_4$ ¹⁰⁹, $\text{Al}_5\text{Ru}_9\text{B}_6$ ⁹⁹ and $\text{Ca}_2\text{Os}_3\text{B}_5$ ¹⁰⁰; in the latter type an interesting B-Os layer is formed, sandwiching the large Ca atoms.

While chain B_5 boron arrangements are still lacking, five-, six- and seven-membered B rings commonly are observed from two-dimensional B nets with B atoms in trigonalprismatic metal coordination (see §6.7.2.3).

Because they exhibit interplay of magnetic and superconducting properties, the formation and crystal chemistry of $\text{M}_{\text{RE}}\text{M}_{\text{T}4}\text{B}_4$ compounds have been examined. Ternary rare-earth and actinide (Th, U, Pu)-transition metal borides of the approxi-

	Mn	Tc	Re	Fe	Ru	Os	Co	Rh	Ir	Ni	Pd	Pt
Sc					b							
Y			d	e	h,i		a	g,h	m			
La			d		k	m	j			l		
Ce			d	f	i	m	a			m		
Pr					i	m	j			m		
Nd			f	i	m	j		g	m			
Pm												
Sm			f	i	m	j		g,h	m			
Eu					i	n			n			
Gd			q	f	i	o	a	g	m			
Tb					i	o	a	g	m			
Dy			q		i	o	a	g				
Ho			q		i	o	a	g				
Er					i	o	a		g,p			
Tm					i	o	a		g,p			
Yb					i	o	r		p			
Lu					i	o	a		g,p			
U					l	l	c					
Pa												
Th					i	l		g,h	l			

■ CeCo_4B_4

▣ NdCo_4B_4

□ LuRh_4B_4

▤ LuRu_4B_4

⊠ YOs_4B_4

⊞ YFe_4B_4

⊠ RERe_4B_4

Figure 2. Formation of ternary borides $\text{M}_{\text{RE}}\text{M}_{\text{T}4}\text{B}_4$ (M_{RE} = rare-earth element, M_{T} = transition metal) and different structure types. ■, CeCo_4B_4 type; ▣, LuRu_4B_4 type; ▤, NdCo_4B_4 type; ⊠, YOs_4B_4 type; ⊞, $\text{Sm}_{1-x}\text{Fe}_x\text{B}_4$ type; ⊠, $\text{M}_{\text{RE}}\text{Re}_4\text{B}_4$ type; □, LuRh_4B_4 type. Refs: a⁷, b⁴¹, c³⁸, d¹¹, e⁴⁴, f⁴³, g³⁶, h¹⁴, i⁸, j⁹, k¹², l¹³, m³⁹, n⁵³, o⁴², p⁴⁶, q⁴⁷, r⁴⁸, s⁵⁴, t⁵¹, u⁵², v¹⁸, w⁷⁴, x⁷⁵, y⁷⁶, z¹⁰¹.

TABLE 3. GEOMETRICAL RELATIONSHIP BETWEEN THE DIFFERENT STRUCTURE TYPES

 $M_{RE}M_{T4}B_4$ ($M_T = Co, Ru, Rh, Os, Ir$)

$LuRu_4B_4-CeCo_4B_4$	$LuRh_4B_4-CeCo_4B_4$	$NdCo_4B_4-CeCo_4B_4$
$a(LuRu_4B_4) \sim \sqrt{2} a(CeCo_4B_4)$	$a(LuRh_4B_4) \sim c(CeCo_4B_4)$	$a(NdCo_4B_4) \sim \sqrt{2} a(CeCo_4B_4)$
$c(LuRu_4B_4) \sim 2a\sqrt{2}(CeCo_4B_4)$	$b(LuRh_4B_4) \sim 3\sqrt{2} a(CeCo_4B_4)$	$c(NdCo_4B_4) \sim \frac{1}{2}c(CeCo_4B_4)$
	$c(LuRh_4B_4) \sim a\sqrt{2}(CeCo_4B_4)$	
$YOs_4B_4-NdCo_4B_4$		
	$a(YOs_4B_4) \sim a(NdCo_4B_4)$	
	$c(YOs_4B_4) \sim 8c(NdCo_4B_4)$	

mate formula $M_{RE}(M_{AN})M_{T4}B_4$ crystallize in at least six different structure types: $CeCo_4B_4$ ⁷, $LuRu_4B_4$ ⁸, $NdCo_4B_4$ ⁹, YOs_4B_4 ¹⁰ and $LuRh_4B_4$ ⁴⁶. For rare-earth compounds (Y, La, Ce, Sm, Gd, Dy, Ho) Re_4B_4 a different but unsolved structure is observed^{11,47}. Superstructures of the $M_{RE_{n+m}}(Fe_4B_4)_n$ formula, the crystal structures of which derive from the $NdCo_4B_4$ type, are either incommensurate or have large repeat units along the c axis and some ambiguity exists as far as crystal symmetry is concerned (compare refs. 44, 54, 113; see also Table 2). A closer inspection of phase equilibria carried out for $Gd_xFe_4B_4$ gives compositions $0.95 \leq x \leq 1.35$, which indicate a homogeneous range at 1000°C, insofar as the Gd subcell parameter changes within $3.40 \leq \tau_{Gd} \leq 3.48$, and decreases with increasing Gd content⁵⁴. Stabilization of the different structures for a specific elemental combination is controlled by B defects; for example, short boron-boron distances of ~ 145 pm observed in $LuRh_{4+\epsilon}B_4$ ($0 < \epsilon < 0.3$)⁴¹ suggest incomplete occupation of the B sites. The formation of $M_{RE}M_TB_4$ borides and distribution of the different structures is reviewed in Table 1 and Fig. 2.

Formation of tetrahedral M_{T4} clusters is the structural unit common to all known $M_{RE}M_{T4}B_4$ -type phases with strong M_TB , but weak $B-M_{RE}$ interaction in accord to the characterization of $M_{RE}-M_TB$ borides. Involving two remote M_{RE} atoms, the B coordination resembles a distorted trigonal metal prism $M_{T4}M_{RE2}$, but with two M_{RE} atoms at large distances this coordination gives a more open polyhedron.

Simple geometric relations exist for the packing mode of the M_{T4} units within the different structure types $M_{RE}M_{T4}B_4$ for details see also Table 3 and Fig. 3^{13,46}.

The structures of YOs_4B_4 ¹⁰, YFe_4B_4 ¹⁶ and $M_{RE_{n+m}}(Fe_4B_4)_n$ ⁵⁴ contain $NdCo_4B_4$ superstructures where edge-connected M_{T4} units are arranged as to form eight-sided infinite tubes along [001] which are centered by infinite and linear chains of the rare-earth atoms.

From crystal symmetry a resemblance is found for the architecture of the $NdCo_4B_4$ and Ti_3P structures, both crystallizing with space group $P4_2/n$. The two intergrown $Ti_4 + P_4$ tetrahedra form a spherical structure element that on substitution by one large rare-earth atom and according to the crystal chemical identity: $(Ti_4 + P_4)_2Ti_8Ti_8 = Nd_2Co_8B_8$ (Fig. 4) yields the $NdCo_4B_4$ structure. Based on this crystallographic correspondence a correlation is derived for the structural series of

6.7.2.2. Borides with Boron Chains

6.7.2.2.1. Structure Types with Chain Fragments.

	Mn	Tc	Re	Fe	Ru	Os	Co	Rh	Ir	Ni	Pd	Pt
Sc					b		r			? w		
Y			d	e	h,i	o	a	g,h	m			
La			d	y	k	m	j		l			
Ce			d	e,s	i	m	a	zP	m			
Pr				s	i*	m	j	z,gP	m			
Nd				f,s	i	m	j	z,g,P	m			
Pm												
Sm			x	f,s	i	m	j	g,h	m			
Eu					i	n			n			
Gd			q	f,s	i	o	a	g	m			
Tb				s	i	o	a	g	m			
Dy			q		i	o	a	g	m*			
Ho			q		i	o	a	g	v*			
Er					i	o	a	g,p	v*			
Tm					i	o	a	g,p	v*			
Yb					i	o	u	p				
Lu					i	o	a	g,p				
Th					i	l		g,h	l			
Pa												
U					l	l	c					
Np												
Pu					t	t			t			

■ CeCo_4B_4

▣ NdCo_4B_4

□ LuRh_4B_4

▤ LuRu_4B_4

⊠ YOs_4B_4

⊞ $\text{Sm}_{1.0}\text{Fe}_4\text{B}_4$

⊠ RERe_4B_4

* metastable

P high pressure phase

Figure 3. (a) Comparison of the crystal structures of CeCo_4B_4 and NdCo_4B_4 , projected along [001]. Largest circles are rare-earth atoms; tetrahedra are formed by transition-metal atoms (Co), their size depending on height in projection. Smallest circles are B atoms. Boron coordination figures are distorted trigonal prisms; distances that exceed the sum of radii are indicated by dashed lines. (b) Structure relation between the crystal structures of CeCo_4B_4 (projected along [001]) and of LuRu_4B_4 [001]. The atomic arrangement of LuRu_4B_4 consists of alternating slabs of CeCo_4B_4 -type structure and its mirrored counterpart.

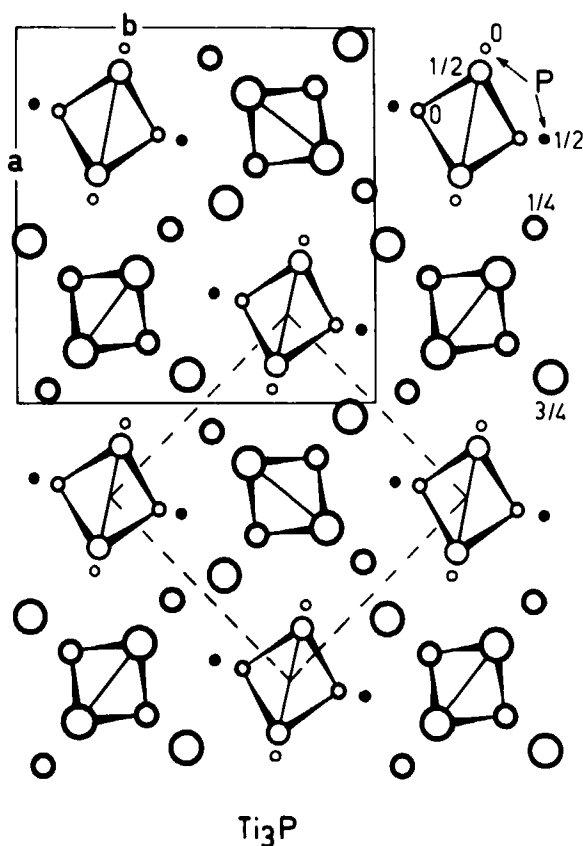
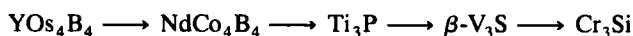


Figure 4. Projection of the crystal structure of Ti_3P along $[001]$ and relation to the structure type of NdCo_4B_4 (broken line).

related structure types:



A crystallographic group-subgroup relationship exists¹⁰ for the pair $\beta\text{-V}_3\text{S}$ – Ti_3P , whereas the relation $\beta\text{-V}_3\text{Si}$ – Cr_3Si (discussed earlier⁷⁷) leads further to the structure of $\text{Cr}_3\text{Si}(\text{Al}_5)$, which is adopted by superconducting compounds with critical temperatures as high as 25 K. Alternatively, both the LuRu_4B_4 and LuRh_4B_4 structures are based upon the CeCo_4B_4 parent and derive by simple shift or rotational operations of CeCo_4B_4 -type slabs. The feature common to these CeCo_4B_4 structures is the alternating sequence of rare-earth atoms and $\text{M}_{\text{T}4}$ units. Therefore, the pattern of the structure of CeCo_4B_4 , LuRu_4B_4 and LuRh_4B_4 can be interpreted in terms of a simple NaCl-type arrangement of rare-earth atoms as well as of $\text{M}_{\text{T}4}$ clusters. Furthermore, one additional M_{T} atom in the B coordination $\text{M}_{\text{RE}2}\text{M}_{\text{T}4+1}$ and no direct $\text{M}_{\text{RE}}\text{--M}_{\text{RE}}$ contacts indicate a better space filling for the CeCo_4B_4 derivative

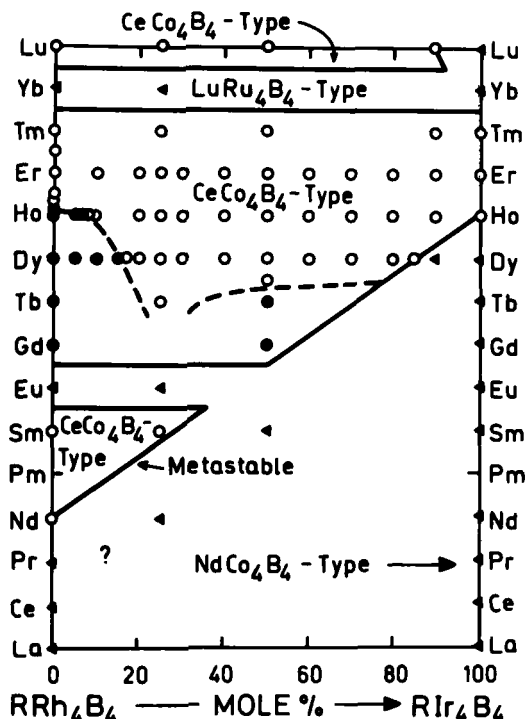


Figure 5. Concentrational sections $M_{RE}(Ir_xRh_{1-x})_4B_4$: phase boundaries (schematic) of different structure types. Open circles indicate the occurrence of superconductivity; filled symbols mean $T_n = 1.2$ K (no superconductivity observed above 1.2 K). Circles denote the existence of a CeCo₄B₄-type phase; the thick solid line represents the (metastable) phase boundary of the CeCo₄B₄-type structure; the dashed line encloses the superconductivity region⁸⁵.

phases with respect to the NdCo₄B₄ type, which consequently is favored by the largest rare-earth members and Th. The influence of size is also supported by the existence of LaRu₄B₄ with a NdCo₄B₄ structure¹². However, differences in the electronic structure of the equally large noble-metal atoms are strong enough to confine the influence of size within each isotopic series of compounds¹³. The critical influence of the electron-atom ratio is reflected in that replacement of as few as 15% of Rh by Ru changes the structure type of $M_{RE}(Rh, Ru)_4B_4$ borides from CeCo₄B₄ to LuRu₄B₄^{8,16}. Therefore, the LuRu₄B₄-type is a metastable polymorph of the $M_{RE}Rh_4B_4$ borides⁸. Boron deficiency, i.e., however, may exert a stabilizing role in the selection of the various structure types; e.g., ErRh₄B₄ is known to exist with the CeCo₄B₄ structure¹⁰² and is claimed to adapt the LuRu₄B₄ structure⁸ and the LuRh_{4+E}B₄ structure⁴⁶ with small deficiencies in the B content.

Metastable compounds crystallizing with CeCo₄B₄ structures⁶⁰ are reported for the combinations $M_{RE}Ir_4B_4$ ($M_{RE} = Ho, Er, Tm$) and for the solid solution $(Y_xLu_{1-x})Ir_4B_4$ with $0.2 \leq x \leq 0.7$. Similarly, neither Ca nor Sc form a $M_{RE}Rh_4B_4$

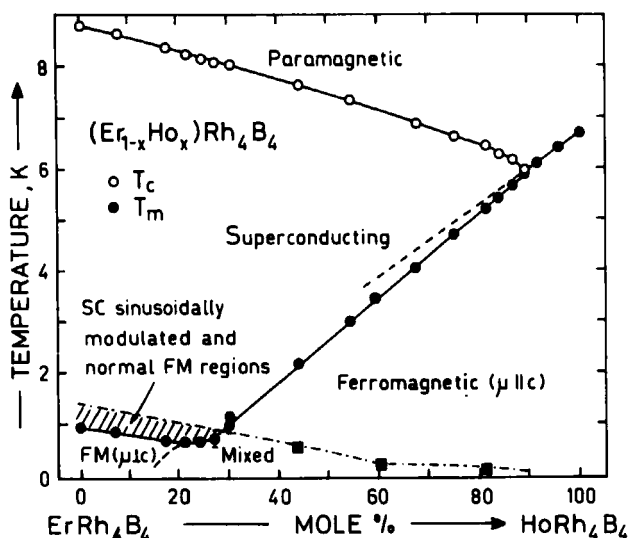


Figure 6. System $\text{Er}_{1-x}\text{Ho}_x\text{Rh}_4\text{B}_4$: low-T phase diagram^{59,72}.

compound, but on substitution of $\sim 30\%$ Ca for Sc, a high-T (CeCo_4B_4 -type) and a low-T (LuRu_4B_4 type?) modification is claimed. Stabilization of a $\text{M}_{\text{RE}}\text{Rh}_4\text{B}_4$ phase is also observed in arc-melted alloys³⁷, $\text{M}_{\text{RE}0.7}\text{Sc}_{0.3}\text{Rh}_4\text{B}_4$. Consequently (Ce, Pr, Nd) Rh_4B_4 are high-pressure modifications synthesized at 3.3 GPa and 1500°C^{101,104,105}.

In the ternary and higher order borides $\text{M}_{\text{RE}}\text{M}_{\text{T4}}\text{B}_4$ -containing platinum metals^{36,37}, the $\text{M}_{\text{RE}}\text{Rh}_4\text{B}_4$ phases are superconducting and exhibit long-range magnetic order below their superconducting transition T. Superconductivity coexists with antiferromagnetic order ($T_N > T_C$ or $T_N < T_C$) but is destroyed by the onset of ferromagnetism at a second, lower critical temperature $T_{C2} \sim T_{\text{Curie}} < T_{C1}$. Investigation of the $\text{Ho}(\text{Rh}_{1-x}\text{Ir}_x)_4\text{B}_4$ system by means of low-T specific heat, ac-magnetic susceptibility and electrical resistance measurements reveals the existence of ferromagnetism for $x \leq 0.2$ (reentrant superconductivity owing to mean field ferromagnetic ordering) and antiferromagnetism for $x > 0.5$ (see Fig. 7)⁷³. For compositions $0.2 < x < 0.5$ two distinct magnetic ordering transitions occur below the superconducting transition T, similar to the antiferromagnetic superconductor NdRh_4B_4 , where the lower transition corresponds to a change in the direction of a sinusoidal modulation of the antiferromagnetically aligned moments on the body-centered tetragonal Nd^{3+} sublattice^{92,93}. Specific heat and neutron diffraction data obtained from $\text{Ho}(\text{Rh}_{1-x}\text{Ir}_x)_4\text{B}_4$ alloys confirms the antiferromagnetic ordering for $x > 0.5$; the magnetic structure at $x = 0.7$ and below $T_N = 2.7$ K is an alternating stacking of antiferromagnetic planes and is a body-centered tetragonal superstructure of the CeCo_4B_4 subcell according⁹¹ to $a_m = \sqrt{2} \cdot a_o$ and $c_m = 2c_o$ (the magnetic structure determination refers to the smaller crystallographic body-centered tetragonal unit). The antiferromagnetic to superconducting transition at $T_c \sim 1.35$ K is second order.

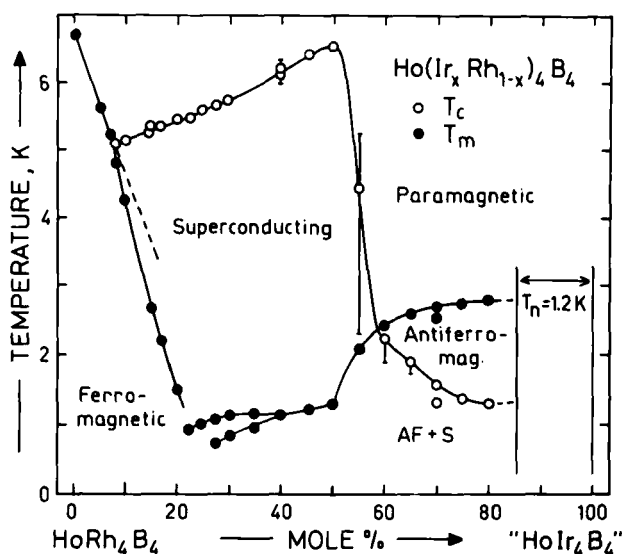


Figure 7. System $\text{Ho}(\text{Rh}_{1-x}\text{Ir}_x)_4\text{B}_4$: low-T phase diagram^{55,66,73}.

In the ferromagnetic superconductors (i.e., ErRh_4B_4 with reentrant superconducting behavior), the compound becomes superconducting at an upper critical T_c , T_{C1} , but loses its superconductivity at a lower second critical T_c , T_{C2} near the Curie temperature. Owing to these superconducting ferromagnetic interactions a sinusoidally modulated magnetic state is formed that coexists with superconductivity in a narrow T range above T_{C2} (neutron diffraction studies^{88,89}). For example, a transverse linearly polarized sinusoidally modulated magnetic structure ($\sim 100 \text{ \AA}$)^{72,88-90} along [010] is observed in ErRh_4B_4 and in the Er-rich section of $(\text{Er}_{1-x}\text{Ho}_x)\text{Rh}_4\text{B}_4$.

A listing of ternary, quaternary and higher order systems is found in Table 1. An extensive and more detailed compilation concerning the structural chemistry and phase equilibria in the low-T phase diagrams⁷⁸ of the $(\text{M}_{\text{RE}1-x}^1\text{M}_{\text{RE}x}^2)(\text{M}_{\text{T}1-x}^1\text{M}_{\text{T}x}^2)_4\text{B}_4$ type is available⁷⁸, along with a discussion of the physical properties and low-T behavior of these alloys (i.e., superconductivity and magnetism)^{17,71-73}.

The formation of CeCo_4B_4 -type compounds within the concentrational sections $\text{M}_{\text{RE}}(\text{Ir}_x\text{Rh}_{1-x})_4\text{B}_4$, the metastable phase boundaries (as derived from as cast alloys), and the occurrence of superconductivity in these systems is summarized⁸⁴ in Fig. 5. The $\text{M}_{\text{RE}}(\text{Rh}_{1-x}\text{M}_{\text{T}x})_4\text{B}_4$ systems reveal a discontinuous drop at x_{cr} in the variation of the superconducting transition T vs. concentration that may arise from a complicated Rh- M_{T} ordering in the $\text{M}_{\text{T}4}$ cluster sites⁶¹. Although this occurs whether the structure is the CeCo_4B_4 type or the LuRu_4B_4 type, and no discontinuity is observed from the corresponding variation of the unit-cell dimensions, the abrupt change^{61,86} in $\text{M}_{\text{RE}}(\text{Rh}_{1-x}\text{Ru}_x)_4\text{B}_4$ ($\text{M}_{\text{RE}} = \text{Y, Er, Lu}$; Ru_4B_4 type) is correlated with the $c:a$ ratio just crossing the value :2.

The system⁸⁶ $\text{Y}(\text{Rh}_{1-x}\text{Ru}_x)_4\text{B}_4$ (LuRu_4B_4 type, $x > 0.15$, x-ray diffraction, electron spectroscopy, ac-magnetic susceptibility measurements) is similar. The abrupt disap-

pearance of superconductivity for $0.6 \leq x \leq 1.0$, and the simultaneous existence corresponds to a minimum in the intracluster distances and a maximum of the intercluster distances at $x = 0.8$.

Analysis of the boron data shows a continuous modification of the hybridization of the Bp and the transition-metal d states in contrast to earlier suggestions of an abrupt change in the electronic structure¹⁸ near x_{cr} . The crystal chemistry of ternary and higher order $M_{RE}M_{T4}B_4$ phases and their low-T behavior is governed by the mode of linking the M_{T4} clusters (also by the different mode of transition-metal atom ordering on the M_{T4} cluster sites), by a ratio of intercluster and intracluster bond lengths as well as by the degree of $M_{RE}-M_{RE}$ atom interaction. The $NdCo_4B_4$ -derived structure types $M_{RE}M_{T4}B_4$ reveal a strong (direct) magnetic interaction among the (magnetic) rare-earth atoms, whereas the interplay superconductivity and magnetic order in the $CeCo_4B_4$ -type derivative structures is based on the weak (indirect) magnetic coupling of remote ($> 5 \text{ \AA}$) rare earths.

(P. ROGL)

1. M. V. Chepiga, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 9, 1688 (1973); *Chem. Abstr.*, 80, 31,242 (1974).
2. W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, 97, 378 (1966); see also H. Jedlicka, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, 99, 1068 (1968).
3. W. Jung, Z. *Naturforsch., Teil B*, 34, 1221 (1979).
4. R. N. Shelton, B. A. Karcher, D. R. Powell, R. A. Jacobson, H. C. Ku, *Mater. Res. Bull.*, 15, 1441 and 1445 (1980).
5. W. Jeitschko, *Acta Crystallogr., Sect. B*, 24, 930 (1968).
6. H. Jedlicka, F. Benesovsky, H. Nowotny, *Monatsh. Chem.*, 100, 844 (1969).
7. P. Rogl, E. Rudy, *J. Solid-State Chem.*, 24, 175 (1978).
8. Yu. B. Kuz'ma, N. S. Bilonizhko, *Sov. Phys.-Crystallogr.*, 16, 897 (1972).
9. D. C. Johnston, *Solid-State Commun.*, 24, 699 (1977).
10. Yu. B. Kuz'ma, N. S. Bilonizhko, *Dopov. Akad. Nauk Ukr. RSR., Ser. A*, 275 (1978); *Chem. Abstr.*, 89, 34,531 (1978).
11. P. Rogl, K. Hiebl, M. J. Sienko, paper presented at the *Proceedings of the 7th International Conference on Solid Compounds of Transition Elements*, Grenoble, June 21–26, II, A4.
12. S. I. Mikhaleiko, Yu. B. Kuz'ma, A. S. Sobolev, *Poroshk. Metall.*, No. 1, 48 (1977); *Chem. Abstr.*, 86, 128,127 (1977).
13. A. Grüttner, K. Yvon, *Acta Crystallogr., Sect. B*, 35, 451 (1979).
14. P. Rogl, *Monatsh. Chem.*, 111, 517 (1980).
15. K. Yvon, A. Grüttner, in *Superconductivity in d- and f-Band Metals*, D. H. Douglass, ed., Academic Press, New York, 1979, p. 515.
16. M. A. Marko, Yu. B. Kuz'ma, E. I. Gladyshevskij, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, No. 6, 555 (1976); *Chem. Abstr.*, 86, 46,295 (1977).
17. N. F. Chaban, Yu. B. Kuz'ma, N. S. Bilonizhko, O. O. Kachmar, N. V. Petriv, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, 875 (1979); *Chem. Abstr.*, 92, 65,384 (1980).
18. See, e.g., *Int. Conf. Ternary Superconductors*, Lake Geneva, Wisconsin, 1980.
19. D. C. Johnston, *Solid-State Commun.*, 42, 453 (1982).
20. M. L. Borlera, G. Pradelli, *Metall. Ital.*, 2, 61 (1971).
21. H. E. Baurecht, H. Boller, H. Nowotny, *Monatsh. Chem.*, 102, 373 (1971).
22. S. Rundqvist, *Acta Chem. Scand.*, 16, 1 (1962).
23. H. Nowotny, R. Kieffer, F. Benesovsky, *Planseeber. Pulvermet.*, 5, 86 (1957); *Monatsh. Chem.*, 88, 180 (1957).
24. N. F. Chagan, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 6, 883 (1970); *Chem. Abstr.*, 73, 59,645 (1970).
25. H. Kudielka, H. Nowotny, G. Findeisen, *Monatsh. Chem.*, 88, 1048 (1957).
26. V. S. Telegus, Yu. B. Kuz'ma, *Porosh. Met.*, 8, 68 (1968); *Chem. Abstr.*, 69, 110,405 (1968).

27. E. Rudy, Compendium of Phase Diagram Data, AFML-TR-65-2-5, 1969; *Chem. Abstr.*, 72, 25,616 (1970).
28. Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 7, 452 (1971); *Chem. Abstr.*, 75, 25,992 (1971).
29. Yu. B. Kuz'ma, V. I. Lakh, B. I. Stadnyk, D. A. Kovalyk, *Porosh. Met.*, 10, 59 (1970); *Chem. Abstr.*, 74, 146,837 (1971).
30. Yu. B. Kuz'ma, V. I. Lakh, B. I. Stadnyk, N. F. Chaban, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, 33, 849 (1971); *Chem. Abstr.*, 75, 144,697 (1971).
31. Yu. B. Kuz'ma, V. S. Telegus, D. A. Kovalyk, *Porosh. Met.*, 9, 79 (1969); *Chem. Abstr.*, 71, 74,691 (1969).
32. V. S. Telegus, Yu. B. Kuz'ma, *Porosh. Met.*, 10, No. 1, 67 (1971); *Chem. Abstr.*, 74, 131,054 (1971).
33. H. Haschke, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, 97, 1459 (1966); 95, 1502 (1964).
34. E. I. Gladyshevskij, T. F. Fedorov, Yu. B. Kuz'ma, R. V. Skolozdra, *Sov. Powder Metall. Met. Ceram.*, 4, 305 (1966).
35. H. Jedlicka, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, 99, 1068 (1968).
36. Yu. B. Kuz'ma, M. V. Chepiga, *Inorg. Mater.*, (USSR), 5, 40 (1969).
37. J. M. Vandenberg, B. T. Matthias, *Proc. Natl. Acad. Sci., USA*, 74, 1334, 1336 (1977).
38. B. T. Matthias, C. K. N. Patel, H. Barz, E. Corenzwit, J. M. Vandenberg, *Phys. Lett.*, 68A, 119 (1978).
39. I. P. Volyovka, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 14, 356 (1978); *Chem. Abstr.*, 88, 177,892 (1978).
40. P. Rogl, *Monatsh. Chem.*, 110, 235 (1979).
41. K. Hiebl, P. Rogl, M. J. Sienko, *J. Less-Common Met.*, 82, 21 (1981).
42. H. C. Ku, D. C. Johnston, B. T. Matthias, H. Barz, G. Burri, L. Rinderer, *Mater. Res. Bull.*, 14, 1591 (1979).
43. P. Rogl, K. Hiebl, M. J. Sienko, paper presented at the *Proceedings of the 7th International Conference on Solid Compounds of Transition Elements*, Grenoble, June 21–26, II, A4.
44. N. F. Chaban, Yu. B. Kuz'ma, N. S. Bilonizhko, O. O. Kachmar, N. V. Petrov, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, 875 (1979); *Chem. Abstr.*, 92, 65,384 (1980).
45. G. F. Stepanchikova, Yu. B. Kuz'ma, *Sov. Powder Metall. Met. Ceram.*, 10, 44 (1980).
46. Yu. B. Kuz'ma, G. F. Stepanchikova, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 10, 1905 (1974); *Chem. Abstr.*, 82, 132,183 (1975).
47. K. Yvon, D. C. Johnston, *Acta Crystallogr., Sect. B*, 38, 247 (1982).
48. S. I. Mikhaleenko, N. F. Chaban, Yu. B. Kuz'ma, paper presented at the *Proceedings of the 7th Symposium on Boron, Borides and Related Compounds*, Uppsala, June, 1981.
49. G. F. Stepanchikova, *Visn. L'viv Politekh. Inst.*, 130, 58 (1979).
50. B. Aronsson, *Acta Chem. Scand.*, 12, 31 (1958).
51. H. Nowotny, F. Benesovsky, E. Rudy, A. Wittmann, *Monatsh. Chem.*, 91, 975 (1960).
52. P. Rogl, H. Haines, P. E. Potter, *J. Nucl. Mater.*, 149, 283 (1987).
53. N. F. Chaban, *Vestn. Univ. L'viv, Ser. Khim.*, 23, 44 (1981).
54. K. Hiebl, P. Rogl, M. J. Sienko, *Inorg. Chem.*, 21, 1128 (1982).
55. H. F. Braun, M. Pelizzzone, K. Yvon, paper presented at the *Proceedings of the 7th International Conference on Solid Compounds of Transition Elements*, Grenoble, June 21–26, 1982, II, B11; see also *Solid-State Commun.*, 55, 131 (1985).
56. H. C. Ku, Thesis, University of California, San Diego, 1980.
57. H. C. Hamaker, M. B. Maple, in *Ternary Superconductors*, *Proc. Int. Conf. Ternary Superconductors*, G. K. Shenoy, B. D. Dunlap, F. Y. Fradin, eds., North Holland, Amsterdam, 1980, p. 201.
58. R. H. Wang, R. J. Laskowski, C. Y. Huang, J. L. Smith, S. W. Chu, *J. Appl. Phys.*, 49, 1392 (1978); 50, 1862 (1979).
59. M. Isino, K. Tsunokuni, H. Iwasaki, Y. Muto, *J. Magn. Magn. Mater.*, 31–34, 519 (1983).
60. D. C. Johnston, W. A. Fertig, M. B. Maple, B. T. Matthias, *Solid-State Commun.*, 26, 141 (1978).
61. H. C. Ku, B. T. Matthias, H. Barz, *Solid-State Commun.*, 32, 937 (1979).
62. H. E. Hornig, R. N. Shelton, in *Ternary Superconductors*, *Proc. Int. Conf. on Ternary Superconductors*, G. K. Shenoy, B. D. Dunlap, F. Y. Fradin, eds., North Holland, Amsterdam, 1981, p. 213.

63. L. D. Woolf, M. B. Maple, in *Ternary Superconductors, Proc. Int. Conf. on Ternary Superconductors*, G. K. Shenoy, B. D. Dunlap, F. Y. Fradin, eds., North Holland, Amsterdam, 1981, p. 181.
64. S. Maekawa, J. L. Smith, C. Y. Huang, *Phys. Rev.*, **B22**, 164 (1980).
65. K. Okuda, Y. Nakakura, K. T. Kadowaki, *J. Magn. Magn. Mater.*, **15-18**, 1575 (1980).
66. H. Adrian, R. Müller, R. Behrle, G. Saemann-Ischenko, G. Voit, *Physica*, **108B**, 1281 (1981).
67. H. C. Hamaker, H. C. Ku, M. B. Maple, H. A. Mook, *Solid-State Commun.*, **43**, 455 (1982).
68. D. C. Johnston, *Physica*, **108B**, 755 (1981).
69. H. C. Ku, R. N. Shelton, *Solid-State Commun.*, **40**, 237 (1981).
70. K. Hiebl, P. Rogl, M. J. Sienko, *J. Less-Common Met.*, **82**, 201 (1981).
71. C. B. Vining, R. N. Shelton, in *Ternary Superconductors, Proc. Int. Conf. on Ternary Superconductors*, G. K. Shenoy, B. D. Dunlap, F. Y. Fradin, eds., North Holland, Amsterdam, 1981, p. 189.
72. S. E. Lambert, L. D. Woolf, M. B. Maple, *J. Low-Temp. Phys.*, **54**, 177 (1984).
73. H. A. Mook, O. A. Pringle, S. Kawarazaki, S. K. Sinha, G. W. Crabtree, D. G. Hinks, M. B. Maple, Z. Fisk, D. C. Johnston, L. D. Woolf, H. C. Hamaker, paper presented at the *Proceedings of the IV Conference on Superconductivity in d- and f-Band Metals*, Karlsruhe, June 28-30, 1982, p. 201; *J. Appl. Phys.*, **53**, 2614 (1982).
74. K. N. Yang, S. E. Lambert, H. C. Hamaker, M. B. Maple, H. A. Mook, H. C. Ku, paper presented at the *Proceedings of the IV Conference on Superconductivity in d- and f-Band Metals*, Karlsruhe, June 28-30, 1982, p. 217.
75. G. F. Stepanchikova, Yu. B. Kuz'ma, *Vestn. Un-ta, L'vov Un-ta, Ser. Khim.*, No. 23, 48 (1981); *Chem. Abstr.*, **95**, 68,813 (1981).
76. S. I. Mikhaleenko, Yu. B. Kuz'ma, D. K. Tschir, *Poroshk. Metall. (Kiev)*, No. 9, 50 (1982); *Chem. Abstr.*, **98**, 112,030 (1982).
77. Yu. B. Kuz'ma, N. S. Bilonizhko, S. I. Svarichevskaya, in *Tugoplavkie Boridie Silizidi*, G. V. Samsonov, ed., *Nauka Dumka*, Kiev, 1977, p. 67.
78. B. Pedersen, F. Gronvold, *Acta Crystallogr., Sect., B*, **12**, 1022 (1959).
79. P. Rogl, in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 6, K. A. Gschneidner Jr., L. Eyring, eds., North Holland, Amsterdam, 1983.
80. M. B. Maple, in *Proceedings of the International School of Low-Temperature Physics, 3rd Course, Advances in Superconductivity*, B. Deaver, J. Ruvald, eds., July, Erice, Italy, 1982.
81. M. B. Maple, *J. Magn. Magn. Mater.*, **31-34**, 479.
82. M. B. Maple, in *Proc. Mater. Res Soc., Annu. Meet.*, 1982.
83. M. B. Maple, H. C. Hamaker, L. D. Woolf, in *Topics in Current Physics, Superconductivity in Ternary Compounds, II*, Vol. 34, Springer-Verlag, Berlin, 1982, p. 99.
84. D. C. Johnston, H. F. Braun, in *Superconductivity in Ternary Compounds*, Ø. Fischer, M. B. Maple, eds., Springer-Verlag, Berlin, 1982, p. 11.
85. Ø. Fischer, M. B. Maple, in *Topics of Current Physics, Superconductivity in Ternary Compounds, I*, Vol. 32, Ø. Fischer, M. B. Maple, eds. Springer-Verlag, Berlin, 1982, p. 1.
86. H. C. Ku, H. Barz, in *Ternary Superconductors, Proc. Int. Conf. on Ternary Superconductors*, Lake Geneva, WI, G. K. Shenoy, B. D. Dunlap, F. Y. Fradin, eds. North Holland, Amsterdam, 1981, p. 209.
87. R. N. Shelton, H. E. Hornig, A. J. Bevolo, J. W. Richardson, R. A. Jacobson, S. D. Bader, H. C. Hamaker, *Phys. Rev.*, **B27**, 6713, 1983.
88. H. C. Hamaker, G. Zajac, S. D. Bader, *Phys. Rev.*, **B27**, 6713, 1983.
89. D. E. Moncton, D. B. McWhan, P. H. Schmidt, G. Shirane, W. Thomlinson, M. B. Maple, H. B. MacKay, L. D. Woolf, Z. Fisk, D. C. Johnston, *Phys. Rev. Lett.*, **45**, 2060 (1980).
90. S. K. Sinha, G. W. Crabtree, D. G. Hinks, H. A. Mook, *Phys. Rev. Lett.*, **48**, 950 (1982).
91. H. A. Mook, W. C. Koehler, M. B. Maple, Z. Fisk, D. C. Johnston, L. D. Woolf, *Phys. Rev.*, **B25**, 372 (1982).
92. H. C. Hamaker, H. C. Ku, M. B. Maple, H. A. Mook, *Solid-State Commun.*, **43**, 455 (1982).
93. C. F. Majkrzak, D. E. Cox, G. Shirane, H. A. Mook, H. C. Hamaker, H. B. MacKay, Z. Fisk, M. B. Maple, *Phys. Rev.*, **B26**, 245 (1982).
94. C. F. Majkrzak, S. K. Satija, G. Shirane, H. C. Hamaker, Z. Fisk, M. B. Maple, *Phys. Rev.*, **B27**, 2889 (1983).

6.7.2.2. Borides with Boron Chains

6.7.2.2.2. Ternary Borides with Boron-Boron Chain Formation.

95. G. V. Chernyak, N. F. Chaban, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 6, 65 (1983).
96. C. Horvath, P. Rogl, *Mater. Res. Bull.*, 20, 1273 (1985).
97. P. Rogl, P. Potter, H. R. Haines, *J. Less-Common Met.*, 121, 431 (1986).
98. W. Jung, B. Schmidt, *Z. Anorg. Allg. Chem.*, 543, 89 (1986).
99. W. Jung, K. Petry, *Z. Kristallogr.*, 182, 153 (1988).
100. K. Schweitzer, W. Jung, *Z. Anorg. Allg. Chem.*, 533, 30 (1986).
101. M. Shimotomai, J. Ohta, H. Fujisawa, K. Suito, T. Ooyama, K. Kumagai, *J. Less-Common Met.*, 135, 161 (1987).
102. Y. Watanabe, H. Iwasaki, H. Takei, *Acta Crystallogr.*, C40, 1644 (1984).
103. Y. Watanabe, H. Iwasaki, Y. Muto, *Acta Crystallogr.*, C42, 1469 (1986).
104. M. Shimotomai, M. Enoki, M. Doyama, H. Fujisawa, *Physica*, 130B, 501 (1985).
105. M. Shimotomai, J. Ohta, H. Fujisawa, K. Suito, T. Ooyama, K. Kumagai, *J. Less-Common Met.*, 135, 161 (1987).
106. P. Rogl, H. Klesnar, P. Fischer, *J. Am. Ceram. Soc.*, in press.
107. D. B. DeMooij, K. H. Buschow, *Philips J. Res.*, 41, 400 (1986).
108. Yu. B. Kuz'ma, O. M. Dub, V. A. Bruskov, N. F. Chaban, L. V. Zavali, *Sov. Phys. Crystallogr.*, 33, 496 (1989).
109. Yu. B. Kuz'ma, L. G. Akselrud, V. A. Bruskov, N. S. Bilonizhko, *Sov. Phys. Crystallogr.*, 30, 585 (1985).
110. Yu. B. Kuz'ma, S. N. Mikhaleenko, V. A. Bruskov, *Vses. Konf. Kristallochim. Intermet. Soeden*, Tesizy Dokladov, Lviv, Oct. 1989, p. 44.
111. Yu. B. Kuz'ma, S. V. Orishchin, T. Glovyak, I. B. Gubich, N. F. Chaban, S. I. Chikhrij, *Vses. Konf. Kristallochim. Intermet. Soeden*, Tesizy Dokladov, Lviv, Oct. 1989, p. 102.
112. N. V. Ivych, N. F. Chaban, *Vses. Konf. Kristallochim. Intermet. Soeden*, Tesizy Dokladov, Lviv, Oct. 1989, p. 46.
113. D. Givord, P. Tenaud, J. M. Moreau, *J. Less-Common Met.*, 115, L7 91986; 123, 109 (1986).
114. D. R. Noakes, A. M. Umarji, G. K. Shenoy, D. G. Hinks, *J. Appl. Phys.* 55(6), 1847 (1984).
115. R. H. Heffner, D. W. Cooke, R. L. Hutson, M. Leon, M. E. Schillaci, J. L. Smith, A. Yaouanc, S. A. Dodds, L. C. Gupta, D. E. MacLaughlin, C. Boekema, *J. Appl. Phys.*, 55, 2007 (1984).
116. R. N. Shelton, H. E. Horng, A. J. Bevolo, J. W. Richardson, R. A. Jacobsen, S. D. Bader, H. C. Hamaker, *Phys. Rev. Ser. B*, 27, 6703 (1983).
117. R. Mirgel, W. Jung, *J. Less-Common Met.*, 143, 49 (1988).

6.7.2.2.2. Ternary Borides with Boron-Boron Chain Formation.

Boron atoms in infinite boron zigzag chains form covalent B—B bonds at 165–190 pm with bond angles of $\sim 115^\circ$. The boron coordination is trigonal prismatic, giving rise to coordinated rows of face-connected trigonal metal prisms (Table 1). Most typical are the binary transition-metal monoborides such as the FeB, CrB and MoB structure types. Transformations between pairs by simple geometric shifts^{1,40} (FeB \longrightarrow CrB, CrB \longrightarrow α -MoB) explain the close structural relationship among monoborides, which from near-neighbor diagrams are characterized by strong M_T —B interactions³. Including ternary representatives, a systematic transformation between these competing structure types is derived², depending on the metal-metal substitution and therefore primarily on the electron-atom ratio, $e : a$, i.e., RuB (WC-type) \longrightarrow $Mo_{0.5}Ru_{0.5}B$ (FeB) \longrightarrow $Mo_{0.7}Ru_{0.3}B$ (CrB) \longrightarrow α -MoB (α -MoB).

The number of CrB representatives is highly increased by ternary compounds observed in the isothermal sections M_T —Mo—B and M_T —W—B just below the transformation T of the CrB-type high-T modifications of MoB and WB into low-T α -MoB or α -WB. These ternary compounds therefore represent a stabilization of the high-T form of MoB and WB, respectively, toward lower T by statistical Mo(W)/metal substitution. Transition T (T_{tr}) range⁴ for WB from 2100°C (W rich) to 2180°C (B

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97. P. Rogl, P. Potter, H. R. Haines, *J. Less-Common Met.*, 121, 431 (1986).
98. W. Jung, B. Schmidt, *Z. Anorg. Allg. Chem.*, 543, 89 (1986).
99. W. Jung, K. Petry, *Z. Kristallogr.*, 182, 153 (1988).
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102. Y. Watanabe, H. Iwasaki, H. Takei, *Acta Crystallogr.*, C40, 1644 (1984).
103. Y. Watanabe, H. Iwasaki, Y. Muto, *Acta Crystallogr.*, C42, 1469 (1986).
104. M. Shimotomai, M. Enoki, M. Doyama, H. Fujisawa, *Physica*, 130B, 501 (1985).
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106. P. Rogl, H. Klesnar, P. Fischer, *J. Am. Ceram. Soc.*, in press.
107. D. B. DeMooij, K. H. Buschow, *Philips J. Res.*, 41, 400 (1986).
108. Yu. B. Kuz'ma, O. M. Dub, V. A. Bruskov, N. F. Chaban, L. V. Zavali, *Sov. Phys. Crystallogr.*, 33, 496 (1989).
109. Yu. B. Kuz'ma, L. G. Akselrud, V. A. Bruskov, N. S. Bilonizhko, *Sov. Phys. Crystallogr.*, 30, 585 (1985).
110. Yu. B. Kuz'ma, S. N. Mikhaleenko, V. A. Bruskov, *Vses. Konf. Kristallochim. Intermet. Soeden*, Tesizy Dokladov, Lviv, Oct. 1989, p. 44.
111. Yu. B. Kuz'ma, S. V. Orishchin, T. Glovyak, I. B. Gubich, N. F. Chaban, S. I. Chikhrij, *Vses. Konf. Kristallochim. Intermet. Soeden*, Tesizy Dokladov, Lviv, Oct. 1989, p. 102.
112. N. V. Ivych, N. F. Chaban, *Vses. Konf. Kristallochim. Intermet. Soeden*, Tesizy Dokladov, Lviv, Oct. 1989, p. 46.
113. D. Givord, P. Tenaud, J. M. Moreau, *J. Less-Common Met.*, 115, L7 91986; 123, 109 (1986).
114. D. R. Noakes, A. M. Umarji, G. K. Shenoy, D. G. Hinks, *J. Appl. Phys.* 55(6), 1847 (1984).
115. R. H. Heffner, D. W. Cooke, R. L. Hutson, M. Leon, M. E. Schillaci, J. L. Smith, A. Yaouanc, S. A. Dodds, L. C. Gupta, D. E. MacLaughlin, C. Boekema, *J. Appl. Phys.*, 55, 2007 (1984).
116. R. N. Shelton, H. E. Horng, A. J. Bevolo, J. W. Richardson, R. A. Jacobsen, S. D. Bader, H. C. Hamaker, *Phys. Rev. Ser. B*, 27, 6703 (1983).
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TABLE 1. METAL BORIDES AND BOROCARBIDES: STRUCTURE TYPES AND REPRESENTATIVES WITH B CHAINS

Structure type	Boron aggregation; boron coordination	Binary representatives	Ternary representatives	Refs.
A. Metal borides				
CrB Cmcm	Zigzag chains; trigonal prisms	VB, NbB, TaB, β -CrB, β -MoB β -WB, NiB, α -MnB ^a (see Ref. 7)	Stabilization of β -MoB (β -WB) toward lower temperatures by Mo(W) metal substitution: Mo _{1-x} Ga _x B ¹⁸ , Mo _{0.9} Al _{0.1} B ¹⁸ , Mo _{0.4} Ti _{0.6} B ¹⁹ , W ₃ Ti ₂ B ₅ ²⁰ , Mo ₄ HfB ₅ ²¹ , W ₄ HfB ₅ ²³ , Mo ₄ MnB ₅ ²² , W ₄ MnB ₅ ²² , Mo _{0.7} Fe _{0.1} B ²⁴ , W _{0.7} Fe _{0.1} B ²⁴ , Mo _{0.9} Co _{0.1} B ²⁴ , W _{0.9} Co _{0.1} B ²⁴ , Mo _{0.7} Ni _{0.1} B ²⁴ , Mo _{0.7} Ru _{0.2} B ²⁵ , Mo ₄ YB ₅ ⁴⁶ , W ₄ YB ₅ ⁴⁶ Cr _{0.25} Re _{0.75} B _{1-x} ²⁷ V _{0.4} Re _{0.6} ²⁸	
α -MoB 14 ₁ /amd	Two sets of zigzag chains; trigonal prisms	α -CrB ^a , α -MoB ²⁶ α -WB ²⁶		
FeB Pnma	Zigzag chains; trigonal prisms	TiB, HfB, β -MnB ^a , β -FeB ^a CoB (see Ref. 7)	Cr _{0.6} Re _{0.4} B ²⁷ ; Cr _{0.67-0.4} Ru _{0.33-0.6} B, Cr _{0.67-0.5} Os _{0.33-0.5} B, Mo _{0.5} Ru _{0.5} B, W _{0.5} Ru _{0.5} B, V _{0.4-0.6} Ru _{0.6-0.4} B, Ni _{0.75-0.4} Ru _{0.25-0.6} B NG ₃ Co ₄ B ₇ Ta ₃ Co ₄ B ₇ NbCoB ₂ ⁶ ; TaCoB ₂ , NbNiB ₂ , TaNiB ₂ M _T Ir ₃ B ₄ , M _T = Sc, Zr, Hf	2 56 57
NG ₃ Co ₄ B, NbCoB ₂ Pnma ZrIr ₃ B _{4-x} P6 ₃ /m	Boron chain-net type; trigonal prism Zigzag chains; trigonal prisms Linear chains; B-chain atoms in octahedron and isolated boron atoms in trigonal prisms	— — —		29 30
α -Ni ₄ B _{3-x} Pnma	Zigzag chains; isolated prisms	α -Ni ₄ B _{3-x} ⁸	—	

m-Ni ₄ B _{3-x} C2/c	Zigzag chains; trigonal prisms and archimedean antiprism	m-Ni ₄ B _{3-x} ⁸	—		
Ru ₁₁ B ₈ Pbam	Branched zigzag chains and isolated boron atoms;	Ru ₁₁ B ₈ ³²	—		
V ₅ B ₆ Ammm	trigonal prisms Single and double zigzag chains; trigonal prism	V ₅ B ₆ ⁹ , NG ₅ B ₆ ⁵³	Cr ₂ Ni ₃ B ₅ ³³	34	
Ta ₃ B ₄ Immm	Double chains; trigonal prisms	Ti ₃ B ₄ ⁵² , V ₃ B ₄ , Nb ₃ B ₄ , Ta ₃ B ₄ , Cr ₃ B ₄ , Mn ₃ B ₄ (see Ref. 7)	MoCo ₂ B ₄ (ordered type, 800°C) (Mo _{0.33-0.4} Ru _{0.67-0.6}) ₃ B ₄ (1300°C) (Mo _{0.67} Fe _{0.33}) ₃ B ₄ (ordered type, 1050°C) (Mo _{0.33} Fe _{0.67}) ₃ B ₄ (disordered?, 1000°C) (W _{0.67} Fe _{0.33}) ₃ B ₄ (stable below 850°C; ordered) VCoB ₃ ³⁵ (Cr _{0.75} Ni _{0.25}) ₂ B ₃ ³³ La ₂ Re ₃ B ₇	10 24 49 24	
V ₂ B ₃ Cmcm	Triple chains; trigonal prisms	V ₂ B ₃ ⁹ , Cr ₂ B ₃ ⁵⁴		45	
La ₂ Re ₃ B ₇ Pcca	Boron zigzag chains; distorted trigonal prisms; distorted octahedron	—			
Lu ₂ Ni ₃ B ₆ Cmmm	Boron chains linked to form open nets; trigonal prism	—	Lu ₂ Ni ₃ B ₆	59	
Pr ₂ Re ₃ B ₆ C2/c	Zigzag chains with side chains; trigonal prism	—	Pr ₂ Re ₃ B ₆	60	
W ₂ Ir ₃ B _{6-x} Immm	Zigzag chains at 200-pm distance, and boron pairs; trigonal prisms	—	W ₂ Ir ₃ B ₅ ¹⁰ Mo _{2.5} Ir _{2.5} B ₅ ¹⁰		
Er ₃ CrB ₇	Boron net fragments,	—	M _{RE3} CrB ₇ , M _{RE} = Er M _{RE3} MnB ₇ , M _{RE} = Y, Gd M _{RE3} ReB ₇ , M _{RE} = Y, Gd, Tb, Dy, Ho, Er, Tm	11 11 11	(continued)

TABLE 1. METAL BORIDES AND BOROCARBIDES: STRUCTURE TYPES AND REPRESENTATIVES WITH B CHAINS

Structure type	Boron aggregation; boron coordination	Binary representatives	Ternary representatives	Refs.
B. Ternary aluminum borides				
MoAlB	chain-like Cmcm connected by boron atoms in trigonal prisms	—	$M_{RE}FeB_7$, $M_{RE} = Y, Tb, Dy, Ho, Er$ $M_{RE}MoB_7$, $M_{RE} = Tb, Du, Ho$ $M_{RE}WB_7$, $M_{RE} = Gd (?)$	11 ^a 58 44
Zigzag chains;				
Cmcm	trigonal prisms	—	$TaNiB^{37}$, $MoAlB^{51}$ $NbNiB^{36}$	
Mn_2AlB_2	Zigzag chains;	—	Cr_2AlB_2 , Mn_2AlB_2 ,	38
Cmcm	trigonal prisms	—	$Fe_2AlB_2^{42}$	
$Ru_3Al_2B_2$	Zigzag chains;	—	$Ru_3Al_2B_2$	55
Cmcm	trigonal prisms	—		
Cr_3AlB_4	Double chains;	—	$Cr_3AlB_4^{38}$	
Pmm	trigonal prisms	—		
C. Transition-metal borocarbides				
Mo_2BC	Zigzag boron	—	Mo_2BC^{39} , Nb_2BN^{61}	
Cmcm	chains branched with carbon atoms; trigonal prisms	—		
YBC	—	—	YBC ¹⁶	
Cmcm	—	—	UBC ³¹ , UBN ⁶²	
UBC	—	—	$PuBc^{65}$, $NpBC^{63}$	
ThBC	Boron chains dissolved into C—B—B—C groups	—	ThBC ¹³	
P4 ₁ 22	Boron chains dissolved into C—B—B—C groups	—		
$Th_3B_2C_3$ P2/m	Boron chains dissolved into C—B—B—C groups	—	$Th_3B_2C_3^{17}$	

^a For the existence of different low- and high-T modifications, see text.

rich), and from 1800°C (Mo rich) to 1520°C (B rich) for MoB. A similar transition is observed for CrB ($T_{tr} \sim 1000^\circ\text{C}$)⁵ and its α -MoB-type low-T form ($T_{tr} = 1120^\circ\text{C}$)⁴⁸. From bandstructure calculations⁴¹ of the binary FeB-type monoborides (TiB, MnB, FeB, CoB) the electron transfer $M_T \longrightarrow B$ becomes smaller for increasing atomic numbers of the transition metal, finally reaching a zero value for Co. Nickel also forms a monoboride, but with a different structure (CrB type).

Thermodynamic phase equilibria and the occurrence and stability of the low-T phases of CrB, FeB and MnB are obtained from the concentrational sections $\text{Cr}_{1-x}\text{Mn}_x\text{B}$ and $\text{Mn}_{1-x}\text{Fe}_x\text{B}$ between 800°C and melting⁴⁸. These boride systems have invar-like properties⁴⁸. An orthorhombic low-T modification⁴⁷ of FeB based on a random stacking of CrB and FeB-type units⁴⁸ and claimed to exist $< 650^\circ\text{C}$, represents only a transposition-type behavior, with irregular shifts of FeB units with respect to a long-range order CrB-type arrangement⁶⁴. At $T < 650^\circ\text{C}$ FeB decompose into $B + \text{Fe}_2\text{B}$. For MnB an orthorhombic low-T form with the CrB type exists⁵.

A mixed type CrB + FeB with an alternating sequence of slabs of FeB and CrB units is also known from the NbCoB_2 structure⁶, which can be written as the topochemical sum:



Besides these chain borides there are binary structure types (no ternary representatives so far), which are classified⁷ by their more irregular stacking of trigonal metal prisms: Ru_{11}B_8 , monoclinic Ni_4B_3 and orthorhombic Ni_4B_3 . Corresponding to the ratio $M_T : B > 1$, orthorhombic Ni_4B_3 and Ru_{11}B_8 contain additional isolated B atoms in trigonal prisms, which form a branched chain in Ru_{11}B_8 . For monoclinic Ni_4B_3 the ratio $M_T : B > 1$ results in a higher coordination number for one half of the B atoms; B atoms at the center of trigonal prisms and at the centers of antiprisms alternate in a chain⁸.

With decreasing $M_T : B$ ratio, two or three B zigzag chains are connected at bonding distances, thus forming double or triple chains (Fig. 1). This tendency toward two-dimensional boron net formation (i.e., AlB_2 type) is recognized from the structural series within the V-B system: $\text{V}_n\text{B}_{n+1} = (n-1)\text{VB} + \text{VB}_2$ ($n = 1, 2, 3, 5$; not known for $n = 4$)⁹.

Metal ordering occurs among the ternary representatives of the Ta_3B_4 type (see Table 1) (metal sites are 2c and 4g of Immm). The pair Mo, Ru in $(\text{Mo}_{0.43-0.33}\text{Ru}_{0.57-0.67})_3\text{B}_4$ lacks neutron diffraction data, but from an x-ray single-crystal refinement there is preferential occupation of Ru in the 4g sites¹⁰. Similarly, MoCo_2B_4 ³⁴ and MoFe_2B_4 ⁴⁴ possesses an ordered metal arrangement (Mo in 2c); the latter phase, however, also is observed²⁴ with a composition Mo_2FeB_4 ; Mo occupies the 4g sites; W_2FeB_4 decomposes above 850°C but again reveals ordering with W atoms in 4g.

Preferential occupation of the 4g site by the larger transition-metal atoms accompanies ferromagnetism in solid solutions of $(\text{Mn}_{1-x}\text{M}_x)_3\text{B}_4$ ($M_T = \text{Ta, Cr, Mo, W, Ni}$)⁵⁰. The discontinuity in the variation of the lattice parameters vs. x in $(\text{Ta}_x\text{Mn}_{1-x})_3\text{B}_4$ at $x \sim 0.5$ corresponds to a change in the Mn-Ta exchange: for compositions $x < 0.4$ Ta atoms preferentially occupy 4g sites; but Mn/Ta substitution in the 2c sites starts⁵⁰ at concentrations of $x > 0.4$. Intermediates with statistical distributions are conceivable. The structure of Ta_3B_4 is characterized by B—B band

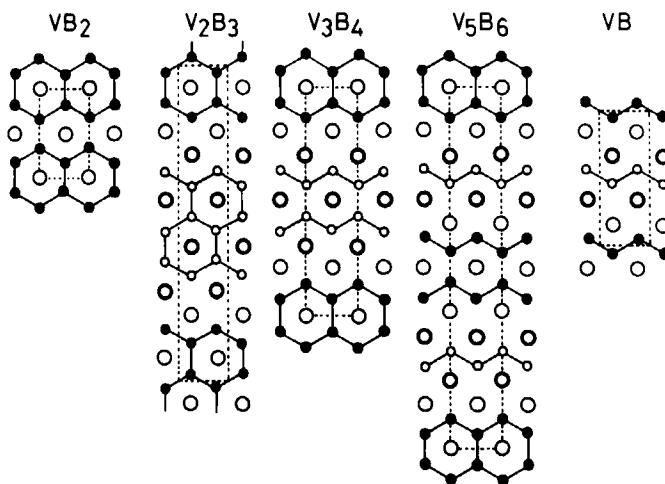


Figure 1. Structural series of vanadium borides and mode of formation: $V_nB_{n+1} = (n-1)VB + VB_2$; $n = 1, 2, 3, 5$. The structures⁹ are projected along [100]; large circles are metal atoms; small circles are B atoms; filled circles are atoms in $x = 1/2$, open circles are atoms in $x = 0$.

nets, owing to the combination of two B zigzag chains; metal atoms in the 2c sites are those with the higher B coordination above and below the net bands. The existence of Cr_2NiB_4 with ordered Ta_3B_4 structure¹² is not confirmed.

Higher B aggregates also are found in ternary borides, such as $W_2Ir_3B_{-5}^{10}$, where B—B chains come close together (~ 200 pm) to form a folded 6^3 -B layer, as in the structure of $RuB_2(OsB_2)$. Similarly, combinations of B-chain elements and B-network fragments are found in the $M_{RE3}M_TB_7$ borides (M_{RE} = small rare earths and M_T = Re, Fe; see also Table 1 and references therein) and in the structure⁴⁵ of $La_2Re_3B_7$, which combines a distorted trigonal-prismatic as well as an orthorhombic metal coordination about the B atoms. The B zigzag chains are connected by small net fragments (B_3 triangles). Similarly, zigzag chains of B with side branches are found⁶⁰ in $Pr_2Re_3B_6$, and zigzag chains linked at every fourth B atom form open nets in⁵⁹ $Lu_2Ni_3B_6$, similar to those in $CeCr_2B_6$ (see §6.7.2.3).

Although Al behaves like a transition metal in its binary borides AlB_2 and AlB_{12} , B atoms in ternary Al-containing borides are located within the transition-metal building elements, the Al now behaving as a typical B-class metal. The structural series found with Cr–Al borides³⁸, $Cr_{1+n}AlB_{2n} = CrAl + nCrB_2$, $n = 1, 2$, demonstrates the topochemical mode of combining structural building blocks of simple borides and of intermetallic phases³⁰ (Fig. 2). Accordingly, Al-containing ternary borides can be classified by their B aggregation, depending on the ratio of transition metal to B. For example, $MoAlB$ and $(Cr, Mn, Fe)_2AlB_2$ are chain borides ($M_T : B = 1$), but Cr_3AlB_4 ($M_T : B = 3 : 4$) exhibits double chains as in Ta_3B_4 . There is a formal site correspondence between the crystal structures of $MoAlB$ and UCB (see below).

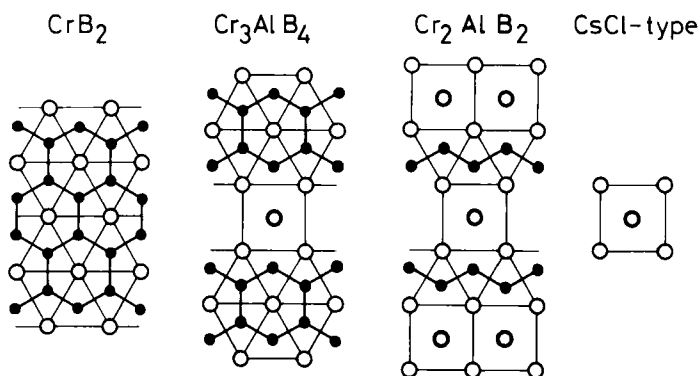


Figure 2. Structural series of Cr–Al borides and mode of formation: $\text{Cr}_{1+n}\text{AlB}_{2n} = \text{CrAl} + n\text{CrB}_2$, $n = 1, 2$. The structures³⁸ are projected along [001]; the B net and Al atoms in $z = 1/2$; Cr atoms are in $z = 0$.

Rare-earth (and actinide)-B–carbon compounds resemble metal borides in B-rich carboborides, whereas the physical and structural properties of C-rich borocarbides tend to a more carbide-like behavior (which will not be covered in this context).

Infinite zigzag B chains with C strongly bonded to B constitute the basic building element of transition-metal carboborides ($\text{M}_\text{T}\text{BC}$). The boron coordination is trigonal prismatic $\text{BM}_\text{T}6$, whereas carbon coordination is a $\text{M}_\text{T}3\text{BO}_\text{h}$. However, with an increasing ratio of radii $R_\text{M}_\text{T} : R_\text{B}$ the B-chain elements are replaced by B pairs or more precisely by B–C groups, C–B–B–C, as derived from the crystal chemistry of ThBC and $\text{Th}_3\text{B}_2\text{C}_3$ compounds¹³ (topochemical mode: $\text{Th}_3\text{B}_2\text{C}_3 = 2 \text{ThBC} + \text{ThC}$). The ThBC and UBC structure are related because the unit cell of ThBC is obtained^{13,17} by a simple shift of two slabs of UBC. Furthermore, a crystallographic group–subgroup relationship is established¹⁴ for the pair α -MoB–ThBC and with respect to the correspondence of the metal–B sublattices of UBC and CrB type, the shift operation ThBC–UBC is an analog of the example⁴⁰ α -MoB–MoB among actinide borocarbides (see Fig. 3)¹⁴. Owing to the smaller $R_\text{M}_\text{T} : R_\text{B}$ ratio, the O_h voids in monoborides are too small to accommodate carbon atoms, which explains their low b/c values as well as the absence of carbon solubility as found from the phase equilibria (see Fig. 1, §6.7.2).

Based on the topochemical description of the structure³⁹ of $\text{Mo}_2\text{BC} = \text{MoB} + \text{MoC}$, the typical B-chain element within the MoB unit becomes conceivable.

Phase equilibria reveal the formation of stable $\text{M}_\text{RE}\text{BC}$ compounds for all the lanthanides, including Sc and Y. According to the atomic size of Th comparable to the larger rare earths, the structure and bonding in ThBC resembles $\text{M}_\text{RE}\text{BC}$ for the Ce– M_RE . The smaller Y– M_RE members and Sc, however, show a different stacking¹⁵. From simple shift operations the structure¹³ of YBC is intermediate¹⁶ between the AlB_2 and ThSi_2 types.

The first two examples of boron nitrides with N atoms branching off a typical B–B zigzag chain are⁶¹ UBN (UBC type) and NG_2BN .

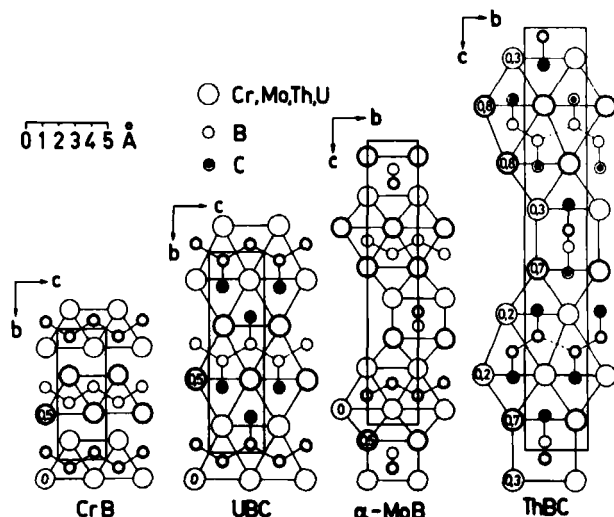


Figure 3. Relation between the orthorhombic structure types of CrB and UBC (projected along [100]) as well as between the tetragonal structure types of α -MoB and ThBC (projected along [100]). Boron atoms are at the centers of trigonal metal prisms, carbon atoms at the centers of M_5B-O_n . The numbers given indicate the heights in projection.

Some compounds with B:metal ratios that would group them among chain borides form extended B defects, isolated B atoms or B-chain fragments rather than B—B chains: e.g., RuB_{2-x} , OsB_{2-x} , $Th-IrB_{2-x}$ (x in all cases ~ 1 , WC type or defect AlB_2 type); RhB , $PtB_{0.7}$ (anti-NiAs type); $IrB_{0.7}$ (IrB_{1-x} type, low-T modification), $ZrIr_3B_{4-x}$ type (see §6.7.2.1.3, Table 1).

(P. ROGL)

1. D. Hohnke, E. Parthé, *Acta Crystallogr.*, **20**, 572 (1966).
2. P. Rogl, H. Nowotny, *Monatsh. Chem.*, **104**, 943 (1973).
3. W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley-Interscience, New York, 1972.
4. E. Rudy, Compendium of Phase Diagram Data, AFML-TR-65-2-5, 1969; *Chem. Abstr.*, **72**, 25,616 (1970).
5. G. Papesch, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **104**, 933 (1973).
6. Yu. B. Kuz'ma, *Sov. Phys.-Crystallogr.*, **20**, 636 (1976).
7. T. Lundström, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 351.
8. S. Rundqvist, S. Pramatus, *Acta Chem. Scand.*, **21**, 191 (1967).
9. K. E. Spear, P. W. Gilles, *High Temp. Sci.*, **1**, 86 (1969).
10. P. Rogl, F. Benesovsky, H. Nowotny, *Monatsh. Chem.*, **103**, 965 (1972).
11. Yu. B. Kuz'ma, S. I. Mikhaleenko, L. G. Aksel'rud, *J. Less-Common Met.*, **117**, 29 (1986).
12. B. Post, E. Pipitz, W. H. Herz, *Powder Met. Bull.*, **7**, 149 (1956).
13. P. Rogl, *J. Nucl. Mater.*, **73**, 198 (1978).
14. P. Rogl, *J. Nucl. Mater.*, **80**, 187 (1979).

15. J. Bauer, private communication, 1981.
16. J. Bauer, H. Nowotny, *Monatsh. Chem.*, **102**, 1129 (1971).
17. P. Rogl, *J. Nucl. Mater.*, **79**, 154 (1979).
18. W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **96**, 844 (1965).
19. A. Wittmann, H. Nowotny, H. Boller, *Monatsh. Chem.*, **91**, 608 (1965).
20. Yu. B. Kuz'ma, S. N. Svarichevskaya, V. S. Telegus, *Sov. Powder Metall. Met. Ceram.*, **6**, 61 (1969).
21. P. Rogl, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **102**, 971 (1971).
22. V. S. Telegus, Yu. B. Kuz'ma, *Porosh. Met.*, **11**, No. 1, 67 (1971); *Chem. Abstr.*, **74**, 131,055 (1971).
23. Yu. B. Kuz'ma, V. I. Lakh, B. I. Stadnyk, D. A. Kovalyk, *Porosh. Met.*, **10**, No. 12, 59 (1970); *Chem. Abstr.*, **74**, 146,837 (1971).
24. H. Haschke, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **97**, 1459 (1966).
25. H. Haschke, Thesis, University of Vienna, 1965.
26. R. Kiessling, *Acta Chem. Scand.*, **1**, 893 (1947).
27. V. S. Telegus, Yu. B. Kuz'ma, C. K. Stefanishina, *Porosh. Met.*, **9**, No. 2, 64 (1969); *Chem. Abstr.*, **71**, 7101 (1969).
28. Yu. B. Kuz'ma, D. A. Kovalyk, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **5**, 1428 (1969); *Chem. Abstr.*, **72**, 71,708 (1970).
29. W. Steurer, P. Rogl, H. Nowotny, *Monatsh. Chem.*, **109**, 919 (1978).
30. P. Rogl, H. Nowotny, *J. Less-Common Met.*, **67**, 41 (1979).
31. L. Toth, H. Nowotny, F. Benesovsky, E. Rudy, *Monatsh. Chem.*, **92**, 794 (1961).
32. J. Aselius, *Acta Chem. Scand.*, **14**, 2169 (1960).
33. E. Lugscheider, O. Knotek, H. Reimann, *Monatsh. Chem.*, **105**, 80 (1974).
34. Yu. B. Kuz'ma, O. V. Nych, R. V. Skolozdra, *Inorg. Mater. (USSR)*, **2**, 1709 (1966).
35. Yu. B. Kuz'ma, P. K. Starodub, *Izv. Akad. Nauk SSSR*, **9**, 337 (1973); *Chem. Abstr.*, **79**, 10,889 (1973).
36. A. S. Sobolev, Yu. B. Kuz'ma, T. F. Fedorov, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **3**, 536 (1967); *Chem. Abstr.*, **67**, 68,032 (1967).
37. Yu. B. Kuz'ma, A. S. Sobolev, T. F. Fedorov, *Sov. Powder Metall. Met. Ceram.*, **5**, 81 (1971).
38. N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, **9**, 1696 (1973); see also *Str. Svoistva Primen. Metallid. (Mater. Simp.) 2nd*, 1972, I. I. Kornilov, N. M. Matveeva, eds., Nauka, Moscow, p. 102; *Chem. Abstr.*, **82**, 178,302 (1975).
39. W. Jeitschko, H. Nowotny, F. Benesovsky, *Monatsh.*, *Chem.*, **94**, 565 (1963).
40. H. Boller, W. Rieger, H. Nowotny, *Monatsh. Chem.*, **95**, 1497 (1964).
41. D. R. Armstrong, E. Cetina, P. G. Perkins, paper presented at the 7th International Symposium on Boron, Borides and Related Compounds, Uppsala, June, 1981.
42. W. Jeitschko, *Acta Crystallogr., Sect. B*, **25**, 163 (1969).
43. G. F. Stepanchikova, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 10, 214, 44 (1980); *Chem. Abstr.*, **94**, 21,153 (1981).
44. N. F. Chaban, *Sov. Powder Metall. Met. Ceram.*, **229**, 61 (1982).
45. Yu. B. Kuz'ma, S. I. Mikhaleiko, B. Ya. Kotyr, Ya. P. Yamiokyuk, *Dopov. Akad. Nauk Ukr. RSR, Ser. B*, **3**, 25 (1982); *Chem. Abstr.*, **97**, 172,756 (1982).
46. Yu. B. Kuz'ma, S. I. Svarichevskaya, A. S. Sobolev, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **9**, 1512 (1973); *Chem. Abstr.*, **80**, 31,241 (1974).
47. R. Fruchart, *Ann. Chem.*, **4**, 1247 (1959).
48. T. Kanaizuka, *J. Solid-State Chem.*, **41**, 195 (1982); *Mater. Res. Bull.*, **16**, 1601 (1981).
49. E. I. Gladyshevskij, T. F. Fedorov, Yu. B. Kuz'ma, R. V. Skolozdra, *Sov. Powder Metall. Met. Ceram.*, **4**, 305 (1966).
50. T. Ishii, M. Shimada, M. Koizumi, *J. Magn. Magn. Mater.* **31-34**, 151 (1983); *Solid-State Commun.*, **47**, 303 (1983); *J. Chem. Phys.*, **78**, Part I, 3294 (1983); **79**, 1511 (1983).
51. W. Jeitschko, *Monatsh. Chem.*, **17**, 1472 (1966).
52. K. E. Spear, P. McDowell, F. McMahon, *J. Am. Ceram. Soc.*, **69**(1), C4 (1986).
53. H. Klesnar, P. Rogl, research at University of Vienna, 1987, to be published.
54. S. Okada, T. Atoda, I. Higashi, Y. Takahashi, *J. Less-Common Met.*, **113**, 331 (1985).
55. W. Jung, K. Schweitzer, *Z. Kristallogr.*, **174**, 109 (1986).

56. Yu. B. Kuz'ma, L. G. Aksel'rud, *Sov. Phys. Crystallogr.*, **31**, 108 (1986).
57. P. Rogl, unpublished results.
58. Yu. B. Kuz'ma, N. P. Sacharyuk, L. T. Maksymova, *Poroshk. Metall.*, **9**, 70 (1988).
59. O. M. Dub, Yu. B. Kuz'ma, M. D. Masys, N. F. Chaban, T. I. Malinovskij, *Dokl. Akad. Nauk Ukr. SSR* **2**, 35 (1987).
60. S. I. Mikhaleiko, Yu. B. Kuz'ma, V. A. Bryskov, *Dokl. Akad. Nauk Ukr. SSR, Ser. B8*, **43** (1986).
61. P. Rogl, H. Klesnar, P. Fischer, *J. Am. Ceram. Soc.*, **71**, C450 (1988).
62. H. Klesnar, P. Rogl, Proc. 20emes Journées des Actinides, Prague, April 1990, CSSR
63. P. Rogl, M. Beauvy, J. Larroque, Proc. 19emes Journées des Actinides, Madonna di Campiglio, March 1989, Italy.
64. I. Smid, P. Rogl, in *Science of Hard Materials*, Inst. of Physics Conf. Series No. 75, E. A. Almond, C. A. Brookes, R. Warren, eds., Adam Hilger Ltd., Bristol, Boston, 1986, pp. 249–257.
65. P. Rogl, H. Haines, P. E. Potter, to be published.

6.7.2.3. Borides with Two-Dimensional Boron Networks

With a B–transition metal ratio, $B:M_T > 1.5$ boron networks are formed resulting in metal–B layer structures, such as transition-metal diborides (see Table 1). The binary structures¹ are classified by their modes of stacking of closely packed (3^6) metal-atom layers as well as planar or puckered (6^3) B layers (for the B nets K, K', H, H', see Fig. 1). Boron coordination is either a trigonal-metal prism or a metal T_d . Although defects may occur in both sublattices (such as in Ru_2B_{3-x} or $Mo_{1-x}B_3$) borides reveal small homogeneous regions; the few exceptions are the diborides of Nb, Ta and to a lesser degree MoB_{2-x} (AlB_2 type).

Orthorhombic distortion, owing to puckered metal as well as B layers, occurs in the RuB_2 type, whereas for monoclinic Ir_2B_{3-x} ($IrB_{1.35}$) a sequence of puckered B and metal double layers containing isolated B atoms is established².

The occurrence of binary and ternary ReB_2 phases is regulated⁴ by a constant electron–atom ratio $e:a = 4.4$.

The graphite-like 6^3 boron nets in AlB_2 -type borides are rigid^{6–8}. No diborides are expected for the larger values of $R_{M_T}:R_B$ and, accordingly, GdB_2 is a high-T phase and SmB_2 , with the largest radius ratio, can be obtained only from high-T, high-pressure synthesis⁹.

The electronic structures of the binary first-row transition-metal diborides, ScB_2 , TiB_2 , VB_2 , CrB_2 and MnB_2 (all AlB_2 type), extrapolated to a hypothetical FeB_2 reveals a negative charge on the Fe atoms, and so no compound formation is expected. However, the existence of a thermodynamically stable FeB_2 with AlB_2 type is claimed⁵² on poor agreement between observed and calculated d values and x-ray intensities. The rigid B net cannot accommodate metal atoms much smaller than Mn; hence Co and Ni diborides do not exist and MnB_2 is limited to a high-T compound⁶⁵ that decomposes into Mn_3B_4 and MnB_4 below $\sim 1075^\circ C$.

Despite possible electron-acceptor B sp^3 combining with the group I and II main-group elements, only metastable AlB_2 phases, AgB_2 and AuB_2 , are known, and the Ag–B and Au–B systems exhibit simple monotectics and eutectics, respectively.

6.7. Formation of Borides

6.7.2. Existence and Crystal Chemistry of Borides

6.7.2.3. Borides with Two-Dimensional Boron Networks

56. Yu. B. Kuz'ma, L. G. Aksel'rud, *Sov. Phys. Crystallogr.*, **31**, 108 (1986).
57. P. Rogl, unpublished results.
58. Yu. B. Kuz'ma, N. P. Sacharyuk, L. T. Maksymova, *Poroshk. Metall.*, **9**, 70 (1988).
59. O. M. Dub, Yu. B. Kuz'ma, M. D. Masys, N. F. Chaban, T. I. Malinovskij, *Dokl. Akad. Nauk Ukr. SSR* **2**, 35 (1987).
60. S. I. Mikhaleenko, Yu. B. Kuz'ma, V. A. Bryskov, *Dokl. Akad. Nauk Ukr. SSR, Ser. B8*, **43** (1986).
61. P. Rogl, H. Klesnar, P. Fischer, *J. Am. Ceram. Soc.*, **71**, C450 (1988).
62. H. Klesnar, P. Rogl, Proc. 20emes Journées des Actinides, Prague, April 1990, CSSR
63. P. Rogl, M. Beauvy, J. Larroque, Proc. 19emes Journées des Actinides, Madonna di Campiglio, March 1989, Italy.
64. I. Smid, P. Rogl, in *Science of Hard Materials*, Inst. of Physics Conf. Series No. 75, E. A. Almond, C. A. Brookes, R. Warren, eds., Adam Hilger Ltd., Bristol, Boston, 1986, pp. 249–257.
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TABLE 1. METAL BORIDES: STRUCTURE TYPES AND REPRESENTATIVES WITH TWO-DIMENSIONAL B NETWORKS

Structure type	Stacking sequence (see Fig. 1)	Boron aggregation; boron coordination	Binary representatives	Ternary representatives	Refs.
AlB_2 $P6_3/mmm$	AHAH...	Planar 6^3 net; trigonal prism	(see Refs. 1, 8) MgB_2 , AlB_2 , TiB_2 , VB_2 , CrB_2 , MnB_2 , ZrB_2 , NbB_2 , MoB_2 , ^a HfB_2 , TaB_2 , WB_2 (impurity stabil.?) REB_2 , RE = Sm(hP phase) ⁹ , Gd (hT phase) ⁵⁴ Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y (see Ref. 23) AnB ₂ , An = U, Np, Pu	$\text{Mo}_x\text{Mn}_{1-x}\text{B}_2$, $x = 0.37-0.45$, 800°C	3
ReB_2 $P6_3/mmc$	AK'BK'AK'BK'...	puckered 6^3 net; T_d	TeB_2 , ²⁵ ReB_2 , ²⁶	$\text{Mo}_{0.3}\text{Ru}_{0.7}\text{B}_2$ $\text{W}_{0.3}\text{Ru}_{0.7}\text{B}_2$ $\text{V}_{0.4}\text{Os}_{0.6}\text{B}_2$ $\text{Mo}_{0.3}\text{Os}_{0.7}\text{B}_2$ $\text{W}_{0.3}\text{Os}_{0.7}\text{B}_2$ $\text{Mo}_{0.6}\text{Ir}_{0.4}\text{B}_2$ $\text{W}_{0.56}\text{Ir}_{0.44}\text{B}_2$ —	5
$\text{Ru}_2\text{B}_{3-x}$ $P6_3/mmc$	AH'AK'BH'BK'AH'	Puckered 6^3 net and isolated boron atoms; trigonal prism, T_d	Ru_2B_3 , ²⁷ Os_2B_3 ¹	($\text{W}_{0.67}\text{Pd}_{0.33}$) ₂ B ₅ , 950°C	30
$\text{Mo}_2\text{B}_{5-x}$ $R\bar{3}m$	AHAK'BHBK'CHCK'AH...	Puckered and planar 6^3 nets; trigonal prism and T_d	$\text{MoB}_{2.3}$, ^{28,a} ²⁹ W_2B_{5-x}	—	30
W_2B_{5-x} $P6_3/mmc$	AHAK'BHBK'AH...	Puckered and planar 6^3 net; T_d and trigonal prism	$\text{WB}_{2.0}$ ²⁷	—	30
$\text{Mo}_{1-x}\text{B}_3$ $P6_3/mmc$	A'HB'HA'H...	Planar 6^3 net; T_d	$\text{MoB}_{3.75}$, ³¹ $\text{WB}_{\sim 4}$ ^{1,4}	($\text{Mo}_{0.5}\text{Rh}_{0.5}$) _{1-x} B ₃ , above 1150°C ($\text{W}_{0.67}\text{Ni}_{0.33}$) _{1-x} B ₃ , 1000°C	30

(continued)

TABLE 1. (continued)

Structure type	Stacking sequence (see Fig. 1)	Boron aggregation; boron coordination	Binary representatives	Ternary representatives	Refs.
RuB_2		Corrugated 6^3 net;		$(W_{0.33}Rh_{0.67})_{1-x}B_3$, 1100°C	30
Pmmn		T_d	RuB_2 ³² OsB_2 ³²		
Ir_2B_{3-x}		Isolated B atoms,	$IrB_{1.35}$ ²		30
$C2/m$		puckered 6.4.6.4 net; T_d trigonal prism			
$Pr_{5-x}Co_{2+x}B_6$		Planar 6^3 net;			
$R\bar{3}m$		trigonal prism		$M_{RE5-x}Fe_{2+x}B_6$, $M_{RE} = Y, Ce, Pr^{73}$, Nd, Sm, Eu, Gd, Tb, Dy, Yb	72
				$M_{RE5-x}Co_{2+x}B_6$, $M_{RE} = Y, La, Ce, Pr$, Nd, Sm, Gd, Tb, Dy, Ho, Er	72
$CeCr_2B_6$		Corrugated 6^3 -net fragments; B_6 groups connected at 210 pm;		$M_{RE}Cr_2B_6$: $M_{RE} = Ce^{14,33}$, Pr, Nd, Sm	34
Immm		trigonal prism, T_d			
Y_2ReB_6		Planar nets of five-, six- and seven-membered rings of B atoms;		$M_{RE2}ReB_6$: $M_{RE} = Y, Gd, Tb, Dy$, Ho, Er, Tm, Lu	13
Pbam		trigonal prism		Yb_2AlB_6 ¹⁷ $M_{RE2}RuB_6$: $M_{RE} = Y, Gd, Tb, Dy$, Ho, Er, Tm, Yb, Lu	48, 49, 69
				$M_{RE2}OsB_6$: $M_{RE} = Y, Gd, Tb, Dy$, Ho, Er, Tm, Yb, Lu	48, 49, 69
				$U_2M_TB_6$, $M_T = W^{56}$, Mo, Re, Os	49

ThMoB ₄ Cmmm	Planar nets of five- and seven-membered B rings; trigonal prism	—	Pu ₂ M _T B ₆ , M _T = Tc, Re, Ru, Os ThM _T B ₄ , M _T = V, Mo, W, Re UM _T B ₄ , M _T = Mo, W, Re M _T = Ru, Os M _{RE} VB ₄ , M _{RE} = Y, Gd, Tb, Dy Ho, Er M _{RE} CrB ₄ , M _{RE} = Y, Ce ³³ , Pr ³⁴ , Nd ³⁴ , Sm ³⁴ , Gd, Tb, Dy, Ho, Er, Tm ¹¹ , Lu M _{RE} MnB ₄ , M _{RE} = Y, Ce ³⁸ , Gd, Tb, Dy, Ho, Er M _{RE} FeB ₄ , M _{RE} = Y, Ce, Sm ⁴¹ , Gd, Tb, Dy, Ho, Er, Tm, Yb ⁷⁴ , Lu M _{RE} CoB ₄ , M _{RE} = Y, Ce ⁵⁹ , Gd, Tb, Dy, Ho, Er, Tm, Yb ⁷⁴ , Lu M _{RE} NiB ₄ , M _{RE} = Er, Tm, Yb ⁷⁴ , Lu M _{RE} MoB ₄ , M _{RE} = Y, Gd, Tb, Dy, Ho, Er M _{RE} RuB ₄ , M _{RE} = Y, Gd, Tb, Dy, Ho, Er, Tm, Yb ⁴⁰ , Lu ⁴⁹ M _{RE} WB ₄ , M _{RE} = Y, Gd, Tb, Dy, Ho, Er M _{RE} ReB ₄ , M _{RE} = Y, Ce ⁶¹ , Sm ⁶⁰ , Gd, Tb, Dy, Ho, Er, Tm ³⁷ M _{RE} OsB ₄ , M _{RE} = Y, Gd, Tb, Dy, Ho, Er, Tm, Yb ⁴⁰ , Lu ⁴⁹	55 12 35 49 36 10 36 42 42 50 11 39 11 11 39
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(continued)

6.7. Formation of Borides
 6.7.2. Existence and Crystal Chemistry of Borides
 6.7.2.3. Borides with Two-Dimensional Boron Networks

TABLE 1. (continued)

Structure type	Stacking sequence (see Fig. 1)	Boron aggregation; boron coordination	Binary representatives	Ternary representatives	Refs.
ErNiB_4 14/mmm		Planar net of eight-membered B rings linked by a B pair	—	$\text{M}_{\text{RE}}\text{AlB}_4$, $\text{M}_{\text{RE}} = \text{Yb}^{17}, \text{Lu}^{17}$ UM_TB_4 , $\text{M}_T = \text{V}, \text{Cr}$, Mn, Fe, Co PuM_TB_4 , $\text{M}_T = \text{Mo}$, W, Tc, Re, Ru, Os $\text{M}_{\text{RE}}\text{NiB}_4$, $\text{M}_{\text{RE}} = \text{Y}$, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er UNiB_4 $\text{M}_{\text{RE}}\text{NiB}_{13}$, $\text{M}_{\text{RE}} = \text{Y}$, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu $\text{U}_4\text{NiB}_{13}$ $\text{M}_T\text{B}_2\text{C}_2$, $\text{M}_T = \text{Ca}$, Y, Ln	35, 62 55 77 77
$\text{Er}_4\text{NiB}_{13}$ 14/mmm		Puckered nets of seven- and four-membered rings of B atoms plus isolated borons	—		78 79
LaB_2C_2 P42c		Planar 8.4.8, ordered B—C net; B—C—B—C group centering a metal cube	—		18
YB_2C P4 ₂ /mbc		Planar 7.4.7 ordered B—C nets; trigonal prism, B—C—B—C group centering a metal cube	—	$\text{M}_{\text{RE}}\text{B}_2\text{C}$, $\text{M}_{\text{RE}} = \text{Y}$, Tb, Dy, Ho, Er, Tm, Yb $\text{M}_{\text{RE}} = \text{Sc}, \text{Lu}$	19 57
ThB_2C R3m		Puckered B—C nets	—	ThB_2C , UB_2C (high-T phase) ²⁰ PuB_2C	20 76

^a The composition range of the Mo borides MoB_2 and $\text{Mo}_2\text{B}_{5-x}$ is $\text{MoB}_{1.55-2.0}$ at 2073 K and $\text{MoB}_{2.00-2.16}$ (1800–2100 K), with a large B deficiency⁵¹; see also refs. 70, 71.

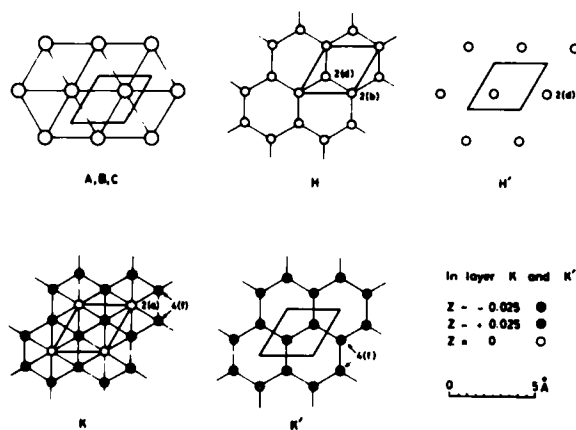


Figure 1. Metal-atom layers (A, B, C) and B-atom layers: H, H' are planar layers; K, K' are puckered layers¹.

Despite the occurrence of binary AlB_2 borides (see also Fig. 2), no ternary representatives are known; $(\text{Mn}, \text{Mo})\text{B}_2$ found from isothermal sections³ is a stabilized high-T phase by conversion to lower T by a statistical (?) metal-metal substitution. Both MnB_2 and MoB_2 are high-T compounds stable above 1075°C ⁶⁵ and 1517°C ⁵³, respectively; WB_2 is claimed but is either metastable or impurity stabilized²⁷. Similar examples⁴ are observed with $(\text{W}, \text{Pd})_2\text{B}_5$ (Mo_2B_5 type) as well as $(\text{Mo}, \text{Rh})_{1-x}\text{B}_3$ and $(\text{W}, \text{Ni})_{1-x}\text{B}_3$ ($\text{Mo}_{1-x}\text{B}_3$ type). The phase relations in the B-rich section of the $\text{Mo}(\text{W})\text{-B}$ binaries, however, are not known precisely.

For large $R_{\text{M}_T} : R_{\text{M}_T}$ ratios in ternary compounds, however, a different approach to accommodate large and small transition-metal atoms allows formation of B nets consisting of irregular, five-, six- and seven-membered B rings, as in the YCrB_4 (5, 7), ThMoB_4 (5, 7) and Y_2ReB_6 (5-7) structures (see Fig. 3¹⁰⁻¹³). In all three structures the five-membered boron rings are above and below the smaller of the two transition-metal components. Therefore, the YCrB_4 representatives (see Table 1) also comprise those elemental combinations for which a restrictive size factor $R_B : R_{\text{M}_T}$, and a resulting inability to form net-type borides based only upon six-membered B rings is well known, e.g., $\text{M}_{\text{RE}}\text{NiB}_4$ (no Ni diboride), CeReB_4 (no Ce diboride). For the larger rare-earth elements $\text{M}_{\text{RE}}\text{NiB}_4$ borides alternatively adopt a structure type with planar eight-membered boron rings linked by a boron pair to form an open three-dimensional network⁷⁷. Similarly, the structure type of $\text{M}_{\text{RE}4}\text{NiB}_{13}$ consists^{78,79} of four- and seven-membered boron rings plus isolated B atoms above and below the B_4 group to form a B_6 octahedron such as in UB_4 .

For the larger rare-earth metals ternary diborides are formed, having the CeCr_2B_6 structure¹⁴. Here puckered B nets are incompletely developed, with B_6 groups in the form of loosely attached 6³-network fragments ($\text{B-B} \sim 210$ pm). There is a resemblance to the structures of $\text{W}_3\text{IrB}_{6-x}$ ¹⁵ and W_2CoB_2 ¹⁶ (see Fig. 4).

Thorium is one of the largest metals to form $\text{M}_T\text{M}'_T\text{B}_4$ borides. The ThMoB_4 type, however, has a different arrangement of the five- and seven-membered B rings

	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W	Mn	Tc	Re	Fe	Ru	Os	Co	Rh	Ir	Ni	Pd	Pt	Al
Sc													y						y			
Y				b			a	c	c	b		c,s	d	i,t	i,t	m			λ			r
La							r	r	r			r	r			r			r			r
Ce				r	r		q	r	r	x		α	m			y			ε			r
Pr							p												ε			
Nd							p						r			r			ε			
Pm																						
Sm							p					z	l			r			ε			
Eu																						
Gd	r	r	r	b			ja	c	c	j,b		c,s	jo	i,t	i,t	jn			λ			
Tb				b			a	c	c	b		c,s	m	i,t	i,t	m			λ			
Dy				b			a	c	c	b		c,s	m	i,t	i,t	m			λ			
Ho				b			a	c	c	b		c,s	m	i,t	i,t	m			λ			
Er				b			a	c	c	b		c,s	m	i,t	i,t	m			λ			
Tm							c					e,s	m	i,t	i,t	m			λ			
Yb													δ	j	j	δ			λ			
Lu							a					s	m	t,u	t,u	m			λ			k
Th			h				h	h	h			h										
Pa																						
U				g			g	g	g	g	u	g	g	g	g	g	g		λ	u		
Np																						
Pu							w	w				w	w			w	w					

■ YCrB₄
 ■ ThMoB₄
 ■ Y₂ReB₆
 ■ CeCr₂B₆
 ■ AlB₂
 ■ ReB₂
 ■ Er₄NiB₁₃
 ■ ErNiB₄
 □ RuB₂
 □ type unknown

Figure 2. Formation of ternary borides $M_{RE}M_TB_4$ (M_{RE} = rare-earth metal, M_T = transition-metal element) and different structure types. ■, YCrB₄ type; ■, ThMoB₄ type; ■, Y₂ReB₆ type; ■, CeCr₂B₆ type; ■, Er₄NiB₁₃ type; ■, ErNiB₄ type; □, compound formation observed but structure type unknown. Refs: a¹⁰, b³⁶, c¹¹, d⁴⁶, e³⁷, f³⁸, g³⁵, h¹², i³⁹, j⁴⁰, k¹⁷, l⁴¹, m⁴², n⁴⁴, o⁴⁵, p³⁴, q³³, r⁴³, s⁴⁷, t⁴⁸, u⁴⁹, v⁵⁰, w⁵⁵, x⁵⁸, y⁵⁹, z⁶⁰, α⁶¹, β⁶³, γ⁶⁴, δ⁷⁴, ε⁷⁷, λ⁷⁸, ν⁷⁹. Binary diborides are indicated for comparison: ■, AlB₂ type; ■, ReB₂ type; □, RuB₂ type.

compared to the YCrB₄ type, which are related by a simple transposition. Uranium as a smaller atom (comparable to one of the smaller rare earths) favors the YCrB₄-type structure for larger ratios, $R_U : R_{M_T}$, e.g., in combination with the 3d metals V, Cr, Mn, Fe, Co, but combinations with 4d or 5d elements form ThMoB₄-type crystals (see also Table 1 and refs. therein).

Aluminum-containing compounds LuAlB₄, YbAlB₄ (YCrB₄ type) as well as Yb₂AlB₆ (Y₂ReB₆ type) are prepared from Al flux methods; Al in these compounds behaves as a transition metal¹⁷.

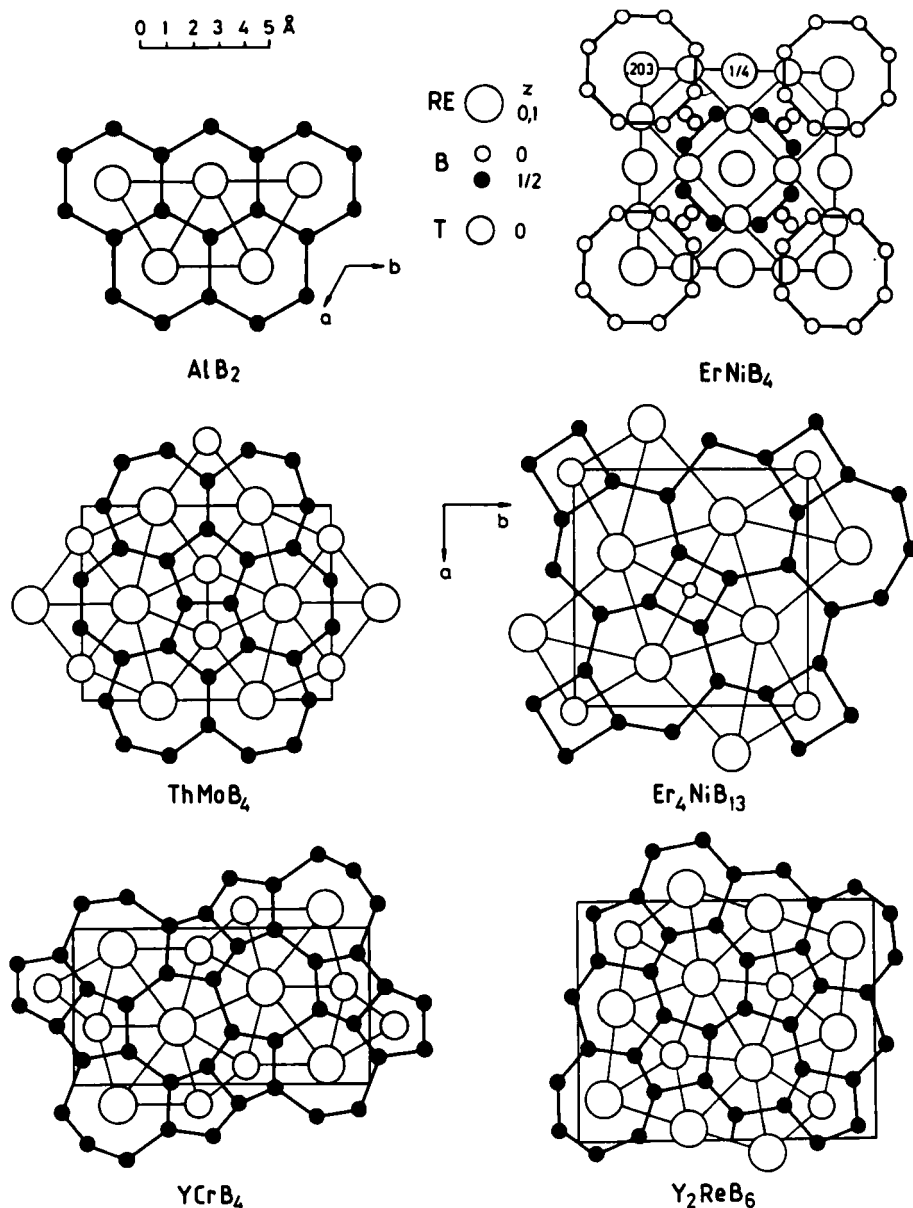


Figure 3. Comparison of boron net-type diboride structures, ThMoB_4 , YCrB_4 , Y_2ReB_6 , ErNiB_4 , $\text{Er}_4\text{NiB}_{13}$, and AlB_2 projected along $[001]$.

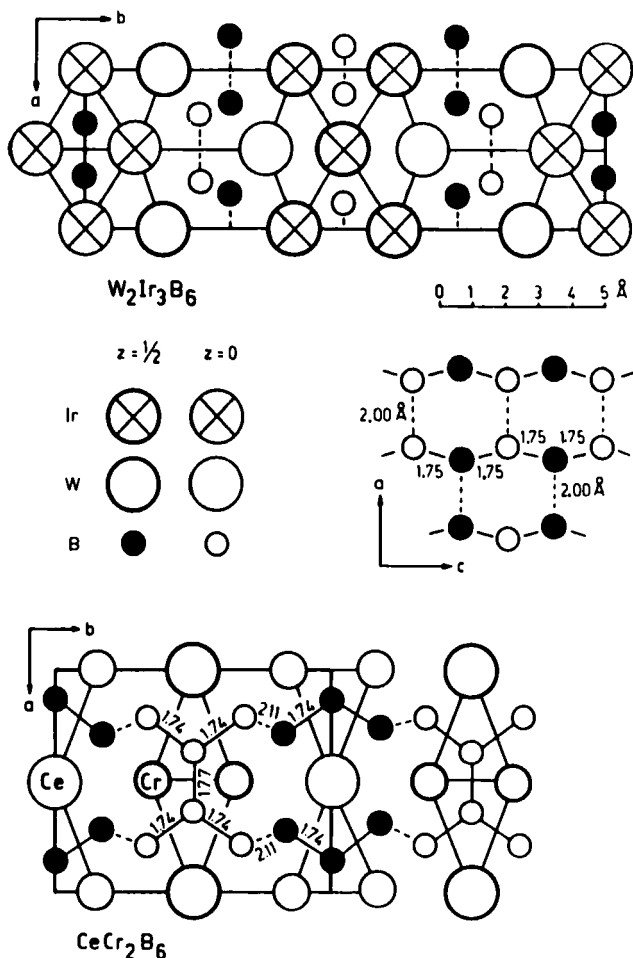
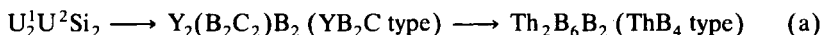


Figure 4. Comparison between the structure types of $CeCr_2B_6$ and $W_2Ir_3B_{6-x}$ ($x \sim 1$) as seen in a projection along [001].

Planar hexagonal boron layers are also found in a lower boride structure⁷² $Pr_{5-x}Co_{2+x}B_6$ ($0 \leq x \leq 1$), where B and Co atoms are substituting each other to some extent.

The structures of Y_2ReB_6 and $YCrB_4$, as well as $YCr(B_4)$ and $Sc\Box(B_2C_2)$, are related¹⁰. Although no carbon layer compounds exist, there are B—C net-type carboborides (borocarbides) such as the YB_2C - or the YB_2C_2 -type structures with planar or corrugated networks exhibiting complicated ordering among B and C atoms^{18,19}. Similar ThB_2C and UB_2C structures, which derive from simple hexagonal metal layers (AlB_2 -type) and B—C networks²⁰, are found within the actinide—B—C

systems, Th(U, Pu, Np)-B-C. The U_3Si_2 ($U_2^1U^2Si_2$), YB_2C and ThB_4 structures are related, especially with respect to their identical $4.3^2.4.3$ metal layers (formed by U^1 atoms in U_3Si_2) (see Fig. 3 in §6.7.2.1.2):



Accordingly, the replacement of the U^2 atoms in U_3Si_2 by planar B_2C_2 arrangements generates the YB_2C structure type²¹; further replacement of the B_2C_2 groups by regular B_6O_6 results in the ThB_4 structure, thus forming a branch to the three-dimensional B framework structures as typical for ratios $B:M_T \geq 4$.

(P. ROGL)

1. T. Lundström, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 351.
2. T. Lundström, L. E. Tergenius, *Acta Chem. Scand.*, **27**, 3705 (1973).
3. V. S. Telegus, Yu. B. Kuz'ma, *Porosh. Met.*, **11**, No. 1, 67 (1971); *Chem. Abstr.*, **74**, 131,054 (1971).
4. H. Nowotny, H. Haschke, F. Benesovsky, *Monatsh. Chem.*, **98**, 547 (1967).
5. P. Rogl, E. Rudy, *J. Solid-State Chem.*, **24**, 195 (1978).
6. W. N. Lipscomb, D. Britton, *J. Chem. Phys.*, **33**, 275 (1960).
7. P. G. Perkins, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 31.
8. K. E. Spear, *J. Less-Common Met.*, **47**, 195 (1976).
9. J. F. Cannon, D. M. Cannon, H. T. Hall, *J. Less-Common Met.*, **56**, 83 (1977).
10. Yu. B. Kuz'ma, *Sov. Phys. Crystallogr.*, **15**, 312 (1970).
11. Yu. B. Kuz'ma, S. I. Svarichevskaya, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, **34**, 166 (1972); *Chem. Abstr.*, **76**, 132,557 (1972).
12. P. Rogl, H. Nowotny, *Monatsh. Chem.*, **105**, 1082 (1974).
13. Yu. B. Kuz'ma, S. I. Svarichevskaya, *Sov. Phys. Crystallogr.*, **17**, 569 (1972).
14. Yu. B. Kuz'ma, S. I. Svarichevskaya, *Sov. Phys. Crystallogr.*, **17**, 830 (1973).
15. P. Rogl, F. Benesovsky, H. Nowotny, *Monatsh. Chem.*, **103**, 965 (1972).
16. W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.*, **97**, 378 (1966).
17. S. I. Mikhaleenko, Yu. B. Kuz'ma, M. M. Korsukova, V. N. Gurin, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **16**, 1325 (1980); *Chem. Abstr.*, **94**, 75,868 (1981).
18. J. Bauer, O. Bars, *Acta Crystallogr., Sect. B*, **36**, 1540 (1980).
19. J. Bauer, J. Debuigne, *J. Inorg. Nucl. Chem.*, **37**, 2473 (1975).
20. P. Rogl, J. Bauer, J. Debuigne, *J. Less-Common Met.*, **82**, 366 (1981); *J. Nucl. Mater.*, **165**, 74 (1989).
21. V. I. Matkovich, J. Economy, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 78.
22. H. P. Woods, F. E. Wawner, B. G. Fox, *Science*, **151**, 75 (1966).
23. J. Bauer, J. Debuigne, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **277**, 851 (1973).
24. P. E. Potter, in *MTP Int. Rev. Sci., Inorg. Chem.*, Vol. 7, 2nd ed., K. W. Bagnall, ed., Butterworths, London, 1975, p. 257.
25. W. Trzebiatowsky, J. Rudzinski, *J. Less-Common Met.*, **6**, 244 (1964).
26. S. La Placa, B. Post, *Acta Crystallogr.*, **15**, 97 (1962).
27. T. Lundström, *Ark. Kem.*, **30**, 115 (1968).

28. R. Kiessling, *Acta Chem. Scand.*, **1**, 893 (1947).
29. Yu. B. Kuz'ma, T. S. Serebriyakova, A. M. Plakhina, *Zh. Neorg. Khim.*, **12**, 288 (1967); *Chem. Abstr.*, **67**, 26,678 (1967).
30. H. Haschke, Thesis, University of Vienna, 1965.
31. T. Lundström, I. Rosenberg, *J. Solid-State Chem.*, **6**, 299 (1973).
32. B. Aronsson, *Acta Chem. Scand.*, **17**, 2036 (1963).
33. Yu. B. Kuz'ma, S. N. Svarichevskaya, V. I. Fomenko, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **9**, 1372 (1973); *Chem. Abstr.*, **79**, 150,265 (1973).
34. S. I. Mikhaleiko, Yu. B. Kuz'ma, *Dopov. Akad. Nauk Ukr. SSR. Ser. A*, 951 (1977); **5A**, 465 (1975); *Chem. Abstr.*, **88**, 30,613 (1978).
35. P. Rogl, H. Nowotny, *Monatsh. Chem.*, **106**, 381 (1975).
36. Yu. B. Kuz'ma, *Dopov. Akad. Nauk Ukr. RSR, Ser. A* **32**, 756 (1970); *Chem. Abstr.*, **74**, 7461 (1971).
37. S. I. Mikhaleiko, *Vistn. Lvov Univ., Ser. Khim.*, **16**, 58 (1974).
38. I. P. Valyovka, Yu. B. Kuz'ma, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, No. 7, 652 (1975); *Chem. Abstr.*, **83**, 156,107 (1975).
39. P. Rogl, *Mater. Res. Bull.*, **13**, 519 (1978).
40. R. Sobczak, P. Rogl, *J. Solid-State Chem.*, **27**, 343 (1979).
41. H. F. Braun, K. Yvon, *Acta Crystallogr., Sect. B*, **36**, 2400 (1980).
42. G. F. Stepanchikova, Yu. B. Kuz'ma, *Vestn. L'vov, Ser. Khim.*, **19**, 37 (1977); *Chem. Abstr.*, **88**, 201,447 (1978).
43. No compound formation observed; see isothermal section from Fig. 1, §6.7.2.
44. N. F. Chaban, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **13**, 757 (1977); *Chem. Abstr.*, **87**, 29,793 (1977).
45. N. F. Chaban, Yu. B. Kuz'ma, N. S. Bilonizhko, O. O. Kachmar, N. V. Petrov, *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, 875 (1979); *Chem. Abstr.*, **92**, 65,384 (1980).
46. G. F. Stepanchikova, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 10, 44 (1980); *Chem. Abstr.*, **94**, 21,153 (1981).
47. Yu. B. Kuz'ma, S. I. Svarichevskaya, *Sov. Phys. Crystallogr.*, **17**, 569 (1972).
48. P. Rogl, H. Nowotny, in *The Rare Earths in Modern Science and Technology*, Vol. 3, G. J. McCarthy, J. J. Rhyne, Silber, eds., Plenum Press, New York, 1982, p. 353.
49. P. Rogl, L. DeLong, *J. Less-Common Met.*, **91**, 97 (1983).
50. N. F. Chaban, G. V. Chernyak, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **17**, 1120 (1981); *Chem. Abstr.*, **95**, 195,521 (1981).
51. D. R. Armstrong, paper presented at the 7th International Symposium on Boron, Borides and Related Compounds, Uppsala, June, 1981.
52. L. G. Voroshnin, L. S. Lyakhovich, G. G. Panich, G. F. Protasevich, *Metalloved. Term. Obrab. Met.* No. 9, 14 (1970); *Chem. Abstr.*, **73**, 133,426 (1970).
53. E. Storms, B. Mueller, *J. Phys. Chem.*, **81**, 318 (1977).
54. J. H. Blanks, K. E. Spear, paper presented at the 76th Annual Meeting of the American Ceramics Society, Chicago, 1974.
55. P. Rogl, H. Haines, P. E. Potter, *J. Nucl. Mater.*, **160**, 107 (1988).
56. I. P. Valyovka, Yu. B. Kuz'ma, *Poroshk. Metall. (Kiev)*, No. 8, 224, 71 (1981); *Chem. Abstr.*, **97**, 116,152 (1982).
57. J. Bauer, *J. Less-Common Met.*, **87**, 45 (1982).
58. Yu. B. Kuz'ma, V. E. Romashov, *Vistn. L'viv. Derzh. Univ., Ser. Khim.*, **17**, 26 (1975).
59. N. S. Bilonizhko, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **10**, 227 (1974); *Chem. Abstr.*, **81**, 7050 (1974).
60. S. N. Mikhaleiko, Yu. B. Kuz'ma, O. K. Tschyr, *Poroshk. Metall. (Kiev)*, No. 9, 50 (1982); *Chem. Abstr.*, **98**, 112,030 (1983).
61. Yu. B. Kuz'ma, S. I. Svarichevskaya, in *Bor. Pluch. Strukt. Svoistva, Mater. Mezhdunar. Simp. Boru 4*, Vol. 2, F. N. Tavazde, V. Metsuieraba, eds., Tiflis, USSR, 1974, p. 124.
62. N. I. Valyovka, Yu. B. Kuz'ma, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **14**, 356 (1978); *Chem. Abstr.*, **88**, 177,892 (1978).
63. G. F. Stepanchikova, *Vistn. L'vov Politekh. Inst.*, **130**, 58 (1979).
64. L. V. Zavteli, Yu. B. Kuz'ma, S. I. Mikhaleiko, *Inorg. Mater. (USSR)*, **24**, 1549 (1988).
65. S. Andersson, J. O. Carlsson, *Acta Chem. Scand.*, **24**, 1791 (1970).
66. W. Obrowski, *Naturwissenschaften*, **48**, 428 (1961).

67. V. N. Gurin, M. M. Korsukova, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 293.
68. N. S. Bilonizhko, N. F. Chaban, Yu. B. Kuz'ma, M. D. Ugrin, *Dopov. Akad. Nauk Ukr. SSR*, No. 6, 26 (1983); *Chem. Abstr.*, 99, 94,463 (1983).
69. K. Hiebl, P. Rogl, H. Nowotny, *J. Solid-State Chem.*, 54, 414 (1984).
70. K. E. Spear, P. K. Liao, *Bull. Alloy Phase Diagr.*, 9(4), 457 (1988).
71. I. Higashi, Y. Takahashi, S. Okada, *J. Less-Common Met.*, 123, 277 (1986). See also S. Okada, T. Atoda, I. Higashi, Y. Takahashi, *J. Mater. Sci.*, 22, 2993 (1987).
72. O. M. Dub, N. F. Chaban, Yu. B. Kuz'ma, *J. Less-Common Met.*, 117, 297 (1986).
73. Yu. B. Kuz'ma, L. G. Akselrud, N. F. Chaban, V. A. Bryskov, *Dokl. Akad. Nauk Ukr. SSR, Ser. B*, 10, 51 (1983).
74. O. M. Dub, N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 21, 1718 (1985).
75. I. P. Valyovka, Yu. B. Kuz'ma, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 288, 186 (1986).
76. P. Rogl, Proceedings of a NATO-meeting, Manchester, Sept. 1989.
77. Yu. B. Kuz'ma, N. S. Bilonizhko, V. K. Pecharskij, L. G. Akselrud, *Kristallografia*, 29, 431 (1984).
78. Yu. B. Kuz'ma, G. V. Chernjak, L. G. Akselrud, B. Ya. Kotur, N. F. Chaban, *Sov. Phys. Crystallogr.*, 28, 711 (1983).
79. P. Rogl, C. Horvath, research at the University of Vienna, to be published.

6.7.2.4. Borides with Three-Dimensional Boron Networks

The structures of B-rich borides, with the ratio $B/M > 2$, are characterized by a three-dimensional, covalent boron framework built up of B_n units ($n = 6, 12, 156$) whose complexity increases with the atomic ratio B/M . The B_n clusters can be connected directly or indirectly via isolated B atoms or pairs. This association is responsible for the existence of high-coordination boron cages, which are occupied by metal atoms. In a B_n cluster, B atomic orbitals are hybridized in a complex way, the B—B distances being longer than those between two adjacent units. Metal atoms contribute, both geometrically and electronically, to the stabilization of the boron framework (electron transfer from metal to B). The large size of the boron cages implies that only metals with large atomic radii can give B-rich borides; this explains the large number of these phases for the rare-earth or actinide elements, but only few for the other transition elements (e.g., ZrB_{12} , $r_{Zr} = 1.60 \times 10^2$ pm).

The CrB_4 structure can be regarded as a transition between the structures of the metal-rich borides and the B-rich phases with complex boron clusters. The crystal structures of CrB_4 and MnB_4 are closely related, although the former is orthorhombic, with $a = 4.744 \times 10^2$ pm, $b = 5.477 \times 10^2$ pm and $c = 2.866 \times 10^2$ pm, and the latter monoclinic, with $a = 5.503 \times 10^2$ pm, $b = 5.367 \times 10^2$ pm, $c = 2.949 \times 10^2$ pm and $\beta = 122.71^\circ$. The MnB_4 structure may be regarded as a monoclinic distortion of the CrB_4 structure involving minor changes in the interatomic distances but no changes in coordination^{1,2}. The B_4 basic unit in CrB_4 is a square of four B atoms (B—B: 1.662 to 1.693×10^2 pm; see Fig. 1). The B_4 units, linked together by weak B—B bonds (1.991×10^2 pm), give rise to channels where chains of Cr atoms are located. Chromium ($r_{Cr} = 1.27 \times 10^2$ pm) occupies the center of a small boron cage ($r_s \approx 1.30 \times 10^2$ pm being the radii of the site for metal occupancy).

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6.7.2.4. Borides with Three-Dimensional Boron Networks

67. V. N. Gurin, M. M. Korsukova, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 293.
68. N. S. Bilonizhko, N. F. Chaban, Yu. B. Kuz'ma, M. D. Ugrin, *Dopov. Akad. Nauk Ukr. SSR*, No. 6, 26 (1983); *Chem. Abstr.*, 99, 94,463 (1983).
69. K. Hiebl, P. Rogl, H. Nowotny, *J. Solid-State Chem.*, 54, 414 (1984).
70. K. E. Spear, P. K. Liao, *Bull. Alloy Phase Diagr.*, 9(4), 457 (1988).
71. I. Higashi, Y. Takahashi, S. Okada, *J. Less-Common Met.*, 123, 277 (1986). See also S. Okada, T. Atoda, I. Higashi, Y. Takahashi, *J. Mater. Sci.*, 22, 2993 (1987).
72. O. M. Dub, N. F. Chaban, Yu. B. Kuz'ma, *J. Less-Common Met.*, 117, 297 (1986).
73. Yu. B. Kuz'ma, L. G. Akselrud, N. F. Chaban, V. A. Bryskov, *Dokl. Akad. Nauk Ukr. SSR, Ser. B*, 10, 51 (1983).
74. O. M. Dub, N. F. Chaban, Yu. B. Kuz'ma, *Inorg. Mater. (USSR)*, 21, 1718 (1985).
75. I. P. Valyovka, Yu. B. Kuz'ma, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 288, 186 (1986).
76. P. Rogl, Proceedings of a NATO-meeting, Manchester, Sept. 1989.
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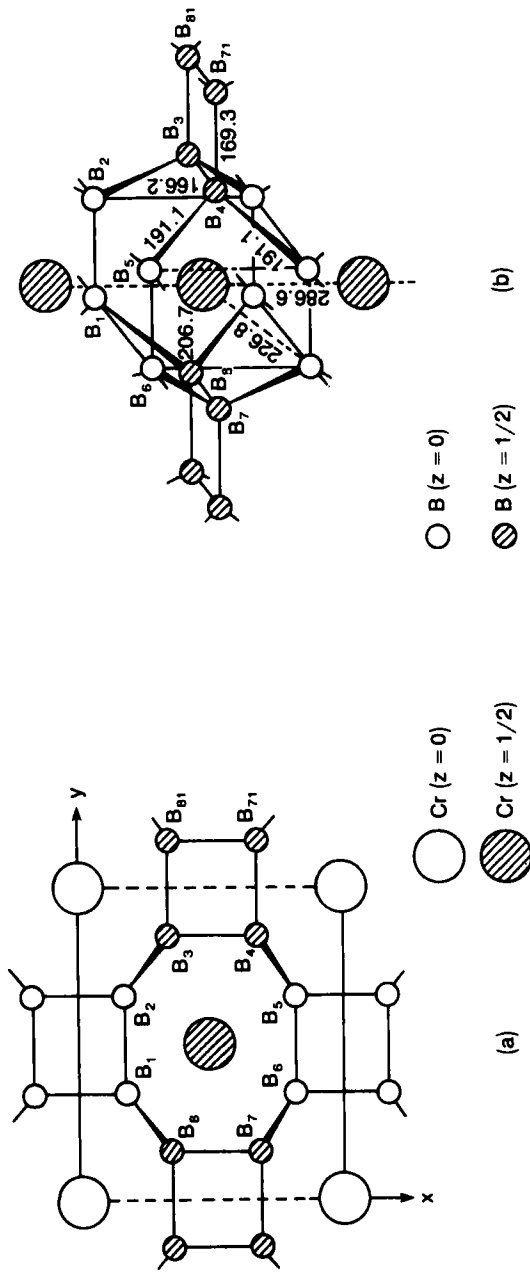


Figure 1. The crystal structure of CrB_4 . (a) Projection onto the x_0y plane. (b) The boron and chromium environments.

1. T. Lundström, *Ark. Kemi*, 31, 227 (1969); *Chem. Abstr.*, 71, 34,034 (1969).
2. T. Lundström, *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 351.

6.7.2.4.1. ThB_4 -Type Tetraborides.

Elements likely to form tetraborides of a ThB_4 type are Y, lanthanides except Eu, as well as some actinides, Th, U, Np, Pu and Am¹⁻³.

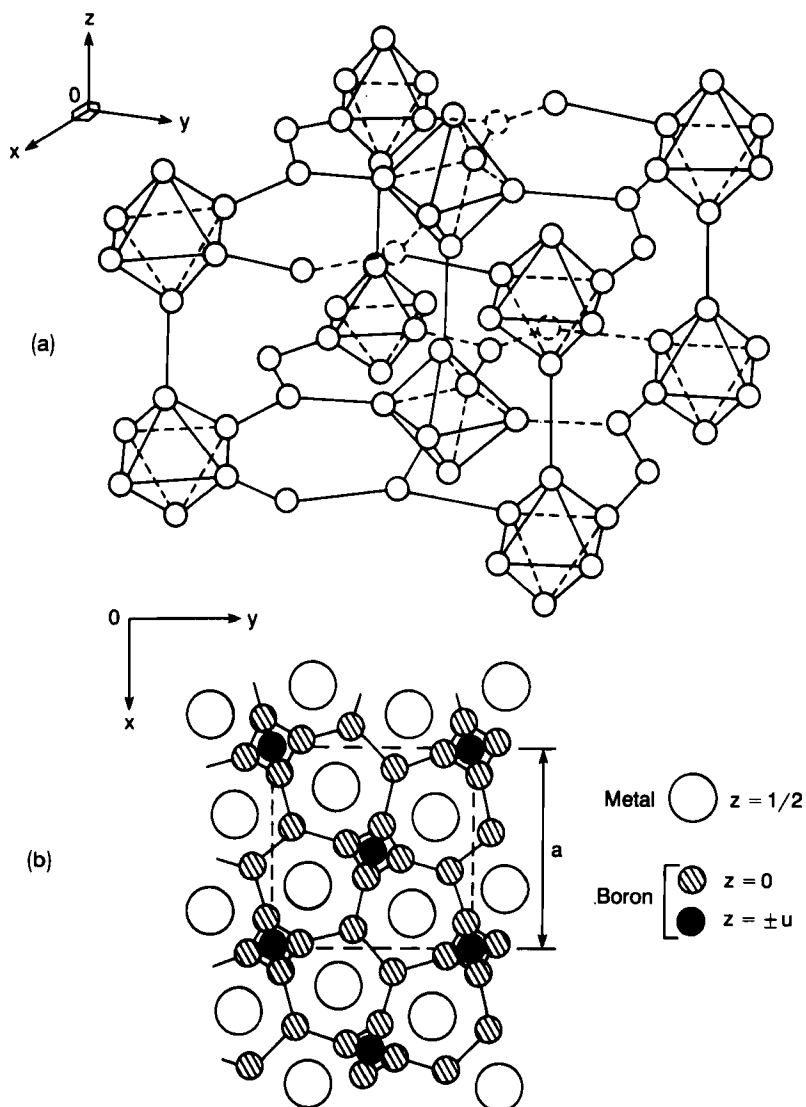


Figure 1. The crystal structure of ThB_4 -type tetraborides. (a) The covalent boron skeleton. (b) Atomic arrangement in MB_4 (projected along \bar{c}).

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 6.7.2.4.1. ThB_4 -Type Tetraborides.

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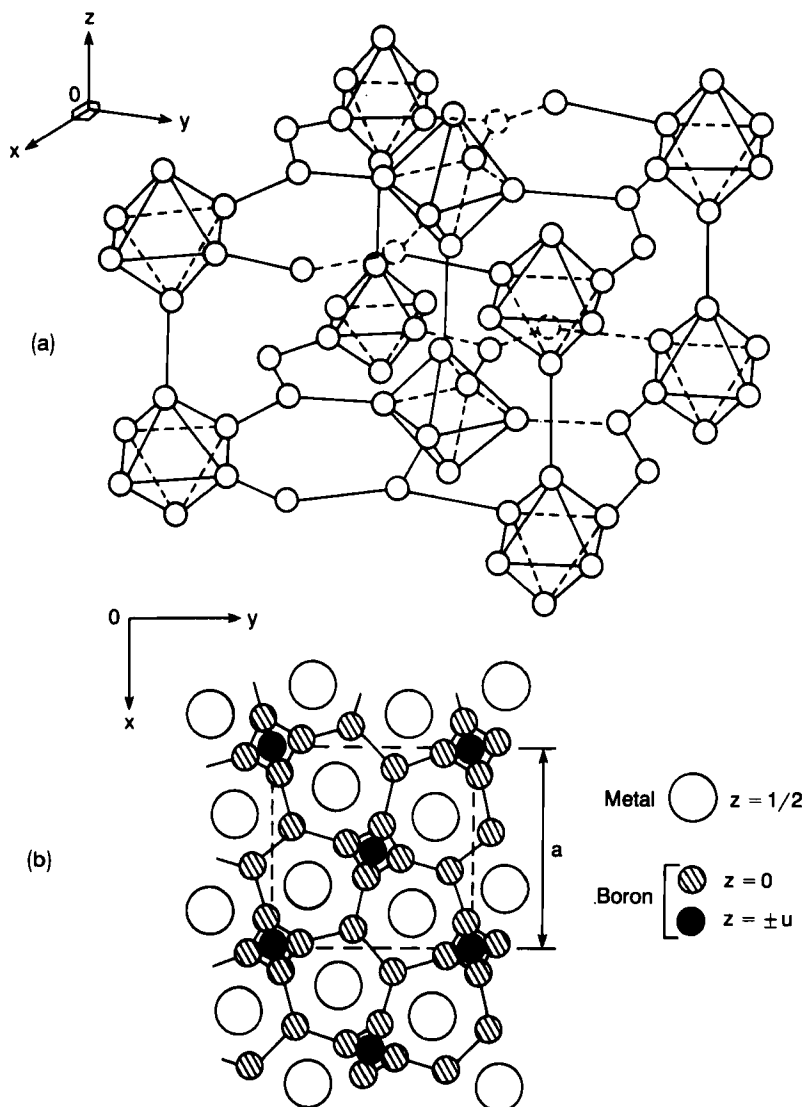


Figure 1. The crystal structure of ThB_4 -type tetraborides. (a) The covalent boron skeleton. (b) Atomic arrangement in MB_4 (projected along \vec{c}).

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 6.7.2.4. Borides with Three-Dimensional Boron Networks
 6.7.2.4.1. ThB₄-Type Tetraborides.

In the crystal structure of these phases with tetragonal symmetry (P_4/mbm , D_4^5h): the boron covalent sublattice is formed by chains of B₆ octahedra, developing along the c axis and by pairs of B atoms, bonding the octahedra in the xOy plane (see Fig. 1). The resulting three-dimensional skeleton contains tunnels parallel to the c axis that are filled by metal atoms^{1,2}.

Structure determinations for YB₄ (x-ray) and ErB₄ (neutron) confirm the structure described above and indicate that the length of the B—B bonds between two octahedra is shorter than the length of the B—B bonds in an octahedron. Moreover, Er and B atoms exhibit a strong anisotropic thermal movement in ErB₄^{7,8}.

Lattice constant data for the tetraborides are given in Table 1.

TABLE 1. LATTICE CONSTANT DATA FOR THE
TETRAGONAL ThB₄-TYPE TETRABORIDES

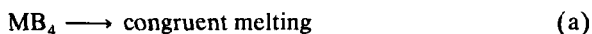
Metal	a (10 ² pm)	c (10 ² pm)	Refs.
Y	7.111 ± 0.002	4.017 ± 0.002	8
La	7.32462	4.18091	9
Ce	7.208	4.091	10
Pr	7.246	4.121	11
	7.241	4.119	10
	7.235	4.116	12
Nd	7.219	4.102	13
	7.220	4.102	10
Sm	7.178	4.071	10
	7.179	4.067	12
Gd	7.141	4.044	12
	7.144	4.048	13
	7.145	4.048	10
Tb	7.119	4.029	10
	7.121	4.031	12
Dy	7.097	4.016	12
	7.101	4.017	13
	7.102	4.017	10
Ho	7.075	4.004	13
	7.085	4.004	12
	7.087	4.008	10
Er	7.060	4.002	12
	7.071	3.997	10, 13
Tm	7.057	3.987	10
	7.05	3.99	14
Yb	7.055	4.004	12
	7.064	3.989	10
Lu	6.997	3.938	15
	7.036	3.974	10
Th	7.256	4.113	1
U	7.080	3.978	17
Np	7.0901 ± 0.0006	3.9938 ± 0.0001	3
Pu	7.102	4.003	16
Am	7.105 ± 0.003	4.006 ± 0.004	3

The self-bonding tendency of B results in strong boron frameworks, which leads to predictions of defect structures that primarily involve changes in the fraction of the metal sites occupied.

The homogeneity range in SmB_4 is indicated by the change in lattice constants with composition of this tetragonal phase. Both a_0 and c_0 values increase by $\sim 1\%$ as the composition changes from the Sm-rich to the B-rich phase boundary⁴. The lattice constants of AmB_4 decrease by $\sim 1\%$ as the composition changes from Am rich to B rich⁵, and LaB_4 has a wide range of homogeneity, but the lattice constants do not vary with composition and provide no evidence for nonstoichiometry⁵. The homogeneity range of LaB_4 is narrow⁶; with DyB_4 , there is no difference in lattice constants of Dy-rich and B-rich samples annealed at 1800°C ¹⁸. Lattice parameter measurements on several tetraborides give no evidence of solid solution ranges¹³. These lattice constant results are the only studies of possible homogeneity ranges in tetraborides.

There are two classes of tetraborides from the point of view of thermal stability¹⁹⁻²²:

1. for $M = \text{Y, Gd, Tb, Dy, Ho, Er, Tm, Lu, Th, U or Pu}$:



2. for $M = \text{La, Ce, Pr, Nd, Sm, Yb or Am}$:

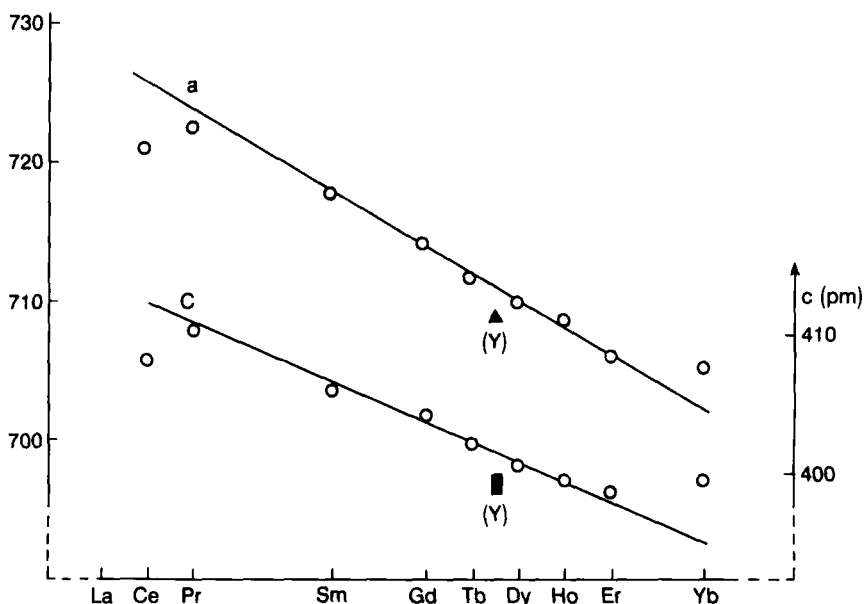


Figure 2. Lattice parameters of the rare-earth tetraborides.

The thermal behavior of tetraborides is based on two factors: the saturation vapor pressure of the metal, an increase of which increases the dissociation, and the stability of the B—B bonds within the boron sublattice, the strength of the B—B bonds decreasing as the size of the cubic lattice parameter increases.

The temperatures at which dissociation of tetraborides (under 10^{-4} N m $^{-2}$) begins are LaB_4 , 1850°C; CeB_4 , 2200°C; PrB_4 , 1950°C, NdB_4 , 1850°C and SmB_4 , 1650°C. Thus, while the thermal stability increases from LaB_4 to CeB_4 , there is a monotonic decrease with increasing atomic number from CeB_4 to SmB_4 .

Rare-earth ions inserted in the tetraborides have the 3+ oxidation state, except for CeB_4 and YbB_4 (see Fig. 2)¹¹⁻¹². The abnormal volume contraction for the CeB_4 unit cell can be explained by the presence of some Ce^{4+} ions^{10,23}. Recoilless γ -ray emission spectra and magnetic measurements indicate that ytterbium in YbB_4 has an intermediate valence state as in YbAl_3 ^{12,24}.

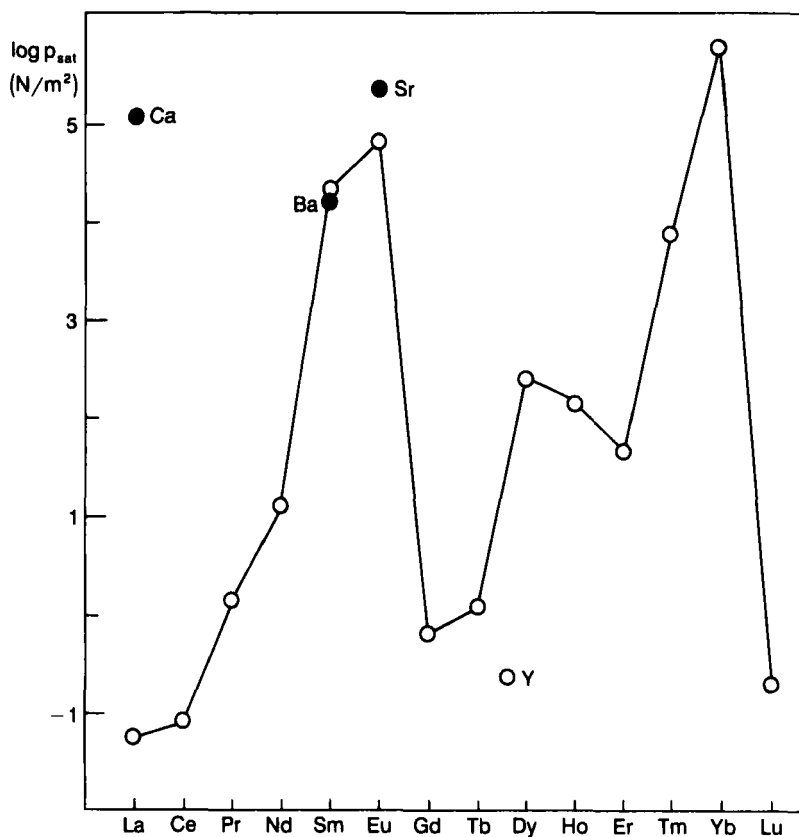


Figure 3. Saturation vapor pressures of rare-earth and alkaline-earth metals at 1800 K.

The trend in thermal stability observed for LaB_4 , CeB_4 , PrB_4 , NdB_4 and SmB_4 is explainable by the counteracting effects of increasing metal volatility and decreasing unit cell volume (see Figs. 2 and 3). The first effect accounts for lesser stability of LaB_4 relative to SmB_4 and the second for the maximum at CeB_4 .

For comparable metal volatilities, the tendency to dissociate decreases with shortening of B—B distances. The high thermal stability of YB_4 , GdB_4 , TbB_4 , DyB_4 , HoB_4 and ErB_4 results from both a relatively low metal volatility and a small unit cell volume.

Because of the high vapor pressure of the metals EuB_4 and YbB_4 are difficult to obtain. However, this factor is not sufficient to explain why EuB_4 cannot be prepared; an equally important factor may be the large unit cell resulting for a 2+ oxidation state of Eu.

The stability of the boron framework requires a transfer of electrons from the metal atoms, but the electronic structure of the tetraborides is not known²⁵. The rare-earth and actinide tetraborides are metallic. Only the rare-earth tetraborides show magnetic ordering temperatures (except for YB_4 , CeB_4 and YbB_4) and some exhibit both a strong magnetic anisotropy and magnetic phase transitions^{11,12,26-28}. While UB_4 does not exhibit magnetic ordering, the solid solutions $\text{U}_{1-x}\text{M}_x\text{B}_4$ ($\text{M} = \text{Y, La, Lu}$) are ferromagnetic at low T ^{29,30}.

(J. R. ETOURNEAU)

1. A. Zalkin, D. H. Templeton, *Acta Crystallogr.*, **6**, 269 (1953).
2. F. Bertaut, P. Blum, *C.R. Hebd. Seances Acad. Sci.*, **229**, 666 (1949).
3. H. A. Eick, R. N. R. Mulford, *J. Inorg. Nucl. Chem.*, **31**, 371 (1969).
4. G. Y. Solov'ev, K. E. Spear, *J. Am. Ceram. Soc.*, **55**, 475 (1972).
5. E. J. Felten, I. Binder, B. Post, *J. Am. Chem. Soc.*, **80**, 3479 (1958).
6. R. W. Johnson, A. H. Daane, *J. Phys. Chem.*, **65**, 909 (1961).
7. G. Will, F. Pfeiffer, W. Schäfer, J. Etourneau, R. Georges, *Rev. Chim. Miner.*, **17**, 541 (1980).
8. A. Guette, M. Vlasse, J. Etourneau, R. Naslain, *C.R. Hebd. Seances Acad. Sci.*, **291**, C145 (1980).
9. J. A. Deacon, S. E. R. Hiscocks, *J. Mater. Sci.*, **6**, 309 (1971).
10. Z. Fisk, A. S. Cooper, P. H. Schmidt, R. N. Castellano, *Mater. Res. Bull.*, **7**, 285 (1972).
11. K. H. J. Buschow, *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 494.
12. A. Berrada, J. P. Mercurio, B. Chevalier, J. Etourneau, P. Hagenmuller, M. Lalanne, J. C. Gianduzzo, R. Georges, *Mater. Res. Bull.*, **11**, 1519 (1976).
13. H. A. Eick, P. W. Gilles, *J. Am. Chem. Soc.*, **81**, 5030 (1959).
14. Yu. B. Paderno, G. V. Samsonov, *Zh. Struct. Khim.*, **2**, 213 (1961).
15. A. A. Stepanova, N. N. Zhuravlev, *Kristallografiya*, **3**, 94 (1958).
16. H. A. Eick, *Inorg. Chem.*, **4**, 1237 (1965).
17. P. Blum, F. Bertaut, *Acta Crystallogr.*, **7**, 81 (1954).
18. K. E. Spear, in *Proc. Int. Symp., Boron and Borides*, Tbilisi, USSR, 1972.
19. J. Etourneau, J. P. Mercurio, R. Naslain, P. Hagenmuller, *C.R. Hebd. Seances Acad. Sci.*, **274**, 1688 (1972).
20. L. G. McGrath, Ph. D. Thesis, New Mexico State University, Las Cruces, NM, 1972.
21. P. K. Smith, Ph. D. Thesis, University of Kansas Lawrence, KS, 1964; also USAEC Rept. No. COO-1140-103, May 1, 1964.
22. J. Etourneau, J. P. Mercurio, P. Hagenmuller, *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 115; J. P. Mercurio, These Doct. Sci. Phys. Univ. Bordeaux-I, No. 434 (1974).

23. K. A. Gschneider, *Rare Earth Alloys*, Van Nostrand, Princeton, 1961.
24. P. Bonville, P. Imbert, G. Hehanno, F. Gonzalez-Jimenez, *J. Phys. Chem. Solids*, **39**, 1273 (1978).
25. W. N. Lipscomb, D. Britton, *J. Chem. Phys.*, **33**, 275 (1960).
26. A. Berrada, J. P. Mercurio, B. Chevalier, J. Etourneau, M. Lalanne, J. C. Gianduzzo, R. Georges, P. Hagenmuller, *Mater. Res. Bull.*, **11**, 1519, 1976.
27. J. Etourneau, J. P. Mercurio, P. Hagenmuller, A. Berrada, R. Georges, R. Bourezg, J. C. Gianduzzo, *J. Less-Common Met.*, **67**, 539 (1979).
28. F. Pfeiffer, W. Schafer, G. Will, J. Etourneau, R. Georges, *J. Magn. Magn. Mater.*, **14**, 306 (1979).
29. A. L. Giorgi, E. G. Szklarz, R. W. White, H. H. Hill, *J. Less-Common Met.*, **34**, 348 (1974).
30. H. H. Hill, A. L. Giorgi, E. G. Szklarz, J. L. Smith, *J. Less-Common Met.*, **38**, 239, 1974.

6.7.2.4.2. CaB_6 -Type Hexaborides.

Hexaborides of a CaB_6 type are formed by K, the alkaline earths, Y and the larger lanthanides, as well as Th and some actinides¹⁻⁴. The crystal structure of these compounds with cubic symmetry ($\text{Pm}\bar{3}\text{m}$, O_h) (see Fig. 1) is characterized by a three-dimensional skeleton of B_6 boron octahedra, the interstices of which are filled by metal atoms. The connection between two octahedra is by a B—B bond of length $\sim 1.66 \times 10^2$ pm, whereas the B—B bond lengths in one octahedron are $\sim 1.76 \times 10^2$ pm⁵⁻⁸.

The homogeneity ranges and defect structures of the hexaborides lead to deviations from stoichiometry through the cation defects (see Table 1).

Studies of ThB_6 and SmB_6 are the most extensive. Thorium boride forms B:Th ratios of 6–24; the compositional dependence of the ThB_6 lattice constant, both x-ray and neutron diffraction intensities and density indicate that composition changes produce no change in the boron sublattice, but the occupancy of the metal sites decreases from $\sim 100\%$ to $\sim 78\%$ with increasing boron content¹⁶. Measurements of x-ray diffraction intensities, density, and resistivity as a function of composition show SmB_6 to be stable between SmB_6 and $\text{Sm}_{0.68}\text{B}_6$ ¹³, and the hexaborides of Ce, Pr, Gd and Tb give similar results¹². Lattice constant values measured for the respective metal-rich and boron-rich phase boundaries of DyB_6 show a difference similar to those for the neighboring hexaborides of Gd and Tb. The homogeneity range of DyB_6 is similar to those exhibited by these hexaborides¹⁸.

It is difficult to decide whether EuB_6 has a homogeneity range or lattice constant values. As the EuB_6 composition changes from Eu-rich to single-phase to B-rich, the lattice constant increases from 4.170 to 4.178 to 4.184×10^2 pm, respectively¹⁹, but other results indicate a decrease in lattice constant with increasing B content²⁰. The lattice constants of EuB_6 may remain constant for samples prepared with different atomic ratios $\text{B}/\text{Eu} > 6$, so the homogeneity range is probably narrow, $\leq 1\%$ for the cation vacancies. The scattering observed in the values of the lattice constant is likely caused by contamination of the samples by C coming from starting materials (boron or boron carbide) used to prepare EuB_6 . The substitution of B by C leads to the borocarbides, $\text{EuB}_{6-x}\text{C}_x$ ($0 < x \leq 0.20$), for which the lattice constant decreases as x increases; YbB_6 and SrB_6 behave similarly^{14,15,21}.

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6.7.2. Existence and Crystal Chemistry of Borides

6.7.2.4. Borides with Three-Dimensional Boron Networks

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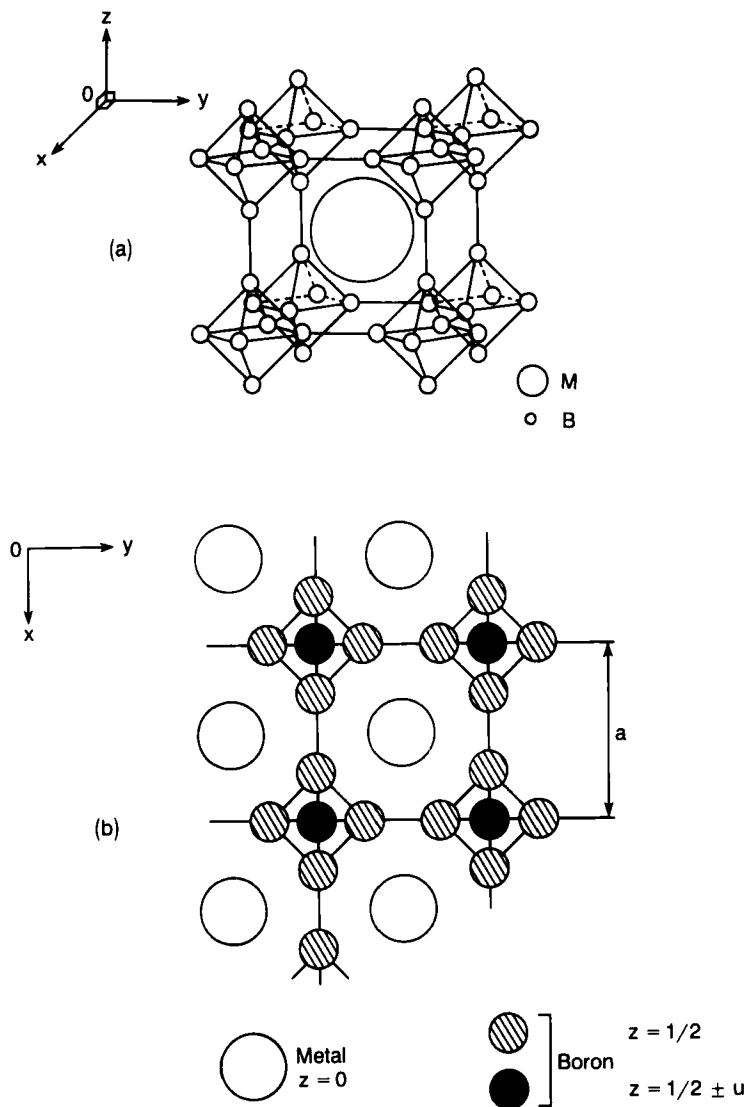


Figure 1. The structure of the CaB_6 -type hexaborides. (a) The [24]-coordination boron cage. (b) Projection onto the $x0y$ plane.

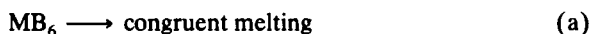
6.7.2. Existence and Crystal Chemistry of Borides
 6.7.2.4. Borides with Three-Dimensional Boron Networks
 6.7.2.4.2. CaB_6 -Type Hexaborides.

TABLE 1. HOMOGENEITY RANGES AND LATTICE
 CONSTANT DATA FOR THE CUBIC HEXABORIDES

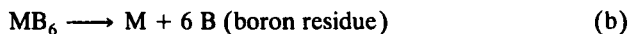
Metal	x in M_xB_6	a (10^2 pm)	Refs.
K	1	4.2320	4, 9
Ca	1	4.1522	9, 10
Sr	1	4.1980	9, 10
Ba	1	4.2690	5
Y	1	4.1022	10
La	1	4.1561	8, 11
	0.77	4.1561	11
Ce	1	4.1396	12
	0.70	4.1415	12
Pr	1	4.1329	12
	0.69	4.1355	12
Nd	1	4.1265	9
Sm	1	4.1352	9
	1	4.1304	13
	0.68	4.1278	13
Eu	1	4.185	14, 15
Gd	1	4.109	9
	1	4.1065	12
	0.70	4.1113	12
Tb	1	4.1036	9
	1	4.1008	12
	0.75	4.1052	12
Dy	1	4.1002	9
	—	4.0969	16
	—	4.1008	16
Yb	1	4.1478	9, 15
Th	1	4.1105	16
	0.78	4.1125	16
Np	1	4.1129	1
Pu	—	4.115	17
		4.140	
Am	1	4.1154	1

There are four classes of hexaborides from the point of view of thermal stability:

1. $\text{M} = \text{La, Ce, Pr, Nd, Sm or Am}$:



2. $\text{M} = \text{K, Ca, Sr, Ba or Eu}$:



3. $\text{M} = \text{Y, Gd, Tb, Dy or Th}$:



4. $\text{M} = \text{Yb}$:



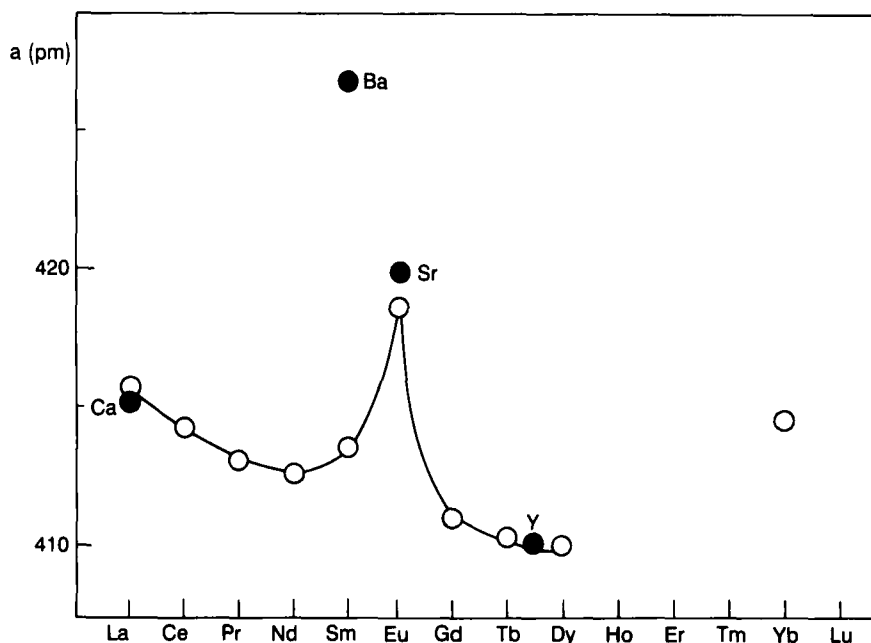


Figure 2. Cubic lattice parameters of the rare-earth and alkaline-earth hexaborides.

The thermal behavior of the hexaborides is like that of the tetraborides^{22,23}.

The great stability of hexaborides from La to Nd can be explained by progressive contraction of the lattice, which compensates for increasing volatility of the metal. Samarium hexaboride, thermally very stable, is the limiting case with regard to metal volatility, which is high, although the lattice parameter is still relatively small, being intermediate between those of CeB_6 and PrB_6 (see Figs. 3, §6.7.2.4.1., and 2).

The lack of thermal stability of EuB_6 and YbB_6 results from the high volatility of the metals and the great dilatation of the unit cell and, consequently, the fragility of the B—B bonds. The exceptional volatility of Yb explains why YbB_6 is less stable than LaB_6 , although their unit cells have nearly the same size.

The dissociation of YbB_6 , GdB_6 , TbB_6 and DyB_6 hexaborides into tetraborides with loss of boron at 1550°C is a consequence of the volatility of B at this T, and also of the high stability of the corresponding tetraborides.

The interpretation proposed for the LnB_6 phases can be extended to alkaline-earth and potassium hexaborides. These dissociate through metal evaporation, yielding a β -rhombohedral boron residue at the mp for CaB_6 , SrB_6 and BaB_6 , and at 750°C for KB_6 .

For a given volume of the unit cell, the most stable hexaborides are those of the least volatile metals; LaB_6 is then more stable than CaB_6 , in spite of their identical parameters.

For comparable metal-vapor pressures, the most stable hexaboride is that which has the smallest unit cell; SmB_6 is more stable than BaB_6 , which has a larger unit cell.

Europium and Sr have comparable volatilities and B—B bonds of identical strength, accounting for the similar thermal behavior of EuB_6 and SrB_6 .

The easy dissociation of KB_6 ($a_{\text{KB}_6} = 4.232 \cdot 10^2 \text{ pm}$, $p_K^{1700 \text{ K}} \approx 27 \times 10^5 \text{ N m}^{-2}$) can be explained in the same way.

The structure of CaB_6 contains bonding bands typical of the boron sublattice and capable of accommodating 20 electrons per CaB_6 formula, and separated from antibonding bands by a relatively narrow gap (from 1.5 to 4.4 eV)^{24,25}. The B atoms of the B_6 octahedron yield only 18 electrons; thus a transfer of two electrons from the metal to the boron sublattice is necessary to stabilize the crystalline framework. The semiconducting properties of M^{2+}B_6 phases ($\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Eu}^{2+}, \text{Yb}^{2+}$) and the metallic ones of M^{3+}B_6 or M^{4+}B_6 phases ($\text{Y}^{3+}, \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}$ and Th^{4+}) are directly explained by this model^{9,15,26}. The validity of these models may be questionable because of the existence and stability of $\text{Na}_x\text{Ba}_{1-x}\text{B}_6$ solid solutions and of KB_6 , since they prove that the CaB_6 -type structure is still stable when the electron contribution of the inserted atom is less than two^{4,27}. A detailed description of physical properties of hexaborides involves not only the bonding and antibonding B bands, but also bonds originating in the atomic orbitals of the inserted metal^{9,28–32}.

The hexaborides for which the oxidation state of the metal is $2+$ are CaB_6 , SrB_6 , BaB_6 , EuB_6 , YbB_6 . They are diamagnetic except EuB_6 , which is ferromagnetic ($T_C = 12.5 \text{ K}$)¹⁵. The other rare-earth hexaborides are characterized by the $3+$ oxidation state, except for SmB_6 , in which samarium is in a mixed valence state. They exhibit antiferromagnetic order at low T except LaB_6 , YB_6 and SmB_6 ^{9,15,33,34}.

(J. R. ETourneau)

1. H. A. Eick, R. N. R. Mulford, *J. Inorg. Nucl. Chem.*, **31**, 371 (1969).
2. A. L. Giorgi, E. G. Szklarz, R. W. White, H. H. Hill, *J. Less-Common Met.*, **34**, 348 (1974).
3. H. H. Hill, A. L. Giorgi, E. G. Szklarz, J. L. Smith, *J. Less-Common Met.*, **38**, 239, 1974.
4. R. Naslain, J. Etourneau, *C.R. Hebd. Seances Acad. Sci.*, **263**, 484 (1966).
5. P. Blum, F. Bertaut, *Acta Crystallogr.*, **7**, 81 (1954).
6. M. Von Stackelberg, F. Neumann, *Z. Phys. Chem.*, **B19**, 314 (1932).
7. L. Pauling, S. Weinbaum, *Z. Kristallogr.*, **187**, 181 (1934).
8. J. Etourneau, Thesis, Université de Bordeaux, No. 285, 1970.
9. J. Etourneau, J. P. Mercurio, P. Hagenmuller, *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 115; J. P. Mercurio, Thèse Doct. Sci. Phys., Univ. Bordeaux-I, No. 434 (1974).
10. R. W. Johnson, A. H. Daane, *J. Chem. Phys.*, **38**, 425 (1963).
11. R. W. Johnson, A. H. Daane, *J. Phys. Chem.*, **65**, 909 (1961).
12. S. Yajima, K. Niihara, 9th. Rare Earth Research Conference, Blacksburg, VA, 1971.
13. K. Niihara, *Bull. Chem. Soc. Jpn.*, **44**, 963 (1971).
14. M. Kasaya, J. M. Tarascon, J. Etourneau, P. Hagenmuller, *Mater. Res. Bull.*, **13**, 751 (1978).
15. J. M. Tarascon, J. Etourneau, P. Dordor, P. Hagenmuller, M. Kasaya, J. M. D. Coey, *J. Appl. Phys.*, **51**, 574 (1980).
16. J. Etourneau, R. Naslain, *J. Less-Common Met.*, **24**, 183 (1971).
17. B. J. McDonald, W. I. Stuart, *Acta Crystallogr.*, **13**, 447 (1960).
18. K. E. Spear, in *Proc. Int. Symp. Boron and Borides*, Tbilisi, USSR, 1972.
19. E. J. Felten, I. Binder, B. Post, *J. Am. Chem. Soc.*, **80**, 3479 (1958).
20. E. M. Savitskii, B. G. Arabei, V. I. Bkarinova, S. E. Salibekov, V. M. Ramashov, N. I. Timofeeva, *Inorg. Mater.*, **7**, 539 (1971).

21. K. A. Schwetz, M. Hoerle, J. Bauer, *Ceram. Int.*, **5**, 105 (1979).
22. P. Bonville, P. Imbert, G. Hehanno, F. Gonzalez-Jimenez, *J. Phys. Chem. Solids*, **39**, 1273 (1978).
23. J. Etourneau, J. P. Mercurio, R. Naslain, *C.R. Hebd. Seances Acad. Sci.*, **275**, 273 (1972).
24. H. C. Longuet-Higgins, M. de V. Roberts, *Proc. Roy. Soc. (London)*, **224**, 336 (1954).
25. M. Yamazaki, *J. Phys. Jpn.*, **12**, 1 (1957).
26. J. P. Mercurio, J. Etourneau, R. Naslain, P. Hagenmuller, J. B. Goodenough, *J. Solid State Chem.*, **9**, 37 (1974).
27. F. Bertaut, P. Blum, *C.R. Hebd. Seances Acad. Sci.*, **234**, 2621 (1952).
28. Tran Minh Duc, G. Hollinger, Y. Jugnet, J. P. Mercurio, A. Berrada, J. Etourneau, P. Hagenmuller, *Inst. Phys. Conf. Ser.*, **37**, 134 (1978).
29. A. J. Arko, G. Crabtree, D. Karim, F. M. Mueller, L. R. Windmiller, J. B. Ketterson, Z. Fisk, *Phys. Rev.*, **B**, **13**, 5240 (1976).
30. A. Hasegawa, A. Yanase, *J. Phys.*, **F**, **7**, 1245 (1977).
31. A. Hasegawa, A. Yanase, *J. Phys.*, **41**, 377 (1980).
32. A. Hasegawa, A. Yanase, *J. Phys.*, **C**, **12**, 5431 (1979).
33. J. M. Tarascon, Y. Isikawa, B. Chevalier, J. Etourneau, P. Hagenmuller, M. Kasaya, *J. Phys.*, **41**, 1141 (1980).
34. K. H. J. Buschow, *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 494.

6.7.2.4.3. UB_{12} -Type Dodecaborides.

Metals able to form dodecaborides with the UB_{12} -type structure are Zr, most of the rare earths (Y, Gd \rightarrow Lu) and some actinides (Th, U, Np, Pu).

The cubic UB_{12} -type boride structure with space group $Fm\bar{3}m$ can be described on the basis of a B_{12} -cubooctahedron (see Fig. 1)¹⁻³. The association of the B_{12} -polyhedra by oriented B—B bonds gives rise to a three-dimensional skeleton with boron cages. Formally, the arrangement of the B_{12} -units and of the metals atoms is of the NaCl-type. Each metal is located in the center of a B_{24} -cubooctahedron.

The dodecaboride lattice constants are listed in Table 1.

Little information is available on homogeneity ranges and defect structures in the dodecaborides. The only variation from stoichiometry in these borides is for YB_{12} ; the limiting phase determined by density measurements is $Y_{0.92}B_{12}$. This result can be attributed to the size of Y which is the maximum for metals that form the dodecaborides⁴. Attempts to prepare DyB_{12} with a nonstoichiometric composition are conclusive⁶.

High-pressure syntheses yield GdB_{12} and ThB_{12} ⁵ (see §6.7.2.4.6).

Binary phase diagrams indicate that the rare-earth dodecaborides do not melt congruently⁷. Owing to the difficulty in preparation of single-phase and single-crystal dodecaborides, little information is available on their physical properties.

The rare earths in their dodecaborides have the 3+ oxidation state except for Yb and Tm which have an intermediate valence state. A recoilless γ -ray emission spectrum study of TmB_{12} shows no magnetic ordering at 1.35 K; the spectra of YbB_{12} reveal no magnetic structure to 1.35 K⁸. The compounds HoB_{12} , ErB_{12} order antiferromagnetically, and ZrB_{12} and LuB_{12} become superconducting ≤ 5.8 K and ≤ 0.48 K, respectively⁹.

The energy spectrum of the dodecaborides (YB_{12} , YbB_{12} , LuB_{12}) computed by the MO-linear combination of atomic orbitals (LCAO) method shows that the direction of the electron transfer is uncertain¹⁰.

6.7.2. Existence and Crystal Chemistry of Borides
 6.7.2.4. Borides with Three-Dimensional Boron Networks
 6.7.2.4.3. UB_{12} -Type Dodecaborides.

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21. K. A. Schwetz, M. Hoerle, J. Bauer, *Ceram. Int.*, **5**, 105 (1979).
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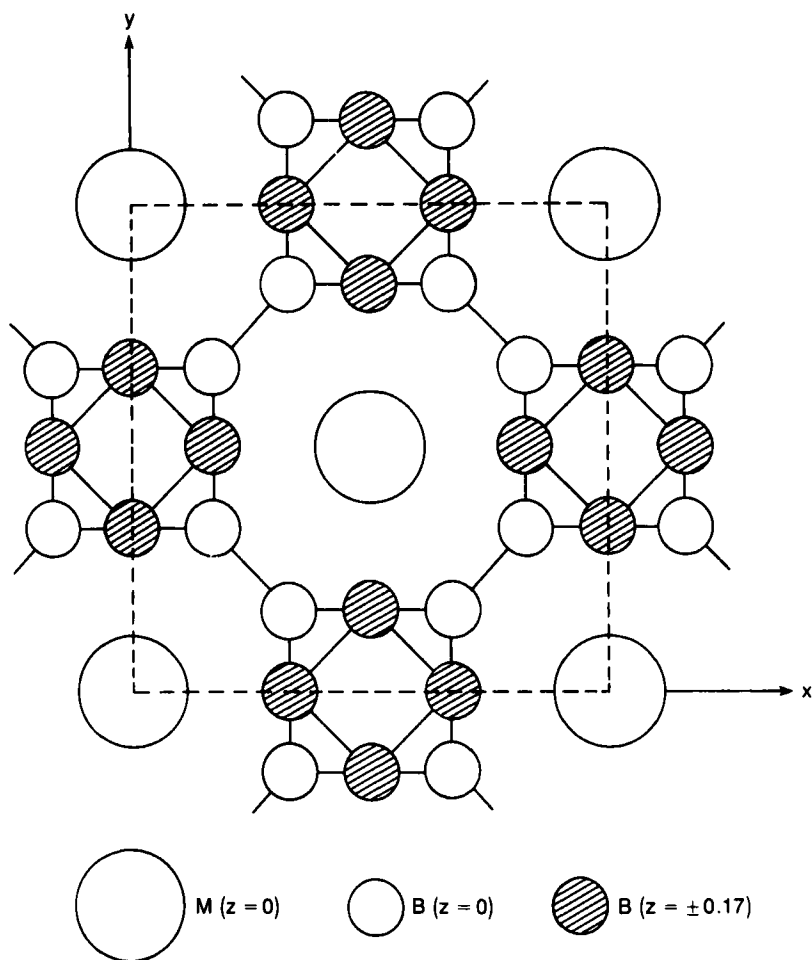
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The energy spectrum of the dodecaborides (YB_{12} , YbB_{12} , LuB_{12}) computed by the MO—linear combination of atomic orbitals (LCAO) method shows that the direction of the electron transfer is uncertain¹⁰.



M = U, Zr, Y, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pu

Figure 1. The structure of the UB_{12} -type dodecaborides (projected onto the x_0y plane).

Assuming perfect stoichiometric structures, the stabilization of the boron frameworks of MB_2 , MB_4 , MB_6 , MB_{12} and elemental B requires the addition of two electrons from each metal atom¹¹. Whatever the B_{12} unit, icosahedron or cuboctahedron, 26 electrons are required for internal bonding and 12 for external bonding. Since the 12 B possesses only 36 electrons, the metal must supply two electrons to each B_{12} group. The results for YB_{12} are consistent with this model; measurements indicate that one electron per Y is delocalized in the conduction band⁴.

(J. R. ETOURNEAU)

TABLE 1. LATTICE CONSTANT DATA FOR
THE CUBIC DODECABORIDES

Metal	a (10^2 pm)	Refs.
Zr	7.408	12
Y	7.5008	13-15
Gd	7.524	15
Tb	7.504	13, 14
Dy	7.4992	6, 14
Ho	7.492	14, 17
Er	7.4832	14, 16, 17
Tm	7.476	14, 17
Yb	7.469	13, 14, 16
Lu	7.464	14, 17
Th	7.611	15
U	7.473	20
Np	7.478	18
Pu	7.484	19

1. F. Bertaut, P. Blum, *C.R. Hebd. Seances Acad. Sci.*, 229, 666 (1949).
2. P. Blum, F. Bertaut, *Acta Crystallogr.*, 7, 81 (1954).
3. V. I. Matkovich, J. Economy, R. F. Giese, R. Barrett, *Acta Crystallogr.*, 19, 1056 (1965).
4. R. W. Johnson, A. H. Daane, *J. Chem. Phys.*, 38, 425 (1963).
5. J. F. Cannon, H. T. Hall, in *The Rare Earths in Modern Science and Technology*, G. J. McCarthy, J. J. Rhyne, ed., Plenum Press, New York, 1977, p. 219.
6. K. E. Spear, in *Proc. Int. Symp. Boron and Borides*, Tbilisi, USSR, 1972.
7. K. E. Spear, *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 439.
8. P. Bonville, P. Imbert, G. Hehanno, F. Gonzalez-Jimenez, *J. Phys. Chem. Solids*, 39, 1273 (1978).
9. B. T. Matthias, T. H. Geballe, K. Andres, G. Corenzwit, G. W. Hull, J. P. Maita, *Science*, 159, 530 (1968).
10. Yu. M. Goryachev, V. V. Odintsov, Yu. B. Paderno, *Metallofizika*, No. 37, p. 29 (1971); *Chem. Abstr.*, 77, 81,514 (1972).
11. W. N. Lipscomb, D. Britton, *J. Chem. Phys.*, 33, 275 (1960).
12. B. Post, F. W. Glaser, *J. Met.*, 4, 631 (1952).
13. S. La Placa, D. Noonan, B. Post, *Acta Crystallogr.*, 16, 1182 (1963).
14. Yu. B. Pavlekno, V. V. Odintsov, I. I. Timofeeva, I. A. Klochov, *High Temp.*, 9, 175 (1971).
15. J. F. Cannon, H. T. Hall, in *The Rare Earths in Modern Science and Technology*, G. J. McCarthy, J. J. Rhyne, eds., Plenum Press, New York, 1977, p. 219.
16. K. Schwetz, P. Etmayek, R. Keiffek, A. Lipp, *Radex Rundsch.*, 314, 257 (1972); *Chem. Abstr.*, 78, 8801 (1973).
17. S. La Placa, I. Binder, B. Post, *J. Inorg. Nucl. Chem.*, 18, 113 (1961).
18. H. A. Eick, R. N. R. Mulford, *J. Inorg. Nucl. Chem.*, 31, 371 (1969).
19. H. A. Eick, *Inorg. Chem.*, 4, 1237 (1965).
20. E. M. Savitskii, B. G. Akabet, V. I. Bkarinova, S. E. Salibekov, V. M. Romashov, N. I. Timofeeva, *Inorg. Mater.*, 7, 539 (1971).

6.7.2. Existence and Crystal Chemistry of Borides

6.7.2.4. Borides with Three-Dimensional Boron Networks

6.7.2.4.4. YB₆₆-Type Borides.6.7.2.4.4. YB₆₆-Type Borides.

Boron phases with formulas MB₅₀, MB₆₆ and MB₁₀₀ (M = Y, Sm, Gd, Tb, Dy, Ho, Er, Yb, Tm, Lu, Th and Pu) are the same cubic phase from x-ray powder data¹⁻⁸, with the Fm3c space group. Single crystals of yttrium and thorium borides lead to the formula MB₆₆^{8,9}. The MB₆₆ lattice constant data are given in Table 1.

The B atoms in the YB₆₆ structure are of the B₁₂-icosahedral type (Fig. 1). The basic unit of the structure is a 156-atom super-icosahedron composed of 13 B₁₂ icosahedra, a B₁₂(B₁₂)₁₂ group (Fig. 2). One B₁₂ icosahedron is in the center of an icosahedron formed by 12 B₁₂ icosahedra⁹.

As schematically represented in Fig. 3 the structure can be considered two interpenetrating fcc lattices of B₁₂(B₁₂)₁₂ units; the B₁₂(B₁₂)₁₂ units of each fcc lattice differ only by the 90° rotation of these units. Thus there are eight of these B₁₂(B₁₂)₁₂ units or 1248 B atoms in the unit cell. The metal atom positions and the location of the remaining B atoms in the structure can be pictured in the octant of the cell shown in Fig. 3. Six metal atom sites exist in each octant of the cell, and these are statistically half-filled. The sites are located 1.27 10² pm (for YB₆₆) inside the cell from the center of each face of an octant; one such site is depicted in Fig. 3. The center of each octant is occupied by either a 36- or a 48-B atom group, which are labeled, respectively, configurations I and II (Fig. 4). Half of the octants contain configuration I, and half contain II in a random fashion⁹.

Only fragmentary information is available concerning the homogeneity ranges in MB₆₆-phases, mostly for DyB₆₆ and YB₆₆. The observed compositional dependence of

TABLE 1. LATTICE CONSTANT DATA FOR THE CUBIC MB₆₆-TYPE PHASES (B / M INDICATES THE ATOMIC RATIO USED IN PREPARATION)

Metal	a ₀ (10 ² pm)					
	B/M < 66	Ref.	B/M = 66	Ref.	B/M > 66	Ref.
Y	23.451	5			23.446	6
	23.445	11			23.440	9
	(B/M = 61.7)					
Nd	23.508	5				
Sm			23.474	5		
Gd	23.476	5			23.474	6
Tb					23.457	6
			23.441	6		
Dy	23.466	12	23.422	5	23.419	
Ho					23.441	6
Er	23.428	6	23.438	5		
Tm					23.433	6
Yb			23.415	5	23.422	6
Lu					23.412	6
Th			23.530	8		
Pu					23.420	10
					(B/M = 100)	

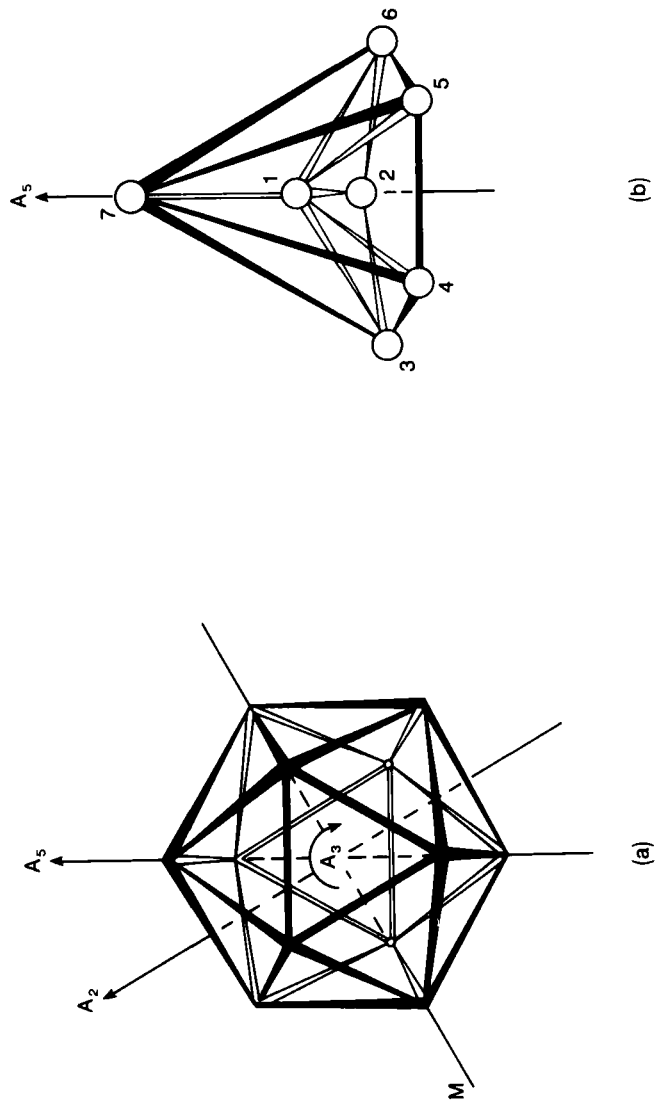


Figure 1. The boron B_{12} icosahedron. (a) Some of its symmetry elements. (b) Ideal coordination polyhedron of boron.

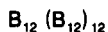
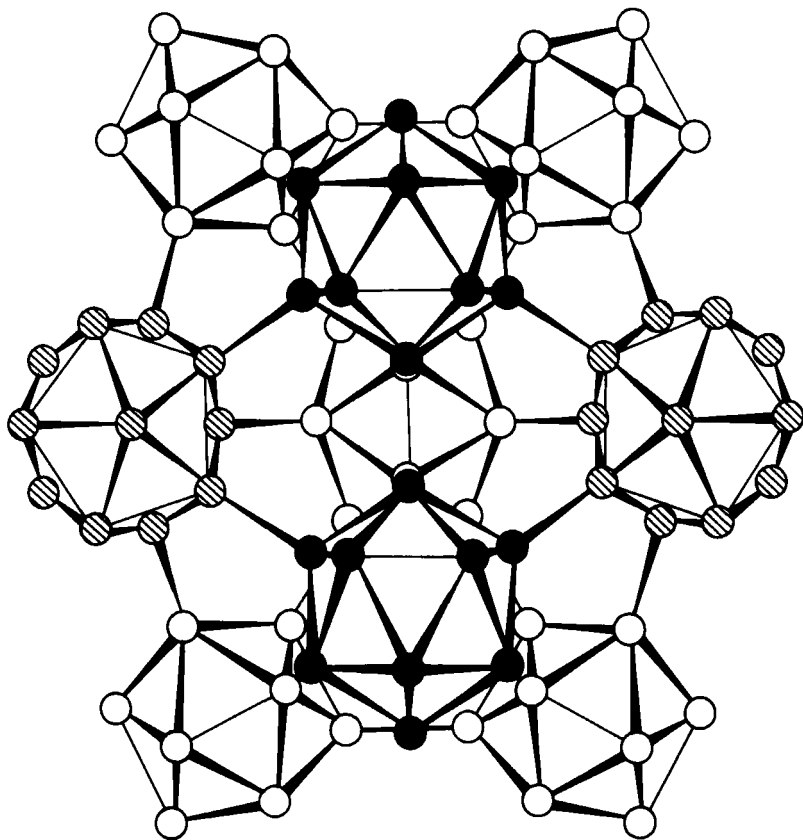


Figure 2. The $\text{B}_{12}(\text{B}_{12})_{12}$ unit.

the DyB_{66} lattice constant indicates that a measurable homogeneity range exists (Table 1)¹². For single crystals of yttrium boride, YB_n with $n = 61 \pm 3$, lattice parameter measurements¹¹ indicate a congruent melting point at $n = 61.7$ and a stoichiometric composition at $n = 68$. The formula of the most B-rich yttrium boride corresponds to YB_{68} , involving 1632 B atoms per unit cell instead of 1584 for YB_{66} ⁹. This difference can be explained if it is assumed there are eight units of $\text{B}_{12}(\text{B}_{12})_{12}$ icosahedra plus eight units of configuration-II B-atom groups. This model avoids the necessity of statistically placing units of both configuration I (with 36 B atoms) and

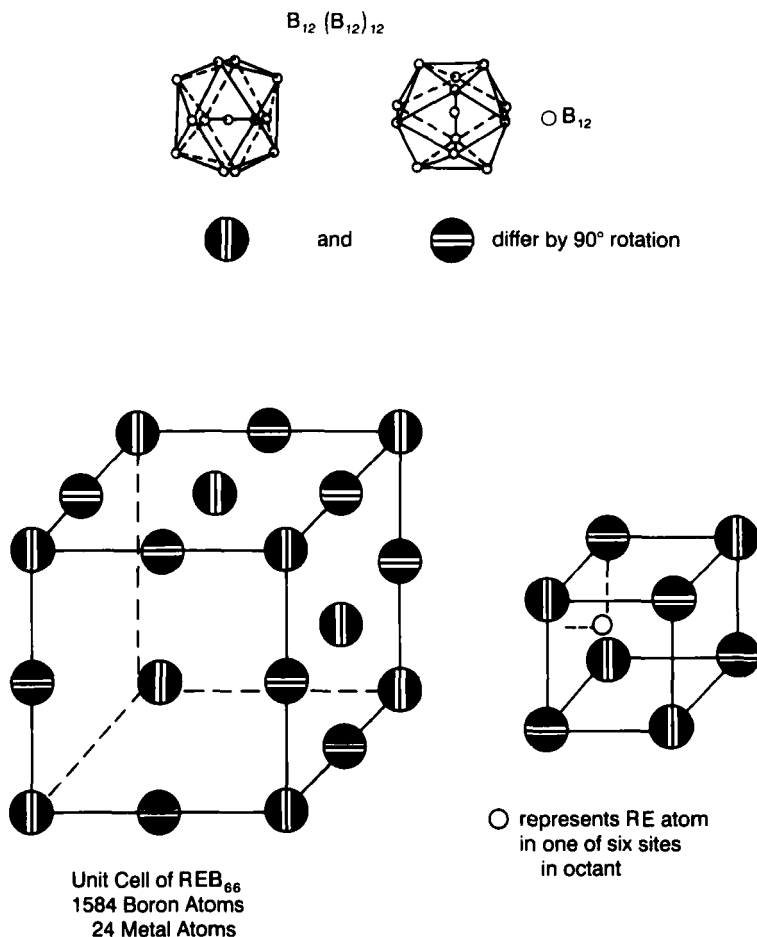


Figure 3. Schematic drawing of the face-centered cubic YB₆₆-type borides (from ref. 13).

configuration II (with 48 B atoms) in the center of each octant as mentioned above in the description of the structure.

The structure of PuB₁₀₀ is not yet clear. A satisfactory indexing can be made for a primitive cubic cell with $a = 23.42 \text{ \AA}$, but with 10 reflections not characteristic of space group Fm3c¹⁴.

The MB₆₆ borides melt congruently and the melting T, at about $2150 \pm 100^\circ\text{C}$, is approximately the same for all of them¹³.

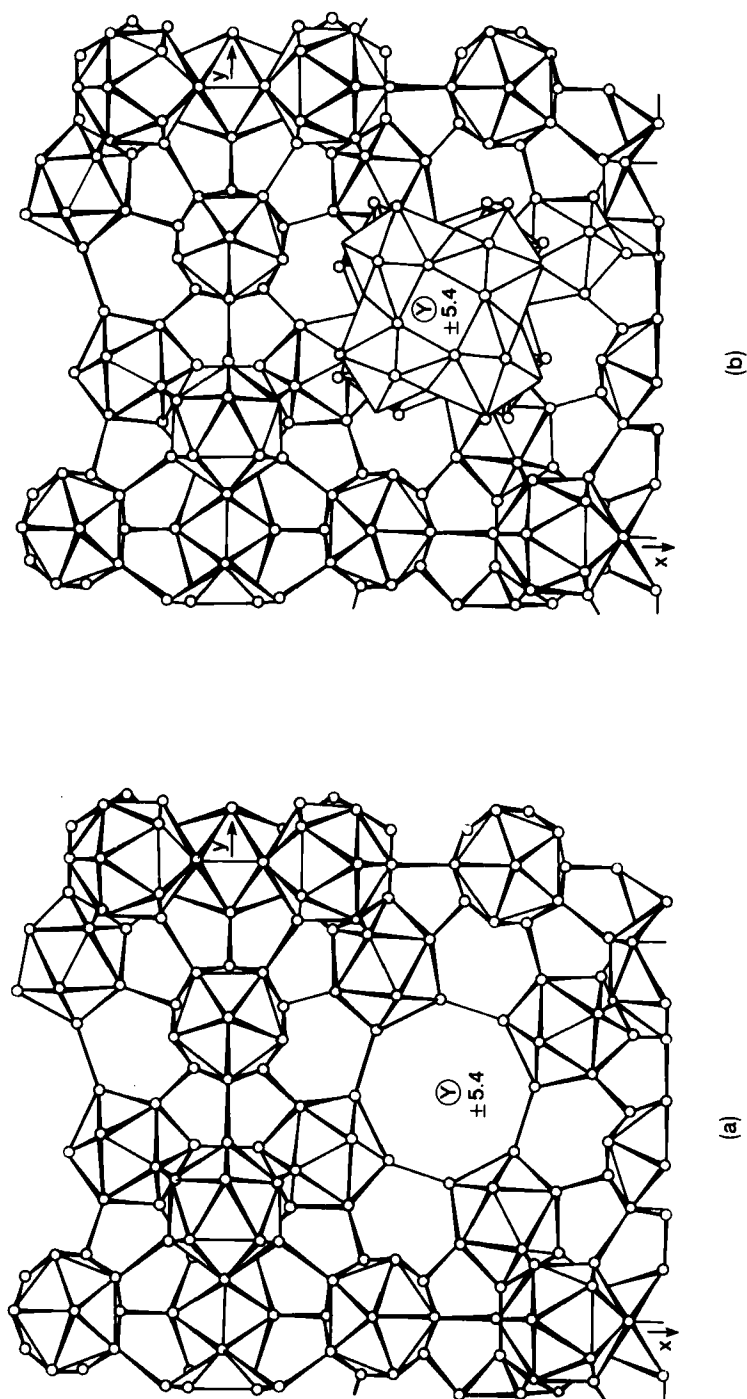


Figure 4. Association of $B_{12}(B_{12})_{12}$ polyhedra in YB_{66} showing: (a) the directed character of intericosahedral bonds, as well as the existence of large voids in the boron framework, (b) the filling of voids by additional B and Y atoms (partial projection onto the ac plane according to ref. 9).

The $\text{YB}_{61.5}$ and YbB_{66} single crystals are p-type semiconductors with a band gap of 0.8 eV for $\text{YB}_{61.5}$ and of 0.73 eV for $\text{YbB}_{66}^{11,15}$.

The acoustic attenuation in $\text{YB}_{61.5}$ is higher than in β -boron¹¹.

(J. R. ETOURNEAU)

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6.7.2.4.5. Other Types.

Nonclassical type structures of borides involving different basic units of B atoms, e.g., the B_5 pentagonal pyramid in MgB_4 , the B_6 octahedron in Sm_2B_5 and finally the B_{12} octahedra in Mg_2B_{14} , MgAlB_{14} and $\text{Na}_x\text{B}_{0.8}\text{B}_{14}$, are considered here.

(i) MgB_4 Type. The structure of single-crystal MgB_4 is orthorhombic, space group Pnam with $a = 5.464 \cdot 10^2$ pm; $b = 7.472 \cdot 10^2$ pm; $c = 4.428 \cdot 10^2$ pm and $Z = 4$, and is based on chains on boron pentagonal pyramids in which the average B—B bond is $1.787 \cdot 10^2$ pm. These chains, labeled C_1 , C_2 , C_3 , C_4 , directed along the \vec{c} axis and bonded by B—B bonds of $1.730 \cdot 10^2$ pm are responsible for the three-dimensional boron framework (Figs. 1a and 1b). The B_5 boron pentagonal pyramids are linked by a common edge. The Mg atoms, located in tunnels parallel to the \vec{c} axis, form zigzag chains; the Mg—Mg distance is of $3.075 \cdot 10^2$ pm. The average B—Mg distance of $3.075 \cdot 10^2$ pm, relatively short, suggests that there is an electronic transfer from metal to boron^{1,2}.

No information is available on the thermal stability of MgB_4 .

(ii) Sm_2B_5 Type. A new type of metal-rich boride, Sm_2B_5 , is monoclinic with space group $\text{P2}_1\text{c}$ and contains four Re_2B_5 formula weights per unit cell ($a_0 = 7.183 \pm 0.006 \cdot 10^2$ pm, $b_0 = 7.191 \pm 0.006 \cdot 10^2$ pm, $c_0 = 7.216 \pm 0.006 \cdot 10^2$ pm and $\beta = 102.03 \pm 0.04^\circ$)^{3,4}.

This structure can be visualized qualitatively from the ThB_4 -type structure described in §6.7.2.4.1. The Sm_2B_5 structure contains parallel layers that are virtually identical to layers found in the xOy plane of the ThB_4 -type structure (Fig. 1, §6.7.2.4.1.). While in ThB_4 direct linkages between B_6 octahedra occur in the \vec{c} axis direction, in Sm_2B_5 the B_6 octahedra are connected by intervening B_2 units.

Only Gd_2B_5 and Nd_2B_5 have the Sm_2B_5 -type structure^{5,6}. These borides melt peritectically to give the tetraboride plus a metal-rich liquid.

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6.7.2.4. Borides with Three-Dimensional Boron Networks

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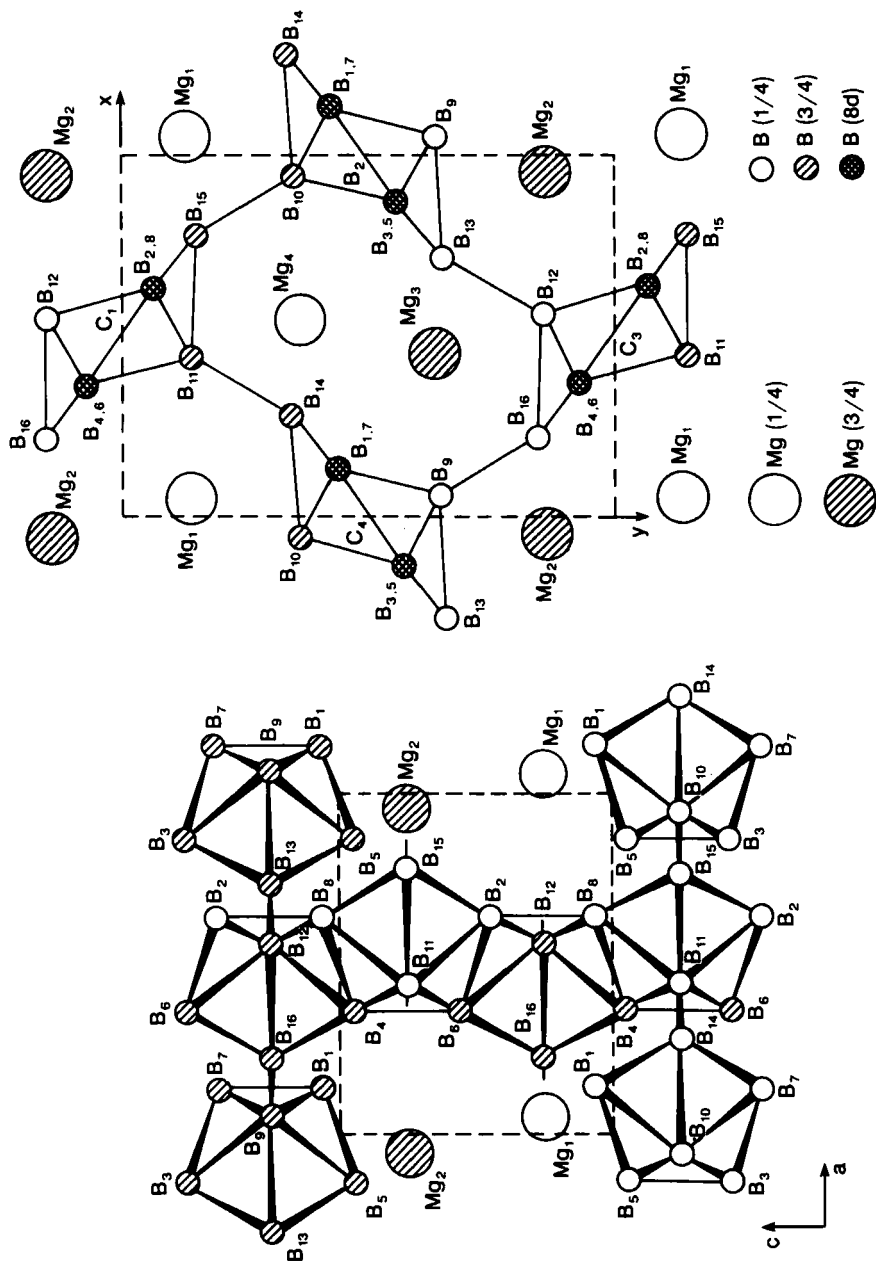
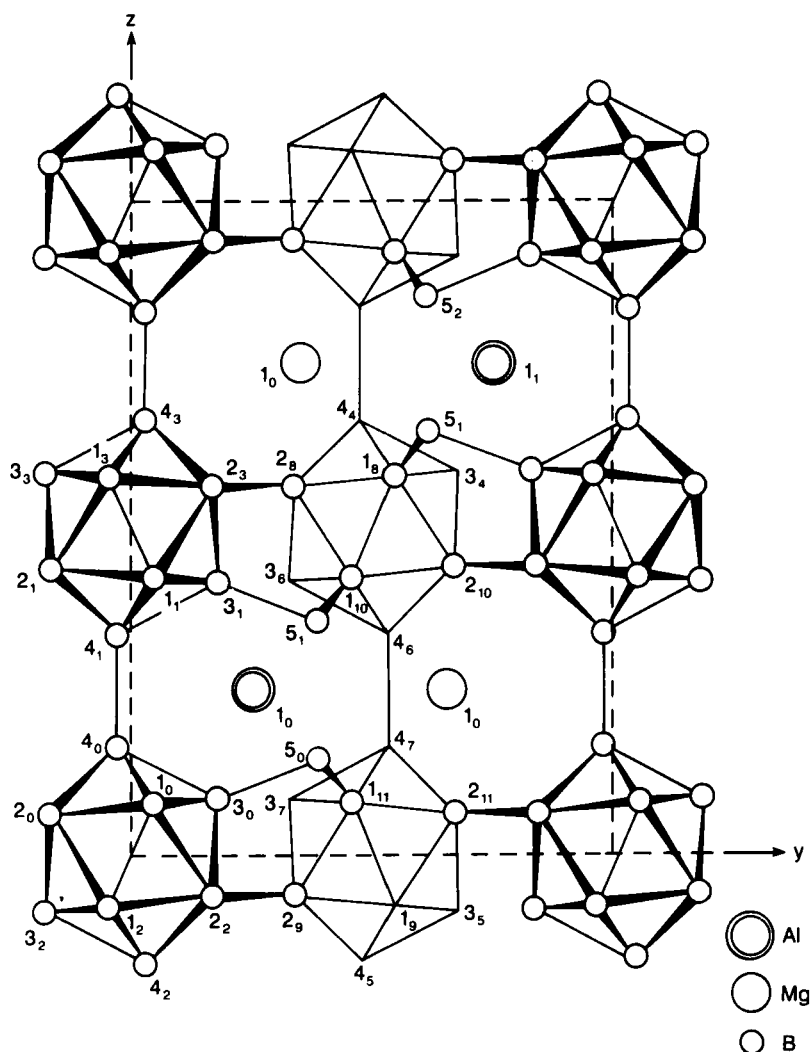


Figure 1. The structure of MgB_4 (from ref. 1). (a) Projection onto the xy plane. (b) Projection onto the $x0z$ plane.

(iii) MgAlB_{14} , Mg_2B_{14} and $\text{Na}_x\text{B}_{0.8}\text{B}_{14}$ Types. These crystallize in the orthorhombic system (space group Imam) with closely related lattice parameters and four $\text{MM}'\text{B}_{14}$ or M_2B_{14} formulas in the unit cell. Their crystal structures have, neglecting details, the same boron skeleton built from simple B_{12} units. They differ from one another by the nature, number and position of the isolated atoms⁷⁻¹¹. While single-crystal structures of MgAlB_{14} and $\text{Na}_x\text{B}_{0.8}\text{B}_{14}$ are available, that of Mg_2B_{14} is established only from powder patterns according to a profile refinement technique, on the basis of isotypy with MgAlB_{14} ¹⁰.

The structures of MgAlB_{14} , Mg_2B_{14} and $\text{Na}_x\text{B}_{0.8}\text{B}_{14}$ are given in projection on the bc plane in Figs. 2, 3 and 4, respectively. These figures show the boron skeleton is



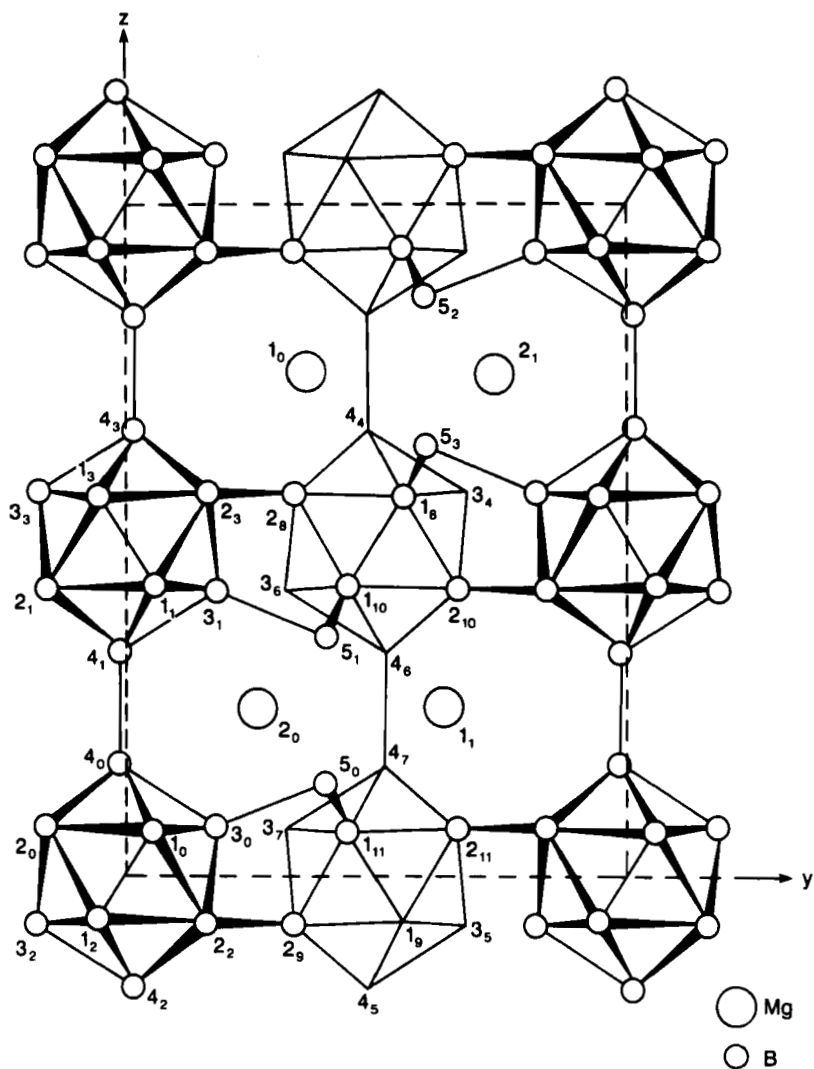


Figure 3. The structure of Mg_2B_{14} in projection on the y_0z plane (from ref. 10).

the same for the three borides. For all of them the icosahedra are bonded together in a chain by direct intericosahedral B—B bonds parallel to the c axis (e.g., 4_0-4_1).

The differences between these structures result first from the intericosahedral B—B bonds linking the chains (e.g., the bridges involving isolated B5 atoms in MgAlB_{14} or Mg_2B_{14} and B5 and B6 atoms in $\text{Na}_x\text{B}_{0.8}\text{B}_{14}$), and second from the positions of the metal atoms and their occupancy. Metal atoms occupy interstitial

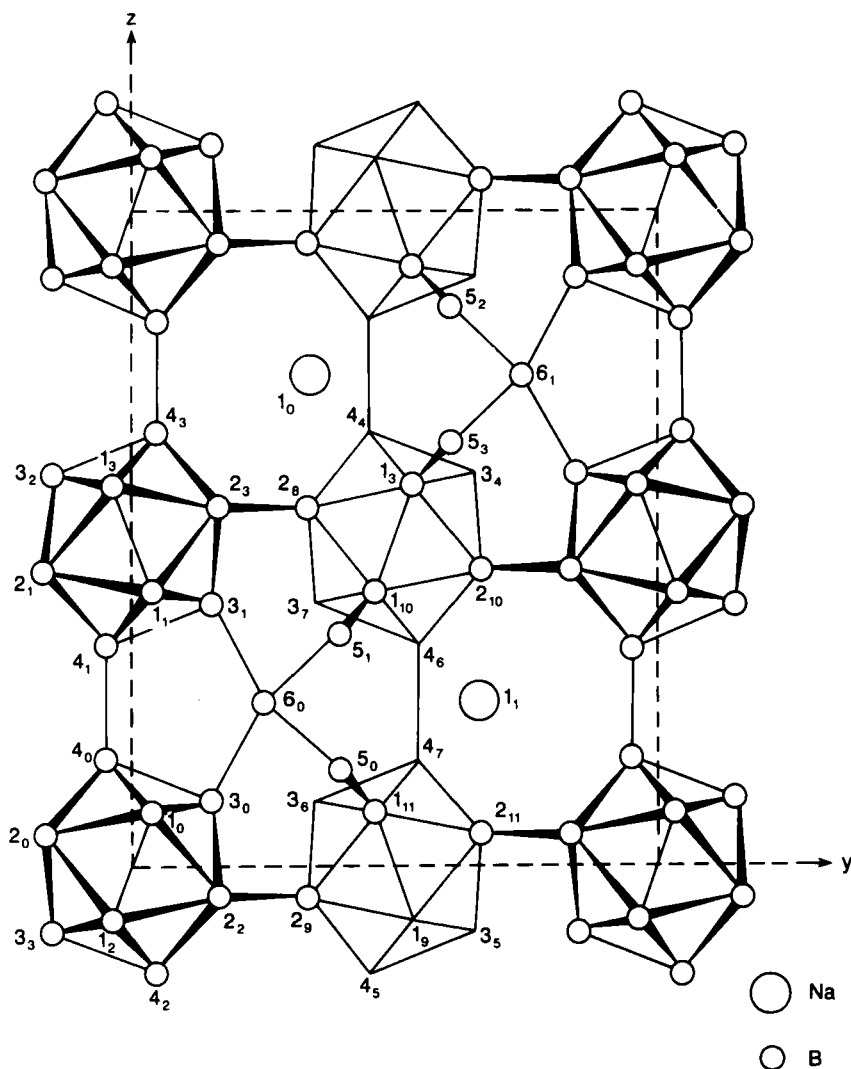


Figure 4. The structure $\text{Na}_x \text{B}_{0.8} \text{B}_{14}$ ($x = 0.8$) in projection on the $y0z$ plane (from ref. 7).

holes in the boron network: the larger site, site I, of type 4(e), lies in the center of a 16-B atom cage; the smaller-cage, site II, of type 4(d) is formed by 12 B atoms.

In $\text{Mg}_2 \text{B}_{14}$, sites I and II are fully occupied by Mg atoms, but not in MgAlB_{14} , where the occupancy for both sites is ca. 75%. The formula that minimizes the R factor ($R = 0.12$) for the crystal studied is $\text{Mg}_{0.5} \text{AlB}_{14}$ (25% Al in site I, 75% Al in site II and 50% Mg in site I)⁹.

Only the larger sites (sites I) are partially occupied by Na and B in the $\text{Na}_x\text{B}_{0.8}\text{B}_{14}$ structure. The occupancy of the interstitial sites depends on the conditions of synthesis, being maximum for preparations in sealed tubes but low for products obtained under a pressure of 1 atm of an inert gas, owing to the high vapor pressure of the Na metal at high T. Two single-crystal structures justify the hypothesis of a nonstoichiometry owing to vacancies in the Na sublattice, leading to the formulas¹¹ $\text{Na}_{0.85}\text{B}_{0.82}\text{B}_{14}$ and $\text{Na}_{0.72}\text{B}_{0.84}\text{B}_{14}$.

While it is possible to obtain a stoichiometric $\text{Na}_x\text{B}_{0.8}\text{B}_{14}$ sodium boride when operating under Na pressure, the pyrolysis of the compound at low T and in high vacuum leads to $\text{Na}_x\text{B}_{0.8}\text{B}_{14}$ sodium-deficient phases where x can reach a value of 0 without the collapse of the boron skeleton¹².

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5. Z. Fisk, A. S. Cooper, P. H. Schmidt, R. N. Castellano, *Mater. Res. Bull.*, **7**, 285 (1972).
6. K. E. Spear, D. W. Petsinger, *Proc. 74th. Ann. Meet. Am. Ceram. Soc.*, (1972).
7. R. Naslain, A. Guette, P. Hagenmuller, *J. Less-Common Met.*, **47**, 1 (1976).
8. V. I. Matkovich, R. F. Giese, J. Economy, *Z. Kristallogr.*, **122**, 166 (1965).
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12. A. Guette, Thesis No. 462, Univ. Bordeaux-I, 1974; Centre Doc. CNRS, Paris, No. AO 10799 (1974).

6.7.2.4.6. Summary.

A number of metals that form MB_4 and MB_6 borides, and virtually all of those that contribute to the MB_{12} and MB_{66} series also form MB_2 borides (Table 1).

Most of the known borides are compounds of the rare-earth metals. In these metals magnetic criteria are used to decide how many electrons from each rare-earth atom contribute to the bonding (usually three), and this metallic valence is also reflected in the value of the metallic radius, r_M° (metallic radii for 12 coordination)¹. Similar behavior appears in the borides of the rare-earth metals and r_M° becomes a useful indicator for the properties and the relative stabilities of these compounds (Fig. 1). The use of r_M° as a correlation parameter in discussing the higher borides of other metals is consistent with the observed distribution of these compounds among the five structural types pointed out above; the borides of the actinides metals, U, Pu and Am lead to complications that require special comment.

The distribution of the observed higher borides among the five structural types (MB_2 , MB_4 , MB_6 , MB_{12} and MB_{66}) is presented in Table 1, which shows correlations with the metallic radius r_M° , values of which are in order of decreasing magnitude (r_M° corresponds to coordination number 12). In order to discuss the existence of the actinide borides, the table also shows the unit cell volume V_m of the borides MB_4 , MB_6 and MB_{12} .

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TABLE 1. CORRELATION OF METALLIC RADII WITH THE EXISTENCE OF THE VARIOUS TYPE STRUCTURES OF THE HIGHER BORIDES

Element	Metallic radius r_M^o (12 coordinated) (10^2 pm)	V_m (10^6 pm ³) Type structure ^a				
		AlB ₂	ThB ₄	CaB ₆	UB ₁₂	YB ₆₆
K	2.35			x 75.79		
Ba	2.25			x 77.80		
Sr	2.15			x 73.90		
Eu	2.035			x 73.30		
Ca	1.973			x 71.58		
Yb	1.938		x 199.29	x 71.36	416.66	12849
Na	1.920			o		
La	1.876		x 224.27	x 71.78		
Ce	1.825		x 212.55	x 70.93		
Pr	1.820		x 216.37	x 70.60		
Nd	1.820		x 213.77	x 70.26		x 12991
Sm	1.802	x(P)	x 209.75	x 70.71		x 12934
Gd	1.804	x	x 206.21	x 69.37	x(P) 425.93	x 12934
Y	1.800	x	x 203.12	x 69.03	x 422.01	x 12888
Th	1.790		x 216.5	x 69.45	x(P) 440.90	x 13027
Tb	1.781	x	x 204.20	x 69.10	x 422.55	x 12906
Dy	1.775	x	x 202.27	x 68.93	x 421.74	x 12844
Ho	1.766	x	x 200.42		x 420.52	x 12880
Er	1.757	x	x 199.47		x 419.04	x 12875
Tm	1.747	x	x 198.55		x 417.84	x 12867
Am	1.730		x 202.3	x 69.70		
Lu	1.735	x	x 192.80		x 415.83	x 12832
Zr	1.60	x			x 406.53	
Sc	1.60	x			o	
Mg	1.60	x	o			
Pu	1.59	x	x 201.8	x 69.60	x 419.2	x 12845
Hf	1.58	x				
U	1.56	x	x 199.3		x 417.9	
Np	1.55	x	x 200.8	x 69.57	x 418.2	
Nb	1.47	x				
Ta	1.46	x				
Ti	1.45	x				
Al	1.43	x			o	
Mn	1.31	x	o			
Cr	1.28	x	o			

^a x indicates existence of the borides, x(P) borides prepared under high pressure, o borides having another structure.

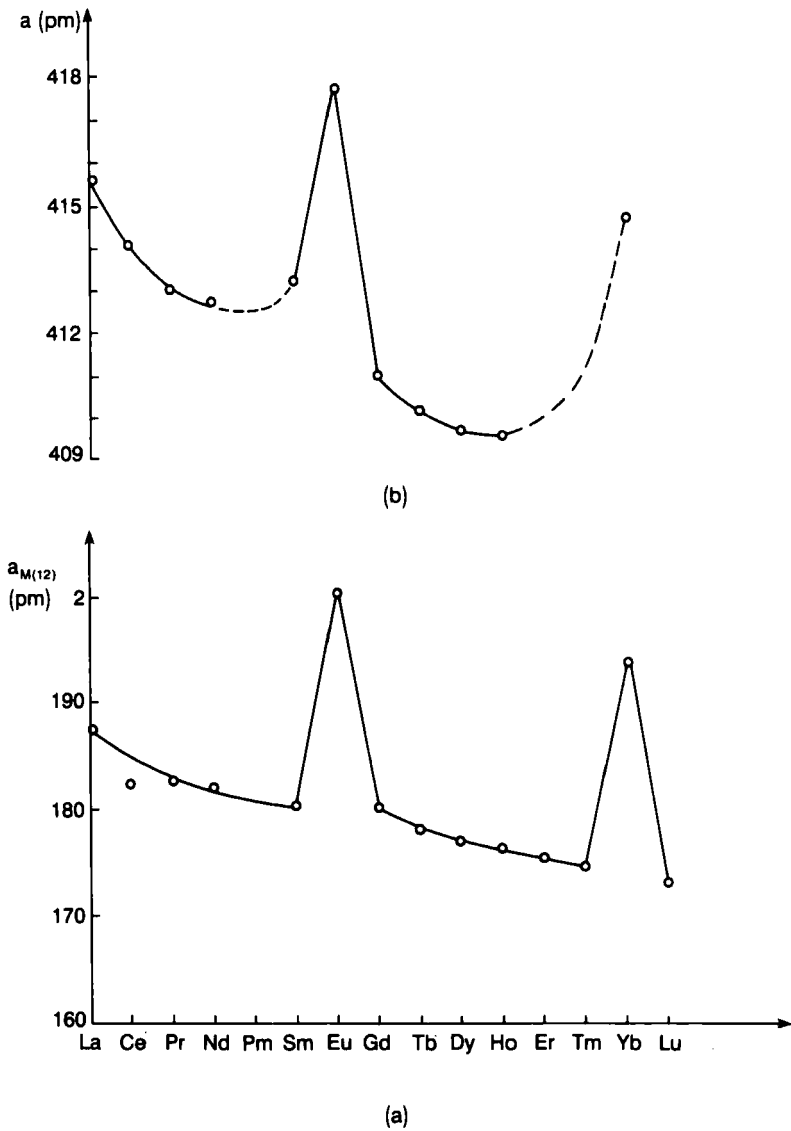


Figure 1. Metallic radii of rare-earth metals and cubic lattice parameters of the rare-earth hexaborides.

TABLE 2. THE RANGES IN r_M° APPROPRIATE TO THE SEVERAL STRUCTURAL TYPE (BORIDES OF THE ACTINIDES ARE EXCLUDED)

Structure type	Range in r_M° (10^2 pm)
CaB_6	2.35–1.77
ThB_4	1.94–1.73
YB_{66}	1.80–1.73
UB_{12}	1.80–1.60
AlB_2	1.80–1.28

Inspection of Table 1 indicates that the unit cell volume of MB_4 , MB_6 , MB_{12} and MB_{66} borides varies as r_M° except for the actinides.

A rather definite range in r_M° is associated with each structural type, but there is a broad zone of overlap ($1.58 \cdot 10^2 \text{ pm} < r_M^\circ < 1.98 \cdot 10^2 \text{ pm}$) in which more than one structural type is observed. Particularly large atoms ($r_M^\circ > 1.97 \cdot 10^2 \text{ pm}$) form only hexaborides and the smallest atoms ($r_M^\circ < 1.55 \cdot 10^2 \text{ pm}$) only diborides. Metal atoms for which $1.60 \cdot 10^2 \text{ pm} < r_M^\circ < 1.82 \cdot 10^2 \text{ pm}$ form borides in four structural types.

In Table 2 is summarized the r_M° appropriate to each structural type for all borides except those of the actinides.

The actinide borides must be considered a special case. The metallic radii exhibited in the borides are correlated with the abilities of the metals to form various

TABLE 3. EXISTENCE OF THE ACTINIDES BORIDES: COMPARISON OF THE UNIT CELL VOLUME OF THE ACTINIDE TETRABORIDES WITH THOSE OF COMPARABLE RARE-EARTH TETRABORIDES

Element			Existence of borides (x) and V_m for MB_4			
Actinide	Rare earth	r_M° (10^2 pm)	MB_2	MB_4 (10^6 pm^3)	MB_6	MB_{12}
Th	Pr	1.790		216.50 (x)	(x)	(x)
		1.820		216.37 (x)	(x)	
Am	Dy	1.730		202.20 (x)	(x)	
		1.775		202.27 (x)	(x)	
Pu	Ho	1.590	(x)	201.80 (x)	(x)	(x)
		1.766	(x)	200.42 (x)		(x)
Np	Ho	1.550	(x)	200.80 (x)	(x)	
		1.766	(x)	200.42 (x)		(x)
U	Er	1.560	(x)	199.30 (x)		(x)
		1.757	(x)	199.47 (x)		(x)

phases. For this purpose the unit cell volume is considered to be proportional to the metallic radius, since this is a convenient way of comparing structures of other than cubic symmetry. It also allows for the possibility that the cation radii in the boride structure may not follow the same trend that the metallic radii do. The V_m of the actinide borides and r_M° of the actinides are given in Table 3.

Among the tetraborides, UB_4 has the smallest volume and hence the smallest effective radius. Thus an actinide element having a metallic radius of 1.59 Å (Pu) or smaller forms a diboride, while those having larger radii do not. As in the rare-earth series, the actinides able to form MB_4 , MB_6 and MB_{12} borides form also MB_2 diborides (Table 1).

Although U has a r_M° close to that of Np, Np forms a hexaboride while U does not. This observation can be explained by considering in the rare-earth series the tetraborides having V_m comparable to those of actinides (Table 3). The V_m of PuB_4 and NpB_4 are intermediate between those of HoB_4 and DyB_4 , and the V_m of UB_4 is smaller than that of HoB_4 . Thus in the tetraborides the size of Np or Pu is larger and the size of U smaller than that of Ho. This hypothesis extended to the hexaborides explains why Pu and Np form hexaborides and U does not.

While HoB_6 and ErB_6 do not exist, the solid solutions $Ho_{1-x}La_xB_6$ ($0.2 < x < 1$) and $Ho_{0.8}Ca_{0.2}B_6$ are known^{2,3}.

The size of the metallic site in the ThB_4 -type structure is relatively large ($r = 1.91 \times 10^2$ pm for YB_4) and accepts only large metal atoms, e.g., rare earths or actinides. Smaller metallic atoms, e.g., Mg, Cr and Mn, form tetraborides having other structures described previously, in which the size of the metallic site is 1.58×10^2 pm for MgB_4 and 1.32×10^2 pm for CrB_4 .

Although Zr and Sc have close metallic radii, the former has the UB_{12} -type structure and the latter exhibits a tetragonal symmetry, but its structure is not known. This indicates that in the series of the metals able to form borides with UB_{12} -type structure the metallic radius of Zr corresponds to the lowest limit ($r_{Zr}^\circ \approx 1.60 \times 10^2$ pm).

Finally, the high-pressure synthesis favors the formation of borides that are difficult to prepare under standard conditions. In this way SmB_2 with the AlB_2 -type structure and GdB_{12} and ThB_{12} with the UB_{12} -type structure are prepared⁴.

(J. R. ETOURNEAU)

1. F. Laves, in *Theory of Alloy Phases*, American Society for Metals, Cleveland, OH, 1956, p. 124.
2. A. Berrada, J. P. Mercurio, J. Etourneau, P. Hagenmuller, *Mater. Res. Bull.*, **11**, 947 (1976).
3. M. C. Nichols, R. W. Mar, Q. Johnson, *J. Less-Common Met.*, **33**, 317 (1973).
4. J. F. Cannon, H. T. Hall, in *The Rare Earths in Modern Science and Technology*, G. J. McCarthy, J. J. Rhyne, eds., Plenum Press, New York, 1977, p. 219.

6.7.2.5. Solid Solution of Transition and Inner Transition Metals in Boron

6.7.2.5.1. The Solubility in the Various Modifications of Boron.

Several of the claimed crystalline modifications of boron are not truly boron modifications but consist of phase mixtures or B-rich compounds formed under favorable kinetic conditions. The existence of the α - and β -rhombohedral (α -rh and

6.7.2. Existence and Crystal Chemistry of Borides**6.7.2.5. Solid Solution of Transition and Inner Transition Metals****6.7.2.5.1. The Solubility in the Various Modifications of Boron.**

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β -rh) modifications¹ as stable phases is not in doubt; neither is² that of β -tetragonal boron, although with less certainty. The α -tetragonal form ($a = 875$ pm; $c = 506$ pm)³ is a B-rich carbide, a nitride or a mixture of both. The α -tetragonal structure also can accommodate transition-metal atoms, e.g., Ti^{4,5}, V⁶ or Ni⁷.

The solubility of transition elements in α -rh boron is low⁸. The purity of α -rh boron prepared by thermal decomposition of BI_3 is high, although that of β -rh prepared from the same reactants is low. Crystallization of α -rh boron from a Pt melt⁹ requires pure chemicals. The solubility of transition and inner transition elements in β -tetragonal boron is not known, but that in β -rh boron is described in §6.7.2.5.2 and 6.7.2.5.3.

Elements dissolved in boron influence its crystal structure. Dissolved impurities also influence the physical and chemical properties of boron, especially the electrical properties, because boron is a semiconductor. Preparation of solid solutions in β -rh boron requires a careful choice of crucible material. To avoid contamination, boron nitride or a cold, coinage-metal crucible should be used or the levitation or floating-zone melting techniques applied.

(T. LUNDSTRÖM)

1. R. Naslain, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 139.
2. M. Vlasse, R. Naslain, J. S. Kasper, K. Ploog, *J. Less-Common Met.*, **67**, 1 (1979).
3. K. Ploog, E. Amberger, *J. Less-Common Met.*, **23**, 33 (1971).
4. E. Amberger, K. Polborn, *Acta Crystallogr., Sect. B*, **31**, 949 (1975).
5. K. Ploog, *Acta Crystallogr., Sect. B*, **32**, 981 (1976).
6. E. Amberger, H. P. Gerster, *Acta Crystallogr., Sect. B*, **36**, 672 (1980).
7. B. F. Decker, J. S. Kasper, *Acta Crystallogr.*, **13**, 1030 (1960).
8. J. A. Ugai, N. E. Soloviev, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 227.
9. F. H. Horn, in *Boron: Synthesis, Structure and Properties*, J. A. Kohn, W. F. Nye, G. K. Gaulé, eds., Plenum Press, New York, 1960, p. 110.

6.7.2.5.2. Solid Solutions in β -Rhombohedral Boron.

The materials for solid solutions of transition elements in β -rh boron are prepared by arc melting the component elements or by solid-state diffusion of the metal into β -rhombohedral (β -rh) boron. Compositions as determined by crystal structure and electron microprobe analyses together with the unit cell dimensions are given in Table 1. The volume of the unit cell (V_m) increases when the solid solution is formed. As illustrated in Fig. 1, V_m increases nearly linearly with metal content for the solid solution of Cu in β -rh boron. In addition to the elements listed in Table 1, the expansion of the unit cell exceeds 7.0×10^{-6} pm³ for saturated solid solutions¹⁻³ of Ti, V, Co, Ni, As, Se and Hf in β -rh boron, whereas the increase is smaller for the remaining elements. The solubility of these elements does not exceed a few tenths at %. The microhardness of the solid solution increases¹² with V_m . Boron is a brittle material, indicating the accommodation of transition-element atoms in the β -rh boron structure is associated with an increase in the cohesion energy of the solid.

Nuclear γ -ray resonance spectra of solid solutions of Fe¹⁶ and Co¹⁷ in β -rh boron give inconclusive results, although the large isomer shifts as compared to Fe metal¹⁴ indicate that the accommodation of Fe atoms in the boron structure is associated with changes in the electronic state. The magnitudes of the shifts are

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6.7.2.5. Solid Solution of Transition and Inner Transition Metals

6.7.2.5.2. Solid Solutions in β -Rhombohedral Boron.

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5. K. Ploog, *Acta Crystallogr., Sect. B*, **32**, 981 (1976).
6. E. Amberger, H. P. Gerster, *Acta Crystallogr., Sect. B*, **36**, 672 (1980).
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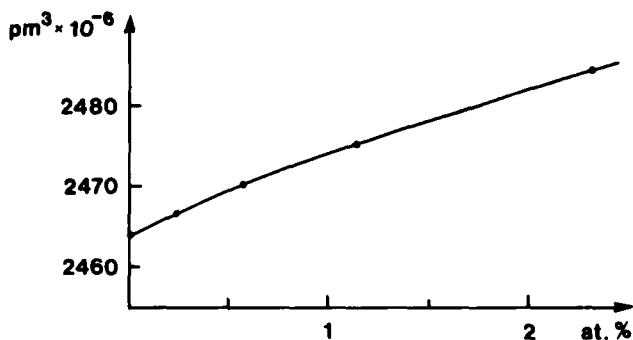
TABLE 1. DATA ON SOLID SOLUTIONS IN β -RHOMBOHEDRAL BORON

Structure	Metal content (at %)		$(\text{pm}^3 \times 10^{-6})$	ΔV $(\text{pm}^3 \times 10^{-6})$	Ref.
	Refinement	Electron microprobe			
β -rh boron	—	—	2462.7	—	1
ScB \sim_{28}	3.5	3.2 ± 0.5	2508.4	45.7	2
CrB \sim_{41}	2.4	—	2482.5	19.8	3
MnB \sim_{23}	4.1	3.6 ± 0.4	2508.6	45.9	4
FeB \sim_{49}	2.0	—	2473.3	10.6	5
NiB _{48.5}	2.06	1.85 ± 0.04	2482.2	19.5	13
CuB \sim_{23}	3.8	4.17 ± 0.02	2500.2	37.5	6
CuB \sim_{28}	3.5	2.7 ± 0.4	2489.9	27.2	4
Cu ₂ Al _{2.7} B ₁₀₄	—	1.8 Cu, 2.5 Al ^a	2508.3	45.6	7
GeB \sim_{90}	1.1	—	2482.0	19.3	1, 8
ZrB \sim_{51}	1.9	—	2497.1	34.4	9
WB _x	—	0.27 ± 0.01	2469.7	7.0	1
SiB \sim_{36}	2.70	2.74 ± 0.14	2509.0	46.3	10
AlB ₃₁	3.13	—	2485.2	22.5	14
ZnB \sim_{25}	3.9	—	2510.2	25.1	15

^a From chemical analyses.

compatible with the presence of Fe(III) as well as Fe(II). Static magnetic and electron paramagnetic resonance studies of Fe¹⁸ and Mn¹⁹ show the Fe(II) to be in the D hole (§6.7.2.5.3) and Fe(III) in the A hole²⁰.

The solubility of rare-earth metals in β -rh boron is unknown. Rare-earth-boron systems are cubic borides^{21,22} with an EB₆₆ composition (E = Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb). The occurrence of this phase excludes extensive solid solutions in

Figure 1. Unit cell volume¹³ vs. Cu content in β -rh boron.

these systems. From spatial considerations the larger La, Ce, Pr, Pm and Eu atoms should not dissolve²³ in β -rh boron.

(T. LUNDSTRÖM)

1. A. Jimenez Crespo, L.-E. Tergenius, T. Lundström, *J. Less-Common Met.*, **77**, 147 (1981).
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4. S. Andersson, B. Callmer, *J. Solid-State Chem.*, **10**, 219 (1974).
5. B. Callmer, T. Lundström, *J. Solid-State Chem.*, **17**, 165 (1976).
6. I. Higashi, T. Sakurai, T. Atoda, *J. Less-Common Met.*, **45**, 283 (1976).
7. R. Mattes, L. Marosi, H. Neidhard, *J. Less-Common Met.*, **20**, 223 (1970).
8. L.-E. Tergenius, T. Lundström, *J. Less-Common Met.*, **82**, 341 (1981).
9. B. Callmer, L.-E. Tergenius, J. O. Thomas, *J. Solid-State Chem.*, **26**, 275 (1978).
10. M. Vlasse, J.-C. Viala, *J. Solid-State Chem.*, in press.
11. L. Bsenko, T. Lundström, *J. Less-Common Met.*, **34**, 273 (1974).
12. J.-O. Carlsson, T. Lundström, *J. Less-Common Met.*, **22**, 317 (1970).
13. T. Lundström, L.-E. Tergenius, *J. Less-Common Met.*, **47**, 23 (1976).
14. Yu. B. Kuz'ma, V. N. Gurin, M. M. Korsukova, L. G. Aksel'rud, *Inorg. Mater. (Engl. Transl.)*, **23**, 500 (1987).
15. I. Higashi, H. Iwasaki, T. Ito, T. Lundström, S. Okada, L.-E. Tergenius, *J. Solid State Chem.*, **82**, 230 (1989).
16. R. Wäppling, L. Häggström, S. Devanarayanan, *Phys. Scr.*, **5**, 97 (1972).
17. F. Stanke, F. Parak, *Phys. Status Solidi*, **52b**, 69 (1972).
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19. G. P. Tsiakarishvili, T. Lundström, L. Lundgren, G. V. Tsagareishvili, D. N. Tsikaridze, F. N. Tavadze, *J. Less-Common Met.*, **147**, 41 (1989).
20. A brief discussion of thermodynamics and chemical bonding appears in: T. Lundström, in *Boron-Rich Solids*, D. Emin, T. Aselage, C. L. Beckel, I. A. Howard, eds., American Institute of Physics, New York, 1986, p. 19.
21. K. Spear, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 439.
22. J. S. Kasper, *Less-Common Met.*, **47**, 17 (1976).
23. Yu. B. Paderno, T. Lundström, *Acta Chem. Scand., Ser. A*, **37**, 609 (1983).

6.7.2.5.3. Crystallographic Data on Solid Solutions of β -Rhombohedral Boron.

The β -rhombohedral (β -rh) structure¹ contains a complex B_{84} unit, three of which make up the hexagonal unit cell ($a = 1092.51$ pm; $c = 2381.4$ pm). A B_{84} unit consists of one central B icosahedron and 12 half-icosahedra, each situated outside a vertex atom of the central icosahedron. Two half-icosahedra can be distinguished; one is combined directly with the corresponding half-icosahedra in the neighboring B_{84} units, forming new complete icosahedra. The second type, with its quasi-fivefold axes nearly perpendicular to the hexagonal axis, is linked via B_{10} units and consists of a condensate of three half-icosahedra. In the B_{10} unit the vertex atom of the three half-icosahedra share one triangular face in pairs. The position of one of the B atoms, B13, in the B_{10} unit is occupied only partially. The linkage of the B_{84} and B_{10} units leads to a rigid, three-dimensional framework of B atoms in which all B atoms form part of an icosahedron. There are two nonequivalent B atoms that do not form part of any icosahedron. One of these, B15, is 6-coordinated and situated between two B_{10} units. The other position, B16, is 8-coordinated and displays a low occupancy. Furthermore, the occupancy of B16 at interstitial position G is influenced in the formation of a solid solution (Table 1).

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23. Yu. B. Paderno, T. Lundström, *Acta Chem. Scand., Ser. A*, **37**, 609 (1983).

6.7.2.5.3. Crystallographic Data on Solid Solutions of β -Rhombohedral Boron.

The β -rhombohedral (β -rh) structure¹ contains a complex B_{84} unit, three of which make up the hexagonal unit cell ($a = 1092.51$ pm; $c = 2381.4$ pm). A B_{84} unit consists of one central B icosahedron and 12 half-icosahedra, each situated outside a vertex atom of the central icosahedron. Two half-icosahedra can be distinguished; one is combined directly with the corresponding half-icosahedra in the neighboring B_{84} units, forming new complete icosahedra. The second type, with its quasi-fivefold axes nearly perpendicular to the hexagonal axis, is linked via B_{10} units and consists of a condensate of three half-icosahedra. In the B_{10} unit the vertex atom of the three half-icosahedra share one triangular face in pairs. The position of one of the B atoms, B13, in the B_{10} unit is occupied only partially. The linkage of the B_{84} and B_{10} units leads to a rigid, three-dimensional framework of B atoms in which all B atoms form part of an icosahedron. There are two nonequivalent B atoms that do not form part of any icosahedron. One of these, B15, is 6-coordinated and situated between two B_{10} units. The other position, B16, is 8-coordinated and displays a low occupancy. Furthermore, the occupancy of B16 at interstitial position G is influenced in the formation of a solid solution (Table 1).

TABLE 1. OCCUPANCY (%) OF INTERSTITIAL² AND SUBSTITUTIONAL POSITIONS IN β -Rh BORON

Composition	Interstitial positions					Substitutional positions			Ref.
	A1	A2	D	E	G	B1	B4	B13	
β -rh B	—	—	—	—	25	100	100	73	3
SiB ~ ₃₆	46.4	4.8	0	0	0	13.3 Si 86.7 B	100	74	4
ScB ~ ₂₈	0	0	31.4	72.7	0	100	5.7 Sc 92.5 B	61.3	5
CrB ~ ₄₁	71.9	0	18.0	0	0	100	100	71.7	2
MnB ~ ₂₃	25.6	0	43.1	66.2	0	100	100	65.0	6
FeB ~ ₄₉	50.7	0	18.5	0	0	100	100	72.6	7
NiB _{48.5}	44.7	0	10.8 ^d	0	18.0	100	100	61.7	15
CuB ~ ₂₈	6.1	0	43.1 ^b	50.5	20.9	100	100	61.1	6
CuB ₂₃	8	0	46	61	13	100	100	69	8
Cu ₂ Al _{2.7} B ₁₀₄	42 Cu	0	18 Cu 17 Al	0	0	100	100	< 100	9
GeB ~ ₉₀	20.8	0.5	3.0 ^c	0	0	3.5 Ge 96.5 B	100	73	10
ZrB ~ ₅₁	0	0	27.9	18.1	14	100	100	53	11

^a Two positions, situated 98 pm from each other.^b Two positions, situated 40 pm from each other.^c Two positions, situated 80 pm from each other.^d Contains a new interstitial position at 0.1127, 0.1744, 0.4753 with occupancy 0.58% Ni.**TABLE 2. HOLES (NOTATION ACCORDING TO REF. 2) AND SUBSTITUTIONAL POSITIONS IN β -Rh BORON**

Hole	Position	Approximate coordinates		
		x	y	z
A1 [M1]	6(c)	0	0	0.14
A2	18(h)	0.11	0.22	0.10
A3 ^a	36(i)	0.28	0.25	0.05
D [M2]	18(h)	0.20	0.40	0.17
D'	18(h)	0.19	0.38	0.15
E [M3]	6(c)	0	0	0.23
F1 ^a	18(h)	0.07	0.14	0.25
F2 ²	18(h)	0.12	0.24	0.25
G [B16]	18(h)	0.06	0.12	0.12
Substitution				
B1 ^b	36(i)	0.17	0.17	0.18
B4 ^c	36(i)	0.24	0.25	0.35

^a No occupancy found.^b B1 can be replaced partially by Si or Ge.^c Two B4 atoms can be replaced partially by Sc.

Although the icosahedron is a compact arrangement (the radius of the central hole is $0.90 r_B$) the linking of these units leads to an open structure. The space filling is only 36% in β -rh boron, assuming the covalent radius of B to be 88 pm. The structure contains several holes that are sufficiently large to accommodate transition-metal atoms. The approximate positions of the holes² are given in Table 2, which also shows which of the B atoms can be replaced by metal atoms. The hole occupancies, obtained from single-crystal diffractometry, are collected in Table 1. The holes are incompletely filled and the occupancy can be low.

Holes of the A1, A2 and A3 types lie outside the triangular faces of the central icosahedron of the B_{84} unit. Each hole is surrounded by 12 neighboring B atoms. The A1 hole accommodates smaller atoms and not Sc or Zr. Silicon and Ge atoms can be accommodated in the A2 hole. There is no evidence for the accommodation of any atoms in the A3, F1 or F2 holes.

The D and E positions have 15 B near neighbors. The E position can be occupied by transition metals. The D hole is occupied except in the Si solution. The center of the D hole is poorly defined¹². Within this hole, Cu or Ge atoms are distributed on two separate positions, situated 40 pm and 80 pm apart, respectively.

Scandium⁵ substitutes for two B atoms at position B4, as well as the substitution of Si¹³ and Ge¹⁰ for B1; the accommodation of Ge is in a small hole at (0.158; 0; 0.5).

Copper preferentially occupies the holes in β -rh boron as shown by powder diffraction¹⁴. In the CuB_x solid solution the D hole is represented by two crystallographic positions (denoted 2' and 2'' in Fig. 1)¹⁵ situated 40 pm from each other. The accommodation of the Cu atoms in three (or four) different holes in the preferred order shown in Fig 1 demonstrates the complex nature of the solid solution.

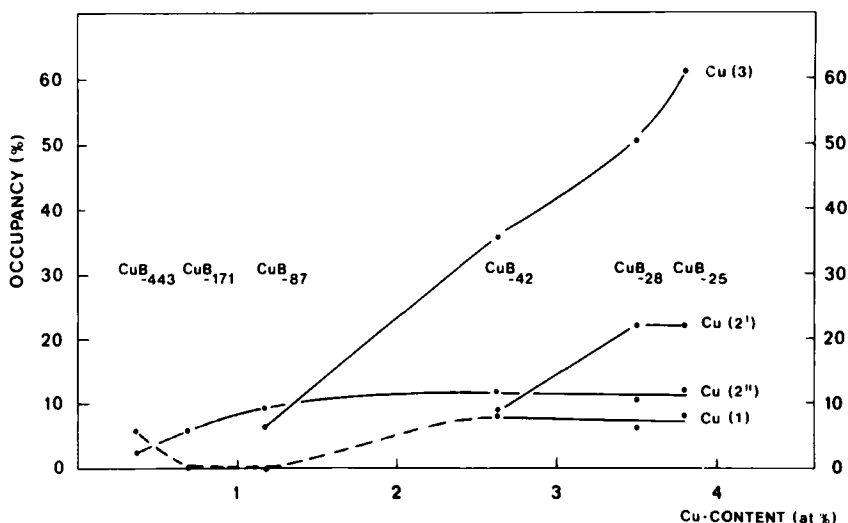


Figure 1. Preferential occupancy of holes in β -rh boron expressed as the occupancy of the crystallographic positions vs. total Cu content^{6,8,14}.

Other single-crystal x-ray diffraction studies^{16,17} of transition element dopants in β -rh boron are based on the results of a refinement of the β -rh boron structure¹⁸ that establishes the occurrence of four new low-occupancy (3.7, 6.6, 6.8 and 8.5%) B positions in addition to the earlier known ones¹⁹. The dopant elements studied, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Hf and Ta, do not enter B positions in the framework, but they enter the A1, A2, D and E positions. In some cases the doping elements have been studied at several concentrations for each element and for different cooling rates. The percentage occupancies of certain positions are correlated with the atomic sizes of the dopants. The bond distances between the polyhedra are shorter than those within the polyhedra. The mechanism of doping for some cases is denoted "displacive," rather than interstitial or substitutional, because of competing interactions between the six different partially occupied B positions and dopant atoms.

(T. LUNDSTRÖM)

1. J. L. Hoard, D. B. Sullenger, C. H. L. Kennard, R. E. Hughes, *J. Solid State Chem.*, **1**, 268 (1970).
2. S. Andersson, T. Lundström, *J. Solid State Chem.*, **2**, 603 (1970).
3. B. Callmer, *Acta Crystallogr., Sect. B*, **33**, 1951 (1977).
4. M. Vlasse, J.-C. Viala, *J. Solid State Chem.*, **37**, 181 (1981).
5. B. Callmer, *J. Solid State Chem.*, **23**, 391 (1978).
6. S. Andersson, B. Callmer, *J. Solid State Chem.*, **10**, 219 (1974).
7. B. Callmer, T. Lundström, *J. Solid State Chem.*, **17**, 165 (1976).
8. I. Higashi, T. Sakurai, T. Atoda, *J. Less-Common Met.*, **45**, 283 (1976).
9. R. Mattes, L. Marosi, H. Neidhard, *J. Less-Common Met.*, **20**, 223 (1970).
10. L.-E. Tergenius, T. Lundström, *J. Less-Common Met.*, **82**, 341 (1981).
11. B. Callmer, L.-E. Tergenius, J. O. Thomas, *J. Solid State Chem.*, **26**, 275 (1978).
12. T. Lundström, L.-E. Tergenius, *J. Less-Common Met.*, **47**, 23 (1976).
13. T. Lundström, in *Boron: Preparation, Structure and Properties*, F. N. Tavadze, ed., Nauka, Moscow, 1974, p. 44; *Chem. Abstr.*, **83**, 12,447 (1975).
14. B. Callmer, Ph.D. Thesis, Acta Universitatis Upsaliensis No. 434, Uppsala, 1977.
15. T. Lundström, L.-E. Tergenius, I. Higashi, *Z. Kristallogr.*, **167**, 235 (1984).
16. M. F. Garbauskas, J. S. Kasper, G. A. Slack, *J. Solid State Chem.*, **63**, 424 (1986).
17. G. A. Slack, C. I. Hejna, M. Garbauskas, J. S. Kasper, *J. Solid State Chem.*, **76**, 64 (1988).
18. G. A. Slack, C. I. Hejna, M. F. Garbauskas, J. S. Kasper, *J. Solid State Chem.*, **76**, 52 (1988).
19. B. Callmer, *Acta Crystallogr., Sect. B*, **33**, 1951 (1977).

6.7.3. Preparation of Borides

The synthetic method used in preparing a particular boride phase depends primarily on its intended use. Whereas for basic research borides of high purity are desirable, for industrial applications, e.g., in coatings, tools and crucibles, as a refining agent in metallurgy or in control rods in nuclear energy plants, pure borides are unnecessary.

The methods for preparing polycrystalline borides¹⁻⁶ often require high T. The only exceptions are precipitations of a few Fe and Pt group borides from aq soln: however high-T treatments are necessary to form crystalline compounds.

Other single-crystal x-ray diffraction studies^{16,17} of transition element dopants in β -rh boron are based on the results of a refinement of the β -rh boron structure¹⁸ that establishes the occurrence of four new low-occupancy (3.7, 6.6, 6.8 and 8.5%) B positions in addition to the earlier known ones¹⁹. The dopant elements studied, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Hf and Ta, do not enter B positions in the framework, but they enter the A1, A2, D and E positions. In some cases the doping elements have been studied at several concentrations for each element and for different cooling rates. The percentage occupancies of certain positions are correlated with the atomic sizes of the dopants. The bond distances between the polyhedra are shorter than those within the polyhedra. The mechanism of doping for some cases is denoted "displacive," rather than interstitial or substitutional, because of competing interactions between the six different partially occupied B positions and dopant atoms.

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5. B. Callmer, *J. Solid State Chem.*, **23**, 391 (1978).
6. S. Andersson, B. Callmer, *J. Solid State Chem.*, **10**, 219 (1974).
7. B. Callmer, T. Lundström, *J. Solid State Chem.*, **17**, 165 (1976).
8. I. Higashi, T. Sakurai, T. Atoda, *J. Less-Common Met.*, **45**, 283 (1976).
9. R. Mattes, L. Marosi, H. Neidhard, *J. Less-Common Met.*, **20**, 223 (1970).
10. L.-E. Tergenius, T. Lundström, *J. Less-Common Met.*, **82**, 341 (1981).
11. B. Callmer, L.-E. Tergenius, J. O. Thomas, *J. Solid State Chem.*, **26**, 275 (1978).
12. T. Lundström, L.-E. Tergenius, *J. Less-Common Met.*, **47**, 23 (1976).
13. T. Lundström, in *Boron: Preparation, Structure and Properties*, F. N. Tavazde, ed., Nauka, Moscow, 1974, p. 44; *Chem. Abstr.*, **83**, 12,447 (1975).
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16. M. F. Garbaskas, J. S. Kasper, G. A. Slack, *J. Solid State Chem.*, **63**, 424 (1986).
17. G. A. Slack, C. I. Hejna, M. Garbaskas, J. S. Kasper, *J. Solid State Chem.*, **76**, 64 (1988).
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The methods of preparing borides may be classified as follows:

1. Direct combination of the elements
2. Reduction of a metal compound and boron halide with hydrogen
3. Fused-salt electrolysis
4. Reduction of a metal oxide or other metal compound using C, B or boron carbide
5. Reduction of boron oxide or boron halides by metals
6. Low-T precipitation of borides from solution
7. Other methods

(J. R. ETourneau)

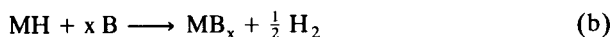
1. R. Kieffer, F. Benesovski, *Hartstoffe*, Springer-Verlag, Berlin, 1963.
2. G. V. Samsonov, L. Ya. Markovski, A. F. Zhigach, M. G. Valyashko, *Boron, Its Compounds and Alloys*. (Engl. Transl.), Office of Technical Services, Department of Commerce, Washington, DC, 1962.
3. C. F. Powell, in *High-Temperature Materials and Technology*, I. E. Campbell, E. M. Sherwood, eds., J. Wiley and Sons, New York, 1967, p. 349.
4. R. Thompson, *Prog. Boron Chem.*, 2, 173 (1970).
5. D. R. Glasson, J. A. Jones, *J. Appl. Chem.*, 19, 125 (1969).
6. R. Naslain, J. Etourneau, P. Hagenmuller, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 263.

6.7.3.1. by Direct Combination of the Elements

Preparations from the metals and boron is common since metals and pure B are readily available. The direct combination of the elements has advantages, especially if control over composition and purity is required.

A pellet is pressed of an intimate mixture of finely divided reactants and reaction induced either by arc melting and high-T annealing or by solid-state sintering in an electrical or high-frequency furnace. Isolating the borides from reactive container components can be a problem. The use of boron nitride liners has proved effective. In some cases the protective liner is made of sintered boride containing the same elements as the boride in preparation.

The metal or its hydride may be used according to the reactions:



Experimental work can be difficult owing to both the high volatility of the metals and their reactivity toward O_2 (e.g., alkali-metals, alkali-earth metals, rare earths). Once reaction begins it often is highly exothermic judging by the enthalpies of formation of borides¹.

The choice of the specific experimental technique is determined by the degree of volatility of the metal.

(i) **Direct Synthesis Involving Metals with Low Volatility.** The reactions are generally carried out in vacuum or under argon. To facilitate solid-state diffusion, the B and the metal or its hydride are shaped into tablets under high pressure (ca. $15 \times 10^5 \text{ N m}^{-2}$). Alternatively, the reactants may be melted together in a water-cooled copper crucible or under levitation conditions within an induction coil at

6.7. Formation of Borides
 6.7.3. Preparation of Borides
 6.7.3.1. by Direct Combination of the Elements

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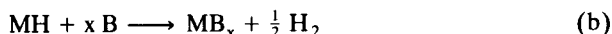
1. R. Kieffer, F. Benesovski, *Hartstoffe*, Springer-Verlag, Berlin, 1963.
2. G. V. Samsonov, L. Ya. Markovski, A. F. Zhigach, M. G. Valyashko, *Boron, Its Compounds and Alloys*. (Engl. Transl.), Office of Technical Services, Department of Commerce, Washington, DC, 1962.
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4. R. Thompson, *Prog. Boron Chem.*, 2, 173 (1970).
5. D. R. Glasson, J. A. Jones, *J. Appl. Chem.*, 19, 125 (1969).
6. R. Naslain, J. Etourneau, P. Hagenmuller, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 263.

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suitable frequency². Borides may be synthesized by diffusion of B from a heated, pressed pellet of the powdered element (or of another boride) in which the metal, e.g., Fe, Co, Ni or Ta is wrapped³⁻⁸.

(ii) **Direct Synthesis in the Presence of the Vapor Phase.** This technique is utilized when the metals involved have high vapor pressures at the T required for synthesis, e.g., for Sm, Eu, Tm, Yb, alkali and alkali-earth metals. The utilization of these relatively volatile metals requires sealed containers that resist the corrosive action of B and of metal gases under pressure⁹⁻¹³.

Since metals react with B only at $\geq 700^\circ\text{C}$, and since alkali-metal borides are thermally unstable, the preparation of these borides by direct synthesis can be carried out at high T only with an excess of metal in sealed containers.

The formation of alkali-metal borides by direct synthesis requires temperatures of $750\text{--}1200^\circ\text{C}$, depending on the variety of boron utilized and the specific metal. This leads to two important consequences:

1. Since the synthesis temperatures are higher than the dissociation temperatures of the phases that are formed (at a pressure of 10^5 N m^{-2}), it is necessary to react the alkali metal with boron under metal pressure in excess of that defined by Eq. (a), in sealed vessels. The alkali metal is present as a liquid in equilibrium with the vapor phase, the pressure of which is determined by the T of the coldest point. This pressure (greater the more volatile the metal) favors the synthetic reaction relative to the reverse dissociation reaction.

2. The reactivity of alkali metals with B decreases as their atomic number increases: Li reacts completely with B at 700°C , whereas with K the reaction is not complete until 1200°C , at which T the pressure of the alkali metal is ca. $20 \times 10^5 \text{ N m}^{-2}$. These pressures demand the use of thick-walled reaction vessels. The boron-alkali metal mixture is placed in a Mo crucible inside such a container made of Fe or Mo, depending on the reaction T.

By using a large metal excess, which can also act as a flux, well-crystallized borides can be obtained. After reaction, the excess is eliminated either by distillation at low T (Na, 350°C ; K, 300°C) and in high vacuum (10^{-3} to 10^{-4} N m^{-2}), or by washing with NH_3 .

The parameters controlling the synthesis are the temperature, the vapor pressure of the alkali metal and the crystalline state of boron. The reactions are unaffected by the atomic ratio, M/B, provided it is much larger than the M/B ratios characteristic of the phases that are to be prepared: values of, e.g., ca. 1/2, 1 or 2, are satisfactory.

The reaction of Li with boron noticeable at 680°C ⁹ or at 600°C ¹⁴, is rapid at 750°C and different; boron samples are attacked equally regardless of crystalline form or particle size.

The reaction of Na with B, detectable at 850°C , becomes complete at 900°C after 24 h. At 1000°C , the reaction rate is independent of the variety of boron (α - or β -rh), if the particle size is the same. The B-Na system contains two borides with the formulas NaB_6 and Na_xB_{15} ^{11,12,15}.

Liquid K, in equilibrium with its vapor, does not react with B $\leq 1100^\circ\text{C}$ ($p_K^\circ = 10.7 \times 10^5 \text{ N m}^{-2}$). Above this T, a selective reaction is observed, leading to the formation of the hexaboride, KB_6 . Whereas Li and Na react equally with both α - and β -rh boron prepared at 800°C by reducing BBr_3 with hydrogen in a quartz tube^{10,16}, K combines only with the α -rh variety. The reaction of Li and Na with B is instantaneous; that of K is slower: to be complete, it requires about 18 h at 1100°C .

($p_K^0 = 10.7 \times 10^5 \text{ N m}^{-2}$) and 5 h at 1200°C ($p_K^0 = 17.5 \times 10^5 \text{ N m}^{-2}$). Above 1200°C , the action of K on α -rh boron leads to products that contain both potassium hexaboride and β -rh boron; this latter phase can result either from the early stages of decomposition of the hexaboride, or from an α -rh \longrightarrow β -rh transformation.

The selective reaction of K with the α -rh boron is explained by the metastable character of this variety at high T and by the existence in the structure of weak, three-center B—B bonds that correspond to particularly long B—B distances ($2.03 \times 10^2 \text{ pm}$; a normal covalent B—B bond is $1.76 \times 10^2 \text{ pm}$).

The thermal stability of alkali-metal borides is relatively low, which is expected from the high vapor pressures of the corresponding metals at high T. Consequently, the alkali-metal vapor pressure is an important parameter, and synthesis of alkali-metal boride is carried out in isothermal reactors that permit maximum alkali-metal pressure and hence optimum preparation conditions.

The B—Na system includes two phases with different thermal stabilities. Either of these two borides can be obtained by direct synthesis on adjusting the alkali-metal pressure in the vapor phase. Thus, the preparation of NaB_6 can be carried out in isothermal reactors at $\leq 1100^\circ\text{C}$ ($p_{\text{Na}}^0 = 45 \times 10^5 \text{ N m}^{-2}$) where the equilibrium $\text{Na}_{\text{liq}} \rightleftharpoons \text{Na}_{\text{vapor}}$ exists. Above this T, the sodium pressure is no longer sufficient to prevent the thermal dissociation of NaB_6 and syntheses lead to a second phase with a lower Na content, Na_xB_{15} . However, Na_xB_{15} can be prepared at $< 1100^\circ\text{C}$, as long as the sodium pressure in the vapor phase is kept low by having a cold wall in the reactor or, e.g., by substituting a Na-K alloy for sodium⁹.

The problems raised by the preparation of some rare-earth borides such as SmB_4 , YbB_4 and TmB_2 are comparable to those found for the alkali borides from the point of view of the volatility of the metals. They dissociate through metal evaporation, yielding boron-rich borides as indicated in §6.7.2.4.

(J. R. ETourneau)

1. O. H. Krikorian, UCRL-51043 (U.S. AEC Rept.); *Chem. Abstr.*, 76, 50,890 (1972).
2. R. Thompson, *Prog. Boron Chem.*, 2, 173 (1970).
3. W. Hodge, R. M. Evans, A. F. Haskins, *J. Metals*, 7, 824 (1955).
4. W. P. Roe, U.S. Patent 2,852,409 (1958); *Chem. Abstr.*, 53, 1082 (1959).
5. R. Fruchart, A. Michel, *Bull. Soc. Chim. Fr.*, 422 (1959).
6. R. Fruchart, A. Michel, *C.R. Hebd. Seances Acad. Sci.*, 245, 171 (1957).
7. H. M. Feder, *Proc. Symp. High Temp*, Berkeley, CA, 159 (1956); *Chem. Abstr.*, 52, 8875 (1958).
8. U.S. Atomic Energy Commission, Br. Pat. 840,203 1960; *Chem. Abstr.*, 55, 342 (1961).
9. R. Naslain, J. Etourneau, P. Hagenmuller, *Bull. Soc. Chim. Fr.*, 2529 (1967).
10. R. Naslain, J. Etourneau, P. Hagenmuller, in *Boron*, Vol. III, *Preparation and Properties*, T. Niemyski, ed., Polish Scientific Publishers, Warsaw, 1970, p. 35.
11. P. Hagenmuller, R. Naslain, *C.R. Hebd. Seances Acad. Sci.*, 257, 1294 (1963).
12. R. Naslain, J. Etourneau, P. Hagenmuller, *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 263.
13. R. Naslain, J. Etourneau, *C.R. Hebd. Seances Acad. Sci.*, 263, 484 (1966).
14. D. R. Secrist, W. J. Childs, U.S. Atomic Energy Commission Report TID-17149 (1962); *Chem. Abstr.*, 61, 11,601 (1964).
15. R. Naslain, A. Guette, P. Hagenmuller, *J. Less-Common Met.*, 47, 1 (1976).
16. R. Naslain, in *Preparative Methods in Solid State Chemistry*, P. Hagenmuller, ed., Academic Press, New York, 1972, p. 439.

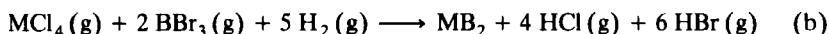
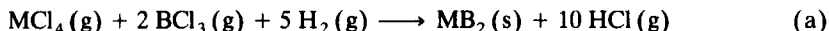
6.7. Formation of Borides

6.7.3. Preparation of Borides

6.7.3.3. by Fused-Salt Electrolysis

6.7.3.2. by Reduction of a Metal Compound and Boron Halide with Hydrogen

This method consists of mixing a boron halide with the metal halide and heating to ca. 1000–1300°C in the presence of hydrogen¹⁻³, e.g.:



Borides of Al, Ti, Zr and Hf are prepared according to reaction (a), although even with careful measuring of reactants it is not always possible to form the metal boride in stoichiometric ratio, and free metal B may be deposited^{2,4,5}. This method is not suitable when the free metal deposits at T below those required for boride formation, as in the cases² of Nb, Ta, Mo and W.

Fibers of titanium diboride can be prepared by reaction (a) at 400°C in an electrical discharge⁶. Adherent layers of certain metal borides on metal substrate surfaces are obtained by thermal decomposition of metal (Mo, W, Nb, Ta) halides and BBr₃ on a metallic substrate using a solar furnace or induction heating⁷⁻⁹.

The halide is not the only metal compound used as source of metal. Metal oxides and sulfides are employed to prepare vanadium, chromium, iron and nickel borides in this way from sulfides at lower reaction T than those required by reaction sintering of the elements¹⁰.

(J. R. ETOURNEAU)

1. R. E. Gannon, R. C. Folweiler, T. Vasilos, *J. Am. Ceram. Soc.*, **46**, 496 (1963).
2. C. F. Powell, I. E. Campbell, B. W. Gosner, *Vapor Plating*, Wiley, New York, 1955, p. 104.
3. A. E. van Arkel, *Chem. Weekbl.*, **24**, 90 (1927).
4. J. J. Gebhardt, R. F. Cree, *J. Am. Ceram. Soc.*, **48**, 262 (1965).
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6. T. Takahashi, K. Sugiyama, Y. Suzuki, *J. Cryst. Growth*, **10**, 139 (1971).
7. B. Armas, F. Trombe, *C.R. Hebd. Seances Acad. Sci.*, **272**, 286 (1971).
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10. J. Cueilleron, G. Lahet, F. Thevenot, R. A. Pâris, *J. Less-Common Met.*, **24**, 317 (1971).

6.7.3.3. by Fused-Salt Electrolysis

In this method¹⁻¹³ the melt contains boric oxide and the metal oxide in a suitable electrolyte, usually an alkali or alkaline-earth halide or fluoroborate. The cell is operated at 700–1000°C depending on electrolyte composition. To limit corrosion, the container serving as cathode is made of mild steel or of the metal whose boride is sought. The anode is graphite or Fe. Numerous borides are prepared in this way, e.g., alkaline-earth and rare-earth hexaborides¹⁴⁻¹⁶ and transition-metal borides, e.g., TiB₂¹⁷, Ni₂B, NiB¹⁸ and TaB¹⁹.

The mechanism of boride formation is not always well known. However, many studies have sought to understand the chemical processes involved in fused-salt electrolysis.

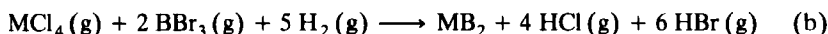
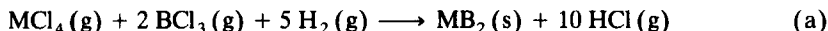
6.7. Formation of Borides

6.7.3. Preparation of Borides

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This method consists of mixing a boron halide with the metal halide and heating to ca. 1000–1300°C in the presence of hydrogen^{1–3}, e.g.:



Borides of Al, Ti, Zr and Hf are prepared according to reaction (a), although even with careful measuring of reactants it is not always possible to form the metal boride in stoichiometric ratio, and free metal B may be deposited^{2,4,5}. This method is not suitable when the free metal deposits at T below those required for boride formation, as in the cases² of Nb, Ta, Mo and W.

Fibers of titanium diboride can be prepared by reaction (a) at 400°C in an electrical discharge⁶. Adherent layers of certain metal borides on metal substrate surfaces are obtained by thermal decomposition of metal (Mo, W, Nb, Ta) halides and BBr₃ on a metallic substrate using a solar furnace or induction heating^{7–9}.

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The fused-salt electrolysis method is not suitable for obtaining pure materials of definite stoichiometry.

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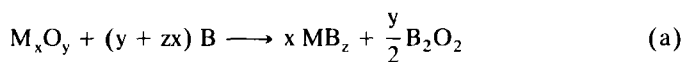
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19. J. J. Rameau, *Rev. Int. Hautes Temp. Refract.*, **8**, 59 (1971).

6.7.3.4. by Reduction of a Metal Oxide or Other Metal Compound Using Carbon, Boron or Boron Carbide

The reduction of a metal oxide or other metal compound by C, B or boron carbide requires higher T than in the other methods available for boride preparation.

An intimate mixture of the starting materials is pelleted and placed in a crucible and heated to 1500–2000°C under vacuum or in a vented furnace.

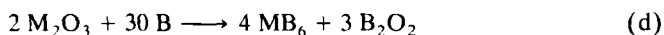
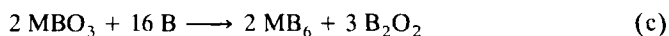
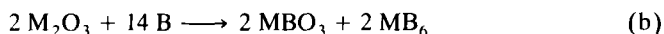
i. Boro-thermic Reduction of a Metal Oxide.



The volatile B_2O_2 is formed in this boro-thermic process for preparing diborides, tetraborides or hexaborides¹⁻³. This method is a means of preparing pure borides.

Two types of formation mechanism for rare-earth hexaboride are distinguished, depending on the hexaboride⁴.

(a) For MB_6 ($M = La, Ce, Nd, Sm, Eu, Gd, Tb$ and Yb):



At 1100°C the borate and the hexaboride are formed simultaneously [reaction (b)]. The observed borates are the aragonite type for La, Ce, Nd and the vaterite type

6.7. Formation of Borides

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6.7.3. Preparation of Borides

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(J. R. ETOURNEAU)

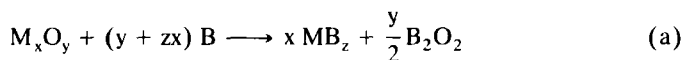
1. L. Andrieux, *C.R. Hebd. Seances Acad. Sci.*, **186**, 1537 (1928).
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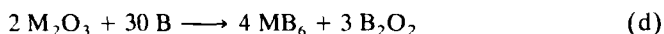
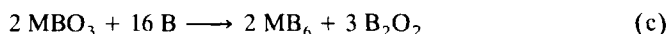
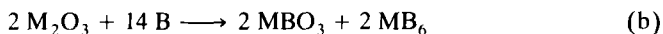
i. Borothermic Reduction of a Metal Oxide.



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Two types of formation mechanism for rare-earth hexaboride are distinguished, depending on the hexaboride⁴.

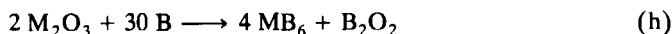
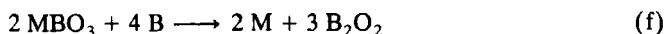
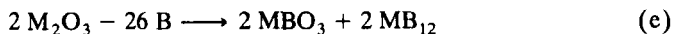
(a) For MB_6 (M = La, Ce, Nd, Sm, Eu, Gd, Tb and Yb):



At 1100°C the borate and the hexaboride are formed simultaneously [reaction (b)]. The observed borates are the aragonite type for La, Ce, Nd and the vaterite type

for the other rare earths. Between 1100 and 1500°C the borate is reduced by the free B in excess [reaction (c)].

(b) For MB_6 ($M = Y$ and Dy):

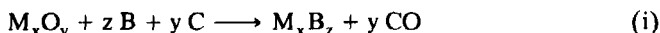


At 1100°C only the borate and the dodecaboride, MB_{12} , are formed [reaction (e)]. At 1100–1500°C the borate is reduced by the xs free B to give the metal, which reacts with MB_{12} to form the hexaboride [reaction (g)].

The boro-thermic reduction of a metal oxide is easiest when there is no formation of dodecaboride. The boric oxide is volatile and is completely eliminated > 1500°C under vacuum.

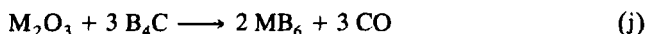
This method is used extensively in the laboratory because it is particularly suitable for preparing borides of rare or expensive metals, e.g., the transition-metal-rich borides CrB , Cr_3B_4 , CrB_2 (except Cr_3B_2 and Cr_4B)⁵, the diborides ScB_2 , TiB_2 ⁶, the rare-earth hexaborides^{6–8}, dodecaborides and MB_{66} -type borides.

ii. Reduction of a Metal Oxide by a Mixture of Boron and Carbon.

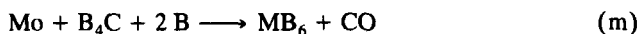
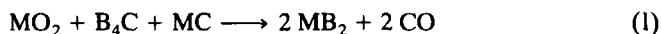
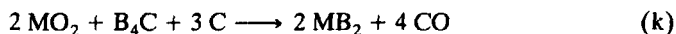


The reduction of a metal oxide by a mixture of B and C is easier than the reduction by the boro-thermic process described above. The rate of reduction depends on the removal of CO, so operation under vacuum increases the rate and allows the reaction to proceed at a lower T than the boro-thermic process. The metal oxide may be volatile and the borides can be contaminated by C. Accordingly, this method is not suitable for preparing pure alkaline-earth and rare-earth hexaborides because in all cases borocarbides of formula $MB_{6-x}C_x$ (e.g., $M = Sr, Eu, Yb$) are formed⁹.

iii. Reduction of a Metal Oxide by Boron Carbide or a Mixture of Boron Carbide and Carbon or a Mixture of Boron Carbide and Boron. Boron carbide is the source of both B and C. It reacts with metal oxides forming the rare-earth hexaborides^{3,7}:



Depending on the desired boride (e.g., diborides or hexaborides) free C, metal carbide or free B are included in addition to the boron carbide^{7,10–16}:



The metal oxide can be replaced by the metal itself¹⁷:



The volatility of the metal oxide is a critical factor, because some metal oxides are too volatile and cannot be used unless an excess is employed, e.g., as for tungsten¹⁸.

(J. R. ETourneau)

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13. P. Peshev, *Rev. Int. Hautes Temp Refract.*, **4**, 289 (1967).
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6.7.3.5. by Reduction of Boron Oxide or Boron Halides with Metals

This method is the simplest and cheapest for making borides. It is used to prepare transition-metal borides and alkaline-earth metal hexaborides.

The reduction of a transition-metal oxide and boron oxide by an electropositive metal such as Al, Mg or an alkali metal has been used as a pathway to titanium, iron, chromium, tungsten and alkali-earth borides¹⁻⁶.

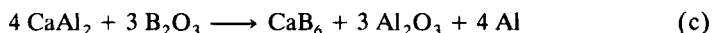
The following reactions illustrate the aluminothermic and magnesiothermic processes:



This reaction can be helped by addition of carbon:



The CaB_6 can be obtained by reduction of boric oxide with calcium aluminide at 800°C ⁷:



To increase the yield a mixture of B_2O_3 and CaO can be added to react with aluminum in excess.

6.7. Formation of Borides

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6.7.3. Preparation of Borides

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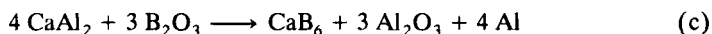
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This reaction can be helped by addition of carbon:



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To increase the yield a mixture of B_2O_3 and CaO can be added to react with aluminum in excess.

The reactions described above can be carried out by replacing Al by Mg



The purity of the products obtained is low since the refractory oxides that result can be difficult to remove. However, purities > 99.5% are obtained using Mg as the reducing agent².

The metal of the desired boride can also be used directly as the reducing agent, the source of B being either boric oxide or boron halides. Examples in which the reducing metal forms the boride include AlB_2 and AlB_{12} (reduction of B_2O_3 by Al)⁸, MnB (reduction of B_2O_3 or borax by Mn)⁹, magnesium borides (reduction of B_2O_3 or NaBF_4 by Mn)^{10,11} and TiB_2 (reaction between boron trifluoride or trichloride and Ti powder¹²).

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6.7.3.6. by Low-Temperature Precipitation of Borides from Solution

Little information exists on low-T precipitation of borides from solution. Chromium, cobalt and platinum borides are the only ones claimed to have been obtained from aqueous solution¹⁻⁶. Ni_2B and Co_2B are precipitated from a solution of nickel or cobalt acetates by adding a solution of sodium tetrahydroborate¹⁻⁴. The formation of these borides at RT gives amorphous products. Hence, heat treatment at 300–700°C leads to crystalline Ni_3B as the main constituent, although the average composition of the precipitate corresponds to $\text{Ni}_2\text{B}^{7-10}$.

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6.7.3.7. by Other Methods

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6.7.4. Crystal Growth of Borides

6.7.4.1. by Gas-Phase Methods

6.7.4.1.1. by Chemical Vapor Deposition (CVD).

6.7.4.1. by Gas-Phase Methods

The crystal growth of metal borides by gas-phase methods permits preparation of products at moderate T (1000–1500°C). This is an important advantage since most borides melt at high T (ca. 3000°C), which makes their crystal growth from melts difficult. In addition, the gas-phase methods lead to the formation of single crystals and solid films of incongruently melting borides.

The gas-phase methods usually applied to the crystal growth of borides are two: chemical vapor deposition (CVD) and chemical vapor transport (CVT).

(P. PESHEV)

6.7.4.1.1. by Chemical Vapor Deposition (CVD).

In CVD gaseous reactants pass over a heated substrate where chemical reactions or thermal decomposition occur and solid material deposits and grows. The CVD systems for the preparation of borides differ in design; however, their basic element is always a reactor (mostly of fused silica) ensuring controllable introduction and good preliminary mixing of the gaseous species before their coming into contact with the substrate. The latter can be a W^{1,2}, Mo³ or Ta⁴ wire directly heated by passing electric current through it. However, more often substrates are made of various profiles of pure graphite^{5–15}, boron-coated graphite^{16–18}, quartz^{19–23}, Ti¹⁰, Nb and Ta^{24–29}. Heating is effected with a rf generator^{5,8,11,12,14–18} a resistance graphite⁶ or silicon carbide^{7,13,20–23} furnace, by concentration of solar radiation^{24–29} or using a.c. discharge between constant-distance electrodes^{19,30}. The process variables that should be manipulated include substrate T, total pressure, total flow rate and ratio between the components in the reactant gas mixture.

Chemical vapor deposition processes are complex. Chemical thermodynamics, mass transfer, reaction kinetics and crystal growth all play important roles³¹. Equilibrium thermodynamic analysis is the first step in understanding any CVD process. Thermodynamic calculations are useful in predicting limiting deposition rates and condensed phases in the systems which can deposit under the limiting equilibrium state. These calculations are made for CVD of titanium^{12,16,17,32,33} and tantalum¹⁵ diborides, but in dynamic CVD systems equilibrium is rarely achieved and kinetic factors often govern the deposition rate behavior.

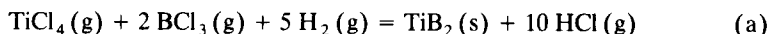
Mass transfer and chemical kinetic factors in CVD include the flow of initial substances and gaseous products through the system, the transport of reactants from the gas phase to the substrate surface, the transport of the gaseous products from the substrate surface to the bulk gas, as well as the reactions taking place at the substrate surface³¹.

A combination of thermodynamic analysis and experimental data on the deposition rates, efficiencies and deposit morphologies as a function of CVD variables may be used to develop models for the deposition processes. In the case of CVD of borides such a predictive model has been created so far only for a CVD system in which TiB₂ is obtained by reduction of TiCl₄ and BCl₃ with H₂³⁴.

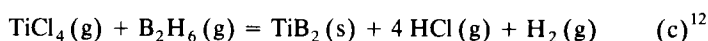
Because of its stability and unusual properties, the crystal growth of TiB₂ is the most studied process of boride preparation by CVD. It is interesting from both a scientific and an engineering viewpoint, and because of the availability, low cost and

easy handling of TiCl_4 and the availability of exhaustive and reliable thermodynamic data concerning TiB_2 and titanium chlorides.

(i) **Crystal Growth of Titanium Diboride.** The overall reaction in the crystal growth of TiB_2 by CVD is^{3-11,14-17,19,20,33,34}:



The reactions



are also utilized.

Detailed equilibrium thermodynamic analysis of the Ti-Bi-Cl-H system^{32,33} indicates that the gaseous species present in greatest abundance at equilibrium are TiCl_3 , TiCl_4 , BCl_3 , H_2 , HBCl_2 and HCl . The deposition of solid Ti and TiB phases is thermodynamically improbable; however, B can be deposited as a second phase at high B/Ti ratios in the gas phase¹⁰. The CVD of TiB_2 is thermodynamically favored at elevated T, low $\text{Cl}/(\text{Cl} + \text{H})$ fractions and reduced pressures. However, the advantages of the reduced pressure in terms of higher reaction efficiency, are small and should not warrant the increased complexity of a low-pressure reactor³⁵.

According to the kinetic model of the deposition process expressed by Eq. (a)³⁴, at high T ($> 1373 \text{ K}$) the principal rate-limiting mechanism is the diffusion of gaseous species through a gas boundary layer above the substrate surface. Below 1373 K a chemical kinetic mechanism dominates the TiB_2 deposition because equilibrium no longer exists at the substrate surface. Variations in the composition of the reactant gaseous mixture change the rate-limiting mechanism at high T. For ratios $\text{B}/(\text{B} + \text{Ti}) > 2/3$ and $\text{Cl}/(\text{Cl} + \text{H}) < 1/3$, a chemical kinetic mechanism becomes predominant instead of the diffusion one³⁴.

The theoretical considerations are qualitatively confirmed by experimental studies^{7,9,16,17,34}. However, quantitative results are strongly affected by reactor and substrate geometry, and this must be taken into account when the data are compared³⁵.

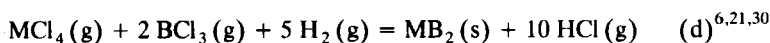
The morphology of chemical-vapor-deposited TiB_2 depends on the deposition conditions^{5-9,16,17}. Titanium diboride begins to grow at 650°C ⁹. At $\leq 900\text{--}1000^\circ\text{C}$ it forms a coherent, relatively smooth film with nodular surface^{6,8,16,17}. Deposition at higher T results in film surfaces with clearly defined crystal facets^{5,8,16,17}. The film orientation is not affected by the substrate orientation^{6,8}. The high deposition temperatures ($\geq 1400^\circ\text{C}$) favor the growth of TiB_2 single crystals in the form of hexagonal platelets measuring up to several mm^2 in the gas phase $\text{TiCl}_4:\text{BCl}_3 \geq 1/2$ ^{4,9,16,17}. Larger and better formed single crystals are obtained at higher T^{16,17} and with xs HCl in the gas phase⁴. Dendritic TiB_2 crystallites form at higher BCl_3 concentrations^{8,16,17}.

Equation (a) proceeds under an a.c. discharge leading to fibrous TiB_2 ¹⁹. The discharge current determines the growth rate and diameter of the fiber. When the current is $0.4\text{--}0.5 \text{ mA}$, the TiB_2 fibers obtained have a diameter of $13 \mu\text{m}$ and grow with a rate of 8 mm/min . Using reaction (a), TiB_2 whiskers $250 \mu\text{m}$ in length and $0.1\text{--}1 \mu\text{m}$ in diameter can be grown for 30 min at $1050\text{--}1070^\circ\text{C}$ ²⁰. Whisker growth is favored by Au, Pt and Pd impurities painted on the substrate surface. The growth mechanism is supposed to be a vapor-liquid-solid (VLS) mechanism²⁰.

Another source of boron in CVD of TiB_2 is diborane. A substantial yield increase, greater deposition rate, lower deposition T and a reduction in HCl byproducts make Eq. (c) attractive^{12,33}. At deposition temperatures $\geq 700^\circ\text{C}$, the deposits are essentially stoichiometric titanium diboride. However, Eq. (c) is accompanied by side reactions leading to the formation of subchlorides (e.g., TiCl_3) and higher boranes. These solid compounds deposit on the cooler portion of the reactor and are oxidized in contact with air after opening the reactor¹². Another disadvantage of B_2H_6 as a boron source, especially when crystals are to be grown, is the relatively high retention of chlorine in the TiB_2 deposits which is not reduced by annealing¹².

Crystalline films of TiB_2 obtained by CVD are used at lower temperatures as protective coatings. The interaction of these films with various substrates is studied^{11,35,36} and desirable properties of the substrate in cases when the coating is deposited according to Eq. (a) are formulated. Substances meeting the requirements in this respect are W, Ta, Mo, WC, TiC, graphite, Fe-Ni-Co-Mn alloy (Kovar) and some high-chrome steels.

(ii) **Crystal Growth of Zirconium and Hafnium Diborides.** Hydrogen reduction of MCl_4 ($\text{M} = \text{Zr}, \text{Hf}$) and BCl_3 is used in CVD of ZrB_2 and HfB_2 :

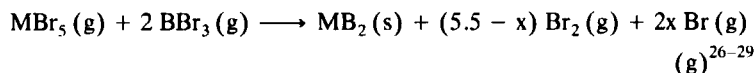
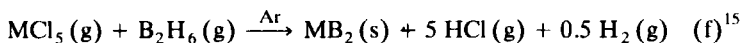
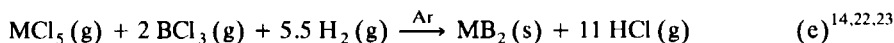


At 1400°C and reduced pressure, ZrB_2 and HfB_2 codeposit with considerable amounts of β -rh boron owing to the low vapor pressure of Zr and Hf tetrachlorides. Excess hydrogen and metal tetrachloride are necessary to minimize the formation of uncombined boron⁶.

Fibrous growth of ZrB_2 occurs under a.c. discharge at 0.5–1 mA, the growth being accelerated by argon addition. Zirconium diboride fibers with a diameter of 9 μm are obtained³⁰.

In the presence of gold as an impurity and at 1040 – 1060°C , ZrB_2 whiskers of $\leq 500 \mu\text{m}$ length and a diameter of $0.5 \mu\text{m}$ can be grown for 30 min on a quartz substrate. As in the case of TiB_2 , a VLS mechanism of growth is proposed²¹.

(iii) **Crystal Growth of Niobium and Tantalum Diborides.** In the CVD of NbB_2 and TaB_2 :



where $\text{M} = \text{Nb}$ or Ta .

According to reaction (e), NbB_2 deposits as a homogeneous crystalline film on a quartz substrate at 950 – 1050°C . At 1050 – 1200°C , pillar crystals of NbB_2 are formed. These results correspond to a composition of the gas phase lying in the NbCl_5 -rich region ($\text{BCl}_3/\text{NbCl}_5 = 1$) and to low flow rates of the reactants. At high flow rates elemental B and Nb are codeposited. In the presence of Ni impurities, the growth of regular hexagonal pillar crystals (10 μm in edge and 50 μm in length) according to a VLS mechanism occurs²².

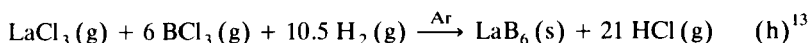
Single-phase tantalum diboride of composition $TaB_{1.90}$ – $TaB_{1.95}$ is deposited using reaction (e) on a quartz substrate when the B/Ta ratio in the source gas is higher than 1.5, and $T > 1000^\circ\text{C}$. At lower T and B/Ta ratios, deposition of metallic Ta is predominant. On substrates containing Ni or Pd impurities, woolly crystals up to $100\ \mu\text{m}$ in length can be grown in 30 min at 1050°C . As in the case of NbB_2 , a tip-VLS mechanism of growth is presumed²³.

Thermodynamic considerations postulate B_2H_6 to be a better boron source than BCl_3 in CVD of TaB_2 ¹⁵. Using reaction (f) at $< 1200\ \text{K}$ deposits with extremely small crystal sizes are obtained on graphite substrates¹⁵. They contain amorphous B at deposition temperatures $< 873\ \text{K}$ and are substoichiometric in B above this T. Carbon from the substrate substitutes for B, thereby stabilizing the diboride structure at high deposition T¹⁵.

Crystalline films of NbB_2 and TaB_2 are deposited on Ta and Nb substrates, respectively, according to the dissociation reaction (g) when the process is carried out at a reduced pressure, a temperature of 1100°C for NbB_2 and 1150°C for TaB_2 and with source gases containing MBr_5 and BBr_3 in a stoichiometric ratio^{26–29}. At temperatures below 1000°C only a metal deposit is obtained, whereas at 1000 – 1100°C deposition of metals, lower borides and MB_2 occurs^{26–29}.

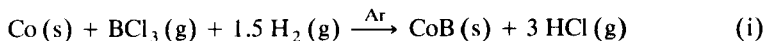
(iv) **Crystal Growth of Molybdenum and Tungsten Borides.** Chemical vapor deposition of molybdenum and tungsten boride films is performed on Nb substrates using the thermal dissociation of BBr_3 and $MoCl_5$ (or WCl_6) under reduced pressure^{24,25,29}. The preparation of single-phase products is difficult. For the Mo–B system, only Mo is deposited $< 1060^\circ\text{C}$. At 1060 – 1260°C the deposit composition changes from $Mo + Mo_2B$ through Mo_2B to $Mo_2B + MoB$. Pure MoB is deposited at 1260 – 1450°C . Mixtures of MoB and Mo_2B_3 are obtained above these T. For W metal, deposition proceeds at $\leq 1150^\circ\text{C}$, after which $W + W_2B$, pure W_2B and $W_2B + WB$ are successively deposited with increasing temperature $\leq 1300^\circ\text{C}$. Pure phases of WB and W_2B_3 are obtained at 1400 and 1600°C , respectively.

(v) **Crystal Growth of Lanthanum Hexaboride.** The overall reaction



is used in CVD crystal growth of LaB_6 on a graphite substrate. A $BCl_3 : LaCl_3$ ratio < 2 in the reactant gas mixture is necessary to avoid deposition of elemental B. Whiskers of 1 – $20\ \mu\text{m}$ thickness and 2 – $5\ \text{mm}$ length are obtained at 1150°C after 1 h of growth. At $\geq 1250^\circ\text{C}$ square pyramidal pillars and isometric crystals grow. The crystal color changes from reddish-purple to blue as the BCl_3 concentration is increased. This is associated with deviations from the stoichiometric composition within LaB_6 homogeneity range and is also established on the basis of the crystal lattice parameter change.

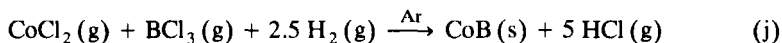
(vi) **Crystal Growth of Cobalt Monoboride.** Chemical vapor deposition is used to prepare CoB layers and crystals³⁷. The layers are obtained on Co substrates according to:



at 650 – 1000°C . When the process takes place at 1000°C , admixtures of Co_2B are found occasionally in the layers in addition to the main CoB phase. The layers prepared below 900°C are very dense and fine grained. Above 900°C their surface

becomes roughened and has many large wrinkles, cavities or voids. Arrays of hollow CoB pillar crystals with square or rectangular cross sections, a random orientation and a length of 20–50 μm are formed at 1100°C.

Cobalt monoboride crystals are deposited on a graphite substrate by simultaneous reduction with hydrogen of a mixture of CoCl_2 (prepared in situ by chlorination of Co powder at 800°C) and BCl_3 in an Ar flow:



The crystals obtained at 800°C have a square pillar form and almost all of them are hollowed in the central part of the cross section. At 1100°C the formation of specially shaped deposits is observed along with the growth of dendritic crystals of CoB (about 5 mm in length).

(vii) Crystal Growth of Boride Solid Solutions. Chemical vapor deposition is applied in the preparation of films of boride solid solutions $(\text{Ti}, \text{Zr})\text{B}_2$ ^{14,38} and $(\text{Ta}, \text{Ti})\text{B}_2$ ¹⁴ by hydrogen reduction of metal chlorides and BCl_3 on graphite substrates^{14,38}. When the gas phase contains TiCl_4 and ZrCl_4 vapors, Zr is incorporated in the deposit only at substrate temperatures $> 900^\circ\text{C}$. With increasing deposition temperature Zr incorporates more readily. Dense uniform $(\text{Ti}, \text{Zr})\text{B}_2$ films with columnar microstructure are grown under high metal chloride partial pressures. For $(\text{Ta}, \text{Ti})\text{B}_2$ solid solutions an alloy containing 10 ± 2 at % Ti is deposited at 850°C, irrespective of the Ta : Ti ratio in the gas phase. The diboride solid solution phase is accompanied by a second phase identified as essentially pure Ta_2B ¹⁴.

(P. PESHEV)

1. A. Moers, *Z. Anorg. Allg. Chem.*, **198**, 243 (1931).
2. K.-Th. Wilke, *Z. Phys. Chem. (Leipzig)*, **220**, 137 (1962).
3. A. N. Pilyankevich, V. S. Sinel'nikova, L. V. Strashinskaya, T. I. Shaposhnikova, in *High-Temperature Borides and Silicides*, T. Ya. Kosolapova, ed., Naukova Dumka, Kiev, 1978, p. 29.
4. K. Sugiyama, S. Iwakoshi, S. Motojima, Y. Takahashi, *J. Cryst. Growth*, **43**, 533 (1978).
5. R. E. Gannon, R. C. Folweiler, T. Vasilos, *J. Am. Ceram. Soc.*, **46**, 496 (1963).
6. J. J. Gebhardt, R. F. Cree, *J. Am. Ceram. Soc.*, **48**, 262 (1965).
7. T. Takahashi, H. Kamiya, *J. Cryst. Growth*, **26**, 203 (1974).
8. T. M. Besmann, K. E. Spear, *J. Cryst. Growth*, **31**, 60 (1975).
9. N. Tamari, Y. Otsubo, A. Kato, *Kyushu Daigaku Kogaku Shuno*, **49**, 531 (1976); *Chem. Abstr.*, **86**, 59,469p (1977).
10. G. Blandenet, Y. Lagarde, J. P. Morlevat, G. Uny, in *Proc. 6th Int. Conf. Chem. Vapor Deposition*, Electrochemical Society, New York, 1977, p. 330.
11. H. O. Pierson, E. Randich, D. M. Mattox, *J. Less-Common Met.*, **67**, 381 (1979).
12. H. O. Pierson, A. W. Mullendore, *Thin Solid Films*, **72**, 511 (1980).
13. S. Motojima, Y. Takahashi, K. Sugiyama, *J. Cryst. Growth*, **44**, 106 (1978).
14. E. Randich, *Thin Solid Films*, **63**, 309 (1979).
15. E. Randich, *Thin Solid Films*, **72**, 517 (1980).
16. P. Peshev, T. Niemyski, *J. Less-Common Met.*, **10**, 133 (1965).
17. P. Peshev, *Izv. Inst. Obshta Neorg. Khim., Bulg. Akad. Nauk*, **4**, 53 (1966); *Chem. Abstr.*, **66**, 68558t (1967).
18. G. Bliznakov, P. Peshev, T. Niemyski, *J. Less-Common Met.*, **12**, 405 (1967).
19. T. Takahashi, K. Sugiyama, Y. Suzuki, *J. Cryst. Growth*, **10**, 139 (1971).
20. S. Motojima, F. Sugimori, Y. Takahashi, K. Sugiyama, *Bull. Chem. Soc. Jpn.*, **48**, 3156 (1975).
21. S. Motojima, F. Sugimori, Y. Takahashi, K. Sugiyama, *Denki Kagaku Oyobi Kogyo Butsuri Kagaku*, **43**, 323 (1975).
22. S. Motojima, K. Sugiyama, Y. Takahashi, *J. Cryst. Growth*, **30**, 233 (1975).

23. S. Motojima, K. Sugiyama, *J. Mater. Sci.*, **14**, 2859 (1979).
24. B. Armas, F. Trombe, *C.R. Hebd. Seances Acad. Sci., Ser. C*, **272**, 286 (1971).
25. B. Armas, F. Trombe, *Sol. Energy*, **15**, 67 (1973).
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27. B. Armas, F. Trombe, *C.R. Hebd. Seances Acad. Sci., Ser. C*, **280**, 435 (1975).
28. B. Armas, C. Combescure, F. Trombe, *J. Electrochem. Soc.*, **123**, 308 (1976).
29. B. Armas, *Rev. Int. Hautes Temp. Refract.*, **12**, 255 (1975).
30. K. Sugiyama, T. Takahashi, *Kogyo Kagaku Zasshi* **73**, 1959 (1970); *Chem. Abstr.*, **74**, 68636v (1971).
31. M. E. Jones, D. W. Shaw, in *Treatise on Solid State Chemistry*, Vol. 5, *Changes of State*, N. B. Hannay, ed., Plenum Press, New York, 1975, p. 283.
32. T. M. Besmann, K. E. Spear, *J. Electrochem. Soc.*, **124**, 786 (1977).
33. E. Randich, T. M. Gerlach, *Thin Solid Films*, **75**, 271 (1981).
34. T. M. Besmann, K. E. Spear, *J. Electrochem. Soc.*, **124**, 790 (1977).
35. H. O. Pierson, E. Randich, *Thin Solid Films*, **54**, 119 (1978).
36. H. O. Pierson, E. Randich, in *Proc. 6th Int. Conf. Chem. Vapor Deposition, Electrochemical Society*, New York, 1977, p. 304.
37. S. Motojima, Y. Ihama, *J. Crystal Growth*, **76**, 373 (1986).
38. T. Takahashi, H. Kamiya, *High Temp.-High Pressures*, **9**, 437 (1977).

6.7.4.1.2. Crystal Growth of Borides by Chemical Vapor Transport.

In processes of crystal growth by CVT the initial polycrystalline solid substance interacts with a gaseous substance (transport agent) according to a reversible chemical reaction in a zone with a given temperature (source zone) as a result of which only gaseous products are obtained. These products are transferred to another zone with another temperature (crystallization zone) where, under differing equilibrium conditions, the initial solid substance is deposited in form of single crystals.

Close-spaced CVT is usually applied to the growth of single crystals. The reaction space here is a sealed tube (mostly of fused silica), different temperatures being maintained at its two ends. This technique is used to prepare TiB_2^{1-3} , ZrB_2^1 , VB_2^1 , NbB_2^4 , TaB_2^4 and LaB_6^5 single crystals.

As in the case of crystal growth by CVD, available data concern mostly TiB_2 single-crystal preparation. The CVT of TiB_2 can be carried out with the following transport agents: I_2 , BI_3 , BBr_3 and TeCl_4^{1-3} . In accordance with data from the thermodynamic analysis of the corresponding transport processes^{2,3}, at $< 1000^\circ\text{C}$ crystal growth takes place at the hotter end of the tube when I_2 and BI_3 are used as transport agents and at the colder end, when BBr_3 and TeCl_4 are applied. The efficient chemical species with the first two transport agents are BX_3 and TiX_4 , whereas with the remaining agents the transport is due principally to BX_3 and TiX_3 . The best results are achieved with TeCl_4 . The single crystals obtained at 1255 K (source zone) and 1125 K (crystallization zone) for 30 days are well-formed, hexagonal-based prisms of TiB_2 ranging from 1 to 3 mm long³. When iodine is used, a three-times lower transport rate is observed at the same transport duration and T in the source and crystallization zones of 1125 and 1225 K, respectively, and the single crystals formed are hexagonal platelets about 1 mm long and 0.1 mm thick. With BI_3 and BBr_3 , no well-formed crystals are obtained.

The crystal compositions vary, depending on the transport agent used, from $\text{TiB}_{1.89}$ (I_2) and $\text{TiB}_{1.94}$ (TeCl_4)³. At process temperatures $> 1000^\circ\text{C}$ and with I_2 , the transport direction is reversed. Crystals grow in the cold zone of the tube, but only microscopic needle-like crystals are obtained¹.

6.7.4. Crystal Growth of Borides

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6.7.4.1. by Gas-Phase Methods

6.7.4.1.2. Crystal Growth of Borides by Chemical Vapor Transport.

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At a maximum T of 1373 K in the source zone and a gradient of 120–150 K, microscopic ZrB_2 and VB_2 crystals grow in the cold crystallization zone when I_2 is used¹. With the same transfer agent for NbB_2 and TaB_2 , the transport direction is again hot \rightarrow cold. A temperature gradient of 150 K and a temperature in the source zone < 1173 K, lead to the formation of an amorphous boride layer in the crystallization zone. When the temperature increases to ≤ 1273 K, a crystalline deposit is obtained and > 1273 K well-shaped crystals are formed. At a constant T difference, the transport rate increases with increasing I conc and T in the source zone.

The CVT of borides is difficult since silica tubes are attacked by the gaseous products of the transport reactions unless the tube walls are coated with BN, which is chemically inert toward halogens and halides. Such a coating can be obtained by CVD using thermal decomposition at 900–950°C of the cyclic hexachloroborazine, $B_3N_3Cl_3$ ⁶. Another possibility is to use alumina or Pythagoras material [$Al_2O_3(60\%)-SiO_2(37\%)-Na_2O(3\%)$] tubes, as for instance in CVT of lanthanum hexaboride⁵.

Single-crystal LaB_6 in well-formed parallelepipeds ($0.15 \times 0.15 \times 2$ m) grows when $LaBr_3$ is used as transport agent in an Ar atmosphere with T in the source and crystallization zones of 1150 and 900°C, respectively. The transport probably proceeds through the subhalide. The amount of transported LaB_6 is increased by a factor of 10 when oxygen is replacing Ar, and $LaCl_3$ is substituted for $LaBr_3$. The more efficient transport in this case is due to the formation⁵ of $LaOCl$.

Open-tube transport is another technique of CVT crystal growth. This technique can also be applied for growing LaB_6 single crystals⁷. During the interaction of La_2O_3 , BCl_3 and H_2 at 1000°C, unidentified volatile products are formed and transferred by the hydrogen to the hotter zone. Hydrogen is present in a large excess so that it plays the role of a carrier. When the hot zone temperature is $< 1300^\circ C$, crystal films of LaB_6 are deposited. At 1350–1450°C cubic crystals of LaB_6 up to 1 mm long are obtained.

CAUTION: Diborane is a toxic gas which burns explosively in air. Its handling requires adequate precautions⁸.

(P. PESHEV)

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2. R. Feurer, C. Bernard, G. Constant, *C.R. Hebd. Seances Acad. Sci., Ser. C*, **282**, 1117 (1976).
3. R. Feurer, G. Constant, C. Bernard, *J. Less-Common Met.*, **67**, 107 (1979).
4. B. Armas, J. H. E. Jeffes, M. G. Hocking, *J. Cryst. Growth*, **44**, 609 (1978).
5. H. Klotz, *Naturwissenschaften*, **52**, 451 (1965).
6. G. Constant, R. Feurer, *J. Less-Common Met.*, **82**, 113 (1981).
7. T. Niemyski, E. Kierzek-Pecold, *J. Cryst. Growth*, **3–4**, 162 (1968).
8. *Diborane*, in *Tech. Bull.*, Callery Chemical Co., Callery, PA, May, 1976; H. C. Miller, E. L. Muetterties, in *Inorganic Syntheses*, vol. 10, E. L. Muetterties, ed., McGraw-Hill, New York, 1967, p. 81.

6.7.4.2. Liquid-Phase Methods

A temperature gradient is applied to the compound to be crystallized in which the compound can exist as a liquid or as liquid and solid.

It is impossible to find inert containers owing to both the high mp of borides ($> 2000^\circ C$) and their reactivity with refractory materials. The problem is solved by melting borides either in water-cooled boats or pedestals. Water-cooled, metal

6.7. Formation of Borides

6.7.4. Crystal Growth of Borides

6.7.4.2. Liquid-Phase Methods

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7. T. Niemyski, E. Kierzek-Pecold, *J. Cryst. Growth*, **3–4**, 162 (1968).
8. *Diborane*, in *Tech. Bull.*, Callery Chemical Co., Callery, PA, May, 1976; H. C. Miller, E. L. Muettterties, in *Inorganic Syntheses*, vol. 10, E. L. Muettterties, ed., McGraw-Hill, New York, 1967, p. 81.

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crucibles for use with rf heating^{1,2} are applied for synthesis, zone purification and crystal growth of semiconductors and metals³⁻⁶.

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2. H. F. Sterling, R. W. Warren, *Metallurgiya*, 67, 301 (1963); *Chem. Abstr.*, 59, 8398 (1963).
3. A. Berghezan, E. Bull Simonsen, *Trans. AIME*, 221, 1029 (1961).
4. T. Niemyski, in *Boron, Preparation, Properties and Applications*, Vol. 2, G. K. Gaule, ed., Plenum Press, New York, 1965, p. 35.
5. S. Hornfeldt, J. B. Kelterson, L. R. Windmiller, *J. Cryst. Growth*, 5, 289 (1969).
6. C. A. Brookes, M. E. Packer, in *Special Ceramics*, Vol. 4, P. Popper, ed., British Ceramics Association, 1968, p. 15.

6.7.4.2.1. Crystal Pulling.

Boride single crystals having high congruent mp ($> 2000^{\circ}\text{C}$) can be pulled from melts, e.g., diborides TiB_2 , ZrB_2 ¹, rare-earth tetraborides REB_4 ² and hexaborides REB_6 ³, YB_6 ^{4,5}.

Synthesis, purification and crystal growth of refractory semiconductors and metals can be carried out in the same rf heating apparatus⁵. As shown in Fig. 1, the charge is in a water-cooled Cu or Ag boat that can move laterally inside a quartz envelope. Purified gas is admitted through one end cap and exits by a bubbler. The quartz envelope can withstand either pressures of a few atmospheres or a vacuum. A side arm is connected to a pulling head via a metal bellows and an O-ring seal. One end cap is fitted with a packing gland through which rods may be inserted so that a W, Zr or Mo susceptor can be positioned over the charge. This susceptor is used primarily for preheating to initiate coupling between the charge and rf-power source

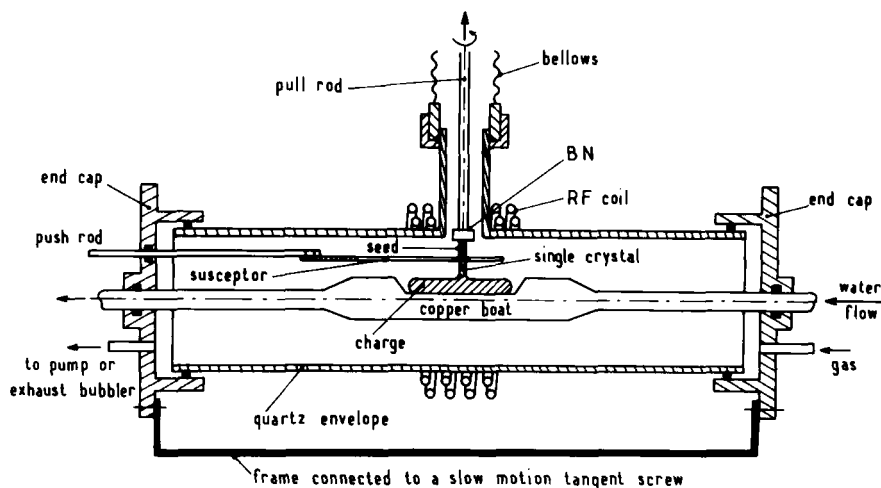


Figure 1. Schematic diagram of the cold metal crucible system used for synthesis, zone melting and crystal pulling crystal growth (from ref. 5).

6.7.4. Crystal Growth of Borides

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6.7.4.2. Liquid-Phase Methods

6.7.4.2.1. Crystal Pulling.

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2. H. F. Sterling, R. W. Warren, *Metallurgiya*, 67, 301 (1963); *Chem. Abstr.*, 59, 8398 (1963).
3. A. Berghezan, E. Bull Simonsen, *Trans. AIME*, 221, 1029 (1961).
4. T. Niemyski, in *Boron, Preparation, Properties and Applications*, Vol. 2, G. K. Gaule, ed., Plenum Press, New York, 1965, p. 35.
5. S. Hornfeldt, J. B. Kelterson, L. R. Windmiller, *J. Cryst. Growth*, 5, 289 (1969).
6. C. A. Brookes, M. E. Packer, in *Special Ceramics*, Vol. 4, P. Popper, ed., British Ceramics Association, 1968, p. 15.

6.7.4.2.1. Crystal Pulling.

Boride single crystals having high congruent mp ($> 2000^{\circ}\text{C}$) can be pulled from melts, e.g., diborides TiB_2 , ZrB_2 ¹, rare-earth tetraborides REB_4 ² and hexaborides REB_6 ³, YB_{66} ^{4,5}.

Synthesis, purification and crystal growth of refractory semiconductors and metals can be carried out in the same rf heating apparatus⁵. As shown in Fig. 1, the charge is in a water-cooled Cu or Ag boat that can move laterally inside a quartz envelope. Purified gas is admitted through one end cap and exits by a bubbler. The quartz envelope can withstand either pressures of a few atmospheres or a vacuum. A side arm is connected to a pulling head via a metal bellows and an O-ring seal. One end cap is fitted with a packing gland through which rods may be inserted so that a W, Zr or Mo susceptor can be positioned over the charge. This susceptor is used primarily for preheating to initiate coupling between the charge and rf-power source

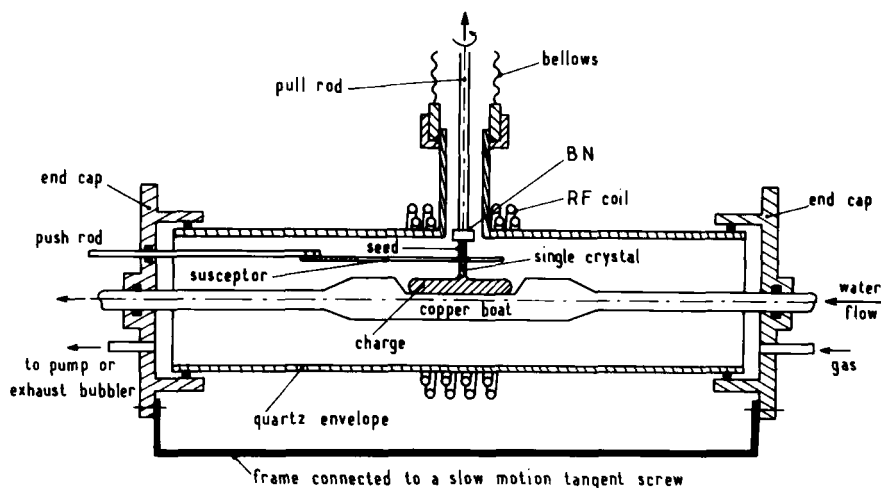


Figure 1. Schematic diagram of the cold metal crucible system used for synthesis, zone melting and crystal pulling crystal growth (from ref. 5).

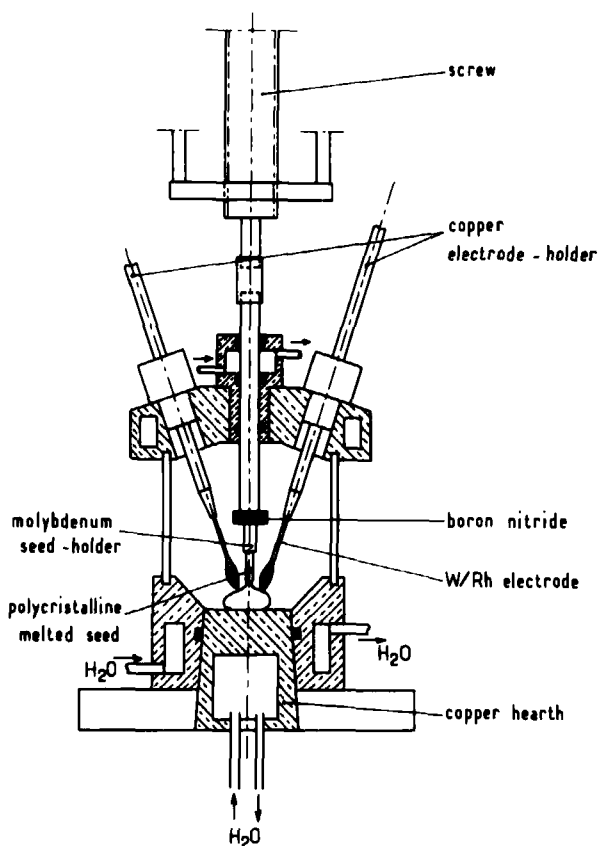


Figure 2. Schematic diagram of a tri-arc furnace for crystal pulling.

and to supply radiation to the melt just above the edges of the metal boat. This ensures that an adequate area of molten surface can be maintained for crystal growth. The seed, which can be a small single crystal or a melted sample of boride, is held in a boron nitride (stainless steel) chuck. For zone refining only, a cylindrical envelope with no side arm is used, and the boat and frame may be translated with respect to the fixed rf coil.

Large single crystals of YB_{66} (e.g., 2×10^{-2} m long and 5×10^{-3} m in diameter) have been obtained in this type of apparatus^{4,5}.

In a crystal-pulling procedure using a tri-arc furnace (Fig. 2)², a resistor box, a d.c. power supply (300 A, 80/40 V) and a set of water-cooled power cables are used to bring power and water to the electrodes. The upper part of the furnace is equipped with three equally spaced copper cathodes, to which are fixed W-Rh electrodes. The upper part (cathode) is separated from the lower part (anode) by a transparent quartz glass tube. In the bottom of the furnace there is a tapered opening for a water-cooled copper hearth containing the boride melt. All parts of the furnace are also water

TABLE 1. GROWTH RATE AND GROWTH DIRECTION
OF SOME RARE-EARTH TETRABORIDES

Crystals	Growth rate (m/min)	Growth direction	
		Axes	Deviation (°)
YB ₄	10 ⁻³	001	0
YB ₄	2 × 10 ⁻³	011	10
TbB ₄	1.5 × 10 ⁻³	001	10
ErB ₄	0.7 × 10 ⁻³	001	17

cooled. A Mo seed holder is rotatable and can be raised or lowered by a screw connected to a variable-speed d.c. motor. The seed holder is isolated electrically and thermally from the pulling copper rod by a boron nitride holder both to avoid an electric arc between the seed and the molten sample (both metallic conductors) and to limit the T gradient along the seed. In this way single crystals of the tetraborides YB₄, TbB₄ and ErB₄ (10⁻² m long and ca. 3 × 10⁻³ m diameter) are grown from a melted seed under the experimental conditions indicated in Table 1; crystals of LaB₆ and YbB₆₆ can also be obtained.

(J. R. ETOURNEAU)

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6.7.4.2.2. Floating-Zone Technique.

As with the crystal-pulling technique described above, floating-zone melting avoids the problem of the crucible. This technique was proposed for the refinement of congruently melting materials¹. In zone melting a short molten zone travels through a relatively long charge (ingot or rod) of solid, carrying with it a portion of the soluble impurities in the charge.

Zone melting is often accompanied by sufficient crystal growth to allow single crystals to be cut from the rod. Horizontal refining using a water-cooled boat on which lies the solid rod of material produces polycrystalline melted ingots containing large single-crystal grains. The nucleation of crystals takes place at the surface of the cold boat, and these crystals extend into the bead for at least a few millimeters.

In floating zone melting the liquid zone is held by surface tension between two vertically aligned solid rods of material as shown in Fig. 1. Generally, induction heating using an eddy current concentrator is suitable for producing a molten zone at T as high as 3000°C².

6.7.4. Crystal Growth of Borides

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6.7.4.2. Liquid-Phase Methods

6.7.4.2.2. Floating-Zone Technique.

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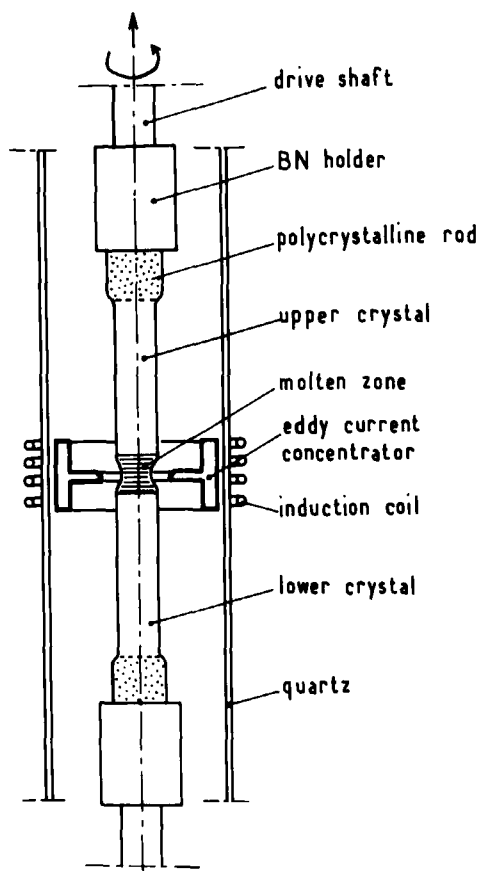


Figure 1. Schematic diagram of a zone-melting furnace.

Single crystals of transition-metal diborides (e.g., ZrB_2 , HfB_2)²⁻⁵ and rare-earth hexaborides (e.g., LaB_6)⁶⁻⁸ are obtained by the floating-zone process under purified Ar. Usually, after one or more passages of the molten zone from bottom to top the solid rod of boride consists of several single crystals per cross section. Single-crystal grains $4\text{--}10 \times 10^{-3}$ m long and $1\text{--}2 \times 10^{-3}$ m across are obtained⁶ for LaB_6 . However, filamentary LaB_6 single crystals (10^{-3} m in diameter and 5×10^{-2} m long, with a [100] growth axis) are prepared by a laser-heated floating-zone method⁸.

The floating-zone technique appears valid only for single crystals of congruent melting materials; however, single-phase samples of peritectic compound may be prepared by zone leveling⁹. This method differs from ordinary zone melting in that the latter has a molten zone at the composition of the compound required and at a T just above its mp, while the former uses a zone having a composition and T corresponding to a point on an adjacent liquidus line. In zone leveling, movement of the zone causes the compound in question to precipitate from solution; in zone

melting, solidification is by normal freezing. In zone leveling, the zone maintains its composition as it moves since the material going into solution at one liquid–solid interface has the same composition as the compound coming out of solution at the other interface. This method is used to prepare single crystals of the peritectic compound YB_6 ; the stable molten zone moving at $5 \times 10^{-3} \text{ m h}^{-1}$ is established at a zone T slightly below 2600°C ¹⁰.

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4. J. S. Haggerty, J. F. Wenckus, D. W. Lee, in *High Temperature Technology*, Butterworths, London, 1969, p. 547.
5. J. S. Haggerty, D. W. Lee, *J. Am. Ceram. Soc.*, **54**, 572 (1971).
6. B. J. Curtis, H. Graffenberger, *Mater. Res. Bull.*, **1**, 27 (1966).
7. T. Tanaka, E. Bannai, S. Kawai, T. Yamane, *J. Cryst. Growth*, **30**, 194 (1975).
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6.7.4.2.3. Flame-Fusion Technique.

Flame fusion is employed for growing of TiB_2 crystals, which melt congruently at ca. 2900°C ¹⁻⁶.

The powdered raw material TiB_2 is deposited in a hot gas onto the molten surface of the crystal being grown. An arc is used instead of a combustion heat source. The growing crystal is shielded from air with Ar.

The growing crystal, or boule, is a cylinder supported by its vertical axis. The top of the crystal is kept molten by impinging a flame upon it. Fine adjustment of the head is not critical because the diameter of the boule can change to accommodate variations in heat input.

The crystal grows when a supply of powdered raw material is dropped through the flame onto the molten surface. The powder is added to the flame from a screen, which is tapped intermittently.

The best crystals obtained are ca. $13 \times 10^{-3} \text{ m}$ long and $7 \times 10^{-3} \text{ m}$ in diameter.

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3. A. D. Kiffer, USAF Rept. WADD-TR-60-52 (1960).
4. C. T. Lynch, S. A. Mersol, F. W. Vahldiek, *J. Less-Common Met.*, **10**, 206 (1966).
5. F. W. Vahldiek, *J. Less-Common Met.*, **10**, 202 (1967).
6. S. A. Mersol, C. T. Lynch, F. W. Vahldiek, in *Anisotropy in Single-Crystal Refractory Compounds*, Vol. 2, Plenum Press, New York, 1968, p. 41.

6.7.4.3. Flux Methods

The production of boride single crystals from their own melt presents difficulties because they have high mp and melt incongruently. The crystallization of borides

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6.7.4.3. Flux Methods

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TABLE 1. GROWTH CONDITIONS OF SOME BORIDE SINGLE CRYSTALS OBTAINED BY THE FLUX METHOD

Borides M_xB_y	Metal solvent, M(s)	Atomic ratio		Crucible	Max. and corresponding time		Cooling rate (°C h ⁻¹)	Ref.
		M(s), M	Boron, M(s)		°C	h		
M = IIA								
CaB ₆	Al			Al ₂ O ₃	1200–1450	4	150	1
SrB ₆	Al			Al ₂ O ₃				
SrB ₆	Sr		< 6	Ta	1800	4	—	2
M = IIIA								
ErB ₂	Er		0.25	Ta	1750	0.1–0.3	Quenching	3
TmB ₂	Tm		0.25	Ta	1750	0.1–0.3	Quenching	3
LaB ₄	La				1700	—	16	2
LaB ₄	La		0.65	Ta	1700	0.2	Quenching	4
CeB ₄	Ce		0.65	Ta	1700	0.2	Quenching	4
PrB ₄	Pr		3	Ta	1700	0.2	Quenching	4
PrB ₄	Pr		2	Mo	1500	2	1000	5
NdB ₄	Nd			Ta	1700	0.2	Quenching	4
SmB ₄	Al	20		Al ₂ O ₃	1550	0.2–2	3300–200 Down to 1000°C and quenching	4, 5 4
↓								
LuB ₄	Al							
LaB ₆	Al	200		Al ₂ O ₃	1200	5–10	6–75	6
LaB ₆	Al	300		Al ₂ O ₃	1500	8	30	7
↓								
SmB ₆	Al			Al ₂ O ₃				8

EuB ₆	Al	Al ₂ O ₃	1200–1450	4	150	9
YbB ₆	Al	Al ₂ O ₃	1450	2	150	9
YB ₆	95 at% Ga	Al ₂ O ₃				
GdB ₆	+					
ThB ₆	5 at% Al	Al ₂ O ₃	1550	24	—	10
M = IVA						
TiB ₂	Fe	ZrO ₂	1700	3–4	5	11–13
	Co	ZrO ₂	1650	3–4	5	13
	Ni	ZrO ₂	1600	3–4	5	13
	Al	Al ₂ O ₃	1500	10	Slow cooling	14, 15
ZrB ₂	Fe	ZrO ₂	1700	3–4	5	11–13
	Al	Al ₂ O ₃	1500	10	Slow cooling	14, 15
HfB ₂	Fe	ZrO ₂	1720	3–4	5	11–13
	Al	Al ₂ O ₃	1500	10	5	14, 15
M = VA						
VB	Al	Al ₂ O ₃	1500	10	Slow cooling	14, 15
V ₃ B ₄	Al	Al ₂ O ₃	1500	10	Slow cooling	14, 15
NbB ₂	Al	Al ₂ O ₃	1500	10	Slow cooling	14, 15
TaB	Al	Al ₂ O ₃	1500	10	Slow cooling	14, 15
M = VIA						
Mo ₂ B ₅	Al	Al ₂ O ₃	1500	10	Slow cooling	14–16
W ₂ B ₅	Al	Al ₂ O ₃	1500	10	Slow cooling	14–16

from flux or solutions in metallic melts is attractive because of its simplicity, its low-T operation and its quickness.

Single crystals of borides of group-IIA, -IIIA, -IVA, -VA and -VIA metals are grown by using various molten metals as solvents. Table 1 summarizes the experimental conditions. The procedure consists of heating a mixture of either the elements (metal, B and the solvent metal) or the boride and the solvent metal. Crystal growth is carried out in an Ar atmosphere, either in a sealed refractory metal crucible (Mo or Ta) or in an open refractory oxide crucible (Al_2O_3 or CaO-stabilized zirconia). The crystals obtained have sizes $1\text{--}10 \times 10^{-3}$ m at least in one direction, depending on the experimental growth conditions.

The flux or solution method is practically the only means of preparing perfect single crystals. Whereas the liquid-phase methods (crystal pulling or zone melting) are more suited to preparing large single crystals of congruently melting borides, the solution and gas-phase methods should be more practical for obtaining smaller crystals as well as films and whiskers of noncongruently melting borides. In the gas-phase method, the corresponding T are somewhat lower than in the solution method, but the time required is the longest of all the methods proposed for the crystal growth of borides.

(J. R. ETourneau)

1. J. M. Tarascon, J. Etourneau, private communication.
2. R. W. Johnson, A. H. Daane, *J. Phys. Chem.*, **65**, 909 (1961).
3. R. N. Castellano, *Mater. Res. Bull.*, **7**, 261 (1972).
4. Z. Fisk, A. S. Cooper, P. H. Schmidt, R. N. Castellano, *Mater. Res. Bull.*, **7**, 285 (1972).
5. J. Etourneau, J. P. Mercurio, A. Berrada, P. Hagenmuller, R. Georges, R. Bourezg, J. C. Gianduzzo, *J. Less-Common Met.*, **67**, 539 (1979).
6. T. Aita, U. Kawabe, Y. Honda, *Jpn. J. Appl. Phys.*, **13**, 251 (1974).
7. M. Futamoto, T. Aita, U. Kawabe, *Jpn. J. Appl. Phys.*, **14**, 1263 (1975).
8. G. D. Sturgeon, J. P. Mercurio, J. Etourneau, P. Hagenmuller, *Mater. Res. Bull.*, **9**, 117 (1974).
9. J. M. Tarascon, J. Etourneau, P. Dordor, P. Hagenmuller, M. Kasaya, J. M. D. Coey, *J. Appl. Phys.*, **51**, 574 (1980).
10. Z. Fisk, P. H. Schmidt, L. D. Longinotti, *Mater. Res. Bull.*, **11**, 1019 (1976).
11. B. A. Gruber, U.S. Pat. 3,096,149 (1963); *Chem. Abstr.*, **59**, 8462 (1963).
12. K. Nakano, H. Hayashi, T. Imura, *Jpn. J. Appl. Phys.*, **10**, 513 (1971).
13. K. Nakano, H. Hayashi, *J. Cryst. Growth*, **24**, 679 (1974).
14. I. Higashi, T. Atoda, *J. Cryst. Growth*, **7**, 251 (1970).
15. I. Higashi, Y. Takahashi, T. Atoda, *J. Cryst. Growth*, **33**, 207 (1976).
16. V. N. Gurin, V. N. Sinelnikova, *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 377.

6.7.5. Sintering Methods

Powder metallurgy uses two ways to manufacture products from boride powders: conventional sintering, involving the molding or compacting of products from the powder with subsequent sintering, or hot pressing, which combines the pressing and sintering processes. For both procedures the raw boride material must be milled sufficiently fine.

(H. PASTOR)

from flux or solutions in metallic melts is attractive because of its simplicity, its low-T operation and its quickness.

Single crystals of borides of group-IIA, -IIIA, -IVA, -VA and -VIA metals are grown by using various molten metals as solvents. Table 1 summarizes the experimental conditions. The procedure consists of heating a mixture of either the elements (metal, B and the solvent metal) or the boride and the solvent metal. Crystal growth is carried out in an Ar atmosphere, either in a sealed refractory metal crucible (Mo or Ta) or in an open refractory oxide crucible (Al_2O_3 or CaO-stabilized zirconia). The crystals obtained have sizes $1\text{--}10 \times 10^{-3}$ m at least in one direction, depending on the experimental growth conditions.

The flux or solution method is practically the only means of preparing perfect single crystals. Whereas the liquid-phase methods (crystal pulling or zone melting) are more suited to preparing large single crystals of congruently melting borides, the solution and gas-phase methods should be more practical for obtaining smaller crystals as well as films and whiskers of noncongruently melting borides. In the gas-phase method, the corresponding T are somewhat lower than in the solution method, but the time required is the longest of all the methods proposed for the crystal growth of borides.

(J. R. ETourneau)

1. J. M. Tarascon, J. Etourneau, private communication.
2. R. W. Johnson, A. H. Daane, *J. Phys. Chem.*, **65**, 909 (1961).
3. R. N. Castellano, *Mater. Res. Bull.*, **7**, 261 (1972).
4. Z. Fisk, A. S. Cooper, P. H. Schmidt, R. N. Castellano, *Mater. Res. Bull.*, **7**, 285 (1972).
5. J. Etourneau, J. P. Mercurio, A. Berrada, P. Hagenmuller, R. Georges, R. Bourezg, J. C. Gianduzzo, *J. Less-Common Met.*, **67**, 539 (1979).
6. T. Aita, U. Kawabe, Y. Honda, *Jpn. J. Appl. Phys.*, **13**, 251 (1974).
7. M. Futamoto, T. Aita, U. Kawabe, *Jpn. J. Appl. Phys.*, **14**, 1263 (1975).
8. G. D. Sturgeon, J. P. Mercurio, J. Etourneau, P. Hagenmuller, *Mater. Res. Bull.*, **9**, 117 (1974).
9. J. M. Tarascon, J. Etourneau, P. Dordor, P. Hagenmuller, M. Kasaya, J. M. D. Coey, *J. Appl. Phys.*, **51**, 574 (1980).
10. Z. Fisk, P. H. Schmidt, L. D. Longinotti, *Mater. Res. Bull.*, **11**, 1019 (1976).
11. B. A. Gruber, U.S. Pat. 3,096,149 (1963); *Chem. Abstr.*, **59**, 8462 (1963).
12. K. Nakano, H. Hayashi, T. Imura, *Jpn. J. Appl. Phys.*, **10**, 513 (1971).
13. K. Nakano, H. Hayashi, *J. Cryst. Growth*, **24**, 679 (1974).
14. I. Higashi, T. Atoda, *J. Cryst. Growth*, **7**, 251 (1970).
15. I. Higashi, Y. Takahashi, T. Atoda, *J. Cryst. Growth*, **33**, 207 (1976).
16. V. N. Gurin, V. N. Sinelnikova, *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer-Verlag, Berlin, 1977, p. 377.

6.7.5. Sintering Methods

Powder metallurgy uses two ways to manufacture products from boride powders: conventional sintering, involving the molding or compacting of products from the powder with subsequent sintering, or hot pressing, which combines the pressing and sintering processes. For both procedures the raw boride material must be milled sufficiently fine.

(H. PASTOR)

6.7.5.1. Sintering of Pure Borides

6.7.5.1.1. Comminution of Powders.

In order to obtain dense products, fine powders must be used, i.e., with a mean particle size of 0.1–10 μm , or preferably 0.1–5 μm , achieved by milling the raw boride powder.

Ball, planetary-centrifugal, vibratory or ultrasonic mills are used for milling TiB_2 and ZrB_2 powders. The milling elements are balls of cemented carbide (WC-Co) or ball-bearing steel.

During ball milling¹ the mean particle diameter, d , gas adsorption isotherm specific surface area (BET) and contamination (wt% contaminant) conform to the general law:

$$\log(\text{property}) = A \cdot \log(\text{time}) + B \quad (\text{a})$$

where A and B are constants.

Iron can be removed² by chemical washing with 10 N aq HCl. Cemented carbide balls must be avoided owing to the high contamination level and because the tungsten carbide cannot be removed without attacking the boride.

The operational parameters for the comminution for TiB_2 and ZrB_2 powders in a planetary centrifugal mill³ have been optimized^{4,5}, allowing a 1- μm mean particle size to be obtained within a few minutes (starting from a powder passing through a 56- μm mesh), with an iron contamination of 3–4 wt%. Comminutability of materials increases with increasing stretch modulus, shear modulus, microhardness and brittleness, and the same holds true for vibratory milling. The comminution of ZrB_2 powder in a vibratory mill^{6,7} increases contamination rapidly with increasing milling time and is always higher than in a ball mill.

Ultrasonic milling^{8,9} is promising because its intensity reaches a maximum during the first 2–5 min, so there is not enough time for contamination to occur.

(H. PASTOR)

1. H. Pastor, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer Verlag, Berlin, 1977, p. 457.
2. R. Meyer, H. Pastor, *Bull. Soc. Fr. Ceram.*, 59 (1965).
3. A. G. Dobrovol'skii, Yu. I. Nikitin, M. S. Sokhin, O. V. Tutakov, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 429 (1967); *Chem. Abstr.*, 67, 75,781 (1967).
4. V. E. Matsera, V. S. Pugin, A. G. Dobrovol'skii, V. F. Gornostaev, L. V. Strashinskaya, N. A. Derenovskaya, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 447 (1973); *Chem. Abstr.*, 80, 6461 (1974).
5. V. E. Matsera, V. S. Pugin, L. V. Strashinskaya, A. G. Dobrovol'skii, Yu. I. Nikitin, B. V. Pogorelyi, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 525 (1973); *Chem. Abstr.*, 80, 18,255 (1974).
6. L. V. D'Yakonova, P. S. Kyslyi, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 1 (1972).
7. E. A. Smith, *Metall. Mater.*, 4, 426 (1970).
8. V. E. Matsera, V. S. Pugin, A. G. Dobrovol'skii, Yu. I. Nikitin, S. V. Pogorelyi, L. V. Strashinskaya, V. F. Gornostaev, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 941 (1971); *Chem. Abstr.*, 76, 103,228 (1972).
9. F. A. Fekhetdinov, V. I. Drozhalova, V. B. Ivanova, N. G. Kovaleva, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 316 (1977); *Chem. Abstr.*, 87, 72,336 (1977).

6.7.5. Sintering Methods

6.7.5.1. Sintering of Pure Borides

6.7.5.1.2. Compacting or Molding of Powders.

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Pressing is carried out within a cemented carbide die between two steel or cemented carbide punches. In order to impart enough mechanical strength to the blank to permit further manipulation without risk, removable organic binders (camphor, natural or synthetic waxes, latex or synthetic rubber, methyl polymethacrylate, polyvinyl alcohol, carboxymethylcellulose, ammonium alginate) are mixed into the powder, dissolved in a convenient volatile solvent. Some of these also act as lubricants thus minimizing the wear on the die.

The compressibility of group-IVA and -VIA transition-metal boride powders is measured by the dimensions and weights of the blanks, by measuring the stroke of the punches with a cathetometer, or alternatively by electrical conductivity (based upon the metallic conductivity of most borides). The process of densification by pressing is defined by^{1,2}:

$$\log P = A \cdot \log \beta + B \quad (a)$$

where P = compacting pressure $0.5 \times 10^6 - 7 \times 10^6 \text{ N m}^{-2}$; β = relative volume, or bulk to blank density ratio and A, B = constants.

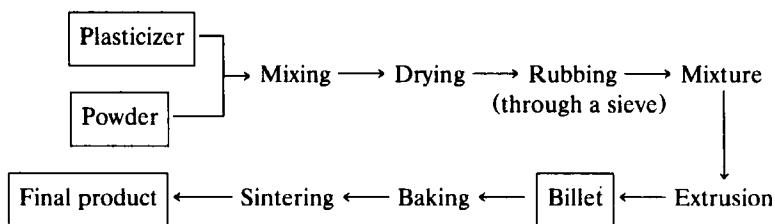
The springback of these materials is significant, and its relationship to pressure is associated with the material brittleness. Stratification occurs in the pressure range $3 \times 10^6 \text{ N m}^{-2}$.

When electrical conductivity is used^{3,4} to investigate the compressibility of boride powders at a pressure of $0.19 - 1.7 \times 10^6 \text{ N m}^{-2}$, the variation of the specific electrical conductivity χ with the relative density θ (apparent density of the blank/density of the bulk material) is:

$$\chi = K \cdot \exp\left(-\frac{A}{\theta}\right) \quad (b)$$

where K and A are constants, A being related to brittleness. Little has been published⁵ on isostatic pressing.

The principles of the extrusion-die pressing production of pipes and rods from powders are well known⁶. The flow diagram of the production of parts is as follows:



Starch, bakelite, polyvinyl alcohol, rubber, paraffin, etc., may be used as plasticizers.

Hot casting under pressure is used for the manufacture of complex shaped parts in the ceramics industry, e.g., in the shaping of parts of LaB_6 , using 10.5 wt% of a binder (85 wt% paraffin-15 wt% beeswax) and casting at a pressure of $5 - 8 \times 10^5 \text{ N m}^{-2}$.

Slip casting is common in the ceramics industry. The material to be cast is milled to a mean particle size of a few microns. A slip is made by mixing the finely divided material with a liquid suspending medium. The slip is then poured into a suitable mold (e.g., of plaster of paris). The liquid in the slip is drawn into the mold by capillary forces and the solids are deposited in a coherent form. For TiB_2 , ZrB_2 and CrB_2 a suspending medium of 5–7 wt% cyclopentadiene in xylene is recommended⁸. A 3 wt% aqueous solution of carboxymethylcellulose is the best dispersing medium for ZrB_2 ^{9,10}.

(H. PASTOR)

1. B. N. Babich, K. I. Portnoi, G. V. Samsonov, *Metalloved. Term. Obrab. Met.*, 1, 31 (1960); Engl. Transl., AD 273 601 O.T.S., Washington, DC, (1962); *Chem. Abstr.*, 54, 10,727c (1960).
2. G. V. Samsonov, L. Y. Markovskii, A. F. Zhigach, M. G. Valyashko, *Bor, ego soedineniya i splavy*, Izdat. Akad. Nauk Ukr. SSR, Kiev, 1960; Engl. Transl.: *Boron, Its Compounds and Alloys*, AEC-tr-5032 (1962), OTS, Washington, DC.
3. G. V. Samsonov, V. S. Neshpor, *Dokl. Akad. Nauk, SSSR*, 104, 405 (1955).
4. L. I. Struk, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 184 (1966).
5. H. Bumm, H. Liepelt, *Z. Werkstofftech.*, 3, 364 (1972).
6. P. S. Kislyi, G. V. Samsonov, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 164 (1962).
7. O. G. Medvedev, G. V. Trunov, L. V. Chernyak, V. Y. Shlyuko, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 250 (1971).
8. R. L. Reddy, L. C. Montgomery, C. A. Grulke, Br. Pat. 1,052,590, (Dec. 30, 1966); *Chem. Abstr.*, 66, 48,757s (1967).
9. A. G. Dobrovol'skii, G. G. Dobrovol'skii, T. A. Lyudvinskaya, E. Y. Popichenko, *Inorg. Mater. (Engl. Transl.)*, 2, 735 (1966).
10. A. I. Avgustinik, G. V. Drozdetskaya, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 10, 556 (1967); *Chem. Abstr.*, 67, 102,466 (1967).

6.7.5.1.3. Sintering: Miscellaneous.

Sintering, activated sintering and reaction sintering are used to produce maximum density in sintered bodies and to make special parts with controlled porosity.

The uncured compacts are presintered in vacuum or in a stream of neutral gas (Ar , H_2) at 800–1400°C. Presintering ensures the removal of the organic binder to avoid later contamination of the sintering furnace by pyrolysis of the by-products. It also facilitates machining and finishing, which are difficult and expensive after final sintering because of the hardness of borides.

Sintering is carried out in vacuum in a resistance furnace equipped with a graphite, Ta or W resistor, or in a high-frequency furnace with a graphite resistor. Sintering is also done in a stream of neutral gas (Ar , H_2). Graphite plates are used as supports, but on contact with graphite some borides form eutectics which melt at 2200–2500°C. In order to limit interaction between the graphite plate and the parts being sintered, the plate is sprinkled with boride powder. The best but not the cheapest way is to use supports of the same material as that being sintered, although some adhesion is to be expected.

Owing to the high sintering temperatures employed, losses of material (by volatilization of boron or boride) and grain growth are observed. In order to limit these losses, the part to be sintered can be embedded in a powder of the same boride. Sintering of pure refractory borides requires $> 0.7T_f$ (T_f = absolute melting temper-

6.7.5. Sintering Methods

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6.7.5.1. Sintering of Pure Borides

6.7.5.1.3. Sintering: Miscellaneous.

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2. G. V. Samsonov, L. Y. Markovskii, A. F. Zhigach, M. G. Valyashko, *Bor, ego soedineniya i splavy*, Izdat. Akad. Nauk Ukr. SSR, Kiev, 1960; Engl. Transl.: *Boron, Its Compounds and Alloys*, AEC-tr-5032 (1962), OTS, Washington, DC.
3. G. V. Samsonov, V. S. Neshpor, *Dokl. Akad. Nauk, SSSR*, 104, 405 (1955).
4. L. I. Struk, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 184 (1966).
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8. R. L. Reddy, L. C. Montgomery, C. A. Grulke, Br. Pat. 1,052,590, (Dec. 30, 1966); *Chem. Abstr.*, 66, 48,757s (1967).
9. A. G. Dobrovolskii, G. G. Dobrovolskii, T. A. Lyudvinskaya, E. Y. Popichenko, *Inorg. Mater. (Engl. Transl.)*, 2, 735 (1966).
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ature) and rarely leads to fully dense parts. These facts invite further study into activated sintering.

Activation methods can be divided into two groups. Activation by addition of selected metals (a few wt%), mainly transition metals, e.g., fine powders of Fe, Ni, Co, Cr, Pt, Pd, etc.¹⁻³, or chlorides of these metals when these are reducible to the metal by hydrogen during presintering. The mechanism of activation is not understood (surface tension, surface diffusion, etc.) but is related to the electronic structure of the metal additive. Activation by carbon is also effective⁴. Alternatively, activation utilizes powders in a specially activated state, e.g., very fine (submicronic) powders⁵.

Reaction sintering is related to activated sintering. It consists of preparing and sintering the boride in a single step by compacting reactants able to generate the pure boride (and gaseous or volatile by-products) at the sintering temperature⁶. In the case of direct synthesis (metal + boron) fully dense pure boride parts are formed but for reactants (e.g., metal oxide + boron carbide) generating gases, the gas prevents densification and leads to porous parts.

Sometimes fully dense bodies are not required; e.g., filters are prepared by sintering. Porous sintered bodies can be prepared by using coarse grain or granulated powders by forming without pressure (e.g., loosely molded powders⁷⁻⁹), or by adding a pore generating agent (a removable organic material in powder form); or by using fibers^{10,11}.

Shrinkage during sintering at high T can be determined experimentally by dilatometry, electrical conductivity, acoustic waves or thermal analysis¹².

(H. PASTOR)

1. R. L. Coble, H. A. Hobbs, in *Investigation of Boride Compounds for Very High Temperature Applications*, L. Kaufman, E. V. Clougherty, eds., Report AD 428 006, N.T.I.S., Springfield, Va, 1973, p. 82.
2. B. Cech, P. Olivierus, J. Sejbál, *Powder Metall. Met. Ceram. (Engl. Transl.)*, 8, 142 (1965).
3. N. I. Rasskazov, in *Third International Powder Metallurgy Conference*, Vol. 2, Karlovy-Vary, Czechoslovakia, 1970, p. 228.
4. G. A. Meerson, A. F. Gorbunov, *Inorg. Mater. (Engl. Transl.)*, 4, 267 (1968).
5. V. M. Gropyanov, *Refractories (USSR)*, 34, 769 (1969).
6. Pechiney, Fr. Pat. 1,216,522 (April 26, 1960); *Chem. Abstr.*, 55, 18,051e (1961).
7. V. M. Sleptsov, E. M. Prshedromirskaya, Y. P. Kukota, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 849 (1965).
8. E. M. Prshedromirskaya, V. M. Sleptsov, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 269 (1966).
9. V. M. Sleptsov, E. M. Prshedromirskaya, V. K. Vitryanyuk, *Rev. Int. Hautes Temp Refract.*, 6, 131 (1969).
10. G. V. Samsonov, V. E. Matsera, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 719 (1972).
11. G. V. Samsonov, V. E. Matsera, *Powder Met. Int.*, 5, 133 (1973).
12. P. S. Kislyi, M. A. Kuzenkova, "Spekanie tupoplavkikh soedinenii" (*Sintering of Refractory Compounds*), Naukova Dumka, Kiev, 1980.

6.7.5.1.4. Sintering: Characteristics.

Tables 1 to 5 summarize the sintering characteristics of borides of groups IIIA to VIA transition metals.

6.7.5. Sintering Methods

6.7.5.1. Sintering of Pure Borides

6.7.5.1.4. Sintering: Characteristics.

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Shrinkage during sintering at high T can be determined experimentally by dilatometry, electrical conductivity, acoustic waves or thermal analysis¹².

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2. B. Cech, P. Olivierus, J. Sejbál, *Powder Metall. Met. Ceram. (Engl. Transl.)*, **8**, 142 (1965).
3. N. I. Rasskazov, in *Third International Powder Metallurgy Conference*, Vol. 2, Karlovy-Vary, Czechoslovakia, 1970, p. 228.
4. G. A. Meerson, A. F. Gorbunov, *Inorg. Mater. (Engl. Transl.)*, **4**, 267 (1968).
5. V. M. Gropyanov, *Refractories (USSR)*, **34**, 769 (1969).
6. Pechiney, Fr. Pat. 1,216,522 (April 26, 1960); *Chem. Abstr.*, **55**, 18,051e (1961).
7. V. M. Sleptsov, E. M. Prshedromirskaya, Y. P. Kukota, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, **849** (1965).
8. E. M. Prshedromirskaya, V. M. Sleptsov, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, **269** (1966).
9. V. M. Sleptsov, E. M. Prshedromirskaya, V. K. Vitryanyuk, *Rev. Int. Hautes Temp Refract.*, **6**, 131 (1969).
10. G. V. Samsonov, V. E. Matsera, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, **719** (1972).
11. G. V. Samsonov, V. E. Matsera, *Powder Met. Int.*, **5**, 133 (1973).
12. P. S. Kislyi, M. A. Kuzenkova, "Spekanie tupoplavkikh soedinenii" (*Sintering of Refractory Compounds*), Naukova Dumka, Kiev, 1980.

6.7.5.1.4. Sintering: Characteristics.

Tables 1 to 5 summarize the sintering characteristics of borides of groups IIIA to VIA transition metals.

TABLE 1. SINTERING CHARACTERISTICS OF BORIDES OF RARE-EARTH METALS

Boride	Binder nature and content (wt%)	Compacting pressure $\times 10^{-5}$ (N m ⁻²)	Sintering T (°C)	Holding time (min)	Sintering atmosphere or vacuum V (pressure in torr) ^b	Relative density (%)	Remarks	Ref.
YB ₆	Aq soln 10% PVA ^a	4-5	2327	30	V: $1-3 \times 10^{-5}$	71	Weight loss: 10%	See 1
EuB ₆	none	3.35	2227-2727	960	V: ?	63	Weight loss: 40%	
LaB ₆	—	—	1375	15	—	—	—	
LaB ₆	Aq soln 10% PVA	4-5	2407	30	V: $1-3 \times 10^{-5}$	82	Weight loss: 15%	
LaB ₆	Aq soln 2% PVA	6-7	2300-2350	60	V: $5 \times 10 \times 10^{-3}$	99.2	LaB ₆ powder packing	
LaB ₆	Glycerine + alcohol	8	2000	120	V: 10^{-5}	81	Weight loss: 9%	
LaB ₆	Glycerine + alcohol	8	2000	120	Ar: 798-836	89.5	Weight loss: 5%	
LaB ₆	Glycerine + alcohol	8	2000	120	H ₂ : 798-836	100	Weight loss: 6%	
LaB ₆	85% paraffin + 25% beeswax	Hot casting P = 5-8	2300-2350	60	V: $5-10 \times 10^{-3}$	95-97	LaB ₆ powder packing	
LaB ₆	Aq soln 3% PVA	1.5-2.5	2350-2400	60-90	V: ?	100	Weight loss and grain growth	
LaB ₆	—	—	1900-2400	30	V: $5-10 \times 10^{-5}$	60-82	Initial powder	2
LaB ₆	—	—	1900-2400	30	V: $5-10 \times 10^{-5}$	70-94	Ultrasonic milling	2
LaB ₆	—	—	1900-2400	30	V: $5-10 \times 10^{-5}$	84-94	Detonation milling	2
LaB ₆	—	1	2000	60	—	84-88	Ultrasonic milling	3
LaB ₆	Aq soln 2.5% PVA	4	2000	60	V: ?	80	+ 2 wt% Y ₂ O ₃	4
LaB ₆	Aq soln 2.5% PVA	4	2200	60	V: ?	93	+ 2 wt% Y ₂ O ₃	4

^a PVA = polyvinyl alcohol.

^b To convert torr into Pascal, multiply by 133.3.

TABLE 2. SINTERING CHARACTERISTICS OF DIBORIDES OF GROUP-IV METALS (TiB_2 , ZrB_2 , HfB_2)

Boride	Mean particle size (μm)	Binder nature and content (wt%)	Compacting pressure (N m^{-2})	Sintering T ($^{\circ}\text{C}$)	Holding time (min)	Sintering atmosphere or vacuum V: (pressure in torr) ^d	Relative density (%) (theoretical)	Remarks	Ref.
TiB_2	2-3	FeCl_3 + alcohol: 1% Fe	3	1800	60	V: 10^{-1}	74.5	Increasing holding time above 60 min has practically no effect on densification	
TiB_2	2-3	FeCl_3 + alcohol: 1% Fe	3	2000	60	V: 10^{-1}	78.4		
TiB_2	2-3	FeCl_3 + alcohol: 1% Fe	3	2200	60	V: 10^{-1}	81.6		
TiB_2	2-3	FeCl_3 + alcohol: 1% Fe	3	2300	60	V: 10^{-1}	85.7		
TiB_2	2-3	FeCl_3 + alcohol: 1% Fe	3	2400	60	V: 10^{-1}	90.9		
TiB_2	250	Polyester: 7%	1	1900	360	H_2 : 760	57.5	Reaction sintering	
TiB_2	—	None	1	1900	360	V: 10^{-1}	—		
TiB_2	5-20	Starch + water (300 g L ⁻¹); 15-20% Aq soln 10% PVA ^a	None	2225	15	H_2 : 760	93-97		
TiB_2	—		10.1	2200	45	V: 10^{-4}	81	Extrusion-die pressing	See 1
TiB_2	5	Paraffin wax: 2%	0.28	2300	120	H_2 or He: 760	80	Weight loss: a few %	
TiB_2	—	Epoxy resin + acetone: 3%	1.5	1850	180	Ar: 760	85.7		
TiB_2	—	Epoxy resin + acetone: 3%	1.5	2000	180	Ar: 760	84.6		
TiB_2	—	Epoxy resin + acetone: 3%	1.5	2130	180	Ar: 760	85.6		
TiB_2	4.2	Camphor (2%) + ether	5	2000	60	V: 5×10^{-2}	69.0	Fe content: 0.35%	
TiB_2	4.2	Camphor (2%) + ether	5	2000	60	V: 5×10^{-2}	92.4	Fe content: 0.58%	
TiB_2	-177, +149	Aq soln 5% PVA	1	2100	60	H_2 : 760	71		
TiB_2	-177, +149	Aq soln 5% PVA	1	2250	60	H_2 : 760	75		
TiB_2	2.5	Xylene/CPD ^b (85/15): 16%	None	2000	120	Ar: 760	92-94	Slip casting	

TiB ₂	—	Aq soln 1% PVA	0.5	2175	30	—	77.5	- 74 + 44 Pore size - 420 + 177 Isostatic pressing Loss of B above 2200°C Ball milling: 48 h 0.6% Fe + 0.08% Cr 1.4% Fe + 1.6% Cr	See 1
TiB ₂	—	Aq soln 1% PVA	0.5	2175	30	—	73.0		
TiB ₂	—	None	12	1900	720	Ar: 760	90		
TiB ₂	—	None	12	2200	10	Ar: 760	90		
TiB ₂	—	—	1	1750	15	—	100	0.6% Fe + 0.08% Cr 1.4% Fe + 1.6% Cr	5 6 7 7
TiB ₂	1	6% petroleum wax	1.3	2100	60	V: ?	99		
TiB ₂	—	—	1	1750	30	V: 10 ⁻⁴	66		
TiB ₂	—	—	1	1750	30	V: 10 ⁻⁴	100		
ZrB ₂	—	Starch + water (300 g/l); 15–20%	None	2300	15	H ₂ : 760	94–97	Extrusion-die pressing Extrusion-die pressing; 2% C inhibits sintering Weight loss: 3.1% + 3% Ni or Co	See 1
ZrB ₂	—	Aq soln 5% PVA	None	2075	60–80	H ₂ : 760	88–94		
ZrB ₂	—	Aq soln 10% PVA	10.1	2200	45	V: 10 ⁻⁴	86		
ZrB ₂	—75, + 44	Rubber (5%) or PVA (3%)	0.6	2000	30	—	63		
ZrB ₂	5	Paraffin wax: 2%	0.28	2200	60–120	H ₂ or He: 760	80	Powder containing ZrB ₁₂ Powder without ZrB ₁₂ Slip casting Slip casting 0.5–0.7% Fe content without additives	See 1
ZrB ₂	20	Rubber + benzene	1.5(?)	2000	60	V: 10 ⁻²	78.2		
ZrB ₂	3	—	—	2225	40	H ₂ : 760	85.8		
ZrB ₂	5.2	Aq soln 5% PVA	1	2100	240	Ar: 760	90		
ZrB ₂	5.2	Aq soln 5% PVA	1	2100	240	Ar: 760	69	Slip casting Slip casting 0.5–0.7% Fe content without additives	See 1
ZrB ₂	—177, + 149	Aq soln 5% PVA	1	2000	60	H ₂ : 760	61		
ZrB ₂	—177, + 149	Aq soln 5% PVA	1	2150	60	H ₂ : 760	66		
ZrB ₂	3	Xylene/CPD (93/7)	None	2000	120	Ar: 760	89		
ZrB ₂	40	Aq soln (3%) CMC ^c : 22%	None	2200	40	H ₂ : 760	88	0.5–0.7% Fe content without additives	(continued)
ZrB ₂	7	Rubber + benzene (Fe content 0.08%)	0.5–1	1900	120	V: 5 × 10 ⁻⁴	80.7		
ZrB ₂	7	Rubber + benzene (Fe content 0.08%)	0.5–1	2100	120	V: 5 × 10 ⁻⁴	83.0		

TABLE 2. (continued)

Boride	Mean particle size (μm)	Binder nature and content (wt%)	Compacting pressure (N m^{-2}) $\times 10^{-5}$	Sintering T ($^{\circ}\text{C}$)	Holding time (min)	Sintering atmosphere or vacuum V: (pressure in torr) ^d	Relative density (%) (theoretical)	Remarks	Ref.
ZrB ₂	7	Rubber + benzene (Fe content 0.08%)	0.5-1	1800	120	V: 5×10^{-4}	85.3	Without ZrO ₂ + B additions See 1 S: $1.4 \text{ m}^2 \text{ g}^{-1}$ Specific S: $1.9 \text{ m}^2 \text{ g}^{-1}$ surface S: $2.3 \text{ m}^2 \text{ g}^{-1}$ of the S: $4.0 \text{ m}^2 \text{ g}^{-1}$ powder	
ZrB ₂	7	Rubber + benzene (Fe content 0.08%)	0.5-1	1900	120	V: 5×10^{-4}	98.8		
ZrB ₂	7	Rubber + benzene (Fe content 0.08%)	0.5-1	2100	120	V: 5×10^{-4}	99.5		
ZrB ₂	See remarks	—	—	2200	60	V: 10^{-4} - 10^{-5}	59.8		
ZrB ₂	See remarks	—	—	2200	60	V: 10^{-4} - 10^{-5}	64.8		
ZrB ₂	See remarks	—	—	2200	60	V: 10^{-4} - 10^{-5}	68.2		
ZrB ₂	See remarks	—	—	2200	60	V: 10^{-4} - 10^{-5}	72.7		
ZrB ₂	1	Starch: 2%	1	2200	90	Ar: 760	82-85		8
ZrB ₂	—	—	1	1800	45	V: ?	100	Ball milling: 72h (1.8% Cr + 3.1% Fe)	
HfB ₂	5	Paraffin wax: 2%	0.28	2200	60-120	H ₂ or He: 760	80	—	1

^a PV/A = polyvinyl alcohol.
^b CPD = cyclopentadiene.
^c CMC = carboxymethylcellulose.
^d To convert torr into Pascal, multiply by 133.3.

TABLE 3. ACTIVATED SINTERING OF TiB_2 AND ZrB_2

Boride	Nature and content (wt%) of activating addition	Nature and content (wt%) of binder	Compacting pressure $\times 10^{-5}$ ($N\ m^{-2}$)	Sintering T ($^{\circ}C$)	Holding time (min)	Atmosphere	Relative density (%)	Ref.
TiB_2	None	Aqueous 10% solution of polyvinyl alcohol	1.7-10.1	2200	45	Vacuum 10^{-4} torr ^a	81.0	See 1
	1 Co				8		87.5	
	5 Co				8		84.9	
	1 Ni				30		89.0	
	10 Ni				30		83.5	
	1 Cr				15		78.5	
	10 Cr				15		95.5	
	5 Si				10		82.0	
	None	Solution of synthetic rubber in benzene	1.5	2000	60	V	78.2	
	1 Fe			2200	60	V	89.2	
ZrB_2	1 Co			2000	60	Ar	99.2	See 1
	1 Ni			2000	60	Ar	98.2	
	0.5 Ni + 0.5 Fe			2000	60	Ar	96.6	
	0.5 Ni + 0.5 Co			2000	60	Ar	98.4	
	1 Ti			2200	60	V	67.7	
	1 Zr			2200	60	Ar	98.0	
	1 Nb			2200	60	Ar	99.0	
	1 Cr			2000	60	Ar	99.7	
	1 Re			2000	60	Ar	97.4	
	1 Re			2200	60	Ar	100	
	0.5 Ti + 0.5 Cr			2200	60	Ar	100	
	0.5 Re + 0.5 Cr			2200	60	V	88.7	

(continued)

TABLE 3. (continued)

Boride	Nature and content (wt%) of activating addition	Nature and content (wt%) of binder	Compacting pressure $\times 10^{-5}$ (N m ⁻²)	Sintering T (°C)	Holding time (min)	Atmosphere	Relative density (%)	Ref.
ZrB ₂	1 Mo	Alcoholic 2% solution of polyvinyl-butyl	1.5	1800	60	—	73.5	See 1
	2 Mo			1800	60		73.0	
	3 Mo			1800	60		71.5	
	4 Mo			1800	60		70.0	
	5 Mo			1800	60		69.5	
	10 Mo			1800	60		75.5	
ZrB ₂	1 W	None	Hot casting	1900	60		71.5	9
	2 W			1900	60		67.8	
	3 W			1900	60		66.5	
	4 W			1900	60		65.5	
	5 W			1900	60		64.3	
	4.3 Mo			2000	60		94-97	
	8.6 Mo			2000	60		97	
	0.9 Mo + 4.4 Cr			1950	60		95	
				1950	60		96	
					60			

^a To convert torr into Pascal, multiply by 133.3.

TABLE 4. SINTERING CHARACTERISTICS OF DIBORIDES OF GROUP-VB METALS (VB₂, NbB₂, TaB₂)

Boride	Binder nature and content (wt%)	Mean particle size (μm)	Compacting pressure $\times 10^{-5}$ (N m ⁻²)	Sintering T (°C)	Holding time (min)	Sintering atmosphere or Vacuum V (pressure in torr) ^a	Relative density (%)	Remarks	Ref.
VB ₂	Paraffin: 2	5	0.28	2000	120	H ₂ or He: 760	80	—	} See 1
NbB ₂	Aq soln 10% PVA ^b	—	10.1	2420	2	V: 10 ⁻⁴	76	—	
NbB ₂	Aq soln 10% PVA ^b	—	10.1	2650	14	V: 10 ⁻⁴	73.4	Weight loss: 3%	
NbB ₂	Paraffin: 2	5	0.28	2300	120	H ₂ or He: 760	80	—	
TaB ₂	Paraffin: 2	5	0.28	2300	120	H ₂ or He: 760	80	—	
TaB ₂	None	4	2.11	2100	30	V: 10 ⁻⁵	94	—	

^a To convert torr to Pa, multiply by 133.3.

^b PVA = polyvinyl alcohol.

TABLE 5. SINTERING CHARACTERISTICS OF BORIDES OF GROUP-VIB METALS

Boride	Binder nature and content (wt%)	Mean particle size (μm)	Compacting pressure $\times 10^{-5}$ (N m ⁻²)	Sintering T (°C)	Holding time (min)	Sintering atmosphere or vacuum V (pressure in torr) ^a	Relative density (%)	Remarks	Ref.
CrB ₂	—	53	5	1600–1700	30	—	—	—	} See 1
CrB ₂	Alcohol soln of FeCl ₃ (1% Fe)	2–3	3	2000	60	V: 10 ⁻¹	76	CrB ₂ melts at 2100°C	
CrB ₂	Paraffin: 2	5	0.28	1900	10	H ₂ or He: 760	80	—	
CrB ₂	Xylene + 7% CPD ^b : 46.2 vol%	2.2	None	1700	60–180	Ar: 760	—	Slip casting	
MoB ₂	Paraffin: 2	5	0.28	1900	60	H ₂ or He: 760	80	—	
W ₂ B ₅	Benzine soln of 5% rubber	—	—	2000	45	V: 10 ⁻⁴	92	Weight loss: 8%	10

^a To convert torr into Pascal, multiply by 133.3.

^b CPD = cyclopentadiene.

(H. PASTOR)

1. H. Pastor, in *Boron and Refractory Borides*, V. I. Matkovich, ed., Springer Verlag, Berlin, 1977, p. 457.
2. G. A. Meerson, V. Kh. Nurmukhamedov, R. M. Manelis, A. N. Dremin, G. A. Adadurov, O. N. Breusov, S. V. Pershin, V. F. Tatsii, *Fiz. Khim. Obrab. Mater.*, 140 (1974); *Chem. Abstr.*, 82, 63,396x (1975).
3. F. A. Fekhetdinov, V. I. Drozhalova, V. B. Ivanova, N. G. Kovaleva, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 316 (1977).
4. V. Ya. Shlyuko, V. V. Morozov, A. V. Besov, L. V. Chernyak, L. V. Guzenko, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 544 (1974).

6.7.5. Sintering Methods

6.7.5.2. Hot Pressing of Pure Borides

6.7.5.2.1. Technology of Hot Pressing.

5. S. S. Kiparisov, G. A. Libenson, A. P. Pankevich, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 145 (1974).
6. R. A. Steiger, F. G. Stroke, U.S. Pat. 4,108,670 (Aug. 22, 1978); *Chem. Abstr.*, 90, 91,404g (1979).
7. A. P. Pankevich, L. A. Gasparyan, *Prom. st. Arm.*, 36 (1979); *Chem. Abstr.*, 92, 27,250t (1980).
8. S. S. Kiparisov, G. A. Libenson, A. P. Pankevich, *Sov. J. Non-ferrous Met.*, 73 (1975).
9. J. Hofmann, J. Adam, V. Prochazka, D. Friedl, *Pokroky Praskové Metall.*, 3 (1974).
10. M. A. Kuzenkova, V. G. Kayuk, P. S. Kislyi, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 184 (1977).

6.7.5.1.5. Sintering of Boride-Metal Composites.

The sintering of boride-metal composites cannot be developed here, although it allows obtaining fully dense parts. For a review, limited to MB_x-M' pseudo-binary systems containing more than 50 vol% boride and excluding infiltrated borides, see ref. 1, §6.7.5.1.4.

(H. PASTOR)

6.7.5.2. Hot Pressing of Pure Borides

Hot pressing (or pressure sintering) is the simultaneous application of pressure and heat to a powder mass enclosed in a die. This technique allows the use of lower temperatures and pressures and shorter processing times than those for conventional sintering and thus permits the production of bodies with finer grain size, lower porosity and higher purity.

(H. PASTOR)

6.7.5.2.1. Technology of Hot Pressing.

Hot pressing^{1,2} requires a refractory die, pressure and heat sources and temperature- and pressure-indicating devices. For many applications the die containing the sample to be hot pressed is heated either by a separate furnace (for $< 1000^\circ\text{C}$) or by inductive or resistance heating of the die body itself. Uniaxial pressure is applied through the ram of a hydraulic or pneumatic press.

The most delicate part of this system is obviously the die, whose material must resist the simultaneous action of heat and pressure (adequate strength and creep resistance); must not react chemically with the material being hot pressed and with the environment; must have a low thermal expansion coefficient, i.e. lower than the material being sintered (otherwise hot ejection is necessary to avoid the sample cracking or the die splitting); and must have good thermal-shock resistance.

Refractory Ni-Cr-Al-Ti-W-Mo alloys (Nimonic type) are used $< 800-900^\circ\text{C}$ for die material; between 900 and 1000°C cemented carbide (WC-Co) is preferred; $> 1000^\circ\text{C}$ graphite is the only convenient material provided that the operating pressure is $< 35 \text{ MN m}^{-2}$ for commercial graphites or $< 140 \text{ MN m}^{-2}$ for special graphites.

Hot pressing has advantages over conventional sintering in reaching maximal densification; controlling the microstructure of the sample (hot pressing lasts only a few minutes, thus allowing control of or preventing grain growth); obtaining a dense, fine-grained structure guaranteeing the best mechanical properties; shaping compos-

6.7.5. Sintering Methods**6.7.5.2. Hot Pressing of Pure Borides****6.7.5.2.1. Technology of Hot Pressing.**

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6. R. A. Steiger, F. G. Stroke, U.S. Pat. 4,108,670 (Aug. 22, 1978); *Chem. Abstr.*, 90, 91,404g (1979).
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The most delicate part of this system is obviously the die, whose material must resist the simultaneous action of heat and pressure (adequate strength and creep resistance); must not react chemically with the material being hot pressed and with the environment; must have a low thermal expansion coefficient, i.e. lower than the material being sintered (otherwise hot ejection is necessary to avoid the sample cracking or the die splitting); and must have good thermal-shock resistance.

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Hot pressing has advantages over conventional sintering in reaching maximal densification; controlling the microstructure of the sample (hot pressing lasts only a few minutes, thus allowing control of or preventing grain growth); obtaining a dense, fine-grained structure guaranteeing the best mechanical properties; shaping compos-

ite materials (fiber-reinforced ceramics, multiphase ceramics, ceramic metal systems, etc.), where hot pressing neutralizes shrinkage that occurs during conventional sintering or in joining a ceramic material to another one or to a metal.

Hot pressing under vacuum³⁻⁵ allows the elimination of absorbed or chemisorbed gases, which are possible sources of pores; elimination of volatile impurities; an increase in the graphite die life; cancelling of convection streams (which are sources of temperature gradients), thus permitting a reduction of the thickness of the thermal insulator; and the rapid heating or cooling of the sample (in the absence of a thermal insulator), thus limiting grain growth.

A special die assembly⁶⁻⁸ operates $< 2000^{\circ}\text{C}$ and $< 1000\text{--}2000 \text{ MN m}^{-2}$. The powdered sample is cold pressed inside a graphite tube (heating element) internally coated with insulating boron nitride; this assembly is then fitted into a high-pressure cemented carbide die equipped with an internal pyrophyllite insulating coating. A $1000\text{--}2000 \text{ MN m}^{-2}$ pressure is applied at RT to the sample, which is then brought to $1500\text{--}2000^{\circ}\text{C}$ within a few minutes by passing an electric current through the graphite tube while maintaining the pressure. Such high pressures inhibit grain growth.

The process of hot-isostatic pressing avoids the heterogeneities inherent to uniaxial compression and produces nonporous components⁹⁻¹¹. Cold-wall isostatic presses are used, the pressure being transmitted to the sample by either Ar or He, and care is required to contain the gas or to prevent convection effects which can lead to large T gradients and rapid failure of the furnace. Specimen preparation is lengthy and expensive. The powdered sample is first sintered to the highest possible density and then machined to give a form that is easily encapsulated to produce a preform that gives the required final shape. Thin-walled cans are used for encapsulation: stainless or mild steel is used $< 1200^{\circ}\text{C}$; Ta is used at higher T. The can is electron-beam welded to maintain a minimum quantity of gas inside the capsule. The metal of the can must be compatible with the compact at the hot-pressing temperature. The capsule is then fitted into a heating device and the assembly placed inside the isostatic press. After hot-isostatic pressing the can must be removed from the compact either by machining or by pickling.

Activating additives (mainly transition metals) can be used as in conventional sintering allowing maximal densification at much lower T, thus preventing only chemical interaction between the sample and the die¹².

Reaction sintering under pressure is used to prepare LaB_6 , UB_2 and UB_4 compacts¹³.

Many theories describe the shrinkage kinetics during hot pressing¹⁴.

(H. PASTOR)

1. G. V. Samsonov, M. S. Koval'chenko, *Goryachee Pressovanie (Hot Pressing)*, Gosudarstvennoe Izdatel'stvo tekhnicheskoi Literatury, Ukr. SSR, Kiev, 1962.
2. H. Pastor, *Ind. Ceram.*, 89 (1969).
3. E. G. Wolff, *Powder Metall.*, 93 (1963).
4. L. Ramqvist, *Powder Metall.*, 24 (1966).
5. R. D. Holliday, R. Mogstad, J. L. Henry, *Electrochem. Technol.*, 1, 183 (1963).
6. E. V. Clougherty, in *Investigation of Boride Compounds for Very High Temperature Applications*, L. Kaufman, E. V. Clougherty, eds., Report RTD-TDR-63-4096, Part I, 1963, (AD 428 006), p. 67; *Chem. Abstr.*, 61, 42,800g (1964).
7. E. V. Clougherty, D. Kalish, in *Strengthening Mechanisms. Metals and Ceramics*, Syracuse Univ. Press, Syracuse, 1966, p. 431.

8. E. V. Clougherty, R. L. Pober, L. Kaufman, in *Modern Developments in Powder Metallurgy*, Vol. 2, Plenum Press, New York, 1966, p. 321.
9. R. P. Levey, *Isostatic Hot-Pressing*, Report No. Y-1487, 1965; *Chem. Abstr.*, 65, 13,254 (1966).
10. E. S. Hodge, *Powder Met.*, 7, 168 (1964).
11. E. S. Hodge, *Mater. Design Eng.*, 61, 92 (1965).
12. R. Meyer, H. Pastor, *Planseeber, Pulvermetall.*, 17, 111 (1969).
13. J. Schmitt, R. Setton, *Verres Refract.*, 319 (1964).
14. H. Pastor, *Rev. Int. Hautes Temp. Refract.*, 9, 251 (1972).

6.7.5.2.2. Hot-Pressing Characteristics of Pure Borides.

Tables 1-5 give the hot-pressing characteristics of pure borides.

(H. PASTOR)

TABLE 1. HOT-PRESSING CHARACTERISTICS OF GROUP-VIA METAL BORIDES

Boride	T (°C)	Pressure, P (MN m ⁻²)	Time (min)	Mean grain size ϕ (μ m)	Relative density (%)	Ref.	Remarks
CrB ₂	2000	18	11		97	41	Gives d = f (T, time, P)
CrB ₂	1900	12.7	10	3.5	94	36	
CrB ₂	2000	12.7	10	3.5	97	36	
CrB ₂	2100	12.7	10	3.5	100	36	
CrB ₂	1900	20	40	< 44	90	9	
CrB	1900	20	33	< 44	90	9	HIP; Ti can. Gives d = f (T, ϕ)
CrB ₂	1350	170	120		100	42	
CrB ₂	1700-2000	20	20		~ 100	43	
					48		
Mo ₂ B ₅	1900	18.5	5		59	14	
MoB	1750	20	35	< 44	75	9	Gives d = f (T, time, P)
MoB ₂	1875	20	40	< 44	90	9	
Mo ₂ B ₅	1900	15.6	10		~ 88	44	
Mo ₂ B ₅	2000	15.6	10		~ 92	44	
Mo ₂ B ₆	2050	15.6	10		~ 100	44	
MoB ₄	1900	11.5	10		~ 90	44	Gives d = f (T, time, P)
MoB ₄	1950	11.5	10		~ 93	44	
MoB ₄	2050	11.5	10		~ 99	44	
WB	1875	20	40	< 44	90	9	
W ₂ B ₅	2100	38.8	12		93	44	
W ₂ B ₅	2200	38.8	12		100	44	
WB ₄	1950	15.6	12		88	44	
WB ₄	2100	15.6	12		99	44	

6.7.5. Sintering Methods

6.7.5.2. Hot Pressing of Pure Borides

6.7.5.2.2. Hot-Pressing Characteristics of Pure Borides.

8. E. V. Clougherty, R. L. Pober, L. Kaufman, in *Modern Developments in Powder Metallurgy*, Vol. 2, Plenum Press, New York, 1966, p. 321.
9. R. P. Levey, *Isostatic Hot-Pressing*, Report No. Y-1487, 1965; *Chem. Abstr.*, 65, 13,254 (1966).
10. E. S. Hodge, *Powder Met.*, 7, 168 (1964).
11. E. S. Hodge, *Mater. Design Eng.*, 61, 92 (1965).
12. R. Meyer, H. Pastor, *Planseeber., Pulvermetall.*, 17, 111 (1969).
13. J. Schmitt, R. Setton, *Verres Refract.*, 319 (1964).
14. H. Pastor, *Rev. Int. Hautes Temp. Refract.*, 9, 251 (1972).

6.7.5.2.2. Hot-Pressing Characteristics of Pure Borides.

Tables 1–5 give the hot-pressing characteristics of pure borides.

(H. PASTOR)

TABLE 1. HOT-PRESSING CHARACTERISTICS OF GROUP-VIA METAL BORIDES

Boride	T (°C)	Pressure, P (MN m ⁻²)	Time (min)	Mean grain size ϕ (μ m)	Relative density (%)	Ref.	Remarks
CrB ₂	2000	18	11		97	41	Gives d = f (T, time, P)
CrB ₂	1900	12.7	10	3.5	94	36	
CrB ₂	2000	12.7	10	3.5	97	36	
CrB ₂	2100	12.7	10	3.5	100	36	
CrB ₂	1900	20	40	< 44	90	9	
CrB	1900	20	33	< 44	90	9	HIP; Ti can. Gives d = f (T, ϕ)
CrB ₂	1350	170	120		100	42	
CrB ₂	1700–2000	20	20		~ 100 4s	43	
Mo ₂ B ₅	1900	18.5	5		59	14	
MoB	1750	20	35	< 44	75	9	
MoB ₂	1875	20	40	< 44	90	9	Gives d = f (T, time, P)
Mo ₂ B ₅	1900	15.6	10		~ 88	44	
Mo ₂ B ₅	2000	15.6	10		~ 92	44	
Mo ₂ B ₆	2050	15.6	10		~ 100	44	
MoB ₄	1900	11.5	10		~ 90	44	
MoB ₄	1950	11.5	10		~ 93	44	Gives d = f (T, time, P)
MoB ₄	2050	11.5	10		~ 99	44	
WB	1875	20	40	< 44	90	9	
W ₂ B ₅	2100	38.8	12		93	44	
W ₂ B ₅	2200	38.8	12		100	44	
WB ₄	1950	15.6	12		88	44	
WB ₄	2100	15.6	12		99	44	

Boride	T (°C)	Pressure, P (MN m ⁻²)	Time (min)	Mean grain size ϕ (μ m)	Relative density (%)	Ref.	Remarks
YB ₄	1927	21	50	30	96	3	
YB ₆	2227	16	60	12	93	3	
SmB ₆	2227	23	60	12	87	3	
EuB ₆	2227	26	90	16	90	3	
LaB ₆	2400	30	60	5-8	98	4	
LaB ₆	1600	60	120		89	5	
LaB ₆	2000	49	5		97	6	Gives d = f(T, time, P)
SmB ₆	2050	49	5		97	6	
EuB ₆	1960	49	5		96	6	
DyB ₆	2000	49	5		95	6	
YB ₆	2150	12.5	5		98.2	7	
LaB ₆	2000	12.5	10		99.0	7	
CeB ₆	2150	12.5	5		98.0	7	
NdB ₆	2200	15.0	15		97.0	7	
SmB ₆	2000	15.0	20		98.8	7	
GdB ₆	1900	15.0	10		97.2	7	
YbB ₆	2000	12.5	10		98.9	7	
LaB ₆	982	690	10		?	8	
LaB ₆	1800	20	40		80	9	Gives d = f(T, time) for P = 20 LaB ₆ decomposes LaB ₆ → LaB ₉
LaB ₂	1650	7500				10	
LaB ₆	2300	8500				10	
LaB ₆	2000	20	45	3.4	92.2	11	
LaB ₆	1800	5000	2		100	12	Gives d = f(P) for T = 1800°C, time = 2 min.
LaB ₆	1800	1000	2		92	12	
LaB ₆	1700	3000	2		96	13	Initial powder
LaB ₆	1500	3000	2		96	13	After impact milling
UB ₂	1600	55	120		95	5	Contains UB ₄ + UO ₂
UB ₄	1800	50	90		85	5	Contains UO ₂
LaB ₆	1827 to 2077	9.8-19.6 29.4	0 to 20		—	46	Gives d = f(time) for 3P and 3T
EuB ₆	> 2100	34	—	7	—	47	Beginning of densification
EuB ₆	1700	34	—	< 1	92	47	Ball milling of the 7- μ m powder

TABLE 3. HOT-PRESSING CHARACTERISTICS OF GROUP-IVA METAL BORIDES

Boride	T (°C)	Pressure (MN m ⁻²)	Time (min)	Mean grain size ϕ (μ m)	Relative density (%)	Ref.	Remarks
TiB ₂	2350	12	5		92.7	14	Cooled under pressure
TiB ₂	2227	20.3	60	22	95	3	
TiB ₂	2450	1000	5.5		99	6 of §6.7.5.2.1	
TiB ₂	2040	9.7	10		88.9	5 of §6.7.5.2.1 contains 3.25 TiC + 0.13 B ₄ C + 1% B	
TiB ₂	1900	16	?		95	15	
TiB ₂	2150	30	5		99.5	16	
TiB ₂	1600	1725	0.5	$\left\{ \begin{array}{l} 4.2 \\ 6\% < 5 \\ 36\% < 10 \\ 84\% < 20 \\ 100\% < 44 \end{array} \right.$	89.6	8	
TiB ₂	1600	1725	18		98.6	of §6.7.5.2.1	
TiB ₂	1700	1725	2		98.6		
TiB ₂	1700	1728	18		96.6		
TiB ₂	1800	13.8	60		97	17	
TiB ₂	2000	20	60		100	18	
TiB ₂	2200	20	60	< 44	94	19	+ 6% Cr (activation)
TiB ₂	1900	769	10		98	20	
TiB ₂	1900	27.6	—		97	21	
TiB ₂	2000	15.5	120	5	97	22	
TiB ₂	1800	27.6	30	3.3	99	23	
TiB ₂	2200	60	30	5.6	100	24	
TiB ₂	2200	60	30	39	91	24	
TiB ₂	2200	15.5	20	< 1	92	25	
TiB ₂	2400	15.5	20	Vibration milling	98	25	
TiB ₂	1900	20	40		90	9	
TiB ₂	1750	50	20		98	26	
TiB ₂	1500	2500	3.3		99.5	27	
TiB ₂	1450	275	180		100	42	HIP: Ti can.

TiB ₂	2095	40	—	—	92	48	Under Ar (10 ⁵ × Pa) Under H ₂ (10 ⁵ × Pa) Under vacuum (330 Pa)
ZrB ₂	2800	18	3	5	93-95.5	28	
ZrB ₂	2227	16.9	90	100	99	3	
ZrB ₂	2475	1000	6		98.5	6 of \$6.7.5.2.1	
ZrB ₂	2000	34.5	1		72.6	3	Initial powder + 6% Cr Gives d = f (time) + 6% W
ZrB ₂	1950	34.5	5		96.5	of \$6.7.5.2.1	
ZrB ₂	2025	34.5	10		94.4		
ZrB ₂	2100	30	10	3.5	99.7	16	
ZrB ₂	2200	20	60	< 44	100	19	Many different powders are used
ZrB ₂	1970	20	40	3-5	85	29	
ZrB ₂	1970	20	40	7	92	29	
ZrB ₂	2100	27.6	80	3-5	99.95	30	
ZrB ₂	2100	20.7	20	< 44	97.9	31	HfB ₂ : Zr can
ZrB ₂	2200	20	30	?	100	32	
ZrB ₂	1350	100	?		99.95	33	
ZrB ₂	1850	27.6	60		88.3	34	
ZrB ₂	2050	27.6	60		100	34	Many different powders are used
ZrB ₂	2000	17.3	260	3-8	99.2	35	
ZrB ₂	2100	12.7	20	7.6	88	36	
ZrB ₂	2300	12.7	20	7.6	96	36	
ZrB ₂	1350	100	120		100	42	HfB ₂ : Zr can
ZrB ₂	2050	80	30	10	99	37	
HfB ₂	2650	15	5		84.9	38	
HfB ₂	3240	12.6	45	18	94	3	
HfB ₂	1900	759	10		~ 100	8, 20	Many different powders are used
HfB ₂	1790	1552	10	5	~ 100	39	
HfB ₂	2160	27.6	260		95.6	34	
HfB ₂	2200	20.7	200	25	98	35	
HfB ₂	2550	1000	4		97.9	6 of \$6.7.5.2.1	

TABLE 4. HOT-PRESSING CHARACTERISTICS OF GROUP-VA METAL BORIDES

Boride	T (°C)	Pressure, P (MN m ⁻²)	Time (min)	Mean grain size ϕ (μ m)	Relative density (%)	Ref.	Remarks
VB ₂	2127	22	40	22	92	3	
NbB ₂ , TaB ₂	870-1100	414-2242	2-60		83.5-91.0	8 and 6	
NbB ₂	2060	80	?	2-4	97	40	Gives d = f(T, P) for T = 1650-2240°C, P = 5.90 MN m ⁻²

TABLE 5. HOT-PRESSING CHARACTERISTICS OF ALKALINE-EARTH METAL BORIDES

Boride	T (°C)	Pressure (MN m ⁻²)	Time (min)	Mean grain size ϕ (μ m)	Relative density (%)	Ref.	Remarks
Be ₄ B	1030	20.7	60	11	99.7	1	
Be ₄ B	1010	34.5	8		97.6	45	
CaB ₆	1600	41.4	120		98.5	2	Gives d = f(T, time)

1. S. K. Dutta, J. A. Rubin, *J. Am. Ceram. Soc.*, **56**, 609 (1973).
2. S. K. Dutta, *Am. Ceram. Soc. Bull.*, **54**, 727 (1975).
3. E. W. Hoyt, J. Chrone, *Preparation of Self-Bonded Borides*, Report USAEC-GEAP-3332, 1960; *Chem. Abstr.*, **55**, 1338c (1961).
4. S. Scholz, in *Special Ceramics 1962*, P. Popper, ed., Academic Press, New York, 1963, p. 293.
5. J. Schmitt, R. Setton, *Verres Refract.*, **319** (1964).
6. B. G. Arabei, E. N. Shtrom, Yu. A. Lapitskii, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, **406** (1964).
7. G. V. Samsonov, in *Tugoplavkie soedineniya redkozemel'nykh metallov s nemetallami*, Izdat. Metallurgiya, Moskva, 1964, 61; Engl. Transl.: report JPRS-28165, 1965.
8. D. Kalish, E. V. Clougherty, *Am. Ceram. Soc. Bull.*, **48**, 570 (1969).
9. M. Kinoshita, S. Kose, Y. Hamano, *Osaka Kogyo Gijutsu Shikensho Kiho*, **24**, 85 (1973); *Chem. Abstr.*, **80**, 30,093b (1974).
10. N. N. Zhuravlev, R. M. Manelis, I. A. Belousova, V. Kh. Nurmukhamedov, *Inorg. Mater.*, **9**, 1033 (1973).
11. M. Ishii, S. Watanabe, H. Hiraoko, *Jpn. Pat.* 77-36120 (Mar. 19, 1977); *Chem. Abstr.*, **87**, 27,752e (1977).
12. A. V. Bochko, V. M. Volkogon, G. G. Karyuk, V. N. Paderno, Yu. B. Paderno, A. N. Pilyankevich, in *Goryachee-pressovanie* (Hot-Pressing), M. S. Koval'chenko *et al.*, eds., Institut Problem Materialovedenie, Kiev, 1977, p. 3.
13. V. M. Volkogon, Yu. B. Paderno, Yu. A. Chernyavskii, A. N. Martynenko, in *Vliyanie vysokikh davlenii na veshchestvo* (Influence of High Pressures on Matter), I. N. Frantsevich, ed., Naukova Dumka, Kiev, 1978, p. 67.

14. M. S. Koval'chenko, G. V. Samsonov, *Izv. Akad. Nauk SSSR, Otdel. Tekh. Nauk, Metall. Topl.*, 143 (1959); *Chem. Abstr.*, 55, 14,225e (1961).
15. U.S. Borax & Chemical Corp., Fr. Pat. 1,382,681 (Nov. 9, 1964).
16. R. Meyer, H. Pastor, *Bull. Soc. Fr. Ceram.*, 59 (1965).
17. R. W. Reidel, J. Hartwig, Union Carbide Corp., U.S. Pat. 3,215,545 (Nov. 2, 1965); *Chem. Abstr.*, 64, 3184 (1966).
18. Y. Hamano, M. Kinoshita, S. Kose, *Yogyo Kyokai Shi*, 74, 295 (1966); *Chem. Abstr.*, 69, 79,858s (1968); *Osaka Kogyo Gijutsu Shikenjo Kiho*, 18, 149 (1967).
19. Y. Toibana, H. Hashimoto, *Osaka Kogyo Gijutsu Shikenjo Kiho*, 18, 216 (1967); *Chem. Abstr.*, 69, 45,774w (1968).
20. D. Kalish, E. V. Clougherty, *High Pressure Hot-Pressing of Refractory Materials*, Report AD-665 315, 1968; *Chem. Abstr.*, 69, 54,039n (1968).
21. G. D. Barbaras, U.S. Pat. 3,455,682 (July 15, 1969); *Chem. Abstr.*, 71, 63,743f (1969).
22. R. H. Biddulph, U.S. Pat. 3,505,438 (April 7, 1970); *Chem. Abstr.*, 72, 135,968d (1970).
23. V. Mandorf Jr., R. G. Fenish, U.S. Pat. 3,632,708 (Jan. 4, 1972); *Chem. Abstr.*, 76, 89,535t (1972).
24. E. Fitzer, *Arch. Eisenhüttenwes.*, 44, 703 (1973).
25. M. S. Koval'chenko, M. M. Mai, *Sov. Powder Metall.*, 622 (1973); *Phys. Sintering*, 5, 307 (1973).
26. S. S. Kiparisov, G. A. Libenson, A. P. Pankevich, *Izvest. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 17, 145 (1974).
27. T. Watanabe, in *Proceedings of the 4th International Conference on High Pressure*, Kyoto, 1974, p. 138; *Chem. Abstr.*, 83, 83,912m (1975); *Kyushu Kogyo Gijutsu Shikensho Hokoku*, 21, 1238 (1978); *Chem. Abstr.*, 91, 43,053r (1979).
28. F. W. Glaser, *Powder Metall. Bull.*, 6, 51 (1951).
29. M. Kinoshita, S. Kose, Y. Hamano, *J. Ceram. Assoc. Jpn.*, 75, 84 (1967).
30. J. Chown, in *Science of Ceramics*, Vol. 4, The British Ceramic Society, 1968, p. 53.
31. W. C. Allen, W. A. Taebel, U.S. Pat. 3,433,656 (Mar. 18, 1969); *Chem. Abstr.*, 70, 99,310t (1969).
32. S. Janes, J. Nixdorf, *Ber. Deutsch. Keram. Ges.*, 46, 60 (1969).
33. R. Johansson, S. E. Isaksson, *Powder Metall. Int.*, 2, 49 (1970).
34. E. V. Clougherty, R. J. Hill, W. H. Rhodes, E. T. Peters, *Research and Development of Refractory Oxidation-Resistant Diborides. Processing and Characterization*; Report AD-866 558 (1970); *Chem. Abstr.*, 78, 61,571u (1973).
35. J. R. Fenter, *SAMPE Quart.*, 2, 1 (1971).
36. M. S. Koval'chenko, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 272 (1973).
37. R. Hayami, M. Iwasa, M. Kinoshita, *Yogyo Kyokai Shi*, 86, 352 (1978); *Chem. Abstr.*, 89, 151,358m (1978).
38. Yu. B. Paderno, T. I. Serebryakova, G. V. Samsonov, *Tsvetn. Metall.*, 32, 48 (1959).
39. D. Kalish, E. V. Clougherty, *J. Am. Ceram. Soc.*, 52, 26 (1969).
40. M. Iwasa, M. Kinoshita, R. Hayami, T. Yamazaki, *Yogyo Kyokai Shi*, 87, 284 (1979).
41. V. S. Neshpor, P. S. Kislyi, *Ogneupory*, 24, 231 (1959); *Chem. Abstr.*, 53, 15,683h (1959).
42. J. Adlerborn, S. E. Isaksson, H. Larker, Ger. Pat. DE 2,344,648 A1 (Mar. 28, 1974); A.S.E.A., U.S. Pat. 4,007,251 (Feb. 8, 1977); *Chem. Abstr.*, 81, 28,814 (1974).
43. Y. Toibana, S. Ueda, *Osaka Kogyo Gijutsu Shikensho Kiho*, 28, 164 (1977); *Chem. Abstr.*, 88, 125,288y (1978).
44. M. S. Koval'chenko, L. G. Bodrova, E. K. Fen, *Sov. Powder Metall. Met. Ceram. (Engl. Transl.)*, 469 (1975).
45. R. L. Landingham, A. W. Casey, *Semiannual Progress Report of the Light-Armor Materials Program*, Technical Report UCRL-51066, 1971, p. 23.
46. A. I. Kondrashev, Yu. B. Paderno, V. N. Paderno, *Poroshkov. Met.* (6), 16 (1982); *Soviet Powder Met.* (6), 437 (1982).
47. G. W. Hollenberg, P. B. Beutler, *Am. Ceram. Soc. Bull.* 60 (4), 478 (1981).
48. C. Brodhag, M. Bouchacourt, F. Thevenot, *Silic.-Ind.*, 46 (4/5), 91 (1981).

7. Formation of Bonds to the Group-IA (Li, Na, K, Rb, Cs, Fr) or Group-IIA (Be, Mg, Ca, Sr, Ba, Ra) Metals

7.1. Introduction

This chapter describes the formation of bonds of the group-IA and group-IIA metals to the group-IA, group-IIA, group-IB and group-IIB metals, as well as to the transition and inner transition metals.

(M. G. BARKER)

7.2. Formation of Group-IA (Li, Na, K, Rb, Cs, Fr) or Group-IIA (Be, Mg, Ca, Sr, Ba, Ra)–Group-IA (Li, Na, K, Rb, Cs, Fr) or –Group-IIA (Be, Mg, Ca, Sr, Ba, Ra) Metal Bonds

7.2.1. Introduction

The diversity of lithium chemistry has been described¹. The reaction chemistry² of the group-IA metals and their applied chemistry³ have been reviewed. Physical data have also been compiled⁴. These sources update several earlier reviews^{5–9}.

(M. G. BARKER)

1. R. O. Bach, ed., *Lithium, Current Applications in Science, Medicine and Technology*, Wiley Interscience, New York, 1985.
2. C. C. Addison, *The Chemistry of the Liquid Alkali Metals*, John Wiley & Sons, Chichester, UK, 1984.
3. H. U. Borgstedt, C. K. Mathews, *Applied Chemistry of the Alkali Metals*, Plenum Press, New York, 1987.
4. R. W. Ohse, ed., *Handbook of Thermodynamic and Transport Properties of Alkali Metals*, IUPAC Chemical Data Series No. 30, Blackwell, Oxford, 1985.
5. R. N. Lyon, ed., *Liquid Metals Handbook*, 2nd ed., U.S. Government Printing Office, Washington, D.C., 1952.
6. O. J. Foust, ed., *Na-NaK Engineering Handbook*, Vol. 1, *Sodium Chemistry and Physical Properties*, U.S. Government Printing Office, Washington, D.C., 1965.
7. J. W. Mausteller, F. T. Pepper, S. J. Rodgers, *Alkali Metal Handling and Systems Operating Techniques*, Gordon & Breach, New York, 1967.
8. M. Sittig, *Sodium, Its Manufacture, Properties and Uses*, Rheinhold, New York, 1956.
9. F. M. Perel'man, *Rubidium and Caesium*, Macmillan, New York, 1965.

7.2.2. in the Group-IA Elements

7.2.2.1. in Lithium

7.2.2.1.1. Industrial Manufacture.

Lithium is extracted from the ores lepidolite and spodumene, which contain up to 8% lithium oxide. The ore is converted first to lithium sulfate by acid roasting at 250°C and then to lithium chloride via the carbonate. Electrolysis of the fused

7.2. Formation of Group-IA (Li, Na, K, Rb, Cs, Fr) or Group-IIA (Be, Mg, Ca, Sr, Ba, Ra)–Group-IA (Li, Na, K, Rb, Cs, Fr) or –Group-IIA (Be, Mg, Ca, Sr, Ba, Ra) Metal Bonds

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5. R. N. Lyon, ed., *Liquid Metals Handbook*, 2nd ed., U.S. Government Printing Office, Washington, D.C., 1952.
6. O. J. Foust, ed., *Na-NaK Engineering Handbook*, Vol. 1, *Sodium Chemistry and Physical Properties*, U.S. Government Printing Office, Washington, D.C., 1965.
7. J. W. Mausteller, F. T. Pepper, S. J. Rodgers, *Alkali Metal Handling and Systems Operating Techniques*, Gordon & Breach, New York, 1967.
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7.2.2. in the Group-IA Elements
 7.2.2.1. in Lithium
 7.2.2.1.3. The Purification of Lithium.

TABLE 1. THE IMPURITIES IN LIQUID LITHIUM (ppm)¹

% Li	99.2	99.8	99.9-99.97	99.98	99.9	99.7	99.96
N		50-200	16	28-50	100	300	45
Cl		100-2000	41	13-40	40	30	10
Si		10-100	10	10	60	150	10
Na	6000	900-1500	75-150	30-50	70	200	82
K	100	100-1000	80-100	50-75			62
Ca		2-4	10	10	200	600	1
Al		10-100	10	10	}		10
Fe	100	10-100	100	10		300	100
Co, Ni				10			
Others				Cr 10			
				Cr 10			

chloride is hampered by its high melting point (614°C) and by severe corrosion of the components by the product Li and its salts. Current processes use a mixed electrolyte of LiCl-48% KCl which is liquid at the operating temperature of 460°C with graphite anodes and steel cathodes. Since the decomposition voltage of LiCl is lower than that of the other alkali metal chlorides the process produces 97% pure Li¹. Potassium is only slightly miscible with Li and remelting reduces its content to less than 100 ppm.

A laboratory preparation of pure Li uses a finely powdered mixture of Li₂O and a noble metal (Pt, Pd or Ir), which is heated > 1100°C in a stream of H₂. The pure intermetallic phase so produced is then heated under vacuum and the Li can be isolated by condensation from the vapor phase².

(M. G. BARKER)

1. J. S. Smatko, FIAT Report. 783, 1946.

2. U. Berndt, B. Erdmann, C. Keller, *Angew. Chem., Int. Ed. Engl.*, 11, 515 (1972).

7.2.2.1.2. The Purity of Commercial Lithium.

Purity values for lithium are usually calculated on the basis of metallic impurities¹, with only chloride being quoted for nonmetallic impurities. Typical analyses are shown in Table 1.

(M. G. BARKER)

1. A. Hatterer, *The Alkali Metals*, Spec. Publ. No. 22, The Chemical Society, London, 1967. A comprehensive review.

7.2.2.1.3. The Purification of Lithium.

Many of the techniques available to purify alkali metals were initially developed to use with liquid sodium as a consequence of its large-scale application in liquid-metal-cooled fast-breeder reactors¹. These techniques can be summarized as filtration or cold trapping distillation or chemical (gettering).

7.2.2. in the Group-IA Elements

7.2.2.1. in Lithium

7.2.2.1.3. The Purification of Lithium.

TABLE 1. THE IMPURITIES IN LIQUID LITHIUM (ppm)¹

% Li	99.2	99.8	99.9-99.97	99.98	99.9	99.7	99.96
N		50-200	16	28-50	100	300	45
Cl		100-2000	41	13-40	40	30	10
Si		10-100	10	10	60	150	10
Na	6000	900-1500	75-150	30-50	70	200	82
K	100	100-1000	80-100	50-75			62
Ca		2-4	10	10	200	600	1
Al		10-100	10	10	}		10
Fe	100	10-100	100	10		300	100
Co, Ni				10			
Others				Cr 10			
				Cr 10			

chloride is hampered by its high melting point (614°C) and by severe corrosion of the components by the product Li and its salts. Current processes use a mixed electrolyte of LiCl-48% KCl which is liquid at the operating temperature of 460°C with graphite anodes and steel cathodes. Since the decomposition voltage of LiCl is lower than that of the other alkali metal chlorides the process produces 97% pure Li¹. Potassium is only slightly miscible with Li and remelting reduces its content to less than 100 ppm.

A laboratory preparation of pure Li uses a finely powdered mixture of Li₂O and a noble metal (Pt, Pd or Ir), which is heated > 1100°C in a stream of H₂. The pure intermetallic phase so produced is then heated under vacuum and the Li can be isolated by condensation from the vapor phase².

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Purity values for lithium are usually calculated on the basis of metallic impurities¹, with only chloride being quoted for nonmetallic impurities. Typical analyses are shown in Table 1.

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Many of the techniques available to purify alkali metals were initially developed to use with liquid sodium as a consequence of its large-scale application in liquid-metal-cooled fast-breeder reactors¹. These techniques can be summarized as filtration or cold trapping distillation or chemical (gettering).

7.2.2. in the Group-IA Elements

7.2.2.1. in Lithium

7.2.2.1.3. The Purification of Lithium.

TABLE 1. THE IMPURITIES IN LIQUID LITHIUM (ppm)¹

% Li	99.2	99.8	99.9-99.97	99.98	99.9	99.7	99.96
N		50-200	16	28-50	100	300	45
Cl		100-2000	41	13-40	40	30	10
Si		10-100	10	10	60	150	10
Na	6000	900-1500	75-150	30-50	70	200	82
K	100	100-1000	80-100	50-75			62
Ca		2-4	10	10	200	600	1
Al		10-100	10	10	}		10
Fe	100	10-100	100	10		300	100
Co, Ni				10			
Others				Cr 10			
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(i) Filtration or Cold Trapping. Filtration of the molten metal at a T just above its melting point removes insoluble surface contamination, but the high solubilities of nonmetals in Li render this technique less effective than with Na. The solubilities (in wppm) of the more important impurities at 200°C in Li are given in Table 1. Specific analytical data for the efficiency of filtration as a means of lowering the nonmetal content of lithium are not readily available. Filtration is unable to remove small solid particulates from the liquid. This leads to a wide spread in analytical values. Lithium must be filtered through metal sinters, since liq Li rapidly attacks glass and ceramics above its melting point. Early work on the solubility of N₂ and O₂ in Li employed a 20- μ m stainless steel filter. Oxygen solubility values were found to vary from 58 to 121 ppm on filtration at 250°C, and a similar spread was observed for nitrogen⁷. Filtration is therefore suitable only for removing gross impurities and is not a means of purification.

Cold trapping is a technique widely used in Na loops for the continuous control of impurity levels⁸. This technique can control the levels of carbon, oxygen and hydrogen^{7,9}, but nitrogen does not appear to be influenced by changes in the cold-trap temperature and its high solubility in liq Li means that nitrogen cannot be maintained at acceptable levels (a few hundred wppm or less) by cold trapping.

(ii) Distillation. Lithium may be distilled at 600°C and a pressure of 10⁻⁴ torr, but the rate of distillation is somewhat low (0.38 hr⁻¹ cm⁻² of liquid-vapor interface area). This technique removes metallic impurities, hydrogen, oxygen and carbon, and similar fractional distillation of more volatile impurities should be possible. Removal of nitrogen is not possible by distillation. Lithium nitride is known to decompose under vacuum at 600°C to the elements. The N₂ thus produced recombines with the distillate and no purification results¹⁰.

(iii) Chemical Methods of Purification. The addition to liq Li of solid metals whose oxides, nitrides, carbides and hydrides are more thermodynamically stable than those of Li is the best purification method. These methods are best carried out at the highest practical temperature, generally > 500°C, since the rate at which the non-metal impurity is removed from solution in the Li is generally governed by the rate at which the nonmetal can diffuse from the surface into the bulk of the solid metal being employed. A stainless steel clad V-15Cr loop is used to study impurity (oxygen, nitrogen, hydrogen) redistribution between Li and selected refractory metals. Operation of a Zr getter at 600°C for ~ 1000 h leads to a reduction in nitrogen level from 670 to 18 appm¹³. Yttrium gettering has shown promise, however, using the metal in sponge form to remove hydrogen from liq Li at the relatively low T of 400°C^{3,11}. The

TABLE 1. SOLUBILITIES OF SOME NONMETALS IN LIQUID LI AT 200°C²

	wppm	appm	Refs.
C	2	1	6
N	1461	724	3, 4
O	7	3	5
H	63	437	3

gettering reaction followed by distillation has also been described. This method fixes the nonmetals in a nonvolatile form, allowing the distillation of pure Li from the getters. A mixed getter is used with the metals being chosen for their specificity toward the nonmetals. The high stability of Li_2O precludes the use of many transition metals whose oxides are of lower stability¹². The removal of oxygen from Li can be effected by nitrogen dissolved in the Li¹³.

Molten salt extraction to remove hydrogen isotopes and other impurities from liq Li is also used. Liquid Li is mixed with an all lithium halide molten salt (LiF-LiCl-LiBr , 22:31:47 mol%, mp 445°C). During mixing the saltlike impurities (LiH , LiT , Li_2C_2 , Li_3N) are preferentially extracted into the molten salt phase. After separation of the two phases (specific gravities Li 0.5, halide molten salt 2.2), the salt is electrolyzed and the impurities are removed as H_2 , T_2 , N_2 and CH_4 . This method of purification is now under development for large-scale use. The one disadvantage of this method is the high halide content of the Li after purification, nearly 500 appm⁹.

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7.2.2.1.4. Analysis of Lithium for Impurities.

No standard analytical procedure is available for lithium or for the nonmetallic impurities. Metallic impurities are generally determined by distillation of xs Li and solution of the residue, followed by atomic absorption analysis. The determination of oxygen in Li by the vacuum distillation method has been shown to give reproducibility at the 30-80 ppm level as evaluated by quantitative oxygen additions and recovery¹. Since this method converts the alkalinity of solutions of the vacuum distillation residue to oxygen concentrations, it is not specific to oxygen but also includes carbide and hydride. Oxygen can be determined by solution of lithium in liq NH_3 , followed by filtration and titration of the insoluble oxide². Oxygen and nitrogen can be determined by high-T fluorination with KBrF_4 , and a good degree of self-consistency is obtained³. The simultaneous determination of carbide and nitride by measuring the HCCl and NH_3 evolved when a sample of lithium is dissolved in water⁴ gives satisfactory results⁵.

Oxygen determination utilizing methanol and coulometric moisture analysis reagent⁶ does not yield as reproducible results⁵ as the activation analysis method⁷.

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Oxygen determination utilizing methanol and coulometric moisture analysis reagent⁶ does not yield as reproducible results⁵ as the activation analysis method⁷.

The continuous monitoring of liquid lithium for O, C, H and H uses electrochemical cells based on $\text{ThO}_2\text{-Y}_2\text{O}_3$ electrolytes and diffusion meters. No continuous method for N analysis is yet available^{8,9}.

Lowering of the electrical resistivity of liquid and solid lithium can be achieved by filtering the metal through a stainless steel sinter just above its mp (180.5°C). It was thought that this was probably due to the removal of nitrogen as solid Li_3N . The effect of hydrogen removal by gettering with Yt is also known, and it may be possible to use this technique for the continuous monitoring of nitrogen in Li¹⁰. The possibility of interactions between nonmetals dissolved in Li, however, could implicate the interpretation of these data¹¹.

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7.2.2.2. in Sodium

7.2.2.2.1. Industrial Manufacture.

The processes for the production of metallic Na, Na-Ha or Na-Pb alloy have been reviewed¹.

The major process for producing sodium since the 1930s² involves electrolysis of fused NaCl-CaCl_2 eutectic mixtures in a fire brick-lined cell at 590°C. Previous to this process, Na was produced by the electrolysis of molten NaOH within +20°C of the bath mp³. Production of Na by electrolysis of pure NaCl is not efficient, since the salt has a high melting point (801°C) and at this T the high solubility of Na in NaCl enhances back diffusion of the metal to the anode. The use of CaCl_2 as a component of the electrolyte is also disadvantageous in that Ca is soluble in the electrolyte to about 4-5 wt%, thus introducing a significant Ca impurity. On the laboratory scale, the in situ preparation of pure Na may be employed using the thermal decomposition of NaN_3 to free Na and N_2 . This method has been employed to prepare Na_2O ⁴ and some sodium-transition-metal ternary oxides such as Na_3CrO_4 ^{5,6}. **Such relations should be treated with extreme caution, however, as they may occur with explosive violence⁷.**

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7.2.2.2.2. The Purity of Commercial Sodium.

Commercial sodium contains up to 500 ppm Ca. The use of Na as a coolant in liquid-metal cooled fast-breeder reactors has led to the availability of so-called reactor-grade sodium¹⁻⁴. This product differs from the normal commercial sodium in having a much reduced Ca content (≤ 1.0 ppm). Sodium also contains ~ 20 ppm Li and ≤ 100 ppm K. Transition metals are only slightly soluble in Na, but significant quantities of iron are often found in commercial Na. The high reactivity of Na with air (H_2O , CO_2 , O_2 , but not N_2) precludes the evaluation of oxygen, hydrogen and carbon contents. Commercial Na is always covered with a crust of Na_2CO_3 , Na_2O and NaOH . A comprehensive collection of analytical data from Na from various manufacturers⁵ is reproduced in Table 1.

Since the largest scale usage of Na is as a coolant in nuclear fast reactors, purity information on this Na is included as a separate section.

Data are available for metallic impurities in the primary coolant of in-pile test loops at MOL which uses I.C.I. Na, and from Degussa Na which is used as the

TABLE 1. IMPURITIES IN COMMERCIAL SODIUM (ppm)

% Na	99.94	99.99	99.90	99.9				99.9
O	30?		26					
N	10	20	10					
Cl	10	15	15	15	40	20-40	30	6
$[\text{SO}_4]^{2-}$	20	20	20	10	10			
$[\text{PO}_4]^{3-}$	5	10						
SiO_2				16	10	20		
Others					As 0.1	B 5	B 5	
Li			10			2	20	5
K			600	100	200	200-250	150	
Mg			20		6	20		
Ca	500		400	500	450	350-450	10	10
Sr			30	20				
Ba			10	10	10	10	10	
Al			10	1	20			
Fe		10	3		8	20-40		8
Co, Ni	5?		10		0.1	20		0.2-4
Pb		10	5		0.6	20		7
Mn			10		0.1	20		5
Others			5		Cu 1	Cu 20		Re 100
						Sn 20		Sn 2
						Ag 5 Hg 50		Hg 35

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Li			10			2	20	5
K			600	100	200	200-250	150	
Mg			20		6	20		
Ca	500		400	500	450	350-450	10	10
Sr			30	20				
Ba			10	10	10	10	10	
Al			10	1	20			
Fe		10	3		8	20-40		8
Co, Ni	5?		10		0.1	20		0.2-4
Pb		10	5		0.6	20		7
Mn			10		0.1	20		5
Others			5		Cu 1	Cu 20		Re 100
						Sn 20		Sn 2
						Ag 5 Hg 50		Hg 35

TABLE 2. IMPURITY LEVELS IN REACTOR SODIUM

Element	Primary system (ppm)	Secondary system (ppm)	Method of analysis
O	2-5	2-5	Amalgamation
C	1-2	1-2	Oxyacidic flux
H	1-2	1-2	Isotope dilution
Al	0.6	0.6	
Bi	2	0.1	
Ca	~ 0.05	0.01	
Co	0.04	0.02	
Cr	0.03	0.03	Atomic absorption spectrophotometry following vacuum distillation from a tantalum crucible
Cu	0.02	0.02	
Fe	0.06-0.1	0.1	
Mg	0.01-0.06	0.02	
Mn	0.005	~ 0.005	
Mo	0.07	0.07	
Ni	0.05	0.05	
Pb	10-12	0.7	
Sn	20-25	0.5	

primary and secondary coolant for the fast reactor K.N.K. at Karlsruhe^{1,2}. The iron data for the K.N.K. reactor fluctuates between determinations, using activation analysis and x-ray fluorescence, and also with time. The oxygen level was 30-50 ppm.

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(M. G. BARKER)

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3. W. E. Ruther, T. D. Claar, S. Greenberg, R. V. Štrain, U.S. Atomic Energy Comm. ANL-7670 (1970); *Chem. Abstr.*, 74, 1,496,965 (1971).
4. W. H. Olsen, C. C. Miles, D. W. Cissel, U.S. Atomic Energy Comm. ANL-7520 (1968) (Pt. 2) pp. 222-226; *Chem. Abstr.*, 72, 95,901 (1970).
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7.2.2.2.3. The Purification of Sodium.

Sodium purification methods are generally identical to those for lithium (see §7.2.2.1.3), but the relative efficiencies of the methods differ¹⁻³.

(i) Filtration or Cold Trapping. The simplest and most efficient method of purifying sodium on a laboratory scale is filtration through a glass sinter. This method readily removes gross oxide, hydride, carbonate and hydroxide impurities and is carried out at T just above the mp of Na (~100°C). Filtration also lowers the calcium content of sodium^{4,5}, although this may be merely the removal of Ca as CaO, formed

7.2.2. in the Group-IA Elements

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7.2.2.2. in Sodium

7.2.2.2.3. The Purification of Sodium.

TABLE 2. IMPURITY LEVELS IN REACTOR SODIUM

Element	Primary system (ppm)	Secondary system (ppm)	Method of analysis
O	2-5	2-5	Amalgamation
C	1-2	1-2	Oxyacidic flux
H	1-2	1-2	Isotope dilution
Al	0.6	0.6	
Bi	2	0.1	
Ca	~ 0.05	0.01	
Co	0.04	0.02	
Cr	0.03	0.03	Atomic absorption spectrophotometry following vacuum distillation from a tantalum crucible
Cu	0.02	0.02	
Fe	0.06-0.1	0.1	
Mg	0.01-0.06	0.02	
Mn	0.005	~ 0.005	
Mo	0.07	0.07	
Ni	0.05	0.05	
Pb	10-12	0.7	
Sn	20-25	0.5	

primary and secondary coolant for the fast reactor K.N.K. at Karlsruhe^{1,2}. The iron data for the K.N.K. reactor fluctuates between determinations, using activation analysis and x-ray fluorescence, and also with time. The oxygen level was 30-50 ppm.

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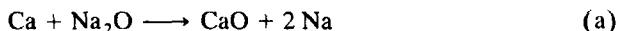
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by reaction with Na_2O in the molten Na:



Equation (a) forms the basis removing Ca from sodium. The free-energy change for the reaction is highly favorable, and even at small concentrations of Ca in sodium the addition of oxygen should result in the formation of insoluble CaO.

The major impurity removed by filtration is oxygen. Solubility data for oxygen in sodium are somewhat variable, but oxygen levels of ~ 5 wppm are readily attainable by filtration. Carbon is insoluble $\leq 600^\circ\text{C}$ and is easily removed by filtration methods. Hydrogen may be removed by filtration, having a solubility ≤ 1 ppm at low T. The high dissociation pressure of sodium hydride also enables hydrogen to be pumped out by vacuum outgassing.

Cold trapping is the method most widely used to purify large volumes of sodium. A dynamic sodium loop with a cold trap³ or smaller diffusion cold traps that are more suitable for laboratory-scale work⁶ have been described. Cold trapping is especially suitable for contaminants that show a large variation in solubility with T. Thus the control of oxygen and hydrogen levels in sodium is generally achieved by this means. The operation and design of cold traps has been extensively reported².

(ii) Distillation. A greater variety of impurities may be removed by distillation than by any other means. Purification by vacuum distillation is practicable at $T \geq 350^\circ\text{C}$ to remove all impurities except K, which can be removed to ≤ 10 ppm, but only after half the Na has been distilled⁷. Both single-⁸ and triple-stage³ distillation units have been tested³. Using high vacuum, Na can be distilled at only 250°C from glass apparatus since Na does not attack glass appreciably $\leq 350^\circ\text{C}$.

(iii) Chemical Methods of Purification. Most nonmetallic impurities can be removed by high-T reaction with elements whose compounds are more stable than those of Na. Zirconium foil at $600\text{--}650^\circ\text{C}$ reduces Na_2O with the formation of ZrO_2 , which is held in the vessel by a stainless steel filter. Using this technique oxygen levels of ≤ 2 ppm have been reported³. Zirconium is assumed to remove hydrogen, but it does not lower hydrogen levels as much as cold trapping⁹. Uranium foil has been used as an alternative to Zr¹⁰.

Carbon has been removed to very low levels in sodium at 600°C by the use of Type 316 stainless steel¹¹. Neither Zr nor Nb is efficient at C removal, since oxide films inhibit carbide formation².

It should be possible to purify sodium by electrolysis through a β -alumina electrolyte; this only conducts Na^+ ions, and, therefore, only pure Na should pass through the material.

(M. G. BARKER)

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3. A. W. Thorley, A. C. Raine, *The Alkali Metals*, Spec. Publ. No. 22, The Chemical Society, London, 1967. A very good paper giving details of methods used at present.
4. C. C. Addison, D. Kerridge, J. Lewis, *J. Chem. Soc.*, 2861 (1954).
5. C. C. Addison, E. Iberson, J. A. Manning, *J. Chem. Soc.*, 2699 (1962).
6. I. W. Cavell, M. G. Nicholas, *J. Nucl. Mater.*, 95, 129 (1980).
7. G. W. Horsley, Report A.E.R.E. M/R 1152 (1953).

8. G. W. Horsley, *J. Appl. Chem.*, **8**, 13 (1958).
9. V. M. Sinclair, R. A. H. Pool, A. E. Ross, *Proc. 2nd Conf. on Nuclear Reactor Technol.*, TID 7622, p. 35 (1961); *Chem. Abstr.*, **57**, 16092 (1963).
10. H. S. Isaacs, *J. Electrochem. Soc.*, **119**, 455 (1972).
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7.2.2.2.4. Analysis of Sodium for Impurities.

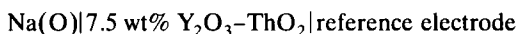
Sodium analytical techniques have been reviewed^{1,2}, most comprehensively regarding reactor applications³.

(i) **Separation and Preconcentration Methods.** Since many of the impurities are in the ppm range, it is necessary to preconcentrate the impurity for analysis. Vacuum distillation is the method most widely used to separate Na from non-volatile impurities⁴. The vapor pressure of Na at various T indicates that quite low vacuum may be used in distillation, e.g., at 623 K a vacuum of 10^{-2} kN m⁻² is required, but a vacuum of at least 1.3×10^{-4} kN m⁻² avoids sample contamination particularly in the case of oxygen and carbon analysis³. The technique can be used for concentrates of some metallic impurities, e.g., Fe, Cr, Ni, but cannot be used for the more volatile metallic impurities such as K, Rb, Cs or Hg.

The reaction of Na with Hg to form an amalgam that can then be separated from the Na₂O for oxygen analysis⁵ has been compared with the vacuum distillation technique^{6,7}. Ion-exchange techniques in which the sample is dissolved in a suitable solvent and the resulting separation of elements is achieved by an ion-exchange resin is less common. This technique is particularly suited to separating the volatile impurities such as K, Rb and Co⁸.

(ii) **Sodium Sampling.** Since analysis in sodium is at ppm levels, contamination of the metal during analysis is a major problem. Since the sampling of reactor sodium is carried out at high T, this problem has received widespread attention and designs have been proposed for both large- and small-scale application⁹⁻¹¹.

(iii) **Specialized Analytical Methods.** Analytical methods for metallic impurities are well documented³ and are not covered here. A major advance in the continuous monitoring of impurities in liquid sodium down to the lowest levels of detection has been the development of analysis using electrochemical cells. Oxygen analysis in sodium may be carried out using a cell of the type



Reference electrodes of Pt-air¹² and In-In₂O₃¹³ are useful to measure oxygen in sodium at 700–1100 K. Problems in the stability of the electrolyte tubes require the use of ThO₂ and Y₂O₃^{14,15}.

Electrochemical cells have also been proposed for carbon that employ a eutectic molten salt mixture of Li₂CO₃–Na₂CO₃¹⁶ or LiCl–CaCl₂–CaC₂¹⁵ as the electrolyte. A diffusion-type meter has also been developed for both small-scale and reactor sodium¹⁷.

Hydrogen may also be determined by both electrochemical and diffusion meters. The electrochemical meter is a hydride-activated concentration cell that employs an electrolyte consisting of a CaH₂–CaCl₂ mixture¹⁸. The diffusion meter is based on the equilibrium pressures attained on either side of a thin membrane, usually nickel.

7.2.2. in the Group-IA Elements

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7.2.2.2. in Sodium

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-
8. G. W. Horsley, *J. Appl. Chem.*, **8**, 13 (1958).
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Hydrogen detection in this type of meter is achieved using an ion pump, mass spectrometry or thermal conductivity detectors¹⁹.

Two other methods of monitoring impurity levels in loop or reactor systems are based on the equilibration of metals with the solution of the nonmetal in sodium. Oxygen may be evaluated by the vanadium wire equilibrium method²⁰ and carbon by the use of stainless steel or nickel equilibration²¹. Neither of these methods gives continuous monitoring of the impurity, but each is employed in a regular sampling system.

(M. G. BARKER)

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3. E. A. Trevillion, *A Review of Sodium Analytical Techniques*, C.E.G.B. Report RD/B/N/3031, (1974); *Chem. Abstr.*, 83, 90,220 (1975). An excellent review of up-to-date methods of analysis.
4. J. R. Humphreys, *Amer. Inst. Chem. Eng. Nuclear Eng. and Science Congress*, Reprint 67 (1955).
5. L. P. Pepkowitz, W. C. Judd, *Anal. Chem.*, 22, 1285 (1950).
6. K. T. Claxton, *J. Nucl. Energy*, 19, 849 (1965).
7. J. A. J. Walker, E. D. France, J. L. Drummond, A. W. Smith, *The Alkali Metals*, Spec. Publ. No. 22, The Chemical Society, London, 1967.
8. L. Burris, B. Singer, *Proc. 65th Annual A.I.Ch.E. Meeting*, New York (1972).
9. G. M. Kesser, A.N.L. Report 7997 (1973).
10. L. Bos, *Liquid Alkali Metals*, Proc. Int. Conf. British Nuclear Energy Soc., London, 1973; *Chem. Abstr.*, 81, 19,858 (1974).
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13. M. G. Adamson, E. A. Aitken, *Thermodynamics of Nuclear Materials*, Proc. Symp., 4th, 1974; Vol. 1, pp. 233–250, IAEA, Vienna, 1975.
14. C. A. Smith, C.E.G.B. Report RD/B/N2331 (1972); *Chem. Abstr.*, 81, 9346 (1974).
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18. C. A. Smith, *Liquid Alkali Metals*, Proc. Int. Conf. British Nuclear Energy Soc., London, 1973; *Chem. Abstr.*, 81, 9346 (1974).
19. A. W. Smith, *I.A.E.A. Specialist Meeting on Impurity Monitoring in Sodium*, Cadarache, 1972. Not abstracted.
20. D. L. Smith, *Met. Trans.*, 2, 579 (1971).
21. J. J. McCown, C. Bagnall, *I.A.E.A. Specialist Meeting on Carbon in Sodium*, Harwell, 1979. Not abstracted.

7.2.2.3. In Potassium

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The reaction is unfavorable for the production of potassium at 870°C, but the removal of K by distillation drives the equilibrium to the right. A variation in the condenser temperature can be used to produce Na-K alloys or potassium with a typical Na content of 1.0 wt%. A high-purity grade of potassium, with Na contents ≤ 50 ppm, is produced commercially by distillation in a multiplate tower².

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7.2.2.3.2. Impurities in Commercial Potassium.

The major metallic impurities are Na, Ca and Si. Typical analytical data for both commercial and high-purity potassium are given in Tables 1 and 2.

Nonmetallic impurities such as hydrogen and oxygen, are generally not quoted by the manufacturers but are very high. Carbon and nitrogen levels are much lower—especially nitrogen, but carbon present as surface carbonate may be extensive. The oxygen impurity is³ ≤ 800 ppm and hydrogen 200–1000 ppm.

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TABLE 1. TYPICAL ANALYSIS OF COMMERCIAL POTASSIUM METAL SHOWING IMPURITIES IN ppm¹

Al	50	Cu	20	Si	100
Ba	20	Fe	50	Ag	10
Be	10	Pb	50	Na	250
B	10	Mg	30	Sr	10
Ca	100	Mn	10	Sn	30
Cr	50	Mo	50	Ti	30
Co	50	Ni	20	V	30

7.2.2. in the Group-IA Elements

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7.2.2.3. in Potassium

7.2.2.3.2. Impurities in Commercial Potassium.

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B	10	Mg	30	Sr	10
Ca	100	Mn	10	Sn	30
Cr	50	Mo	50	Ti	30
Co	50	Ni	20	V	30

TABLE 2. IMPURITY CONTENT OF POTASSIUM²

Element	As received ^a (ppm)	After purification ^b (ppm)
O	65 ^c , 300 ^d	20 ^c , 50 ^d
Li	ND ^e	1
Na	55	60
Rb	ND ^e	130
Cs	ND ^e	20
Mg	2	2
Ca	15	11
B	10	10
Si	25	10
Cr	5	1
Fe	5	20
Ni	5	7
Nb	10	5
Ti	5	5
Mo	3	5
Va	1	1
Zr	10	20

^a Vendor analysis.^b Oak Ridge National Laboratory analysis.^c By amalgamation method.^d By gettering-vacuum-fusion procedure.^e Not determined.

7.2.2.3.3. Purification of Potassium.

The purification of potassium has been studied less. The methods that have been applied to sodium may also be applicable to potassium, but those depending upon solubility may be less efficient in potassium since the nonmetals are more soluble in potassium.

The relatively low reactivity of potassium with SiO₂ allows purification of the metal by filtration to be conveniently carried out in glass apparatus. Such a purification has been described in which the oxygen content of potassium was reduced to about ~100 ppm by filtration through a borosilicate glass sinter¹. Commercial potassium is supplied under hydrocarbon oil, which may then be removed by reflux under nitrogen with low-boiling petroleum, decanting of the organic layer and degassing at 250°C under vacuum.

A more comprehensive purification procedure² uses a sequence of steps as follows: filtration at 200°C through a stainless steel powder compact filter of 10-μm pore size reduces the oxygen content and removes any solid impurities. Gettering with Zr foil for 46 h at 760°C reduces the oxygen concentration to ~200 ppm. The weight ratio of K to Zr is 13:1 with a surface area to volume ratio of Zr to K 4:1. A second gettering with zirconium foil for 72 h at 800°C reduces the oxygen content ~50 ppm.

(M. G. BARKER)

1. C. C. Addison, M. G. Barker, R. M. Lintonbon, *J. Chem. Soc. A*, 1465 (1970).2. A. P. Litman, U.S. Atomic Energy Comm. ORNL-3751 (1965); *Chem. Abstr.*, 63, 9558 (1965).

7.2.2. in the Group-IA Elements

7.2.2.3. in Potassium

7.2.2.3.3. Purification of Potassium.

TABLE 2. IMPURITY CONTENT OF POTASSIUM²

Element	As received ^a (ppm)	After purification ^b (ppm)
O	65 ^c , 300 ^d	20 ^c , 50 ^d
Li	ND ^e	1
Na	55	60
Rb	ND ^e	130
Cs	ND ^e	20
Mg	2	2
Ca	15	11
B	10	10
Si	25	10
Cr	5	1
Fe	5	20
Ni	5	7
Nb	10	5
Ti	5	5
Mo	3	5
Va	1	1
Zr	10	20

^a Vendor analysis.^b Oak Ridge National Laboratory analysis.^c By amalgamation method.^d By gettering-vacuum-fusion procedure.^e Not determined.

7.2.2.3.3. Purification of Potassium.

The purification of potassium has been studied less. The methods that have been applied to sodium may also be applicable to potassium, but those depending upon solubility may be less efficient in potassium since the nonmetals are more soluble in potassium.

The relatively low reactivity of potassium with SiO₂ allows purification of the metal by filtration to be conveniently carried out in glass apparatus. Such a purification has been described in which the oxygen content of potassium was reduced to about ~100 ppm by filtration through a borosilicate glass sinter¹. Commercial potassium is supplied under hydrocarbon oil, which may then be removed by reflux under nitrogen with low-boiling petroleum, decanting of the organic layer and degassing at 250°C under vacuum.

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7.2.2. in the Group-IA Elements

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7.2.2.3. in Potassium

7.2.2.3.4. Analysis of Potassium.

7.2.2.3.4. Analysis of Potassium.

The same analytical methods as for liquid sodium have been applied. Distillation separates and concentrates the impurities prior to analysis. Amalgamation has poor recovery value for oxygen compared to distillation (Table 1)¹.

In the equilibrium technique for oxygen, potassium containing 100–1000 ppm oxygen is exposed to zirconium metal at 815°C, and the zirconium analyzed for oxygen

TABLE 1. OXYGEN RECOVERED FROM POTASSIUM BY AMALGAMATION AND VACUUM DISTILLATION ANALYSES

Analytical method	Oxygen added (ppm)	Total oxygen (ppm)	T ^a (°C)	Oxygen found (ppm)	Oxygen recovery (%)
Amalgamation	620	670	70	735	110
	585, 505	635, 555	400	75, 200	12, 36
	540, 575	590, 625	600	190, 230	32, 37
	745	880	815	305	35
	410	455	70	500	110
Vacuum distillation ^b	515	590	400	455	77
	505	580	800	375	65
	605	740	815	280	38

^a Heated in molybdenum, nickel or niobium containers for times varying from 1 to 100 h before analysis.

^b Conditions: 375°C; 2 h; 5×10^{-5} torr.

TABLE 2. OXYGEN RECOVERED FROM POTASSIUM BY GETTERING-VACUUM-FUSION ANALYSIS^a

Oxygen added (ppm)	Total oxygen (ppm)	T ^b (°C)	Oxygen found (ppm)	Oxygen recovery (%)
905	955	200	960	102
1045	1095	200	1135	104
15	65	600	60	92
155	205	600	225	110
340	360	800	355	99
1100	1225	800	1210	99
1375	1500	800	1650	110
2780	2905	800	2820	97
250	300	815	275	92
610	745	815	740	99
1380	1430	815	1565	109

^a Zirconium specimen thickness, 0.5–1.65 mm; T, 815°C; time, 100 h.

^b Heated in molybdenum, nickel or niobium containers for times varying from 1 to 100 h before analysis.

by a platinum bath-vacuum fusion technique. The weight gained by the zirconium arises from oxygen gettered from the potassium. Oxygen recovery values by this method vary from 92 to 110% (Table 2).

Little work has been carried out using electrochemical cells to analyze for impurities. Thermodynamic data have been measured for the interaction of nuclear fuels with liquid potassium using cells based on $\text{ThO}_2\text{-Y}_2\text{O}_3$ electrolytes², so such cells could be used to monitor oxygen. Both the diffusion and electrochemical types of hydrogen and carbon meters should function satisfactorily in liquid potassium.

(M. G. BARKER)

1. A. P. Litman, U.S. Atomic Energy Comm. ORNL-3751 (1965); *Chem. Abstr.*, 63, 9558 (1965).
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7.2.2.4. in Rubidium and Cesium

7.2.2.4.1. Industrial Manufacture.

Rubidium is widely dispersed in nature, making up 99 ppm of the earth's crust but forming no minerals of its own and being always incorporated (up to 3%) in K (the only major element Rb can replace owing to similarity in size, charge and electronegativity) minerals such as lepidolites $\text{KLi}_2\text{Al}(\text{Si}_4\text{O}_{10})(\text{OH})_2$, biotites $\text{K}(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$, potash feldspars $\text{KAl}(\text{Al}, \text{Si})\text{Si}_2\text{O}_8$ and deposits of carnallite $\text{KMgCl}_3 \cdot 6 \text{H}_2\text{O}$. It is always found associated with Cs which creates difficulty in separation owing to their chemical and physical similarity. Cesium is less abundant (3 ppm of earth's crust) but forms two natural minerals, pollucite, $\text{Cs}_4\text{Al}_4\text{Si}_9\text{O}_{26} \cdot \text{H}_2\text{O}$ (up to 30% Cs), and rhodizite, a hydrated borate of Al, Be, Na and Cs (up to 0.3% Cs). The lepidolites, which are a source of Li, have assumed the most practical importance because Rb and Cs can be extracted together. Cesium is now extracted in appreciable quantities from pollucite, but the greatest potential source of these elements lies in the trace quantities held in the vast carnallite deposits^{1,2}.

Depending on the extraction method and the source of Rb and Cs, the elements are obtained in industry as chlorides, nitrates and carbonates. Methods of preparing and purifying all of the alkali metals are described with examples³. Methods for Rb and Cs are governed by the relative ease of reduction of their compounds, the volatility of the extracted metal and the extreme chemical reactivity of these heavier alkali metals toward air and moisture.

Rubidium and Cs metals were first obtained by electrolyzing their fused salts, but owing to the high chemical reactivity of the metals, special precautions are necessary that incur severe losses. Other methods based on the reduction at moderate temperatures by strong reducing elements (C, Si, Al, Fe, Zr, Na, Mg, Ca, Ba) of salts (M_2CO_3 , MCl , MOH , MCN , MCNS , MNO_3 , M_2SO_4 , M_2CrO_4 where $\text{M} = \text{Rb}$ or Cs) in an inert atmosphere or under vacuum have proved more suitable, especially if there are no gaseous products to contaminate the liberated alkali metal, which is invariably distilled. The combinations of starting material and reductant reviewed in refs. 1 and 4 are listed in Table 1. Reduction takes place only after intimate mixing and commences when the alkali metal salt or reducing metal melts. Hydrogen can provide a protective atmosphere, but the alkali metals form hydrides at relatively low T.

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Rubidium and Cs metals were first obtained by electrolyzing their fused salts, but owing to the high chemical reactivity of the metals, special precautions are necessary that incur severe losses. Other methods based on the reduction at moderate temperatures by strong reducing elements (C, Si, Al, Fe, Zr, Na, Mg, Ca, Ba) of salts (M_2CO_3 , MCl , MOH , MCN , MCNS , MNO_3 , M_2SO_4 , M_2CrO_4 where $\text{M} = \text{Rb}$ or Cs) in an inert atmosphere or under vacuum have proved more suitable, especially if there are no gaseous products to contaminate the liberated alkali metal, which is invariably distilled. The combinations of starting material and reductant reviewed in refs. 1 and 4 are listed in Table 1. Reduction takes place only after intimate mixing and commences when the alkali metal salt or reducing metal melts. Hydrogen can provide a protective atmosphere, but the alkali metals form hydrides at relatively low T.

TABLE 1. REAGENTS FOR THE PRODUCTION^a OF METALLIC R OR Cs

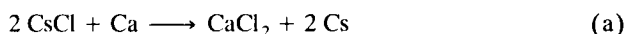
M salt	Reducing agent	M salt	Reducing agent
M ₂ O	Mg	M ₂ SO ₄	Fe
MOH	Al, C, Fe	M ₂ Cr ₂ O ₄	Al
M ₂ CO ₃	Mg + H ₂ , Fe	M ₂ Cr ₂ O ₇	Si-Al
MAIO ₂	Mg + H ₂	MMnO ₄	Si-Al
MCN	NiO	MHSO ₄	Zr
MNO ₃	Fe	M ₂ CrO ₄	Zr, Si ^b
MCl	Fe-CaC ₂	M ₂ Cr ₂ O ₇	Zr
		M ₂ SO ₄	Zr

^a Data from refs. 1 and 4.

^b C. Norris, L. Wallden, *Phys. Status Solidi*, A, 2, 381 (1970).

Contamination of metal with other distillates is largely overcome when reducing selected compounds with Zr since the alkali metal is then the only volatile species. **Mixtures of CsHSO₄ and Cs₂CrO₄ react explosively**, however, carrying particulates over, unless slow heating rates and a large excess of Zr are employed.

Reduction of the chlorides by Ba, Na or Ca is a satisfactory method of preparing small amounts of pure Rb and Cs. Rubidium chloride is dissolved in barium azide aq sol and evaporated at 25°C to dryness. The intimate mixture is then heated under vacuum. The Ba(N₃)₂ decomposes at ca. 100–200°C to Ba metal, which reduces RbCl to Rb; this distills at temperatures low enough to prevent contamination by Ba vapor. The most widely employed method uses Ca as the reducing agent:



The chloride is mixed on a laboratory scale with xs Ca (powder or chips) in an Fe tube in a high-T glass distillation vessel. The Fe tube protects the glass from corrosive attack by the alkali-metal vapors. The vessel is inclined and evacuated while slowly heating to 700–800°C. The liberated Rb or Cs distills onto the cooler upper walls of the vessel and runs into integral glass ampules, which are sealed under vacuum for storage. Further purification is achieved by repeated vacuum distillation at 300°C. Yields are theoretical.

Alternatively, Rb and Cs are prepared in small but hydride-free quantities for specialist purposes by the gradual thermal decomposition (ca. 390°C) of the metal azides, MN₃, under high vacuum. The evolved nitrogen is inert to these heavier alkali metals¹.

(R. J. PULHAM)

1. F. M. Perel'man, *Rubidium and Caesium*, Pergamon Press, Oxford, 1965.
2. B. Mason, *Principles of Geochemistry*, John Wiley & Sons, New York, 1966.
3. A. Hatterer, in *The Alkali Metals*, Spec. Publ. No. 22, The Chemical Society, London, 1967, pp. 317–369.
4. A. A. Eldridge, G. W. Dysun, A. J. E. Welch, D. A. Pantony, eds., *Mellors Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. II, Suppl. III, *The Alkali Metals*, Part 2. Longmans Green, London, 1963.

7.2.2. in the Group-IA Elements
 7.2.2.4. in Rubidium and Cesium
 7.2.2.4.3. Purification.

TABLE 1. TYPICAL PURITY OF Rb AND Cs

		Rubidium Purity (ppm)										
										Mg Ca Pb Cr		
		Cs	K	Na	Li	Fe	Al	Si		Mn	Ni	Cu
High-purity typical	99.93%	500	100	50	10	5	1	1				1
High-purity specification	99.8% (min.)	1000	1000	200	50	20	20	20				5
Technical typical	99.6%	2000	1000	1000	10	20	30	20				10
		Cesium Purity (ppm)										
										Mg Ca Pb Cr		
		Rb	Na	K	Li	Fe	Al	Si		Mn	Ni	Cu
High-purity typical	99.99%	40	40	20	10	5	5	1				1
High-purity specification	99.98% (min.)	100	100	100	10	10	10	5				5
Technical typical	99.7%	1000	1000	1000	10	20	20	20				10

7.2.2.4.2. Purity of the Commercial Metals.

Manufacturers usually supply both technical and high-purity grade metals, and these can be available as 1 g in glass ampules up to 4.5 kg in steel cylinders. One manufacturer's specification are reproduced in Table 1 to show what the buyer can expect. As might be expected, the other alkali metals are the major impurities in both Rb and Cs. There is less Rb in Cs than Cs in Rb owing to the specificity of pollucite for Cs, and Cs is purer overall than Rb. These metals are so easily contaminated by air during transfer to laboratory apparatus that Cs_2O (or lower oxides) become the major impurity. Manufacturers offer containers with valves or breaker seals for sealing directly on to apparatus.

(R. J. PULHAM)

7.2.2.4.3. Purification.

Three kinds of impurities are found in Rb and Cs: (a) foreign alkali and alkaline-earth metals, (b) transition and heavy metals and (c) nonmetals in the form of salts, e.g., M_2O , MOH , MH and M_2CO_3 . Whereas (a) and (b) are introduced either from the source mineral, the extraction method or the containment, the nonmetals in (c) are usually introduced during the subsequent handling. Reclamation of Rb and Cs, therefore, usually involves removal of the nonmetals. With such low-melting metals as Rb (mp 38.980°C) and Cs (mp 28.592°C), all purification processes involve the liquid state, and a first consideration is the choice of inert container and structural material. Borosilicate glass is used up to 300°C, but higher T encourages chemical replacement of B and Si in the boroaluminosilicate glass by Rb and Cs and contamination of the liquid metal by soluble metal oxide. Stainless steel is necessary for higher T. Solubilities of transition metals in liq Rb and Cs are collected in ref. 1. Values range from 1 to 30 ppm in Rb for Ti, Zr, V, Mo and W between 760 and 1100°C, with Fe showing

greater solubility at 10–125 ppm between 540 and 925°C. Cesium dissolves about 10 ppm Nb and Mo at 137°C. The solubilities of elements in all of the alkali metals are collected^{2,3} and the interactions of alkali metals with each other when dissolved in the liquid metal are described⁴.

(i) **Distillation.** Slow distillation under vacuum at low T successfully removes transition and heavy metals but is less efficient for the more volatile alkali metals and least effective for the separation of Rb from Cs owing to the similarity in their vapor pressures. Distillation cannot remove salts that are volatile or that decompose to give gases. Thus RbH and CsH, the least thermally stable of the alkali-metal hydrides, may dissociate and can lead to contamination of the distilland by subsequent recombination with hydrogen. When the distillates are remelted, the metal hydrides redissolve in the liquid metals; the solubility of H₂ in liq Cs (from 1.02 to 1.73 mol% H) has been determined⁵ over the range 300–400°C from pressure–composition isotherms:

$$\log(\text{ppm H}_2) = 3.46 - 900/T \text{ (K)} \quad (\text{a})$$

The T dependence of the solubility of CsH in Cs differs significantly from those for solutions of the hydrides in the other alkali metals². Distillation leaves behind involatile impurity salts, but oxygen transport from distilland to receiver has been observed³. Oxygen can be carried over with the distillate in the form of CO₂ or CO, the former being produced by decomposition of carbonate and the latter by reduction of oxides with a carbon impurity under dry conditions near the end of distillation. The identification of CO among the noncondensable gases during the distillation of Cs lends support to this⁷.

(ii) **Filtration.** The solubilities of salts in the liquid metals often diminish with decreasing temperature, being least just above the freezing point. Thus liq Na (mp 97.8°C) is purified by filtering the precipitated Na₂O impurity at 100°C, thereby reducing the concentration to ca. 1 ppm. Rubidium⁸ and Cs^{9–11}, however, dissolve large quantities of oxide at low T; the freezing point of Cs (28.592°C) is depressed by 40°C to form a eutectic at 16 mol% O before the hypereutectic liquidus subsequently rises through a succession of steps to the mp of Cs₂O, 485°C (Fig. 1). Thus liq Cs that has been filtered at 28.6°C can still hold up to 20 mol% O. Similarly for Rb. The steeper hypereutectic liquidi at lower oxygen concentrations in the analogous K (Fig. 1) and Na systems means that filtration at the freezing points becomes progressively more efficient at removing oxide impurity from Cs (and Rb) through K to Na¹².

(iii) **Gettering.** Liquid Rb and Cs are exposed to Zr, Ti, or Y, which extract the dissolved nonmetals from solution to form more thermodynamically stable, insoluble oxides, carbides, hydrides, etc., which adhere to the gettering metal. By this means the last traces of nonmetals may be removed, and gettering (or hot trapping) appears in principle to be the method most suitable for purifying these metals. The use of soluble getters such as Ca, Sr and Ba also reduces the nonmetal content by forming insoluble alkaline-earth compounds that can be filtered, but the disadvantage is that unused getter remains dissolved in the Rb or Cs.

(iv) **Recommended Purification.** The choice of methods for purifying Rb and Cs depends on the prior history of the metal. The metals can be purchased in sufficient purity that the only impurities of concern are those introduced from containers and by atmospheric contamination. When transition or heavy metals are present, then distillation is recommended. Filtration through a 10-μm sintered steel filter at

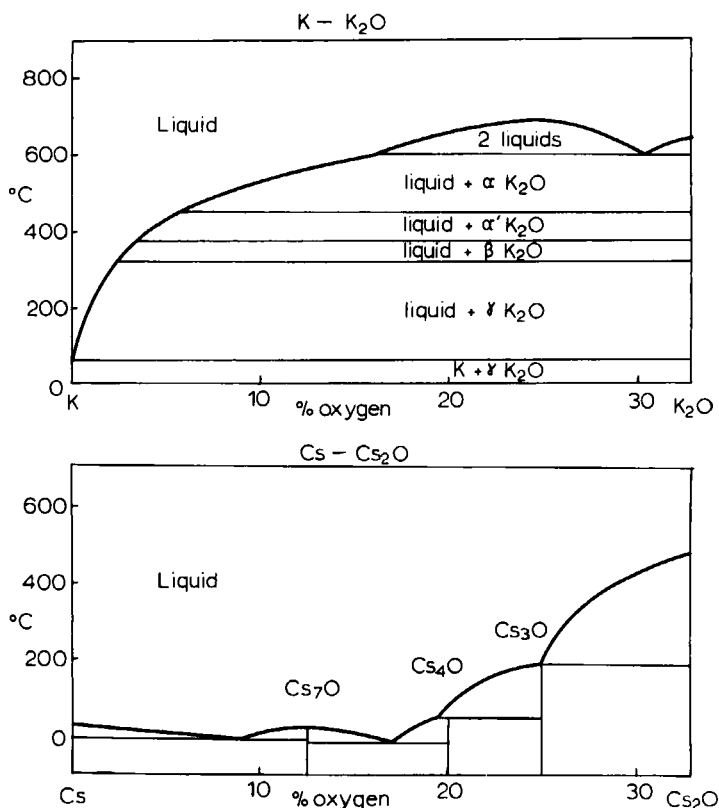


Figure 1. The Cs-O and K-O Phase Diagrams.

55–65°C removes metal particulates and C¹. Gettering with Zr foil (sponge gives a larger surface area) at 700°C for 24 h is recommended for the removal of the nonmetals, O, H and C¹. Stainless steel turnings also reduce both O and C contents.

(R. J. PULHAM)

1. J. W. Mausteller, F. Tepper, S. J. Rodgers, *Alkali-Metal Handling and Systems Operating Techniques*, Gordon & Breach, New York, 1967.
2. H. U. Borgstedt, C. K. Mathews, *Applied Chemistry of the Alkali Metals*, Plenum Press, New York, 1987.
3. R. W. Ohse, ed., *Handbook of Thermodynamic and Transport Properties of the Alkali Metals*, IUPAC, Blackwell Scientific Publications, Oxford, 1985.
4. C. C. Addison, *The Chemistry of the Liquid Alkali Metals*, John Wiley and Sons, Chichester, UK, 1984.
5. M. N. Arno'ldov, Yu. V. Bogdanov, M. N. Ivanovskii, B. A. Morozov, *Izv. Akad. Nauk. SSSR, Met.*, 4, 30 (1976).
6. W. Klemm, N. J. Scharf, *Z. Anorg. Allg. Chem.*, 303, 262 (1960).
7. T. Atharris, Natl. Co. Rept. ML-TDP-64-200, 1964, Malden, Mass.
8. Ph. Touzain, *Can. J. Chem.*, 47, 2639 (1969).

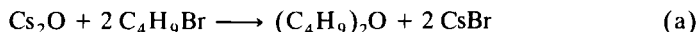
9. G. Braner, *Z. Anorg. Allg. Chem.*, 255, 101 (1947).
10. M. E. Rengade, *C.R. Hebd. Seances Acad. Sci.*, 148, 1199 (1909).
11. A. Simon, *Z. Anorg. Allg. Chem.*, 395, 310 (1973).
12. R. J. Pulham, *J. Pure Appl. Chem.* 49, 83 (1977).

7.2.2.4.4. Analysis for Impurities.

Reviews of analytical methods for impurities in alkali metals are largely devoted to Na and K owing to their use as liquid coolants in fast-breeder nuclear reactors¹⁻⁵. These methods may be extended to Rb and Cs except the analysis for oxygen. In analytical work with the alkali metals, care is necessary during sampling and handling to avoid contamination in transit. The impurities usually considered are O, C, N, H and metals.

(i) **Oxygen.** (a) **Amalgamation.** The metal sample is dissolved in Hg, leaving a residue of M_2O for titration with aqueous acid. The residue can contain M_2O , MOH , MH , M_2CO_3 and M_2C_2 , however, which also give alkali on hydrolysis. Therefore, the constituents of the residue are determined separately or the conditions prior to sampling are arranged to convert MOH and M_2CO_3 to M_2O and to dissociate MH . This method may not be applicable to Rb and Cs because the oxides may be soluble in both Hg and the amalgam.

(b) **Butyl halide.** The metal sample is consumed by C_4H_9Br , leaving a residue of M_2O , MOH , M_2CO_3 , and MH for analysis. The method may not be applicable to Rb and Cs owing to the formation of organometallic compounds that hydrolyze to increase the alkalinity. The analysis is also complicated by the reaction:



so that quantitative determination of $(C_4H_9)_2O$ by gas chromatography is also necessary.

(c) **Vacuum distillation.** The alkali metal is distilled leaving an involatile residue of salts for analysis. The oxides Rb_2O and Cs_2O may thermally decompose, giving oxygen that transfers with the distilland.

(d) **Vacuum fusion of getters.** The Zr or V getter, which has been equilibrated with the liquid alkali metal, is analyzed by vacuum fusion. The distribution coefficient for oxygen between the liquid metal and getter is needed. The method is applicable to Rb and Cs.

(e) **Activation methods.** All oxygen-containing species undergo the neutron activation process $^{16}O(n,p)^{16}N$, and the ^{16}N MeV γ radiation is measured by scintillation spectrometry. This method is applicable to all alkali metals and abolishes the need for blanks.

(f) **γ -Photon activation analysis.** This has been applied^{6,7} to Cs (and Na) to determine O and C using a linear accelerator to induce the reactions $^{16}O(\gamma,n)^{15}O$ and $^{12}C(\gamma,n)^{11}C$. The radioactive ^{15}O and ^{11}C species can be separated chemically for counting, thereby making the method applicable to impure as well as nearly pure metal. Impurity levels of 6 ppm O and 1 ppm C are found⁶ in distilled Cs.

(g) **Methanolysis.** The metal sample is dissolved in MeOH and the solution is neutralized with salicylic acid, *o*- $C_6H_4(OH)COOH$. The H_2O liberated from the M_2O is determined by Karl Fischer reagent (traditionally $I_2-SO_2-py-MeOH$). Possibly Rb_2O and Cs_2O react with the organic reagents and reduce the applicability.

7.2.2. in the Group-IA Elements
 7.2.2.4. in Rubidium and Cesium
 7.2.2.4.4. Analysis for Impurities.

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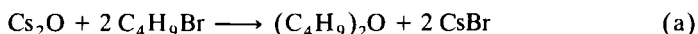
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(c) **Vacuum distillation.** The alkali metal is distilled leaving an involatile residue of salts for analysis. The oxides Rb₂O and Cs₂O may thermally decompose, giving oxygen that transfers with the distilland.

(d) **Vacuum fusion of getters.** The Zr or V getter, which has been equilibrated with the liquid alkali metal, is analyzed by vacuum fusion. The distribution coefficient for oxygen between the liquid metal and getter is needed. The method is applicable to Rb and Cs.

(e) **Activation methods.** All oxygen-containing species undergo the neutron activation process ¹⁶O(n,p)¹⁶N, and the ¹⁶N MeV γ radiation is measured by scintillation spectrometry. This method is applicable to all alkali metals and abolishes the need for blanks.

(f) **γ-Photon activation analysis.** This has been applied^{6,7} to Cs (and Na) to determine O and C using a linear accelerator to induce the reactions ¹⁶O(γ,n)¹⁵O and ¹²C(γ,n)¹¹C. The radioactive ¹⁵O and ¹¹C species can be separated chemically for counting, thereby making the method applicable to impure as well as nearly pure metal. Impurity levels of 6 ppm O and 1 ppm C are found⁶ in distilled Cs.

(g) **Methanolysis.** The metal sample is dissolved in MeOH and the solution is neutralized with salicylic acid, *o*-C₆H₄(OH)COOH. The H₂O liberated from the M₂O is determined by Karl Fischer reagent (traditionally I₂-SO₂-py-MeOH). Possibly Rb₂O and Cs₂O react with the organic reagents and reduce the applicability.

(h) Ammonolysis. The metal sample is dissolved in liq NH_3 , leaving a residue of M_2O for analysis. The formation of RbNH_2 and CsNH_2 can render the method inapplicable to Rb and Cs.

(i) Vacuum fusion with C. The oxide is converted to CO for analysis. The process may be complicated in the case of Rb or Cs by retention of metal in intercalation compounds of the type MC_8 .

(j) Depression of the freezing point. The depression of the freezing point of the metal is proportional to the concentration of dissolved oxide. This is the method most applicable to Rb and Cs, which show well-defined eutectic points in the $\text{M}-\text{M}_2\text{O}$ phase diagrams at high oxygen concentrations. It is not specific to O in theory, but O is the only nonmetal that depresses the fp of Rb and Cs. The depression is linear for both Rb and Cs up to 500 ppm, and the coefficients are $0.0017^\circ\text{C}/\text{ppm O}_2$ and $0.0024^\circ\text{C}/\text{ppm O}_2$, respectively¹.

(k) Electrochemical oxygen concentration cell. A galvanic cell comprising a $\text{Cu}-\text{Cu}_2\text{O}$ reference electrode and a solid $\text{ThO}_2-\text{Y}_2\text{O}_3$ electrolyte permeable only to O^{2-} ions dips into the liquid metal, which becomes the other electrode. The emf gives a measure of the M_2O activity or concentration in the liquid metal. The method is theoretically applicable to Na, K, Rb and Cs.

(ii) Carbon. Methods are designed to determine the different forms of carbon impurity: M_2C_2 or MHC_2 is converted to C_2H_2 ; M_2CO_3 to CO_2 ; and elemental C to CO_2 . All methods seem applicable, after modification, to Rb and Cs.

(a) Oxidation. This method relies on hydrolysis and analysis of liberated hydrocarbons followed by neutralization, giving CO_2 . Oxidation of residual C to CO_2 is by a mixture of $\text{H}_2\text{SO}_4-\text{H}_3\text{PO}_4-\text{K}_2\text{Cr}_2\text{O}_7$.

(b) Low-T combustion. Direct combustion of the metal sample in O_2 at 600°C is followed by acidification of the residue and estimation of the evolved CO_2 .

(c) High-T combustion. Direct combustion of metal in O_2 at 1100°C gives CO_2 directly for analysis.

(d) Low-T combustion of hydrolyzed metal. The metal is hydrolyzed to obtain hydrocarbon. Acidification then gives CO_2 from M_2CO_3 . Combustion of the evaporated solution at 600°C in O_2 gives CO_2 from elemental C.

(iii) Nitrogen. Although Rb and Cs do not form nitrides, the element is held in the metals as nitrides of impurity Li, Mg, Ca, Sr or Ba.

(a) Micronitride hydrolysis. Nitrides in sample are hydrolyzed to NH_3 , which is titrated with acid.

(iv) Hydrogen. Hydrogen can exist in the metals as MH or MOH, the latter being converted to MH and M_2O by the metal at high T; MH dissociates⁸ to H_2 and M.

(a) Vacuum extraction. The sample of metal is sealed into an Fe (or Ni) capsule and heated under vacuum to 700°C to liberate H, which diffuses through the capsule wall for measurement.

(b) Isotope dilution. The metal is equilibrated with D_2 , and the isotopic ratio H:D of the gas phase is determined by mass spectrometry.

(c) Low-T amalgamation. The sample is dissolved in Hg below 300°C to prevent MOH decomposition and the isolated MH is hydrolyzed to H_2 .

(v) Metallic impurities. The methods² for determining metallic impurities in Na, K and NaK are also applicable to Rb and Cs. Wet chemical methods involving colorimetric determinations are used for Al, Ca, Cr, Cu, Fe, Ni, Nb, Ti, W and Zr.

Flame photometry and atomic absorption can be used to determine one alkali metal in the presence of others. Emission spectrographic analysis is both rapid and sensitive; the limit of detection, e.g., of Na or K in Rb and Cs is 10 ppm but can be as low as 1 ppm in certain cases. Neutron activation analysis is one of the most sensitive analytical techniques available and is also capable of determining one alkali metal in the presence of another. Sensitivities (ppm), e.g., are Fe, Mg, Ca (1); Sr (0.1); K, Al, Ba, Cs, Rb (0.01); Na (0.001)¹.

(R. J. PULHAM)

1. J. W. Mausteller, F. Tepper, S. J. Rodgers, *Alkali-Metals Handling and Systems Operating Techniques*, Gordon & Breach, New York, 1967.
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3. A. W. Thorley, A. C. Raine, in *The Alkali Metals*, Spec. Publ. No. 22, The Chemical Society, London, 1967, pp. 374–392.
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5. R. W. Ohse, ed., *Handbook of Thermodynamic and Transport Properties of the Alkali Metals*, IUPAC, Blackwell Scientific, Oxford, 1985.
6. C. Engleman, F. Nordman, G. Tinelli, in *Liquid Alkali-Metals*, British Nuclear Energy Soc., London, 1973, pp. 71–75.
7. C. Persianic, J. Spira, R. Bastian, *Talanta*, 14, 565 (1967).
8. C. C. Addison, *The Chemistry of the Liquid Alkali Metals*, John Wiley and Sons, Chichester, UK, 1984.

7.2.2.5. In Francium

Francium is produced by the α decay of Ac, which decays mostly by β emission. However, ca. 1% of the decays are by α emission, giving ^{223}Fr , the isotope with the longest half life ($t_{1/2} = 1260$ s). Rapid separation techniques are necessary to isolate this short-lived species from the complex mixture. One way is to separate the ^{227}Th and ^{223}Ra daughters from the Ac mother and then separate the monovalent Fr from the trivalent Ac. Other major isotopes of Fr have even shorter lifetimes.

Isotope	203	204	205	206	207	208	209	210	
$t_{1/2}$ (s)	0.7	3.3	3.7	16	15	60	52	192	
Isotope	211	212	213	218	219	220	221	222	224
$t_{1/2}$ (s)	180	1140	34	0.0005	0.02	27.5	288	900	120

These are produced by bombarding Th or U with 100-MeV protons, or lighter targets with 100-MeV heavier ions produced in cyclotrons or linear accelerators. Thus the complete fusion of targets such as Pb, Au or Tl with the projectiles B, C, O, N or Ne produces¹ Fr isotopes below mass number 223.

The nonnuclear chemistry of Fr reduces to studies of coprecipitation in which Fr shows the behavior of the heavier alkali metal. Coprecipitation is followed by ion exchange to concentrate Fr². Physical (mp, density, crystal parameters) and chemical (thermodynamics, solvation entropies) properties are theoretically derived or extrapolated from the trends exhibited by the other alkali metals.

(R. J. PULHAM)

7.2. Formation of Group-IA or -IIA-IA or -IIA Metal Bonds

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7.2.2. in the Group-IA Elements

7.2.2.5. In Francium

Flame photometry and atomic absorption can be used to determine one alkali metal in the presence of others. Emission spectrographic analysis is both rapid and sensitive; the limit of detection, e.g., of Na or K in Rb and Cs is 10 ppm but can be as low as 1 ppm in certain cases. Neutron activation analysis is one of the most sensitive analytical techniques available and is also capable of determining one alkali metal in the presence of another. Sensitivities (ppm), e.g., are Fe, Mg, Ca (1); Sr (0.1); K, Al, Ba, Cs, Rb (0.01); Na (0.001)¹.

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7.2.3. In the Group-IIA Elements

The natural occurrence of the group-IIA elements ranges from common to rare; e.g., Ca is 5th in the order of atomic abundance of the elements in the earth's crust, Mg is 7th, Ba and Sr are 21st and 22nd, respectively, and Be is 32nd¹. Radium is of extremely limited availability. It does occur naturally, although it has neither stable nor long-lived radioactive isotopes; it is found in association with U, since ^{230}Ra ($t_{1/2} = 1.6 \times 10^3$ years) is a daughter product in the radioactive decay of ^{238}U ². Selected data on the distribution of these elements in various natural environments are collected in Table 1.

The electronic configuration of the group-IIA elements, [inert gas] ns^2 , render them so reactive that they never occur native but are always combined with other elements. Thus, Be is found in complex silicate minerals; Mg, Ca, Sr and Ba, however, occur in carbonate, sulfate or phosphate ores. Consequently, whereas the extractive metallurgy of Be is relatively complex, that for the other elements is quite straightforward.

Although Be is a light, strong metal with a very high melting point, it is rather brittle and of limited ductility; hence it is little used as a structural material. Nonetheless, its nuclear properties (low neutron capture cross-section and high neutron scattering cross-section) render it very effective as a moderator in nuclear reactor technology. The principal use for metallic Be, however, is as an alloying component; it imparts hardness to Cu, Ni, Ni-Fe and Ni-Cr-Fe alloys, oxidation resistance to Mg and fluidity to Al alloys.

Magnesium is a light, moderately strong metal with good ductility and malleability. Its structural integrity can be improved by alloying with Al and/or Zn; other elements such as Mn, Th and the lanthanides are also added for special purposes. Magnesium is also employed as an alloying component. When added to commercial Al, it imparts better mechanical properties and improves weldability as well as corrosion resistance; it is also added to Zn to improve creep strength. These Mg and Mg-containing alloys are used primarily in the aircraft and automotive industries for applications where a high strength to weight ratio is desirable.

TABLE 1. NATURAL ABUNDANCE OF THE GROUP-IIA METALS (wt%)

Element	Igneous rocks	Clays and shales	Meteorites	Lunar rocks	Oceans
Be	3.8×10^{-4}	3.0×10^{-4}	3.6×10^{-4}	3.3×10^{-4}	—
Mg	1.87	1.34	14.0	4.4	0.131
Ca	2.96	2.53	1.40	10.3	4.2×10^{-2}
Sr	3.4×10^{-2}	4.5×10^{-2}	1.0×10^{-3}	1.7×10^{-2}	1.0×10^{-3}
Ba	6.5×10^{-2}	8.0×10^{-2}	6.0×10^{-4}	2.1×10^{-2}	3.0×10^{-6}

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The chemical reactivity of metallic Mg has been utilized in several ways. It is employed in the reduction step in the manufacture of Ti, in the deoxidation and desulfurization of steels and in the nodularization of cast iron. It has also been used for the preparation of photoengraving plates, in dry batteries, and as a sacrificial anode for cathodic protection of other metals.

Neither Ca, Sr nor Ba metal has any structural integrity. The principal application of metallic Ca is as a reducing agent in the preparation of metals, such as Th and Zr. Like Mg, it can be used in the deoxidation and desulfurization of steels. Small quantities are used for alloying with Al and for the removal of Bi from Pb. Neither Sr nor Ba have any significant commercial uses. Barium is used to a limited extent as a getter to remove reactive gases from vacuum tubes.

(P. HUBBERSTEY)

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7.2.3.1. in Beryllium

The principal minerals of Be are listed in Table 1, the most abundant being beryl, the only one of commercial significance. Phenacite, chrysoberyl, bertrandite and barylite are constituents of recently discovered Be-containing deposits; future extraction of Be from these ores is currently being considered. The other minerals are not found in sufficient quantities to constitute possible commercial sources of Be. The majority of the ores, including beryl, are complex silicate materials from which it is difficult to extract the metal; consequently, Be extractive metallurgy is both complex and expensive.

Beryllium and its compounds are toxic: they must be handled with extreme caution.

(P. HUBBERSTEY)

TABLE 1. BERYLLIUM MINERALS

Mineral	Composition	Approximate Be content (wt%)
Beryl	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	5
Phenacite	Be_3SiO_4	16
Chrysoberyl	BeAl_2O_4	7
Bertrandite	$\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$	15
Barylite	$\text{BaBe}_2\text{Si}_2\text{O}_7$	6
Helvite	$[\text{Mn, Fe, Zn}]_4\text{Be}_3\text{Si}_3\text{O}_{12}\text{S}$	5
Herderite	$\text{CaBe}(\text{PO}_4)(\text{OH, F})$	6
Euclase	$\text{BeAlSiO}_4(\text{OH})$	6
Gadolinite	$\text{Be}_2\text{Y}_2\text{FeSi}_2\text{O}_{10}$	4

7.2. Formation of Group-IA or -IIA-IA or -IIA Metal Bonds

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7.2.3. in the Group-IIA Elements

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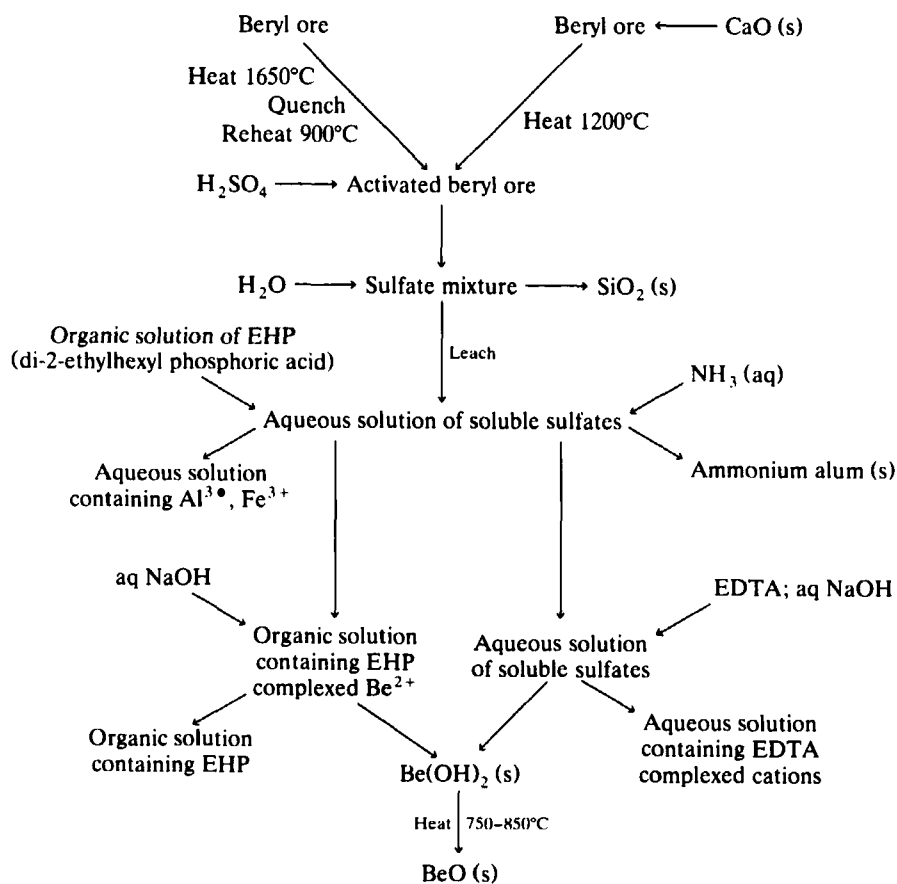
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Bertrandite	$\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$	15
Berylite	$\text{BaBe}_2\text{Si}_2\text{O}_7$	6
Helvite	$[\text{Mn}, \text{Fe}, \text{Zn}]_4\text{Be}_3\text{Si}_3\text{O}_{12}\text{S}$	5
Herderite	$\text{CaBe}(\text{PO}_4)(\text{OH}, \text{F})$	6
Euclase	$\text{BeAlSiO}_4(\text{OH})$	6
Gadolinite	$\text{Be}_2\text{Y}_2\text{FeSi}_2\text{O}_{10}$	4

7.2.3.1.1. Industrial Manufacture.

Commercial methods for extracting Be are of two types. Initially, beryl is converted in a multistage chemical process into pure BeO [or $\text{Be}(\text{OH})_2$]; the oxide is subsequently reduced to metallic Be using chemical or electrolytic methods. Many processes have been patented for the extraction of BeO [or $\text{Be}(\text{OH})_2$] from beryl, but only two are currently commercial; these are the sulfate and the complex fluoride processes.

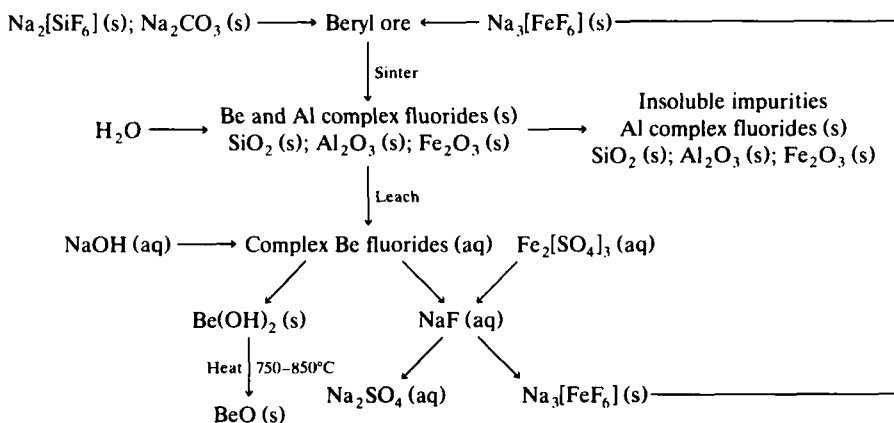
The sulfate process is based on the attack of activated beryl by sulfuric acid to form water-soluble Be and Al sulfates and insoluble silica. A flow diagram summarizing this process is given in Scheme 1. Activated beryl must be used since the natural ore is resistant to acid attack except by HF , which is prohibitively expensive. High-grade beryl ore ($> 10\%$ BeO) is normally activated by a heat-treatment process


Scheme 1

in which the ore is melted (mp 1650°C) and then quenched in water. The resultant glass is reheated to 900°C for a short time to increase further its chemical reactivity. The increase in reactivity is thought to be due to the crystallization of, e.g., BeAl_2O_4 , BeO and $\text{Al}_6\text{Si}_2\text{O}_{13}$. Low-grade beryl ore (<10% BeO) is rendered active by alkali attack. A friable, reactive product is obtained by fusing the ore with an alkali (normally CaO , but NaOH , KOH , Na_2CO_3 or K_2CO_3 may be used) and quenching the molten mixture in water. Amended versions of this method involve sintering (rather than fusion) of the ore- CaO charge, and using hot aqueous alkalis under pressure. The mechanism of the alkali attack is uncertain, but it leads to complete chemical breakdown of the beryl ore.

The activated beryl is treated with sulfuric acid; the soluble metal sulfates so formed are leached with water and separated from the insoluble products, principally silica. The traditional method for Be recovery from the sulfate solution is a two-stage process; initially, Al is removed by crystallization as ammonium alum, $[\text{NH}_4]_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$, by adding $[\text{NH}_4]_2\text{SO}_4$ or simply NH_3 . The BeSO_4 -rich filtrate is then treated with chelating agents (e.g., EDTA) to retain impurities such as Fe in solution, before precipitation of granular $\text{Be}(\text{OH})_2$ by addition of NaOH . This method is now being superseded by solvent extraction methods using cation-exchange solvents such as di-(2-ethylhexyl) phosphoric acid; the selectivity of this solvent for Be^{2+} in the presence of Al^{3+} and Fe^{3+} is satisfactory in the pH range 0–3. The Be is recovered from the solvent by washing with aqueous alkali. Alternatively, 1-(3-ethylpentyl)-4-ethylodolamine, can be used to extract Be^{2+} selectively from the sulfate liquors in the pH range 2–3. The Be is recovered by treatment of the solvent with molar H_2SO_4 . The Be is extracted from the resultant solutions by precipitation as $\text{Be}(\text{OH})_2$, which may be converted readily to BeO by calcining at ca. 750–850°C.

The complex fluoride process consists of roasting beryl with $\text{Na}_2[\text{SiF}_6]$ (or $\text{Na}_3[\text{FeF}_6]$) at 700–750°C and leaching the product with water to extract the soluble beryllium fluorides. A flow diagram summarizing this process is given in Scheme 2.



Scheme 2

The process consists of heating a 1 : 6 beryl : $\text{Na}_2[\text{SiF}_6]$ molar ratio to a temperature of 750°C . The ensuing reaction is complex, the principal products being $\text{Na}[\text{BeF}_3]$, $\text{Na}_2[\text{BeF}_4]$, $\text{Na}_2[\text{AlF}_5]$, $\text{Na}_3[\text{AlF}_6]$ and SiO_2 . The roast material is extracted with water, when the soluble Be-containing products are separated from the insoluble Al- and Si-containing products; this procedure is highly selective for Be, and the filtrate is remarkably free of impurities. The Be is precipitated as $\text{Be}(\text{OH})_2$ at pH 12 by adding NaOH ; the hydroxide is converted readily to BeO by calcining at about $750\text{--}850^\circ\text{C}$. A slightly purer product may be obtained by redissolving the $\text{Be}(\text{OH})_2$ in a minimum amount of xs NaOH , heating the solution to $45\text{--}50^\circ\text{C}$ to coagulate the alkali-insoluble impurities [principally $\text{Fe}(\text{OH})_3$], filtering and precipitating granular $\text{Be}(\text{OH})_2$ by boiling the clarified beryllate solution.

The process is improved by minimizing the loss of fluorine (as NaF solution effluent) by precipitating it from the effluent as $\text{Na}_3[\text{FeF}_6]$ by the addition of $\text{Fe}_2[\text{SO}_4]_3$; this complex fluoride can then be substituted for $\text{Na}_2[\text{SiF}_6]$ in the original process. A further improvement reduces loss of SiF_4 (a decomposition product of $\text{Na}_2[\text{SiF}_6]$) from the reaction mixture by addition of NaF or Na_2CO_3 . Addition of NaF suppresses the decomposition equilibrium:



whereas addition of Na_2CO_3 leads to the production of more $\text{Na}_2[\text{SiF}_6]$:

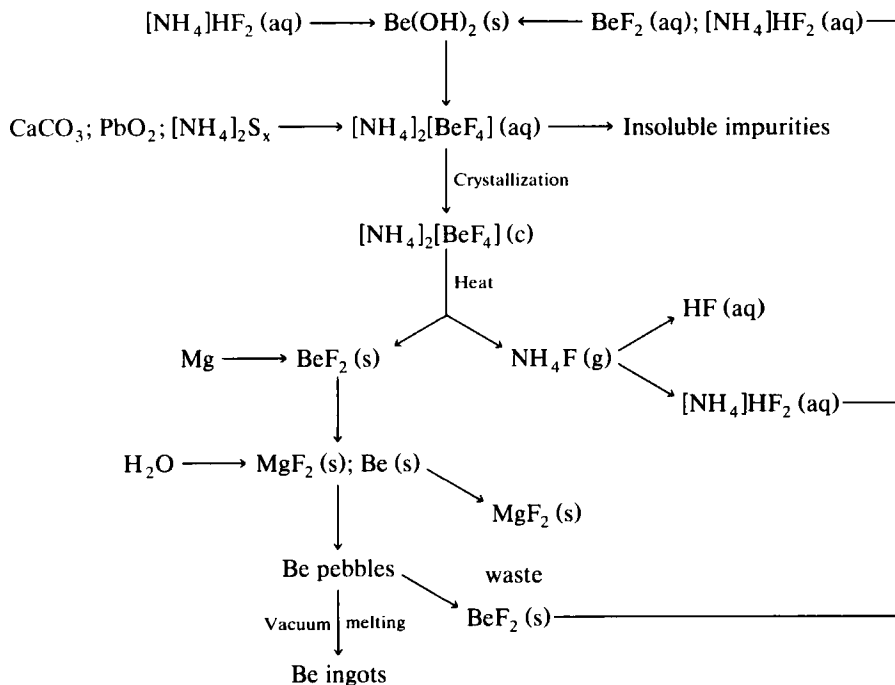


In addition to the complex fluorides described above (i.e., $\text{Na}_2[\text{SiF}_6]$ and $\text{Na}_3[\text{FeF}_6]$, several other materials have been tried as fluorinating agents, including HF , either in the free gaseous form, or combined as in the acid fluorides, NaHF_2 and $[\text{NH}_4]\text{HF}_2$, and the salts, CaF_2 , NaF , NH_4F , $\text{FeF}_3 \cdot x \text{H}_2\text{O}$ and $\text{AlF}_3 \cdot x \text{H}_2\text{O}$; with the exception of NaHF_2 , none of these fluorinating agents is commercial.

Several other processes for extracting Be from beryl have been patented; the most feasible involves the formation of BeCl_2 by direct chlorination of beryl under reducing conditions; several volatile chlorides are produced by this reaction (BeCl_2 , AlCl_3 , SiCl_4 and FeCl_3) and are separated by fractional condensation to give the product in a pure state. Other methods involve the fusion of beryl with carbon and pyrites, with calcium carbide and with silicon.

Only two processes for the manufacture of Be are of industrial importance: (i). the thermal reduction of BeF_2 using Mg , and (ii) the electrolysis of BeCl_2 in a molten chloride electrolyte. Direct reduction of the oxide is ineffective because of its thermodynamic stability; only Ca reduces BeO to the metal; unfortunately, Ca cannot be used since it forms a stable intermetallic compound with Be, Be_{13}Ca .

The principal method for the manufacture of Be from BeO involves formation of BeF_2 via $\text{Be}(\text{OH})_2$ and $[\text{NH}_4]_2\text{BeF}_4$, followed by reduction using Mg metal; the process is summarized in the flow diagram in Scheme 3. Solution of $\text{Be}(\text{OH})_2$, together with scrap Be and BeO , in aq $[\text{NH}_4]\text{HF}_2$ gives an impure $[\text{NH}_4]_2\text{BeF}_4$ solution, which can be purified by successive addition of: (i) CaCO_3 to precipitate Al as $\text{Al}(\text{OH})_3$, (ii) PbO_2 to precipitate Mn and Cr as MnO_2 and PbCrO_4 and (iii) $[\text{NH}_4]_2\text{S}_x$ to precipitate Cu, Pb and Ni as Cu_2S , PbS and NiS . After filtration of these

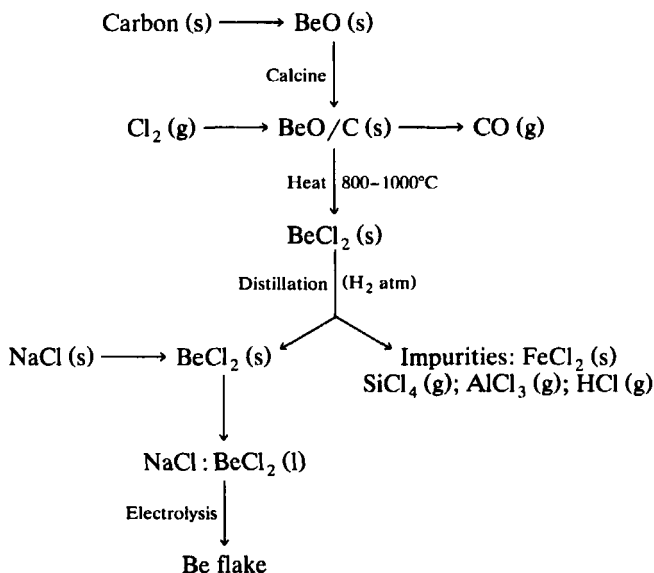


Scheme 3

insoluble impurities, the solution is concentrated to yield crystalline $[\text{NH}_4]_2\text{BeF}_4$. Thermal decomposition gives BeF_2 and volatile NH_4F , which is trapped and recycled. Excess BeF_2 is then heated with Mg to form Be ; the reaction proceeds rapidly at 900°C , but heating above 1300°C (i.e., above the mp of Be and MgF_2) facilitates separation of the products.

The alternative method for the manufacture of Be is based on the electrolysis of BeCl_2 produced by carbon reduction of BeO in the presence of Cl_2 ; a flow diagram summarizing the process is given in Scheme 4. Beryllium oxide is mixed with carbon and a binder such as wood tar; the mixture is fabricated into a briquette, calcined to form a dry, porous BeO-C mixture and heated in Cl_2 to $800\text{--}1000^\circ\text{C}$ to form BeCl_2 . Distillation in a stream of H_2 at $500\text{--}550^\circ\text{C}$ separates the BeCl_2 from the other volatile impurities (e.g., HCl , AlCl_3 , SiCl_4), the nonvolatile impurities (e.g., FeCl_2 , produced by H_2 reduction of FeCl_3) being retained in the furnace. Electrolysis of an equimolar $\text{BeCl}_2\text{--NaCl}$ mixture, fused in a Ni crucible under a protective Cl_2 atmosphere, is used, although use of BeCl_2 in a LiCl-KCl eutectic mixture has been suggested. Normally, the cathode is Ni or Fe , and the anode is graphite or Fe . The operating T are $350\text{--}400^\circ\text{C}$ for the $\text{BeCl}_2\text{--NaCl}$ electrolyte and $450\text{--}550^\circ\text{C}$ for the $\text{BeCl}_2\text{--LiCl-KCl}$ electrolyte. The Be flake so obtained is 99.5% pure.

Other methods include thermal reduction of BeO , using either Ti or Zr , thermal reduction of BeCl_2 , using either Li , Na , K , Mg or Ca , and thermal decomposition of



Scheme 4

BeI₂ using a hot wire technique, but none of these processes has industrial application.

(P. HUBBERSTEY)

7.2.3.1.2. Laboratory Preparation.

Since Be is readily available in various forms and specifications, there is little reason to prepare it in the laboratory; however, it is possible to adapt any of the extraction processes described previously (see §7.2.3.1.1) to small-scale experiment. Also Be powder can be prepared by gas-phase reduction of BeCl₂ using Na vapor¹ or H₂². Thermal reduction methods include high-T reduction of BeO using Ti, in a vacuum or an atmosphere of H₂³, and reduction of a mixture of BeF₂ and either NaF or KF with Na or Mg at 850°C in a partial vacuum⁴. Electrodeposition of Be metal from solutions of BeCl₂⁵, BeNO₃⁵, Be[CH₃COO]₂¹ and Be₄O[CH₃COO]₆¹ in liq NH₃ has also been reported.

(P. HUBBERSTEY)

1. J. M. Tien, *Trans. Electrochem. Soc.*, **89**, 237 (1946).
2. L. Hackspill, J. Besson, *Bull. Soc. Chim. Fr.*, **16**, 113 (1949).
3. W. Kroll, *Z. Anorg. Allg. Chem.*, **240**, 331 (1939).
4. R. Rohrer, *C.R. Hebd. Seances Acad. Sci.*, **214**, 744 (1942).
5. H. S. Booth, G. G. Torrey, *J. Phys. Chem.*, **35**, 3111 (1931).

7.2.3. in the Group-IIA Elements

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7.2.3.1. in Beryllium

7.2.3.1.3. Purity and Purification.

7.2.3.1.3. Purity and Purification.

Metallic Be prepared using the commercial methods outlined in §7.2.3.1.1 is impure; whereas Be pebbles from thermal reduction processes (typical assay 97%) contain Mg (1.5 wt%), flakes produced by electrolytic methods (typical assay 99.5%) contain some Cl (0.15 wt%), but few metallic impurities. Vacuum melting and casting is the standard technique for purifying Be pebbles and has been used to treat flake Be; Mg and Cl content can be reduced to 0.05 and 0.005 wt%, respectively. Since powder metallurgy is preferred for Be fabrication, flake Be is treated by methods that do not involve consolidation; the flake is dry ball-milled, sieved, leached with 10% oxalic acid and vacuum dried. The Cl content is reduced to 0.02 wt%. Analysis of typical commercial-grade vacuum-cast Be ingots and milled and leached Be flake are given in Table 1.

TABLE 1. TYPICAL ANALYTICAL DATA^a FOR PURIFIED SAMPLES OF BERYLLIUM ($\mu\text{g g}^{-1}$)

Impurity	Al	Cr	Cu	Fe	Mg	Mn	N	Ni	O	Si
Commercially available beryllium ¹										
Vacuum melted and cast	600	90	—	1100	500	70	—	130	—	—
Milled flake	40	6	—	200	20	7	80	—	3000	30
Vacuum distillation, single-cycle ²										
As received	25	8	145	60	15	25	12	70	2240	40
1st distillate	20	50	50	110	8	35	—	70	10	20
Vacuum distillation, two-cycle ³										
As received	1000	200	250	6500	—	500	100	300	—	3000
1st distillate	20	40	5	60	—	20	10	10	—	100
2nd distillate	10	—	5	12	—	10	10	10	—	30
Vacuum distillation, five-cycle ⁴										
As received	200	200	500	4000	100	200	—	50	4000	3000
1st distillate	25	50	170	500	6	5	—	20	100	50
2nd distillate	25	20	50	100	4	3	—	20	—	30
5th distillate	10	20	6	10	2	2	—	20	70	16
Zone refined, five passes ¹⁷										
As received	75	10	85	225	—	20	—	115	—	20
Front sample	20	5	—	50	—	5	—	220	—	20
Rear sample	960	110	10	1290	—	230	—	30	—	40
Zone refined, six passes ¹⁷										
As received	50	—	5	15	—	—	—	30	—	20
Front sample	5	—	10	5	—	—	—	80	—	20
Rear sample	50	—	5	76	—	—	—	10	—	20
Crystallization from Be-Al alloys ¹⁶										
As received	9	—	5	5	8	25	—	30	—	—
Crystalline sample	1200	—	120	0.3	—	3	—	3	—	—

^a All quoted data are maximum values.

Ultra-high-purity Be is normally prepared from commercially available Be flake by vacuum distillation²⁻⁹, zone refining¹⁰⁻¹⁵ and crystallization from a liquid metal solvent¹⁶. Single-cycle vacuum distillation² of high-purity Be flake, previously vacuum melted and cast, from a Ta crucible heated by an electron bombardment furnace at 1400–1500°C gives products whose analytical figures are included in Table 1². Two-³ and five-cycle⁴ Be distillation give analytical figures, collated in Table 1, indicative of the effectiveness of the technique. A crucible-free vacuum induction, melting, casting and distillation process for preparing very high-purity polycrystalline Be has been reported⁶⁻⁸.

The zone-refining technique has been applied to Be purification. Typical analytical data for zone-refined samples are given in Table 1¹⁷. These data show that zone refining concentrates Fe, Al, Mn and Cr at the front of the sample and Ni and Cr at its base; furthermore, it appears to have no effect at all on Si distribution¹⁷. The influence of an electric field¹³ and the effect of H₂¹⁴, N₂¹⁴ and Al¹⁵ on zone-refining purification techniques have also been assessed.

Crystallization of Be from a Be-Al alloy is effective for removing Fe, Mn and Ni but leads to an enrichment in Al, Cu and Mg; typical analytical data are included in Table 1¹⁶.

Finally¹⁸, remarkable analytical figures result for Be purified by a sequence of techniques. Thus, commercially available, vacuum-melted and hot-extracted Be was given two floating-zone passes, followed by distillation using a high-vacuum crucible-free technique. The highest purity distillate produced contains only 8×10^{-4} at% impurities, $5 \mu\text{g g}^{-1}$ oxygen, $3 \mu\text{g g}^{-1}$ carbon, with the balance being the sum of the other elements¹⁸.

(P. HUBBERSTEY)

1. G. E. Darwin, J. H. Buddery, *Metallurgy of the Rarer Metals—Beryllium*, Butterworths, London, 1960, pp. 99, 102.
2. C. S. Pearsall, U.S. Atomic Energy Commission Rept., MIT-1104 (1952).
3. K. D. Sinelnikov, V. E. Ivanov, V. M. Amonenko, V. D. Burlakov, *Proc. 2nd U.N. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 3, Geneva, 1958; *Chem. Abstr.*, 54, 6457d (1960).
4. G. F. Tikhinskii, I. N. Khristenko, *Izv. Akad. Nauk SSSR, Met.*, 90 (1969).
5. V. E. Ivanov, B. M. Amonenko, G. F. Tikhinskii, I. I. Papirov, L. N. Ryabchikov, V. N. Grinyuk, in 3rd Int. Conf. Met. Beryllium, Grenoble, France, 1965, p. 33; *Chem. Abstr.*, 67, 84,259 (1967).
6. R. F. Bunshah, in 3rd Int. Conf. Met. Beryllium, Grenoble, France, 1965, p. 63; *Chem. Abstr.*, 67, 86,903 (1967).
7. R. F. Bunshah, R. S. Juntz, *Met. Soc. Conf.*, 33, 1 (1964), publ. 1966; *Chem. Abstr.*, 66, 87,975 (1967).
8. R. F. Bunshah, U.S. Atomic Energy Commission Rept., UCRL-12253 (1965); *Chem. Abstr.*, 63, 10,950c (1965).
9. B. L. Blanc, in 3rd Int. Conf. Met. Beryllium, Grenoble, France, 1965, p. 39; *Chem. Abstr.*, 67, 102,331 (1967).
10. C. S. Pearsall, U.S. Atomic Energy Commission Rept., MIT-1103 (1952); *Chem. Abstr.*, 48, 93i (1954).
11. V. N. Grinyuk, I. I. Papirov, G. P. Tikhinskii, I. G. D'yakov, *Izv. Akad. Nauk SSSR, Met.*, 77 (1967); *Chem. Abstr.*, 67, 110,956 (1967).
12. B. Schaub, G. Cabanne, *C.R. Hebd. Seances Acad. Sci.*, 257, 444 (1963).
13. B. Schaub, C. Potard, in 3rd Int. Conf. Met. Beryllium, Grenoble, France, 1965, p. 87; *Chem. Abstr.*, 67, 102,333 (1969).
14. B. Schaub, R. Kuentz, J. P. Nolin, in 3rd Int. Conf. Met. Beryllium, Grenoble, France, 1965, p. 81; *Chem. Abstr.*, 67, 102,332 (1967).

15. B. Schaub, P. Desre, in 3rd Int. Conf. Met. Beryllium, Grenoble, France, 1965, p. 93; *Chem. Abstr.*, 67, 102,336 (1967).
16. C. Potard, in 3rd Int. Conf. Met. Beryllium, Grenoble, France, 1965, p. 95; *Chem. Abstr.*, 67, 102,337 (1967).
17. S. Talbot, in *Monographies sur les Metaux de Haute Purete*, G. Chaudron, ed., Vol. 2, Masson, Paris, 1977, p. 88; *Chem. Abstr.*, 88, 125,140 (1978).
18. G. J. London, M. Herman, in 3rd Int. Conf. Met. Beryllium, Grenoble, France, 1965, p. 21; *Chem. Abstr.*, 67, 84,263 (1967).

7.2.3.2. in Magnesium

The principal minerals of Mg are listed in Table 1. The carbonates and silicates are widely distributed in large deposits; dolomite and magnesite are often used for Mg production, the extractive metallurgy being relatively simple. Other minerals employed as commercial sources of Mg are the sulfates and chlorides, particularly carnallite, which are found in salt beds and are constituents of saline springs, salt lakes and the oceans. Indeed, the majority of Mg produced is derived from the oceans, which contain 0.3% MgCl_2 , 0.18% MgSO_4 and 0.04% MgBr_2 .

(P. HUBBERSTEY)

7.2.3.2.1. Industrial Manufacture.

Metallic Mg is produced industrially using both electrolytic and thermal reduction methods. The electrolytic processes differ primarily in the choice of electrolyte—anhyd MgCl_2 , partially hydrated $\text{MgCl}_2 \cdot x \text{H}_2\text{O}$ and MgO . The more important thermal reduction processes use FeSi, Al alloys or C as reducing agents.

Most Mg metal is manufactured by electrolysis of either anhydrous or partially hydrated MgCl_2 from sea water. Addition of CaO to sea water precipitates Mg(OH)_2 ,

TABLE 1. MAGNESIUM MINERALS

Mineral	Composition	Approximate Mg content (wt%)
Magnesite	MgCO_3	28
Hydromagnesite	$3 \text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 3 \text{H}_2\text{O}$	27
Dolomite	$\text{MgCO}_3, \text{CaCO}_3$	13
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	19
Serpentine } Chrysotile }	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	26
Olivine	$[\text{Mg}, \text{Fe}]_2\text{SiO}_4$	28
Enstatite	MgSiO_3	24
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	18
Epsomite	$\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$	10
Langbeinite	$2 \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$	12
Kainite	$\text{MgSO}_4 \cdot \text{KCl} \cdot 3 \text{H}_2\text{O}$	10
Bischofite	$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	12
Carnallite	$\text{MgCl}_2 \cdot \text{KCl} \cdot 6 \text{H}_2\text{O}$	9

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7.2.3.2. in Magnesium

7.2.3.2.1. Industrial Manufacture.

15. B. Schaub, P. Desre, in 3rd Int. Conf. Met. Beryllium, Grenoble, France, 1965, p. 93; *Chem. Abstr.*, 67, 102,336 (1967).
16. C. Potard, in 3rd Int. Conf. Met. Beryllium, Grenoble, France, 1965, p. 95; *Chem. Abstr.*, 67, 102,337 (1967).
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(P. HUBBERSTEY)

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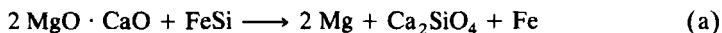
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which after filtration is dissolved in aq HCl and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ crystallizes from the resultant solution. Thermal decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in air leads to partially hydrated MgCl_2 ; thermal decomposition in the presence of MCl (M = Li, Na, K), Cl_2 or HCl, however, gives anhyd MgCl_2 .

Anhydrous MgCl_2 is electrolyzed in a suitable mixture with NaCl or KCl at 675–725°C; the Cl_2 formed as a by-product is employed to produce more MgCl_2 by reaction with MgO (or MgCO_3) and carbon. A similar electrolyte is used for electrolysis of partially hydrated MgCl_2 ; consumable carbon electrodes must be employed, however, to facilitate the chlorination (by MgCl_2) of the MgO formed by reaction of the water with MgCl_2 . The Cl_2 and HCl produced as by-products of this process are used to generate more $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Electrolysis of MgO uses an electrolyte comprising MgO dissolved in molten fluoride (e.g., equimol MgF_2 : BaF_2); since MgO is only slightly soluble in the fluoride the process is not a direct electrolysis of MgO but an electrolysis of MgF_2 formed by fluorination of MgO. As in the electrolysis of partially hydrated MgCl_2 , consumable carbon electrodes must be used to enhance the fluorination process.

The most widely employed thermal reduction process for preparing Mg metal uses FeSi as reducing agent. Mixtures of the substrate, usually calcined dolomite (i.e., MgO, CaO) and FeSi are fabricated into briquettes with a hydrocarbon binder and loaded into Ni–Cr steel (15/28) retorts. After evacuation the retort is subjected to a temperature gradient; Mg distills from the hot mixture (at 1150°C) and high-purity Mg crystals collect at the water-cooled end of the retort:



Aluminum or one of its alloys (Al–Si, Al–Ca–Si, Al–Ca–Fe–Si) can be substituted for FeSi in this process. The alternative thermal reduction process is based on the reduction of pure MgO by carbon in an arc furnace at temperatures above 1800°C. Since the reaction:



is reversible and both products are volatile, rapid quenching, using refrigerated H_2 , natural gas or oil, is necessary to disturb the equilibrium and recover the Mg. An alternative method of quenching the equilibrium is to cool the gaseous mixture instantly by forcing it through a diverging nozzle at supersonic velocity. The metallic Mg powder resulting from this process is extremely pyrophoric and must be stored and handled under He or Ar.

(P. HUBBERSTEY)

7.2.3.2.2. Laboratory Preparation.

Laboratory preparation is best effected by adapting the commercial process in which MgO is reduced by FeSi in the presence of CaO (Eq. c)¹. The reaction should be carried out in a long, narrow steel bomb, heated to 1150°C at the end containing the charge, and air cooled at the other end. The Mg forms slowly and sublimes and condenses at the cooler end. Evacuation, although preferable, is not necessary since the metal produced initially scavenges the O_2 and N_2 from the bomb. After reaction

is complete, the system is cooled and filled with Ar and the metal is collected in an Ar-filled glove-box.

Finely divided, highly reactive Mg powders are required for laboratory applications in synthetic organic chemistry. Although commercially available powders are often used, much more active powders can be prepared, in situ, by alkali-metal (Li, Na, K) reduction of magnesium halides in anhydrous, aprotic, organic solvents (THF, DME)²⁻⁴; the reaction efficiency can be increased by both introducing the corresponding alkali metal iodide^{4,5} and using ultrasonic techniques to disperse the alkali metal⁶. The addition of catalytic amounts of naphthalene, which acts as an electron carrier, has also been described^{7,8}; this modification obviates the need to reflux the reaction mixture. An alternative route to highly active Mg powders is thermal decomposition of MgH_2 , magnesium-anthracene, magnesium-butadiene or their derivatives⁹.

(P. HUBBERSTEY)

1. L. M. Pidgeon, W. A. Alexander, *Trans. Am. Inst. Mining Eng.*, **159**, 315 (1944).
2. R. D. Rieke, U.S. Department of Energy Rept., DOE/ER/10603-T3 (1985).
3. R. D. Rieke, P. M. Hudnall, *J. Am. Chem. Soc.*, **94**, 7178 (1972).
4. R. D. Rieke, S. E. Bales, *J. Am. Chem. Soc.*, **96**, 1775 (1975).
5. R. D. Rieke, S. E. Bales, *J. Chem. Soc., Chem. Commun.*, 879 (1973).
6. B. H. Han, *Tachan Hwahakhoe Chi*, **29**, 557 (1985); *Chem. Abstr.*, **105**, 46,679 (1986).
7. R. T. Arnold, S. T. Kulenovic, *Synth. Commun.*, **7**, 223 (1977).
8. R. D. Rieke, P. T.-J. Li, T. P. Burns, S. T. Uhm, *J. Org. Chem.*, **46**, 4324 (1981).
9. B. Bogdanovic, Ger. Pat. 3,340,492; *Chem. Abstr.*, **103**, P196,226 (1985).

7.2.3.2.3. Purity and Purification.

Electrolytic Mg is less pure than Mg obtained by thermal reduction methods and is purified commercially by sublimation under vacuum, a process inherent in thermal reduction. Typical analyses for crude electrolytic Mg (assay 99.8%), for sublimed material (assay 99.95%) and for twice sublimed material (assay 99.99%) are collected in Table 1¹. Sublimation reduces most impurity levels (by $\sim 10^{-2}$) but leads to increased Zn content.

The removal of Fe from electrolytic Mg by adding Ti-containing materials²⁻¹¹ depends on the formation of intermetallic compounds such as FeTi and Fe_2Ti ; typical additives include metallic Ti, TiCl_4 and K_2TiF_6 . The Fe content of Mg can be reduced to $40 \mu\text{g g}^{-1}$, with a concomitant increase in Ti content to $100 \mu\text{g g}^{-1}$; this is of little significance since the Mg is generally used in the manufacture of ultra-high-purity Ti. The addition of Zr-bearing materials has also been considered⁹⁻¹⁴ and the effect of these additives on the removal of Si, N, O, H and first-row transition metals has been elucidated. Impurity removal from Mg has also been achieved by injecting boron halides¹⁵; Mn, Fe and Si inventories of < 30 , < 20 , and $10 \mu\text{g g}^{-1}$, respectively, are obtained. Refinement of Mg melts by a molten salt flux has also been considered^{6,16}; as yet few details are available.

Ultra-high-purity Mg has been prepared by either zone refining or vacuum distillation. Zone refining¹⁷⁻²³ is a difficult process because of the high volatility and reactivity of the metal. Nevertheless, the process can be carried out in SO_2 atmospheres where protective films of MgSO_4 and MgO are formed¹⁷⁻¹⁹, or in ultra-pure Ar atmospheres²⁰⁻²². Zone refining²³ removes a number of major impurities, includ-

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7.2.3.2. in Magnesium

7.2.3.2.3. Purity and Purification.

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4. R. D. Rieke, S. E. Bales, *J. Am. Chem. Soc.*, **96**, 1775 (1975).
5. R. D. Rieke, S. E. Bales, *J. Chem. Soc., Chem. Commun.*, 879 (1973).
6. B. H. Han, *Tachan Hwahakhoe Chi*, **29**, 557 (1985); *Chem. Abstr.*, **105**, 46,679 (1986).
7. R. T. Arnold, S. T. Kulenovic, *Synth. Commun.*, **7**, 223 (1977).
8. R. D. Rieke, P. T.-J. Li, T. P. Burns, S. T. Uhm, *J. Org. Chem.*, **46**, 4324 (1981).
9. B. Bogdanovic, Ger. Pat. 3,340,492; *Chem. Abstr.*, **103**, P196,226 (1985).

7.2.3.2.3. Purity and Purification.

Electrolytic Mg is less pure than Mg obtained by thermal reduction methods and is purified commercially by sublimation under vacuum, a process inherent in thermal reduction. Typical analyses for crude electrolytic Mg (assay 99.8%), for sublimed material (assay 99.95%) and for twice sublimed material (assay 99.99%) are collected in Table 1¹. Sublimation reduces most impurity levels (by $\sim 10^{-2}$) but leads to increased Zn content.

The removal of Fe from electrolytic Mg by adding Ti-containing materials²⁻¹¹ depends on the formation of intermetallic compounds such as FeTi and Fe_2Ti ; typical additives include metallic Ti, TiCl_4 and K_2TiF_6 . The Fe content of Mg can be reduced to $40 \mu\text{g g}^{-1}$, with a concomitant increase in Ti content to $100 \mu\text{g g}^{-1}$; this is of little significance since the Mg is generally used in the manufacture of ultra-high-purity Ti. The addition of Zr-bearing materials has also been considered⁹⁻¹⁴ and the effect of these additives on the removal of Si, N, O, H and first-row transition metals has been elucidated. Impurity removal from Mg has also been achieved by injecting boron halides¹⁵; Mn, Fe and Si inventories of < 30 , < 20 , and $10 \mu\text{g g}^{-1}$, respectively, are obtained. Refinement of Mg melts by a molten salt flux has also been considered^{6,16}; as yet few details are available.

Ultra-high-purity Mg has been prepared by either zone refining or vacuum distillation. Zone refining¹⁷⁻²³ is a difficult process because of the high volatility and reactivity of the metal. Nevertheless, the process can be carried out in SO_2 atmospheres where protective films of MgSO_4 and MgO are formed¹⁷⁻¹⁹, or in ultra-pure Ar atmospheres²⁰⁻²². Zone refining²³ removes a number of major impurities, includ-

TABLE 1. TYPICAL ANALYTICAL DATA^a FOR PURIFIED SAMPLES OF MAGNESIUM ($\mu\text{g g}^{-1}$)

Impurity	As	Ba	Co	Cu	Cr	Fe	Ga	Mn	Sb	Zn	Zr
Commercially available magnesium ¹											
Crude electrolytic	—	—	1	30	0.14	500	—	585	0.08	—	—
Sublimed	—	—	0.05	22	0.07	96	—	300	0.07	33	—
Twice sublimed	—	—	0.02	1	0.02	6	—	1	0.01	112	—
Zone-refined magnesium, 20 passes ²³											
As received	—	—	0.02	1	0.02	6	—	1	0.01	112	—
Zone refined	—	—	0.01	0.05	0.01	0.25	—	0.5	0.004	0.4	—
Vacuum-distilled magnesium ^{b 27}											
As received	0.008	0.12	0.08	3	0.15	97	0.6	18	0.03	55	0.8
Singly distilled (a)	0.001	0.05	0.001	0.8	0.5	0.07	0.1	0.2	0.006	17	0.09
Singly distilled (b)	0.001	0.03	0.001	0.6	0.01	0.04	0.008	0.05	0.002	16	0.08
Singly distilled (c)	0.01	0.3	0.002	0.05	0.013	0.6	0.002	0.01	0.001	17	0.7
Doubly distilled (d)	0.001	0.07	0.001	0.08	0.02	0.04	0.004	0.03	0.001	3	0.08

^a All quoted data are maximum values.^b Distillation conditions: (a) 24 g h^{-1} 55% distilled, (b) 3.5 g h^{-1} 72% distilled, (c) 3.5 g h^{-1} 83% distilled, (d) 3.5 g h^{-1} 99% & 99% distilled.

ing Fe, Cu and Zn, but has virtually no effect on Mn. Analytical data²³ for a sample of twice sublimed Mg subjected to a total of 20 passes (final assay 99.9999%) are included in Table 1.

Multicycle vacuum distillations have been assessed²⁴⁻²⁸. The distillations were effected at 700°C . Data on the effect of distillation rate and of fraction distilled on the purity of the sample are collected in Table 1. These data show that the technique is effective in removing the less volatile impurities As, Co, Cu, Cr, Fe, Ga, Mn and Sb from Mg but has little effect on more volatile species, Ba, Zn and Zr. Increase of the distillation rate or the fraction distilled leads to a decrease in the effective purification. Double (99% fraction) distillation gives a product of similar purity to that of a single (72% fraction) distillation^{27,28}. Single (78% fraction) distillation of a Mg sample (assay 99.9%) unusually rich in Mn ($300 \mu\text{g g}^{-1}$) at 3.5 g h^{-1} gave a decrease ($\times 10^{-4}$) in Mn content (to $0.025 \mu\text{g g}^{-1}$); a similar value ($0.04 \mu\text{g g}^{-1}$) was obtained from a doubly (99% fraction) distilled sample. This technique gives Mg with assays of 99.9995%^{27,28}.

(P. HUBBERSTEY)

1. R. Fromageau, in *Monographies sur les Metaux de Haute Purete*, G. Chaudron, ed., Vol. 2, Masson, Paris, 1977, p. 113.
2. I. A. Baranik, A. I. Baronovskii, L. N. Antipin, O. G. Kiselev, V. M. Kargin, A. F. Vikharev, USSR Pat. 233933,24-12-1968; *Chem. Abstr.*, 70, 117,300 (1969).
3. I. A. Baranik, A. I. Baronovskii, A. F. Vikharev, V. V. Rodyakin, O. G. Kiselev, V. M. Kargin, USSR Pat. 244619,28-5-1969; *Chem. Abstr.*, 72, P15,189 (1970).
4. A. F. Vikharev, O. M. Shapovalova, V. V. Rodyakin, V. D. Ponomarev, *Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall.*, 10, 80 (1967); *Chem. Abstr.*, 68, 32,170 (1968).
5. V. A. Kechin, N. M. Demido, *Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall.*, 95 (1978); *Chem. Abstr.*, 90, 207,814 (1979).

6. V. V. Rodyakin, *Issled. Obl. Khlornoj Met. Titana*, 180 (1969); *Chem. Abstr.*, 73, 117,620 (1970).
7. I. P. Vyatkin, V. A. Kechin, *Tsvet. Metall.*, 45, 36 (1972); *Chem. Abstr.*, 77, 23,306 (1972).
8. O. A. Putina, A. I. Gulyakin, I. P. Vyatkin, O. P. Brandman, A. A. Putin, *Tsvet. Metall.*, 43 (1976); *Chem. Abstr.*, 86, 76,406 (1977).
9. V. A. Kechin, A. S. Malyagin, A. D. Pogorelyi, *Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall.*, 143 (1977); *Chem. Abstr.*, 87, 26,554 (1977).
10. A. F. Vikharev, V. V. Rodyakin, *Sb. Tr. Vses. Nauk.-Issled. Proekt. Inst. Titana*, 2, 293 (1968); *Chem. Abstr.*, 70, 70,601 (1969).
11. V. A. Kechin, N. M. Demido, *Izv. Vyssh. Uchebn. Zavod., Tsevt. Metall.*, 56 (1980); *Chem. Abstr.*, 93, 51,409 (1980).
12. M. V. Chukhrov, V. A. Kechin, A. P. Vyatkin, *Tsvet. Metall.*, 44, 83 (1971); *Chem. Abstr.*, 76, 88,919 (1972).
13. A. I. Panin, N. A. Baitenev, V. Z. Tarasenko, K. Sh. Valiev, deposited document, VINITI 7767-73 (1973); *Chem. Abstr.*, 86, 143,526 (1977).
14. N. A. Baitenev, A. I. Panin, V. V. Rodyakin, V. Z. Tarasenko, L. B. Furschik, *Kompleksn. Ispol'z. Miner. Syr'ya*, 17 (1979); *Chem. Abstr.*, 91, 143,986 (1979).
15. A. Mena, J. M. Charriere, J. Desbrest, Fr. Pat. 2,516,940; *Chem. Abstr.*, 99, 143,860 (1983).
16. G. Emod, *Femip. Kut. Intez. Kozlem*, 10, 157 (1971); *Chem. Abstr.*, 76, 36,302 (1972).
17. A. S. Yue, J. B. Clark, *Trans. Am. Inst. Mining Eng.*, 212, 881 (1958).
18. F. Montariol, J. P. Catteau, C. Boucheron, A. Vanderschaege, *C.R. Hebd. Seances Acad. Sci.*, 261, 3605 (1965).
19. A. P. Kazakov, A. I. Belyayev, V. N. Vigdorovich, *Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall.*, 9, 79 (1966); *Chem. Abstr.*, 66, 109,025 (1967).
20. T. Chaudron, G. Revel, *C.R. Hebd. Seances Acad. Sci.*, 260, 1957 (1965).
21. A. Lesblats, T. Chaudron, G. Revel, P. Albert, *C.R. Hebd. Seances Acad. Sci.*, 261, 3125 (1965).
22. T. Chaudron, G. Revel, *Mem. Sci. Rev., Met.*, 64, 561 (1967).
23. T. Chaudron, G. Revel, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 263, 120 (1966).
24. J. Herenguel, G. Chaudron, *C.R. Hebd. Seances Acad. Sci.*, 193, 771 (1931).
25. A. J. Martin, *Met. Indust.*, 88, 495 (1956).
26. M. M. Spivak, R. A. Isakova, V. D. Ponomarev, *Tr. Inst. Met. Obogashch. Akad. Nauk Kaz. SSR.*, 31, 39 (1968); *Chem. Abstr.*, 72, 23,733 (1970).
27. G. Revel, J. L. Pastol, J. C. Rouchard, R. Fromageau, *Metall. Trans.*, 9B, 665 (1978).
28. G. Revel, J. L. Pastol, J. C. Rouchard, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 281, 1065 (1975).

7.2.3.3. in Calcium

Of the principal minerals of Ca listed in Table 1, the most important ores are the various deposits of CaCO_3 , especially limestones, which occur as immense sedimentary beds over extensive parts of the earth's surface. Extraction of Ca from CaCO_3 is a simple and relatively inexpensive process. Although the other Ca-bearing minerals are rarely considered as potential Ca sources, they are widely distributed and extensively mined: fluorite and apatite for their fluoride and phosphate content, gypsum and anhydrite for their use in construction.

(P. HUBBERSTEY)

7.2.3.3.1. Industrial Manufacture.

Metallic Ca is manufactured using techniques similar to those employed for metallic Mg (see §7.2.3.2.1). Contrary to practice in Mg technology, however, where the major proportion of the metal is obtained electrolytically, for Ca production, the

7.2.3. in the Group-IIA Elements

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7.2.3.3. in Calcium

7.2.3.3.1. Industrial Manufacture.

6. V. V. Rodyakin, *Issled. Obl. Khlorno Met. Titana*, 180 (1969); *Chem. Abstr.*, 73, 117,620 (1970).
7. I. P. Vyatkin, V. A. Kechin, *Tsvet. Metall.*, 45, 36 (1972); *Chem. Abstr.*, 77, 23,306 (1972).
8. O. A. Putina, A. I. Gulyakin, I. P. Vyatkin, O. P. Brandman, A. A. Putin, *Tsvet. Metall.*, 43 (1976); *Chem. Abstr.*, 86, 76,406 (1977).
9. V. A. Kechin, A. S. Malyagin, A. D. Pogorelyi, *Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall.*, 143 (1977); *Chem. Abstr.*, 87, 26,554 (1977).
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14. N. A. Baitenev, A. I. Panin, V. V. Rodyakin, V. Z. Tarasenko, L. B. Furschik, *Kompleksn. Ispol'z. Miner. Syr'ya*, 17 (1979); *Chem. Abstr.*, 91, 143,986 (1979).
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16. G. Emod, *Femip. Kut. Intez. Kozlem*, 10, 157 (1971); *Chem. Abstr.*, 76, 36,302 (1972).
17. A. S. Yue, J. B. Clark, *Trans. Am. Inst. Mining Eng.*, 212, 881 (1958).
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23. T. Chaudron, G. Revel, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 263, 120 (1966).
24. J. Herenguel, G. Chaudron, *C.R. Hebd. Seances Acad. Sci.*, 193, 771 (1931).
25. A. J. Martin, *Met. Indust.*, 88, 495 (1956).
26. M. M. Spivak, R. A. Isakova, V. D. Ponomarev, *Tr. Inst. Met. Obogashch. Akad. Nauk Kaz. SSR.*, 31, 39 (1968); *Chem. Abstr.*, 72, 23,733 (1970).
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(P. HUBBERSTEY)

7.2.3.3.1. Industrial Manufacture.

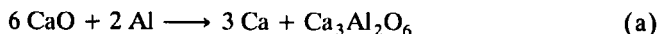
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TABLE 1. CALCIUM MINERALS

Mineral	Composition	Approximate Ca content (wt%)
Limestone	CaCO ₃	40
Chalk		
Marble		
Iceland spar		
Dolomite	MgCO ₃ , CaCO ₃	22
Fluorspar	CaF ₂	51
Fluorite		
Apatite	3 Ca ₃ (PO ₄) ₂ · CaF ₂	40
Wollastonite	CaSiO ₃	34
Anorthite	CaAl ₂ Si ₂ O ₈	14
Anhydrite	CaSO ₄	29
Gypsum	CaSO ₄ · 2 H ₂ O	23

thermal reduction methods are currently superseding the electrolytic methods on both economic and practical grounds. Indeed, electrolysis of Ca salts is difficult since: (i) it is difficult to prepare anhyd CaCl₂ free from basic salts and CaO, and (ii) it is impossible to run a Ca cell using partially hydrated CaCl₂ as feed material as for Mg manufacture.

In the principal thermal reduction process, CaO, obtained by calcination of high-purity CaCO₃, is reduced with Al or one of its alloys:



Briquettes of CaO with 5–20% excess powdered Al are heated under vacuum to 1170°C in a Ni-Cr steel (15/28) retort in which the Ca vapor, produced by reduction of solid CaO by Al vapor, is condensed in a zone at 680–740°C. Any Mg impurity is condensed in a zone at 275–350°C; a mixture of the two metals condenses in an intermediate zone. The Al content of the product can be reduced by passing the metal vapor, before it condenses, through a vessel filled with solid CaO. The adaptation of the FeSi thermal reduction process for Mg production (see §7.2.3.2.1) to Ca manufacture has also been described but is not economically viable in comparison with the above process. The thermal reduction of CaO with carbon has been proposed; as for Mg production, however, the reversibility of the equilibrium:



renders this process less attractive than the one using Al as reductant.

Electrolysis of a melt of anhyd CaCl₂ containing CaF₂ or KCl is conducted above the mp (839°C) of the metal, which is deposited on water-cooled cathodes of Fe or graphite that are slowly raised to permit solidification of the accumulated metal. The product is a coherent mass that is protected from oxidation by an electrolyte crust; deposition below the melting point would yield a voluminous spongy product, full of electrolyte and susceptible to oxidation and hydrolysis.

A minor source of metallic Ca is the recovery of the Ca that crystallizes from the liq Na produced in the electrochemical cell. This can be effected either by filtration of the liquid metal or by alcohol leaching of the residual Na–Ca sludge.

(P. HUBBERSTEY)

7.2.3.3.2. Laboratory Preparation.

Metallic Ca is prepared in the laboratory by reducing CaO with Al powder¹. The reaction mixture is charged in an evacuable steel bomb, designed such that one end can be heated while the other end is water cooled. After the bomb has been evacuated, the charge is heated to 1200–1300°C in vacuum and the Ca condenses at the cooler end of the bomb. After cooling, the bomb is filled with Ar and the metal recovered. Metallic Ca can also be prepared² by reducing CaCl₂ with metallic Na.

(P. HUBBERSTEY)

1. A. Guntz, F. Benoit, *Bull. Soc. Chim. Fr.*, 35, 712 (1924).
2. T. P. Whaley, *Inorg. Synth.*, 6, 18 (1960).

7.2.3.3.3. Purity and Purification.

The relatively impure crude Ca obtained from both thermal reduction and electrolytic sources (97–98%) is distilled to give a 99% pure product. Volatile impurities such as the alkali metals are removed in a predistillation mode at 800°C; subsequent distillation of the bulk metal at 825–850°C under vacuum removes most of the involatile impurities, such as Al, Cl, Fe and Si. The N content is often not reduced because of atmospheric contamination after distillation. Unfortunately, these commercial methods have no effect on Mg, which is the major impurity (up to 1 wt%). Typical analytical data¹ for Ca samples prepared by electrolysis, thermal reduction (using Al) and distillation are collated in Table 1.

Analytical data for samples obtained using vacuum distillation^{2,3}, fractional distillation^{4,5}, multiple distillation^{6,7} and ultra-high-vacuum reactive distillation^{8–10} techniques are included in Table 1. The ultra-high-vacuum reactive distillation process is a variant in which the Ca is distilled from a Mo crucible into a distillation column subjected to a slight temperature gradient and allowed to condense on a series of Mo baffles. Analytical data for specimens taken from both ends of the temperature gradient in a single-cycle distillation and from the hot end of a two-cycle distillation are collected in Table 1; the variation in the effectiveness of the separation along the temperature gradient is quite marked, diverse elements being concentrated at the two ends (e.g., Ba, Cl and Mn are concentrated at the hot end, whereas H and O are concentrated at the cold end). Nonetheless, a marked improvement in purity is attained (Table 1); the major impurities remaining include the heavier alkaline-earth metals, Sr and Ba, together with Mn, presumably because of their similar volatility to that of Ca, and N, which arises by atmospheric contamination. A development of this technique¹¹ involves metallothermic reduction of high-purity CaO with high-purity Al in a vacuum followed by ultra-high-vacuum reactive distillation (at 880°C). This gives extremely pure samples of Ca, with markedly reduced Mg, Sr and Ba contents¹¹; analytical data are included in Table 1.

7.2.3. in the Group-IIA Elements

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7.2.3.3. in Calcium

7.2.3.3.3. Purity and Purification.

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TABLE 1. TYPICAL ANALYTICAL DATA^a FOR SAMPLES OF PURIFIED CALCIUM ($\mu\text{g g}^{-1}$)

Impurity	Al	Ba	Cl	Fe	H	Mg	Mn	N	Na	O	Si	Sr
Commercially available calcium ¹												
Electrolytic	3,000	—	16,000	3,000	—	200	70	30	—	—	500	—
Thermally reduced	2,000	—	—	100	—	6,000	200	1,000	—	—	200	—
Distilled	3	—	—	5	—	3,000	45	175	—	—	1	—
Vacuum distillation, single cycle ^{2,3}												
Distillate	—	—	—	20	—	500	10	50	—	—	100	500
Vacuum distillation, single cycle following predistillation ⁴												
As received	1,000	—	—	30	—	9,800	120	—	—	—	—	—
Distillate	10	—	—	10	—	60	80	—	—	—	—	—
Vacuum distillation, fractional ⁵												
As received	3	—	—	5	—	3,000	45	175	—	—	1	—
Distillate	2	—	—	3	—	3	50	10	—	—	2	—
Vacuum distillation, multicycle ^{6,7}												
Distillate	—	3	—	3	—	2	1	260	—	—	2	3
Ultra-high-vacuum reactive distillation ⁸⁻¹⁰												
As received	—	72	6	—	11	473	25	6	8	440	—	658
1st distillate (hot end)	—	688	38	—	2	79	372	—	4	40	—	77
1st distillate (cold end)	—	6	1	—	28	67	3	—	6	80	—	241
2nd distillate (hot end)	—	55	10	—	6	5	18	—	13	14	—	116
Ultra-high-vacuum reactive distillation following ultra-high-vacuum metallothermic (Al) reduction ¹¹												
Distillate	22	1	—	—	17	< 1	—	5	—	—	—	16

^a All quoted data are maximum values.

Multiple recrystallizations (three or more) from the molten metal give specimens free of the other alkaline-earth metals and a final assay of 99.9999%¹²⁻¹⁴. Combined vacuum distillation and zone melting (five passes at 880–900°C under He) reduces the alkaline-earth metal impurity levels below the detection limits¹⁵.

(P. HUBBERSTEY)

1. R. Fromageau, in *Monographies sur les Metaux de Haute Purete*, G. Chaudron, ed., Vol. 2, Masson, Paris, 1977, p. 153.
2. D. T. Peterson, Proc. Int. Am. Conf. Mater. Technol., San Antonio, Texas, p. 45 (1968).
3. D. T. Peterson, V. G. Fattore, *J. Phys. Chem.*, **65**, 2062 (1961).
4. Showa Denko KK Jpn. Pat. 58,141,349; *Chem. Abstr.*, **99**, 198,647 (1983).
5. W. J. MacCreary, *J. Met.*, **10**, 615 (1958).
6. R. P. Rand, L. D. Calvert, *Can. J. Chem.*, **40**, 705 (1962).
7. W. A. Alexander, L. D. Calvert, A. Desaulniers, H. S. Dunsmore, D. F. Sargent, *Can. J. Chem.*, **47**, 611 (1969).
8. J. Evers, A. Weiss, E. Kaldis, J. Muheim, *J. Less-Common Met.*, **30**, 83 (1973).
9. J. Evers, E. Kaldis, J. Muheim, *Helv. Phys. Acta*, **46**, 402 (1973).
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7.2.3.4. in Strontium and in Barium

The principal minerals of Sr are strontionite (SrCO_3) and celestite (SrSO_4); those of Ba are barite (BaSO_4) and witherite (BaCO_3). Strontionite and barite are the usual sources of metallic Sr and Ba, respectively. Traces of both elements occur in nearly all limestones and dolomites and small amounts are usually present in natural limes. Furthermore, although neither element occurs as an independent silicate, traces of each may replace part of the Ca, Pb or K in compounds containing one or more of these elements.

(P. HUBBERSTEY)

7.2.3.4.1. Industrial Manufacture.

The demand for metallic Sr and Ba is severely limited. Consequently, they are speciality products and are extracted from their ores in small-scale batch processes.

Metallic Sr can be prepared by methods similar to those used for Ca manufacture (see §7.2.3.3.1). Thus thermal reduction of SrO using Al and electrolysis of anhyd SrCl_2 both yield pure Sr. Reduction of SrO by CH_4 is also successful on a pilot scale. Metallic Ba is produced by thermal reduction of BaO by Al; alternative reducing agents are Na, Mg, Si and FeSi. Electrolysis of fused anhydrous halides (e.g., BaCl_2) is not applicable since the reaction yields a subhalide rather than the pure metal.

Starting materials are obtained from the ores; SrO is readily prepared from SrCO_3 , the principal ore, by calcination, and SrCl_2 is obtained by thermal decomposition, in an HCl atmosphere, of $\text{SrCl}_2 \cdot 6 \text{H}_2\text{O}$, the product of the dissolution of SrCO_3 in aq HCl. Conversion of BaSO_4 , the major source of Ba, into BaO is effected via BaS and BaCO_3 . Thus BaSO_4 is reduced to BaS by heating with carbon in a rotary kiln; BaCO_3 is precipitated when BaS is dissolved in water and treated with CO_2 ; production of BaO is achieved by heating an intimate mixture of BaCO_3 and carbon.

In the thermal reduction process SrO (BaO) is briquetted with 5–20% xs Al powder and charged into Ni–Cr steel (15/28) retorts similar to those used for Ca production (see §7.2.3.3.1). The retorts are evacuated and subjected to a T gradient, the end containing the charge being heated to 1000°C , the other end being water cooled. The Al vaporizes, attacks the SrO (BaO) and releases the Sr (Ba), which distills and crystallizes in a pure state at the cooler end of the retort. Electrolysis of anhyd SrCl_2 , mixed with small quantities of KCl, above the mp of Sr (772°C), provides an alternative route to metallic Sr. The molten metal is deposited on water-cooled cathodes of Fe or graphite that are slowly lifted from the melt to permit solidification of the accumulated metal. This process gives a coherent mass that is protected from oxidation and hydrolysis by an electrolyte crust. Deposition at a $T < \text{mp}$ yields a voluminous spongy product full of electrolyte and susceptible to oxidation and hydrolysis.

7.2.3. in the Group-IIA Elements
7.2.3.4. in Strontium and in Barium
7.2.3.4.1. Industrial Manufacture.

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Metallic Sr (Ba) can also be obtained by thermal decomposition of SrH_2 (BaH_2), $\text{Sr}(\text{N}_3)_2$ [$\text{Ba}(\text{N}_3)_2$] and Sr (Ba) amalgams.

(P. HUBBERSTEY)

7.2.3.4.2. Laboratory Preparation.

A laboratory adaptation of the commercial thermal reduction method¹ utilizes reduction of SrO (BaO) by Al powder:



carried out in an evacuable steel bomb designed such that one end can be heated while the other is water cooled. The charge is heated to 1300–1400°C (1200–1300°C) in vacuum. Metallic Sr (Ba), formed by reaction of Al vapor with SrO (BaO), distills and condenses at the cooler end. After cooling, the Sr (Ba) is retrieved in Ar. N.B.: Sr forms as a solid, but Ba condenses as a liquid; the bomb should be designed with this difference taken into account². A similar process for preparing pure Sr (Ba) has been described³.

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3. P. S. Danner, *J. Am. Chem. Soc.*, 46, 2382, (1924).
4. B. C. Marklein, *Inorg. Synth.*, 1, 11 (1939).

7.2.3.4.3. Purity and Purification.

Commercial Sr and Ba are quite impure, typical assays being 98.5 and 98.0%, respectively, with the major impurities being the other alkaline-earth metals (with the exception of Be) and the nonmetals H, C, N and O. The former are obtained from the ores and the latter from reaction with the constituents of the atmosphere.

Atmospheric sensitivity renders the preparation of ultrapure samples difficult. Nevertheless, vacuum distillation^{1–4}, ultra-high-vacuum reactive distillation^{5–9} and crystal growth purification methods^{10–12} are described; zone-refining methods have been applied on a limited scale only^{12,13}, presumably because of the high volatility of the metals and the unfavorable distribution coefficients.

Vacuum distillation of Sr¹ and of Ba² and ultra-high-vacuum reactive distillation of Sr^{5,7,8} (to give a 99.97% assay) and of Ba^{6–8} (to give a 99.997% assay) has been reported. In the latter technique the metal is distilled under ultra-high vacuum from a Ta crucible through a series of Ta baffles sited in a T gradient. Analytical data for the products appear in Table 1; data for vacuum-distilled metal are included in the table for comparison. Even better assays have been obtained (99.99% for Sr and 99.999% for Ba) using a development⁹ of vacuum distillation in which metallothermic reduction of high-purity MO (M = Sr, Ba) with high-purity Al in vacuum, followed by ultra-high-vacuum reactive distillation (at 760°C for Sr and 880°C for Ba), is em-

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TABLE 1. TYPICAL ANALYTICAL DATA^a FOR SAMPLES OF PURIFIED STRONTIUM AND BARIUM ($\mu\text{g g}^{-1}$)

Strontium													
Impurity	Al	Ba	C	Ca	Cl	Fe	H	Mg	Mn	N	Na	O	
Vacuum distillation ¹													
Distillate	—	1000	200	1000	—	15	350	500	50	60	—	—	
Ultra-high-vacuum reactive distillation ^{5,7,8}													
As received	—	440	400	1600	10	1	34	1	90	15	1	290	
Distillate	—	170	55	290	1	1	1	10	3	1	1	20	
Ultra-high-vacuum reactive distillation following ultra-high-vacuum metallothemic (Al) reduction ⁹													
Distillate	13	< 1	—	46	—	—	42	< 1	—	5	—	—	
Barium													
Impurity	Al	C	Ca	Cl	Fe	H	Mg	Mn	N	Na	O	Sr	
Vacuum distillation ²													
Distillate	—	35	50	—	23	—	50	80	73	—	—	50	
Ultra-high-vacuum reactive distillation ⁶⁻⁸													
As received	—	52	555	14	3	371	73	64	5	40	1750	1850	
1st distillate	—	1	28	4	1	7	1	5	1	1	36	77	
2nd distillate	—	1	3	8	1	7	1	8	2	2	36	2	
Ultra-high-vacuum reactive distillation following ultra-high-vacuum metallothemic (Al) reduction ⁹													
Distillate	< 2	—	< 1	—	—	15	< 1	—	5	—	—	< 1	

^a All quoted data are maximum values.

ployed⁹; analytical data for these specimens are included in Table 1. An apparatus for the purification of Ba by repeated distillation has been described³; no analytical data are given, but the purity of the metal is assessed by resistance measurements.

Crystallization from the liquid metal has been assessed theoretically and experimentally as a purification method for both Sr^{10,11} and Ba^{10,12}. After five recrystallizations, metals of 99.9999% purity can be produced. The purification of Ba by zone refining^{12,13} is inefficient, many passes being required for the removal of the other alkaline-earth metals. The application of combined methods (i.e., vacuum distillation plus crystal growth^{12,14,15} or vacuum distillation plus zone refining¹²) to the purification of both metals has also been described.

(P. HUBBERSTEY)

1. D. T. Peterson, R. P. Colburn, *J. Phys. Chem.*, **70**, 468 (1966).
2. D. T. Peterson, C. C. Hammerberg, *J. Less-Common Met.*, **16**, 457 (1968).
3. T. E. Brown, K. A. McEwen, *J. Phys., D, Appl. Phys.*, **3**, 980 (1970).
4. A. V. Vakhobov, V. N. Vigdorovich, V. G. Khudaiberdiev, *Izv. Vyssh. Ucheb. Zaved., Tsvet. Metall.*, **17**, 93 (1974); *Chem. Abstr.*, **81**, 66,941 (1974).
5. E. Kaldis, J. Muheim, J. Evers, A. Weiss, *J. Less-Common Met.*, **31**, 169 (1973).

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7.2.4. Formation of Alloys Between Group-IA Elements

7.2.4.1. Binary Alloys

7.2.4.1.1. Phase Diagrams.

Alloying has been investigated between all pairs of group-IA elements. The alloying is dominated by the increase in metallic radius with increasing atomic number¹: metals similar in size give mixed crystals, slight differences between metals give eutectic systems and greater differences result in either immiscibility in the liquid state or compound formation. Thus Rb and Cs are completely miscible and form mixed crystals; Na forms eutectics with the heavier metals, but Li is only partly miscible with Na and is even less miscible with K, Rb and Cs. These trends are summarized in Fig. 1.

(i) Li–Na. The phase diagram (Fig. 2) shows a considerable degree of immiscibility. The miscibility gap (two immiscible liquids) is not symmetrical, however, so Li is more soluble in Na than vice versa. The consolute point occurs at $305 \pm 1^\circ\text{C}$ and 27 mol% Na. This is 137 and 75°C below that calculated in refs. 3 and 4, respectively. Whereas the experimental points (by chemical analysis) in ref. 4 fall close to the liquidus shown in Fig. 2 and only the interpolation differs, those (by thermal analysis) in ref. 3 differ considerably. Corroboration of the liquidus is provided by other studies^{5–7} but the earlier reported interpolated liquid^{8,9} has not been confirmed. The amendments, however, are incorporated in ref. 10. The solid solubility of Na in Li is below 0.64 mol% Na and that of Li in Na is no more than 1.90 mol% Li and may be even less since the terminal solid solubility is very small in this system¹¹.

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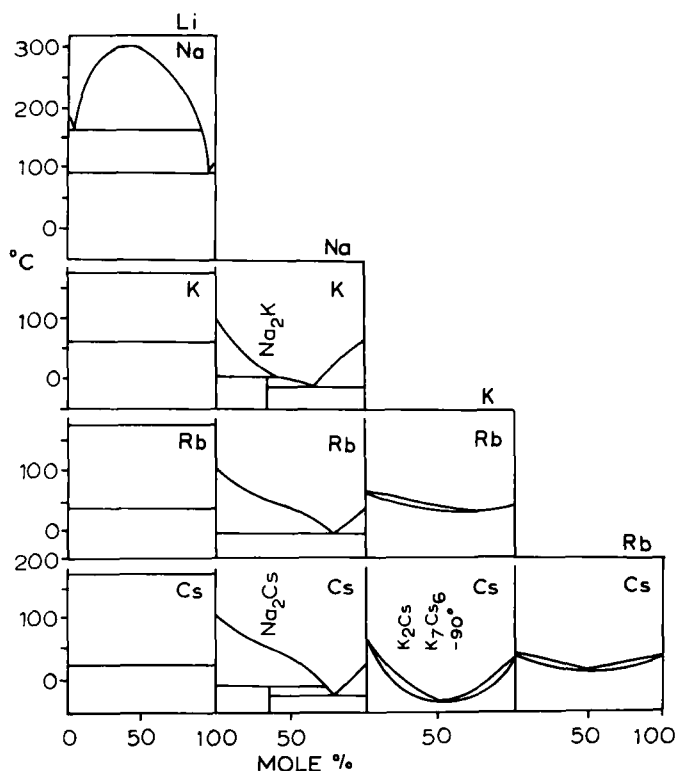


Figure 1. Summary of group IA-group IA phase diagrams (updated from ref. 1).

Li at 321, 427 and 538°C, respectively, and 0.018, 0.034, 0.125 and 0.471 at 321, 427, 538 and 660°C, respectively¹². Between 63 and 180°C, a K-rich liquid phase is in equilibrium with solid Li (i.e., Li dissolves in K but not vice versa)¹³. Above 180°C, K begins to dissolve in Li, giving two immiscible liquids, and these are filtered and chemically analyzed to give the solubilities:

$$\log (\text{wt Li in K, ppm}) = 6.09 - 1837/T \text{ (K) } 63\text{--}450^\circ\text{C} \quad (\text{a})$$

$$\log (\text{wt K in Li, ppm}) = 5.50 - 1362/T \text{ (K) } 180\text{--}550^\circ\text{C} \quad (\text{b})$$

On an atomic basis, Li is much more soluble in K than vice versa (0.07, 0.43, 1.29 and 1.99 mol% Li compared with 0.007, 0.02, 0.05 and 0.07 mol% K). Although these solubilities are larger than those given by eqs. (a) and (b), both investigations point to a two-immiscible-liquid-type of phase diagram with a consolute $T > 1000^\circ\text{C}$, and with the consolute composition being on the Li-rich side as in the Li-Na system.

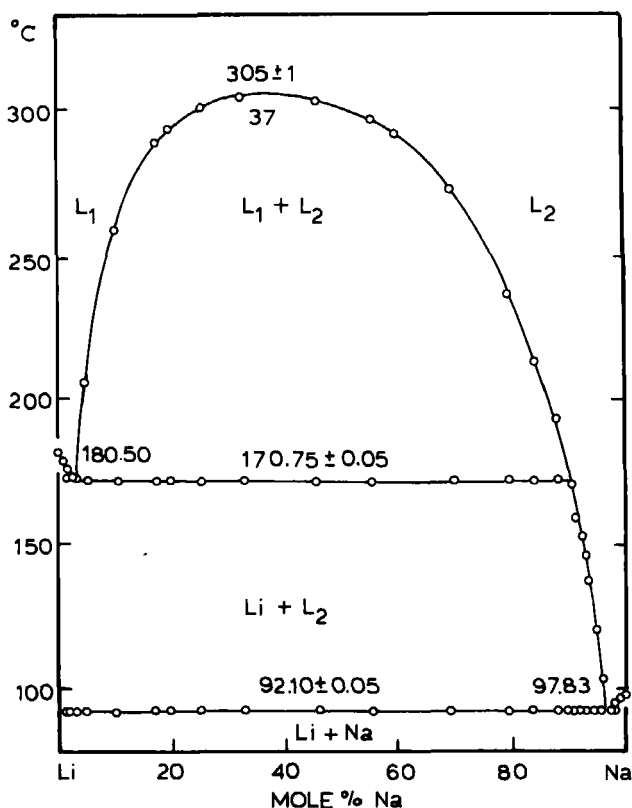


Figure 2. The Li-Na phase diagram (based on ref. 2).

(iii) Li-Rb and Li-Cs. An early thermal investigation indicated that Li and Cs were immiscible in both liquid and solid states⁸, but a more recent investigation has detected slight solubility of Cs in Li at high T. At 760°C the values are 0.007 and 0.018 mol% Cs for two separate experiments; at 982°C, 0.174 and 0.179; at 1038°C, 0.159 and 0.200; and at 1093°C, 0.336 and 0.704 mol% Cs¹⁴.

(iv) Na-K. The Na-K phase diagram is reported in ref. 15, which does not include, however, a precise study in ref. 16. This information is now augmented by the data in ref. 16 which gives the peritectic invariant point at 40.2 mol% K and $6.92 \pm 0.05^\circ\text{C}$, the eutectic at $-12.62 \pm 0.05^\circ\text{C}$ and 68.1 mol% K and maximum solid solubilities of α , 0.8 ± 0.1 mol% K, and β , 4.6 ± 0.3 mol% Na (Fig. 3). Resistance-temperature measurements in the K-rich region locate the eutectic concentration at 67.8 mol% K (78.2 wt%) and include the points from other investigations in this composition region¹⁷.

(v) Na-Rb and Na-Cs. These systems are similar to Na-K in forming simple eutectic systems; like Na-K, Na-Cs also contains a compound, Na_2Cs (74.29 wt%

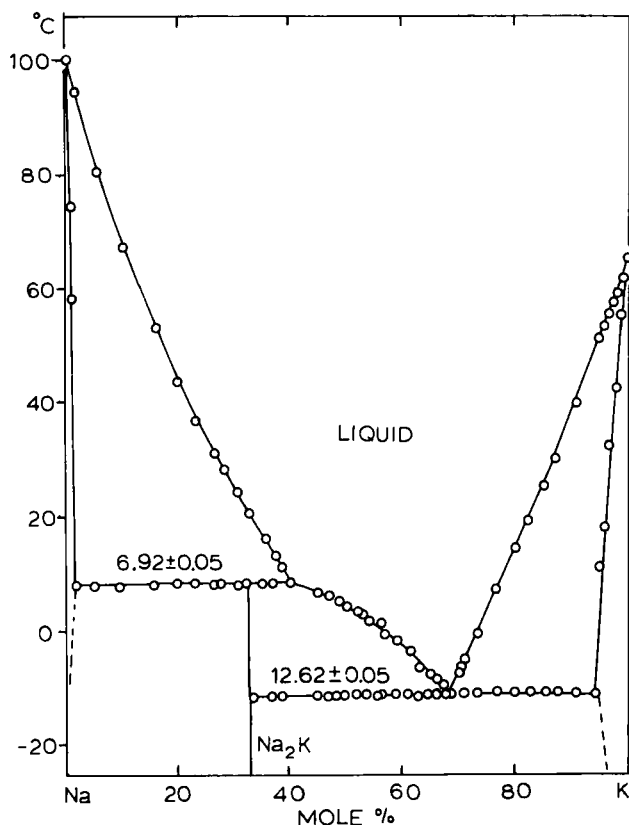


Figure 3. The Na-K phase diagram.

Cs), that forms peritectically at -8°C . For Na-Rb, the eutectic point is variously located⁸ at -4.5 , -5.2°C and 75, 75.6 mol% Rb. A reinvestigation of the liquidus gives the eutectic at $-4.50 \pm 0.05^{\circ}\text{C}$ and 82.1 mol% Rb and this is shown in Fig. 5¹⁸. For Na-Cs, the eutectic data⁸ are -30 , -28°C at 75, ca. 70 mol% Cs. A reinvestigation gives $-31.83 \pm 0.10^{\circ}\text{C}$ at 79.1 mol% Cs and also a peritectic halt at $-7.90 \pm 0.20^{\circ}\text{C}$ and 70.4 mol% Cs¹⁹. These data are shown in Fig. 4.

(vi) K-Rb, K-Cs and Rb-Cs. These phase diagrams are so similar that they can be considered together. The salient feature is extreme miscibility; K-Rb and Rb-Cs form a continuous series of solid solutions and the solid solution lattice parameter in K-Cs changes linearly with composition. The slight difference in K-Cs may be due to a greater size difference. The minimum in the K-Rb liquidus occurs at 66.7 mol% Rb and 32.8°C (alternatively at 72.2 and 34°C)⁸, later reported at 66.7 mol% Rb and 33.85°C ²⁰. In K-Cs and Rb-Cs, the minimum is near 50 mol% (-37.5 for K-Cs and 9°C for Rb-Cs)⁸. More recent redeterminations of the K-Cs²¹ and Rb-Cs²⁰ liquid

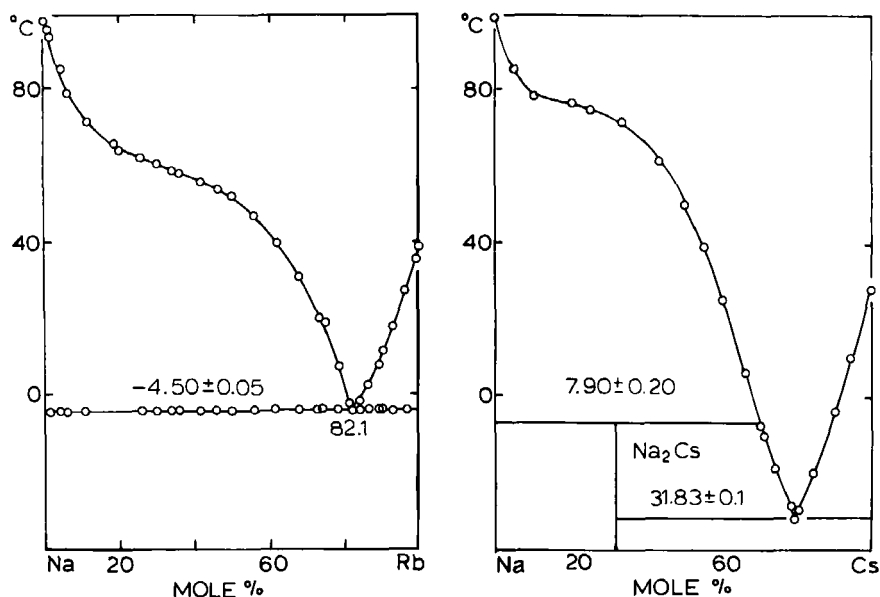


Figure 4. The Na-Rb and Na-Cs phase diagrams.

locate the minima at 49.8 ± 0.5 mol% Cs (-38.03°C) and 53.0 mol% Cs (9.70°C), respectively. Two compounds, K_2Cs and K_7Cs_6 , have been detected below -90°C by thermal analysis and x-ray diffraction²². The phase relationships are shown in Fig. 5.

(R. J. PULHAM)

1. W. Klemm, D. Kunze, in *The Alkali Metals*, Spec. Publ. No. 22, The Chemical Society, London, 1967, pp. 3–22.
2. M. G. Down, P. Hubberstey, R. J. Pulham, *J. Chem. Soc., Dalton Trans.*, 1490 (1975).
3. W. H. Howland, L. F. Epstein, *Handling and Use of Alkali Metals*, Adv. Chem. Ser. No. 19, American Chemical Society, Washington, D.C., 1957, p. 34.
4. O. N. Salmon, D. H. Ahmann, *J. Phys. Chem.*, **60**, 13 (1956).
5. F. A. Kanda, R. C. Saxon, D. V. Keller, *J. Phys. Chem. Liquids*, **1**, 61 (1968).
6. H. K. Schurmann, R. D. Parks, *Phys. Rev. Lett.*, **27**, 1790 (1971).
7. P. D. Feitsma, J. J. Hallers, F. B. D. Werff, W. Van der Lugt, *Physica*, B,C, **79–80**, 35 (1975).
8. M. Hansen, ed., *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
9. R. P. Elliot, ed., *Constitution of Binary Alloys*, First Suppl., McGraw-Hill, New York, 1965.
10. R. W. Ohse, ed., *Handbook of Thermodynamic and Transport Properties of the Alkali Metals*, IUPAC, Blackwell Scientific, Oxford, 1985.
11. W. B. Pearson, *Int. Ser. Monographs Metallurgical Physics and Phys. Metallurgy*, **4**, 717 (1964).
12. W. G. Moffatt, ed., *Handbook of Binary Phase Diagrams*, Vols. 1–3, General Electric, Schenectady, NY, 1978.
13. F. J. Smith, *J. Less-Common Met.*, **35**, 147 (1974).
14. F. A. Shunk, ed., *Constitution of Binary Alloys*, Second Suppl., McGraw-Hill, New York, 1969.
15. O. J. Foust, ed., *Sodium-NaK Engineering Handbook*, Vol. 1, Gordon & Breach, New York, 1972, pp. 19–21.

7.2.4.1. Binary Alloys

7.2.4.1.2. Compound Formation.

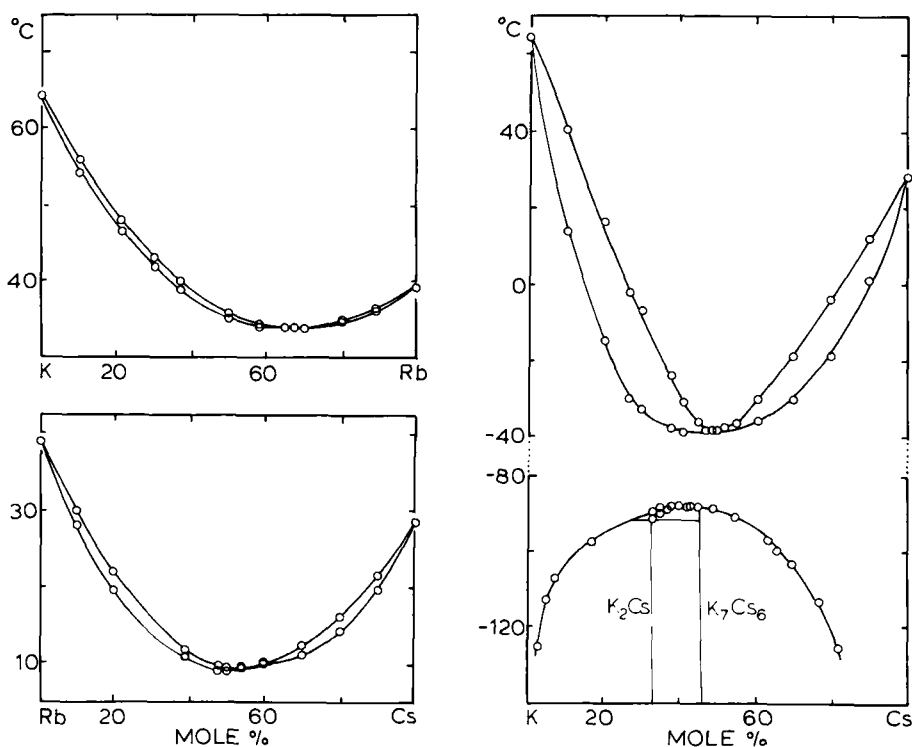


Figure 5. The K-Rb, Rb-Cs and K-Cs phase diagrams.

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18. J. R. Goates, J. B. Ott, C. C. Hsu, *Trans. Farad. Soc.*, **66**, 25 (1970).
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7.2.4.1.2. Compound Formation.

The only effective way to identify and distinguish the intermetallic phases depicted in the phase diagrams (see §7.2.4.1.1) is by x-ray diffraction, so their structures are included here.

Four compounds have been identified: Na_2K , Na_2Cs , K_2Cs and K_7Cs_6 . The formula of Na_2K (45.95 wt% K)¹ was later shown to have the hexagonal $MgZn_2$ (C14) structure with $a = 748 \pm 2$, $c = 1227 \pm 7$ pm, $Z = 4$, and space group $P6/mmc$ ^{2,3}. The structure of the compound Na_2Cs , which forms peritectically at $-8^\circ C$, is unknown but K_2Cs resembles Na_2K and has the $MgZn_2$ structure with $a = 906.5$ and

7.2.4. Formation of Alloys Between Group-IA Elements

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7.2.4.1. Binary Alloys

7.2.4.1.2. Compound Formation.

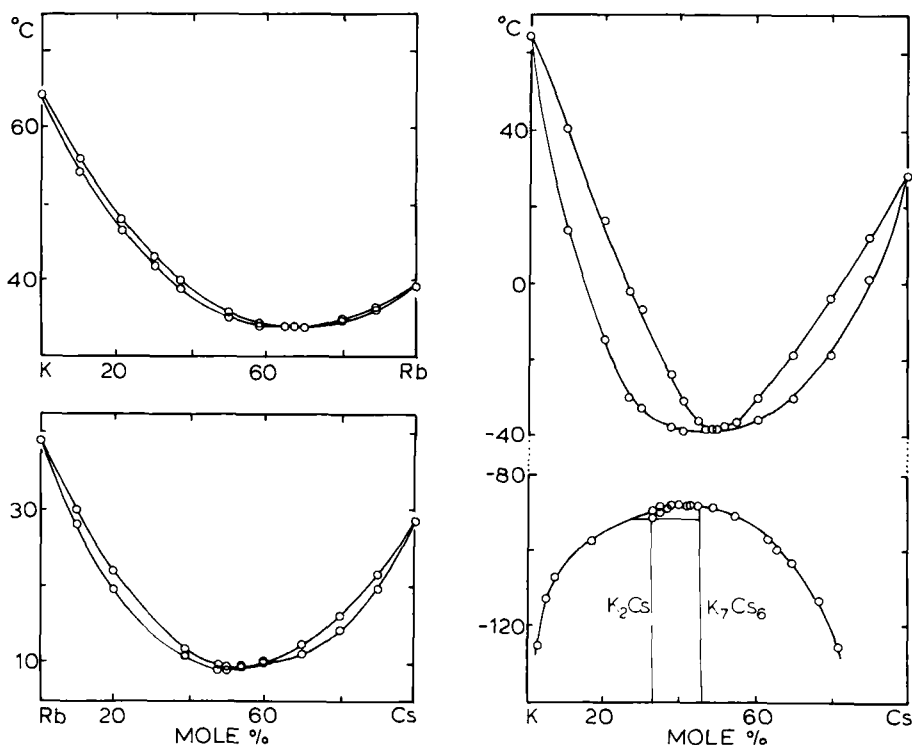


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$c = 1477.5$ pm at -95°C . Additionally, K and Cs form the phase K_7Cs_6 , and single crystals grown at -100°C have $a = 907.8$, $c = 32950$ pm and space group $\text{P}6_3/\text{mmm}$ ⁴.

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7.2.4.1.3. Preparations.

These chemically reactive phases are prepared by slow cooling of melts with the appropriate composition under an inert atmosphere or vacuum. Equilibrium is slow to be attained at the low temperatures necessary to prevent dissociation; at 6.9°C Na_2K dissociates into α (solid solution of K in Na) and liquid (60/40 Na/K). The K_2Cs and K_7Cs_6 phases are even less stable and result from cooling mixtures of the elements of the desired stoichiometry to -100°C in a metal beaker under argon¹.

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7.2.4.2. Multicomponent Alloys

Three-component mixtures selected from Na, K, Rb and Cs have been investigated to determine the minimum melting point in each ternary mixture, characterizing low-melting portions of the Na-K-Cs phase diagram and measuring the physical

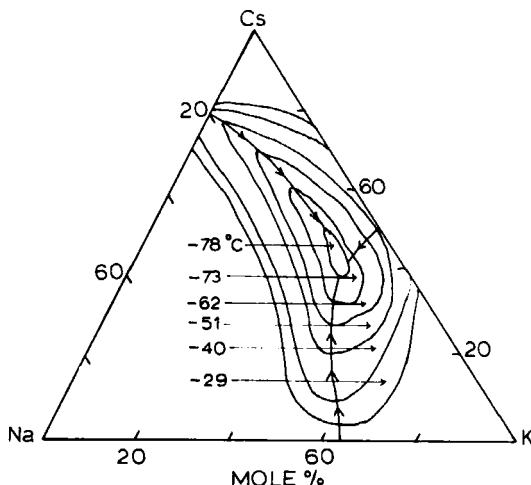


Figure 1. Part of the Na-K-Cs phase diagram showing the ternary eutectic at -78°C .

7.2. Formation of Group-IA or -IIA-IA or -IIA Metal Bonds

7.2.4. Formation of Alloys Between Group-IA Elements

7.2.4.2. Multicomponent Alloys

$c = 1477.5$ pm at -95°C . Additionally, K and Cs form the phase K_7Cs_6 , and single crystals grown at -100°C have $a = 907.8$, $c = 32950$ pm and space group $\text{P}6_3/\text{mmm}$ ⁴.

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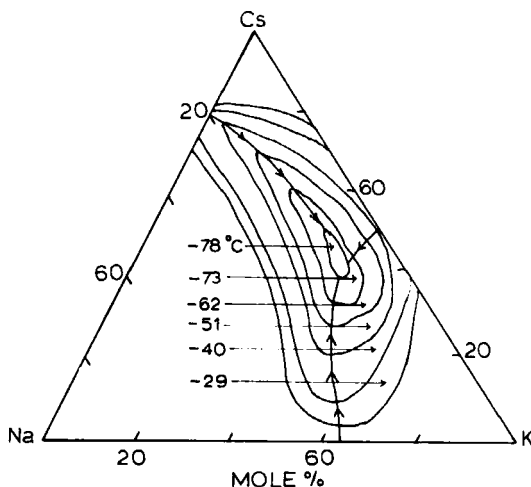


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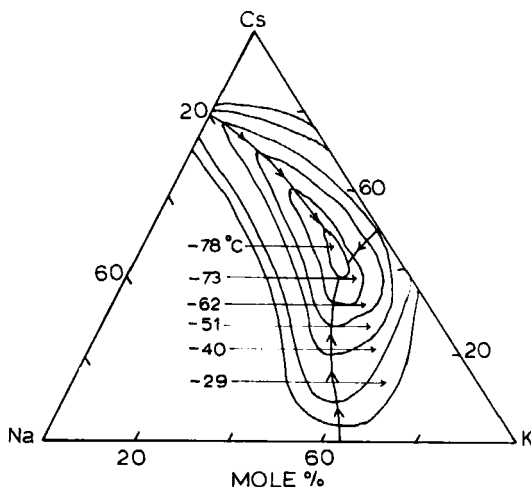


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7.2.5. Formation of Alloys Between Group-IIA Elements

7.2.5.1. Binary Alloys

7.2.5.1.1. Phase Diagrams.

The heavier group-IIA metals are similar to the heavier alkali metals in that they are miscible with one another and form mixed crystals. The lighter metals, Be and Mg, however, show a strong tendency to form intermetallic compounds which is not prevalent among the alkali metals. Thus Be and Mg form Be_{13}M ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}$ and Ba) and Mg_2M ($\text{M} = \text{Ca}, \text{Sr}$ and Ba), respectively. A convenient summary of alloying behavior is shown in Fig. 1 which is an updated version of that of ref. 1. There are signs that Be will form similar phase diagrams with each of the other group-IIA metals. The general feature is extreme immiscibility which diminishes slightly from $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$. This is shown (Table 1 and Fig. 1) by the increasing solubility in Be of these metals with increasing atomic number, and the progressive movement of the eutectic to higher Be concentrations^{1,2}. At the other end of the phase diagram, M is in equilibrium with Be_{13}M as shown by heating Be in Mg and finding that Be is always coated with Be_{13}M and no other compound¹.

The general features of the Mg-Ca, Mg-Sr and Mg-Ba phase diagrams are outlined in Fig. 1. The fine details of each can be found in refs. 3-5. The notable

7.2.5. Formation of Alloys Between Group-IIA Elements

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The general features of the Mg–Ca, Mg–Sr and Mg–Ba phase diagrams are outlined in Fig. 1. The fine details of each can be found in refs. 3–5. The notable

features are the simple phase equilibria between Mg and Ca in which the compound Mg_2Ca dominates. In Mg–Sr and Mg–Ba the additional compounds $Mg_{23}M_6$ ($M = Sr$ or Ba), $Mg_{17}M_2$ ($M = Sr$ or Ba) and Mg_4Sr make an appearance, and it seems that Mg_2M ($M = Ca, Sr$ or Ba) diminishes in stability (as measured by their relative mps) with increasing atomic number at the expense of $Mg_{17}M_2$ ($M = Sr$ or Ba) which is the highest melting compound in Mg–Ba.

Calcium is miscible with Sr in the liquid and in all the solid bcc, hcp and fcc allotropic forms (Fig. 1). Barium exhibits no hcp or fcc forms, however, so that solid solubility between the close-packed structures of Ca and Sr, and the bcc structure of Ba is restricted in the Ca–Ba and also in the Sr–Ba systems. A continuous series of solid solutions is only achieved in Ca–Ba and Sr–Ba for the high-T bcc modifications. In Ca–Ba, the solid solutions are separated by a narrow heterogeneous field between 32 and 36 mol% Ba; in Sr–Ba this occurs between 24 and 30 mol% Ba (Fig. 1).

In these group-IIA–group-IIA alloys, there is evidently great difficulty in obtaining and maintaining the pure metals, Ca, Sr and Ba. Thus the mps reported vary from

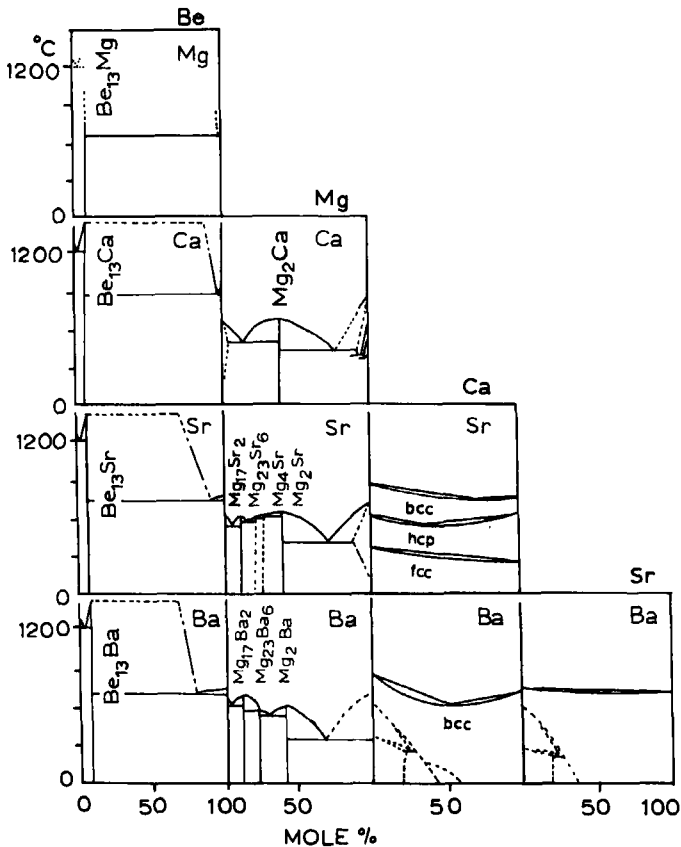


Figure 1. Summary of group IIA–group IIA phase diagrams.

TABLE 1. SOLUBILITY (mol%) OF Be IN THE GROUP-IIA METALS

T (°C)	Solubility in Mg
700	0.027 to 0.040
780	0.081 to 0.11
T (°C)	Solubility in Sr
900	15.8
1000	16.5
1100	18.6
T (°C)	Solubility in Ca
1000	5.1
1100	6.3
T (°C)	Solubility in Ba
800	16.7
900	18.9
1000	21.7
1100	25.5

836 to 850 for Ca, 768 to 774 for Sr and 708 to 725°C for Ba, which must reflect the variation in purity.

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7.2.5.1.2. Compound Formation.

In this group, the metals form compounds of the type Be_{13}M ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}$ or Ba), Mg_2M ($\text{M} = \text{Ca}, \text{Sr}$ or Ba) Mg_4M or Mg_{23}M_6 ($\text{M} = \text{Sr}$ or Ba) and Mg_9M or Mg_{17}M_2 ($\text{M} = \text{Sr}$ or Ba)^{1–5}. These intermetallic phases are essentially identified and distinguished one from another by their x-ray diffraction patterns so their structures are included in this section.

7.2.5. Formation of Alloys Between Group-IIA Elements

299

7.2.5.1. Binary Alloys

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(i) Be_{13}M . All the group-IIA metals combine with Be to form compounds with the stoichiometry Be_{13}M (where $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}$ or Ba ; this is a widely found composition since in addition $\text{M} = \text{Sc}, \text{Y}, \text{Ln}, \text{Zr}, \text{Hg}$ and Th , and Be can be replaced by Cu, Zn and others). The Be_{13}M compounds have the fcc $\text{NaZn}_{13}(\text{D}2)$ type structure with space group $\text{Fm}\bar{3}\text{c}$ and $Z = 8$. The lattice constant a (pm) increases with increasing size of M :

$$\text{Be}_{13}\text{Mg} \quad a = 1016.6 \pm 0.5^6, 1016 \pm 1^7, 1015.8 \pm 0.5^8$$

$$\text{Be}_{13}\text{Ca} \quad a = 1031.2 \pm 0.1^{6,9}$$

$$\text{Be}_{13}\text{Sr} \quad a = 1045.7 \pm 0.1^{10}, 1046.0 \pm 0.5^{11}$$

$$\text{Be}_{13}\text{Ba} \quad a = 1048.5 \pm 0.5^{11}$$

The structures are like that of CsCl , in which there are M atoms and B_{13} groups, the latter forming slightly distorted icositetrahedra. Each M has 24 neighboring Be atoms, whereas the coordination of Be is 12. Within the icositetrahedra the distance between the central Be atom and the 12 Be atoms at the corners is constant and smaller than in elemental Be. These bonds are very strong and inflexible, giving a rigid Be sublattice that is not greatly influenced by the size of the inserted M atoms, whereas the distances between the icositetrahedra are not constant but increase with increasing size of M ¹¹.

(ii) Mg_2M . The compounds Mg_2Ca , Mg_2Sr and Mg_2Ba all form with the hexagonal $\text{MgZn}_2(\text{C}14)$ type of structure with space group $\text{P}6_3/\text{mmc}$ and $Z = 4$. The cell dimensions (pm) are:

$$\text{Mg}_2\text{Ca}^{12} \quad a = 623 \quad c = 1012$$

$$\text{Mg}_2\text{Sr}^{13} \quad a = 643.9 \quad c = 1049.4$$

$$\text{Mg}_2\text{Ba}^{13} \quad a = 664.9 \quad c = 1067.6$$

(iii) Mg_{23}M_6 . Compounds originally thought to be Mg_4Sr and Mg_4Ba have been identified as $\text{Mg}_{23}\text{Sr}_6$ and $\text{Mg}_{23}\text{Ba}_6$, respectively, but there appears still to be one phase that can justifiably be called Mg_4Sr . The Mg_{23}M_6 ($\text{M} = \text{Sr}$ or Ba) compounds have the fcc $\text{Mn}_{23}\text{Th}_6(\text{D}8_a)$ type of structure with space group $\text{Fm}\bar{3}\text{m}$ and $Z = 4$. Cell dimensions (pm) are:

$$\text{Mg}_{23}\text{Sr}_6 \quad a = 1491.4^{14}, 1491^{15}$$

$$\text{Mg}_{23}\text{Ba}_6 \quad a = 1526.3, 1.8^{14}, 1521^{15}$$

The remaining compound Mg_4Sr is hexagonal with $a = 1051.1 \pm 0.8$ pm, $c = 2836.2 \pm 1.1$ pm, $Z = 18$ and space group $\text{P}6_3/\text{mmc}$ ¹⁴.

(iv) Mg_{17}M_2 . These compounds have caused confusion by their stoichiometry. The phases richest in Mg , Mg_9M ($\text{M} = \text{Sr}$ or Ba), have now been assigned the stoichiometry Mg_{17}M_2 and thereby resemble $\text{Zn}_{17}\text{Th}_2$. The compound $\text{Mg}_{17}\text{Sr}_2$ is hexagonal with $a = 1053.3 \pm 0.7$ pm, $c = 1034 \pm 0.7$ pm, $Z = 2$ and space group $\text{P}6/\text{mmc}$ ¹⁶. For $\text{Mg}_{17}\text{Ba}_2$, the structure is hexagonal/rhombohedral with $a = 1066.4 \pm 0.5^{16}$ (or 1061)¹⁷, $c = 1559.3 \pm 0.7^{16}$ (or 1552)¹⁷ pm, $Z = 3$ and space group $\text{R}\bar{3}\text{m}$.

7.2.5.1. Binary Alloys

7.2.5.1.3. Preparations.

There is little evidence for 1 : 1 compounds between elements in this group under normal conditions. The diatomic van der Waals molecules, CaMg, SrMg and SrCa, however, have been synthesized by codepositing the atoms from separate sources with argon or krypton into solid matrices at 12 K. These low-T species are identified from their laser-induced fluorescence spectra. The ground-state spectroscopic data for these alkaline-earth dimers form a sensible series between the parent molecules Mg₂, Ca₂ and Sr₂¹⁸.

(R. J. PULHAM)

1. M. Hansen, ed., *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
2. R. P. Elliott, ed., *Constitution of Binary Alloys*, First Suppl., McGraw-Hill, New York, 1965.
3. F. A. Shunk, ed., *Constitution of Binary Alloys*, Second Suppl., McGraw-Hill, New York, 1969.
4. W. G. Moffatt, ed., *Handbook of Binary Phase Diagrams*, Vols. 1–3, General Electric, Schenectady, NY, 1978.
5. W. B. Pearson, ed., *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vols. 1 and 2, Pergamon Press, Toronto, 1967.
6. T. W. Baker, J. Williams, *Acta Crystallogr.*, **8**, 519 (1955).
7. R. O. Elliott, E. M. Cramer, F. H. Ellinger, U.S. Atomic Energy Commission, Rept. La-2184, 1958; *Chem. Abstr.*, **52**, 14,496 (1958).
8. G. A. Abdullaev, N. D. Nagorskaya, A. V. Novoselova, G. N. Ronami, *Vestnik Moskov. Univ. Khim.*, **14**, 109 (1973); *Chem. Abstr.*, **78**, 165,595 (1973).
9. T. W. Baker, *Acta Crystallogr.*, **15**, 175 (1962).
10. N. N. Matyushenko, L. F. Verkhorobin, V. A. Karev, *Kristallografiya*, **9**, 273 (1964); *Sov. Phys. Crystallogr.*, **9**, 213 (1964).
11. W. Klemm, D. Kunze, in *The Alkali-Metals*, Spec. Publ. No. 22, The Chemical Society, London, 1967, pp. 3–22.
12. H. Witte, *Naturwissenschaften*, **25**, 795 (1937).
13. E. Hellner, F. Laves, *Z. Kristallogr.*, **A105**, 134 (1943).
14. F. E. Wang, F. A. Kanda, C. F. Miskell, A. J. King, *Acta Crystallogr.*, **18**, 24 (1965).
15. E. I. Gladyshevskii, P. I. Kripyakevich, Ju. B. Kuz'ma, M. Ju. Teslyuk, *Kristallografiya*, **6**, 769 (1961).
16. P. I. Kripyakevich, V. I. Edzokimenko, *Kristallografiya*, **7**, 31 (1962).
17. F. E. Wang, F. A. Kanda, C. F. Miskell, A. J. King, *Acta Crystallogr.*, **16**, 697 (1963).
18. J. C. Miller, L. Andrews, *J. Am. Chem. Soc.*, **100**, 6956 (1978).

7.2.5.1.3. Preparations.

The preparations of the intermetallic phases of the group-IIA metals are not complicated, but some problems arise owing to their chemical reactivity and reaction with containment vessels; the latter is particularly troublesome with Be which alloys easily with many metals. The compound Be₁₃Mg has been prepared by cold pressing Be powder followed by immersion in a bath of molten Mg at 750°C for 30 min (1800 s) under Ar, with final water quench. The phase Be₁₃Mg is also produced by the Ca reduction of BeO¹. When the Ca melts, reaction gives Be₁₃Ca and CaO and goes to completion with xs Ca. This and CaO are leached out with dil H₂SO₄, leaving the more resistant Be₁₃Ca². Dilution of the Be can be an advantage, and Be₁₃Mg is produced by quenching or slowly cooling the Al-Be-Mg or Al-Be-Mg-Zn alloys, which contain up to 2% of Be³. Alternatively, turnings of Be are sealed with Ca (or Ba) into iron vessels at 1100–1200°C for 60 h but even then the formation of Be₁₃Ca (or Be₁₃Ba) may not be quite complete, and iron is not the best container; BeO or Be–Ca spinel ceramics are better. The preparation of Be₁₃Sr is easier; turnings of Be are

7.2.5. Formation of Alloys Between Group-IIA Elements

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4. W. G. Moffatt, ed., *Handbook of Binary Phase Diagrams*, Vols. 1–3, General Electric, Schenectady, NY, 1978.
5. W. B. Pearson, ed., *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vols. 1 and 2, Pergamon Press, Toronto, 1967.
6. T. W. Baker, J. Williams, *Acta Crystallogr.*, **8**, 519 (1955).
7. R. O. Elliott, E. M. Cramer, F. H. Ellinger, U.S. Atomic Energy Commission, Rept. La-2184, 1958; *Chem. Abstr.*, **52**, 14,496 (1958).
8. G. A. Abdullaev, N. D. Nagorskaya, A. V. Novoselova, G. N. Ronami, *Vestnik Moskov. Univ. Khim.*, **14**, 109 (1973); *Chem. Abstr.*, **78**, 165,595 (1973).
9. T. W. Baker, *Acta Crystallogr.*, **15**, 175 (1962).
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12. H. Witte, *Naturwissenschaften*, **25**, 795 (1937).
13. E. Hellner, F. Laves, *Z. Kristallogr.*, **A105**, 134 (1943).
14. F. E. Wang, F. A. Kanda, C. F. Miskell, A. J. King, *Acta Crystallogr.*, **18**, 24 (1965).
15. E. I. Gladyshevskii, P. I. Kripyakevich, Ju. B. Kuz'ma, M. Ju. Teslyuk, *Kristallografiya*, **6**, 769 (1961).
16. P. I. Kripyakevich, V. I. Edzokimenko, *Kristallografiya*, **7**, 31 (1962).
17. F. E. Wang, F. A. Kanda, C. F. Miskell, A. J. King, *Acta Crystallogr.*, **16**, 697 (1963).
18. J. C. Miller, L. Andrews, *J. Am. Chem. Soc.*, **100**, 6956 (1978).

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7.2.6.1. Binary Alloys

7.2.6.1.1. Phase Diagrams.

mixed with the calculated amount of Sr and heated to 1000°C for 20 h, which ensures complete reaction⁴. Strontium may be generated in situ by using a mixture of SrO with Be⁵.

The compounds of Mg with Ca, Sr and Ba are also simply prepared; mixtures of different proportions are heated to above the liquidus temperature and cooled for examination under inert conditions. Single crystals can be picked out from those alloys that contain a distinct compound phase as detected by x-rays⁶.

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4. W. Klemm, D. Kunze, in *The Alkali-Metals*, Spec. Publ. No. 22, The Chemical Society, London, 1967, pp. 3–22.
5. N. N. Matyushenko, V. N. Karev, L. F. Verkhorobin, *Russ. J. Inorg. Chem.*, **8**, 928 (1963).
6. F. E. Wang, F. A. Kanda, C. F. Miskell, A. J. King, *Acta Crystallogr.*, **18**, 24 (1965).

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(i) **Systems Containing Lithium.** (a) Li–Be. An approximate value of 0.17 mol% Be at 1000°C is the smallest reported value of the solubility of Be in molten Li, even after 200 h of equilibration². Higher values of 0.23 mol% Be at 732°C and 1.08 mol% Be at 1016°C, and 3 mol% Be at 900°C and 12 mol% Be at 1200°C have been reported⁵. The system contains no compounds, and there is restricted solid solubility or possibly a eutectic.

(b) Li–Mg. There is considerable variance in the determinations of the liquidus and solidus up to 70 mol% Mg. The maximum, however, is located at 594°C (ca. 70.8 mol% Mg) and the eutectic at 588°C (77 mol% Mg). There is better agreement for the Mg-rich region, and most interest has centered on the solid solutions (their limits, structures and variation in lattice parameters with composition) owing to the industrial interest^{2,3}.

(c) Li–Ca. Estimations for the eutectic point are 7.7, 8.0 mol% Ca at 141.8, 165, 140°C^{2,3}, or more recently 8.2 mol% Ca and $141 \pm 1^\circ\text{C}$ ⁴. Similarly, with the peritectic arrest early values were at 230.9, 225 and ca. 230°C^{2,3} but these have been refined to $230 \pm 2^\circ\text{C}$ from ca. 29 to 90 mol% Ca⁴. Early terminal solubilities were estimated at

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4. W. Klemm, D. Kunze, in *The Alkali-Metals*, Spec. Publ. No. 22, The Chemical Society, London, 1967, pp. 3–22.
5. N. N. Matyushenko, V. N. Karev, L. F. Verkhorobin, *Russ. J. Inorg. Chem.*, **8**, 928 (1963).
6. F. E. Wang, F. A. Kanda, C. F. Miskell, A. J. King, *Acta Crystallogr.*, **18**, 24 (1965).

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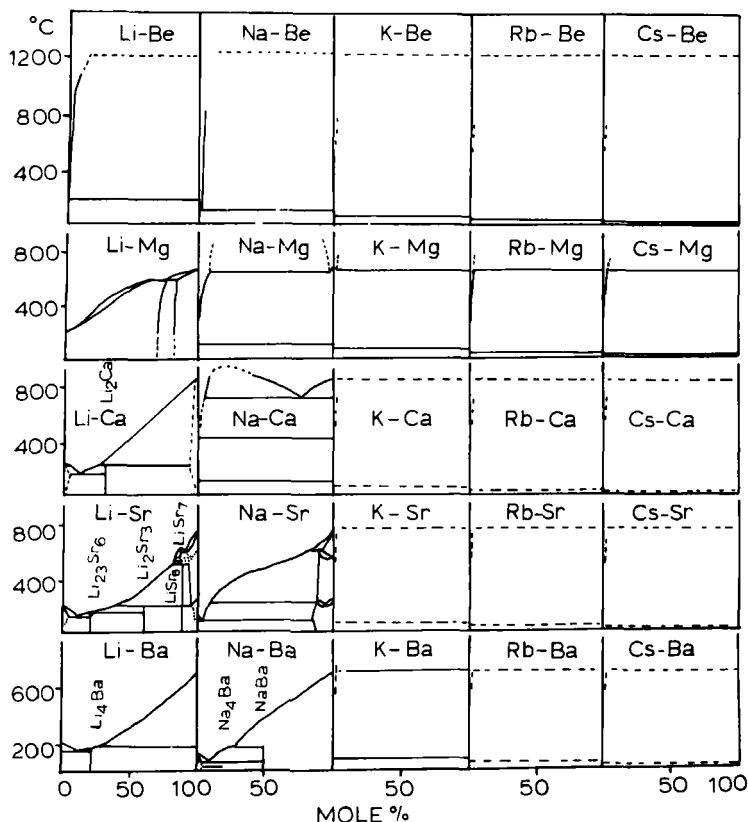


Figure 1. Summary of group IA-group IIA phase diagrams (updated from ref. 1).

2.1 mol% Ca and 3 mol% Li, with a later value of 0.43 mol% Ca at the eutectic temperature⁴.

(d) Li-Sr. Available information is collected in ref. 4. The phase diagram is summarized in Fig. 1. This system is the most complicated of the Li-group-IIA mixtures, particularly at the Sr-rich end, which is shown in detail in ref. 4.

(e) Li-Ba. This simple system has a eutectic point at 10.5 mol% Ba and 143°C and contains one compound, Li_4Ba , that forms peritectically at 156°C. The solid solubility is less than 0.51 mol% Ba in Li, and less than 10% Li in Ba⁴.

(ii) Systems Containing Sodium. (a) Na-Be. There is probably restricted liquid miscibility in this system, and the possibility of a eutectic system with a flat liquidus cannot be excluded. Sodium dissolves ca. 3 mol% Be at 875°C, which is close to the bp of Na (881°C)^{1,5}.

(b) Na-Mg. This pair of elements shows extremely limited miscibility. Up to about 8.2% Mg is shown to dissolve in molten Na at 637°C^{1,5}, but this conflicts with earlier data showing that the two immiscible liquids in mutual contact at 638°C contain ca. 1.2 mol% Mg and 2.1 mol% Na, respectively². This agrees more with a

value of 2.1 mol% Na at 638°C, rising to 2.7 mol% Na at 700°C, for the solubility of Na in molten Mg from a later source⁶.

(c) Na–Ca. This is a much neglected system, although parts of the phase diagram are probably still undetermined (the liquidus up to 4 mol% Ca in Na and the consolute temperature region, 16–40 mol% Ca). Difficulty arises from the sluggish separation of the two immiscible liquids. Calcium forms a eutectic with Na at 77.9 mol% Ca and 710°C, but no eutectic point for Ca in Na has been found².

(d) Na–Sr. The phase diagram displayed in Fig. 1 is from refs. 7 and 8; the original may be found in ref. 8. Early work identified a eutectic at 3.2 mol% Sr and 92.5°C³, but more extensive (0–100 mol%) investigation has amended this to 1.3 mol% Sr at 94°C and established the entire liquidus and the solid solubility regions of the Sr-rich end⁷. Considerable revision of the Na-rich (up to 38 mol% Sr) liquidus ensued, and the eutectic point was relocated at 0.65 mol% Sr and 94.80°C, with estimated terminal solid solubility of Sr in Na of 0.04 mol% at the eutectic temperature⁸.

(e) Na–Ba. Early forms of the Na–Ba phase diagram³ have been superseded by the less complex and more reliable version⁴. A more recent study of the 0–44 mol% Ba liquidus relocates the eutectic, which is examined in detail at 4.5 mol% Ba and 83°C (previously 5.5 mol% Ba and 82°C^{4,9}), and shows a convex rather than concave liquidus reflecting lower solubility of Sr in molten Na¹⁰. The liquidus^{9,10} meets the peritectic horizontal (197°C) at 24 mol% Ba. A composite diagram from refs. 9 and 10 is shown in Fig. 1.

(iii) Systems Containing Potassium. (a) K–Be, K–Mg, K–Sr and K–Ba. Liquid potassium is immiscible with the group-IIA metals; the maximum solubility in molten Mg is 1.0 mol% at 700°C⁶.

(iv) Systems Containing Rubidium. (a) Rb–Be. Small solubilities of Be in molten Rb have been detected, but there is little agreement between the values. After equilibration of Be with molten Rb for 40 h at 100°C in an iron container, the liquid contains 0.16 mol% Be, and there is no measurable solubility at 400°C and no evidence of intermediate compounds in the system. Earlier work shows a lower solubility of less than 0.001 mol% Be for materials held at 540–760°C in sealed Ta containers⁵.

(b) Rb–Mg, –Ca, –Sr, –Ba. These systems are virtually immiscible; mutual liquid solubilities are small reaching 1.2 mol% for Mg in Rb at the monotectic temperature 650°C. There are no compounds, and the melting point of Mg is not measurably lowered by dissolved Rb⁵.

(v) Systems Containing Cesium. (a) Cs–Be, –Mg, –Ca, –Sr, –Ba. Cesium is immiscible in both liquid and solid states with the group-IIA metals. At 600°C, the solubility of Be in molten Cs is 0.18 mol%, falling to undetectable amounts at 100°C. No more than 1.8 mol% Mg dissolves in liquid Cs at the monotectic temperature 650°C, and the mp of Mg is not measurably lowered by Cs. There are no compounds in these systems⁵.

(R. J. PULHAM)

1. W. Klemm, D. Kunze, in *The Alkali-Metals*, Spec. Publ. No. 22, The Chemical Society, London, 1967, pp. 3–22.
2. M. Hansen, ed., *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
3. R. P. Elliott, ed., *Constitution of Binary Alloys*, First Suppl., McGraw-Hill, New York, 1965.

7.2.6.1. Binary Alloys

7.2.6.1.2. Compound Formation.

4. F. A. Shunk, ed., *Constitution of Binary Alloys*, Second Suppl., McGraw-Hill, New York, 1972.
5. W. G. Moffatt, ed., *Handbook of Binary Phase Diagrams*, Vols. 1-3, General Electric, Schenectady, NY, 1978.
6. M. F. Lantratov, *Zh. Priklad. Khim.*, 46, 1982 (1973); *Chem. Abstr.*, 79, 150,100 (1973).
7. W. O. Roberts, U.S. Atomic Energy Commission, Rept. TID-20639, 1964; *Chem. Abstr.*, 62, 2285f (1964).
8. P. R. Bussey, P. Hubberstey, R. J. Pulham, *J. Chem. Soc., Dalton Trans.*, 2327 (1976).
9. F. A. Kanda, R. M. Stevens, D. V. Keller, *J. Phys. Chem.*, 69, 3867 (1965).
10. C. C. Addison, G. K. Creffield, P. Hubberstey, R. J. Pulham, *J. Chem. Soc., A*, 2688 (1971).

7.2.6.1.2. Compound Formation.

Lithium forms compounds with Ca, Sr and Ba, but there is no stoichiometry common to all three systems. The phases are identified and distinguished by their x-ray diffraction patterns. The phase Li_2Ca is hexagonal¹, analogous to Mg_2Ca , and of the $\text{MgZn}_2(\text{C14})$ structure with space group $\text{P6}_3/\text{mmc}$, $Z = 4$ and with $a = 626.0 \pm 0.8$ pm, $c = 1025 \pm 2$ pm. This structure was subsequently confirmed using single crystals, but giving slightly different cell dimensions of $a = 631 \pm 1$ pm and $c = 1028 \pm 1$ pm².

In the Li-Sr system, four phases $\text{Li}_{23}\text{Sr}_6$, Li_2Sr_3 , LiSr_8 and LiSr_7 are recognized and their structures refined^{3,4}. The compound $\text{Li}_{23}\text{Sr}_6$ is fcc with the $\text{Mn}_{23}\text{Th}_6$ type of structure having space group $\text{Fm}3\text{m}$ with $a = 1488 \pm 5$ (or 1503)⁵ and $Z = 4$ ^{3,4}. The compound Li_2Sr_3 is tetragonal with space group $\text{P4}_2/\text{mmn}$, $a = 962.8 \pm 0.4$ pm, $c = 855.0 \pm 0.3$ pm and $Z = 4$. From 530 to 548°C, LiSr_7 exists with a body-centered tetragonal structure having $a = 761$ pm and $c = 650$ pm. The compound LiSr_8 shows two polymorphic forms, one above and one below $197 \pm 1^\circ\text{C}$. The low-T form (25–197°C) is tetragonal with $a = 616$ and $c = 886$ pm. From 198 to 496°C, the structure is hcp with $a = 431$ and $c = 1385$ pm^{3,4}.

In the Li-Ba system, powder diffraction data for Li_4Ba indicated a hexagonal cell with $a = 1092 \pm 1$ pm and $c = 894 \pm 1$ pm⁶, subsequently refined to $a = 1102.6 \pm 2.3$, $c = 889.1 \pm 1.0$ pm and $Z = 6$ ¹.

Early reports claimed the existence of Na_{12}Ba , Na_6Ba , NaBa , Na_2Ba_5 and Na_2Ba , but the two compounds that have most credence are NaBa and Na_4Ba . The former is orthorhombic with $a = 426 \pm 2$, $b = 588 \pm 2$ and $c = 965 \pm 2$ pm, while Na_4Ba is tetragonal with $a = 916 \pm 3$ and $c = 1728 \pm 3$ pm⁸.

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1. E. Hellner, F. Laves, *Z. Kristallogr.*, 105A, 134 (1943).
2. F. A. Kanda, A. J. King, U.S. Atomic Energy Commission, Rept. TID-15150, 1962; *Chem. Abstr.*, 57, 14,481f (1962).
3. F. E. Wang, F. A. Kanda, A. J. King, *J. Phys. Chem.*, 66, 2138 (1962).
4. F. E. Wang, A. J. King, F. A. Kanda, *J. Phys. Chem.*, 66, 2142 (1962).
5. P. I. Kripyakevich, G. I. Oleksiv, *Dopov. Akad. Nauk Ukr. RSR*, 11, 1489 (1963); *Chem. Abstr.*, 60, 11,445 (1964).
6. D. V. Keller, F. A. Kanda, A. J. King, *J. Phys. Chem.*, 62, 732 (1958).
7. F. E. Wang, F. A. Kanda, C. F. Miskell, A. J. King, *Acta Crystallogr.*, 18, 24 (1965).
8. F. A. Kanda, R. M. Stevens, D. V. Keller, *J. Phys. Chem.*, 69, 3867 (1965).

7.2.6. Formation of Alloys Between Group-IA and Group-IIA Elements 305

7.2.6.1. Binary Alloys

7.2.6.1.2. Compound Formation.

4. F. A. Shunk, ed., *Constitution of Binary Alloys*, Second Suppl., McGraw-Hill, New York, 1972.
5. W. G. Moffatt, ed., *Handbook of Binary Phase Diagrams*, Vols. 1–3, General Electric, Schenectady, NY, 1978.
6. M. F. Lantratov, *Zh. Priklad. Khim.*, 46, 1982 (1973); *Chem. Abstr.*, 79, 150,100 (1973).
7. W. O. Roberts, U.S. Atomic Energy Commission, Rept. TID-20639, 1964; *Chem. Abstr.*, 62, 2285f (1964).
8. P. R. Bussey, P. Hubberstey, R. J. Pulham, *J. Chem. Soc., Dalton Trans.*, 2327 (1976).
9. F. A. Kanda, R. M. Stevens, D. V. Keller, *J. Phys. Chem.*, 69, 3867 (1965).
10. C. C. Addison, G. K. Creffield, P. Hubberstey, R. J. Pulham, *J. Chem. Soc., A*, 2688 (1971).

7.2.6.1.2. Compound Formation.

Lithium forms compounds with Ca, Sr and Ba, but there is no stoichiometry common to all three systems. The phases are identified and distinguished by their x-ray diffraction patterns. The phase Li_2Ca is hexagonal¹, analogous to Mg_2Ca , and of the $\text{MgZn}_2(\text{C14})$ structure with space group $\text{P6}_3/\text{mmc}$, $Z = 4$ and with $a = 626.0 \pm 0.8$ pm, $c = 1025 \pm 2$ pm. This structure was subsequently confirmed using single crystals, but giving slightly different cell dimensions of $a = 631 \pm 1$ pm and $c = 1028 \pm 1$ pm².

In the Li–Sr system, four phases $\text{Li}_{23}\text{Sr}_6$, Li_2Sr_3 , LiSr_8 and LiSr_7 are recognized and their structures refined^{3,4}. The compound $\text{Li}_{23}\text{Sr}_6$ is fcc with the $\text{Mn}_{23}\text{Th}_6$ type of structure having space group $\text{Fm}3\text{m}$ with $a = 1488 \pm 5$ (or 1503)⁵ and $Z = 4$ ^{3,4}. The compound Li_2Sr_3 is tetragonal with space group $\text{P4}_2/\text{mmn}$, $a = 962.8 \pm 0.4$ pm, $c = 855.0 \pm 0.3$ pm and $Z = 4$. From 530 to 548°C, LiSr_7 exists with a body-centered tetragonal structure having $a = 761$ pm and $c = 650$ pm. The compound LiSr_8 shows two polymorphic forms, one above and one below $197 \pm 1^\circ\text{C}$. The low-T form (25–197°C) is tetragonal with $a = 616$ and $c = 886$ pm. From 198 to 496°C, the structure is hcp with $a = 431$ and $c = 1385$ pm^{3,4}.

In the Li–Ba system, powder diffraction data for Li_4Ba indicated a hexagonal cell with $a = 1092 \pm 1$ pm and $c = 894 \pm 1$ pm⁶, subsequently refined to $a = 1102.6 \pm 2.3$, $c = 889.1 \pm 1.0$ pm and $Z = 6$ ¹.

Early reports claimed the existence of Na_{12}Ba , Na_6Ba , NaBa , Na_2Ba_5 and Na_2Ba , but the two compounds that have most credence are NaBa and Na_4Ba . The former is orthorhombic with $a = 426 \pm 2$, $b = 588 \pm 2$ and $c = 965 \pm 2$ pm, while Na_4Ba is tetragonal with $a = 916 \pm 3$ and $c = 1728 \pm 3$ pm⁸.

(R. J. PULHAM)

1. E. Hellner, F. Laves, *Z. Kristallogr.*, 105A, 134 (1943).
2. F. A. Kanda, A. J. King, U.S. Atomic Energy Commission, Rept. TID-15150, 1962; *Chem. Abstr.*, 57, 14,481f (1962).
3. F. E. Wang, F. A. Kanda, A. J. King, *J. Phys. Chem.*, 66, 2138 (1962).
4. F. E. Wang, A. J. King, F. A. Kanda, *J. Phys. Chem.*, 66, 2142 (1962).
5. P. I. Kripyakevich, G. I. Oleksiv, *Dopov. Akad. Nauk Ukr. RSR*, 11, 1489 (1963); *Chem. Abstr.*, 60, 11,445 (1964).
6. D. V. Keller, F. A. Kanda, A. J. King, *J. Phys. Chem.*, 62, 732 (1958).
7. F. E. Wang, F. A. Kanda, C. F. Miskell, A. J. King, *Acta Crystallogr.*, 18, 24 (1965).
8. F. A. Kanda, R. M. Stevens, D. V. Keller, *J. Phys. Chem.*, 69, 3867 (1965).

306 7.2.6. Formation of Alloys Between Group-IA and Group-IIA Elements**7.2.6.1. Binary Alloys****7.2.6.1.3. Preparations.****7.2.6.1.3. Preparations.**

The Li-group-IIA intermetallic compounds are prepared simply by heating the components in the appropriate ratios. Thus, when melted and homogenized at 100° above the peritectic T (152°C; see §7.2.6.1.1) and subsequently cooled, an alloy of 79.2% Li and 20.8% Sr gives a brittle alloy containing single crystals of $\text{Li}_{23}\text{Sr}_6$ ¹. Crystals of Li_2Sr_3 cannot be grown like this because its composition is too far away from the junction of the peritectic isothermal with the liquidus. Instead, this phase is formed by reacting liquid with solid LiSr_8 for alloys of higher Sr content than 40 mol%. Primary crystals of Li_2Sr_3 form, however, from cooled melts in the composition range 21–40% Sr, although they react with the liquid matrix at 152°C to form $\text{Li}_{23}\text{Sr}_6$ by the peritectic reaction. To obtain Li_2Sr_3 , a 40 mol% Sr alloy is melted and mixed at 270°C, then cooled at 10^{-2}°C s^{-1} and held at 160°C for 2 h before quenching in ice water. The slow cooling and subsequent soaking ensures good crystals. The quenching prevents the crystals reacting with the liquid to give $\text{Li}_{23}\text{Sr}_6$ ². Alloys (Na_4Ba) are prepared by weighing under Ar ³, and the liquid alloys (Li_4Ba , Na_4Ba) may be contained in low-carbon steel, stoppered crucibles⁴.

(R. J. PULHAM)

1. F. E. Wang, A. J. King, F. A. Kanda, *J. Phys. Chem.*, **66**, 2142 (1962).
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3. F. A. Kanda, R. M. Stevens, D. V. Keller, *J. Phys. Chem.*, **69**, 3867 (1965).
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7.3. Formation of the Group-IA or -IIA–Group-IB or -IIB Element Bonds

7.3.1. Formation of the Group-IA–Group-IB Element Bonds

7.3.1.1. Phase Diagrams

7.3.1.1.1. Lithium Systems.

Two phase diagrams are available for lithium–copper systems. No intermetallic phases were found¹, but LiCu_4 was later observed². Substantial solid solubility of lithium in copper approaching 20 at% at the melting point of Li has been observed.

A first study of the Li–Ag system showed only two phases of fixed composition³; however, a much more complex system of phases was found later⁴ using thermal, micrographic and x-ray diffraction methods.

The phase diagram of the Li–Au system reveals a great deal of complexity, with separate intermetallic phases being formed⁵ based on thermal analysis supported by x-ray diffraction at specific compositions. Annealing, sometimes over long time periods, has been undertaken in some cases.

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4. W. E. Freeth, G. V. Raynor, *J. Inst. Metals*, **82**, 569 (1953/4).
5. G. Kienast, J. Verma, *Z. Anorg. Allg. Chem.*, **310**, 143 (1961).

7.3.1.1.2. Sodium Systems.

No phase diagram is available for the sodium–copper system.

Although early determinations^{1,2} found no compounds in the sodium–silver system³, thermal arrests at 322 and 744°C and x-ray diffraction revealed the existence of an intermediate phase of composition NaAg_2 . The lower T arrest was thought to arise from a phase transformation of the compound. Three intermetallic phases have also been observed in the sodium–gold phase diagram^{3,4}. Both diagrams are in agreement in the Au-rich side, but the more recent diagram³ is the more reliable.

(M. G. BARKER)

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7.3.1.1.3. Potassium Systems.

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7.3.1.1.4. Rubidium and Cesium Systems.

No phase diagram is available for systems involving either Cu or Ag. The Rb–Au system shows three intermediate phases¹, although RbAu_4 was later shown² to be RbAu_5 . No compound Rb_2Au has been observed corresponding to K_2Au .

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7.3.1.2. Compound Formation

The compounds observed in the phase diagrams reported in the previous section are collected in Table 1.

(M. G. BARKER)

7.3.1.3. Preparations

Intermetallic compounds are generally prepared by simply heating the elements in the correct molar proportion at or just below the liquidus temperature specified in the phase diagram. The major experimental problems associated with these methods are first, attack of the container material by the alkali metal or the intermetallic compound in the molten state; second, the temperature chosen must be such as to attain true homogeneity of the intermetallic compound.

(M. G. BARKER)

7.3.1.3.1. of Alkali-Metal–Copper Compounds.

Lithium reacts with copper powder in a copper crucible at 200°C to yield yellow mixed crystals of the variable-phase LiCu_4 , whose formulation represents a maximum content of Li¹. A crystalline LiCu_4 product is observed on copper surfaces exposed to liquid lithium².

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7.3.1. Formation of the Group-IA–Group-IB Element Bonds

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Intermetallic compounds are generally prepared by simply heating the elements in the correct molar proportion at or just below the liquidus temperature specified in the phase diagram. The major experimental problems associated with these methods are first, attack of the container material by the alkali metal or the intermetallic compound in the molten state; second, the temperature chosen must be such as to attain true homogeneity of the intermetallic compound.

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TABLE 1. COMPOUNDS OBSERVED BETWEEN THE ELEMENTS OF GROUP IA AND GROUP IB

Li with					
Cu	LiCu ₄				
Ag	LiAg	Li ₉ Ag ₄	Li ₁₀ Ag ₃	Li ₁₂ Ag	
Au	Au ₃ Li	Au ₅ Li ₄	Au ₃ Li ₅	Li ₃ Au	Li ₁₅ Au ₄
Na with					
Cu	None				
Ag	NaAg ₂				
Au	NaAu ₂	NaAu	Na ₂ Au		
K with					
Cu	None				
Ag	None				
Au	KAu ₅	KAu ₂	KAu	K ₂ Au	
Rb with					
Cu	None				
Ag	None				
Au	RbAu ₅	RbAu ₂	RbAu		
Cs with					
Cu	None				
Ag	None				
Au	CsAu				

No compound has been reported for other alkali-metal–copper systems.

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1. W. Klemm, B. Volavsek, *Z. Anorg. Allg. Chem.*, **29b**, 184 (1958).
2. C. F. Old, P. Trevena, Report AERE R9853 (1980); *Met. Sci.*, **15**, 281 (1981).

7.3.1.3.2. of Alkali-Metal–Silver Compounds.

Numerous compounds are observed in the Li–Ag phase diagram. The alloys are heated under Ar and cast in mild steel crucibles for metallographic examination, with homogeneity achieved by remelting under vacuum¹. Similar procedures were employed in an earlier study², except that H₂ was used in place of Ar. An Ar cover gas was also employed to prepare the brasslike γ_3 phase in the Li–Ag system for structural study. The silver and lithium were melted together in an iron crucible for 15–30 s before cooling without quenching to minimize the loss of lithium³.

Both LiAg and NaAg have been investigated as gas-phase molecular species using high-T effusion techniques^{4,5}. In determining the dissociation energy of LiAg, mixtures of Ag and Li₂O were evaporated using molybdenum or zirconia liners⁵.

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5. A. Neubert, K. F. Zmbov, *J. Chem. Soc., Faraday I*, **70**, 2219 (1974).

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7.3.1.3. Preparations

7.3.1.3.2. of Alkali-Metal–Silver Compounds.

TABLE 1. COMPOUNDS OBSERVED BETWEEN THE ELEMENTS OF GROUP IA AND GROUP IB

Li with					
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Ag	LiAg	Li ₉ Ag ₄	Li ₁₀ Ag ₃	Li ₁₂ Ag	
Au	Au ₃ Li	Au ₅ Li ₄	Au ₃ Li ₅	Li ₃ Au	Li ₁₅ Au ₄
Na with					
Cu	None				
Ag	NaAg ₂				
Au	NaAu ₂	NaAu	Na ₂ Au		
K with					
Cu	None				
Ag	None				
Au	KAu ₅	KAu ₂	KAu	K ₂ Au	
Rb with					
Cu	None				
Ag	None				
Au	RbAu ₅	RbAu ₂	RbAu		
Cs with					
Cu	None				
Ag	None				
Au	CsAu				

No compound has been reported for other alkali-metal–copper systems.

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310 7.3. Formation of the Group-IA or -IIA-Group-IB or -IIB Element Bonds

7.3.1. Formation of the Group-IA-Group-IB Element Bonds

7.3.1.4. Ionic Compounds

7.3.1.3.3. of Alkali-Metal-Gold Compounds.

Only compounds formed with Li, Na and K are discussed here; the ionic Rb-Au and Cs-Au compounds are treated in the next section.

A vapor generator for the successive deposition of Na, K and Cs on photocathodes without emission of solid particles may be used to prepare alkali-metal-gold compounds¹.

The Li-Au phase diagram was studied² by heating lithium and gold at 100–200°C above the melting point of Li for 6 h followed by heating at 100°C above the melting point of the alloy for 1 h. Certain alloys require long annealing times; e.g., LiAu₃ must be heated at 360°C for a long time before its cubic structure is observed. The α' -LiAu₃ phase gives extra reflections, which disappear after long annealing at 350°C.

Sodium-gold compounds were prepared by melting the metals together at 980°C in an iron crucible under N₂ and then quenching^{3,4}, or by melting the two metals in alumina crucibles under Ar, homogenizing at 100–200°C below the melting point and then cooling rapidly⁵. This rapid quenching indicates that NaAu₂ may have a high-T modification that is not observed in slowly cooled melts. The Na-Au, K-Au and Rb-Au alloys are prepared by melting the high-purity elements under vacuum in cells made from sintered nonporous alumina and pure Mo. Both materials are compatible with the alkali metals and with the molten alloys. However, the ceramic container cannot be used to prepare LiAu since liq Li readily attacks Al₂O₃, so a thin-walled Mo cell is used⁶. Gold powder reacts with liquid sodium at 170°C in a quartz vessel to give Na₂Au⁷.

The compounds KAu₅ and RbAu₅ have been prepared by melting the pure metals in an alumina container sealed in an iron bomb⁸.

The ternary compounds Na₂AuSn, KAu₄Sn₂ and Na₂AuGe are known; KAu₄Sn₂ is prepared⁹ by heating a mixture of the three elements in tantalum crucibles under Ar for 14 h at 500°C, followed by a long (3–4 d) equilibration at 400–600°C; Na₂AuGe forms¹⁰ from the reaction of NaAu and NaGe at 1000°C.

(M. G. BARKER)

1. J. H. N. Van Vucht, J. J. B. Fransen, Ger. Pat., 2,326,957 (1974); *Chem. Abstr.*, 80, 76,584 (1974).
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7.3.1.4. Ionic Compounds

The compound CsAu is ionic, Cs⁺ Au⁻; RbAu was also thought to be ionic owing to xs Rb in the lattice but is now thought of as being a semiconductor. The preparation of CsAu is from¹ a gold film with Cs vapor. The gold film is first

310 7.3. Formation of the Group-IA or -IIA-Group-IB or -IIB Element Bonds

7.3.1. Formation of the Group-IA-Group-IB Element Bonds

7.3.1.4. Ionic Compounds

7.3.1.3.3. of Alkali-Metal-Gold Compounds.

Only compounds formed with Li, Na and K are discussed here; the ionic Rb-Au and Cs-Au compounds are treated in the next section.

A vapor generator for the successive deposition of Na, K and Cs on photocathodes without emission of solid particles may be used to prepare alkali-metal-gold compounds¹.

The Li-Au phase diagram was studied² by heating lithium and gold at 100–200°C above the melting point of Li for 6 h followed by heating at 100°C above the melting point of the alloy for 1 h. Certain alloys require long annealing times; e.g., LiAu₃ must be heated at 360°C for a long time before its cubic structure is observed. The α' -LiAu₃ phase gives extra reflections, which disappear after long annealing at 350°C.

Sodium-gold compounds were prepared by melting the metals together at 980°C in an iron crucible under N₂ and then quenching^{3,4}, or by melting the two metals in alumina crucibles under Ar, homogenizing at 100–200°C below the melting point and then cooling rapidly⁵. This rapid quenching indicates that NaAu₂ may have a high-T modification that is not observed in slowly cooled melts. The Na-Au, K-Au and Rb-Au alloys are prepared by melting the high-purity elements under vacuum in cells made from sintered nonporous alumina and pure Mo. Both materials are compatible with the alkali metals and with the molten alloys. However, the ceramic container cannot be used to prepare LiAu since liq Li readily attacks Al₂O₃, so a thin-walled Mo cell is used⁶. Gold powder reacts with liquid sodium at 170°C in a quartz vessel to give Na₂Au⁷.

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7.3.2.1. Phase Diagrams

7.3.2.1.1. Lithium Systems.

evaporated onto the walls of a borosilicate glass or quartz tube to a depth of several hundred Ångströms, and Cs vapor deposited onto the gold at 150–200°C under vacuum². The white crystalline CsAu film decomposes at temperatures $\geq 250^\circ\text{C}$.

Bulk samples, as opposed to thin films, are prepared by exposing gold powder to Cs vapor at 200°C in evacuated quartz tubes³. A later publication indicated that the reaction between gold films and Cs vapor did in fact take place at RT. This study involved the in situ generation of Cs by the heating of Cs_2CrO_4 and silicon powder in a nickel side arm⁴. Ionic CsAu not only reacts with oxygen, but corrodes SiO_2 in the molten state. Current preparative methods involve the heating of ultrapure Au and Cs metals at 650°C for several hours under Ar in molybdenum cells^{5,6} fitted with tantalum gaskets⁷. Alumina cells have been used above the melting point of CsAu (590°C)⁸. The reaction of cesium with gold powder is complete within 10 min at 612°C, and the reaction of rubidium within 15 min at 500°C. Attempts to prepare CsAu and RbAu by solid-state reactions did not give single-phased products: the CsAu contained traces of Au_2Cs ⁹. The preparations of CsAu and RbAu suitable for structure determinations have been described¹⁰.

The existence of cesium auride molecules from cesium and gold heated briefly at the melting temperature of and then annealed at 700°C for 5–6 h in a molybdenum high-T cell has been proposed. The mass spectrum showed, in addition to Cs^+ , Cs^{2+} and Au^+ , a distinct signal for CsAu^+ . At 1200–1500K the intensity of the signal at $m/e = 330$ was weaker by a factor of about 10^3 than that of the Cs^+ signal. A bond energy of $\sim 460 \text{ kJ mol}^{-1}$ is consistent with the formation of an ionic bond¹¹.

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7.3.2. Formation of the Group-IA–Group-IIB Element Bonds

7.3.2.1. Phase Diagrams

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The Li–Zn phase diagram shows the presence of eight intermediate phases¹. Later x-ray diffraction results confirm the existence of five intermediate RT phases^{2–3}. Polymorphism is shown by the three compounds shown in the Li–Cd phase system⁴, and this has confused the interpretation of x-ray diffraction patterns^{5–8}.

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The composition of the Li–Hg system was investigated, and seven phases were postulated^{9,10}.

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7.3.2.1.2. Sodium Systems.

In contrast to the lithium system, the Na–Zn phase diagram¹ shows only NaZn_{13} ^{2,3}.

The Cd–Na phase diagram, established with 5–85 wt% Na⁴, shows two intermetallic phases, NaCd_2 and $\text{Na}_2\text{Cd}_{11}$. The latter was earlier reported as either NaCd_5 or NaCd_6 , but more recent work indicates a cubic structure isomorphous with $\text{Mg}_2\text{Zn}_{11}$ in which some electron transfer occurs between the two types of atom^{5,6}.

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The K–Zn phase diagram is analogous to that of Na–Zn in that only one compound, KZn_{13} , is formed¹. Similarly, KCd_{13} is the only compound occurring in the K–Cd system²; KCd_7 has not been confirmed².

The complete K–Hg phase diagram³ is compiled from three studies^{4–6}, and shows the formation of six intermetallic phases. A determination in the range 22–30 at% K indicates the formation of $\text{KHg}_{2.7}$ ⁷.

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4. G. Tammann, *Z. Anorg. Allg. Chem.*, **37**, 303 (1903).
5. E. Jancke, *Z. Phys. Chem.*, **58**, 245 (1907).

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7. H. Schuhmann, K. Kaltwasser, *Z. Phys. Chem. (Leipzig)*, 219, 168 (1962).

7.3.2.1.4. Rubidium Systems.

No phase diagram for the Rb-Zn or Rb-Cd systems is available.

The Rb-Hg system shows eight intermetallic phases¹.

(M. G. BARKER)

1. W. Biltz, F. Weibke, H. Eggers, *Z. Anorg. Allg. Chem.*, 219, 119 (1934).

7.3.2.1.5. Cesium Systems.

No phase diagram is available for the Cs-Zn or Cs-Cd systems. The Cs-Hg system shows six intermetallic phases, but the accuracy of this determination is in doubt¹.

(M. G. BARKER)

1. N. S. Kurnakov, G. J. Zukovsky, *Z. Anorg. Allg. Chem.*, 52, 416 (1907).

7.3.2.2. Compound Formation

The compounds formed between the group-IA and group-IIB elements are collected in Table 1. Some compounds have been inserted into the table that are not

TABLE 1. COMPOUNDS FORMED BETWEEN GROUP-IA AND GROUP-IIB ELEMENTS

Li with								
Zn	LiZn	Li ₂ Zn ₃	LiZn ₂	Li ₂ Zn ₅	LiZn ₄			
Cd	Li ₃ Cd	LiCd	LiCd ₃					
Hg	Li ₆ Hg	Li ₃ Hg	Li ₂ Hg	LiHg	LiHg ₂	LiHg ₃		
Na with								
Zn	NaZn ₁₃							
Cd	NaCd ₂	Na ₂ Cd ₁₁						
Hg	Na ₃ Hg	Na ₅ Hg ₂	Na ₃ Hg ₂	NaHg	Na ₇ Hg ₈	NaHg ₂	NaHg ₆	NaHg ₁₆
K with								
Zn	KZn ₁₃	KZn						
Cd	KCd ₁₃							
Hg	KHg	K ₅ Hg ₇	KHg ₂	KHg _{2.7}	KHg ₃	KHg ₄	KHg ₈	KHg ₁₁
Rb with								
Zn	No data							
Cd	RbCd ₁₃							
Hg	Rb ₇ Hg ₈	Rb ₃ Hg ₄	RbHg ₂	Rb ₂ Hg ₇	Rb ₅ Hg ₁₈	Rb ₂ Hg ₉	RbHg ₆	RbHg ₁₁
Cs with								
Zn	No data							
Cd	CsCd ₁₃							
Hg		CsHg	Cs ₃ Hg ₄	CsHg ₂	CsHg ₄	CsHg ₆	CsHg ₁₂	

7.3. Formation of the Group-IA or -IIA-Group-IB or -IIB Element Bonds 313

7.3.2. Formation of the Group-IA-Group-IIB Element Bonds

7.3.2.2. Compound Formation

6. E. Janেকে, *Z. Metallk.*, 20, 113 (1928).

7. H. Schuhmann, K. Kaltwasser, *Z. Phys. Chem. (Leipzig)*, 219, 168 (1962).

7.3.2.1.4. Rubidium Systems.

No phase diagram for the Rb-Zn or Rb-Cd systems is available.

The Rb-Hg system shows eight intermetallic phases¹.

(M. G. BARKER)

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7.3.2.1.5. Cesium Systems.

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The compounds formed between the group-IA and group-IIB elements are collected in Table 1. Some compounds have been inserted into the table that are not

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Li with								
Zn	LiZn	Li ₂ Zn ₃	LiZn ₂	Li ₂ Zn ₅	LiZn ₄			
Cd	Li ₃ Cd	LiCd	LiCd ₃					
Hg	Li ₆ Hg	Li ₃ Hg	Li ₂ Hg	LiHg	LiHg ₂	LiHg ₃		
Na with								
Zn	NaZn ₁₃							
Cd	NaCd ₂	Na ₂ Cd ₁₁						
Hg	Na ₃ Hg	Na ₅ Hg ₂	Na ₃ Hg ₂	NaHg	Na ₇ Hg ₈	NaHg ₂	NaHg ₆	NaHg ₁₆
K with								
Zn	KZn ₁₃	KZn						
Cd	KCd ₁₃							
Hg	KHg	K ₅ Hg ₇	KHg ₂	KHg _{2.7}	KHg ₃	KHg ₄	KHg ₈	KHg ₁₁
Rb with								
Zn	No data							
Cd	RbCd ₁₃							
Hg	Rb ₇ Hg ₈	Rb ₃ Hg ₄	RbHg ₂	Rb ₂ Hg ₇	Rb ₅ Hg ₁₈	Rb ₂ Hg ₉	RbHg ₆	RbHg ₁₁
Cs with								
Zn	No data							
Cd	CsCd ₁₃							
Hg		CsHg	Cs ₃ Hg ₄	CsHg ₂	CsHg ₄	CsHg ₆	CsHg ₁₂	

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Hg	Li ₆ Hg	Li ₃ Hg	Li ₂ Hg	LiHg	LiHg ₂	LiHg ₃		
Na with								
Zn	NaZn ₁₃							
Cd	NaCd ₂	Na ₂ Cd ₁₁						
Hg	Na ₃ Hg	Na ₅ Hg ₂	Na ₃ Hg ₂	NaHg	Na ₇ Hg ₈	NaHg ₂	NaHg ₆	NaHg ₁₆
K with								
Zn	KZn ₁₃	KZn						
Cd	KCd ₁₃							
Hg	KHg	K ₅ Hg ₇	KHg ₂	KHg _{2.7}	KHg ₃	KHg ₄	KHg ₈	KHg ₁₁
Rb with								
Zn	No data							
Cd	RbCd ₁₃							
Hg	Rb ₇ Hg ₈	Rb ₃ Hg ₄	RbHg ₂	Rb ₂ Hg ₇	Rb ₅ Hg ₁₈	Rb ₂ Hg ₉	RbHg ₆	RbHg ₁₁
Cs with								
Zn	No data							
Cd	CsCd ₁₃							
Hg		CsHg	Cs ₃ Hg ₄	CsHg ₂	CsHg ₄	CsHg ₆	CsHg ₁₂	

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Na with								
Zn	NaZn ₁₃							
Cd	NaCd ₂	Na ₂ Cd ₁₁						
Hg	Na ₃ Hg	Na ₅ Hg ₂	Na ₃ Hg ₂	NaHg	Na ₇ Hg ₈	NaHg ₂	NaHg ₆	NaHg ₁₆
K with								
Zn	KZn ₁₃	KZn						
Cd	KCd ₁₃							
Hg	KHg	K ₅ Hg ₇	KHg ₂	KHg _{2.7}	KHg ₃	KHg ₄	KHg ₈	KHg ₁₁
Rb with								
Zn	No data							
Cd	RbCd ₁₃							
Hg	Rb ₇ Hg ₈	Rb ₃ Hg ₄	RbHg ₂	Rb ₂ Hg ₇	Rb ₅ Hg ₁₈	Rb ₂ Hg ₉	RbHg ₆	RbHg ₁₁
Cs with								
Zn	No data							
Cd	CsCd ₁₃							
Hg		CsHg	Cs ₃ Hg ₄	CsHg ₂	CsHg ₄	CsHg ₆	CsHg ₁₂	

shown on the phase diagrams: NaHg_6 or NaHg_{16} on the basis of thermodynamic data for the dilute-Na end of the phase system¹. The compound KZn was formed as a solid phase from solutions of K and Zn in mercury².

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7.3.2.3. Preparative Methods

Alloys are generally prepared by the melting of stoichiometric ratios of the elements in graphite or iron crucibles under Ar or N_2 (not for Li compounds). Variations on this method are outlined below.

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7.3.2.3.1. of Alkali-Metal–Zinc Compounds.

Sodium–zinc alloys for phase diagram determination are prepared¹ by melting the elements in glass tubes under H_2 . Samples of NaZn_{13} are prepared by heating zinc for several hours above the melting point of NaZn_{13} (557°C) with xs Na in alundum extraction thimbles with N_2 or Ar in a steel bomb sealed with copper gaskets. Excess Na was removed by extraction with liq NH_3 . Both KZn_{13} and KCd_{12} were prepared in this manner².

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314 7.3.2. Formation of the Group-IA–Group-IB Element Bonds

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8. C. Coquant, R. Houdart, *C. R. Hebd. Seances Acad. Sci.*, 284B, 171 (1977).
9. K. A. Gingerich, U. V. Choudary, *J. Chem. Phys.*, 68, 3265 (1978).
10. P. H. Kasai, D. McLeod, *J. Phys. Chem.*, 82, 1554 (1978).
11. P. H. Kasai, D. McLeod, *Ber. Bunsenges. Phys. Chem.*, 82, 103 (1978).
12. P. H. Kasai, D. McLeod, *Faraday Symp., Roy. Soc. Chem.*, 14, 65 (1980).

13. M. Hansen, K. Anderko, eds., *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, (1958).
14. R. P. Elliott, ed., *Constitution of Binary Alloys*, First Suppl., McGraw-Hill, New York, 1965.
15. F. A. Shunk, ed., *Constitution of Binary Alloys*, Second Suppl., McGraw-Hill, New York, 1969.
16. W. G. Moffatt, ed., *Handbook of Binary Phase Diagrams*, General Electric, Schenectady, NY, 1977.
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7.3.3.1. Phase Diagrams, Intermetallic Phases and Compounds

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(P. HUBBERSTEY)

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The recommended Be–Ag phase diagram is that in ref. 4, an amended version of that in ref. 1. Only one intermediate phase, δ -Be₂Ag, is confirmed. Since the existence of both the γ phase (included in ref. 1) and the more recently reported compound Be₁₂Ag has been queried⁴, neither is included in the recommended phase diagram. The lack of confirmatory evidence for Be₁₂Ag is somewhat surprising since an x-ray study of single crystals electrolytically extracted from arc-melted alloys is available¹¹. The intermediate phase δ -Be₂Ag, which has an extended homogeneity range and deviates considerably from stoichiometry, has a limited stability range, being formed in a eutectoid reaction at 740°C and decomposing peritectically at 1010°C.

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2. M. L. Hammond, A. T. Davinroy, M. I. Jacobsen, Tech. Rept. AFML-TR-65-223, 1965.
3. S. H. Gelles, J. J. Pickett, E. D. Levine, W. B. Novak, in *The Metallurgy of Beryllium*, Inst. Metals, Monograph Rept. Ser. No. 28, Institute of Metals, 1963, pp. 588–600; *Chem. Abstr.*, 60, 11,695 (1964).
4. F. Aldinger, G. Petzov, *Beryllium Sci. Technol.*, 1, 235 (1979).
5. J. Garcia-Rocha, R. J. Rioja, D. E. Laughlin, *Metall. Trans. A*, 15, 939 (1984).
6. L. S. Magomedova, G. V. Davydov, *Uch. Zap., Dagestan Gos. Pedagog. Inst.*, 5, 39 (1966); *Chem. Abstr.*, 68, 90,650 (1968).
7. L. S. Patskherova, *Izv. Vyssh. Ucheb. Zaved., Fiz.*, 12, 122 (1969); *Chem. Abstr.*, 71, 85,631 (1969).
8. Y. D. Tyapkin, V. A. Golikov, *Fiz. Metal Metalloved.*, 35, 336 (1973); *Chem. Abstr.*, 79, 8825 (1973).
9. Y. D. Tyapkin, V. A. Golikov, *Fiz. Metal Metalloved.*, 36, 1058 (1973); *Chem. Abstr.*, 80, 86,430 (1974).
10. V. A. Golikov, Y. D. Tyapkin, *Fiz. Metal Metalloved.*, 37, 322 (1974); *Chem. Abstr.*, 81, 67,399 (1974).
11. F. W. von Batchelder, R. F. Raeuchle, *Acta Crystallogr.*, 1, 122 (1958).
12. M. H. Mueller, L. H. Schartz, S. S. Sidhu, *Progr. and Abstr. 16th Annual Pittsburgh Diffn. Conf.*, Nov. 1958, p. 38 (1958).
13. G. P. Chatterjee, *J. Mines, Metals, Fuels*, 10, 20 (1962).
14. G. P. Chatterjee, *J. Mines, Metals, Fuels*, 11, 17 (1963).

7.3.3.1.2. Magnesium Systems.

Phase relationships in the Mg–Cu^1 and Mg–Ag^2 systems have been critically reassessed, giving rise to new recommended phase diagrams. In the absence of a similar review of the Mg–Au system, the recommended phase diagram is the original compilation³.

In the Mg–Cu phase diagram¹, there are two intermetallic compounds, both of which melt congruently: Mg_2Cu (568°C) and MgCu_2 (819°C). Whereas the former has a limited homogeneity range, the latter's is extensive. Structural evidence is claimed⁴ for the formation, by rapid quenching, of a phase with approximate composition MgCu_4 , stable below 300°C. In the absence of corroborative data, this phase is omitted from the phase diagram.

Three intermediate phases, $\gamma\text{-Mg}_3\text{Ag}$, $\beta\text{-MgAg}$ and $\alpha'\text{-MgAg}_3$, occur in the Mg–Ag phase diagram². The $\alpha'\text{-MgAg}_3$ superlattice is formed in an order–disorder transformation in the α phase at 25 at% Mg; the transformation T at the stoichiometric composition is $\sim 387^\circ\text{C}^5$. The $\beta\text{-MgAg}$ phase has a wide homogeneity range and melts congruently (820°C); $\gamma\text{-Mg}_3\text{Ag}$, however, has a more restricted homogeneity range and decomposes in a peritectic reaction (492°C).

The recommended Mg–Au phase diagram is that of ref. 3 amended by the addition of several new compounds close to MgAu_3 ; they are a family of close-packed structures modulated both by antiphase boundaries of the superstructure and by a

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7.3.3.1.2. Magnesium Systems.

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3. S. H. Gelles, J. J. Pickett, E. D. Levine, W. B. Novak, in *The Metallurgy of Beryllium*, Inst. Metals, Monograph Rept. Ser. No. 28, Institute of Metals, 1963, pp. 588–600; *Chem. Abstr.*, 60, 11,695 (1964).
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The recommended Mg–Au phase diagram is that of ref. 3 amended by the addition of several new compounds close to MgAu_3 ; they are a family of close-packed structures modulated both by antiphase boundaries of the superstructure and by a

special stacking sequence of the substructure⁶⁻¹¹. Of the well-established phases, β -MgAu is a congruently melting (1150°C) phase with a wide homogeneity range, Mg_2Au (788°C) and Mg_3Au (818°C) are congruently melting stoichiometric compounds and Mg_5Au_2 is a stoichiometric compound of limited stability range, being formed in a peritectoid reaction (721°C) and decomposing peritectically (796°C). Detailed crystallographic data indicating existence of superstructures for Mg_3Au and Mg_2Au have also been reported¹²⁻¹⁴.

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5. L. M. Clareborough, J. F. Nicholas, *Aust. J. Sci. Res.*, A3, 284 (1950).
6. K. Schubert, K. Burkhardt, W. Gold, P. K. Panday, *Naturwissenschaften*, 52, 301 (1965).
7. K. Burkhardt, K. Schubert, *Z. Metallkd.*, 56, 864 (1965).
8. K. Schubert, *Metallurgia*, 20, 424 (1966).
9. K. Burkhardt, K. Schubert, R. S. Toth, H. Sato, *Acta Crystallogr., Sect. B*, 24, 137 (1968).
10. P. Airo, *Phys. Status Solidi*, A, 47, K107 (1978).
11. M. van Sande, G. van Tendeloo, S. Amelinckx, P. Airo, *Phys. Status Solidi*, A, 54, 499 (1978).
12. G. van Tendeloo, S. Amelinckx, *Phys. Status Solidi*, A, 69, 103 (1982).
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7.3.3.1.3. Calcium Systems.

The Ca-Cu system has been reexamined using thermal analysis and x-ray diffraction methods¹; an independent study of the CaCu_5 -Cu section has also been completed². The resultant phase diagram¹, although similar to that in ref. 3 at the Cu-rich end, differs markedly for Ca-rich alloys. Supporting evidence for the modifications has been obtained from the Ca-Mg-Cu ternary system⁴. Three intermediate compounds are formed in the system; CaCu_5 (950°C) melts congruently, whereas Ca_2Cu (488°C) and CaCu (567°C) are formed in peritectic reactions. Single-crystal x-ray diffraction studies verify the stoichiometry of Ca_2Cu ⁵ and examine the polymorphism of CaCu ⁶.

The original Ca-Ag diagram in ref. 3 has been superseded⁷⁻⁹; it is essentially that reported in ref. 7, modified by the observation in refs. 8 and 9. Of the six intermetallic compounds formed in this system, only CaAg (666°C) and Ca_2Ag_7 (731°C) melt congruently; the others, Ca_3Ag (475°C), Ca_5Ag_3 (555°C), CaAg_2 (597°C) and Ca_2Ag_9 (687°C), decompose in peritectic reactions. A single-crystal x-ray diffraction study of a further compound, Ca_3Ag_8 , has been described¹⁰, although thermal analysis has shown no evidence of its presence⁷⁻⁹.

Phase relationships in the Ca-Au system are extremely complex and have yet to be delineated satisfactorily. Six intermediate phases, three of which melt congruently, are described³. The phase of variable composition designated β -CaAu (1015°C), CaAu_2 (864°C) and CaAu_4 (880°C), and three others are formed in peritectic reactions, Ca_2Au (798°C), Ca_4Au_3 (849°C) and CaAu_3 (853°C). The homogeneity

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ranges of the Au-rich phases, CaAu_5 (previously designated CaAu_4), Ca_2Au_9 , Ca_2Au_7 and CaAu_2 , have been determined from emf measurements of both solid and liquid Ca–Au alloys¹¹. The existence of the Ca-rich phases, Ca_3Au ¹², Ca_5Au_2 ¹², Ca_7Au_3 ¹³, Ca_5Au_3 ¹⁴, Ca_5Au_4 ¹³, and CaAu ¹⁵ has been confirmed in a detailed single-crystal x-ray diffraction investigation. Independent physicochemical studies of the compound previously designated CaAu_4 ³ show that it is better described as CaAu_5 ¹⁶ and that it exhibits superconducting properties¹⁷. The phase relationships are considered so ill defined that a phase diagram cannot be recommended unreservedly.

(P. HUBBERSTEY)

1. G. Bruzzone, *J. Less-Common Met.*, **25**, 361 (1971).
2. G. M. Kuznetsov, V. N. Fedorov, A. Rodnyanskaya, S. V. Kokovikhin, T. Yu. Byakovskaya, *Izv. Vyssh. Uchebn. Zaved., Tsvet. Metall.*, **94** (1980); *Chem. Abstr.*, **93**, 121,068 (1980).
3. M. Hansen, K. Anderko, eds., *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958.
4. K. M. Myles, *J. Less-Common Met.*, **20**, 149 (1970).
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8. B. Pascal, M. Caillet, M. Allibert, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **270**, 520 (1970).
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10. L. D. Calvert, C. Rand, *Acta Crystallogr.*, **17**, 1175 (1964).
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12. M. L. Fornasini, F. Merlo, M. Pani, *Rev. Chim. Miner.*, **22**, 791 (1986).
13. M. L. Fornasini, F. Merlo, *J. Solid-State Chem.*, **59**, 65 (1985).
14. F. Merlo, M. L. Fornasini, *Rev. Chim. Miner.*, **21**, 273 (1984).
15. F. Merlo, *J. Less-Common Met.*, **86**, 241 (1982).
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17. D. C. Hamilton, C. J. Raub, B. T. Matthias, E. Corenzwit, G. W. Hall, *J. Phys. Chem. Solids*, **26**, 665 (1965).

7.3.3.1.4. Strontium Systems.

The Sr–Cu system has been critically assessed¹. The most recent phase diagram², determined by combining differential thermal analysis and x-ray diffraction techniques, contains two intermediate compounds, both of which form in peritectic reactions, SrCu (588°C) and SrCu_5 (845°C); SrCu has also been prepared for independent structural analysis³.

A recent study of the phase relationships in the 0–30 at% Sr region⁴ of the Sr–Ag system shows that the phase diagram in ref. 5 is in error in this section. Combination of the data shows five compounds; of these, four melt congruently, Sr_3Ag_2 (665°C), SrAg (680°C), SrAg_2 (760°C) and SrAg_5 (783°C); the other, SrAg_4 (713°C) is formed in a peritectic reaction. Confirmatory evidence for Sr_3Ag_2 ⁶, SrAg ⁷ and SrAg_5 ⁸ comes from structural investigations; similar studies suggest the existence of a novel phase, Sr_7Ag_3 ⁶.

The phase diagram for the Sr–Au system shows three congruently melting phases, β - SrAu (970°C), SrAu_2 (1085°C) and SrAu_5 (1040°C); four phases formed in peritectic reactions are also observed, Sr_9Au (640°C), Sr_3Au (590°C), γ - Sr_2Au (750°C) and δ - Sr_3Au_2 , which has a limited stability range from the eutectoid (725°C) to the peritectic reaction (770°C)⁹. Independent structural investigations confirm the forma-

7.3.3. Formation of the Group-IIA–Group-IB Element Bond

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7.3.3.1. Phase Diagrams, Intermetallic Phases and Compounds

7.3.3.1.4. Strontium Systems.

ranges of the Au-rich phases, CaAu_5 (previously designated CaAu_4), Ca_2Au_9 , Ca_2Au_7 and CaAu_2 , have been determined from emf measurements of both solid and liquid Ca–Au alloys¹¹. The existence of the Ca-rich phases, Ca_3Au ¹², Ca_5Au_2 ¹², Ca_7Au_3 ¹³, Ca_5Au_3 ¹⁴, Ca_5Au_4 ¹³, and CaAu ¹⁵ has been confirmed in a detailed single-crystal x-ray diffraction investigation. Independent physicochemical studies of the compound previously designated CaAu_4 ³ show that it is better described as CaAu_5 ¹⁶ and that it exhibits superconducting properties¹⁷. The phase relationships are considered so ill defined that a phase diagram cannot be recommended unreservedly.

(P. HUBBERSTEY)

1. G. Bruzzone, *J. Less-Common Met.*, **25**, 361 (1971).
2. G. M. Kuznetsov, V. N. Fedorov, A. Rodnyanskaya, S. V. Kokovikhin, T. Yu. Byakovskaya, *Izv. Vyssh. Uchebn. Zaved., Tsvet. Metall.*, **94** (1980); *Chem. Abstr.*, **93**, 121,068 (1980).
3. M. Hansen, K. Anderko, eds., *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958.
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tion of Sr_3Au_2 ¹⁰, SrAu ¹¹, SrAu_2 ¹² and SrAu_5 ⁸ and provide evidence for the novel material, Sr_7Au_3 ⁶.

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7.3.3.1.5. Barium Systems.

The entire Ba–Cu system has been examined¹; a partial study (0–50 at% Ba) has also been carried out². Where comparable the two sets of data are in agreement; consequently, the recommended phase diagram is that in ref. 1. Two compounds exist in the system; BaCu (570°C) melts congruently, whereas BaCu₁₃ (670°C) is formed in a peritectic reaction. Further evidence for BaCu has come from a structural study³.

The phase diagram for the Ba–Ag system is only poorly characterized. A study⁴ of the phase relationships is based on thermal analysis data of alloys prepared using Ba that contained 1.9% Sr and 0.15% N. The existence of three compounds, Ba₂Ag₃, Ba₃Ag₅ and BaAg₄ is claimed, and some evidence for two additional compounds, Ba₃Ag and Ba₄Ag₃, is also quoted. Crystallographic studies have shown that a phase of stoichiometry BaAg exists in the system⁵ and that the phase previously designated BaAg₄ is better described⁶ as BaAg₅. The data are considered speculative, and the phase diagram in ref. 7 cannot be recommended.

Few data pertinent to the Ba–Au phase diagram have been published. The crystal structure of the intermetallic BaAu₅ has been determined^{6,8,9} and it has been shown to be superconducting^{8,9}. Early reports¹⁰ suggest that the compounds Ba₂Au₃ and BaAu₂ exist and that there are one or more compounds richer in Ba. More recent structural studies have demonstrated the formation of Ba₃Au₂¹¹ and BaAu¹².

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3. M. L. Fornasini, F. Merlo, *Acta Crystallogr., Sect. B*, 36, 1288 (1980).
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7. M. Hansen, K. Anderko, eds., *Constitution of Binary Alloys*, 2nd ed. McGraw-Hill, New York, 1958.
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7.3.3. Formation of the Group-IIA-Group-IB Element Bond

7.3.3.1. Phase Diagrams, Intermetallic Phases and Compounds

7.3.3.1.5. Barium Systems.

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7.3.3.2. Preparative Techniques.

Group-IIA–group-IB binary alloys and intermetallic phases or compounds are prepared by heating a mixture of the metals to a T close to ($\pm 50^\circ\text{C}$) the liquidus or melting point, mixing thoroughly, annealing and cooling or quenching to RT.

A major problem is the reactivity of the metals, particularly the group-IIA metals, to the atmosphere and the containment vessel. Products containing Ca, Sr and Ba are often as reactive as the metals; Be- and Mg-containing products, however, are generally chemically inert. As a result, much of the original work was undertaken on impure samples and products (quoted metal purities of 98% were not uncommon).

Thus care must be taken when preparing and purifying the constituent metals, handling the reactants and products and choosing material for the containment vessel. The mixtures are normally prepared from ultrapure group-IB metal and multidistilled group-IIA metal; ideally the final distillation is undertaken *in situ*¹. The metals and products must either be handled in a vacuum or protected by a purified inert cover gas, preferably Ar or He (N_2 cannot be used because of its reactivity to group-IIA metals). The containment vessel is usually fabricated from a refractory material.

Typically, Be-containing alloys and intermetallic phases have been prepared in beryllia² or alumina crucibles³; Mg-containing products have been synthesized in graphite⁴, magnesia⁵ or alumina⁶ crucibles. Alloys and compounds containing Ca, Sr and Ba have been synthesized in alumina⁷, boron nitride⁸, zircon⁸, molybdenum⁹, iron⁹, or steel¹ crucibles. Both zircon and molybdenum are satisfactory only for alloys with low group-IIA metal content and are replaced by boron nitride and iron, respectively, for group-IIA metal-rich systems^{8,9}. Crucibles are sealed in silica, quartz, iron or steel vessels, usually under either vacuum or purified inert cover gas; in a few cases, the samples were melted under a halide flux¹⁰.

Several techniques for preparing specialty products have been described. For example, the growth of small spherical single crystals of MgCu_2 has been achieved in a MgCl_2 – KCl – NaCl molten salt bath¹¹. Powdered alloy, prepared by metallurgical methods, is added to the molten salt and heated to just above the melting point of the alloy. The molten particles became spherical in the melt and after slow cooling spherical single crystals are picked out after dissolution of the salt in water¹¹. Fine particles (< 500 nm diam.) of Mg–Cu intermetallic phases are prepared by chemical vapor deposition methods¹². The two metals are evaporated simultaneously from separate sources in an Ar atmosphere (2×10^{-3} Pa) and deposited in a convenient growth zone; the composition of the deposit is dictated by that of the metal vapor¹². Conditions for the growth of single-, bi and tricrystals of MgAg have also been reported¹³.

7.3. Formation of the Group-IA or -IIA–Group-IB or -IIB Element Bonds 321**7.3.3. Formation of the Group-IIA–Group-IB Element Bond****7.3.3.2. Preparative Techniques.**

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9. D. C. Hamilton, C. J. Raub, B. T. Matthias, E. Corenzwit, G. W. Hall, *J. Phys. Chem. Solids*, **26**, 665 (1965).
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Thus care must be taken when preparing and purifying the constituent metals, handling the reactants and products and choosing material for the containment vessel. The mixtures are normally prepared from ultrapure group-IB metal and multidistilled group-IIA metal; ideally the final distillation is undertaken *in situ*¹. The metals and products must either be handled in a vacuum or protected by a purified inert cover gas, preferably Ar or He (N_2 cannot be used because of its reactivity to group-IIA metals). The containment vessel is usually fabricated from a refractory material.

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322 7.3. Formation of the Group-IA or -IIA–Group-IB or -IIB Element Bonds
 7.3.4. Formation of the Group-IIA–Group-IIB Element Bond
 7.3.4.1. Phase Diagrams, Intermetallic Phases and Compounds

1. W. A. Alexander, L. D. Calvert, A. Desaulniers, H. S. Dunsmore, D. F. Sargent, *Can. J. Chem.*, **47**, 611 (1969).
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4. S. P. Garg, V. J. Bhatt, C. V. Sunderam, *Met. Trans.*, **4**, 283 (1973).
5. G. Brauer, W. Haucke, *Z. Phys. Chem.*, **B33**, 304 (1936).
6. M. van Sande, G. van Tendeloo, S. Amelinckx, P. Airo, *Phys. Status Solidi*, **A54**, 499 (1979).
7. C. J. Raub, D. C. Hamilton, *J. Less-Common Met.*, **6**, 486 (1964).
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13. H. A. Domian, G. F. Bolling, *Met. Rev.*, **3**, 394 (1969).

7.3.4. Formation of the Group-IIA–Group-IIB Element Bond

The sole interest in the chemistry of species containing group-IIA–group-IIB element bonds is metallurgical. The available data on phase equilibria have been reviewed^{1–3} and a handbook of phase diagrams published⁴. Furthermore, structural data for intermetallic phases and compounds have been critically assessed^{5,6}.

(P. HUBBERSTEY)

1. M. Hansen, K. Anderko, eds., *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958.
2. R. P. Elliott, ed., *Constitution of Binary Alloys*, First Suppl., McGraw-Hill, New York, 1965.
3. F. A. Shunk, ed., *Constitution of Binary Alloys*, Second Suppl., McGraw-Hill, New York, 1969.
4. W. G. Moffatt, ed., *Handbook of Binary Phase Diagrams*, General Electric, Schenectady, NY, 1977.
5. W. B. Pearson, ed., *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 1, Pergamon Press, Oxford, 1958.
6. W. B. Pearson, ed., *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2, Pergamon Press, Oxford, 1967.

7.3.4.1. Phase Diagrams, Intermetallic Phases and Compounds

Equilibrium conditions for the synthesis of intermetallic phases and compounds are concisely summarized as a function of temperature and composition in the form of phase diagrams. Consequently, in the following subsections, these relationships for group-IIA–group-IIB metal systems are reviewed. The phase diagrams in ref. 1 are used as a baseline; work published before this compilation is not specifically referred to, but that reported subsequently is used, as appropriate, to modify or replace these phase diagrams.

(P. HUBBERSTEY)

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322 7.3. Formation of the Group-IA or -IIA-Group-IB or -IIB Element Bonds**7.3.4. Formation of the Group-IIA-Group-IIB Element Bond****7.3.4.1. Phase Diagrams, Intermetallic Phases and Compounds**

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3. F. A. Shunk, ed., *Constitution of Binary Alloys*, Second Suppl., McGraw-Hill, New York, 1969.
4. W. G. Moffatt, ed., *Handbook of Binary Phase Diagrams*, General Electric, Schenectady, NY, 1977.
5. W. B. Pearson, ed., *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 1, Pergamon Press, Oxford, 1958.
6. W. B. Pearson, ed., *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2, Pergamon Press, Oxford, 1967.

7.3.4.1. Phase Diagrams, Intermetallic Phases and Compounds

Equilibrium conditions for the synthesis of intermetallic phases and compounds are concisely summarized as a function of temperature and composition in the form of phase diagrams. Consequently, in the following subsections, these relationships for group-IIA-group-IIB metal systems are reviewed. The phase diagrams in ref. 1 are used as a baseline; work published before this compilation is not specifically referred to, but that reported subsequently is used, as appropriate, to modify or replace these phase diagrams.

(P. HUBBERSTEY)

1. M. Hansen, K. Anderko, eds., *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958.

322 7.3. Formation of the Group-IA or -IIA–Group-IB or -IIB Element Bonds
 7.3.4. Formation of the Group-IIA–Group-IIB Element Bond
 7.3.4.1. Phase Diagrams, Intermetallic Phases and Compounds

1. W. A. Alexander, L. D. Calvert, A. Desaulniers, H. S. Dunsmore, D. F. Sargent, *Can. J. Chem.*, **47**, 611 (1969).
2. G. P. Chatterjee, *J. Mines Metals Fuels*, **10**, 20 (1962).
3. O. Winkler, *Z. Metallkd.*, **30**, 162 (1938).
4. S. P. Garg, V. J. Bhatt, C. V. Sunderam, *Met. Trans.*, **4**, 283 (1973).
5. G. Brauer, W. Haucke, *Z. Phys. Chem.*, **B33**, 304 (1936).
6. M. van Sande, G. van Tendeloo, S. Amelinckx, P. Airo, *Phys. Status Solidi*, **A54**, 499 (1979).
7. C. J. Raub, D. C. Hamilton, *J. Less-Common Met.*, **6**, 486 (1964).
8. A. N. Campbell, W. H. W. Wood, *Can. J. Chem.*, **49**, 1315 (1971).
9. G. Bruzzone, *J. Less-Common Met.*, **25**, 361 (1971).
10. S. Busk, *J. Metals*, **2**, 1460 (1950).
11. I. Nakatani, Y. Kitano, M. Korekado, Y. Komura, *Jpn. J. Appl. Phys.*, **9**, 842 (1970).
12. T. Ohno, *J. Cryst. Growth*, **70**, 541 (1984).
13. H. A. Domian, G. F. Bolling, *Met. Rev.*, **3**, 394 (1969).

7.3.4. Formation of the Group-IIA–Group-IIB Element Bond

The sole interest in the chemistry of species containing group-IIA–group-IIB element bonds is metallurgical. The available data on phase equilibria have been reviewed^{1–3} and a handbook of phase diagrams published⁴. Furthermore, structural data for intermetallic phases and compounds have been critically assessed^{5,6}.

(P. HUBBERSTEY)

1. M. Hansen, K. Anderko, eds., *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958.
2. R. P. Elliott, ed., *Constitution of Binary Alloys*, First Suppl., McGraw-Hill, New York, 1965.
3. F. A. Shunk, ed., *Constitution of Binary Alloys*, Second Suppl., McGraw-Hill, New York, 1969.
4. W. G. Moffatt, ed., *Handbook of Binary Phase Diagrams*, General Electric, Schenectady, NY, 1977.
5. W. B. Pearson, ed., *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 1, Pergamon Press, Oxford, 1958.
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(P. HUBBERSTEY)

1. M. Hansen, K. Anderko, eds., *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958.

7.3.4. Formation of the Group-IIA–Group-IIB Element Bond

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7.3.4.1. Phase Diagrams, Intermetallic Phases and Compounds

7.3.4.1.2. Magnesium Systems.

7.3.4.1.1. Beryllium Systems.

Data for these systems are limited. There is no evidence for the formation of intermediate phases in either the Be–Zn¹ or the Be–Cd^{2,3} system; in the Be–Hg system, however, the existence of BeHg₂ has been postulated on the basis of the properties of the amalgam formed by electrolyzing a NaCl–BeCl₂ molten salt mixture into the Hg cathode^{4,5}.

(P. HUBBERSTEY)

1. I. F. Nichkov, M. V. Smirnov, *Izv. Vyssh. Ucheb. Zaved., Tsevt. Metall.*, 105 (1961); *Chem. Abstr.*, 56, 1248i (1962).
2. F. M. Yans, U.S. Atomic Energy Commission, Report NMI-1240 (1960).
3. J. Klein, L. Perelman, W. W. Beaver, U.S. Atomic Energy Commission, Report WADC-58-478 part II (1960).
4. M. C. Kells, R. B. Holden, C. I. Whitman, *J. Am. Chem. Soc.*, 79, 3925 (1957).
5. R. B. Holden, M. C. Kells, C. I. Whitman, *Proc. 2nd. U.N. Int. Conf. Peaceful Uses Atomic Energy*, Geneva 1958, Vol. 4, pp. 306–308, 1958; *Chem. Abstr.*, 54, 7375 (1960).

7.3.4.1.2. Magnesium Systems.

The Mg–Zn system has been extensively researched. The recommended phase diagram is given in ref. 1; it is effectively that of ref. 2, modified at the Mg-rich end (0–67 at% Zn) using the collaborative data from refs. 3–5. Five intermetallic compounds exist; of these, one melts congruently, MgZn₂ (588°C), the other four, Mg₇Zn₃ (342°C), MgZn (347°C), Mg₂Zn₃ (416°C) and Mg₂Zn₁₁ (381°C) being formed in peritectic reactions. Although controversy remains over the temperature range of stability of the intermetallic phases, particularly MgZn and Mg₂Zn₃^{5–7}, it is accepted that Mg₇Zn₃ has a limited range, extending for only 30°C from the peritectic reaction (342°C) to the eutectoid reaction (312°C). Single-crystal x-ray diffraction studies of the latter phase⁸ suggest it is more correctly designated Mg₅₁Zn₂₀.

The recommended phase diagram in the Mg–Cd system is that of ref. 2. Above 250°C the two metals are mutually soluble in the solid state, forming a disordered hexagonal phase. At lower T, however, ordering occurs to give three phases; an ordered hexagonal phase based on Mg₃Cd, an ordered orthorhombic phase based on MgCd and an ordered hexagonal phase based on MgCd₃. The transformation curve consists of three branches with a single maximum at ~ 50 and two points of inflection at ~ 36 and 68 at% Cd; disorder–order transformation temperatures of alloys having the compositions, Mg₃Cd, MgCd and MgCd₃ have been reported as 150–160°C, 246–258°C and 80–94°C, respectively.

Three structural reports^{9–11}, a theoretical analysis of alloying behavior¹² and a report describing thermodynamic properties¹³ are the only publications on the Mg–Hg system since ref. 2; consequently, the recommended phase diagram is that of ref. 2. There are six intermediate compounds; three melt congruently, Mg₂Hg (580°C), Mg₅Hg₃ (562°C), MgHg (627°C), and three are formed on peritectic reactions, Mg₃Hg (508°C), Mg₅Hg₂ (519°C) and MgHg₂ (170°C).

(P. HUBBERSTEY)

1. R. P. Elliott, ed., *Constitution of Binary Alloys*, First Suppl., McGraw-Hill, New York (1965).
2. M. Hansen, K. Anderko, eds., *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958.

7.3.4. Formation of the Group-IIA–Group-IIB Element Bond

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2. F. M. Yans, U.S. Atomic Energy Commission, Report NMI-1240 (1960).
3. J. Klein, L. Perelman, W. W. Beaver, U.S. Atomic Energy Commission, Report WADC-58-478 part II (1960).
4. M. C. Kells, R. B. Holden, C. I. Whitman, *J. Am. Chem. Soc.*, 79, 3925 (1957).
5. R. B. Holden, M. C. Kells, C. I. Whitman, *Proc. 2nd. U.N. Int. Conf. Peaceful Uses Atomic Energy*, Geneva 1958, Vol. 4, pp. 306–308, 1958; *Chem. Abstr.*, 54, 7375 (1960).

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2. M. Hansen, K. Anderko, eds., *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958.

3. J. J. Park, L. L. Wyman, Tech. Report WADC-57-504 (1957); *Chem. Abstr.*, 55, 17,439c (1961).
4. K. Anderko, E. J. Klimek, D. W. Levinson, W. Rostoker, *Trans. Am. Soc. Met.*, 49, 778 (1957).
5. J. B. Clark, F. N. Rhines, *Trans. Am. Inst. Mining Eng.*, 209, 425 (1957).
6. J. Gullott, R. Graf, C. R. Hebd. *Seances Acad. Sci.*, 262B, 1219 (1966).
7. W. Kitchingman, I. M. Vesey, *J. Inst. Metals*, 98, 52 (1970).
8. I. Higashi, N. Shiotani, M. Uda, T. Mizoguchi, H. Katoh, *J. Solid-State Chem.*, 36, 225 (1981).
9. J. L. C. Daams, J. H. N. van Vucht, *Philips J. Res.*, 39, 275 (1984).
10. E. Cruceanu, D. Nicolescu, O. Ivanciu, *J. Mater. Sci.*, 9, 1389 (1974).
11. T. N. Lipchin, S. V. Muchkov, I. P. Vyatkin, *Metalloved. Term. Obrab. Met.*, 36 (1974).
12. J. E. Inglesfield, *J. Phys. C, Solid State Phys.*, 2, 1293 (1969).
13. M. Y. Vyaznev, I. P. Vyatkin, S. Mushkov, E. I. Mishkin, O. I. Brandman, *Zh. Prikl. Khim.*, 48, 77 (1975).

7.3.4.1.3. Calcium Systems.

The derived phase relationships in all three Ca systems differ markedly from and supersede those quoted in ref. 1. The phase diagram for the Ca–Zn system² shows evidence for eight compounds; three melt congruently, CaZn_2 (704°C), CaZn_5 (695°C) and CaZn_{11} (724°C), and five are formed in peritectic reactions, Ca_3Zn (394°C), Ca_7Zn_4 (414°C), CaZn (439°C), $\text{Ca}_7\text{Zn}_{20}$ (642°C) and CaZn_{13} (669°C). Although the stoichiometries of Ca_3Zn , Ca_7Zn_4 and $\text{Ca}_7\text{Zn}_{20}$ are based solely on differential thermal analysis data², their existence, together with that of the other five compounds, is confirmed in a vapor pressure study of both liquid and solid Ca–Zn alloys³; Ca_3Zn^4 , Ca_5Zn_3 ⁵ (previously designated Ca_7Zn_4), CaZn^4 , CaZn_3 ⁶ (previously designated $\text{Ca}_7\text{Zn}_{20}$), CaZn_{11} ⁷ and CaZn_{13} ⁷ have also been prepared and studied structurally.

Six intermediate compounds exist in the Ca–Cd system⁸. The compounds CaCd (685°C), CaCd_2 (701°C) and Ca_2Cd_7 (622°C) melt congruently; the other compounds, Ca_3Cd_2 (527°C), $\text{Ca}_3\text{Cd}_{17}$ (595°C), and CaCd_6 (565°C), are formed in peritectic reactions. The compound CaCd_2 exists in two modifications, the $\alpha = \beta$ transition occurring at 650°C. The compound Ca_3Cd_2 has also been synthesized and studied structurally⁹.

The phase diagram for the Ca–Hg system is effectively that obtained by combination of the data in ref. 10 with those quoted in ref. 1 for Hg-rich (0–25 at% Ca) alloys. Nine compounds are present in the system; three melt congruently, Ca_3Hg (523°C), CaHg (961°C) and CaHg_2 (746°C), and six are formed in a peritectic reactions, Ca_2Hg (530°C), Ca_5Hg_3 (587°C), Ca_3Hg_2 (660°C), CaHg_3 (570°C), $\text{CaHg}_{3.6}$ (264°C) and CaHg_{11} (84°C). The stoichiometry of CaHg_{11} is ascertained from an independent structural study¹¹; the compounds, Ca_3Hg ¹¹, CaHg_{10} , CaHg_2 ¹² and CaHg_3 ¹³ have also been prepared for independent structural analysis.

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3. P. Chioti, R. J. Hecht, *Trans. Metall. Soc. Am. Inst. Mining Eng.*, 239, 536 (1967).
4. M. L. Fornasini, F. Merlo, K. Schubert, *J. Less-Common Met.*, 79, 111 (1981).
5. G. Bruzzone, E. Franceschi, F. Merlo, *J. Less-Common Met.*, 60, 59 (1978).

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3. J. J. Park, L. L. Wyman, Tech. Report WADC-57-504 (1957); *Chem. Abstr.*, 55, 17,439c (1961).
4. K. Anderko, E. J. Klimek, D. W. Levinson, W. Rostoker, *Trans. Am. Soc. Met.*, 49, 778 (1957).
5. J. B. Clark, F. N. Rhines, *Trans. Am. Inst. Mining Eng.*, 209, 425 (1957).
6. J. Gullott, R. Graf, *C. R. Hebd. Seances Acad. Sci.*, 262B, 1219 (1966).
7. W. Kitchingman, I. M. Vesey, *J. Inst. Metals*, 98, 52 (1970).
8. I. Higashi, N. Shiotani, M. Uda, T. Mizoguchi, H. Katoh, *J. Solid-State Chem.*, 36, 225 (1981).
9. J. L. C. Daams, J. H. N. van Vucht, *Philips J. Res.*, 39, 275 (1984).
10. E. Cruceanu, D. Nicolescu, O. Ivanciu, *J. Mater. Sci.*, 9, 1389 (1974).
11. T. N. Lipchin, S. V. Muchkov, I. P. Vyatkin, *Metalloved. Term. Obrab. Met.*, 36 (1974).
12. J. E. Inglesfield, *J. Phys. C, Solid State Phys.*, 2, 1293 (1969).
13. M. Y. Vyaznev, I. P. Vyatkin, S. Mushkov, E. I. Mishkin, O. I. Brandman, *Zh. Prikl. Khim.*, 48, 77 (1975).

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5. G. Bruzzone, E. Franceschi, F. Merlo, *J. Less-Common Met.*, 60, 59 (1978).

6. M. L. Fornasini, F. Merlo, *Acta Crystallogr., Sect. B*, **36**, 1739 (1980).
7. I. Iandelli, A. Palenzona, *J. Less-Common Met.*, **12**, 333 (1967).
8. G. Bruzzone, *Gazz. Chim. Ital.*, **102**, 234 (1972).
9. F. Merlo, *J. Less-Common Met.*, **50**, 275 (1976).
10. G. Bruzzone, F. Merlo, *J. Less-Common Met.*, **32**, 237 (1973).
11. M. Pusej, Z. Ban, *Croat. Chem. Acta*, **51**, 75 (1978); *Chem. Abstr.*, **89**, 121,138 (1978).
12. A. Iandelli, A. Palenzona, *Atti. Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.*, **37**, 165 (1964); *Chem. Abstr.*, **62**, 15,518d (1965).
13. A. Iandelli, A. Palenzona, *J. Less-Common Met.*, **15**, 273 (1968).

7.3.4.1.4. Strontium Systems.

The Sr–Zn phase diagram has been determined using differential thermal analytical and x-ray diffraction methods¹. Of the four intermediate compounds found, SrZn_2 (575°C) and SrZn_{13} (830°C) melt congruently, and SrZn (434°C) and SrZn_5 (650°C) are formed in peritectic reactions. The last also undergoes a polymorphic transition (620°C). The structural data for the five phases¹ extend previous data for SrZn^2 , SrZn_2^3 , low-T SrZn_5^4 and $\text{SrZn}_{13}^{5,6}$. Solubility⁷ and thermodynamic⁸ data for dilute solutions of Sr in liquid Zn are also available; in both reports, SrZn_{13} is in equilibrium with the saturated liquid.

The Sr–Cd phase diagram has been elucidated⁹. Of the six intermediate compounds found in the system, two, SrCd_2 (730°C) and Sr_2Cd_9 (629°C), melt congruently; the other four compounds, Sr_2Cd (430°C), SrCd (580°C), SrCd_6 (600°C) and SrCd_{11} (531°C), are formed in peritectic reactions. A single-crystal x-ray diffraction study of a seventh compound, Sr_5Cd_3 , has been reported¹⁰; how this material fits into the phase relationships is uncertain. The formation of SrCd^{11} , $\text{Sr}_2\text{Cd}_9^{12}$, SrCd_6^{12} and SrCd_{11}^{13} has been confirmed in structural investigations.

The Sr–Hg phase diagram has been determined¹⁴. Ten compounds are formed in this system; two melt congruently, SrHg (850°C) and SrHg_2 (772°C), and eight are formed from peritectic reactions, Sr_3Hg (458°C), Sr_2Hg (478°C), Sr_3Hg_2 (545°C), SrHg_3 (512°C), $\text{SrHg}_{3.6}$ (481°C), Sr_2Hg_9 (427°C), SrHg_{11} (289°C) and SrHg_x ($x \sim 13$; 62°C). The synthesis of SrHg^{15} , SrHg_2^{16} , SrHg_3^{17} and SrHg_{11}^{18} has also been reported in separate structural studies.

(P. HUBBERSTEY)

1. G. Bruzzone, F. Merlo, *J. Less-Common Met.*, **92**, 75 (1983).
2. F. Merlo, *J. Less-Common Met.*, **86**, 241 (1982).
3. B. G. Bergman, P. J. Shlichta, *Acta Crystallogr.*, **17**, 65 (1964).
4. N. C. Baenziger, J. W. Conant, *Acta Crystallogr.*, **9**, 361 (1956).
5. J. A. A. Ketelaar, *J. Chem. Phys.*, **5**, 668 (1937).
6. I. Iandelli, A. Palenzona, *J. Less-Common Met.*, **12**, 333 (1967).
7. I. Johnson, K. E. Anderson, J. Bartos, U.S. Atomic Energy Commission, Rept. ANL 6596, pp. 108–110 (1962).
8. A. V. Volkovich, A. V. Krivopushkin, I. F. Nichkov, *Izv. Vyssh. Ucheb. Zaved., Tsevt. Metall.*, **37** (1978); *Chem. Abstr.*, **91**, 61,295 (1979).
9. W. Koester, J. Meixner, *Z. Metallkd.*, **56**, 695 (1965).
10. G. Bruzzone, E. Franceschi, F. Merlo, *J. Less-Common Met.*, **60**, 59 (1978).
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12. G. Bruzzone, *Gazz. Chim. Ital.*, **102**, 234 (1972).
13. M. J. Sanderson, N. C. Baenziger, *Acta Crystallogr.*, **6**, 627 (1953).
14. G. Bruzzone, F. Merlo, *J. Less-Common Met.*, **35**, 153 (1974).
15. R. Ferro, *Acta Crystallogr.*, **7**, 781 (1954).

7.3.4. Formation of the Group-IIA–Group-IIB Element Bond

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6. M. L. Fornasini, F. Merlo, *Acta Crystallogr., Sect. B*, **36**, 1739 (1980).
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7.3.4.1.4. Strontium Systems.

The Sr–Zn phase diagram has been determined using differential thermal analytical and x-ray diffraction methods¹. Of the four intermediate compounds found, SrZn₂ (575°C) and SrZn₁₃ (830°C) melt congruently, and SrZn (434°C) and SrZn₅ (650°C) are formed in peritectic reactions. The last also undergoes a polymorphic transition (620°C). The structural data for the five phases¹ extend previous data for SrZn², SrZn₂³, low-T SrZn₅⁴ and SrZn₁₃^{5,6}. Solubility⁷ and thermodynamic⁸ data for dilute solutions of Sr in liquid Zn are also available; in both reports, SrZn₁₃ is in equilibrium with the saturated liquid.

The Sr–Cd phase diagram has been elucidated⁹. Of the six intermediate compounds found in the system, two, SrCd₂ (730°C) and Sr₂Cd₉ (629°C), melt congruently; the other four compounds, Sr₂Cd (430°C), SrCd (580°C), SrCd₆ (600°C) and SrCd₁₁ (531°C), are formed in peritectic reactions. A single-crystal x-ray diffraction study of a seventh compound, Sr₅Cd₃, has been reported¹⁰; how this material fits into the phase relationships is uncertain. The formation of SrCd¹¹, Sr₂Cd₉¹², SrCd₆¹² and SrCd₁₁¹³ has been confirmed in structural investigations.

The Sr–Hg phase diagram has been determined¹⁴. Ten compounds are formed in this system; two melt congruently, SrHg (850°C) and SrHg₂ (772°C), and eight are formed from peritectic reactions, Sr₃Hg (458°C), Sr₂Hg (478°C), Sr₃Hg₂ (545°C), SrHg₃ (512°C), SrHg_{3,6} (481°C), Sr₂Hg₉ (427°C), SrHg₁₁ (289°C) and SrHg_x (x ~ 13; 62°C). The synthesis of SrHg₂¹⁵, SrHg₃¹⁶ and SrHg₁₁¹⁷ has also been reported in separate structural studies.

(P. HUBBERSTEY)

1. G. Bruzzone, F. Merlo, *J. Less-Common Met.*, **92**, 75 (1983).
2. F. Merlo, *J. Less-Common Met.*, **86**, 241 (1982).
3. B. G. Bergman, P. J. Shlichta, *Acta Crystallogr.*, **17**, 65 (1964).
4. N. C. Baenziger, J. W. Conant, *Acta Crystallogr.*, **9**, 361 (1956).
5. J. A. A. Ketelaar, *J. Chem. Phys.*, **5**, 668 (1937).
6. I. Iandelli, A. Palenzona, *J. Less-Common Met.*, **12**, 333 (1967).
7. I. Johnson, K. E. Anderson, J. Bartos, U.S. Atomic Energy Commission, Rept. ANL 6596, pp. 108–110 (1962).
8. A. V. Volkovich, A. V. Krivopushkin, I. F. Nichkov, *Izv. Vyssh. Ucheb. Zaved., Tsevt. Metall.*, **37** (1978); *Chem. Abstr.*, **91**, 61,295 (1979).
9. W. Koester, J. Meixner, *Z. Metallkd.*, **56**, 695 (1965).
10. G. Bruzzone, E. Franceschi, F. Merlo, *J. Less-Common Met.*, **60**, 59 (1978).
11. A. Palenzona, *J. Less-Common Met.*, **25**, 367 (1971).
12. G. Bruzzone, *Gazz. Chim. Ital.*, **102**, 234 (1972).
13. M. J. Sanderson, N. C. Baenziger, *Acta Crystallogr.*, **6**, 627 (1953).
14. G. Bruzzone, F. Merlo, *J. Less-Common Met.*, **35**, 153 (1974).
15. R. Ferro, *Acta Crystallogr.*, **7**, 781 (1954).

16. G. Bruzzone, *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.*, **48**, 235 (1970); *Chem. Abstr.* **73**, 103,005 (1970).
17. A. Iandelli, A. Palenzona, *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.*, **37**, 165 (1964); *Chem. Abstr.*, **62**, 15,518d (1965).
18. E. J. Duwell, N. C. Baenziger, *Acta Crystallogr.*, **8**, 709 (1955).

7.3.4.1.5. Barium Systems.

Paralleling the corresponding Sr systems, the Ba-Zn system is the last for which a reliable phase diagram is published¹. Using differential thermal analytical and x-ray diffraction techniques, five compounds have been found in the system: Ba₂Zn (360°C), BaZn (340°C) and BaZn₁₃ (885°C), which melt congruently, and BaZn₂ (380°C) and BaZn₅ (635°C), which are formed in peritectic reactions. Structural studies¹ confirm previous data for BaZn², BaZn₅³ and BaZn₁₃⁴ and have generated novel data for Ba₂Zn and BaZn₂.

Two versions of the Ba-Cd phase diagram^{5,6} are very similar and, but for some minor differences in the critical point parameters, differ only in the stoichiometry of the compound at 17 at% Ba-Ba₂Cd₉⁵ or BaCd₅⁶. Since ref. 5 includes a structural analysis of the intermediate compounds, this phase diagram is recommended. There are five intermediate compounds in the system. Four of these melt congruently, BaCd (588°C), BaCd₂ (642°C), Ba₂Cd₉ (620°C) and BaCd₁₁ (672°C); the other, Ba₂Cd (409°C), is formed in a peritectic reaction. The existence of Ba₂Cd⁷, BaCd⁸, BaCd₂⁹, and BaCd₁₁¹⁰ has been verified in separate crystallographic studies.

There are eight compounds in the Ba-Hg system¹¹. The three compounds BaHg (822°C), BaHg₂ (726°C) and BaHg₄ (517°C) melt congruently; the other five compounds, however, Ba₂Hg (434°C), Ba₂Hg₉ (505°C), BaHg₆ (410°C), BaHg₁₁ (255°C) and BaHg₁₃ (160°C), are formed in peritectic reactions. The synthesis of Ba₂Hg⁷, BaHg⁸, BaHg₂⁹ and BaHg₁₁^{12,13} has been reported in related structural studies.

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3. N. C. Baenziger, J. W. Conant, *Acta Crystallogr.*, **9**, 361 (1956).
4. J. A. A. Ketelaar, *J. Chem. Phys.*, **5**, 668 (1937).
5. G. Bruzzone, *Gazz. Chim. Ital.*, **102**, 234 (1972).
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8. R. Ferro, *Acta Crystallogr.*, **7**, 781 (1954).
9. G. Bruzzone, *Atti Accad. Naz. Lincei. Cl. Sci. Fis. Mat. Nat. Rend.*, **48**, 235 (1970); *Chem. Abstr.*, **73**, 103,005 (1970).
10. M. J. Sanderson, N. C. Baenziger, *Acta Crystallogr.*, **6**, 627 (1953).
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7.3.4.2. Preparative Techniques

Group-IIA-group-IIB binary alloys and intermetallic compounds are prepared by heating the constituent metals in the appropriate molar ratio to a temperature close ($\pm 50^\circ\text{C}$) to the liquidus or melting point, mixing thoroughly, annealing and cooling or quenching to RT. The annealing process is generally brief, but in some

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17. A. Iandelli, A. Palenzona, *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.*, **37**, 165 (1964); *Chem. Abstr.*, **62**, 15,518d (1965).
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5. G. Bruzzone, *Gazz. Chim. Ital.*, **102**, 234 (1972).
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7. F. Merlo, *J. Less-Common Met.*, **50**, 275 (1976).
8. R. Ferro, *Acta Crystallogr.*, **7**, 781 (1954).
9. G. Bruzzone, *Atti Accad. Naz. Lincei. Cl. Sci. Fis. Mat. Nat. Rend.*, **48**, 235 (1970); *Chem. Abstr.*, **73**, 103,005 (1970).
10. M. J. Sanderson, N. C. Baenziger, *Acta Crystallogr.*, **6**, 627 (1953).
11. G. Bruzzone, F. Merlo, *J. Less-Common Met.*, **39**, 271 (1975).
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13. E. J. Duwell, N. C. Baenziger, *Acta Crystallogr.*, **8**, 705 (1955).

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cases, especially the Mg-Cd system, long periods (typically 16 d at 300°C¹) are necessary for complete homogenization.

The group-IIA elements and their products, especially those containing Ca, Sr or Ba, are reactive; this must be remembered when assessing the early literature, since a major proportion of the work was undertaken on impure materials (metal purities of only 98% were not uncommon).

As a result of their reactivity, particular attention must be given to preparation and purification of the metals, the conditions under which the metals, alloys and compounds are handled and the choice of material for the containment vessel. Ultrapure group-IIB metals may be used without further purification, but it is advisable to purify the group-IIA metals by a multidistillation process, the final distillation preferably being carried out in situ. The reactants and products are best handled in an atmosphere of a purified inert gas, usually He or Ar (N₂ cannot be used because of the ready formation of group-IIA metal nitrides); alternatively, they can be handled under vacuum or, in rare cases, under halide fluxes. The containment vessel is normally fabricated from a refractory.

Preparative details for Be-containing species are limited, since the only compound mentioned is BeHg₂; its existence has been postulated on the basis of the properties of the amalgam prepared by electrolyzing a NaCl-BeCl₂ molten salt mixture into a Hg cathode^{2,3}.

Typical preparative routes to Mg-Zn alloys and compounds involve the melting of the metals in Mo crucibles under Ar⁴. Alternatively, the metals have been melted in graphite crucibles sealed in silica tubes⁵. A number of preparative techniques for Mg-Zn alloys and compounds for specialized applications have also been devised⁶⁻⁹. Thus, films of Mg-Zn alloys are produced on glass plates by vacuum deposition of the vapor generated by simultaneous evaporation of the two metals⁶. Polycrystals of MgZn₂ are obtained by subjecting a graphite crucible containing the molten alloy to continuous mechanical vibration⁷; the dependence of the size of the polycrystals on the frequency and amplitude of the vibration has been ascertained. Single crystals of MgZn₂ are grown in a glass tube by vapor deposition of polycrystalline MgZn₂⁸. Spherical single crystals of MgZn₂ are prepared by crystallization in a molten salt (MgCl₂, NaCl, KCl)⁹. Powdered MgZn₂, prepared by metallurgical methods, is added to the molten salt and heated to just above the melting point of the alloy. On melting, the particles assume a spherical shape and, after slow cooling, spherical single crystals are retrieved by dissolving the salts in water⁹.

Preparation of a Mg-Cd alloy involves melting the purified metals under a halide flux in a graphite crucible, cooling to 300°C and annealing/homogenizing the sample for 16 d, followed by quenching to RT¹. Iron¹⁰ and alumina-lined, unglazed porcelain¹¹ crucibles have also been used; annealing/homogenizing temperatures have varied from 250 to 380°C for periods up to 35 d^{1,10-13}; in a limited number of examples, the metals have been protected by either He or Ar¹³.

Mg-Hg alloys and compounds have been produced by mixing the two metals in either Ar-filled Fe crucibles¹⁴ or evacuated silica tubes¹⁵.

Alloys and compounds containing Ca, Sr or Ba have been prepared by melting the component metals in Fe crucibles sealed under Ar¹⁶⁻²⁰. Alternative methods have involved the use of either Ta crucibles sealed under He²¹, steel crucibles sealed under Ar²² or evacuated silica tubes²³.

328 7.3. Formation of the Group-IA or -IIA-Group-IB or -IIB Element Bonds
7.3.4. Formation of the Group-IIA-Group-IIB Element Bond
7.3.4.2. Preparative Techniques

1. N. V. Ageev, D. L. Ageeva, *Izv. Akad. Nauk SSSR (Khim.)*, 143 (1946).
2. M. G. Kells, R. B. Holden, C. I. Whitman, *J. Am. Chem. Soc.*, 79, 3925 (1957).
3. R. B. Holden, M. C. Kells, C. I. Whitman, *Proc. 2nd. U.N. Int. Conf. Peaceful Uses Atomic Energy*, Geneva, 1958, Vol. 4, pp. 306-308 (1958); *Chem. Abstr.*, 54, 7375 (1960).
4. K. Anderko, E. J. Klimek, D. W. Levinson, W. Rostoker, *Trans. Metall. Soc., Am. Inst. Mining Eng.*, 49, 778 (1957).
5. S. Sansom, *Acta Chem. Scand.*, 3, 835 (1949).
6. I. L. Roikh, L. N. Koltunova, V. E. Tolkachev, V. P. Kirichenko, *Dokl. Akad. Nauk SSSR*, 159, 413 (1964).
7. S. Siegel, *Krist. Tech.*, 10, 217 (1975).
8. C. Kirsten, U. Kraemer, *Krist. Tech.*, 1, 175 (1966).
9. I. Nakatani, Y. Kitano, M. Korekado, Y. Komura, *Jpn. J. Appl. Phys.*, 9, 842 (1970).
10. H. Steeple, *Acta Crystallogr.*, 5, 247 (1952).
11. K. Riederer, *Z. Metallkd.*, 29, 423 (1937).
12. N. Ridley, *J. Inst. Met.*, 93, 46 (1964-5).
13. D. A. Edwards, W. E. Wallace, R. S. Craig, *J. Am. Chem. Soc.*, 74, 5256 (1952).
14. G. Brauer, R. Randolph, *Z. Anorg. Allg. Chem.*, 248, 405 (1941).
15. E. Cruceanu, D. Niculescu, O. Ivanciu, *J. Mater. Sci.*, 9, 1389 (1974).
16. G. Bruzzone, F. Merlo, *J. Less-Common Met.*, 32, 237 (1973).
17. G. Bruzzone, E. Franceschi, F. Merlo, *J. Less-Common Met.*, 60, 59 (1978).
18. G. Bruzzone, F. Merlo, *J. Less-Common Met.*, 35, 153 (1974).
19. R. Ferro, *Acta Crystallogr.*, 7, 781 (1954).
20. G. Bruzzone, F. Merlo, *J. Less-Common Met.*, 39, 271 (1975).
21. A. F. Messing, M. D. Adams, R. K. Steunenberg, *Trans. Am. Soc. Met.*, 56, 345 (1963).
22. R. T. Dirstine, *J. Less-Common Met.*, 39, 181 (1975).
23. M. Puselj, Z. Ban, *Croat. Chem. Acta*, 51, 75 (1978); *Chem. Abstr.*, 89, 121,318 (1978).

7.4. Formation of the Group-IA or -IIA–Transition- and –Inner Transition-Metal Bond

7.4.1. Formation of the Group-IA–Transition- and –Inner Transition-Metal Bond

7.4.1.1. in Metallic Systems

The alkali metals do not form intermetallic compounds with the transition metals. Both Na and Li dissolve only ppm quantities of most transition metals, although the solubilities are greater in Li. Nickel is very soluble in Li (900 ppm at 600°C), but no intermetallic compound forms¹. Intermetallic compound formation is, however, observed between Li and the noble metals Rh, Ir, Pd and Pt, so this section concentrates on the preparation of these compounds.

In the Li–Rh system LiRh is prepared² from rhodium metal foil and liq Li in a 25 at% excess of the 1 : 1 molar ratio. The mixture is heated in an iron crucible to 750–880°C in Ar. The direct reaction of the elements in a molybdenum crucible at 800°C for 7 d produces³ LiRh. Identical methods produce LiIr and LiIr₃ with which the rhodium compounds are isostructural³. The reaction of Rh metal with LiH at 600°C gives^{4,5} the ternary hydrides Li₄RhH₄ and Li₄RhH₅.

The Li–Pd phase diagram⁶ shows the intermetallic compounds LiPd₇, LiPd₂, LiPd, Li₃Pd₂, Li₃Pd, Li₁₅Pd₄ and possibly Li₅Pd. The phase diagram was established by differential thermal analysis of elemental mixtures, and the compounds identified by x-ray powder diffraction and metallographic methods. Melting T increased from the eutectic at 145°C (12 at% Pd) to 1500°C at LiPd₇.

The Li–Pd intermetallics⁷, including LiPd₂, are prepared by sealing the elements in molybdenum containers under a reduced pressure of Ar and heating at 800°C for several hours, followed by annealing at a lower temperature (600 or 330°C). Structures have been determined⁸.

The Li–Pt phase diagram shows the four intermetallic phases Li₉Pt (mp 171°C), Li₅Pt (mp 290°C), Li₁₅Pt₄ (mp 313°C) and Li₂Pt (mp 955°C) in the range 0–40 at% Pt⁹, along with LiPt¹⁰, LiPt₂¹¹ and LiPt₇¹². Compounds Li₂Pt and LiPt were prepared from LiH with elemental Pt. Whereas Li₂Pt was obtained directly at 600°C, LiPt was prepared by the vacuum decomposition of a ternary hydride at 450°C and isolated from the reaction of equimolar amounts of LiH and Pt at 600°C¹⁰. The intermetallic LiPt₂ was prepared by heating a mixture of lithium and platinum strip to > 540°C when the mixture ignited and Li was distilled (a tenfold mole excess was used to compensate for this loss). Excess Li was removed by solution in H₂O or 3 mol L⁻¹ HCl and the product identified by x-ray powder diffraction¹¹. The ternary hydride LiPtH_{0.66} has also been prepared by the reaction of LiH and Pt at 450°C¹³.

The compound NaPt₂ has been proposed as the product of the reaction of Na and Pt at 650°C in Ar. The yield was poor, but a lattice dimension of 7.48 Å was found¹¹.

330 7.4. Formation of the Group-IA or IIA- and -Inner Transition-Metal Bond
7.4.1. Formation of the Group-IA-Transition- and -Inner Transition-Metal Bond
7.4.1.2. Group-IA – Transition-Metal or Inner-Transition-Metal Bond

An unusual reaction is used to form a $KRe \cdot 4 H_2O$. The reduction of potassium perrhenate in en- H_2O solutions by potassium metal yields a white solid containing the Rh^- ion mixed with KOH. Extraction with isopropyl alcohol gives a colloidal brown liquid containing a mixture of KOH, isopropyl alcohol and the rhenide. Fractional extraction of the liquid gives a gray solid that contains 55–60% $KRe \cdot 4 H_2O$ ¹⁴.

Flame spectrometry of mixtures of NaCl or KCl with NH_4ReO_4 shows no compounds containing Na—Re bonds, but K_2Re was obtained¹⁵ with KCl.

(M. G. BARKER)

1. H. U. Borgstedt, *Mater. Chem.*, 5, 95 (1980).
2. S. S. Sidhu, K. D. Anderson, D. D. Zamberis, *Acta Crystallogr.*, 18, 906 (1965).
3. H. C. Donkersloot, J. H. N. Van Vucht, *J. Less-Common Met.*, 50, 279 (1976).
4. J. D. Farr, *J. Inorg. Nucl. Chem.*, 14, 202 (1960).
5. H. G. Wheat, C-Y. Cheng, R. J. Bayuzick, R. W. Sullivan, C. B. Magee, *J. Less-Common Met.*, 58, P13 (1978).
6. O. Loebich, Ch. J. Raub, *J. Less-Common Met.*, 55, 67 (1977).
7. J. H. N. Van Vucht, K. H. J. Buschow, *J. Less-Common Met.*, 48, 345 (1976).
8. O. Loebich, W. Wopersnow, *J. Less-Common Met.*, 63, P83 (1979).
9. O. Loebich, Ch. J. Raub, *J. Less-Common Met.*, 70, P47 (1980).
10. W. Bronger, B. Nacken, K. Ploog, *J. Less-Common Met.*, 43, 143 (1975).
11. C. P. Nash, F. M. Boyden, L. D. Whittig, *J. Am. Chem. Soc.*, 82, 6203 (1960).
12. W. Bronger, W. Klemm, *Z. Anorg. Allg. Chem.*, 319, 58 (1962).
13. B. Nacken, W. Bronger, *J. Less-Common Met.*, 52, 323 (1977).
14. J. B. Bravo, E. Griswold, J. Kleinberg, *J. Am. Chem. Soc.*, 58, 18 (1936).
15. M. I. Ermolaev, Yu. Ya. Gukova, *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.*, 15, 9 (1972).

7.4.1.2. in Coordination Compounds Containing a Group-IA – Transition-Metal or Inner-Transition-Metal Bond

Only covalent bonds between Li and Na and transition metals are known, there being none with the lower group-IA metals or with inner transition elements. Bonding is inferred from metal–metal distances^{1–3}, as well as calculations⁴.

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330 7.4. Formation of the Group-IA or IIA- and -Inner Transition-Metal Bond**7.4.1. Formation of the Group-IA-Transition- and -Inner Transition-Metal Bond****7.4.1.2. Group-IA – Transition-Metal or Inner-Transition-Metal Bond**

An unusual reaction is used to form a $KRe \cdot 4 H_2O$. The reduction of potassium perrhenate in en- H_2O solutions by potassium metal yields a white solid containing the Rh^- ion mixed with KOH. Extraction with isopropyl alcohol gives a colloidal brown liquid containing a mixture of KOH, isopropyl alcohol and the rhenide. Fractional extraction of the liquid gives a gray solid that contains 55–60% $KRe \cdot 4 H_2O$ ¹⁴.

Flame spectrometry of mixtures of NaCl or KCl with NH_4ReO_4 shows no compounds containing Na—Re bonds, but K_2Re was obtained¹⁵ with KCl.

(M. G. BARKER)

1. H. U. Borgstedt, *Mater. Chem.*, **5**, 95 (1980).
2. S. S. Sidhu, K. D. Anderson, D. D. Zamberis, *Acta Crystallogr.*, **18**, 906 (1965).
3. H. C. Donkersloot, J. H. N. Van Vucht, *J. Less-Common Met.*, **50**, 279 (1976).
4. J. D. Farr, *J. Inorg. Nucl. Chem.*, **14**, 202 (1960).
5. H. G. Wheat, C-Y. Cheng, R. J. Bayuzick, R. W. Sullivan, C. B. Magee, *J. Less-Common Met.*, **58**, P13 (1978).
6. O. Loebich, Ch. J. Raub, *J. Less-Common Met.*, **55**, 67 (1977).
7. J. H. N. Van Vucht, K. H. J. Buschow, *J. Less-Common Met.*, **48**, 345 (1976).
8. O. Loebich, W. Wopersnow, *J. Less-Common Met.*, **63**, P83 (1979).
9. O. Loebich, Ch. J. Raub, *J. Less-Common Met.*, **70**, P47 (1980).
10. W. Bronger, B. Nacken, K. Ploog, *J. Less-Common Met.*, **43**, 143 (1975).
11. C. P. Nash, F. M. Boyden, L. D. Whittig, *J. Am. Chem. Soc.*, **82**, 6203 (1960).
12. W. Bronger, W. Klemm, *Z. Anorg. Allg. Chem.*, **319**, 58 (1962).
13. B. Nacken, W. Bronger, *J. Less-Common Met.*, **52**, 323 (1977).
14. J. B. Bravo, E. Griswold, J. Kleinberg, *J. Am. Chem. Soc.*, **58**, 18 (1936).
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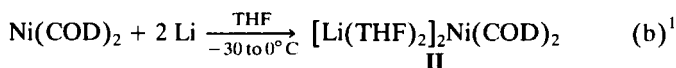
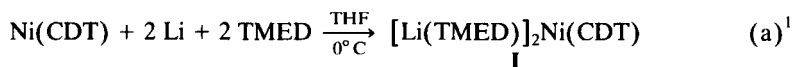
7.4.1. Formation of the Group-IA-Transition- and -Inner Transition-Metal Bond 331

7.4.1.2. Group-IA - Transition-Metal or Inner-Transition-Metal Bond

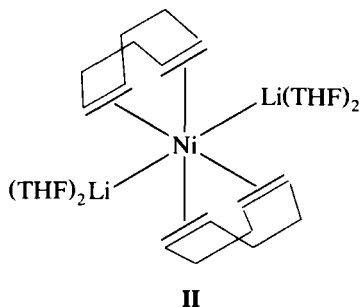
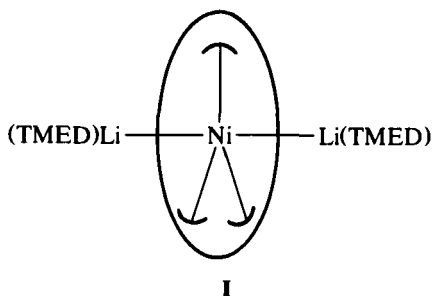
7.4.1.2.1. Compounds Containing Lithium Bonded to a Transition Metal.

7.4.1.2.1. In Synthesis of Compounds Containing Lithium Bonded to a Transition Metal.

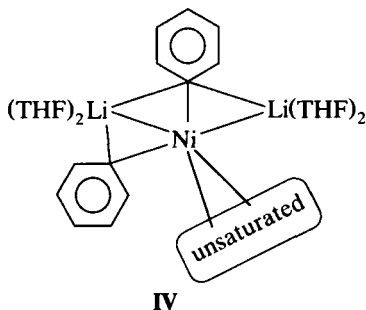
Lithium-transition metal compounds are formed by reactions of, e.g., Ni^0CDT :



The Ni—Li bond is stable in these compounds, and **II**, which is fluxional, reacts with mono- and diolefins to give further compounds containing Li—Ni bonds.



Other compounds containing Li—Ni bonds result from the reaction of $\text{Ni}(\text{CDT})$ and PhLi in Et_2O to give a solution of $[(\text{PhLi})_2(\text{Et}_2\text{O})_x]\text{Ni}(\text{CDT})$. When treated with THF or TMED, this solution gives crystalline $[\text{PhLi}(\text{THF})_2]_2\text{Ni}(\text{CDT})$ **III** and $[\text{PhLi}(\text{TMED})]_2\text{Ni}(\text{CDT})$, respectively. Analogous reactions occur² with $\text{Ni}(\text{COD})_2$, and $\text{Co}(\text{COD})\text{cyclooctenyl}$ reacts with PhLi to give a compound containing a Li—Co bond³. Reaction of **III** with unsaturated alkenes, alkynes, arenes, ketones or nitriles in Et_2O or THF gives $[(\text{PhLi})_2(\text{THF})_n] \text{Ni}(\text{unsaturated})$ **IV** and related compounds. Reaction of NiCDT with a salt-free mixture of NaPh and LiPh in the presence of C_2H_4 gives $[(\text{PhLi})_2\text{Et}_2\text{O}]\text{Ni}(\text{C}_2\text{H}_4)$.

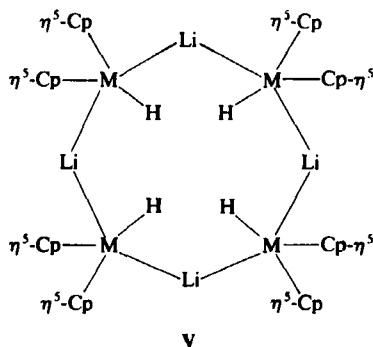


In $[\text{Li}(\text{TMED})_2][\text{MnMe}_n]$ ($n = 4, 5$ or 6) the Li—Mn distance of 2.831 \AA is regarded to be too long for Mn—Li bonding⁴.

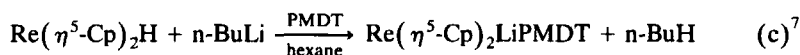
When $\text{M}(\eta^5\text{-Cp})_2\text{H}_2$ ($\text{M} = \text{Mo}, \text{W}$) reacts with $n\text{-BuLi}$ in toluene, the tetrameric $[\text{M}(\eta^5\text{-Cp})_2(\text{H})\text{Li}]_4$ (**V**) is formed with an eight-membered ring of alternating M and Li

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 7.4.1.2.2. Compounds Containing Sodium Bonded to a Transition Metal.

atoms linked by metal–metal bonds^{5,6}:

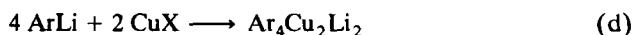


The Re derivative, $\text{Re}(\eta^5\text{-Cp})_2\text{H}$, reacts similarly:

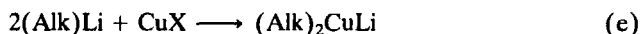


and the yellow monomeric product contains a Re—Li bond.

The nature of alkyl- and arylcuprates is still not clear, but both the arylcuprates, which are formed from aryllithiums and Cu(I) salts:



where X = Cl, Br, I, and the alkylcuprates:



contain weak Li—Cu bonds bridged by organic groups^{8,9}.

(J. R. CHIPPERFIELD)

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7.4.1.2.2. In Synthesis of Compounds Containing Sodium Bonded to a Transition Metal.

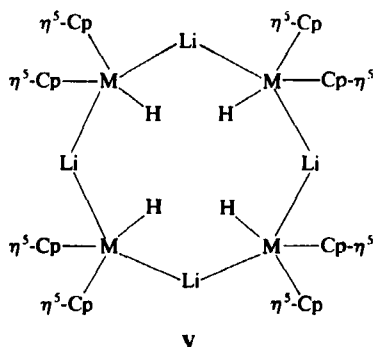
There are fewer examples of sodium-bonded compounds than of those containing Li. When (CDT)Ni is treated with a salt-free NaPh—LiPh mixture (Na : Li = 2–4) in the mole ratio (NaPh + LiPh) : Ni = 4 in ether in the presence of C_2H_4 , the complex $[(\text{PhNa})_2(\text{Et}_2\text{O})_2]\text{Ni}(\text{C}_2\text{H}_4)$ (I) precipitates as an orange-red powder, whereas

332 7.4.1. Formation of the Group-IA-Transition- and -Inner Transition-Metal Bond

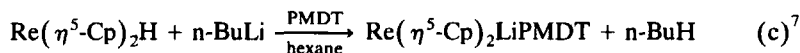
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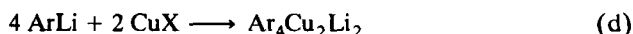


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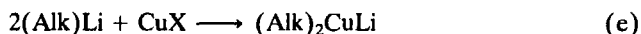


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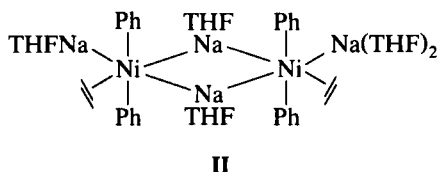
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7.4.2. Formation of the Group-IIA-Transition- and -Inner Transition-Metal Bond

7.4.2.1. in Metallic Systems

Beryllium forms intermetallic compounds with transition metals and phase diagrams are available¹⁻⁴. Some 26 phase diagrams have also been published for Mg-transition metal systems, and intermetallic compound formation is widespread in these systems also. The extent of intermetallic compound formation decreases down group IIA, such that Ca, Sr and Ba show much less tendency for compound formation to the extent that compounds are observed⁵ only in the Ba-Pd system.

Heating of mixtures of the elements at high T in the required stoichiometry results in compound formation, but there are several difficulties, the worst being the disparity in melting points of the two elements concerned. For complete reaction and the formation of homogeneous samples long heating times at T near to the liquidus are required. This leads to loss of the most volatile component in the system, namely the group IIA element. For example, Be_{12}Mo and Be_2Mo are prepared by heating Mo and Be for 100 h at 1100°C ⁶ and Be_2Nb_3 by heating the powders Be and Nb at 1550°C under Ar. In the latter the material has to be repeatedly crushed and blended and reheated under vacuum at $1600\text{--}1750^\circ\text{C}$ to ensure homogeneity. During vacuum treatment extensive loss of Be occurs, leading to a final composition of $\text{NbBe}_{0.4}$ ⁷. Sealed containers are used for CaNi_5 , Ca_2Ni_7 , CaNi_3 and CaNi_2 . Here problems are encountered from the low boiling point of Ca (1600°C) compared with the melting point of Ni (1455°C). The mixtures are placed in Mo containers sealed into silica capsules and heated for 3 weeks slightly above the melting point of Ca, but homogeneity was not attained. Better results were obtained for the Ni-rich phases by heating the mixtures gradually to 1450°C and then cooling to RT⁸.

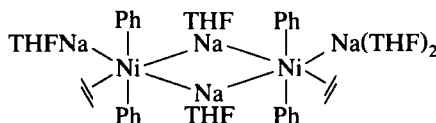
A halide flux enhances the growth of single crystals of intermetallic compounds such as CaNi_5 ⁹ and compounds in the Dy-Mg and Ce-Mg¹⁰ systems which have

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II

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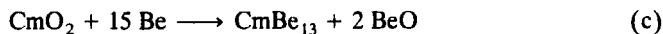
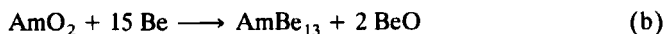
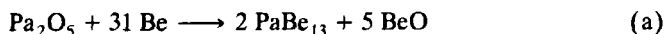
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A halide flux enhances the growth of single crystals of intermetallic compounds such as CaNi_5 ⁹ and compounds in the Dy-Mg and Ce-Mg¹⁰ systems which have

been prepared from the elements in a LiCl-KCl flux. Crystals of Mg_2Th and $\text{Mg}_{23}\text{Th}_6$ have also been grown from molten Mg contained in thorium crucibles¹¹.

Several preparative methods do not use elemental mixtures. Group IIA-Pt intermetallic compounds have been prepared¹² by reacting platinum metal with the group-IIA oxide under hydrogen or ammonia at 900–1200°C. Beryllium metal reacts¹³ with neptunium fluoride under vacuum at 1100–1200°C to form Be_{13}Np .

The compounds Be_{13}M ($\text{M} = \text{Pa}, \text{Am}$ or Cm) have been prepared by reacting Be with the appropriate actinide oxide at 1500°C in He:



Precautions must be taken to shield the apparatus because of neutron emission from (α, n) reactions, and the neutron emission rate may be used in a novel fashion to detect reaction. In the reaction of Pa_2O_5 with Be (20% xs) in the form of platelets, the T was increased to the mp of Be when a sharp increase in neutron emission showed that reaction had taken place. The mixtures were then maintained at temperature until the neutron emission rate became constant¹⁴.

A series of Be-Pt intermetallic compounds are prepared during the electrodeposition of Be on Pt from a solution of BeCl_2 in an equimol NaCl-KCl mixture at 710°C. x-Ray diffraction of the electrode surface shows¹⁵ the presence of BePt , Be_3Pt . Electrolytic methods are also used¹⁶ to extract single crystals of Be_{13}V from alloys prepared by arc melting Be and the transition metal in the proportion 15:1.

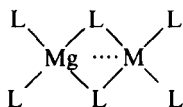
(M. G. BARKER)

1. M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
2. R. P. Elliott, *Constitution of Binary Alloys*, First Suppl., McGraw-Hill, New York, 1965.
3. F. A. Shunk, *Constitution of Binary Alloys*, Second Suppl., McGraw-Hill, New York, 1969.
4. W. G. Moffatt, *The Handbook of Binary Phase Diagrams*, General Electric Co., Schenectady, NY, 1977. Looseleaf system in three volumes with regular updating. Contains excellent index to material contained in refs. 1–3.
5. E. M. Savitskiy, V. P. Polyakova, E. M. Khorlin, *Russ. Metallur. (Metally)*, 6, 88 (1970).
6. S. G. Gordon, J. A. McGurty, G. E. Klein, W. J. Koshuba, *J. Met.*, 3, 637 (1951).
7. A. Zalkyn, D. E. Sands, O. H. Krikorian, *Acta Crystallogr.*, 13, 160 (1960).
8. K. H. J. Buschow, *J. Less-Common Met.*, 38, 95 (1974).
9. H. Nowotny, E. Wormnes, A. Mornheim, *Z. Metallk.*, 32, 39 (1940).
10. V. I. Evdokimenko, P. I. Kripyakevich, *Sov. Phys. Crystallogr.*, 9, 463 (1964).
11. E. I. Gladyshevskii, P. I. Kripyakevich, Ju. B. Kuzma, M. Ju. Teslyuk, *Sov. Phys. Crystallogr.*, 6, 615 (1961).
12. W. Bronger, W. Klemm, *Z. Anorg. Allg. Chem.*, 319, 58 (1962).
13. O. C. J. Runnalls, *Acta Crystallogr.*, 7, 222 (1954).
14. U. Benedict, K. Buijs, C. Dufour, J. C. Toussaint, *J. Less-Common Met.*, 42, 345 (1975).
15. Yu. K. Delimarskii, E. L. Khandros, V. M. Baranenko, *Ukr. Khim. Zh. (Russ. Ed.)*, 4, 3 (1976); *Chem. Abstr.*, 84, 142,475 (1976).
16. F. W. Batchelde, R. F. Raeuchle, *Acta Crystallogr.*, 10, 648 (1957).

7.4. Formation of the Group-IA or IIA- and -Inner Transition-Metal Bond 335
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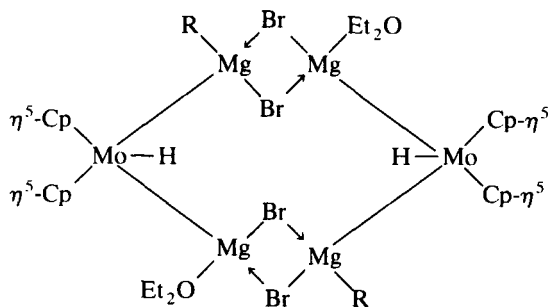
7.4.2.2. in Coordination Compounds Containing a Group-IIA – Transition- and Inner-Transition-Metal Bond

Compounds containing Mg bonded to an inner transition metal or other group-IIA metals bonded to transition metals are not known. Compounds such as **I**, in which there are only weak interactions between Mg and M, are excluded from this discussion.

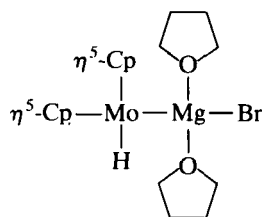


I

Organomagnesium halide reagents RMgX (RX = C₆H₁₁Br, i-PrBr, n-BuBr, PhBr) react in toluene-ether with (η⁵-Cp)₂MoH₂ to form compounds **II**, in which each molecule contains four Mo—Mg bonds¹⁻³. When **II** is dissolved in THF a red solution is formed, which after concentration yields⁴ orange crystals of **III**. Compound **III** is monomeric with a Mo—Mg bond of length 273.2 pm, consistent for Mo as a one-electron donor.

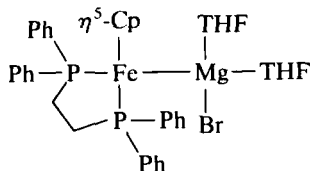


II



III

An Mg—Fe bond is formed in **IV** by the reaction of η⁵-CpFe(dppe)Br with Mg in THF^{5,6}, and η⁵-Cp(PPh₃)NiMgBr forms similarly in solution when η⁵-CpNi(PPh₃)Br reacts with Mg in Et₂O-THF or Et₂O-C₆H₆, but this is not isolated⁷.

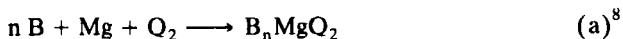


IV

Further compounds are formed from dimeric carbonyl derivatives, Q₂ [Q = Fe(CO)₂Cp-η⁵; Mo(CO)₂(L)Cp-η⁵, where L = CO, PBu-n₃, PMePh₂; Co(CO)₃L,

336 7.4. Formation of the Group-IA or IIA- and -Inner Transition-Metal Bond
 7.4.2. Formation of the Group-IIA-Transition- and -Inner Transition-Metal Bond
 7.4.2.2. Group-IIA - Transition- and Inner-Transition-Metal Bond

where $L = CO, PMePh_2$], with $Mg-Hg$ in the presence of bases (B) such as THF or py:



where $n = 2$ or 4 . These derivatives may contain either carbonyl-bridged $Mg-M$ bonds or direct $Mg-M$ bonds. When Mg is 6 coordinated ($n = 4$), bridging carbonyl groups are present, but when Mg is 4 coordinated ($n = 2$), direct metal-metal bonds may be present. Therefore, IR spectra of $(THF)_2Mg[Fe(CO)_2Cp-\eta^5]_2$ and $(THF)_2Mg[Co(CO)_3PBu-n_3]_2$ in C_6H_6 suggest direct $Mg-Fe$ and $Mg-Co$ bonds, whereas these are absent in $py_4Mg[Fe(CO)_2Cp-\eta^5]_2$ $py =$ pyridine and $(THF)_4Mg[Co(CO)_3PBu-n_3]_2$.

Other compounds with $Mg-Ni^9$ and $Mg-Co^{10}$ bonds have been made.

(J. R. CHIPPERFIELD)

1. M. L. H. Green, G. A. Moser, I. Packer, F. Pettit, R. A. Forder, K. Prout, *J. Chem. Soc., Chem. Commun.*, 839 (1974).
2. K. Prout, R. A. Forder, *Acta Crystallogr., Sect. B*, 31, 852 (1975).
3. M. L. H. Green, T. Luong-thi, G. A. Moser, I. Packer, F. Pettit, D. M. Roe, *J. Chem. Soc., Dalton Trans.*, 1988 (1976).
4. S. G. Davies, M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1510 (1978).
5. H. Felkin, P. J. Knowles, B. Meunier, A. Mitschler, L. Ricard, R. Weiss, *J. Chem. Soc., Chem. Commun.*, 44 (1974).
6. H. Felkin, P. J. Knowles, B. Meunier, *J. Organomet. Chem.*, 146, 151 (1978).
7. H. Felkin, P. J. Knowles, *J. Organomet. Chem.*, 37, C14 (1972).
8. G. B. McVicar, *Inorg. Chem.*, 14, 2087 (1975).
9. W. Kaschube, K.-R. Pörschke, K. Angermund, C. Krüger, G. Wilke, *Chem. Ber.*, 121, 1921 (1988).
10. K. Jonas, G. Koepe, K. Krüger, *Angew. Chem., Int. Ed. Engl.*, 25, 923 (1986).

7.5. The Formation of the Group IA or IIA–Group 0 Element Bond

The electron affinities of the group 0 elements are not sufficiently favorable to allow for salt formation even with the most electropositive of these elements, Cs. The electropositive nature of the group-IA and -IIA elements excludes the possibility of bonding such as that discussed in §2.10.

(N. BARTLETT)

8. Formation of the Bond to the Group-IB (Cu, Ag, Au) or -IIB (Zn, Cd, Hg) Elements

8.1. Introduction

This chapter examines bonds to and among group-IB and -IIB, the transition and inner transition metals.

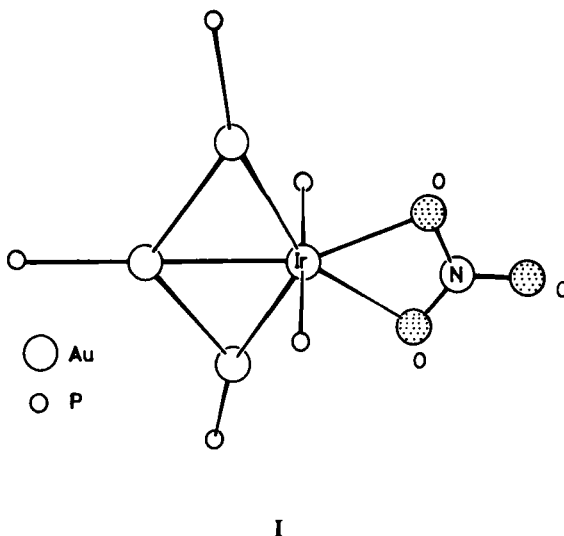
(A. P. HAGEN)

8.2. Formation of the Group-IB or -IIB–Group-IB or -IIB Metal Bonds

8.2.1. in Gold Cluster Compounds Containing the Au_3 , Au_4 , Au_5 , Au_6 , Au_7 , Au_8 , Au_9 , Au_{11} , Au_{13} and Au_{55} Cores

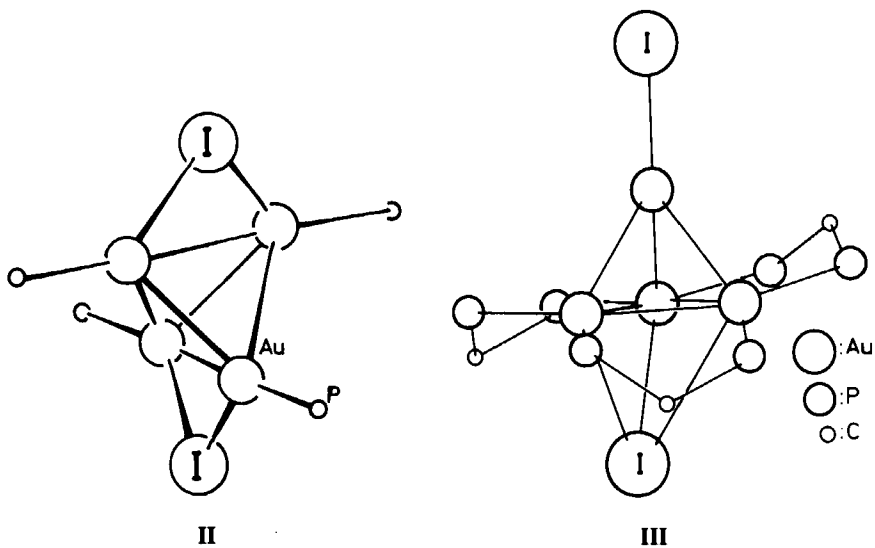
Whereas many high-nuclearity metal clusters have CO as a ligand¹, all known high-nuclearity Au clusters are coordinated with tertiary phosphines.

The smallest known gold clusters are the heterometallics^{2,3} $(\text{AuPh}_3)_3\text{V}(\text{CO})_5$ and $[(\text{AuPPh}_3)_3\text{Ir}(\text{PPh}_3)_2\text{NO}_3]$. The first can be described as a triangle of Au capped by the $\text{V}(\text{CO})_5$ group, whereas the second (I) contains a planar Au_3Ir in which the $\text{Au}_3(\text{PPh}_3)_3$ looks like a coordinated allyl group to the $\text{Ir}(\text{PPh}_3)_2\text{NO}_3$ entity.

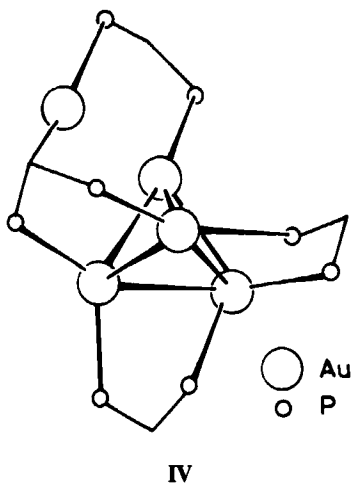


The smallest monometallic Au clusters are the two Au_4 clusters, $\text{Au}_4(\text{PPh}_3)_4\text{I}_2$ and $\text{Au}_4(\text{dppm})_3\text{I}_2$. Both clusters contain a tetrahedral Au_4 core^{4,5}. In $\text{Au}_4(\text{PPh}_3)_4\text{I}_2$ the

Its are μ_2 bridged between two opposite Au–Au edges (II), whereas in $\text{Au}_4(\text{dppm})_3\text{I}_2$ one I is coordinated to one Au, and the other I is μ_3 coordinated (III).

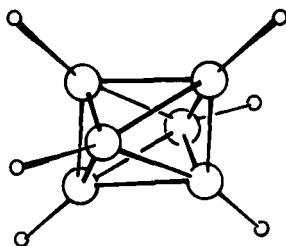


A cluster with five Au atoms exists in $\{\text{Au}_5(\text{dppm})_3[(\text{P}_2\text{H}_2\text{P})_2\text{CH}]\}(\text{NO}_3)_2$. This cluster has a Au_4 core, with an additional Au incorporated in the phosphine ligand, linearly coordinated between a phosphorus and a carbon from the methanido bridge (**IV**)^{6,7}:



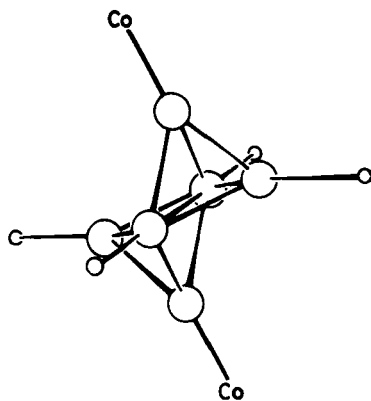
An Au cluster containing six metal atoms is found^{8,9} in {Au₆[P(p-MeC₆H₄)₃]₂}[BPh₄]₂ (**V**). This cluster, with the geometry of a slightly distorted O_h, was originally thought to be noncentered. It has been established that there is a C

atom in the center, so the composition is³³ $[\text{C}(\text{AuPh}_3)_6]^{2+}$. A similar C-centered cluster with composition $\text{C}(\text{AuPPh}_3)_5$ is also reported³⁴.



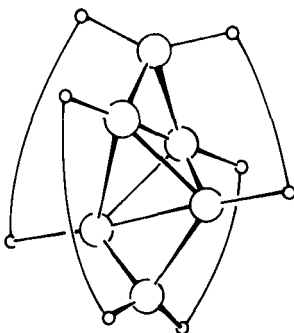
V

The Au_6 core in the $\text{Au}_6(\text{PPh}_3)_4[\text{Co}(\text{CO})_4]_2$ cluster (VI) is a bitetrahedron with one common edge¹⁰:



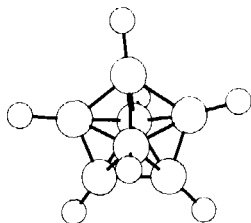
VI

In $\text{Au}_6(\text{dppp})_4(\text{NO}_3)_2$, there is a tetrahedron of four Au atoms and an Au bridge between two opposite edges¹¹ (VII):



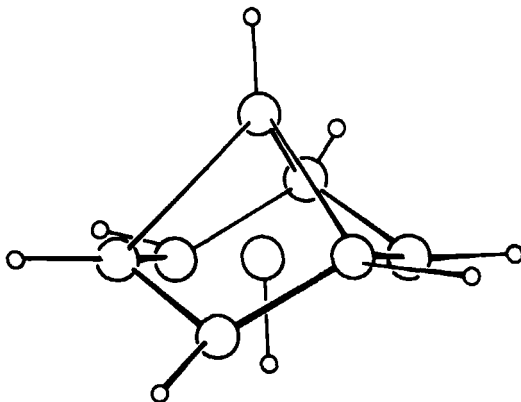
VII

An Au cluster with seven metals is found in $[\text{Au}_7(\text{PPh}_3)_7]^+$ (VIII). The Au core is a pentagonal bipyramid¹².



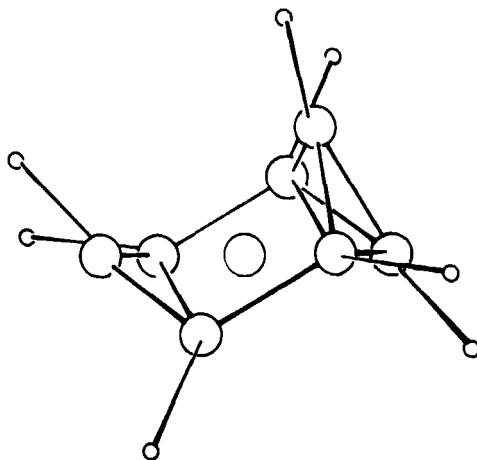
VIII

An Au_8 core is present¹³⁻¹⁵ in $[\text{Au}_8(\text{PPh}_3)_8](\text{PF}_6)_2$ (IX). The Au_8 skeleton is derived from that of the Au_{11} cluster by removing three Au atoms from the basal triangle. Each Au atom, including the central Au atom, is coordinated to a phosphine.



IX

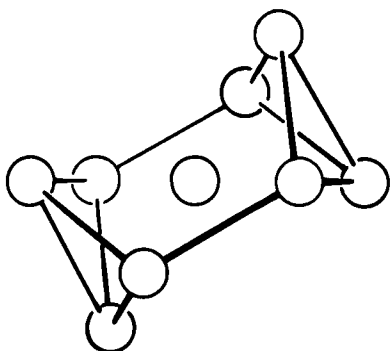
The Au-P skeleton in $[\text{Au}_8(\text{PPh}_3)_7](\text{NO}_3)_2$ (X)^{10,15} is derived from the $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ cluster by removing one Au(I)-phosphine entry:



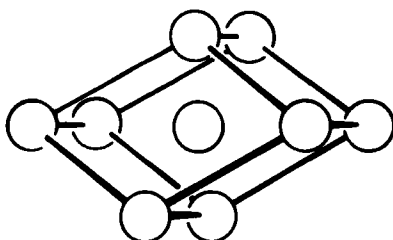
X

The Au_8 cluster in $[\text{Au}_8(\text{PPh}_3)_6]\text{PF}_6$ may be isostructural¹² with that in $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$.

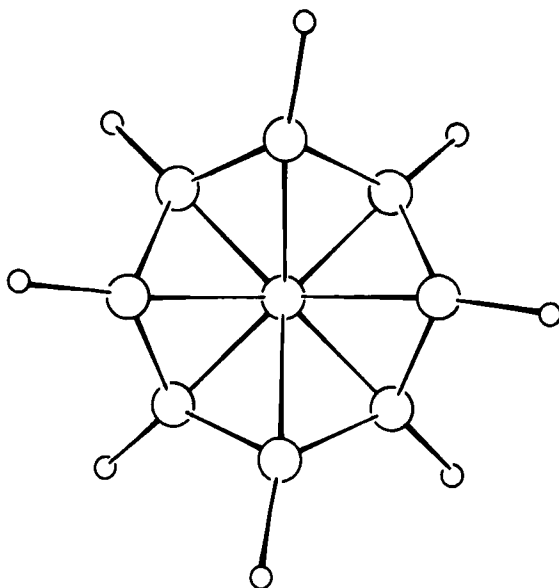
An Au_9 core exists in the $[\text{Au}_9(\text{PAr}_3)_8]\text{Y}_3$ compounds (**XI**)¹⁶ [$\text{Y} = \text{NO}_3$, PF_6 , ClO_4 , $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}$], $\text{Au}_9(\text{PPh}_3)_8\text{PF}_6$ (**XII**)¹⁷ and $\text{Au}_9[\text{P}(\text{p-C}_6\text{H}_4\text{OCH}_3)_3]_8[\text{BF}_4]_3$ (**XIII**)¹⁸.



XI



XII

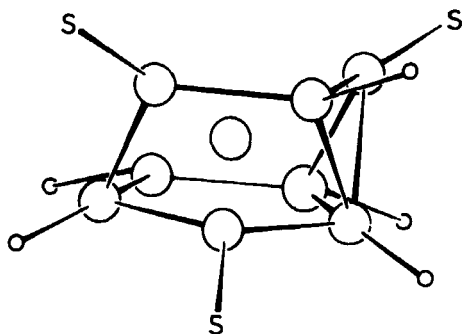


XIII

In the 3+- and 1+-charged complexes there is a central Au atom and eight peripheral Au atoms, all coordinated to phosphine ligands, but there are differences in the geometry of the Au cores (respectively, **XI**, **XII**, and **XIII**).

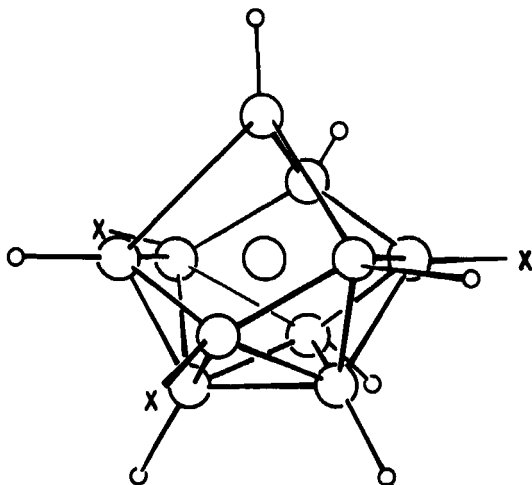
In $\text{Au}_9[\text{P}(\text{C}_6\text{H}_{11})_5]_5(\text{SCN})_3$ five peripheral Au atoms are coordinated to phosphine and three to SCN ¹⁹. The geometry of the Au cluster deviates slightly from

those of the other Au_9 clusters (XIV):



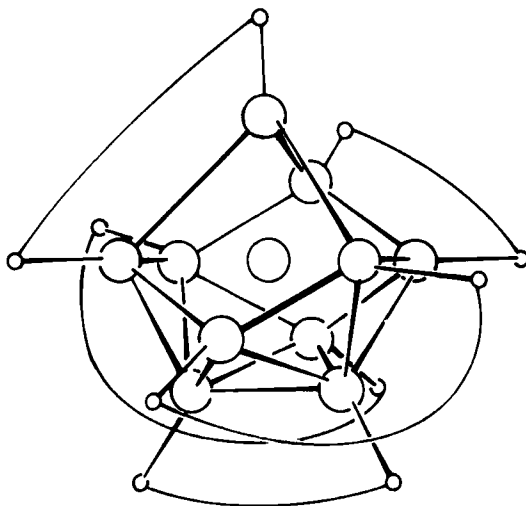
XIV

Gold clusters with 11 metal atoms exist in the $\text{Au}_{11}(\text{PAr}_3)_7\text{Y}_3$ compounds (Ar = phenyl or para-substituted phenyl, Y = SCN, CN, I) (XV) and in $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$. In $\text{Au}_{11}[\text{P}(\text{C}_6\text{H}_5)_3]_7[\text{SCN}]_3$, $\text{Au}_{11}[\text{P}(\text{p-ClC}_6\text{H}_4)_3]_7\text{I}_3$ and $\text{Au}_{11}[\text{P}(\text{p-FC}_6\text{H}_4)_3]_7\text{I}_3$, a central Au atom is surrounded by 10 peripheral Au atoms²⁰⁻²², which are bonded to either phosphine or the Y.



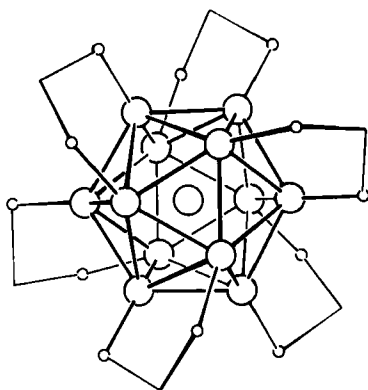
XV

In $[\text{Au}_{11}(\text{PPh}_2(\text{CH}_2)_3\text{PPh}_2)_5][\text{SCN}_3]$ (XVI), an Au_{11} cluster, phosphines are bonded to all the peripheral Au atoms²³:

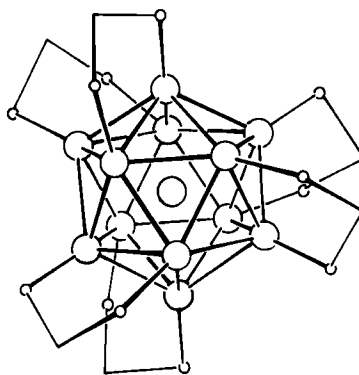


XVI

A central Au atom is surrounded by 12 Au atoms at the vertices of an icosahedron in⁷ $[\text{Au}_{13}(\text{dppm})_6]^n+$ and in²⁴ $[\text{Au}_{13}(\text{PPhMe}_2)_{10}\text{Cl}_2](\text{PF}_6)_3$ (XVII and XVIII, respectively):

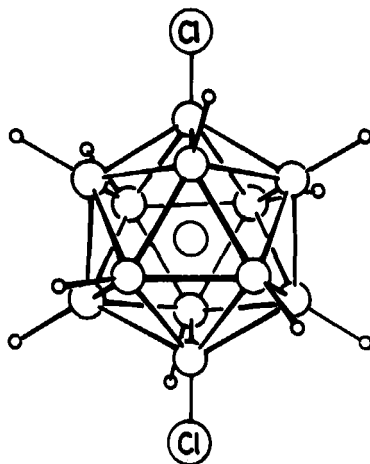


a



b

XVII



XVIII

The skeletal geometries of the centered Au clusters described above can be derived from a centered icosahedron. The Au_{13} clusters form a complete icosahedron, whereas Au_{11} can be obtained by replacing a triangle of Au atoms by one Au atom and Au_9 can be derived from an icosahedron by removing two pairs of adjacent atoms that together form a rectangle. The Au_8 cluster is obtained when one triangle of atoms is removed from the Au_{11} cluster. The $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ ion is related to the Au_9 cluster by removal of a Au(I) phosphine entity from the latter. The common feature of all centered Au clusters is the centered hexagon²³.

However, in $^{18}\text{Au}_9[\text{P}(\text{p-C}_6\text{H}_4\text{OCH}_3)_3]_8[\text{BF}_4]_3$ there is a centered eight-membered crown and $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ has²⁵ a hexagonal closest packed structure. The structure of the Au_{55} cluster has been questioned³⁵. Most of the noncentered smaller clusters have a tetrahedral buildup. However, $[\text{Au}_6(\text{PPh}_3)_6]^{2+}$ has an octahedral framework, and $[\text{Au}_7(\text{PPh}_3)_7]^+$ is pentagonal bipyramidal.

The composition of stable compounds seems to depend on the steric demands of the phosphines coordinated to the periphery of the Au cluster. Not more than eight PPh_3 ligands can be accommodated around a small Au framework, giving a maximum of nine Au atoms in a homoleptic, centered cluster; $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ reacts with $x\text{s PPh}_3$ to give $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$, where the eightfold phosphine cover is not exceeded, but where also the central Au is bonded to PPh_3 . In $[\text{Au}_{11}(\text{PPh}_3)_8\text{X}_2]^+$ two small ligands, such as Cl^- or $[\text{SCN}]^-$, are needed. With the bulky $[\text{P}(\text{C}_6\text{H}_{11})_3]$ ligand a heteroleptic composition is necessary for a stable Au_9 compound: $[\text{Au}_9[\text{P}(\text{C}_6\text{H}_{11})_3]_5][\text{SCN}]_3$. With sterically less demanding phosphines, such as dppm ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$), dpppH ($\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$) and PMe_2Ph , the compositions $[\text{Au}_{11}(\text{dppp})_5]^{3+}$, $[\text{Au}_{13}(\text{dppm})_6]^{n+}$ and $[\text{Au}_{13}[\text{P}(\text{Me}_2\text{Ph})_3]_{10}\text{Cl}_2]^{3+}$ can be achieved. When a complete coverage of ligands is not realized, as in $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$, the exposed, coordinatively unsaturated Au atom causes a high reactivity. High-nuclearity Au clusters have been synthesized in which the central atom is not Au but Pd³⁶, Rh³⁷ or Pt³⁸.

The magnitude of the positive charge on all Au cluster compounds can be rationalized by simple MO calculations^{23,26}. The reactivity and structure of the

clusters can be understood with the aid of a theoretical bonding model³⁹; simple electron counting rules predict the symmetry and the possibility for addition and other reactions^{40,41}.

Chemical bonding and dynamic properties of Au clusters are obtained by recoilless γ -ray spectroscopy^{23,27,28}, XPS^{29,30} and³¹ P NMR investigations^{31,32}.

Gold clusters can be synthesized by three methods: reduction of Au(I) compounds, evaporation of Au metal and conversions of Au clusters.

(F. A. VOLLENBROEK, J. W. A. VAN DER VELDEN, J. J. BOUR, J. J. STEGGERDA)

1. P. Chini, G. Longoni, C. G. Albana, in *Advances in Organometallic Chemistry*, F. G. A. Stone, R. West, eds., Academic Press, New York, 1976, p. 285.
2. J. E. Ellis, *J. Am. Chem. Soc.*, **103**, 6106 (1981).
3. A. J. Casalnuovo, L. H. Pignolet, J. W. A. van der Velden, J. J. Bour, J. J. Steggerda, *J. Am. Chem. Soc.*, **105**, 5957 (1984).
4. F. Demartin, M. Manassero, L. Naldini, R. Ruggeri, M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 222 (1981).
5. J. W. A. van der Velden, J. J. Bour, R. Pet, W. P. Bosman, J. H. Noordik, *Inorg. Chem.*, **22**, 3112 (1983).
6. J. W. A. van der Velden, J. J. Bour, F. A. Vollenbroek, P. T. Beurskens, J. M. M. Smits, *J. Chem. Soc., Chem. Commun.*, 1162 (1979).
7. J. W. A. van der Velden, F. A. Vollenbroek, J. J. Bour, P. T. Beurskens, J. M. M. Smits, W. P. Bosman, *Recl. Trav. Chim. Pays-Bas*, **100** 148 (1981).
8. P. L. Bellon, M. Manassero, C. Naldini, M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 1035 (1972).
9. P. L. Bellon, M. Manassero, M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 2423 (1973).
10. J. W. A. van der Velden, J. J. Bour, B. F. Otterloo, W. P. Bosman, J. H. Noordik, *J. Chem. Soc., Chem. Commun.*, 583 (1981).
11. J. W. A. van der Velden, J. J. Bour, J. J. Steggerda, P. T. Beurskens, M. Roseboom, J. H. Noordik, *Inorg. Chem.*, **21**, 4324 (1982).
12. J. W. A. van der Velden, P. T. Beurskens, J. J. Bour, W. P. Bosman, J. H. Noordik, M. Kolenbrander, J. A. K. M. Buskes, *Inorg. Chem.*, **23**, 146 (1984).
13. F. A. Vollenbroek, W. P. Bosman, J. J. Bour, J. H. Noordik, P. T. Beurskens, *J. Chem. Soc., Chem. Commun.*, 387 (1979).
14. M. Manassero, L. Naldini, M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 385 (1979).
15. F. A. Vollenbroek, J. J. Bour, J. W. A. van der Velden, *Recl. Trav. Chim. Pays-Bas*, **99**, 137 (1980).
16. P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 1423 (1971).
17. J. G. M. van der Linden, M. L. H. Paulissen, J. E. J. Schmitz, *J. Am. Chem. Soc.*, **105**, 1903 (1983).
18. K. P. Hall, B. R. C. Theobald, D. I. Gilmour, D. M. Mingos, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 528 (1982).
19. M. K. Cooper, G. R. Denis, K. Henrick, M. McPartlin, *Inorg. Chim. Acta*, **45**, L151 (1980).
20. M. McPartlin, R. Mason, L. Malatesta, *J. Chem. Soc., Chem. Commun.*, 334 (1969).
21. V. G. Alcano, P. L. Bellon, M. Manassero, M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 1210 (1970).
22. P. L. Bellon, M. Manassero, M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1481 (1972).
23. F. A. Vollenbroek, Thesis, Univ. Nijmegen, The Netherlands, 1979.
24. C. E. Briant, B. R. C. Theobald, J. W. White, L. K. Bell, D. M. P. Mingos, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 201 (1981).
25. G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyer, G. H. M. Calis, J. W. A. van der Velden, *Chem. Ber.*, **114**, 3634 (1981).
26. D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1163 (1976).
27. F. A. Vollenbroek, P. C. P. Bouten, J. M. Trooster, J. P. van den Berg, J. J. Bour, *Inorg. Chem.*, **17**, 1345 (1978).

28. F. A. Vollenbroek, J. J. Bour, J. M. Trooster, J. W. A. van der Velden, *J. Chem. Soc., Chem. Commun.*, 907 (1978).
29. P. M. Th. M. van Attekum, J. W. A. van der Velden, J. M. Trooster, *Inorg. Chem.*, 19, 701 (1980).
30. C. Battisoni, G. Mattogno, F. Cariati, L. Naldini, A. Sgamellotti, *Inorg. Chim. Acta*, 24, 207 (1977).
31. F. A. Vollenbroek, J. P. van den Berg, J. W. A. van der Velden, J. J. Bour, *Inorg. Chem.*, 19, 2685 (1980).
32. J. W. A. van der Velden, Thesis, Univ. Nijmegen, The Netherlands (1983).
33. F. Scherbaum, A. Grohmann, B. Huber, C. Krüger, H. Schmidbaur, *Angew. Chem.*, 100, 1602 (1988).
34. F. Scherbaum, A. Grohmann, G. Müller, H. Schmidbaur, *Angew. Chem.*, 101, 464 (1989).
35. J. P. Fackler Jr., C. J. McNeal, R. N. P. Winpenny, L. H. Pignolet, *J. Am. Chem. Soc.*, 111, 6434 (1989).
36. L. N. Ito, B. J. Johnson, A. M. Mueting, L. H. Pignolet, *Inorg. Chem.*, 28, 2028 (1989).
37. S. G. Bott, M. P. Mingos, M. J. Watson, *J. Chem. Soc., Chem. Commun.*, 1192 (1989).
38. J. J. Bour, R. P. F. Kanters, P. P. J. Schlebos, J. J. Steggerda, *Recl. Trav. Chim. Pays-Bas*, 107, 211 (1988).
39. A. J. Stone, *Inorg. Chem.*, 20, 563 (1981).
40. K. P. Hall, D. M. P. Mingos, in *Progress in Inorganic Chemistry*, Vol. 32, S. J. Lippard, ed., 237, John Wiley and Sons, New York, 1984, p. 237.
41. R. P. F. Kanters, Ph.D. Thesis, University of Nijmegen, The Netherlands, 1990.

8.2.1.1. by Reduction of Au(I) Complexes

Sodium borohydride reductions of gold(I) complexes give Au clusters at RT if sodium borohydride in ethanol is dropped slowly into a suspension of the Au(I) complex in the same solvent. The immediate coloring of the reaction mixture (mostly red), even after only a few drops of the borohydride have been added, indicates fast formation of Au clusters. In view of the complicated composition of these compounds the fast formation is surprising. The use of H_2 and CO with H_2O as reducing agents in the synthesis of gold clusters has been described (see Table 1, Method A, §8.2.2.2).

To remove any metallic Au, the reaction mixture is evaporated to dryness and subsequently passed over a commercial terra infusorii column in a minimal volume of solvent. Crystallization may be performed by slow diffusion of a two-layer system. Yields are low (10–60%). The metal evaporation technique (see §8.2.1.2) gives higher yields than the sodium borohydride method.

Reduction of $ClAuP(PhMe_2)_3$ by $Ti(\mu-C_7H_8)_2$ in toluene leads to precipitation. When this is dissolved in ethanol, and a large counterion is added, it crystallizes¹ as the cationic $[Au_{11}(PPhMe_2)_{10}]^{3+}$. Also, $Ti(\mu-C_7H_8-\eta^7)_2$ is used as the reducing agent in the preparation of $[Au_9\{P(p-C_6H_4OCH_3)_3\}_8]^{3+}$ from $AuCIP(p-C_6H_4OCH_3)_3$.

The reduction of $AuPPh_3Cl$ with B_2H_6 in benzene yields $Au_{55}(PPh_3)_{12}Cl_6$.

Heteronuclear clusters can be prepared by the reduction of $AuCIPPh_3$ with $Cs_3V(CO)_5$ or $Au(NO_3)PPh_3$ with $[Ir_2(\mu-H)_3(H)_2(PPh_3)_4][PF_6]$, which yield, respectively, $(AuPPh_3)_3V(CO)_5$ and $[Au_3Ir(NO_3)(PPh_3)_5][PF_6]$.

(F. A. VOLLENBROEK, J. W. A. VAN DER VELDEN, J. J. BOUR, J. J. STEGGERDA)

1. C. E. Briant, B. R. C. Theobald, J. W. White, L. K. Bell, D. M. R. Mingos, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 201 (1981).
2. W. Bos, J. J. Bour, J. J. Steggerda, L. H. Pignolet, *Inorg. Chem.*, 24, 4298 (1985).

350 8.2. Formation of the Group-IB or -IIB-Group-IB or -IIB Metal Bonds

8.2.1. in Gold Cluster Compounds

8.2.1.1. by Reduction of Au(I) Complexes

28. F. A. Vollenbroek, J. J. Bour, J. M. Trooster, J. W. A. van der Velden, *J. Chem. Soc., Chem. Commun.*, 907 (1978).
29. P. M. Th. M. van Attekum, J. W. A. van der Velden, J. M. Trooster, *Inorg. Chem.*, 19, 701 (1980).
30. C. Battisoni, G. Mattogno, F. Cariati, L. Naldini, A. Sgamellotti, *Inorg. Chim. Acta*, 24, 207 (1977).
31. F. A. Vollenbroek, J. P. van den Berg, J. W. A. van der Velden, J. J. Bour, *Inorg. Chem.*, 19, 2685 (1980).
32. J. W. A. van der Velden, Thesis, Univ. Nijmegen, The Netherlands (1983).
33. F. Scherbaum, A. Grohmann, B. Huber, C. Krüger, H. Schmidbaur, *Angew. Chem.*, 100, 1602 (1988).
34. F. Scherbaum, A. Grohmann, G. Müller, H. Schmidbaur, *Angew. Chem.*, 101, 464 (1989).
35. J. P. Fackler Jr., C. J. McNeal, R. N. P. Winpenny, L. H. Pignolet, *J. Am. Chem. Soc.*, 111, 6434 (1989).
36. L. N. Ito, B. J. Johnson, A. M. Mueting, L. H. Pignolet, *Inorg. Chem.*, 28, 2028 (1989).
37. S. G. Bott, M. P. Mingos, M. J. Watson, *J. Chem. Soc., Chem. Commun.*, 1192 (1989).
38. J. J. Bour, R. P. F. Kanters, P. P. J. Schlebos, J. J. Steggerda, *Recl. Trav. Chim. Pays-Bas*, 107, 211 (1988).
39. A. J. Stone, *Inorg. Chem.*, 20, 563 (1981).
40. K. P. Hall, D. M. P. Mingos, in *Progress in Inorganic Chemistry*, Vol. 32, S. J. Lippard, ed., 237, John Wiley and Sons, New York, 1984, p. 237.
41. R. P. F. Kanters, Ph.D. Thesis, University of Nijmegen, The Netherlands, 1990.

8.2.1.1. by Reduction of Au(I) Complexes

Sodium borohydride reductions of gold(I) complexes give Au clusters at RT if sodium borohydride in ethanol is dropped slowly into a suspension of the Au(I) complex in the same solvent. The immediate coloring of the reaction mixture (mostly red), even after only a few drops of the borohydride have been added, indicates fast formation of Au clusters. In view of the complicated composition of these compounds the fast formation is surprising. The use of H_2 and CO with H_2O as reducing agents in the synthesis of gold clusters has been described (see Table 1, Method A, §8.2.2.2).

To remove any metallic Au, the reaction mixture is evaporated to dryness and subsequently passed over a commercial terra infusorii column in a minimal volume of solvent. Crystallization may be performed by slow diffusion of a two-layer system. Yields are low (10–60%). The metal evaporation technique (see §8.2.1.2) gives higher yields than the sodium borohydride method.

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8.2. Formation of the Group-IB or -IIB-Group-IB or -IIB Metal Bonds 351

8.2.1. in Gold Cluster Compounds

8.2.1.3. from the Conversion of Clusters

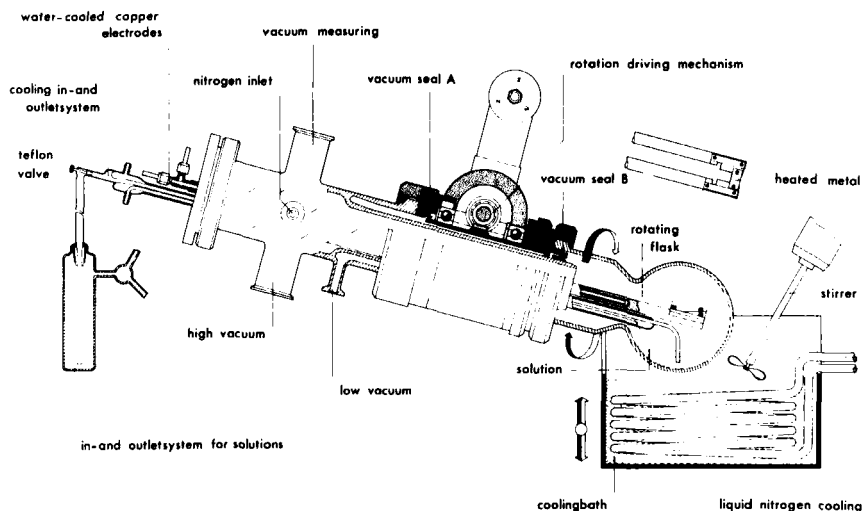


Figure 1. Rotary metal evaporator.

8.2.1.2. from Reactions of Evaporated Au with Au(I) Complexes

A rotary apparatus is used¹ for metal evaporation as shown in Fig. 1. Similar equipment is employed for the preparation of organometallics. For Au clusters, Au metal is evaporated from a resistively heated W boat onto an ethanol film, in which the reactants, e.g., $\text{Au}(\text{PAr}_3)\text{X}$ and/or PAr_3 , are dissolved (see Table 1, method B, §8.2.2.2).

For the preparation of $[\text{Au}_5(\text{PPh}_2\text{CH}_2\text{PPh}_2)_3(\text{NO}_3)_2]$ different mole ratios of $\text{Au}:\text{PPh}_2\text{CH}_2\text{PPh}_2:\text{NH}_4\text{NO}_3$ are used, all of which result in the same product.

To prepare $[\text{Au}_9(\text{PAr}_3)_8]^{3+}$ a mole ratio $\text{Au}:\text{Au}(\text{PAr}_3)_2\text{NO}_3:\text{PAr}_3 = 6:3:2$ and for $\text{Au}_{11}(\text{PAr}_3)_7\text{X}_3$ a mole ratio $\text{Au}:\text{Au}(\text{PAr}_3)\text{X}:\text{PAr}_3 = 8:3:4$ is needed; the amount of Au taken is 30% xs.

This procedure results in higher yields (60–80%) than achieved with the sodium borohydride method (10–60%). Apart from the preparation route described above, $[\text{Au}_{11}(\text{PPh}_3)_7][\text{SCN}]_3$ may be prepared through evaporation of Au onto an ethanolic solution of KSCN and PPh_3 .

The $[\text{Au}_7(\text{PPh}_3)_7]^+$ cation cluster is prepared by evaporating 4 mmol Au onto a solution of 6 mmol PPh_3 in 300 mL toluene. The yield is 20–30% (based on Au).

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8.2.1.3. from the Conversion of Clusters

This method (see Table 1, method C, §8.2.2.2) yields Au clusters in high yield; e.g. $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ as prepared by the Au evaporation or the borohydride route is an attractive starting material for the synthesis of most Au clusters. Scheme I shows the reaction pathways of $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ with electron-pair donor bases.

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8.2.1. in Gold Cluster Compounds

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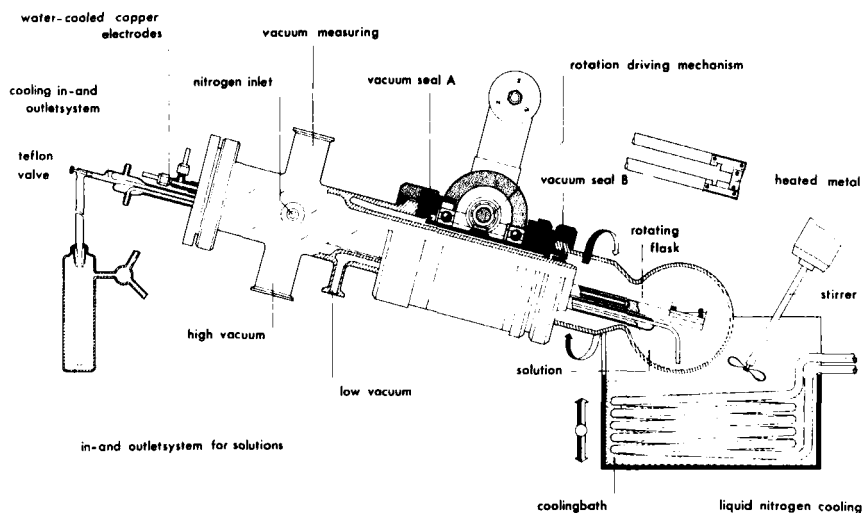


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A rotary apparatus is used¹ for metal evaporation as shown in Fig. 1. Similar equipment is employed for the preparation of organometallics. For Au clusters, Au metal is evaporated from a resistively heated W boat onto an ethanol film, in which the reactants, e.g., $\text{Au}(\text{PAR}_3)\text{X}$ and/or PAR_3 , are dissolved (see Table 1, method B, §8.2.2.2).

For the preparation of $[\text{Au}_5(\text{PPh}_2\text{CH}_2\text{PPh}_2)_3](\text{NO}_3)_2$ different mole ratios of $\text{Au} : \text{PPh}_2\text{CH}_2\text{PPh}_2 : \text{NH}_4\text{NO}_3$ are used, all of which result in the same product.

To prepare $[\text{Au}_9(\text{PAR}_3)_8]^{3+}$ a mole ratio $\text{Au} : \text{Au}(\text{PAR}_3)_2\text{NO}_3 : \text{PAR}_3 = 6 : 3 : 2$ and for $\text{Au}_{11}(\text{PAR}_3)_7\text{X}_3$ a mole ratio $\text{Au} : \text{Au}(\text{PAR}_3)\text{X} : \text{PAR}_3 = 8 : 3 : 4$ is needed; the amount of Au taken is 30% xs.

This procedure results in higher yields (60–80%) than achieved with the sodium borohydride method (10–60%). Apart from the preparation route described above, $[\text{Au}_{11}(\text{PPh}_3)_7][\text{SCN}]_3$ may be prepared through evaporation of Au onto an ethanolic solution of KSCN and PPh_3 .

The $[\text{Au}_7(\text{PPh}_3)_7]^+$ cation cluster is prepared by evaporating 4 mmol Au onto a solution of 6 mmol PPh_3 in 300 mL toluene. The yield is 20–30% (based on Au).

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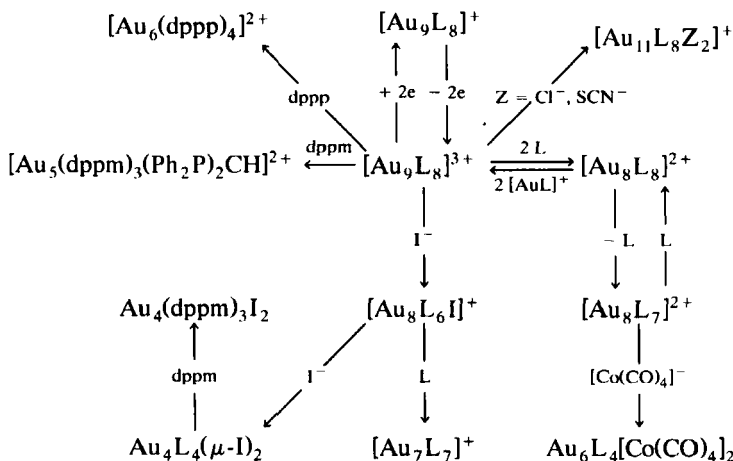
This method (see Table 1, method C, §8.2.2.2) yields Au clusters in high yield; e.g. $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ as prepared by the Au evaporation or the borohydride route is an attractive starting material for the synthesis of most Au clusters. Scheme I shows the reaction pathways of $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ with electron-pair donor bases.

TABLE 1. SURVEY OF GOLD-CLUSTER COMPOUNDS

Cluster ^a	Crystal structure	Method of preparation ^b	Refs.
[Au ₃ Ir(PPh ₃) ₅ (NO ₃)] [PF ₆]	+	A	3
Au ₃ V(PPh ₃) ₅ (CO) ₅	+	A	2
Au ₄ (PPh ₃) ₄ I ₂	+	C	4
Au ₄ (dppm) ₃ I ₂	+	C	5
[Au ₅ (dppm) ₃ (Ph ₂ P) ₂ CH] [NO ₃] ₂	+	A, B	6, 7
[Au ₆ (P(p-MeC ₆ H ₄) ₃) ₆] [B(C ₆ H ₅) ₄] ₂	+	A	8, 9
Au ₆ (PPh ₃) ₄ [Co(CO) ₄] ₂	+	C	10
[Au ₆ (dppp) ₄] [NO ₃] ₂	+	C	11
[Au ₇ (PPh ₃) ₇] ⁺	+	B	12
[Au ₈ (PPh ₃) ₈] [NO ₃] ₂	+	C	13–15
[Au ₈ (PPh ₃) ₇] [NO ₃] ₂	+	C	10, 15
[Au ₈ (PPh ₃) ₆ I] [PF ₆]	–	C	12
Au ₉ (PAr ₃) ₈ Z ₃	+	A, B, C	15, 16, 23, 28
[Au ₉ (PPh ₃) ₈] [PF ₆]	+	C	17, 32
Au ₉ [(P(p-C ₆ H ₄ OCH ₃) ₃) ₈][BF ₄] ₃	+	A	18
Au ₉ (P(C ₆ H ₁₁) ₃) ₅ [SCN] ₃	+	A	19
[Au ₉ (PPh ₃) ₆ (CN-Pr- <i>i</i>) ₂] [PF ₆] ₃	–	C	33
Au ₁₁ (PAr ₃) ₇ Z ₃	+	A, B	20–22, 23, 28
[Au ₁₁ (PPh ₃) ₈ Cl ₂] [–]	–	C	23
[Au ₁₁ (dppp) ₅] [SCN] ₃	+	C	23
[Au ₁₁ (Me ₂ PhP) ₁₀] [PF ₆] ₃	–	A	24
[Au ₁₃ (dppm) ₆] ⁿ⁺	+	A	7
[Au ₁₃ (PPhMe ₂) ₁₀ Cl ₂] [PF ₆] ₃	+	C	24
Au ₅₅ (PPh ₃) ₁₂ Cl ₆	–	A	25

^a dppm = bis(diphenylphosphino)methane; dppp = 1,3-bis(diphenylphosphino)propane; Z = [NO₃][–], [PF₆][–], [ClO₄][–], [C₆H₂(NO₂)₃O][–], [SCN][–], [CN][–], I[–], Cl[–].

^b Methods of preparation: A, reduction of Au(I) complexes; B, evaporation of Au; C, conversion of clusters.

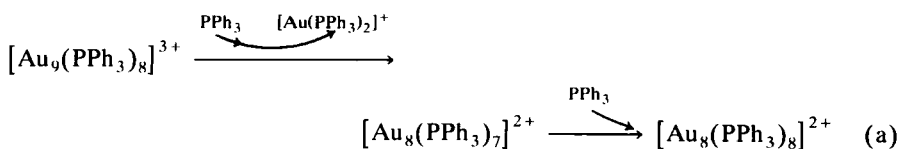


where dppm = bis(diphenylphosphino)methane, dppp = bis(1,3-diphenylphosphino)-propane.

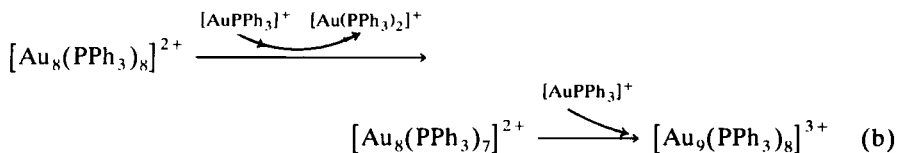
Scheme I. Reactions of [Au₉(PPh₃)₈]³⁺.

The speed of reaction of cationic Au clusters with neutral and anionic electron-pair donor bases is amazingly fast. Such reactions occur via complicated fragmentation and recombination reactions and new Au clusters are formed within minutes. Four types of reaction can be discerned (as follows), and examples of each can be found in the scheme.

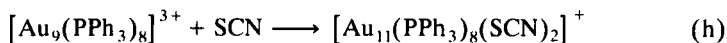
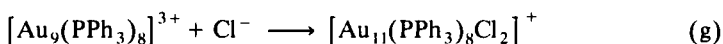
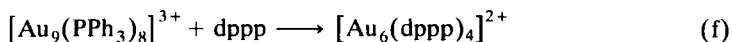
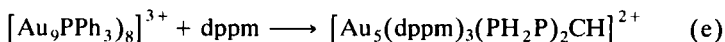
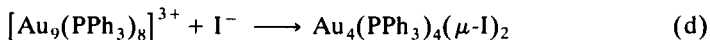
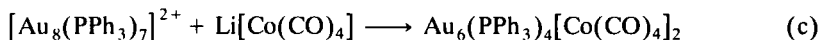
(i) **Dissociation-Association.** The reactivity of $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ is ascribed to the partial dissociation into two coordinatively unsaturated compounds, $[\text{Au}(\text{PPh}_3)]^+$ and $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$. Both react with PPh_3 ; $[\text{Au}(\text{PPh}_3)_2]^+$ is formed preferentially, but if sufficient PPh_3 is added $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$ is formed also.



The reverse reaction also is possible according to the scheme:



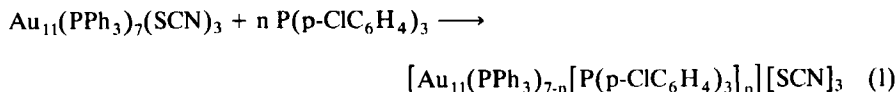
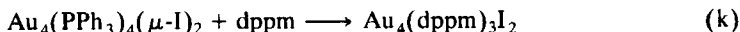
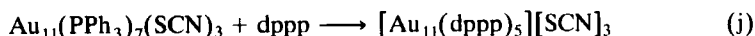
(ii) **Fragmentation-Recombination.** Complicated fragmentation and recombination reactions can occur, leading to smaller clusters, as in the reaction of a cationic Au cluster with $[\text{Co}(\text{CO})_4]^-$, iodide or bidentate phosphines, but also to larger clusters, as in the reactions of $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ with Cl^- or $[\text{SCN}]^-$ and of $[\text{Au}_{11}(\text{P}(\text{PhMe}_2))_{10}]^{3+}$ with Cl^- :



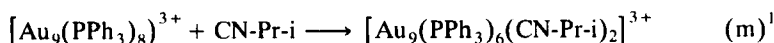
(iii) **Substitution.** Here the metal skeleton is maintained while the ligands are exchanged. Substitution of monodentate for bidentate phosphine ligands proceeds readily.

354 8.2.2. in Other Metal-Metal Bonded Dimers and Clusters of Group-IB
 8.2.2.1. Bare Metal Dimers and Clusters
 8.2.2.1.1. Metal-Vapor Cryochemistry

Substitution of monodentate phosphine ligands by other monodentate phosphines is slow:



where $n = 1-7$;



(iv) Redox. Electrochemical investigations² show that $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ in acetone undergoes two consecutive, reversible, one-electron reductions at -0.36 V and -0.40 V (vs. Ag-AgCl ref.) to form $[\text{Au}_9(\text{PPh}_3)_8]^+$. The intermediate product $[\text{Au}_9(\text{PPh}_3)_9]^{2+}$ is detected by EPR, but owing to its disproportionation into $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ and $[\text{Au}_9(\text{PPh}_3)_8]^+$, isolation of pure products is not possible.

In recent years a great number of mixed metal-gold clusters have been reported⁴⁻⁶.

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8.2.2. In Other Metal-Metal Bonded Dimers and Clusters of Group-IB Elements

8.2.2.1. Bare Metal Dimers and Clusters

8.2.2.1.1. Metal-Vapor Cryochemistry¹⁻⁷

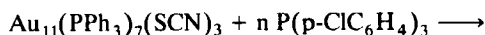
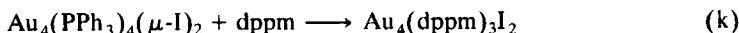
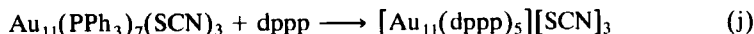
The vapor above molten Cu, Ag or Au contains predominantly atoms, but dimers are also present to ca. 0.1%. Study of these in the vapor is impeded³ by the high concentration of atomic metal. When these vaporized metals are cocondensed with an inert substance, such as Ar, CH₄, Kr, Xe at 10-12 K, a solid containing metal atoms in the inert matrix is obtained. As the proportion of metal to inert substance is

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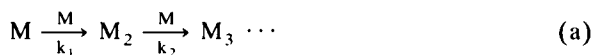
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8.2.2.1. Bare Metal Dimers and Clusters

8.2.2.1.2. Other Methods.

raised, metal dimers, trimers, etc., are formed as well as the atoms by the aggregation reaction:



Techniques of converting metal atoms in an inert matrix into small metal clusters are well developed.

Silver vapor cocondensed with matrices of H_2O or paraffin wax ($C_{22}H_{46}$) at 12 K gives mainly an atomic dispersion of Ag. However when these Ag atom matrices are warmed briefly (to 77 K for H_2O and up to 80 K for $C_{22}H_{46}$), thermal diffusion takes place with aggregation of the Ag atoms into small clusters of up to Ag_4 . These thermal aggregation methods can be used to prepare small clusters, but a mixture of metal polymers is usually obtained.

A more selective method for aggregation of metal atoms in an inert matrix is cryophotoaggregation; e.g., atomic Ag is irradiated in an Ar matrix with UV at the atomic resonance absorption of the entrapped Ag atoms, i.e., 315 nm. After ca. 1 h irradiation, the UV spectrum of the matrix shows that the concentration of atomic Ag has decreased and that new absorptions corresponding to Ag_2 and Ag_3 have appeared. Aggregates up to Ag_5 can be prepared in this way, and clusters of Cu_2 and Cu_3 in a matrix of Ar may be obtained similarly.

These methods may be used to prepare mixed metal clusters. Simultaneous codeposition of Ag and Cu vapors in Ar at 10–12 K yields a mixture including atomic Ag and Cu, dimers Ag_2 and Cu_2 , together with $AgCu$. At 77 K, $CuAg_4$ and Cu_2Ag_3 clusters occur⁶. The amount of $AgCu$ can be increased by photoexcitation with 305 nm Ag or Cu atomic radiation. The trimer $AuAgCu$ is produced⁶ when a mixture of Au, Ag and Cu vapors is condensed at 77 K.

(J. R. CHIPPERFIELD)

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8.2.2.1.2. Other Methods.

Small Ag clusters can be formed in a zeolite matrix^{1,2}. A single crystal of the Na-exchanged zeolite 4A exchanges Na^+ for Ag^+ when treated with aq $AgNO_3$ to give a black product. On dehydration at 400–425°C the black crystal changes through brick red to yellow. A bulk preparation of the same dehydrated material is dark gold. This material contains octahedral Ag_6 clusters, that are enclosed by cubes of eight Ag^+ cations. The $Ag(0)$ is produced by reduction of Ag^+ by oxide ions:

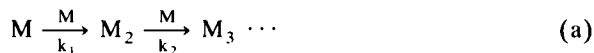


8.2.2. in Other Metal-Metal Bonded Dimers and Clusters of Group-IB 355

8.2.2.1. Bare Metal Dimers and Clusters

8.2.2.1.2. Other Methods.

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Further dehydration of the yellow crystals at 475°C leads to further reduction to silver colored product that contains Ag powder.

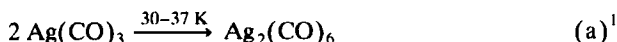
(J. R. CHIPPERFIELD)

1. Y. Kim, K. Seff, *J. Am. Chem. Soc.*, **99**, 7055 (1977).
2. L. R. Gellens, J. V. Smith, J. J. Pluth, *J. Am. Chem. Soc.*, **105**, 51 (1983); and refs. therein.

8.2.2.2. Dimers and Clusters with Nonbridging Ligands

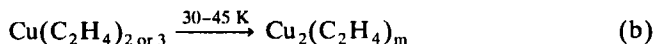
8.2.2.2.1. Syntheses from Metal Vapors.

When Ag vapor is cocondensed with CO at 10–12 K the compound $\text{Ag}(\text{CO})_3$ is formed as separate molecules in a CO matrix. When this is warmed to 30–37 K for about 1 h dimerization takes place:



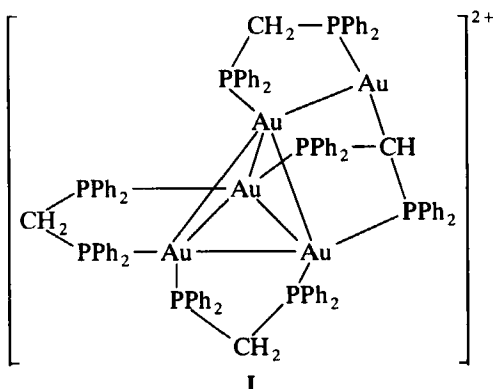
This reaction is diffusion controlled in solid CO. The binuclear carbonyl is unstable and even at these low T decomposes to Ag_2 or higher clusters. Similarly, Au forms $\text{Au}(\text{CO})_1$ or 2 , which does not dimerize. However, Cu cocondensed with CO and Ar forms compounds $\text{Cu}_n(\text{CO})$ ($n = 1-4$), which after warming to 35 K decompose to larger Cu carbonyl clusters of indeterminate composition, the IR spectra of which resemble CO chemisorbed onto bulk Cu.

Similarly, cocondensation of Cu and C_2H_4 or Cu and $\text{C}_2\text{H}_4\text{-Ar}$ at 10–12 K under conditions that favor the production of atomic Cu leads to formation of $\text{Cu}(\text{C}_2\text{H}_4)_n$ ($n = 1-3$). When this product is annealed at 30–45 K, binuclear derivatives form:



with an undefined number (m) of C_2H_4 molecules¹.

If Au atoms from heated Au react with $(\text{Ph}_2\text{P})_2\text{CH}_2$ and NH_4NO_3 in EtOH the cation $[\text{Au}_5(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_3(\text{Ph}_2\text{PCHPPh}_2)]^{2+}$ (I) is formed:



This contains both bridged and unbridged Au—Au bonds².

(J. R. CHIPPERFIELD)

356 8.2.2. in Other Metal-Metal Bonded Dimers and Clusters of Group-IB
 8.2.2.2. Dimers and Clusters with Nonbridging Ligands
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(J. R. CHIPPERFIELD)

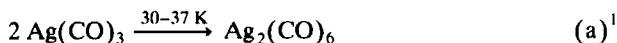
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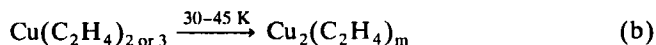
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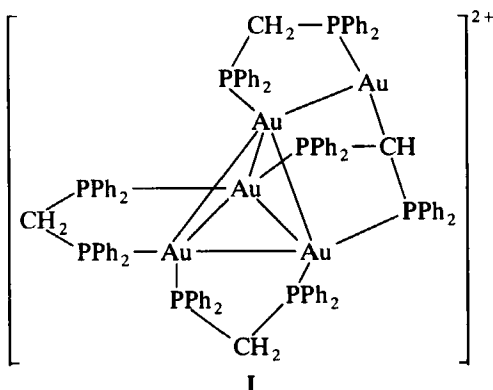
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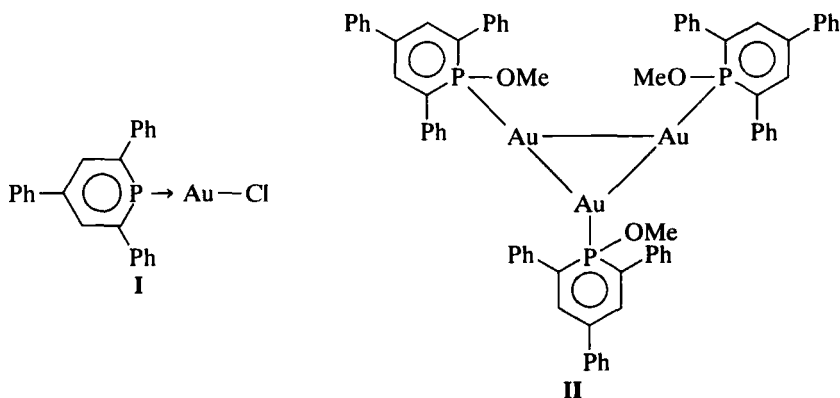
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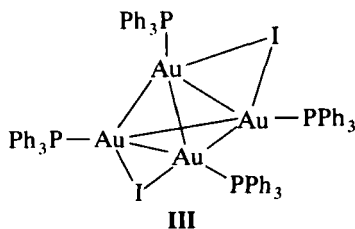
8.2.2.2.2. Other Methods.

Gold clusters can be prepared that contain species other than the Au_6 , Au_8 , Au_9 and Au_{11} described in §8.2.1. There is little strategic method in the synthesis, products often arising by chance.

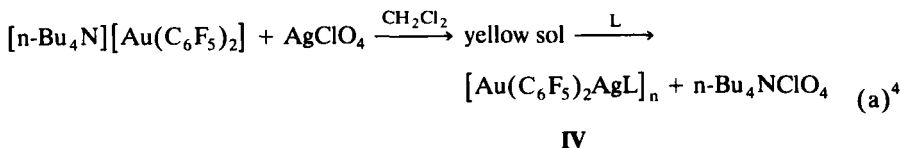
When the heterocyclic phosphine complex of Au (I) is treated with NaOMe in $\text{MeOH}-\text{C}_6\text{H}_6$ for 15 min, the trinuclear Au complex (II) is formed¹.



One Au cluster can be converted to another. Addition of Et_4NCl to a solution of the Au_{11} cation $[\text{Au}_{11}(\text{PPhMe}_2)_{10}]^{3+}$ gives high yields of a Au_{13} cation that can be obtained as $[\text{Au}_{13}(\text{PPhMe}_2)_{10}\text{Cl}_2][\text{PF}_6]_3$ in the presence² of NH_4PF_6 . Moreover, $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$ reacts with KI in acetone to give the pale yellow cluster $\text{Au}_4(\mu\text{-I})_2(\text{PPh}_3)_4$ in 15% yield; its structure (III) contains bridged and unbridged $\text{Au}-\text{Au}$ bonds³.



A polymer containing both $\text{Au}-\text{Ag}$ and $\text{Au}-\text{Au}$ bonds can be prepared by:



8.2.2. in Other Metal-Metal Bonded Dimers and Clusters of Group-IB 357

8.2.2.2. Dimers and Clusters with Nonbridging Ligands

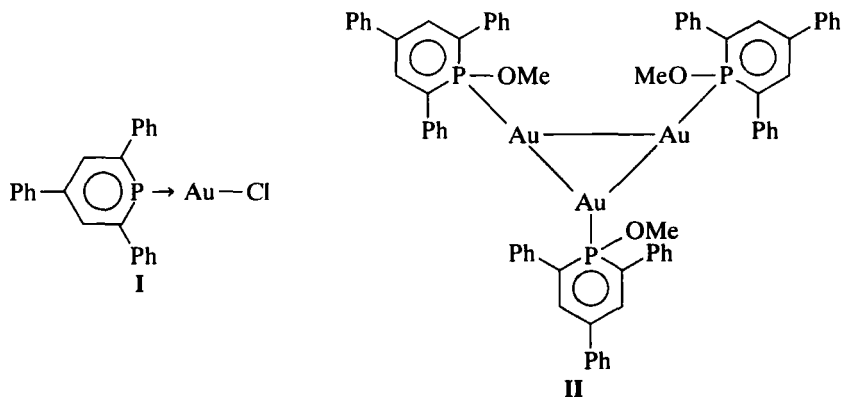
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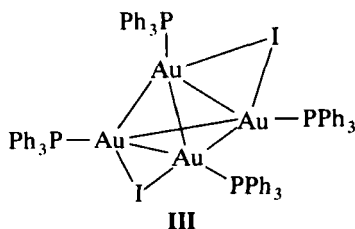
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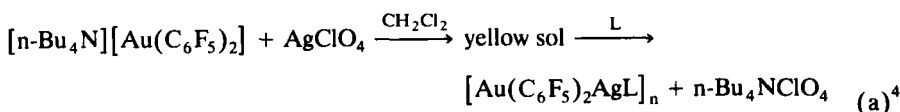
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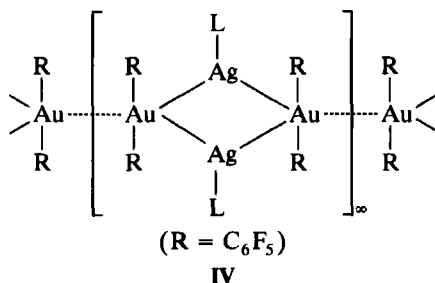
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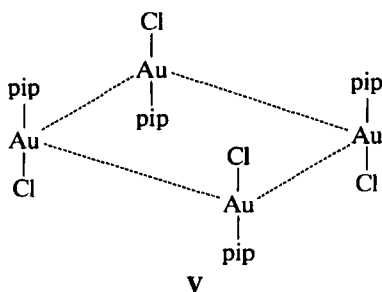
A polymer containing both Au—Ag and Au—Au bonds can be prepared by:



The product (IV) is precipitated on addition of L (L = THT, py, pyridine N-oxide or PPh₂Me). The yellow-orange compounds (IV) contain four-membered rings bonded by Au—Au bonds of length 288.9 pm; the Au—Ag bonds are 272 pm long.



A by-product of the reaction of Cl(Me₂S)Au(I) with excess piperidine (pip) is the tetramer⁵ [pipAuCl]₄ (V):



The Au(I)—Au(I) distance of 330.1 pm is longer than in metallic Au (288 pm), and in view of the d¹⁰ configuration in Au(I) compounds, such structures as V arise by packing factors in the solid rather than by metal-metal bonding (see §8.2.2.3). Similarly long Au—Au bonds are found in other Au(I) compounds^{6,7} and in mixed Au(I)—Au(III) compounds⁸. Many other cluster compounds are known⁹.

(J. R. CHIPPERFIELD)

1. H. Kanter, K. Dimroth, *Tetrahedron Lett.*, 545 (1975).
2. C. E. Briant, B. R. C. Theobald, J. W. White, L. K. Bell, D. M. P. Mingos, A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 201 (1981).
3. F. Demartin, M. Manassero, L. Naldini, R. Ruggeri, M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 222 (1981).
4. R. Uson, A. Laguna, M. Laguna, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1097 (1981).
5. J. J. Guy, P. G. Jones, M. J. Mays, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 8 (1977).
6. R. J. Puddephatt, *The Chemistry of Gold*, Elsevier, Amsterdam, 1978, p. 157.
7. M. K. Cooper, K. Hendrick, M. McPartlin, J. L. Latten, *Inorg. Chim. Acta*, 65, L185 (1982).
8. L. S. Hollis, S. L. Lippard, *J. Am. Chem. Soc.*, 105, 4293 (1983).
9. K. P. Hall, D. M. P. Mingos, *Prog. Inorg. Chem.*, 32, 237 (1984).

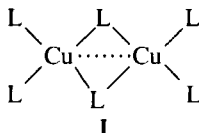
8.2.2. in Other Metal-Metal Bonded Dimers and Clusters of Group-IB 359
 8.2.2.3. Dimers and Clusters with Bridging Ligands
 8.2.2.3.2. Compounds of Silver.

8.2.2.3. Dimers and Clusters with Bridging Ligands

8.2.2.3.1. Compounds of Copper.

Many Cu(I) compounds have polymeric structures with weak Cu—Cu bonds that are bridged by atoms or groups. These include Cu(I) carboxylates, alkyls and aryls, alkoxides and $(\text{CuXL})_n$ complexes (X = halide, L = ligand). In Cu(I) compounds Cu has a filled 3d shell, $3d^{10}$, that does not participate in metal-metal bonding, so the extent of metal-metal bonding in these compounds is questionable. Calculations show that the metal-metal bonding is at best weak¹⁻³. These compounds arise from the same syntheses as would be used to prepare the monomer, and so they are not considered further here.

Similarly, Cu(II) carboxylates^{4,5} have bridged structures with an uncertain amount of metal-metal bonding, and many Cu(II) complexes, such as I, are prepared by the reaction of the ligand with Cu^{2+} for investigations of the extent of metal-metal bonding⁶.



However, it is difficult to separate direct Cu—Cu interactions from Cu—Cu interactions taking place through the bridging ligand atoms.

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3. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, 1988, p. 793.
4. M. Melnik, *Coord. Chem. Rev.*, **36**, 1 (1981).
5. J. Catterick, P. Thornton, *Adv. Inorg. Chem. Radiochem.*, **20**, 291 (1977).
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8.2.2.3.2. Compounds of Silver.

Alkyl, aryl and thiolate derivatives of Ag(I) have bridged Ag—Ag bonds of uncertain strength. These, like the Cu(I) derivatives (see §8.2.2.3.1), are best described as aggregates, rather than compounds containing metal-metal bonds^{1,2}.

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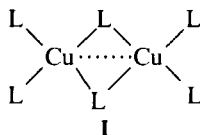
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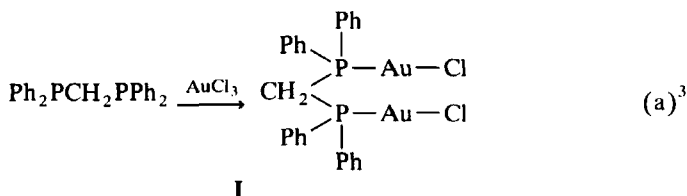
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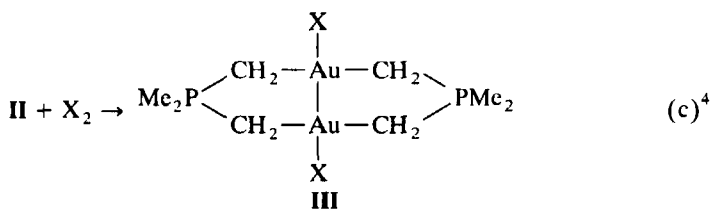
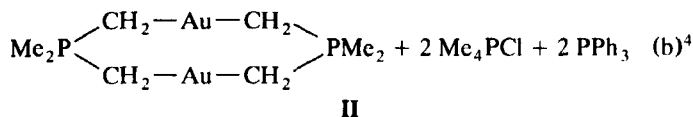
360 8.2.2. in Other Metal-Metal Bonded Dimers and Clusters of Group-IB
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8.2.2.3.3. Compounds of Gold.

The dithiocarbamate complex of Au(I), $[\text{AuS}_2\text{CNPr}_2]_2$, is dimeric with a short bridged Au—Au bond, but as in the Cu(I) and Ag(I) compounds (see §8.2.2.3.1) and (8.3.2.3.2), the extent of Au—Au bonding is not clear^{1,2}. Similarly, in such compounds as **I**, which is prepared by the reaction:



there is little direct Au(I)—Au(I) bonding. Bridged Au—Au bonds are present in Au(II) compounds⁴⁻⁶ such as **III**, which are prepared by the reactions:



where $\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2$. Whereas **II**, a Au(I) derivative, does not contain a Au—Au bond, **III**, which has a Au—Au distance of 260 pm ($\text{X} = \text{Cl}$), has a metal-metal bond. Reaction of **II** with MeI gives a compound analogous to **III** containing a Au—Au bond, with one Au bonded to Me and the other to I.

(J. R. CHIPPERFIELD)

1. F. J. Farrell, T. G. Spiro, *Inorg. Chem.*, **10**, 1606 (1971).
2. H. Schmidbaur, K. C. Dash, *Adv. Inorg. Chem. Radiochem.*, **25**, 239 (1982).
3. H. Schmidbaur, A. Wohlleben, F. Wagner, O. Orama, G. Huttner, *Chem. Ber.*, **110**, 1748 (1977).
4. H. Schmidbaur, *Acc. Chem. Res.*, **8**, 62 (1975).
5. D. C. Calabro, B. A. Harrison, G. T. Palmer, M. K. Moguel, R. L. Rebert, J. L. Burmeister, *Inorg. Chem.*, **20**, 4311 (1981).
6. See *Gmelin Handbook of Inorganic Chemistry, Au. Organogold Compounds*, Springer-Verlag, Berlin, 1980, p. 260, for a good review of these compounds.

8.2. Formation of the Group-IB or -IIB-Group-IB or -IIB Metal Bonds	361
8.2.3. In Univalent Compounds of Zinc and Cadmium	
8.2.3.2. Univalent Compounds of Cadmium	

8.2.3. In Univalent Compounds of Zinc and Cadmium

8.2.3.1. Univalent Compounds of Zinc

Univalent Zn(I) compounds are not formed because they are unstable with respect to disproportionation to Zn(II) and Zn(0):



If enthalpies alone are considered, the only compound of the oxide and halides of Zn(I) that should be stable is ZnI, but entropy prevents this being isolated¹.

At 570 K Zn metal is involatile, but at this T it sublimes into a vapor of Zn dichloride. The sublimate analyzes² as ca. ZnCl. With similar experiments involving the vapors of ZnBr₂ and ZnI₂, Zn metal also sublimes, but analysis of the sublimates shows only ca. 20% of ZnBr from Zn + ZnBr₂ and 10% of ZnI from Zn + ZnI₂. The monohalides may form at 570 K, but they disproportionate on cooling, in agreement with the known formation of halides³ ZnX at high T.

The solubilities of Zn in ZnCl₂ at 500–700°C are⁴ ca. 0.78–1.97 mol%. On rapid cooling of these solutions a stable yellow glass is obtained. The glass is diamagnetic (showing absence of Zn⁺) and is soluble in saturated aq ZnCl₂, MeOH, Me₂CO, AcOEt and Et₂O. The visible, UV and ESR spectra of the yellow glass are consistent with the presence of Zn₂²⁺, and a band at 175 cm⁻¹ in the Raman spectrum is attributed to Zn₂²⁺. Metallic Zn precipitates from an ether solution of the yellow glass after 5–10 min.

No compound containing the Zn₂²⁺ species is isolated, and there is no evidence for other polynuclear cations, such as Zn₃²⁺, analogous to those found for Cd and Hg.

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4. D. H. Kerridge, S. A. Tariq, *J. Chem. Soc., A*, 1122 (1967).

8.2.3.2. Univalent Compounds of Cadmium

The vapor above mixtures of Cd and CdCl₂ contains¹ Cd(I) as CdCl. Solutions of Cd in anhyd Cd(II) salts² are deep red-black and diamagnetic, which implies an absence of Cd⁺ ions. At 600°C the solubility of Cd in the molten halides drops from 18 and 14 mol% for CdCl₂ and CdBr₂, respectively, to 1.5 mol% for CdI₂. The equilibrium:



lies well to the left, because halide ions coordinate better to Cd²⁺ than to Cd₂²⁺. If AlCl₃ is added to Cd in CdCl₂, the anion [AlCl₄]⁻ is formed and the solubility of Cd increases. The lattice energies of Cd²⁺ and Cd₂²⁺ salts with this anion should be more similar than those with Cl⁻, and in the ternary system Cd–CdCl₂–AlCl₃ a new

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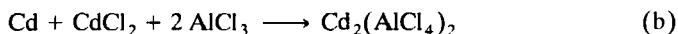
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phase with the composition CdAlCl_4 appears³. Complete reduction of Cd(II) to Cd(I) does not take place, however. Refluxing the cooled mixture with benzene gives a crystalline deposit from which crystals of $\text{Cd}_2(\text{AlCl}_4)_2$ can be hand picked:



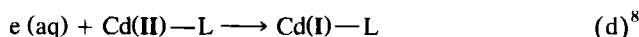
Slow cooling of a twofold excess of Cd with $\text{Cd}(\text{AlCl}_4)_2$ from 340°C to RT gives the same product⁴. In spite of spectroscopic evidence⁵ for Cd_2^{2+} in solutions of Cd in CdCl_2 and AlCl_3 , there are no other isolatable derivatives of Cd_2^{2+} .

Low concentrations of Cd(I) species can be obtained by allowing Cd vapor to react with Cd^{2+} and trapping the resultant Cd(I) species in a zeolite⁶. When Cd^{2+} -exchanged zeolite A is exposed to Cd metal vapor at 350°C for 2.5 d, both Cd^+ and Cd_2^{2+} are formed, the latter having a Cd-Cd internuclear distance of 235 pm.

Solutions of Cd(II) compounds can be reduced to Cd(I) by hydrated electrons formed by pulse radiolysis:



These solutions of Cd^+ are powerful reducing agents, and after tens of microseconds all Cd^+ has disappeared. If Cd^{2+} complexes of such ligands as glycine, en, EDTA and NTA are subjected to pulse radiolysis, the Cd^+ produced is present as a complex:

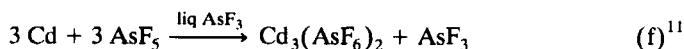


Exposure of frozen solutions of CdSO_4 in H_2SO_4 to γ rays at 77 K results in the formation of a species with ESR and UV spectra consistent with Cd^+ . When annealed at 120 K the Cd^+ reacts with xs Cd^{2+} :

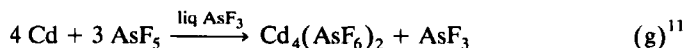


Similar reactions take place in frozen solutions of $\text{Cd}(\text{ClO}_4)_2$ in⁹ MeOH and EtOH, and in¹⁰ the γ irradiation of solid $\text{K}_2\text{Cd}(\text{CN})_4$.

Attempts to prepare $\text{Cd}_2(\text{AsF}_6)_2$ and $\text{Cd}_2(\text{SbF}_6)_2$ by reacting Cd with the corresponding pentafluoride in liq SO_2 yield only Cd(II) products, unlike the analogous reaction¹¹ of Hg. More successful is the use of AsF_3 as a solvent. When Cd is oxidized with AsF_5 in liq AsF_3 the expected product of $\text{Cd}_2(\text{AsF}_6)_2$ is not formed, but a derivative of Cd_3^{2+} is obtained quantitatively:



The first product slowly reacts with atmospheric moisture to give an unidentified white product and Cd metal. At low $\text{AsF}_5 : \text{Cd}$ ratios a brown product, $\text{Cd}_4(\text{AsF}_6)_2$, is formed:



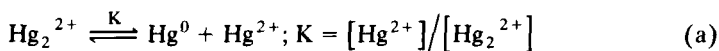
which is a derivative of the polyatomic cation, Cd_4^{2+} . Neither Cd_3^{2+} nor Cd_4^{2+} has been characterized as well as have the corresponding polyatomic cations of Hg.

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5. J. D. Corbett, *Inorg. Chem.*, **1**, 700 (1962).
6. L. B. McCusker, K. Seff, *J. Am. Chem. Soc.*, **101**, 5235 (1979).
7. D. Meyerstein, W. A. Mulac, *J. Phys. Chem.*, **72**, 784 (1968).
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8.2.4. in Mercury(I) Compounds from Mercury(II) Compounds

The range of stable Hg(I) compounds that can be formed in solution is limited by the tendency of Hg(I) to disproportionate:



The equilibrium constant K has a value in H_2O of about 10^{-2} at RT. Although Hg_2^{2+} ions are therefore stable when alone in H_2O , any factor that causes a reduction in the equilibrium concentration of Hg^{2+} relative to that of Hg_2^{2+} forces the disproportionation in favor of the disproportionation products. There are three ways in which the concentration of Hg^{2+} may be so lowered. First, many Hg(II) compounds are almost completely insoluble. Therefore, attempts to prepare Hg_2S_2 by treating Hg_2^{2+} with S^{2-} give a mixture of Hg and insoluble HgS rather than Hg_2S_2 . Second, some Hg(II) derivatives, although soluble, are only slightly dissociated into ions. Therefore, attempts to prepare $\text{Hg}_2(\text{CN})_2$ by the action of $[\text{CN}]^-$ on Hg_2^{2+} give Hg and undissociated $\text{Hg}(\text{CN})_2$. Third, many Hg(II) complexes are more stable than the Hg(I) complex of the same ligand. Therefore, the action of many amines on Hg_2^{2+} is to give Hg and an Hg(II)-amine complex rather than the Hg(I)-amine complex. These three factors greatly reduce the number of Hg(I) compounds that can be made from soluble Hg(I) compounds. In preparations starting from Hg(I) compounds solutions must not be allowed to become alkaline, as $[\text{OH}]^-$ ions cause the disproportionation of Hg_2^{2+} to give Hg and the insoluble red-yellow HgO .

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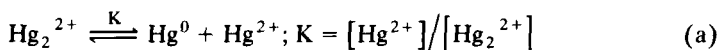
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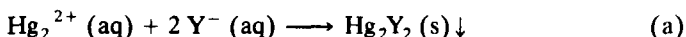
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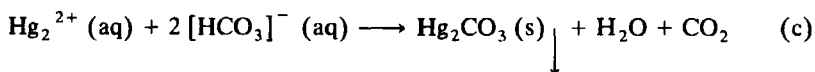
364 8.2. Formation of the Group-IB or -IIB-Group-IB or -IIB Metal Bonds
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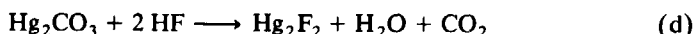
The two most soluble (in H_2O) compounds of Hg(I) are $\text{Hg}_2(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ and $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4 \text{H}_2\text{O}$, and these are used as sources of aq Hg_2^{2+} ions for the preparation of less soluble Hg(I) compounds. They are both made by redox reactions involving Hg(0) and Hg(II) . Solutions of these two salts do not disproportionate because the anions $[\text{NO}_3]^-$ and $[\text{ClO}_4]^-$ are poor complexing ligands and form only weak complexes with Hg(II) . Sparingly soluble Hg(I) derivatives can be formed by addition of a soluble salt of a univalent anion, Y^- , or divalent anion, Y^{2-} , to an aq soln of $\text{Hg}_2(\text{NO}_3)_2$ or $\text{Hg}_2(\text{ClO}_4)_2$:



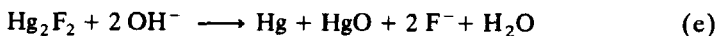
The trivalent $[\text{PO}_4]^{3-}$ and $[\text{AsO}_4]^{3-}$ ions react similarly. Examples of anions that give insoluble Hg(I) compounds in this way include halides, pseudohalides, halates, carboxylates and sulfate. A trace of HNO_3 or HClO_4 is often added to the solution of the Hg(I) nitrate or perchlorate to prevent disproportionation induced by alkali. Table 1 lists common Hg(I) derivatives prepared in this way and includes values of the solubility products of the sparingly soluble Hg(I) compounds where these are measured. A similar reaction is used to prepare Hg_2CO_3 from a soluble bicarbonate:



The fluoride Hg_2F_2 can be made from Hg_2CO_3 by reaction with 40% HF :



The solid can be isolated⁶ by evaporation of the H_2O and HF . This compound is not stable in H_2O and quickly disproportionates when acid is not present:



There are a number of Hg(I) compounds that can be made by reacting Hg_2CO_3 or $\text{Hg}_2(\text{NO}_3)_2$ with compounds containing acidic NH groups. Instead of complexes (see §8.2.5.2.3), simple Hg(I) compounds are formed. For example, Hg_2CO_3 reacts with the amide derivatives $\text{NH}(\text{SO}_2\text{F})\text{R}$ in benzene:



where⁷ $\text{R} = \text{SO}_2\text{F}$, CO_2Et , CO_2Me and CONEt_2 . A similar compound, **I**, is formed by the imide (**II**):

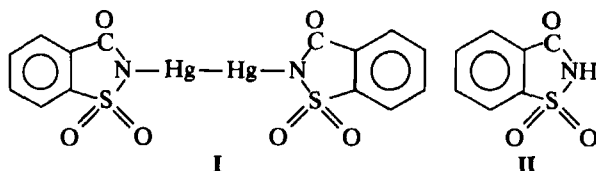
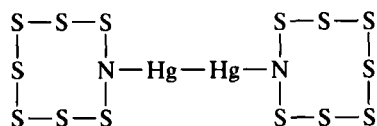


TABLE I. MERCURY(I) DERIVATIVES FORMED FROM Aq Hg_2^{2+} AND ANIONS

Compound	Solubility product ^a	Refs.
Hg_2Cl_2	- 17.9	1
Hg_2Br_2	- 22.2	1
Hg_2I_2	- 28.3	1
$\text{Hg}_2(\text{CNO})_2$		3
$\text{Hg}_2(\text{SCN})_2$	- 19.5	1, 2
$\text{Hg}_2(\text{N}_3)_2$	- 9.2	1
$\text{Hg}_2(\text{BrO}_3)_2$		2
$\text{Hg}_2(\text{IO}_3)_2$	- 17.9	1
Hg_2CO_3	- 16.1	1, 5
Hg_2SO_4	- 6.1	1, 2
Hg_2SeO_4		2
Hg_2CrO_4	- 8.7	1
$\text{Hg}_2(\text{VO}_3)_2$		4
$(\text{Hg}_2)_3(\text{PO}_4)_2$	- 12.4	1
$(\text{Hg}_2)_3(\text{AsO}_4)_2$		4
$\text{Hg}_2(\text{BF}_4)_2$		5
$\text{Hg}_2(\text{OAc})_2$		2
$\text{Hg}_2(\text{EtCO}_2)_2$		2
$\text{Hg}_2(\text{PrCO}_2)_2$		2
$\text{Hg}_2(\text{o-O}_2\text{CC}_6\text{H}_4\text{CO}_2)$		2
$\text{Hg}_2(\text{ClCH}_2\text{CO}_2)_2$		2
$\text{Hg}_2(\text{Cl}_2\text{CHCO}_2)_2$		2
$\text{Hg}_2(\text{CCl}_3\text{CO}_2)_2$		2
$\text{Hg}_2[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]_2$		4

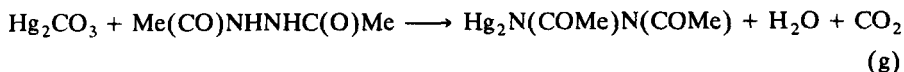
^a Log K for the equilibrium between the solid and Hg_2^{2+} and anions.

and reaction of S_7NH with $\text{Hg}_2(\text{NO}_3)_2$ in DMF yields⁸ a similar product (III):

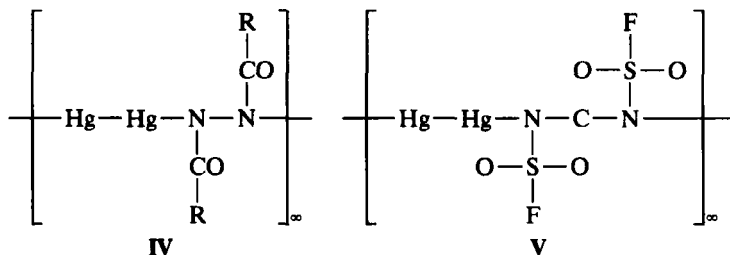


III

Organic compounds that have two or more acidic NH groups give rise to Hg(I) derivatives that are chain polymers. N,N' -Diacetylhydrazine reacts with Hg_2CO_3 in slightly acidic H_2O :



to form a product that has the chain structure⁹ IV (R = Me):



Other hydrazine derivatives, RC(O)NHNHC(O)R , react similarly in benzene (R = CF_3 , CCl_3) and $(\text{FSO}_2)\text{NH}\cdot\text{CO}\cdot\text{NH}(\text{SO}_2\text{F})$ reacts with Hg_2CO_3 in benzene to give V⁷. Tetrasulfurtetranitridetetrahydride, $\text{S}_4\text{N}_4\text{H}_4$, has four NH groups that react with $\text{Hg}_2(\text{NO}_3)_2$ in DMF at -70°C to give a polymer with the empirical formula⁸ $(\text{HgSN})_x$.

Sulfonyl and acyl cyanamides, $\text{HL} = \text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NHCN}$, $\text{C}_5\text{H}_4\text{N}\cdot\text{SO}_2\text{NHCN}$ and $\text{C}_5\text{H}_4\text{N}\cdot\text{CONHCN}$, react with $\text{Hg}_2(\text{NO}_3)_2$ in H_2O to precipitate Hg_2L_2 . Under similar conditions, however, $\text{NH}_2\text{C}_6\text{H}_4\text{C(O)NHCN}$ gives a precipitate of Hg_2LNO_3 that has a chain structure¹⁰ (see §8.2.5.2.3).

The two sulfonic acids, pyridine-3-sulfonic and sulfanilic (HL), react to form the Hg(I) compounds Hg_2L_2 with $\text{Hg}_2(\text{NO}_3)_2$ in H_2O . In these derivatives in Hg atoms are bonded¹¹ to nitrogen atoms in L.

An acetylide of Hg(I), $\text{Hg}_2\text{C}_2\cdot\text{H}_2\text{O}$, is formed when acetylene is passed through a suspension of $\text{Hg}_2(\text{OAc})_2$ in H_2O for 30 h in the dark. The white acetylide precipitates but decomposes on attempted drying under gentle heat¹². Compounds Hg_2XA and $\text{Hg}_2\text{XX}'$ (X, X' = halogen, A = $[\text{ClO}_4]^-$, $[\text{HSO}_4]^-$) can be made from mixtures of Hg_2X_2 and Hg_2A_2 or Hg_2X_2 and $\text{Hg}_2\text{X}'_2$ under controlled conditions¹³.

(J. R. CHIPPERFIELD)

1. R. M. Smith, A. E. Martell, *Critical Stability Constants*, Vols. 2-4, Plenum Press, New York, 1975-1977; these give references to the original literature.
2. E. Dorm, B. Lindh, *Acta Chem. Scand.*, 21, 1661 (1967).
3. E. Söderbäck, *Acta Chem. Scand.*, 11, 1622 (1957).
4. D. T. Burns, A. Townshend, A. H. Carter, *Inorganic Reaction Chemistry*, Vol. 2, *Reactions of the Elements and Their Compounds, Part A: Alkali Metals to Nitrogen*, Ellis Horwood, Chichester, 1981, p. 243.
5. O. G. Sheintsis, *J. Appl. Chem. USSR*, 13, 1101 (1940); *Chem. Abstr.*, 35, 2087 (1941).
6. G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Vol. 1, 2nd ed., Academic Press, New York, 1963, p. 243.
7. D. Breiting, K. Brodersen, J. Limmer, *Chem. Ber.*, 103, 2388 (1970).
8. M. Goehring, G. Zirker, *Z. Anorg. Allg. Chem.*, 285, 70 (1956).
9. K. Brodersen, L. Kunkel, *Chem. Ber.*, 91, 2698 (1958).
10. K. Brodersen, R. Dölling, *Z. Anorg. Allg. Chem.*, 475, 67 (1981).
11. K. Brodersen, R. Dölling, G. Liehr, *Z. Anorg. Allg. Chem.*, 464, 17 (1980).
12. W. A. Frad, *Adv. Inorg. Chem. Radiochem.*, 11, 207 (1968).
13. K. Brodersen, J. Hoffmann, *Z. Anorg. Allg. Chem.*, 482, 226 (1981).

8.2.4. in Mercury(I) Compounds from Mercury(II) Compounds 367

8.2.4.2. Complexes of Mercury(I)

8.2.4.2.1. Complexes of Mercury(I) with Oxygen-Donor Ligands.

8.2.4.2. Complexes of Mercury(I)

Ligands that reduce the activity of Hg(II) more than that of Hg(I) lead to disproportionation products when added to a solution containing Hg_2^{2+} ions. Because the smaller Hg^{2+} ion is a better electron-pair acceptor acid than the larger Hg_2^{2+} ion, the number of Hg(I) complexes may be limited, but many complexes of Hg(I) are formed by reactions of Hg_2^{2+} with ligands containing donor atoms from groups VB and VIB. Polyethers and polyesters are good solvents for these reactions¹.

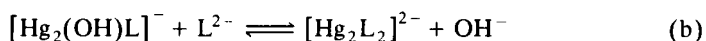
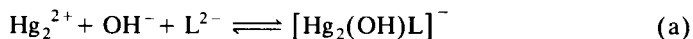
(J. R. CHIPPERFIELD)

1. K. Brodersen, H.-U. Hummel, in *Comprehensive Coordination Chemistry*, Vol. 5, G. Wilkinson, R. D. Gillard, J. A. McLeverty, eds., Pergamon Press, Oxford, 1987, p. 1047.
2. K. Brodersen, J. Hoffmann, R. Erdmann, *Z. Anorg. Allg. Chem.*, **482**, 217 (1981).

8.2.4.2.1. Complexes of Mercury(I) with Oxygen-Donor Ligands.

Oxygen-donor ligands that form alkaline solutions can lead to disproportionation products when added to a Hg(I) salt solution. There must be sufficient H^+ present to prevent this.

In aq soln $\text{Hg}_2(\text{NO}_3)_2$ reacts with $\text{Na}_4\text{P}_2\text{O}_7$ (Na_4L) to form complex ions with the formulas¹ $[\text{Hg}_2(\text{OH})\text{L}]^{3-}$ and $[\text{Hg}_2\text{L}_2]^{6-}$. The tripolyphosphate $[\text{P}_3\text{O}_{10}]^{5-}$ and tetrapolyphosphate $[\text{P}_4\text{O}_{13}]^{7-}$ ions² form similar complex ions. The stability of these complex phosphates decreases as the chain length increases². The dicarboxylic acids oxalic, dimethylmalonic and succinic, H_2L , form complexes with Hg_2^{2+} ions¹:



The formation constants and conditions are shown in Table 1. The complexes formed

TABLE 1. COMPLEXES FORMED BY Hg_2^{2+} IN H_2O

Ligand (L)	Formation constants ^a		pH ^d
	$\log_{10} K^b$	$\log_{10} K^c$	
$[\text{SO}_4]^{2-}$	3.54	1.3 ^c	-1
$[\text{P}_2\text{O}_7]^{4-}$	15.64	12.38	7.5-9.6
$[\text{P}_3\text{O}_{10}]^{5-}$	11.23	15.0	7.2-9.0
$[\text{P}_4\text{O}_{13}]^{6-}$	15.26	9.88	6.0-8.6
$[\text{C}_2\text{O}_4]^{2-}$	13.04	6.98	5.1-7.6
$[\text{O}_2\text{CCMe}_2\text{CO}_2]^{2-}$	13.58	7.52	4.9-6.3
$[\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2]^{2-}$	13.45	7.28	7.0-7.7
$[\text{o-O}_2\text{CC}_6\text{H}_4\text{CO}_2]^{2-}$	4.9 ^c	—	2.4-4.7
$[\text{HN}(\text{CH}_2\text{CO}_2)_2]^{2-}$	10.81 ^c	—	1.3-1.9
PhNH_2	3.71 ^c	—	≈ 2.8

^a From Refs. 11 and 12 at ea. 25°C.^b For reaction: $\text{Hg}_2^{2+} + 2 \text{L} \rightleftharpoons [\text{Hg}_2\text{L}_2]^{2+}$ except where indicated.^c For reaction: $\text{Hg}_2^{2+} + \text{OH}^- + \text{L} \rightleftharpoons [\text{Hg}_2(\text{OH})\text{L}]^+$.^d Range of pH over which K is measured.^e For reaction: $\text{Hg}_2^{2+} + \text{L} \rightleftharpoons [\text{Hg}_2\text{L}]^{2+}$.

8.2.4. in Mercury(I) Compounds from Mercury(II) Compounds 367

8.2.4.2. Complexes of Mercury(I)

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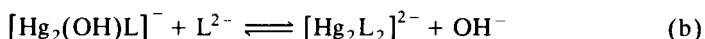
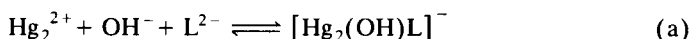
(J. R. CHIPPERFIELD)

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2. K. Brodersen, J. Hoffmann, R. Erdmann, *Z. Anorg. Allg. Chem.*, **482**, 217 (1981).

8.2.4.2.1. Complexes of Mercury(I) with Oxygen-Donor Ligands.

Oxygen-donor ligands that form alkaline solutions can lead to disproportionation products when added to a Hg(I) salt solution. There must be sufficient H^+ present to prevent this.

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The formation constants and conditions are shown in Table 1. The complexes formed

TABLE 1. COMPLEXES FORMED BY Hg_2^{2+} IN H_2O

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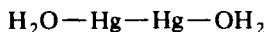
^c For reaction: $\text{Hg}_2^{2+} + \text{OH}^- + \text{L} \rightleftharpoons [\text{Hg}_2(\text{OH})\text{L}]^+$.

^d Range of pH over which K is measured.

^e For reaction: $\text{Hg}_2^{2+} + \text{L} \rightleftharpoons [\text{Hg}_2\text{L}]^{2+}$.

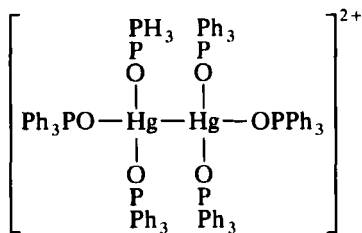
by the dicarboxylic acids are less stable than those formed by the polyphosphates, and high concentrations of the ligand are needed to keep them in solution.

Complexes with oxygen-donor ligands can be isolated as solids. The hydrated salts, $\text{Hg}_2(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ ³ and $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4 \text{H}_2\text{O}$ ⁴, both contain the aquo complex ion **I**:



I

Pyridine-1-oxide reacts with $\text{Hg}_2(\text{ClO}_4)_2$ in MeOH to form $\text{Hg}_2(\text{C}_5\text{H}_5\text{NO})_4(\text{ClO}_4)_2$ (**II**), which crystallizes from the solution^{5,6}. Similarly the same ligand with Hg_2SiF_6 yields⁵ $\text{Hg}_2\text{SiF}_6 \cdot 5 \text{C}_5\text{H}_5\text{NO}$. In a similar way^{5,7} the ligand Ph_3PO forms the complexes $\text{Hg}_2(\text{Ph}_3\text{PO})_4(\text{ClO}_4)_2$, $\text{Hg}_2(\text{Ph}_3\text{PO})_6(\text{ClO}_4)_2$, which contain the cation **III** and $\text{Hg}_2\text{SiF}_6 \cdot 5 \text{Ph}_3\text{PO}$:



III

In **II** and **III** the Hg coordination is different from that shown (2 or 3 coordination) in complexes of **Hg(I)** with N-donor ligands (see §8.2.4.2.3). In **II**, three of the four pyridine-1-oxide molecules bridge adjacent Hg—Hg units, giving the Hg atom a coordination number of 4 or 5, whereas in **III** there are 4-coordinated Hg atoms. Attempts to prepare analogous complexes with Ph_3AsO lead to disproportionation products⁵.

Some common oxygen-containing solvents give isolatable **Hg(I)** complexes. For example, both diglyme and 1,4-dioxane form $\text{Hg}_2(\text{solvent})_2(\text{NO}_3)_2$ complexes⁸. The diglyme complex forms when $\text{Hg}_2(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ is dissolved in diglyme containing a little $\text{CH}(\text{OEt})_3$ to remove H_2O . The dioxane complex forms in MeOH.

Complexes can be formed by DMSO; e.g., $\text{Hg}_2(\text{DMSO})_3(\text{ClO}_4)_2$ forms when $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4 \text{H}_2\text{O}$ is mixed with DMSO in MeOH and crystallizes^{5,9} at 5°C. Similarly, $\text{Hg}_2(\text{DMSO})\text{SiF}_6 \cdot x \text{H}_2\text{O}$ is formed⁹ with Hg_2SiF_6 , and $\text{Hg}_2(\text{DMSO})_2(\text{CF}_3\text{SO}_3)_2$ can be isolated¹⁰ from $\text{Hg}_2(\text{CF}_3\text{SO}_3)_2$ in MeOH containing a little DMSO. Excess DMSO leads to disproportionation. Two sulfoxides similar to DMSO, Ph_2SO and $n\text{-Pr}_2\text{SO}$, react in MeOH with $\text{Hg}_2(\text{ClO}_4)_2$ to give the complexes $\text{Hg}_2(\text{Ph}_2\text{SO})_{2,6}(\text{ClO}_4)_2$ and $\text{Hg}_2(n\text{-Pr}_2\text{SO})_4(\text{ClO}_4)_2$.

(J. R. CHIPPERFIELD)

1. T. Yamane, N. Davidson, *J. Am. Chem. Soc.*, **82**, 2123 (1960).
2. J. I. Watters, R. A. Simonaitis, *Talanta*, **11**, 247 (1964).
3. D. Grdenić, *J. Chem. Soc.*, 1312 (1956).
4. G. Johansson, *Acta Chem. Scand.*, **20**, 553 (1966).
5. R. A. Potts, A. L. Allred, *Inorg. Chem.*, **5**, 1066 (1966).
6. D. L. Kepert, D. Taylor, A. H. White, *J. Chem. Soc., Dalton Trans.*, 392 (1973).

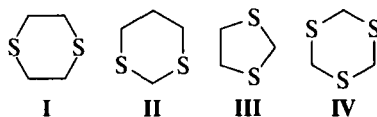
8.2.4.2. Complexes of Mercury(I)

8.2.4.2.2. with Sulfur- and Selenium-Donor Ligands.

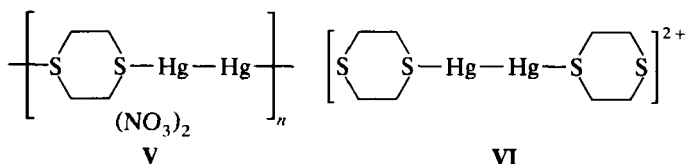
7. D. L. Kepert, D. Taylor, A. H. White, *J. Chem. Soc., Dalton Trans.*, 1658 (1973).
8. K. Brodersen, R. Eder, *Chem. Ber.*, 110, 2392 (1977).
9. S. Åhrland, I. Persson, *Acta Chem. Scand.*, A34, 645 (1980).
10. P. Peringer, *J. Inorg. Nucl. Chem.*, 42, 1501 (1980).
11. L. G. Sillén, A. E. Martell, *Stability Constants of Metal-Ion Complexes*, Spec. Publ. 17 and 25 (Supplement 1), The Chemical Society, London, 1964, 1971; contain data on formation constants of complexes with references to the original literature.
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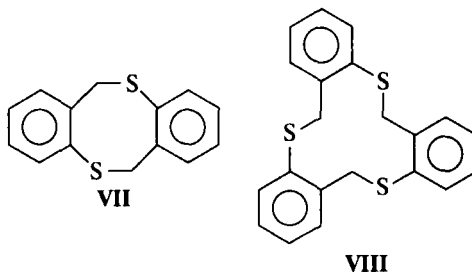
Sulfur-containing ligands form complexes with Hg(I). Ligands I–III form $\text{Hg}_2\text{L}(\text{NO}_3)_2$ complexes with $\text{Hg}_2(\text{NO}_3)_2$ in MeOH, whereas with $\text{Hg}_2(\text{ClO}_4)_2$ 2 mol of ligand react^{1,2} to give $\text{Hg}_2\text{L}_2(\text{ClO}_4)_2$. The 1,3,5-trithiane ligand (IV) also forms a complex $\text{Hg}_2\text{L}(\text{NO}_3)_2$.



The complexes formed with $\text{Hg}_2(\text{NO}_3)_2$ have a chain structure with the ligand joining Hg—Hg units together as in V, whereas those with $\text{Hg}_2(\text{ClO}_4)_2$ contain complex cations as in VI:



No complexes can be isolated with hindered sulfur-containing ligands such as VII and VIII:



In addition, $\text{PhCH}_2\text{SCH}_2\text{Ph}$ forms 1:1 adducts with $\text{Hg}_2(\text{NO}_3)_2$ and 1:2 adducts with $\text{Hg}_2(\text{ClO}_4)_2$. Two-phase systems can be used to isolate these complexes. The Hg(I) salt is dissolved in H_2O or MeOH, the organic sulfur ligand is dissolved in benzene or CH_2Cl_2 and the two solutions are stirred together.

Sulfur-containing ligands form complexes with Hg(I) salts other than the nitrate and perchlorate. The ligand $\text{PhCH}_2\text{SCH}_2\text{Ph}$ forms a 1:1 complex with² Hg_2SiF_6 .

8.2.4. in Mercury(I) Compounds from Mercury(II) Compounds

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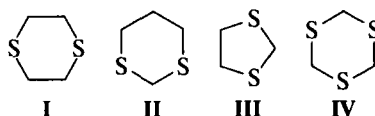
8.2.4.2. Complexes of Mercury(I)

8.2.4.2.2. with Sulfur- and Selenium-Donor Ligands.

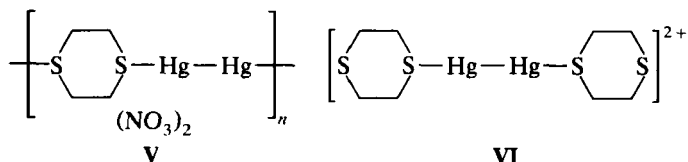
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8.2.4.2.2. Complexes of Mercury(I) with Sulfur- and Selenium-Donor Ligands.

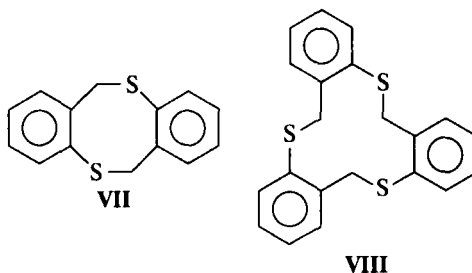
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The complexes formed with $\text{Hg}_2(\text{NO}_3)_2$ have a chain structure with the ligand joining Hg—Hg units together as in V, whereas those with $\text{Hg}_2(\text{ClO}_4)_2$ contain complex cations as in VI:



No complexes can be isolated with hindered sulfur-containing ligands such as VII and VIII:



In addition, $\text{PhCH}_2\text{SCH}_2\text{Ph}$ forms 1:1 adducts with $\text{Hg}_2(\text{NO}_3)_2$ and 1:2 adducts with $\text{Hg}_2(\text{ClO}_4)_2$. Two-phase systems can be used to isolate these complexes. The Hg(I) salt is dissolved in H_2O or MeOH, the organic sulfur ligand is dissolved in benzene or CH_2Cl_2 and the two solutions are stirred together.

Sulfur-containing ligands form complexes with Hg(I) salts other than the nitrate and perchlorate. The ligand $\text{PhCH}_2\text{SCH}_2\text{Ph}$ forms a 1:1 complex with² Hg_2SiF_6

and, in liq SO_2 , $\text{Hg}_2(\text{AsF}_6)_2$ forms 1:1 complexes with Ph_3PS , $(p\text{-FC}_6\text{H}_4)_3\text{PS}$ and Ph_3PSe . These latter complexes can be isolated if the ligand: Hg_2^{2+} ratio is ≤ 1 , but when ligand: $\text{Hg}_2^{2+} > 1$ disproportionation takes place and no complex can be isolated³.

(J. R. CHIPPERFIELD)

1. K. Brodersen, G. Liehr, W. Rölz, *Chem. Ber.*, 108, 3243 (1975).

2. K. Brodersen, W. Rölz, *Chem. Ber.*, 110, 1042 (1977).

3. P. A. W. Dean, D. G. Ibbott, *Can. J. Chem.*, 54, 177 (1976).

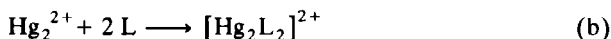
8.2.4.2.3. Complexes of Mercury(I) with Nitrogen-Donor Ligands.

When N-donor ligands, such as amines, are added to Hg(I) in H_2O disproportionation occurs:

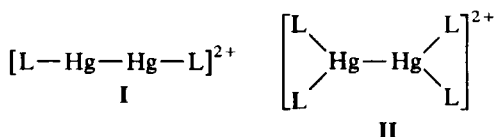


as Hg^{2+} forms stable complexes. Only PhNH_2 forms a stable amine complex, $[\text{Hg}_2\text{PhNH}_2]^{2+}$, in acidic solution¹ (see entry under PhNH_2 in Table 1, §8.2.4.2.1). Many Hg(I) -nitrogen-donor complexes are crystalline solids. They are prepared by adding a solution of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ or $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4 \text{H}_2\text{O}$ in MeOH to the ligand in MeOH . Complexes crystallize either spontaneously or after cooling. A little $\text{CH}(\text{OEt})_3$ removes any H_2O present, and sometimes a trace of HNO_3 or HClO_4 is added to minimize alkaline disproportionation.

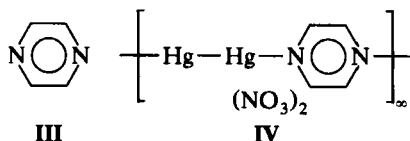
Sensitivity toward disproportionation is illustrated in the Hg(I) complexes of substituted pyridines², L:



When $\text{L} = 4\text{-CNC}_5\text{H}_4\text{N}$ ($\text{pK}_a = 1.86$), $2\text{-ClC}_5\text{H}_4\text{N}$ ($\text{pK}_a = 2.81$), or $4\text{-PhCOC}_5\text{H}_4\text{N}$ ($\text{pK}_a = 3.35$) $[\text{Hg}_2\text{L}_2] [\text{ClO}_4]_2$ can be isolated as solids. However, under the same conditions the more basic unsubstituted pyridine ($\text{pK}_a = 5.21$) leads to disproportionation, and no complex can be isolated. Complexes of Hg(I) of these more basic substituted pyridines can be prepared³ under a N_2 atmosphere in MeOH at -70°C . Table 1 shows some Hg(I) complexes prepared with N-donor ligands. The majority contain an Hg_2^{2+} ion with each atom coordinated to one or two N atoms as in I or II.



With Hg_2^{2+} bidentate nitrogen ligands form complexes that have chain structures. For example, 1,4-diazine **III** forms a complex $[\text{Hg}_2(\text{C}_4\text{H}_4\text{N}_2)(\text{NO}_3)_2]_n$ (**IV**) that has Hg—Hg units joined in infinite chains, with the $[\text{NO}_3]^-$ groups between the chains⁹.



370 8.2.4. in Mercury(I) Compounds from Mercury(II) Compounds
 8.2.4.2. Complexes of Mercury(I)
 8.2.4.2.3. Complexes of Mercury(I) with Nitrogen-Donor Ligands.

and, in liq SO_2 , $\text{Hg}_2(\text{AsF}_6)_2$ forms 1:1 complexes with Ph_3PS , $(p\text{-FC}_6\text{H}_4)_3\text{PS}$ and Ph_3PSe . These latter complexes can be isolated if the ligand: Hg_2^{2+} ratio is ≤ 1 , but when ligand: $\text{Hg}_2^{2+} > 1$ disproportionation takes place and no complex can be isolated³.

(J. R. CHIPPERFIELD)

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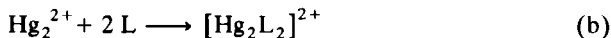
8.2.4.2.3. Complexes of Mercury(I) with Nitrogen-Donor Ligands.

When N-donor ligands, such as amines, are added to Hg(I) in H_2O disproportionation occurs:

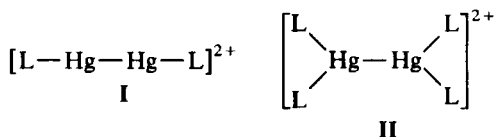


as Hg_2^{2+} forms stable complexes. Only PhNH_2 forms a stable amine complex, $[\text{Hg}_2\text{PhNH}_2]^{2+}$, in acidic solution¹ (see entry under PhNH_2 in Table 1, §8.2.4.2.1). Many Hg(I) -nitrogen-donor complexes are crystalline solids. They are prepared by adding a solution of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ or $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4 \text{H}_2\text{O}$ in MeOH to the ligand in MeOH . Complexes crystallize either spontaneously or after cooling. A little $\text{CH}(\text{OEt})_3$ removes any H_2O present, and sometimes a trace of HNO_3 or HClO_4 is added to minimize alkaline disproportionation.

Sensitivity toward disproportionation is illustrated in the Hg(I) complexes of substituted pyridines², L:



When $\text{L} = 4\text{-CNC}_5\text{H}_4\text{N}$ ($\text{pK}_a = 1.86$), $2\text{-ClC}_5\text{H}_4\text{N}$ ($\text{pK}_a = 2.81$), or $4\text{-PhCOC}_5\text{H}_4\text{N}$ ($\text{pK}_a = 3.35$) $[\text{Hg}_2\text{L}_2][\text{ClO}_4]_2$ can be isolated as solids. However, under the same conditions the more basic unsubstituted pyridine ($\text{pK}_a = 5.21$) leads to disproportionation, and no complex can be isolated. Complexes of Hg(I) of these more basic substituted pyridines can be prepared³ under a N_2 atmosphere in MeOH at -70°C . Table 1 shows some Hg(I) complexes prepared with N-donor ligands. The majority contain an Hg_2^{2+} ion with each atom coordinated to one or two N atoms as in I or II.



With Hg_2^{2+} bidentate nitrogen ligands form complexes that have chain structures. For example, 1,4-diazine **III** forms a complex $[\text{Hg}_2(\text{C}_4\text{H}_4\text{N}_2)(\text{NO}_3)_2]_n$ (**IV**) that has $\text{Hg}-\text{Hg}$ units joined in infinite chains, with the $[\text{NO}_3]^-$ groups between the chains⁹.

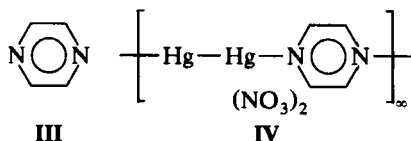


TABLE 1. MERCURY(I) COMPLEXES $\text{Hg}_2\text{L}_n\text{Z}_2$ FORMED WITH N-DONOR LIGANDS

Ligand, L	n	Z	Refs.
Pyridine	1	NO_3	5
	4	ClO_4	3
2-Me-Pyridine	2	ClO_4	3
4-CN-Pyridine	2	ClO_4	2, 3
2,4-Dimethylpyridine	2	ClO_4	3
4-Ph-Pyridine	2	NO_3	8
3-NH ₂ -Pyridine	2	ClO_4	4
	1	NO_3	4
3-Trichloroacetamido-pyridine	2	NO_3	4
Aniline	1	ClO_4	1
	6	NO_3	8
2-Cl-Aniline	2	NO_3	5
2-CN-Aniline	2	ClO_4	5
2-Me-Aniline	4	NO_3	5
4-Ph-Aniline	2	NO_3	8
4-F-Aniline	4	NO_3	10
	2	NO_3	10
2-NH ₂ -Naphthalene	2	NO_3	8
Pyridazine	2	NO_3	10
2,2'-Bipyridyl	2	ClO_4	3
1,10-Phenanthroline	2	ClO_4	3
	2	NO_3	10, 15
	1	NO_3	10, 12
Hexamethylenetetramine	1	ClO_4	3
	2	ClO_4	3
Quinoline	2	ClO_4	2
	2	NO_3	8, 11
1,8-Naphthyridine	1	ClO_4	13
Acridine	1	ClO_4	14

Other ligands that react to form these Hg(I) complexes are 1,2- and 1,4-diaminobenzene⁸, 1,10-phenanthroline¹⁰, and the bridged ring compound⁵:



(J. R. CHIPPERFIELD)

1. T. W. Wirth, N. Davidson, *J. Am. Chem. Soc.*, **86**, 4314 (1964).
2. D. L. Kepert, D. Taylor, *Aust. J. Chem.*, **27**, 1199 (1974).
3. K.-H. Tan, M. J. Taylor, *Aust. J. Chem.*, **33**, 1753 (1980).
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Both AsPh_3 and SbPh_3 react with $\text{Hg}_2(\text{AsF}_6)_2$ in liq SO_2 to give insoluble complexes¹ $\text{Hg}_2\text{L}(\text{AsF}_6)_2$ ($\text{L} = \text{AsPh}_3, \text{SbPh}_3$). Phosphine derivatives tend to disproportionate. At low $\text{L}:\text{Hg}_2^{2+}$ ratios there is evidence for complex ions $[\text{Hg}_2\text{L}]^{2+}$ [$\text{L} = \text{P}(\text{CF}_3)_2, \text{PF}_3$] and also $[\text{Hg}_2\text{L}_2]^{2+}$ ($\text{L} = \text{PF}_3$) in liq SO_2 . Other phosphines, including PPh_3 and PCl_3 , lead to the disproportionation of Hg(I) under these conditions¹.

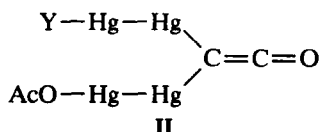
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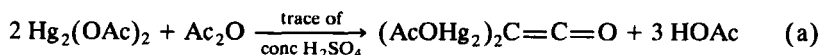
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Reaction of Hg(I) salts, such as $\text{Hg}_2(\text{OAc})_2$, with acetic anhydride forms Hg(I) ketenides (II)³:



where $\text{Y} = \text{OAc}, \text{NO}_3\text{ClO}_4$;



The ketenides separate as insoluble, infusible solids. The perchlorate derivative II ($\text{Y} = \text{ClO}_4$) is dangerously explosive.

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372 8.2. Formation of the Group-IB or -IIB–Group-IB or -IIB Metal Bonds
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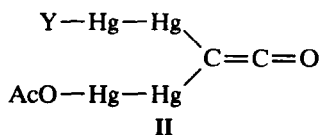
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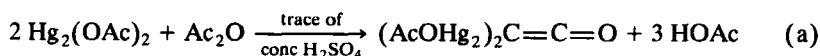
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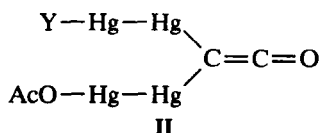
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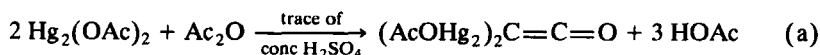
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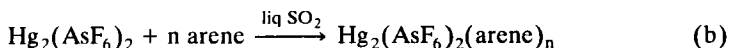
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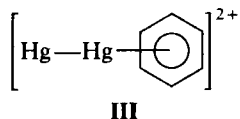
8.2.5. Mercury Chain Compounds

8.2.5.1. Mercury Chain Compounds in Liquid SO₂

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The complexes precipitate immediately on mixing; 1:1 complexes (n = 1) are prepared from arenes such as benzene, biphenyl, naphthalene, acenaphthalene, fluorene, phenanthrene, anthracene and m-dinitrobenzene. These complexes contain a complex Hg(I) cation with the arene π coordinated to one Hg as in III:



The aromatic compound, 9,10-benzophenanthrene, L, gives two complexes with the constitution Hg₂(AsF₆)₂L₃ and [Hg₂(AsF₆)₂]₂L.

(J. R. CHIPPERFIELD)

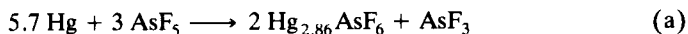
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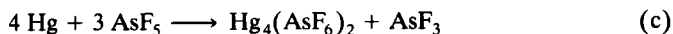
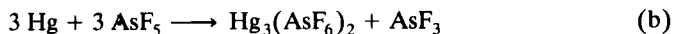
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Mercury(I) compounds containing a covalent Hg—Hg bond are well known, but those containing more than two Hg atoms covalently bonded are rare.

If AsF₅ dissolved in liq SO₂ is allowed to react with Hg at RT, pale-golden metallic crystals of Hg_{2.86}AsF₆ are obtained¹:



This material, previously thought to be Hg₆(AsF₆)₂, contains infinite linear chains of Hg atoms in two mutually perpendicular directions. Each Hg atom bears a charge of 0.35. On further reaction of AsF₅ with Hg in liq SO₂, a deep red solution is obtained as well as the golden crystals. From this red solution two further polynuclear Hg derivatives, Hg₃(AsF₆)₂¹ and Hg₄(AsF₆)₂², crystallize:



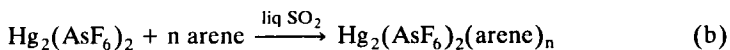
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8.2. Formation of the Group-IB or -IIB–Group-IB or -IIB Metal Bonds 373

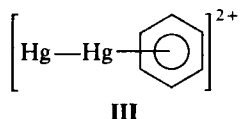
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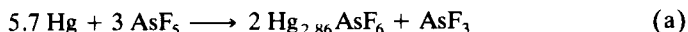
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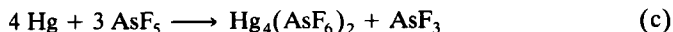
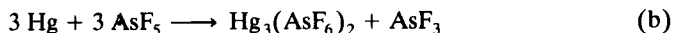
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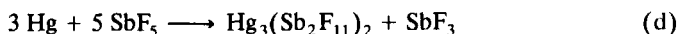


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 8.2.5.2. Mercury Chain Compounds in Molten AlCl_3

Hg in liq SO_2 when both the golden $\text{Hg}_{2.86}\text{AsF}_6$ and $\text{Hg}_4(\text{AsF}_6)_2$ are converted into the light yellow $\text{Hg}_3(\text{AsF}_6)_2$.

When SbF_5 reacts with Hg in liq SO_2 at RT the pale yellow compound $\text{Hg}_3(\text{Sb}_2\text{F}_{11})_2$ can be isolated:



This compound reacts with Hg in liq SO_2 at -20°C to oxidize Hg to metallic golden $\text{Hg}_{2.91}\text{SbF}_6$:



This compound has a constitution similar to $\text{Hg}_{2.86}\text{AsF}_6$.

Compounds claimed as Hg_3AsF_6 and HgSbF_6 (likely $\text{Hg}_{2.86}\text{AsF}_6$ and $\text{Hg}_{2.91}\text{SbF}_6$) are prepared by electrolysis of SO_2 solution of $[\text{AsF}_6]^-$ or $[\text{SbF}_6]^-$ with a Hg anode³.

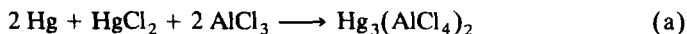
Reacting Hg with $\text{Hg}(\text{MF}_6)_2$ ($\text{M} = \text{Nb}, \text{Ta}$) gives golden crystals of $\text{Hg}_{3-\delta}\text{MF}_6$, which subsequently are transformed into silver crystals of Hg_3MF_6 ^{4,5}. Under these conditions small amounts of $\text{Hg}_3(\text{MF}_5)_2\text{SO}_4$ ($\text{M} = \text{Nb}, \text{Ta}$) and $\text{Hg}_4(\text{Ta}_2\text{F}_{11})_2$ form⁶.

(J. R. CHIPPERFIELD)

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Electrochemical measurements show that the Hg_3^{2+} species becomes more stable in AlCl_3 -rich melts, and its production also is favored by low temperatures. Like the similar compound $\text{Hg}_3(\text{AsF}_6)_2$ (see §8.2.5.1) it contains an almost linear Hg_3 unit².

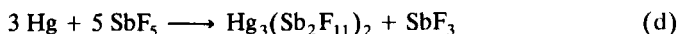
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374 8.2. Formation of the Group-IB or -IIB–Group-IB or -IIB Metal Bonds**8.2.5. Mercury Chain Compounds****8.2.5.2. Mercury Chain Compounds in Molten AlCl_3**

Hg in liq SO_2 when both the golden $\text{Hg}_{2.86}\text{AsF}_6$ and $\text{Hg}_4(\text{AsF}_6)_2$ are converted into the light yellow $\text{Hg}_3(\text{AsF}_6)_2$.

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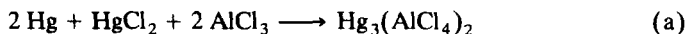
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8.3. Formation of the Group-IB (Cu, Ag, Au) or Group-IIB (Zn, Cd, Hg)–Transition-Metal Bonds

8.3.1. Introduction

Group-IB bonds are described, followed by group-IIB–transition-metal bonds.

8.3.2. Group IB – Transition- and Inner Transition-Metal Bonds

8.3.2.1. by Coupling Carbonyl Anions with Complexes of the Group-IB Monohalides¹

Bonds are formed between Cu, Ag or Au and transition metals by:



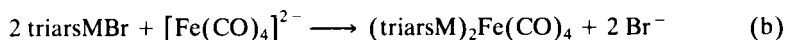
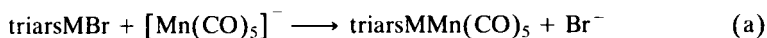
where M is a group-IB element, M' a transition metal and L a ligand. Ethers, such as THF or diglyme, are used as solvents. Alkali-metal cations such as Na⁺, precipitate the halide NaX. The complex is obtained in good yield from the supernatant solvent (see also §8.3.3.1).

(J. R. CHIPPERFIELD)

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8.3.2.1.1. Formation of Bonds Between Transition Metals and Copper or Silver.

Anions derived from transition-metal carbonyls (see also §8.3.3.1) react with Cu– or Ag–halogen bonds; e.g., triarsMBr (M = Cu, Ag) reacts with univalent or divalent carbonyl anions^{1,2}:



These reactions can be extended to many carbonyl derivatives that form carbonyl anions, such as those of V³, Mo and W^{4,5} and Co¹, e.g., to form a cluster containing

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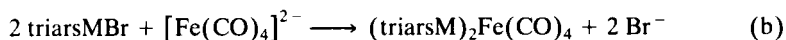
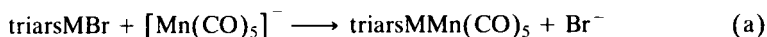
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These reactions can be extended to many carbonyl derivatives that form carbonyl anions, such as those of V³, Mo and W^{4,5} and Co¹, e.g., to form a cluster containing

Fe—Cu bonds:



The product is crystallized as the tetraethylammonium derivative⁶ $[\text{Et}_4\text{N}][\text{Fe}_5\text{CuC}(\text{CO})_{14}\text{MeCN}]$. Similarly the salt $[\text{N}(\text{PPh}_3)_2]_2[\text{FeC}(\text{CO})_{12}]$ reacts with $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ in THF to yield, after 2 h, black crystals⁷ of $[\text{N}(\text{PPh}_3)_2][\text{CuFe}_4\text{C}(\text{CO})_{12}\text{MeCN}]$. Clusters containing Cu—Os^{8,9}, Cu—Ru^{10,11} and Ag—Ru^{10,12} bonds are prepared this way.

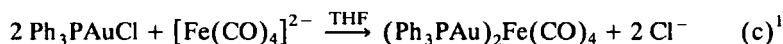
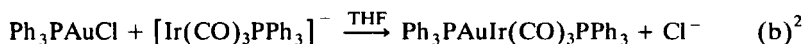
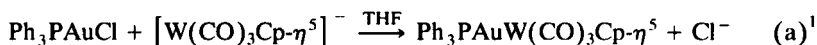
Strategies for synthesizing compounds containing clusters of Cu or Ag and transition metals are available¹³.

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8.3.2.1.2. Formation of Bonds Between Transition Metals and Gold.

Whereas Cu and Ag form complexes with derivatives of transition-metal carbonyls in which the Cu or Ag are 4 coordinated in both the reactant and in the final product, many analogous Au complexes exhibit only 2 coordination. For example, the simple Au complex Ph_3PAuCl reacts with transition-metal carbonyl anions in THF to give complexes with transition-metal to Au bonds, e.g.:



376 8.3.2. Group IB – Transition- and Inner Transition-Metal Bonds¹
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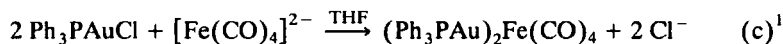
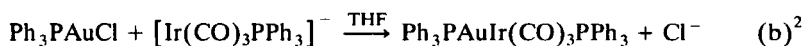
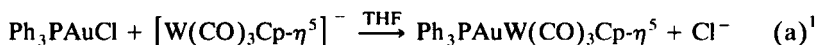
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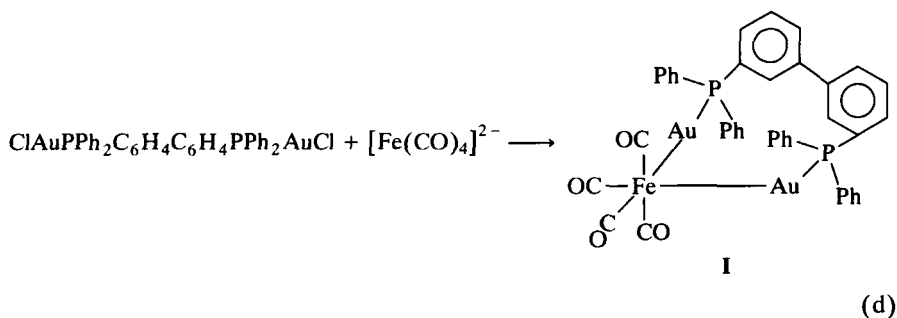
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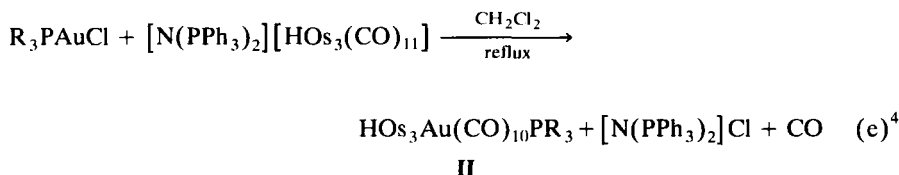
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The bidentate ligand of the Au derivative of 3,3'-diphenylphosphinobiphenyl also reacts³ with $[\text{Fe}(\text{CO})_4]^{2-}$:

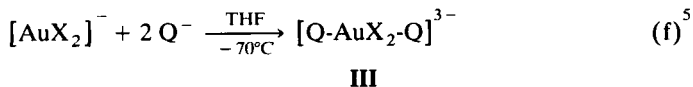


A more complex variation is:



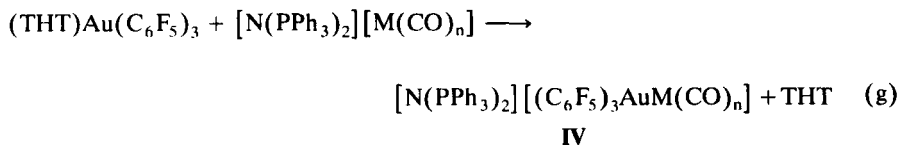
where R = Et, Ph. The product (II) contains a Au atom bridging two Os atoms.

Anionic complexes containing two transition-metal to Au bonds can be formed by reacting $\text{R}_4\text{N}[\text{AuX}_2]$ (R = Et, n-Bu; X = Cl, Br) with carbonyl anions:

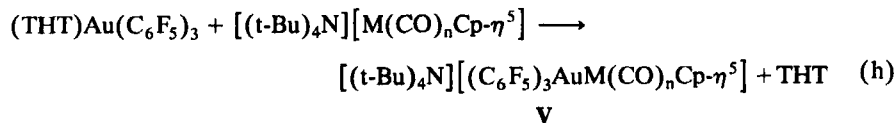


where Q = $\text{Mn}(\text{CO})_5$, $\text{Co}(\text{CO})_4$, $\text{Mo}(\text{CO})_3\text{Cp-}\eta^5$, $\text{Fe}(\text{CO})_2\text{Cp-}\eta^5$. Then products (III) precipitate when pentane is added. Care is needed in selecting the nature of X and R. Whereas $\text{Et}_4\text{N}[\text{AuCl}_2]$ gives the required products with carbonyl anions of Mn and Mo, $\text{Et}_4\text{N}[\text{AuBr}_2]$ is best for reaction with $[\text{Co}(\text{CO})_4]^-$, and n-Bu₄N[AuBr₂] for reaction with $[\text{Fe}(\text{CO})_2\text{Cp-}\eta^5]^-$.

Anionic complexes also can be prepared from $(\text{THT})\text{Au}(\text{C}_6\text{F}_5)_3$, which reacts with carbonyl anions in CH_2Cl_2 to give compounds with Au to transition-metal bonds:



where $M(CO)_n = Mn(CO)_5$, $Co(CO)_4$ and:



where⁶ $M(CO)_n = Fe(CO)_2$ and $Mo(CO)_3$. In the presence of $(THT)Au(C_6F_5)_3$ the products IV and V disproportionate to give $[N(PPh_3)_2][Au\{M(CO)_n\}_2]$ and $[NBu-t_4][Au\{M(CO)_n Cp-\eta^5\}_2]$. Action of anions derived from transition-metal clusters with Au derivatives yields $Au-Fe^{7-10}$, $Au-Co^{11}$, $Au-Ru^{9,12-17}$, $Au-Os^{15,18,19}$ and $Au-W^{20}$ clusters. Successful cluster synthesis strategies are available²¹.

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1. C. E. Coffey, J. Lewis, R. S. Nyholm, *J. Chem. Soc.*, 1741 (1964).
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3. B. Chiswell, L. M. Venanzi, *J. Chem. Soc., A*, 901 (1966).
4. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, *J. Organomet. Chem.*, 215, C33 (1981).
5. P. Braunstein, J. Dehand, *J. Organomet. Chem.*, 88, C24 (1975).
6. R. Uson, A. Laguna, M. Laguna, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 366 (1981).
7. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, M. J. Rosales, *J. Organomet. Chem.*, 231, C59 (1982).
8. B. F. G. Johnson, D. A. Kaner, J. Lewis, M. J. Rosales, *J. Organomet. Chem.*, 238, C73 (1982).
9. E. Roland, K. Fischer, H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 22, 326 (1983).
10. C. E. Briant, K. P. Hall, D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 843 (1983).
11. J. W. Lauher, K. Wald, *J. Am. Chem. Soc.*, 103, 7648 (1981).
12. P. Braunstein, G. Predieri, A. Tiripicchio, E. Sappa, *Inorg. Chem. Acta*, 63, 113 (1982).
13. B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. Puga, P. R. Raithby, D. Braga, M. McPartlin, W. Clegg, *J. Organomet. Chem.*, 243, C13 (1983).
14. M. I. Bruce, B. K. Nicholson, *J. Organomet. Chem.*, 252, 243 (1983).
15. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 314 (1982).
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19. B. F. G. Johnson, J. Lewis, W. J. H. Nelson, P. R. Raithby, M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 608 (1983).
20. G. A. Carriedo, D. Hodgson, J. A. K. Howard, K. Marsden, F. G. A. Stone, M. J. Went, P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1006 (1982).
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8.3.2.2. by Other Methods

8.3.2.2.1. Reaction of Carbonyl Anions with Uncomplexed Derivatives of Group-IB Metals.

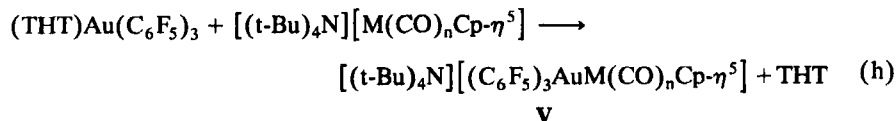
Formation of bonds between group-IB and transition metals by reacting carbonyl anions with complexed derivatives of group-IB metals is discussed in §8.3.2.1. Car-

378 8.3.2. Group IB – Transition- and Inner Transition-Metal Bonds¹

8.3.2.2. by Other Methods

8.3.2.2.1. Reaction of Carbonyl Anions with Derivatives of Group-IB.

where $M(CO)_n = Mn(CO)_5$, $Co(CO)_4$ and:



where⁶ $M(CO)_n = Fe(CO)_2$ and $Mo(CO)_3$. In the presence of $(THT)Au(C_6F_5)_3$ the products IV and V disproportionate to give $[N(PPh_3)_2][Au\{M(CO)_n\}_2]$ and $[NBu-t_4][Au\{M(CO)_n Cp-\eta^5\}_2]$. Action of anions derived from transition-metal clusters with Au derivatives yields $Au-Fe^{7-10}$, $Au-Co^{11}$, $Au-Ru^{9,12-17}$, $Au-Os^{15,18,19}$ and $Au-W^{20}$ clusters. Successful cluster synthesis strategies are available²¹.

(J. R. CHIPPERFIELD)

1. C. E. Coffey, J. Lewis, R. S. Nyholm, *J. Chem. Soc.*, 1741 (1964).
2. J. P. Collman, F. D. Vastine, W. R. Roper, *J. Am. Chem. Soc.*, 88, 5035 (1966).
3. B. Chiswell, L. M. Venanzi, *J. Chem. Soc., A*, 901 (1966).
4. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, *J. Organomet. Chem.*, 215, C33 (1981).
5. P. Braunstein, J. Dehand, *J. Organomet. Chem.*, 88, C24 (1975).
6. R. Uson, A. Laguna, M. Laguna, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 366 (1981).
7. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, M. J. Rosales, *J. Organomet. Chem.*, 231, C59 (1982).
8. B. F. G. Johnson, D. A. Kaner, J. Lewis, M. J. Rosales, *J. Organomet. Chem.*, 238, C73 (1982).
9. E. Roland, K. Fischer, H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 22, 326 (1983).
10. C. E. Briant, K. P. Hall, D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 843 (1983).
11. J. W. Lauher, K. Wald, *J. Am. Chem. Soc.*, 103, 7648 (1981).
12. P. Braunstein, G. Predieri, A. Tiripicchio, E. Sappa, *Inorg. Chem. Acta*, 63, 113 (1982).
13. B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. Puga, P. R. Raithby, D. Braga, M. McPartlin, W. Clegg, *J. Organomet. Chem.*, 243, C13 (1983).
14. M. I. Bruce, B. K. Nicholson, *J. Organomet. Chem.*, 252, 243 (1983).
15. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 314 (1982).
16. M. I. Bruce, B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 1141 (1982).
17. M. J. Freeman, M. Green, A. G. Orpen, I. D. Salter, F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1332 (1983).
18. B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. N. Nicholls, J. Puga, P. R. Raithby, M. J. Rosales, M. Schröder, M. D. Vargas, *J. Chem. Soc., Dalton Trans.*, 2447 (1983).
19. B. F. G. Johnson, J. Lewis, W. J. H. Nelson, P. R. Raithby, M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 608 (1983).
20. G. A. Carriedo, D. Hodgson, J. A. K. Howard, K. Marsden, F. G. A. Stone, M. J. Went, P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1006 (1982).
21. I. D. Salter, in *Advances in Organometallic Chemistry*, Vol. 29, F. G. A. Stone, R. West, eds., Academic Press, New York, 1989, p. 249.

8.3.2.2. by Other Methods

8.3.2.2.1. Reaction of Carbonyl Anions with Uncomplexed Derivatives of Group-IB Metals.

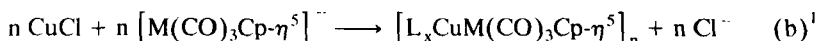
Formation of bonds between group-IB and transition metals by reacting carbonyl anions with complexed derivatives of group-IB metals is discussed in §8.3.2.1. Car-

bonyl anions also react with uncomplexed group-IB compounds to form compounds containing metal–metal bonds.

Carbonyl anions react with AgNO₃ or CuCl in aqueous bis(2-methoxyethyl)ether to form covalent oligomers (n = 3 or 4):



where M = Cr, Mo, W, and also:



where M = Cr, Mo, W; L_x = H₂O or $\frac{1}{2} \text{ NH}_3 \cdot \frac{1}{2} \text{ H}_2\text{O}$. On addition of Me₄NCl compounds [Me₄N][M'(M(CO)₃Cp-η⁵)₂] are formed where M = Cr, Mo, W, and M' = Cu, Ag. Similar compounds can be made using the carbonyl anions² [Co(CO)₄][−] and [Fe(CO)₂Cp-η⁵][−].

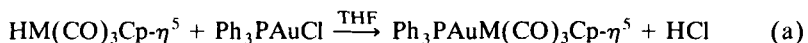
(J. R. CHIPPERFIELD)

1. P. Hackett, A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1606 (1975).

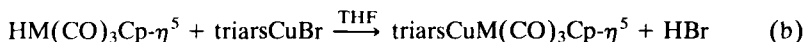
2. P. Chini, S. Martinengo, G. Longoni, *Gazz. Chim. Ital.*, 105, 203 (1975).

8.3.2.2.2. Reaction of Carbonyl Hydrides with Complexes of Group-IB Metals.

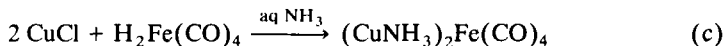
These reactions give products similar to those described in §8.3.2.1. Transition-metal hydrido complexes react with a halogen derivative of a group-IB metal to form a hydrogen halide and the required metal–metal bond¹:



where M = Cr, Mo, W, and:



where M = Mo, W. Analogous complexes of Ag do not form under these conditions, but H₂Fe(CO)₄ reacts² similarly with CuCl:



and the Os-containing cluster hydrido complex H₂Os₃(CO)₁₀ reacts^{3,4} with Ph₃PAuMe:



Clusters containing Au—I⁵ and Au—Ru^{6–8} bonds are formed by similar reactions.

1. R. J. Haines, R. S. Nyholm, M. H. B. Stiddard, *J. Chem. Soc., A*, 46 (1968).

2. W. Hieber, E. Fack, *Z. Anorg. Allg. Chem.*, 236, 83 (1938).

3. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, *J. Organomet. Chem.* 215, C33 (1981).

4. L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, J. L. Spencer, F. G. A. Stone, P. Woodward, *J. Chem. Soc., Chem. Commun.*, 260 (1978).

8.3.2. Group IB – Transition- and Inner Transition-Metal Bonds¹

379

8.3.2.2. by Other Methods

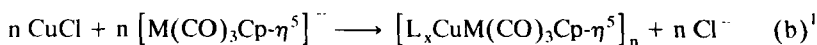
8.3.2.2.2. Reaction of Carbonyl Hydrides with Complexes of Group-IB.

bonyl anions also react with uncomplexed group-IB compounds to form compounds containing metal–metal bonds.

Carbonyl anions react with AgNO₃ or CuCl in aqueous bis(2-methoxyethyl)ether to form covalent oligomers (n = 3 or 4):



where M = Cr, Mo, W, and also:



where M = Cr, Mo, W; L_x = H₂O or $\frac{1}{2} \text{ NH}_3 \cdot \frac{1}{2} \text{ H}_2\text{O}$. On addition of Me₄NCl compounds [Me₄N][M'(M(CO)₃Cp-η⁵)₂] are formed where M = Cr, Mo, W, and M' = Cu, Ag. Similar compounds can be made using the carbonyl anions² [Co(CO)₄][−] and [Fe(CO)₂Cp-η⁵][−].

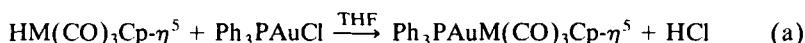
(J. R. CHIPPERFIELD)

1. P. Hackett, A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1606 (1975).

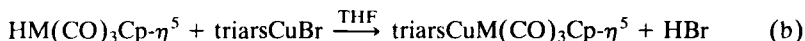
2. P. Chini, S. Martinengo, G. Longoni, *Gazz. Chim. Ital.*, 105, 203 (1975).

8.3.2.2.2. Reaction of Carbonyl Hydrides with Complexes of Group-IB Metals.

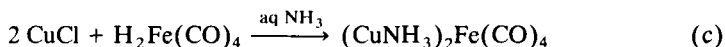
These reactions give products similar to those described in §8.3.2.1. Transition-metal hydrido complexes react with a halogen derivative of a group-IB metal to form a hydrogen halide and the required metal–metal bond¹:



where M = Cr, Mo, W, and:



where M = Mo, W. Analogous complexes of Ag do not form under these conditions, but H₂Fe(CO)₄ reacts² similarly with CuCl:



and the Os-containing cluster hydrido complex H₂Os₃(CO)₁₀ reacts^{3,4} with Ph₃PAuMe:



Clusters containing Au—I⁵ and Au—Ru^{6–8} bonds are formed by similar reactions.

1. R. J. Haines, R. S. Nyholm, M. H. B. Stiddard, *J. Chem. Soc., A*, 46 (1968).

2. W. Hieber, E. Fack, *Z. Anorg. Allg. Chem.*, 236, 83 (1938).

3. B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, *J. Organomet. Chem.* 215, C33 (1981).

4. L. J. Farrugia, J. A. K. Howard, P. Mitprachachon, J. L. Spencer, F. G. A. Stone, P. Woodward, *J. Chem. Soc., Chem. Commun.*, 260 (1978).

380 8.3.2. Group IB – Transition- and Inner Transition-Metal Bonds¹

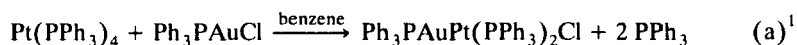
8.3.2.2. by Other Methods

8.3.2.2.3. Reactions of Other Transition-Metal Complexes with Group-IB.

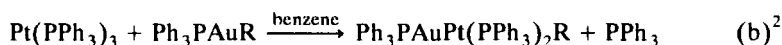
5. A. L. Casalnuovo, L. H. Pignolet, J. W. A. van der Velden, J. J. Bour, J. J. Steggerda, *J. Am. Chem. Soc.*, **105**, 5957 (1983).
6. M. I. Bruce, B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 1141 (1982).
7. L. J. Farrugia, M. J. Freeman, M. Green, A. G. Orpen, F. G. A. Stone, I. D. Salter, *J. Organomet. Chem.*, **249**, 273 (1983).
8. L. W. Bateman, M. Green, K. A. Mead, R. M. Mills, I. D. Salter, F. G. A. Stone, P. Woodward, *J. Chem. Soc., Dalton Trans.*, 2599 (1983).

8.3.2.2.3. Reactions of Other Transition-Metal Complexes with Group-IB Compounds.

The Pt(0) derivative $\text{Pt}(\text{PPh}_3)_4$ reacts with Au complexes to form a Au—Pt bond:

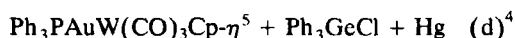
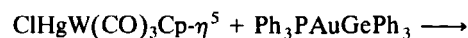
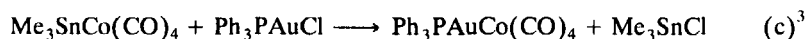


Organometallic Au complexes react similarly with $\text{Pt}(\text{PPh}_3)_3$:

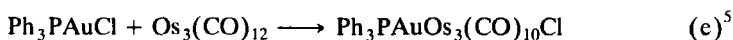


where $\text{R} = \text{C}_6\text{Cl}_5$ or Me. In this reaction the organic group is transferred from Au to Pt to form organometallic derivatives of Pt.

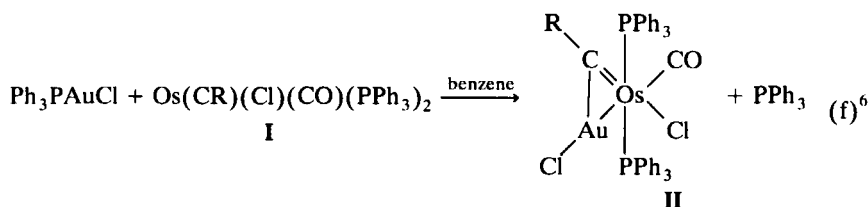
Compounds containing transition metals bonded to main-group elements, such as Hg and Sn, react with Au derivatives to form metal-metal bonds with the elimination of R_3MCl :



More complicated are reactions of Ph_3PAuCl with Os carbonyls and derivatives. The carbonyl $\text{Os}_3(\text{CO})_{12}$ reacts with Ph_3PAuCl by oxidative addition:



whereas the Os carbyne (I) reacts with Ph_3PAuCl :



380 8.3.2. Group IB – Transition- and Inner Transition-Metal Bonds¹

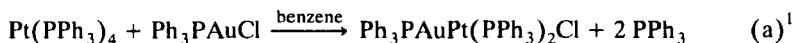
8.3.2.2. by Other Methods

8.3.2.2.3. Reactions of Other Transition-Metal Complexes with Group-IB.

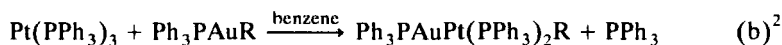
5. A. L. Casalnuovo, L. H. Pignolet, J. W. A. van der Velden, J. J. Bour, J. J. Steggerda, *J. Am. Chem. Soc.*, **105**, 5957 (1983).
6. M. I. Bruce, B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 1141 (1982).
7. L. J. Farrugia, M. J. Freeman, M. Green, A. G. Orpen, F. G. A. Stone, I. D. Salter, *J. Organomet. Chem.*, **249**, 273 (1983).
8. L. W. Bateman, M. Green, K. A. Mead, R. M. Mills, I. D. Salter, F. G. A. Stone, P. Woodward, *J. Chem. Soc., Dalton Trans.*, 2599 (1983).

8.3.2.2.3. Reactions of Other Transition-Metal Complexes with Group-IB Compounds.

The Pt(0) derivative $\text{Pt}(\text{PPh}_3)_4$ reacts with Au complexes to form a Au—Pt bond:

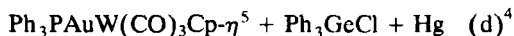
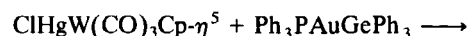
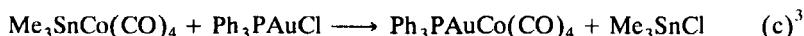


Organometallic Au complexes react similarly with $\text{Pt}(\text{PPh}_3)_3$:

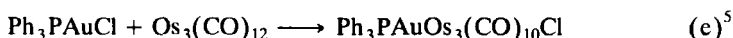


where $\text{R} = \text{C}_6\text{Cl}_5$ or Me. In this reaction the organic group is transferred from Au to Pt to form organometallic derivatives of Pt.

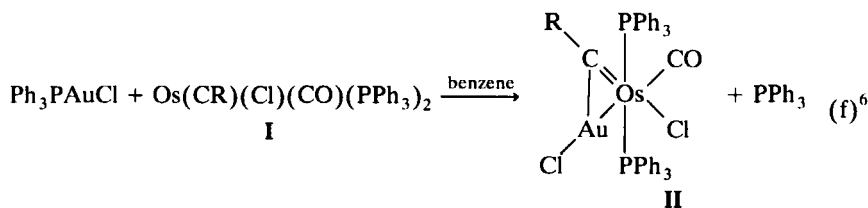
Compounds containing transition metals bonded to main-group elements, such as Hg and Sn, react with Au derivatives to form metal-metal bonds with the elimination of R_3MCl :



More complicated are reactions of Ph_3PAuCl with Os carbonyls and derivatives. The carbonyl $\text{Os}_3(\text{CO})_{12}$ reacts with Ph_3PAuCl by oxidative addition:

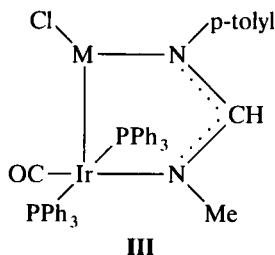


whereas the Os carbyne (I) reacts with Ph_3PAuCl :

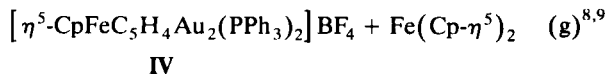


to give a product (II) containing a three-membered ring ($R = p\text{-MeC}_6\text{H}_4$). Complex I reacts with AgCl or CuI to form complexes similar to II.

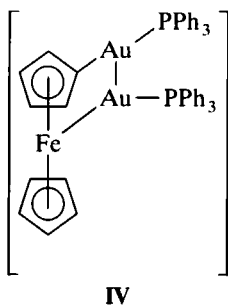
Small-ring formation is also seen in the reaction of $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ with $[\text{M}(\text{RNC}(\text{H})(\text{NR}'))_n]$ ($M = \text{Cu}, \text{Ag}$; $R = \text{Me}, \text{Et}, i\text{-Pr}, t\text{-Bu}, \text{cyclohexyl}$; $n = 2, 4$; $R' = p\text{-MeC}_6\text{H}_4$) to give complexes (III) where the Ir—M bond is stabilized by a bridging formamido group⁷:



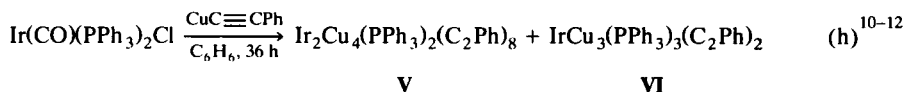
Reaction of ferrocenyl(triphenylphosphine)gold(I) with a deficiency of HBF_4 forms a bond between Au and Fe:



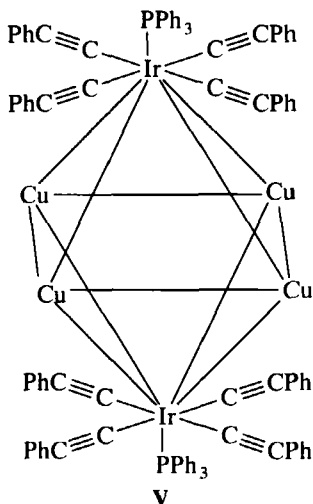
The product (IV) has the Fe atom in the sandwich bonded to a Au, which itself is bonded both to a cyclopentadiene ring and to a second Au.



Clusters can be formed by reacting transition-metal complexes with group-IB derivatives. The reaction of $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ with Cu phenylacetylide gives rise to two cluster products:



The main product V contains an O_h of metal atoms:



The other product (VI) is formed in traces. These reactions form Au–Ru^{13,14}, Au–Os^{15–17}, Ag–Fe¹⁸ and Ag–Rh¹⁹ clusters and compounds with bridged Ag–Pt^{20,21} and Au–W²² bonds. Syntheses of cluster compounds containing Cu, Ag or Au and other transition metals are available²³.

(J. R. CHIPPERFIELD)

1. A J. Layton, R. S. Nyholm, G. A. Pneumaticakis, M. L. Tobe, *Chem. Ind. (London)*, 465 (1967).
2. O. Rossell, J. Sales, *Inorg. Chim. Acta*, 53, L1 (1981).
3. E. W. Abel, G. V. Hutson, *J. Inorg. Nucl. Chem.*, 30, 2339 (1968).
4. A. Carrick, F. Glockling, *J. Chem. Soc.*, A, 913 (1968).
5. C.W. Bradford, W. van Bronswijk, R. J. H. Clark, R. S. Nyholm, *J. Chem. Soc.*, A, 2889 (1970).
6. G. R. Clark, C. M. Cochrane, W. R. Roper, L. J. Wright, *J. Organomet. Chem.*, 199, C35 (1980).
7. P. I. van Vliet, G. van Koten, K. Vrieze, *J. Organomet. Chem.*, 182, 105 (1979).
8. V. G. Andrianov, Yu. T. Struchkov, E. R. Rossinskaja, *J. Chem. Soc., Chem. Commun.*, 338 (1973).
9. *Gmelin Handbook of Inorganic Chemistry, Au. Organogold Compounds*. Springer-Verlag, Berlin, 1980, p. 240; good discussion of these compounds and synthetic routes.
10. O. M. Abu Salah, M. I. Bruce, M. R. Churchill, S. A. Bezman, *J. Chem. Soc., Chem. Commun.*, 858 (1972).
11. M. R. Churchill, S. A. Bezman, *Inorg. Chem.*, 13, 1418 (1974).
12. O. M. Abu Salah, M. I. Bruce, *Aust. J. Chem.*, 29, 531 (1976).
13. B. F. G. Johnson, J. Lewis, J. N. Nicholls, J. Puga, K. H. Whitmire, *J. Chem. Soc., Dalton Trans.*, 787 (1983).
14. M. Green, K. A. Mead, R. M. Mills, I. D. Salter, F. G. A. Stone, P. Woodward, *J. Chem. Soc., Chem. Commun.*, 51 (1982).
15. K. Burgess, B. F. G. Johnson, J. Lewis, *J. Organomet. Chem.*, 247, C42 (1983).
16. K. Burgess, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1179 (1983).
17. K. Burgess, B. F. G. Johnson, J. Lewis, P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1661 (1983).
18. G. N. Mott, N. J. Taylor, A. J. Carty, *Organometallics*, 2, 447 (1983).

8.3. Group-IB (Cu, Ag, Au) or -IIB (Zn, Cd, Hg)–Transition-Metal Bonds 383

8.3.3. Group IIB–Transition- and Inner-Transition-Metal Bonds

19. N. G. Connelly, A. R. Lucy, J. D. Payne, A. M. R. Galas, W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1879 (1983).
20. A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze, *Inorg. Chem.*, **21**, 2026 (1982).
21. B. Lippert, D. Neugebauer, *Inorg. Chem.*, **21**, 451 (1982).
22. M. R. Awang, G. A. Carriedo, J. A. K. Howard, K. A. Mead, I. Moore, C. M. Nunn, F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 964 (1983).
23. I. D. Salter, in *Advances in Organometallic Chemistry*, Vol. 29, F. G. A. Stone, R. West, eds., Academic Press, New York, 1989, p. 249.

8.3.2.2.4. Codeposition of Group-IB and Transition Metals To Give Bimetallic Clusters.

By using the technique of metal-vapor cryochemistry diatomic bimetallic clusters MM' (M = group IB metal, M' = transition metal) can be generated in quantities large enough to study their chemistry. For example, cocondensation of metal vapors at 10–12 K in Ar matrices gives such species as $AgCu$, $AgMo$, $AgMn$ and $CuFe$. Amounts formed are small, but sufficient for spectroscopic investigation^{1,2} (see §8.2.3.1.1).

(J. R. CHIPPERFIELD)

1. W. J. Power, *Adv. Inorg. Chem. Radiochem.*, **23**, 79 (1980).
2. J. A. Howard, R. Sutcliffe, B. Mile, *Surf. Sci.*, **156**, 214 (1985).

8.3.2.2.5. Formation of Clusters Containing Group-IB and Transition Metals¹.

Clusters can be formed that contain group-IB–transition-metal bonds. Such clusters include those with only one atom of the group-IB metal, but more than one atom of the transition metal, such as $Os_3AuX(CO)_{10}PPh_3$ ($X = Cl, Br, I, SCN, H$); those such as $IrCu_3(C_2Ph)_2(PPh_3)_3$ which contain one transition-metal atom and more than one group-IB atom; and those containing several atoms of both group-IB and transition metals, such as $Ir_2Cu_4(C_2Ph)_8(PPh_3)_2$.

Examples of these clusters are described in the preceding sections.

(J. R. CHIPPERFIELD)

1. W. L. Gladfelter, G. L. Geoffroy, *Adv. Organomet. Chem.*, **18**, 207 (1980).
2. I. D. Salter, in *Advances in Organometallic Chemistry*, Vol. 29, F. G. A. Stone, R. West, eds., Academic Press, New York, 1989, p. 249.

8.3.3. Synthesis of Group IIB–Transition- and Inner-Transition-Metal Bonds

Compounds containing group-IIB–transition-metal bonds are characterized for almost every transition metal¹. Although there are more derivatives containing Hg than Zn or Cd, there is no difficulty in producing analogous compounds of each of these metals. No compound is known in which Zn, Cd or Hg is bonded to either lanthanide or actinide elements.

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8.3. Group-IB (Cu, Ag, Au) or -IIB (Zn, Cd, Hg)–Transition-Metal Bonds 383

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8.3.2.2.4. Codeposition of Group-IB and Transition Metals To Give Bimetallic Clusters.

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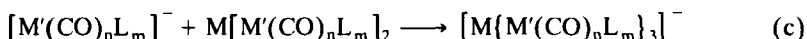
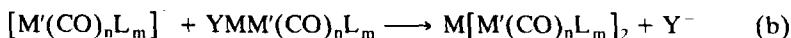
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384 8.3.3. Group IIB–Transition- and Inner-Transition-Metal Bonds
 8.3.3.1. by Reactions of Carbonyl Anions with Divalent Group-IIB Salts
 8.3.3.1.1. Derivatives of Zinc and Cadmium.

8.3.3.1. by Reactions of Carbonyl Anions with Divalent Group-IIB Salts

Anions of transition-metal carbonyls are prepared by reducing the carbonyl and react with derivatives of group-IIB metals to yield mono-, di- and even trisubstituted derivatives:



where M = group-IIB metal, M' = transition metal, L = ligand other than CO, Y = halide, CN, etc. Carbonyl anions can be prepared by reducing a carbonyl dimer, such as $Mn_2(CO)_{10}$, with 1% Na amalgam in THF:



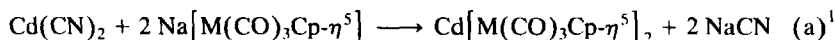
After separation of excess amalgam a solution of MX_2 is added. Reaction is rapid and the desired product can be separated from the Na halide or NaCN produced. If the separation of the amalgam is incomplete it is possible for Hg to be incorporated into the product (see §8.3.3.4). To avoid this, other methods of preparing carbonyl anions can be used, such as reaction with $NaBH_4$, Na–K and other reducing agents^{1–5}, or phase-transfer methods⁶.

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Although reaction of carbonyl anions with group-IIB salts is seldom used to prepare derivatives of Zn and Cd, it works when used. Compounds containing Mo–Cd and W–Cd bonds can be synthesized by reacting aq $Cd(CN)_2$ with dry $Na[M(CO)_3Cp-\eta^5]$ (M = Mo, W):



Potentiometry in H_2O of the equilibrium between Zn^{2+} and $[Fe(CO)_4]^{2-}$:

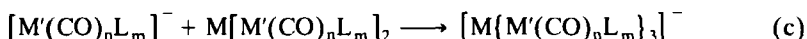
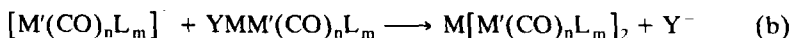


confirms that this reaction takes place², with an equilibrium constant K of $4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1}$. Electrochemically generated carbonyl anions $[Co(CO)_4]^-$ and

384 8.3.3. Group IIB–Transition- and Inner-Transition-Metal Bonds
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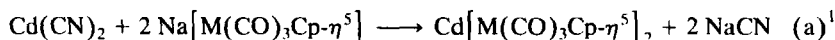
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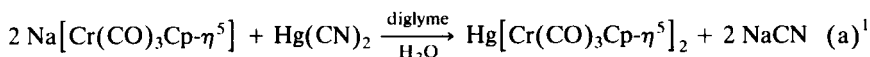
$[\text{Mn}(\text{CO})_5]^-$ react with anodically oxidized Zn in C_6H_6 -MeOH in the presence of bipy to give³ $\text{Zn}[\text{Co}(\text{CO})_4]_2\text{bipy}$ and $\text{Zn}[\text{Mn}(\text{CO})_5]_2\text{bipy}$.

(J. R. CHIPPERFIELD)

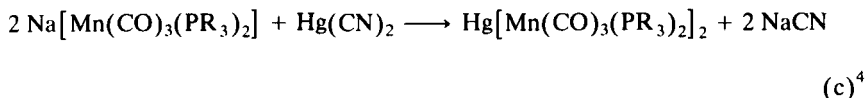
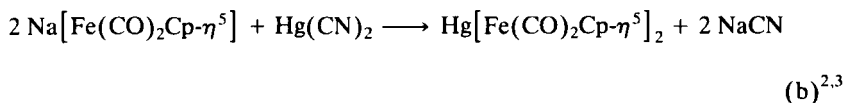
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8.3.3.1.2. Derivatives of Mercury.

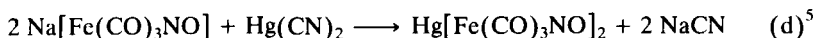
Transition-metal to Hg bonds are prepared by this method in excellent yields, e.g.:



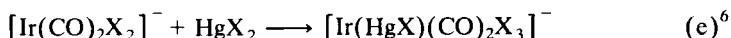
In an excess of carbonyl anion two transition-metal to Hg bonds form:



where R = Ph, OPh, and:



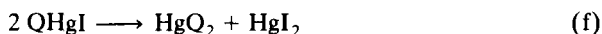
However, reactions can be stopped after only one such bond has formed, e.g.:



where X = Cl, Br.

Conversion of the Hg—X-bonded products to those containing two transition-metal—Hg bonds can be accomplished by adding a second equivalent of the carbonyl anion.

Compounds containing both Hg—X and Hg-transition-metal bonds can rearrange:



in the presence of alkaline Na_2SnO_2 [if $\text{Q} = \text{W}(\text{CO})_3\text{Cp-}\eta^5$ or $\text{Fe}(\text{CO})_2\text{Cp-}\eta^5$] or alkaline $\text{Na}_2\text{S}_2\text{O}_3$ [if $\text{Q} = \text{Mo}(\text{CO})_3\text{Cp-}\eta^5$]⁷.

If only one reactive Hg—X bond is available in RHgX , only one Hg-transition-metal bond is formed:



8.3.3. Group IIB—Transition- and Inner-Transition-Metal Bonds 385
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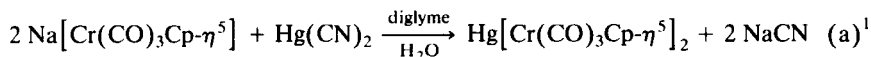
$[\text{Mn}(\text{CO})_5]^-$ react with anodically oxidized Zn in C_6H_6 –MeOH in the presence of bipy to give³ $\text{Zn}[\text{Co}(\text{CO})_4]_2\text{bipy}$ and $\text{Zn}[\text{Mn}(\text{CO})_5]_2\text{bipy}$.

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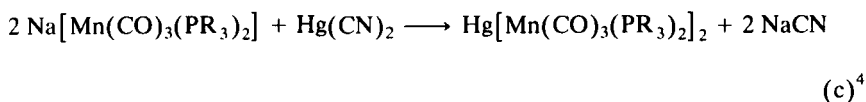
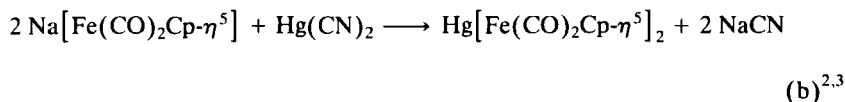
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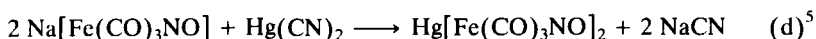
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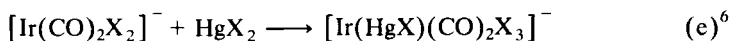
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where R = Ph, OPh, and:



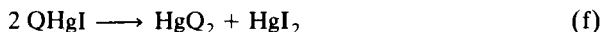
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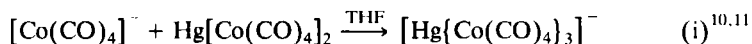


where M = V, Nb, Ta; L = CO, PPh₃ R = Et; and:

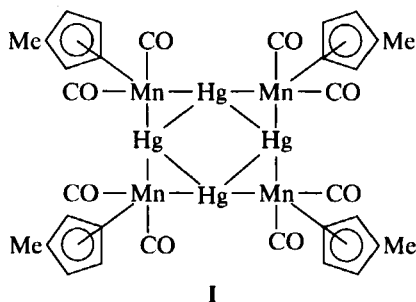


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The compound $\text{Hg}[\text{Co}(\text{CO})_4]_2$ reacts with a further equivalent of the carbonyl anion to give a product containing three Co—Hg bonds:



This method is not limited to the preparation of simple complexes; e.g., $\text{K}[\text{Mn}(\text{CO})_2(\eta\text{-MeC}_5\text{H}_4\text{GeH}_3)]$ reacts with aq HgCl_2 to give I:



which contains both Hg—Mn and Hg—Hg bonds¹² and $[\text{Ru}_3(\text{CO})_9\text{C}_2\text{-Bu-t}]^-$ reacts¹³ with $\text{t-Bu-C}_2\text{Ru}_3(\text{CO})_9\text{HgBr}$ to give $\text{Hg}[\text{Ru}_3(\text{CO})_9\text{C}_2\text{-Bu-t}]_2$. The anions $[\text{M}_3\text{H}(\text{CO})_{11}]^-$, (M = Ru, Os) react with Hg(I) or Hg(II) salts in dry MeOH to give $[\text{M}_3(\text{CO})_{11}\text{Hg}]_3$ clusters¹⁴.

(J. R. CHIPPERFIELD)

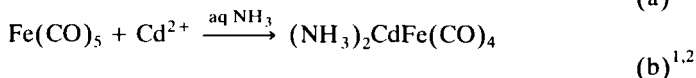
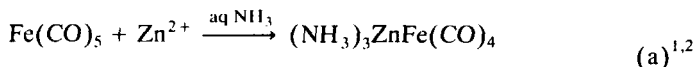
1. R. B. King, F. G. A. Stone, *Inorg. Synth.*, **7**, 99 (1963).
2. E. O. Fischer, R. Böttcher, *Z. Naturforsch., Teil B*, **10b**, 600 (1955).
3. E. O. Fischer, W. Hafner, H. O. Stahl, *Z. Anorg. Allg. Chem.*, **282**, 47 (1955).
4. W. Hieber, M. Höfler, J. Muschi, *Chem. Ber.*, **98**, 311 (1965).
5. W. Hieber, H. Beunter, *Z. Anorg. Allg. Chem.*, **320**, 320, 101 (1963).
6. D. Forster, *Inorg. Chem.*, **11**, 473 (1972).
7. A. N. Nesmeyanov, L. G. Makarova, V. N. Vinogradova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2605 (1972).
8. A. Davison, J. E. Ellis, *J. Organomet. Chem.*, **36**, 113 (1972).
9. K. A. Keblyns, M. Dubeck, *Inorg. Chem.*, **3**, 1646 (1964).
10. A. Vizi-Orosz, L. Papp, L. Markó, *Inorg. Chem. Acta*, **3**, 103 (1969).
11. J. M. Burlitch, R. B. Petersen, H. L. Conder, W. R. Robinson, *J. Am. Chem. Soc.*, **92**, 1783 (1970).
12. W. Gäde, E. Weiss, *Angew. Chem., Int. Ed. Engl.*, **20**, 803 (1981).
13. S. Ermer, K. King, K. I. Hardcastle, E. Rosenberg, A. M. M. Lanfredi, A. Tiripicchio, M. T. Camellini, *Inorg. Chem.*, **22**, 1339 (1983).
14. M. Fajardo, H. D. Holden, B. F. G. Johnson, J. Lewis, P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 24 (1984).

8.3.3. Group IIB–Transition- and Inner-Transition-Metal Bonds	387
8.3.3.2. Reactions of Carbonyls with Divalent Group-IIB Salts	
8.3.3.2.1. Derivatives of Zinc and Cadmium.	

8.3.3.2. Reactions of Carbonyls and Substituted Carbonyls with Divalent Group-IIB Salts

8.3.3.2.1. Derivatives of Zinc and Cadmium.

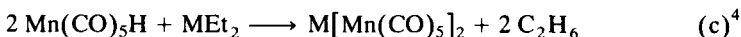
Iron pentacarbonyl reacts with Zn or Cd salts in aq NH_3 to give well-defined, colorless compounds:



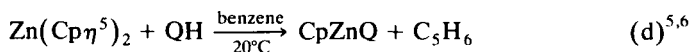
I

If I is treated with dil HOAc, yellow $\text{CdFe}(\text{CO})_4$ is formed. In the presence of a complexing ligand, such derivatives as $\text{py}_2\text{CdFe}(\text{CO})_4$, $(\text{NH}_3)(\text{bipy})\text{ZnFe}(\text{CO})_4$ and $\text{bipyZnFe}(\text{CO})_4$ can be isolated³.

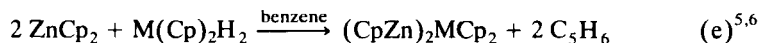
Carbonyl hydrides react similarly with derivatives of Zn or Cd; e.g., $\text{Mn}(\text{CO})_5\text{H}$ and MEt_2 ($\text{M} = \text{Zn}, \text{Cd}$) react on warming to give compounds containing $\text{Mn}-\text{M}$ bonds:



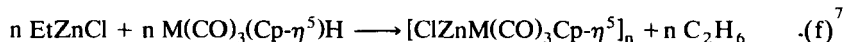
Similarly, $\text{Zn}(\text{Cp})_2$ reacts with $\text{Mo}(\text{CO})_3(\text{Cp}-\eta^5)\text{H}$ or $\text{Mn}(\text{CO})_5\text{H}$:



where $\text{Q} = \text{Mo}(\text{CO})_3\text{Cp}-\eta^5$ or $\text{Mn}(\text{CO})_5$, and with the dihydrido complexes $\text{M}(\text{Cp}-\eta^5)_2\text{H}_2$ ($\text{M} = \text{Mo}, \text{W}$):



When a transition-metal hydride reacts with EtZnCl the organic moiety, rather than the halogen, is replaced:



II

to give a polymer II ($\text{M} = \text{Mo}, \text{W}$).

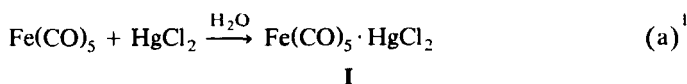
(J. R. CHIPPERFIELD)

1. F. Feigl, P. Krumholz, *Z. Anorg. Allg. Chem.*, **215**, 242 (1933).
2. W. Hieber, E. Fack, *Z. Anorg. Allg. Chem.*, **236**, 83 (1938); see also R. D. Ernst, T. J. Marks, *Inorg. Chem.*, **17**, 1477 (1978).
3. A. T. T. Hsieh, M. J. Mays, R. H. Platt, *J. Chem. Soc., A*, 3296 (1971).
4. N. A. D. Carey, J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 1471 (1968).
5. P. H. M. Budzelaar, J. Boersma, G. J. M. van der Kerk, *J. Organomet. Chem.*, **202**, C71 (1980).
6. P. H. M. Budzelaar, J. Boersma, G. J. M. van der Kerk, A. L. Spek, A. J. M. Duisenberg, *Inorg. Chem.*, **21**, 3777 (1982).
7. J. St. Denis, W. Butler, M. D. Glick, J. P. Oliver, *J. Am. Chem. Soc.*, **96**, 5427 (1924).

388 8.3.3. Group IIB–Transition- and Inner-Transition-Metal Bonds
 8.3.3.2. Reactions of Carbonyls with Divalent Group-IIB Salts
 8.3.3.2.2. Derivatives of Mercury.

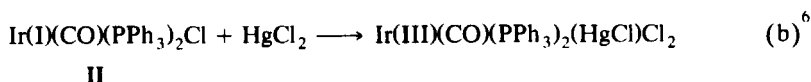
8.3.3.2.2. Derivatives of Mercury.

Carbonyls react with derivatives of Hg(II) to form transition-metal to Hg bonds, the simplest manner being adduct formation. For example, $\text{Fe}(\text{CO})_5$ and HgCl_2 react:

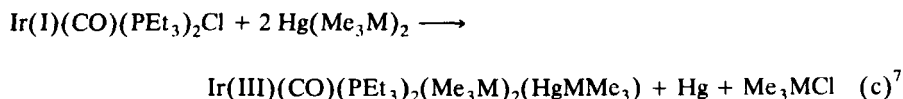


to form the adduct (I). Many adducts can form, e.g., $\text{Co}(\text{CO})_2\text{Cp-}\eta^5 \cdot n \text{HgCl}_2$ ($n = 1$ or 3)^{2,3}, $\text{Fe}(\text{CO})_3[\text{P}(\text{OMe})_3]_2 \cdot \text{HgX}_2$ ⁴, $\text{bipyM}(\text{CO})_3 \cdot \text{HgX}_2$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{Cl}, \text{Br}$)⁵.

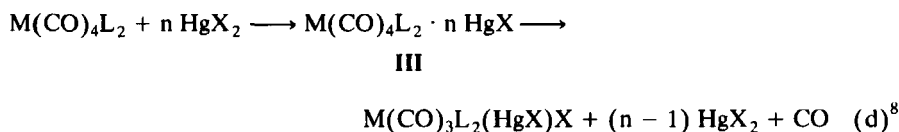
Oxidative addition is another possibility:



After oxidative addition an elimination can take place. For example, $\text{Ir(I)}(\text{CO})(\text{PEt}_3)_2\text{Cl}$, which is similar to **II**, reacts with a Hg derivative with oxidative elimination:

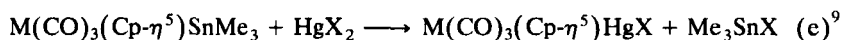


where $\text{M} = \text{Si}$ or Ge . Kinetic study confirms that adduct formation precedes oxidative elimination in the mercuriation of $\text{M}(\text{CO})_4\text{L}_2$:



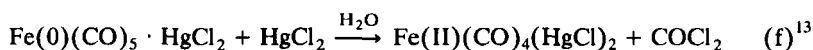
where $\text{M} = \text{Mo}, \text{W}$; $\text{L}_2 = \text{bipy}$ or phen ; $\text{X} = \text{Cl}, \text{Br}$. The nature of the intermediate **III** depends on the solvent; in acetone $n = 2$ and in CH_2Cl_2 $n = 1$.

Mercury(II) halides displace Me_3Sn groups from a transition-metal carbonyl derivative:



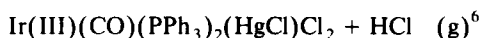
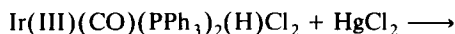
where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$. Similar reactions take place for derivatives of Fe ^{10,11}, Mn and Re ¹¹, and for $\text{Fe}(\text{CO})_2(\text{Cp-}\eta^5)\text{MMe}_3$, where¹² $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$. These reactions take place by initial adduct formation¹¹.

The Fe adduct (I) may react with a further HgCl_2 to form a compound with two Fe—Hg bonds by oxidative elimination:



A similar reaction not involving oxidation is that of a hydrido complex with HgCl_2

with the elimination of HCl:



Reactions of hydrides are therefore similar to those of carbonyls, and by appropriate choice of reactants a product often can be made by either route, as is shown for the mercuration of trinuclear Ru complexes¹⁴:



where X = Br, I and $\text{C}_6\text{H}_9 = \text{t-BuC}\equiv\text{C}-$. These reactions also can produce Mo—Hg¹⁵, W—Hg¹⁵, Ir—Hg^{16,17}, Co—Hg¹⁸ and Ru—Hg¹⁹ bonds.

(J. R. CHIPPERFIELD)

1. H. Hock, H. Stuhlmann, *Chem. Ber.*, **61**, 2097 (1928); **62**, 431 (1929).
2. I. W. Nowell, D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 2393 (1972).
3. I. W. Nowell, D. R. Russell, *J. Chem., Soc., Dalton Trans.*, 2396 (1972).
4. B. Demerseman, G. Bouquet, M. Bigorgne, *J. Organomet. Chem.*, **35**, 341 (1972).
5. K. Edgar, B. F. G. Johnson, J. Lewis, S. B. Wild, *J. Chem. Soc., A*, 2851 (1968).
6. R. S. Nyholm, K. Vrieze, *J. Chem. Soc.*, 5337 (1965).
7. K. A. Hooton, *J. Chem. Soc., A*, 1251 (1971).
8. J. W. McDonald, F. Basolo, *Inorg. Chem.*, **10**, 492 (1971).
9. R. M. G. Roberts, *J. Organomet. Chem.*, **40**, 359 (1972).
10. R. M. G. Roberts, *J. Organomet. Chem.*, **47**, 359 (1973).
11. J. R. Chipperfield, A. C. Hayter, D. E. Webster, *J. Chem. Soc., Dalton Trans.*, 485 (1977).
12. J. R. Chipperfield, A. C. Hayter, D. E. Webster, *J. Chem. Soc., Dalton Trans.*, 921 (1977).
13. J. Lewis, S. B. Wild, *J. Chem. Soc., A*, 69 (1966).
14. R. Fahmy, K. King, E. Rosenberg, A. Tiripicchio, M. T. Camellini, *J. Am. Chem. Soc.*, **102**, 3626 (1980).
15. M. A. Lobo, M. F. Perpignan, M. P. Pardo, M. Cano, *J. Organomet. Chem.*, **254**, 325 (1983).
16. O. Rossel, M. Seco, *Inorg. Chim. Acta*, **74**, 119 (1983).
17. M. Kretschmer, P. S. Pregosin, P. Favre, C. W. Schlaepfer, *J. Organomet. Chem.*, **253**, 17 (1983).
18. L. B. Anderson, H. L. Conder, R. A. Kudaroski, C. Kriley, K. J. Holibaugh, J. Winland, *Inorg. Chem.*, **21**, 2095 (1982).
19. G. R. Clark, S. V. Hoskins, W. R. Roper, *J. Organomet. Chem.*, **234**, C9 (1982).

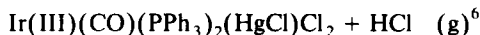
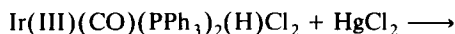
8.3.3.3. by Reactions of Other Transition-Metal Complexes with Group-IIB Derivatives

Compounds containing transition-metal to Hg bonds are prepared this way, but few Zn and Cd compounds are.

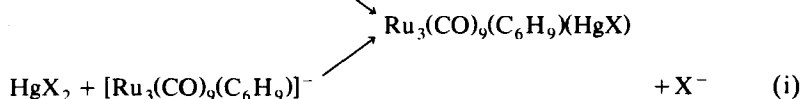
Ferrocene reacts with HgCl_2 in Et_2O to give¹ the adducts red $\text{Fe}(\text{Cp-}\eta^5)_2 \cdot 7 \text{HgCl}_2$ and blue $\text{Fe}(\text{Cp-}\eta^5)_2 \cdot 2 \text{HgCl}_2$, and $\text{Ru}(\text{Cp-}\eta^5)_2$ undergoes a similar reaction². Other adducts are $\text{Ru}(\text{EtCN})_4\text{Cl}_2 \cdot \text{HgCl}_2$ ³, $\text{Rh}(\text{MeCN})(\text{PPh}_3)_2\text{Cl} \cdot \text{HgCl}_2$ ⁴ and $\text{Rh}(\text{RCH}=\text{CH}_2)_2 \cdot \text{HgCl}_2$ ⁵ (R = H or $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$). Hydrido complexes

8.3. Group-IB (Cu, Ag, Au) or -IIB (Zn, Cd, Hg)–Transition-Metal Bonds 389**8.3.3. Group IIB–Transition- and Inner-Transition-Metal Bonds****8.3.3.3. by Reactions of Other Transition-Metal Complexes**

with the elimination of HCl:



Reactions of hydrides are therefore similar to those of carbonyls, and by appropriate choice of reactants a product often can be made by either route, as is shown for the mercuration of trinuclear Ru complexes¹⁴:



where X = Br, I and $\text{C}_6\text{H}_9 = \text{t-BuC}\equiv\text{C}-$. These reactions also can produce Mo—Hg¹⁵, W—Hg¹⁵, Ir—Hg^{16,17}, Co—Hg¹⁸ and Ru—Hg¹⁹ bonds.

(J. R. CHIPPERFIELD)

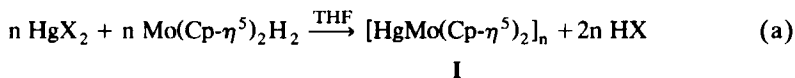
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8.3.3.3. by Reactions of Other Transition-Metal Complexes with Group-IIB Derivatives

Compounds containing transition-metal to Hg bonds are prepared this way, but few Zn and Cd compounds are.

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$M(\text{Cp-}\eta^5)_2\text{H}_2$ ($M = \text{Mo}$ or W) react with HgX_2 ($X = \text{Cl, Br, I, SCN, OAc, CN}$) in THF to give the insoluble derivatives⁶ $M(\text{Cp-}\eta^5)_2(\text{HgX})_2 \cdot n \text{HgX}_2$ ($n = 0, 1/3, 1/2, 2/3, 1$) quantitatively. When low mole ratios of $\text{Mo}(\text{Cp-}\eta^5)_2\text{H}_2$ to HgX_2 are used, polymer I is formed:

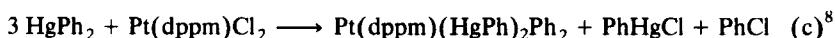


where $Y = \text{Cn, OAc}$. A similar reaction involving elimination of a hydrogen halide is:

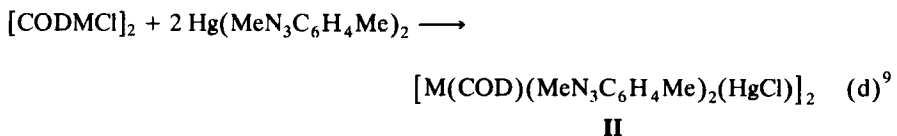


where $X = \text{Cl, Br}$; $Y = \text{F, Cl, Br, I, OAc}$.

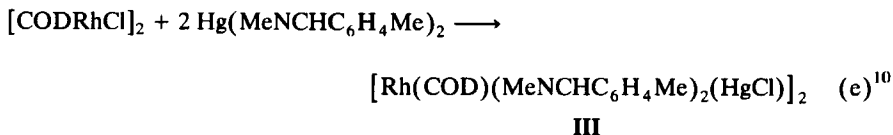
Transition-metal halides also can react with Hg(II) derivatives. For example, Pt(dppm)Cl_2 undergoes oxidative addition with HgPh_2 :



whereas dimeric complexes of Ir and Rh react with Hg triazenides and amidines:

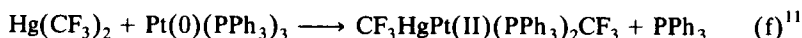


where $M = \text{Ir}$ or Rh , and:

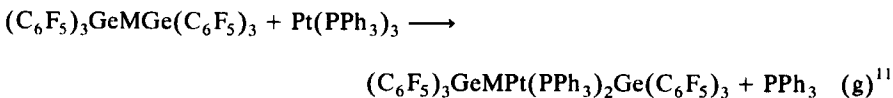


The products of these reactions, **II** and **III**, contain Hg—Rh and Hg—Ir bonds that are bridged by triazenide (**II**) and amidino (**III**) groups.

The Pt complex $\text{Pt(PPh}_3)_3$ reacts with Hg derivatives, such as $\text{Hg}(\text{CF}_3)_2$, by oxidative addition:

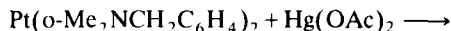
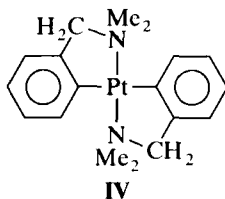


and inserts into an $M\text{—Ge}$ bond ($M = \text{Zn, Cd, Hg}$):

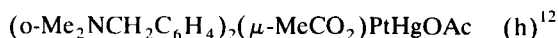


Although the Pt compounds L_2PtR_2 react with Hg(II) derivatives HgX_2 , to give unstable intermediates that eliminate RHgX or Hg , some stable derivatives containing Hg—Pt bonds can be isolated. For example, $\text{Pt(o-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2$ (**IV**) reacts

with $\text{Hg}(\text{OAc})_2$:

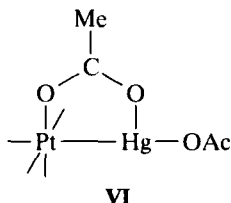


IV

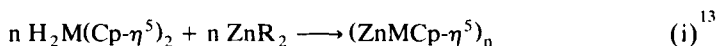


V

to yield a product (**V**) that has a carboxylate-bridge Hg—Pt bond as shown in **VI**:



The analogous reactions of Zn and Cd derivatives are less well studied. Zinc alkyls ZnR_2 ($\text{R} = \text{Et}$, $n\text{-Bu}$) react with transition-metal hydrido complexes, $\text{H}_2\text{M}(\text{Cp-}\eta^5)_2$ ($\text{M} = \text{Mo}$, W):



VII

to yield the polymer **VII**, which either contains linear chains or is a tetramer. The Cd derivative $\text{Cd}(\text{GePh}_3)_2$ also reacts with $\text{Pd}(\text{PPh}_3)_3$ in a manner similar¹¹ to eq. (g), whereas with $\text{Ni}(\text{Cp-}\eta^5)_2$ in toluene at 20°C dark red crystals of $\text{Cd}[\text{Ni}(\text{Cp-}\eta^5)(\text{GePh}_3)(\text{CdGePh}_3)]_2$ are formed¹⁴. These methods also can yield Zn—Ni ¹⁵, Hg—Pt ^{16–19}, Hg—Pd ²⁰, Hg—Nb ²¹, Hg—Ni ²² and Hg—Co ²³ bonds.

(J. R. CHIPPERFIELD)

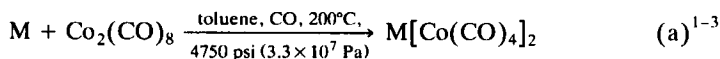
1. R. M. G. Roberts, J. Silver, I. E. G. Morrison, *J. Organomet. Chem.*, **209**, 385 (1981); see also W. H. Morrison, D. N. Hendrickson, *Inorg. Chem.*, **11**, 2912 (1972).
2. A. I. Gusev, Yu. T. Struchkov, *J. Struct. Chem. (Engl. Transl.)*, **12**, 1044 (1971).
3. B. E. Prater, *J. Organomet. Chem.*, **33**, 215 (1971).
4. A. L. Balch, J. Miller, *J. Organomet. Chem.*, **32**, 263 (1971).
5. R. Cramer, J. J. Mrowca, *Inorg. Chim. Acta*, **5**, 528 (1971).
6. M. M. Kubicki, R. Kergoat, J. E. Guerschais, C. Bois, P. L'Haridon, *Inorg. Chem. Acta*, **43**, 17 (1980).
7. R. S. Nyholm, K. Vrieze, *J. Chem. Soc.*, 5331 (1965). R. S. Nyholm, K. Vrieze, *J. Chem. Soc.*, 5337 (1965).
8. F. Glockling, R. J. I. Pollock, *J. Chem. Soc., Dalton Trans.*, 2259 (1974).

392 8.3. Group-IIB (Cu, Ag, Au) or -IIB (Zn, Cd, Hg)–Transition-Metal Bonds
 8.3.3. Group IIB–Transition- and Inner-Transition-Metal Bonds
 8.3.3.4. by Insertion into a Bond Insertion of a Group-IIB Element

9. P. I. van Vliet, M. Kokkes, G. van Koten, K. Vrieze, *J. Organomet. Chem.*, **187**, 413 (1980).
10. P. I. van Vliet, G. van Koten, K. Vrieze, *J. Organomet. Chem.*, **188**, 301 (1980).
11. V. I. Sokolov, O. A. Reutov, *Coord. Chem. Rev.*, **27**, 89 (1978).
12. A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze, A. L. Spek, A. J. M. Duisenberg, *J. Chem. Soc., Chem. Commun.*, 469 (1980).
13. B. R. Francis, M. L. H. Green, T. Luong-thi, G. A. Moser, *J. Chem. Soc., Dalton Trans.*, 1339 (1976).
14. S. N. Titova, V. T. Bychkov, G. A. Domrachev, G. A. Razuvaev, Yu. T. Struchkov, L. N. Zakharov, *J. Organomet. Chem.*, **187**, 167 (1980).
15. P. H. M. Budzelaar, J. Boersma, G. J. M. van der Kerk, *Angew. Chem., Int. Ed. Engl.*, **22**, 329 (1983).
16. M. N. Bochkarev, N. L. Ermolaev, G. A. Razuvaev, Yu. K. Grishin, Yu. A. Ustynyuk, *J. Organomet. Chem.*, **229**, C1 (1982).
17. O. Rossell, J. Sales, M. Seco, *J. Organomet. Chem.*, **236**, 415 (1982).
18. Y. Yamamoto, H. Yamazaki, T. Sakurai, *J. Am. Chem. Soc.*, **104**, 2329 (1982).
19. A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze, A. L. Spek, *Inorg. Chem.*, **21**, 2014 (1982).
20. E. D. Mednikov, V. V. Bashilov, V. I. Sokolov, Yu. L. Slovokhotov, Yu. T. Struchkov, *Polyhedron*, **2**, 141 (1983).
21. R. Kergoat, M. M. Kubicki, J. E. Guerschais, N. C. Norman, A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 633 (1982).
22. L. S. Isaeva, L. N. Morozova, V. V. Bashilov, P. V. Petrovskii, V. I. Sokolov, O. A. Reutov, *J. Organomet. Chem.*, **243**, 253 (1983).
23. F. Cecconi, C. A. Ghilardi, S. Midollini, S. Moneti, *J. Chem. Soc., Dalton Trans.*, 349 (1983).

8.3.3.4. by Insertion into a Metal–Metal Bond Insertion of a Group-IIB Element into Transition-Metal to Transition-Metal Bonds

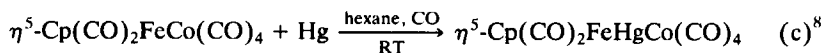
Insertion of Zn, Cd or Hg into a metal–metal bond occurs at high T and pressure:



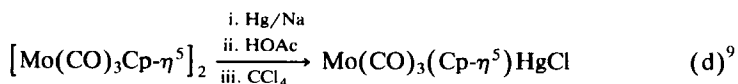
where M = Zn, Cd or Hg, and:



where M = Zn, Cd. These derivatives also can be formed in solution at RT and one of the problems of using Na–Hg as a reducing agent in the preparation of carbonyl anions from carbonyl dimers is the formation of Hg derivatives as side products. Mercury inserts more readily into carbonyls, such as $\text{Co}_2(\text{CO})_8$ or $[\text{Fe}(\text{CO})_2\text{Cp-}\eta^5]_2$, which favor bridging, than into such carbonyls as $\text{Mn}_2(\text{CO})_{10}$, which allows less tendency for bridged metal–metal bonds⁵⁻⁷. Mixed carbonyls, such as $\eta^5\text{-Cp}(\text{CO})_2\text{FeCo}(\text{CO})_4$, also insert Hg:



Under some conditions carbonyl dimers can give rise to noninsertion products:

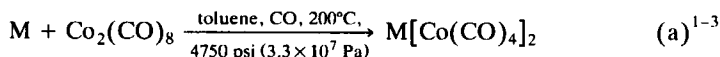


392 8.3. Group-IB (Cu, Ag, Au) or -IIB (Zn, Cd, Hg)–Transition-Metal Bonds
 8.3.3. Group IIB–Transition- and Inner-Transition-Metal Bonds
 8.3.3.4. by Insertion into a Bond Insertion of a Group-IIB Element

9. P. I. van Vliet, M. Kokkes, G. van Koten, K. Vrieze, *J. Organomet. Chem.*, **187**, 413 (1980).
10. P. I. van Vliet, G. van Koten, K. Vrieze, *J. Organomet. Chem.*, **188**, 301 (1980).
11. V. I. Sokolov, O. A. Reutov, *Coord. Chem. Rev.*, **27**, 89 (1978).
12. A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze, A. L. Spek, A. J. M. Duisenberg, *J. Chem. Soc., Chem. Commun.*, 469 (1980).
13. B. R. Francis, M. L. H. Green, T. Luong-thi, G. A. Moser, *J. Chem. Soc., Dalton Trans.*, 1339 (1976).
14. S. N. Titova, V. T. Bychkov, G. A. Domrachev, G. A. Razuvaev, Yu. T. Struchkov, L. N. Zakharov, *J. Organomet. Chem.*, **187**, 167 (1980).
15. P. H. M. Budzelaar, J. Boersma, G. J. M. van der Kerk, *Angew. Chem., Int. Ed. Engl.*, **22**, 329 (1983).
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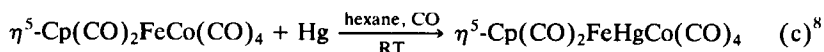
Insertion of Zn, Cd or Hg into a metal–metal bond occurs at high T and pressure:



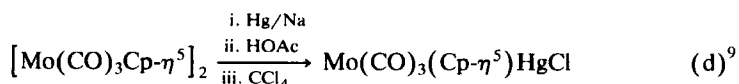
where M = Zn, Cd or Hg, and:



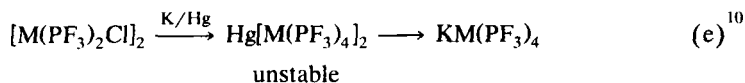
where M = Zn, Cd. These derivatives also can be formed in solution at RT and one of the problems of using Na–Hg as a reducing agent in the preparation of carbonyl anions from carbonyl dimers is the formation of Hg derivatives as side products. Mercury inserts more readily into carbonyls, such as $\text{Co}_2(\text{CO})_8$ or $[\text{Fe}(\text{CO})_2\text{Cp-}\eta^5]_2$, which favor bridging, than into such carbonyls as $\text{Mn}_2(\text{CO})_{10}$, which allows less tendency for bridged metal–metal bonds⁵⁻⁷. Mixed carbonyls, such as $\eta^5\text{-Cp}(\text{CO})_2\text{FeCo}(\text{CO})_4$, also insert Hg:



Under some conditions carbonyl dimers can give rise to noninsertion products:

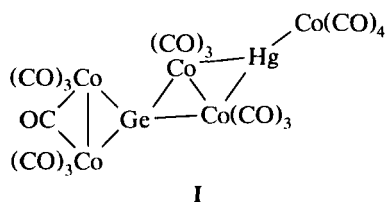


whereas dimers of heavier elements react to form unstable insertion products:

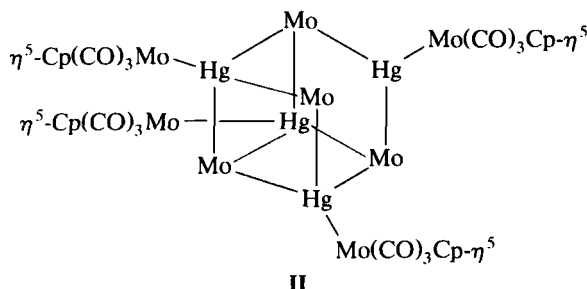


where M = Ir or Rh.

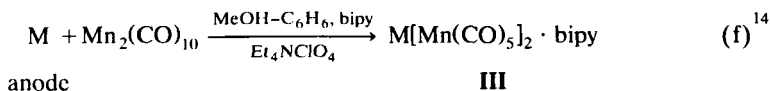
Compound **I** is formed in 5% yield as a by-product in the reduction of $Co_2(CO)_8$ with Na/Hg in benzene–hexane followed by reaction¹¹ with GeI_4 :



It contains a Hg atom bridging two Co atoms. Similarly, $[\eta^5-Cp(CO)_3MoMoHg]_4$ forms by reduction of $[Mo(CO)_3Cp-\eta^5]_2$ by Na/Hg in the presence of 2-chlorobutene and THF. The central metal atoms are arranged in a cubane structure (**II**)¹²:



Metals can be inserted into metal–metal bonds during electrochemical oxidation reactions. The compounds $Hg[M(CO)_5]_2$ (M = Mn or Re), $Hg[Mo(CO)_3Cp-\eta^5]_2$ and $Hg[Fe(CO)_2Cp-\eta^5]_2$ are formed during electrolysis of the carbonyl dimers in dimethoxyethane with Hg electrodes¹³. The electrolytic syntheses of Zn and Cd derivatives:



where M = Zn and Cd, includes **III** and $M[Co(CO)_4]_2 \cdot \text{bipy}$ (M = Zn, Cd). Reaction of Hg with Pd¹⁵ or Pt¹⁶ clusters incorporates Hg atoms.

(J. R. CHIPPERFIELD)

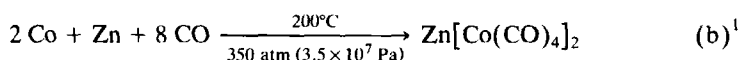
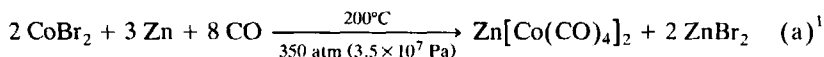
1. G. N. Schrauzer, B. N. Bastian, G. A. Fosselius, *J. Am. Chem. Soc.*, **88**, 4890 (1966).
2. B. Lee, J. M. Burlitch, J. L. Hoard, *J. Am. Chem. Soc.*, **89**, 6362 (1967).
3. W. Hieber, U. Teller, *Z. Anorg. Allg. Chem.*, **249**, 43 (1942).

4. J. M. Burlitch, *J. Chem. Soc., Chem. Commun.*, 887 (1968).
5. R. B. King, in *Advances in Organometallic Chemistry*, Vol. 2, F. G. A. Stone, R. West, eds., Academic Press, New York, 1964, p. 157.
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9. C. Bueno, M. R. Churchill, *Inorg. Chem.*, **20**, 2197 (1981).
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8.3.3.5. Other Synthetic Methods

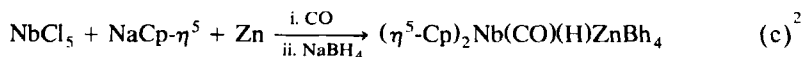
8.3.3.5.1. Reactions of Metals Not Involving Insertion or Exchange

Because transition-metal carbonyls react with Zn, Cd and Hg to form compounds containing metal-metal bonds (see §8.3.3.4), the derivatives can be prepared by combining reactants under carbonyl-forming conditions:



The derivatives $\text{Cd}[\text{Co}(\text{CO})_4]_2$ and $\text{Hg}[\text{Co}(\text{CO})_4]_2$ can be formed similarly.

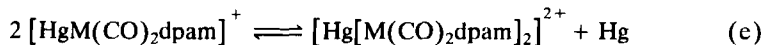
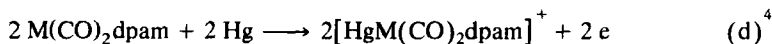
When NbCl_5 is treated under reducing conditions with Zn:



I

the yellow prisms of **I** that are formed contain both H-bridged and direct Nb—Zn bonds. Zinc can be oxidized by $(\eta^5\text{-Cp})_2\text{TiCl}_2$ in toluene to give $[(\eta^5\text{-Cp})_2\text{TiCl}_2\text{ZnCl}_2]$, which contains Cl-bridged Zn—Ti bonds³.

Electrochemical oxidation of the group-IIB metal can generate metal-metal bonds analogously to the manner described in §8.3.3.4. For example, cyclic voltammetry with Hg electrodes shows that $\text{M}(\text{CO})_2\text{dpam}$ ($\text{M} = \text{Cr}, \text{Mo}$) reacts to form Hg—M bonds in two stages:



Similarly, electrochemical oxidation of $\text{Ru}(\text{Cp-}\eta^5)_2$ at Hg electrodes yields $[(\eta^5\text{-Cp})_2\text{RuHgRu}(\text{Cp-}\eta^5)_2]^{2+}$ derivatives that can be isolated as salts^{5,6}.

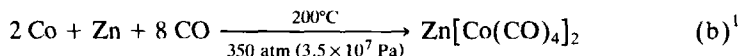
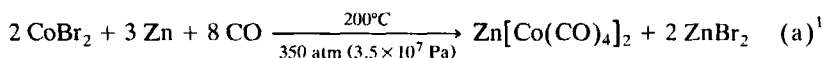
394 **8.3.3. Group IIB—Transition- and Inner-Transition-Metal Bonds**
 8.3.3.5. Other Synthetic Methods
 8.3.3.5.1. Reactions of Metals Not Involving Insertion or Exchange

4. J. M. Burlitch, *J. Chem. Soc., Chem. Commun.*, 887 (1968).
5. R. B. King, in *Advances in Organometallic Chemistry*, Vol. 2, F. G. A. Stone, R. West, eds., Academic Press, New York, 1964, p. 157.
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12. J. Deutscher, S. Fadel, M. L. Ziegler, *Chem. Ber.*, **112**, 2413 (1979).
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8.3.3.5. Other Synthetic Methods

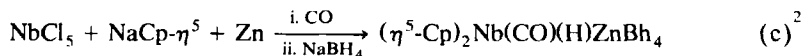
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The derivatives $\text{Cd}[\text{Co}(\text{CO})_4]_2$ and $\text{Hg}[\text{Co}(\text{CO})_4]_2$ can be formed similarly.

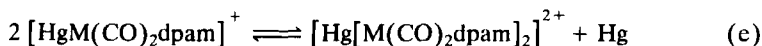
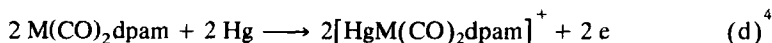
When NbCl_5 is treated under reducing conditions with Zn:



I

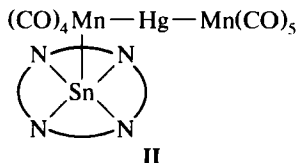
the yellow prisms of **I** that are formed contain both H-bridged and direct Nb—Zn bonds. Zinc can be oxidized by $(\eta^5\text{-Cp})_2\text{TiCl}_2$ in toluene to give $[(\eta^5\text{-Cp})_2\text{TiCl}_2\text{ZnCl}_2]$, which contains Cl-bridged Zn—Ti bonds³.

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When Na-Hg is used as a reducing agent, care must be taken to insure that no undesired Hg is incorporated into the product; e.g., reduction of $[\text{Co}(\text{Cl})\text{np}]\text{BPh}_4$ in THF with Na-Hg followed by BuOH gave the red-brown dimeric npCoHgHgConp in 65% yield⁷, and the reaction of Hg with $[\text{NaMn}(\text{CO})_5]$ and tetraphenylporphyrin-SnCl₂ in THF gave a porphyrin derivative (II) with a Sn—Mn—Hg—Mn chain⁸.



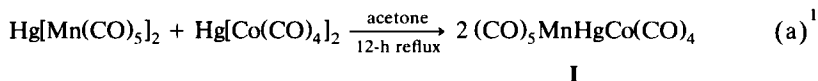
When Na or Hg is mixed with $[\text{Rh}(\text{PMe}_3)_4]\text{Cl}$ or $\text{Rh}(\text{PMe}_3)_3\text{Cl}$ in THF, the cluster $\text{Hg}_6\text{Rh}_4(\text{PMe}_3)_{12}$ forms⁹.

(J. R. CHIPPERFIELD)

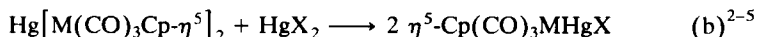
1. W. Hieber, U. Teller, *Z. Anorg. Allg. Chem.*, **249**, 43 (1943).
2. M. A. Porai-Koshits, A. S. Antsyshkina, A. A. Pasynskii, G. G. Sadikov, Yu. V. Skripkin, V. N. Ostrikova, *Inorg. Chem. Acta*, **34**, L285 (1979).
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4. A. M. Bond, R. Colton, J. J. Lackowski, *Inorg. Chem.*, **18**, 1977 (1979).
5. D. N. Hendrickson, Y. S. Sohn, W. H. Morrison, H. B. Gray, *Inorg. Chem.*, **11**, 808 (1972).
6. W. H. Morrison, D. N. Hendrickson, *Inorg. Chem.*, **11**, 2912 (1972).
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8. S. Onaka, Y. Kondo, K. Toriumi, T. Ito, *Chem. Lett.*, 1605 (1980).
9. R. A. Jones, F. M. Real, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 126 (1981).

8.3.3.5.2. Exchange.

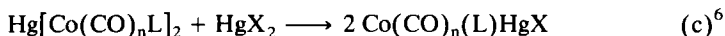
When $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ is mixed with $\text{Hg}[\text{Co}(\text{CO})_4]_2$ in boiling acetone a scrambling takes place, with metal-metal bonds being broken and reformed to give the trimetallic product I:



Similarly, Hg(II) halides yield compounds containing two transition-metal-Hg bonds:



where if M = Cr, X = Cl, Br, I; if M = Mo, X = Cl; if M = W, X = Br. Similar exchanges take place for substituted carbonyls:



where if L = AsMePh₂, n = 3 and X = Br; if L = Ph₂PCH₂CH₂PPh₂, n = 2 and

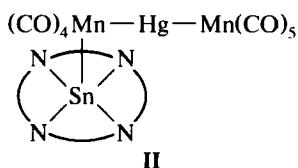
8.3.3. Group IIB–Transition- and Inner-Transition-Metal Bonds

395

8.3.3.5. Other Synthetic Methods

8.3.3.5.2. Exchange.

When Na–Hg is used as a reducing agent, care must be taken to insure that no undesired Hg is incorporated into the product; e.g., reduction of $[\text{Co}(\text{Cl})\text{np}]\text{BPh}_4$ in THF with Na–Hg followed by BuOH gave the red-brown dimeric npCoHgHgConp in 65% yield⁷, and the reaction of Hg with $[\text{NaMn}(\text{CO})_5]$ and tetraphenylporphyrin– SnCl_2 in THF gave a porphyrin derivative (II) with a $\text{Sn}—\text{Mn}—\text{Hg}—\text{Mn}$ chain⁸.



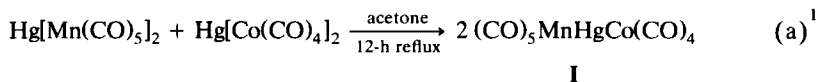
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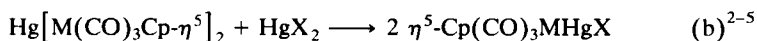
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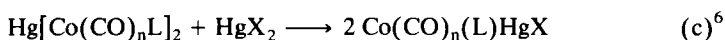
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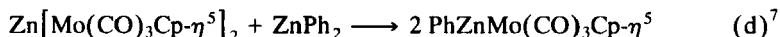


where if $\text{M} = \text{Cr}$, $\text{X} = \text{Cl}$, Br , I ; if $\text{M} = \text{Mo}$, $\text{X} = \text{Cl}$; if $\text{M} = \text{W}$, $\text{X} = \text{Br}$. Similar exchanges take place for substituted carbonyls:

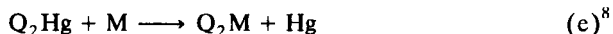


where if $\text{L} = \text{AsMePh}_2$, $n = 3$ and $\text{X} = \text{Br}$; if $\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $n = 2$ and

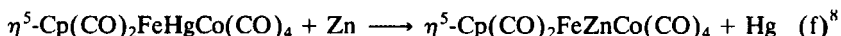
X = Cl. Zinc and Cd complexes react similarly, e.g.:



Another exchange involves Zn or Cd metal in a polar solvent, such as THF or diglyme:



where M = Zn or Cd and Q = $\text{Co}(\text{CO})_4$, $\text{Fe}(\text{CO})_2\text{Cp-}\eta^5$, $\text{Cr}(\text{CO})_3\text{Cp-}\eta^5$, $\text{Mo}(\text{CO})_3\text{Cp-}\eta^5$ and $\text{W}(\text{CO})_3\text{Cp-}\eta^5$. A similar reaction takes place with trimetallic complexes:



These reactions can give unexpected products. When $\text{Hg}[\text{Co}(\text{CO})_4]_2$ reacts with $\text{Hg}(\text{CN})_2$ in alkaline MeOH the cluster $\text{Hg}_9\text{Co}_6(\text{CO})_{18}$ forms⁹.

(J. R. CHIPPERFIELD)

1. M. Zöller, M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, **15**, 162 (1976).
2. A. R. Manning, D. J. Thornhill, *J. Chem. Soc., A*, 637 (1971).
3. M. J. Albright, M. D. Glick, J. P. Oliver, *J. Organomet. Chem.*, **161**, 221 (1978).
4. M. J. Albright, J. P. Oliver, *J. Organomet. Chem.*, **172**, 99 (1979).
5. M. J. Mays, J. D. Robb, *J. Chem. Soc., A*, 329 (1968).
6. J. Newman, A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 241 (1972).
7. J. N. St. Denis, W. Butler, M. D. Glick, J. P. Oliver, *J. Organomet. Chem.*, **129**, 1 (1977).
8. J. M. Burlitch, A. Ferrari, *Inorg. Chem.*, **9**, 563 (1970).
9. J. M. Ragosta, J. M. Burlitch, *J. Chem. Soc., Chem. Commun.*, 1187 (1985).

8.4. The Formation of the Group-IB or -IIB-Group 0 Element Bond

The electropositive nature of the group-IB and -IIB elements excludes the possibility of bonding such as that discussed in §2.10, unless the group-IB or -IIB element is itself bound to a highly electron-withdrawing ligand or ligands. An example of such a case has been demonstrated theoretically¹ for He atom binding to the Be end of BeO. The O atom in BeO captures the Be valence electron pair so effectively, in making the Be—O bond, that the Be end of that molecule trans to the O atom appears almost as Be²⁺. Thus the Be of BeO is a sufficiently powerful σ electron-pair acceptor to engage the 2s pair of He in donation to it. The other noble gases may be capable of similar binding to BeO but they also possess p-orbital electron pairs in their outermost electron shells; because of the filled O atom p-orbitals, these have antibonding π character, which somewhat offsets the favorable σ bonding.

(N. BARTLETT)

1. W. Koch, G. Frenking, J. Gauss, D. Cremer, J. R. Collins, *J. Am. Chem. Soc.*, **109**, 5917 (1987).

Abbreviations

abs	absolute
a.c.	alternating current
Ac	acetyl, CH_3CO
acac	acetylacetonate anion
acacH	acetylacetone, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$
AcO	acetate anion, $\text{CH}_3\text{C}(\text{O})\text{O}$
Ad	adamantyl
ads	adsorbed
AIBN	2,2'-azobis(isobutyronitrile), $2,2'-[(\text{CH}_3)_2\text{CCN}]_2\text{N}_2$
Alk	alkyl
am	amine
amt	amount
Am	amyl, C_5H_{11}
amu	atomic mass unit
anhyd	anhydrous
aq	aqueous
Ar	aryl
asym	asymmetrical, asymmetric
at	atom (not atomic, except in atomic weight)
atm	atmosphere (not atmospheric)
av	average
BBN	9-Borabicyclo[3.3.1]nonane
bcc	body-centered cubic
BD	butadiene
bipy	2,2'-bipyridyl
bipyH	protonated 2,2'-bipyridyl
bp	boiling point
Bu	butyl, C_4H_9
Bz	benzyl, $\text{C}_6\text{H}_5\text{CH}_2$
c-	cyclo (used in formulas)
ca.	circa, about, approximately
catal	catalyst (not catalyzing, catalysis, catalyzed, etc.)
CDT	cyclododecatriene
cf.	compare
Ch.	chapter
CHD	1,3-cycloheptadiene
Chx	cyclohexyl
ChxD	1,3-cyclohexadiene
CI	configuration interaction
Cob	cobalamine
COD	cyclooctadiene
COE	cyclooctene
conc	concentrated (not concentration)
const.	constant
COT	cyclooctatriene
COTe	cyclooctatetraene
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
DCM	dicyclopentadienylmethane
DCME	$\text{Cl}_2\text{CHC}(\text{O})\text{CH}_3$
DCP	1,3-dicyclopentadienylpropane
DDT	dichlorodiphenyltrichloroethane, 1,1,1',-trichloro-2,2-bis-(4-chlorophenyl)ethane
dec	decomposed
DED	1,1-bis(ethoxycarbonyl)ethene-2,2-dithiolate, $[(\text{H}_5\text{C}_2\text{OC}(\text{O}))_2\text{C}=\text{CS}_2]^2$
depe	1,2-bis(diphenylphosphino)ethene, $(\text{C}_6\text{H}_5)_2\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$
DIAD	diindenylanthracenyl
diars	1,2-bis(dimethylarsino)benzene, o-phenylenebis(dimethylarsine), 1,2-(CH_3) ₂ AsC ₆ H ₄ As(CH ₃) ₂
dien	diethylenetriamine, $[\text{H}_2\text{N}(\text{CH}_2)_2]_2\text{NH}$
diglyme	diethyleneglycol dimethylether, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})\text{CH}_3$
dil	dilute
diop	2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}[\text{OCH}(\text{CH}_3)=\text{CH}_2]\text{CH}[\text{OCH}(\text{CH}_3)=\text{CH}_2]\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$
dipda	p-i-PrC ₆ H ₄ CH=CHC ₆ H ₄ -c-p
diphos	1,2-bis(diphenylphosphino)benzene, 1,2-(C_6H_5) ₂ PC ₆ H ₄ P(C_6H_5) ₂
Div.	division
DMA	dimethylacetamide
dme	dropping mercury electrode
DME	1,2-dimethoxyethane, glyme, $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OCH}_3$
DMF	N,N-dimethylformamide, $\text{HC}(\text{O})\text{N}(\text{CH}_3)_2$
DMG	dimethylglyoxime, $\text{CH}_3\text{C}(=\text{NOH})\text{C}(=\text{NOH})\text{CH}_3$
DMP	1,2-dimethoxybenzene, 1,2-(CH_3O) ₂ C ₆ 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-(C_6H_5) ₂ P(CH ₂) ₄ P(C_6H_5) ₂
dppe	1,2-bis(diphenylphosphino)ethane, 1,2-(C_6H_5) ₂ P(CH ₂) ₂ P(C_6H_5) ₂
dppm	bis(diphenylphosphino)methane, $[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{CH}_2$
dppoe	bis(diphenylphosphoryl)ethane
dppp	1,3-bis(diphenylphosphino)propane, 1,3-(C_6H_5) ₂ P(CH ₂) ₃ P(C_6H_5) ₂

dptpe	1,2-bis(di-p-tolylphosphino)ethane, 1,2-(4-CH ₃ C ₆ H ₄) ₂ P(CH ₂) ₂ P (C ₆ H ₄ 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-HS(CH ₂) ₄ SH
DTS	dithiosquarate
ed.	edition, editor
eds.	editors
EDTA	ethylenediaminetetraacetic acid, [HOC(O)] ₂ N(CH ₂) ₂ N[C(O)OH] ₂
e.g.	exempli gratia, for example
EHMO	extended Hückel molecular orbital
emf	electromotive force
en	ethylenediamine, H ₂ N(CH ₂) ₂ 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 ₃ CH ₂
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
Fc	ferrocenyl
fcc	face-centered cubic
ff.	following
Fig	figure
Fl	fluorenyl
Fp	η^5 -C ₅ H ₅ Fe(CO) ₂
fp	freezing point
g	gas
g-at	gram-atom
GLC	gas-liquid chromatography
glyme	1,2-dimethoxyethane, CH ₃ O(CH ₂) ₂ OCH ₃
graph	graphite
GS	ground state
h	hour, hours
H-Cob	cobalamine
HD	1,5-hexadiene
hept	heptyl
Hex	hexyl
HMDB	hexamethyl(Dewar benzene)
hmde	hanging mercury drop electrode
MHI	heptamethylindenyl

HPMA	hexamethylphosphoramide, $[(CH_3)_2N]_3PO$
HOMO	highest occupied molecular orbital
HPLC	high-pressure liquid chromatography
i.e.	id est, that is
Im	imidazole
inter alia	among other things
IPC	isopinocampylborane
IR	infrared
irrev	irreversible
ISC	intersystem crossing
isn	isonicotinamide
l	liquid
L	ligand
LC	ligand centered
LF	ligand field
LFER	linear free-energy relationship
liq	liquid
LMCT	ligand-to-metal charge transfer
Ln	lanthanides, rare earths
LSV	linear-scan voltammetry
LUMO	lowest unoccupied molecular orbital
m	meta
max	maximum
M	metal
MC	metal centered
Me	methyl, CH_3
Men	menthyl
mes	mesitylene, 1,3,5-trimethylbenzene derivative
MeOH	methanol, CH_3OH
mer	meridional; the repeating unit of an oligomer or polymer
mhp	2-hydroxy-6-methylpyridine, 2-HO, 6- $CH_3C_5H_3N$
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
Nuc	nucleophile
NPP	normal pulse polarography
NQR	nuclear quadrupole resonance
NTA	nitritotriacetate
o	ortho
obs	observed

Oct	octyl
ocp	octaethylporphyrin
O _F	oxidation factor
O _h	octahedral
Oq	oxyquinolate
ox.	oxidation
p	para
p.	page
P	pressure
Pat.	patent
pet.	petroleum
Ph	phenyl, C ₆ H ₅
phen	1,10-phenanthroline
Ph ₂ PPy	2-(diphenylphosphino)pyridine, 2-(C ₆ H ₅) ₂ PC ₅ H ₄ N
pip	piperidine, C ₅ H ₁₀ N
PMDT	pentamethyldiethylenetriamine, (CH ₃) ₂ N(CH ₂) ₂ N(CH ₃)(CH ₂) ₂ N(CH ₃) ₂
PMR	proton magnetic resonance
pn	propylene-1,3-diamine, 1,3-H ₂ NCH ₂ CH ₂ CH ₂ NH ₂
pos	positive
Po-tol ₃	tri-o-tolylphosphine
pp.	pages
ppb	parts per billion
ppm	parts per million
ppn	bis(diphenylphosphino)amine, [(C ₆ H ₅) ₂ P] ₂ NH
ppt	precipitate
Pr	propyl, C ₃ H ₇
PSS	photostationary state
PVC	poly(vinyl chloride)
py	pyridine, C ₅ H ₅ N
pyr	pyrazine
pz	pyrazolyl
PZE	potential of zero charge
rac	racemic mixture, racemate
R	organic group; universal gas constant
RDE	rotated disk electrode
RE	rare earths, lanthanides
red.	reduction
Redox	reduction-oxidation reactions
ref.	reference
rev	reversible
rf	radiofrequency
RF	reduction factor
R _F	R group with substituted F
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	sepulchrate, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane

Sia	Diisamyl
SMAD	solvated metal-atom dispersed
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
TGL	triethyleneglycol dimethylether
THF	tetrahydrofuran
THP	tetrahydropyran
THT	tetrahydrothiophene
Thx	thexyl
TLC	thin-layer chromatography
TMED	N,N,N',N'-tetramethylethylenediamine, (CH ₃) ₂ N(CH ₂) ₂ N(CH ₃) ₂
tmen	N,N,N',N'-tetramethylethylenediamine
TMP	2,2,6,6-tetramethylpiperidyl
TMPH	2,2,6,6-tetramethylpiperidine, 2,2,6,6-(CH ₃) ₄ C ₅ H ₇ N
Tol	tolyl, C ₆ H ₄ CH ₃ , p-tolyl
Tos	tosyl, tolylsulfonyl, 4-CH ₃ C ₆ H ₄ SO ₂
TPA	tetraphenylarsonium ion, [(C ₆ H ₅) ₄ As] ⁺
TPPO	triphenylphosphineoxide
triars	bis-[-(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] ₂ 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
Y	often used for S, Se
yr.	year
§	section
η	hapto designator

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.

AcB₂

B₂Ac

Crystal chemistry: 6.7.2.3

Ag

Ag

Reaction with CO: 8.2.2.2.1

AgAuCu

AgAuCu

Formation: 8.2.2.1.1

AgBa

BaAg

Formation: 7.3.3.1.5

AgBa₃

Ba₃Ag

Formation: 7.3.3.1.5

AgBe₁₂

Be₁₂Ag

Formation: 7.3.3.1.1

- AgCa**
 CaAg
 Formation: 7.3.3.1.3
AgCa₃
 Ca₃Ag
 Formation: 7.3.3.1.3
AgCu
 AgCu
 Formation: 8.3.2.2.4
AgLi
 LiAg
 Dissociation energy: 7.3.1.3.2
 Formation: 7.3.1.2
AgLi₁₂
 Li₁₂Ag
 Formation: 7.3.1.2
AgMg₃
 Mg₃Ag
 Formation: 7.3.3.1.2
AgMn
 AgMn
 Formation: 8.3.2.2.4
AgMo
 AgMo
 Formation: 8.3.2.2.4
AgO₃*C₃
AgSr
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Ag₂
 Ag₂
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 CaAg₂
 Formation: 7.3.3.1.3
Ag₂Na
 NaAg₂
 Formation: 7.3.1.1.2, 7.3.1.2
Ag₂O₆*C₆
Ag₂Sr
 SrAg₂
 Formation: 7.3.3.1.4
Ag₂Sr₃
 Sr₃Ag₂
 Formation: 7.3.3.1.4
Ag₃
 Ag₃
 Formation: 8.2.2.1.1
Ag₃Ba₂
 Ba₂Ag₃
 Formation: 7.3.3.1.5
Ag₃Ba₄
 Ba₄Ag₃
 Formation: 7.3.3.1.5
Ag₃Ca₅
 Ca₅Ag₃
 Formation: 7.3.3.1.3
Ag₃Cu₂
 Ag₃Cu₂
 Formation: 8.2.2.1.1
Ag₃Li₁₀
 Li₁₀Ag₃
 Formation: 7.3.1.2
Ag₃Sr₇
 Sr₇Ag₃
 Formation: 7.3.3.1.4
Ag₄
 Ag₄
 Formation: 8.2.2.1.1
Ag₄Ba
 BaAg₄
 Formation: 7.3.3.1.5
Ag₄Cu
 Ag₄Cu
 Formation: 8.2.2.1.1
Ag₄Li₉
 Li₉Ag₄
 Formation: 7.3.1.2
Ag₅
 Ag₅
 Formation: 8.2.2.1.1
Ag₅Ba
 BaAg₅
 Formation: 7.3.3.1.5
Ag₅Ba₃
 Ba₃Ag₅
 Formation: 7.3.3.1.5
Ag₅Sr
 SrAg₅
 Formation: 7.3.3.1.4
Ag₆
 Ag₆
 Formation: 8.2.2.1.2
Ag₇Ca₂
 Ca₂Ag₇
 Formation: 7.3.3.1.3
Ag₈Ca₃
 Ca₃Ag₈
 Formation: 7.3.3.1.3
Ag₉Ca₂
 Ca₂Ag₉
 Formation: 7.3.3.1.3
Al_{0.5}B_{0.05}Hf_{0.45}
B_{0.05}Al_{0.5}Hf_{0.45}
 Crystal chemistry: 6.7.2.1

Al**Al**Reaction with AlX_3 : 6.2.2.1Reaction with elemental S, Se, Te:
6.2.3**(Al,Hf)₉(Al,Mo)₄B** $\text{B}(\text{Al,Hf})_9(\text{Al,Mo})_4$

Crystal chemistry: 6.7.2.1

(Al,Mo)₄B*(Al,Hf)₉**AlBMo** $\text{B}(\text{Al,Mo})$

Crystal chemistry: 6.7.2.2

 BAlMo

Crystal chemistry: 6.7.2.2

AlB₂ AlB_2

Crystal structure: 6.7.2.3, 6.7.2.4

Preparation: 6.7.3.2, 6.7.3.5

AlB₂Cr₂ B_2AlCr_2

Crystal chemistry: 6.7.2.2

AlB₂Fe₂ B_2AlFe_2

Crystal chemistry: 6.7.2.2

AlB₂Mn₂ B_2AlMn_2

Crystal chemistry: 6.7.2.2

AlB₄Cr₃ B_4AlCr_3

Crystal chemistry: 6.7.2.2

AlB₄Lu B_4AlLu

Crystal chemistry: 6.7.2.3

AlB₄Yb B_4AlYb

Crystal chemistry: 6.7.2.3

AlB₆Yb₂ B_6AlYb_2

Crystal chemistry: 6.7.2.3

AlB₁₂ AlB_{12}

Crystal structure: 6.7.2.4

Preparation: 6.7.3.5

AlB₁₄Mg MgAlB_{14} Crystal structure and lattice
parameters: 6.7.2.4.5**AlBr₃** AlBr_3

Reaction with elemental Al: 6.2.2.1

Al*C₃H₉**Al*C₆H₁₅****Al*C₈H₁₉****Al*C₁₂H₂₇****AlCl** AlCl

Formation: 6.2.2.1

AlCl₃ AlCl_3

Reaction with elemental Al: 6.2.2.1

AlCoNO₄P₂*C₅₈H₄₅**AlFeNO₂*C₃₃H₄₀****AlK*C₆H₁₅****AlK*C₈H₂₀****Al₂BRe₃** BAl_2Re_3

Crystal chemistry: 6.7.2.1

Al₂B₄H₈ $\text{Al}_2(\text{BH}_2)_4$

Formation: 6.2.2.2

Al₂Br₄ $(\text{AlBr}_2)_2$

Formation: 6.2.2.1

Al₂*C₁₆H₃₆**Al₂CdCl₈** $\text{Cd}(\text{AlCl}_4)_2$

Formation: 8.2.3.2

Al₂Cd₂Cl₈ $\text{Cd}_2(\text{AlCl}_4)_2$

Formation: 8.2.3.2

Al₂Cl₄ $(\text{AlCl}_2)_2$

Formation: 6.2.2.1

Al₂K₂*C₂₄H₅₄**Al₂P₂Pt*C₄₂H₄₈****Al₂Si₈*C₂₈H₇₆****Al_{2.7}BNi_{20.3}** $\text{BAl}_{2.7}\text{Ni}_{20.3}$

Crystal chemistry: 6.7.2.1

Al_{2.7}B₁₀₄Cu₂ $\text{Al}_{2.7}\text{B}_{104}\text{Cu}_2$

Formation: 6.7.2.5.2

Structure: 6.7.2.5.3

Al₃BCo₂₀ $\text{BAl}_3\text{Co}_{20}$

Crystal chemistry: 6.7.2.1

Al₃BHf₅ BAl_3Hf_5

Crystal chemistry: 6.7.2.1

Al₃BTa₅ BAl_3Ta_5

Crystal chemistry: 6.7.2.1

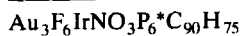
Al₃BZr₅ BAl_3Zr_5

Crystal chemistry: 6.7.2.1

Al₃N₂*C₇H₂₁**Al₄BN₃*C₁₂H₃₆**

- Al₅B₆Ru₉**
 Al₅B₆Ru₉
 Crystal chemistry: 6.7.2.2
Al₅K₃*C₄₀H₉₀
Al₆B₆N₆*C₂₄H₇₂
Al₇Te₁₀
 Al₇Te₁₀
 Formation: 6.2.3
AmB₂
 AmB₂
 Crystal structure: 6.7.2.4
AmB₄
 AmB₄
 Crystal structure and lattice parameters: 6.7.2.4.1
 Thermal stability: 6.7.2.4.1
AmB₆
 AmB₆
 Crystal structure and lattice parameters: 6.7.2.4.2
 Thermal stability: 6.7.2.4.2
AmBe₁₃
 AmBe₁₃
 Formation: 7.4.2.1
AsB₃CoN₄O₄*C₆₂H₅₇
AsB₄F₆H₃
 (BF₂)₃B·AsH₃
 Formation: 6.2.2.1
AsB₁₀Cl₂*C₂H₁₁
As*C₁₈H₁₅
AsF₅
 AsF₅
 Reaction with elemental Cd: 8.2.3.2
 Reaction with elemental Hg: 8.2.5.1
AsF₆Hg₃
 Hg₃(AsF₆)
 Formation: 8.2.5.1
AsH₃
 AsH₃
 Reaction with BF: 6.2.2.1
As₂Cd₃F₁₂
 Cd₃(AsF₆)₂
 Formation: 8.2.3.2
As₂Cd₄F₁₂
 Cd₄(AsF₆)₂
 Formation: 8.2.3.2
As₂Cl₂Rh*C₂₆H₂₇
As₂Cl₃HgRh*C₂₆H₂₆
As₂F₁₂Hg₂
 Hg₂(AsF₆)₂
 Reaction with ArH: 8.2.4.3
 Reaction with EPh₃: 8.2.4.2.4
As₂F₁₂Hg₃
 Hg₃(AsF₆)₂
 Formation: 8.2.5.1
As₂F₁₂Hg₄
 Hg₄(AsF₆)₂
 Formation: 8.2.5.1
As₃F₁₂Hg₂*C₁₈H₁₅
Au
 Au
 Reaction with (Ph₂P)₂CH₂: 8.2.2.2.1
 Reaction with CO: 8.2.2.2.1
AuBFe₄O₁₂P*C₃₀H₁₇
AuB₂CoP*C₃₀H₃₃
AuB₂PRh*C₃₄H₄₃
AuB₄P*C₂₀H₂₂
AuB₅P*C₁₈H₂₃
AuB₆NS₂*C₅H₂₂
AuB₉NP*C₂₅H₃₀
AuB₉NS₂*C₇H₂₁
AuB₁₈N*C₂₀H₄₂
AuBa
 BaAu
 Formation: 7.3.3.1.5
AuBe
 BeAu
 Formation: 7.3.3.1.1
AuBe₅
 Be₅Au
 Formation: 7.3.3.1.1
AuCa
 CaAu
 Formation: 7.3.3.1.3
AuCa₂
 Ca₂Au
 Formation: 7.3.3.1.3
AuClO₁₀Os₃P*C₂₈H₁₅
AuClP*C₁₈H₁₅
AuClP₃Pt*C₅₄H₄₅
AuCl₃
 AuCl₃
 Reaction with R₂PCH₂PR₂: 8.2.2.3.3
AuCoO₄P*C₂₂H₁₅
AuCrO₃P*C₂₆H₂₀
AuCs
 CsAu
 Dissociation energy: 7.3.1.4
 Formation: 7.3.1.2, 7.3.1.4
AuCu*Ag
AuGeNa₂
 Na₂AuGe
 Formation: 7.3.1.3.3
AuGeP*C₃₆H₃₀

- AuK**
 KAu
 Formation: 7.3.1.2
- AuK₂**
 K₂Au
 Formation: 7.3.1.2
- AuLi₃**
 Li₃Au
 Formation: 7.3.1.2
- AuMg**
 MgAu
 Formation: 7.3.3
- AuMg₂**
 Mg₂Au
 Formation: 7.3.3.1.2
- AuMg₃**
 Mg₃Au
 Formation: 7.3.3.1.2
- AuMoO₃P*C₂₆H₂₀
 AuNP₃S*C₄₉H₄₂
- AuNa**
 NaAu
 Formation: 7.3.1.2, 7.3.1.3.3
- AuNa₂**
 Na₂Au
 Formation: 7.3.1.2
- AuNa₂Sn**
 Na₂AuSn
 Formation: 7.3.1.3.3
- AuO*C
 AuO₂*C₂
 AuO₃PW*C₂₆H₂₀
 AuO₁₀Os₃P*C₂₈H₁₆
 AuP*C₁₉H₁₈
 AuP₂S₂Tl*C₂₆H₂₄
- AuRb**
 RbAu
 Formation: 7.3.1.2
- AuSr**
 SrAu
 Formation: 7.3.3.1.4
- AuSr₂**
 Sr₂Au
 Formation: 7.3.3.1.4
- AuSr₃**
 Sr₃Au
 Formation: 7.3.3.1.4
- Au₂**
 Au₂
 Formation: 8.2.2.1.1
 Au₂BFe₄O₁₂P₂*C₂₄H₃₁
 Au₂BFe₄O₁₂P₂*C₃₆H₃₁
 Au₂BFe₄O₁₂P₂*C₄₈H₃₁
- Au₂B₈N₂S₄*C₁₀H₃₀
 Au₂B₁₈N₂S₄*C₁₄H₄₂
- Au₂Ba**
 BaAu₂
 Formation: 7.3.3.1.5
- Au₂Ba₃**
 Ba₃Au₂
 Formation: 7.3.3.1.5
- Au₂Be**
 BeAu₂
 Formation: 7.3.3.1.1
- Au₂Ca**
 CaAu₂
 Formation: 7.3.3.1.3
- Au₂Ca₅**
 Ca₅Au₂
 Formation: 7.3.3.1.3
- Au₂Cl₂P₂*C₂₅H₂₂
- Au₂K**
 KAu₂
 Formation: 7.3.1.2
- Au₂Mg₅**
 Mg₅Au₂
 Formation: 7.3.3.1.2
- Au₂Na**
 NaAu₂
 Formation: 7.3.1.2
- Au₂Rb**
 RbAu₂
 Formation: 7.3.1.2
- Au₂Sr**
 SrAu₂
 Formation: 7.3.3.1.4
- Au₂Sr₃**
 Sr₃Au₂
 Formation: 7.3.3.1.4
- Au₃Ba₂**
 Ba₂Au₃
 Formation: 7.3.3.1.5
- Au₃Ca**
 CaAu₃
 Formation: 7.3.3.1.3
- Au₃Ca₄**
 Ca₄Au₃
 Formation: 7.3.3.1.3
- Au₃Ca₅**
 Ca₅Au₃
 Formation: 7.3.3.1.3
- Au₃Ca₇**
 Ca₇Au₃
 Formation: 7.3.3.1.3



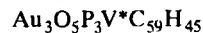
Formation: 7.3.1.2



Formation: 7.3.1.2



Formation: 7.3.3.1.2



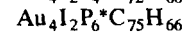
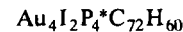
Formation: 7.3.3.1.1



Formation: 7.3.3.1.3



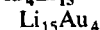
Formation: 7.3.3.1.3



Formation: 7.3.1.1.3



Formation: 7.3.1.3.3



Formation: 7.3.1.2



Formation: 7.3.3.1.5



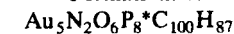
Formation: 7.3.3.1.3



Formation: 7.3.1.1.3, 7.3.1.2



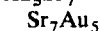
Formation: 7.3.1.2



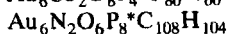
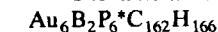
Formation: 7.3.1.2



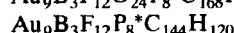
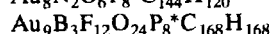
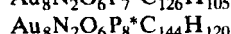
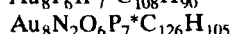
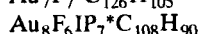
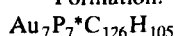
Formation: 7.3.3.1.4



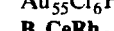
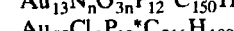
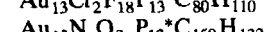
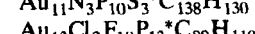
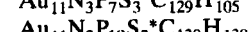
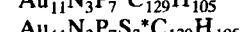
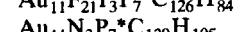
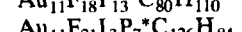
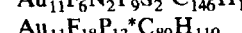
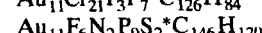
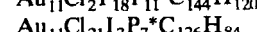
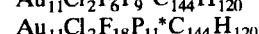
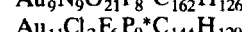
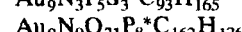
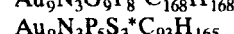
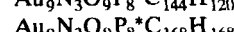
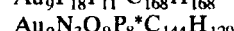
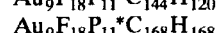
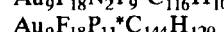
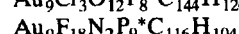
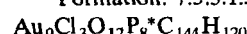
Formation: 7.3.3.1.4



Formation: 7.3.3.1.3



Formation: 7.3.3.1.3



Crystal chemistry: 6.7.2.1



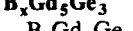
Crystal chemistry: 6.7.2.1



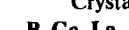
Crystal chemistry: 6.7.2.1



Crystal chemistry: 6.7.2.1



Crystal chemistry: 6.7.2.1



Crystal chemistry: 6.7.2.1

B_xGe₃Tb₅
 B_xGe₃Tb₅
 Crystal chemistry: 6.7.2.1
B_xHoRh₃
 B_xHoRh₃
 Crystal chemistry: 6.7.2.1
B_xIn₃Sc
 B_xIn₃Sc
 Crystal chemistry: 6.7.2.1
B_xIr₃Sc
 B_xIr₃Sc
 Crystal chemistry: 6.7.2.1
B_xIr₃Zr
 B_xIr₃Zr
 Crystal chemistry: 6.7.2.1
B_xLaRh₃
 B_xLaRh₃
 Crystal chemistry: 6.7.2.1
B_xLuRh₃
 B_xLuRh₃
 Crystal chemistry: 6.7.2.1
B_xNdRh₃
 B_xNdRh₃
 Crystal chemistry: 6.7.2.1
B_xNd₅Si₃
 B_xNd₅Si₃
 Crystal chemistry: 6.7.2.1
B_xPb₃Sc
 B_xPb₃Sc
 Crystal chemistry: 6.7.2.1
B_xRh₃Sc
 B_xRh₃Sc
 Crystal chemistry: 6.7.2.1
B_xRh₃Sm
 B_xRh₃Sm
 Crystal chemistry: 6.7.2.1
B_xRh₃Tb
 B_xRh₃Tb
 Crystal chemistry: 6.7.2.1
B_xRh₃Th
 B_xRh₃Th
 Crystal chemistry: 6.7.2.1
B_xRh₃Tm
 B_xRh₃Tm
 Crystal chemistry: 6.7.2.1
B_xRh₃U
 B_xRh₃U
 Crystal chemistry: 6.7.2.1
B_xRh₃Y
 B_xRh₃Y
 Crystal chemistry: 6.7.2.1
B_xRh₃Yb
 B_xRh₃Yb
 Crystal chemistry: 6.7.2.1

B_xScSn₃
 B_xScSn₃
 Crystal chemistry: 6.7.2.1
B_xScTi₃
 B_xScTi₃
 Crystal chemistry: 6.7.2.1
B_xSi₃Tb₅
 B_xSi₃Tb₅
 Crystal chemistry: 6.7.2.1
B_xW
 B_xW
 Formation: 6.7.2.5.2
B_{0.05}Fe_{0.95}
 Fe₂₃B₆
 Crystal chemistry: 6.7.2.1
B_{0.05}Hf_{0.45}*Al_{0.5}
B_{0.15}Fe_{0.85}
 Fe₃B
 Crystal chemistry: 6.7.2.1
B_{0.20}Fe_{0.80}
 Fe₃B
 Crystal chemistry: 6.7.2.1
B_{0.48}Si₃V₅
 B_{0.48}Si₃V₅
 Crystal chemistry: 6.7.2.1
B_{0.5}InNi₃
 B_{0.5}InNi₃
 Crystal chemistry: 6.7.2.1
B_{0.7}Pt
 B_{0.7}Pt
 Crystal chemistry: 6.7.2.1
B
 B,β-rhombohedral
 Structure: 6.7.2.5.3
B
 Reaction with B₂O₃: 6.2.3
 Reaction with BX₃: 6.2.2.1
B*(Al,Hf)₉(Al,Mo)₄
BBe₄
 Be₄B
 Hot-pressing: 6.7.5.2
BBr*C₂H₆
BBr*C₁₂H₁₀
BBrFeNO₃*C₇H₉
BBrN₂*C₄H₁₂
BBrO₂*C₂H₆
BBr₃
 BBr₃
 Reaction with BX: 6.2.2.1
 Reaction with elemental Hg: 6.2.2.2
 Reaction with H₂ and MCl₄: 6.7.3.2
BBr₃N*C₆H₁₅
B*C₃H₉
B*C₅H₉

- B***C₁₀H₁₁
B*C₁₀H₁₇
B*C₁₁H₁₁
B*C₁₂H₁₃
B*C₁₂H₂₇
B*C₃₄H₂₅
BCa₂Ni₂₁
 BCa₂Ni₂₁
 Crystal chemistry: 6.7.2.1
BCeCo₄
 BCeCo₄
 Crystal chemistry: 6.7.2.1
BCe₂Fe₁₄
 BCe₂Fe₁₄
 Crystal chemistry: 6.7.2.1
BClF₁₅IrOP₂*C₅₅H₃₀
BClMn₂O₈P₂*C₄₄H₃₀
BClN₂*C₄H₁₂
BClO₂*C₂H₆
BClO₃Ru*C₇H₆
BCl₃MnO₄P*C₂₂H₁₅
BCl₂N₂Pd*C₅H₁₅
BCl₃
 BCl₃
 Reaction with B₂O₂: 6.2.3
 Reaction with BX: 6.2.2.1
 Reaction with Cu atoms: 6.2.2.4
 Reaction with elemental Hg: 6.2.2.2
 Reaction with H₂ and MCl₄: 6.7.3.2
 Reaction with L₂Pt(C₂H₄),
 L₂Pt(BF₃)₂: 6.5.2.1
 Reaction with L₃Pt, L₂PtSiF₄: 6.5.2.1
 Reaction with TiCl₄, CoCl₂, TaBr₅:
 6.7.4.1.1
BCl₃P₂Pt*C₃₆H₃₀
BCo
 BCo
 Crystal chemistry: 6.7.2.2
 CoB
 Formation: 6.7.4.1.1
BCo*C₁₁H₁₃
BCo*C₁₄H₂₀
BCo*C₁₆H₁₅
BCo*C₂₁H₂₆
BCoMo
 BCoMo
 Crystal chemistry: 6.7.2.1
BCoN*C₁₃H₂₀
BCoN*C₂₁H₁₉
BCoNSi*C₁₅H₂₇
BCoN₃O₃*C₃H₉
BCoNb
 BCoNb-l,h
 Crystal chemistry: 6.7.2.1
BCoO₂*C₁₃H₁₁
BCoO₃*C₁₄H₁₂
BCoRe
 BCoRe
 Crystal chemistry: 6.7.2.1
BCoTa
 BCoTa-l,h
 Crystal chemistry: 6.7.2.1
BCoW
 BCoW
 Crystal chemistry: 6.7.2.1
B(Co,Mo)
 B(Co,Mo)
 Crystal chemistry: 6.7.2.2
B(Co,W)
 B(Co,W)
 Crystal chemistry: 6.7.2.2
BCo₂
 BCo₂
 Crystal chemistry: 6.7.2.1
 Co₂B
 Preparation: 6.7.3.6
BCo₂NO₆*C₁₄H₁₈
BCo₂Nb
 BCo₂Nb
 Crystal chemistry: 6.7.2.1
B(Co,Ni)₂Nb
 B(Co,Ni)₂Nb
 Crystal chemistry: 6.7.2.1
B(Co,Ni)₂Ta
 B(Co,Ni)₂Ta
 Crystal chemistry: 6.7.2.1
BCo₃
 BCo₃
 Crystal chemistry: 6.7.2.1
BCo₃NO₉*C₁₅H₁₅
B(Co,Re)₃
 B(Co,Re)₃
 Crystal chemistry: 6.7.2.1
BCo₄Dy
 BCo₄Dy
 Crystal chemistry: 6.7.2.1
BCo₄Er
 BCo₄Er
 Crystal chemistry: 6.7.2.1
BCo₄Gd
 BCo₄Gd
 Crystal chemistry: 6.7.2.1
BCo₄Ho
 BCo₄Ho
 Crystal chemistry: 6.7.2.1
BCo₄La
 BCo₄La
 Crystal chemistry: 6.7.2.1

- B₂Co₄Lu**
 B₂Co₄Lu
 Crystal chemistry: 6.7.2.1
- B₂Co₄Nd**
 B₂Co₄Nd
 Crystal chemistry: 6.7.2.1
- B₂Co₄Pr**
 B₂Co₄Pr
 Crystal chemistry: 6.7.2.1
- B₂Co₄Sm**
 B₂Co₄Sm
 Crystal chemistry: 6.7.2.1
- B₂Co₄Tb**
 B₂Co₄Tb
 Crystal chemistry: 6.7.2.1
- B₂Co₄Tm**
 B₂Co₄Tm
 Crystal chemistry: 6.7.2.1
- B₂Co₄Y**
 B₂Co₄Y
 Crystal chemistry: 6.7.2.1
- B₂Co_{4.6}Si₂**
 B₂Co_{4.6}Si₂
 Crystal chemistry: 6.7.2.1
- B₂Co₂₀*Al₃**
- B₂Cr**
 B₂Cr-l,h
 Crystal chemistry: 6.7.2.2
 CrB
 Hot-pressing: 6.7.5.1
 Preparation: 6.7.3.4
 Sintering: 6.7.5.1
- B₂CrNaO₇*C₁₇H₂₄**
- B₂(Cr,Os)**
 B₂(Cr,Os)
 Crystal chemistry: 6.7.2.2
- B₂(Cr,Re)**
 B₂(Cr,Re)
 Crystal chemistry: 6.7.2.2
- B₂(Cr,Ru)**
 B₂(Cr,Ru)
 Crystal chemistry: 6.7.2.2
- B₂Cr₂**
 B₂Cr₂
 Crystal chemistry: 6.7.2.1
- B₂(Cr,Mo)₂**
 B₂(Cr,Mo)₂
 Crystal chemistry: 6.7.2.1
- B₂(Cr,V)₂**
 B₂(Cr,V)₂
 Crystal chemistry: 6.7.2.1
- B₂Cr_{4.5}P₂**
 B₂Cr_{4.5}P₂
 Crystal chemistry: 6.7.2.1
- B₂Cr₅Si₃**
 B₂Cr₅Si₃
 Crystal chemistry: 6.7.2.1
- B₂DyRh₃**
 B₂DyRh₃
 Crystal chemistry: 6.7.2.1
- B₂Dy₂Fe₁₄**
 B₂Dy₂Fe₁₄
 Crystal chemistry: 6.7.2.1
- B₂Dy₅Ge₃**
 B₂Dy₅Ge₃
 Crystal chemistry: 6.7.2.1
- B₂Dy₅Si₃**
 B₂Dy₅Si₃
 Crystal chemistry: 6.7.2.1
- B₂Er₂Fe₁₄**
 B₂Er₂Fe₁₄
 Crystal chemistry: 6.7.2.1
- B₂EuRh₃**
 B₂EuRh₃
 Crystal chemistry: 6.7.2.1
- B₂F**
 B₂F
 Formation: 6.2.2.1
 Reaction with EX₃, EH₃, SR₂, CO,
 BX₃: 6.2.2.1
- B₂F₃**
 B₂F₃
 Reaction with elemental B: 6.2.2.1
 Reaction with L₆WH₂: 6.5.2.1
- B₂F₃MoO₃P*C₂₆H₁₉**
- B₂F₃O₃PW*C₂₆H₁₉**
- B₂F₃Re*C₁₀H₁₁**
- B₂F₃W*C₁₀H₁₂**
- B₂F₄Na**
 NaBF₄
 Reaction with magnesium: 6.7.3.5
- B₂F₆FeNOP₃*C₁₅H₃₃**
- B₂F₆FeNO₉P₄*C₁₇H₄₂**
- B₂F₆FeNP*C₁₆H₂₅**
- B₂F₆FeNP₄*C₁₇H₄₂**
- B₂F₆FeN₂P₃*C₁₆H₃₆**
- B₂F₆IrP*C₂₁H₂₅**
- B₂F₆PRh*C₂₁H₂₅**
- B₂F₆PRu*C₁₇H₁₆**
- B₂F₁₅*C₁₈**
- B₂Fe**
 B₂Fe
 Crystal chemistry: 6.7.2.2
- B₂Fe*C₁₇H₁₇**
- B₂FeNO₃*C₁₃H₂₀**
- B₂FeNO₃Si*C₁₃H₂₂**
- B₂FeNO₃Si*C₁₅H₂₄**
- B₂FeN₂O₃*C₈H₁₅**

BFeNb
 BFeNb
 Crystal chemistry: 6.7.2.1
BFeO₃*C₁₃H₉
BFeO₃*C₁₅H₁₃
BFeO₃*C₃₇H₂₅
BFeO₄*C₉H₉
BFeTa
 BFeTa
 Crystal chemistry: 6.7.2.1
BFeW
 BFeW
 Crystal chemistry: 6.7.2.1
B(Fe,Mo)
 B(Fe,Mo)
 Crystal chemistry: 6.7.2.2
B(Fe,W)
 B(Fe,W)
 Crystal chemistry: 6.7.2.2
BFe₂
 BFe₂
 Crystal chemistry: 6.7.2.1
BFe₂*C₂₂H₂₃
BFe_{2.2}Ir_{0.8}
 BFe_{2.2}Ir_{0.8}
 Crystal chemistry: 6.7.2.1
BFe_{2.2}Rh_{0.8}
 BFe_{2.2}Rh_{0.8}
 Crystal chemistry: 6.7.2.1
BFe_{2.6}Mo_{0.4}
 BFe_{2.6}Mo_{0.4}
 Crystal chemistry: 6.7.2.1
BFe_{2.6}Re_{0.4}
 BFe_{2.6}Re_{0.4}
 Crystal chemistry: 6.7.2.1
BFe_{2.6}Ru_{0.4}
 BFe_{2.6}Ru_{0.4}
 Crystal chemistry: 6.7.2.1
BFe₄NO₁₂P₂*C₄₈H₃₂
BFe₄O₁₂*C₁₂H₃
BFe₄O₁₂P*C₃₀H₁₇Au
BFe₄O₁₂P₂*C₂₄H₃₁Au₂
BFe₄O₁₂P₂*C₃₆H₃₁Au₂
BFe₄O₁₂P₂*C₄₈H₃₁Au₂
BFe_{4.8}Si₂
 BFe_{4.8}Si₂
 Crystal chemistry: 6.7.2.1
BFe₁₄Gd₂
 BFe₁₄Gd₂
 Crystal chemistry: 6.7.2.1
BFe₁₄H₄Nd₂
 BFe₁₄H₄Nd₂
 Crystal chemistry: 6.7.2.1

BFe₁₄Ho₂
 BFe₁₄Ho₂
 Crystal chemistry: 6.7.2.1
BFe₁₄La₂
 BFe₁₄La₂
 Crystal chemistry: 6.7.2.1
BFe₁₄Nd₂
 BFe₁₄Nd₂
 Crystal chemistry: 6.7.2.1
BFe₁₄Pr₂
 BFe₁₄Pr₂
 Crystal chemistry: 6.7.2.1
BFe₁₄Sm₂
 BFe₁₄Sm₂
 Crystal chemistry: 6.7.2.1
BFe₁₄Tb₂
 BFe₁₄Tb₂
 Crystal chemistry: 6.7.2.1
BFe₁₄Th₂
 BFe₁₄Th₂
 Crystal chemistry: 6.7.2.1
BFe₁₄Tm₂
 BFe₁₄Tm₂
 Crystal chemistry: 6.7.2.1
BFe₁₄Y₂
 BFe₁₄Y₂
 Crystal chemistry: 6.7.2.1
B(Ga,Mo)
 B(Ga,Mo)
 Crystal chemistry: 6.7.2.2
BGe_{0.3}Mo_{1.7}
 BGe_{0.3}Mo_{1.7}
 Crystal chemistry: 6.7.2.1
BGe₃Nb₅
 BGe₃Nb₅
 Crystal chemistry: 6.7.2.1
BGe₃Ta₅
 BGe₃Ta₅
 Crystal chemistry: 6.7.2.1
BGe₃V₅
 BGe₃V₅
 Crystal chemistry: 6.7.2.1
BHf
 BHf
 Crystal chemistry: 6.7.2.2
BHfIr₃
 BHfIr₃
 Crystal chemistry: 6.7.2.1
BHf₂Ni₂₁
 BHf₂Ni₂₁
 Crystal chemistry: 6.7.2.1
BHf₅*Al₃

BHf₉Mo₄
 BHf₉Mo₄
 Crystal chemistry: 6.7.2.1
BHf₉Os₄
 BHf₉Os₄
 Crystal chemistry: 6.7.2.1
BHf₉Re₄
 BHf₉Re₄
 Crystal chemistry: 6.7.2.1
BHf₉W₄
 BHf₉W₄
 Crystal chemistry: 6.7.2.1
BI₃
 BI₃
 Reaction with BX: 6.2.2.1
 Reaction with elemental Hg: 6.2.2.2
 Reaction with TiCl₄, CoCl₂, TaBr₅:
 6.7.4.1.1
BIr
 BIr-l,h
 Crystal chemistry: 6.7.2.1
 BIr
 Crystal chemistry: 6.7.2.1
 BK₂N₃Rh*C₁₃H₉
 BLiN*C₈H₁₅
 BLiNSi*C₇H₁₅
BLiPt₃
 BLiPt₃
 Crystal chemistry: 6.7.2.1
 BLi₂N*C₁₀H₂₀
BMn_{0.5}Re_{1.5}
 BRe_{1.5}Mn_{0.5}
 Crystal chemistry: 6.7.2.1
BMn
 BMn
 Crystal chemistry: 6.7.2.2
 MnB
 Preparation: 6.7.3.5
 BMnNO₃*C₁₁H₁₅
 BMnN₂O₄P*C₂₆H₂₇
 BMnN₂O₅*C₉H₁₂
 BMnO₄P*C₃₀H₃₃
 BMnO₄P*C₃₄H₂₃
 BMnO₄P*C₃₄H₂₅
BMn₂
 BMn₂
 Crystal chemistry: 6.7.2.1
 BMn₂O₆*C₁₆H₉
 BMn₂O₆*C₁₈H₁₃
BMn₄
 BMn₄
 Crystal chemistry: 6.7.2.1

BMo
 BMo-l,h
 Crystal chemistry: 6.7.2.2
 MoB
 Hot-pressing: 6.7.5.2
BMo*Al
B(Mo,Ni)
 B(Mo,Ni)
 Crystal chemistry: 6.7.2.2
B(Mo,Ru)
 B(Mo,Ru)
 Crystal chemistry: 6.7.2.2
B(Mo,Ti)
 B(Mo,Ti)
 Crystal chemistry: 6.7.2.2
BMo₂
 BMo₂
 Crystal chemistry: 6.7.2.1
BMo₄Zr₉
 BMo₄Zr₉
 Crystal chemistry: 6.7.2.1
BMo_{4.5}Re_{15.5}
 (Mo,Re)₃(Mo,Re)₂B_{1-x}
 Crystal chemistry: 6.7.2.1
 BN*C₈H₁₆
 BN*C₈H₁₈
 BNNb*C₁₈H₂₉
 BNRu*C₂₂H₃₈
 BNSi*C₇H₁₆
 BNSi*C₁₀H₂₂
 BNSi*C₁₂H₂₄
BNU
 BNU
 Crystal chemistry: 6.7.2.2
 BN₂*C₅H₁₅
 BN₂NbSi*C₂₁H₃₈
 BN₂Ni₂*C₂₀H₃₀
 BN₂O₅Re*C₉H₁₂
 BN₂Si*C₁₁H₂₇
 BN₃*C₁₂H₃₆Al₄
 BNa*C₆H₈
BNb
 BNb
 Crystal chemistry: 6.7.2.2
BNbNi
 BNbNi
 Crystal chemistry: 6.7.2.2
 BNbOZn*C₁₁H₁₅
BNi
 BNi
 Crystal chemistry: 6.7.2.2
 BNi*C₁₉H₂₃
 BNiO₂*C₃₆H₂₅
 BNiP₂*C₄₈H₄₀

BNiTa**BNiTa**

Crystal chemistry: 6.7.2.2

B(Ni,Ru)**B(Ni,Ru)**

Crystal chemistry: 6.7.2.2

BNi₂**BNi₂**

Crystal chemistry: 6.7.2.1

Ni₂B

Formation: 6.7.3.6

BNi₃**BNi₃**

Crystal chemistry: 6.7.2.1

Ni₃B

Formation: 6.7.3.6

BNi₄U**BNi₄U**

Crystal chemistry: 6.7.2.1

BNi₆Si₂**BSi₂Ni₆**

Crystal chemistry: 6.7.2.1

BNi_{20.3}*Al_{2.7}**BNp*C****BO****BO**

Formation: 6.2.3

BO*C₅H₉**BO*C₆H₉****BORh*C₁₅H₂₄****BOs****BOs**

Crystal chemistry: 6.7.2.1

BPd₂**BPd₂**

Crystal chemistry: 6.7.2.1

BPd₃**BPd₃**

Crystal chemistry: 6.7.2.1

BPrRh₃**BPrRh₃**

Crystal chemistry: 6.7.2.1

BPt*C₄₂H₃₇**BPt₂****BPt₂**

Crystal chemistry: 6.7.2.1

BPt₄**BPt₄**

Crystal chemistry: 6.7.2.1

B(Re,V)**B(Re,V)**

Crystal chemistry: 6.7.2.2

BRe_{1.05-1.37}V_{0.95-0.63}**(Re,V)₂B**

Crystal chemistry: 6.7.2.1

BRe_{1.49-1.64}V_{0.51-0.36}**(Re,V)₂B**

Crystal chemistry: 6.7.2.1

BRe₃**BRe₃**

Crystal chemistry: 6.7.2.1

BRe₃*Al₂**BRe₄Zr₉****BRe₄Zr₉**

Crystal chemistry: 6.7.2.1

BRe_{13.3}W_{6.7}**(W,Re)₃(W,Re)₂B**

Crystal chemistry: 6.7.2.1

BRh**BRh**

Crystal chemistry: 6.7.2.1

BRh*C₁₀H₁₂**BRh*C₁₅H₁₄****BRh*C₁₅H₂₄****BRu****BRu**

Crystal chemistry: 6.7.2.1

B(Ru,V)**B(Ru,V)**

Crystal chemistry: 6.7.2.2

B(Ru,W)**B(Ru,W)**

Crystal chemistry: 6.7.2.2

BRu₃U**BRu₃U**

Crystal chemistry: 6.7.2.1

BTa**BTa**

Crystal chemistry: 6.7.2.2

Crystal growth: 6.7.4.3

BTa₂**BTa₂**

Crystal chemistry: 6.7.2.1

BTa₅*Al₃**BTc₃****BTc₃**

Crystal chemistry: 6.7.2.1

BTh*C**BTi****BTi**

Crystal chemistry: 6.7.2.2

BTi*C₆H₈**BTi*C₁₁H₁₀****BU*C**

BV**BV**

Crystal chemistry: 6.7.2.2

Crystal growth: 6.7.2.4.3

BW**BW-I,h**

Crystal chemistry: 6.7.2.2

WB

Hot-pressing: 6.7.5.2

BW₂**BW₂**

Crystal chemistry: 6.7.2.1

BW₄Zr₉**BW₄Zr₉**

Crystal chemistry: 6.7.2.1

BYC*****BZr₅*Al₃****(B,P)Fe₃****(B,P)Fe₃**

Crystal chemistry: 6.7.2.1

B_{1.35}Ir**Ir₂B₃**

Crystal chemistry: 6.7.2.3

B_{1.43}Ni_{4.29}Si₂**B_{1.43}Ni_{4.29}Si₂**

Crystal chemistry: 6.7.2.1

B₂*Ac**B₂*Al****B₂*Am****B₂BaRh₂****B₂BaRh₂**

Crystal chemistry: 6.7.2.1

B₂BrP₂Pt*C₄₀H₄₂**B₂Br₂N₂Ti*C₁₆H₃₀****B₂Br₄****B₂Br₄**

Formation: 6.2.2.1, 6.2.2.2

B₂Br₄CoP₂*C₂₆H₂₄**B₂Br₄CoP₄*C₅₂H₄₈****B₂*C₁₂H₂₄****B₂Ca*C₂****B₂CaIr₂****B₂CaIr₂**

Crystal chemistry: 6.7.2.1

B₂CaRh₂**B₂CaRh₂**

Crystal chemistry: 6.7.2.1

B₂CeCo₃**B₂CeCo₃**

Crystal chemistry: 6.7.2.1

B₂CeCo₅**B₂CeCo₅**

Crystal chemistry: 6.7.2.1

B₂CeIr₃**B₂CeIr₃**

Crystal chemistry: 6.7.2.1

B₂CeOs₂**B₂CeOs₂**

Crystal chemistry: 6.7.2.1

B₂CeRh₃**B₂CeRh₃**

Crystal chemistry: 6.7.2.1

B₂CeRu₂**B₂CeRu₂**

Crystal chemistry: 6.7.2.1

B₂CeRu₃**B₂CeRu₃**

Crystal chemistry: 6.7.2.1

B₂Ce₃N₄**B₂Ce₃N₄**

Crystal chemistry: 6.7.2.2

B₂ClN₂Si₂V*C₁₄H₃₀**B₂Cl₂CoP₄*C₆₄H₅₈****B₂Cl₂N₂Si₂Ti*C₁₄H₃₀****B₂Cl₄****B₂Cl₄**

Formation: 6.2.2.1, 6.2.2.2, 6.2.2.4

Reaction with B₂H₆: 6.2.2.2Reaction with CCl₃F: 6.2.2.2Reaction with CCl₄: 6.2.2.3Reaction with H₂O: 6.2.3Reaction with LiBH₄: 6.2.1

Thermal decomposition: 6.2.2.3

B₂Cl₄N₂Ti*C₁₄H₃₄**B₂Cl₆P₂Pt*C₃₆H₃₀****B₂Cl₆P₃Pt*C₅₄H₄₅****B₂Co*C₁₂H₁₆****B₂Co*C₁₂H₁₉****B₂Co*C₁₄H₂₃****B₂Co*C₁₇H₂₉****B₂Co*C₂₂H₂₀****B₂CoF₂*C₁₃H₁₇****B₂CoFe*C₁₉H₂₇****B₂CoFe*C₂₂H₃₃****B₂CoFeNiO₃*C₂₄H₃₃****B₂CoI₄P₄*C₅₂H₄₈****B₂CoKN₄O₄P*C₅₀H₄₇****B₂CoMo₂****B₂CoMo₂**

Crystal chemistry: 6.7.2.2

B₂CoN*C₁₄H₂₃**B₂CoN₄O₄P*C₅₀H₄₇****B₂CoNb****B₂CoNb**

Crystal chemistry: 6.7.2.2

B₂CoNi*C₁₉H₂₇**B₂CoNi*C₂₂H₃₃**

- B₂CoP*C₃₀H₃₃Au**
B₂CoP₄*C₄₄H₄₈
B₂CoP₄*C₄₄H₅₂
B₂CoP₄*C₇₆H₅₂
B₂CoP₄*C₇₆H₆₈
B₂CoS*C₁₃H₂₁
B₂CoTa
 B₂CoTa
 Crystal chemistry: 6.7.2.2
B₂CoW₂
 B₂CoW₂
 Crystal chemistry: 6.7.2.2
B₂Co₂*C₁₉H₂₇
B₂Co₂*C₂₂H₃₃
B₂Co₂Dy
 B₂Co₂Dy
 Crystal chemistry: 6.7.2.1
B₂Co₂Gd
 B₂Co₂Gd
 Crystal chemistry: 6.7.2.1
B₂Co₂Ho
 B₂Co₂Ho
 Crystal chemistry: 6.7.2.1
B₂Co₂La
 B₂Co₂La
 Crystal chemistry: 6.7.2.1
B₂Co₂N₂O₄*C₂₄H₄₀
B₂Co₂Nd
 B₂Co₂Nd
 Crystal chemistry: 6.7.2.1
B₂Co₂O₄*C₁₄H₁₄
B₂Co₂O₄*C₂₄H₁₈
B₂Co₂Pr
 B₂Co₂Pr
 Crystal chemistry: 6.7.2.1
B₂Co₂S₂*C₁₀H₁₂
B₂Co₂Sc
 B₂Co₂Sc
 Crystal chemistry: 6.7.2.1
B₂Co₂Sm
 B₂Co₂Sm
 Crystal chemistry: 6.7.2.1
B₂Co₂Ta
 B₂Co₂Ta
 Crystal chemistry: 6.7.2.1
B₂Co₂Tb
 B₂Co₂Tb
 Crystal chemistry: 6.7.2.1
B₂Co₂Y
 B₂Co₂Y
 Crystal chemistry: 6.7.2.1
B₂Co₃Dy
 B₂Co₃Dy
 Crystal chemistry: 6.7.2.1
B₂Co₃Er
 B₂Co₃Er
 Crystal chemistry: 6.7.2.1
B₂Co₃Gd
 B₂Co₃Gd
 Crystal chemistry: 6.7.2.1
B₂Co₃Hf
 B₂Co₃Hf
 Crystal chemistry: 6.7.2.1
B₂Co₃Ho
 B₂Co₃Ho
 Crystal chemistry: 6.7.2.1
B₂Co₃Lu
 B₂Co₃Lu
 Crystal chemistry: 6.7.2.1
B₂Co₃Sc
 B₂Co₃Sc
 Crystal chemistry: 6.7.2.1
B₂Co₃Sm
 B₂Co₃Sm
 Crystal chemistry: 6.7.2.1
B₂Co₃Tb
 B₂Co₃Tb
 Crystal chemistry: 6.7.2.1
B₂Co₃Tm
 B₂Co₃Tm
 Crystal chemistry: 6.7.2.1
B₂Co₃U
 B₂Co₃U
 Crystal chemistry: 6.7.2.1
B₂Co₃Y
 B₂Co₃Y
 Crystal chemistry: 6.7.2.1
B₂Co₃Yb
 B₂Co₃Yb
 Crystal chemistry: 6.7.2.1
B₂Co₃Zr
 B₂Co₃Zr
 Crystal chemistry: 6.7.2.1
B₂Co₄Nd
 B₂Co₄Nd
 Crystal chemistry: 6.7.2.2
B₂Co₅P
 B₂Co₅P
 Crystal chemistry: 6.7.2.2
B₂Co₅Ta₃
 B₂Co₅Ta₃
 Crystal chemistry: 6.7.2.1
B₂Co₅Ti₃
 B₂Co₅Ti₃
 Crystal chemistry: 6.7.2.1
B₂Co₇Dy₃
 B₂Co₇Dy₃
 Crystal chemistry: 6.7.2.1

B₂Co₇Gd₃
 B₂Co₇Gd₃
 Crystal chemistry: 6.7.2.1
B₂Co₇U₃
 B₂Co₇U₃
 Crystal chemistry: 6.7.2.1
B₂Co₁₁*C
B₂Cr
 CrB₂
 Crystal chemistry: 6.7.2.3
 Crystal structure: 6.7.2.4
 Hot-pressing: 6.7.5.2
 Preparation: 6.7.3.4
 Sintering: 6.7.5.1
B₂CrN₂O₄*C₂₀H₃₆
B₂CrO₄S*C₁₂H₁₆
B₂Cr₂*Al
B₂Cr₂Ir
 B₂Cr₂Ir
 Crystal chemistry: 6.7.2.2
B₂(Cr,Mo)₃
 B₂(Cr,Mo)₃
 Crystal chemistry: 6.7.2.2
B₂Cr₅P
 B₂PCr₅
 Crystal chemistry: 6.7.2.2
B₂Dy
 DyB₂
 Crystal chemistry: 6.7.2.3
 Crystal structure: 6.7.2.4
B₂Dy*C
B₂Dy*C₂
B₂DyFe₂
 B₂DyFe₂
 Crystal chemistry: 6.7.2.1
B₂DyIr₃
 B₂DyIr₃
 Crystal chemistry: 6.7.2.1
B₂DyOs
 B₂DyOs
 Crystal chemistry: 6.7.2.2
B₂DyRh₃
 B₂DyRh₃
 Crystal chemistry: 6.7.2.1
B₂DyRu
 B₂DyRu
 Crystal chemistry: 6.7.2.2
B₂DyRu₃
 B₂DyRu₃
 Crystal chemistry: 6.7.2.1

B₂Er
 ErB₂
 Crystal chemistry: 6.7.2.3
 Crystal growth: 6.7.4.3
 Crystal structure: 6.7.2.4
B₂Er*C₂
B₂ErFe₂
 B₂ErFe₂
 Crystal chemistry: 6.7.2.1
B₂ErIr₃
 B₂ErIr₃
 Crystal chemistry: 6.7.2.1
B₂ErOs
 B₂ErOs
 Crystal chemistry: 6.7.2.2
B₂ErOs₃
 B₂ErOs₃
 Crystal chemistry: 6.7.2.1
B₂ErRh₃
 B₂ErRh₃
 Crystal chemistry: 6.7.2.1
B₂ErRu
 B₂ErRu
 Crystal chemistry: 6.7.2.2
B₂ErRu₃
 B₂ErRu₃
 Crystal chemistry: 6.7.2.1
B₂Eu*C₂
B₂EuRh₃
 B₂EuRh₃
 Crystal chemistry: 6.7.2.1
B₂F₂*C₈H₁₂
B₂F₂FeO₃*C₁₁H₁₂
B₂F₂FeS*C₁₄H₂₀
B₂F₂Ni*C₁₆H₂₄
B₂F₂NiO₂*C₁₀H₁₂
B₂F₂Pt*C₁₆H₂₄
B₂F₄
 B₂F₄
 Formation: 6.2.2.1, 6.2.2.2, 6.2.3
B₂F₆FePS*C₁₃H₂₁
B₂F₆MnO₃PS*C₁₁H₁₆
B₂F₆P₂Pt*C₃₆H₃₀
B₂FeMnO₃S*C₁₆H₂₁
B₂FeMo₂
 B₂FeMo₂
 Crystal chemistry: 6.7.2.2
B₂FeNO₃*C₁₂H₁₉
B₂FeN₂*C₁₆H₃₀
B₂FeN₂O*C₂₁H₄₀
B₂FeN₂O₃*C₁₃H₂₀
B₂FeNiO₃*C₁₇H₂₂
B₂FeO₂*C₁₂H₁₈

- $B_2FeO_3 \cdot C_{15}H_{24}$
 $B_2FeO_3S \cdot C_{11}H_{16}$
 $B_2FeS \cdot C_{14}H_{22}$
 $B_2FeS \cdot C_{15}H_{24}$
 $B_2FeS \cdot C_{16}H_{26}$
 B_2FeW_2
 B_2FeW_2
 Crystal chemistry: 6.7.2.2
 $B_2Fe_2 \cdot Al$
 $B_2Fe_2 \cdot C_{44}H_{44}$
 B_2Fe_2Gd
 B_2Fe_2Gd
 Crystal chemistry: 6.7.2.1
 B_2Fe_2Ho
 B_2Fe_2Ho
 Crystal chemistry: 6.7.2.1
 B_2Fe_2Lu
 B_2Fe_2Lu
 Crystal chemistry: 6.7.2.1
 $B_2Fe_2NiO_6 \cdot C_{20}H_{22}$
 $B_2Fe_2O_3 \cdot C_{17}H_{22}$
 $B_2Fe_2O_4 \cdot C_{26}H_{22}$
 $B_2Fe_2S \cdot C_{18}H_{26}$
 B_2Fe_2Tb
 B_2Fe_2Tb
 Crystal chemistry: 6.7.2.1
 B_2Fe_2Tm
 B_2Fe_2Tm
 Crystal chemistry: 6.7.2.1
 B_2Fe_2Y
 B_2Fe_2Y
 Crystal chemistry: 6.7.2.1
 B_2Fe_3U
 B_2Fe_3U
 Crystal chemistry: 6.7.2.1
 $B_2(Fe,W)_3$
 $B_2(Fe,W)_3$
 Crystal chemistry: 6.7.2.2
 B_2Fe_5P
 B_2Fe_5P
 Crystal chemistry: 6.7.2.2
 B_2Fe_5Si
 B_2Fe_5Si
 Crystal chemistry: 6.7.2.2
 B_2Gd
 GdB_2
 Crystal chemistry: 6.7.2.3
 Crystal structure: 6.7.2.4
 $B_2Gd \cdot C_2$
 B_2GdIr_3
 B_2GdIr_3
 Crystal chemistry: 6.7.2.1
 B_2GdOs_2
 Crystal chemistry: 6.7.2.1
 B_2GdRh_3
 $B_2GdRh_{3-h,l}$
 Crystal chemistry: 6.7.2.1
 B_2GdRu_2
 B_2GdRu_2
 Crystal chemistry: 6.7.2.1
 B_2GdRu_3
 B_2GdRu_3
 Crystal chemistry: 6.7.2.1
 B_2H_4
 H_2BBH_2
 Formation: 6.2.1
 Structure: 6.2.1
 B_2H_6
 B_2H_6
 Reaction with B_2Cl_4 : 6.2.2.2
 Reaction with MX_5 , MX_2 : 6.7.4.1.1
 B_2Hf
 HfB_2
 Crystal chemistry: 6.7.2.3
 Crystal growth: 6.7.4.2.1, 6.7.4.3
 Crystal structure: 6.7.2.4
 Hot-pressing: 6.7.5.2
 Preparation: 6.7.3.1, 6.7.3.2, 6.7.3.4
 Sintering: 6.7.5.1
 $B_2Hf_3Ir_5$
 $B_2Hf_3Ir_5$
 Crystal chemistry: 6.7.2.1
 B_2Ho
 HoB_2
 Crystal chemistry: 6.7.2.3
 Crystal structure: 6.7.2.4
 Preparation: 6.7.3.1
 $B_2Ho \cdot C$
 $B_2Ho \cdot C_2$
 B_2HoIr_3
 B_2HoIr_3
 Crystal chemistry: 6.7.2.1
 B_2HoOs
 B_2HoOs
 Crystal chemistry: 6.7.2.2
 B_2HoRh_3
 B_2HoRh_3
 Crystal chemistry: 6.7.2.1
 B_2HoRu
 B_2HoRu
 Crystal chemistry: 6.7.2.2
 B_2HoRu_3
 B_2HoRu_3
 Crystal chemistry: 6.7.2.1

- B₂I₄**
 B₂I₄
 Formation: 6.2.2.1, 6.2.2.2
 Thermal decomposition: 6.2.2.3
- B₂IrMg₂**
 B₂IrMg₂
 Crystal chemistry: 6.7.2.2
- B₂IrMo**
 B₂(Ir,Mo)
 Crystal chemistry: 6.7.2.3
- B₂IrMo₂**
 B₂IrMo₂
 Crystal chemistry: 6.7.2.2
- B₂IrV₂**
 B₂IrV₂
 Crystal chemistry: 6.7.2.2
- B₂IrW**
 B₂(Ir,W)
 Crystal chemistry: 6.7.2.3
- B₂Ir₂Sr**
 B₂Ir₂Sr
 Crystal chemistry: 6.7.2.1
- B₂Ir₃La**
 B₂Ir₃La
 Crystal chemistry: 6.7.2.1
- B₂Ir₃Lu**
 B₂Ir₃Lu
 Crystal chemistry: 6.7.2.1
- B₂Ir₃Nd**
 B₂Ir₃Nd
 Crystal chemistry: 6.7.2.1
 B₂NdIr₃
 Crystal chemistry: 6.7.2.1
- B₂Ir₃Pr**
 B₂Ir₃Pr
 Crystal chemistry: 6.7.2.1
- B₂Ir₃Sc**
 B₂Ir₃Sc
 Crystal chemistry: 6.7.2.1
- B₂Ir₃Sm**
 B₂Ir₃Sm
 Crystal chemistry: 6.7.2.1
- B₂Ir₃Tb**
 B₂Ir₃Tb
 Crystal chemistry: 6.7.2.1
- B₂Ir₃Th**
 B₂Ir₃Th
 Crystal chemistry: 6.7.2.1
- B₂Ir₃Tm**
 B₂Ir₃Tm
 Crystal chemistry: 6.7.2.1
- B₂Ir₃U**
 B₂Ir₃U
 Crystal chemistry: 6.7.2.1
- B₂Ir₃Y**
 B₂Ir₃Y
 Crystal chemistry: 6.7.2.1
- B₂Ir₃Yb**
 B₂Ir₃Yb
 Crystal chemistry: 6.7.2.1
- B₂La*C₂**
 B₂LaOs₂
 B₂LaOs₂
 Crystal chemistry: 6.7.2.1
- B₂LaRh₃**
 B₂LaRh₃
 Crystal chemistry: 6.7.2.1
- B₂LaRu₂**
 B₂LaRu₂
 Crystal chemistry: 6.7.2.1
- B₂La₃N₄**
 B₂La₃N₄
 Crystal chemistry: 6.7.2.2
- B₂Li_{1.2}Ni_{2.5}**
 B₂Li_{1.2}Ni_{2.5}
 Crystal chemistry: 6.7.2.1
- B₂Lu**
 LuB₂
 Crystal chemistry: 6.7.2.3
 Crystal structure: 6.7.2.4
- B₂Lu*C₂**
 B₂LuOs
 B₂LuOs
 Crystal chemistry: 6.7.2.2
- B₂LuOs₃**
 B₂LuOs₃
 Crystal chemistry: 6.7.2.1
- B₂LuRh₃**
 B₂LuRh₃
 Crystal chemistry: 6.7.2.1
- B₂LuRu**
 B₂LuRu
 Crystal chemistry: 6.7.2.2
- B₂LuRu₃**
 B₂LuRu₃
 Crystal chemistry: 6.7.2.1
- B₂Mg**
 MgB₂
 Crystal chemistry: 6.7.2.3
 Crystal structure: 6.7.2.4
- B₂MgNi_{2.5}**
 B₂MgNi_{2.5}
 Crystal chemistry: 6.7.2.1
- B₂Mn**
 B₂Mn
 Crystal chemistry: 6.7.2.3

- B₂MnMo**
 B₂(Mn,Mo)
 Crystal chemistry: 6.7.2.3
B₂MnV
 B₂(Mn,V)
 Crystal chemistry: 6.7.2.3
B₂MnW
 B₂(Mn,W)
 Crystal chemistry: 6.7.2.3
B₂Mn₂*Al
B₂Mn₂O₆S*C₁₄H₁₆
B₂(Mn,Mo)₃
 B₂(Mn,Mo)₃
 Crystal chemistry: 6.7.2.2
B₂Mn₅P
 B₂Mn₅P
 Crystal chemistry: 6.7.2.2
B₂Mn₅Si
 B₂Mn₅Si
 Crystal chemistry: 6.7.2.2
B₂Mo
 MoB₂
 Crystal chemistry: 6.7.2.3
 Hot-pressing: 6.7.5.2
 Sintering: 6.7.5.1
B₂Mo*C
B₂MoOs
 B₂(Mo,Os)
 Crystal chemistry: 6.7.2.3
B₂MoRu
 B₂(Mo,Ru)
 Crystal chemistry: 6.7.2.3
B₂Mo₂Ni
 B₂Mo₂Ni
 Crystal chemistry: 6.7.2.2
B₂Mo₂Os
 B₂Mo₂Os
 Crystal chemistry: 6.7.2.2
B₂(Mo,Ru)₃
 B₂(Mo,Ru)₃
 Crystal chemistry: 6.7.2.2
B₂Mo₅Si
 B₂Mo₅Si
 Crystal chemistry: 6.7.2.2
B₂N*C₉H₁₉
B₂NO₅Re*C₁₃H₂₆
B₂N₂*C₆H₂₂
B₂N₂*C₁₀H₃₀
B₂N₂*C₁₄H₃₄
B₂N₂Ni*C₂₀H₄₀
B₂N₂Ni₂Si₂*C₂₂H₄₈
B₂N₂O₂*C₆H₁₈
B₂N₂O₄*C₂₀H₃₆
B₂N₂O₄Rh₂*C₂₄H₄₀
B₂N₂O₄W*C₂₀H₃₆
B₂N₂Rh₂*C₂₄H₄₀
B₂N₂Ru*C₂₀H₃₄
B₂N₄*C₈H₂₄
B₂N₄Nd₃
 B₂N₄Nd₃
 Crystal chemistry: 6.7.2.2
B₂N₄Pr₃
 B₂N₄Pr₃
 Crystal chemistry: 6.7.2.2
B₂NaPt₃
 B₂NaPt₃
 Crystal chemistry: 6.7.2.1
B₂NaRh*C₁₀H₁₄
B₂NaRh*C₂₀H₁₈
B₂Nb
 NbB₂
 Crystal chemistry: 6.7.2.3
 Crystal growth: 6.7.4.3
 Crystal structure: 6.7.2.4
 Formation: 6.7.4.1.1, 6.7.4.1.2
 Hot-pressing: 6.7.5.2
 Sintering: 6.7.5.1
B₂NbNi
 B₂NbNi
 Crystal chemistry: 6.7.2.2
B₂Nb₃
 B₂Nb₃
 Crystal chemistry: 6.7.2.2
B₂(Nb,Re)₃
 B₂(Nb,Re)₃
 Crystal chemistry: 6.7.2.2
B₂Nb₅Si₃
 B₂Nb₅Si₃
 Crystal chemistry: 6.7.2.1
B₂Nd
 B₂Nd
 Crystal chemistry: 6.7.2.3
B₂Nd*C₂
B₂NdOs₂
 B₂NdOs₂
 Crystal chemistry: 6.7.2.1
B₂NdRh₃
 B₂NdRh₃
 Crystal chemistry: 6.7.2.1
B₂NdRu₂
 B₂NdRu₂
 Crystal chemistry: 6.7.2.1
B₂NdRu₃
 B₂NdRu₃
 Crystal chemistry: 6.7.2.1
B₂Ni*C₁₄H₂₂
B₂Ni*C₁₇H₂₂
B₂Ni*C₁₇H₂₈

- $B_2Ni^*C_{22}H_{22}$
 $B_2Ni^*C_{24}H_{26}$
 $B_2Ni^*C_{26}H_{30}$
 $B_2NiO_2S^*C_{10}H_{16}$
 $B_2NiS^*C_{13}H_{21}$
 B_2NiTa
 B_2NiTa
 Crystal chemistry: 6.7.2.2
 B_2NiW_2
 B_2NiW_2
 Crystal chemistry: 6.7.2.2
 $B_2Ni_2^*C_{16}H_{28}$
 $B_2Ni_2^*C_{17}H_{31}$
 $B_2Ni_2^*C_{19}H_{27}$
 $B_2Ni_2^*C_{22}H_{33}$
 B_2Ni_3Y
 B_2Ni_3Y
 Crystal chemistry: 6.7.2.1
 B_2Np
 NpB_2
 Crystal chemistry: 6.7.2.3
 Crystal structure: 6.7.2.4
 $B_2ORh_2^*C_{24}H_{36}$
 B_2O_2
 OBBO
 Formation: 6.2.3, 6.7.3.4
 Reaction with BCl_3 : 6.2.3
 Reaction with SF_4 : 6.2.3
 $B_2O_2Rh^*C_{15}H_{23}$
 B_2O_3
 B_2O_3
 Reaction with B_4C and transition metals: 6.7.3.5
 Reaction with elemental boron: 6.2.3
 $B_2O_4^*C_4H_{12}$
 B_2Os
 B_2Os
 Crystal chemistry: 6.7.2.3
 B_2OsSc
 B_2OsSc
 Crystal chemistry: 6.7.2.2
 B_2OsTb
 B_2OsTb
 Crystal chemistry: 6.7.2.2
 B_2OsTm
 B_2OsTm
 Crystal chemistry: 6.7.2.2
 B_2OsV
 $B_2(Os,V)$
 Crystal chemistry: 6.7.2.3
 B_2OsW
 $B_2(Os,W)$
 Crystal chemistry: 6.7.2.3
 B_2OsY
 B_2OsY
 Crystal chemistry: 6.7.2.2
 B_2Os_2Pr
 B_2Os_2Pr
 Crystal chemistry: 6.7.2.1
 B_2Os_2Sm
 B_2Os_2Sm
 Crystal chemistry: 6.7.2.1
 B_2Os_2Th
 B_2Os_2Th
 Crystal chemistry: 6.7.2.1
 B_2Os_3U
 B_2Os_3U
 Crystal chemistry: 6.7.2.1
 $B_2(Os,V)_3$
 $B_2(Os,V)_3$
 Crystal chemistry: 6.7.2.2
 $B_2(Os,W)_3$
 $B_2(Os,W)_3$
 Crystal chemistry: 6.7.2.2
 $B_2PRh^*C_{34}H_{43}Au$
 $B_2P_2^*C_6H_{22}$
 $B_2P_2^*C_{36}H_{34}$
 $B_2P_6^*C_{162}H_{166}Au_6$
 B_2Pd_5
 B_2Pd_5
 Crystal chemistry: 6.7.3.1
 $B_2Pr^*C_2$
 B_2PrRh_3
 B_2PrRh_3
 Crystal chemistry: 6.7.2.1
 B_2PrRu_2
 B_2PrRu_2
 Crystal chemistry: 6.7.2.1
 B_2PrRu_3
 B_2PrRu_3
 Crystal chemistry: 6.7.2.1
 B_2Pu
 PuB_2
 Crystal chemistry: 6.7.2.3
 Crystal structure: 6.7.2.4
 B_2Re
 B_2Re
 Crystal chemistry: 6.7.2.3
 B_2ReTi_2
 B_2ReTi_2
 Crystal chemistry: 6.7.2.2
 $B_2(Re,Ta)_3$
 $B_2(Re,Ta)_3$
 Crystal chemistry: 6.7.2.2

- B₂Rh*C₁₀H₁₅**
B₂Rh*C₁₇H₂₉
B₂Rh*C₂₀H₁₉
B₂Rh₂Sr
 B₂Rh₂Sr
 Crystal chemistry: 6.7.2.1
B₂Rh₃Sm
 B₂Rh₃Sm
 Crystal chemistry: 6.7.2.1
B₂Rh₃Tb
 B₂Rh₃Tb
 Crystal chemistry: 6.7.2.1
B₂Rh₃Tm
 B₂Rh₃Tm
 Crystal chemistry: 6.7.2.1
B₂Rh₃Y
 B₂Rh₃Y
 Crystal chemistry: 6.7.2.1
B₂Rh₃Yb
 B₂Rh₃Yb
 Crystal chemistry: 6.7.2.1
B₂Ru
 B₂Ru
 Crystal chemistry: 6.7.2.3
B₂RuTb
 B₂RuTb
 Crystal chemistry: 6.7.2.2
B₂RuTm
 B₂RuTm
 Crystal chemistry: 6.7.2.2
B₂RuW
 B₂(Ru,W)
 Crystal chemistry: 6.7.2.3
B₂RuY
 B₂RuY
 Crystal chemistry: 6.7.2.2
B₂Ru₂Sm
 B₂Ru₂Sm
 Crystal chemistry: 6.7.2.1
B₂Ru₂Th
 B₂Ru₂Th
 Crystal chemistry: 6.7.2.1
B₂Ru₃Sm
 B₂Ru₃Sm
 Crystal chemistry: 6.7.2.1
B₂Ru₃Tb
 B₂Ru₃Tb
 Crystal chemistry: 6.7.2.1
B₂Ru₃Th
 B₂Ru₃Th
 Crystal chemistry: 6.7.2.1
B₂Ru₃Tm
 B₂Ru₃Tm
 Crystal chemistry: 6.7.2.1
B₂Ru₃U
 B₂Ru₃U
 Crystal chemistry: 6.7.2.1
B₂(Ru,W)₃
 B₂(Ru,W)₃
 Crystal chemistry: 6.7.2.2
B₂S*C₈H₁₆
B₂Sc
 B₂Sc
 Crystal chemistry: 6.7.2.3
B₂Sc*C
B₂Sc*C₂
B₂SiV₅
 B₂SiV₅
 Crystal chemistry: 6.7.2.2
B₂Si₃Ta₅
 B₂Si₃Ta₅
 Crystal chemistry: 6.7.2.1
B₂Sm
 SmB₂
 Crystal chemistry: 6.7.2.3
 Crystal structure: 6.7.2.4
B₂Sm*C₂
B₂Ta
 TaB₂
 Crystal chemistry: 6.7.2.3
 Formation: 6.7.4.1.2
 Hot-pressing: 6.7.5.2
 Sintering: 6.7.5.1
B₂Ta₃
 B₂Ta₃
 Crystal chemistry: 6.7.2.2
B₂Tb
 TbB₂
 Crystal chemistry: 6.7.2.3
 Crystal structure: 6.7.2.4
B₂Tb*C
B₂Tb*C₂
B₂Tc
 B₂Tc
 Crystal chemistry: 6.7.2.3
B₂Th*C
B₂Th₃*C₃
B₂Ti
 TiB₂
 Activated-sintering: 6.7.5.1
 Comminution: 6.7.5.1.1
 Crystal chemistry: 6.7.2.3
 Crystal growth: 6.7.4.2.1, 6.7.4.2.3, 6.7.4.3
 Crystal structure: 6.7.2.4
 Formation: 6.7.4.1.1, 6.7.4.1.2
 Hot-pressing: 6.7.5.2

- Preparation: 6.7.3.1, 6.7.3.2, 6.7.3.3,
6.7.3.4, 6.7.3.5
Sintering: 6.7.5.1
Thermal stability: 6.7.4.2.1
- B₂Tm**
TmB₂
Crystal chemistry: 6.7.2.3
Crystal structure: 6.7.2.4
- B₂Tm*C
B₂Tm*C₂
- B₂U**
UB₂
Crystal chemistry: 6.7.2.3
Crystal structure: 6.7.2.4
Hot-pressing: 6.7.5.2
- B₂U*C
- B₂V**
VB₂
Crystal chemistry: 6.7.2.3
Formation: 6.7.4.1.2
Hot-pressing: 6.7.5.2
Sintering: 6.7.5.1
- B₂V₃**
B₂V₃
Crystal chemistry: 6.7.2.2
- B₂W**
B₂W
Crystal chemistry: 6.7.2.3
- B₂Y**
YB₂
Crystal chemistry: 6.7.2.3
Crystal structure: 6.7.2.4
- B₂Y*C
B₂Y*C₂
- B₂Yb**
B₂Yb
Crystal chemistry: 6.7.2.3
- B₂Yb*C
B₂Yb*C₂
- B₂Zr**
ZrB₂
Activated-sintering: 6.7.5.1
Comminution: 6.7.5.1.1
Crystal chemistry: 6.7.2.3
Crystal growth: 6.7.4.2.1, 6.7.4.2.3,
6.7.4.3
Crystal structure: 6.7.2.4
Formation: 6.7.4.1.1, 6.7.4.1.2
Hot-pressing: 6.7.5.2
Preparation: 6.7.3.1, 6.7.3.2, 6.7.3.3,
6.7.3.4, 6.7.3.5
Sintering: 6.7.5.1
Thermal stability: 6.7.4.2.1
- (B,Be)₂(Ni,Be)**
(B,Be)₂(Ni,Be)
Crystal chemistry: 6.7.2.1
- B_{2,3}Mo**
B_{2,3}Mo
Crystal chemistry: 6.7.2.3
- B₃*C₂H₅
B₃Ce₂Co₇
B₃Ce₂Co₇
Crystal chemistry: 6.7.2.1
- B₃Cl₆N₃**
B₃N₃Cl₆
Boron transport material: 6.7.4.1.2
- B₃Cl₆P₄Rh*C₇₆H₆₈
B₃Co*C₇H₁₂
- B₃CoMo₃**
B₃CoMo₃
Crystal chemistry: 6.7.2.2
- B₃CoN₄O₄*C₆₂H₅₇As
B₃CoN₄O₄P*C₅₄H₇₃
B₃CoP₂*C₁₄H₃₆
- B₃CoV**
B₃CoV
Crystal chemistry: 6.7.2.2
- B₃CoW₃**
B₃CoW₃
Crystal chemistry: 6.7.2.2
- B₃Co₂*C₁₂H₁₅
B₃Co₂*C₁₅H₁₉
B₃Co₂*C₂₄H₃₉
B₃Co₂N₃*C₃₀H₆₀
B₃Co₃*C₁₅H₂₀
- B₃Co₇Dy₂**
B₃Co₇Dy₂
Crystal chemistry: 6.7.2.1
- B₃Co₇Er₂**
B₃Co₇Er₂
Crystal chemistry: 6.7.2.1
- B₃Co₇Gd₂**
B₃Co₇Gd₂
Crystal chemistry: 6.7.2.1
- B₃Co₇Ho₂**
B₃Co₇Ho₂
Crystal chemistry: 6.7.2.1
- B₃Co₇Nd₂**
B₃Co₇Nd₂
Crystal chemistry: 6.7.2.1.
- B₃Co₇Pr₂**
B₃Co₇Pr₂
Crystal chemistry: 6.7.2.1
- B₃Co₇Tb₂**
B₃Co₇Tb₂
Crystal chemistry: 6.7.2.1

B₃Co₇Tm₂
 B₃Co₇Tm₂
 Crystal chemistry: 6.7.2.1
B₃Co₇Y₂
 B₃Co₇Y₂
 Crystal chemistry: 6.7.2.1
B₃CrN₃O₃*C₁₀H₂₀
B₃CrN₃O₃*C₁₄H₂₀
B₃Cr₂
 B₃Cr₂
 Crystal chemistry: 6.7.2.2
B₃(Cr,Ni)₂
 B₃(Cr,Ni)₂
 Crystal chemistry: 6.7.2.2
B₃Cr₅
 B₃Cr₅
 Crystal chemistry: 6.7.2.2
B₃(Cr,W)₅
 B₃(Cr,W)₅
 Crystal chemistry: 6.7.2.2
B₃F₅
 (BF₂)₂BF
 Formation: 6.2.2.1
B₃F₁₂O₂₄P₈*C₁₆₈H₁₆₈Au₉
B₃F₁₂P₈*C₁₄₄H₁₂₀Au₉
B₃Fe*C₂₀H₃₃
B₃FeMo₃
 B₃FeMo₃
 Crystal chemistry: 6.7.2.2
B₃FeO₃*C₅H₇
B₃FeW₃
 B₃FeW₃
 Crystal chemistry: 6.7.2.2
B₃Fe₂₃Nd₂
 B₃Fe₂₃Nd₂
 Crystal chemistry: 6.7.2.2
B₃IrOP₂*C₃₇H₃₈
B₃MnO₃*C₇H₈
B₃Mo_{1-x}
 B₃Mo_{1-x}
 Crystal chemistry: 6.7.2.3
B₃Mo_{1-x}Rh_{1-x}
 B₃(Mo,Rh)_{1-x}
 Crystal chemistry: 6.7.2.3
B₃Mo₃Ni
 B₃Mo₃Ni
 Crystal chemistry: 6.7.2.2
B₃NRh₂*C₃₅H₃₆
B₃N₃*C₇H₂₀
B₃N₃*C₁₁H₂₀
B₃Ni_{1-x}W_{1-x}
 B₃(Ni,W)_{1-x}
 Crystal chemistry: 6.7.2.3
B₃Ni*C₁₆H₃₁

B₃NiW₃
 B₃NiW₃
 Crystal chemistry: 6.7.2.2
B₃Ni₄
 B₃Ni_{4-o,m}
 Crystal chemistry: 6.7.2.2
B₃O*C₄H₁₅
B₃O₉P₃Rh₂*C₃₉H₅₄
B₃Os₂
 B₃Os₂
 Crystal chemistry: 6.7.2.3
B₃P₂Pd*C₂₆H₃₁
B₃P₂Pt*C₁₂H₃₇
B₃P₂Pt*C₁₆H₂₉
B₃P₂Pt*C₂₈H₃₇
B₃P₂Pt*C₄₂H₄₉
B₃P₃Rh₂*C₃₉H₅₄
B₃Pd_{1-x}W_{1-x}
 B₃(W,Pd)_{1-x}
 Crystal chemistry: 6.7.2.3
B₃Re₇
 B₃Re₇
 Crystal chemistry: 6.7.2.1
B₃Rh_{1-x}W_{1-x}
 B₃(Rh,W)_{1-x}
 Crystal chemistry: 6.7.2.3
B₃Rh₂*C₁₅H₂₁
B₃Rh₂*C₃₀H₂₇
B₃Rh₇
 B₃Rh₇
 Crystal chemistry: 6.7.2.1
B₃Ru₂
 B₃Ru₂
 Crystal chemistry: 6.7.2.3
B₃Ru₇
 B₃Ru₇
 Crystal chemistry: 6.7.2.1
B₃Tc₇
 B₃Tc₇
 Crystal chemistry: 6.7.2.1
B₃V₂
 B₃V₂
 Crystal chemistry: 6.7.2.2
B₃W_{1-x}
 W_{1-x}B₃
 Crystal chemistry: 6.7.2.3
(B,Si)₃W₅
 (B,Si)₃W₅
 Crystal chemistry: 6.7.2.2
B₄*Am
B₄*C
B₄*C₂H₈
B₄*C₄H₁₂
B₄*C₆H₁₆

- B₄(Ca,Sc)Rh₄**
 B₄(Ca,Sc)Rh₄
 Crystal chemistry: 6.7.2.2
- B₄Ca₂Rh₅**
 B₄Ca₂Rh₅
 Crystal chemistry: 6.7.2.1
- B₄Ce**
 CeB₄
 Crystal growth: 6.7.4.3
 Crystal structure and lattice parameters: 6.7.2.4.1
 Electrical and magnetic properties: 6.7.2.4.1
 Preparation: 6.7.3.1
 Thermal stability: 6.7.2.4.1
- B₄CeCo₄**
 B₄CeCo₄
 Crystal chemistry: 6.7.2.2
- B₄CeCr**
 B₄CeCr
 Crystal chemistry: 6.7.2.3
- B₄CeFe**
 B₄CeFe
 Crystal chemistry: 6.7.2.3
- B₄CeFe₄**
 B₄CeFe₄
 Crystal chemistry: 6.7.2.2
- B₄CeIr₄**
 B₄CeIr₄
 Crystal chemistry: 6.7.2.2
- B₄CeMn**
 B₄CeMn
 Crystal chemistry: 6.7.2.3
- B₄CeNi**
 B₄CeNi
 Crystal chemistry: 6.7.2.3
- B₄CeOs₄**
 B₄CeOs₄
 Crystal chemistry: 6.7.2.2
- B₄CeRu₄**
 B₄CeRu₄
 Crystal chemistry: 6.7.2.2
- B₄Ce₃Co₁₁**
 B₄Ce₃Co₁₁
 Crystal chemistry: 6.7.2.1
- B₄Cl₂Rh₂*C₂₄H₄₆
 B₄Cl₂Rh₂*C₂₄H₄₈
- B₄Cl₃F₆P**
 (BF₂)₃B·PCl₃
 Formation: 6.2.2.1
- B₄Cl₄**
 B₄Cl₄
 Formation: 6.2.2.2
- B₄Co*C₅H₁₃
- B₄Co*C₇H₁₁
 B₄Co*C₉H₁₅
 B₄Co*C₁₀H₂₃
 B₄Co*C₁₄H₂₅
- B₄CoDy**
 B₄CoDy
 Crystal chemistry: 6.7.2.3
- B₄CoEr**
 B₄CoEr
 Crystal chemistry: 6.7.2.3
- B₄CoFe₂O₆*C₁₅H₁₅
- B₄CoGd**
 B₄CoGd
 Crystal chemistry: 6.7.2.3
- B₄CoHo**
 B₄CoHo
 Crystal chemistry: 6.7.2.3
- B₄CoLu**
 B₄CoLu
 Crystal chemistry: 6.7.2.3
- B₄CoMn₂O₆S*C₂₂H₃₂
 B₄CoN₂*C₂₃H₄₃
 B₄CoSi₂*C₁₃H₂₇
- B₄CoTb**
 B₄CoTb
 Crystal chemistry: 6.7.2.3
- B₄CoTm**
 B₄CoTm
 Crystal chemistry: 6.7.2.3
- B₄CoU**
 B₄CoU
 Crystal chemistry: 6.7.2.3
- B₄CoY**
 B₄CoY
 Crystal chemistry: 6.7.2.3
- B₄Co₂*C₁₀H₁₆
 B₄Co₂*C₁₂H₁₆
 B₄Co₂*C₂₀H₃₆
 B₄Co₂F₆PS₂*C₁₆H₃₂
 B₄Co₂Fe*C₂₈H₄₄
 B₄Co₂N₂O₄*C₂₂H₃₈
 B₄Co₂Ni₂O₂*C₃₆H₅₆
 B₄Co₃*C₁₂H₃₄
 B₄Co₄*C₂₀H₂₄
- B₄Co₄Dy**
 B₄DyCo₄
 Crystal chemistry: 6.7.2.2
- B₄Co₄Er**
 B₄ErCo₄
 Crystal chemistry: 6.7.2.2
- B₄Co₄Gd**
 B₄GdCo₄
 Crystal chemistry: 6.7.2.2

B₄Co₄Ho
 B₄HoCo₄
 Crystal chemistry: 6.7.2.2
B₄Co₄La
 B₄LaCo₄
 Crystal chemistry: 6.7.2.2
B₄Co₄Lu
 B₄LuCo₄
 Crystal chemistry: 6.7.2.2
B₄Co₄Pr
 B₄Co₄Pr
 Crystal chemistry: 6.7.2.2
B₄Co₄Sm
 B₄Co₄Sm
 Crystal chemistry: 6.7.2.2
B₄Co₄Tb
 B₄Co₄Tb
 Crystal chemistry: 6.7.2.2
B₄Co₄Tm
 B₄Co₄Tm
 Crystal chemistry: 6.7.2.2
B₄Co₄U
 B₄Co₄U
 Crystal chemistry: 6.7.2.2
B₄Co₄Y
 B₄Co₄Y
 Crystal chemistry: 6.7.2.2
B₄(Co,Re)₇
 B₄(Co,Re)₇
 Crystal chemistry: 6.7.2.1
B₄Co₁₁Dy₃
 B₄Co₁₁Dy₃
 Crystal chemistry: 6.7.2.1
B₄Co₁₁Er₃
 B₄Co₁₁Er₃
 Crystal chemistry: 6.7.2.1
B₄Co₁₁Gd₃
 B₄Co₁₁Gd₃
 Crystal chemistry: 6.7.2.1
B₄Co₁₁Ho₃
 B₄Co₁₁Ho₃
 Crystal chemistry: 6.7.2.1
B₄Co₁₁La₃
 B₄Co₁₁La₃
 Crystal chemistry: 6.7.2.1
B₄Co₁₁Lu
 B₄Co₁₁Lu
 Crystal chemistry: 6.7.2.1
B₄Co₁₁Nd₃
 B₄Co₁₁Nd₃
 Crystal chemistry: 6.7.2.1
B₄Co₁₁Pr₃
 B₄Co₁₁Pr₃
 Crystal chemistry: 6.7.2.1

B₄Co₁₁Sm₃
 B₄Co₁₁Sm₃
 Crystal chemistry: 6.7.2.1
B₄Co₁₁Tm₃
 B₄Co₁₁Tm₃
 Crystal chemistry: 6.7.2.1
B₄Co₁₁Y₃
 B₄Co₁₁Y₃
 Crystal chemistry: 6.7.2.1
B₄Cr
 CrB₄
 Crystal structure and lattice parameters: 6.7.2.4
B₄CrDy
 B₄CrDy
 Crystal chemistry: 6.7.2.3
B₄CrEr
 B₄CrEr
 Crystal chemistry: 6.7.2.3
B₄CrGd
 B₄CrGd
 Crystal chemistry: 6.7.2.3
B₄CrHo
 B₄CrHo
 Crystal chemistry: 6.7.2.3
B₄CrLu
 B₄CrLu
 Crystal chemistry: 6.7.2.3
B₄CrNd
 B₄CrNd
 Crystal chemistry: 6.7.2.3
B₄CrO₂S₂*C₁₈H₃₂
B₄CrPr
 B₄CrPr
 Crystal chemistry: 6.7.2.3
B₄CrSm
 B₄CrSm
 Crystal chemistry: 6.7.2.3
B₄CrTb
 B₄CrTb
 Crystal chemistry: 6.7.2.3
B₄CrTm
 B₄CrTm
 Crystal chemistry: 6.7.2.3
B₄CrU
 B₄CrU
 Crystal chemistry: 6.7.2.3
B₄CrY
 B₄CrY
 Crystal chemistry: 6.7.2.3
B₄Cr₃
 B₄Cr₃
 Crystal chemistry: 6.7.2.2

- Cr_3B_4
Preparation: 6.7.3.4
- $\text{B}_4\text{Cr}_3^*\text{Al}$
- $\text{B}_4\text{CuP}_2^*\text{C}_{36}\text{H}_{39}$
- B_4Dy**
 DyB_4
Crystal growth: 6.7.4.2.1, 6.7.4.2.2, 6.7.4.3
Crystal structure and lattice parameters: 6.7.2.4.1
Electrical and magnetic properties: 6.7.2.4.1
Preparation: 6.7.3.1, 6.7.3.4
Thermal stability: 6.7.2.4.1
- B_4DyEr**
 B_4DyEr
Crystal chemistry: 6.7.2.3
- B_4DyFe**
 B_4DyFe
Crystal chemistry: 6.7.2.3
- B_4DyHo**
 B_4DyHo
Crystal chemistry: 6.7.2.3
- B_4DyMn**
 B_4DyMn
Crystal chemistry: 6.7.2.3
- B_4DyMo**
 B_4DyMo
Crystal chemistry: 6.7.2.3
- B_4DyNi**
 B_4DyNi
Crystal chemistry: 6.7.2.3
- B_4DyOs**
 B_4DyOs
Crystal chemistry: 6.7.2.3
- B_4DyOs_4**
 B_4DyOs_4
Crystal chemistry: 6.7.2.2
- B_4DyRe**
 B_4DyRe
Crystal chemistry: 6.7.2.3
- B_4DyRh_4**
 B_4DyRh_4
Crystal chemistry: 6.7.2.2
- B_4DyRu**
 B_4DyRu
Crystal chemistry: 6.7.2.3
- B_4DyRu_4**
 B_4DyRu_4
Crystal chemistry: 6.7.2.2
- B_4DyV**
 B_4DyV
Crystal chemistry: 6.7.2.3
- B_4DyW**
 B_4DyW
Crystal chemistry: 6.7.2.3
- B_4Er**
 ErB_4
Crystal growth: 6.7.4.2.1, 6.7.4.2.2, 6.7.4.3
Crystal structure and lattice parameters: 6.7.2.4.1
Electrical and magnetic properties: 6.7.2.4.1
Preparation: 6.7.3.1, 6.7.3.4
Thermal stability: 6.7.2.4.1
- B_4ErFe**
 B_4ErFe
Crystal chemistry: 6.7.2.3
- B_4ErIr_4**
 B_4ErIr_4
Crystal chemistry: 6.7.2.2
- B_4ErMn**
 B_4ErMn
Crystal chemistry: 6.7.2.3
- B_4ErMo**
 B_4ErMo
Crystal chemistry: 6.7.2.3
- B_4ErOs**
 B_4ErOs
Crystal chemistry: 6.7.2.3
- B_4ErOs_4**
 B_4ErOs_4
Crystal chemistry: 6.7.2.2
- B_4ErRe**
 B_4ErRe
Crystal chemistry: 6.7.2.3
- B_4ErRh_4**
 B_4ErRh_4
Crystal chemistry: 6.7.2.2
- B_4ErRu**
 B_4ErRu
Crystal chemistry: 6.7.2.3
- B_4ErRu_4**
 B_4ErRu_4
Crystal chemistry: 6.7.2.2
- B_4ErV**
 B_4ErV
Crystal chemistry: 6.7.2.3
- B_4ErW**
 B_4ErW
Crystal chemistry: 6.7.2.3
- B_4EuIr_4**
 B_4EuIr_4
Crystal chemistry: 6.7.2.2

- B₄EuOs₄**
 B₄EuOs₄
 Crystal chemistry: 6.7.2.2
- B₄EuPd₆**
 B₄EuPd₆
 Crystal chemistry: 6.7.2.1
- B₄EuRh₆**
 B₄EuRh₆
 Crystal chemistry: 6.7.2.1
- B₄EuRu₄**
 B₄EuRu₄
 Crystal chemistry: 6.7.2.2
- B₄F₄Ni*C₁₆H₂₄**
- B₄F₆**
 (BF₂)₃B
 Formation: 6.2.2.1
- B₄F₆H₃*As**
- B₄F₆H₃P**
 (BF₂)₃B·PH₃
 Formation: 6.2.2.1
- B₄F₆O*C**
- B₄F₆S*C₂H₆**
- B₄F₉P**
 (BF₂)₃B·PF₃
 Formation: 6.2.2.1
- B₄Fe*C₇H₁₁**
- B₄Fe*C₁₂H₂₀**
- B₄Fe*C₁₃H₂₂**
- B₄Fe*C₁₆H₂₈**
- B₄FeGd**
 B₄FeGd
 Crystal chemistry: 6.7.2.3
- B₄FeHo**
 B₄FeHo
 Crystal chemistry: 6.7.2.3
- B₄FeLu**
 B₄FeLu
 Crystal chemistry: 6.7.2.3
- B₄FeNi*C₃₀H₅₄**
- B₄FeOS₂*C₁₇H₃₂**
- B₄FeO₂*C₉H₁₂**
- B₄FeO₃*C₅H₆**
- B₄FeSm**
 B₄FeSm
 Crystal chemistry: 6.7.2.3
- B₄FeTb**
 B₄FeTb
 Crystal chemistry: 6.7.2.3
- B₄FeTm**
 B₄FeTm
 Crystal chemistry: 6.7.2.3
- B₄FeU**
 B₄FeU
 Crystal chemistry: 6.7.2.3
- B₄FeY**
 B₄FeY
 Crystal chemistry: 6.7.2.3
- B₄Fe₂S₂Zn*C₂₆H₄₂**
- B₄Fe₃O₆*C₂₄H₃₄**
- B₄(Fe,Mo)₃**
 B₄(Fe,Mo)₃
 Crystal chemistry: 6.7.2.2
- B₄(Fe,W)₃**
 B₄(Fe,W)₃
 Crystal chemistry: 6.7.2.2
- B₄Fe₄Nd**
 B₄Fe₄Nd
 Crystal chemistry: 6.7.2.2
- B₄Fe₄Sm**
 B₄Fe₄Sm
 Crystal chemistry: 6.7.2.2
- B₄Fe₄Y**
 B₄Fe₄Y
 Crystal chemistry: 6.7.2.2
- B₄Gd**
 GdB₄
 Crystal growth: 6.7.2.4.1, 6.7.4.2.2,
 6.7.4.3
 Crystal structure and lattice
 parameters: 6.7.2.4.1
 Electrical and magnetic properties:
 6.7.2.4.1
 Preparation: 6.7.3.1, 6.7.3.4
 Thermal stability: 6.7.2.4.1
- B₄GdIr₄**
 B₄GdIr₄
 Crystal chemistry: 6.7.2.2
- B₄GdMn**
 B₄GdMn
 Crystal chemistry: 6.7.2.3
- B₄GdMo**
 B₄GdMo
 Crystal chemistry: 6.7.2.3
- B₄GdNi**
 B₄GdNi
 Crystal chemistry: 6.7.2.3
- B₄GdOs**
 B₄GdOs
 Crystal chemistry: 6.7.2.3
- B₄GdOs₄**
 B₄GdOs₄
 Crystal chemistry: 6.7.2.2
- B₄GdRe**
 B₄GdRe
 Crystal chemistry: 6.7.2.3
- B₄GdRh₄**
 B₄GdRh₄
 Crystal chemistry: 6.7.2.2

B₄GdRu

Crystal chemistry: 6.7.2.3

B₄GdRu₄

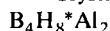
Crystal chemistry: 6.7.2.2

B₄GdV

Crystal chemistry: 6.7.2.3

B₄GdW

Crystal chemistry: 6.7.2.3

**B₄H₉K**Reaction with [(C₆H₅)₃P]₃CuCl: 6.4**B₄H₁₀**

Formation: 6.2.1

Reaction with ER₃: 6.2.1**B₄HfIr₃**

Crystal chemistry: 6.7.2.2

B₄HoIr₄

Crystal chemistry: 6.7.2.2

B₄HoMn

Crystal chemistry: 6.7.2.3

B₄HoMo

Crystal chemistry: 6.7.2.3

B₄HoOs

Crystal chemistry: 6.7.2.3

B₄HoOs₄

Crystal chemistry: 6.7.2.2

B₄HoRe

Crystal chemistry: 6.7.2.3

B₄HoRh₄

Crystal chemistry: 6.7.2.2

B₄HoRu

Crystal chemistry: 6.7.2.3

B₄HoRu₄

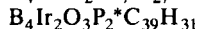
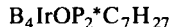
Crystal chemistry: 6.7.2.2

B₄HoV

Crystal chemistry: 6.7.2.3

B₄HoW

Crystal chemistry: 6.7.2.3

**B₄Ir₃Sc**

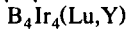
Crystal chemistry: 6.7.2.2

B₄Ir₃Zr

Crystal chemistry: 6.7.2.2

B₄Ir₄La

Crystal chemistry: 6.7.2.2

B₄Ir₄(Lu,Y)

Crystal chemistry: 6.7.2.2

B₄Ir₄Nd

Crystal chemistry: 6.7.2.2

B₄Ir₄Pr

Crystal chemistry: 6.7.2.2

B₄Ir₄Sm

Crystal chemistry: 6.7.2.2

B₄Ir₄Tb

Crystal chemistry: 6.7.2.2

B₄Ir₄Th

Crystal chemistry: 6.7.2.2

B₄Ir₄Y

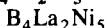
Crystal chemistry: 6.7.2.2

B₄LaOs₄

Crystal chemistry: 6.7.2.2

B₄LaRu₄

Crystal chemistry: 6.7.2.2

B₄La₂Ni₅

Crystal chemistry: 6.7.2.2

B₄Lu

Crystal growth: 6.7.4.3

Crystal structure and lattice parameters: 6.7.2.4.1

Electrical and magnetic properties: 6.7.2.4.1

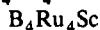
Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.1

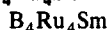


- B₄LuOs₄**
 B₄LuOs₄
 Crystal chemistry: 6.7.2.2
- B₄LuRh₄**
 B₄LuRh₄
 Crystal chemistry: 6.7.2.2
- B₄LuRu₄**
 B₄LuRu₄
 Crystal chemistry: 6.7.2.2
- B₄Mg**
 MgB₄
 Crystal structure and lattice parameters: 6.7.2.4.5
- B₄Mn**
 MnB₄
 Crystal structure and lattice parameters: 6.7.2.4
- B₄MnTb**
 B₄MnTb
 Crystal chemistry: 6.7.2.3
- B₄MnU**
 B₄MnU
 Crystal chemistry: 6.7.2.3
- B₄MnY**
 B₄MnY
 Crystal chemistry: 6.7.2.3
- B₄Mn₃**
 B₄Mn₃
 Crystal chemistry: 6.7.2.2
- B₄Mo**
 MoB₄
 Hot-pressing: 6.7.5.2
- B₄MoTb**
 B₄MoTb
 Crystal chemistry: 6.7.2.3
- B₄MoTh**
 B₄MoTh
 Crystal chemistry: 6.7.2.3
- B₄MoU**
 B₄MoU
 Crystal chemistry: 6.7.2.3
- B₄MoY**
 B₄MoY
 Crystal chemistry: 6.7.2.3
- B₄(Mo,Ru)₃**
 B₄(Mo,Ru)₃
 Crystal chemistry: 6.7.2.2
- B₄N₂Ni*C₁₈H₃₈
 B₄Na*C₄H₁₁
- B₄Nb₃**
 B₄Nb₃
 Crystal chemistry: 6.7.2.2
- B₄Nd**
 NdB₄
 Crystal growth: 6.7.4.3
 Crystal structure and lattice parameters: 6.7.2.4.1
 Electrical and magnetic properties: 6.7.2.4.1
 Preparation: 6.7.3.1
 Thermal stability: 6.7.2.4.1
- B₄NdNi**
 B₄NdNi
 Crystal chemistry: 6.7.2.3
- B₄NdOs₄**
 B₄NdOs₄
 Crystal chemistry: 6.7.2.2
- B₄NdRh₄**
 B₄NdRh₄
 Crystal chemistry: 6.7.2.2
- B₄NdRu₄**
 B₄NdRu₄
 Crystal chemistry: 6.7.2.2
- B₄Nd₂Ni₅**
 B₄Nd₂Ni₅
 Crystal chemistry: 6.7.2.2
- B₄Ni*C₁₄H₂₈
 B₄Ni*C₂₄H₄₈
 B₄NiP₄*C₅₄H₅₄
- B₄NiPr**
 B₄NiPr
 Crystal chemistry: 6.7.2.3
- B₄NiS₂*C₁₆H₃₂
- B₄NiSm**
 B₄NiSm
 Crystal chemistry: 6.7.2.3
- B₄NiTb**
 B₄NiTb
 Crystal chemistry: 6.7.2.3
- B₄NiU**
 B₄NiU
 Crystal chemistry: 6.7.2.3
- B₄NiY**
 B₄NiY
 Crystal chemistry: 6.7.2.3
- B₄Np**
 NpB₄
 Crystal structure and lattice parameters: 6.7.2.4.1
- B₄OOsP₂*C₃₇H₃₈
 B₄O₃OsSi₂*C₁₁H₂₂
- B₄OsTb**
 B₄OsTb
 Crystal chemistry: 6.7.2.3

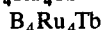
- B₄OsTm**
 B₄OsTm
 Crystal chemistry: 6.7.2.3
- B₄OsY**
 B₄OsY
 Crystal chemistry: 6.7.2.3
- B₄OsYb**
 B₄OsYb
 Crystal chemistry: 6.7.2.3
- B₄Os₄Pr**
 B₄Os₄Pr
 Crystal chemistry: 6.7.2.2
- B₄Os₄Sm**
 B₄Os₄Sm
 Crystal chemistry: 6.7.2.2
- B₄Os₄Tb**
 B₄Os₄Tb
 Crystal chemistry: 6.7.2.2
- B₄Os₄Th**
 B₄Os₄Th
 Crystal chemistry: 6.7.2.2
- B₄Os₄Tm**
 B₄Os₄Tm
 Crystal chemistry: 6.7.2.2
- B₄Os₄U**
 B₄Os₄U
 Crystal chemistry: 6.7.2.2
- B₄Os₄Y**
 B₄Os₄Y
 Crystal chemistry: 6.7.2.2
- B₄Os₄Yb**
 B₄Os₄Yb
 Crystal chemistry: 6.7.2.2
- B₄P*C₂₀H₂₂Au**
B₄PRh*C₂₁H₂₂
B₄P₂Pt*C₁₄H₃₆
B₄P₂Pt*C₁₄H₃₇
B₄P₂Pt*C₁₄H₃₈
B₄P₂Pt*C₁₆H₄₂
- B₄Pr**
 PrB₄
 Crystal growth: 6.7.4.3
 Crystal structure and lattice parameters: 6.7.2.4.1
 Electrical and magnetic properties: 6.7.2.4.1
 Preparation: 6.7.3.1
 Thermal stability: 6.7.2.4.1
- B₄PrRu₄**
 B₄PrRu₄
 Crystal chemistry: 6.7.2.2
- B₄Pt*C₂₄H₄₆**
B₄Pt*C₂₄H₄₈
- B₄Pu**
- PuB₄**
 Crystal structure and lattice parameters: 6.7.2.4.1
 Thermal stability: 6.7.2.4.1
- B₄ReTb**
 B₄ReTb
 Crystal chemistry: 6.7.2.3
- B₄ReTh**
 B₄ReTh
 Crystal chemistry: 6.7.2.3
- B₄ReTm**
 B₄ReTm
 Crystal chemistry: 6.7.2.3
- B₄ReU**
 B₄ReU
 Crystal chemistry: 6.7.2.3
- B₄ReY**
 B₄ReY
 Crystal chemistry: 6.7.2.3
- B₄Rh*C₂₄H₄₇**
B₄Rh₄(Sc,Th)
 B₄Rh₄(Sc,Th)
 Crystal chemistry: 6.7.2.2
- B₄Rh₄Sm**
 B₄Rh₄Sm
 Crystal chemistry: 6.7.2.2
- B₄Rh₄Tb**
 B₄Rh₄Tb
 Crystal chemistry: 6.7.2.2
- B₄Rh₄Th**
 B₄Rh₄Th
 Crystal chemistry: 6.7.2.2
- B₄Rh₄Tm**
 B₄Rh₄Tm
 Crystal chemistry: 6.7.2.2
- B₄Rh₄Y**
 B₄Rh₄Y
 Crystal chemistry: 6.7.2.2
- B₄Rh₅Sr₂**
 B₄Rh₅Sr₂
 Crystal chemistry: 6.7.2.1
- B₄RuTb**
 B₄RuTb
 Crystal chemistry: 6.7.2.3
- B₄RuTm**
 B₄RuTm
 Crystal chemistry: 6.7.2.3
- B₄RuY**
 B₄RuY
 Crystal chemistry: 6.7.2.3
- B₄RuYb**
 B₄RuYb
 Crystal chemistry: 6.7.2.3

B₄Ru₄Sc

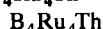
Crystal chemistry: 6.7.2.2

B₄Ru₄Sm

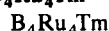
Crystal chemistry: 6.7.2.2

B₄Ru₄Tb

Crystal chemistry: 6.7.2.2

B₄Ru₄Th

Crystal chemistry: 6.7.2.2

B₄Ru₄Tm

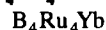
Crystal chemistry: 6.7.2.2

B₄Ru₄U

Crystal chemistry: 6.7.2.2

B₄Ru₄Y

Crystal chemistry: 6.7.2.2

B₄Ru₄Yb

Crystal chemistry: 6.7.2.2

B₄Sm

Crystal growth: 6.7.4.3

Crystal structure and lattice
parameters: 6.7.2.4.1Electrical and magnetic properties:
6.7.2.4.1

Preparation: 6.7.3.1

Thermal stability: 6.7.2.4.1

B₄Ta₃

Crystal chemistry: 6.7.2.2

B₄Tb

Crystal growth: 6.7.4.2.1, 6.7.4.3

Crystal structure and lattice
parameters: 6.7.2.4.1Electrical and magnetic properties:
6.7.2.4.1

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.1

B₄TbV

Crystal chemistry: 6.7.2.3

B₄TbW

Crystal chemistry: 6.7.2.3

B₄Tb₃*C₁₁**B₄Th**

Crystal growth: 6.7.4.2.1, 6.7.4.2.2

Crystal structure and lattice
parameters: 6.7.2.4.1Electrical and magnetic properties:
6.7.2.4.1

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.1

B₄ThV

Crystal chemistry: 6.7.2.3

B₄ThW

Crystal chemistry: 6.7.2.3

B₄Ti₃

Crystal chemistry: 6.7.2.2

B₄Tm

Crystal growth: 6.7.4.3

Crystal structure and lattice
parameters: 6.7.2.4.1Electrical and magnetic properties:
6.7.2.4.1

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.1

B₄UCrystal structure and lattice
parameters: 6.7.2.4.1Electrical and magnetic properties:
6.7.2.4.1

Hot-pressing: 6.7.5.2

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.1

B₄UV

Crystal chemistry: 6.7.2.3

B₄UW

Crystal chemistry: 6.7.2.3

B₄V*C₁₄H₂₂**B₄V₃**

Crystal chemistry: 6.7.2.2



Crystal growth: 6.7.4.3

B₄W

Hot-pressing: 6.7.5.2

B₄WY

Crystal chemistry: 6.7.2.3

B₄Y**YB₄**

Crystal growth: 6.7.4.2.1, 6.7.4.3
 Crystal structure and lattice parameters: 6.7.2.4.1
 Electrical and magnetic properties: 6.7.2.4.2
 Hot-pressing: 6.7.5.2
 Preparation: 6.7.3.1, 6.7.3.4
 Thermal stability: 6.7.2.4.1

B₄Yb**YbB₄**

Crystal growth: 6.7.4.3
 Crystal structure and lattice parameters: 6.7.2.4.1
 Electrical and magnetic properties: 6.7.2.4.1
 Preparation: 6.7.3.1
 Thermal stability: 6.7.2.4.1

B₄Yb*Al**B₅*C₂H₇****B₅*C₄H₁₁****B₅Ca₂Os₃****B₅Ca₂Os₃**

Crystal chemistry: 6.7.2.2

B₅CdClP*C₁₈H₂₃**B₅ClIrOP₂*C₃₇H₃₈****B₅ClOOSp₃Pt*C₄₅H₄₉****B₅Co*C₅H₁₄****B₅Co*C₇H₁₂****B₅CoO₄*C₄H₈****B₅CoSi₂*C₁₃H₂₈****B₅Co₂*C₁₂H₁₇****B₅Co₂*C₂₀H₃₅****B₅Co₂*C₂₀H₃₇****B₅Co₂P₃*C₂₀H₅₁****B₅Co₂S₂*C₁₀H₁₇****B₅Co₂S₂*C₁₀H₁₅****B₅CuP₂*C₃₆H₃₈****B₅Eu₂Os₃****B₅Eu₂Os₃**

Crystal chemistry: 6.7.2.2

B₅Fe*C₅H₁₅**B₅Fe*C₁₅H₂₅****B₅FeN₃*C₁₉H₃₈****B₅FeO₂*C₇H₁₃****B₅Gd₂****Gd₂B₅**

Crystal structure: 6.7.2.4.5

B₅H₈K**K[B₅H₈]**

Reaction with [(C₆H₅)₃P]₂CdCl₂: 6.4

Reaction with [(C₆H₅)₃P]₃CuCl: 6.4

B₅H₈Li**Li[B₅H₈]**

Reaction with (C₆H₅)₃PAuNO₃: 6.4

B₅H₉**B₅H₉**

Reaction with η⁵-CpCo(CO)₂ and Fe(CO)₅: 6.5.3.1

Reaction with Co atoms: 6.5.3.3

Reaction with ER₃: 6.2.1

Reaction with HMn(CO)₅: 6.5.2.2

B₅H₁₂K**K[B₅H₁₂]**

Reaction with [(C₆H₅)₃P]₃CuCl: 6.4

B₅HfMo₄**B₅HfMo₄**

Crystal chemistry: 6.7.2.2

B₅HfW₄**B₅HfW₄**

Crystal chemistry: 6.7.2.2

B₅IrOP₂*C₃₇H₃₈**B₅Ir_{2.5}Mo_{2.5}****B₅Ir_{2.5}Mo_{2.5}**

Crystal chemistry: 6.7.2.2

B₅MnMo₄**B₅MnMo₄**

Crystal chemistry: 6.7.2.2

B₅MnO₃*C₃H₁₀**B₅MnW₄****B₅MnW₄**

Crystal chemistry: 6.7.2.2

B₅Mo₂**Mo₂B₅**

Crystal growth: 6.7.4.3

Hot-pressing: 6.7.5.2

B₅Na₃Pt₉**B₅Na₃Pt₉**

Crystal chemistry: 6.7.2.1

B₅Nd₂**Nd₂B₅**

Crystal structure: 6.7.2.4.5

B₅Ni₂*C₁₂H₁₇**B₅OOSp₂*C₃₇H₃₉****B₅P*C₁₈H₂₃Au****B₅P₂Pt*C₁₃H₃₈****B₅P₂Pt*C₁₃H₃₉****B₅P₄Pt₂*C₂₈H₇₁****B₅Pd₂W₂****B₅(W,Pd)₂**

Crystal chemistry: 6.7.2.3

B₅Sm₂**Sm₂B₅**

Crystal structure: 6.7.2.4.5

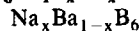
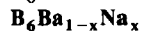
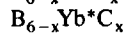
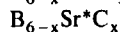
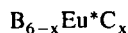
B₅W₂

Crystal chemistry: 6.7.2.3

Crystal growth: 6.7.4.3

Hot-pressing: 6.7.5.2

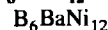
Sintering: 6.7.5.1



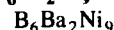
Existence: 6.7.2.4.2

B₆BaCrystal structure and lattice
parameters: 6.7.2.4.2Electrical and magnetic properties:
6.7.2.4.2Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4,
6.7.3.5

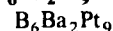
Thermal stability: 6.7.2.4.2

B₆BaNi₁₂

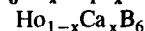
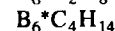
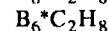
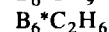
Crystal chemistry: 6.7.2.1

B₆Ba₂Ni₉

Crystal chemistry: 6.7.2.1

B₆Ba₂Pt₉

Crystal chemistry: 6.7.2.1



Formation: 6.7.2.4.6

B₆Ca

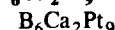
Crystal growth: 6.7.4.3

Crystal structure and lattice
parameters: 6.7.4.2Electrical and magnetic properties:
6.7.2.4.2

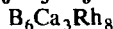
Hot-pressing: 6.7.5.2

Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4,
6.7.3.5

Thermal stability: 6.7.2.4.2

B₆Ca₂Pt₉

Crystal chemistry: 6.7.2.1

B₆Ca₃Rh₈

Crystal chemistry: 6.7.2.1

B₆CeCrystal growth: 6.7.4.2.1, 6.7.4.2.2,
6.7.4.3Crystal structure and lattice
parameters: 6.7.2.4.2Electrical and magnetic properties:
6.7.2.4.2

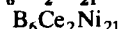
Hot-pressing: 6.7.5.2

Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4,
6.7.3.5

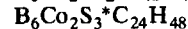
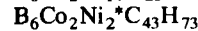
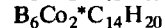
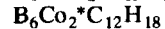
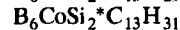
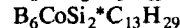
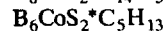
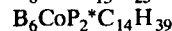
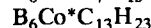
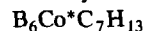
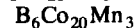
Thermal stability: 6.7.2.4.2

B₆CeCr₂

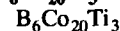
Crystal chemistry: 6.7.2.3

B₆Ce₂Ni₂₁

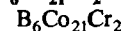
Crystal chemistry: 6.7.2.1

**B₆Co₂₀Mn₃**

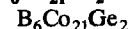
Crystal chemistry: 6.7.2.1

B₆Co₂₀Ti₃

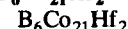
Crystal chemistry: 6.7.2.1

B₆Co₂₁Cr₂

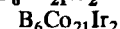
Crystal chemistry: 6.7.2.1

B₆Co₂₁Ge₂

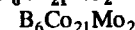
Crystal chemistry: 6.7.2.1

B₆Co₂₁Hf₂

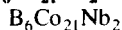
Crystal chemistry: 6.7.2.1

B₆Co₂₁Ir₂

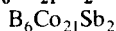
Crystal chemistry: 6.7.2.1

B₆Co₂₁Mo₂

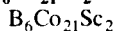
Crystal chemistry: 6.7.2.1

B₆Co₂₁Nb₂

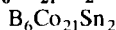
Crystal chemistry: 6.7.2.1

B₆Co₂₁Sb₂

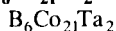
Crystal chemistry: 6.7.2.1

B₆Co₂₁Sc₂

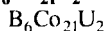
Crystal chemistry: 6.7.2.1

B₆Co₂₁Sn₂

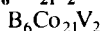
Crystal chemistry: 6.7.2.1

B₆Co₂₁Ta₂

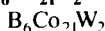
Crystal chemistry: 6.7.2.1

B₆Co₂₁U₂

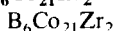
Crystal chemistry: 6.7.2.1

B₆Co₂₁V₂

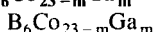
Crystal chemistry: 6.7.2.1

B₆Co₂₁W₂

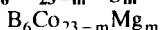
Crystal chemistry: 6.7.2.1

B₆Co₂₁Zr₂

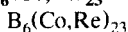
Crystal chemistry: 6.7.2.1

B₆Co_{23-m}Ga_m

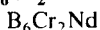
Crystal chemistry: 6.7.2.1

B₆Co_{23-m}Mg_m

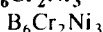
Crystal chemistry: 6.7.2.1

B₆(Co,Re)₂₃

Crystal chemistry: 6.7.2.1

B₆Cr₂Nd

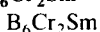
Crystal chemistry: 6.7.2.3

B₆Cr₂Ni₃

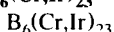
Crystal chemistry: 6.7.2.2

B₆Cr₂Pr

Crystal chemistry: 6.7.2.3

B₆Cr₂Sm

Crystal chemistry: 6.7.2.3

B₆(Cr,Ir)₂₃

Crystal chemistry: 6.7.2.1

B₆CuP₂*C₃₆H₃₉**B₆Dy**

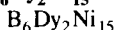
Crystal growth: 6.7.4.3

Crystal structure and lattice
parameters: 6.7.2.4.2Electrical and magnetic properties:
6.7.2.4.2

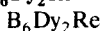
Hot-pressing: 6.7.5.2

Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4,
6.7.3.5

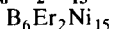
Thermal stability: 6.7.2.4.2

B₆Dy₂Ni₁₅

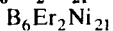
Crystal chemistry: 6.7.2.2

B₆Dy₂Re

Crystal chemistry: 6.7.2.3

B₆Er₂Ni₁₅

Crystal chemistry: 6.7.2.2

B₆Er₂Ni₂₁

Crystal chemistry: 6.7.2.1

B₆Er₂Re

Crystal chemistry: 6.7.2.3

B₆Eu

Crystal growth: 6.7.4.3

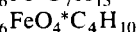
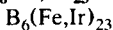
Crystal structure and lattice
parameters: 6.7.2.4.2Electrical and magnetic properties:
6.7.2.4.2

Hot-pressing: 6.7.5.2

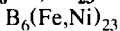
Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4,
6.7.3.5

Sintering: 6.7.5.1

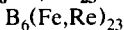
Thermal stability: 6.7.2.4.2

B₆Fe*C₇H₁₃**B₆Fe₂*C₁₂H₁₈****B₆Fe₂Ni₂*C₅₀H₈₅****B₆(Fe,Ir)₂₃**

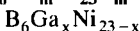
Crystal chemistry: 6.7.2.1

B₆(Fe,Ni)₂₃

Crystal chemistry: 6.7.2.1

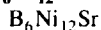
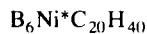
B₆(Fe,Re)₂₃

Crystal chemistry: 6.7.2.1

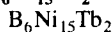
B₆Ga_mNi_{23-m}

Crystal chemistry: 6.7.2.1

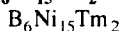
- B₆Gd**
GdB₆
 Crystal growth: 6.7.4.3
 Crystal structure and lattice parameters: 6.7.2.4.2
 Electrical and magnetic properties: 6.7.2.4.2
 Hot-pressing: 6.7.5.2
 Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4, 6.7.3.5
 Thermal stability: 6.7.2.4.2
- B₆Gd₂Re**
B₆Gd₂Re
 Crystal chemistry: 6.7.2.3
- B₆Ge_{1.4}Ni_{21.6}**
B₆Ge_{1.4}Ni_{21.6}
 Crystal chemistry: 6.7.2.1
- B₆H₉K**
K[B₆H₉]
 Reaction with [(C₆H₅)₃P]₃CuCl: 6.4
- B₆H₁₀**
B₆H₁₀
 Reaction with Co atoms: 6.5.3.3
 Reaction with Fe₂(CO)₉: 6.5.3.1
- B₆Ho_{1-x}La_x**
Ho_{1-x}La_xB₆
 Formation: 6.7.2.4.6
- B₆Ho₂Ni₁₅**
B₆Ho₂Ni₁₅
 Crystal chemistry: 6.7.2.2
- B₆Ho₂Re**
B₆Ho₂Re
 Crystal chemistry: 6.7.2.3
- B₆In₂Ni₂₁**
B₆In₂Ni₂₁
 Crystal chemistry: 6.7.2.1
- B₆Ir₃W₂**
B₆Ir₃W₂
 Crystal chemistry: 6.7.2.2
- B₆(Ir,Mn)₂₃**
B₆(Ir,Mn)₂₃
 Crystal chemistry: 6.7.2.1
- B₆K**
KB₆
 Crystal structure and lattice parameters: 6.7.2.4.2
 Preparation: 6.7.3.1
 Thermal stability: 6.7.2.4.2
- B₆La**
LaB₆
 Crystal growth: 6.7.4.2.1, 6.7.4.2.2, 6.7.4.3
 Crystal structure and lattice parameters: 6.7.2.4.2
- Electrical and magnetic properties: 6.7.2.4.2
 Formation: 6.7.1, 6.7.4.1.2
 Hot-pressing: 6.7.5.2
 Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4, 6.7.3.5, 6.7.3.7
 Sintering: 6.7.5.1
 Thermal stability: 6.7.2.4.2
- B₆Li₃Ni₂₀**
B₆Li₃Ni₂₀
 Crystal chemistry: 6.7.2.1
- B₆Lu₂Ni₃**
B₆Lu₂Ni₃
 Crystal chemistry: 6.7.2.2
- B₆Lu₂Ni₁₅**
B₆Lu₂Ni₁₅
 Crystal chemistry: 6.7.2.2
- B₆Lu₂Ni₂₁**
B₆Lu₂Ni₂₁
 Crystal chemistry: 6.7.2.1
- B₆Lu₅Ni₁₉**
B₆Lu₅Ni₁₉
 Crystal chemistry: 6.7.2.1
- B₆Mg_{3.5}Ni_{19.5}**
B₆Mg_{3.5}Ni_{19.5}
 Crystal chemistry: 6.7.2.1
- B₆Mn₂Ni₂₁**
B₆Mn₂Ni₂₁
 Crystal chemistry: 6.7.2.1
- B₆(Mn,Re)₂₃**
B₆(Mn,Re)₂₃
 Crystal chemistry: 6.7.2.1
- B₆N₆*C₂₄H₇₂Al₆**
- B₆Na**
NaB₆
 Thermal stability preparation: 6.7.3.1
- B₆Nb₂Ni₂₁**
B₆Nb₂Ni₂₁
 Crystal chemistry: 6.7.2.1
- B₆Nb₅**
B₆Nb₅
 Crystal chemistry: 6.7.2.2
- B₆(Nb,Ru)₂₁**
B₆(Nb,Ru)₂₁
 Crystal chemistry: 6.7.2.1
- B₆Nd**
NdB₆
 Crystal growth: 6.7.4.3
 Crystal structure and lattice parameters: 6.7.2.4.2
 Electrical and magnetic properties: 6.7.2.4.2
 Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4, 6.7.3.5
 Thermal stability: 6.7.2.4.2



Crystal chemistry: 6.7.2.1



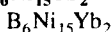
Crystal chemistry: 6.7.2.2



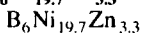
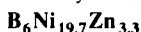
Crystal chemistry: 6.7.2.2



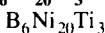
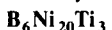
Crystal chemistry: 6.7.2.2



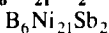
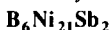
Crystal chemistry: 6.7.2.2



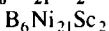
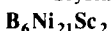
Crystal chemistry: 6.7.2.1



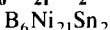
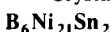
Crystal chemistry: 6.7.2.1



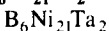
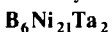
Crystal chemistry: 6.7.2.1



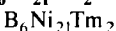
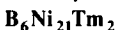
Crystal chemistry: 6.7.2.1



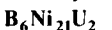
Crystal chemistry: 6.7.2.1



Crystal chemistry: 6.7.2.1



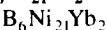
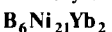
Crystal chemistry: 6.7.2.1



Crystal chemistry: 6.7.2.1



Crystal chemistry: 6.7.2.1



Crystal chemistry: 6.7.2.1



Crystal chemistry: 6.7.2.1



Crystal structure and lattice parameters: 6.7.2.4.2



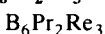
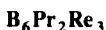
Crystal growth: 6.7.4.2.1, 6.7.4.2.2, 6.7.4.3

Crystal structure and lattice parameters: 6.7.2.4.2

Electrical and magnetic properties: 6.7.2.4.2

Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4, 6.7.3.5

Thermal stability: 6.7.2.4.2



Crystal chemistry: 6.7.2.2



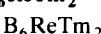
Crystal chemistry: 6.7.2.1



Crystal structure and lattice parameters: 6.7.2.4.2



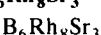
Crystal chemistry: 6.7.2.3



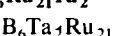
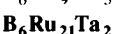
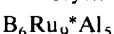
Crystal chemistry: 6.7.2.3



Crystal chemistry: 6.7.2.3



Crystal chemistry: 6.7.2.1



Crystal chemistry: 6.7.2.1



Crystal growth: 6.7.4.2.1, 6.7.4.2.2, 6.7.4.3

Crystal structure and lattice parameters: 6.7.2.4.2

Electrical and magnetic properties: 6.7.2.4.2

Hot-pressing: 6.7.5.2

Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4, 6.7.3.5

Thermal stability: 6.7.2.4.2

B₆Sr

Crystal growth: 6.7.4.3

Crystal structure and lattice
parameters: 6.7.2.4.2Electrical and magnetic properties:
6.7.2.4.2Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4,
6.7.3.5

Thermal stability: 6.7.2.4.2

B₆Tb

Crystal growth: 6.7.4.3

Crystal structure and lattice
parameters: 6.7.2.4.2Electrical and magnetic properties:
6.7.2.4.2Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4,
6.7.3.5

Thermal stability: 6.7.2.4.2

B₆Th

Crystal growth: 6.7.4.3

Crystal structure and lattice
parameters: 6.7.2.4.2Electrical and magnetic properties:
6.7.2.4.2Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4,
6.7.3.5

Thermal stability: 6.7.2.4.2

B₆V₅

Crystal chemistry: 6.7.2.2

B₆Y

Crystal growth: 6.7.4.3

Crystal structure and lattice
parameters: 6.7.4.2Electrical and magnetic properties:
6.7.2.4.2

Hot-pressing: 6.7.5.2

Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4,
6.7.3.5

Sintering: 6.7.5.1

B₆Yb

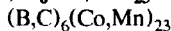
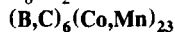
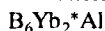
Crystal growth: 6.7.4.3

Crystal structure and lattice
parameters: 6.7.2.4.2Electrical and magnetic properties:
6.7.2.4.2

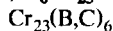
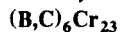
Hot-pressing: 6.7.5.2

Preparation: 6.7.3.1, 6.7.3.3, 6.7.3.4,
6.7.3.5

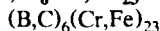
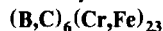
Thermal stability: 6.7.2.4.2



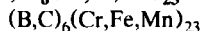
Crystal chemistry: 6.7.2.1



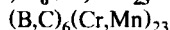
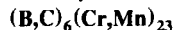
Crystal chemistry: 6.7.2.1



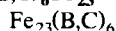
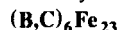
Crystal chemistry: 6.7.2.1



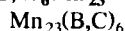
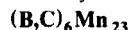
Crystal chemistry: 6.7.2.1



Crystal chemistry: 6.7.2.1



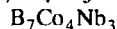
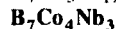
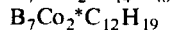
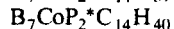
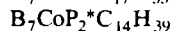
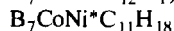
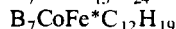
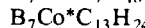
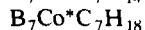
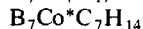
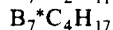
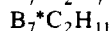
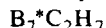
Crystal chemistry: 6.7.2.1



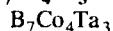
Crystal chemistry: 6.7.2.1



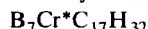
Crystal chemistry: 6.7.2.2



Crystal chemistry: 6.7.2.2

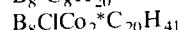
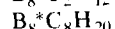
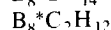
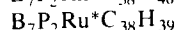
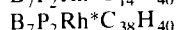
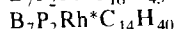
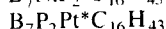
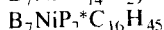
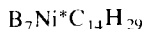


Crystal chemistry: 6.7.2.2

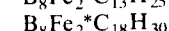
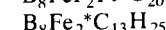
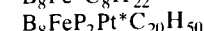
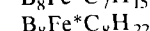
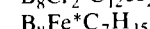
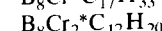
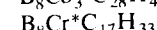
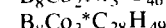
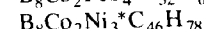
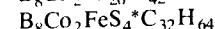
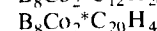
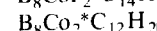
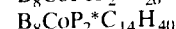
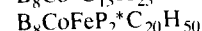
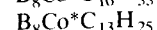
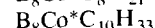
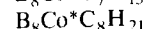
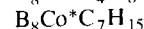
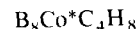


B₇I₇

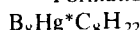
Formation: 6.2.2.3

**B₈Cl₈**

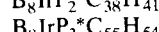
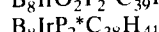
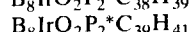
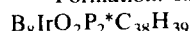
Formation: 6.2.2.3

**B₈H₁₈**

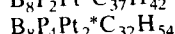
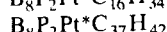
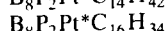
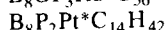
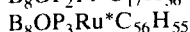
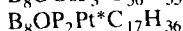
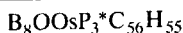
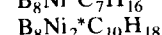
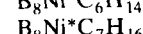
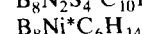
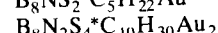
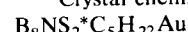
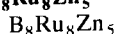
Formation: 6.2.1

**B₈I₈**

Formation: 6.2.2.3

**B₈Li₃Ni₁₆**

Crystal chemistry: 6.7.2.1

**B₈Ru₈Zn₅**

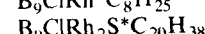
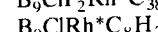
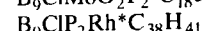
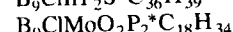
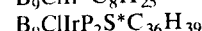
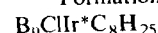
Crystal chemistry: 6.7.2.2

B₈Ru₁₁

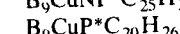
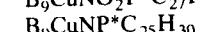
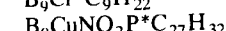
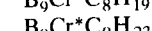
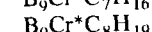
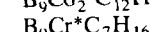
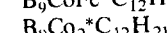
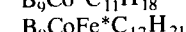
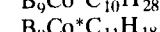
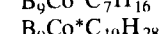
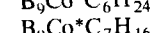
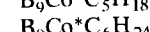
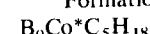
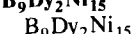
Crystal chemistry: 6.7.2.2

B₉Br₉

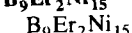
Formation: 6.2.2.3

**B₉Cl₉**

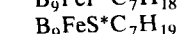
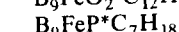
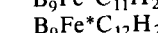
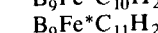
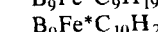
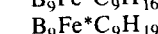
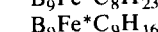
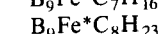
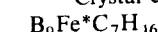
Formation: 6.2.2.3

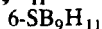
**B₉Dy₂Ni₁₅**

Crystal chemistry: 6.7.2.2

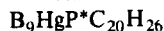
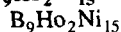
B₉Er₂Ni₁₅

Crystal chemistry: 6.7.2.2



B₉H₁₁S

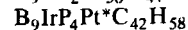
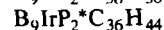
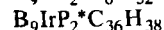
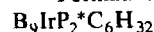
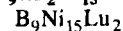
Reaction with Fe atoms: 6.5.3.3

**B₉Ho₂Ni₁₅**

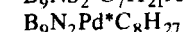
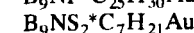
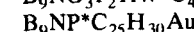
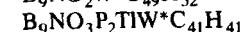
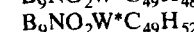
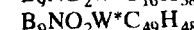
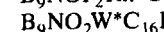
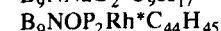
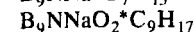
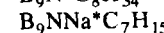
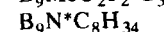
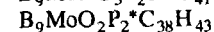
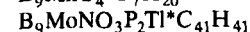
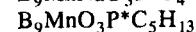
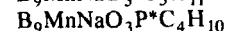
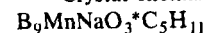
Crystal chemistry: 6.7.2.2

B₉I₉

Formation: 6.2.2.3

**B₉Lu₂Ni₁₅**

Crystal chemistry: 6.7.2.2

**B₉Ni₁₅Tb₂**

Crystal chemistry: 6.7.2.2

B₉Ni₁₅Tm₂

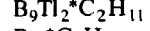
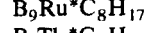
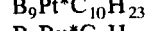
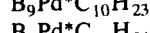
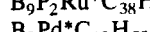
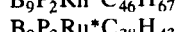
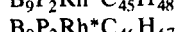
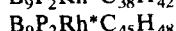
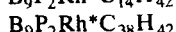
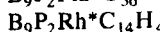
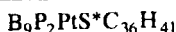
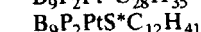
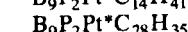
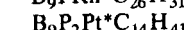
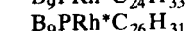
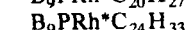
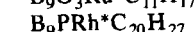
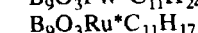
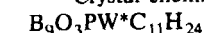
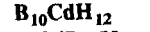
Crystal chemistry: 6.7.2.2

B₉Ni₁₅Y₂

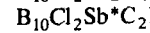
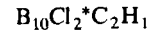
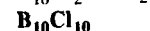
Crystal chemistry: 6.7.2.2

B₉Ni₁₅Yb₂

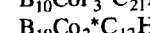
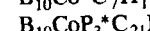
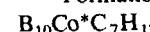
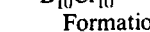
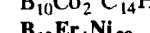
Crystal chemistry: 6.7.2.2

**B₁₀CdH₁₂**

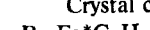
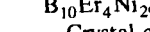
Formation: 6.4

**B₁₀Cl₁₀**

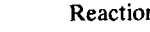
Formation: 6.2.2.3

**B₁₀Er₄Ni₂₉**

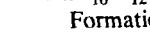
Crystal chemistry: 6.7.2.2

**B₁₀H₁₂S**

Reaction with Fe atoms: 6.5.3.3

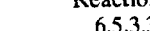
B₁₀H₁₂Zn

Formation: 6.4

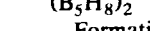
B₁₀H₁₄Reaction with (CH₃)₂Cd: 6.4Reaction with (CH₃)₂Zn: 6.4

Reaction with Fe atoms and arenes:

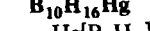
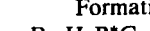
6.5.3.3

B₁₀H₁₆

Formation: 6.2.1

B₁₀H₁₆Hg

Formation: 6.4

**B₁₀Ho₃Ni₁₉**

Crystal chemistry: 6.7.2.2

- B₁₀I₁₀**
 B₁₀I₁₀
 Formation: 6.2.2.3
 Electrical and magnetic properties:
 6.7.2.4.3
 Preparation: 6.7.3.4
 Thermal stability: 6.7.2.4.3
- B₁₀Lu₄Ni₂₉**
 B₁₀Lu₄Ni₂₉
 Crystal chemistry: 6.7.2.2
- B₁₀N*C₃H₁₆**
B₁₀N*C₄H₂₅
B₁₀Ni*C₆H₁₆
B₁₀Ni₂*C₁₀H₂₀
B₁₀Ni₃*C₃₀H₅₈
B₁₀Ni₂₉Sc₄
 B₁₀Ni₂₉Sc₄
 Crystal chemistry: 6.7.2.2
- B₁₀Ni₂₉Tm₄**
 B₁₀Ni₂₉Tm₄
 Crystal chemistry: 6.7.2.2
- B₁₀Ni₂₉Yb₄**
 B₁₀Ni₂₉Yb₄
 Crystal chemistry: 6.7.2.2
- B₁₀P₂Pd*C₂₆H₃₆**
B₁₀P₂Pd*C₂₈H₃₆
B₁₀P₂Pd*C₃₆H₄₂
B₁₀P₂Pt*C₁₂H₄₂
B₁₀P₂Pt*C₂₄H₆₆
B₁₀P₂Pt*C₂₆H₃₆
B₁₀P₂Pt*C₃₆H₄₂
B₁₀P₂Rh*C₃₈H₄₃
B₁₀P₂RhS*C₃₆H₄₁
B₁₀Rh₁₄Sr₅
 B₁₀Rh₁₄Sr₅
 Crystal chemistry: 6.7.2.1
- B₁₁Cl₁₁**
 B₁₁Cl₁₁
 Formation: 6.2.2.3
- B₁₁Co*C₈H₂₃**
B₁₁Mg₅Rh₁₃
 B₁₁Mg₅Rh₁₃
 Crystal chemistry: 6.7.2.1
- B₁₂*Al**
B₁₂Cl₁₂
 B₁₂Cl₁₂
 Formation: 6.2.2.3
- B₁₂CoO*C₁₀H₃₅**
B₁₂(Co,Ir)₂₃
 B₆(Co,Ir)₂₃B₆
 Crystal chemistry: 6.7.2.1
- B₁₂Dy**
 DyB₁₂
 Crystal structure and lattice
 parameters: 6.7.2.4.3
- B₁₂Er**
 ErB₁₂
 Crystal structure and lattice
 parameters: 6.7.2.4.3
 Electrical and magnetic properties:
 6.7.2.4.3
 Preparation: 6.7.3.4
 Thermal stability: 6.7.2.4.3
- B₁₂Gd**
 GdB₁₂
 Crystal structure and lattice
 parameters: 6.7.2.4.3
 Electrical and magnetic properties:
 6.7.2.4.3
 Preparation: 6.7.3.7
 Thermal stability: 6.7.2.4.3
- B₁₂Np**
 NpB₁₂
 Crystal structure and lattice
 parameters: 6.7.2.4.3
- B₁₂P₂Pt₂*C₁₆H₄₀**
B₁₂Pr₈Re₁₃
 B₁₂Pr₈Re₁₃
 Crystal chemistry: 6.7.2.2
- B₁₂Tb**
 TbB₁₂
 Crystal structure and lattice
 parameters: 6.7.2.4.3
 Electrical and magnetic properties:
 6.7.2.4.3
 Thermal stability: 6.7.2.4.3
- B₁₂Th**
 ThB₁₂
 Crystal structure and lattice
 parameters: 6.7.2.4.3
 Preparation: 6.7.3.7
- B₁₂Tm**
 TmB₁₂
 Crystal structure and lattice
 parameters: 6.7.2.4.3
 Thermal stability: 6.7.2.4.3
- B₁₂U**
 UB₁₂
 Crystal structure and lattice
 parameters: 6.7.2.4.3
 Thermal stability: 6.7.2.4.3

- B₁₂Y**
YB₁₂
 Crystal structure and lattice parameters: 6.7.2.4.3
 Electrical and magnetic properties: 6.7.2.4.3
 Thermal stability: 6.7.2.4.3
- B₁₂Yb**
YbB₁₂
 Crystal structure and lattice parameters: 6.7.2.4.3
 Thermal stability: 6.7.2.4.3
- B₁₂Zr**
ZrB₁₂
 Crystal structure and lattice parameters: 6.7.2.4.3
- B₁₃CoO*C₁₀H₃₄**
- B₁₄Ca₇Rh₂₀**
B₁₄Ca₇Rh₂₀
 Crystal chemistry: 6.7.2.1
- B₁₄Mg*Al**
- B₁₄Mg₂**
Mg₂B₁₄
 Crystal structure and lattice parameters: 6.7.2.4.5
- B₁₅Na_x**
Na_xBB₁₄
 Crystal structure and lattice parameters: 6.7.2.4.5
 Preparation: 6.7.3.1
 Thermal stability: 6.7.3.1
- B₁₆CoO*C₁₀H₃₇**
- B₁₆P₂Pt*C₁₆H₄₀**
- B₁₇Co*C₅H₂₆**
- B₁₈Co*C₄H₂₂**
- B₁₈CoNa*C₄H₂₂**
- B₁₈CoNa*C₈H₃₄**
- B₁₈CoNaP₂*C₂H₂₀**
- B₁₈CoNa₂*C₄H₂₂**
- B₁₈CoP₂*C₄H₂₆**
- B₁₈CuN*C₁₂H₄₂**
- B₁₈CuN₂*C₂₀H₆₂**
- B₁₈FeP₂*C₄H₂₆**
- B₁₈Fe₂*C₉H₂₇**
- B₁₈H₂₂**
 n-B₁₈H₂₂
 Reaction with Co atoms: 6.5.3.3
- B₁₈H₂₂NiS₂**
 11,11'-Ni(6-SB₉H₁₁)₂
 Formation: 6.5.3.4, 6.5.3.4
- B₁₈H₂₂PdS₂**
 11,11'-Pd(6-SB₉H₁₁)₂
 Formation: 6.5.3.4, 6.5.3.4
- B₁₈HgN₂*C₁₄H₃₀**
- B₁₈N*C₂₀H₄₂Au**
- B₁₈NO₂P₂Sm₃*C₄₈H₆₈**
- B₁₈N₂S₄*C₁₄H₄₂Au₂**
- B₁₈Ni₂O₂P₂*C₄₂H₅₀**
- B₁₈P₂Pt*C₁₆H₄₂**
- B₁₈P₂Rh₂*C₁₆H₅₂**
- B₁₈P₂Rh₂*C₂₄H₆₆**
- B₁₈P₂Rh₂*C₄₀H₅₄**
- B₁₈P₂Rh₂*C₅₂H₆₂**
- B₁₈P₄Pt₂*C₃₂H₆₀**
- B₁₉Na₂Ni*C₄H₂₄**
- B₁₉P₃Rh*C₅₈H₆₇**
- B₂₀H₂₆**
 (B₁₀H₁₃)₂
 Formation: 6.2.1
- B₂₀Hg*C₄H₂₂**
- B₂₀HgN*C₄H₃₆**
- B₂₀HgSe*C₄H₂₂**
- B₂₀HgTe*C₄H₂₂**
- B₂₀Ni*C₂H₂₂**
- B₂₃Cu**
B₂₃Cu
 Formation: 6.7.2.5.2
 Structure: 6.7.2.5.3
- B₂₃Mn**
B₂₃Mn
 Formation: 6.7.2.5.2
 Structure: 6.7.2.5.3
- B₂₇Cu₃N₃O₆*C₂₇H₃₉**
- B₂₈Cu**
B₂₈Cu
 Formation: 6.7.2.5.2
 Structure: 6.7.2.5.3
- B₂₈Sc**
B₂₈Sc
 Formation: 6.7.2.5.2
 Structure: 6.7.2.5.3
- B₃₆Si**
B₃₆Si
 Formation: 6.7.2.5.2
 Structure: 6.7.2.5.3
- B₄₁Cr**
B₄₁Cr
 Formation: 6.7.2.5.2
 Structure: 6.7.2.5.3
- B_{48.5}Ni**
B_{48.5}Ni
 Formation: 6.7.2.5.2
 Structure: 6.7.2.5.3
- B₄₉Fe**
B₄₉Fe
 Formation: 6.7.2.5.2
 Structure: 6.7.2.5.3
- B₅₁Zr**
B₅₁Zr
 Formation: 6.7.2.5.2
 Structure: 6.7.2.5.3

B₆₆Dy

Crystal structure and lattice
parameters: 6.7.2.4.4

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.4

B₆₆Er

Crystal structure and lattice
parameters: 6.7.2.4.4

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.4

B₆₆Gd

Crystal structure and lattice
parameters: 6.7.2.4.4

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.4

B₆₆Ho

Crystal structure and lattice
parameters: 6.7.2.4.4

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.4

B₆₆Nd

Crystal structure and lattice
parameters: 6.7.2.4.2

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.4

B₆₆Sm

Crystal structure and lattice
parameters: 6.7.2.4.4

Thermal stability: 6.7.2.4.4

B₆₆Tb

Crystal structure and lattice
parameters: 6.7.2.4.4

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.4

B₆₆Th

Crystal structure and lattice
parameters: 6.7.2.4.4

Preparation: 6.7.3.1

Thermal stability: 6.7.2.4.4

B₆₆Tm

Crystal structure and lattice
parameters: 6.7.2.4.4

Preparation: 6.7.3.1

Thermal stability: 6.7.2.4.4

B₆₆Y

Crystal growth: 6.7.4.2.1, 6.7.4.2.2

Crystal structure and lattice
parameters: 6.7.2.4.4

Electrical and magnetic properties:
6.7.2.4.4

Preparation: 6.7.3.1, 6.7.3.4

Thermal stability: 6.7.2.4.4

B₆₆Yb

Crystal structure and lattice
parameters: 6.7.2.4.4

Electrical and magnetic properties:
6.7.2.4.4

Thermal stability: 6.7.2.4.4

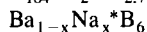
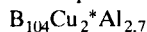
B₉₀Ge

Formation: 6.7.2.5.2

Structure: 6.7.2.5.3

B₁₀₀Pu

Crystal structure and lattice
parameters: 6.7.2.4.4

**BaBe₁₃**

In phase diagram: 7.2.5.1.1

Preparation: 7.2.5.1.3

X-ray identification: 7.2.5.1.2

BaCd

Formation: 7.3.4.1.5

BaCd₂

Formation: 7.3.4.1.5

BaCd₅

Formation: 7.3.4.1.5

BaCd₁₁

Formation: 7.3.4.1.5

BaCu

Formation: 7.3.3.1.5

- BaCu₁₃**
 BaCu₁₃
 Formation: 7.3.3.1.5
BaHg
 BaHg
 Formation: 7.3.4.1.5
BaHg₂
 BaHg₂
 Formation: 7.3.4.1.5
BaHg₄
 BaHg₄
 Formation: 7.3.4.1.5
BaIr₁₂*B₇
BaLi₄
 Li₄Ba
 In phase diagram: 7.2.6.1.1
 Preparation: 7.2.6.1.3
 X-ray identification: 7.2.6.1.2
BaMg₂
 Mg₂Ba
 In phase diagram: 7.2.5.1.1
 Preparation: 7.2.5.1.3
 X-ray identification: 7.2.5.1.1,
 7.2.5.1.2
BaN₆
 Ba(N₃)₂
 Thermal decomposition: 7.2.2.4.1
BaNa
 NaBa
 In phase diagram: 7.2.6.1.1
 Preparation: 7.2.6.1.3
 X-ray identification: 7.2.6.1.2
BaNa₄
 Na₄Ba
 In phase diagram: 7.2.6.1.1
 Preparation: 7.2.6.1.3
 X-ray identification: 7.2.6.1.2
BaNi₁₂*B₆
BaRh₂*B₂
BaZn
 BaZn
 Formation: 7.3.4.1.5
BaZn₂
 BaZn₂
 Formation: 7.3.4.1.5
BaZn₅
 BaZn₅
 Formation: 7.3.4.1.5
BaZn₁₃
 BaZn₁₃
 Formation: 7.3.4.1.5
Ba₂*Ag₃
Ba₂*Au₃
Ba₂Cd₉
- Ba₂Cd₉**
 Formation: 7.3.4.1.5
Ba₂Hg
 Ba₂Hg
 Formation: 7.3.4.1.5
Ba₂Mg₁₇
 Mg₁₇Ba₂
 In phase diagram: 7.2.5.1.1
 Preparation: 7.2.5.1.3
 X-ray identification: 7.2.5.1.1,
 7.2.5.1.2
Ba₂Ni₉*B₆
Ba₂Pt₉*B₆
Ba₂Zn
 Ba₂Zn
 Formation: 7.3.4.1.5
Ba₃*Ag
Ba₃*Ag₅
Ba₃*Au₂
Ba₄*Ag₃
Ba₆Mg₂₃
 Mg₂₃Ba₆
 In phase diagram: 7.2.5.1.1
 Preparation: 7.2.5.1.3
 X-ray identification: 7.2.5.1.1,
 7.2.5.1.2
Be_{0.4}Nb
 NbBe_{0.4}
 Formation: 7.4.2.1
Be
 Be
 Safety: 7.2.3.1.1
Be*Au
Be*Au₂
BeCu₂
 BeCu₂
 Formation: 7.3.3.1.1
BePt
 BePt
 Formation: 7.4.2.1
Be₂Cu
 Be₂Cu
 Formation: 7.3.3.1.1
Be₂Mo
 Be₂Mo
 Formation: 7.4.2.1
Be₂Nb₃
 Be₂Nb₃
 Formation: 7.4.2.1
Be₃*Au₄
Be₃Cu
 Be₃Cu
 Formation: 7.3.3.1.1

Be₃Pt

Formation: 7.4.2.1

Be₄*B**Be₅*Au****Be₁₂*Ag****Be₁₂Mo**

Formation: 7.4.2.1

Be₁₃*Am**Be₁₃*Ba****Be₁₃Ca**

In phase diagram: 7.2.5.1.1

Preparation: 7.2.5.1.3

X-ray identification: 7.2.5.1.1,
7.2.5.1.2**Be₁₃Cm**

Formation: 7.4.2.1

Be₁₃Mg

In phase diagram: 7.2.5.1.1

Preparation: 7.2.5.1.3

X-ray identification: 7.2.5.1.1,
7.2.5.1.2**Be₁₃Pa**

Formation: 7.4.2.1

Be₁₃Sr

In phase diagram: 7.2.5.1.1

Preparation: 7.2.5.1.3

X-ray identification: 7.2.5.1.1,
7.2.5.1.2**Be₁₃V**

Formation: 7.4.2.1

Br*C₂H₆B**Br*C₄H₉****Br*C₁₂H₁₀B****BrCo₂InO₉*C₁₂H₈****BrFeNO₃*C₇H₉B****BrHgO₃W*C₈H₅****BrInMo₂O₆*C₁₆H₁₀****BrLi**Reaction with GaX₂: 6.2.2.1**BrN₂*C₄H₁₂B****BrO₂*C₂H₆B****BrP₂Pt*C₄₀H₄₂B₂****Br₂**

Reaction with elemental Ga: 6.2.2.1

Br₂CoGaO₅*C₈H₈**Br₂Ga**

Reaction with electron pair bases:

6.2.2.1

Reaction with LiX: 6.2.2.1

see Ga[GaBr₄]: 6.2.2.1**Br₂Hg**

Reaction with elemental Ga: 6.2.2.1

Reaction with M(CO)₄L₂: 8.3.3.2.2**Br₂In**Reaction with electron pair bases:
6.2.2.1

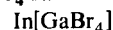
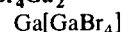
Reaction with MX: 6.2.2.1

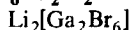
Reaction with PR₃: 6.2.2.1**Br₂N₂Ti*C₁₆H₃₀B₂****Br₃*Al****Br₃*B****Br₃Co₄In₃O₁₆*C₁₆****Br₃FeGaNa₂O₄*C₄****Br₃FeInNa₂O₄*C₄****Br₃Ga**Reaction with Co₂(CO)₈: 6.5.2.3

Reaction with elemental Ga: 6.2.2.1

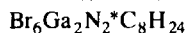
Br₃Ga₂

Formation: 6.2.2.1

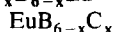
Br₃InReaction with Co₂(CO)₈: 6.5.2.3**Br₃N*C₆H₁₅B****Br₄*Al₂****Br₄*B₂****Br₄CoP₂*C₂₆H₂₄B₂****Br₄CoP₄*C₅₂H₄₈B₂****Br₄Co₂GaO₆*C₆****Br₄Co₂InO₆*C₆****Br₄GaIn**Reaction with electron pair bases:
6.2.2.1**Br₄GaN*C₄H₁₂****Br₄Ga₂**see GaBr₂: 6.2.2.1**Br₄In₂P₂*C₁₂H₃₀****Br₅Nb**Reaction with BX₃, B₂H₆: 6.7.4.1.1

Br₅TaReaction with BX₃, B₂H₆: 6.7.4.1.1**Br₆Ga₂Li₂**

Formation: 6.2.2.1

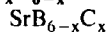
**Br₆Ga₄**

Formation: 6.2.2.1

**C_xB_{6-x}Eu**

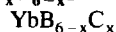
Crystal structure: 6.7.2.4.2

Preparation: 6.7.3.4

C_xB_{6-x}Sr

Crystal structure: 6.7.2.4.2

Preparation: 6.7.3.4

C_xB_{6-x}Yb

Crystal structure: 6.7.2.4.2

Preparation: 6.7.3.4

CAuO

Formation: 8.2.2.2.1

CBNp

Crystal chemistry: 6.7.2.2

CBTh

Crystal chemistry: 6.7.2.2

CBU

Crystal chemistry: 6.7.2.2

CBY

Crystal chemistry: 6.7.2.2

CB₂Co₁₁

Crystal chemistry: 6.7.2.1

CB₂Dy

Crystal chemistry: 6.7.2.3

CB₂Ho

Crystal chemistry: 6.7.2.3

CB₂Mo

Crystal chemistry: 6.7.2.2

CB₂Sc

Crystal chemistry: 6.7.2.3

CB₂Tb

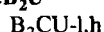
Crystal chemistry: 6.7.2.3

CB₂Th

Crystal chemistry: 6.7.2.3

CB₂Tm

Crystal chemistry: 6.7.2.3

CB₂U

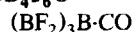
Crystal chemistry: 6.7.2.3

CB₂Y

Crystal chemistry: 6.7.2.3

CB₂Yb

Crystal chemistry: 6.7.2.3

CB₄Reaction with B₂O₃, MO, MO₂,
M₂O₃: 6.7.3.4**CB₄F₆O**

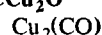
Formation: 6.2.2.1

CCl₂FeHgO₅

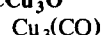
Formation: 8.3.3.2.2

CCuO

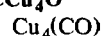
Formation: 8.2.2.2.1

CCu₂O

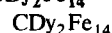
Formation: 8.2.2.2.1

CCu₃O

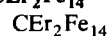
Formation: 8.2.2.2.1

CCu₄O

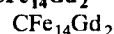
Formation: 8.2.2.2.1

CDy₂Fe₁₄

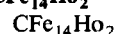
Crystal chemistry: 6.7.2.1

CEr₂Fe₁₄

Crystal chemistry: 6.7.2.1

CFe₁₄Gd₂

Crystal chemistry: 6.7.2.1

CFe₁₄Ho₂

Crystal chemistry: 6.7.2.1

- CFe₁₄Nd₂**
 CFe₁₄Nd₂
 Crystal chemistry: 6.7.2.1
- CFe₁₄Tb₂**
 CFe₁₄Tb₂
 Crystal chemistry: 6.7.2.1
- CH₉B₆**
 CB₆H₉
 Reaction with μ -(C₈H₁₂)L₄Pt₂:
 6.5.3.3
- CH₁₄B₈**
 4-CB₈H₁₄
 Reaction with L₄Pt, η^5 -Cp₂Ni:
 6.5.3.3
- CHg₂O₃**
 Hg₂CO₃
 Reaction with HF: 8.2.4.1
- CNa₂O₃**
 Na₂CO₃
 Reaction with SiF₄: 7.2.3.1.1
- CO**
 CO
 Reaction with BF: 6.2.2.1
 Reaction with Cu, Ag, Au: 8.2.2.2.1
- C₂AuO₂**
 Au(CO)₂
 Formation: 8.2.2.2.1
- C₂B₂Ca**
 B₂C₂Ca
 Crystal chemistry: 6.7.2.3
- C₂B₂Dy**
 B₂C₂Dy
 Crystal chemistry: 6.7.2.3
- C₂B₂Er**
 B₂C₂Er
 Crystal chemistry: 6.7.2.3
- C₂B₂Eu**
 B₂C₂Eu
 Crystal chemistry: 6.7.2.3
- C₂B₂Gd**
 B₂C₂Gd
 Crystal chemistry: 6.7.2.3
- C₂B₂Ho**
 B₂C₂Ho
 Crystal chemistry: 6.7.2.3
- C₂B₂La**
 B₂C₂La
 Crystal chemistry: 6.7.2.3
- C₂B₂Lu**
 B₂C₂Lu
 Crystal chemistry: 6.7.2.3
- C₂B₂Nd**
 B₂C₂Nd
 Crystal chemistry: 6.7.2.3
- C₂B₂Pr**
 B₂C₂Pr
 Crystal chemistry: 6.7.2.3
- C₂B₂Sc**
 B₂C₂Sc
 Crystal chemistry: 6.7.2.3
- C₂B₂Sm**
 B₂C₂Sm
 Crystal chemistry: 6.7.2.3
- C₂B₂Tb**
 B₂C₂Tb
 Crystal chemistry: 6.7.2.3
- C₂B₂Tm**
 B₂C₂Tm
 Crystal chemistry: 6.7.2.3
- C₂B₂Y**
 B₂C₂Y
 Crystal chemistry: 6.7.2.3
- C₂B₂Yb**
 B₂C₂Yb
 Crystal chemistry: 6.7.2.3
- C₂Cl₂Hg₄O₉**
 (O₃ClOHg₂)₂C=C=O
 Formation and safety: 8.2.4.3
- C₂F₆Hg**
 Hg(CF₃)₂
 Reaction with PtL₃: 8.3.3.3
- C₂H₄**
 C₂H₄
 Reaction with Cu: 8.2.2.2.1
- C₂H₅B₃**
 1,5-C₂B₃H₅
 Reaction with [(C₂H₅)₃P]₄Pt: 6.5.3.1
- C₂H₅Gal₂**
 C₂H₅Gal₂
 Reaction with Na₂[Fe(CO)₄]: 6.5.2.2
- C₂H₆BBr**
 (CH₃)₂BBr
 Reaction with L₄Pt: 6.5.2.3
 Reaction with M: 6.2.2.2
- C₂H₆BBrO₂**
 (CH₃O)₂BBr
 Reaction with M: 6.2.2.2
- C₂H₆BClO₂**
 (CH₃O)₂BCl
 Reaction with M: 6.2.2.2
- C₂H₆B₄F₆S**
 (BF₂)₃B-S(CH₃)₂
 Formation: 6.2.2.1
- C₂H₆B₆**
 1,7-C₂B₆H₆
 Reaction with [(C₂H₅)₃P]₄Pt: 6.5.3.1

- C₂H₆Cd**
(CH₃)₂Cd
Reaction with B₁₀H₁₄: 6.4
- C₂H₆ClGa**
(CH₃)₂GaCl
Reaction with M: 6.2.2.2
- C₂H₆S**
S(CH₃)₂
Reaction with BF₃, GaX₂: 6.2.2.1
- C₂H₆Zn**
(CH₃)₂Zn
Reaction with B₁₀H₁₄: 6.4
- C₂H₇B₅**
2,4-C₂B₅H₇
Reaction with (C₅H₅)Co(CO)₂: 6.5.3.1
- C₂H₇B₇**
1,6-C₂B₇H₇
Reaction with [(C₂H₅)₃P]₃Pt: 6.5.3.1
- C₂H₈B₄**
2,3-C₂B₄H₈
Reaction with [(C₂H₅)₃P]₂Pt: 6.5.3.1
- C₂H₈B₆**
2,3-C₂B₆H₈
Reaction with μ-(C₈H₁₂)L₄Pt₂: 6.5.3.3
- C₂H₈GaN**
(CH₃)₂GaNH₂
Formation: 6.2.2.2
- C₂H₁₁AsB₁₀Cl₂**
(C₂H₂B₁₀H₉)AsCl₂
Formation: 6.4
- C₂H₁₁B₇**
2,6-C₂B₇H₁₁
Reaction with metal atoms: 6.5.3.3
- C₂H₁₁B₉Tl₂**
Tl₂[7,8-C₂B₉H₁₁]
Reaction with (C₆H₅)₃PCuCl: 6.4
- C₂H₁₁B₁₀Cl₂Sb**
(C₂H₂B₁₀H₉)SbCl₂
Formation: 6.4
- C₂H₁₁B₁₀Cl₂Sn**
(C₂H₂B₁₀H₉)SnCl₂
Formation: 6.4
- C₂H₁₂B₈**
5,6-C₂B₈H₁₂
Reaction with μ-(C₈H₁₂)(C₂H₅)₃P]₄Pt₂: 6.5.3.3
- C₂H₂₀B₁₈CoNaP₂**
Na[3,3'-Co(1,2-CPB₉H₁₀)₂]
Formation: 6.5.3.4
Na[3,3'-Co(1,7-CPB₉H₁₀)₂]
Formation: 6.5.3.4
- C₂H₂₂B₂₀Ni**
2,2'-Ni(7-CB₁₀H₁₁)₂
Formation: 6.5.3.4
- C₃AgO₃**
Ag(CO)₃
Formation: 8.2.2.2.1
- C₃B₂Th₃**
B₂C₃Th₃
Crystal chemistry: 6.7.2.2
- C₃H₆S₂**
SCH₂SCH₂CH₂
Reaction with Hg₂(NO₃)₂: 8.2.4.2.2
- C₃H₆S₃**
SCH₂SCH₂SCH₂
Reaction with Hg₂(NO₃)₂: 8.2.4.2.2
- C₃H₉Al**
(CH₃)₃Al
Addition to [(C₆H₅)₃P]₃Pt: 6.5.3.1
Reaction with B₂(NR₂)₄: 6.2.4
Reaction with LiMR₃: 6.2.4
- C₃H₉B**
B(CH₃)₃
Addition to Co(NO)₃: 6.5.3.1
- C₃H₉BCoN₃O₃**
(NO)₃CoB(CH₃)₃
Formation: 6.5.3.1
- C₃H₉ClSi**
(CH₃)₃SiCl
Reaction with K₂[R₆Al₂]: 6.2.4
- C₃H₉Ga**
(CH₃)₃Ga
Reaction with elemental Na: 6.2.4
Reaction with LiMR₃: 6.2.4
- C₃H₉GeLi**
LiGe(CH₃)₃
Reaction with R₃E: 6.2.4
- C₃H₉In**
(CH₃)₃In
Reaction with LiMR₃: 6.2.4
- C₃H₉LiSi**
LiSi(CH₃)₃
Reaction with R₃E: 6.2.4
- C₃H₉LiSn**
LiSn(CH₃)₃
Reaction with R₃E: 6.2.4
- C₃H₉N**
N(CH₃)₃
Reaction with B₅H₉, B₄H₁₀: 6.2.1
- C₃H₉P**
P(CH₃)₃
Reaction with B₅H₉, B₄H₁₀: 6.2.1

- C₃H₉Tl**
 (CH₃)₃Tl
 Reaction with elemental K: 6.2.4
 Reaction with LiMR₃: 6.2.4
- C₃H₁₀B₅MnO₃**
 2,2,2-(CO)₃-2-MnB₅H₁₀
 Formation: 6.5.2.2
- C₃H₁₄B₁₀**
 1-CH₃-1,2-C₂B₁₀H₁₁
 Reaction with L₄Co: 6.5.3.3
- C₃H₁₆B₁₀N**
 2-N(CH₃)₂-2-CB₁₀H₁₀
 Reaction with nitrile and phosphine complexes: 6.5.3.1
- C₄Br₃FeGaNa₂O₄**
 Na₂[(CO)₄FeGaBr₃]
 Formation: 6.5.2.2
- C₄Br₃FeInNa₂O₄**
 Na₂[(CO)₄FeInBr₃]
 Formation: 6.5.2.2
- C₄CdFeO₄**
 CdFe(CO)₄
 Formation: 8.3.3.2.1
- C₄Cl₂FeHg₂O₄**
 Fe(CO)₄(HgCl)₂
 Formation: 8.3.3.2.2
- C₄CoNaO₄**
 Na[Co(CO)₄]
 Reaction with octaethylporphyrinato-indium and thalliumchloride: 6.5.2.2
 Reaction with tetraphenylporphyrinato-indiumchloride: 6.5.2.2
- C₄H₂FeO₄**
 H₂Fe(CO)₄
 Reaction with CuCl: 8.3.2.2.2
- C₄H₆CdFeN₂O₄**
 (NH₃)₂CdFe(CO)₄
 Formation: 8.3.3.2.1
- C₄H₆Cu₂FeN₂O₄**
 (CuNH₃)₂Fe(CO)₄
 Formation: 8.3.2.2.2
- C₄H₈B₅CoO₄**
 2-[Co(CO)₄]B₅H₈
 Formation: 6.5.2.2
- C₄H₈B₈Co**
 6,1,3,9,13-CoC₄B₈H₈
 Formation: 6.5.3.4
- C₄H₈Cl₄Pt₂**
 [C₂H₄PtCl₂]₂
 Reaction with (C₂H₅)₂C₂B₂(C₂H₅)₂CHCH₃: 6.5.3.3
- C₄H₈Cu**
 Cu(C₂H₄)₂
 Formation: 8.2.2.2.1
- C₄H₈S₂**
 $\overline{\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2}$
 Reaction with Hg₂(NO₃)₂: 8.2.4.2.2
 $\overline{\text{SCH}_2\text{SCH}_2\text{CH}_2\text{CH}_2}$
 Reaction with Hg₂(NO₃)₂: 8.2.4.2.2
- C₄H₉Br**
 C₄H₉Br
 Reaction with Cs₂O: 7.2.2.4.4
- C₄H₉FeN₃O₄Zn**
 (NH₃)₃ZnFe(CO)₄
 Formation: 8.3.3.2.1
- C₄H₁₀B₄FeO₄**
 μ-[3,4-Fe(CO)₄]B₆H₁₀
 Formation: 6.5.3.3
- C₄H₁₀B₉MnNaO₃P**
 Na[3,3,3-(CO)₃-3,1,7-MnCPB₉H₁₀]
 Formation: 6.5.3.4
- C₄H₁₀Cd**
 (C₂H₅)₂Cd
 Reaction with HMn(CO)₅: 8.3.3.2.1
- C₄H₁₀Zn**
 (C₂H₅)₂Zn
 Reaction with (η⁵-Cp)₂MH₂: 8.3.3.3
 Reaction with HMn(CO)₅: 8.3.3.2.1
- C₄H₁₁B₄Na**
 Na[(CH₃)₂C₂B₄H₅]
 Reaction with HgCl₂: 6.4
- C₄H₁₁B₅**
 2,4-(CH₃)₂-2,4-C₂B₅H₅
 Reaction with Co[(C₂H₅)₃]₄ and Fe[CN(C₄H₉)]₅: 6.5.3.1
- C₄H₁₂BBrN₂**
 [(CH₃)₂N]₂BBr
 Reaction with M: 6.2.2.2
- C₄H₁₂BClN₂**
 [(CH₃)₂N]₂BCl
 Reaction with M: 6.2.2.2
 Reaction with Na[Mn(CO)₅]: 6.5.2.2
 Reaction with Na[Re(CO)₅]: 6.5.2.2
- C₄H₁₂B₂O₄**
 B₂(OCH₃)₄
 Formation: 6.2.2.2
- C₄H₁₂B₄**
 2,3-(CH₃)₂-2,3-C₂B₄H₆
 Reaction with [(C₂H₅)₃P]₂Pt: 6.5.3.1
- C₄H₁₂Br₄GaN**
 [(CH₃)₄N]GaBr₄
 Formation: 6.2.5
- C₄H₁₂Cl₄GaN**
 [(CH₃)₄N]GaCl₄
 Formation: 6.2.5

- C₄H₁₂GaI₄N**
[(CH₃)₄N]GaI₄
Formation: 6.2.5
- C₄H₁₂Ga₂**
(CH₃)₄Ga₂
Formation: 6.2.2.2
- C₄H₁₄B₆**
2,3-(CH₃)₂-2,3-C₂B₆H₈
Reaction with μ -(C₈H₁₂)L₄Pt₂:
6.5.3.3
- C₄H₁₅B₃O**
B₃H₇OC₄H₈
Reaction with ER₃: 6.2.1
- C₄H₁₇B₇**
5,9-(CH₃)₂-5,9-C₂B₇H₁₁
Reaction with
(C₈H₁₂)(C₂H₅)₃P]₂Ni: 6.5.3.1
- C₄H₁₈Ga₂N₂**
Ga₂(CH₃)₄(NH₃)₂
Formation: 6.2.2.2
- C₄H₂₂B₁₈Co**
3,3'-Co(1,7-C₂B₉H₁₁)₂
Formation: 6.5.3.4
- C₄H₂₂B₁₈CoNa**
Na[3,3'-Co(1,2-C₂B₉H₁₁)₂]
Formation: 6.5.3.4
- C₄H₂₂B₁₈CoNa₂**
Na₂[3,3'-Co(1,2-C₂B₉H₁₁)₂]
Formation: 6.5.3.4
- C₄H₂₂B₂₀Hg**
Hg[C₂H₂B₁₀H₉]₂
Reaction with Se, Te, SnCl₂, AsCl₃,
SbCl₃: 6.4
- C₄H₂₂B₂₀HgSe**
[C₂H₂B₁₀H₉]₂HgSeB₁₀H₉C₂H₂
Formation: 6.4
- C₄H₂₂B₂₀HgTe**
[C₂H₂B₁₀H₉]₂HgTeB₁₀H₉C₂H₂
Formation: 6.4
- C₄H₂₄B₁₉Na₂Ni**
Na₂[13,13'-Ni(7,9-C₂B₁₀H₁₂)(7',11'-
C₂B₉H₁₂)]
Formation: 6.5.3.4
- C₄H₂₅B₁₀N**
[(CH₃)₄N][B₁₀H₁₃]
Reaction with HgCl₂: 6.4
- C₄H₂₆B₁₈CoP₂**
3,3'-Co(2-CH₃-1,2-CPB₉H₁₀)₂
Formation: 6.5.3.4
- 3,3'-Co(7-CH₃-1,7-CPB₉H₁₀)₂
Formation: 6.5.3.4
- C₄H₂₆B₁₈FeP₂**
3,3'-Fe(2-CH₃-1,2-CPB₉H₁₀)₂
Formation: 6.5.3.4
- 3,3'-Fe(7-CH₃-1,7-CPB₉H₁₀)₂
Formation: 6.5.3.4
- C₄H₃₆B₂₀HgN**
[(CH₃)₄N][Hg(B₁₀H₁₂)₂]
Formation: 6.4
- C₄NiO₄**
Ni(CO)₄
Reaction with cyclic divinyl: 6.5.3.1
- C₅Cl₂FeHgO₅**
Fe(CO)₅·HgCl₂
Reaction with HgX₂: 8.3.3.2.2
- C₅FeO₅**
Fe(CO)₅
Reaction with 2,5-dihydro-1H-1,2-
azaboroles: 6.5.3.3
- Reaction with borolenes: 6.5.3.1
- Reaction with cyclic divinyl boranes:
6.5.3.1
- Reaction with HgX₂: 8.3.3.2.2
- Reaction with Zn²⁺, Cd²⁺: 8.3.3.2.1
- C₅H₆B₄FeO₃**
7,7,7-(CO)₃-7,2,3-FeC₂B₄H₆
Formation: 6.5.3.3
- C₅H₇B₃FeO₃**
6,6,6-(CO)₃-6,1,2-FeC₂B₃H₇
Formation: 6.5.3.3
- C₅H₉B**
C₄H₆BCH₃
Reaction with metal carbonyls: 6.5.3.1
- C₅H₉BO**
C₄H₆BOCH₃
Reaction with metal carbonyls: 6.5.3.1
- C₅H₁₁B₉MnNaO₃**
Na[3,3,3-(CO)₃-3,1,2-MnC₂B₉H₁₁]
Formation: 6.5.3.4
- C₅H₁₃B₄Co**
2-(η^5 -C₅H₅)-2-CoB₄H₈
Formation: 6.5.3.4
- C₅H₁₃B₆CoS₂**
7-(η^5 -C₅H₅)-7,6,8-CoS₂B₆H₈
Formation: 6.5.3.4
- C₅H₁₃B₉MnO₃P**
3,3,3-(CO)₃-7-CH₃-3,1,7-MnCPB₉H₁₀
Formation: 6.5.3.4
- C₅H₁₃LiSi₂**
LiCH[Si(CH₃)₂]₂
Reaction with Ga₂Br₄·L₂,
In₂Br₄·L₂: 6.2.2.1
- C₅H₁₄B₅Co**
1-(C₅H₅)-1-CoB₅H₉
Formation: 6.5.3.1

- C₅H₁₅BCl₂N₂Pd**
Cl₂Pd[(CH₃)₂N]₂BCH₃
Formation: 6.5.3.1
- C₅H₁₅BN₂**
[(CH₃)₂N]₂BCH₃
Reaction with (C₆H₅CN)₂PdCl₂:
6.5.3.1
Reaction with Fe₂(CO)₉: 6.5.3.1
- C₅H₁₅B₅Fe**
1-(η⁵-C₅H₅)-1-FeB₅H₁₀
Formation: 6.5.3.4
2-(η⁵-C₅H₅)-2-FeB₅H₁₀
Formation: 6.5.3.4
- C₅H₁₈B₉Co**
2-(η⁵-C₅H₅)-2-CoB₉H₁₃
Formation: 6.5.3.1
5-(η⁵-C₅H₅)-5-CoB₉H₁₃
Formation: 6.5.3.4
- C₅H₂₀B₁₀Fe**
2-(η⁵-C₅H₅)-2-FeB₁₀H₁₅
Formation: 6.5.3.4
- C₅H₂₂AuB₈NS₂**
4-[S₂CN(C₂H₅)₂]-4-AuB₈H₁₂
Formation: 6.4
- C₅H₂₆B₁₇Co**
iso-8-(η⁵-C₅H₅)CoB₁₇H₂₁
Formation: 6.5.3.3
- C₅MnNaO₅**
Na[Mn(CO)₅]
Formation: 8.3.3.1
Reaction with octaethylporphyrinato-indium and thalliumchloride:
6.5.2.2
Reaction with tetraphenylporphyrinato-indiumchloride: 6.5.2.2
- C₅NaO₅Re**
Na[Re(CO)₅]
Reaction with InCl₃·3 H₂O: 6.5.2.2
- C_{5n}H_{5n}Mo_nZn_n**
(η⁵-C₅H₅MoZn)_n
Formation: 8.3.3.3
- C_{5n}H_{5n}W_nZn_n**
(η⁵-C₅H₅WZn)_n
Formation: 8.3.3.3
- C₆Ag₂O₆**
Ag₂(CO)₆
Formation: 8.2.2.2.1
- C₆Br₄Co₂GaO₆**
GaCo₂Br₄(CO)₆
Formation: 6.5.2.3
- C₆Br₄Co₂InO₆**
InCo₂Br₄(CO)₆
Formation: 6.5.2.3
- C₆Fe₂HgN₂O₈**
Hg[Fe(CO)₃NO]₂
Formation: 8.3.3.1.2
- C₆H₈BNa**
Na[CH₃BC₅H₅]
Reaction with (CO)₃Cr(NH₃)₃:
6.5.3.4
- C₆H₈BTl**
Tl[(C₅H₅BCH₃)
Reaction with [(CH₃)₄C₄]Co(CO)₂I:
6.5.3.4
- C₆H₉BO**
CHCHCH₂CHCHBOCH₃
Reaction with Fe₂(CO)₉: 6.5.3.3
- C₆H₁₀Ni**
(η³-C₃H₅)₂Ni
Reaction with
(CH₃)₂C₂B₂(CH₃)₂CH₂: 6.5.3.3
Reaction with 2,3-dihydro-1,3-diboroles: 6.5.3.1, 6.5.3.3
- C₆H₁₂Cu**
Cu(C₂H₄)₃
Formation: 8.2.2.2.1
- C₆H₁₂Ni**
Ni(C₂H₄)₃
Reaction with 2,3-dihydro-1,3-diboroles: 6.5.3.1
- C₆H₁₄B₈Ni**
10-(η⁵-C₅H₅)-10,1-NiCB₈H₉
Formation: 6.5.3.4
- C₆H₁₅Al**
(C₂H₅)₃Al
Reaction with elemental K: 6.3
- C₆H₁₅AlK**
K[(C₂H₅)₃Al]
Formation: 6.3
- C₆H₁₅BBr₃N**
(C₂H₅)₃NBBBr₃
Reaction with Tl[Co(CO)₄]: 6.5.2.2
- C₆H₁₆B₄**
2,3-(C₂H₅)₂C₂B₄H₆
Reaction with Fe atoms and toluene:
6.5.3.3
- C₆H₁₆B₁₀Ni**
2-(η⁵-C₅H₅)-2,7-NiCB₁₀H₁₁
Formation: 6.5.3.4
10-(η⁵-C₅H₅)-10,1-NiCB₁₀H₁₁
Formation: 6.5.3.4
- C₆H₁₈B₂N₂O₂**
[(CH₃)₂N]₂B₂(OCH₃)₂
Formation: 6.2.2.2
- C₆H₁₈Ga₂Na₂**
Na₂[(CH₃)₆Ga₂]
Formation: 6.2.4

- C₆H₁₈Ge₂Hg**
 Hg[Ge(CH₃)₃]₂
 Reaction with Ir(CO)ClL₂: 8.3.3.2.2
- C₆H₁₈HgSi₂**
 Hg[Si(CH₃)₃]₂
 Reaction with Ir(CO)ClL₂: 8.3.3.2.2
- C₆H₁₈K₂Tl₂**
 K₂[(CH₃)₆Tl₂]
 Formation: 6.2.4
- C₆H₁₈Sn₂**
 (CH₃)₆Sn₂
 Formation: 6.2.4
- C₆H₂₂B₂N₂**
 B₂H₄[N(CH₃)₃]₂
 Formation: 6.2.1
- C₆H₂₂B₂P₂**
 B₂H₄[P(CH₃)₃]₂
 Formation: 6.2.1
- C₆H₂₄B₉Co**
 [2,3-(C₂H₅)₂-2,3-C₂B₄H₄]-2-CoB₅H₁₀
 Formation: 6.5.3.4
- C₆H₃₂B₉IrP₂**
 6-H-6,6-[P(CH₃)₃]₂-6-IrB₉H₁₃
 Formation: 6.5.3.4
- C₇H₃HgO₆Ta**
 CH₃HgTa(CO)₆
 Formation: 8.3.3.1.2
- C₇H₅Cl₂CoHgO₂**
 η⁵-C₅H₅Co(CO)₂·HgCl₂
 Formation: 8.3.3.2.2
- C₇H₅FeIO₂**
 η⁵-C₅H₅Fe(CO)₂I
 Reaction with
 η⁵-CPCo[(C₂H₅)₂C₂B₂(CH₃)₃]:
 6.5.3.4
- C₇H₆BClO₃Ru**
 (CO)₃Ru[η⁵-(C₂H₃)₂BCl]
 Formation: 6.5.3.1
- C₇H₈B₃MnO₃**
 1,1,1-(CO)₃-2-CH₃-1,2,3,4-MnC₃B₃H₅
 Formation: 6.5.3.4
- C₇H₉BBrFeNO₃**
 [H₂C=CH-B(Br)N(CH₃)₂]Fe(CO)₃
 Formation: 6.5.2.1
- C₇H₉CoO₄Sn**
 (CH₃)₃SnCo(CO)₄
 Reaction with R₃PAuCl: 8.3.2.2.3
- C₇H₁₁B₄Co**
 1-(η⁵-C₅H₅)-1,2,4-CoC₂B₄H₆
 Formation: 6.5.3.4
- C₇H₁₁B₄Fe**
 1-(η⁵-C₅H₅)-1,2,4-FeC₂B₄H₆
 Formation: 6.5.3.4
- C₇H₁₂B₃Co**
 1-(η⁵-C₅H₅)-1,2,3-CoC₂B₃H₇
 Formation: 6.5.3.4
- C₇H₁₂B₃Co**
 4-(η⁵-C₅H₅)-4,1,8-CoC₂B₃H₇
 Formation: 6.5.3.4
- C₇H₁₃B₅FeO₂**
 2-(η⁵-C₅H₅)-2,2-(CO)₂-2-FeB₅H₈
 Formation: 6.5.3.4
 2-(η⁵-C₅H₅)Fe(CO)₂B₅H₈
 Formation: 6.5.3.4
 2-[(η⁵-C₅H₅)(CO)₂Fe]B₅H₈
 Formation: 6.5.3.4
- C₇H₁₃B₆Co**
 1-(η⁵-C₅H₅)-1,4,5-CoC₂B₆H₈
 Formation: 6.5.3.4
- C₇H₁₃B₆Fe**
 4-(η⁵-C₅H₅)-4,1,8-FeC₂B₆H₈
 Formation: 6.5.3.4
- C₇H₁₄B₇Co**
 2-(η⁵-C₅H₅)-2,1,10-CoC₂B₇H₉
 Formation: 6.5.3.4
 2-(η⁵-C₅H₅)-2,1,6-CoC₂B₇H₉
 Formation: 6.5.3.4
 2-(η⁵-C₅H₅)-2,3,10-CoC₂B₇H₉
 Formation: 6.5.3.4
 2-η⁵-C₅H₅Co-1,4-C₂B₇H₉
 Formation: 6.5.3.3
 4-η⁵-C₅H₅Co-1,4-C₂B₇H₉
 Formation: 6.5.3.3
- C₇H₁₅BLiNSi**
 Li[(CH₃)₃SiN—C₃H₃—B—CH₃]
 Reaction with transition metal
 halides: 6.5.3.4
- C₇H₁₅B₈Co**
 1-(η⁵-C₅H₅)-1,2,3-CoC₂B₈H₁₀
 Formation: 6.5.3.4
- C₇H₁₅B₈Fe**
 1-(η⁵-C₅H₅)-1,2,3-FeC₂B₈H₁₀
 Formation: 6.5.3.4
- C₇H₁₅B₉NNa**
 Na[(C₅H₅N)C₂B₉H₁₀]
 Reaction with HgCl₂: 6.4
- C₇H₁₆BNSi**
 (CH₃)₃SiNCH₂CH=CHBCH₃
 Reaction with metal atoms: 6.5.3.3
 (CH₃)₃SiN—CH₂—
 CH=CH—BuCH₃
 Lithiation: 6.5.3.4
- C₇H₁₆B₈Ni**
 9-(C₅H₅)-9,7,8-NiC₂B₈H₁₁
 Formation: 6.5.3.3

- C₇H₁₆B₉Co**
2-(η^5 -C₅H₅)-2,1,12-CoC₂B₉H₁₁
Formation: 6.5.3.4
3-(η^5 -C₅H₅)-3,1,2-CoC₂B₉H₁₁
Formation: 6.5.3.4
- C₇H₁₆B₉Cr**
3-(η^5 -C₅H₅)-3,1,2-CrC₂B₉H₁₁
Formation: 6.5.3.4
- C₇H₁₆B₉Fe**
3-(η^5 -C₅H₅)-3,1,2-FeC₂B₉H₁₁
Formation: 6.5.3.4
- C₇H₁₇B₁₀Co**
13-(η^5 -C₅H₅)-13,7,9-CoC₂B₁₀H₁₂
Formation: 6.5.3.4
- C₇H₁₈B₇Co**
4- η^5 -C₅H₅Co-2,3-C₂B₇H₁₃
Formation: 6.5.3.3
- C₇H₁₈B₉FeP**
 η^5 -C₅H₅-Fe(7-CH₃-1,7-CPB₉H₁₀)
Formation: 6.5.3.4
- C₇H₁₈B₁₀FeS**
2-[(η^6 -CH₃C₆H₅)-2,1-Fe]SB₁₀H₁₀
Formation: 6.5.3.3
- C₇H₁₉B₉FeS**
8-(η^6 -CH₃C₆H₅)-8,7-FeSB₉H₁₁
Formation: 6.5.3.3
- C₇H₂₀B₃N₃**
C₂H₅(CH₃)₂B₃N₃(CH₃)₃
Reaction with metal carbonyl derivatives: 6.5.3.1
- C₇H₂₀B₉MnO₄**
6,6,6-(CO)₃-2-C₄H₈O-6-MnB₉H₁₂
Formation: 6.5.3.4
- C₇H₂₁Al₃N₂**
(CH₃)₃Al₃[N(CH₃)₂]₂
Formation: 6.2.4
- C₇H₂₁AuB₉NS₂**
3-[(C₂H₅)₂NCS₂]-3,1,2-AuC₂B₉H₁₁
Formation: 6.4
- C₇H₂₇B₄IrOP₂**
1-CO-1,1-[P(CH₃)₃]₂-1-IrB₄H₉
Formation: 6.5.3.4
- C₈CdCo₂O₈**
Cd[Co(CO)₄]₂
Formation: 8.3.3.4, 8.3.3.5.1
- C₈Co₂HgO₈**
Hg[Co(CO)₄]₂
Formation: 8.3.3.4, 8.3.3.5.1
- C₈Co₂O₈**
Co₂(CO)₈
Reaction with borolenes: 6.5.3.1
Reaction with GaCl₂: 6.5.2.1
- Reaction with tetraphenyl- and octaethylporphyrinatoindium-chloride: 6.5.2.3
Reaction with Zn, Cd, Hg: 8.3.3.4
- C₈Co₂O₈Zn**
Zn[Co(CO)₄]₂
Formation: 8.3.3.4, 8.3.3.5.1
- C₈H₅BrHgO₃W**
 η^5 -C₅H₅W(CO)₃HgBr
Formation: 8.3.3.5.2
- C₈H₅ClCrHgO₃**
 η^5 -C₅H₅Cr(CO)₃HgCl
Formation: 8.3.3.5.2
- C₈H₅ClHgMoO₃**
 η^5 -C₅H₅Mo(CO)₃HgCl
Formation: 8.3.3.4, 8.3.3.5.2
- C₈H₅ClHgO₃W**
ClHgW(CO)₃C₅H₅- η^5
Reaction with R₃PAuGeR₃: 8.3.2.2.3
- C₈H₅Cl₂InMoO₃**
Cl₂InMo(CO)₃(C₅H₅- η^5)
Formation: 6.5.2.2
- C₈H₅CrNaO₃**
Na[Cr(CO)₃(C₅H₅- η^5)]
Reaction with octaethylporphyrinato-indium and thalliumchloride: 6.5.2.2
- C₈H₅MoNaO₃**
Na[Mo(CO)₃(C₅H₅- η^5)]
Reaction with InCl₃: 6.5.2.2
Reaction with octaethylporphyrinato-indium and thalliumchloride: 6.5.2.2
- C₈H₅NaO₃W**
Na[W(CO)₃(C₅H₅- η^5)]
Reaction with octaethylporphyrinato-indium and thalliumchloride: 6.5.2.2
- C₈H₆CrO₃**
HCr(CO)₃C₅H₅- η^5
Reaction with R₃PAuCl: 8.3.2.2.2
- C₈H₆MoO₃**
HMo(CO)₃C₅H₅- η^5
Reaction with R₃PAuCl: 8.3.2.2.2
- C₈H₆O₃W**
HW(CO)₃C₅H₅- η^5
Reaction with R₃PAuCl: 8.3.2.2.2
- C₈H₈Br₂CoGaO₅**
Br₂GaCo(CO)₄·OC₄H₈
Formation: 6.5.2.1
- C₈H₈Cl₂CoGaO₅**
Cl₂GaCo(CO)₄·OC₄H₈
Formation: 6.5.2.1, 6.5.2.2

- C₈H₈CoGaI₂O₅**
I₂GaCo(CO)₄·OC₄H₈
Formation: 6.5.2.1
- C₈H₁₀Ni**
η³-C₃H₅NiC₅H₅-η⁵
Reaction with 2,3-dihydro-1,3-diboroles: 6.5.3.3
- C₈H₁₂B₂F₂**
(CH₃)₄C₄B₂F₂
Reaction with metal carbonyls: 6.5.3.1
Reaction with Pt(C₈H₁₂)₂: 6.5.3.1
Reaction with [(CH₃)₄C₄]NiCl₂: 6.5.3.1
- C₈H₁₄Ni**
(η³-B-C₃H₄CH₃)₂Ni
Reaction with
(C₂H₅)₂C₂B₂(CH₃)₂CH₂: 6.5.3.3
- C₈H₁₅BF₂FeN₂O₃**
(CO)₃Fe{[(CH₃)₂N]₂BCH₃}
Formation: 6.5.3.1
- C₈H₁₅BLiN**
Li[C₃H₃NC(CH₃)₃BCH₃]
Reaction with M(CO)₆: 6.5.3.4
Reaction with transition metal halides and [(CH₃CN)₃Mn(CO)₃]PF₆: 6.5.3.4
- C₈H₁₆BN**
CH₂—CH=CH—B(CH₃)—
N[C(CH₃)₃]
Reaction with η⁵-CpCo(C₂H₄)₂: 6.5.3.1
- C₈H₁₆B₂S**
(C₂H₅)₂C₂B₂(CH₃)₂S
Reaction with (arene)₂Fe complexes: 6.5.3.1
Reaction with metal carbonyls and metal carbonyl derivatives: 6.5.3.1
- C₈H₁₆Cl₂Rh₂**
[Rh(C₂H₄)₂Cl]₂
Reaction with borolenes: 6.5.3.1
- C₈H₁₇B₉Ru**
3-(η⁶-C₆H₆)-3,1,2-RuC₂B₉H₁₁
Formation: 6.5.3.4
- C₈H₁₈BN**
(CH₃)₃CBNC(CH₃)₃
Reaction with Co₂(CO)₈ and (C₅H₅)₂NbH₃: 6.5.3.1
n-C₄H₉BNC(CH₃)₃
Reaction with Cr(CO)₅·THF and W(CO)₅·THF: 6.5.3.1
- C₈H₁₈Si₂**
(CH₃)₃SiC≡CSi(CH₃)₃
Reaction with Co atoms and B₆H₁₀: 6.5.3.3
- C₈H₁₈Zn**
(n-C₄H₉)₂Zn
Reaction with (η⁵-Cp)₂MH₂: 8.3.3.3
- C₈H₁₉Al**
(i-C₄H₉)₂AlH
Reaction with K: 6.2.4
- C₈H₁₉B₉Cr**
3-(η⁵-C₅H₅)-1-CH₃-3,1,2-CrC₂B₉H₁₁
Formation: 6.5.3.4
- C₈H₂₀AlK**
K[(C₂H₅)₄Al]
Formation: 6.3
- C₈H₂₀B₈**
(CH₃)₄C₄B₈H₈
Reaction with η⁵-CpCo(CO)₂: 6.5.3.1
- C₈H₂₁B₈Co**
1,1'-CoH-[2,3-(CH₃)₂-2,3-C₂B₄H₄]₂
Formation: 6.5.3.4
- C₈H₂₂B₈Fe**
H₂Fe[2,3-(CH₃)₂-2,3-C₂B₄H₄]₂
Reaction with Co[P(C₂H₅)₃]₄, (C₈-H₁₂)Pt[P(C₂H₅)₃]₄, (C₈H₁₂)Fe(C₅H₅): 6.5.3.1
- C₈H₂₂B₈Hg**
μ-4,5,4',5'-Hg[2,3-(CH₃)₂-2,3-C₂B₄H₅]-[2',3'-(CH₃)₂-2',3'-C₂B₄H₅]
Formation: 6.4
- C₈H₂₃B₉Fe**
1,1'-(FeH₂)-[2,3-(CH₃)₂-2,3-C₂B₄H₄]-[2,3-(CH₃)₂-2,3-C₂B₅H₅]
Formation: 6.5.3.4
- C₈H₂₃B₁₁Co**
1,1'-Co-[2,3-(CH₃)₂-2,3-C₂B₄H₄]-[2,2-(CH₃)₂-2,3-C₂B₇H₇]
Formation: 6.5.3.4
- C₈H₂₄B₂N₄**
B₂[N(CH₃)₂]₄
Formation: 6.2.2.2
[(CH₃)₂N]₄B₂
Reaction with R₃Al: 6.2.4
- C₈H₂₄Br₆Ga₂N₂**
[(CH₃)₄N]₂Ga₂Br₆
Formation: 6.2.5
- C₈H₂₄Cl₆Ga₂N₂**
[(CH₃)₄N]₂Ga₂Cl₆
Formation: 6.2.5
- C₈H₂₄Ga₂I₆N₂**
[(CH₃)₄N]₂Ga₂I₆
Formation: 6.2.5
- C₈H₂₅B₉ClIr**
6-(C₈H₁₂)-6-Cl-6-IrB₉H₁₃
Formation: 6.5.3.4

- C₈H₂₅B₉ClRh**
6-(C₈H₁₂)₂-6-Cl-6-RhB₉H₁₃
Formation: 6.5.3.4
- C₈H₂₇B₉N₂Pd**
3-[(CH₃)₂N(CH₂)₂N(CH₃)₂]-3,1,2-PdC₂B₉H₁₁
Formation: 6.5.3.4
- C₈H₃₄B₉N**
[(C₂H₅)₄N][B₉H₁₄]
Reaction with Br₂Au[S₂CN(C₂H₅)₂]: 6.4
- C₈H₃₄B₁₈CoNa**
Na[3,3'-Co(1,2-(CH₃)₂-1,2-C₂B₉H₁₁)₂]
Formation: 6.5.3.4
- C₉CoHgMnO₉**
(CO)₅MnHgCo(CO)₄
Formation: 8.3.3.5.2
- C₉Fe₂O₉**
Fe₂(CO)₉
Reaction with C₄H₆BC₆H₅: 6.5.3.1
Reaction with divinyl boranes: 6.5.3.1
- C₉H₉BFeO₄**
(η⁴-CHCHCH₂CHCHBOCH₃)-Fe(CO)₃
Formation: 6.5.3.3
- C₉H₁₂BMnN₂O₅**
[(CH₃)₂N]₂BMn(CO)₅
Formation: 6.5.2.2
- C₉H₁₂BN₂O₅Re**
[(CH₃)₂N]₂BRe(CO)₅
Formation: 6.5.2.2
- C₉H₁₂B₄FeO₂**
μ-4,5-[Fe(CO)₂(η⁵-C₅H₅)]-2,3-C₂B₄H₇
Formation: 6.5.3.4
- C₉H₁₅B₄Co**
1-(η⁵-C₅H₅)-2,3-(CH₃)₂-1,2,3-CoC₂B₄H₄
Formation: 6.5.3.4
1-(C₅H₅)-2,2-(CH₃)₂-1,2,3-CoC₂B₄H₄
Reaction with Fe(CO)₅: 6.5.3.1
- C₉H₁₆B₉Fe**
1-η⁵-C₅H₅-6-(2,4-C₂B₅H₆)-1,2,4-FeC₂B₄H₅
Formation: 6.5.3.4
- C₉H₁₇B₇Fe**
2-(η⁶-CH₃C₆H₅)Fe-1,6-C₂B₇H₉
Formation: 6.5.3.3
2-(η⁶-CH₃C₆H₅)Fe-6,9-C₂B₇H₉
Formation: 6.5.3.3
- C₉H₁₇B₉NNaO₂**
Na[9-[4-(C₅H₄N)CO₂CH₃]-7,8-C₂B₉H₁₀]
Reaction with CuCl: 6.4
- C₉H₁₉B₂N**
(C₂H₅)₂C₂B₂(CH₃)₂NCH₃
Reaction with metal carbonyls and carbonyl derivatives: 6.5.3.1
- C₉H₁₉B₉Fe**
3-(η³-CH₃C₆H₅)-3,1,2-FeC₂B₉H₁₁
Formation: 6.5.3.4
- C₉H₂₂B₉Cr**
3-(η⁵-C₅H₅)-1,2-(CH₃)₂-3,1,2-CrC₂B₉H₁₁
Formation: 6.5.3.4
- C₉H₂₇B₁₈Fe₂**
4-(η⁵-C₅H₅)-5-(1,2-C₂B₉H₁₁)-4,5,2,3-Fe₂C₂B₉H₁₁
Formation: 6.5.3.4
- C₁₀CdMn₂O₁₀**
Cd[Mn(CO)₅]₂
Formation: 8.3.3.2.1, 8.3.3.4
- C₁₀ClMn₂O₁₀Tl**
ClTl[Mn(CO)₅]₂
Formation: 6.5.2.2
- C₁₀H₂O₁₀Os₃**
H₂Os₃(CO)₁₀
Reaction with R₃PAuR: 8.3.2.2.2
- C₁₀H₁₀Cl₄FeHg₂**
(η⁵-C₅H₅)₂Fe-2 HgCl₂
Formation: 8.3.3.3
- C₁₀H₁₀Cl₁₄FeHg₇**
(η⁵-C₅H₅)₂Fe-7 HgCl₂
Formation: 8.3.3.3
- C₁₀H₁₀Co**
(η⁵-C₅H₅)₂Co
Reaction with organoboron dihalides: 6.5.2.3
- C₁₀H₁₀Cr**
(η⁵-C₅H₅)₂Cr
Reaction with 5,6-C₂B₈H₁₂: 6.5.3.3
- C₁₀H₁₀Fe**
(η⁵-C₅H₅)₂Fe
Reaction with HgX₂: 8.3.3.3
- C₁₀H₁₀HgMo**
(η⁵-C₅H₅)₂MoHg
Formation: 8.3.3.3
- C₁₀H₁₀Ru**
(η⁵-C₅H₅)₂Ru
Reaction with HgX₂: 8.3.3.3
- C₁₀H₁₀Zn**
(C₅H₅)₂Zn
Reaction with HMn(CO)₅: 8.3.3.2.1
- C₁₀H₁₁B**
C₄H₆BC₆H₅
Reaction with metal carbonyls: 6.5.3.1
Reaction with Ru₃(CO)₁₂, Mn₂(CO)₁₀: 6.5.3.3

- C₁₀H₁₁BF₃Re**
 $(\eta^5\text{-C}_5\text{H}_5)_2\text{ReH}\cdot\text{BF}_3$
 Formation: 6.5.2.1
- C₁₀H₁₁Re**
 $(\eta^5\text{-C}_5\text{H}_5)_2\text{ReH}$
 Reaction with BF_3 : 6.5.2.1
- C₁₀H₁₂BF₃W**
 $(\eta^5\text{-C}_5\text{H}_5)_2\text{WH}_2\cdot\text{BF}_3$
 Formation: 6.5.2.1
- C₁₀H₁₂BRh**
 $\eta^5\text{-C}_5\text{H}_5\text{Rh}(\text{C}_4\text{H}_4\text{BCH}_3)$
 Formation: 6.5.3.1
- C₁₀H₁₂B₂Co₂S₂**
 $4,6\text{-(}\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{-}3,5\text{-S}_2\text{B}_2\text{H}_2$
 Formation: 6.5.3.3
- C₁₀H₁₂B₂F₂NiO₂**
 $[(\text{CH}_3)_4\text{C}_4\text{B}_2\text{F}_2]\text{Ni}(\text{CO})_2$
 Formation: 6.5.3.1
- C₁₀H₁₂Mo**
 $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}_2$
 Reaction with HgX_2 : 8.3.3.3
 Reaction with R_2Zn : 8.3.3.3
- C₁₀H₁₂W**
 $(\eta^5\text{-C}_5\text{H}_5)_2\text{WH}_2$
 Reaction with BF_3 : 6.5.2.1
 Reaction with R_2Zn : 8.3.3.3
- C₁₀H₁₃FeGaO₅**
 $\text{C}_2\text{H}_5\text{GaFe}(\text{CO})_4\cdot\text{OC}_4\text{H}_8$
 Formation: 6.5.2.2
- C₁₀H₁₄B₂NaRh**
 $\text{Na}[\text{Rh}(\text{C}_4\text{H}_4\text{BCH}_3)_2]$
 Formation: 6.5.3.1
- C₁₀H₁₄FeGeO₂**
 $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Ge}(\text{CH}_3)_3$
 Reaction with HgX_2 : 8.3.3.2.2
- C₁₀H₁₄FeO₂Si**
 $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Si}(\text{CH}_3)_3$
 Reaction with HgX_2 : 8.3.3.2.2
- C₁₀H₁₄FeO₂Sn**
 $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Sn}(\text{CH}_3)_3$
 Reaction with HgX_2 : 8.3.3.2.2
- C₁₀H₁₅B₂Rh**
 $\text{HRh}(\text{C}_4\text{H}_4\text{BCH}_3)_2$
 Formation: 6.5.3.1
- C₁₀H₁₅B₅Co₂S₂**
 $6,8\text{-(}\eta^5\text{-C}_5\text{H}_5)_2\text{-}6,8,7,9\text{-Co}_2\text{S}_2\text{B}_5\text{H}_5$
 Formation: 6.5.3.4
 $6,8\text{-(}\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{-}7,9\text{-S}_2\text{B}_5\text{H}_5$
 Formation: 6.5.3.3
- C₁₀H₁₆B₂NiO₂S**
 $[(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_2(\text{CH}_3)_2\text{S}]\text{Ni}(\text{CO})_2$
 Formation: 6.5.3.1
- C₁₀H₁₆B₄Co₂**
 $1,2\text{-(}\eta^5\text{-C}_5\text{H}_5)_2\text{-}1,2\text{-Co}_2\text{B}_4\text{H}_6$
 Formation: 6.5.3.4
- C₁₀H₁₇B**
 $\text{C}_4\text{H}_6\text{BC}_6\text{H}_{11}$
 Reaction with metal carbonyls: 6.5.3.1
- C₁₀H₁₇B₅Co₂S**
 $2,3\text{-(}\eta^5\text{-C}_5\text{H}_5)_2\text{-}2,3,6\text{-Co}_2\text{SB}_5\text{H}_7$
 Formation: 6.5.3.4
 $2,3\text{-(}\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{-}6\text{-SB}_5\text{H}_7$
 Formation: 6.5.3.3
- C₁₀H₁₈B₈Ni₂**
 $1,6\text{-(}\eta^5\text{-C}_5\text{H}_5)_2\text{-}1,6\text{-Ni}_2\text{B}_8\text{H}_8$
 Formation: 6.5.3.4
- C₁₀H₂₀BLi₂N**
 $\text{Li}_2[\text{C}_4\text{H}_4\text{BN}(\text{C}_3\text{H}_8\text{-i})_2]$
 Reaction with transition metal halides: 6.5.3.4
- C₁₀H₂₀B₃CrN₃O₃**
 $[\text{C}_2\text{H}_5(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]\text{Cr}(\text{CO})_3$
 Formation: 6.5.3.1
- C₁₀H₂₀B₁₀Ni₂**
 $1,7\text{-(}\eta^5\text{-C}_5\text{H}_5)_2\text{-}1,6\text{-Ni}_2\text{B}_{10}\text{H}_{10}$
 Formation: 6.5.3.4
- C₁₀H₂₁B₉Fe**
 $3\text{-(}\eta^6\text{-}1,4\text{-(CH}_3)_2\text{C}_6\text{H}_4\text{)}\text{-}3,1,2\text{-FeC}_2\text{B}_9\text{H}_{11}$
 Formation: 6.5.3.4
- C₁₀H₂₂BNSi**
 $\text{C}_2\text{H}_5\text{C}\equiv\text{C}(\text{CH}_3)\text{-Si}(\text{CH}_3)_2\text{-N}(\text{CH}_3)\text{-BC}_2\text{H}_5$
 Reaction with $\eta^5\text{-CpCo}(\text{C}_2\text{H}_4)_2$: 6.5.3.1
 $\text{C}_2\text{H}_5\text{C}\equiv\text{C}(\text{CH}_3)\text{-Si}(\text{CH}_3)_2\text{-N}(\text{CH}_3)\text{-BC}_2\text{H}_5$
 Reaction with $\text{Fe}_2(\text{CO})_9$: 6.5.3.1
 $\text{C}_2\text{H}_5\text{C}\equiv\text{C}(\text{CH}_3)\text{-Si}(\text{CH}_3)_2\text{-N}(\text{CH}_3)\text{BC}_2\text{H}_5$
 Reaction with metal atoms: 6.5.3.1
- C₁₀H₂₃B₄Co**
 $1\text{-(}\eta^5\text{-(CH}_3)_5\text{C}_5\text{)}\text{-}1\text{-CoB}_4\text{H}_8$
 Formation: 6.5.3.4
 $2\text{-(}\eta^5\text{-(CH}_3)_5\text{C}_5\text{)}\text{-}2\text{-CoB}_4\text{H}_8$
 Formation: 6.5.3.4
- C₁₀H₂₃B₉Pd**
 $3\text{-(}\eta^2\text{-C}_8\text{H}_{12}\text{)}\text{-}3,1,2\text{-PdC}_2\text{B}_9\text{H}_{11}$
 Formation: 6.5.3.4
- C₁₀H₂₃B₉Pt**
 $3\text{-(C}_8\text{H}_{12}\text{)}\text{-}3,1,2\text{-PtC}_2\text{B}_9\text{H}_{11}$

- Formation: 6.5.3.4
C₁₀H₂₈B₉Co
 6-[η^5 -(CH₃)₅C₅]-6-CoB₉H₁₃
 Formation: 6.5.3.4
C₁₀H₃₀Au₂B₈N₂S₄
 6,9-[S₂CN(C₂H₅)₂]₂-6,9-Au₂B₈H₁₀
 Formation: 6.4
C₁₀H₃₀B₂N₂
 (CH₃)₄B₂[N(CH₃)₃]₂
 Formation: 6.2.2.2
C₁₀H₃₃B₈Co
 6-[η^5 -(CH₃)₅C₅]-6-CoB₈H₁₈
 Formation: 6.5.3.4
C₁₀H₃₄B₁₃CoO
 [2,3-(C₂H₅)₂-2,3-C₂B₄H₄]-5-CoB₉H₁₂-1-O(CH₂)₄
 Formation: 6.5.3.4
C₁₀H₃₅B₁₂CoO
 [2,3-(C₂H₅)₂C₂B₃H₅]-5-CoB₉H₁₂-1-O(CH₂)₄
 Formation: 6.5.3.4
C₁₀H₃₇B₁₆CoO
 (1,2-(C₂H₅)₂C₂B₇H₇)-6-CoB₉H₁₂-2-O(CH₂)₄
 Formation: 6.5.3.4
C₁₀HgMn₂O₁₀
 Hg[Mn(CO)₅]₂
 Formation: 8.3.3.4
C₁₀Mn₂O₁₀
 Mn₂(CO)₁₀
 Reaction with Na-Hg: 8.3.3.1
 Reaction with tetraphenylporphyrinatoindiumchloride: 6.5.2.3
 Reaction with Zn, Cd, Hg: 8.3.3.4
C₁₀Mn₂O₁₀Zn
 Zn[Mn(CO)₅]₂
 Formation: 8.3.3.2.1, 8.3.3.4
C₁₁B₄Tb₃
 B₄C₁₁Tb₃
 Crystal chemistry: 6.7.2.1
C₁₁H₁₀BTl
 Tl(C₅H₅BC₆H₅)
 Reaction with [(CH₃)₄C₄]Co(CO)₂I: 6.5.3.4
 Reaction with IrC₅(CH₃)₅Cl₂: 6.5.3.4
 Reaction with RhCl₂C₅(CH₃)₅: 6.5.3.4
 Reaction with [RuCl₂(C₆H₆)₂]₂: 6.5.3.4
C₁₁H₁₁B
 CHCHCH₂CHCHBC₆H₅
 Reaction with Co₂(CO)₈: 6.5.3.3
C₁₁H₁₂B₂F₂FeO₃
 [(CH₃)₄C₄B₂F₂]Fe(CO)₃
 Formation: 6.5.3.1
C₁₁H₁₃BCo
 η^5 -C₅H₅Co(η^5 -C₅H₅BCH₃)
 Formation: 6.5.2.3
C₁₁H₁₄MoO₃Sn
 η^5 -C₅H₅Mo(CO)₃Sn(CH₃)₃
 Reaction with HgX₂: 8.3.3.2.2
C₁₁H₁₅BMnNO₃
 [C₃H₃NC(CH₃)₃BCH₃]Mn(CO)₃
 Formation: 6.5.3.4
C₁₁H₁₅BNbOZn
 (η^5 -C₅H₅)₂Nb(CO)(H)ZnBH₄
 Formation: 8.3.3.5.1
C₁₁H₁₆B₂F₆MnO₃PS
 [(C₂H₅)₂C₂B₂(CH₃)₂S]-Mn(CO)₃[PF₆]
 Reaction with transition metal halides to give triple-decked and tetra-decked complexes: 6.5.3.4
C₁₁H₁₆B₂FeO₃S
 [(C₂H₅)₂C₂B₂(CH₃)₂S]Fe(CO)₃
 Formation: 6.5.3.1
C₁₁H₁₇B₉O₃Ru
 3,3,3-(CO)₃-3,1,2-RuC₂B₉H₁₁-0,5C₆H₆
 Formation: 6.5.3.4
C₁₁H₁₈B₇CoNi
 2,3-(η^5 -C₅H₅)₂-2,3,10-NiCoCB₇H₈
 Formation: 6.5.3.4
 3,5-(η^5 -C₅H₅)₂-3,5,10-NiCoCB₇H₈
 Formation: 6.5.3.4
C₁₁H₁₈B₉Co
 3-(η^5 -C₉H₇)-3,1,2-CoC₂B₉H₁₁
 Formation: 6.5.3.4
C₁₁H₂₀B₃N₃
 C₆H₅(CH₃)₂B₃N₃(CH₃)₃
 Reaction with metal carbonyl derivatives: 6.5.3.1
C₁₁H₂₁B₇Fe
 2-[η^6 -(CH₃)₃C₆H₃]Fe-1,6-C₂B₇H₉
 Formation: 6.5.3.3
C₁₁H₂₂B₄O₃OsSi₂
 1-Os(CO)₃-2,3-[(CH₃)₃Si]₂-2,3-C₂B₄H₄
 Formation: 6.5.3.3
C₁₁H₂₂B₉Fe
 1-C₆H₄CH₃-2,4-(CH₃)₂-1,2,4-FeC₂B₉H₉
 Formation: 6.5.3.4
C₁₁H₂₃B₇Fe
 6-[η^6 -(CH₃)₃C₆H₃]Fe-9,10-C₂B₇H₁₁
 Formation: 6.5.3.3

- C₁₁H₂₄B₉O₃PW**
6,6,6,6-(CO)₃[P(CH₃)₂(C₆H₅)]-6-
WB₉H₁₃
Formation: 6.5.3.4
- C₁₁H₂₇BN₂Si**
(CH₃)₃Si[(CH₃)₃C]NBNC(CH₃)₃
Reaction with (C₅H₅)₂NbH₃: 6.5.3.1
- C₁₂Co₃InO₁₂**
In[Co(CO)₄]₃
Formation: 6.5.2.2
- C₁₂Co₃O₁₂Tl**
Tl[Co(CO)₄]₃
Formation: 6.5.2.2
- C₁₂Fe₃O₁₂**
Fe₃(CO)₁₂
Reaction with C₄H₆BC₆H₅: 6.5.3.1
- C₁₂H₃BFe₄O₁₂**
HFe₄(BH₂)(CO)₁₂
Formation: 6.5.3.3
- C₁₂H₈BrCo₂InO₉**
BrIn[Co(CO)₄]₂·OC₄H₈
Formation: 6.5.2.1
- C₁₂H₈ClCo₂GaO₉**
ClGa[Co(CO)₄]₂·OC₄H₈
Reaction with Cl₃Ga·THF: 6.5.2.2
- C₁₂H₁₀BBr**
(C₆H₅)₂BBr
Reaction with L₂NiC₂H₄: 6.5.2.3
- C₁₂H₁₃B**
C₆H₈BC₆H₅
Reaction with metal carbonyls and
metal carbonyl derivatives: 6.5.3.1
- C₁₂H₁₅B₃Co₂**
1,7-(η⁵-C₅H₅)₂-1,7,2,3-Co₂C₂B₃H₅
Formation: 6.5.3.4
1,7-(η⁵-C₅H₅)₂-1,7,2,4-Co₂C₂B₃H₅
Formation: 6.5.3.4
- C₁₂H₁₆B₂Co**
Co(η⁵-C₅H₅BCH₃)₂
Formation: 6.5.2.3
- C₁₂H₁₆B₂CrO₄S**
[(C₂H₅)₂C₂B₂(CH₃)₂S]Cr(CO)₄
Formation: 6.5.3.1
- C₁₂H₁₆B₄Co₂**
3,4-(η⁵-C₅H₅)₂-3,4,1,7-Co₂C₂B₄H₆
Formation: 6.5.3.4
- C₁₂H₁₇B₅Co₂**
1,7-(C₅H₅)₂-1,7,5,6-Co₂C₂B₅H₇
Formation: 6.5.3.1
1,8-(C₅H₅)₂-1,8,5,6-Co₂C₂B₅H₇
Formation: 6.5.3.1
3,8-(η⁵-C₅H₅)₂-3,8,1,9-Co₂C₂B₅H₇
Formation: 6.5.3.4
- C₁₂H₁₇B₅Ni₂**
1,2-(η⁵-C₅H₅)₂-1,2,7,8-Ni₂C₂B₅H₇
Formation: 6.5.3.4
- C₁₂H₁₈B₂FeO₂**
(η⁵-CHCHCH₂CHCHBOCH₃)₂Fe
Formation: 6.5.3.3
- C₁₂H₁₈B₆Co₂**
2,7-(η⁵-C₅H₅)₂-2,7,1,10-Co₂C₂B₆H₈
Formation: 6.5.3.4
2,9-(η⁵-C₅H₅)₂-2,9,1,10-Co₂C₂B₆H₈
Formation: 6.5.3.4
7,9-(η⁵-C₅H₅)₂-7,9,1,6-Co₂C₂B₆H₈
Formation: 6.5.3.4
- C₁₂H₁₈B₆Fe₂**
1,6-(η⁵-C₅H₅)₂-1,6,1,2-Fe₂C₂B₆H₈
Formation: 6.5.3.4
- C₁₂H₁₉B₂Co**
η⁵-C₅H₅Co[(CH₃)₂C₂B₂(CH₃)₂CH₂]
Reduction to the anion: 6.5.3.1
- C₁₂H₁₉B₂FeNO₃**
[(C₂H₅)₂C₂B₂(CH₃)₂NCH₃]-
Fe(CO)₃
Formation: 6.5.3.1
- C₁₂H₁₉B₇CoFe**
1,8-(C₅H₅)₂-1,8,2,3-FeCoC₂B₇H₉
Formation: 6.5.3.4
- C₁₂H₁₉B₇Co₂**
1,10-(η⁵-C₅H₅)₂-1,10,2,3-Co₂C₂B₇H₉
Formation: 6.5.3.4
1,8-(η⁵-C₅H₅)₂-1,8,2,3-Co₂C₂B₇H₉
Formation: 6.5.3.4
- C₁₂H₂₀B₄Fe**
1-(C₈H₁₀)-2,3-(CH₃)₂-1,2,3-FeC₂B₄H₄
Formation: 6.5.3.4
- C₁₂H₂₀B₈Co₂**
1,2-(η⁵-C₅H₅)₂-1,2,3,6-Co₂C₂B₈H₁₀
Formation: 6.5.3.4
1,2-(η⁵-C₅H₅)₂-1,2,5,7-Co₂C₂B₈H₁₀
Formation: 6.5.3.4
2,3-(η⁵-C₅H₅)₂-2,3,1,7-Co₂C₂B₈H₁₀
Formation: 6.5.3.4
3,6-(η⁵-C₅H₅)₂-3,6,1,2-Co₂C₂B₈H₁₀
Formation: 6.5.3.4
3,6-(η⁵-C₅H₅)₂-3,6,8,10-Co₂C₂B₈H₁₀
Formation: 6.5.3.4
- C₁₂H₂₀B₈Cr₂**
1,3-(C₅H₅)₂-1,3,2,4-Cr₂C₂B₈H₁₀
Formation: 6.5.3.3
- C₁₂H₂₁B₉CoFe**
4,5-(η⁵-C₅H₅)₂-4,5,1,8-CoFeC₂B₉H₁₁
Formation: 6.5.3.4
- C₁₂H₂₁B₉Co₂**
4,5-(η⁵-C₅H₅)₂-4,5,1,13-Co₂C₂B₉H₁₁
Formation: 6.5.3.4

C₁₂H₂₁B₉Fe4,5-(η^5 -C₅H₅)₂-4,5,2,3-FeC₂B₉H₁₁

Formation: 6.5.3.4

C₁₂H₂₂B₁₀Co₂1,14-(η^5 -C₅H₅)₂-1,14,2,10-Co₂C₂B₁₀H₁₂

Formation: 6.5.3.4

C₁₂H₂₄BNSi $\text{C}_2\text{H}_5\text{C}\equiv\text{C}[\text{C}(\text{CH}_3)=\text{CH}_2]-$ $\text{Si}(\text{CH}_3)_2-\text{N}(\text{CH}_3)-\text{BC}_2\text{H}_5$

Reaction with metal complexes:

6.5.3.1

C₁₂H₂₄B₂(C₂H₅)₂C₂B₂(C₂H₅)₂C(CH₃)HReaction with η^5 -Cp₂Ni or[η^5 -CpCoNi]₂: 6.5.3.3Reaction with η^5 -CpCo(CO)₂: 6.5.3.3Reaction with MX₂ (M = Pd, Pt):

6.5.3.3

Reaction with Pt(C₂H₄)₃: 6.5.3.1**C₁₂H₂₆B₉FeO₂**1-(η^5 -C₅H₅)-2-CH(OC₂H₅)₂-1,2,3-FeC₂B₉H₁₀

Formation: 6.5.3.4

C₁₂H₂₇Al(i-C₄H₉)₃Al

Reaction with K: 6.2.4

C₁₂H₂₇B(C₄H₉)₃BReaction with L₄CoCl: 6.5.2.2**C₁₂H₂₈Ga₂Si₄**Ga₂{CH[Si(CH₃)₂]₄}

Formation: 6.2.2.1

C₁₂H₃₀Br₄In₂P₂In₂Br₄[P(C₂H₅)₃]₂

Formation: 6.2.2.1

C₁₂H₃₀I₄In₂P₂In₂I₄[P(C₂H₅)₃]₂

Formation: 6.2.2.1

C₁₂H₃₃GaSi₃[(CH₃)₃SiCH₂]₃Ga

Reaction with KH: 6.2.4

C₁₂H₃₃InSi₃[(CH₃)₃SiCH₂]₃In

Reaction with KH: 6.2.4

C₁₂H₃₄B₄Co₃1,2,3-[(η^5 -(CH₃)₅C]₂-1,2,3-Co₃B₄H₄

Formation: 6.5.3.4

C₁₂H₃₆Al₄BN₃(CH₃)₆Al₄B[N(CH₃)₂]₃

Formation: 6.2.4

C₁₂H₃₇B₃P₂Pt[(C₂H₅)₃P]₂PtB₃H₇

Formation: 6.5.3.4

C₁₂H₄₁B₉P₂PtS11-H-11,11-[(C₂H₅)₃P]₂-11,6-PtSB₉H₁₀

Formation: 6.5.3.4

C₁₂H₄₂B₁₀P₂Pt7,7-[(C₂H₅)₃P]₂-7-PtB₁₀H₁₂

Formation: 6.5.3.4

C₁₂H₄₂B₁₈CuN[(C₂H₅)₄N][3,3'-Cu(1,2-C₂B₉H₁₁)₂]

Formation: 6.4

C₁₃H₉BFeO₃(C₄H₄BC₆H₅)Fe(CO)₃

Formation: 6.5.3.1

C₁₃H₉BK₂N₃RhK₂[(C₄H₄BC₆H₅)Rh(CN)₃]

Formation: 6.5.3.1

C₁₃H₁₁BCoO₂(CHCHCH₂CHCHBC₆H₅)Co(CO)₂

Formation: 6.5.3.3

C₁₃H₁₇B₂CoF₂[(CH₃)₄C₄B₂F₂]Co(C₅H₅)

Formation: 6.5.3.1

C₁₃H₂₀BCoN η^5 -C₅H₅Co(CH=CH=CH-BCH₃)-N[C(CH₃)₃]

Formation: 6.5.3.1

C₁₃H₂₀BFeNO₃[C₄H₄BN(C₃H₈-i)₂]Fe(CO)₃

Formation: 6.5.3.4

C₁₃H₂₀B₂FeN₂O₃[C₄H₄B₂(N-i-C₃H₈)₂]Fe(CO)₃

Formation: 6.5.3.3

C₁₃H₂₁B₂CoS η^5 -C₅H₅Co[(C₂H₅)₂C₂B₂(CH₃)₂S]

Formation: 6.5.3.4

[(C₂H₅)₂C₂B₂(CH₃)₂S]Co(C₅H₅)

Formation: 6.5.3.1

C₁₃H₂₁B₂F₆FePS[(η^5 -C₅H₅)Fe[(C₂H₅)₂C₂B₂(CH₃)₂S]]-[PF₆]Reaction with transition metal
halides: 6.5.3.4**C₁₃H₂₁B₂NiS**[(C₂H₅)₂C₂B₂(CH₃)₂S]Ni(C₅H₅)

Formation: 6.5.3.1

C₁₃H₂₂BFeNO₃Si[C₂H₅C=C(CH₃)-Si(CH₃)₂-N(CH₃)-BC₂H₅]Fe(CO)₃

Formation: 6.5.3.1

C₁₃H₂₂B₄Fe1-(η^6 -C₆H₅CH₃)-Fe-2,3-(C₂H₅)₂C₂B₄H₄

Formation: 6.5.3.3

C₁₃H₂₃B₆Co

7,8,10,11-(CH₃)₄-7,8,10,11-C₄-2-Co-
(B₆H₆)-C₅H₅-η⁵

Formation: 6.5.3.3

7,8,10,11-(CH₃)₄-7,8,10,11-C₄-9-Co-
(B₆H₆)-C₅H₅-η⁵

Formation: 6.5.3.3

C₁₃H₂₄B₇Co

η⁵-C₅H₅Co(CH₃)₄C₄B₇H₇

Formation: 6.5.3.3

1-(η⁵-C₅H₅)-2,3,7,8-(CH₃)₄-1,2,3,7,8-
CoC₄B₇H₇

Formation: 6.5.3.4

C₁₃H₂₅B₈Co

1-(η⁵-C₅H₅)-2,3,7,8-(CH₃)₄-1,2,3,7,8-
CoC₄B₈H₈

Formation: 6.5.3.4

6:4',5'-[1-(η⁵-C₅H₅)-1-Co-2,3-(CH₃)₂-
2,3-C₂B₄H₃]-[2',3'-(CH₃)₂-
2',3'C₂B₄H₅]

Formation: 6.5.3.4

C₁₃H₂₅B₈Fe₂

Fe₂[(CH₃)₄C₄B₈H₈]-η⁵C₅H₅

Formation: 6.5.3.1

C₁₃H₂₆B₂NO₅Re

[(C₂H₅)₄N][(H₃B)₂Re(CO)₅]

Formation: 6.5.3.2

C₁₃H₂₇B₄CoSi₂

(1-η⁵-C₅H₅)Co-2,3-[(CH₃)₃Si]₂C₂B₄H₄

Formation: 6.5.3.3

C₁₃H₂₈B₅CoSi₂

(5-η⁵-C₅H₅)Co-1,8-[(CH₃)₃Si]₂C₂B₅H₅

Formation: 6.5.3.3

C₁₃H₂₉B₆CoSi₂

(1-η⁵-C₅H₅)Co-4,5-[(CH₃)₃Si]₂C₂B₆H₆

Formation: 6.5.3.3

(1-η⁵-C₅H₅)Co-4,6-[(CH₃)₃Si]₂C₂B₆H₆

Formation: 6.5.3.3

C₁₃H₃₀ClIrOP₂

Ir(CO)Cl[P(C₂H₅)₃]₂

Reaction with Hg(SiR₃)₂,

Hg(GeR₃)₂: 8.3.3.2.2

C₁₃H₃₁B₆CoSi₂

5:1,2'-(1-η⁵-C₅H₅)Co-2,3-

[(CH₃)₃Si]₂C₂B₄H₃[B₂H₅]

Formation: 6.5.3.3

C₁₃H₃₈B₅P₂Pt

μ-4,5-[(C₂H₅)₃P]₂(PtH)-μ-(5,6-H)-2,3-
CB₅H₆

Formation: 6.5.3.3

C₁₃H₃₉B₅P₂Pt

μ-4,5-[(C₂H₅)₃P]₂(PtH)-μ-(3,4-H)-μ-
(5,6-H)-2-CB₅H₆

Formation: 6.5.3.1, 6.5.3.3

C₁₄H₉MnO₃

(C₅H₄C₆H₅)Mn(CO)₃

Formation: 6.5.3.1

C₁₄H₁₀ClFe₂InO₄

Formation: 6.5.2.1

C₁₄H₁₀Fe₂HgO₄

Hg[Fe(CO)₂C₅H₅-η⁵]₂

Formation: 8.3.3.1.2

C₁₄H₁₀Fe₂O₄

[(η⁵-C₅H₅)(CO)₂Fe]₂

Reaction with InCl: 6.5.2.1

[η⁵-C₅H₅Fe(CO)₂]₂

Formation: 6.5.3.4

C₁₄H₁₀MoO₃Zn

C₆H₅ZnMo(CO)₃C₅H₅-η⁵

Formation: 8.3.3.5.2

C₁₄H₁₂BCoO₃

(C₅H₇BC₆H₅)Co(CO)₃

Formation: 6.5.3.3

C₁₄H₁₄B₂Co₂O₄

(C₄H₄BCH₃)₂Co₂(CO)₄

Formation: 6.5.3.1

C₁₄H₁₄S

(C₆H₅CH₂)₂S

Reaction with Hg₂(NO₃)₂: 8.2.4.2.2

Reaction with Hg₂SiF₆: 8.2.4.2.2

C₁₄H₁₆B₂Mn₂O₆S

(CO)₃Mn-μ-[(C₂H₅)₂C₂B₂(CH₃)₂S]-
Mn(CO)₃

Formation: 6.5.3.1

C₁₄H₁₈BCo₂NO₆

[(CH₃)₃CBNC(CH₃)₃][Co₂(CO)₆]

Formation: 6.5.3.1

C₁₄H₂₀BCo

[(CH₃)₄C₄][Co(C₅H₅BCH₃-η⁶)

Formation: 6.5.3.4

C₁₄H₂₀B₂F₂FeS

(1,4-F₂C₆H₄)Fe-

[(C₂H₅)₂C₂B₂(CH₃)₂S]

Formation: 6.5.3.1

C₁₄H₂₀B₃CrN₃O₃

[C₆H₅(CH₃)₂B₃N₃(CH₃)₃][Cr(CO)₃]

Formation: 6.5.3.1

C₁₄H₂₀B₆Co₂

1,12-(η⁵-C₅H₅)₂-1,12,2,3,7,8-

Co₂C₄B₆H₁₀

Formation: 6.5.3.4

C₁₄H₂₂B₂FeS

(C₆H₆)Fe[(C₂H₅)₂C₂B₂(CH₃)₂S]

Formation: 6.5.3.1

C₁₄H₂₂B₂Ni

η⁵-C₅H₅Ni[(C₂H₅)₂C₂B₂(CH₃)₂CH]

Formation: 6.5.3.3

C₁₄H₂₂B₄V1-(C₈H₈)-2,3-(C₂H₅)₂-1,2,3-VC₂B₄H₄

Formation: 6.5.3.4

C₁₄H₂₂B₁₀Co₂3':2-(2',4'-C₂B₅H₆)-1,8-(η⁵-C₅H₅)₂-1,8,5,6-Co₂C₂B₅H₆

Formation: 6.5.3.4

C₁₄H₂₃B₂Coη⁵-C₅H₅Co[(C₂H₅)₂C₂B₂(CH₃)₂CH₂]

Formation: 6.5.3.4

Reaction with K: 6.5.3.4

Reaction with η⁵-CpCo(C₂H₄)₂,
[η⁵-Fe(CO)₂]₂ and η⁵-Fe(C₈H₁₂):
6.5.3.3**C₁₄H₂₃B₂CoN**η⁵-C₅H₅Co[C₃H₃B(CH₃)B-(CH₃)N[C(CH₃)₃]

Formation: 6.5.3.1

C₁₄H₂₅B₄Co1-[η⁵-C₅(CH₃)₅]-2,3-(CH₃)₂-1,2,3-CoC₂B₄H₄

Formation: 6.5.3.4

C₁₄H₂₈B₄Ni[(CH₃)₂C₂B₂(CH₃)₂CH₂]₂Ni

Thermolysis: 6.5.3.3

C₁₄H₂₉B₇Ni5,7,8-(CH₃)₃-11,7,8,10-[η³-C₄(CH₃)₄H]Ni-C₃B₇H₇

Formation: 6.5.3.3

C₁₄H₃₀B₂ClN₂Si₂V[C₃H₃NSi(CH₃)₃BCH₃]₂VCl

Formation: 6.5.3.4

C₁₄H₃₀B₂Cl₂N₂Si₂Ti[C₃H₃NSi(CH₃)₃BCH₃]₂TiCl₂

Formation: 6.5.3.4

C₁₄H₃₀B₁₈HgN₂3,3'-Hg[4-(C₅H₅N)(1,2-C₂B₉H₁₀)]₂

Formation: 6.4

C₁₄H₃₄B₂Cl₄N₂Ti[C₃H₈BNC(CH₃)₃]₂TiCl₄

Formation: 6.5.3.1

C₁₄H₃₄B₂N₂[C₃H₈BNC(CH₃)₃]₂Reaction with TiCl₄: 6.5.3.1**C₁₄H₃₆B₃CoP₂**2,2-[(C₂H₅)₃P]₂-2,1,6-CoC₂B₃H₆

Formation: 6.5.3.1

C₁₄H₃₆B₄P₂Ptμ-4,5-[(C₂H₅)₃P]₂PtH)-μ-(5,6-H)-2,3-C₂B₄H₄

Formation: 6.5.3.1

C₁₄H₃₇B₄P₂Ptμ-4,5-[(C₂H₅)₃P]₂PtH)-(5,6-H)-2,3-C₂B₄H₆

Formation: 6.5.3.1

C₁₄H₃₈B₄P₂Ptμ-4,5-[(C₂H₅)₃P]₂PtH)-μ-(5,6-H)-2,3-C₂B₄H₆

Formation: 6.5.3.3

C₁₄H₃₉B₆CoP₂2-H-2,2-[(C₂H₅)₃P]₂-2,1,8-CoC₂B₆H₈

Formation: 6.5.3.1

C₁₄H₃₉B₇CoP₂6,6-[P(C₂H₅)₃]₂-6,1,2-CoC₂B₇H₉

Formation: 6.5.3.4

C₁₄H₄₀B₇CoP₂2-H-2,2-[P(C₂H₅)₃]₂-2,1,6-CoC₂B₇H₉

Formation: 6.5.3.4

C₁₄H₄₀B₇P₂Rh2-H-2,2-[P(C₂H₅)₃]₂-1,2,6-RhC₂B₇H₉

Formation: 6.5.3.4

C₁₄H₄₀B₈CoP₂1,1-[P(C₂H₅)₃]₂-1,2,4-CoC₂B₈H₁₀

Formation: 6.5.3.4

C₁₄H₄₁B₉P₂Pt3,3-[(C₂H₅)₃P]₂-3,1,2-PtC₂B₉H₁₁

Formation: 6.5.3.1

C₁₄H₄₂Au₂B₁₈N₂S₄{[(C₂H₅)₂NCS]₂Au}[Au(C₂B₉H₁₁)₂]

Formation: 6.4

C₁₄H₄₂B₈P₂Pt9-H-9,9-[(C₂H₅)₃P]₂-μ-(10,11-H)-9,7,8-Pt-C₂B₈H₁₀

Formation: 6.5.3.3

C₁₄H₄₂B₉P₂Rh3-H-3,3-[(C₂H₅)₃P]₂-3,1,2-RhC₂B₉H₁₁

Formation: 6.5.3.4

C₁₅H₁₃BFeO₃(C₆H₈BC₆H₅)Fe(CO)₃

Formation: 6.5.3.1

C₁₅H₁₄BRh(C₅H₅)Rh(C₄H₄BC₆H₅)

Formation: 6.5.3.1

C₁₅H₁₅BCo₃NO₉(C₂H₅)₃NBCo₃(CO)₉

Formation: 6.5.2.2

C₁₅H₁₅B₄CoFe₂O₆1,1,1-(CO)₃-4,4,4-(CO)₃-9-(C₅H₅)-2,8-(CH₃)₂-1,4,9-Fe₂CoC₂B₄H₄

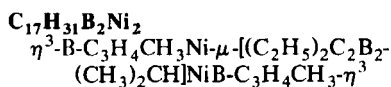
Formation: 6.5.3.1

C₁₅H₁₉B₃Co₂1,7-(η⁵-C₅H₅)₂-μ-(2,3-C₃H₄)-1,7,2,3-Co₂C₂B₃H₅

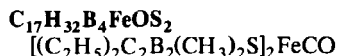
Formation: 6.5.3.4

- C₁₅H₂₀B₃Co₃**
1,2,3-(η^5 -C₅H₅)₃-1,2,3-Co₃B₃H₅
Formation: 6.5.3.4
- C₁₅H₂₁B₃Rh₂**
(C₄H₄BCH₃)Rh- μ -(C₄H₄BCH₃)-
Rh(C₄H₄BCH₃)
Formation: 6.5.3.1
- C₁₅H₂₃B₂O₂Rh**
[(CH₃)₄C₄B₂(OCH₃)₂]Rh(C₅H₅)
Formation: 6.5.3.1
- C₁₅H₂₄BFeNO₃Si**
(CO)₃Fe(C₂H₅ \bar{C} =C[C(CH₃)=CH₂]-Si(CH₃)₂-
N(CH₃)-BC₂H₅)
Formation: 6.5.3.1
- C₁₅H₂₄BORh**
 η^5 -(CH₃)₅C₅Rh[η -(C₂H₃)₂BO(CH₃)]
Formation: 6.5.3.1
- C₁₅H₂₄BRh**
 η^5 -(CH₃)₅C₅Rh[(C₂H₃)₂BCH₃]
Formation: 6.5.3.1
- C₁₅H₂₄B₂FeO₃**
[(C₂H₅)₂C₂B₂(C₂H₅)₂CHCH₃]-
Fe(CO)₃
Formation: 6.5.3.1
- C₁₅H₂₄B₂FeS**
(C₆H₅CH₃)Fe[(C₂H₅)₂C₂B₂-
(CH₃)₂S]
Formation: 6.5.3.1
- C₁₅H₂₅B₅Fe**
2-(η^6 -CH₃C₆H₅)Fe-6,7,9,10-
(CH₃)₄C₄B₅H₅
Formation: 6.5.3.3
- C₁₅H₂₇BCoNSi**
[C₂H₅ \bar{C} =C(CH₃)-Si(CH₃)₂-
N(CH₃)-BC₂H₅]Co(C₅H₅)
Formation: 6.5.3.1
- C₁₅H₃₃BF₆FeNOP₃**
[[C₃H₃NC(CH₃)₃BCH₃]Fe(CO)-
[P(CH₃)₃]₂]PF₆
Formation: 6.5.3.4
- C₁₅InMn₃O₁₅**
In[Mn(CO)₅]₃
Formation: 6.5.2.2
- C₁₅InO₁₅Re₃**
In[Re(CO)₅]₃
Formation: 6.5.2.2
- C₁₅Mn₃O₁₅Tl**
Tl[Mn(CO)₅]₃
Formation: 6.5.2.2
- C₁₆Br₃Co₄In₃O₁₆**
Br₃In₃[Co(CO)₄]₄
Formation: 6.5.2.1
- C₁₆H₉BMn₂O₆**
(CO)₃Mn- μ -(C₄H₄BC₆H₅)Mn(CO)₃
Formation: 6.5.3.1
- C₁₆H₁₀BrInMo₂O₆**
BrIn[Mo(CO)₃(C₅H₅- η^5)]₂
Formation: 6.5.2.2
- C₁₆H₁₀Cr₂HgO₆**
Hg[Cr(CO)₃C₅H₅- η^5]₂
Formation: 8.3.3.1.2
- C₁₆H₁₅BCo**
 η^5 -C₅H₅Co(η^5 -C₅H₅BC₆H₅)
Formation: 6.5.2.3
- C₁₆H₁₅Co₃OS**
(μ_3 -CO)-(C₅H₅)₃Co₃S
Formation: 6.5.3.3
- C₁₆H₂₁B₂FeMnO₃S**
(CO)₃Mn- μ -[(C₂H₅)₂C₂B₂(CH₃)₂S]-
Fe(C₅H₅)
Formation: 6.5.3.1
- C₁₆H₂₄B₂F₂Ni**
[(CH₃)₄C₄]Ni[(CH₃)₄C₄B₂F₂]
Formation: 6.5.3.1
- C₁₆H₂₄B₂F₂Pt**
[(CH₃)₄C₄B₂F₂]Pt(C₈H₁₂)
Formation: 6.5.3.1
- C₁₆H₂₄B₄F₄Ni**
[(CH₃)₄C₄B₂F₂]₂Ni
Formation: 6.5.3.1
- C₁₆H₂₅BF₆FeNP**
[[C₃H₃NC(CH₃)₃BCH₃]Fe[C₆H₄-
(CH₃)₂]PF₆
Formation, reaction with phosphines,
phosphites, CO and CH₃CN:
6.5.3.4
- C₁₆H₂₆B₂FeS**
[p-C₆H₄(CH₃)₂]Fe-
[(C₂H₅)₂C₂B₂(CH₃)₂S]
Formation: 6.5.3.1
- C₁₆H₂₈B₂Ni₂**
 η^3 -C₃H₅Ni- μ -[(CH₃)₂C₂B₂-
(CH₃)₂CH]Ni(C₃H₅- η^3)₂
Formation: 6.5.3.3
- C₁₆H₂₈B₄Fe**
1-[η^6 -(CH₃)₆C₆]Fe-2,3-(CH₃)₂C₂B₄H₄
Formation: 6.5.3.3
- C₁₆H₂₉B₃P₂Pt**
[(C₆H₅)(CH₃)₂P]₂PtB₃H₇
Formation: 6.5.3.4
- C₁₆H₃₀B₂Br₂N₂Ti**
[C₃H₃NC(CH₃)₃BCH₃]₂TiBr₂
Formation: 6.5.3.4

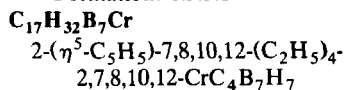
- C₁₆H₃₀B₂FeN₂**
[C₃H₃NC(CH₃)₃BCH₃]₂Fe
Reaction with arenes in the presence
of AlX₃ and Al: 6.5.3.4
- C₁₆H₃₁B₃Ni**
[(CH₃B)(C₂H₅)₂C₂B₂(CH₃)₂CH]Ni-
(CH₃CHCH-CHC₂H₅)
Formation: 6.5.3.3
- C₁₆H₃₂B₄Co₂F₆PS₂**
[(C₂H₅)₂C₂B₂(CH₃)₂S]Co₂[PF₆]
Reaction with FeCl₂: 6.5.3.4
- C₁₆H₃₂B₄NiS₂**
[(C₂H₅)₂C₂B₂(CH₃)₂S]₂Ni
Formation: 6.5.3.1
- C₁₆H₃₄B₈P₂Pt**
4,4-[P(CH₃)₂C₆H₅]₂-4-PtB₈H₁₂
Formation: 6.5.3.4
- C₁₆H₃₆Al₂**
(i-C₄H₉)₄Al₂
Reaction with elemental K: 6.2.4
- C₁₆H₃₆BF₆FeN₂P₃**
[[C₃H₃NC(CH₃)₃BCH₃]₂Fe-
(CH₃CN)[P(CH₃)₃]₂]PF₆
Formation: 6.5.3.4
- C₁₆H₃₈B₉NO₂W**
[(C₂H₅)₄N][CH₃C≡3W(CO)₂-7,8-
C₂B₉H₉(CH₃)₂]
Formation: 6.5.3.4
- C₁₆H₄₀B₁₂P₂Pt₂**
7,7-[(C₆H₅)(CH₃)₂P]₂-7,7'-Pt₂(B₆H₉)₂
Formation: 6.5.3.4
[P(CH₃)₂C₆H₅]₂Pt₂B₁₂H₁₈
Formation: 6.5.3.4
- C₁₆H₄₀B₁₆P₂Pt**
7-[P(CH₃)₂C₆H₅]-7-PtB₁₆H₁₈-9'-
P(CH₃)₂C₆H₅
Formation: 6.5.3.4
[P(CH₃)₂C₆H₅]-(-
PtB₁₆H₁₈)[P(CH₃)₂C₆H₅]
Formation: 6.5.3.4
- C₁₆H₄₂B₄P₂Pt**
μ-4,5-[(C₂H₅)₃P]₂PtH]-μ-(5,6-H)-
2,3(CH₃)₂-2,3-C₂B₄H₄
Formation: 6.5.3.3
- C₁₆H₄₂B₁₈P₂Pt**
[P(CH₃)₂C₆H₅]₂PtB₁₈H₂₀
Formation: 6.5.3.4
- C₁₆H₄₃B₇P₂Pt**
10,10-[(C₂H₅)₃P]₂-2,8-(CH₃)₂-10,2,8-
PtC₂B₇H₇
Formation: 6.5.3.1
- C₁₆H₄₅B₇NiP₂**
6,6-[(C₂H₅)₃P]₂-5,9-(CH₃)₂-6,5,9-
NiC₂B₇H₉
Formation: 6.5.3.3
- C₁₆H₅₂B₁₈P₂Rh₂**
{3-[(C₂H₅)₃P]3-H-3,1,2-RhC₂B₉H₁₀]₂
Formation: 6.5.3.4
- C₁₇H₁₀MnO₅Tl**
(C₆H₅)₂Tl—Mn(CO)₅
Formation: 6.5.2.2
- C₁₇H₁₆BF₆PRu**
[η⁶-C₆H₆Ru(η⁶-C₅H₅BC₆H₅)]PF₆
Formation: 6.5.3.4
- C₁₇H₁₇BFe**
η⁵-C₅H₅Fe[(C₆H₅)BC₅H₄CH₃]
Formation: 6.5.3.1
- C₁₇H₂₂B₂FeNiO₃**
η⁵-C₅H₅Ni-μ-[(C₂H₅)₂C₂B₂-
(CH₃)₂CH]Fe(CO)₃
Formation: 6.5.3.3
- C₁₇H₂₂B₂Fe₂O₃**
η⁵-C₅H₅Fe-
μ-[(C₂H₅)₂C₂B₂(CH₃)₂CH]-
Fe(CO)₃
Formation: 6.5.3.3
- C₁₇H₂₂B₂Ni**
η⁵-C₅H₅Ni[(C₂H₅)₂C₂B₂-
(C₂H₅)₂CCH₃]
Reaction with [η⁵-CpNi(CO)₂]₂:
6.5.3.3
- C₁₇H₂₄BCrNaO₇**
Na[(CH₃BC₅H₅)Cr(CO)₃][C₄H₈O₂]₂
Formation: 6.5.3.4
- C₁₇H₂₄B₇Co₃**
1,2,8-(η⁵-C₅H₅)₃-1,2,8,3,6-Co₃C₂B₇H₉
Formation: 6.5.3.4
2,3,5-(η⁵-C₅H₅)₃-2,3,5,1,7-Co₃C₂B₇H₉
Formation: 6.5.3.4
- C₁₇H₂₈B₂Ni**
η⁵-C₅H₅Ni[(C₂H₅)₂C₂B₂-
(C₂H₅)₂CCH₃]
Formation: 6.5.3.3
- C₁₇H₂₉B₂Co**
η⁵-C₅H₅Co[(C₂H₅)₂C₂B₂-
(C₂H₅)₂CHCH₃]
Reaction with Ni(CO)₄: 6.5.3.1
- C₁₇H₂₉B₂Rh**
η⁵-C₅H₅Rh[(C₂H₅)₂C₂B₂-
(C₂H₅)₂CHCH₃]
Formation: 6.5.3.1
Reduction to the anion: 6.5.3.1



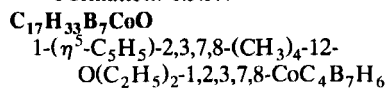
Formation: 6.5.3.3



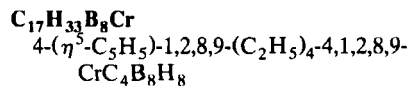
Formation: 6.5.3.1



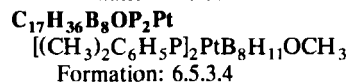
Formation: 6.5.3.4



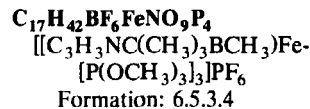
Formation: 6.5.3.4



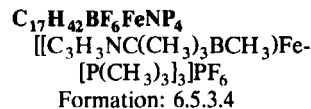
Formation: 6.5.3.4



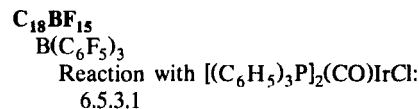
Formation: 6.5.3.4



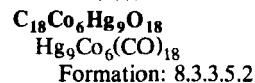
Formation: 6.5.3.4



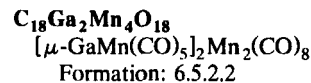
Formation: 6.5.3.4



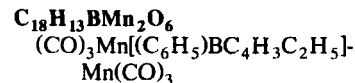
6.5.3.1



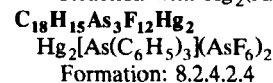
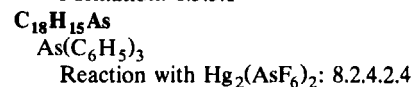
Formation: 8.3.3.5.2



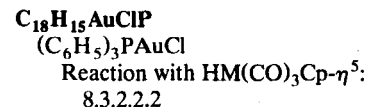
Formation: 6.5.2.2



Formation: 6.5.3.1

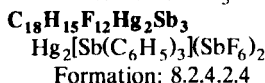


Formation: 8.2.4.2.4

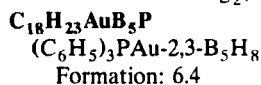
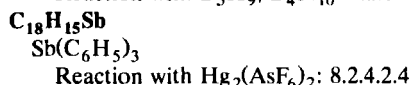
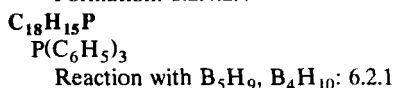


8.3.2.2.2

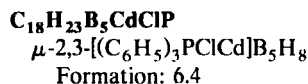
Reaction with $\text{Os}_3(\text{CO})_{12}$: 8.3.2.2.3
 Reaction with PtL_4 : 8.3.2.2.3
 Reaction with $\text{R}_3\text{P=CH}_2$: 8.2.2.3.3



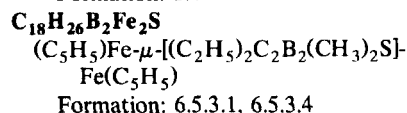
Formation: 8.2.4.2.4



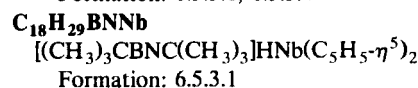
Formation: 6.4



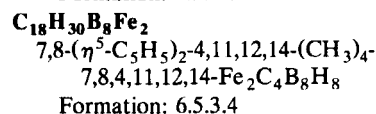
Formation: 6.4



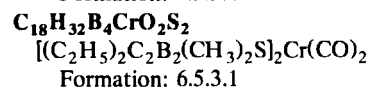
Formation: 6.5.3.1, 6.5.3.4



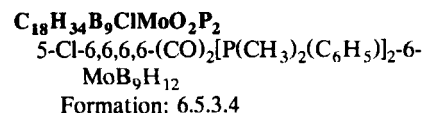
Formation: 6.5.3.1



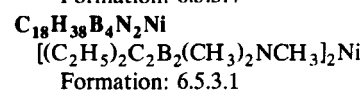
Formation: 6.5.3.4



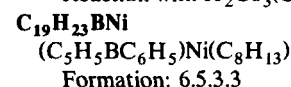
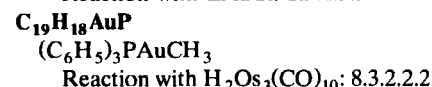
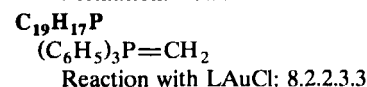
Formation: 6.5.3.1



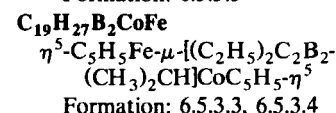
Formation: 6.5.3.4



Formation: 6.5.3.1



Formation: 6.5.3.3



Formation: 6.5.3.3, 6.5.3.4

- C₁₉H₂₇B₂CoNi**
 $\eta^5\text{-C}_5\text{H}_5\text{Ni-}\mu\text{-}[(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_2\text{-}(\text{CH}_3)_2\text{CH}]\text{CoC}_5\text{H}_5\text{-}\eta^5$
 Formation: 6.5.3.3
- C₁₉H₂₇B₂Co₂**
 $\eta^5\text{-C}_5\text{H}_5\text{Co-}\mu\text{-}[(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_2\text{-}(\text{CH}_3)_2\text{CH}]\text{CoC}_5\text{H}_5\text{-}\eta^5$
 Formation: 6.5.3.3, 6.5.3.4
- C₁₉H₂₇B₂Ni₂**
 $\eta^5\text{-C}_5\text{H}_5\text{Ni-}\mu\text{-}[(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_2\text{-}(\text{CH}_3)_2\text{CH}]\text{NiC}_5\text{H}_5\text{-}\eta^5$
 Formation: 6.5.3.3
- C₁₉H₃₈B₅FeN₃**
 4,4,4-[(tC₄H₉)NC]₃-1,7-CH₃)₂-4,1,7-FeC₂B₅H₅
 Formation: 6.5.3.1
- C₂₀H₁₈B₂NaRh**
 Na[Rh(C₄H₄BC₆H₅)₂]
 Formation: 6.5.3.1
- C₂₀H₁₉B₂Rh**
 HRh(C₄H₄BC₆H₅)₂
 Formation: 6.5.3.1
- C₂₀H₂₂AuB₄P**
 $\mu\text{-4,5-}[(\text{C}_6\text{H}_5)_3\text{PAu}]\{2,3\text{-C}_2\text{B}_4\text{H}_7\}$
 Formation: 6.4
- C₂₀H₂₂B₂Fe₂NiO₆**
 $\eta^5\text{-C}_5\text{H}_5(\text{CO})\text{Fe-}(\mu\text{-CO})_2\text{Ni-}\mu\text{-}[(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_2(\text{CH}_3)_2\text{-CH}]\text{-Fe}(\text{CO})_3$
 Formation: 6.5.3.3
- C₂₀H₂₄B₄Co₄**
 1,2,4,7-($\eta^5\text{-C}_5\text{H}_5$)₄-1,2,4,7-Co₄B₄H₄
 Formation: 6.5.3.4
- C₂₀H₂₆B₉CuP**
 {3-[(C₆H₅)₃P]-3,1,2-CuC₂B₉H₁₁}⁻
 Formation: 6.4
- C₂₀H₂₆B₉HgP**
 8-[(C₆H₅)₃PHg][1,2-C₂B₉H₁₁]
 Formation: 6.4
- C₂₀H₂₇B₉PRh**
 1-[(C₆H₅)₃P]-1-H-1,2,3-RhC₂B₉H₁₁
 Formation: 6.5.3.4
- C₂₀H₃₀BN₂Ni₂**
 $\eta^5\text{-C}_5\text{H}_5\text{Ni-}\mu\text{-}[\text{C}_4\text{H}_4\text{BN}(\text{C}_3\text{H}_8\text{-i})_2]\text{-NiC}_5\text{H}_5\text{-}\eta^5$
 Formation: 6.5.3.4
- C₂₀H₃₃B₃Fe**
 1-[($\eta^6\text{-(CH}_3)_6\text{C}_6$)]Fe-4,5,7,8-(CH₃)₄C₄B₃H₃
 Formation: 6.5.3.3
- C₂₀H₃₃B₁₀HgP**
 [(C₆H₅)₃P(CH₃)] [CH₃HgB₁₀H₁₂]
 Formation: 6.4
- C₂₀H₃₃CoP₄**
 {o-C₆H₄[P(CH₃)₂]₂CoH
 Reaction with BX₃: 6.5.2.3
- C₂₀H₃₄B₂N₂Ru**
 $[\eta^6\text{-(CH}_3)_6\text{C}_6]\text{Ru}\{\text{C}_4\text{H}_4\text{B}_2\text{-}[\text{N}(\text{CH}_3)_2]\}$
 Formation: 6.5.3.4
- C₂₀H₃₅B₅Co₂**
 1,2-[($\eta^5\text{-(CH}_3)_5\text{C}_5$)]₂-1,2-Co₂B₅H₅
 Formation: 6.5.3.4
- C₂₀H₃₆B₂CrN₂O₄**
 [n-C₄H₉BN(C(CH₃)₃)₂Cr(CO)]₄
 Formation: 6.5.3.1
- C₂₀H₃₆B₂N₂O₄**
 [(C₄H₉)₂B₂N₂(C₄H₉-t)₂Cr(CO)]₄
 Formation: 6.5.3.1
- C₂₀H₃₆B₂N₂O₄W**
 [n-C₄H₉-BN-C(CH₃)₃]₂W(CO)]₄
 Formation: 6.5.3.1
- C₂₀H₃₆B₄Co₂**
 1,2-[($\eta^5\text{-(CH}_3)_5\text{C}_5$)]₂-1,2-Co₂B₄H₆
 Formation: 6.5.3.4
- C₂₀H₃₇B₅Co₂**
 1,2-[($\eta^5\text{-(CH}_3)_5\text{C}_5$)]₂-1,2-Co₂B₅H₇
 Formation: 6.5.3.4
- C₂₀H₃₈B₉ClRh₂S**
 {[($\eta^5\text{-(CH}_3)_5\text{C}_5$)]Rh}₂(SB₉H₈Cl)
 Formation: 6.5.3.4
- C₂₀H₄₀B₂N₂Ni**
 [C₄H₄BN(C₃H₈-i)₂]₂Ni
 Formation: 6.5.3.4
- C₂₀H₄₀B₆Ni**
 [(CH₃B)(C₂H₅)₂C₂B₂(CH₃)₂CH]₂Ni
 Formation: 6.5.3.3
- C₂₀H₄₁B₈ClCo₂**
 6-Cl-5,7-[($\eta^5\text{-(CH}_3)_5\text{C}_5$)]₂-5,7-Co₂B₈H₁₁
 Formation: 6.5.3.4
- C₂₀H₄₂AuB₁₈N**
 [(C₄H₅)₄N][3,3'-Au(C₂B₉H₁₁)₂]
 Formation: 6.4
- C₂₀H₄₂B₈Co₂**
 5,7-[($\eta^5\text{-(CH}_3)_5\text{C}_5$)]₂-5,7-Co₂B₈H₁₂
 Formation: 6.5.3.4
- C₂₀H₄₂B₈Co₂**
 5,9-[($\eta^5\text{-(CH}_3)_5\text{C}_5$)]₂-5,9-Co₂B₈H₁₂
 Formation: 6.5.3.4
- C₂₀H₄₂B₈Co₂**
 6,9-[($\eta^5\text{-(CH}_3)_5\text{C}_5$)]₂-6,9-Co₂B₈H₁₂
 Formation: 6.5.3.4
- C₂₀H₅₀B₈CoFeP₂**
 CoFe[(CH₃)₄C₄B₈H₈][P(C₂H₅)₃]₂
 Formation: 6.5.3.1
- C₂₀H₅₀B₈FeP₂Pt**
 FePt[(CH₃)₄C₄B₈H₈][P(C₂H₅)₃]₂
 Formation: 6.5.3.1

- C₂₀H₅₁B₅Co₂P₃**
4,8-{Co(H)[P(C₂H₅)₃]₂-μ-H-μ-
[P(C₂H₅)₃]-4,1,7-CoC₂B₅H₄
Formation: 6.5.3.1
- C₂₀H₆₂B₁₈CuN₂**
[(C₂H₅)₄N]₂[3,3'-Cu(1,2-C₂B₉H₁₁)₂]
Formation: 6.4
Oxidation: 6.4
- C₂₁H₁₉BCoN**
[(C₅H₅)₂Co][C₄H₄B(CN)C₆H₅]
Formation: 6.5.3.1
- C₂₁H₂₂B₄PRh**
1-[P(C₆H₅)₃]-1,2,3-RhC₃B₄H₇
Formation: 6.5.3.4
- C₂₁H₂₅BF₆IrP**
[η⁵-(CH₃)₅C₅Ir(η⁶-C₅H₅BC₆H₅)]PF₆
Formation: 6.5.3.4
- C₂₁H₂₅BF₆PRh**
[η⁵-(CH₃)₅(η⁶-C₅RhC₅H₅BC₆H₅)]PF₆
Formation: 6.5.3.4
- C₂₁H₂₆BCo**
{[(CH₃)₂C]₂(CH=CH)BC₆H₅}-
CoC₅H₅
Formation: 6.5.3.1
- C₂₁H₃₈BN₂NbSi**
{(CH₃)₃Si[(CH₃)₃C]NBNC(CH₃)₃}-
HNb(C₅H₅)₂
Formation: 6.5.3.1
- C₂₁H₄₀B₂FeN₂O**
[C₄H₄BN(C₃H_{8-i})₂]₃Fe(CO)
Formation: 6.5.3.4
- C₂₁H₆₀B₁₀CoP₃**
1-CH₃-4-P(C₂H₅)₃-μ-4,6(7)-
{[Co{P(C₂H₅)₃]₂}-μ-(H)₂-4,1,2-
CoC₂B₁₀H₁₀
Formation: 6.5.3.3
- C₂₂H₁₅AuCoO₄P**
(C₆H₅)₃PAuCo(CO)₄
Formation: 8.3.2.2.3
- C₂₂H₁₅BCl₂MnO₄P**
Cl₂BMn(CO)₄P(C₆H₅)₃
Formation: 6.5.2.2
- C₂₂H₁₅MnNaO₄P**
Na[Mn(CO)₄P(C₆H₅)₃]
Reaction with BX₃: 6.5.2.2
- C₂₂H₂₀B₂Co**
Co(η⁵-C₅H₅BC₆H₅)₂
Formation: 6.5.2.3
- C₂₂H₂₂B₂Ni**
(C₅H₅BC₆H₅)Ni(C₅H₇BC₆H₅)
Formation: 6.5.3.3
- C₂₂H₂₃BFe₂**
η⁵-C₅H₅Fe[(C₆H₅)BC₄H₃(C₂H₅)-
FeC₅H₅]-η⁵
Formation: 6.5.3.1
- C₂₂H₃₂B₄CoMn₂O₆S**
(CO)₃Mn-
μ-[(C₂H₅)₂C₂B₂-(CH₃)₂S]Co-
μ-[(C₂H₅)₂C₂B₂(CH₃)₂]-
Mn(CO)₃
Formation: 6.5.3.1
- C₂₂H₃₃B₂CoFe**
η⁵-C₅H₅Fe-μ-[(C₂H₅)₂C₂B₂-
(C₂H₅)₂CCH₃]CoC₅H₅-η⁵
Formation: 6.5.3.3
- C₂₂H₃₃B₂CoNi**
η⁵-C₅H₅Co-μ-[(C₂H₅)₂C₂B₂-
(C₂H₅)₂CCH₃]NiC₅H₅-η⁵
Formation: 6.5.3.3
- η⁵-C₅H₅Ni-μ-[(C₂H₅)₂C₂B₂-
(C₂H₅)₂CCH₃]CoC₅H₅-η⁵
Formation: 6.5.3.3
Reaction with Fe₂(CO)₉: 6.5.3.3
- C₂₂H₃₃B₂Co₂**
η⁵-C₅H₅Co-μ-[(C₂H₅)₂C₂B₂-
(C₂H₅)₂CCH₃]CoC₅H₅-η⁵
Formation: 6.5.3.3
- C₂₂H₃₃B₂Ni₂**
η⁵-C₅H₅Ni-μ-[(C₂H₅)₂C₂B₂-
(C₂H₅)₂CCH₃]NiC₅H₅-η⁵
Formation: 6.5.3.3
- C₂₂H₃₈BNRu**
[(CH₃)₆C₆]Ru[C₄H₄BN(C₃H_{8-i})₂]
Formation: 6.5.3.4
- C₂₂H₃₈B₄Co₂N₂O₄**
[(C₂H₅)₂C₂B₂(CH₃)₂NCH₃]₂-
Co₂(CO)₄
Formation: 6.5.3.1
- C₂₂H₄₈B₂N₂Ni₂Si₂**
{(C₂H₅C≡C[(CH₃)=CH₂]-
Si(CH₃)₂-N(CH₃)-B-
C₂H₅)₂Ni₂
Formation: 6.5.3.1
- C₂₂H₅₇Ge₃HgIrOP₂**
Ir(CO)[P(C₂H₅)₃]₂[Ge(CH₃)₃]₂-
[HgGe(CH₃)₃]
Formation: 8.3.3.2.2
- C₂₂H₅₇HgIrOP₂Si₃**
Ir(CO)[P(C₂H₅)₃]₂[Si(CH₃)₃]₂-
[HgSi(CH₃)₃]
Formation: 8.3.3.2.2
- C₂₃H₄₃B₄CoN₂**
[(C₂H₅)₂C₂B₂(CH₃)₂NCH₃]₂-
Co(C₅H₅)
Formation: 6.5.3.1
- C₂₄H₁₅InMo₃O₉**
In[Mo(CO)₃(C₅H₅-η⁵)]₃
Formation: 6.5.2.2

- C₂₄H₁₈B₂Co₂O₄**
 (C₄H₄BC₆H₅)₂Co₂(CO)₄
 Formation: 6.5.3.1
- C₂₄H₂₀Tl₂**
 (C₆H₅)₄Tl₂
 Formation: 6.2.4
- C₂₄H₂₆B₂Ni**
 (C₆H₈BC₆H₅)₂Ni
 Formation: 6.5.3.1
- C₂₄H₃₁Au₂BFe₄O₁₂P₂**
 Fe₄(CO)₁₂[AuP(C₂H₅)₃]₂BH
 Formation: 6.4
 HFe₄(CO)₁₂[AuP(C₂H₅)₃]₂B
 Structure: 6.4
- C₂₄H₃₃B₂CoFeNiO₃**
 η⁵-C₅H₅(CO)Fe(μ-CO)₂Ni-
 μ-[(C₂H₅)₂C₂B₂(C₂H₅)₂CHCH₃]-
 CoC₅H₅-η⁵
 Formation: 6.5.3.3
- C₂₄H₃₃B₉PRh**
 1,3-μ-(3,4-CH₂=CH-CH₂CH₂)-3-H-3-
 P(C₆H₅)₃-3,1,2-RhC₂B₉H₁₀
 Formation: 6.5.3.4
- C₂₄H₃₄B₄Fe₃O₆**
 (CO)₃Fe-μ-[(C₂H₅)₂C₂B₂(CH₃)₂CH]-
 Fe-μ-[(C₂H₅)₂C₂B₂(CH₃)₂CH]-
 Fe(CO)₃
 Formation: 6.5.3.1
- C₂₄H₃₆B₂ORh₂**
 η⁵-[(CH₃)₅C₅Rh]₂(C₂H₃BOBC₂H₃)
 Formation: 6.5.3.1
- C₂₄H₃₉B₃Co₂**
 1,7-[η⁵-C₅(CH₃)₅]₂-2,3-(CH₃)₂-1,7,2,3-
 Co₂C₂B₃H₃
 Formation: 6.5.3.4
- C₂₄H₄₀B₂Co₂N₂O₄**
 [C₄H₄BN(C₃H₈-i)₂][Co(CO)-μ-(CO)₂-
 Co[C₄H₄BN-(C₃H₈-i)₂]
 Formation: 6.5.3.4
- C₂₄H₄₀B₂N₂O₄Rh₂**
 [C₄H₄BN(C₃H₈-i)₂Rh(CO)-μ-(CO)₂-
 Rh(CO)[C₄-H₄BN-
 (C₃H₈-i)₂]
 Formation: 6.5.3.4
- C₂₄H₄₀B₂N₂Rh₂**
 (C₈H₁₂)Rh-μ-
 {C₄H₄B₂[N(CH₃)₂]₂}Rh(C₈H₁₂)
 Formation: 6.5.3.4
- C₂₄H₄₆B₄Cl₂Rh₂**
 {[(C₂H₅)₂C₂B₂(C₂H₅)₂CCH₃][RhCl]₂
 Dehalogenation with K: 6.5.3.3
- C₂₄H₄₆B₄Pt**
 [(C₂H₅)₂C₂B₂(C₂H₅)₂CCH₃]₂Pt
 Formation, reaction with η⁵-
 CpFe(C₈H₁₂), η⁵-CpCo(C₂H₄)₂,
 [η⁵-CpNi(CO)₂]₂: 6.5.3.3
- C₂₄H₄₇B₄Rh**
 [(C₂H₅)₂C₂B₂(C₂H₅)₂CHCH₃]-
 [(C₂H₅)₂C₂B₂-(C₂H₅)₂CCH₃]₂Rh
 Formation: 6.5.3.1, 6.5.3.3
- C₂₄H₄₈B₄Cl₂Rh₂**
 {[(C₂H₅)₂C₂B₂(C₂H₅)₂CHCH₃]-
 Rh(μ-Cl)₂}
 Formation, Reduction with K: 6.5.3.1
 Reaction with Na[C₅H₅]: 6.5.3.1
- C₂₄H₄₈B₄Ni**
 [(C₂H₅)₂C₂B₂(C₂H₅)₂CHCH₃]₂Ni
 Formation: 6.5.3.1
- C₂₄H₄₈B₄Pt**
 [(C₂H₅)₂C₂B₂(C₂H₅)₂CHCH₃]₂Pt
 Thermolysis: 6.5.3.3
- C₂₄H₄₈B₆Co₂S₃**
 [(C₂H₅)₂C₂B₂(CH₃)₂S]₂Co-
 μ-[(C₂H₅)₂C₂B₂(CH₃)₂S]₂Co-
 [(C₂H₅)₂C₂B₂(CH₃)₂S]
 Formation: 6.5.3.1
- C₂₄H₅₄Al₂K₂**
 K₂[(i-C₄H₉)₆Al₂]
 Formation: 6.2.4
 Reaction with R₃SiX: 6.2.4
- C₂₄H₆₆B₁₀P₂Pt**
 7,7-[(C₄H₉)₃P]₂-7-PtB₁₀H₁₂
 Formation: 6.5.3.4
- C₂₄H₆₆B₁₈P₂Rh₂**
 3'-[(C₈H₁₃)-3'-H-3',1',2'-RhC₂B₉H₁₀-
 3,3-[(C₂H₅)₃-P]₂-μ-7-H-3-H-
 3,1,8-RhC₂B₉H₁₀
 Formation: 6.5.3.4
- C₂₄H₇₂Al₆B₆N₆**
 (CH₃)₁₂Al₆B₆[N(CH₃)₂]₆
 Formation: 6.2.4
- C₂₅H₂₂Au₂Cl₂P₂**
 ClAuP(C₆H₅)₂CH₂P(C₆H₅)₂AuCl
 Formation: 8.2.2.3.3
- C₂₅H₂₂P₂**
 [(C₆H₅)₂P]₂CH₂
 Reaction with Au: 8.2.2.2.1
- C₂₅H₃₀AuB₉NP**
 3-[(C₆H₅)₃P]-4-(C₅H₅N)-3,1,2-
 AuC₂B₉H₁₀
 Formation: 6.4
- C₂₅H₃₀B₉CuNP**
 3-[(C₆H₅)₃P]-4-(C₅H₅N)-3,1,2-
 CuC₂B₉H₁₀
 Formation: 6.4

- C₂₆H₁₉BF₃MoO₃P**
(C₆H₅)₃PC₅H₄MoBF₃(CO)₃
Formation: 6.5.2.1
- C₂₆H₁₉BF₃O₃PW**
(C₆H₅)₃PC₅H₄WBF₃(CO)₃
Formation: 6.5.2.1
- C₂₆H₁₉MoO₃P**
(C₆H₅)₃PC₅H₄Mo(CO)₃
Reaction with BF₃: 6.5.2.1
- C₂₆H₁₉O₃PW**
(C₆H₅)₃PC₅H₄W(CO)₃
Reaction with BF₃: 6.5.2.1
- C₂₆H₂₀AuCrO₃P**
(C₆H₅)₃PAuCr(CO)₃C₅H₅-η⁵
Formation: 8.3.2.2.2
- C₂₆H₂₀AuMoO₃P**
(C₆H₅)₃PAuMo(CO)₃C₅H₅-η⁵
Formation: 8.3.2.2.2
- C₂₆H₂₀AuO₃PW**
(C₆H₅)₃PAuW(CO)₃C₅H₅-η⁵
Formation: 8.3.2.2.2, 8.3.2.2.3
- C₂₆H₂₂B₂Fe₂O₄**
[(CHCHCH₂CHCHBC₆H₅)Fe(CO)₂]₂
Formation: 6.5.3.3
- C₂₆H₂₄AuP₂S₂TI**
AuTI[(C₆H₅)₂P(CH₂)S]₂
Formation: 6.4
- C₂₆H₂₄B₂Br₄CoP₂**
[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]-
Co(BBr₂)₂
Reaction with
[o-(CH₃)₂AsC₆H₄AsCH₃C₆H₄-
As(CH₃)₂-o]CuBBr₂: 6.4
- C₂₆H₂₆As₂Cl₃HgRh**
Rh[As(C₆H₅)₂CH₃]₂(HgCl)Cl₂
Formation: 8.3.3.3
- C₂₆H₂₇As₂Cl₂Rh**
Rh[As(C₆H₅)₂CH₃]₂(H)Cl₂
Reaction with HgX₂: 8.3.3.3
- C₂₆H₂₇BMnN₂O₄P**
[(CH₃)₂N]₂BMn(CO)₄P(C₆H₅)₃
Formation: 6.5.2.2
- C₂₆H₂₉ClCoN₄O₄P**
(C₆H₅)₃P[(CH₃)₂C₂N₂O₂H]₂CoCl
Reaction with K: 6.5.2.2
- C₂₆H₂₉CoKN₄O₄P**
K[(C₆H₅)₃P[(CH₃)₂C₂N₂O₂H]₂Co]
Reaction with R₂BCl: 6.5.2.2
- C₂₆H₃₀B₂Ni**
[4,4-(CH₃)₂C₅H₄BC₆H₅]₂Ni
Formation: 6.5.3.3
- C₂₆H₃₁B₃P₂Pd**
[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]PdB₃H₇
Formation: 6.5.3.4
- C₂₆H₃₁B₉PRh**
1-[(C₆H₅)₃P]-1-C₆H₅-1,2,3-
RhC₂B₉H₁₁
Formation: 6.5.3.4
- C₂₆H₃₆B₁₀P₂Pd**
7,7-[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]-7-
PdB₁₀H₁₂
Formation: 6.5.3.4
- C₂₆H₃₆B₁₀P₂Pt**
7,7-[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]-7-
PtB₁₀H₁₂
Formation: 6.5.3.4
- C₂₆H₄₂B₄Fe₂S₂Zn**
Zn(η⁵-C₅H₅Fe[(C₂H₅)₂C₂B₂-
(CH₃)₂S])₂
Reaction with K: 6.5.3.4
- C₂₇H₃₂B₉CuNO₂P**
3-[(C₆H₅)₃P]-4-[4-(C₅H₄N)CO₂CH₃]-
3,1,2-CuC₂B₉H₁₀
Formation: 6.4
- C₂₇H₃₉B₂₇Cu₃N₃O₆**
Cu₃(μ-H)₃(C₂B₉H₅[4-
(C₅H₄N)CO₂CH₃])₃
Formation: 6.4
- C₂₈H₁₅AuClO₁₀Os₃P**
Os₃AuCl(CO)₁₀P(C₆H₅)₃
Formation: 8.3.2.2.5
- C₂₈H₁₆AuO₁₀Os₃P**
HOs₃Au(CO)₁₀P(C₆H₅)₃
Formation: 8.3.2.1.2, 8.3.2.2.2
- C₂₈H₃₅B₉P₂Pt**
[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]-
PtC₂B₉H₁₁
Formation: 6.5.3.4
- C₂₈H₃₆B₁₀P₂Pd**
[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]-
PdC₂B₁₀H₁₂
Formation: 6.5.3.4
- C₂₈H₃₇B₃P₂Pt**
[(C₆H₅)₂(C₂H₅)P]₂PtB₃H₇
Formation: 6.5.3.4
- C₂₈H₄₄B₄Co₂Fe**
{η⁵-C₅H₅Co[(C₂H₅)₂C₂B₂(CH₃)₂-
CH]}₂Fe
Formation: 6.5.3.4
- C₂₈H₄₉B₆Co₃**
7,7'-[η⁵-C₅(CH₃)₅]₂-1,1',2,2'-(CH₃)₄-
7,7',3,1,1',2,2'-Co₃C₄B₈H₇
Formation: 6.5.3.4
- C₂₈H₇₁B₅P₄Pt₂**
1,1-[(C₂H₅)₃P]₂-6,6-[(C₂H₅)₃P]₂-4,5-
(CH₃)₂-1,6,4,5-Pt₂C₂B₅H₅
Formation: 6.5.3.1

- C₂₈H₇₆Al₂Si₈**
 $\{[(CH_3)_3Si]_2CH\}_4Al_2$
 Formation: 6.2.2.2
- C₂₈H₇₆In₂Si₈**
 $In_2[CH[Si(CH_3)_3]_2]_4$
 Formation: 6.2.2.1
- C₃₀H₁₇AuBF₄O₁₂P**
 $HFe_4(CO)_{12}[AuP(C_6H_5)_3]BH$
 Formation: 6.4
- C₃₀H₂₇B₃Rh₂**
 $(C_4H_4BC_6H_5)Rh-\mu-(C_4H_4BC_6H_5)-$
 $Rh(C_4H_4BC_6H_5)$
 Formation, reaction with phosphines,
 isonitriles: 6.5.3.1
- C₃₀H₃₁B₉Pd**
 $3,3'-[\eta^5-(C_6H_5)_4C_4]-3,1,2-PdC_2B_9H_{11}$
 Formation: 6.5.3.4
- C₃₀H₃₃AuB₂CoP**
 $\eta^5-C_5H_5Co[(CH_3)_2C_2B_2-$
 $(CH_3)_2CHAuP(C_6H_5)_3]$
 Formation: 6.5.3.1
- C₃₀H₃₃BMnO₄P**
 $(C_4H_9)_2BMn(CO)_4P(C_6H_5)_3$
 Formation: 6.5.2.2
- C₃₀H₅₄B₄FeNi**
 $(\eta^6-CH_3C_6H_5)Fe-$
 $-[(C_2H_5)_2C_2B_2(C_2H_5)_2CCH_3]Ni-$
 $[(C_2H_5)_2C_2B_2(C_2H_5)_2CH_3]$
 Formation: 6.5.3.3
- C₃₀H₅₈B₁₀Ni₃**
 $[(CH_3)B(CH_3)_2C_2B_2(CH_3)_2CH]Ni-$
 $\mu-[(CH_3)_2C_2B_2(CH_3)_2CH]Ni-$
 $\mu-[(CH_3)_2C_2B_2(CH_3)_2CH]Ni-$
 $\mu-[(CH_3)B(CH_3)_2C_2B_2(CH_3)_2CH]$
 Formation: 6.5.3.3
- C₃₀H₆₀B₃Co₂N₃**
 $[C_4H_4BN(C_3H_8-i)_2]Co-\mu-$
 $[C_4H_4BN(C_3H_8-i)_2]Co-$
 $[C_4H_4BN(C_3H_8-i)_2]$
 Formation: 6.5.3.4
- C₃₂H₅₄B₈P₄Pt₂**
 $6,6,9,9-[P(CH_3)_2C_6H_5]_4-6,9-Pt_2B_8H_{10}$
 Formation: 6.5.3.4
- C₃₂H₆₀B₁₈P₄Pt₂**
 $[P(CH_3)_2C_6H_5]_4Pt_2B_{18}H_{16}$
 Formation: 6.5.3.4
- C₃₂H₆₄B₈Co₂FeS₄**
 $[(C_2H_5)_2C_2B_2(CH_3)_2S]Co-\mu-$
 $[(C_2H_5)_2C_2B_2(CH_3)_2S]Fe-\mu-$
 $[(C_2H_5)_2C_2B_2(CH_3)_2S]Co-$
 $[(C_2H_5)_2C_2B_2(CH_3)_2S]$
 Formation: 6.5.3.4
- C₃₂H₇₂P₄Pt₂**
 $(C_8H_{12})Pt_2[P(C_2H_5)_3]_4$
 Reaction with carboranes: 6.5.3.1
- C₃₃H₄₀AlFeNO₂**
 $[(C_2H_5)_4N][(C_6H_5)_3AlFe(CO)_2-$
 $(C_5H_5)]$
 Formation: 6.5.3.2
- C₃₃H₄₀FeGaNO₂**
 $[(C_2H_5)_4N][(C_6H_5)_3GaFe(CO)_2-$
 $(C_5H_5)]$
 Formation: 6.5.3.2
- C₃₃H₄₀FeInNO₂**
 $[(C_2H_5)_4N][(C_6H_5)_3InFe(CO)_2-$
 $(C_5H_5)]$
 Formation: 6.5.3.2
- C₃₃H₃O₃₃Os₉**
 $[Os_3(CO)_{11}Hg]_3$
 Formation: 8.3.3.1.2
- C₃₃H₃O₃₃Ru₉**
 $[Ru_3(CO)_{11}Hg]_3$
 Formation: 8.3.3.1.2
- C₃₄H₂₃BMnO₄P**
 $C_{12}H_8BMn(CO)_4P(C_6H_5)_3$
 Formation: 6.5.2.2
- C₃₄H₂₅B**
 $(C_6H_5)_4C_4BC_6H_5$
 Reaction with metallocarbonyls and
 $(1,5-C_8H_{12})_2Pt$: 6.5.3.1
- C₃₄H₂₅BMnO₄P**
 $(C_6H_5)_2BMn(CO)_4P(C_6H_5)_3$
 Formation: 6.5.2.2
- C₃₄H₄₃AuB₂PRh**
 $\eta^5-C_5H_5Rh[(C_2H_5)_2C_2B_2-$
 $(C_2H_5)_2CH_3]AuP(C_6H_5)_3$
 Formation: 6.5.3.1
- C₃₅H₃₆B₃NRh₂**
 $\{[(C_4H_4BC_6H_5)Rh(CNC(CH_3)_3)]-$
 $[(C_4H_4BC_6H_5)_2Rh]\}$
 Formation: 6.5.3.1
- C₃₅H₄₃InMnNO₅**
 $[(C_3H_7)_4N][(C_6H_5)_3InMn(CO)_5]$
 Formation: 6.5.3.2
- C₃₆CdF₃₀Ge₂**
 $(C_6F_5)_3GeCdGe(C_6F_5)_3$
 Reaction with PtL₃: 8.3.3.3
- C₃₆F₃₀Ge₂Hg**
 $(C_6F_5)_3GeHgGe(C_6F_5)_3$
 Reaction with PtL₃: 8.3.3.3
- C₃₆F₃₀Ge₂Zn**
 $(C_6F_5)_3GeZnGe(C_6F_5)_3$
 Reaction with PtL₃: 8.3.3.3
- C₃₆H₂₅BNiO₂**
 $[(C_6H_5)_4C_4BC_6H_5]Ni(CO)_2$
 Formation: 6.5.3.1

- C₃₆H₃₀AuGeP**
 (C₆H₅)₃PAuGe(C₆H₅)₃
 Reaction with ClHgW(CO)₃Cp-η⁵:
 8.3.2.2.3
- C₃₆H₃₀BCl₃P₂Pt**
 [(C₆H₅)₃P]₂PtBCl₃
 Formation: 6.5.2.1
- C₃₆H₃₀B₂Cl₆P₂Pt**
 [(C₆H₅)₃P]₂Pt(BCl₃)₂
 Formation: 6.5.2.1
- C₃₆H₃₀B₂F₆P₂Pt**
 [(C₆H₅)₃P]₂Pt(BF₃)₂
 Formation: 6.5.2.1
 Reaction with BCl₃: 6.5.2.1
- C₃₆H₃₀F₄P₂PtSi**
 [(C₆H₅)₃P]₂PtSiF₄
 Reaction with BCl₃: 6.5.2.1
- C₃₆H₃₁Au₂BFe₄O₁₂P₂**
 Fe₄(CO)₁₂[AuP(C₂H₅)₃]-
 [AuP(C₆H₅)₃]BH
 Formation: 6.4
- C₃₆H₃₄B₂P₂**
 B₂H₄[P(C₆H₅)₃]₂
 Formation: 6.2.1
- C₃₆H₃₈B₅CuP₂**
 μ-2,3-[(C₆H₅)₃P]₂Cu)B₅H₈
 Formation: 6.4
- C₃₆H₃₈B₉IrP₂**
 1-[P(C₆H₅)₃]-1-H-1,2-P(C₆H₅)₂C₆H₄-
 1-IrB₉H₈
 Formation: 6.5.3.4
- C₃₆H₃₉B₄CuP₂**
 μ-2,4-[(C₆H₅)₃P]₂Cu)B₄H₉
 Formation: 6.4
- C₃₆H₃₉B₆CuP₂**
 [(C₆H₅)₃P]₂CuB₆H₉
 Formation: 6.4
- C₃₆H₃₉B₉ClIrP₂S**
 2-[(C₆H₅)₃P]₂(H)(Cl)Ir)-1-SB₉H₈
 Formation: 6.5.3.4
- C₃₆H₄₁B₉P₂PtS**
 11-H-11,11-[(C₆H₅)₃P]₂-11,6-PtSB₉H₁₀
 Formation: 6.5.3.4
- C₃₆H₄₁B₁₀P₂RhS**
 2,2-[(C₆H₅)₃P]₂-2-H-2,1-RhSB₁₀H₁₀
 Formation: 6.5.3.4
- C₃₆H₄₂B₁₀P₂Pd**
 7,7-[(C₆H₅)₃P]₂-7-PdB₁₀H₁₂
 Formation: 6.5.3.4
- C₃₆H₄₂B₁₀P₂Pt**
 7,7-[(C₆H₅)₃P]₂-7-PtB₁₀H₁₂
 Formation: 6.5.3.4
- C₃₆H₄₄B₉IrP₂**
 6-H-6,6-[P(C₆H₅)₃]₂-6-IrB₉H₁₃
 Formation: 6.5.3.4
- C₃₆H₅₆B₄Co₂Ni₂O₂**
 η⁵-C₅H₅Co-μ-[(C₂H₅)₂C₂B₂-
 (C₂H₅)₂CCH₃]-Ni₂(CO)₂-
 μ-[(C₂H₅)₂C₂B₂-
 (C₂H₅)₂CCH₃]Co(C₅H₅)
 Formation and Reaction with
 (C₂H₅)₂C₂B₂(CH₃)₂CH₂: 6.5.3.1,
 6.5.3.3
- C₃₆H₁₀₈Hg₆P₁₂Rh₄**
 Hg₆Rh₄[P(CH₃)₃]₁₂
 Formation: 8.3.3.5.1
- C₃₇H₂₅BFeO₃**
 [(C₆H₅)₄C₄BC₆H₅]Fe(CO)₃
 Formation: 6.5.3.1
- C₃₇H₃₀ClIrOP₂**
 Ir(CO)Cl[P(C₆H₅)₃]₂
 Reaction with HgCl₂: 8.3.3.2.2
- C₃₇H₃₀Cl₃HgIrOP₂**
 Ir(CO)(HgCl)(Cl)₂[P(C₆H₅)₃]₂
 Formation: 8.3.3.2.2
- C₃₇H₃₈B₃IrOP₂**
 1,1-[(C₆H₅)₃P]₂-1-H-1-(CO)-1-IrB₃H₇
 Formation: 6.5.3.4
- C₃₇H₃₈B₄OOSp₂**
 2,2-[P(C₆H₅)₃]₂-2-CO-2-OsB₄H₈
 Formation: 6.5.3.4
- C₃₇H₃₈B₅ClIrOP₂**
 2,2-[(C₆H₅)₃P]₂-2-CO-2-Cl-2-IrB₅H₈
 Formation: 6.5.3.4
- C₃₇H₃₈B₅IrOP₂**
 2,2-[(C₆H₅)₃P]₂-2-CO-2-IrB₅H₈
 Formation: 6.5.3.4
- C₃₇H₃₉B₅OOSp₂**
 4,4-[P(C₆H₅)₃]₂-4-CO-4-OsB₅H₉
 Formation: 6.5.3.4
- C₃₇H₄₂B₈P₂Pt**
 9,6-[(C₆H₅)₃P]₂PtCB₈H₁₂
 Formation: 6.5.3.3
- C₃₈H₃₀F₆HgP₂Pt**
 CF₃HgPt[P(C₆H₅)₃]₂CF₃
 Formation: 8.3.3.3
- C₃₈H₃₄P₂Pt**
 [(C₆H₅)₃P]₂Pt(C₂H₄)
 Reaction with BF₃: 6.5.2.1
- C₃₈H₃₉B₇P₂Ru**
 6,6-[(C₆H₅)₃P]₂-6,2,3-RuC₂B₇H₉
 Formation: 6.5.3.4
- C₃₈H₃₉B₈IrO₂P₂**
 7-P(C₆H₅)₃-7,8-[P(C₆H₅)₂C₆H₄]-3-
 OCH₃-10-OH-7,10-IrCB₈H₆
 Formation: 6.5.3.4

- C₃₈H₄₀B₇P₂Rh**
6,6-[(C₆H₅)₃P]₂-6-H-6,2,3-RhC₂B₇H₉
Formation: 6.5.3.4
- C₃₈H₄₁B₈IrP₂**
1,1-[(C₆H₅)₃P]₂-1-H-1,2,4-IrC₂B₈H₁₀
Formation: 6.5.3.4
- C₃₈H₄₁B₉ClP₂Rh**
1,1-[(C₆H₅)₃P]₂-1-Cl-1,2,3-RhC₂B₉H₁₁
Formation: 6.5.3.4
- C₃₈H₄₂B₉P₂Rh**
2,2-[P(C₆H₅)₃]₂-2-H-2,1,12-
RhC₂B₉H₁₁
Formation: 6.5.3.4
3,3-[(C₆H₅)₃P]₂-3-H-3,1,2-RhC₂B₉H₁₁
Formation: 6.5.3.4
- C₃₈H₄₃B₉MoO₂P₂**
6,6,6,6-(CO)₂[P(C₆H₅)₃]₂-6-MoB₉H₁₃
Formation: 6.5.3.4
- C₃₈H₄₃B₉P₂Ru**
2,2-[(C₆H₅)₃P]₂-2,2-(H)₂-2,1,7-
RuC₂B₉H₁₁
Formation: 6.5.3.4
3,3-[(C₆H₅)₃P]₂-3,3-(H)₂-3,1,2-
RuC₂B₉H₁₁
Formation: 6.5.3.4
- C₃₈H₄₃B₁₀P₂Rh**
1,1[(C₆H₅)₃P]₂-1-H-1,2,4-RhC₂B₁₀H₁₂
Formation: 6.5.3.4
- C₃₉H₃₁B₄Ir₂O₃P₂**
1,1,2-(CO)₃-1-[P(C₆H₅)₃]-2,2,3,5-
[(C₆H₅)₂PC₆H₅]-1,2-Ir₂B₄H₂
Formation: 6.5.3.4
- C₃₉H₄₁B₈IrO₂P₂**
1,2-CH₃CO₂-2-H-2,10-[P(C₆H₅)₃]₂-
2,1-IrCB₈H₇
Formation: 6.5.3.4
- C₃₉H₅₄B₃O₉P₃Rh₂**
[(C₄H₄BC₆H₅)Rh[P(OCH₃)₃]₃]-
[(C₄H₄BC₆H₅)₂Rh]
Formation: 6.5.3.1
- C₃₉H₅₄B₃P₃Rh₂**
[(C₄H₄BC₆H₅)Rh[P(CH₃)₃]₃]-
[(C₄H₄BC₆H₅)₂Rh]
Formation: 6.5.3.1
- C₄₀H₄₂B₂BrP₂Pt**
[(C₆H₅)₃P]₂Pt[B(CH₃)₂]₂Br
Formation: 6.5.2.3
- C₄₀H₅₄B₁₈P₂Rh₂**
{3-[(C₆H₅)₃P]-3-H-3,1,2-RhC₂B₉H₁₁]₂
Formation: 6.5.3.4
- C₄₀H₉₀Al₅K₃**
K₃[(i-C₄H₉)₁₀Al₅]
Formation: 6.2.4
- C₄₁H₄₁B₉MoNO₃P₂TI**
{[(C₆H₅)₃P]₂N}[3,3,3-(CO)₃-3-TI-3,1,2-
MoC₂B₉H₁₁]
Formation: 6.5.3.4
- C₄₁H₄₁B₉NO₃P₂TIW**
{[(C₆H₅)₃P]₂N}[3,3,3-(CO)₃-3-TI-3,1,2-
WC₂B₉H₁₁]
Formation: 6.5.3.4
- C₄₂H₃₇BPt**
[(C₆H₅)₄C₄BC₆H₅]PtC₈H₁₂
Formation: 6.5.3.1
- C₄₂H₄₈Al₃P₂Pt**
[(C₆H₅)₃P]₂Pt[Al(CH₃)₃]₂
Formation: 6.5.3.1
- C₄₂H₄₉B₃P₂Pt**
[(p-CH₃C₆H₄)₃P]₂PtB₃H₇
Formation: 6.5.3.4
- C₄₂H₅₀B₁₈Ni₂O₂P₂**
{3-μ-(CO)-8-[P(C₆H₅)₃]-3,1,2-
NiC₂B₉H₁₀]₂
Formation: 6.5.3.4
- C₄₂H₅₆GaNO₃W**
[(C₄H₉)₄N][(C₆H₅)₃GaW(CO)₃-
(C₅H₅)]
Formation: 6.5.3.2
- C₄₂H₅₆InNO₃W**
[(C₄H₉)₄N][(C₆H₅)₃InW(CO)₃(C₅H₅)]
Formation: 6.5.3.2
- C₄₂H₅₈B₉IrP₄Pt**
7,7-[P(CH₃)₃]₂-9-P(C₆H₅)₃-9,4-
P(C₆H₅)₂C₆H₄-9-H-7,9-PtIrB₉H₁₀
Formation: 6.5.3.4
- C₄₃H₇₃B₆Co₂Ni₂**
η⁵-C₅H₅Co-μ-[(C₂H₅)₂C₂B₂-
(C₂H₅)₂CCH₃]Ni-
μ-[(C₂H₅)₂C₂B₂-(CH₃)₂CH]Ni-
μ-[(C₂H₅)₂C₂B₂(C₂H₅)₂-CCH₃]-
Co-C₅H₅-η⁵
Formation: 6.5.3.1
- C₄₄H₃₀BClMn₂O₈P₂**
ClB[Mn(CO)₄(C₆H₅)₃]₂
Formation: 6.5.2.2
- C₄₄H₄₄B₂Fe₂**
[(C₁₀H₁₀)₂Fe]₂C₄H₄B₂
Reaction with metal carbonyls and
metal carbonyl derivatives: 6.5.3.1
- C₄₄H₄₅B₉NOP₂Rh**
3,3-[(C₆H₅)₃P]₂-3-(CO)-4-C₅H₅N-
3,1,2-RhC₂B₉H₁₀
Formation: 6.5.3.4
- C₄₄H₄₈B₂CoP₄**
{o-C₆H₄[P(CH₃)₂]₂]₂Co(BC₁₂H₈)₂
Formation: 6.5.2.3

C₄₄H₅₂B₂CoP₄
 {o-C₆H₄[P(CH₃)₂]₂]₂Co[B(C₆H₅)₂]₂
 Formation: 6.5.2.3

C₄₅H₄₈B₉P₂Rh
 2,2-[(C₆H₅)₃P]₂-2-H-1-CH₃-7-C₆H₅-
 2,1,7-Rh-C₂B₉H₉
 Formation: 6.5.3.4
 4,9-[(C₆H₅)₃P]₂Rh[4,9-μ-(H)₂-7-CH₃-
 8-C₆H₅-7,8-C₂B₉H₈
 Formation: 6.5.3.4

C₄₅H₄₉B₅ClOOS₃Pt
 2,2,2-(CO)[P(C₆H₅)₃]₂-7,7-
 (Cl)P(CH₃)₂-C₆H₅-μ-2,7-H-2,7-
 OsPtB₅H₇
 Formation: 6.5.3.4

C₄₆H₆₇B₉P₂Rh
 6,10-[(C₆H₅)₃P][(C₆H₁₁)₃P]Rh[6,10-
 μ-(H)₂-7,8-[1',2'-CH₂C₆H₄CH₂]-
 10,11-μ-(H)₂-7,8-C₂B₉H₇
 Formation: 6.5.3.4

C₄₆H₇₈B₈Co₂Ni₃
 η⁵-C₅H₅Co-μ-[(C₂H₅)₂C₂B₂-
 (CH₃)₂CH]Ni]₃-μ-[(C₂H₅)₂C₂B₂-
 (CH₃)₂CH]CoC₅H₅-η⁵
 Formation: 6.5.3.3

C₄₆H₇₉B₆Co₂Ni₂
 η⁵-C₅H₅Co-μ-[(C₂H₅)₂C₂B₂-
 (C₂H₅)₂CCH₃]Ni-μ-
 [(C₂H₅)₂C₂B₂-
 (C₂H₅)₂CCH₃]Ni-
 μ-[(C₂H₅)₂C₂B₂-(C₂H₅)₂CCH₃]-
 CoC₅H₅-η⁵
 Formation: 6.5.3.3

C₄₈H₃₁Au₂BFe₄O₁₂P₂
 Fe₄(CO)₁₂[AuP(C₆H₅)₃]₂BH
 Formation: 6.4

C₄₈H₃₂BFe₄NO₁₂P₂
 [HFe₄(CO)₁₂BH][[(C₆H₅)₃P]₂N]
 Reaction with (C₆H₅)₃PAuCl: 6.4

C₄₈H₄₀BNiP₂
 [(C₆H₅)₃P]₂NiB(C₆H₅)₂
 Formation: 6.5.2.3

C₄₈H₆₈B₁₈NO₂P₂Sm₃
 {[(C₆H₅)₃P]₂N}[3,3-(C₄H₈O)₂-3,3'-
 Sm(3,1,2-SmC₂B₉H₁₁)₂]
 Formation: 6.5.3.4

C₄₉H₄₂AuNP₃S
 [(C₆H₅)₃P]₂N[Au(C₆H₅)₂P(CH₂)S]
 Reaction with Ti⁺: 6.4

C₄₉H₄₈B₉NO₂W
 {[(C₆H₅)₃P]₂N}[4-CH₃C₆H₄≡
 3W(CO)₂-7,8-C₂B₉H₁₁]
 Formation: 6.5.3.4

C₄₉H₅₂B₉NO₂W
 {[(C₆H₅)₃P]₂N}[4-CH₃C₆H₄≡
 W(CO)₂-7,8-C₂B₉H₉-(CH₃)₂]
 Formation: 6.5.3.4

C₅₀H₄₇B₂CoKN₄O₄P
 K[(C₆H₅)₃P][(CH₃)₂C₂N₂O₂-
 B(C₆H₅)₂]₂Co]
 Reaction with BX₃: 6.5.2.2

C₅₀H₄₇B₂CoN₄O₄P
 (C₆H₅)₃P[(CH₃)₂C₂N₂O₂-
 B(C₆H₅)₂]₂Co
 Reaction with K: 6.5.2.2

C₅₀H₈₅B₆Fe₂Ni₂
 (η⁶-CH₃C₆H₅)Fe{μ-[(C₂H₅)₂C₂B₂-
 (C₂H₅)₂CCH₃]Ni]₂-
 μ-[(C₂H₅)₂C₂B₂(C₂H₅)₂CCH₃]-
 Fe(CH₃C₆H₅-η⁶)
 Formation: 6.5.3.3

C₅₂H₄₀Cu₃IrP₂
 IrCu₃(C₂C₆H₅)₂[P(C₆H₅)₃]₂
 Formation: 8.3.2.2.5

C₅₂H₄₈B₂Br₄CoP₄
 [(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]₂-
 Co(BBr₂)₂
 Formation: 6.5.2.3

C₅₂H₄₈B₂CoI₄P₄
 [(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]₂Co(BI₂)₂
 Formation: 6.5.2.3

C₅₂H₄₉CoP₄
 [(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]₂CoH
 Reaction with BX₃: 6.5.2.3

C₅₂H₆₂B₁₈P₂Rh₂
 {3-[(C₆H₅)₃P]-3-H-2-C₆H₅-3,1,2-
 RhC₂B₉H₁₀]₂
 Formation: 6.5.3.4

C₅₄H₄₅AuCIP₃Pt
 (C₆H₅)₃PAuPt[P(C₆H₅)₃]₂Cl
 Formation: 8.3.2.2.3

C₅₄H₄₅B₃Cl₆P₃Pt
 [(C₆H₅)₃P]₃Pt(BCl₃)₂
 Formation: 6.5.2.1

C₅₄H₄₅P₃Pt
 Pt[P(C₆H₅)₃]₃
 Reaction with HgX₂: 8.3.3.3
 Reaction with Zn(ML₃)₂, Cd(ML₃)₂,
 Hg(ML₃)₂: 8.3.3.3
 [(C₆H₅)₃P]₃Pt
 Reaction with BCl₃: 6.5.2.1

C₅₄H₅₄B₄NiP₄
 1-[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]₂-1,2,3-
 NiC₂B₄H₆
 Formation: 6.5.3.4

- C₅₄H₇₃B₃CoN₄O₄P**
 (C₆H₅)₃P[(CH₃)₂C₂-
 N₂O₂B(C₄H₉)₂]₂CoB(C₆H₅)₂
 Formation: 6.5.2.2
- C₅₅H₃₀BClF₁₅IrOP₂**
 [(C₆H₅)₃P]₂(CO)ClIrB(C₆F₅)₃
 Formation: 6.5.3.1
- C₅₅H₅₄B₈IrP₃**
 1-[P(C₆H₅)₃]-2-H-2,2-[P(C₆H₅)₃]₂-
 2,10-IrCB₈H₈
 Formation: 6.5.3.4
- C₅₆H₅₅B₈OOSp₃**
 9,9,9-(CO)[P(C₆H₅)₃]₂-9,6-OSCB₈H₁₀-
 5-[P(C₆H₅)₃]
 Formation: 6.5.3.4
- C₅₆H₅₅B₈OP₃Ru**
 9,9,9-(CO)[P(C₆H₅)₃]₂-9,6-RuCB₈H₁₀-
 5-[P(C₆H₅)₃]
 Formation: 6.5.3.4
- C₅₈H₄₅AlCoNO₄P₂**
 {[(C₆H₅)₃P]₂N}[(C₆H₅)₃AlCo(CO)₄]
 Formation: 6.5.3.2
- C₅₈H₄₅CoGaNO₄P₂**
 {[(C₆H₅)₃P]₂N}[(C₆H₅)₃GaCo(CO)₄]
 Formation: 6.5.3.2
- C₅₈H₄₅CoInNO₄P₂**
 {[(C₆H₅)₃P]₂N}[(C₆H₅)₃InCo(CO)₄]
 Formation: 6.5.3.2
- C₅₈H₆₇B₁₉P₃Rh**
 {[(C₆H₅)₃P]₃[Rh]}⁺[7-{1'-(1',2'-
 C₂B₁₀H₁₁)]-7,8-C₂B₉H₁₁]⁻
 Formation: 6.5.3.4
- C₅₉H₄₅Au₃O₅P₃V**
 Au₃[P(C₆H₅)₃]₃[V(CO)₅]
 Formation: 8.2.1
- C₆₂H₅₇AsB₃CoN₄O₄**
 (C₆H₅)₃As[(CH₃)₂C₂-
 N₂O₂B(C₆H₅)₂]₂CoB(C₆H₅)₂
 Formation: 6.5.2.2
- C₆₄H₅₈B₂Cl₂CoP₄**
 [(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]₂-
 Co[B(C₆H₅)Cl]₂
 Formation: 6.5.2.3
- C₇₂H₃₀CdF₃₀Ge₂P₂Pt**
 (C₆F₅)₃GeCdPt[P(C₆H₅)₃]₂-
 Ge(C₆F₅)₃
 Formation: 8.3.3.3
- C₇₂H₃₀F₃₀Ge₂P₂PtZn**
 (C₆F₅)₃GeZnPt[P(C₆H₅)₃]₂-
 Ge(C₆F₅)₃
 Formation: 8.3.3.3
- C₇₂H₆₀Au₄I₂P₄**
 [Au₄(P(C₆H₅)₃)₄]₂
 Formation: 8.2.1.3
- C₇₂H₆₀P₄Pt**
 Pt[P(C₆H₅)₃]₄
 Reaction with R₃PAuCl: 8.3.2.2.3
- C₇₅H₆₆Au₄I₂P₆**
 [Au₄(C₆H₅)₂PCH₂P(C₆H₅)₂]₃I₂
 Formation: 8.2.1.3
- C₇₆H₅₂B₂CoP₄**
 [(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]₂-
 Co[BC₁₂H₈]₂
 Formation: 6.5.2.3
- C₇₆H₆₈B₂CoP₄**
 [(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]₂-
 Co[B(C₆H₅)₂]₂
 Formation: 6.5.2.3
- C₇₆H₆₈B₃Cl₆P₄Rh**
 {[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]₂-
 Rh(BCl₃)₂}[B(C₆H₅)₄]
 Formation: 6.5.2.1
- C₈₀H₆₀Au₆Co₂O₈P₄**
 [Au₆(C₆H₅)₃P]₄[Co(CO)₄]₂
 Formation: 8.2.1.3
- C₈₀H₁₁₀Au₁₁F₁₈P₁₃**
 [Au₁₁[(CH₃)₂C₆H₅P]₁₀][PF₆]₃
 Formation: 8.2.1
 Reaction with Cl⁻: 8.2.1.3
- C₈₀H₁₁₀Au₁₃Cl₂F₁₈P₁₃**
 [Au₁₃[(CH₃)₂C₆H₅P]₁₀Cl₂][PF₆]₃
 Formation: 8.2.1.3
- C₉₀H₇₅Au₃F₆IrNO₃P₆**
 [Au₃(Et₃P)₃Ir(Et₃P)₂NO₃][PF₆]
 Formation: 8.2.2.1, 8.2.4.1
- C₉₃H₁₆₅Au₉N₃P₅S₃**
 [Au₉(C₆H₁₁)₃P]₅[SCN]₃
 Formation: 8.2.1
- C₁₀₀H₇₀Cu₄Ir₂P₂**
 Ir₂Cu₄(C₂C₆H₅)₈[P(C₆H₅)₃]₂
 Formation: 8.3.2.2.5
- C₁₀₀H₈₇Au₅N₂O₆P₈**
 [Au₅(C₆H₅)₂PCH₂P(C₆H₅)₂]₃-
 [(C₆H₅)₂PCHP(C₆H₅)₂][NO₃]₂
 Formation: 8.2.1, 8.2.1.2
- C₁₀₈H₉₀Au₈F₆IP₇**
 [Au₈(C₆H₅)₃P]₆I][PF₆]
 Formation: 8.2.1.3
- C₁₀₈H₁₀₄Au₆N₂O₆P₈**
 [Au₆(C₆H₅)₂P(CH₂)₃P(C₆H₅)₂]₄-
 [NO₃]₂
 Formation: 8.2.1.3
- C₁₁₆H₁₀₄Au₉F₁₈N₂P₉**
 [Au₉(C₆H₅)₃P]₆[CNCH(CH₃)₂]₂-
 [PF₆]₃
 Formation: 8.2.1.3

- C₁₂₆H₈₄Au₁₁Cl₂₁I₃P₇**
[Au₁₁[(p-Cl-C₆H₄)₃P]₇]₃
Formation: 8.2.1
- C₁₂₆H₈₄Au₁₁F₂₁I₃P₇**
[Au₁₁[(p-F-C₆H₄)₃P]₇]₃
Formation: 8.2.1
- C₁₂₆H₁₀₅Au₇P₇**
[Au₇[(C₆H₅)₃P]₇]⁺
Formation: 8.2.1.2
- C₁₂₆H₁₀₅Au₈N₂O₆P₇**
[Au₈[(C₆H₅)₃P]₇][NO₃]₂
Formation, reaction with LiCo(CO)₄,
PPh₃, [AuPPh₃]⁺: 8.2.1.3
- C₁₂₉H₁₀₅Au₁₁N₃P₇**
[Au₁₁[(C₆H₅)₃P]₇][CN]₃
Formation: 8.2.1
- C₁₂₉H₁₀₅Au₁₁N₃P₇S₃**
[Au₁₁[(C₆H₅)₃P]₇][SCN]₃
Formation: 8.2.1, 8.2.1.2
Reaction with bis(1,3-diphenylphosphino)propane:
8.2.1.3, 8.2.2.3
- C₁₃₈H₁₃₀Au₁₁N₃P₁₀S₃**
[Au₁₁[(C₆H₅)₂P(CH₂)₃P(C₆H₅)₂]₅]-
[SCN]₃
Formation: 8.2.1.3
- C₁₄₄H₁₂₀Au₈N₂O₆P₈**
[Au₈[(C₆H₅)₃P]₈][NO₃]₂
Formation, reaction with
[RhCl(C₈H₄)₂]₂: 8.2.1.3
- C₁₄₄H₁₂₀Au₉B₃F₁₂P₈**
[Au₉[(C₆H₅)₃P]₈][BF₄]₃
Formation: 8.2.1
- C₁₄₄H₁₂₀Au₉Cl₃O₁₂P₈**
[Au₉[(C₆H₅)₃P]₈][ClO₄]₃
Formation: 8.2.1
- C₁₄₄H₁₂₀Au₉F₁₈P₁₁**
[Au₉[(C₆H₅)₃P]₈][PF₆]₃
Formation: 8.2.1, 8.2.1.2
- C₁₄₄H₁₂₀Au₉N₃O₉P₈**
[Au₉[(C₆H₅)₃P]₈][NO₃]₃
Formation: 8.2.1, 8.2.1.2, 8.2.1.3
Reaction with Ph₃P,
Cl⁻[SCN]⁻, I⁻,
bis(diphenylphosphino)methane,
bis(η³-diphenylphosphino)propane,
CN-i-Pr: 8.2.1.3
Formation: 8.2.1, 8.2.2.2
- C₁₄₄H₁₂₀Au₁₁Cl₂F₆P₉**
[Au₁₁[(C₆H₅)₃P]₈Cl₂][PF₆]
Formation: 8.2.1.3
- C₁₄₄H₁₂₀Au₁₁Cl₂F₁₈P₁₁**
[Au₁₁[(C₆H₅)₃P]₈Cl₂][PF₆]₃
Formation: 8.2.1.3
- C₁₄₆H₁₂₀Au₁₁F₆N₂P₉S₂**
[Au₁₁[(C₆H₅)₃P]₈][SCN]₂[PF₆]
Formation: 8.2.1.3
- C₁₅₀H₁₃₂Au₁₃N₆O_{3n}P₁₂**
[Au₁₃[(C₆H₅)₂PCH₂P(C₆H₅)₂]₆]-
[NO₃]_n
Formation: 8.2.1
- C₁₆₂H₁₂₆Au₉N₉O₂₁P₈**
[Au₉[(C₆H₅)₃P]₈][C₆H₂O(NO₂)₃]₃
Formation: 8.2.1
- C₁₆₂H₁₆₆Au₆B₂P₆**
Au₆[(p-MeC₆H₅)₃P]₆[B(C₆H₅)₄]₂
Formation: 8.2.1
[Au₆[(p-Me-C₆H₄)₃P]₆][B(C₆H₅)₄]₂
Formation: 8.2.1
- C₁₆₈H₁₆₈Au₉B₃F₁₂O₂₄P₈**
[Au₉[(p-MeOC₆H₄)₃P]₈][BF₄]₃
Formation: 8.2.1
- C₁₆₈H₁₆₈Au₉F₁₈P₁₁**
Au₉[(p-Me-C₆H₄)₃P]₈[PF₆]₃
Formation: 8.2.1
[Au₉[(p-MeC₆H₄)₃P]₈][PF₆]₃
Formation: 8.2.1
- C₁₆₈H₁₆₈Au₉N₃O₉P₈**
Au₉[(p-Me-C₆H₄)₃P]₈[NO₃]₃
Formation: 8.2.1
[Au₉[(p-MeC₆H₄)₃P]₈][NO₃]₃
Formation: 8.2.1
- C₂₁₆H₁₈₀Au₅₅Cl₆P₁₂**
[Au₅₅[(C₆H₅)₃P]₁₂]₆
Formation: 8.2.1
- Ca_xHo_{1-x}*B₆
Ca
Reaction with Na₂O: 7.2.2.2.3
- Ca*Ag
Ca*Ag₂
Ca*Au
Ca*Au₂
Ca*Au₃
Ca*Au₄
Ca*Au₅
Ca*B₆
Ca*Be₁₃
Ca*C₂B₂
CaCd
CaCd
Formation: 7.3.4.1.3
CaCd₂
CaCd₂
Formation: 7.3.4.1.3
CaCd₆
CaCd₆
Formation: 7.3.4.1.3

CaCu

CaCu

Formation: 7.3.3.1.3

CaCu₅CaCu₅

Formation: 7.3.3.1.3

CaHg

CaHg

Formation: 7.3.4.1.3

CaHg₂CaHg₂

Formation: 7.3.4.1.3

CaHg₃CaHg₃

Formation: 7.3.4.1.3

CaHg₁₁CaHg₁₁

Formation: 7.3.4.1.3

CaIr₂*B₂**CaLi₂**Li₂Ca

In phase diagram: 7.2.6.1.1

Preparation: 7.2.6.1.3

X-ray identification: 7.2.6.1.2

CaMg

CaMg

Matrix isolation: 7.2.5.1.1

CaMg₂Mg₂Ca

In phase diagram: 7.2.5.1.1

Preparation: 7.2.5.1.3

X-ray identification: 7.2.5.1.1

CaNi₂CaNi₂

Formation: 7.4.2.1

CaNi₃CaNi₃

Formation: 7.4.2.1

CaNi₅CaNi₅

Formation: 7.4.2.1

CaRh₂*B₂**CaSr**

CaSr

Matrix isolation: 7.2.5.1.1

CaZn

CaZn

Formation: 7.3.4.1.3

CaZn₃CaZn₃

Formation: 7.3.4.1.3

CaZn₁₁CaZn₁₁

Formation: 7.3.4.1.3

CaZn₁₃CaZn₁₃

Formation: 7.3.4.1.3

(Ca,Sc)Rh₄*B₄Ca₂*Ag₇Ca₂*Ag₉Ca₂*AuCa₂*Au₇Ca₂*Au₉**Ca₂Cd₇**Ca₂Cd₇

Formation: 7.3.4.1.3

Ca₂CuCa₂Cu

Formation: 7.3.3.1.3

Ca₂HgCa₂Hg

Formation: 7.3.4.1.3

Ca₂Mg₁₇Mg₁₇Ca₂

In phase diagram: 7.2.5.1.1

Preparation: 7.2.5.1.3

X-ray identification: 7.2.5.1.1

Ca₂Ni₇Ca₂Ni₇

Formation: 7.4.2.1

Ca₂Ni₂₁*B**Ca₂Os₃*B₅****Ca₂Pt₉*B₆****Ca₂Rh₅*B₄****Ca₃*Ag****Ca₃*Ag₈****Ca₃Cd₂**Ca₃Cd₂

Formation: 7.3.4.1.3

Ca₃Cd₁₇Ca₃Cd₁₇

Formation: 7.3.4.1.3

Ca₃HgCa₃Hg

Formation: 7.3.4.1.3

Ca₃Hg₂Ca₃Hg₂

Formation: 7.3.4.1.3

Ca₃Rh₈*B₆**Ca₃Zn**Ca₃Zn

Formation: 7.3.4.1.3

Ca₄*Au₃**Ca₅*Ag₃****Ca₅*Au₂****Ca₅*Au₃****Ca₅*Au₄**

- Ca₅Hg₃**
 Ca₅Hg₃
 Formation: 7.3.4.1.3
Ca₅Zn₃
 Ca₅Zn₃
 Formation: 7.3.4.1.3
Ca₆Mg₂₃
 Mg₂₃Ca₆
 In phase diagram: 7.2.5.1.1
 Preparation: 7.2.5.1.3
 X-ray identification: 7.2.5.1.1
 Ca₇*Au₃
 Ca₇Rh₂₀*B₁₄
Ca₇Zn₄
 Ca₇Zn₄
 Formation: 7.3.4.1.3
Ca₇Zn₂₀
 Ca₇Zn₂₀
 Formation: 7.3.4.1.3
Cd
 Cd
 Reaction with AsF₅: 8.2.3.2
 Reaction with Co₂(CO)₈, Mn₂(CO)₁₀:
 8.3.3.4
 Cd*Ba
 Cd*C₂H₆
 Cd*C₄H₁₀
 Cd*Ca
CdCl
 CdCl
 Formation: 8.2.3.2
 CdClP*C₁₈H₂₃B₅
 CdCl₈*Al₂
 CdCo₂O₈*C₈
 CdF₃₀Ge₂*C₃₆
 CdF₃₀Ge₂P₂Pt*C₇₂H₃₀
 CdFeN₂O₄*C₄H₆
 CdFeO₄*C₄
 CdH₁₂*B₁₀
CdLi
 LiCd
 Formation: 7.3.2.2
CdLi₃
 Li₃Cd
 Formation: 7.3.2.2
CdMg
 MgCd
 Formation: 7.3.4.1.2
CdMg₃
 Mg₃Cd
 Formation: 7.3.4.1.2
CdMn₂O₁₀*C₁₀
CdSr
 SrCd
 Formation: 7.3.4.1.4
CdSr₂
 Sr₂Cd
 Formation: 7.3.4.1.4
 Cd₂*Ba
 Cd₂*Ca
 Cd₂*Ca₃
 Cd₂Cl₈*Al₂
Cd₂Na
 NaCd₂
 Formation: 7.3.2.1.2, 7.3.2.2
Cd₂Sr
 SrCd₂
 Formation: 7.3.4.1.4
 Cd₃F₁₂*As₂
Cd₃Li
 LiCd₃
 Formation: 7.3.2.2
Cd₃Mg
 MgCd₃
 Formation: 7.3.4.1.2
Cd₃Sr₅
 Sr₅Cd₃
 Formation: 7.3.4.1.4
 Cd₄F₁₂*As₂
 Cd₅*Ba
Cd₅Na
 NaCd₅
 Formation: 7.3.2.1.2
 Cd₆*Ca
Cd₆Sr
 SrCd₆
 Formation: 7.3.4.1.4
 Cd₇*Ca₂
Cd₇K
 KCd₇
 Formation: 7.3.2.1.3
 Cd₉*Ba₂
Cd₉Sr₂
 Sr₂Cd₉
 Formation: 7.3.4.1.4
 Cd₁₁*Ba
Cd₁₁Na₂
 Na₂Cd₁₁
 Formation: 7.3.2.1.2, 7.3.2.2
Cd₁₁Sr
 SrCd₁₁
 Formation: 7.3.4.1.4
Cd₁₃Cs
 CsCd₁₃
 Formation: 7.3.2.2

Cd₁₃KKCd₁₃

Formation: 7.3.2.1.3, 7.3.2.2

Cd₁₃RbRbCd₁₃

Formation: 7.3.2.2

Cd₁₇*Ca₃Ce*B₄Ce*B₆CeCo₃*B₂CeCo₄*BCeCo₄*B₄CeCo₅*B₂CeCr*B₄CeCr₂*B₆CeFe*B₄CeFe₄*B₄CeIr₃*B₂CeIr₄*B₄CeMn*B₄CeNi*B₄CeOs₂*B₂CeOs₄*B₄CeRh₃*B_xCeRh₃*B₂CeRu₂*B₂CeRu₃*B₂CeRu₄*B₄Ce₂Co₇*B₃Ce₂Fe₁₄*BCe₂Ni₂₁*B₆Ce₃Co₁₁*B₄Ce₃N₄*B₂

Cl*Al

Cl*Cd

ClCoN₄O₄*P*C₂₆H₂₉ClCo₂*C₂₀H₄₁B₈ClCo₂GaO₉*C₁₂H₈ClCrHgO₃*C₈H₅**ClCu**

CuCl

Reaction with H₂Fe(CO)₄: 8.3.2.2.2ClF₁₅IrOP₂*C₅₅H₃₀BClFe₂InO₄*C₁₄H₁₀ClGa*C₂H₆ClHgMoO₃*C₈H₅ClHgO₃W*C₈H₅**ClIn**

InCl

Formation: 6.2.2.1

Reaction with [η⁵-Cp(CO)₂Fe]₂:

6.5.2.1

ClIr*C₈H₂₅B₉ClIrOP₂*C₁₃H₃₀ClIrOP₂*C₃₇H₃₀ClIrOP₂*C₃₇H₃₈B₅ClIrP₂S*C₃₆H₃₉B₉**ClK**

KCl

Source of K metal: 7.2.2.3.1

ClMn₂O₈P₂*C₄₄H₃₀BClMn₂O₁₀Tl*C₁₀ClMoO₂P₂*C₁₈H₃₄B₉ClN₂*C₄H₁₂BClN₂Si₃V*C₁₄H₃₀B₂ClOOSp₃Pt*C₄₅H₄₉B₅ClO₂*C₂H₆BClO₃Ru*C₇H₆BClO₁₀Os₃P*C₂₈H₁₅AuClP*C₁₈H₁₅AuClP*C₁₈H₂₃B₅CdClP₂Rh*C₃₈H₄₁B₉ClP₃Pt*C₅₄H₄₅AuClRh*C₈H₂₅B₉ClRh₂S*C₂₀H₃₈B₉ClSi*C₃H₉Cl₂*C₂H₁₁AsB₁₀**Cl₂Co**CoCl₂Reaction with BX₃: 6.7.4.1.1Cl₂CoGaO₅*C₈H₈Cl₂CoHgO₂*C₇H₅Cl₂CoP₄*C₆₄H₅₈B₂Cl₂F₆P₉*C₁₄₄H₁₂₀Au₁₁Cl₂F₁₂Ir₂P₄[Ir(PF₃)₂Cl]₂

Reaction with K-Hg: 8.3.3.4

Cl₂F₁₂P₄Rh₂[Rh(PF₃)₂Cl]₂

Reaction with K-Hg: 8.3.3.4

Cl₂F₁₈P₁₁*C₁₄₄H₁₂₀Au₁₁Cl₂F₁₈P₁₃*C₈₀H₁₁₀Au₁₃Cl₂FeHgO₅*CCl₂FeHgO₅*C₅Cl₂FeHg₂O₄*C₄**Cl₂Ga**GaCl₂Reaction with Co₂(CO)₈: 6.5.2.1

Reaction with electron pair bases:

6.2.2.1

see Ga[GaCl₄]: 6.2.2.1

Structure: 6.2.2.1

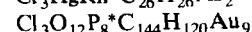
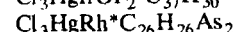
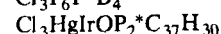
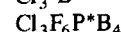
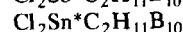
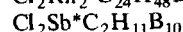
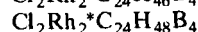
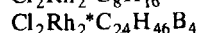
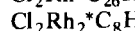
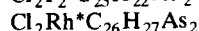
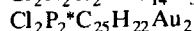
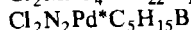
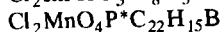
Cl₂HgHgCl₂Reaction with Fe(CO)₅: 8.3.3.2.2Reaction with Fe(Cp-η⁵)₂,Ru(Cp-η⁵)₂: 8.3.3.3Reaction with M(CO)₄L₂: 8.3.3.2.2



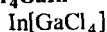
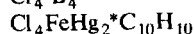
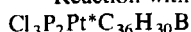
Reaction with electron pair bases:

6.2.2.1

Reaction with MX: 6.2.2.1

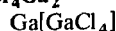
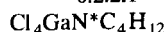


Reaction with BF: 6.2.2.1



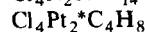
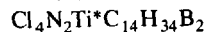
Reaction with electron pair bases:

6.2.2.1



see GaCl_2 : 6.2.2.1

Structure: 6.2.2.1



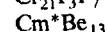
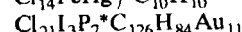
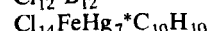
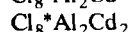
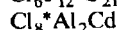
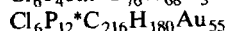
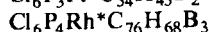
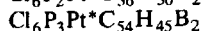
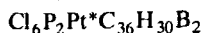
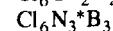
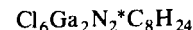
Reaction with BX_3 , B_2H_6 : 6.7.4.1.1



Reaction with BX_3 , B_2H_6 : 6.7.4.1.1



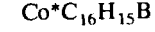
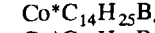
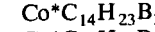
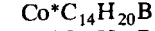
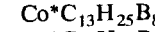
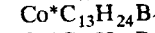
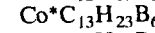
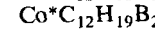
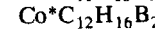
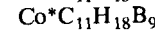
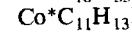
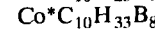
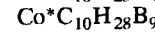
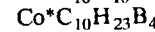
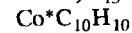
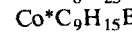
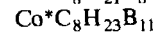
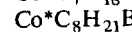
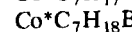
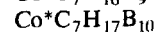
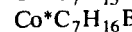
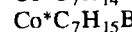
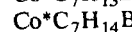
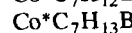
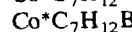
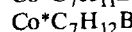
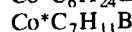
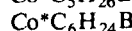
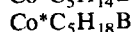
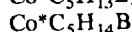
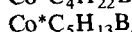
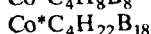
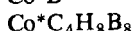
Reaction with BX_3 , B_2H_6 : 6.7.4.1.1



Reaction with boranes or carboranes:

6.5.3.3

Reaction with BX_3 : 6.7.4.1.1



$\text{Co}^*\text{C}_{17}\text{H}_{29}\text{B}_2$
 $\text{Co}^*\text{C}_{21}\text{H}_{26}\text{B}$
 $\text{Co}^*\text{C}_{22}\text{H}_{20}\text{B}_2$
 Co^*Cl_2
 CoDy^*B_4
 CoEr^*B_4
 $\text{CoF}_2^*\text{C}_{13}\text{H}_{17}\text{B}_2$
 $\text{CoFe}^*\text{C}_{12}\text{H}_{19}\text{B}_7$
 $\text{CoFe}^*\text{C}_{12}\text{H}_{21}\text{B}_9$
 $\text{CoFe}^*\text{C}_{19}\text{H}_{27}\text{B}_2$
 $\text{CoFe}^*\text{C}_{22}\text{H}_{33}\text{B}_2$
 $\text{CoFeNiO}_3^*\text{C}_{24}\text{H}_{33}\text{B}_2$
 $\text{CoFeP}_2^*\text{C}_{20}\text{H}_{50}\text{B}_8$
 $\text{CoFe}_2\text{O}_6^*\text{C}_{15}\text{H}_{15}\text{B}_4$
 $\text{CoGaI}_2\text{O}_5^*\text{C}_8\text{H}_8$
 $\text{CoGaNO}_4\text{P}_2^*\text{C}_{58}\text{H}_{45}$
 $\text{CoGaO}_5^*\text{C}_8\text{H}_8\text{Br}_2$
 $\text{CoGaO}_5^*\text{C}_8\text{H}_8\text{Cl}_2$
 CoGd^*B_4
 $\text{CoHgMnO}_9^*\text{C}_9$
 $\text{CoHgO}_2^*\text{C}_7\text{H}_5\text{Cl}_2$
 CoHo^*B_4
 $\text{CoI}_4\text{P}_4^*\text{C}_{52}\text{H}_{48}\text{B}_2$
 $\text{CoInNO}_4\text{P}_2^*\text{C}_{58}\text{H}_{45}$
 $\text{CoKN}_4\text{O}_4\text{P}^*\text{C}_{26}\text{H}_{29}$
 $\text{CoKN}_4\text{O}_4\text{P}^*\text{C}_{50}\text{H}_{47}\text{B}_2$
 CoLu^*B_4
 $\text{CoMn}_2\text{O}_6\text{S}^*\text{C}_{22}\text{H}_{32}\text{B}_4$
 CoMo^*B
 $\text{CoMo}_2^*\text{B}_2$
 $\text{CoMo}_3^*\text{B}_3$
 $\text{CoN}^*\text{C}_{13}\text{H}_{20}\text{B}$
 $\text{CoN}^*\text{C}_{14}\text{H}_{23}\text{B}_2$
 $\text{CoN}^*\text{C}_{21}\text{H}_{19}\text{B}$
 $\text{CoNO}_4\text{P}_2^*\text{C}_{58}\text{H}_{45}\text{Al}$
 $\text{CoNSi}^*\text{C}_{15}\text{H}_{27}\text{B}$
 $\text{CoN}_2^*\text{C}_{23}\text{H}_{43}\text{B}_4$
 $\text{CoN}_3\text{O}_3^*\text{C}_3\text{H}_9\text{B}$
 $\text{CoN}_4\text{O}_4^*\text{C}_{62}\text{H}_{57}\text{AsB}_3$
 $\text{CoN}_4\text{O}_4\text{P}^*\text{C}_{26}\text{H}_{29}\text{Cl}$
 $\text{CoN}_4\text{O}_4\text{P}^*\text{C}_{50}\text{H}_{47}\text{B}_2$
 $\text{CoN}_4\text{O}_4\text{P}^*\text{C}_{54}\text{H}_{73}\text{B}_3$
 $\text{CoNa}^*\text{C}_4\text{H}_{22}\text{B}_{18}$
 $\text{CoNa}^*\text{C}_8\text{H}_{34}\text{B}_{18}$
 $\text{CoNaO}_4^*\text{C}_4$
 $\text{CoNaP}_2^*\text{C}_2\text{H}_{20}\text{B}_{18}$
 $\text{CoNa}_2^*\text{C}_4\text{H}_{22}\text{B}_{18}$
 CoNb^*B
 CoNb^*B_2
 $\text{CoNi}^*\text{C}_{11}\text{H}_{18}\text{B}_7$
 $\text{CoNi}^*\text{C}_{19}\text{H}_{27}\text{B}_2$
 $\text{CoNi}^*\text{C}_{22}\text{H}_{33}\text{B}_2$
 $\text{CoO}^*\text{C}_{10}\text{H}_{34}\text{B}_{13}$
 $\text{CoO}^*\text{C}_{10}\text{H}_{35}\text{B}_{12}$
 $\text{CoO}^*\text{C}_{10}\text{H}_{37}\text{B}_{16}$
 $\text{CoO}^*\text{C}_{17}\text{H}_{33}\text{B}_7$
 $\text{CoO}_2^*\text{C}_{13}\text{H}_{11}\text{B}$
 $\text{CoO}_3^*\text{C}_{14}\text{H}_{12}\text{B}$
 $\text{CoO}_4^*\text{C}_4\text{H}_8\text{B}_5$
 $\text{CoO}_4\text{P}^*\text{C}_{22}\text{H}_{15}\text{Au}$
 $\text{CoO}_4\text{Sn}^*\text{C}_7\text{H}_9$
 $\text{CoP}^*\text{C}_{30}\text{H}_{33}\text{AuB}_2$
 $\text{CoP}_2^*\text{C}_4\text{H}_{26}\text{B}_{18}$
 $\text{CoP}_2^*\text{C}_{14}\text{H}_{36}\text{B}_3$
 $\text{CoP}_2^*\text{C}_{14}\text{H}_{39}\text{B}_6$
 $\text{CoP}_2^*\text{C}_{14}\text{H}_{39}\text{B}_7$
 $\text{CoP}_2^*\text{C}_{14}\text{H}_{40}\text{B}_7$
 $\text{CoP}_2^*\text{C}_{14}\text{H}_{40}\text{B}_8$
 $\text{CoP}_2^*\text{C}_{26}\text{H}_{24}\text{B}_2\text{Br}_4$
 $\text{CoP}_3^*\text{C}_{21}\text{H}_{60}\text{B}_{10}$
 $\text{CoP}_4^*\text{C}_{20}\text{H}_{33}$
 $\text{CoP}_4^*\text{C}_{44}\text{H}_{48}\text{B}_2$
 $\text{CoP}_4^*\text{C}_{44}\text{H}_{52}\text{B}_2$
 $\text{CoP}_4^*\text{C}_{52}\text{H}_{48}\text{B}_2\text{Br}_4$
 $\text{CoP}_4^*\text{C}_{52}\text{H}_{49}$
 $\text{CoP}_4^*\text{C}_{64}\text{H}_{58}\text{B}_2\text{Cl}_2$
 $\text{CoP}_4^*\text{C}_{76}\text{H}_{52}\text{B}_2$
 $\text{CoP}_4^*\text{C}_{76}\text{H}_{68}\text{B}_2$
 CoRe^*B
 $\text{CoS}^*\text{C}_{13}\text{H}_{21}\text{B}_2$
 $\text{CoS}_2^*\text{C}_5\text{H}_{13}\text{B}_6$
 $\text{CoSi}_2^*\text{C}_{13}\text{H}_{27}\text{B}_4$
 $\text{CoSi}_2^*\text{C}_{13}\text{H}_{28}\text{B}_5$
 $\text{CoSi}_2^*\text{C}_{13}\text{H}_{29}\text{B}_6$
 $\text{CoSi}_2^*\text{C}_{13}\text{H}_{31}\text{B}_6$
 CoTa^*B
 CoTa^*B_2
 CoTb^*B_4
 CoTm^*B_4
 CoU^*B_4
 CoV^*B_3
 CoW^*B
 CoW_2^*B_2
 CoW_3^*B_3
 CoY^*B_4
 $(\text{Co},\text{Mo})^*\text{B}$
 $(\text{Co},\text{W})^*\text{B}$
 Co_2^*B
 $\text{Co}_2^*\text{C}_{10}\text{H}_{16}\text{B}_4$
 $\text{Co}_2^*\text{C}_{12}\text{H}_{15}\text{B}_3$
 $\text{Co}_2^*\text{C}_{12}\text{H}_{16}\text{B}_4$
 $\text{Co}_2^*\text{C}_{12}\text{H}_{17}\text{B}_5$
 $\text{Co}_2^*\text{C}_{12}\text{H}_{18}\text{B}_6$
 $\text{Co}_2^*\text{C}_{12}\text{H}_{19}\text{B}_7$
 $\text{Co}_2^*\text{C}_{12}\text{H}_{20}\text{B}_8$
 $\text{Co}_2^*\text{C}_{12}\text{H}_{21}\text{B}_9$
 $\text{Co}_2^*\text{C}_{12}\text{H}_{22}\text{B}_{10}$
 $\text{Co}_2^*\text{C}_{14}\text{H}_{20}\text{B}_6$

- $\text{Co}_2^*\text{C}_{14}\text{H}_{22}\text{B}_{10}$
 $\text{Co}_2^*\text{C}_{15}\text{H}_{19}\text{B}_3$
 $\text{Co}_2^*\text{C}_{19}\text{H}_{27}\text{B}_2$
 $\text{Co}_2^*\text{C}_{20}\text{H}_{35}\text{B}_5$
 $\text{Co}_2^*\text{C}_{20}\text{H}_{36}\text{B}_4$
 $\text{Co}_2^*\text{C}_{20}\text{H}_{37}\text{B}_5$
 $\text{Co}_2^*\text{C}_{20}\text{H}_{41}\text{B}_8\text{Cl}$
 $\text{Co}_2^*\text{C}_{20}\text{H}_{42}\text{B}_8$
 $\text{Co}_2^*\text{C}_{22}\text{H}_{33}\text{B}_2$
 $\text{Co}_2^*\text{C}_{24}\text{H}_{39}\text{B}_3$
 $\text{Co}_2\text{Dy}^*\text{B}_2$
 $\text{Co}_2\text{F}_6\text{PS}_2^*\text{C}_{16}\text{H}_{32}\text{B}_4$
 $\text{Co}_2\text{Fe}^*\text{C}_{28}\text{H}_{44}\text{B}_4$
 $\text{Co}_2\text{FeS}_4^*\text{C}_{32}\text{H}_{64}\text{B}_8$
 $\text{Co}_2\text{GaO}_6^*\text{C}_6\text{Br}_4$
 $\text{Co}_2\text{GaO}_9^*\text{C}_{12}\text{H}_8\text{Cl}$
 $\text{Co}_2\text{Gd}^*\text{B}_2$
 $\text{Co}_2\text{HgO}_8^*\text{C}_8$
 $\text{Co}_2\text{Ho}^*\text{B}_2$
 $\text{Co}_2\text{InO}_6^*\text{C}_6\text{Br}_4$
 $\text{Co}_2\text{InO}_9^*\text{C}_{12}\text{H}_8\text{Br}$
 $\text{Co}_2\text{La}^*\text{B}_2$
 $\text{Co}_2\text{NO}_6^*\text{C}_{14}\text{H}_{18}\text{B}$
 $\text{Co}_2\text{N}_2\text{O}_4^*\text{C}_{22}\text{H}_{38}\text{B}_4$
 $\text{Co}_2\text{N}_2\text{O}_4^*\text{C}_{24}\text{H}_{40}\text{B}_2$
 $\text{Co}_2\text{N}_3^*\text{C}_{30}\text{H}_{60}\text{B}_3$
 $\text{Co}_2\text{Nb}^*\text{B}$
 $\text{Co}_2\text{Nd}^*\text{B}_2$
 $\text{Co}_2\text{Ni}_2^*\text{C}_{43}\text{H}_{73}\text{B}_6$
 $\text{Co}_2\text{Ni}_2^*\text{C}_{46}\text{H}_{79}\text{B}_6$
 $\text{Co}_2\text{Ni}_2\text{O}_2^*\text{C}_{36}\text{H}_{56}\text{B}_4$
 $\text{Co}_2\text{Ni}_3^*\text{C}_{46}\text{H}_{78}\text{B}_8$
 $\text{Co}_2\text{O}_4^*\text{C}_{14}\text{H}_{14}\text{B}_2$
 $\text{Co}_2\text{O}_4^*\text{C}_{24}\text{H}_{18}\text{B}_2$
 $\text{Co}_2\text{O}_8^*\text{C}_8$
 $\text{Co}_2\text{O}_8^*\text{C}_8\text{Cd}$
 $\text{Co}_2\text{O}_8\text{P}_4^*\text{C}_{80}\text{H}_{60}\text{Au}_6$
 $\text{Co}_2\text{O}_8\text{Zn}^*\text{C}_8$
 $\text{Co}_2\text{P}_3^*\text{C}_{20}\text{H}_{51}\text{B}_5$
 $\text{Co}_2\text{Pr}^*\text{B}_2$
 $\text{Co}_2\text{S}^*\text{C}_{10}\text{H}_{17}\text{B}_5$
 $\text{Co}_2\text{S}_2^*\text{C}_{10}\text{H}_{12}\text{B}_2$
 $\text{Co}_2\text{S}_2^*\text{C}_{10}\text{H}_{15}\text{B}_5$
 $\text{Co}_2\text{S}_3^*\text{C}_{24}\text{H}_{48}\text{B}_6$
 $\text{Co}_2\text{Sc}^*\text{B}_2$
 $\text{Co}_2\text{Sm}^*\text{B}_2$
 $\text{Co}_2\text{Ta}^*\text{B}_2$
 $\text{Co}_2\text{Tb}^*\text{B}_2$
 $\text{Co}_2\text{Y}^*\text{B}_2$
 $(\text{Co},\text{Ni})_2\text{Nb}^*\text{B}$
 $(\text{Co},\text{Ni})_2\text{Ta}^*\text{B}$
 Co_3^*B
 $\text{Co}_3^*\text{B}_2\text{Ce}$
 $\text{Co}_3^*\text{C}_{12}\text{H}_{34}\text{B}_4$
 $\text{Co}_3^*\text{C}_{15}\text{H}_{20}\text{B}_3$
 $\text{Co}_3^*\text{C}_{17}\text{H}_{24}\text{B}_7$
 $\text{Co}_3^*\text{C}_{28}\text{H}_{49}\text{B}_8$
 $\text{Co}_3\text{Dy}^*\text{B}_2$
 $\text{Co}_3\text{Er}^*\text{B}_2$
 $\text{Co}_3\text{Gd}^*\text{B}_2$
 $\text{Co}_3\text{Hf}^*\text{B}_2$
 $\text{Co}_3\text{Ho}^*\text{B}_2$
 $\text{Co}_3\text{InO}_{12}^*\text{C}_{12}$
 $\text{Co}_3\text{Lu}^*\text{B}_2$
 $\text{Co}_3\text{NO}_9^*\text{C}_{15}\text{H}_{15}\text{B}$
 $\text{Co}_3\text{OS}^*\text{C}_{16}\text{H}_{15}$
 $\text{Co}_3\text{O}_{12}\text{Ti}^*\text{C}_{12}$
 $\text{Co}_3\text{Sc}^*\text{B}_2$
 $\text{Co}_3\text{Sm}^*\text{B}_2$
 $\text{Co}_3\text{Tb}^*\text{B}_2$
 $\text{Co}_3\text{Tm}^*\text{B}_2$
 $\text{Co}_3\text{U}^*\text{B}_2$
 $\text{Co}_3\text{Y}^*\text{B}_2$
 $\text{Co}_3\text{Yb}^*\text{B}_2$
 $\text{Co}_3\text{Zr}^*\text{B}_2$
 $(\text{Co},\text{Re})_3^*\text{B}$
 Co_4^*BCe
 $\text{Co}_4^*\text{B}_4\text{Ce}$
 $\text{Co}_4^*\text{C}_{20}\text{H}_{24}\text{B}_4$
 $\text{Co}_4\text{Dy}^*\text{B}$
 $\text{Co}_4\text{Dy}^*\text{B}_4$
 $\text{Co}_4\text{Er}^*\text{B}$
 $\text{Co}_4\text{Er}^*\text{B}_4$
 $\text{Co}_4\text{Gd}^*\text{B}$
 $\text{Co}_4\text{Gd}^*\text{B}_4$
 $\text{Co}_4\text{Ho}^*\text{B}$
 $\text{Co}_4\text{Ho}^*\text{B}_4$
 $\text{Co}_4\text{In}_3\text{O}_{16}^*\text{C}_{16}\text{Br}_3$
 $\text{Co}_4\text{La}^*\text{B}$
 $\text{Co}_4\text{La}^*\text{B}_4$
 $\text{Co}_4\text{Lu}^*\text{B}$
 $\text{Co}_4\text{Lu}^*\text{B}_4$
 $\text{Co}_4\text{Nb}_3^*\text{B}_7$
 $\text{Co}_4\text{Nd}^*\text{B}$
 $\text{Co}_4\text{Nd}^*\text{B}_2$
 $\text{Co}_4\text{Pr}^*\text{B}$
 $\text{Co}_4\text{Pr}^*\text{B}_4$
 $\text{Co}_4\text{Sm}^*\text{B}$
 $\text{Co}_4\text{Sm}^*\text{B}_4$
 $\text{Co}_4\text{Ta}_3^*\text{B}_7$
 $\text{Co}_4\text{Tb}^*\text{B}$
 $\text{Co}_4\text{Tb}^*\text{B}_4$
 $\text{Co}_4\text{Tm}^*\text{B}$
 $\text{Co}_4\text{Tm}^*\text{B}_4$
 $\text{Co}_4\text{U}^*\text{B}_4$
 $\text{Co}_4\text{Y}^*\text{B}$
 $\text{Co}_4\text{Y}^*\text{B}_4$
 $\text{Co}_{4.6}\text{Si}_2^*\text{B}$

$\text{Co}_5^*\text{B}_2\text{Ce}$
 $\text{Co}_5^*\text{P}^*\text{B}_2$
 $\text{Co}_5\text{Ta}_3^*\text{B}_2$
 $\text{Co}_5\text{Ti}_3^*\text{B}_2$
 $\text{Co}_6\text{Hg}_9\text{O}_{18}^*\text{C}_{18}$
 $\text{Co}_7^*\text{B}_3\text{Ce}_2$
 $\text{Co}_7\text{Dy}_2^*\text{B}_3$
 $\text{Co}_7\text{Dy}_3^*\text{B}_2$
 $\text{Co}_7\text{Er}_2^*\text{B}_3$
 $\text{Co}_7\text{Gd}_2^*\text{B}_3$
 $\text{Co}_7\text{Gd}_3^*\text{B}_2$
 $\text{Co}_7\text{Ho}_2^*\text{B}_3$
 $\text{Co}_7\text{Nd}_2^*\text{B}_3$
 $\text{Co}_7\text{Pr}_2^*\text{B}_3$
 $\text{Co}_7\text{Tb}_2^*\text{B}_3$
 $\text{Co}_7\text{Tm}_2^*\text{B}_3$
 $\text{Co}_7\text{U}_3^*\text{B}_2$
 $\text{Co}_7\text{Y}_2^*\text{B}_3$
 $(\text{Co},\text{Re})_7^*\text{B}_4$
 $\text{Co}_{11}^*\text{B}_4\text{Ce}_3$
 $\text{Co}_{11}^*\text{CB}_2$
 $\text{Co}_{11}\text{Dy}_3^*\text{B}_4$
 $\text{Co}_{11}\text{Er}_3^*\text{B}_4$
 $\text{Co}_{11}\text{Gd}_3^*\text{B}_4$
 $\text{Co}_{11}\text{Ho}_3^*\text{B}_4$
 $\text{Co}_{11}\text{La}_3^*\text{B}_4$
 $\text{Co}_{11}\text{Lu}^*\text{B}_4$
 $\text{Co}_{11}\text{Nd}_3^*\text{B}_4$
 $\text{Co}_{11}\text{Pr}_3^*\text{B}_4$
 $\text{Co}_{11}\text{Sm}_3^*\text{B}_4$
 $\text{Co}_{11}\text{Tm}_3^*\text{B}_4$
 $\text{Co}_{11}\text{Y}_3^*\text{B}_4$
 $\text{Co}_{20}^*\text{Al}_3\text{B}$
 $\text{Co}_{20}\text{Mn}_3^*\text{B}_6$
 $\text{Co}_{20}\text{Ti}_3^*\text{B}_6$
 $\text{Co}_{21}\text{Cr}_2^*\text{B}_6$
 $\text{Co}_{21}\text{Ge}_2^*\text{B}_6$
 $\text{Co}_{21}\text{Hf}_2^*\text{B}_6$
 $\text{Co}_{21}\text{Ir}_2^*\text{B}_6$
 $\text{Co}_{21}\text{Mo}_2^*\text{B}_6$
 $\text{Co}_{21}\text{Nb}_2^*\text{B}_6$
 $\text{Co}_{21}\text{Sb}_2^*\text{B}_6$
 $\text{Co}_{21}\text{Sc}_2^*\text{B}_6$
 $\text{Co}_{21}\text{Sn}_2^*\text{B}_6$
 $\text{Co}_{21}\text{Ta}_2^*\text{B}_6$
 $\text{Co}_{21}\text{U}_2^*\text{B}_6$
 $\text{Co}_{21}\text{V}_2^*\text{B}_6$
 $\text{Co}_{21}\text{W}_2^*\text{B}_6$
 $\text{Co}_{21}\text{Zr}_2^*\text{B}_6$
 $\text{Co}_{23-m}\text{Ga}_m^*\text{B}_6$
 $\text{Co}_{23-m}\text{Mg}_m^*\text{B}_6$
 $(\text{Co},\text{Re})_{23}^*\text{B}_6$
 $(\text{Co},\text{Mn})_{23}^*(\text{B},\text{C})_6$
 $(\text{Co},\text{Ir})_{23}^*\text{B}_{12}$

Cr^*B
 Cr^*B_2
 Cr^*B_4
 $\text{Cr}^*\text{B}_4\text{Ce}$
 Cr^*B_{41}
 $\text{Cr}^*\text{C}_7\text{H}_{16}\text{B}_9$
 $\text{Cr}^*\text{C}_8\text{H}_{19}\text{B}_9$
 $\text{Cr}^*\text{C}_9\text{H}_{22}\text{B}_9$
 $\text{Cr}^*\text{C}_{10}\text{H}_{10}$
 $\text{Cr}^*\text{C}_{17}\text{H}_{32}\text{B}_7$
 $\text{Cr}^*\text{C}_{17}\text{H}_{33}\text{B}_8$
 CrCs_2O_4
 Cs_2CrO_4
 Explodes when mixed with CsHSO_4 :
 7.2.2.4.1
 CrDy^*B_4
 CrEr^*B_4
 CrGd^*B_4
 $\text{CrHgO}_3^*\text{C}_8\text{H}_5\text{Cl}$
 CrHo^*B_4
 CrLu^*B_4
 $\text{CrN}_2\text{O}_4^*\text{C}_{20}\text{H}_{36}\text{B}_2$
 $\text{CrN}_3\text{O}_3^*\text{C}_{10}\text{H}_{20}\text{B}_3$
 $\text{CrN}_3\text{O}_3^*\text{C}_{14}\text{H}_{20}\text{B}_3$
 $\text{CrNaO}_3^*\text{C}_8\text{H}_5$
 $\text{CrNaO}_7^*\text{C}_{17}\text{H}_{24}\text{B}$
 CrNd^*B_4
 $\text{CrO}_2\text{S}_2^*\text{C}_{18}\text{H}_{32}\text{B}_4$
 $\text{CrO}_3^*\text{C}_8\text{H}_6$
 $\text{CrO}_3\text{P}^*\text{C}_{26}\text{H}_{20}\text{Au}$
 $\text{CrO}_4\text{S}^*\text{C}_{12}\text{H}_{16}\text{B}_2$
 CrPr^*B_4
 CrSm^*B_4
 CrTb^*B_4
 CrTm^*B_4
 CrU^*B_4
 CrY^*B_4
 $(\text{Cr},\text{Os})^*\text{B}$
 $(\text{Cr},\text{Re})^*\text{B}$
 $(\text{Cr},\text{Ru})^*\text{B}$
 $\text{Cr}_2^*\text{AlB}_2$
 Cr_2^*B
 Cr_2^*B_3
 $\text{Cr}_2^*\text{B}_6\text{Ce}$
 $\text{Cr}_2^*\text{B}_6\text{Co}_{21}$
 $\text{Cr}_2^*\text{C}_{12}\text{H}_{20}\text{B}_8$
 $\text{Cr}_2\text{HgO}_6^*\text{C}_{16}\text{H}_{10}$
 $\text{Cr}_2\text{Ir}^*\text{B}_2$
 $\text{Cr}_2\text{Nd}^*\text{B}_6$
 $\text{Cr}_2\text{Ni}_3^*\text{B}_6$
 $\text{Cr}_2\text{Pr}^*\text{B}_6$
 $\text{Cr}_2\text{Sm}^*\text{B}_6$
 $(\text{Cr},\text{Mo})_2^*\text{B}$
 $(\text{Cr},\text{V})_2^*\text{B}$

- (Cr,Ni)₂*B₃
 Cr₃*AlB₄
 Cr₃*B₄
 (Cr,Mo)₃*B₂
 Cr_{4,5}P₂*B
 Cr₅*B₃
 Cr₅P*B₂
 Cr₅Si₃*B
 (Cr,W)₅*B₃
 Cr₂₃*(B,C)₆
 (Cr,Ir)₂₃*B₆
 (Cr,Fe)₂₃*(B,C)₆
 (Cr,Fe,Mn)₂₃*(B,C)₆
 (Cr,Mn)₂₃*(B,C)₆
 Cs*Au
 Cs*Cd₁₃
 CsHO₄S
 CsHSO₄
 Explodes when mixed with Cs₂CrO₄:
 7.2.2.4.1
CsHg
 CsHg
 Formation: 7.3.2.2
CsHg₂
 CsHg₂
 Formation: 7.3.2.2
CsHg₄
 CsHg₄
 Formation: 7.3.2.2
CsHg₆
 CsHg₆
 Formation: 7.3.2.2
CsHg₁₂
 CsHg₁₂
 Formation: 7.3.2.2
Cs₂O
 Cs₂O
 Reaction with RX: 7.2.2.4.4
 Cs₂O₄*Cr
Cs₃Hg₄
 Cs₃Hg₄
 Formation: 7.3.2.2
Cu
 Cu atoms
 Reaction with BX₃: 6.2.2.4
 Cu
 Reaction with C₂H₄: 8.2.2.2.1
 Reaction with CO: 8.2.2.2.1
 Cu*Ag
 Cu*AgAu
 Cu*Ag₄
 Cu*B₂₃
 Cu*B₂₈
 Cu*Ba
 Cu*Be₂
 Cu*Be₃
 Cu*C₄H₈
 Cu*C₆H₁₂
 Cu*Ca
 Cu*Ca₂
 Cu*Cl
CuFe
 CuFe
 Formation: 8.3.2.2.4
CuMg
 MgCu
 Formation: 7.3.3
CuMg₂
 Mg₂Cu
 Formation: 7.3.3.1.2
 CuN*C₁₂H₄₂B₁₈
 CuNO₂P*C₂₇H₃₂B₉
 CuNP*C₂₅H₃₀B₉
 CuN₂*C₂₀H₆₂B₁₈
 CuO*C
 CuP*C₂₀H₂₆B₉
 CuP₂*C₃₆H₃₈B₅
 CuP₂*C₃₆H₃₉B₄
 CuP₂*C₃₆H₃₉B₆
CuSr
 SrCu
 Formation: 7.3.3.1.4
Cu₂
 Cu₂
 Formation: 8.2.2.1.1
 Cu₂*Ag₃
 Cu₂*Al_{2,7}B₁₀₄
 Cu₂*Be
 Cu₂FeN₂O₄*C₄H₆
Cu₂Mg
 MgCu₂
 Formation: 7.3.3.1.2
 Cu₂O*C
Cu₃
 Cu₃
 Formation: 8.2.2.1.1
 Cu₃IrP₂*C₅₂H₄₀
 Cu₃N₃O₆*C₂₇H₃₉B₂₇
 Cu₃O*C
 Cu₄Ir₂P₂*C₁₀₀H₇₀
Cu₄Li
 LiCu₄
 Formation: 7.3.1.1, 7.3.1.2, 7.3.1.3.1
Cu₄Mg
 MgCu₄
 Formation: 7.3.3.1.2
 Cu₄O*C

Cu₅*Ca
Cu₅Sr
 SrCu₅
 Formation: 7.3.3.1.4

Cu₁₃*Ba
 Dy*BCo₄
 Dy*B₂
 Dy*B₂Co₂
 Dy*B₂Co₃
 Dy*B₄
 Dy*B₄Co
 Dy*B₄Co₄
 Dy*B₄Cr
 Dy*B₆
 Dy*B₁₂
 Dy*B₆₆
 Dy*CB₂
 Dy*C₂B₂
 DyEr*B₄
 DyFe*B₄
 DyFe₂*B₂
 DyHo*B₄
 DyIr₃*B₂
 DyMn*B₄
 DyMo*B₄
 DyNi*B₄
 DyOs*B₂
 DyOs*B₄
 DyOs₄*B₄
 DyRe*B₄
 DyRh₃*B
 DyRh₃*B₂
 DyRh₄*B₄
 DyRu*B₂
 DyRu*B₄
 DyRu₃*B₂
 DyRu₄*B₄
 DyV*B₄
 DyW*B₄
 Dy₂*B₃Co₇
 Dy₂Fe₁₄*B
 Dy₂Fe₁₄*C
 Dy₂Ni₁₅*B₆
 Dy₂Ni₁₅*B₉
 Dy₂Re*B₆
 Dy₃*B₂Co₇
 Dy₃*B₄Co₁₁
 Dy₅Ge₃*B
 Dy₅Si₃*B
 Er*BCo₄
 Er*B₂
 Er*B₂Co₃
 Er*B₄
 Er*B₄Co

Er*B₄Co₄
 Er*B₄Cr
 Er*B₄Dy
 Er*B₁₂
 Er*B₆₆
 Er*C₂B₂
 ErFe*B₄
 ErFe₂*B₂
 ErIr₃*B₂
 ErIr₄*B₄
 ErMn*B₄
 ErMo*B₄
 ErOs*B₂
 ErOs*B₄
 ErOs₃*B₂
 ErOs₄*B₄
 ErRe*B₄
 ErRh₃*B_x
 ErRh₃*B₂
 ErRh₄*B₄
 ErRu*B₂
 ErRu*B₄
 ErRu₃*B₂
 ErRu₄*B₄
 ErV*B₄
 ErW*B₄
 Er₂*B₃Co₇
 Er₂Fe₁₄*B
 Er₂Fe₁₄*C
 Er₂Ni₁₅*B₆
 Er₂Ni₁₅*B₉
 Er₂Ni₂₁*B₆
 Er₂Re*B₆
 Er₃*B₄Co₁₁
 Er₄Ni₂₉*B₁₀
 Eu*B₆
 Eu*C_xB_{6-x}
 Eu*C₂B₂
 EuIr₄*B₄
 EuOs₄*B₄
 EuPd₆*B₄
 EuRh₃*B
 EuRh₃*B₂
 EuRh₆*B₄
 EuRu₄*B₄
 Eu₂Os₃*B₅
 F*B
FH

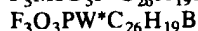
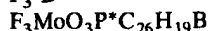
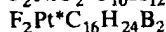
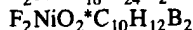
HF

Reaction with Hg₂CO₃: 8.2.4.1

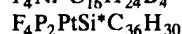
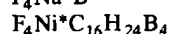
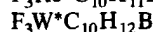
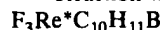
F₂*C₈H₁₂B₂
 F₂*C₁₃H₁₇B₂Co
 F₂FeO₃*C₁₁H₁₂B₂
 F₂FeS*C₁₄H₂₀B₂

F₂Hg₂

Formation: 8.2.4.1



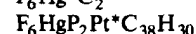
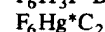
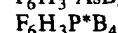
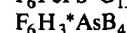
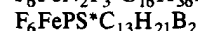
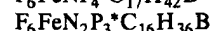
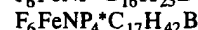
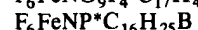
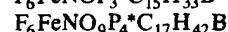
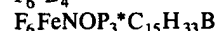
Reaction with BF: 6.2.2.1



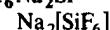
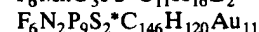
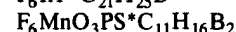
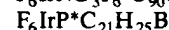
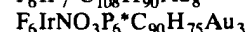
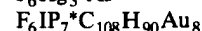
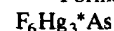
Reaction with OBBO: 6.2.3

Reaction with Na₂CO₃: 7.2.3.1.1

Reaction with elemental Hg: 8.2.5.1

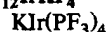
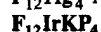
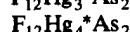
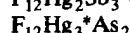
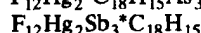
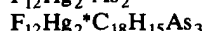
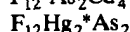
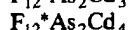
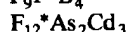
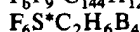
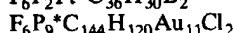
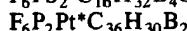
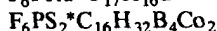
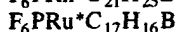
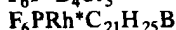
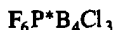
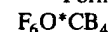


Formation: 8.2.5.1

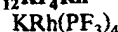
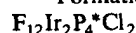


Decomposition: 7.2.3.1.1

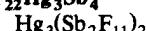
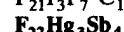
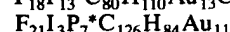
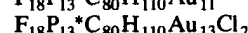
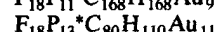
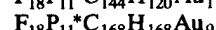
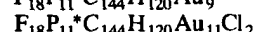
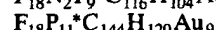
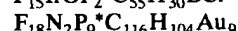
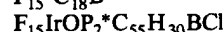
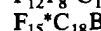
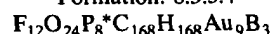
Formation: 7.2.3.1.1



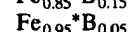
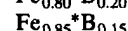
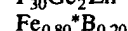
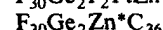
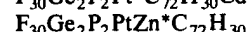
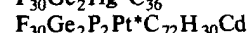
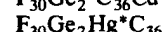
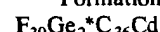
Formation: 8.3.3.4



Formation: 8.3.3.4

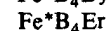
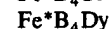
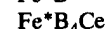


Formation: 8.2.5.1



Reaction with boranes or carboranes:

6.5.3.3



- $\text{Fe}^*\text{C}_5\text{H}_{15}\text{B}_5$
 $\text{Fe}^*\text{C}_5\text{H}_{20}\text{B}_{10}$
 $\text{Fe}^*\text{C}_7\text{H}_{11}\text{B}_4$
 $\text{Fe}^*\text{C}_7\text{H}_{13}\text{B}_6$
 $\text{Fe}^*\text{C}_7\text{H}_{15}\text{B}_8$
 $\text{Fe}^*\text{C}_7\text{H}_{16}\text{B}_9$
 $\text{Fe}^*\text{C}_8\text{H}_{22}\text{B}_8$
 $\text{Fe}^*\text{C}_8\text{H}_{23}\text{B}_9$
 $\text{Fe}^*\text{C}_9\text{H}_{16}\text{B}_9$
 $\text{Fe}^*\text{C}_9\text{H}_{17}\text{B}_7$
 $\text{Fe}^*\text{C}_9\text{H}_{19}\text{B}_9$
 $\text{Fe}^*\text{C}_{10}\text{H}_{10}$
 $\text{Fe}^*\text{C}_{10}\text{H}_{21}\text{B}_9$
 $\text{Fe}^*\text{C}_{11}\text{H}_{21}\text{B}_7$
 $\text{Fe}^*\text{C}_{11}\text{H}_{22}\text{B}_9$
 $\text{Fe}^*\text{C}_{11}\text{H}_{23}\text{B}_7$
 $\text{Fe}^*\text{C}_{12}\text{H}_{19}\text{B}_7\text{Co}$
 $\text{Fe}^*\text{C}_{12}\text{H}_{20}\text{B}_4$
 $\text{Fe}^*\text{C}_{12}\text{H}_{21}\text{B}_9$
 $\text{Fe}^*\text{C}_{12}\text{H}_{21}\text{B}_9\text{Co}$
 $\text{Fe}^*\text{C}_{13}\text{H}_{22}\text{B}_4$
 $\text{Fe}^*\text{C}_{15}\text{H}_{25}\text{B}_5$
 $\text{Fe}^*\text{C}_{16}\text{H}_{28}\text{B}_4$
 $\text{Fe}^*\text{C}_{17}\text{H}_{17}\text{B}$
 $\text{Fe}^*\text{C}_{19}\text{H}_{27}\text{B}_2\text{Co}$
 $\text{Fe}^*\text{C}_{20}\text{H}_{33}\text{B}_3$
 $\text{Fe}^*\text{C}_{22}\text{H}_{33}\text{B}_2\text{Co}$
 $\text{Fe}^*\text{C}_{28}\text{H}_{44}\text{B}_4\text{Co}_2$
 Fe^*Cu
 $\text{FeGaNO}_2^*\text{C}_{33}\text{H}_{40}$
 $\text{FeGaNa}_2\text{O}_4^*\text{C}_4\text{Br}_3$
 $\text{FeGaO}_5^*\text{C}_{10}\text{H}_{13}$
 FeGd^*B_4
 $\text{FeGeO}_2^*\text{C}_{10}\text{H}_{14}$
 $\text{FeHgO}_5^*\text{CCl}_2$
 $\text{FeHgO}_5^*\text{C}_5\text{Cl}_2$
 $\text{FeHg}_2^*\text{C}_{10}\text{H}_{10}\text{Cl}_4$
 $\text{FeHg}_2\text{O}_4^*\text{C}_4\text{Cl}_2$
 $\text{FeHg}_7^*\text{C}_{10}\text{H}_{10}\text{Cl}_{14}$
 FeHo^*B_4
 $\text{FeIO}_2^*\text{C}_7\text{H}_5$
 $\text{FeInNO}_2^*\text{C}_{33}\text{H}_{40}$
 $\text{FeInNa}_2\text{O}_4^*\text{C}_4\text{Br}_3$
 FeLu^*B_4
 $\text{FeMnO}_3\text{S}^*\text{C}_{16}\text{H}_{21}\text{B}_2$
 $\text{FeMo}_2^*\text{B}_2$
 $\text{FeMo}_3^*\text{B}_3$
 $\text{FeNOP}_3^*\text{C}_{15}\text{H}_{33}\text{BF}_6$
 $\text{FeNO}_2^*\text{C}_{33}\text{H}_{40}\text{Al}$
 $\text{FeNO}_3^*\text{C}_7\text{H}_9\text{BBR}$
 $\text{FeNO}_3^*\text{C}_{12}\text{H}_{19}\text{B}_2$
 $\text{FeNO}_3^*\text{C}_{13}\text{H}_{20}\text{B}$
 $\text{FeNO}_3\text{Si}^*\text{C}_{13}\text{H}_{22}\text{B}$
 $\text{FeNO}_3\text{Si}^*\text{C}_{15}\text{H}_{24}\text{B}$
 $\text{FeNO}_9\text{P}_4^*\text{C}_{17}\text{H}_{42}\text{BF}_6$
 $\text{FeNP}^*\text{C}_{16}\text{H}_{25}\text{BF}_6$
 $\text{FeNP}_4^*\text{C}_{17}\text{H}_{42}\text{BF}_6$
 $\text{FeN}_2^*\text{C}_{16}\text{H}_{30}\text{B}_2$
 $\text{FeN}_2\text{O}^*\text{C}_{21}\text{H}_{40}\text{B}_2$
 $\text{FeN}_2\text{O}_3^*\text{C}_8\text{H}_{15}\text{B}$
 $\text{FeN}_2\text{O}_3^*\text{C}_{13}\text{H}_{20}\text{B}_2$
 $\text{FeN}_2\text{O}_4^*\text{C}_4\text{H}_6\text{Cd}$
 $\text{FeN}_2\text{O}_4^*\text{C}_4\text{H}_6\text{Cu}_2$
 $\text{FeN}_2\text{P}_3^*\text{C}_{16}\text{H}_{36}\text{BF}_6$
 $\text{FeN}_3^*\text{C}_{19}\text{H}_{38}\text{B}_5$
 $\text{FeN}_3\text{O}_4\text{Zn}^*\text{C}_4\text{H}_9$
 FeNb^*B
 $\text{FeNi}^*\text{C}_{30}\text{H}_{54}\text{B}_4$
 $\text{FeNiO}_3^*\text{C}_{17}\text{H}_{22}\text{B}_2$
 $\text{FeNiO}_3^*\text{C}_{24}\text{H}_{33}\text{B}_2\text{Co}$
 $\text{FeOS}_2^*\text{C}_{17}\text{H}_{32}\text{B}_4$
 $\text{FeO}_2^*\text{C}_7\text{H}_{13}\text{B}_5$
 $\text{FeO}_2^*\text{C}_9\text{H}_{12}\text{B}_4$
 $\text{FeO}_2^*\text{C}_{12}\text{H}_{18}\text{B}_2$
 $\text{FeO}_2^*\text{C}_{12}\text{H}_{26}\text{B}_9$
 $\text{FeO}_2\text{Si}^*\text{C}_{10}\text{H}_{14}$
 $\text{FeO}_2\text{Sn}^*\text{C}_{10}\text{H}_{14}$
 $\text{FeO}_3^*\text{C}_5\text{H}_6\text{B}_4$
 $\text{FeO}_3^*\text{C}_5\text{H}_7\text{B}_3$
 $\text{FeO}_3^*\text{C}_{11}\text{H}_{12}\text{B}_2\text{F}_2$
 $\text{FeO}_3^*\text{C}_{13}\text{H}_9\text{B}$
 $\text{FeO}_3^*\text{C}_{15}\text{H}_{13}\text{B}$
 $\text{FeO}_3^*\text{C}_{15}\text{H}_{24}\text{B}_2$
 $\text{FeO}_3^*\text{C}_{37}\text{H}_{25}\text{B}$
 $\text{FeO}_3\text{S}^*\text{C}_{11}\text{H}_{16}\text{B}_2$
 $\text{FeO}_4^*\text{C}_4\text{Cd}$
 $\text{FeO}_4^*\text{C}_4\text{H}_2$
 $\text{FeO}_4^*\text{C}_4\text{H}_{10}\text{B}_6$
 $\text{FeO}_4^*\text{C}_9\text{H}_9\text{B}$
 FeO_5^*C_5
 $\text{FeP}^*\text{C}_7\text{H}_{18}\text{B}_9$
 $\text{FePS}^*\text{C}_{13}\text{H}_{21}\text{B}_2\text{F}_6$
 $\text{FeP}_2^*\text{C}_4\text{H}_{26}\text{B}_{18}$
 $\text{FeP}_2^*\text{C}_{20}\text{H}_{50}\text{B}_8\text{Co}$
 $\text{FeP}_2\text{Pt}^*\text{C}_{20}\text{H}_{50}\text{B}_8$
 $\text{FeS}^*\text{C}_7\text{H}_{18}\text{B}_{10}$
 $\text{FeS}^*\text{C}_7\text{H}_{19}\text{B}_9$
 $\text{FeS}^*\text{C}_{14}\text{H}_{20}\text{B}_2\text{F}_2$
 $\text{FeS}^*\text{C}_{14}\text{H}_{22}\text{B}_2$
 $\text{FeS}^*\text{C}_{15}\text{H}_{24}\text{B}_2$
 $\text{FeS}^*\text{C}_{16}\text{H}_{26}\text{B}_2$
 $\text{FeS}_4^*\text{C}_{32}\text{H}_{64}\text{B}_8\text{Co}_2$
 FeSi
 FeSi
 Reducing agent: 7.2.3.2.1
 FeSm^*B_4
 FeTa^*B
 FeTb^*B_4

FeTm^*B_4
 FeU^*B_4
 FeW^*B
 FeW_2^*B_2
 FeW_3^*B_3
 FeY^*B_4
 $(\text{Fe},\text{Mo})^*\text{B}$
 $(\text{Fe},\text{W})^*\text{B}$
 $\text{Fe}_2^*\text{AlB}_2$
 Fe_2^*B
 $\text{Fe}_2^*\text{B}_2\text{Dy}$
 $\text{Fe}_2^*\text{B}_2\text{Er}$
 $\text{Fe}_2^*\text{C}_6\text{H}_{27}\text{B}_{18}$
 $\text{Fe}_2^*\text{C}_{12}\text{H}_{18}\text{B}_6$
 $\text{Fe}_2^*\text{C}_{13}\text{H}_{25}\text{B}_8$
 $\text{Fe}_2^*\text{C}_{18}\text{H}_{30}\text{B}_8$
 $\text{Fe}_2^*\text{C}_{22}\text{H}_{23}\text{B}$
 $\text{Fe}_2^*\text{C}_{44}\text{H}_{44}\text{B}_2$
 $\text{Fe}_2\text{Gd}^*\text{B}_2$
 $\text{Fe}_2\text{HgN}_2\text{O}_8^*\text{C}_6$
 $\text{Fe}_2\text{HgO}_4^*\text{C}_{14}\text{H}_{10}$
 $\text{Fe}_2\text{Ho}^*\text{B}_2$
 $\text{Fe}_2\text{InO}_4^*\text{C}_{14}\text{H}_{10}\text{Cl}$
 $\text{Fe}_2\text{Lu}^*\text{B}_2$
 $\text{Fe}_2\text{NiO}_6^*\text{C}_{20}\text{H}_{22}\text{B}_2$
 $\text{Fe}_2\text{Ni}_2^*\text{C}_{50}\text{H}_{85}\text{B}_6$
 $\text{Fe}_2\text{O}_3^*\text{C}_{17}\text{H}_{22}\text{B}_2$
 $\text{Fe}_2\text{O}_4^*\text{C}_{14}\text{H}_{10}$
 $\text{Fe}_2\text{O}_4^*\text{C}_{26}\text{H}_{22}\text{B}_2$
 $\text{Fe}_2\text{O}_6^*\text{C}_{15}\text{H}_{15}\text{B}_4\text{Co}$
 $\text{Fe}_2\text{O}_9^*\text{C}_9$
 $\text{Fe}_2\text{S}^*\text{C}_{18}\text{H}_{26}\text{B}_2$
 $\text{Fe}_2\text{S}_2\text{Zn}^*\text{C}_{26}\text{H}_{42}\text{B}_4$
 $\text{Fe}_2\text{Tb}^*\text{B}_2$
 $\text{Fe}_2\text{Tm}^*\text{B}_2$
 $\text{Fe}_2\text{Y}^*\text{B}_2$
 $\text{Fe}_{2.2}\text{Ir}_{0.8}^*\text{B}$
 $\text{Fe}_{2.2}\text{Rh}_{0.8}^*\text{B}$
 $\text{Fe}_{2.6}\text{Mo}_{0.4}^*\text{B}$
 $\text{Fe}_{2.6}\text{Re}_{0.4}^*\text{B}$
 $\text{Fe}_{2.6}\text{Ru}_{0.4}^*\text{B}$
 $\text{Fe}_3^*(\text{B},\text{P})$
 $\text{Fe}_3\text{O}_6^*\text{C}_{24}\text{H}_{34}\text{B}_4$
 $\text{Fe}_3\text{O}_{12}^*\text{C}_{12}$
 $\text{Fe}_3\text{U}^*\text{B}_2$
 $(\text{Fe},\text{W})_3^*\text{B}_2$
 $(\text{Fe},\text{Mo})_3^*\text{B}_4$
 $(\text{Fe},\text{W})_3^*\text{B}_4$
 $\text{Fe}_4^*\text{B}_4\text{Ce}$
 $\text{Fe}_4\text{NO}_{12}\text{P}_2^*\text{C}_{48}\text{H}_{32}\text{B}$
 $\text{Fe}_4\text{Nd}^*\text{B}_4$
 $\text{Fe}_4\text{O}_{12}^*\text{C}_{12}\text{H}_3\text{B}$
 $\text{Fe}_4\text{O}_{12}\text{P}^*\text{C}_{30}\text{H}_{17}\text{AuB}$
 $\text{Fe}_4\text{O}_{12}\text{P}_2^*\text{C}_{24}\text{H}_{31}\text{Au}_2\text{B}$

$\text{Fe}_4\text{O}_{12}\text{P}_2^*\text{C}_{36}\text{H}_{31}\text{Au}_2\text{B}$
 $\text{Fe}_4\text{O}_{12}\text{P}_2^*\text{C}_{48}\text{H}_{31}\text{Au}_2\text{B}$
 $\text{Fe}_4\text{Sm}^*\text{B}_4$
 $\text{Fe}_4\text{Y}^*\text{B}_4$
 $\text{Fe}_{4.8}\text{Si}_2^*\text{B}$
 $\text{Fe}_5\text{P}^*\text{B}_2$
 $\text{Fe}_5\text{Si}^*\text{B}_2$
 $\text{Fe}_{14}^*\text{BCe}_2$
 $\text{Fe}_{14}^*\text{BDy}_2$
 $\text{Fe}_{14}^*\text{BER}_2$
 $\text{Fe}_{14}^*\text{CDy}_2$
 $\text{Fe}_{14}^*\text{CER}_2$
 $\text{Fe}_{14}\text{Gd}_2^*\text{B}$
 $\text{Fe}_{14}\text{Gd}_2^*\text{C}$
 $\text{Fe}_{14}\text{H}_4\text{Nd}_2^*\text{B}$
 $\text{Fe}_{14}\text{Ho}_2^*\text{B}$
 $\text{Fe}_{14}\text{Ho}_2^*\text{C}$
 $\text{Fe}_{14}\text{La}_2^*\text{B}$
 $\text{Fe}_{14}\text{Nd}_2^*\text{B}$
 $\text{Fe}_{14}\text{Nd}_2^*\text{C}$
 $\text{Fe}_{14}\text{Pr}_2^*\text{B}$
 $\text{Fe}_{14}\text{Sm}_2^*\text{B}$
 $\text{Fe}_{14}\text{Tb}_2^*\text{B}$
 $\text{Fe}_{14}\text{Tb}_2^*\text{C}$
 $\text{Fe}_{14}\text{Th}_2^*\text{B}$
 $\text{Fe}_{14}\text{Tm}_2^*\text{B}$
 $\text{Fe}_{14}\text{Y}_2^*\text{B}$
 $\text{Fe}_{23}^*(\text{B},\text{C})_6$
 $\text{Fe}_{23}\text{Nd}_2^*\text{B}_3$
 $(\text{Fe},\text{Ir})_{23}^*\text{B}_6$
 $(\text{Fe},\text{Ni})_{23}^*\text{B}_6$
 $(\text{Fe},\text{Re})_{23}^*\text{B}_6$
Fr

Fr

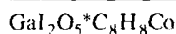
Formation: 7.2.2.5

 $\text{Ga}_m^*\text{B}_6\text{Co}_{23-m}$ $\text{Ga}_m\text{Ni}_{23-m}^*\text{B}_6$ **Ga**

Ga

Reaction with conc. HX: 6.2.5

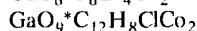
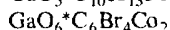
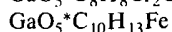
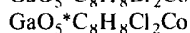
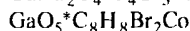
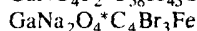
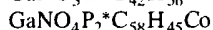
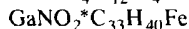
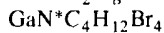
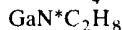
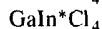
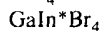
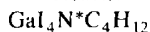
Reaction with elemental K, Na, Li:
6.3Reaction with elemental S, Se, Te:
6.2.3Reaction with GaX_3 : 6.2.2.1Reaction with HgBr_2 : 6.2.2.1Reaction with X_2 : 6.2.2.1Reaction with $[\text{GaCl}_4]^-$: 6.2.2.1 Ga^*Br_2 Ga^*Br_3 $\text{Ga}^*\text{C}_2\text{H}_6\text{Cl}$ $\text{Ga}^*\text{C}_3\text{H}_9$ Ga^*Cl_2 $\text{GaI}_2^*\text{C}_2\text{H}_5$



GaI₃



Reaction with elemental Ga: 6.2.2.1



GaS



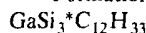
Disproportionation: 6.2.3

Formation: 6.2.3

GaSe



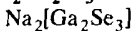
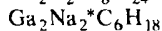
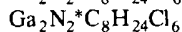
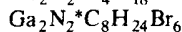
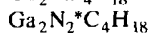
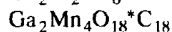
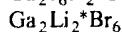
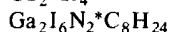
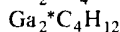
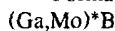
Formation: 6.2.3



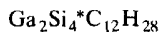
GaTe



Formation: 6.2.3



Formation: 6.2.3



Ga₃K



Formation: 6.3

Ga₃Se₂



Formation: 6.2.3



Ga₄I₆



Formation: 6.2.2.1

Ga₄S₅



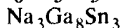
Formation: 6.2.3

Ga₇Rb



Formation: 6.3

Ga₈Na₃Sn₃



Formation: 6.3

Ga₁₃Na₇



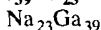
Formation: 6.3

Ga₁₄Li₃

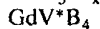
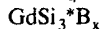
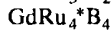
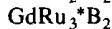
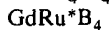
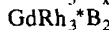
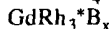
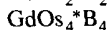
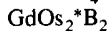
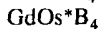
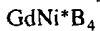
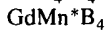
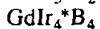
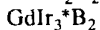
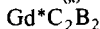
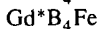
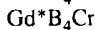
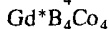
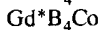
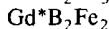
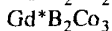
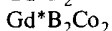


Formation: 6.3

Ga₃₉Na₂₃



Formation: 6.3



$\text{Gd}_2^*\text{BFe}_{14}$
 $\text{Gd}_2^*\text{B}_3\text{Co}_7$
 Gd_2^*B_5
 $\text{Gd}_2^*\text{CFe}_{14}$
 $\text{Gd}_2^*\text{Re}^*\text{B}_6$
 $\text{Gd}_3^*\text{B}_2\text{Co}_7$
 $\text{Gd}_3^*\text{B}_4\text{Co}_{11}$
 $\text{Gd}_5\text{Ge}_3^*\text{B}_x$
 $\text{Ge}_{0.3}\text{Mo}_{1.7}^*\text{B}$
 Ge^*B_{90}
 $\text{GeLi}^*\text{C}_3\text{H}_9$
GeNa
 NaGe

Formation: 7.3.1.3.3

GeNa_2^*Au
 $\text{GeO}_2^*\text{C}_{10}\text{H}_{14}\text{Fe}$
 $\text{GeP}^*\text{C}_{36}\text{H}_{30}\text{Au}$
 $\text{Ge}_{1.4}\text{Ni}_{21.6}^*\text{B}_6$
 $\text{Ge}_2^*\text{B}_6\text{Co}_{21}$
 $\text{Ge}_2^*\text{C}_{36}\text{CdF}_{30}$
 $\text{Ge}_2\text{Hg}^*\text{C}_6\text{H}_{18}$
 $\text{Ge}_2\text{Hg}^*\text{C}_{36}\text{F}_{30}$
 $\text{Ge}_2\text{P}_2\text{Pt}^*\text{C}_{72}\text{H}_{30}\text{CdF}_{30}$
 $\text{Ge}_2\text{P}_2\text{PtZn}^*\text{C}_{72}\text{H}_{30}\text{F}_{30}$
 $\text{Ge}_2\text{Zn}^*\text{C}_{36}\text{F}_{30}$
 $\text{Ge}_3^*\text{B}_x\text{Gd}_5$
 $\text{Ge}_3^*\text{BDy}_5$
 $\text{Ge}_3\text{HgIrOP}_2^*\text{C}_{22}\text{H}_{57}$
 $\text{Ge}_3\text{La}_5^*\text{B}_x$
 $\text{Ge}_3\text{Nb}_5^*\text{B}$
 $\text{Ge}_3\text{Ta}_5^*\text{B}$
 $\text{Ge}_3\text{Tb}_5^*\text{B}_x$
 $\text{Ge}_3\text{V}_5^*\text{B}$
H*F
HK

KH

Reaction with GaR_3 , InR_3 : 6.2.4

HNS₇

S₇NH

Reaction with $\text{Hg}_2(\text{NO}_3)_2$: 8.2.4.1

$\text{HO}_4\text{S}^*\text{Cs}$
 $\text{H}_2\text{FeO}_4^*\text{C}_4$
 $\text{H}_2\text{O}_{10}\text{Os}_3^*\text{C}_{10}$
 H_3^*As
 $\text{H}_3^*\text{AsB}_4\text{F}_6$
 $\text{H}_3\text{BF}_4\text{O}_{12}^*\text{C}_{12}$
 $\text{H}_3\text{HgO}_6\text{Ta}^*\text{C}_7$
H₃N

NH₃

Reaction with alkali metals: 7.2.2.4.4

H₃P

PH₃

Reaction with BF_3 : 6.2.2.1

$\text{H}_3\text{P}^*\text{B}_4\text{F}_6$

H_4^*B_2
 H_4^*C_2
H₄Li₄Rh
 Li_4RhH_4
 Formation: 7.4.1.1, 7.4.2.1
 $\text{H}_4\text{Nd}_2^*\text{BFe}_{14}$
 $\text{H}_5\text{B}_3^*\text{C}_2$
 $\text{H}_5\text{BrHgO}_3\text{W}^*\text{C}_8$
 $\text{H}_5\text{ClCrHgO}_3^*\text{C}_8$
 $\text{H}_5\text{ClHgMoO}_3^*\text{C}_8$
 $\text{H}_5\text{ClHgO}_3\text{W}^*\text{C}_8$
 $\text{H}_5\text{Cl}_2\text{CoHgO}_2^*\text{C}_7$
 $\text{H}_5\text{Cl}_2\text{InMoO}_3^*\text{C}_8$
 $\text{H}_5\text{CrNaO}_3^*\text{C}_8$
 $\text{H}_5\text{FeIO}_2^*\text{C}_7$
 $\text{H}_5\text{GaI}_2^*\text{C}_2$
H₅Li₄Rh
 Li_4RhH_5
 Formation: 7.4.1.1, 7.4.2.1

$\text{H}_5\text{MoNaO}_3^*\text{C}_8$
 $\text{H}_5\text{NaO}_3\text{W}^*\text{C}_8$
 $\text{H}_{5n}\text{Mo}_n\text{Zn}_n^*\text{C}_{5n}$
 $\text{H}_{5n}\text{W}_n\text{Zn}_n^*\text{C}_{5n}$
 $\text{H}_6\text{BBr}^*\text{C}_2$
 $\text{H}_6\text{BBro}_2^*\text{C}_2$
 $\text{H}_6\text{BClO}_2^*\text{C}_2$
 $\text{H}_6\text{BClO}_3\text{Ru}^*\text{C}_7$
 H_6^*B_2
 $\text{H}_6\text{B}_4\text{F}_6\text{S}^*\text{C}_2$
 $\text{H}_6\text{B}_4\text{FeO}_3^*\text{C}_5$
 $\text{H}_6\text{B}_6^*\text{C}_2$
 $\text{H}_6\text{Cd}^*\text{C}_2$
 $\text{H}_6\text{CdFeN}_2\text{O}_4^*\text{C}_4$
 $\text{H}_6\text{ClGa}^*\text{C}_2$
 $\text{H}_6\text{CrO}_3^*\text{C}_8$
 $\text{H}_6\text{Cu}_2\text{FeN}_2\text{O}_4^*\text{C}_4$
 $\text{H}_6\text{MoO}_3^*\text{C}_8$
 $\text{H}_6\text{O}_3\text{W}^*\text{C}_8$
 $\text{H}_6\text{S}^*\text{C}_2$
 $\text{H}_6\text{S}_2^*\text{C}_3$
 $\text{H}_6\text{S}_3^*\text{C}_3$
 $\text{H}_6\text{Zn}^*\text{C}_2$
 $\text{H}_7\text{B}_3\text{FeO}_3^*\text{C}_5$
 $\text{H}_7\text{B}_5^*\text{C}_2$
 $\text{H}_7\text{B}_7^*\text{C}_2$
 $\text{H}_8^*\text{Al}_2\text{B}_4$
 $\text{H}_8\text{BNa}^*\text{C}_6$
 $\text{H}_8\text{BTl}^*\text{C}_6$
 $\text{H}_8\text{B}_3\text{MnO}_3^*\text{C}_7$
 $\text{H}_8\text{B}_4^*\text{C}_2$
 $\text{H}_8\text{B}_5\text{CoO}_4^*\text{C}_4$
 $\text{H}_8\text{B}_6^*\text{C}_2$
 $\text{H}_8\text{B}_8\text{Co}^*\text{C}_4$
 $\text{H}_8\text{BrCo}_2\text{InO}_9^*\text{C}_{12}$

$H_8Br_7CoGaO_5^*C_8$	$H_{10}Cr^*C_{10}$
$H_8ClCo_2GaO_9^*C_{12}$	$H_{10}Cr_2HgO_6^*C_{16}$
$H_8Cl_2CoGaO_5^*C_8$	$H_{10}Fe^*C_{10}$
$H_8Cl_4Pt_2^*C_4$	$H_{10}Fe_2HgO_4^*C_{14}$
$H_8CoGaI_2O_5^*C_8$	$H_{10}Fe_2O_4^*C_{14}$
$H_8Cu^*C_4$	$H_{10}HgMo^*C_{10}$
$H_8GaN^*C_2$	$H_{10}MnO_5Ti^*C_{17}$
$H_8K^*B_5$	$H_{10}MoO_3Zn^*C_{14}$
H_8KO_4Re	$H_{10}Ni^*C_6$
KRe_4H_2O	$H_{10}Ni^*C_8$
Formation: 7.4.1.1	$H_{10}Ru^*C_{10}$
$H_8Li^*B_5$	$H_{10}Zn^*C_4$
$H_8S_2^*C_4$	$H_{10}Zn^*C_{10}$
$H_9Al^*C_3$	$H_{11}AsB_{10}Cl_2^*C_2$
$H_9BBrFeNO_3^*C_7$	$H_{11}B^*C_{10}$
$H_9B^*C_3$	$H_{11}B^*C_{11}$
$H_9B^*C_5$	$H_{11}BCO_2^*C_{13}$
$H_9BCoN_3O_3^*C_3$	$H_{11}BF_3Re^*C_{10}$
$H_9BFeO_3^*C_{13}$	$H_{11}B_4Co^*C_7$
$H_9BFeO_4^*C_9$	$H_{11}B_4Fe^*C_7$
$H_9BK_2N_3Rh^*C_{13}$	$H_{11}B_4Na^*C_4$
$H_9BMn_2O_6^*C_{16}$	$H_{11}B_5^*C_4$
$H_9BO^*C_5$	$H_{11}B_7^*C_2$
$H_9BO^*C_6$	$H_{11}B_9MnNaO_3^*C_5$
$H_9^*B_5$	$H_{11}B_9Ti_2^*C_2$
$H_9B_6^*C$	$H_{11}B_{10}Cl_2Sb^*C_2$
$H_9Br^*C_4$	$H_{11}B_{10}Cl_2Sn^*C_2$
$H_9ClSi^*C_3$	$H_{11}Re^*C_{10}$
$H_9CoO_4Sn^*C_7$	$H_{11}S^*B_9$
$H_9FeN_3O_4Zn^*C_4$	$H_{12}BBRN_2^*C_4$
$H_9Ga^*C_3$	$H_{12}BClN_2^*C_4$
$H_9GeLi^*C_3$	$H_{12}BCO_3^*C_{14}$
$H_9In^*C_3$	$H_{12}BF_3W^*C_{10}$
$H_9K^*B_4$	$H_{12}BMnN_2O_5^*C_9$
$H_9K^*B_6$	$H_{12}BN_2O_5Re^*C_9$
$H_9LiSi^*C_3$	$H_{12}BRh^*C_{10}$
$H_9LiSn^*C_3$	$H_{12}B_2Co_2S_2^*C_{10}$
$H_9MnO_3^*C_{14}$	$H_{12}B_2F_2^*C_8$
$H_9N^*C_3$	$H_{12}B_2F_2FeO_3^*C_{11}$
$H_9P^*C_3$	$H_{12}B_2F_2NiO_2^*C_{10}$
$H_9Ti^*C_3$	$H_{12}B_2O_4^*C_4$
$H_{10}BBR^*C_{12}$	$H_{12}B_3Co^*C_7$
$H_{10}BTi^*C_{11}$	$H_{12}B_4^*C_4$
$H_{10}^*B_4$	$H_{12}B_4FeO_2^*C_9$
$H_{10}B_5MnO_3^*C_3$	$H_{12}B_4Co^*C_7$
$H_{10}^*B_6$	$H_{12}B_8^*C_2$
$H_{10}B_6FeO_4^*C_4$	$H_{12}^*B_{10}Cd$
$H_{10}B_9MnNaO_3P^*C_4$	$H_{12}Br_4GaN^*C_4$
$H_{10}BrInMo_2O_6^*C_{16}$	$H_{12}Cl_4GaN^*C_4$
$H_{10}Cd^*C_4$	$H_{12}Cu^*C_6$
$H_{10}ClFe_2InO_4^*C_{14}$	$H_{12}GaI_4N^*C_4$
$H_{10}Cl_4FeHg_2^*C_{10}$	$H_{12}Ga_2^*C_4$
$H_{10}Cl_{14}FeHg_7^*C_{10}$	$H_{12}K^*B_5$
$H_{10}Co^*C_{10}$	$H_{12}Mo^*C_{10}$

- $H_{12}Ni^*C_6$
 $H_{12}S^*B_{10}$
 $H_{12}W^*C_{10}$
 $H_{12}Zn^*B_{10}$
 $H_{13}B^*C_{12}$
 $H_{13}BCo^*C_{11}$
 $H_{13}BFeO_3^*C_{15}$
 $H_{13}BMn_2O_6^*C_{18}$
 $H_{13}B_4Co^*C_5$
 $H_{13}B_5FeO_2^*C_7$
 $H_{13}B_6Co^*C_7$
 $H_{13}B_6CoS_2^*C_5$
 $H_{13}B_6Fe^*C_7$
 $H_{13}B_9MnO_3P^*C_5$
 $H_{13}FeGaO_5^*C_{10}$
 $H_{13}LiSi_2^*C_5$
 $H_{14}BRh^*C_{15}$
 $H_{14}B_2Co_2O_4^*C_{14}$
 $H_{14}B_2NaRh^*C_{10}$
 $H_{14}B_5Co^*C_5$
 $H_{14}B_6^*C_4$
 $H_{14}B_7Co^*C_7$
 $H_{14}B_8^*C$
 $H_{14}B_8Ni^*C_6$
 $H_{14}^*B_{10}$
 $H_{14}B_{10}^*C_3$
 $H_{14}FeGeO_2^*C_{10}$
 $H_{14}FeO_2Si^*C_{10}$
 $H_{14}FeO_2Sn^*C_{10}$
 $H_{14}MoO_3Sn^*C_{11}$
 $H_{14}Ni^*C_8$
 $H_{14}S^*C_{14}$
 $H_{15}Al^*C_6$
 $H_{15}AlK^*C_6$
 $H_{15}As^*C_{18}$
 $H_{15}As_3F_{12}Hg_2^*C_{18}$
 $H_{15}AuClO_{10}Os_3P^*C_{28}$
 $H_{15}AuClP^*C_{18}$
 $H_{15}AuCoO_4P^*C_{22}$
 $H_{15}BBBr_3N^*C_6$
 $H_{15}BCl_2MnO_4P^*C_{22}$
 $H_{15}BCl_2N_2Pd^*C_5$
 $H_{15}BCo^*C_{16}$
 $H_{15}BCo_3NO_9^*C_{15}$
 $H_{15}BFeN_2O_3^*C_8$
 $H_{15}BLiN^*C_8$
 $H_{15}BLiNSi^*C_7$
 $H_{15}BMnNO_3^*C_{11}$
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 $H_{15}BNbOZn^*C_{11}$
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 $H_{15}B_3Co_2^*C_{12}$
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 $H_{15}B_4Co^*C_9$
 $H_{15}B_4CoFe_2O_6^*C_{15}$
 $H_{15}B_5Co_2S_2^*C_{10}$
 $H_{15}B_5Fe^*C_5$
 $H_{15}B_8Co^*C_7$
 $H_{15}B_8Fe^*C_7$
 $H_{15}B_9NNa^*C_7$
 $H_{15}Co_3OS^*C_{16}$
 $H_{15}F_{12}Hg_2Sb_3^*C_{18}$
 $H_{15}InMo_3O_9^*C_{24}$
 $H_{15}MnNaO_4P^*C_{22}$
 $H_{15}P^*C_{18}$
 $H_{15}Sb^*C_{18}$
 $H_{16}AuO_{10}Os_3P^*C_{28}$
 $H_{16}BF_6PRu^*C_{17}$
 $H_{16}BN^*C_8$
 $H_{16}BNSi^*C_7$
 $H_{16}B_2Co^*C_{12}$
 $H_{16}B_2CrO_4S^*C_{12}$
 $H_{16}B_2F_6MnO_3PS^*C_{11}$
 $H_{16}B_2FeO_3S^*C_{11}$
 $H_{16}B_2Mn_2O_6S^*C_{14}$
 $H_{16}B_2NiO_2S^*C_{10}$
 $H_{16}B_2S^*C_8$
 $H_{16}B_4^*C_6$
 $H_{16}B_4Co_2^*C_{10}$
 $H_{16}B_4Co_2^*C_{12}$
 $H_{16}B_8Ni^*C_7$
 $H_{16}B_9Co^*C_7$
 $H_{16}B_9Cr^*C_7$
 $H_{16}B_9Fe^*C_7$
 $H_{16}B_9Fe^*C_9$
 $H_{16}^*B_{10}$
 $H_{16}B_{10}N^*C_3$
 $H_{16}B_{10}Ni^*C_6$
 $H_{16}Cl_2Rh_2^*C_8$
 $H_{16}Hg^*B_{10}$
 $H_{17}AuBF_4O_{12}P^*C_{30}$
 $H_{17}B^*C_{10}$
 $H_{17}BFe^*C_{17}$
 $H_{17}B_2CoF_2^*C_{13}$
 $H_{17}B_5Co_2^*C_{12}$
 $H_{17}B_5Co_2S^*C_{10}$
 $H_{17}B_5Ni_2^*C_{12}$
 $H_{17}B_7^*C_4$
 $H_{17}B_7Fe^*C_9$
 $H_{17}B_9NNaO_2^*C_9$
 $H_{17}B_9O_3Ru^*C_{11}$
 $H_{17}B_9Ru^*C_8$
 $H_{17}B_{10}Co^*C_7$
 $H_{17}P^*C_{19}$
 $H_{18}AuP^*C_{19}$
 $H_{18}BCo_2NO_6^*C_{14}$
 $H_{18}BN^*C_8$
 $H_{18}B_2Co_2O_4^*C_{24}$

$H_{18}B_2FeO_2^*C_{12}$	$H_{20}B_6Co_2^*C_{14}$
$H_{18}B_2N_2O_2^*C_6$	$H_{20}B_8^*C_8$
$H_{18}B_2NaRh^*C_{20}$	$H_{20}B_8Co_2^*C_{12}$
$H_{18}B_6Co_2^*C_{12}$	$H_{20}B_8Cr_2^*C_{12}$
$H_{18}B_6Fe_3^*C_{12}$	$H_{20}B_9MnO_4^*C_7$
$H_{18}B_7Co^*C_7$	$H_{20}B_{10}Fe^*C_5$
$H_{18}B_7CoNi^*C_{11}$	$H_{20}B_{10}Ni_2^*C_{10}$
$H_{18}^*B_8$	$H_{20}B_{18}CoNaP_2^*C_2$
$H_{18}B_8Ni_2^*C_{10}$	$H_{20}Ti_2^*C_{24}$
$H_{18}B_9Co^*C_5$	$H_{21}Al_3N_2^*C_7$
$H_{18}B_9Co^*C_{11}$	$H_{21}AuB_9NS_2^*C_7$
$H_{18}B_9FeP^*C_7$	$H_{21}B_2CoS^*C_{13}$
$H_{18}B_{10}FeS^*C_7$	$H_{21}B_2F_6FePS^*C_{13}$
$H_{18}Ga_2N_2^*C_4$	$H_{21}B_2FeMnO_3S^*C_{16}$
$H_{18}Ga_2Na_2^*C_6$	$H_{21}B_2NiS^*C_{13}$
$H_{18}Ge_2Hg^*C_6$	$H_{21}B_3Rh_2^*C_{15}$
$H_{18}HgSi_2^*C_6$	$H_{21}B_7Fe^*C_{11}$
$H_{18}K_2Ti_2^*C_6$	$H_{21}B_8Co^*C_8$
$H_{18}Si_2^*C_8$	$H_{21}B_9CoFe^*C_{12}$
$H_{18}Sn_2^*C_6$	$H_{21}B_9Co_2^*C_{12}$
$H_{18}Zn^*C_8$	$H_{21}B_9Fe^*C_{10}$
$H_{19}Al^*C_8$	$H_{21}B_9Fe^*C_{12}$
$H_{19}BCoN^*C_{21}$	$H_{22}AuB_4P^*C_{20}$
$H_{19}BF_3MoO_3P^*C_{26}$	$H_{22}AuB_8NS_2^*C_5$
$H_{19}BF_3O_3PW^*C_{26}$	$H_{22}Au_2Cl_2P_2^*C_{25}$
$H_{19}B_2Co^*C_{12}$	$H_{22}BFeNO_3Si^*C_{13}$
$H_{19}B_2FeNO_3^*C_{12}$	$H_{22}BNSi^*C_{10}$
$H_{19}B_2N^*C_9$	$H_{22}B_2FeNiO_3^*C_{17}$
$H_{19}B_2Rh^*C_{20}$	$H_{22}B_2FeS^*C_{14}$
$H_{19}B_3Co_2^*C_{15}$	$H_{22}B_2Fe_2NiO_6^*C_{20}$
$H_{19}B_3CoFe^*C_{12}$	$H_{22}B_2Fe_2O_3^*C_{17}$
$H_{19}B_3Co_2^*C_{12}$	$H_{22}B_2Fe_2O_4^*C_{26}$
$H_{19}B_9Cr^*C_8$	$H_{22}B_2N_2^*C_6$
$H_{19}B_9Fe^*C_9$	$H_{22}B_2Ni^*C_{14}$
$H_{19}B_9FeS^*C_7$	$H_{22}B_2Ni^*C_{17}$
$H_{19}MoO_3P^*C_{26}$	$H_{22}B_2Ni^*C_{22}$
$H_{19}O_3PW^*C_{26}$	$H_{22}B_2P_2^*C_6$
$H_{20}AlK^*C_8$	$H_{22}B_4Fe^*C_{13}$
$H_{20}AuCrO_3P^*C_{26}$	$H_{22}B_4O_3OsSi_2^*C_{11}$
$H_{20}AuMoO_3P^*C_{26}$	$H_{22}B_4PRh^*C_{21}$
$H_{20}AuO_3PW^*C_{26}$	$H_{22}B_4V^*C_{14}$
$H_{20}BCo^*C_{14}$	$H_{22}B_8Fe^*C_8$
$H_{20}BCoN^*C_{13}$	$H_{22}B_8Hg^*C_8$
$H_{20}BFeNO_3^*C_{13}$	$H_{22}B_9Cr^*C_9$
$H_{20}BLi_2N^*C_{10}$	$H_{22}B_9Fe^*C_{11}$
$H_{20}B_2Co^*C_{22}$	$H_{22}B_{10}Co_2^*C_{12}$
$H_{20}B_2F_2FeS^*C_{14}$	$H_{22}B_{10}Co_2^*C_{14}$
$H_{20}B_2FeN_2O_3^*C_{13}$	$H_{22}^*B_{18}$
$H_{20}B_3Co_3^*C_{15}$	$H_{22}B_{18}Co^*C_4$
$H_{20}B_3CrN_3O_3^*C_{10}$	$H_{22}B_{18}CoNa^*C_4$
$H_{20}B_3CrN_3O_3^*C_{14}$	$H_{22}B_{18}CoNa_2^*C_4$
$H_{20}B_3N_3^*C_7$	$H_{22}B_{20}Hg^*C_4$
$H_{20}B_3N_3^*C_{11}$	$H_{22}B_{20}HgSe^*C_4$
$H_{20}B_4Fe^*C_{12}$	$H_{22}B_{20}HgTe^*C_4$

- $H_{22}B_{20}Ni^*C_2$
 $H_{22}NiS_2^*B_{18}$
 $H_{22}P_2^*C_{25}$
 $H_{22}PdS_2^*B_{18}$
 $H_{23}AuB_5P^*C_{18}$
 $H_{23}BF_2^*C_{22}$
 $H_{23}BMnO_4P^*C_{34}$
 $H_{23}BNi^*C_{19}$
 $H_{23}B_2Co^*C_{14}$
 $H_{23}B_2CoN^*C_{14}$
 $H_{23}B_2O_2Rh^*C_{15}$
 $H_{23}B_4Co^*C_{10}$
 $H_{23}B_5CdClP^*C_{18}$
 $H_{23}B_6Co^*C_{13}$
 $H_{23}B_7Fe^*C_{11}$
 $H_{23}B_9Fe^*C_8$
 $H_{23}B_9Pd^*C_{10}$
 $H_{23}B_9Pt^*C_{10}$
 $H_{23}B_{11}Co^*C_8$
 $H_{24}AuP_2S_2Ti^*C_{26}$
 $H_{24}BCrNaO_7^*C_{17}$
 $H_{24}BFeNO_3Si^*C_{15}$
 $H_{24}BNSi^*C_{12}$
 $H_{24}BORh^*C_{15}$
 $H_{24}BRh^*C_{15}$
 $H_{24}B_2Br_4CoP_2^*C_{26}$
 $H_{24}B_2^*C_{12}$
 $H_{24}B_2F_2Ni^*C_{16}$
 $H_{24}B_2F_2Pt^*C_{16}$
 $H_{24}B_2FeO_3^*C_{15}$
 $H_{24}B_2FeS^*C_{15}$
 $H_{24}B_2N_4^*C_8$
 $H_{24}B_4Co_4^*C_{20}$
 $H_{24}B_4F_4Ni^*C_{16}$
 $H_{24}B_7Co^*C_{13}$
 $H_{24}B_7Co_3^*C_{17}$
 $H_{24}B_9Co^*C_6$
 $H_{24}B_9O_3PW^*C_{11}$
 $H_{24}B_{19}Na_2Ni^*C_4$
 $H_{24}Br_6Ga_2N_2^*C_8$
 $H_{24}Cl_6Ga_2N_2^*C_8$
 $H_{24}Ga_2I_6N_2^*C_8$
 $H_{25}B^*C_{34}$
 $H_{25}BF_6FeNP^*C_{16}$
 $H_{25}BF_6IrP^*C_{21}$
 $H_{25}BF_6PRh^*C_{21}$
 $H_{25}BFeO_3^*C_{37}$
 $H_{25}BMnO_4P^*C_{34}$
 $H_{25}BNiO_2^*C_{36}$
 $H_{25}B_4Co^*C_{14}$
 $H_{25}B_5Fe^*C_{15}$
 $H_{25}B_8Co^*C_{13}$
 $H_{25}B_8Fe^*C_{13}$
 $H_{25}B_9ClIr^*C_8$
 $H_{25}B_9ClRh^*C_8$
 $H_{25}B_{10}N^*C_4$
 $H_{26}As_2Cl_3HgRh^*C_{26}$
 $H_{26}BCo^*C_{21}$
 $H_{26}B_2FeS^*C_{16}$
 $H_{26}B_2Fe_2S^*C_{18}$
 $H_{26}B_2NO_3Re^*C_{13}$
 $H_{26}B_2Ni^*C_{24}$
 $H_{26}B_9CuP^*C_{20}$
 $H_{26}B_9FeO_2^*C_{12}$
 $H_{26}B_9HgP^*C_{20}$
 $H_{26}B_{17}Co^*C_5$
 $H_{26}B_{18}CoP_2^*C_4$
 $H_{26}B_{18}FeP_2^*C_4$
 $H_{26}^*B_{20}$
 $H_{27}Al^*C_{12}$
 $H_{27}As_2Cl_2Rh^*C_{26}$
 $H_{27}B^*C_{12}$
 $H_{27}BCoNSi^*C_{15}$
 $H_{27}BMnN_2O_4P^*C_{26}$
 $H_{27}BN_2Si^*C_{11}$
 $H_{27}B_2CoFe^*C_{19}$
 $H_{27}B_2CoNi^*C_{19}$
 $H_{27}B_2Co_2^*C_{19}$
 $H_{27}B_2Ni_2^*C_{19}$
 $H_{27}B_3Rh_2^*C_{30}$
 $H_{27}B_4CoSi_2^*C_{13}$
 $H_{27}B_4IrOP_2^*C_7$
 $H_{27}B_9N_2Pd^*C_8$
 $H_{27}B_9PRh^*C_{20}$
 $H_{27}B_{18}Fe_2^*C_9$
 $H_{28}B_2Ni^*C_{17}$
 $H_{28}B_2Ni_2^*C_{16}$
 $H_{28}B_4Fe^*C_{16}$
 $H_{28}B_4Ni^*C_{14}$
 $H_{28}B_5CoSi_2^*C_{13}$
 $H_{28}B_9Co^*C_{10}$
 $H_{28}Ga_2Si_4^*C_{12}$
 $H_{29}BNNb^*C_{18}$
 $H_{29}B_2Co^*C_{17}$
 $H_{29}B_2Rh^*C_{17}$
 $H_{29}B_3P_2Pt^*C_{16}$
 $H_{29}B_6CoSi_2^*C_{13}$
 $H_{29}B_7Ni^*C_{14}$
 $H_{29}ClCoN_4O_4P^*C_{26}$
 $H_{29}CoKN_4O_4P^*C_{26}$
 $H_{30}AuB_9NP^*C_{25}$
 $H_{30}AuGeP^*C_{36}$
 $H_{30}Au_2B_8N_2S_4^*C_{10}$
 $H_{30}BClF_{15}IrOP_2^*C_{55}$
 $H_{30}BClMn_2O_8P_2^*C_{44}$
 $H_{30}BCl_3P_2Pt^*C_{36}$
 $H_{30}BN_2Ni_2^*C_{20}$
 $H_{30}B_2Br_2N_2Ti^*C_{16}$

- $\text{H}_{30}\text{B}_2\text{ClN}_2\text{Si}_2\text{V}^*\text{C}_{14}$
 $\text{H}_{30}\text{B}_2\text{Cl}_2\text{N}_2\text{Si}_2\text{Ti}^*\text{C}_{14}$
 $\text{H}_{30}\text{B}_2\text{Cl}_6\text{P}_2\text{Pt}^*\text{C}_{36}$
 $\text{H}_{30}\text{B}_2\text{F}_6\text{P}_2\text{Pt}^*\text{C}_{36}$
 $\text{H}_{30}\text{B}_2\text{FeN}_2^*\text{C}_{16}$
 $\text{H}_{30}\text{B}_2\text{N}_2^*\text{C}_{10}$
 $\text{H}_{30}\text{B}_2\text{Ni}^*\text{C}_{26}$
 $\text{H}_{30}\text{B}_8\text{Fe}_2^*\text{C}_{18}$
 $\text{H}_{30}\text{B}_9\text{CuNP}^*\text{C}_{25}$
 $\text{H}_{30}\text{B}_{18}\text{HgN}_2^*\text{C}_{14}$
 $\text{H}_{30}\text{Br}_4\text{In}_2\text{P}_2^*\text{C}_{12}$
 $\text{H}_{30}\text{CdF}_{30}\text{Ge}_2\text{P}_2\text{Pt}^*\text{C}_{72}$
 $\text{H}_{30}\text{ClIrOP}_2^*\text{C}_{13}$
 $\text{H}_{30}\text{ClIrOP}_2^*\text{C}_{37}$
 $\text{H}_{30}\text{Cl}_3\text{HgIrOP}_2^*\text{C}_{37}$
 $\text{H}_{30}\text{F}_4\text{P}_2\text{PtSi}^*\text{C}_{36}$
 $\text{H}_{30}\text{F}_6\text{HgP}_2\text{Pt}^*\text{C}_{38}$
 $\text{H}_{30}\text{F}_{30}\text{Ge}_2\text{P}_2\text{PtZn}^*\text{C}_{72}$
 $\text{H}_{30}\text{I}_4\text{In}_2\text{P}_2^*\text{C}_{12}$
 $\text{H}_{31}\text{Au}_2\text{BFe}_4\text{O}_{12}\text{P}_2^*\text{C}_{24}$
 $\text{H}_{31}\text{Au}_2\text{BFe}_4\text{O}_{12}\text{P}_2^*\text{C}_{36}$
 $\text{H}_{31}\text{Au}_2\text{BFe}_4\text{O}_{12}\text{P}_2^*\text{C}_{48}$
 $\text{H}_{31}\text{B}_2\text{Ni}_2^*\text{C}_{17}$
 $\text{H}_{31}\text{B}_3\text{Ni}^*\text{C}_{16}$
 $\text{H}_{31}\text{B}_3\text{P}_2\text{Pd}^*\text{C}_{26}$
 $\text{H}_{31}\text{B}_4\text{Ir}_2\text{O}_3\text{P}_2^*\text{C}_{39}$
 $\text{H}_{31}\text{B}_6\text{CoSi}_2^*\text{C}_{13}$
 $\text{H}_{31}\text{B}_9\text{PRh}^*\text{C}_{26}$
 $\text{H}_{31}\text{B}_9\text{Pd}^*\text{C}_{30}$
 $\text{H}_{32}\text{BFe}_4\text{NO}_{12}\text{P}_2^*\text{C}_{48}$
 $\text{H}_{32}\text{B}_4\text{CoMn}_2\text{O}_6\text{S}^*\text{C}_{22}$
 $\text{H}_{32}\text{B}_4\text{Co}_2\text{F}_6\text{PS}_2^*\text{C}_{16}$
 $\text{H}_{32}\text{B}_4\text{CrO}_2\text{S}_2^*\text{C}_{18}$
 $\text{H}_{32}\text{B}_4\text{FeOS}_2^*\text{C}_{17}$
 $\text{H}_{32}\text{B}_4\text{NiS}_2^*\text{C}_{16}$
 $\text{H}_{32}\text{B}_7\text{Cr}^*\text{C}_{17}$
 $\text{H}_{32}\text{B}_9\text{CuNO}_2\text{P}^*\text{C}_{27}$
 $\text{H}_{32}\text{B}_9\text{IrP}_2^*\text{C}_6$
 $\text{H}_{33}\text{AuB}_2\text{CoP}^*\text{C}_{30}$
 $\text{H}_{33}\text{BF}_6\text{FeNOP}_3^*\text{C}_{15}$
 $\text{H}_{33}\text{BMnO}_4\text{P}^*\text{C}_{30}$
 $\text{H}_{33}\text{B}_2\text{CoFe}^*\text{C}_{22}$
 $\text{H}_{33}\text{B}_2\text{CoFeNiO}_3^*\text{C}_{24}$
 $\text{H}_{33}\text{B}_2\text{CoNi}^*\text{C}_{22}$
 $\text{H}_{33}\text{B}_2\text{Co}_2^*\text{C}_{22}$
 $\text{H}_{33}\text{B}_2\text{Ni}_2^*\text{C}_{22}$
 $\text{H}_{33}\text{B}_3\text{Fe}^*\text{C}_{20}$
 $\text{H}_{33}\text{B}_7\text{CoO}^*\text{C}_{17}$
 $\text{H}_{33}\text{B}_8\text{Co}^*\text{C}_{10}$
 $\text{H}_{33}\text{B}_8\text{Cr}^*\text{C}_{17}$
 $\text{H}_{33}\text{B}_9\text{PRh}^*\text{C}_{24}$
 $\text{H}_{33}\text{B}_{10}\text{HgP}^*\text{C}_{20}$
 $\text{H}_{33}\text{CoP}_4^*\text{C}_{20}$
 $\text{H}_{33}\text{GaSi}_3^*\text{C}_{12}$
 $\text{H}_{33}\text{InSi}_3^*\text{C}_{12}$
 $\text{H}_{34}\text{B}_2\text{Cl}_4\text{N}_2\text{Ti}^*\text{C}_{14}$
 $\text{H}_{34}\text{B}_2\text{N}_2^*\text{C}_{14}$
 $\text{H}_{34}\text{B}_2\text{N}_2\text{Ru}^*\text{C}_{20}$
 $\text{H}_{34}\text{B}_2\text{P}_2^*\text{C}_{36}$
 $\text{H}_{34}\text{B}_4\text{Co}_3^*\text{C}_{12}$
 $\text{H}_{34}\text{B}_4\text{Fe}_3\text{O}_6^*\text{C}_{24}$
 $\text{H}_{34}\text{B}_8\text{P}_2\text{Pt}^*\text{C}_{16}$
 $\text{H}_{34}\text{B}_9\text{ClMoO}_2\text{P}_2^*\text{C}_{18}$
 $\text{H}_{34}\text{B}_9\text{N}^*\text{C}_8$
 $\text{H}_{34}\text{B}_{13}\text{CoO}^*\text{C}_{10}$
 $\text{H}_{34}\text{B}_{18}\text{CoNa}^*\text{C}_8$
 $\text{H}_{34}\text{P}_2\text{Pt}^*\text{C}_{38}$
 $\text{H}_{35}\text{B}_5\text{Co}_2^*\text{C}_{20}$
 $\text{H}_{35}\text{B}_9\text{P}_2\text{Pt}^*\text{C}_{28}$
 $\text{H}_{35}\text{B}_{12}\text{CoO}^*\text{C}_{10}$
 $\text{H}_{36}\text{Al}_2^*\text{C}_{16}$
 $\text{H}_{36}\text{Al}_4\text{BN}_3^*\text{C}_{12}$
 $\text{H}_{36}\text{BF}_6\text{FeN}_2\text{P}_3^*\text{C}_{16}$
 $\text{H}_{36}\text{B}_2\text{CrN}_2\text{O}_4^*\text{C}_{20}$
 $\text{H}_{36}\text{B}_2\text{N}_2\text{O}_4^*\text{C}_{20}$
 $\text{H}_{36}\text{B}_2\text{N}_2\text{O}_4\text{W}^*\text{C}_{20}$
 $\text{H}_{36}\text{B}_2\text{ORh}_2^*\text{C}_{24}$
 $\text{H}_{36}\text{B}_3\text{CoP}_2^*\text{C}_{14}$
 $\text{H}_{36}\text{B}_3\text{NRh}_2^*\text{C}_{35}$
 $\text{H}_{36}\text{B}_4\text{Co}_2^*\text{C}_{20}$
 $\text{H}_{36}\text{B}_4\text{P}_2\text{Pt}^*\text{C}_{14}$
 $\text{H}_{36}\text{B}_8\text{OP}_2\text{Pt}^*\text{C}_{17}$
 $\text{H}_{36}\text{B}_{10}\text{P}_2\text{Pd}^*\text{C}_{26}$
 $\text{H}_{36}\text{B}_{10}\text{P}_2\text{Pd}^*\text{C}_{28}$
 $\text{H}_{36}\text{B}_{10}\text{P}_2\text{Pt}^*\text{C}_{26}$
 $\text{H}_{36}\text{B}_{20}\text{HgN}^*\text{C}_4$
 $\text{H}_{37}\text{BPt}^*\text{C}_{42}$
 $\text{H}_{37}\text{B}_3\text{P}_2\text{Pt}^*\text{C}_{12}$
 $\text{H}_{37}\text{B}_3\text{P}_2\text{Pt}^*\text{C}_{28}$
 $\text{H}_{37}\text{B}_4\text{P}_2\text{Pt}^*\text{C}_{14}$
 $\text{H}_{37}\text{B}_5\text{Co}_2^*\text{C}_{20}$
 $\text{H}_{37}\text{B}_{16}\text{CoO}^*\text{C}_{10}$
 $\text{H}_{38}\text{BNRu}^*\text{C}_{22}$
 $\text{H}_{38}\text{BN}_2\text{NbSi}^*\text{C}_{21}$
 $\text{H}_{38}\text{B}_3\text{IrOP}_2^*\text{C}_{37}$
 $\text{H}_{38}\text{B}_4\text{Co}_2\text{N}_2\text{O}_4^*\text{C}_{22}$
 $\text{H}_{38}\text{B}_4\text{N}_2\text{Ni}^*\text{C}_{18}$
 $\text{H}_{38}\text{B}_4\text{OOSp}_2^*\text{C}_{37}$
 $\text{H}_{38}\text{B}_4\text{P}_2\text{Pt}^*\text{C}_{14}$
 $\text{H}_{38}\text{B}_5\text{ClIrOP}_2^*\text{C}_{37}$
 $\text{H}_{38}\text{B}_5\text{CuP}_2^*\text{C}_{36}$
 $\text{H}_{38}\text{B}_5\text{FeN}_3^*\text{C}_{19}$
 $\text{H}_{38}\text{B}_5\text{IrOP}_2^*\text{C}_{37}$
 $\text{H}_{38}\text{B}_5\text{P}_2\text{Pt}^*\text{C}_{13}$
 $\text{H}_{38}\text{B}_9\text{ClRh}_2\text{S}^*\text{C}_{20}$
 $\text{H}_{38}\text{B}_9\text{IrP}_2^*\text{C}_{36}$
 $\text{H}_{38}\text{B}_9\text{NO}_2\text{W}^*\text{C}_{16}$
 $\text{H}_{39}\text{B}_3\text{Co}_2^*\text{C}_{24}$

- $\text{H}_{39}\text{B}_4\text{CuP}_2^*\text{C}_{36}$
 $\text{H}_{39}\text{B}_5\text{OOSp}_2^*\text{C}_{37}$
 $\text{H}_{39}\text{B}_5\text{P}_2\text{Pt}^*\text{C}_{13}$
 $\text{H}_{39}\text{B}_6\text{CoP}_2^*\text{C}_{14}$
 $\text{H}_{39}\text{B}_6\text{CuP}_2^*\text{C}_{36}$
 $\text{H}_{39}\text{B}_7\text{CoP}_2^*\text{C}_{14}$
 $\text{H}_{39}\text{B}_7\text{P}_2\text{Ru}^*\text{C}_{38}$
 $\text{H}_{39}\text{B}_8\text{IrO}_2\text{P}_2^*\text{C}_{38}$
 $\text{H}_{39}\text{B}_9\text{ClIrP}_2\text{S}^*\text{C}_{36}$
 $\text{H}_{39}\text{B}_{27}\text{Cu}_3\text{N}_3\text{O}_6^*\text{C}_{27}$
 $\text{H}_{40}\text{AlFeNO}_2^*\text{C}_{33}$
 $\text{H}_{40}\text{BNiP}_2^*\text{C}_{48}$
 $\text{H}_{40}\text{B}_2\text{Co}_2\text{N}_2\text{O}_4^*\text{C}_{24}$
 $\text{H}_{40}\text{B}_2\text{FeN}_2\text{O}^*\text{C}_{21}$
 $\text{H}_{40}\text{B}_2\text{N}_2\text{Ni}^*\text{C}_{20}$
 $\text{H}_{40}\text{B}_2\text{N}_2\text{O}_4\text{Rh}_2^*\text{C}_{24}$
 $\text{H}_{40}\text{B}_2\text{N}_2\text{Rh}_2^*\text{C}_{24}$
 $\text{H}_{40}\text{B}_6\text{Ni}^*\text{C}_{20}$
 $\text{H}_{40}\text{B}_7\text{CoP}_2^*\text{C}_{14}$
 $\text{H}_{40}\text{B}_7\text{P}_2\text{Rh}^*\text{C}_{14}$
 $\text{H}_{40}\text{B}_7\text{P}_2\text{Rh}^*\text{C}_{38}$
 $\text{H}_{40}\text{B}_8\text{CoP}_2^*\text{C}_{14}$
 $\text{H}_{40}\text{B}_{12}\text{P}_2\text{Pt}_2^*\text{C}_{16}$
 $\text{H}_{40}\text{B}_{16}\text{P}_2\text{Pt}^*\text{C}_{16}$
 $\text{H}_{40}\text{Cu}_3\text{IrP}_2^*\text{C}_{52}$
 $\text{H}_{40}\text{FeGaNO}_2^*\text{C}_{33}$
 $\text{H}_{40}\text{FeInNO}_2^*\text{C}_{33}$
 $\text{H}_{41}\text{B}_8\text{ClCo}_2^*\text{C}_{20}$
 $\text{H}_{41}\text{B}_8\text{IrO}_2\text{P}_2^*\text{C}_{39}$
 $\text{H}_{41}\text{B}_8\text{IrP}_2^*\text{C}_{38}$
 $\text{H}_{41}\text{B}_9\text{ClP}_2\text{Rh}^*\text{C}_{38}$
 $\text{H}_{41}\text{B}_9\text{MoNO}_3\text{P}_2\text{Ti}^*\text{C}_{41}$
 $\text{H}_{41}\text{B}_9\text{NO}_3\text{P}_2\text{TiW}^*\text{C}_{41}$
 $\text{H}_{41}\text{B}_9\text{P}_2\text{Pt}^*\text{C}_{14}$
 $\text{H}_{41}\text{B}_9\text{P}_2\text{PtS}^*\text{C}_{12}$
 $\text{H}_{41}\text{B}_9\text{P}_2\text{PtS}^*\text{C}_{36}$
 $\text{H}_{41}\text{B}_{10}\text{P}_2\text{RhS}^*\text{C}_{36}$
 $\text{H}_{42}\text{AuB}_{18}\text{N}^*\text{C}_{20}$
 $\text{H}_{42}\text{AuNP}_3\text{S}^*\text{C}_{49}$
 $\text{H}_{42}\text{Au}_2\text{B}_{18}\text{N}_2\text{S}_4^*\text{C}_{14}$
 $\text{H}_{42}\text{BF}_6\text{FeNO}_9\text{P}_4^*\text{C}_{17}$
 $\text{H}_{42}\text{BF}_6\text{FeNP}_4^*\text{C}_{17}$
 $\text{H}_{42}\text{B}_2\text{BrP}_2\text{Pt}^*\text{C}_{40}$
 $\text{H}_{42}\text{B}_4\text{Fe}_2\text{S}_2\text{Zn}^*\text{C}_{26}$
 $\text{H}_{42}\text{B}_4\text{P}_2\text{Pt}^*\text{C}_{16}$
 $\text{H}_{42}\text{B}_8\text{Co}_2^*\text{C}_{20}$
 $\text{H}_{42}\text{B}_8\text{P}_2\text{Pt}^*\text{C}_{14}$
 $\text{H}_{42}\text{B}_8\text{P}_2\text{Pt}^*\text{C}_{37}$
 $\text{H}_{42}\text{B}_9\text{P}_2\text{Rh}^*\text{C}_{14}$
 $\text{H}_{42}\text{B}_9\text{P}_2\text{Rh}^*\text{C}_{38}$
 $\text{H}_{42}\text{B}_{10}\text{P}_2\text{Pd}^*\text{C}_{36}$
 $\text{H}_{42}\text{B}_{10}\text{P}_2\text{Pt}^*\text{C}_{12}$
 $\text{H}_{42}\text{B}_{10}\text{P}_2\text{Pt}^*\text{C}_{36}$
 $\text{H}_{42}\text{B}_{18}\text{CuN}^*\text{C}_{12}$
 $\text{H}_{42}\text{B}_{18}\text{P}_2\text{Pt}^*\text{C}_{16}$
 $\text{H}_{43}\text{AuB}_2\text{PRh}^*\text{C}_{34}$
 $\text{H}_{43}\text{B}_4\text{CoN}_2^*\text{C}_{23}$
 $\text{H}_{43}\text{B}_7\text{P}_2\text{Pt}^*\text{C}_{16}$
 $\text{H}_{43}\text{B}_9\text{MoO}_2\text{P}_2^*\text{C}_{38}$
 $\text{H}_{43}\text{B}_9\text{P}_2\text{Ru}^*\text{C}_{38}$
 $\text{H}_{43}\text{B}_{10}\text{P}_2\text{Rh}^*\text{C}_{38}$
 $\text{H}_{43}\text{InMnNO}_5^*\text{C}_{35}$
 $\text{H}_{44}\text{B}_2\text{Fe}_2^*\text{C}_{44}$
 $\text{H}_{44}\text{B}_4\text{Co}_2\text{Fe}^*\text{C}_{28}$
 $\text{H}_{44}\text{B}_9\text{IrP}_2^*\text{C}_{36}$
 $\text{H}_{45}\text{AlCoNO}_4\text{P}_2^*\text{C}_{58}$
 $\text{H}_{45}\text{AuClP}_3\text{Pt}^*\text{C}_{54}$
 $\text{H}_{45}\text{Au}_3\text{O}_5\text{P}_3\text{V}^*\text{C}_{59}$
 $\text{H}_{45}\text{B}_2\text{Cl}_6\text{P}_3\text{Pt}^*\text{C}_{54}$
 $\text{H}_{45}\text{B}_7\text{NiP}_2^*\text{C}_{16}$
 $\text{H}_{45}\text{B}_9\text{NOP}_2\text{Rh}^*\text{C}_{44}$
 $\text{H}_{45}\text{CoGaNO}_4\text{P}_2^*\text{C}_{58}$
 $\text{H}_{45}\text{CoInNO}_4\text{P}_2^*\text{C}_{58}$
 $\text{H}_{45}\text{P}_3\text{Pt}^*\text{C}_{54}$
 $\text{H}_{46}\text{B}_4\text{Cl}_2\text{Rh}_2^*\text{C}_{24}$
 $\text{H}_{46}\text{B}_4\text{Pt}^*\text{C}_{24}$
 $\text{H}_{47}\text{B}_2\text{CoKN}_4\text{O}_4\text{P}^*\text{C}_{50}$
 $\text{H}_{47}\text{B}_2\text{CoN}_4\text{O}_4\text{P}^*\text{C}_{50}$
 $\text{H}_{47}\text{B}_4\text{Rh}^*\text{C}_{24}$
 $\text{H}_{48}\text{Al}_2\text{P}_2\text{Pt}^*\text{C}_{42}$
 $\text{H}_{48}\text{B}_2\text{Br}_4\text{CoP}_4^*\text{C}_{52}$
 $\text{H}_{48}\text{B}_2\text{CoI}_4\text{P}_4^*\text{C}_{52}$
 $\text{H}_{48}\text{B}_2\text{CoP}_4^*\text{C}_{44}$
 $\text{H}_{48}\text{B}_2\text{N}_2\text{Ni}_2\text{Si}_2^*\text{C}_{22}$
 $\text{H}_{48}\text{B}_4\text{Cl}_2\text{Rh}_2^*\text{C}_{24}$
 $\text{H}_{48}\text{B}_4\text{Ni}^*\text{C}_{24}$
 $\text{H}_{48}\text{B}_4\text{Pt}^*\text{C}_{24}$
 $\text{H}_{48}\text{B}_6\text{Co}_2\text{S}_3^*\text{C}_{24}$
 $\text{H}_{48}\text{B}_9\text{NO}_2\text{W}^*\text{C}_{49}$
 $\text{H}_{48}\text{B}_9\text{P}_2\text{Rh}^*\text{C}_{45}$
 $\text{H}_{49}\text{B}_3\text{P}_2\text{Pt}^*\text{C}_{42}$
 $\text{H}_{49}\text{B}_5\text{ClOOSp}_3\text{Pt}^*\text{C}_{45}$
 $\text{H}_{49}\text{B}_8\text{Co}_3^*\text{C}_{28}$
 $\text{H}_{49}\text{CoP}_4^*\text{C}_{52}$
 $\text{H}_{50}\text{B}_8\text{CoFeP}_2^*\text{C}_{20}$
 $\text{H}_{50}\text{B}_8\text{FeP}_2\text{Pt}^*\text{C}_{20}$
 $\text{H}_{50}\text{B}_{18}\text{Ni}_2\text{O}_2\text{P}_2^*\text{C}_{42}$
 $\text{H}_{51}\text{B}_5\text{Co}_2\text{P}_3^*\text{C}_{20}$
 $\text{H}_{52}\text{B}_2\text{CoP}_4^*\text{C}_{44}$
 $\text{H}_{52}\text{B}_2\text{CoP}_4^*\text{C}_{76}$
 $\text{H}_{52}\text{B}_9\text{NO}_2\text{W}^*\text{C}_{49}$
 $\text{H}_{52}\text{B}_{18}\text{P}_2\text{Rh}_2^*\text{C}_{16}$
 $\text{H}_{54}\text{Al}_2\text{K}_2^*\text{C}_{24}$
 $\text{H}_{54}\text{B}_3\text{O}_9\text{P}_3\text{Rh}_2^*\text{C}_{39}$
 $\text{H}_{54}\text{B}_3\text{P}_3\text{Rh}_2^*\text{C}_{39}$
 $\text{H}_{54}\text{B}_4\text{FeNi}^*\text{C}_{30}$
 $\text{H}_{54}\text{B}_4\text{NiP}_4^*\text{C}_{54}$
 $\text{H}_{54}\text{B}_8\text{IrP}_3^*\text{C}_{55}$

$H_{54}B_8P_4Pt_2^*C_{32}$
 $H_{54}B_{18}P_2Rh_2^*C_{40}$
 $H_{55}B_8OOp_3^*C_{56}$
 $H_{55}B_8OP_3Ru^*C_{56}$
 $H_{56}B_4Co_2Ni_2O_2^*C_{36}$
 $H_{56}GaNO_3W^*C_{42}$
 $H_{56}InNO_3W^*C_{42}$
 $H_{57}AsB_3CoN_4O_4^*C_{62}$
 $H_{57}Ge_3HgIrOP_2^*C_{22}$
 $H_{57}HgIrOP_2Si_3^*C_{22}$
 $H_{58}B_2Cl_2CoP_4^*C_{64}$
 $H_{58}B_9IrP_4Pt^*C_{42}$
 $H_{58}B_{10}Ni_3^*C_{30}$
 $H_{60}Au_4I_2P_4^*C_{72}$
 $H_{60}Au_6Co_2O_8P_4^*C_{80}$
 $H_{60}B_3Co_2N_3^*C_{30}$
 $H_{60}B_{10}CoP_3^*C_{21}$
 $H_{60}B_{18}P_4Pt_2^*C_{32}$
 $H_{60}P_4Pt^*C_{72}$
 $H_{62}B_{18}CuN_2^*C_{20}$
 $H_{62}B_{18}P_2Rh_2^*C_{52}$
 $H_{64}B_4Co_2FeS_4^*C_{32}$
 $H_{66}Au_4I_2P_6^*C_{75}$
 $H_{66}B_{10}P_2Pt^*C_{24}$
 $H_{66}B_{18}P_2Rh_2^*C_{24}$
 $H_{67}B_9P_2Rh^*C_{46}$
 $H_{67}B_{19}P_3Rh^*C_{58}$
 $H_{68}B_2CoP_4^*C_{76}$
 $H_{68}B_3Cl_6P_4Rh^*C_{76}$
 $H_{68}B_{18}NO_2P_2Sm_3^*C_{48}$
 $H_{70}Cu_4Ir_2P_2^*C_{100}$
 $H_{71}B_5P_4Pt_2^*C_{28}$
 $H_{72}Al_6B_6N_6^*C_{24}$
 $H_{72}P_4Pt_2^*C_{32}$
 $H_{73}B_3CoN_4O_4P^*C_{54}$
 $H_{73}B_6Co_2Ni_2^*C_{43}$
 $H_{75}Au_3F_6IrNO_3P_6^*C_{90}$
 $H_{76}Al_2Si_8^*C_{28}$
 $H_{76}In_2Si_8^*C_{28}$
 $H_{78}B_8Co_2Ni_3^*C_{46}$
 $H_{79}B_6Co_2Ni_2^*C_{46}$
 $H_{84}Au_{11}Cl_{21}I_3P_7^*C_{126}$
 $H_{84}Au_{11}F_{21}I_3P_7^*C_{126}$
 $H_{85}B_6Fe_2Ni_2^*C_{50}$
 $H_{87}Au_5N_2O_6P_8^*C_{100}$
 $H_{90}Al_5K_3^*C_{40}$
 $H_{90}Au_8F_6IP_7^*C_{108}$
 $H_{104}Au_6N_2O_6P_8^*C_{108}$
 $H_{104}Au_9F_{18}N_2P_9^*C_{116}$
 $H_{105}Au_7P_7^*C_{126}$
 $H_{105}Au_8N_2O_6P_7^*C_{126}$
 $H_{105}Au_{11}N_3P_7^*C_{129}$
 $H_{105}Au_{11}N_3P_7S_3^*C_{129}$
 $H_{108}Hg_6P_{12}Rh_4^*C_{36}$

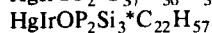
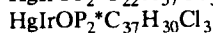
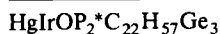
$H_{110}Au_{11}F_{18}P_{13}^*C_{80}$
 $H_{110}Au_{13}Cl_2F_{18}P_{13}^*C_{80}$
 $H_{120}Au_8N_2O_6P_8^*C_{144}$
 $H_{120}Au_9B_3F_{12}P_8^*C_{144}$
 $H_{120}Au_9Cl_3O_{12}P_8^*C_{144}$
 $H_{120}Au_9F_{18}P_{11}^*C_{144}$
 $H_{120}Au_9N_3O_9P_8^*C_{144}$
 $H_{120}Au_{11}Cl_2F_{18}P_{11}^*C_{144}$
 $H_{120}Au_{11}F_6N_2P_9S_2^*C_{146}$
 $H_{126}Au_9N_9O_{21}P_8^*C_{162}$
 $H_{130}Au_{11}N_3P_{10}S_3^*C_{138}$
 $H_{132}Au_{13}N_9O_{30}P_{12}^*C_{150}$
 $H_{165}Au_9N_3P_5S_3^*C_{93}$
 $H_{166}Au_6B_2P_6^*C_{162}$
 $H_{168}Au_9B_3F_{12}O_{24}P_8^*C_{168}$
 $H_{168}Au_9F_{18}P_{11}^*C_{168}$
 $H_{168}Au_9N_3O_9P_8^*C_{168}$
 $H_{180}Au_{55}Cl_6P_{12}^*C_{216}$
 $Hf_{0.45}^*Al_{0.5}B_{0.05}$
 Hf^*B
 Hf^*B_2
 $Hf^*B_2Co_3$
 $HfIr_3^*B$
 $HfIr_3^*B_4$
 $HfMo_4^*B_5$
 $HfW_4^*B_5$
 $Hf_2^*B_6Co_{21}$
 $Hf_2Ni_{21}^*B$
 $Hf_3Ir_5^*B_2$
 $Hf_5^*Al_3B$
 $Hf_9Mo_4^*B$
 $Hf_9Os_4^*B$
 $Hf_9Re_4^*B$
 $Hf_9W_4^*B$
Hg

Hg

Reaction with AsF_5 , SbF_5 : 8.2.5.1

Reaction with $Co_2(CO)_8$, $Mn_2(CO)_{10}$:
8.3.3.4

$Hg^*B_{10}H_{16}$
 Hg^*Ba
 Hg^*Ba_2
 Hg^*Br_2
 $Hg^*C_2F_6$
 $Hg^*C_4H_{22}B_{20}$
 $Hg^*C_6H_{18}Ge_2$
 $Hg^*C_8H_{22}B_8$
 $Hg^*C_{36}F_{30}Ge_2$
 Hg^*Ca
 Hg^*Ca_2
 Hg^*Ca_3
 Hg^*Cl_2
 Hg^*Cs

**HgK**

Formation: 7.3.2.2

HgLi

Formation: 7.3.2.2

HgLi₂

Formation: 7.3.2.2

HgLi₃

Formation: 7.3.2.2

HgLi₆

Formation: 7.3.2.2

HgMg

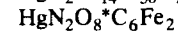
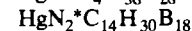
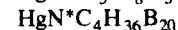
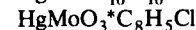
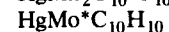
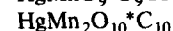
Formation: 7.3.4.1.2

HgMg₂

Formation: 7.3.4.1.2

HgMg₃

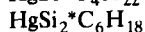
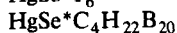
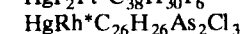
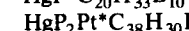
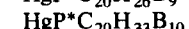
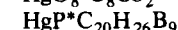
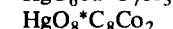
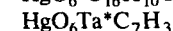
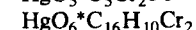
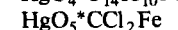
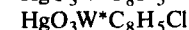
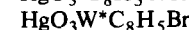
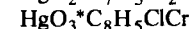
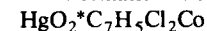
Formation: 7.3.4.1.2

**HgNa**

Formation: 7.3.2.2

HgNa₃

Formation: 7.3.2.2

**HgSr**

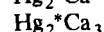
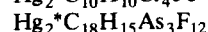
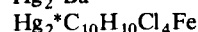
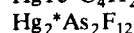
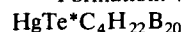
Formation: 7.3.4.1.4

HgSr₂

Formation: 7.3.4.1.4

HgSr₃

Formation: 7.3.4.1.4

**Hg₂K**

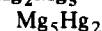
Formation: 7.3.2.2

Hg₂Li

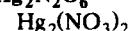
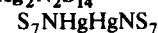
Formation: 7.3.2.2

Hg₂Mg

Formation: 7.3.4.1.2

Hg₂Mg₅

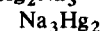
Formation: 7.3.4.1.2

Hg₂N₂O₆Reaction with S_7NH : 8.2.4.1**Hg₂N₂S₁₄**

Formation: 8.2.4.1

Hg₂Na

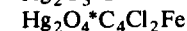
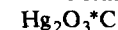
Formation: 7.3.2.2

Hg₂Na₃

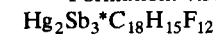
Formation: 7.3.2.2

Hg₂Na₅

Formation: 7.3.2.2

**Hg₂Rb**

Formation: 7.3.2.2



Hg₂Sr
 SrHg₂
 Formation: 7.3.4.1.4

Hg₂Sr₃
 Sr₃Hg₂
 Formation: 7.3.4.1.4

Hg_{2,7}K
 KHg_{2,7}
 Formation: 7.3.2.2

Hg₃*AsF₆
 Hg₃*As₂F₁₂

Hg₃*Ca

Hg₃*Ca₅

Hg₃K
 KHg₃
 Formation: 7.3.2.2

Hg₃Li
 LiHg₃
 Formation: 7.3.2.2

Hg₃Mg₅
 Mg₅Hg₃
 Formation: 7.3.4.1.2

Hg₃O₃₃Os₉*C₃₃

Hg₃O₃₃Ru₉*C₃₃

Hg₃Sb₄*F₂₂

Hg₃Sr
 SrHg₃
 Formation: 7.3.4.1.4

Hg₄*As₂F₁₂

Hg₄*Ba

Hg₄*Cs

Hg₄*Cs₃

Hg₄K
 KHg₄
 Formation: 7.3.2.2

Hg₄O₉*C₂Cl₂

Hg₄Rb₃
 Rb₃Hg₄
 Formation: 7.3.2.2

Hg₆*Cs

Hg₆Na
 NaHg₆
 Formation: 7.3.2.2

Hg₆P₁₂Rh₄*C₃₆H₁₀₈

Hg₆Rb
 RbHg₆
 Formation: 7.3.2.2

Hg₇*C₁₀H₁₀Cl₁₄Fe

Hg₇K₅
 K₅Hg₇
 Formation: 7.3.2.2

Hg₇Rb₂
 Rb₂Hg₇
 Formation: 7.3.2.2

Hg₈K
 KHg₈
 Formation: 7.3.2.2

Hg₈Na₇
 Na₇Hg₈
 Formation: 7.3.2.2

Hg₈Rb₇
 Rb₇Hg₈
 Formation: 7.3.2.2

Hg₉O₁₈*C₁₈Co₆

Hg₉Rb₂
 Rb₂Hg₉
 Formation: 7.3.2.2

Hg₉Sr₂
 Sr₂Hg₉
 Formation: 7.3.4.1.4

Hg₁₁*Ca
Hg₁₁K
 KHg₁₁
 Formation: 7.3.2.2

Hg₁₁Rb
 RbHg₁₁
 Formation: 7.3.2.2

Hg₁₁Sr
 SrHg₁₁
 Formation: 7.3.4.1.4

Hg₁₂*Cs
Hg₁₆Na
 NaHg₁₆
 Formation: 7.3.2.2

Hg₁₈Rb₅
 Rb₅Hg₁₈
 Formation: 7.3.2.2

Ho_{1-x}*B₆Ca_x
 Ho_{1-x}La_x*B₆

Ho*BCo₄

Ho*B₂

Ho*B₂Co₂

Ho*B₂Co₃

Ho*B₂Fe₂

Ho*B₄Co

Ho*B₄Co₄

Ho*B₄Cr

Ho*B₄Dy

Ho*B₄Fe

Ho*B₆₆

Ho*CB₂

Ho*C₂B₂

HoIr₃*B₂

HoIr₄*B₄

HoMn*B₄

HoMo*B₄

HoOs*B₂

HoOs*B₄

$\text{HoOs}_4^*\text{B}_4$
 HoRe^*B_4
 $\text{HoRh}_3^*\text{B}_x$
 $\text{HoRh}_3^*\text{B}_2$
 $\text{HoRh}_4^*\text{B}_4$
 HoRu^*B_2
 HoRu^*B_4
 $\text{HoRu}_3^*\text{B}_2$
 $\text{HoRu}_4^*\text{B}_4$
 HoV^*B_4
 HoW^*B_4
 $\text{Ho}_2^*\text{BFe}_{14}$
 $\text{Ho}_2^*\text{B}_3\text{Co}_7$
 $\text{Ho}_2^*\text{CFe}_{14}$
 $\text{Ho}_2\text{Ni}_{15}^*\text{B}_6$
 $\text{Ho}_2\text{Ni}_{15}^*\text{B}_9$
 $\text{Ho}_2\text{Re}^*\text{B}_6$
 $\text{Ho}_3^*\text{B}_4\text{Co}_{11}$
 $\text{Ho}_3\text{Ni}_{19}^*\text{B}_{10}$
 $\text{IO}_2^*\text{C}_7\text{H}_5\text{Fe}$
 $\text{IP}_7^*\text{C}_{108}\text{H}_{90}\text{Au}_8\text{F}_6$
 $\text{I}_2^*\text{C}_2\text{H}_5\text{Ga}$
 I_2In

InI_2

Reaction with electron pair bases:

6.2.2.1

Reaction with MX: 6.2.2.1

Reaction with PR_3 : 6.2.2.1

$\text{I}_2\text{O}_5^*\text{C}_8\text{H}_8\text{CoGa}$

$\text{I}_2\text{P}_4^*\text{C}_{72}\text{H}_{60}\text{Au}_4$

$\text{I}_2\text{P}_6^*\text{C}_{75}\text{H}_{66}\text{Au}_4$

I_3^*B

I_3^*Ga

$\text{I}_3\text{P}_7^*\text{C}_{126}\text{H}_{84}\text{Au}_{11}\text{Cl}_{21}$

$\text{I}_3\text{P}_7^*\text{C}_{126}\text{H}_{84}\text{Au}_{11}\text{F}_{21}$

I_4^*B_2

$\text{I}_4\text{In}_2\text{P}_2^*\text{C}_{12}\text{H}_{30}$

$\text{I}_4\text{N}^*\text{C}_4\text{H}_{12}\text{Ga}$

$\text{I}_4\text{P}_4^*\text{C}_{52}\text{H}_{48}\text{B}_2\text{Co}$

I_6^*Ga_4

$\text{I}_6\text{N}_2^*\text{C}_8\text{H}_{24}\text{Ga}_2$

I_7^*B_7

I_8^*B_8

I_9^*B_9

$\text{I}_{10}^*\text{B}_{10}$

In

In

Reaction with elemental S, Se, Te:

6.2.3

Reaction with In_2S_3 : 6.2.3

In^*Br_2

In^*Br_3

$\text{In}^*\text{Br}_4\text{Ga}$

$\text{In}^*\text{C}_3\text{H}_9$

In^*Cl

In^*Cl_2

$\text{In}^*\text{Cl}_4\text{Ga}$

In^*I_2

$\text{InMnNO}_5^*\text{C}_{35}\text{H}_{43}$

$\text{InMn}_3\text{O}_{15}^*\text{C}_{15}$

$\text{InMoO}_3^*\text{C}_8\text{H}_5\text{Cl}_2$

$\text{InMo}_2\text{O}_6^*\text{C}_{16}\text{H}_{10}\text{Br}$

$\text{InMo}_3\text{O}_9^*\text{C}_{24}\text{H}_{15}$

$\text{InNO}_2^*\text{C}_{33}\text{H}_{40}\text{Fe}$

$\text{InNO}_3\text{W}^*\text{C}_{42}\text{H}_{56}$

$\text{InNO}_4\text{P}_2^*\text{C}_{58}\text{H}_{45}\text{Co}$

$\text{InNa}_2\text{O}_4^*\text{C}_4\text{Br}_3\text{Fe}$

$\text{InNi}_3^*\text{B}_{0.5}$

$\text{InO}_4^*\text{C}_{14}\text{H}_{10}\text{ClFe}_2$

$\text{InO}_6^*\text{C}_6\text{Br}_4\text{Co}_2$

$\text{InO}_9^*\text{C}_{12}\text{H}_8\text{BrCo}_2$

$\text{InO}_{12}^*\text{C}_{12}\text{Co}_3$

$\text{InO}_{15}\text{Re}_3^*\text{C}_{15}$

InS

InS

Formation: 6.2.3

InSe

InSe

Disproportionation: 6.2.3

Formation: 6.2.3

$\text{InSi}_3^*\text{C}_{12}\text{H}_{33}$

InTe

InTe

Formation: 6.2.3

$\text{In}_2\text{Ni}_{21}^*\text{B}_6$

In_2O_3

In_2O_3

Reaction with M: 6.2.3

$\text{In}_2\text{P}_2^*\text{C}_{12}\text{H}_{30}\text{Br}_4$

$\text{In}_2\text{P}_2^*\text{C}_{12}\text{H}_{30}\text{I}_4$

In_2S_3

In_2S_3

Reaction with elemental In: 6.2.3

Reaction with $\text{La}_2\text{O}_2\text{S}$: 6.2.3

$\text{In}_2\text{Si}_8^*\text{C}_{28}\text{H}_{76}$

$\text{In}_3\text{O}_{16}^*\text{C}_{16}\text{Br}_3\text{Co}_4$

$\text{In}_3\text{Sc}^*\text{B}_x$

In_4Se_3

In_4Se_3

Formation: 6.2.3

In_4Te_4

In_4Te_4

Formation: 6.2.3

$\text{In}_5\text{Na}_{24}\text{O}_{15}$

$\text{Na}_{24}[\text{In}_5\text{O}_{15}]$

Formation: 6.2.3

In_5S_4
 In_5S_4
 Formation: 6.2.3
 $\text{In}_6\text{La}_{10}\text{O}_6\text{S}_{17}$
 $\text{In}_6\text{La}_{10}\text{O}_6\text{S}_{17}$
 Formation: 6.2.3
 In_6S_7
 In_6S_7
 Formation: 6.2.3
 In_6Se_7
 In_6Se_7
 Formation: 6.2.3
 $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$
 $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$
 Formation: 6.2.3
 $\text{Ir}_{0.8}\text{*BFe}_{2.2}$
 Ir*B
 $\text{Ir*B}_{1.35}$
 $\text{Ir*B}_2\text{Cr}_2$
 $\text{Ir*C}_8\text{H}_{25}\text{B}_9\text{Cl}$
 $\text{IrKP}_4\text{*F}_{12}$
 IrLi
 LiIr
 Formation: 7.4.1.1, 7.4.2.1
 $\text{IrMg}_2\text{*B}_2$
 IrMo*B_2
 $\text{IrMo}_2\text{*B}_2$
 $\text{IrNO}_3\text{P}_6\text{*C}_{60}\text{H}_{75}\text{Au}_3\text{F}_6$
 $\text{IrOP}_2\text{*C}_7\text{H}_{27}\text{B}_4$
 $\text{IrOP}_2\text{*C}_{13}\text{H}_{30}\text{Cl}$
 $\text{IrOP}_2\text{*C}_{22}\text{H}_{57}\text{Ge}_3\text{Hg}$
 $\text{IrOP}_2\text{*C}_{37}\text{H}_{30}\text{Cl}$
 $\text{IrOP}_2\text{*C}_{37}\text{H}_{30}\text{Cl}_3\text{Hg}$
 $\text{IrOP}_2\text{*C}_{37}\text{H}_{38}\text{B}_3$
 $\text{IrOP}_2\text{*C}_{37}\text{H}_{38}\text{B}_5$
 $\text{IrOP}_2\text{*C}_{37}\text{H}_{38}\text{B}_5\text{Cl}$
 $\text{IrOP}_2\text{*C}_{55}\text{H}_{30}\text{BClF}_{15}$
 $\text{IrOP}_2\text{Si}_3\text{*C}_{22}\text{H}_{57}\text{Hg}$
 $\text{IrO}_2\text{P}_2\text{*C}_{38}\text{H}_{39}\text{B}_8$
 $\text{IrO}_2\text{P}_2\text{*C}_{39}\text{H}_{41}\text{B}_8$
 $\text{IrP*C}_{21}\text{H}_{25}\text{BF}_6$
 $\text{IrP}_2\text{*C}_6\text{H}_{32}\text{B}_9$
 $\text{IrP}_2\text{*C}_{36}\text{H}_{38}\text{B}_9$
 $\text{IrP}_2\text{*C}_{36}\text{H}_{44}\text{B}_9$
 $\text{IrP}_2\text{*C}_{38}\text{H}_{41}\text{B}_8$
 $\text{IrP}_2\text{*C}_{52}\text{H}_{40}\text{Cu}_3$
 $\text{IrP}_2\text{S*C}_{36}\text{H}_{39}\text{B}_9\text{Cl}$
 $\text{IrP}_3\text{*C}_{55}\text{H}_{54}\text{B}_8$
 $\text{IrP}_4\text{Pt*C}_{42}\text{H}_{58}\text{B}_9$
 $\text{IrV}_2\text{*B}_2$
 IrW*B_2
 $\text{Ir}_2\text{*B}_2\text{Ca}$
 $\text{Ir}_2\text{*B}_6\text{Co}_{21}$
 $\text{Ir}_2\text{O}_3\text{P}_2\text{*C}_{39}\text{H}_{31}\text{B}_4$

$\text{Ir}_2\text{P}_2\text{*C}_{100}\text{H}_{70}\text{Cu}_4$
 $\text{Ir}_2\text{P}_4\text{*Cl}_2\text{F}_{12}$
 $\text{Ir}_2\text{Sr*B}_2$
 $\text{Ir}_{2.5}\text{Mo}_{2.5}\text{*B}_5$
 $\text{Ir}_3\text{*BHf}$
 $\text{Ir}_3\text{*B}_2\text{Ce}$
 $\text{Ir}_3\text{*B}_2\text{Dy}$
 $\text{Ir}_3\text{*B}_2\text{Er}$
 $\text{Ir}_3\text{*B}_2\text{Gd}$
 $\text{Ir}_3\text{*B}_2\text{Ho}$
 $\text{Ir}_3\text{*B}_4\text{Hf}$
 $\text{Ir}_3\text{La*B}_2$
 Ir_3Li
 LiIr_3
 Formation: 7.4.1.1, 7.4.2.1
 $\text{Ir}_3\text{Lu*B}_2$
 $\text{Ir}_3\text{Nd*B}_2$
 $\text{Ir}_3\text{Pr*B}_2$
 $\text{Ir}_3\text{Sc*B}_x$
 $\text{Ir}_3\text{Sc*B}_2$
 $\text{Ir}_3\text{Sc*B}_4$
 $\text{Ir}_3\text{Sm*B}_2$
 $\text{Ir}_3\text{Tb*B}_2$
 $\text{Ir}_3\text{Th*B}_2$
 $\text{Ir}_3\text{Tm*B}_2$
 $\text{Ir}_3\text{U*B}_2$
 $\text{Ir}_3\text{W}_2\text{*B}_6$
 $\text{Ir}_3\text{Y*B}_2$
 $\text{Ir}_3\text{Yb*B}_2$
 $\text{Ir}_3\text{Zr*B}_x$
 $\text{Ir}_3\text{Zr*B}_4$
 $\text{Ir}_4\text{*B}_4\text{Ce}$
 $\text{Ir}_4\text{*B}_4\text{Er}$
 $\text{Ir}_4\text{*B}_4\text{Eu}$
 $\text{Ir}_4\text{*B}_4\text{Gd}$
 $\text{Ir}_4\text{*B}_4\text{Ho}$
 $\text{Ir}_4\text{La*B}_4$
 $\text{Ir}_4(\text{Lu,Y})*\text{B}_4$
 $\text{Ir}_4\text{Nd*B}_4$
 $\text{Ir}_4\text{Pr*B}_4$
 $\text{Ir}_4\text{Sm*B}_4$
 $\text{Ir}_4\text{Tb*B}_4$
 $\text{Ir}_4\text{Th*B}_4$
 $\text{Ir}_4\text{Y*B}_4$
 $\text{Ir}_5\text{*B}_2\text{Hf}_3$
 $\text{Ir}_{12}\text{*B}_7\text{Ba}$
 $(\text{Ir,Mn})_{23}\text{*B}_6$

K

K

Industrial manufacture: 7.2.2.3.1
 Liquid coolant: 7.2.2.4.4
 Reaction with elemental Ga: 6.3
 Reaction with R_3Al , R_4Al_2 , HAIR_2 :
 6.2.4

- K*Au**
K*Au₂
K*Au₄
K*Au₅
K*B₄H₉
K*B₅H₈
K*B₅H₁₂
K*B₆
K*B₆H₉
K*C₆H₁₅Al
K*C₈H₂₀Al
K*Cd₇
K*Cd₁₃
K*Cl
K*Ga₃
K*H
K*Hg
K*Hg₂
K*Hg_{2.7}
K*Hg₃
K*Hg₄
K*Hg₈
K*Hg₁₁
KN₄O₄P*C₂₆H₂₉Co
KN₄O₄P*C₅₀H₄₇B₂Co
KO₄Re*H₈
KP₄*F₁₂Ir
KP₄Rh*F₁₂
KSn₂*Au₄
KZn
KZn
 Formation: 7.3.2.2
KZn₁₃
KZn₁₃
 Formation: 7.3.2.1.3, 7.3.2.2
K₂*Au
K₂*C₂₄H₅₄Al₂
K₂N₃Rh*C₁₃H₉B
K₂Re
K₂Re
 Formation: 7.4.1.1
K₂Tl₂*C₆H₁₈
K₃*C₄₀H₉₀Al₅
K₅*Hg₇
La_x*B₆Ho_{1-x}
La*BCo₄
La*B₂Co₂
La*B₂Ir₃
La*B₄Co₄
La*B₄Ir₄
La*B₆
La*C₂B₂
LaOs₂*B₂
LaOs₄*B₄
LaRh₃*B_x
LaRh₃*B₂
LaRu₂*B₂
LaRu₄*B₄
La₂*BFe₁₄
La₂Ni₅*B₄
La₂O₂S
La₂O₂S
 Reaction with In₂S₃: 6.2.3
La₃*B₄Co₁₁
La₃N₄*B₂
La₅*B₄Ge₃
La₁₀O₆S₁₇*In₆
Li
Li
 Industrial manufacture: 7.2.2.1.1
 Reaction with elemental Ga: 6.3
Li*Ag
Li*Au₃
Li*B₅H₈
Li*Br
Li*C₃H₉Ge
Li*Cd
Li*Cd₃
Li*C_u₄
Li*Hg
Li*Hg₂
Li*Hg₃
Li*Ir
Li*Ir₃
LiN*C₈H₁₅B
LiNSi*C₇H₁₅B
LiPd
LiPd
 Formation: 7.4.1.1, 7.4.2.1
LiPd₂
LiPd₂
 Formation: 7.4.1.1, 7.4.2.1
LiPd₇
LiPd₇
 Formation: 7.4.1.1, 7.4.2.1
LiPt
LiPt
 Formation: 7.4.1.1
LiPt₂
LiPt₂
 Formation: 7.4.1.1
LiPt₃*B
LiPt₇
LiPt₇
 Formation: 7.4.1.1
LiRh
LiRh
 Formation: 7.4.1.1

- LiRh₃**
 LiRh₃
 Formation: 7.4.2.1
- LiSi***C₃H₉
**LiSi₂*C₅H₁₃
LiSn*C₃H₉**
- LiSr₇**
 LiSr₇
 In phase diagram: 7.2.6.1.1
 Preparation: 7.2.6.1.3
 X-ray identification: 7.2.6.1.2
- LiSr₈**
 LiSr₈
 In phase diagram: 7.2.6.1.1
 Preparation: 7.2.6.1.3
 X-ray identification: 7.2.6.1.2
- LiZn**
 LiZn
 Formation: 7.3.2.2
- LiZn₂**
 LiZn₂
 Formation: 7.3.2.2
- LiZn₄**
 LiZn₄
 Formation: 7.3.2.2
- Li_{1,2}Ni_{2,5}***B₂
Li₂*Br₆Ga₂
Li₂*Ca
Li₂*Hg
Li₂N*C₁₀H₂₀B
- Li₂O**
 Li₂O
 Source of Li metal: 7.2.2.1.1
- Li₂Pt**
 Li₂Pt
 Formation: 7.4.1.1
- Li₂Sr₃**
 Li₂Sr₃
 In phase diagram: 7.2.6.1.1
 Preparation: 7.2.6.1.3
 X-ray identification: 7.2.6.1.2
- Li₂Zn₃**
 Li₂Zn₃
 Formation: 7.3.2.2
- Li₂Zn₅**
 Li₂Zn₅
 Formation: 7.3.2.2
- Li₃***Au
Li₃*Cd
Li₃*Ga₁₄
Li₃*Hg
Li₃Ni₁₆*B₈
Li₃Ni₂₀*B₆
Li₃Pd
- Li₃Pd**
 Formation: 7.4.1.1, 7.4.2.1
- Li₃Pd₂**
 Li₃Pd₂
 Formation: 7.4.1.1, 7.4.2.1
- Li₄***Au₅
Li₄*Ba
Li₄Rh*H₄
Li₄Rh*H₅
Li₅*Au₃
Li₅Pd
 Li₅Pd
 Formation: 7.4.1.1, 7.4.2.1
- Li₅Pt**
 Li₅Pt
 Formation: 7.4.1.1, 7.4.2.1
- Li₆***Hg
- Li₇Pd₇**
 Li₇Pd₇
 Formation: 7.4.2.1
- Li₉***Ag₄
Li₉Pt
 Li₉Pt
 Formation: 7.4.1.1, 7.4.2.1
- Li₁₀***Ag₃
Li₁₂*Ag
Li₁₅*Au₄
Li₁₅Pd₄
 Li₁₅Pd₄
 Formation: 7.4.1.1, 7.4.2.1
- Li₁₅Pt₄**
 Li₁₅Pt₄
 Formation: 7.4.1.1
- Li₂₃Sr₆**
 Li₂₃Sr₆
 In phase diagram: 7.2.6.1.1
 Preparation: 7.2.6.1.3
 X-ray identification: 7.2.6.1.2
- Lu***AlB₄
Lu*BCo₄
Lu*B₂
Lu*B₂Co₃
Lu*B₂Fe₂
Lu*B₂Ir₃
Lu*B₄
Lu*B₄Co
Lu*B₄Co₄
Lu*B₄Co₁₁
Lu*B₄Cr
Lu*B₄Fe
Lu*C₂B₂
LuOs*B₂
LuOs₃*B₂
LuOs₄*B₄

- LuRh₃*B_x
 LuRh₃*B₂
 LuRh₄*B₄
 LuRu*B₂
 LuRu₃*B₂
 LuRu₄*B₄
 (Lu,Y)*B₄Ir₄
 Lu₂Ni₃*B₆
 Lu₂Ni₁₅*B₆
 Lu₂Ni₁₅*B₉
 Lu₂Ni₂₁*B₆
 Lu₄Ni₂₉*B₁₀
 Lu₅Ni₁₉*B₆
 Mg_m*B₆Co_{23-m}
 Mg*AlB₁₄
 Mg*Au
 Mg*Au₃
 Mg*B₂
 Mg*B₄
 Mg*Be₁₃
 Mg*Ca
 Mg*Cd
 Mg*Cd₃
 Mg*Cu
 Mg*Cu₂
 Mg*Cu₄
 Mg*Hg
 Mg*Hg₂
 MgNi_{2.5}*B₂
 MgSr
 MgSr
 Matrix isolation: 7.2.5.1.1
 MgZn
 MgZn
 Formation: 7.3.4.1.2
 Mg₂*Au
 Mg₂*B₂Ir
 Mg₂*B₁₄
 Mg₂*Ba
 Mg₂*Ca
 Mg₂*Cu
 Mg₂*Hg
 Mg₂Sr
 Mg₂Sr
 In phase diagram: 7.2.5.1.1
 Preparation: 7.2.5.1.3
 X-ray identification: 7.2.5.1.1
 Mg₂Th
 Mg₂Th
 Formation: 7.4.2.1
 Mg₂Zn₃
 Mg₂Zn₃
 Formation: 7.3.4.1.2
 Mg₂Zn₁₁
 Mg₂Zn₁₁
 Formation: 7.3.2.1.2, 7.3.4.1.2
 Mg₃*Ag
 Mg₃*Au
 Mg₃*Cd
 Mg₃*Hg
 Mg_{3.5}Ni_{19.5}*B₆
 Mg₄Sr
 Mg₄Sr
 In phase diagram: 7.2.5.1.1
 Preparation: 7.2.5.1.3
 X-ray identification: 7.2.5.1.1
 Mg₅*Au₂
 Mg₅*Hg₂
 Mg₅*Hg₃
 Mg₅Rh₁₃*B₁₁
 Mg₇Zn₃
 Mg₇Zn₃
 Formation: 7.3.4.1.2
 Mg₁₇*Ba₂
 Mg₁₇*Ca₂
 Mg₁₇Sr₂
 Mg₁₇Sr₂
 In phase diagram: 7.2.5.1.1
 Preparation: 7.2.5.1.3
 X-ray identification: 7.2.5.1.1
 Mg₂₃*Ba₆
 Mg₂₃*Ca₆
 Mg₂₃Sr₆
 Mg₂₃Sr₆
 In phase diagram: 7.2.5.1.1
 Preparation: 7.2.5.1.3
 X-ray identification: 7.2.5.1.1
 Mg₂₃Th₆
 Mg₂₃Th₆
 Formation: 7.4.2.1
 Mg₅₁Zn₂₀
 Mg₅₁Zn₂₀
 Formation: 7.3.4.1.2
 Mn_{0.5}Re_{1.5}*B
 Mn*Ag
 Mn*B
 Mn*B₂
 Mn*B₄
 Mn*B₄Ce
 Mn*B₄Dy
 Mn*B₄Er
 Mn*B₄Gd
 Mn*B₄Ho
 Mn*B₂₃
 MnMo*B₂
 MnMo₄*B₅
 MnNO₃*C₁₁H₁₅B

$\text{MnNO}_5^*\text{C}_{35}\text{H}_{43}\text{In}$
 $\text{MnN}_2\text{O}_4\text{P}^*\text{C}_{26}\text{H}_{27}\text{B}$
 $\text{MnN}_2\text{O}_5^*\text{C}_9\text{H}_{12}\text{B}$
 $\text{MnNaO}_3^*\text{C}_5\text{H}_{11}\text{B}_9$
 $\text{MnNaO}_3\text{P}^*\text{C}_4\text{H}_{10}\text{B}_9$
 $\text{MnNaO}_4\text{P}^*\text{C}_{22}\text{H}_{15}$
 $\text{MnNaO}_5^*\text{C}_5$
 $\text{MnO}_3^*\text{C}_3\text{H}_{10}\text{B}_5$
 $\text{MnO}_3^*\text{C}_7\text{H}_8\text{B}_3$
 $\text{MnO}_3^*\text{C}_{14}\text{H}_9$
 $\text{MnO}_3\text{P}^*\text{C}_5\text{H}_{13}\text{B}_9$
 $\text{MnO}_3\text{PS}^*\text{C}_{11}\text{H}_{16}\text{B}_2\text{F}_6$
 $\text{MnO}_3\text{S}^*\text{C}_{16}\text{H}_{21}\text{B}_2\text{Fe}$
 $\text{MnO}_4^*\text{C}_7\text{H}_{20}\text{B}_9$
 $\text{MnO}_4\text{P}^*\text{C}_{22}\text{H}_{15}\text{BCl}_2$
 $\text{MnO}_4\text{P}^*\text{C}_{30}\text{H}_{33}\text{B}$
 $\text{MnO}_4\text{P}^*\text{C}_{34}\text{H}_{23}\text{B}$
 $\text{MnO}_4\text{P}^*\text{C}_{34}\text{H}_{25}\text{B}$
 $\text{MnO}_5\text{Ti}^*\text{C}_{17}\text{H}_{10}$
 $\text{MnO}_9^*\text{C}_9\text{CoHg}$
 MnTb^*B_4
 MnU^*B_4
 MnV^*B_2
 MnW^*B_2
 MnW_4^*B_5
 MnY^*B_4
 $\text{Mn}_2^*\text{AlB}_2$
 Mn_2^*B
 $\text{Mn}_2\text{Ni}^*\text{B}_6$
 $\text{Mn}_2\text{O}_6^*\text{C}_{16}\text{H}_9\text{B}$
 $\text{Mn}_2\text{O}_6^*\text{C}_{18}\text{H}_{13}\text{B}$
 $\text{Mn}_2\text{O}_6\text{S}^*\text{C}_{14}\text{H}_{16}\text{B}_2$
 $\text{Mn}_2\text{O}_6\text{S}^*\text{C}_{22}\text{H}_{32}\text{B}_4\text{Co}$
 $\text{Mn}_2\text{O}_8\text{P}_2^*\text{C}_{44}\text{H}_{30}\text{BCl}$
 $\text{Mn}_2\text{O}_{10}^*\text{C}_{10}$
 $\text{Mn}_2\text{O}_{10}^*\text{C}_{10}\text{Cd}$
 $\text{Mn}_2\text{O}_{10}^*\text{C}_{10}\text{Hg}$
 $\text{Mn}_2\text{O}_{10}\text{Ti}^*\text{C}_{10}\text{Cl}$
 $\text{Mn}_2\text{O}_{10}\text{Zn}^*\text{C}_{10}$
 Mn_3^*B_4
 $\text{Mn}_3^*\text{B}_6\text{Co}_{20}$
 $\text{Mn}_3\text{O}_{15}^*\text{C}_{15}\text{In}$
 $\text{Mn}_3\text{O}_{15}\text{Ti}^*\text{C}_{15}$
 $(\text{Mn},\text{Mo})_3^*\text{B}_2$
 Mn_4^*B
 $\text{Mn}_4\text{O}_{18}^*\text{C}_{18}\text{Ga}_2$
 $\text{Mn}_5\text{P}^*\text{B}_2$
 $\text{Mn}_5\text{Si}^*\text{B}_2$
 $\text{Mn}_{23}^*(\text{B},\text{C})_6$
 $(\text{Mn},\text{Re})_{23}^*\text{B}_6$
 $\text{Mo}_n\text{Zn}_n^*\text{C}_{5n}\text{H}_{5n}$
 $\text{Mo}_{0.4}^*\text{BFe}_{2.6}$
 $\text{Mo}_{1-x}^*\text{B}_3$
 $\text{Mo}_{1-x}\text{Rh}_{1-x}^*\text{B}_3$
 Mo^*Ag
 Mo^*AlB
 Mo^*B
 Mo^*BCo
 Mo^*B_2
 $\text{Mo}^*\text{B}_2\text{Ir}$
 $\text{Mo}^*\text{B}_2\text{Mn}$
 $\text{Mo}^*\text{B}_{2.3}$
 Mo^*B_4
 $\text{Mo}^*\text{B}_4\text{Dy}$
 $\text{Mo}^*\text{B}_4\text{Er}$
 $\text{Mo}^*\text{B}_4\text{Gd}$
 $\text{Mo}^*\text{B}_4\text{Ho}$
 Mo^*Be_2
 $\text{Mo}^*\text{Be}_{12}$
 Mo^*CB_2
 $\text{Mo}^*\text{C}_{10}\text{H}_{10}\text{Hg}$
 $\text{Mo}^*\text{C}_{10}\text{H}_{12}$
 $\text{MoNO}_3\text{P}_2\text{Ti}^*\text{C}_{41}\text{H}_{41}\text{B}_9$
 $\text{MoNaO}_3^*\text{C}_8\text{H}_5$
 $\text{MoO}_2\text{P}_2^*\text{C}_{18}\text{H}_{34}\text{B}_9\text{Cl}$
 $\text{MoO}_2\text{P}_2^*\text{C}_{38}\text{H}_{43}\text{B}_9$
 $\text{MoO}_3^*\text{C}_8\text{H}_5\text{CHg}$
 $\text{MoO}_3^*\text{C}_8\text{H}_5\text{Cl}_2\text{In}$
 $\text{MoO}_3^*\text{C}_8\text{H}_6$
 $\text{MoO}_3\text{P}^*\text{C}_{26}\text{H}_{19}$
 $\text{MoO}_3\text{P}^*\text{C}_{26}\text{H}_{19}\text{BF}_3$
 $\text{MoO}_3\text{P}^*\text{C}_{26}\text{H}_{20}\text{Au}$
 $\text{MoO}_3\text{Sn}^*\text{C}_{11}\text{H}_{14}$
 $\text{MoO}_3\text{Zn}^*\text{C}_{14}\text{H}_{10}$
 MoOs^*B_2
 MoRu^*B_2
 MoTb^*B_4
 MoTh^*B_4
 MoU^*B_4
 MoY^*B_4
 $(\text{Mo},\text{Ni})^*\text{B}$
 $(\text{Mo},\text{Ru})^*\text{B}$
 $(\text{Mo},\text{Ti})^*\text{B}$
 $\text{Mo}_{1.7}^*\text{BGe}_{0.3}$
 Mo_2^*B
 $\text{Mo}_2^*\text{B}_2\text{Co}$
 $\text{Mo}_2^*\text{B}_2\text{Fe}$
 $\text{Mo}_2^*\text{B}_2\text{Ir}$
 Mo_2^*B_5
 $\text{Mo}_2^*\text{B}_6\text{Co}_{21}$
 $\text{Mo}_2\text{Ni}^*\text{B}_2$
 $\text{Mo}_2\text{O}_6^*\text{C}_{16}\text{H}_{10}\text{BrIn}$
 $\text{Mo}_2\text{Os}^*\text{B}_2$
 $\text{Mo}_{2.5}^*\text{B}_5\text{Ir}_{2.5}$
 $\text{Mo}_3^*\text{B}_3\text{Co}$
 $\text{Mo}_3^*\text{B}_3\text{Fe}$
 $\text{Mo}_3\text{Ni}^*\text{B}_3$
 $\text{Mo}_3\text{O}_9^*\text{C}_{24}\text{H}_{15}\text{In}$

- (Mo,Ru)₃*B₂
 (Mo,Ru)₃*B₄
 Mo₄*BHf₉
 Mo₄*B₅Hf
 Mo₄*B₅Mn
 Mo₄Zr₉*B
 Mo_{4.5}Re_{15.5}*B
 Mo₅Si*B₂
 Mo₄₀O₆₂*In₁₁
 N_nO_{3n}P₁₂*C₁₅₀H₁₃₂Au₁₃
 N*C₂H₈Ga
 N*C₃H₉
 N*C₃H₁₆B₁₀
 N*C₄H₁₂Br₄Ga
 N*C₄H₁₂Cl₄Ga
 N*C₄H₁₂GaI₄
 N*C₄H₂₅B₁₀
 N*C₄H₃₆B₂₀Hg
 N*C₆H₁₅BBr₃
 N*C₈H₁₅BLi
 N*C₈H₁₆B
 N*C₈H₁₈B
 N*C₈H₃₄B₉
 N*C₉H₁₉B₂
 N*C₁₀H₂₀BLi₂
 N*C₁₂H₄₂B₁₈Cu
 N*C₁₃H₂₀BCo
 N*C₁₄H₂₃B₂Co
 N*C₂₀H₄₂AuB₁₈
 N*C₂₁H₁₉BCo
 N*H₃
 NNa*C₇H₁₅B₉
 NNaO₂*C₉H₁₇B₉
 NNb*C₁₈H₂₉B
 NOP₂Rh*C₄₄H₄₅B₉
 NOP₃*C₁₅H₃₃BF₆Fe
 NO₂*C₃₃H₄₀AlFe
 NO₂*C₃₃H₄₀FeGa
 NO₂*C₃₃H₄₀FeIn
 NO₂P*C₂₇H₃₂B₉Cu
 NO₂P₂Sm₃*C₄₈H₆₈B₁₈
 NO₂W*C₁₆H₃₈B₉
 NO₂W*C₄₉H₄₈B₉
 NO₂W*C₄₉H₅₂B₉
 NO₃*C₇H₉BBrFe
 NO₃*C₁₁H₁₅BMn
 NO₃*C₁₂H₁₉B₂Fe
 NO₃*C₁₃H₂₀BFe
 NO₃P₂Tl*C₄₁H₄₁B₉Mo
 NO₃P₂TlW*C₄₁H₄₁B₉
 NO₃P₈*C₉₀H₇₅Au₃F₈Ir
 NO₃Si*C₁₃H₂₂BFe
 NO₃Si*C₁₅H₂₄BFe
 NO₃W*C₄₂H₅₆Ga
 NO₃W*C₄₂H₅₆In
 NO₄P₂*C₅₈H₄₅AlCo
 NO₄P₂*C₅₈H₄₅CoGa
 NO₄P₂*C₅₈H₄₅CoIn
 NO₅*C₃₅H₄₃InMn
 NO₅Re*C₁₃H₂₆B₂
 NO₆*C₁₄H₁₈BCo₂
 NO₉*C₁₅H₁₅BCo₃
 NO₉P₄*C₁₇H₄₂BF₆Fe
 NO₁₂P₂*C₄₈H₃₂BF₆Fe
 NP*C₁₆H₂₅BF₆Fe
 NP*C₂₅H₃₀AuB₉
 NP*C₂₅H₃₀B₉Cu
 NP₃S*C₄₉H₄₂Au
 NP₄*C₁₇H₄₂BF₆Fe
 NRh₂*C₃₅H₃₆B₃
 NRu*C₂₂H₃₈B
 NS₂*C₅H₂₂AuB₈
 NS₂*C₇H₂₁AuB₉
 NS₇*H
 NSi*C₇H₁₅BLi
 NSi*C₇H₁₆B
 NSi*C₁₀H₂₂B
 NSi*C₁₂H₂₄B
 NSi*C₁₅H₂₇BCo
 NU*B
 N₂*C₄H₁₂BBr
 N₂*C₄H₁₂BCl
 N₂*C₄H₁₈Ga₂
 N₂*C₅H₁₅B
 N₂*C₆H₂₂B₂
 N₂*C₇H₂₁Al₃
 N₂*C₈H₂₄Br₆Ga₂
 N₂*C₈H₂₄Cl₆Ga₂
 N₂*C₈H₂₄Ga₂I₆
 N₂*C₁₀H₃₀B₂
 N₂*C₁₄H₃₀B₁₈Hg
 N₂*C₁₄H₃₄B₂
 N₂*C₁₆H₃₀B₂Fe
 N₂*C₂₀H₆₂B₁₈Cu
 N₂*C₂₃H₄₃B₄Co
 N₂NbSi*C₂₁H₃₈B
 N₂Ni*C₁₈H₃₈B₄
 N₂Ni*C₂₀H₄₀B₂
 N₂Ni₂*C₂₀H₃₀B
 N₂Ni₂Si₂*C₂₂H₄₈B₂
 N₂O*C₂₁H₄₀B₂Fe
 N₂O₂*C₆H₁₈B₂
 N₂O₃*C₈H₁₅BFe
 N₂O₃*C₁₃H₂₀B₂Fe
 N₂O₄*C₄H₆CdFe
 N₂O₄*C₄H₆Cu₂Fe
 N₂O₄*C₂₀H₃₆B₂
 N₂O₄*C₂₀H₃₆B₂Cr

$N_2O_4 \cdot C_{22}H_{38}B_4Co_2$
 $N_2O_4 \cdot C_{24}H_{40}B_2Co_2$
 $N_2O_4P \cdot C_{26}H_{27}BMn$
 $N_2O_4Rh_2 \cdot C_{24}H_{40}B_2$
 $N_2O_4W \cdot C_{20}H_{36}B_2$
 $N_2O_5 \cdot C_9H_{12}BMn$
 $N_2O_5Re \cdot C_9H_{12}B$
 $N_2O_6 \cdot Hg_2$
 $N_2O_6P_7 \cdot C_{126}H_{105}Au_8$
 $N_2O_6P_8 \cdot C_{100}H_{87}Au_5$
 $N_2O_6P_8 \cdot C_{108}H_{104}Au_6$
 $N_2O_6P_8 \cdot C_{144}H_{120}Au_8$
 $N_2O_8 \cdot C_6Fe_2Hg$
 $N_2P_3 \cdot C_{16}H_{36}BF_6Fe$
 $N_2P_9 \cdot C_{116}H_{104}Au_9F_{18}$
 $N_2P_9S_2 \cdot C_{146}H_{120}Au_{11}F_6$
 $N_2Pd \cdot C_5H_{15}BCl_2$
 $N_2Pd \cdot C_8H_{27}B_9$
 $N_2Rh_2 \cdot C_{24}H_{40}B_2$
 $N_2Ru \cdot C_{20}H_{34}B_2$
 $N_2S_4 \cdot C_{10}H_{30}Au_2B_8$
 $N_2S_4 \cdot C_{14}H_{42}Au_2B_{18}$
 $N_2S_{14} \cdot Hg_2$
 $N_2Si \cdot C_{11}H_{27}B$
 $N_2Si_2Ti \cdot C_{14}H_{30}B_2Cl_2$
 $N_2Si_2V \cdot C_{14}H_{30}B_2Cl$
 $N_2Ti \cdot C_{14}H_{34}B_2Cl_4$
 $N_2Ti \cdot C_{16}H_{30}B_2Br_2$
 $N_3 \cdot B_3Cl_6$
 $N_3 \cdot C_7H_{20}B_3$
 $N_3 \cdot C_{11}H_{20}B_3$
 $N_3 \cdot C_{12}H_{36}Al_4B$
 $N_3 \cdot C_{19}H_{38}B_5Fe$
 $N_3 \cdot C_{30}H_{60}B_3Co_2$
 $N_3O_3 \cdot C_3H_9BCo$
 $N_3O_3 \cdot C_{10}H_{20}B_3Cr$
 $N_3O_3 \cdot C_{14}H_{20}B_3Cr$
 $N_3O_4Zn \cdot C_4H_9Fe$
 $N_3O_6 \cdot C_{27}H_{39}B_{27}Cu_3$
 $N_3O_9P_8 \cdot C_{144}H_{120}Au_9$
 $N_3O_9P_8 \cdot C_{168}H_{168}Au_9$
 $N_3P_5S_3 \cdot C_{93}H_{165}Au_9$
 $N_3P_7 \cdot C_{129}H_{105}Au_{11}$
 $N_3P_7S_3 \cdot C_{129}H_{105}Au_{11}$
 $N_3P_{10}S_3 \cdot C_{138}H_{130}Au_{11}$
 $N_3Rh \cdot C_{13}H_9BK_2$
 $N_4 \cdot B_2Ce_3$
 $N_4 \cdot B_2La_3$
 $N_4 \cdot C_8H_{24}B_2$
 $N_4Nd_3 \cdot B_2$
 $N_4O_4 \cdot C_{62}H_{57}AsB_3Co$
 $N_4O_4P \cdot C_{26}H_{29}ClCo$
 $N_4O_4P \cdot C_{26}H_{29}CoK$
 $N_4O_4P \cdot C_{50}H_{47}B_2Co$

$N_4O_4P \cdot C_{50}H_{47}B_2CoK$
 $N_4O_4P \cdot C_{54}H_{73}B_3Co$
 $N_4Pr_3 \cdot B_2$
 $N_6 \cdot Ba$
 $N_6 \cdot C_{24}H_{72}Al_6B_6$
 $N_9O_{21}P_8 \cdot C_{162}H_{126}Au_9$
 $Na_x \cdot B_6Ba_{1-x}$
 $Na_x \cdot B_{15}$
Na

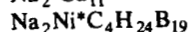
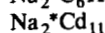
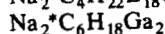
Na

Industrial manufacture: 7.2.2.2.1

Liquid coolant: 7.2.2.4.4

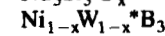
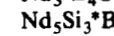
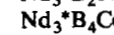
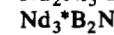
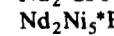
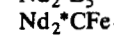
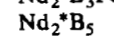
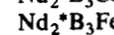
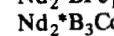
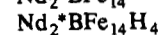
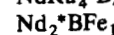
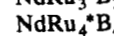
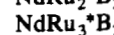
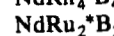
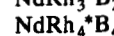
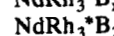
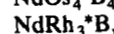
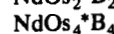
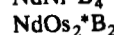
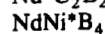
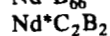
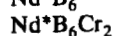
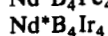
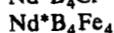
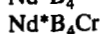
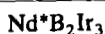
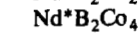
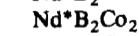
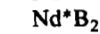
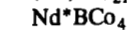
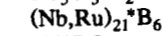
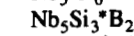
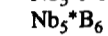
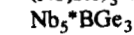
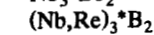
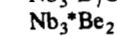
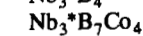
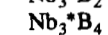
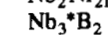
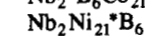
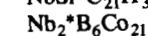
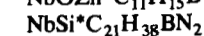
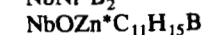
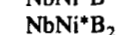
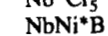
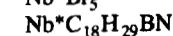
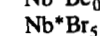
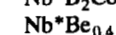
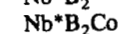
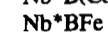
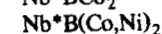
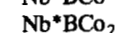
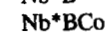
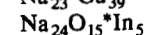
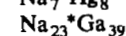
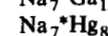
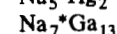
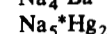
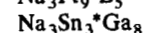
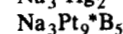
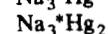
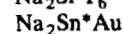
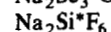
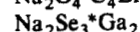
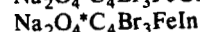
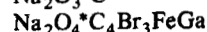
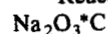
Reaction with elemental Ga: 6.3

$Na \cdot Ag_2$
 $Na \cdot Au$
 $Na \cdot Au_2$
 $Na \cdot BF_4$
 $Na \cdot B_6$
 $Na \cdot Ba$
 $Na \cdot C_4H_{11}B_4$
 $Na \cdot C_4H_{22}B_{18}Co$
 $Na \cdot C_6H_8B$
 $Na \cdot C_7H_{15}B_9N$
 $Na \cdot C_8H_{34}B_{18}Co$
 $Na \cdot Cd_2$
 $Na \cdot Cd_5$
 $Na \cdot Ge$
 $Na \cdot Hg$
 $Na \cdot Hg_2$
 $Na \cdot Hg_6$
 $Na \cdot Hg_{16}$
 $NaO_2 \cdot C_9H_{17}B_9N$
 $NaO_3 \cdot C_5H_{11}B_9Mn$
 $NaO_3 \cdot C_8H_5Cr$
 $NaO_3 \cdot C_8H_5Mo$
 $NaO_3P \cdot C_4H_{10}B_9Mn$
 $NaO_3W \cdot C_8H_5$
 $NaO_4 \cdot C_4Co$
 $NaO_4P \cdot C_{22}H_{15}Mn$
 $NaO_5 \cdot C_5Mn$
 $NaO_5Re \cdot C_5$
 $NaO_7 \cdot C_{17}H_{24}BCr$
 $NaP_2 \cdot C_2H_{20}B_{18}Co$
NaPt₂
 $NaPt_2$
 Formation: 7.4.1.1
 $NaPt_3 \cdot B_2$
 $NaRh \cdot C_{10}H_{14}B_2$
 $NaRh \cdot C_{20}H_{18}B_2$
NaZn₁₃
 $NaZn_{13}$
 Formation: 7.3.2.2
 $Na_2 \cdot Au$
 $Na_2 \cdot AuGe$



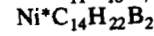
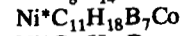
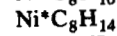
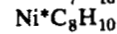
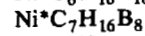
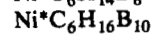
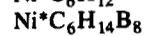
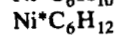
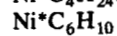
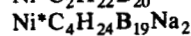
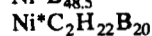
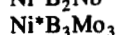
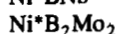
Industrial manufacture: 7.2.2.2.1

Reaction with Ca metal: 7.2.2.2.3



Reaction with boranes or carboranes:

6.5.3.3



- $\text{Ni}^*\text{C}_{14}\text{H}_{28}\text{B}_4$
 $\text{Ni}^*\text{C}_{14}\text{H}_{29}\text{B}_7$
 $\text{Ni}^*\text{C}_{16}\text{H}_{24}\text{B}_2\text{F}_2$
 $\text{Ni}^*\text{C}_{16}\text{H}_{24}\text{B}_4\text{F}_4$
 $\text{Ni}^*\text{C}_{16}\text{H}_{31}\text{B}_3$
 $\text{Ni}^*\text{C}_{17}\text{H}_{22}\text{B}_2$
 $\text{Ni}^*\text{C}_{17}\text{H}_{28}\text{B}_2$
 $\text{Ni}^*\text{C}_{18}\text{H}_{38}\text{B}_4\text{N}_2$
 $\text{Ni}^*\text{C}_{19}\text{H}_{23}\text{B}$
 $\text{Ni}^*\text{C}_{19}\text{H}_{27}\text{B}_2\text{Co}$
 $\text{Ni}^*\text{C}_{20}\text{H}_{40}\text{B}_2\text{N}_2$
 $\text{Ni}^*\text{C}_{20}\text{H}_{40}\text{B}_6$
 $\text{Ni}^*\text{C}_{22}\text{H}_{22}\text{B}_2$
 $\text{Ni}^*\text{C}_{22}\text{H}_{33}\text{B}_2\text{Co}$
 $\text{Ni}^*\text{C}_{24}\text{H}_{26}\text{B}_2$
 $\text{Ni}^*\text{C}_{24}\text{H}_{48}\text{B}_4$
 $\text{Ni}^*\text{C}_{26}\text{H}_{30}\text{B}_2$
 $\text{Ni}^*\text{C}_{30}\text{H}_{54}\text{B}_4\text{Fe}$
 $\text{NiO}_2^*\text{C}_{10}\text{H}_{12}\text{B}_2\text{F}_2$
 $\text{NiO}_2^*\text{C}_{36}\text{H}_{25}\text{B}$
 $\text{NiO}_2\text{S}^*\text{C}_{10}\text{H}_{16}\text{B}_2$
 $\text{NiO}_3^*\text{C}_{17}\text{H}_{22}\text{B}_2\text{Fe}$
 $\text{NiO}_3^*\text{C}_{24}\text{H}_{33}\text{B}_2\text{CoFe}$
 NiO_4^*C_4
 $\text{NiO}_6^*\text{C}_{20}\text{H}_{22}\text{B}_2\text{Fe}_2$
 $\text{NiP}_2^*\text{C}_{16}\text{H}_{45}\text{B}_7$
 $\text{NiP}_2^*\text{C}_{48}\text{H}_{40}\text{B}$
 $\text{NiP}_4^*\text{C}_{54}\text{H}_{54}\text{B}_4$
 NiPr^*B_4
 $\text{NiS}^*\text{C}_{13}\text{H}_{21}\text{B}_2$
 $\text{NiS}_2^*\text{B}_{18}\text{H}_{22}$
 $\text{NiS}_2^*\text{C}_{16}\text{H}_{32}\text{B}_4$
 NiSm^*B_4
 NiTa^*B
 NiTa^*B_2
 NiTb^*B_4
 NiU^*B_4
 NiW_2^*B_2
 NiW_3^*B_3
 NiY^*B_4
 $(\text{Ni,Ru})^*\text{B}$
 $(\text{Ni,Be})^*(\text{B,Be})_2$
 Ni_2^*B
 $\text{Ni}_2^*\text{C}_{10}\text{H}_{18}\text{B}_8$
 $\text{Ni}_2^*\text{C}_{10}\text{H}_{20}\text{B}_{10}$
 $\text{Ni}_2^*\text{C}_{12}\text{H}_{17}\text{B}_5$
 $\text{Ni}_2^*\text{C}_{16}\text{H}_{28}\text{B}_2$
 $\text{Ni}_2^*\text{C}_{17}\text{H}_{31}\text{B}_2$
 $\text{Ni}_2^*\text{C}_{19}\text{H}_{27}\text{B}_2$
 $\text{Ni}_2^*\text{C}_{20}\text{H}_{30}\text{BN}_2$
 $\text{Ni}_2^*\text{C}_{22}\text{H}_{33}\text{B}_2$
 $\text{Ni}_2^*\text{C}_{43}\text{H}_{73}\text{B}_6\text{Co}_2$
 $\text{Ni}_2^*\text{C}_{46}\text{H}_{79}\text{B}_6\text{Co}_2$
 $\text{Ni}_2^*\text{C}_{50}\text{H}_{85}\text{B}_6\text{Fe}_2$
 Ni_2^*Ca
 $\text{Ni}_2\text{O}_2^*\text{C}_{36}\text{H}_{56}\text{B}_4\text{Co}_2$
 $\text{Ni}_2\text{O}_2\text{P}_2^*\text{C}_{42}\text{H}_{50}\text{B}_{18}$
 $\text{Ni}_2\text{Si}_2^*\text{C}_{22}\text{H}_{48}\text{B}_2\text{N}_2$
 $\text{Ni}_{2.5}^*\text{B}_2\text{Li}_{1.2}$
 $\text{Ni}_{2.5}^*\text{B}_2\text{Mg}$
 $\text{Ni}_3^*\text{B}_{0.5}\text{In}$
 Ni_3^*B
 $\text{Ni}_3^*\text{B}_6\text{Cr}_2$
 $\text{Ni}_3^*\text{B}_6\text{Lu}_2$
 $\text{Ni}_3^*\text{C}_{30}\text{H}_{58}\text{B}_{10}$
 $\text{Ni}_3^*\text{C}_{46}\text{H}_{78}\text{B}_8\text{Co}_2$
 Ni_3^*Ca
 $\text{Ni}_3\text{Y}^*\text{B}_2$
 Ni_4^*B_3
 $\text{Ni}_4\text{U}^*\text{B}$
 $\text{Ni}_{4.29}\text{Si}_2^*\text{B}_{1.43}$
 $\text{Ni}_5^*\text{B}_4\text{La}_2$
 $\text{Ni}_5^*\text{B}_4\text{Nd}_2$
 Ni_5^*Ca
 $\text{Ni}_6\text{Si}_2^*\text{B}$
 Ni_7^*Ca_2
 $\text{Ni}_9^*\text{B}_6\text{Ba}_2$
 $\text{Ni}_{12}^*\text{B}_6\text{Ba}$
 $\text{Ni}_{12}\text{Sr}^*\text{B}_6$
 $\text{Ni}_{15}^*\text{B}_6\text{Dy}_2$
 $\text{Ni}_{15}^*\text{B}_6\text{Er}_2$
 $\text{Ni}_{15}^*\text{B}_6\text{Ho}_2$
 $\text{Ni}_{15}^*\text{B}_6\text{Lu}_2$
 $\text{Ni}_{15}^*\text{B}_9\text{Dy}_2$
 $\text{Ni}_{15}^*\text{B}_9\text{Er}_2$
 $\text{Ni}_{15}^*\text{B}_9\text{Ho}_2$
 $\text{Ni}_{15}^*\text{B}_9\text{Lu}_2$
 $\text{Ni}_{15}\text{Tb}_2^*\text{B}_6$
 $\text{Ni}_{15}\text{Tb}_2^*\text{B}_9$
 $\text{Ni}_{15}\text{Tm}_2^*\text{B}_6$
 $\text{Ni}_{15}\text{Tm}_2^*\text{B}_9$
 $\text{Ni}_{15}\text{Y}_2^*\text{B}_6$
 $\text{Ni}_{15}\text{Y}_2^*\text{B}_9$
 $\text{Ni}_{15}\text{Yb}_2^*\text{B}_6$
 $\text{Ni}_{15}\text{Yb}_2^*\text{B}_9$
 $\text{Ni}_{16}^*\text{B}_8\text{Li}_3$
 $\text{Ni}_{19}^*\text{B}_6\text{Lu}_5$
 $\text{Ni}_{19}^*\text{B}_{10}\text{Ho}_3$
 $\text{Ni}_{19.5}^*\text{B}_6\text{Mg}_{3.5}$
 $\text{Ni}_{19.7}\text{Zn}_{3.3}^*\text{B}_6$
 $\text{Ni}_{20}^*\text{B}_6\text{Li}_3$
 $\text{Ni}_{20}\text{Ti}_3^*\text{B}_6$
 $\text{Ni}_{20.3}^*\text{Al}_{2.7}\text{B}$
 $\text{Ni}_{21}^*\text{BCa}_2$
 $\text{Ni}_{21}^*\text{BHf}_2$
 $\text{Ni}_{21}^*\text{B}_6\text{Ce}_2$
 $\text{Ni}_{21}^*\text{B}_6\text{Er}_2$
 $\text{Ni}_{21}^*\text{B}_6\text{In}_2$

- $\text{Ni}_{21}^*\text{B}_6\text{Lu}_2$
 $\text{Ni}_{21}^*\text{B}_6\text{Mn}_2$
 $\text{Ni}_{21}^*\text{B}_6\text{Nb}_2$
 $\text{Ni}_{21}\text{Sb}_2^*\text{B}_6$
 $\text{Ni}_{21}\text{Sc}_2^*\text{B}_6$
 $\text{Ni}_{21}\text{Sn}_2^*\text{B}_6$
 $\text{Ni}_{21}\text{Ta}_2^*\text{B}_6$
 $\text{Ni}_{21}\text{Tm}_2^*\text{B}_6$
 $\text{Ni}_{21}\text{U}_2^*\text{B}_6$
 $\text{Ni}_{21}\text{V}_2^*\text{B}_6$
 $\text{Ni}_{21}\text{Yb}_2^*\text{B}_6$
 $\text{Ni}_{21.6}^*\text{B}_6\text{Ge}_{1.4}$
 $\text{Ni}_{23-m}^*\text{B}_6\text{Ga}_m$
 $(\text{Ni},\text{Re})_{23}^*\text{B}_6$
 $\text{Ni}_{29}^*\text{B}_{10}\text{Er}_4$
 $\text{Ni}_{29}^*\text{B}_{10}\text{Lu}_4$
 $\text{Ni}_{29}\text{Sc}_4^*\text{B}_{10}$
 $\text{Ni}_{29}\text{Tm}_4^*\text{B}_{10}$
 $\text{Ni}_{29}\text{Yb}_4^*\text{B}_{10}$
 Np^*B_2
 Np^*B_4
 Np^*B_6
 Np^*B_{12}
 Np^*CB
 O^*B
 O^*C
 O^*CAu
 $\text{O}^*\text{CB}_4\text{F}_6$
 O^*CCu
 O^*CCu_2
 O^*CCu_3
 O^*CCu_4
 $\text{O}^*\text{C}_4\text{H}_{15}\text{B}_3$
 $\text{O}^*\text{C}_5\text{H}_9\text{B}$
 $\text{O}^*\text{C}_6\text{H}_9\text{B}$
 $\text{O}^*\text{C}_{10}\text{H}_{34}\text{B}_{13}\text{Co}$
 $\text{O}^*\text{C}_{10}\text{H}_{35}\text{B}_{12}\text{Co}$
 $\text{O}^*\text{C}_{10}\text{H}_{37}\text{B}_{16}\text{Co}$
 $\text{O}^*\text{C}_{17}\text{H}_{33}\text{B}_7\text{Co}$
 $\text{O}^*\text{C}_{21}\text{H}_{40}\text{B}_2\text{FeN}_2$
 O^*Cs_2
 O^*Li_2
 O^*Na_2
 $\text{OOSp}_2^*\text{C}_{37}\text{H}_{38}\text{B}_4$
 $\text{OOSp}_2^*\text{C}_{37}\text{H}_{39}\text{B}_5$
 $\text{OOSp}_3^*\text{C}_{56}\text{H}_{55}\text{B}_8$
 $\text{OOSp}_3\text{Pt}^*\text{C}_{45}\text{H}_{49}\text{B}_5\text{Cl}$
 $\text{OP}_2^*\text{C}_7\text{H}_{27}\text{B}_4\text{Ir}$
 $\text{OP}_2^*\text{C}_{13}\text{H}_{30}\text{ClIr}$
 $\text{OP}_2^*\text{C}_{22}\text{H}_{57}\text{Ge}_3\text{HgIr}$
 $\text{OP}_2^*\text{C}_{37}\text{H}_{30}\text{ClIr}$
 $\text{OP}_2^*\text{C}_{37}\text{H}_{30}\text{Cl}_3\text{HgIr}$
 $\text{OP}_2^*\text{C}_{37}\text{H}_{38}\text{B}_3\text{Ir}$
 $\text{OP}_2^*\text{C}_{37}\text{H}_{38}\text{B}_5\text{ClIr}$
 $\text{OP}_2^*\text{C}_{37}\text{H}_{38}\text{B}_5\text{Ir}$
 $\text{OP}_2^*\text{C}_{55}\text{H}_{30}\text{BClF}_{15}\text{Ir}$
 $\text{OP}_2\text{Pt}^*\text{C}_{17}\text{H}_{36}\text{B}_8$
 $\text{OP}_2\text{Rh}^*\text{C}_{44}\text{H}_{45}\text{B}_9\text{N}$
 $\text{OP}_2\text{Si}_3^*\text{C}_{22}\text{H}_{57}\text{HgIr}$
 $\text{OP}_3^*\text{C}_{15}\text{H}_{33}\text{BF}_6\text{FeN}$
 $\text{OP}_3\text{Ru}^*\text{C}_{56}\text{H}_{55}\text{B}_8$
 $\text{ORh}^*\text{C}_{15}\text{H}_{24}\text{B}$
 $\text{ORh}_2^*\text{C}_{24}\text{H}_{36}\text{B}_2$
 $\text{OS}^*\text{C}_{16}\text{H}_{15}\text{Co}_3$
 $\text{OS}_2^*\text{C}_{17}\text{H}_{32}\text{B}_4\text{Fe}$
 $\text{OZn}^*\text{C}_{11}\text{H}_{15}\text{BNb}$
 O_2^*B_2
 $\text{O}_2^*\text{C}_2\text{Au}$
 $\text{O}_2^*\text{C}_2\text{H}_6\text{BBr}$
 $\text{O}_2^*\text{C}_2\text{H}_6\text{BCl}$
 $\text{O}_2^*\text{C}_6\text{H}_{18}\text{B}_2\text{N}_2$
 $\text{O}_2^*\text{C}_7\text{H}_5\text{Cl}_2\text{CoHg}$
 $\text{O}_2^*\text{C}_7\text{H}_5\text{FeI}$
 $\text{O}_2^*\text{C}_7\text{H}_{13}\text{B}_5\text{Fe}$
 $\text{O}_2^*\text{C}_9\text{H}_{12}\text{B}_4\text{Fe}$
 $\text{O}_2^*\text{C}_9\text{H}_{17}\text{B}_9\text{NNa}$
 $\text{O}_2^*\text{C}_{10}\text{H}_{12}\text{B}_2\text{F}_2\text{Ni}$
 $\text{O}_2^*\text{C}_{10}\text{H}_{14}\text{FeGe}$
 $\text{O}_2^*\text{C}_{12}\text{H}_{18}\text{B}_2\text{Fe}$
 $\text{O}_2^*\text{C}_{12}\text{H}_{26}\text{B}_9\text{Fe}$
 $\text{O}_2^*\text{C}_{13}\text{H}_{11}\text{BCo}$
 $\text{O}_2^*\text{C}_{33}\text{H}_{40}\text{AlFeN}$
 $\text{O}_2^*\text{C}_{33}\text{H}_{40}\text{FeGaN}$
 $\text{O}_2^*\text{C}_{33}\text{H}_{40}\text{FeInN}$
 $\text{O}_2^*\text{C}_{36}\text{H}_{25}\text{BNi}$
 $\text{O}_2^*\text{C}_{36}\text{H}_{56}\text{B}_4\text{Co}_2\text{Ni}_2$
 $\text{O}_2\text{P}^*\text{C}_{27}\text{H}_{32}\text{B}_9\text{CuN}$
 $\text{O}_2\text{P}_2^*\text{C}_{18}\text{H}_{34}\text{B}_9\text{ClMo}$
 $\text{O}_2\text{P}_2^*\text{C}_{38}\text{H}_{39}\text{B}_8\text{Ir}$
 $\text{O}_2\text{P}_2^*\text{C}_{38}\text{H}_{43}\text{B}_9\text{Mo}$
 $\text{O}_2\text{P}_2^*\text{C}_{39}\text{H}_{41}\text{B}_8\text{Ir}$
 $\text{O}_2\text{P}_2^*\text{C}_{42}\text{H}_{50}\text{B}_{18}\text{Ni}_2$
 $\text{O}_2\text{P}_2\text{Sm}_3^*\text{C}_{48}\text{H}_{68}\text{B}_{18}\text{N}$
 $\text{O}_2\text{Rh}^*\text{C}_{15}\text{H}_{23}\text{B}_2$
 $\text{O}_2\text{S}^*\text{C}_{10}\text{H}_{16}\text{B}_2\text{Ni}$
 $\text{O}_2\text{S}^*\text{La}_2$
 $\text{O}_2\text{S}_2^*\text{C}_{18}\text{H}_{32}\text{B}_4\text{Cr}$
 $\text{O}_2\text{Si}^*\text{C}_{10}\text{H}_{14}\text{Fe}$
 $\text{O}_2\text{Sn}^*\text{C}_{10}\text{H}_{14}\text{Fe}$
 $\text{O}_2\text{W}^*\text{C}_{16}\text{H}_{38}\text{B}_9\text{N}$
 $\text{O}_2\text{W}^*\text{C}_{49}\text{H}_{48}\text{B}_9\text{N}$
 $\text{O}_2\text{W}^*\text{C}_{49}\text{H}_{52}\text{B}_9\text{N}$
 O_3^*B_2
 O_3^*CHg_2
 O_3^*CNa_2
 $\text{O}_3^*\text{C}_3\text{Ag}$
 $\text{O}_3^*\text{C}_3\text{H}_9\text{BCoN}_3$
 $\text{O}_3^*\text{C}_3\text{H}_{10}\text{B}_5\text{Mn}$

$O_3^*C_5H_6B_4Fe$
 $O_3^*C_5H_7B_3Fe$
 $O_3^*C_5H_{11}B_9MnNa$
 $O_3^*C_7H_8B_3Mn$
 $O_3^*C_7H_9BB_rFeN$
 $O_3^*C_8H_5ClCrHg$
 $O_3^*C_8H_5ClHgMo$
 $O_3^*C_8H_5Cl_2InMo$
 $O_3^*C_8H_5CrNa$
 $O_3^*C_8H_5MoNa$
 $O_3^*C_8H_6Cr$
 $O_3^*C_8H_6Mo$
 $O_3^*C_8H_{15}BFeN_2$
 $O_3^*C_{10}H_{20}B_3CrN_3$
 $O_3^*C_{11}H_{12}B_2F_2Fe$
 $O_3^*C_{11}H_{15}BMnN$
 $O_3^*C_{12}H_{19}B_2FeN$
 $O_3^*C_{13}H_9BFe$
 $O_3^*C_{13}H_{20}BFeN$
 $O_3^*C_{13}H_{20}B_2FeN_2$
 $O_3^*C_{14}H_9Mn$
 $O_3^*C_{14}H_{12}BCo$
 $O_3^*C_{14}H_{20}B_3CrN_3$
 $O_3^*C_{15}H_{13}BFe$
 $O_3^*C_{15}H_{24}B_2Fe$
 $O_3^*C_{17}H_{22}B_2FeNi$
 $O_3^*C_{17}H_{22}B_2Fe_2$
 $O_3^*C_{24}H_{33}B_2CoFeNi$
 $O_3^*C_{37}H_{25}BFe$
 $O_3^*In_2$
 $O_3OsSi_2^*C_{11}H_{22}B_4$
 $O_3P^*C_4H_{10}B_9MnNa$
 $O_3P^*C_5H_{13}B_9Mn$
 $O_3P^*C_{26}H_{19}BF_3Mo$
 $O_3P^*C_{26}H_{19}Mo$
 $O_3P^*C_{26}H_{20}AuCr$
 $O_3P^*C_{26}H_{20}AuMo$
 $O_3PS^*C_{11}H_{16}B_2F_6Mn$
 $O_3PW^*C_{11}H_{24}B_9$
 $O_3PW^*C_{26}H_{19}$
 $O_3PW^*C_{26}H_{19}BF_3$
 $O_3PW^*C_{26}H_{20}Au$
 $O_3P_2^*C_{39}H_{31}B_4Ir_2$
 $O_3P_2Ti^*C_{41}H_{41}B_9MoN$
 $O_3P_2TiW^*C_{41}H_{41}B_9N$
 $O_3P_6^*C_{90}H_{75}Au_3FeIrN$
 $O_3Ru^*C_7H_6BCl$
 $O_3Ru^*C_{11}H_{17}B_9$
 $O_3S^*C_{11}H_{16}B_2Fe$
 $O_3S^*C_{16}H_{21}B_2FeMn$
 $O_3Si^*C_{13}H_{22}BFeN$
 $O_3Si^*C_{15}H_{24}BFeN$
 $O_3Sn^*C_{11}H_{14}Mo$
 $O_3W^*C_8H_5BrHg$
 $O_3W^*C_8H_5ClHg$
 $O_3W^*C_8H_5Na$
 $O_3W^*C_8H_6$
 $O_3W^*C_{42}H_{56}GaN$
 $O_3W^*C_{42}H_{56}InN$
 $O_3Zn^*C_{14}H_{10}Mo$
 $O_{3n}P_{12}^*C_{150}H_{132}Au_{13}N_n$
 $O_4^*C_4Br_3FeGaNa_2$
 $O_4^*C_4Br_3FeInNa_2$
 $O_4^*C_4CdFe$
 $O_4^*C_4Cl_2FeHg_2$
 $O_4^*C_4CoNa$
 $O_4^*C_4H_2Fe$
 $O_4^*C_4H_6CdFeN_2$
 $O_4^*C_4H_6Cu_2FeN_2$
 $O_4^*C_4H_8B_5Co$
 $O_4^*C_4H_{10}B_6Fe$
 $O_4^*C_4H_{12}B_2$
 $O_4^*C_4Ni$
 $O_4^*C_7H_{20}B_9Mn$
 $O_4^*C_9H_9BFe$
 $O_4^*C_{14}H_{10}ClFe_2In$
 $O_4^*C_{14}H_{10}Fe_2$
 $O_4^*C_{14}H_{10}Fe_2Hg$
 $O_4^*C_{14}H_{14}B_2Co_2$
 $O_4^*C_{20}H_{36}B_2CrN_2$
 $O_4^*C_{20}H_{36}B_2N_2$
 $O_4^*C_{22}H_{38}B_4Co_2N_2$
 $O_4^*C_{24}H_{18}B_2Co_2$
 $O_4^*C_{24}H_{40}B_2Co_2N_2$
 $O_4^*C_{26}H_{22}B_2Fe_2$
 $O_4^*C_{62}H_{57}AsB_3CoN_4$
 $O_4^*CrCs_2$
 $O_4P^*C_{22}H_{15}AuCo$
 $O_4P^*C_{22}H_{15}BCl_2Mn$
 $O_4P^*C_{22}H_{15}MnNa$
 $O_4P^*C_{26}H_{27}BMnN_2$
 $O_4P^*C_{26}H_{29}ClCoN_4$
 $O_4P^*C_{26}H_{29}CoKN_4$
 $O_4P^*C_{30}H_{33}BMn$
 $O_4P^*C_{34}H_{23}BMn$
 $O_4P^*C_{34}H_{25}BMn$
 $O_4P^*C_{50}H_{47}B_2CoKN_4$
 $O_4P^*C_{50}H_{47}B_2CoN_4$
 $O_4P^*C_{54}H_{73}B_3CoN_4$
 $O_4P_2^*C_{58}H_{45}AlCoN$
 $O_4P_2^*C_{58}H_{45}CoGaN$
 $O_4P_2^*C_{58}H_{45}CoInN$
 $O_4Re^*H_8K$
 $O_4Rh_2^*C_{24}H_{40}B_2N_2$
 $O_4S^*C_{12}H_{16}B_2Cr$
 O_4S^*CsH
 $O_4Sn^*C_7H_9Co$
 $O_4W^*C_{20}H_{36}B_2N_2$

$O_4Zn^*C_4H_9FeN_3$
 $O_5^*CCl_2FeHg$
 $O_5^*C_5Cl_2FeHg$
 $O_5^*C_5Fe$
 $O_5^*C_5MnNa$
 $O_5^*C_8H_8Br_2CoGa$
 $O_5^*C_8H_8Cl_2CoGa$
 $O_5^*C_8H_8CoGaI_2$
 $O_5^*C_9H_{12}BMnN_2$
 $O_5^*C_{10}H_{13}FeGa$
 $O_5^*C_{35}H_{43}InMnN$
 $O_5P_3V^*C_{59}H_{45}Au_3$
 O_5Pa_2
 Pa_2O_5

Reaction with Be metal: 7.4.2.1

$O_5Re^*C_5Na$
 $O_5Re^*C_9H_{12}BN_2$
 $O_5Re^*C_{13}H_{26}B_2N$
 $O_5Ti^*C_{17}H_{10}Mn$
 $O_6^*C_6Ag_2$
 $O_6^*C_6Br_4Co_2Ga$
 $O_6^*C_6Br_4Co_2In$
 $O_6^*C_{14}H_{18}BCo_2N$
 $O_6^*C_{15}H_{15}B_4CoFe_2$
 $O_6^*C_{16}H_9BMn_2$
 $O_6^*C_{16}H_{10}BrInMo_2$
 $O_6^*C_{16}H_{10}Cr_2Hg$
 $O_6^*C_{18}H_{13}BMn_2$
 $O_6^*C_{20}H_{22}B_2Fe_2Ni$
 $O_6^*C_{24}H_{34}B_4Fe_3$
 $O_6^*C_{27}H_{39}B_{27}Cu_3N_3$
 $O_6^*Hg_2N_2$
 $O_6P_7^*C_{126}H_{105}Au_8N_2$
 $O_6P_8^*C_{100}H_{87}Au_5N_2$
 $O_6P_8^*C_{108}H_{104}Au_6N_2$
 $O_6P_8^*C_{144}H_{120}Au_8N_2$
 $O_6S^*C_{14}H_{16}B_2Mn_2$
 $O_6S^*C_{22}H_{32}B_4CoMn_2$
 $O_6S_{17}^*In_6La_{10}$
 $O_6Ta^*C_7H_3Hg$
 $O_7^*C_{17}H_{24}BCrNa$
 $O_8^*C_6Fe_2HgN_2$
 $O_8^*C_8CdCo_2$
 $O_8^*C_8Co_2$
 $O_8^*C_8Co_2Hg$
 $O_8P_2^*C_{44}H_{30}BClMn_2$
 $O_8P_4^*C_{80}H_{60}Au_6Co_2$
 $O_8Zn^*C_8Co_2$
 $O_9^*C_2Cl_2Hg_4$
 $O_9^*C_9CoHgMn$
 $O_9^*C_9Fe_2$
 $O_9^*C_{12}H_8BrCo_2In$
 $O_9^*C_{12}H_8ClCo_2Ga$
 $O_9^*C_{15}H_{15}BCo_3N$

$O_9^*C_{24}H_{15}InMo_3$
 $O_9P_3Rh_2^*C_{39}H_{54}B_3$
 $O_9P_4^*C_{17}H_{42}BF_6FeN$
 $O_9P_8^*C_{144}H_{120}Au_9N_3$
 $O_9P_8^*C_{168}H_{168}Au_9N_3$
 $O_{10}^*C_{10}CdMn_2$
 $O_{10}^*C_{10}HgMn_2$
 $O_{10}^*C_{10}Mn_2$
 $O_{10}Os_3^*C_{10}H_2$
 $O_{10}Os_3P^*C_{28}H_{15}AuCl$
 $O_{10}Os_3P^*C_{28}H_{16}Au$
 $O_{10}Ti^*C_{10}ClMn_2$
 $O_{10}Zn^*C_{10}Mn_2$
 $O_{12}^*C_{12}Co_3In$
 $O_{12}^*C_{12}Fe_3$
 $O_{12}^*C_{12}H_3BFe_4$
 $O_{12}P^*C_{30}H_{17}AuBFe_4$
 $O_{12}P_2^*C_{24}H_{31}Au_2BFe_4$
 $O_{12}P_2^*C_{36}H_{31}Au_2BFe_4$
 $O_{12}P_2^*C_{48}H_{31}Au_2BFe_4$
 $O_{12}P_2^*C_{48}H_{32}BFe_4N$
 $O_{12}P_8^*C_{144}H_{120}Au_9Cl_3$
 $O_{12}Ti^*C_{12}Co_3$
 $O_{15}^*C_{15}InMn_3$
 $O_{15}^*In_5Na_{24}$
 $O_{15}Re_3^*C_{15}In$
 $O_{15}Ti^*C_{15}Mn_3$
 $O_{16}^*C_{16}Br_3Co_4In_3$
 $O_{18}^*C_{18}Co_6Hg_9$
 $O_{18}^*C_{18}Ga_2Mn_4$
 $O_{21}P_8^*C_{162}H_{126}Au_9N_9$
 $O_{24}P_8^*C_{168}H_{168}Au_9B_3F_{12}$
 $O_{33}Os_9^*C_{33}Hg_3$
 $O_{33}Ru_9^*C_{33}Hg_3$
 $O_{62}^*In_{11}Mo_{40}$
 Os^*B
 Os^*B_2
 Os^*B_2Dy
 Os^*B_2Er
 Os^*B_2Ho
 Os^*B_2Lu
 Os^*B_2Mo
 $Os^*B_2Mo_2$
 Os^*B_4Dy
 Os^*B_4Er
 Os^*B_4Gd
 Os^*B_4Ho
 $OsP_2^*C_{37}H_{38}B_4O$
 $OsP_2^*C_{37}H_{39}B_5O$
 $OsP_3^*C_{56}H_{55}B_8O$
 $OsP_3Pt^*C_{45}H_{49}B_5ClO$
 $OsSc^*B_2$
 $OsSi_2^*C_{11}H_{22}B_4O_3$
 $OsTb^*B_2$

OsTb*B ₄	P*C ₅ H ₁₃ B ₉ MnO ₃
OsTm*B ₂	P*C ₇ H ₁₈ B ₉ Fe
OsTm*B ₄	P*C ₁₆ H ₂₅ BF ₆ FeN
OsV*B ₂	P*C ₁₈ H ₁₅
OsW*B ₂	P*C ₁₈ H ₁₅ AuCl
OsY*B ₂	P*C ₁₈ H ₂₃ AuB ₅
OsY*B ₄	P*C ₁₈ H ₂₃ B ₅ CdCl
OsYb*B ₄	P*C ₁₉ H ₁₇
Os ₂ *B ₂ Ce	P*C ₁₉ H ₁₈ Au
Os ₂ *B ₂ Gd	P*C ₂₀ H ₂₂ AuB ₄
Os ₂ *B ₂ La	P*C ₂₀ H ₂₆ B ₉ Cu
Os ₂ *B ₂ Nd	P*C ₂₀ H ₂₆ B ₉ Hg
Os ₂ *B ₃	P*C ₂₀ H ₃₃ B ₁₀ Hg
Os ₂ Pr*B ₂	P*C ₂₁ H ₂₅ BF ₆ Ir
Os ₂ Sm*B ₂	P*C ₂₂ H ₁₅ AuCoO ₄
Os ₂ Th*B ₂	P*C ₂₂ H ₁₅ BCl ₂ MnO ₄
Os ₃ *B ₂ Er	P*C ₂₂ H ₁₅ MnNaO ₄
Os ₃ *B ₂ Lu	P*C ₂₅ H ₃₀ AuB ₉ N
Os ₃ *B ₅ Ca ₂	P*C ₂₅ H ₃₀ B ₉ CuN
Os ₃ *B ₅ Eu ₂	P*C ₂₆ H ₁₉ BF ₃ MoO ₃
Os ₃ *C ₁₀ H ₂ O ₁₀	P*C ₂₆ H ₁₉ MoO ₃
Os ₃ P*C ₂₈ H ₁₅ AuClO ₁₀	P*C ₂₆ H ₂₀ AuCrO ₃
Os ₃ P*C ₂₈ H ₁₆ AuO ₁₀	P*C ₂₆ H ₂₀ AuMoO ₃
Os ₃ U*B ₂	P*C ₂₆ H ₂₇ BMnN ₂ O ₄
(Os,V) ₃ *B ₂	P*C ₂₆ H ₂₉ ClCoN ₄ O ₄
(Os,W) ₃ *B ₂	P*C ₂₆ H ₂₉ CoKN ₄ O ₄
Os ₄ *BHf ₉	P*C ₂₇ H ₃₂ B ₉ CuNO ₂
Os ₄ *B ₄ Ce	P*C ₂₈ H ₁₅ AuClO ₁₀ Os ₃
Os ₄ *B ₄ Dy	P*C ₂₈ H ₁₆ AuO ₁₀ Os ₃
Os ₄ *B ₄ Er	P*C ₃₀ H ₁₇ AuBF ₆ O ₁₂
Os ₄ *B ₄ Eu	P*C ₃₀ H ₃₃ AuB ₂ Co
Os ₄ *B ₄ Gd	P*C ₃₀ H ₃₃ BMnO ₄
Os ₄ *B ₄ Ho	P*C ₃₄ H ₂₃ BMnO ₄
Os ₄ *B ₄ La	P*C ₃₄ H ₂₅ BMnO ₄
Os ₄ *B ₄ Lu	P*C ₃₆ H ₃₀ AuGe
Os ₄ *B ₄ Nd	P*C ₅₀ H ₄₇ B ₂ CoKN ₄ O ₄
Os ₄ Pr*B ₄	P*C ₅₀ H ₄₇ B ₂ CoN ₄ O ₄
Os ₄ Sm*B ₄	P*C ₅₄ H ₇₃ B ₃ CoN ₄ O ₄
Os ₄ Tb*B ₄	P*Cl ₃
Os ₄ Th*B ₄	P*F ₃
Os ₄ Tm*B ₄	P*H ₃
Os ₄ U*B ₄	PRh*C ₂₀ H ₂₇ B ₉
Os ₄ Y*B ₄	PRh*C ₂₁ H ₂₂ B ₄
Os ₄ Yb*B ₄	PRh*C ₂₁ H ₂₅ BF ₆
Os ₉ *C ₃₃ Hg ₃ O ₃₃	PRh*C ₂₄ H ₃₃ B ₉
P*B ₂ Co ₅	PRh*C ₂₆ H ₃₁ B ₉
P*B ₂ Cr ₅	PRh*C ₃₄ H ₄₃ AuB ₂
P*B ₂ Fe ₅	PRu*C ₁₇ H ₁₆ BF ₆
P*B ₂ Mn ₅	PS*C ₁₁ H ₁₆ B ₂ F ₆ MnO ₃
P*B ₄ Cl ₃ F ₆	PS*C ₁₃ H ₂₁ B ₂ F ₆ Fe
P*B ₄ F ₆ H ₃	PS ₂ *C ₁₆ H ₃₂ B ₄ Co ₂ F ₆
P*B ₄ F ₉	PW*C ₁₁ H ₂₄ B ₉ O ₃
P*C ₃ H ₉	PW*C ₂₆ H ₁₉ BF ₃ O ₃
P*C ₄ H ₁₀ B ₉ MnNaO ₃	PW*C ₂₆ H ₁₉ O ₃

- $PW^*C_{26}H_{20}AuO_3$
 $P_2^*BCr_{4.5}$
 $P_2^*C_2H_{20}B_{18}CoNa$
 $P_2^*C_4H_{26}B_{18}Co$
 $P_2^*C_4H_{26}B_{18}Fe$
 $P_2^*C_6H_{22}B_2$
 $P_2^*C_6H_{32}B_9Ir$
 $P_2^*C_7H_{27}B_4IrO$
 $P_2^*C_{12}H_{30}Br_4In_2$
 $P_2^*C_{12}H_{30}I_4In_2$
 $P_2^*C_{13}H_{30}ClIrO$
 $P_2^*C_{14}H_{36}B_3Co$
 $P_2^*C_{14}H_{39}B_6Co$
 $P_2^*C_{14}H_{39}B_7Co$
 $P_2^*C_{14}H_{40}B_7Co$
 $P_2^*C_{14}H_{40}B_8Co$
 $P_2^*C_{16}H_{45}B_7Ni$
 $P_2^*C_{18}H_{34}B_9ClMoO_2$
 $P_2^*C_{20}H_{50}B_8CoFe$
 $P_2^*C_{22}H_{57}Ge_3HgIrO$
 $P_2^*C_{24}H_{31}Au_2BFe_4O_{12}$
 $P_2^*C_{25}H_{22}$
 $P_2^*C_{25}H_{22}Au_2Cl_2$
 $P_2^*C_{26}H_{24}B_2Br_4Co$
 $P_2^*C_{36}H_{31}Au_2BFe_4O_{12}$
 $P_2^*C_{36}H_{34}B_2$
 $P_2^*C_{36}H_{38}B_5Cu$
 $P_2^*C_{36}H_{38}B_9Ir$
 $P_2^*C_{36}H_{39}B_4Cu$
 $P_2^*C_{36}H_{39}B_6Cu$
 $P_2^*C_{36}H_{44}B_9Ir$
 $P_2^*C_{37}H_{30}ClIrO$
 $P_2^*C_{37}H_{30}Cl_3HgIrO$
 $P_2^*C_{37}H_{38}B_3IrO$
 $P_2^*C_{37}H_{38}B_4OOs$
 $P_2^*C_{37}H_{38}B_5ClIrO$
 $P_2^*C_{37}H_{38}B_5IrO$
 $P_2^*C_{37}H_{39}B_5OOs$
 $P_2^*C_{38}H_{39}B_8IrO_2$
 $P_2^*C_{38}H_{41}B_8Ir$
 $P_2^*C_{38}H_{43}B_9MoO_2$
 $P_2^*C_{39}H_{31}B_4Ir_2O_3$
 $P_2^*C_{39}H_{41}B_8IrO_2$
 $P_2^*C_{42}H_{50}B_{18}Ni_2O_2$
 $P_2^*C_{44}H_{30}BClMn_2O_8$
 $P_2^*C_{48}H_{31}Au_2BFe_4O_{12}$
 $P_2^*C_{48}H_{32}BFe_4NO_{12}$
 $P_2^*C_{48}H_{40}BNi$
 $P_2^*C_{52}H_{40}Cu_3Ir$
 $P_2^*C_{55}H_{30}BClF_{15}IrO$
 $P_2^*C_{58}H_{45}AlCoNO_4$
 $P_2^*C_{58}H_{45}CoGaNO_4$
 $P_2^*C_{58}H_{45}CoInNO_4$
 $P_2^*C_{100}H_{70}Cu_4Ir_2$
 $P_2Pd^*C_{26}H_{31}B_3$
 $P_2Pd^*C_{26}H_{36}B_{10}$
 $P_2Pd^*C_{28}H_{36}B_{10}$
 $P_2Pd^*C_{36}H_{42}B_{10}$
 $P_2Pt^*C_{12}H_{37}B_3$
 $P_2Pt^*C_{12}H_{42}B_{10}$
 $P_2Pt^*C_{13}H_{38}B_5$
 $P_2Pt^*C_{13}H_{39}B_5$
 $P_2Pt^*C_{14}H_{36}B_4$
 $P_2Pt^*C_{14}H_{37}B_4$
 $P_2Pt^*C_{14}H_{38}B_4$
 $P_2Pt^*C_{14}H_{41}B_9$
 $P_2Pt^*C_{14}H_{42}B_8$
 $P_2Pt^*C_{16}H_{29}B_3$
 $P_2Pt^*C_{16}H_{34}B_8$
 $P_2Pt^*C_{16}H_{40}B_{16}$
 $P_2Pt^*C_{16}H_{42}B_4$
 $P_2Pt^*C_{16}H_{42}B_{18}$
 $P_2Pt^*C_{16}H_{43}B_7$
 $P_2Pt^*C_{17}H_{36}B_8O$
 $P_2Pt^*C_{20}H_{50}B_8Fe$
 $P_2Pt^*C_{24}H_{66}B_{10}$
 $P_2Pt^*C_{26}H_{36}B_{10}$
 $P_2Pt^*C_{28}H_{35}B_9$
 $P_2Pt^*C_{28}H_{37}B_3$
 $P_2Pt^*C_{36}H_{30}BCl_3$
 $P_2Pt^*C_{36}H_{30}B_2Cl_6$
 $P_2Pt^*C_{36}H_{30}B_2F_6$
 $P_2Pt^*C_{36}H_{42}B_{10}$
 $P_2Pt^*C_{37}H_{42}B_8$
 $P_2Pt^*C_{38}H_{30}F_6Hg$
 $P_2Pt^*C_{38}H_{34}$
 $P_2Pt^*C_{40}H_{42}B_2Br$
 $P_2Pt^*C_{42}H_{48}Al_2$
 $P_2Pt^*C_{42}H_{49}B_3$
 $P_2Pt^*C_{72}H_{30}CdF_{30}Ge_2$
 $P_2PtS^*C_{12}H_{41}B_9$
 $P_2PtS^*C_{36}H_{41}B_9$
 $P_2PtSi^*C_{36}H_{30}F_4$
 $P_2PtZn^*C_{72}H_{30}F_{30}Ge_2$
 $P_2Pt_2^*C_{16}H_{40}B_{12}$
 $P_2Rh^*C_{14}H_{40}B_7$
 $P_2Rh^*C_{14}H_{42}B_9$
 $P_2Rh^*C_{38}H_{40}B_7$
 $P_2Rh^*C_{38}H_{41}B_9Cl$
 $P_2Rh^*C_{38}H_{42}B_9$
 $P_2Rh^*C_{38}H_{43}B_{10}$
 $P_2Rh^*C_{44}H_{45}B_9NO$
 $P_2Rh^*C_{45}H_{48}B_9$
 $P_2Rh^*C_{46}H_{67}B_9$
 $P_2RhS^*C_{36}H_{41}B_{10}$
 $P_2Rh_2^*C_{16}H_{52}B_{18}$
 $P_2Rh_2^*C_{24}H_{66}B_{18}$
 $P_2Rh_2^*C_{40}H_{54}B_{18}$

- $P_2Rh_2^*C_{52}H_{62}B_{18}$
 $P_2Ru^*C_{38}H_{39}B_7$
 $P_2Ru^*C_{38}H_{43}B_9$
 $P_2S^*C_{36}H_{39}B_9ClIr$
 $P_2S_2Ti^*C_{26}H_{24}Au$
 $P_2Si_3^*C_{22}H_{57}HgIrO$
 $P_2Sm_3^*C_{48}H_{68}B_{18}NO_2$
 $P_2Ti^*C_{41}H_{41}B_9MoNO_3$
 $P_2TiW^*C_{41}H_{41}B_9NO_3$
 $P_3^*C_{15}H_{33}BF_6FeNO$
 $P_3^*C_{16}H_{36}BF_6FeN_2$
 $P_3^*C_{20}H_{51}B_5Co_2$
 $P_3^*C_{21}H_{60}B_{10}Co$
 $P_3^*C_{55}H_{54}B_8Ir$
 $P_3^*C_{56}H_{55}B_8OOs$
 $P_3Pt^*C_{45}H_{49}B_5ClOOs$
 $P_3Pt^*C_{54}H_{45}$
 $P_3Pt^*C_{54}H_{45}AuCl$
 $P_3Pt^*C_{54}H_{45}B_2Cl_6$
 $P_3Rh^*C_{58}H_{67}B_{19}$
 $P_3Rh_2^*C_{39}H_{54}B_3$
 $P_3Rh_2^*C_{39}H_{54}B_3O_9$
 $P_3Ru^*C_{56}H_{55}B_8O$
 $P_3S^*C_{49}H_{42}AuN$
 $P_3V^*C_{59}H_{45}Au_3O_5$
 $P_4^*C_{17}H_{42}BF_6FeN$
 $P_4^*C_{17}H_{42}BF_6FeNO_9$
 $P_4^*C_{20}H_{33}Co$
 $P_4^*C_{44}H_{48}B_2Co$
 $P_4^*C_{44}H_{52}B_2Co$
 $P_4^*C_{52}H_{48}B_2Br_4Co$
 $P_4^*C_{52}H_{48}B_2CoI_4$
 $P_4^*C_{52}H_{49}Co$
 $P_4^*C_{54}H_{54}B_4Ni$
 $P_4^*C_{64}H_{58}B_2Cl_2Co$
 $P_4^*C_{72}H_{60}Au_4I_2$
 $P_4^*C_{76}H_{52}B_2Co$
 $P_4^*C_{76}H_{68}B_2Co$
 $P_4^*C_{80}H_{60}Au_6Co_2O_8$
 $P_4^*Cl_2F_{12}Ir_2$
 $P_4^*F_{12}IrK$
 $P_4Pt^*C_{42}H_{58}B_9Ir$
 $P_4Pt^*C_{72}H_{60}$
 $P_4Pt_2^*C_{28}H_{71}B_5$
 $P_4Pt_2^*C_{32}H_{54}B_8$
 $P_4Pt_2^*C_{32}H_{60}B_{18}$
 $P_4Pt_2^*C_{32}H_{72}$
 $P_4Rh^*C_{76}H_{68}B_3Cl_6$
 $P_4Rh^*F_{12}K$
 $P_4Rh_2^*Cl_2F_{12}$
 $P_5S_3^*C_{93}H_{165}Au_9N_3$
 $P_6^*C_{75}H_{66}Au_4I_2$
 $P_6^*C_{90}H_{75}Au_3F_6IrNO_3$
 $P_6^*C_{162}H_{166}Au_6B_2$
 $P_7^*C_{108}H_{90}Au_8F_6I$
 $P_7^*C_{126}H_{84}Au_{11}Cl_{21}I_3$
 $P_7^*C_{126}H_{84}Au_{11}F_{21}I_3$
 $P_7^*C_{126}H_{105}Au_7$
 $P_7^*C_{126}H_{105}Au_8N_2O_6$
 $P_7^*C_{129}H_{105}Au_{11}N_3$
 $P_7S_3^*C_{129}H_{105}Au_{11}N_3$
 $P_8^*C_{100}H_{87}Au_5N_2O_6$
 $P_8^*C_{108}H_{104}Au_6N_2O_6$
 $P_8^*C_{144}H_{120}Au_8N_2O_6$
 $P_8^*C_{144}H_{120}Au_9B_3F_{12}$
 $P_8^*C_{144}H_{120}Au_9Cl_3O_{12}$
 $P_8^*C_{144}H_{120}Au_9N_3O_9$
 $P_8^*C_{162}H_{126}Au_9N_9O_{21}$
 $P_8^*C_{168}H_{168}Au_9B_3F_{12}O_{24}$
 $P_8^*C_{168}H_{168}Au_9N_3O_9$
 $P_9^*C_{116}H_{104}Au_9F_{18}N_2$
 $P_9^*C_{144}H_{120}Au_{11}Cl_2F_6$
 $P_9S_2^*C_{146}H_{120}Au_{11}F_6N_2$
 $P_{10}S_3^*C_{138}H_{130}Au_{11}N_3$
 $P_{11}^*C_{144}H_{120}Au_9F_{18}$
 $P_{11}^*C_{144}H_{120}Au_{11}Cl_2F_{18}$
 $P_{11}^*C_{168}H_{168}Au_9F_{18}$
 $P_{12}^*C_{150}H_{132}Au_{13}N_nO_{3n}$
 $P_{12}^*C_{216}H_{180}Au_{55}Cl_6$
 $P_{12}Rh_4^*C_{36}H_{108}Hg_6$
 $P_{13}^*C_{80}H_{110}Au_{11}F_{18}$
 $P_{13}^*C_{80}H_{110}Au_{13}Cl_2F_{18}$
 Pa^*Be_{13}
 $Pa_2^*O_5$
 $Pb_3Sc^*B_x$
 $Pd_{1-x}W_{1-x}^*B_3$
 $Pd^*C_5H_{15}BCl_2N_2$
 $Pd^*C_8H_{27}B_9N_2$
 $Pd^*C_{10}H_{23}B_9$
 $Pd^*C_{26}H_{31}B_3P_2$
 $Pd^*C_{26}H_{36}B_{10}P_2$
 $Pd^*C_{28}H_{36}B_{10}P_2$
 $Pd^*C_{30}H_{31}B_9$
 $Pd^*C_{36}H_{42}B_{10}P_2$
 Pd^*Li
 Pd^*Li_3
 Pd^*Li_5
 $PdS_2^*B_{18}H_{22}$
 Pd_2^*B
 Pd_2^*Li
 $Pd_2^*Li_3$
 $Pd_2W_2^*B_5$
 Pd_3^*B
 $Pd_4^*Li_{15}$
 $Pd_5^*B_2$
 $Pd_6^*B_4Eu$
 Pd_7^*Li
 $Pd_7^*Li_7$

- Pr*BCo₄
 Pr*B₂Co₂
 Pr*B₂Ir₃
 Pr*B₂Os₂
 Pr*B₄
 Pr*B₄Co₄
 Pr*B₄Cr
 Pr*B₄Ir₄
 Pr*B₄Ni
 Pr*B₄Os₄
 Pr*B₆
 Pr*B₆Cr₂
 Pr*C₂B₂
 PrRh₃*B
 PrRh₃*B₂
 PrRu₂*B₂
 PrRu₃*B₂
 PrRu₄*B₄
 Pr₂*BFe₁₄
 Pr₂*B₃Co₇
 Pr₂Re₃*B₆
 Pr₃*B₂N₄
 Pr₃*B₄Co₁₁
 Pr₈Re₁₃*B₁₂
 Pt*B_{0.7}
 Pt*Be
 Pt*Be₃
 Pt*C₁₀H₂₃B₉
 Pt*C₁₂H₃₇B₃P₂
 Pt*C₁₂H₄₂B₁₀P₂
 Pt*C₁₃H₃₈B₅P₂
 Pt*C₁₃H₃₉B₅P₂
 Pt*C₁₄H₃₆B₄P₂
 Pt*C₁₄H₃₇B₄P₂
 Pt*C₁₄H₃₈B₄P₂
 Pt*C₁₄H₄₁B₉P₂
 Pt*C₁₄H₄₂B₈P₂
 Pt*C₁₆H₂₄B₂F₂
 Pt*C₁₆H₂₉B₃P₂
 Pt*C₁₆H₃₄B₈P₂
 Pt*C₁₆H₄₀B₁₆P₂
 Pt*C₁₆H₄₂B₄P₂
 Pt*C₁₆H₄₂B₁₈P₂
 Pt*C₁₆H₄₃B₇P₂
 Pt*C₁₇H₃₆B₈OP₂
 Pt*C₂₀H₅₀B₈FeP₂
 Pt*C₂₄H₄₆B₄
 Pt*C₂₄H₄₈B₄
 Pt*C₂₄H₆₆B₁₀P₂
 Pt*C₂₆H₃₆B₁₀P₂
 Pt*C₂₈H₃₅B₉P₂
 Pt*C₂₈H₃₇B₃P₂
 Pt*C₃₆H₃₀BCl₃P₂
 Pt*C₃₆H₃₀B₂Cl₆P₂
 Pt*C₃₆H₃₀B₂F₆P₂
 Pt*C₃₆H₄₂B₁₀P₂
 Pt*C₃₇H₄₂B₈P₂
 Pt*C₃₈H₃₀F₆HgP₂
 Pt*C₃₈H₃₄P₂
 Pt*C₄₀H₄₂B₂BrP₂
 Pt*C₄₂H₃₇B
 Pt*C₄₂H₄₈Al₂P₂
 Pt*C₄₂H₄₉B₃P₂
 Pt*C₄₂H₅₈B₉IrP₄
 Pt*C₄₅H₄₉B₅ClOOSp₃
 Pt*C₅₄H₄₅AuClP₃
 Pt*C₅₄H₄₅B₂Cl₆P₃
 Pt*C₅₄H₄₅P₃
 Pt*C₇₂H₃₀CdF₃₀Ge₂P₂
 Pt*C₇₂H₆₀P₄
 Pt*Li
 Pt*Li₂
 Pt*Li₅
 Pt*Li₉
 PtS*C₁₂H₄₁B₉P₂
 PtS*C₃₆H₄₁B₉P₂
 PtSi*C₃₆H₃₀F₄P₂
 PtZn*C₇₂H₃₀F₃₀Ge₂P₂
 Pt₂*B
 Pt₂*C₄H₈Cl₄
 Pt₂*C₁₆H₄₀B₁₂P₂
 Pt₂*C₂₈H₇₁B₅P₄
 Pt₂*C₃₂H₅₄B₈P₄
 Pt₂*C₃₂H₆₀B₁₈P₄
 Pt₂*C₃₂H₇₂P₄
 Pt₂*Li
 Pt₂*Na
 Pt₃*BLi
 Pt₃*B₂Na
 Pt₄*B
 Pt₄*Li₁₅
 Pt₇*Li
 Pt₉*B₅Na₃
 Pt₉*B₆Ba₂
 Pt₉*B₆Ca₂
 Pt₉Sr₂*B₆
 Pu*B₂
 Pu*B₄
 Pu*B₆
 Pu*B₁₀₀
 Rb*Au
 Rb*Au₂
 Rb*Au₅
 Rb*Cd₁₃
 Rb*Ga₇
 Rb*Hg₂
 Rb*Hg₆
 Rb*Hg₁₁

- Rb_2^*Hg_7
 Rb_2^*Hg_9
 Rb_3^*Hg_4
 $\text{Rb}_5^*\text{Hg}_{18}$
 Rb_7^*Hg_8
 $\text{Re}_{0.4}^*\text{BFe}_{2.6}$
 Re^*BCo
 Re^*B_2
 $\text{Re}^*\text{B}_4\text{Dy}$
 $\text{Re}^*\text{B}_4\text{Er}$
 $\text{Re}^*\text{B}_4\text{Gd}$
 $\text{Re}^*\text{B}_4\text{Ho}$
 $\text{Re}^*\text{B}_6\text{Dy}_2$
 $\text{Re}^*\text{B}_6\text{Er}_2$
 $\text{Re}^*\text{B}_6\text{Gd}_2$
 $\text{Re}^*\text{B}_6\text{Ho}_2$
 $\text{Re}^*\text{C}_5\text{NaO}_5$
 $\text{Re}^*\text{C}_9\text{H}_{12}\text{BN}_2\text{O}_5$
 $\text{Re}^*\text{C}_{10}\text{H}_{11}$
 $\text{Re}^*\text{C}_{10}\text{H}_{11}\text{BF}_3$
 $\text{Re}^*\text{C}_{13}\text{H}_{26}\text{B}_2\text{NO}_5$
 $\text{Re}^*\text{H}_8\text{KO}_4$
 Re^*K_2
 ReTb^*B_4
 $\text{ReTb}_2^*\text{B}_6$
 ReTh^*B_4
 $\text{ReTi}_2^*\text{B}_2$
 ReTm^*B_4
 $\text{ReTm}_2^*\text{B}_6$
 ReU^*B_4
 ReY^*B_4
 ReY_2^*B_6
 $(\text{Re},\text{V})^*\text{B}$
 $\text{Re}_{1.05-1.37}^*\text{V}_{0.95-0.63}^*\text{B}$
 $\text{Re}_{1.49-1.64}^*\text{V}_{0.51-0.36}^*\text{B}$
 $\text{Re}_{1.5}^*\text{BMn}_{0.5}$
 $\text{Re}_3^*\text{Al}_2\text{B}$
 Re_3^*B
 $\text{Re}_3^*\text{B}_6\text{Pr}_2$
 $\text{Re}_3^*\text{C}_{15}\text{InO}_{15}$
 $(\text{Re},\text{Ta})_3^*\text{B}_2$
 $\text{Re}_4^*\text{BHf}_9$
 $\text{Re}_4\text{Zr}_9^*\text{B}$
 Re_7^*B_3
 $\text{Re}_{13}^*\text{B}_{12}\text{Pr}_8$
 $\text{Re}_{13.3}^*\text{W}_{6.7}^*\text{B}$
 $\text{Re}_{15.5}^*\text{BMo}_{4.5}$
 $\text{Rh}_{0.8}^*\text{BFe}_{2.2}$
 $\text{Rh}_{1-x}^*\text{B}_3\text{Mo}_{1-x}$
 $\text{Rh}_{1-x}\text{W}_{1-x}^*\text{B}_3$
 Rh^*B
 $\text{Rh}^*\text{C}_8\text{H}_{25}\text{B}_9\text{Cl}$
 $\text{Rh}^*\text{C}_{10}\text{H}_{12}\text{B}$
 $\text{Rh}^*\text{C}_{10}\text{H}_{14}\text{B}_2\text{Na}$
 $\text{Rh}^*\text{C}_{10}\text{H}_{15}\text{B}_2$
 $\text{Rh}^*\text{C}_{13}\text{H}_9\text{BK}_2\text{N}_3$
 $\text{Rh}^*\text{C}_{14}\text{H}_{40}\text{B}_7\text{P}_2$
 $\text{Rh}^*\text{C}_{14}\text{H}_{42}\text{B}_9\text{P}_2$
 $\text{Rh}^*\text{C}_{15}\text{H}_{14}\text{B}$
 $\text{Rh}^*\text{C}_{15}\text{H}_{23}\text{B}_2\text{O}_2$
 $\text{Rh}^*\text{C}_{15}\text{H}_{24}\text{B}$
 $\text{Rh}^*\text{C}_{15}\text{H}_{24}\text{BO}$
 $\text{Rh}^*\text{C}_{17}\text{H}_{29}\text{B}_2$
 $\text{Rh}^*\text{C}_{20}\text{H}_{18}\text{B}_2\text{Na}$
 $\text{Rh}^*\text{C}_{20}\text{H}_{19}\text{B}_2$
 $\text{Rh}^*\text{C}_{20}\text{H}_{27}\text{B}_9\text{P}$
 $\text{Rh}^*\text{C}_{21}\text{H}_{22}\text{B}_4\text{P}$
 $\text{Rh}^*\text{C}_{21}\text{H}_{25}\text{BF}_6\text{P}$
 $\text{Rh}^*\text{C}_{24}\text{H}_{33}\text{B}_9\text{P}$
 $\text{Rh}^*\text{C}_{24}\text{H}_{47}\text{B}_4$
 $\text{Rh}^*\text{C}_{26}\text{H}_{26}\text{As}_2\text{Cl}_3\text{Hg}$
 $\text{Rh}^*\text{C}_{26}\text{H}_{27}\text{As}_2\text{Cl}_2$
 $\text{Rh}^*\text{C}_{26}\text{H}_{31}\text{B}_9\text{P}$
 $\text{Rh}^*\text{C}_{34}\text{H}_{43}\text{AuB}_2\text{P}$
 $\text{Rh}^*\text{C}_{38}\text{H}_{40}\text{B}_7\text{P}_2$
 $\text{Rh}^*\text{C}_{38}\text{H}_{41}\text{B}_9\text{ClP}_2$
 $\text{Rh}^*\text{C}_{38}\text{H}_{42}\text{B}_9\text{P}_2$
 $\text{Rh}^*\text{C}_{38}\text{H}_{43}\text{B}_{10}\text{P}_2$
 $\text{Rh}^*\text{C}_{44}\text{H}_{45}\text{B}_9\text{NOP}_2$
 $\text{Rh}^*\text{C}_{45}\text{H}_{48}\text{B}_9\text{P}_2$
 $\text{Rh}^*\text{C}_{46}\text{H}_{67}\text{B}_9\text{P}_2$
 $\text{Rh}^*\text{C}_{58}\text{H}_{67}\text{B}_{19}\text{P}_3$
 $\text{Rh}^*\text{C}_{76}\text{H}_{68}\text{B}_3\text{Cl}_6\text{P}_4$
 $\text{Rh}^*\text{F}_{12}\text{KP}_4$
 $\text{Rh}^*\text{H}_4\text{Li}_4$
 $\text{Rh}^*\text{H}_5\text{Li}_4$
 Rh^*Li
 $\text{RhS}^*\text{C}_{36}\text{H}_{41}\text{B}_{10}\text{P}_2$
 $\text{Rh}_2^*\text{B}_2\text{Ba}$
 $\text{Rh}_2^*\text{B}_2\text{Ca}$
 $\text{Rh}_2^*\text{C}_8\text{H}_{16}\text{Cl}_2$
 $\text{Rh}_2^*\text{C}_{15}\text{H}_{21}\text{B}_3$
 $\text{Rh}_2^*\text{C}_{16}\text{H}_{52}\text{B}_{18}\text{P}_2$
 $\text{Rh}_2^*\text{C}_{24}\text{H}_{36}\text{B}_2\text{O}$
 $\text{Rh}_2^*\text{C}_{24}\text{H}_{40}\text{B}_2\text{N}_2$
 $\text{Rh}_2^*\text{C}_{24}\text{H}_{40}\text{B}_2\text{N}_2\text{O}_4$
 $\text{Rh}_2^*\text{C}_{24}\text{H}_{46}\text{B}_4\text{Cl}_2$
 $\text{Rh}_2^*\text{C}_{24}\text{H}_{48}\text{B}_4\text{Cl}_2$
 $\text{Rh}_2^*\text{C}_{24}\text{H}_{66}\text{B}_{18}\text{P}_2$
 $\text{Rh}_2^*\text{C}_{30}\text{H}_{27}\text{B}_3$
 $\text{Rh}_2^*\text{C}_{35}\text{H}_{36}\text{B}_3\text{N}$
 $\text{Rh}_2^*\text{C}_{39}\text{H}_{54}\text{B}_3\text{O}_9\text{P}_3$
 $\text{Rh}_2^*\text{C}_{39}\text{H}_{54}\text{B}_3\text{P}_3$
 $\text{Rh}_2^*\text{C}_{40}\text{H}_{54}\text{B}_{18}\text{P}_2$
 $\text{Rh}_2^*\text{C}_{52}\text{H}_{62}\text{B}_{18}\text{P}_2$
 $\text{Rh}_2^*\text{Cl}_2\text{F}_{12}\text{P}_4$
 $\text{Rh}_2\text{S}^*\text{C}_{20}\text{H}_{38}\text{B}_9\text{Cl}$
 $\text{Rh}_2\text{Sr}^*\text{B}_2$

$\text{Rh}_3^*\text{B}_x\text{Ce}$	$\text{Rh}_{13}^*\text{B}_{11}\text{Mg}_5$
$\text{Rh}_3^*\text{B}_x\text{Er}$	$\text{Rh}_{14}\text{Sr}_5^*\text{B}_{10}$
$\text{Rh}_3^*\text{B}_x\text{Gd}$	$\text{Rh}_{20}^*\text{B}_{14}\text{Ca}_7$
$\text{Rh}_3^*\text{B}_x\text{Ho}$	$\text{Ru}_{0.4}^*\text{BFe}_{2.6}$
$\text{Rh}_3^*\text{B}_x\text{La}$	Ru^*B
$\text{Rh}_3^*\text{B}_x\text{Lu}$	Ru^*B_2
$\text{Rh}_3^*\text{B}_x\text{Nd}$	$\text{Ru}^*\text{B}_2\text{Dy}$
Rh_3^*BDy	$\text{Ru}^*\text{B}_2\text{Er}$
Rh_3^*BEu	$\text{Ru}^*\text{B}_2\text{Ho}$
Rh_3^*BPr	$\text{Ru}^*\text{B}_2\text{Lu}$
$\text{Rh}_3^*\text{B}_2\text{Ce}$	$\text{Ru}^*\text{B}_2\text{Mo}$
$\text{Rh}_3^*\text{B}_2\text{Dy}$	$\text{Ru}^*\text{B}_4\text{Dy}$
$\text{Rh}_3^*\text{B}_2\text{Er}$	$\text{Ru}^*\text{B}_4\text{Er}$
$\text{Rh}_3^*\text{B}_2\text{Eu}$	$\text{Ru}^*\text{B}_4\text{Gd}$
$\text{Rh}_3^*\text{B}_2\text{Gd}$	$\text{Ru}^*\text{B}_4\text{Ho}$
$\text{Rh}_3^*\text{B}_2\text{Ho}$	$\text{Ru}^*\text{C}_7\text{H}_6\text{BClO}_3$
$\text{Rh}_3^*\text{B}_2\text{La}$	$\text{Ru}^*\text{C}_8\text{H}_{17}\text{B}_9$
$\text{Rh}_3^*\text{B}_2\text{Lu}$	$\text{Ru}^*\text{C}_{10}\text{H}_{10}$
$\text{Rh}_3^*\text{B}_2\text{Nd}$	$\text{Ru}^*\text{C}_{11}\text{H}_{17}\text{B}_9\text{O}_3$
$\text{Rh}_3^*\text{B}_2\text{Pr}$	$\text{Ru}^*\text{C}_{17}\text{H}_{16}\text{BF}_6\text{P}$
Rh_3^*Li	$\text{Ru}^*\text{C}_{20}\text{H}_{34}\text{B}_2\text{N}_2$
$\text{Rh}_3\text{Sc}^*\text{B}_x$	$\text{Ru}^*\text{C}_{22}\text{H}_{38}\text{BN}$
$\text{Rh}_3\text{Sm}^*\text{B}_x$	$\text{Ru}^*\text{C}_{38}\text{H}_{39}\text{B}_7\text{P}_2$
$\text{Rh}_3\text{Sm}^*\text{B}_2$	$\text{Ru}^*\text{C}_{38}\text{H}_{43}\text{B}_9\text{P}_2$
$\text{Rh}_3\text{Tb}^*\text{B}_x$	$\text{Ru}^*\text{C}_{56}\text{H}_{55}\text{B}_8\text{OP}_3$
$\text{Rh}_3\text{Tb}^*\text{B}_2$	RuTb^*B_2
$\text{Rh}_3\text{Th}^*\text{B}_x$	RuTb^*B_4
$\text{Rh}_3\text{Tm}^*\text{B}_x$	RuTm^*B_2
$\text{Rh}_3\text{Tm}^*\text{B}_2$	RuTm^*B_4
$\text{Rh}_3\text{U}^*\text{B}_x$	RuW^*B_2
$\text{Rh}_3\text{Y}^*\text{B}_x$	RuY^*B_2
$\text{Rh}_3\text{Y}^*\text{B}_2$	RuY^*B_4
$\text{Rh}_3\text{Yb}^*\text{B}_x$	RuYb^*B_4
$\text{Rh}_3\text{Yb}^*\text{B}_2$	$(\text{Ru},\text{V})^*\text{B}$
$\text{Rh}_4^*\text{B}_4(\text{Ca},\text{Sc})$	$(\text{Ru},\text{W})^*\text{B}$
$\text{Rh}_4^*\text{B}_4\text{Dy}$	$\text{Ru}_2^*\text{B}_2\text{Ce}$
$\text{Rh}_4^*\text{B}_4\text{Er}$	$\text{Ru}_2^*\text{B}_2\text{Gd}$
$\text{Rh}_4^*\text{B}_4\text{Gd}$	$\text{Ru}_2^*\text{B}_2\text{La}$
$\text{Rh}_4^*\text{B}_4\text{Ho}$	$\text{Ru}_2^*\text{B}_2\text{Nd}$
$\text{Rh}_4^*\text{B}_4\text{Lu}$	$\text{Ru}_2^*\text{B}_2\text{Pr}$
$\text{Rh}_4^*\text{B}_4\text{Nd}$	Ru_2^*B_3
$\text{Rh}_4^*\text{C}_{36}\text{H}_{108}\text{Hg}_6\text{P}_{12}$	$\text{Ru}_2\text{Sm}^*\text{B}_2$
$\text{Rh}_4(\text{Sc},\text{Th})^*\text{B}_4$	$\text{Ru}_2\text{Th}^*\text{B}_2$
$\text{Rh}_4\text{Sm}^*\text{B}_4$	$\text{Ru}_3^*\text{B}_2\text{Ce}$
$\text{Rh}_4\text{Tb}^*\text{B}_4$	$\text{Ru}_3^*\text{B}_2\text{Dy}$
$\text{Rh}_4\text{Th}^*\text{B}_4$	$\text{Ru}_3^*\text{B}_2\text{Er}$
$\text{Rh}_4\text{Tm}^*\text{B}_4$	$\text{Ru}_3^*\text{B}_2\text{Gd}$
$\text{Rh}_4\text{Y}^*\text{B}_4$	$\text{Ru}_3^*\text{B}_2\text{Ho}$
$\text{Rh}_5^*\text{B}_4\text{Ca}_2$	$\text{Ru}_3^*\text{B}_2\text{Lu}$
$\text{Rh}_5\text{Sr}_2^*\text{B}_4$	$\text{Ru}_3^*\text{B}_2\text{Nd}$
$\text{Rh}_6^*\text{B}_4\text{Eu}$	$\text{Ru}_3^*\text{B}_2\text{Pr}$
Rh_7^*B_3	$\text{Ru}_3\text{Sm}^*\text{B}_2$
$\text{Rh}_8^*\text{B}_6\text{Ca}_3$	$\text{Ru}_3\text{Tb}^*\text{B}_2$
$\text{Rh}_8\text{Sr}_3^*\text{B}_6$	$\text{Ru}_3\text{Th}^*\text{B}_2$

$\text{Ru}_3\text{Tm}^*\text{B}_2$
 $\text{Ru}_3\text{U}^*\text{B}$
 $\text{Ru}_3\text{U}^*\text{B}_2$
 $(\text{Ru},\text{W})_3^*\text{B}_2$
 $\text{Ru}_4^*\text{B}_4\text{Ce}$
 $\text{Ru}_4^*\text{B}_4\text{Dy}$
 $\text{Ru}_4^*\text{B}_4\text{Er}$
 $\text{Ru}_4^*\text{B}_4\text{Eu}$
 $\text{Ru}_4^*\text{B}_4\text{Gd}$
 $\text{Ru}_4^*\text{B}_4\text{Ho}$
 $\text{Ru}_4^*\text{B}_4\text{La}$
 $\text{Ru}_4^*\text{B}_4\text{Lu}$
 $\text{Ru}_4^*\text{B}_4\text{Nd}$
 $\text{Ru}_4^*\text{B}_4\text{Pr}$
 $\text{Ru}_4\text{Sc}^*\text{B}_4$
 $\text{Ru}_4\text{Sm}^*\text{B}_4$
 $\text{Ru}_4\text{Tb}^*\text{B}_4$
 $\text{Ru}_4\text{Th}^*\text{B}_4$
 $\text{Ru}_4\text{Tm}^*\text{B}_4$
 $\text{Ru}_4\text{U}^*\text{B}_4$
 $\text{Ru}_4\text{Y}^*\text{B}_4$
 $\text{Ru}_4\text{Yb}^*\text{B}_4$
 Ru_7^*B_3
 $\text{Ru}_8\text{Zn}_5^*\text{B}_8$
 $\text{Ru}_9^*\text{Al}_5\text{B}_6$
 $\text{Ru}_9^*\text{C}_{33}\text{Hg}_3\text{O}_{33}$
 $\text{Ru}_{11}^*\text{B}_8$
 $\text{Ru}_{21}\text{Ta}_2^*\text{B}_6$
S

S

Reaction with elemental Al, Ga, In:

6.2.3

Reaction with elemental In: 6.2.3

$\text{S}^*\text{B}_9\text{H}_{11}$
 $\text{S}^*\text{B}_{10}\text{H}_{12}$
 $\text{S}^*\text{C}_2\text{H}_6$
 $\text{S}^*\text{C}_2\text{H}_6\text{B}_4\text{F}_6$
 $\text{S}^*\text{C}_7\text{H}_{18}\text{B}_{10}\text{Fe}$
 $\text{S}^*\text{C}_7\text{H}_{19}\text{B}_9\text{Fe}$
 $\text{S}^*\text{C}_8\text{H}_{16}\text{B}_2$
 $\text{S}^*\text{C}_{10}\text{H}_{16}\text{B}_2\text{NiO}_2$
 $\text{S}^*\text{C}_{10}\text{H}_{17}\text{B}_5\text{Co}_2$
 $\text{S}^*\text{C}_{11}\text{H}_{16}\text{B}_2\text{F}_6\text{MnO}_3\text{P}$
 $\text{S}^*\text{C}_{11}\text{H}_{16}\text{B}_2\text{FeO}_3$
 $\text{S}^*\text{C}_{12}\text{H}_{16}\text{B}_2\text{CrO}_4$
 $\text{S}^*\text{C}_{12}\text{H}_{41}\text{B}_9\text{P}_2\text{Pt}$
 $\text{S}^*\text{C}_{13}\text{H}_{21}\text{B}_2\text{Co}$
 $\text{S}^*\text{C}_{13}\text{H}_{21}\text{B}_2\text{F}_6\text{FeP}$
 $\text{S}^*\text{C}_{13}\text{H}_{21}\text{B}_2\text{Ni}$
 $\text{S}^*\text{C}_{14}\text{H}_{14}$
 $\text{S}^*\text{C}_{14}\text{H}_{16}\text{B}_2\text{Mn}_2\text{O}_6$
 $\text{S}^*\text{C}_{14}\text{H}_{20}\text{B}_2\text{F}_2\text{Fe}$
 $\text{S}^*\text{C}_{14}\text{H}_{22}\text{B}_2\text{Fe}$
 $\text{S}^*\text{C}_{15}\text{H}_{24}\text{B}_2\text{Fe}$

$\text{S}^*\text{C}_{16}\text{H}_{15}\text{Co}_3\text{O}$
 $\text{S}^*\text{C}_{16}\text{H}_{21}\text{B}_2\text{FeMnO}_3$
 $\text{S}^*\text{C}_{16}\text{H}_{26}\text{B}_2\text{Fe}$
 $\text{S}^*\text{C}_{18}\text{H}_{26}\text{B}_2\text{Fe}_2$
 $\text{S}^*\text{C}_{20}\text{H}_{38}\text{B}_9\text{ClRh}_2$
 $\text{S}^*\text{C}_{22}\text{H}_{32}\text{B}_4\text{CoMn}_2\text{O}_6$
 $\text{S}^*\text{C}_{36}\text{H}_{39}\text{B}_9\text{ClIrP}_2$
 $\text{S}^*\text{C}_{36}\text{H}_{41}\text{B}_9\text{P}_2\text{Pt}$
 $\text{S}^*\text{C}_{36}\text{H}_{41}\text{B}_{10}\text{P}_2\text{Rh}$
 $\text{S}^*\text{C}_{49}\text{H}_{42}\text{AuNP}_3$
 S^*CsHO_4
 S^*F_4
 S^*Ga
 S^*In
 $\text{S}^*\text{La}_2\text{O}_2$
 $\text{S}_2^*\text{B}_{18}\text{H}_{22}\text{Ni}$
 $\text{S}_2^*\text{B}_{18}\text{H}_{22}\text{Pd}$
 $\text{S}_2^*\text{C}_3\text{H}_6$
 $\text{S}_2^*\text{C}_4\text{H}_8$
 $\text{S}_2^*\text{C}_5\text{H}_{13}\text{B}_6\text{Co}$
 $\text{S}_2^*\text{C}_5\text{H}_{22}\text{AuB}_8\text{N}$
 $\text{S}_2^*\text{C}_7\text{H}_{21}\text{AuB}_9\text{N}$
 $\text{S}_2^*\text{C}_{10}\text{H}_{12}\text{B}_2\text{Co}_2$
 $\text{S}_2^*\text{C}_{10}\text{H}_{15}\text{B}_5\text{Co}_2$
 $\text{S}_2^*\text{C}_{16}\text{H}_{32}\text{B}_4\text{Co}_2\text{F}_6\text{P}$
 $\text{S}_2^*\text{C}_{16}\text{H}_{32}\text{B}_4\text{Ni}$
 $\text{S}_2^*\text{C}_{17}\text{H}_{32}\text{B}_4\text{FeO}$
 $\text{S}_2^*\text{C}_{18}\text{H}_{32}\text{B}_4\text{CrO}_2$
 $\text{S}_2^*\text{C}_{146}\text{H}_{120}\text{Au}_{11}\text{F}_6\text{N}_2\text{P}_9$
 $\text{S}_2\text{Ti}^*\text{C}_{26}\text{H}_{24}\text{AuP}_2$
 $\text{S}_2\text{Zn}^*\text{C}_{26}\text{H}_{42}\text{B}_4\text{Fe}_2$
 $\text{S}_3^*\text{C}_3\text{H}_6$
 $\text{S}_3^*\text{C}_{24}\text{H}_{48}\text{B}_6\text{Co}_2$
 $\text{S}_3^*\text{C}_{93}\text{H}_{165}\text{Au}_9\text{N}_3\text{P}_5$
 $\text{S}_3^*\text{C}_{129}\text{H}_{105}\text{Au}_{11}\text{N}_3\text{P}_7$
 $\text{S}_3^*\text{C}_{138}\text{H}_{130}\text{Au}_{11}\text{N}_3\text{P}_{10}$
 S_3^*In_2
 $\text{S}_4^*\text{C}_{10}\text{H}_{30}\text{Au}_2\text{B}_8\text{N}_2$
 $\text{S}_4^*\text{C}_{14}\text{H}_{42}\text{Au}_2\text{B}_{18}\text{N}_2$
 $\text{S}_4^*\text{C}_{32}\text{H}_{64}\text{B}_8\text{Co}_2\text{Fe}$
 S_4^*In_5
 S_5^*Ga_4
 S_7^*HN
 S_7^*In_6
 $\text{S}_{14}^*\text{Hg}_2\text{N}_2$
 $\text{S}_{17}^*\text{In}_6\text{La}_{10}\text{O}_6$
 $\text{Sb}^*\text{C}_2\text{H}_{11}\text{B}_{10}\text{Cl}_2$
 $\text{Sb}^*\text{C}_{18}\text{H}_{15}$
 Sb^*F_5
 $\text{Sb}^*\text{F}_6\text{Hg}$
 $\text{Sb}_2^*\text{B}_6\text{Co}_{21}$
 $\text{Sb}_2^*\text{B}_6\text{Ni}_{21}$
 $\text{Sb}_3^*\text{C}_{18}\text{H}_{15}\text{F}_{12}\text{Hg}_2$
 $\text{Sb}_4^*\text{F}_{22}\text{Hg}_3$

$\text{Sc}^*\text{B}_x\text{In}_3$
 $\text{Sc}^*\text{B}_x\text{Ir}_3$
 $\text{Sc}^*\text{B}_x\text{Pb}_3$
 $\text{Sc}^*\text{B}_x\text{Rh}_3$
 Sc^*B_2
 $\text{Sc}^*\text{B}_2\text{Co}_2$
 $\text{Sc}^*\text{B}_2\text{Co}_3$
 $\text{Sc}^*\text{B}_2\text{Ir}_3$
 $\text{Sc}^*\text{B}_2\text{Os}$
 $\text{Sc}^*\text{B}_4\text{Ir}_3$
 $\text{Sc}^*\text{B}_4\text{Ru}_4$
 Sc^*B_{28}
 Sc^*CB_2
 $\text{Sc}^*\text{C}_2\text{B}_2$
 $\text{ScSn}_3^*\text{B}_x$
 $\text{ScTi}_3^*\text{B}_x$
 $(\text{Sc,Th})^*\text{B}_4\text{Rh}_4$
 $\text{Sc}_2^*\text{B}_6\text{Co}_{21}$
 $\text{Sc}_2^*\text{B}_6\text{Ni}_{21}$
 $\text{Sc}_4^*\text{B}_{10}\text{Ni}_{29}$
 Se

Se

Reaction with elemental Al, Ga, In:

6.2.3

$\text{Se}^*\text{C}_4\text{H}_{22}\text{B}_{20}\text{Hg}$
 Se^*Ga
 Se^*In
 Se_2^*Ga_3
 $\text{Se}_3^*\text{Ga}_2\text{Na}_2$
 Se_3^*In_4
 Se_7^*In_6
 $\text{Si}^*\text{B}_2\text{Fe}_5$
 $\text{Si}^*\text{B}_2\text{Mn}_5$
 $\text{Si}^*\text{B}_2\text{Mo}_5$
 Si^*B_{36}
 $\text{Si}^*\text{C}_3\text{H}_9\text{Cl}$
 $\text{Si}^*\text{C}_3\text{H}_9\text{Li}$
 $\text{Si}^*\text{C}_7\text{H}_{15}\text{BLiN}$
 $\text{Si}^*\text{C}_7\text{H}_{16}\text{BN}$
 $\text{Si}^*\text{C}_{10}\text{H}_{14}\text{FeO}_2$
 $\text{Si}^*\text{C}_{10}\text{H}_{22}\text{BN}$
 $\text{Si}^*\text{C}_{11}\text{H}_{27}\text{BN}_2$
 $\text{Si}^*\text{C}_{12}\text{H}_{24}\text{BN}$
 $\text{Si}^*\text{C}_{13}\text{H}_{22}\text{BFeNO}_3$
 $\text{Si}^*\text{C}_{15}\text{H}_{24}\text{BFeNO}_3$
 $\text{Si}^*\text{C}_{15}\text{H}_{27}\text{BCoN}$
 $\text{Si}^*\text{C}_{21}\text{H}_{38}\text{BN}_2\text{Nb}$
 $\text{Si}^*\text{C}_{36}\text{H}_{30}\text{F}_4\text{P}_2\text{Pt}$
 Si^*F_4
 $\text{Si}^*\text{F}_6\text{Na}_2$
 Si^*Fe
 SiV_5^*B_2
 $\text{Si}_2^*\text{BCo}_{4.6}$
 $\text{Si}_2^*\text{BFe}_{4.8}$

$\text{Si}_2^*\text{BNi}_6$
 $\text{Si}_2^*\text{B}_{1.43}\text{Ni}_{4.29}$
 $\text{Si}_2^*\text{C}_5\text{H}_{13}\text{Li}$
 $\text{Si}_2^*\text{C}_6\text{H}_{18}\text{Hg}$
 $\text{Si}_2^*\text{C}_8\text{H}_{18}$
 $\text{Si}_2^*\text{C}_{11}\text{H}_{22}\text{B}_4\text{O}_3\text{Os}$
 $\text{Si}_2^*\text{C}_{13}\text{H}_{27}\text{B}_4\text{Co}$
 $\text{Si}_2^*\text{C}_{13}\text{H}_{28}\text{B}_5\text{Co}$
 $\text{Si}_2^*\text{C}_{13}\text{H}_{29}\text{B}_6\text{Co}$
 $\text{Si}_2^*\text{C}_{13}\text{H}_{31}\text{B}_6\text{Co}$
 $\text{Si}_2^*\text{C}_{22}\text{H}_{48}\text{B}_2\text{N}_2\text{Ni}_2$
 $\text{Si}_2\text{Ti}^*\text{C}_{14}\text{H}_{30}\text{B}_2\text{Cl}_2\text{N}_2$
 $\text{Si}_2\text{V}^*\text{C}_{14}\text{H}_{30}\text{B}_2\text{ClN}_2$
 $\text{Si}_3^*\text{B}_x\text{Gd}$
 $\text{Si}_3^*\text{B}_x\text{Nd}_5$
 $\text{Si}_3^*\text{BCr}_5$
 $\text{Si}_3^*\text{BDy}_5$
 $\text{Si}_3^*\text{B}_2\text{Nb}_5$
 $\text{Si}_3^*\text{C}_{12}\text{H}_{33}\text{Ga}$
 $\text{Si}_3^*\text{C}_{12}\text{H}_{33}\text{In}$
 $\text{Si}_3^*\text{C}_{22}\text{H}_{57}\text{HgIrOP}_2$
 $\text{Si}_3\text{Ta}_5^*\text{B}_2$
 $\text{Si}_3\text{Tb}_5^*\text{B}_x$
 $\text{Si}_3\text{V}_5^*\text{B}_{0.48}$
 $\text{Si}_4^*\text{C}_{12}\text{H}_{28}\text{Ga}_2$
 $\text{Si}_8^*\text{C}_{28}\text{H}_{76}\text{Al}_2$
 $\text{Si}_8^*\text{C}_{28}\text{H}_{76}\text{In}_2$
 $\text{Sm}^*\text{B}_x\text{Rh}_3$
 Sm^*BCo_4
 Sm^*B_2
 $\text{Sm}^*\text{B}_2\text{Co}_2$
 $\text{Sm}^*\text{B}_2\text{Co}_3$
 $\text{Sm}^*\text{B}_2\text{Ir}_3$
 $\text{Sm}^*\text{B}_2\text{Os}_2$
 $\text{Sm}^*\text{B}_2\text{Rh}_3$
 $\text{Sm}^*\text{B}_2\text{Ru}_2$
 $\text{Sm}^*\text{B}_2\text{Ru}_3$
 Sm^*B_4
 $\text{Sm}^*\text{B}_4\text{Co}_4$
 $\text{Sm}^*\text{B}_4\text{Cr}$
 $\text{Sm}^*\text{B}_4\text{Fe}$
 $\text{Sm}^*\text{B}_4\text{Fe}_4$
 $\text{Sm}^*\text{B}_4\text{Ir}_4$
 $\text{Sm}^*\text{B}_4\text{Ni}$
 $\text{Sm}^*\text{B}_4\text{Os}_4$
 $\text{Sm}^*\text{B}_4\text{Rh}_4$
 $\text{Sm}^*\text{B}_4\text{Ru}_4$
 Sm^*B_6
 $\text{Sm}^*\text{B}_6\text{Cr}_2$
 Sm^*B_{66}
 $\text{Sm}^*\text{C}_2\text{B}_2$
 $\text{Sm}_2^*\text{BFe}_{14}$
 Sm_7^*B_5
 $\text{Sm}_3^*\text{B}_4\text{Co}_{11}$

$\text{Sm}_3^*\text{C}_{48}\text{H}_{68}\text{B}_{18}\text{NO}_2\text{P}_2$	Sr_2^*Cd
Sn^*AuNa_2	Sr_2^*Cd_9
$\text{Sn}^*\text{C}_2\text{H}_{11}\text{B}_{10}\text{Cl}_2$	Sr_2^*Hg
$\text{Sn}^*\text{C}_3\text{H}_9\text{Li}$	Sr_2^*Hg_9
$\text{Sn}^*\text{C}_7\text{H}_9\text{CoO}_4$	$\text{Sr}_2^*\text{Mg}_{17}$
$\text{Sn}^*\text{C}_{10}\text{H}_{14}\text{FeO}_2$	Sr_3^*Ag_2
$\text{Sn}^*\text{C}_{11}\text{H}_{14}\text{MoO}_3$	Sr_3^*Au
$\text{Sn}_2^*\text{Au}_4\text{K}$	Sr_3^*Au_2
$\text{Sn}_2^*\text{B}_6\text{Co}_{21}$	$\text{Sr}_3^*\text{B}_6\text{Rh}_8$
$\text{Sn}_2^*\text{B}_6\text{Ni}_{21}$	Sr_3^*Hg
$\text{Sn}_2^*\text{C}_6\text{H}_{18}$	Sr_3^*Hg_2
$\text{Sn}_3^*\text{B}_x\text{Sc}$	Sr_3^*Li_2
$\text{Sn}_3^*\text{Ga}_8\text{Na}_3$	$\text{Sr}_5^*\text{B}_{10}\text{Rh}_{14}$
Sr^*Ag	Sr_5^*Cd_3
Sr^*Ag_2	$\text{Sr}_6^*\text{Li}_{23}$
Sr^*Ag_5	$\text{Sr}_6^*\text{Mg}_{23}$
Sr^*Au	Sr_7^*Ag_3
Sr^*Au_2	Sr_7^*Au_5
Sr^*Au_5	Sr_7^*Li
$\text{Sr}^*\text{B}_2\text{Ir}_2$	Sr_8^*Li
$\text{Sr}^*\text{B}_2\text{Rh}_2$	Ta^*B
Sr^*B_6	Ta^*BCo
$\text{Sr}^*\text{B}_6\text{Ni}_{12}$	$\text{Ta}^*\text{B}(\text{Co},\text{Ni})_2$
$\text{Sr}^*\text{Be}_{13}$	Ta^*BFe
$\text{Sr}^*\text{C}_x\text{B}_{6-x}$	Ta^*BNi
Sr^*Ca	Ta^*B_2
Sr^*Cd	$\text{Ta}^*\text{B}_2\text{Co}$
Sr^*Cd_2	$\text{Ta}^*\text{B}_2\text{Co}_2$
Sr^*Cd_6	$\text{Ta}^*\text{B}_2\text{Ni}$
$\text{Sr}^*\text{Cd}_{11}$	Ta^*Br_5
Sr^*Cu	$\text{Ta}^*\text{C}_7\text{H}_3\text{HgO}_6$
Sr^*Cu_5	Ta^*Cl_5
Sr^*Hg	Ta_2^*B
Sr^*Hg_2	$\text{Ta}_2^*\text{B}_6\text{Co}_{21}$
Sr^*Hg_3	$\text{Ta}_2^*\text{B}_6\text{Ni}_{21}$
$\text{Sr}^*\text{Hg}_{11}$	$\text{Ta}_2^*\text{B}_6\text{Ru}_{21}$
Sr^*Mg	Ta_3^*B_2
Sr^*Mg_2	$\text{Ta}_3^*\text{B}_2\text{Co}_5$
Sr^*Mg_4	Ta_3^*B_4
SrZn	$\text{Ta}_3^*\text{B}_7\text{Co}_4$
SrZn	$\text{Ta}_5^*\text{Al}_3\text{B}$
Formation: 7.3.4.1.4	$\text{Ta}_5^*\text{BGe}_3$
SrZn_2	$\text{Ta}_5^*\text{B}_2\text{Si}_3$
SrZn_2	$\text{Tb}^*\text{B}_x\text{Rh}_3$
Formation: 7.3.4.1.4	Tb^*BCo_4
SrZn_5	Tb^*B_2
SrZn_5	$\text{Tb}^*\text{B}_2\text{Co}_2$
Formation: 7.3.4.1.4	$\text{Tb}^*\text{B}_2\text{Co}_3$
SrZn_{13}	$\text{Tb}^*\text{B}_2\text{Fe}_2$
SrZn_{13}	$\text{Tb}^*\text{B}_2\text{Ir}_3$
Formation: 7.3.4.1.4	$\text{Tb}^*\text{B}_2\text{Os}$
Sr_2^*Au	$\text{Tb}^*\text{B}_2\text{Rh}_3$
$\text{Sr}_2^*\text{B}_4\text{Rh}_5$	$\text{Tb}^*\text{B}_2\text{Ru}$
$\text{Sr}_2^*\text{B}_6\text{Pt}_9$	$\text{Tb}^*\text{B}_2\text{Ru}_3$

Tb*B ₄	Th*B ₄ Ru ₄
Tb*B ₄ Co	Th*B ₆
Tb*B ₄ Co ₄	Th*B ₁₂
Tb*B ₄ Cr	Th*B ₆₆
Tb*B ₄ Fe	Th*CB
Tb*B ₄ Ir ₄	Th*CB ₂
Tb*B ₄ Mn	Th*Mg ₂
Tb*B ₄ Mo	ThV*B ₄
Tb*B ₄ Ni	ThW*B ₄
Tb*B ₄ Os	Th ₂ *BFe ₁₄
Tb*B ₄ Os ₄	Th ₃ *C ₃ B ₂
Tb*B ₄ Re	Th ₆ *Mg ₂₃
Tb*B ₄ Rh ₄	Ti*B
Tb*B ₄ Ru	Ti*B ₂
Tb*B ₄ Ru ₄	Ti*C ₁₄ H ₃₀ B ₂ Cl ₂ N ₂ Si ₂
Tb*B ₆	Ti*C ₁₄ H ₃₄ B ₂ Cl ₄ N ₂
Tb*B ₁₂	Ti*C ₁₆ H ₃₀ B ₂ Br ₂ N ₂
Tb*B ₆₆	Ti*Cl ₄
Tb*CB ₂	Ti ₂ *B ₂ Re
Tb*C ₂ B ₂	Ti ₃ *B ₂ Co ₅
TbV*B ₄	Ti ₃ *B ₄
TbW*B ₄	Ti ₃ *B ₆ Co ₂₀
Tb ₂ *BFe ₁₄	Ti ₃ *B ₆ Ni ₂₀
Tb ₂ *B ₃ Co ₇	Tl*C ₃ H ₉
Tb ₂ *B ₆ Ni ₁₅	Tl*C ₆ H ₈ B
Tb ₂ *B ₆ Re	Tl*C ₁₀ ClMn ₂ O ₁₀
Tb ₂ *B ₉ Ni ₁₅	Tl*C ₁₁ H ₁₀ B
Tb ₂ *CFe ₁₄	Tl*C ₁₂ Co ₃ O ₁₂
Tb ₃ *C ₁₁ B ₄	Tl*C ₁₅ Mn ₃ O ₁₅
Tb ₅ *B _x Ge ₃	Tl*C ₁₇ H ₁₀ MnO ₅
Tb ₅ *B _x Si ₃	Tl*C ₂₆ H ₂₄ AuP ₂ S ₂
Tc*B ₂	Tl*C ₄₁ H ₄₁ B ₉ MoNO ₃ P ₂
Tc ₃ *B	TlW*C ₄₁ H ₄₁ B ₉ NO ₃ P ₂
Tc ₇ *B ₃	Tl ₂ *C ₂ H ₁₁ B ₉
Te	Tl ₂ *C ₆ H ₁₈ K ₂
Te	Tl ₂ *C ₂₄ H ₂₀
Reaction with elemental Al, Ga, In:	Tl ₃ *B _x Sc
6.2.3	Tm*B _x Rh ₃
Te*C ₄ H ₂₂ B ₂₀ Hg	Tm*BCo ₄
Te*Ga	Tm*B ₂
Te*In	Tm*B ₂ Co ₃
Te ₄ *In ₄	Tm*B ₂ Fe ₂
Te ₁₀ *Al ₇	Tm*B ₂ Ir ₃
Th*B _x Rh ₃	Tm*B ₂ Os
Th*B ₂ Ir ₃	Tm*B ₂ Rh ₃
Th*B ₂ Os ₂	Tm*B ₂ Ru
Th*B ₂ Ru ₂	Tm*B ₂ Ru ₃
Th*B ₂ Ru ₃	Tm*B ₄
Th*B ₄	Tm*B ₄ Co
Th*B ₄ Ir ₄	Tm*B ₄ Co ₄
Th*B ₄ Mo	Tm*B ₄ Cr
Th*B ₄ Os ₄	Tm*B ₄ Fe
Th*B ₄ Re	Tm*B ₄ Os
Th*B ₄ Rh ₄	Tm*B ₄ Os ₄

Tm*B ₄ Re	V*B ₄ Gd
Tm*B ₄ Rh ₄	V*B ₄ Ho
Tm*B ₄ Ru	V*B ₄ Tb
Tm*B ₄ Ru ₄	V*B ₄ Th
Tm*B ₁₂	V*B ₄ U
Tm*B ₆₆	V*Be ₁₃
Tm*CB ₂	V*C ₁₄ H ₂₂ B ₄
Tm*C ₂ B ₂	V*C ₁₄ H ₃₀ B ₂ ClN ₂ Si ₂
Tm ₂ *BFe ₁₄	V*C ₅₉ H ₄₅ Au ₃ O ₅ P ₃
Tm ₂ *B ₃ Co ₇	V ₂ *B ₂ Ir
Tm ₂ *B ₆ Ni ₁₅	V ₂ *B ₃
Tm ₂ *B ₆ Ni ₂₁	V ₂ *B ₆ Co ₂₁
Tm ₂ *B ₆ Re	V ₂ *B ₆ Ni ₂₁
Tm ₂ *B ₉ Ni ₁₅	V ₃ *B ₂
Tm ₃ *B ₄ Co ₁₁	V ₃ *B ₄
Tm ₄ *B ₁₀ Ni ₂₉	V ₅ *B _{0.48} Si ₃
U*B _x Rh ₃	V ₅ *BGe ₃
U*BN	V ₅ *B ₂ Si
U*BNi ₄	V ₅ *B ₆
U*BRu ₃	W _n Zn _n *C _{5n} H _{5n}
U*B ₂	W _{1-x} *B ₃
U*B ₂ Co ₃	W _{1-x} *B ₃ Ni _{1-x}
U*B ₂ Fe ₃	W _{1-x} *B ₃ Pd _{1-x}
U*B ₂ Ir ₃	W _{1-x} *B ₃ Rh _{1-x}
U*B ₂ Os ₃	W*B _x
U*B ₂ Ru ₃	W*B
U*B ₄	W*BCo
U*B ₄ Co	W*BFe
U*B ₄ Co ₄	W*B ₂
U*B ₄ Cr	W*B ₂ Ir
U*B ₄ Fe	W*B ₂ Mn
U*B ₄ Mn	W*B ₂ Os
U*B ₄ Mo	W*B ₂ Ru
U*B ₄ Ni	W*B ₄
U*B ₄ Os ₄	W*B ₄ Dy
U*B ₄ Re	W*B ₄ Er
U*B ₄ Ru ₄	W*B ₄ Gd
U*B ₁₂	W*B ₄ Ho
U*CB	W*B ₄ Tb
U*CB ₂	W*B ₄ Th
UV*B ₄	W*B ₄ U
UW*B ₄	W*C ₈ H ₅ BrHgO ₃
U ₂ *B ₆ Co ₂₁	W*C ₈ H ₅ ClHgO ₃
U ₂ *B ₆ Ni ₂₁	W*C ₈ H ₅ NaO ₃
U ₃ *B ₂ Co ₇	W*C ₈ H ₆ O ₃
V _{0.51-0.36} *BRe _{1.49-1.64}	W*C ₁₀ H ₁₂
V _{0.95-0.63} *BRe _{1.05-1.37}	W*C ₁₀ H ₁₂ BF ₃
V*B	W*C ₁₁ H ₂₄ B ₉ O ₃ P
V*B ₂	W*C ₁₆ H ₃₈ B ₉ NO ₂
V*B ₂ Mn	W*C ₂₀ H ₃₆ B ₂ N ₂ O ₄
V*B ₂ Os	W*C ₂₆ H ₁₉ BF ₃ O ₃ P
V*B ₃ Co	W*C ₂₆ H ₁₉ O ₃ P
V*B ₄ Dy	W*C ₂₆ H ₂₀ AuO ₃ P
V*B ₄ Er	W*C ₄₁ H ₄₁ B ₉ NO ₃ P ₂ Tl

$W^*C_{42}H_{56}GaNO_3$	Y^*CB_2
$W^*C_{42}H_{56}InNO_3$	$Y^*C_2B_2$
$W^*C_{49}H_{48}B_9NO_2$	$Y_2^*BFe_{14}$
$W^*C_{49}H_{52}B_9NO_2$	$Y_2^*B_3Co_7$
WY^*B_4	$Y_2^*B_6Ni_{15}$
W_2^*B	$Y_2^*B_6Re$
$W_2^*B_2Co$	$Y_2^*B_9Ni_{15}$
$W_2^*B_2Fe$	$Y_3^*B_4Co_{11}$
$W_2^*B_2Ni$	Yb^*AlB_4
$W_2^*B_5$	$Yb^*B_xRh_3$
$W_2^*B_5Pd_2$	Yb^*B_2
$W_2^*B_6Co_{21}$	$Yb^*B_2Co_3$
$W_2^*B_6Ir_3$	$Yb^*B_2Ir_3$
$W_3^*B_3Co$	$Yb^*B_2Rh_3$
$W_3^*B_3Fe$	Yb^*B_4
$W_3^*B_3Ni$	Yb^*B_4Os
$W_4^*BHf_9$	$Yb^*B_4Os_4$
$W_4^*B_5Hf$	Yb^*B_4Ru
$W_4^*B_5Mn$	$Yb^*B_4Ru_4$
$W_4Zr_9^*B$	Yb^*B_6
$W_5^*(B,Si)_3$	Yb^*B_{12}
$W_{6.7}^*BRe_{13.3}$	Yb^*B_{66}
$Y^*B_xRh_3$	$Yb^*C_xB_{6-x}$
Y^*BCo_4	Yb^*CB_2
Y^*B_2	$Yb^*C_2B_2$
$Y^*B_2Co_2$	$Yb_2^*AlB_6$
$Y^*B_2Co_3$	$Yb_2^*B_6Ni_{15}$
$Y^*B_2Fe_2$	$Yb_2^*B_6Ni_{21}$
$Y^*B_2Ir_3$	$Yb_2^*B_9Ni_{15}$
$Y^*B_2Ni_3$	$Yb_4^*B_{10}Ni_{29}$
Y^*B_2Os	$Zn_n^*C_{5n}H_{5n}Mo_n$
$Y^*B_2Rh_3$	$Zn_n^*C_{5n}H_{5n}W_n$
Y^*B_2Ru	Zn
Y^*B_4	Zn
Y^*B_4Co	Reaction with $Co_2(CO)_8$, $Mn_2(CO)_{10}$:
$Y^*B_4Co_4$	8.3.3.4
Y^*B_4Cr	$Zn^*B_{10}H_{12}$
Y^*B_4Fe	Zn^*Ba
$Y^*B_4Fe_4$	Zn^*Ba_2
$Y^*B_4Ir_4$	$Zn^*C_2H_6$
Y^*B_4Mn	$Zn^*C_4H_9FeN_3O_4$
Y^*B_4Mo	$Zn^*C_4H_{10}$
Y^*B_4Ni	$Zn^*C_8Co_2O_8$
Y^*B_4Os	$Zn^*C_8H_{18}$
$Y^*B_4Os_4$	$Zn^*C_{10}H_{10}$
Y^*B_4Re	$Zn^*C_{10}Mn_2O_{10}$
$Y^*B_4Rh_4$	$Zn^*C_{11}H_{15}BNbO$
Y^*B_4Ru	$Zn^*C_{14}H_{10}MoO_3$
$Y^*B_4Ru_4$	$Zn^*C_{26}H_{42}B_4Fe_2S_2$
Y^*B_4W	$Zn^*C_{36}F_{30}Ge_2$
Y^*B_6	$Zn^*C_{72}H_{30}F_{30}Ge_2P_2Pt$
Y^*B_{12}	Zn^*Ca
Y^*B_{66}	Zn^*Ca_3
Y^*CB	Zn^*K

Zn*Li	Zn ₁₁ *Mg ₂
Zn*Mg	Zn ₁₃ *Ba
Zn*Sr	Zn ₁₃ *Ca
Zn ₂ *Ba	Zn ₁₃ *K
Zn ₂ *Li	Zn ₁₃ *Na
Zn ₂ *Sr	Zn ₁₃ *Sr
Zn ₃ *Ca	Zn ₂₀ *Ca ₇
Zn ₃ *Ca ₅	Zn ₂₀ *Mg ₅₁
Zn ₃ *Li ₂	Zr*B _x Ir ₃
Zn ₃ *Mg ₂	Zr*B ₂
Zn ₃ *Mg ₇	Zr*B ₂ Co ₃
Zn _{3,3} *B ₆ Ni _{19,7}	Zr*B ₄ Ir ₃
Zn ₄ *Ca ₇	Zr*B ₁₂
Zn ₄ *Li	Zr*B ₅₁
Zn ₅ *B ₈ Ru ₈	Zr ₂ *B ₆ Co ₂₁
Zn ₅ *Ba	Zr ₅ *Al ₃ B
Zn ₅ *Li ₂	Zr ₉ *BMo ₄
Zn ₅ *Sr	Zr ₉ *BRe ₄
Zn ₁₁ *Ca	Zr ₉ *BW ₄

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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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