BORON HYDRIDES, HETEROBORANES, AND THEIR METALLA DERIVATIVES

1. Introduction

The boron hydrides, including the polyhedral boranes, heteroboranes, and their metalla derivatives, encompass an amazingly diverse area of chemistry. This class contains the most extensive array of structurally characterized cluster compounds known. Included here are many unique clusters possessing idealized molecular geometries ranging over every point group symmetry from identity (C_1) to icosahedral (I_h). Because boron hydride clusters may be considered in some respects to be progenitorial models of metal clusters, their development has provided a framework for the development of cluster chemistry in general as well as for chemical bonding theory.

The first definitive studies of boron hydrides were carried out by Alfred Stock in Germany starting ~1912 (1). Through extensive and now classic synthetic studies, the field of boron hydride chemistry was founded with the isolation of a series of highly reactive, air-sensitive, and volatile compounds of general composition B_nH_{n+4} and B_nH_{n+6}. This accomplishment required the development of basic vacuum line techniques for the manipulation of air-sensitive compounds. An American effort in boron hydride research was subsequently initiated by Hermann I. Schlesinger. His students, including Anton Burg and Herbert C. Brown, went on to make great contributions to boron chemistry. Brown pursued the practical development of hydroboration procedures that are now so important to organic and pharmaceutical chemistry and for which, in 1979, he received a Nobel Prize (2).

Following World War II, activity in boron hydride research increased tremendously in the United States A and Russia as a result of classified government research programs on high energy fuels. In the United States, these included projects HERMES, HEF, and ZIP (3). Research was initially directed toward the development of new fuels for strategic aircraft, such as the B-70A Valkyrie long-range bomber, and eventually led to research on solid rocket propellants. The United States and Russia nearly simultaneously declassified these programs in the early 1960s revealing many important findings, including the discovery of carboranes. Although much information from these enormous governmental efforts has never been published, boron hydride materials have since resulted from government stockpiles produced during this period.

The structural and theoretical aspects of boron hydrides were delineated through X-ray diffraction, theoretical analyses of bonding, and structure and reactivity studies. William N. Lipscomb received the 1976 Nobel Prize for his definitive work on the structure and bonding of boron hydride chemistry, leading to the development of valence bond theory (4). The emergence of a theoretical understanding of boron hydrides and the residual momentum of the high energy fuels program led to a rapid proliferation of significant new boron hydride compounds and the elaboration of their chemistry. The polyhedral borane anions, carboranes, and metallacarboranes were discovered a half-century after the first report of highly reactive boron hydrides, the most stable classes of boron hydrides. The isomeric icosahedral carborane $C_2B_{10}H_{12}$ was reported almost simultaneously in 1963 by American industrial chemists and by workers in Russia (5). The highly fruitful marriage of transition metal and carborane cluster chemistry leading to the metallacarboranes soon followed (6).

2. Nomenclature

The nomenclature of boron hydride derivatives has been somewhat confusing and many inconsistencies exist in the literature. The structures of some reported boron hydride clusters are so complicated that only a structural drawing or graph, often accompanied by explanatory text, is used to describe them. Nomenclature systems often can be used to describe compounds unambiguously, but the resulting descriptions may be so unwieldy that they are of little use. The International Union of Pure and Applid Chemestry (IUPAC) (7) and the Chemical Abstract Service (CAS) (8) have made recommendations, and nomenclature methods have now been developed that can adequately handle nearly all cluster compounds; however, these methods have yet to be widely adopted. For the most part, the nomenclature used in the original literature is retained herein.

The neutral boron hydrides are termed boranes. The molecule BH_3 is called borane or borane(3) [13283-31-3]. For more complex polyboranes, the number of boron atoms is indicated by the common prefixes di-, tri-, tetra-, etc, and the number of hydrogens (substituents) is given by an arabic numeral in parentheses following the name. For example, B_5H_{11} is named pentaborane(11) [18433-84-6], $B_{20}H_{16}$ is named eicosaborane(16) [12008-84-3], and $B_{10}H_{12}I_2$ is diiododecaborane(14) [23835-60-1]. The position of the substituents can be designated precisely from framework numbering conventions. The numbering conventions for selected polyhedra are given in Figure 1. Because other numbering systems are often also used, it is advisable to refer to structural diagrams.

Borane polyhedra have both closed and open skeletons and it has become common practice to include the appropriate structural classification in the compound's name. Closed polyhedra having only triangular faces are termed *closo*, and open structures are designated *nido, arachno*, or *hypho*. For example, more complete names for the previous examples are *arachno*-pentaborane(11), *closo*-icosaborane(16), and 2,4-diiodo-*nido*-decaborane(14). Boron hydride anions are generally termed hydroborates using prefixes to designate the number of hydrogens and borons; the charge follows the name in parentheses. For example, $NaBH_4$ is sodium tetrahydroborate(1−) [16940-66-2], $K_2B_{10}H_{10}$ is potassium decahydro-*closo*-decaborate(2−) [12447-89-1], and the 2,4-dichlorododecahydro*nido*-decaborate(2−) anion [51668-03-2] is $(2,4\text{-}Cl_2B_{10}H_{12})^{2-}$.

When a boron atom of a borane is replaced by a heteroelement, the compounds are called carbaboranes, phosphaboranes, thiaboranes, azaboranes, etc, by an adaptation of organic replacement nomenclature. The original term carborane has been widely adopted in preference to carbaborane, the more systematic name. The numbering of the skeleton in heteroboranes is such that the

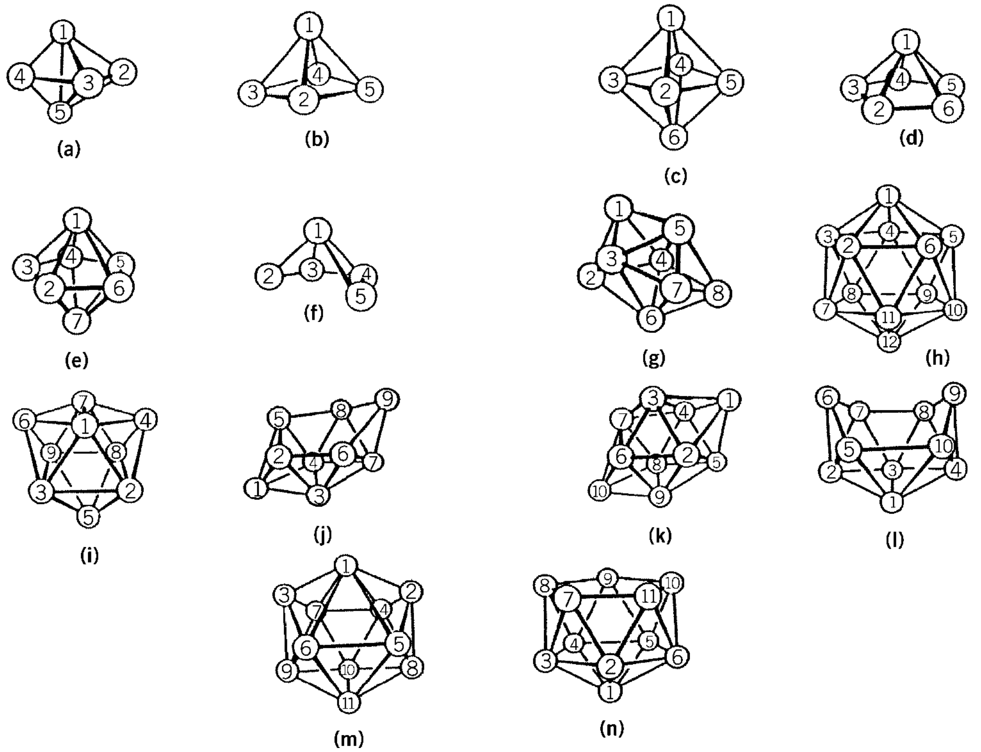


Fig. 1. Numbering conventions for selected borane polyhedra (7) discussed in the text.

heteroelement is given the lowest possible number consistent with the conventions of the parent borane. Thus $C_2B_3H_5$ is dicarba-*closo*-pentaborane(5) and could occur as the 1,2-, 2,3-, or 1,5-isomeric forms (1,2-dicarba-*closo*-pentaborane(5) [23777-70-0], 2,3-dicarba-*closo*-pentaborane(5) [30396-61-3], and 1,5-dicarba-*closo*-pentaborane(5) [20693-66-7]) (see Fig. 1**a**). When different heteroelements occur in combination in a polyhedron, *Chemical Abstracts* gives priority by descending group number and increasing atomic number within a group, eg, 1,2-$PCB_{10}H_{11}$ is 1-phospha-2-carba-*closo*-decaborane(11) [30112-97-1]; however, the hierarchy in the original literature often gives the lowest number to the element of lowest atomic number, eg, 1,2-$CPB_{10}H_{11}$ or 1-carba-2-phospha-*closo*-dodecaborane(11) [30112-97-1]. This convention carries over to the metallaboranes and metallaheteroboranes when a metal occupies a polyhedral vertex. Examples are 9,9-bis(triphenylphosphine)-6-thia-9-platina-*nido*-decaborane(10) [52628-81-6], 9,9-$[P(C_6H_5)_3]_2$-6,9-$SPtB_8H_{10}$, 3-η^5 -cyclopentadienyl-2-dimethyl-1,2-dicarba-3-ferra-*closo*-dodecaborane(11) [66750-82-1], 3-(η^5-C_5H_5)-1,2-$(CH_3)_2$ -3,1,2-$FeC_2B_9H_9$. The arabic numeral in parentheses following the name does not include exopolyhedral ligands bonded to the metal, only the total of the hydrogen atoms plus other substituents bonded to boron and main group heteroelements in the skeletal framework. Examples of metallaborane anions are the 1-η^5-cyclopentadienyl-1-nickela-undecahydro-*closo*-undecaborate(1−) ion, $[(\eta^5\text{-}C_5H_5)Ni(B_{11}H_{11})]^-$, and the 2-$\eta^5$-cyclopentadienyl-2-cobalta-heptahydro-*nido*-tetraborate (1−) ion, $[2\text{-}(\eta^5\text{-}C_5H_5)\text{-}2\text{-}CoB_4H_7]^-$.

A variety of heteroboranes, metallaboranes, and metallaheteroboranes exist that contain more than one interconnected polyhedral cluster. These complex clusters are referred to as conjuncto-boranes. Conjuncto-boranes may be interconnected by sharing a single common boron atom, having a direct B–B bond between two clusters, sharing two boron atoms at a polyhedral edge or three boron atoms at a face, or more extensive polyhedral fusion by the sharing of four or more boron atoms between clusters. Examples include the *commo*-7,7′-bis(dodecahydro-7-nickela-*nido*-undecaborate)(2−) dianion [31388-28-0], [7,7′(-Ni$(B_{10}H_{12})_2]^{2-}$, and the decahydro-2,11-bis(η^5-cyclopentadienyl)-2,11-dicobalt-1-carba-*closo*-dodecaborate(1−) ion [59422-34-3], $[2,11\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}2,11,1\text{-}Co_2\text{-}CB_9H_{10}]^-$. The *commo* prefix is often used to indicate that the metal vertex is shared by two polyhedra. The *commo* nomenclature of metallaboranes and metallaheteroboranes is a widely used special case of the IUPAC recommended conjuncto nomenclature.

3. Structural Systematics

Because the polyhedral boron hydrides are cage molecules, which usually possess triangular faces, their idealized geometries can be described accurately as deltahedra or deltahedral fragments. The left-hand column of Figure 2 illustrates the deltahedra containing $n = 6–12$ vertices: the octahedron, pentagonal bipyramid, bisdisphenoid, symmetrically tricapped trigonal prism, bicapped square antiprism, octadecahedron, and icosahedron. These idealized structures are convex deltahedra except for the octahedron, which is not a regular polyhedron. The left-hand column of Figure 2 also represents the class of deltahedral *closo* molecules from which the other idealized structures (deltahedral fragments) can be generated systematically. Any *nido* or *arachno* cluster can be generated from the appropriate deltahedron by ascending a diagonal from left to right. This progression generates the *nido* structure (center column) by removing the most highly connected vertex of the deltahedron, and the *arachno* structure (right column) by removal of the most highly connected atom of the open (nontriangular) face of the *nido* cluster. The structural correlations shown in Figure 2 were formulated in 1971 (9), and subsequently elaborated (10,11). The terms *closo, nido, arachno*, and *hypho* are derived from Greek and Latin and imply closed, nestlike, weblike, and netlike structures, respectively. These classifications apply equally well to boranes, heteroboranes, and their metalla analogues, and are intimately connected to a quantity known as the framework, or skeletal, electron count. The partitioning of electrons into framework and exopolyhedral classes allows for predictions of structures in most cases, even though these systematics are not concerned explicitly with the assignments of localized bonds within the polyhedral skeletons of these molecules. That is, the lines depicting the skeletons of the structures illustrated are not electron-pair, or "electron precise", bonds. The lines merely serve to join nearest neighbors and illustrate cluster geometries. However, exopolyhedral lines do represent the usual electron precise bonds.

Proposal of a structure from Figure 2 for a given borane or heteroborane proceeds by (*1*) selecting the row that corresponds to the number of framework

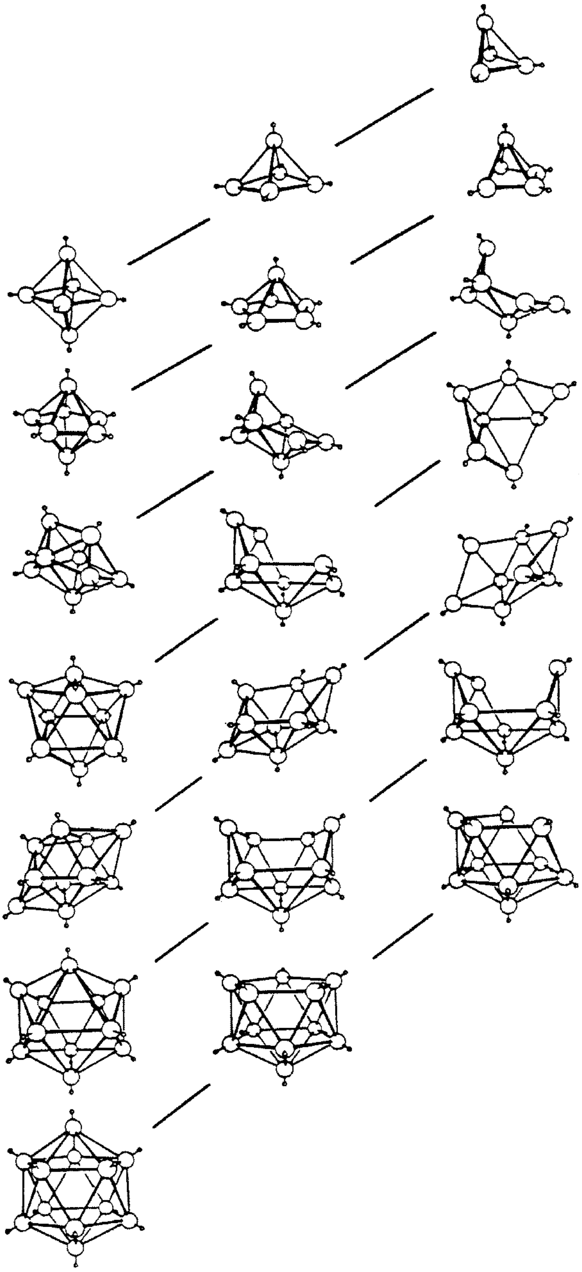


Fig. 2. Idealized deltahedra and deltahedral fragments for *closo, nido*, and *arachno* boranes and heteroboranes. From left to right, the vertical columns give generic *closo, nido*, and *arachno* frameworks; bridge hydrogens and BH_2 groups are not shown, but when appropriate they are placed around the open (nontriangular) face of the framework (see text).

atoms, or polyhedral vertices, n; and (*2*) determining the number of electrons that can reasonably be assigned to bonding within the polyhedral skeleton as opposed to exopolyhedral bonds. According to what are known as the Williams-Wade rules, framework electron counts of $2n+2$, $2n+4$, $2n+6$, and $2n+8$ correspond to the cluster classifications *closo, nido, arachno*, and *hypho*, respectively. For *closo, nido*, and *arachno* electron counts, a structure in the appropriate column of Figure 2 is suggested. These systematics emphasize the oxidation–reduction relationship of *closo–nido–arachno–hypho* interconversions for clusters having the same number of vertices. Boranes of the hypho class are relatively rare and are not included in Figure 2. The term *klado* is recommended by the IUPAC to designate the equally rare class of compounds having a $2n{+}10$ framework electron count. The term *capo* has been proposed to describe boranes, such as $B_{10}H_{10}$, having a $2n$ framework electron count. Compounds having an apparent *closo* structure and possess $<2n{+}2$ skeletal electrons are referred to as *hypercloso*. Other empirical rules refer to the preferred placement of heteroatoms and so-called extra hydrogen atoms in these clusters. The correlation of skeletal electron count with structure is generally applicable to the metallaborane and metallacarborane derivatives as well as to other non-boron types of cluster molecules such as carbocations (12) and metal clusters (11,13,14).

Note that the eight-vertex *nido* cage shown in Figure 2 is more open than would be expected for a cluster resulting from the simple removal of one vertex from the nine-vertex *closo* cage. However, this is the observed geometry for known eight-vertex boranes and carboranes. This apparent anomaly reflects a pattern that exists for *nido* cages containing only boron and/or carbon framework atoms in which, once cages become large enough, there is an alternation of five- and six-membered open faces (15). That is, 6-, 8-, 10-, and 12-vertex *nido* boranes and carboranes have six-membered open faces and 7-, 9-, and 11-vertex boranes and carboranes have five-membered open faces. This observed pattern can be rationalized in terms of charge density of atoms at the open face.

The assignment of valence electrons and the factoring out of those electrons involved in exopolyhedral bonds provides $2n$ framework electrons for a B_nH_n molecule, two electrons short of the $2n+2$ *closo* count. In fact, stable neutral B_nH_n molecules are not known; however, the $[B_nH_n]^{2-}$ anions ($n=6$–12) and the neutral isoelectronic $C_2B_{n-2}H_n$ carboranes ($n=5$–12) are very stable. These are the best known examples of *closo* molecules. Thus, in these respective cases, the double negative charge and the two C–H groups that donate one more valence electron each than a B–H group, furnish the two electrons required to achieve the $2n+2$ framework electron count. In general, substitution of other moieties for a B–H vertex alters the number of framework electrons contributed by a particular vertex, but as long as the total remains $2n+2$, the molecule is classified as *closo*. The number of electrons contributed to the framework electron count by a specific vertex group has been generalized in the form of an equation (14). For main group elements the number of framework electrons contributed is equal to $(v+x-2)$ where v is the number of valence shell electrons of that element, and x is the number of electrons from ligands, eg, for H, $x=1$, and for Lewis bases, $x=2$. Examples of $2n+2$ electron count boranes and heteroboranes, and the number of framework electrons contributed by their skeletal atoms, are given in Table 1.

Table 1. **Electron Counting for $2n+2$, $2n+$, and $2n+6$ Systems**[a]

			Framework electron contribution				
Compound	Extra boron[b]	Carbon[b]	Heteroatom[b]	Hydrogens	Charge	Total	Reference
			Closo$(2n+2)e^-$*systems*				
$C_2B_3H_5$	3(2)	2(3)			0	12	16
$[B_6H_6]^{2-}$	6(2)				2	14	17
$(CH_3)GaC_2B_4H_6$[c]	4(2)	2(3)	1(2)		0	16	18
$[B_8H_8]^{2-}$	8(2)				2	18	16
$C_2B_7H_9$	7(2)	2(3)			0	20	19
$[CB_9H_9]^-$	9(2)	1(3)			1	22	20
$C_2B_9H_{11}$	9(2)	2(3)			1	24	21
$SB_{11}H_{11}$	11(2)		1(4)		0	26	22
$SnC_2B_9H_{11}$	9(2)	2(3)	1(2)		0	26	23
$CPB_{10}H_{11}$	10(2)	1(3)	1(3)		0	26	24
			Nido$(2n+4)e^-$*systems*				
$C_2B_3H_7$	3(2)	2(3)		2	0	14	25
$C_3B_3H_7$	3(2)	3(3)		1	0	16	26
$C_4B_2H_6$	2(2)	4(3)			0	16	27
SB_8H_{10}	8(2)		1(4)	2	0	22	22
SB_9H_{11}	9(2)		1(4)	2	0	24	22
			$[CPB_9H_{10}]^{2-}$	9(2)	1(3)	1(3)	
	2	26	24				
			Arachno$(2n+6)e^-$*systems*				
B_5H_{11}	5(2)			6	0	16	28
$C_2B_7H_{13}$	7(2)	2(3)		4	0	24	29
$[SB_9H_{13}]^-$	9(2)		1(4)	3	1	26	22

[a] Where n is the number of non-hydrogen atoms in the cage structure.

[b] Number of atoms multiplied by, in parentheses, the number of electrons contributed to the framework gives the total electron contribution for the element.

[c] The CH_3 groups are outside the cage.

3.1. *Nido* Clusters ($2n+4$ Systems).

Many *closo* boranes and heteroboranes add two electrons and undergo a concomitant structural transformation from a deltahedron to a deltahedral fragment. For example, *closo*-2,6-$C_2B_9H_{11}$ [17764-89-0] ($2n+2=24$ e^-) is readily reduced to [*nido*-7,9-$C_2B_9H_{11}]^{2-}$ [39469-99-3] ($2n+4=26$ e^-) and conversely [*nido*-7,9-$C_2B_9H_{11}]^{2-}$, may be oxidized to the *closo* cage (30). An effective reduction also occurs upon addition of donors to these molecules, eg, the molecules *closo*-$C_2B_4H_6$ and *closo*-$C_2B_9H_{11}$ open upon addition of amines to give *nido*-$C_2B_4H_6 \cdot NR_3$ (31) and *nido*-$C_2B_9H_{11} \cdot NR_3$ (32), where R is an alkyl group. Such additions of donor groups can formally be regarded as equivalent to additions of H^-, ie, *nido*-$C_2B_4H_6 \cdot L$ and *nido*-$C_2B_9H_{11} \cdot L$, where L is a Lewis base, are analogous to $[C_2B_4H_7]^-$ and $[C_2B_9H_{12}]^-$, respectively. Other examples of *nido* molecules are given in Table 1.

In molecules such as $C_2B_3H_7$ it can be recognized that there are extra hydrogens, extra in the sense that there are more hydrogens than necessary for each vertex atom to have one exopolyhedral hydrogen atom. Extra hydrogens are generally regarded as contributing to the framework electron count. Usually extra hydrogens are found at open, or nontrigonal, faces of deltahedral fragments in the form of bridging hydrogens in B–H–B groups or as second hydrogen atoms in BH_2 groups. Both of these types of hydrogen locations are reminiscent of framework positions in that the bridge positions usually reside close to a spheroidal extension of the polyhedral surface, and in that one hydrogen of the BH_2 group is usually *endo* (close to a framework extension) and the other *exo*. In addition, extra hydrogens are often acidic and can be removed using bases to give anions, frequently without substantially altering framework geometry. In this respect, extra hydrogens may be regarded conceptually as protonated framework electrons. This concept suggests that the addition of a lone-pair donor, such as a hydride ion H^-, to a polyhedral framework adds two electrons and changes the molecule's classification accordingly.

3.2. *Arachno* Clusters ($2n + 6$ Systems). In comparison to the number of known *closo* and *nido* boranes and heteroboranes, there are relatively fewer *arachno* species. Partly because of the lack of a large number of structures on which to base empirical rules, *arachno* structures appear to be less predictable than their *closo* and *nido* counterparts. For example, there are two isomeric forms of B_9H_{15}, one with the *arachno* [19465-30-6] framework shown in Figure 2 (33), the other with a framework more reminiscent of that shown for the nine-atom *nido* classification (34). Structures of *arachno* molecules involve the presence of even more extra hydrogens or other electron-donating heteroatoms than *nido* molecules. Typical examples are given in Table 1.

3.3. *Hypho* Clusters ($2n + 8$ Systems). *Hypho* molecules are even more electron rich. Members of the *hypho* class are fairly rare and, therefore, examples of their structures have not been included in Figure 2. The compounds $B_5H_6[P(CH_3)_3]_2$ [39661-74-0], $[B_5H_{12}]^-$ [11056-98-7], and $B_6H_{10}[P(CH_3)_3]_2$ [57034-29-4], three molecules that contain $2n+8$ framework electrons and that represent members of the *hypho* class of boron hydrides, have been prepared and structurally characterized (35). As expected, this class adopts structures that are more open than their *arachno* and *nido* counterparts. The *hypho* molecule $B_5H_9[P(CH_3)_3]_2$, illustrated in Figure 3, contains two nonbonding basal B–B distances (those not bridged by hydrogen). In *arachno*-B_5H_{11} [18433-84-6] there is only one nonbonding basal B–B distance and in *nido*-B_5H_9 [19624-22-7] all basal distances of the pyramid are bonding (see the $n = 5$ horizontal row of Fig. 2). Another example of a *hypho* molecule is $B_4H_6[P(CH_3)_3]_2$ [66750-83-2] (36).

3.4. Metalla Derivatives. Compounds formed from main group metals and borane or heteroborane cages can be treated using the electron-counting systematics described. For example, the metallacarborane complexes *closo*-$MC_2B_9H_{11}$ (M = Ge [27071-59-9], Sn [23151-46-4], Pb [27071-51-8]) may be regarded as tricarbaborane analogues in which the Group 14 (IVA) metals are present as bare vertices (37). The metals in these clusters in theory possess a nonbonding lone pair of electrons (38) and contribute their remaining two valence electrons to the framework to give a 26-electron *closo* icosahedron.

In addition to satisfying the framework electron requirements of the cage, transition-metal metallaboranes and metallaheteroboranes also generally adhere to the 18 electron rule, and therefore require a somewhat different electron accounting treatment. Assuming that the metal vertex uses only three

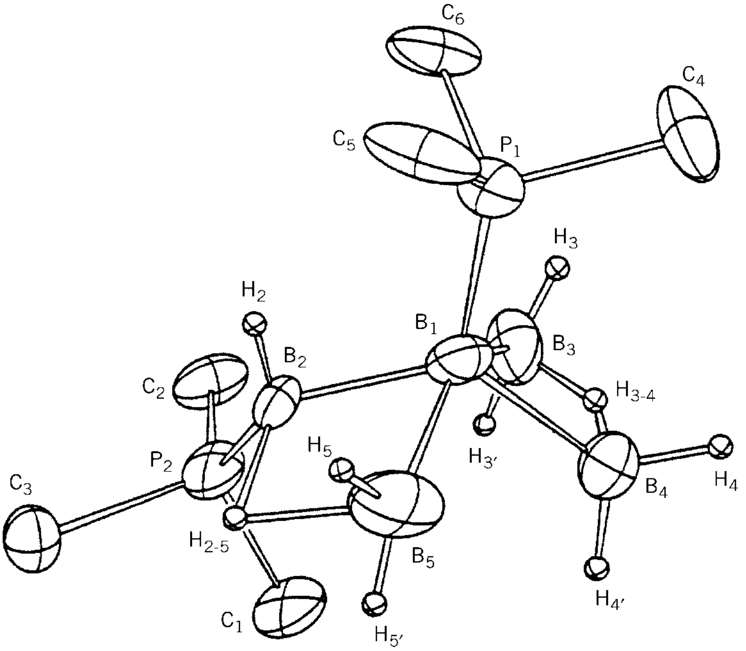


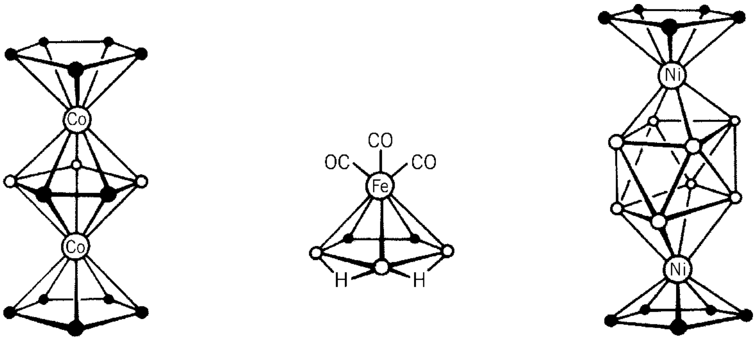
Fig. 3. The *hypho* molecule $B_5H_9[P(CH_3)_3]_2$. Courtesy of the American Chemical Society.

orbitals in cluster bonding, then 12 of the 18 valence electrons available at a metal vertex are not involved in cluster bonding. Thus the metal *d*-electrons may effectively be treated as not included as framework electrons. These premises have been generalized to give the number of skeletal electrons per metal vertex as ($v + x$-12), where v is the number of valence electrons of the metal and x is the number of electrons donated by exopolyhedral substituents and ligands (39). In this formalism, moieties such as $(CO)_3Fe$ and $(\eta^5\text{-}C_5H_5)Co$ can be regarded as donating two electrons to cage bonding and are analogous to a B−H vertex. In the same way, the $(\eta^5\text{-}C_5H_5)Ni$ moiety functions as a three-electron donor vertex analogous to a C−H vertex. Other examples of common vertex groups and their electron contributions to framework bonding are given in Table 2 (14) and Figure 4. The extension of these principles to organometallics

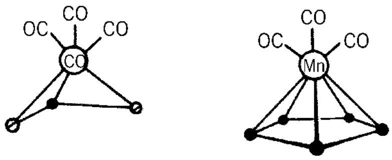
Table 2. **Framework Electron Contributions for Metal Moieties**[a]

Metal (M)	v	$M(CO)_2 x = 4$	$M(\eta^5\text{-}C_5H_5) x = 5$	$M(CO)_3 x = 6$
Cr	6	(−2)	(−1)	0
Mn	7	(−1)	0	1
Fe	8	0	1	2
Co	9	1	2	3
Ni	10	2	3	4

[a] The general contribution for a metal with v valence electrons and exopolyhedral ligands donating x electrons is $v + x - 12$ framework electrons (see text).



closo-$[(\eta^5\text{-}C_5H_5)Co]_2C_2B_3H_5$ *nido*-$(C_2B_3H_7)Fe(CO)_3$ *closo*-$[(\eta^5\text{-}C_5H_5)Co]_2C_2B_3H_5$



arachno-$(C_3H_5)Co(Co(CO)_3$ *nido*-$(\eta^5\text{-}C_5H_5)Mn(CO)_3$

Fig. 4. Metallaboranes and organometallics of the *closo, nido*, and *arachno* classification.

is straightforward: $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and $(C_3H_5)Co(CO)_3$ may be considered to be *nido* and *arachno* species, respectively, as indicated in Figure 4.

3.5. Placement of Heteroatoms. Many of the deltahedra and deltahedral fragments of Figure 2 have two or more nonequivalent vertices. Nonequivalent vertices are recognized as having a different order; ie, a different number of nearest neighbor vertices within the framework. Heteroatoms generally exhibit a positional preference based on the order of the polyhedral vertex and the electron richness of the heteroatom relative to boron. Electron-rich heteroatom groupings contribute more framework electrons than a : electrondots B−H moiety, which has two framework electrons, and generally prefer low order vertices, ie, those having fewer neighbors (40). For example, two of the three isomeric forms of $C_2B_8H_{10}$ can be isomerized thermally to the 1,10-isomer [13653-23-8] (19), the molecule with the carbons at the lowest order vertices. The pyrolysis of *nido*-6-SB_9H_{11} [59120-72-8] gives *closo*-1-SB_9H_9 [41646-56-4], with sulfur at the lowest order vertex (22) (see Fig. 1 for numbering conventions). When the heteroatom is in the same group as boron it preferably adopts a high order vertex; eg, $CH_3GaC_2B_4H_6$ [36607-02-2] (18). The transition metal moieties occur predominantly at high order vertices. The carborane *nido*-1,2-dicarbapentaborane [26249-71-8], $C_2B_3H_7$, presents a notable exception to the predilection of the carbon for low order vertices. It has been suggested that this exception is related to the placement of bridge hydrogens on the open face (10).

3.6. Placement of Extra Hydrogens. The placement of extra hydrogens plays a crucial role in determining the structures adopted by boranes and carboranes. However, the exact position of extra hydrogens sometimes depends on the physical state of the molecule, eg, the tridecahydrodecaborate(1−) anion,

$[B_{10}H_{13}]^-$ [36928-50-4] exhibits different bridge hydrogen placements in the crystal (41) and in solution (42) as can be inferred from experimental evidence, but the solution data are also consistent with a dynamic process of bridge hydrogen tautomerism.

A well-documented example of fluxionality for bridge hydrogens is provided by B_6H_{10} (43). In spite of the controversy regarding hydrogen placement in certain boranes, some empirical rules are evident: (*1*) bridging hydrogens generally occur only between two adjacent boron atoms at an open nontriangular face of the skeleton, and only occasionally bridging a triangular array of borons (44); (*2*) when possible, the bridge termini are the low order vertices of the open face; and (*3*) there is only one bridging hydrogen per edge. Generally, BH_2 groups may be postulated as tautomeric intermediates in fluxional *nido* boranes, but they occur as ground state moieties in *arachno* molecules and then at vertices of order three or lower. In the metallaboranes, hydrogen atoms often bridge between boron and a metal.

The placement of bridge hydrogens may be the most important variable in the determination of relative isomer stabilities, outranking placement of heteroatoms (10,40). A number of cases exist where heteroatoms adopt high order vertices in deference to bridge hydrogen placement at low order vertices, eg, in *nido*-1,2-$C_2B_3H_7$ one of the carbon atoms is at an unanticipated high order vertex, apparently because of bridge hydrogen atom placement (45,46).

3.7. M–H–B Bridges.

Numerous metallaboranes and metallaheteroboranes are known to contain hydrogens bridging between a metal atom and a skeletal boron atom, but complexes containing covalently bound tetrahydroborate(1–) [16971-29-2], $[BH_4]^-$, constitute the prototypical class (47). Metal tetrahydroborates have been reviewed (48). Polyboranes coordinate through bridge hydrogens in a variety of ways as shown in Figure 5. Although the bonds utilize B–H hydrogens in bridging to the metal just as for the tetrahydroborates, the presence of the cage atoms affords distinctly different structural possibilities. The B–H can be regarded as a two-electron donor to metals and often plays a role similar to that of CO in metal carbonyls to stabilize clusters.

3.8. Exceptions to Structural Systematics.

When strong electron-donating or electron-withdrawing groups are present as substituents attached

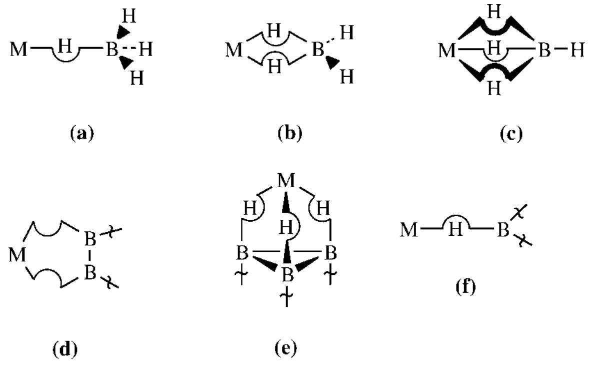


Fig. 5. Modes of M–H–B bonding where M–H–B represents a three-center hydrogen bridge bond for (**a**), (**b**), (**c**) tetrahydroborates and for (**d**), (**e**), (**f**) polyhedral boranes.

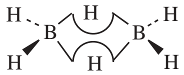
to boron in polyboranes, there is the possibility of structural anomalies. In some cases, electron deficiency of boron apparently can be ameliorated by back-donation instead of by the multicenter bonding afforded in a cage framework. Thus it has been suggested that exceptions to the electron-counting paradigms may occur where back-donation from the substituent to a cluster boron is possible. For example, although $C_4B_2H_6$ [12403-20-2] has a pyramidal *nido* geometry, the structural evidence for $C_4B_2F_2H_4$ [20534-09-2] favors a planar form where B−H has been replaced by B−F (49).

Some metallacarboranes present anomalies to the electron-counting formalisms. Symmetrical [*commo*-3,1,2-$M^n + (C_2B_9H_{11})_2]^{(n-4)}-$ sandwich complexes of the d^6 metals, where M is Fe^{2+} [51868-94-1] and Co^{3+} [11078-84-5] fit the paradigm nicely (50). However, the corresponding d^8 complexes, where M is, eg, Cu^{3+} [15721-63-8] or Ni^{2+} [36733-09-2], might be expected to show an unsymmetrically distorted partially open structure. However, symmetrically "slipped" sandwich structures are observed, suggestive of electron delocalization. The slipped structure can be explained in terms of a reduction of the *closo* molecule with a concomitant distortion as observed for *closo* carboranes (49–51). In accord with these ideas, the d^9 copper(II) complex is opened slightly more than the d^8 complex (50) and this distortion can be rationalized in terms of Jahn-Teller arguments (52). Alternatively, it is sometimes more satisfactory to view borane and carborane cages in their metal complexes as donor ligands that coordinate to metals in an appropriate fashion to contribute the number of electrons required by the specific metal center to produce a filled shell. For example, the [*nido*-7,8-$C_2B_9H_{11}]^{2-}$ cage can generally be regarded as a two-, four-, or six-electron donor when bound to transition metals in the η^1, η^3, or η^5 bonding modes, respectively. The η^3 π-bonding mode, which can be considered to occur in the d^8 metal complexes, involves the B_3 set of the five-membered carborane cage face and produces complexes that may be considered analogous to the well-known metal allyl complexes of traditional organometallic chemistry.

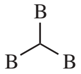
Because the electron-counting paradigm incorporates the 18-electron rule when applied to transition-metal complexes, exceptions can be expected as found for classical coordination complexes. Relatively minor exceptions are found in $(\eta^5\text{-}C_5H_5)_2Fe_2C_2B_6H_8$ [54854-86-3] (53) and $[Ni(B_{10}H_{12})_2]^{2-}$ [11141-32-5] (54). The former (2*n* electrons) is noticeably distorted from an idealized structure, and the latter is reminiscent of the d^8 and d^9 complexes discussed above. An extremely deficient electron count is obtained for complexes such as $[Cr(C_2B_9H_{11})_2]^-$ [37036-06-9], which have essentially undistorted *closo* structures (55). Exceptional cases occur for certain other metallacarboranes that contain electron-rich d^8, d^9, and d^{10} metals. For example, electron-counting formalisms predict *closo* structures for 3-$[(C_2H_5)_2NCS_2]$-3,1,2-$AuC_2B_9H_{11}$ [62572-50-3] (56) and 8,8-$[(CH_3)_3P]_2$-7,8,10-Pt-$C_2B_8H_{10}$ [58348-40-6] (57), but *nido* structures are observed by X-ray crystallography. In some cases, ambiguities arise because bridging hydrogen atoms have not been observed in X-ray crystallographic studies.

4. Bonding

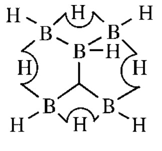
4.1. Localized Bonds. Because boron has more valence orbitals than valence electrons, its compounds are often called electron deficient. This electron deficiency is partly responsible for the great interest surrounding boron hydride chemistry and molecular structure. The structure of even the simplest boron hydride, diborane(6) [19287-45-7], B_2H_6, was sufficiently challenging that it was debated for years before finally being resolved (58) as the hydrogen bridged structure shown.



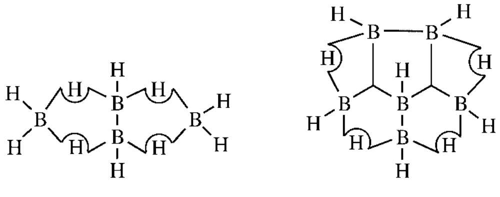
The elucidation of the structure of diborane(6) led to the description of a new bond type, the three-center two-electron bond, in which one electron pair is shared by three atomic centers (59). The delocalization of a bonding pair over a three-center bond allows for the utilization of all the available orbitals in an electron-deficient system. This key point led to the formulation of a valence bond description of the bonding in boron hydrides, sometimes termed a topological description (60). The valence structures of this topological approach give localized bonding descriptions that include delocalized three-center bonds in the basis set of bond types. In addition to the B–H–B three-center bridge bond depicted, a B–B–B three-center bond was introduced to describe bonding in the framework.



The valence theory (4) includes both types of three-center bonds shown as well as normal two-center, B–B and B–H, bonds. For example, one resonance structure of pentaborane(9) is given in projection in Figure 6. An octet of electrons about each boron atom is attained only if three-center bonds are used in addition to



4120 B_5H_9



4012 B_4H_{10} 4220 B_6H_{10}

Fig. 6. The valence structures and *styx* numbers of B_5H_9, B_4H_{10}, and B_6H_{10}.

two-center bonds. In many cases involving boron hydrides the valence structure can be deduced. First, the total number of orbitals and valence electrons available for bonding are determined. Next, the B–H and B–H–B bonds are accounted for. Finally, the remaining orbitals and valence electrons are used in framework bonding. Alternative placements of hydrogen atoms require different valence structures.

The possible number of valence structures for a given boron hydride has been defined exactly using three general equations of balance. For a borane of composition $[B_pH_{q\,+\,p\,+\,c}]^c$, where c is the charge, the equations are

$$s + x = q + c \tag{1}$$

$$s + t = p + c \tag{2}$$

$$t + y = p - c - \frac{1}{2}q \tag{3}$$

where p is the number of terminal B–H units, s is the number of B–H–B three-center bonds, t is the number of B–B–B three-center bonds, y is the number of B–B bonds, and x is the number of BH_2 groups. There are usually several possible solutions to the equations of balance differentiated by a so-called *styx* number, a four-digit number that gives the respective values of s, t, y, and x. The 2D representation of B_5H_9 shown in Figure 6 has the *styx* number 4120. Representations of B_4H_{10} and B_6H_{10}, also shown in Figure 6, have *styx* numbers of 4012 and 4220, respectively. The *styx* formalism is equally applicable to carboranes and carbocations.

The correct *styx* number reflects the true molecular geometry, but the other *styx* structures may be transition states for fluxional molecules. Hexaborane(10) provides an example of bridge hydrogen tautomerism that is detectable by nmr (43). The tautomerism proceeds through a 3311 valence structure in which a bridge hydrogen of 4220 ground state has been converted to a BH_2 group. Note that the sum of the digits of the *styx* number gives one-half of the electrons involved in framework bonding, ie, the $2n + 2$, $2n + 4$, and $2n + 6$ framework electrons of the electron-counting formalism (10,11) and the topological descriptions are intimately related. Therefore, after using the electron-counting formalism to arrive at a framework structure, a valence bond description of the localized bonds can be determined from the *styx* formalism (4). The simultaneous application of these two formalisms allows the prediction of rearrangement during certain reactions and the prediction of transition state structure. Significant skeletal rearrangement would not be anticipated as long as the number of skeletal electrons remained unchanged, as would be the case for both associative and dissociative electrophilic mechanisms, because H^+ is the model electrophile. For the model nucleophile H^-, associative and dissociative nucleophilic mechanisms increase and decrease the framework count, respectively, and framework rearrangement would be expected during the course of the reaction (61).

Although the *styx* numbers quantify the various structural features present in a compound, molecules that are closely related may have very different *styx* numbers. For example, $[C_6H_6]^{2+}$ and B_6H_{10} have similar structures, but *styx* numbers of 0260 and 4220, respectively. A simplified styx system has been introduced that solves this problem (15). In this system, the *s* and *y* of *styx* are added together and identified as *S* of *Stx*. This number has been termed the *Chop-Stx* number. It can be readily seen that compounds structurally related to B_6H_{10} have the *Chop-Stx* number 620. Although at first sight it appears that information regarding the number of B–H–B groups is lost in converting styx to *Chop-Stx*, it turns out that nothing is actually lost. This is because the styx number is always used in conjunction with an empirical formula revealing the number of B–H–B groups. For example, the formula B_6H_{10} indicates that there are four more hydrogen atoms than boron atoms and the *Stx* number 620 indicates that there are no ($x = 0$) BH_2 groups, therefore all extra hydrogens are present as B–H–B groups. The *Chop-Stx* numbers are very useful for making structural correlations. The cataloging of all boron hydride compounds using a 10-digit number, which includes the number of framework electrons over $2n$ (n = number of vertices), the number of boron atoms, the *Chop-Stx* number, the size of the largest open face, and the number of bridging hydrogens has also been proposed (15).

4.2. Molecular Orbital Descriptions. In addition to the localized bond descriptions, molecular orbital (MO) descriptions of bonding in boranes and carboranes have been developed (4). Early work on boranes helped develop one of the most widely applicable approximate methods, the extended Hückel method. Molecular orbital descriptions are particularly useful for *closo* molecules where localized bond descriptions become cumbersome because of the large number of resonance structures that do not accurately reflect molecular symmetry. Such descriptions show that the highest occupied molecular orbital (HOMO) is degenerate for most deltahedral B_nH_n molecules, but that a closed shell is obtained for the corresponding $[B_nH_n]^{2-}$ anions. After accounting for the electrons in exopolyhedral bonds, $2n + 2$ electrons remain for framework bonding giving some theoretical justification for the electron-counting formalisms (10,11). Symmetry considerations (62) also give justification for the opening of *closo* boranes (63) or carboranes (45) upon addition of electrons.

The *ab initio* MO calculations for smaller boranes and carboranes have progressed to the point where definitive answers to structural problems can be provided in many cases. The correlation of experimental boron nmr chemical shifts with those calculated ab initio using the method known as individual gauge for localized molecular orbitals (IGLO) (64) has proven to be a valuable technique for solving structural problems. This method is especially useful when calculated chemical shifts are sensitive to geometrical changes. For example, comparison of the observed and calculated ^{11}B nmr chemical shifts for *nido*-$C_2B_6H_{10}$ strongly favors a symmetrical structure having a six-membered open face out of the three candidate structures for this compound (63). Also, the proposed existence of three separate structures for [*closo*-$B_8H_8]^{2-}$, one in the crystal, D_{2d}, and two in solution, C_{2v} and D_{4d}, has been reinvestigated using experimental–theoretical ^{11}B nmr chemical shift comparisons (65). These studies indicated that the higher temperature solution structure of [*closo*-$B_8H_8]^{2-}$ is D_{2d}, the same as seen in the crystal, and is fluxional involving a somewhat less stable C_{2v} configuration intermediate having a square open face. The structure of the third isomer is unknown. Ab initio calculations of the relative energies of isomeric structures of boranes and carboranes provide quantitative measures that reinforce, extend, and provide a basis for the formerly qualitative rules governing structural features and carbon and bridge-hydrogen placement (40). These rules now allow precise predictions of borane and carborane geometries and structural features.

5. Boranes

5.1. Nido and Arachno Boranes. These boranes are generally more reactive and less stable thermally than the corresponding *closo* boranes. The most extensively studied boranes include diborane(6), B_2H_6, tetraborane(10), B_4H_{10}, pentaborane(9), B_5H_9, and decaborane(14), $B_{10}H_{14}$. This subject has been reviewed (58). A great deal of early work in this area was associated with the government-sponsored high energy fuels programs. Some of this work is summarized (3). The *nido* and *arachno* boranes smaller than $B_{10}H_{14}$ are quite reactive toward oxygen and water. The properties of selected boranes are given in Table 3.

Diborane(6). This compound is manufactured by Callery Chemical Co. in Pennsylvania and Voltaix Inc. in New Jersey. Laboratory-scale preparations are given in equations 4–6, of which the last may be the most convenient method. Diborane is an important starting material for many other boron hydrides.

$$3\ NaBH_4 + 4\ (C_2H_5)_2 \cdot BF_3 \xrightarrow{\text{diglyme}} 2\ B_2H_6 + 3\ NaBF_4 + 4\ (C_2H_5)_2O \qquad (4)$$

$$2\ NaBH_4 + H_2SO_4 \longrightarrow B_2H_6 + 2\ H_2 + Na_2SO_4 \qquad (5)$$

$$2\ NaBH_4 + I_2 \xrightarrow{\text{diglyme}} B_2O_6 + 2\ NaI + 2\ H_2 \qquad (6)$$

It is a spontaneously flammable gas having an extremely high heat of combustion.

$$B_2H_6 + 3\ O_2 \longrightarrow B_2O_6 + 3\ H_2O \qquad \Delta H = -2165\ \text{kJ/mol}\ (-517.4\ \text{kcal/mol}) \qquad (7)$$

Only H_2, BeH_2, and $Be(BH_4)_2$ have higher heats of combustion. When diborane is pyrolyzed >100°C in a sealed tube, it is decomposed to higher boron

Table 3. **Physical Properties of Boranes**

Borane	CAS Registry Number	Molecular formula	Mp, °C	ΔS°_{298}, Bp, °C	ΔH°_f, kJ/mol[a]	ΔG°_f, kJ/mol[a]	J/(K · mol)[a]
diborane(6)	[19287-45-7]	B_2H_6	−164.9	−92.6	35.5	86.6	232.0
tetraborane(10)	[18283-93-7]	B_4H_{10}	−120	18	66.1		
pentaborane(9)	[19624-22-7]	B_5H_9	−46.6	48	73.2	174	275.8
pentaborane(11)	[18433-84-6]	B_5H_{11}	−123	63	103.0		
hexaborane(10)	[23777-80-2]	B_6H_{10}	−62.3	108	94.6		
decaborane(14)	[17702-41-9]	$B_{10}H_{14}$	99.7	213	31.5	216.1	353.0

[a] To convert J to cal, divide by 4.184.

hydrides and hydrogen gas in a complex sequence of reactions. This reaction has been investigated in considerable detail (66).

Octahydrotriborate(1−). The octahydrotriborate(1−) anion [12429-74-2], $[B_3H_8]^-$, commonly referred to as the triborohydride ion, is produced by the reduction of diborane with sodium amalgam. Large quantities can be prepared more conveniently by the reaction of sodium tetrahydroborate and iodine.

$$3\,NaBH_4 + I_2 \xrightarrow[100^\circ C]{diglyme} Na[B_3H_8] + 2\,H_2 + 2\,NaI \tag{8}$$

The tetraalkylammonium salts of $[B_3H_8]^-$ formed by ion-exchange reactions are useful synthetic reagents because of their thermal and air stabilities. The structure of the $[B_3H_8]^-$ ion has been determined by an X-ray study (67) and shown to have the 2013 *styx* structure, C_{2v} symmetry. Mechanisms for the formation of this ion have been proposed (68). Tetraborane(10) can be easily obtained from salts of $[B_3H_8]^-$ (eq. 9).

$$4\,HCl + 4\,Na[B_3H_8] \longrightarrow 2\,B_4H_{10} + 4\,NaCl + 3\,H_2 \tag{9}$$

Pentaborane(9). Pentaborane(9) and $B_{10}H_{14}$ can be prepared by gas-phase pyrolysis of B_2H_6 under different conditions. Pentaborane(9) is a low boiling, highly flammable, and extremely toxic material. It is not commercially available in any significant quantities. Callery Chemical Co., which produced pentaborane in the 1950s for the military, issued a safety bulletin in 1998 describing the neurotoxic properties and hazards of handling and disposing of this material. Despite its hazardous nature, pentaborane is a useful reagent for the preparation of other less dangerous boron hydride compounds. In addition to metalla derivatives, pentaborane(9) can be used to selectively prepare a number of higher boranes, such as $B_9H_{13} \cdot O(C_2H_5)_2$, $K[B_{11}H_{14}]^-$, and carboranes (69) (eqs. 10−13). In most cases, these reactions can be carried out as one-pot procedures, such as by combining the reactions shown in equations 10 and 11 with other reactions.

$$1.8\,B_5H_9 + NaH \xrightarrow{diglyme} Na[B_9H_{14}] + H_2 + \text{minor products} \tag{10}$$

$$Na[B_9H_{14}] + HCl + (C_2H_5)_2O \longrightarrow B_9H_{14} \cdot O(C_2H_5)_2 + NaCl + H_2 \tag{11}$$

$$Na[B_9H_{14}] + BCl_3 + [(CH_3)_4N]Cl \xrightarrow[BCl_3]{diglyme}$$

$$B_{10}H_{14} + O(C_2H_5)_2 + [(CH_3)_4N]\,[BCl_3H] + NaCl \tag{12}$$

$$B_9H_{13} \cdot O(C_2H_5)_2 + 4\,HC{\equiv}CH \longrightarrow$$

$$5,6-C_2B_8H_{12} + (C_2H_5)_2O \cdot B(CH{=}CH_2)_3 \tag{13}$$

Decaborane(14). As one of the most important and intensely studied of the polyhedral boron hydrides, this colorless, flammable, crystalline solid has been produced in large quantities for military use from the 1940s to the 1970s. It can be handled in air and purified by sublimation. Decaborane(14) can be prepared on a laboratory scale by the pyrolysis of B_2H_6 at 100–200°C in the presence of a catalytic amount of a Lewis base such as dimethylether, $(CH_3)_2O$. In addition to the gas-phase pyrolysis of diborane, $B_{10}H_{14}$ can be prepared by a solution-phase process developed at Union Carbide Corp. Decaborane is a key intermediate in the preparation of many carboranes and metalla derivatives. This important compound is not currently manufactured on a large scale and is only available in laboratory quantities. Prices for decaborane are in the \$10–15,000/kg range.

5.2. Reactions of Boranes with Lewis Bases. Boranes that contain a BH_2 moiety, eg, B_2H_6, B_4H_{10}, B_5H_{11}, hexaborane (12) [28375-94-2], B_6H_{12}, and Nonaborane (15) [19465-30-6], B_9H_{15}, can generally be cleaved by nucleophiles in two ways termed symmetrical and unsymmetrical bridge cleavage (70). By using neutral bases, the two modes of cleavage lead to molecular and ionic fragments, respectively, as illustrated in equations 14–19.

$$B_2H_6 + 2\,NH_3 \longrightarrow \left[H_2B(NH_3)_2\right]^+ (BH_4)^- \tag{14}$$

$$B_2H_6 + 2(CH_3)_2S \longrightarrow 2(CH_3)_2S \cdot BH_3 \tag{15}$$

$$B_4H_{10} + 2\,NH_3 \longrightarrow \left[H_2B(NH_3)_2\right]^+ [B_3H_8]^- \tag{16}$$

$$B_4H_{10} + 2\,N(CH_3)_3 \longrightarrow (CH_3)_2N \cdot BH_3 + (CH_3)_3N \cdot B_3H_7 \tag{17}$$

$$B_5H_{11} + 2\,NH_3 \longrightarrow \left[H_2B(NH_3)_2\right]^+ [B_4H_9]^- \tag{18}$$

$$B_5H_{11} + 2\,CO \longrightarrow BH_3(CO) + B_4H_8(CO) \tag{19}$$

Certain base adducts of borane, BH_3, such as triethylamine borane [1722-26-5], $(C_2H_5)_3N \cdot BH_3$, dimethylsulfide borane [13292-87-0], $(CH_3)_2S \cdot BH_3$, and tetrahydrofuran borane [14044-65-6], $C_4H_8O \cdot BH_3$, are more easily and safely handled than B_2H_6 and are commercially available. These compounds find wide use as reducing agents and in hydroboration reactions (57). Base displacement reactions can be used to convert one adduct to another. The relative stabilities of BH_3 adducts as a function of Groups 15 (V A) and 16 (VI A) donor atoms are $P > N$ and $S > O$. This order has sparked controversy because the trend opposes the normal order established by BF_3. In the case of anionic nucleophiles, base displacement leads to ionic hydroborate adducts (eqs. 20 and 21).

$$(C_2H_5)_2O \cdot BH_3 + KF \longrightarrow K^+[BH_3F]^- + (C_2H_5)_2O \tag{20}$$

$$(C_2H_5)_2O \cdot BH_3 + Na(SCN) \longrightarrow Na^+(BH_3SCN)^- + (C_2H_5)_2O \tag{21}$$

Unsymmetrical cleavage of B_2H_6 by metal hydrides gives metal tetrahydroborate salts, also called metal borohydrides or hydroborates.

$$2\,MH + B_2H_6 \longrightarrow 2\,MBH_4 \qquad (M = Li,\ Na,\ K) \tag{22}$$

Decaborane is a multifunctional species that simultaneously acts as a Brønsted acid and a Lewis acid. Weak bases fail to directly deprotonate decaborane but do react resulting in the evolution of H_2 and the formation of species that contain ligands coordinated at the six- and nine-positions of the decaborane skeleton (see Fig. 1).

$$B_{10}H_{14} + 2\,L \longrightarrow B_{10}H_{12}L_2 + H_2 \tag{23}$$

Base displacement reactions (71) have been used to establish the relative basicities of a number of ligands toward $B_{10}H_{12}$ to be as follows: $(C_6H_5)_3P >$ pyridine $> (C_2H_5)_3N > CH_3CON(CH_3)_2 > HCON(CH_3)_2 > (C_2H_5)_2NCN > CH_3CN > (CH_3)_2S$. The $B_{10}H_{12}L_2$ species are important intermediates in the synthesis of two-key *closo* species, $[B_{10}H_{10}]^{2-}$ and 1,2-$C_2B_{10}H_{12}$.

In addition to borane adducts with Lewis bases, the organoboron products resulting from the hydroboration of olefins are widely used in commercial organic syntheses to carry out a variety of highly selective reductions. These are especially important in the pharmaceutical industry. These include 9-borabicyclo[3.3.1]nonane (9-BBN), obtained by hydroboration of 1,5-cyclooctene, and diispinocamphenylborane (DIP_2BH), produced by hydroboration of α-pinene. The latter, being optically active, is useful for asymmetric syntheses. A wide variety of borane reducing agents and hydroborating agents is available from Aldrich Chemical Co., Inc. and Callery Chemical Co.

5.3. Proton Abstraction. Although the exopolyhedral hydrogens of *nido* and *arachno* boranes are generally considered hydridic, the bridge hydrogens are acidic as first demonstrated by titration of $B_{10}H_{14}$ and deuterium exchange (72). Some typical reactions are

$$B_{10}H_{14} + NaOH \longrightarrow Na[B_{10}H_{13}] + H_2O \tag{24}$$

$$B_{10}H_{14} + NaH \longrightarrow Na[B_{10}H_{13}] + H_2 \tag{25}$$

$$B_5H_9 + n - C_4H_9Li \longrightarrow Li[B_5H_8] + C_4H_{10} \tag{26}$$

$$B_4H_{10} + NaH \longrightarrow Na[B_4H_9] + H_2 \tag{27}$$

$$B_6H_{10} + KH \longrightarrow K[B_6H_9] + H_2 \tag{28}$$

The deprotonation of $B_{10}H_{14}$ at a B–H–B bridge position produces the yellow species $[B_{10}H_{13}]^-$ (73–76). Reaction of the $[B_{10}H_{13}]^-$ anion and an electron-pair donor L, produces $[B_{10}H_{13}L]^-$ (77). Hydration of $B_{10}H_{14}$ results in the acidic species $B_{10}H_{14}OH_2$, which ionizes to form the colorless $[B_{10}H_{14}OH]^-$ anion (76). Both $B_{10}H_{14}OH_2$ and $[B_{10}H_{14}OH]^-$ are isoelectronic with the $[B_{10}H_{15}]^-$ anion (78). The hydropolyborate ions formed by proton abstraction from decaborane are useful intermediates for the preparation of metallaboranes and heteroboranes.

5.4. Polyhedral Expansion. The term polyhedral expansion is used to describe a host of reactions in which the size of the polyhedron is increased by the addition of new vertex atoms whether boron, heteroelements, or metals. In the case of the boranes, the pyrolysis of B_2H_6 has been used to obtain B_5H_9 and

$B_{10}H_{14}$ industrially. Although a subject of much study, the mechanism of such pyrolytic expansions is not well understood.

Expansion of $B_{10}H_{14}$ to $[B_{11}H_{14}]^-$ is brought about by a reaction with $[BH_4]^-$ (79).

$$[BH_4]^- + B_{10}H_{14} \longrightarrow [B_{11}H_{14}]^- + 2\,H_2 \qquad (29)$$

Other expansion reactions between diborane and borane anions with a B–B edge bond have been reported (80), eg,

$$2[B_4H_9]^- + B_2H_6 \longrightarrow 2[B_5H_{12}]^- \qquad (30)$$

$$2[B_5H_8]^- + B_2H_6 \longrightarrow 2[B_6H_{11}]^- \qquad (31)$$

Boron halides have also been shown to insert into B–B bonds to give initial products with the new boryl moiety in a bridge position (81).

$$[B_5H_8]^- + (CH_3)_2BCl \longrightarrow \mu - \left[(CH_3)_2B\right] \cdot B_5H_8 + Cl^- \qquad (32)$$

$$\mu - [(CH_3)_2B] \cdot B_5H_8 \xrightarrow{(C_2H_5)_2O} (CH_3)_2B_6H_8 \qquad (33)$$

5.5. Electrophilic Attack. A variety of boranes, heteroboranes, and metallaboranes undergo electrophilic substitution. Susceptibility of boranes to electrophilic attack is often detected by deuteron–proton exchange experiments. For example, electrophilic hydrogen–deuterium exchange of $B_{10}H_{14}$ occurs at the 1-,2-,3-, and 4-positions when exposed to DCl in the presence of $AlCl_3$ (82,83). The trend to increasing positive sites in $B_{10}H_{14}$ is 2,4 $<$ 1,3 $<$ 5,7,8,10 $<$ 6,9. Initial halogenation and alkylation of $B_{10}H_{14}$ also occurs at the 2,4-positions (82,84). Electrophilic substitution of pentaborane(9) has also been observed to give halogenation, alkylation, and deuteration. The more negative apical site (1-position) is substituted preferentially, but the 1-isomer can be catalytically converted to the basally substituted isomer (2-position) (85) (Fig. 1**a**). The basal B–B bond of B_6H_{10} can be protonated to give the isolable polyhedral borane cation, $[B_6H_{11}]^+$ (86) (Fig. 1**d**).

5.6. Closo Borane Anions. This group contains a homologous series of very stable polyhedral anions, $[closo\text{-}B_nH_n]^{2-}$, $n = 6–12$. Just as the previously known boron hydrides might be considered as analogues of aliphatic hydrocarbons, the *closo* borane anions are analogues of aromatic hydrocarbons. The stability of the *closo* anions is attributable to electron delocalization in a unique 3D aromaticity. Unlike their *nido* and *arachno* counterparts with bridging hydrogens, proton abstraction does not, for practical purposes, occur in *closo* borane chemistry. Instead, acid catalysis is important in their substitution chemistry. The best known members of this series, $[closo\text{-}B_{10}H_{10}]^{2-}$ [12356-12-6] and $[closo\text{-}B_{12}H_{12}]^{2-}$ [12356-13-7], were first reported in 1959 and 1960 (87) and were the subject of detailed studies (88).

In aqueous solution, *closo* borane anions are very stable as their conjugate acids, which possess acidity similar to sulfuric acid, yet their chemistry is remarkably different. Large unipositive cations, such as Tl^+, Cs^+, Rb^+,

$[(CH_3)_4N]^+$, and $[(CH_3)_3S]^+$, yield water-insoluble salts of $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ (89). Small unipositive cations and most dipositive cations, such as Ba^{2+} and Ca^{2+}, form water-soluble salts that are strong electrolytes and give hydrates on evaporation. The divalent transition and rare-earth elements also give soluble salts and hydrates, but solubilities decrease when the water of the coordination sphere is replaced by ligands such as NH_3. Polarizable cations, such as Ag^+, Cu^+, Tl^+, and Hg^{2+} form water-insoluble salts. The latter compounds contain M–H–B interactions in the solid state. Salts of cations, which are not readily reducible, display exceptional thermal stabilities. Thus $Cs_2[B_{12}H_{12}]$ and $Cs_2[B_{10}H_{10}]$ can be heated to 810 and 600°C, respectively, in a sealed, evacuated tube and recovered unchanged.

Salts of $[B_6H_6]^{2-}$ [12429-97-9], $[B_7H_7]^{2-}$ [12430-07-8], $[B_8H_8]^{2-}$ [12430-13-6], $[B_9H_9]^{2-}$ [12430-00-0], and $[B_{11}H_{11}]^{2-}$ [12430-44-3] appear to exhibit similar behavior, but less definitive data are available. Although silver salts of $[B_6H_6]^{2-}$, $[B_9H_9]^{2-}$, and $[B_{11}H_{11}]^{2-}$ have been isolated, they are shock-, heat-, and light-sensitive (90,91). Anhydrous $Cs_2[B_6H_6]$, $Cs_2[B_8H_8]$, and $Cs_2[B_9H_9]$ are thermally stable to 600°C, but $Cs_2[B_{11}H_{11}]$ disproportionates to $Cs_2[B_{10}H_{10}]$ and $Cs_2[B_{12}H_{12}]$ at temperatures >400°C (17).

The base-promoted closure of Decaborane(14) yields salts of the $[B_{10}H_{10}]^{2-}$ anion (eq. 34). Relatively strong Lewis bases, such as trialkylamines, are required to accomplish this reaction as weaker bases, such as diethyl sulfide and acetonitrile, form stable 6,9-$L_2B_{10}H_{12}$ species where L = $(C_2H_5)_2S$, H_3CCN, etc, which are important synthetic intermediates (92).

$$B_{10}H_{14} + 2\,N(C_2H_5)_3 \xrightarrow{-H_2} 6,9\text{–}[(C_2H_5)_2N]_2\,[B_{10}H_{12}] \longrightarrow$$
$$6,9\text{–}[(C_2H_5)_2NH]_2\,[B_{10}H_{10}] \qquad (34)$$

The reaction of B_2H_6 with $NaBH_4$ or $(C_2H_5)_3N \cdot BH_3$ at 180°C in $N(C_2H_5)_3$ at high pressure gives $[B_{12}H_{12}]^{2-}$ in nearly quantitative yield (93). In diglyme at 162°C, the same reactants give a 5–10% yield of $[B_6H_6]^{2-}$ at even lower (85°C) temperatures and at atmospheric pressure $Na[B_3H_8]$ [12429-74-2] is obtained (91,94).

$$2\,NaBH_4 + 5\,B_2H_6 \longrightarrow Na_2[B_{12}H_{12}] + 13\,H_2 \qquad (35)$$

$$2\left[(C_2H_5)_3N\right] \cdot BH_3 + 5\,B_2H_6 \longrightarrow [(C_2H_5)_3NH][B_{12}H_{12}] + 11\,H_2 \qquad (36)$$

Pyrolysis of $Cs[B_3H_8]$ at 230°C gives $Cs_2[B_9H_9]$ (60%) along with some $Cs_2[B_{10}H_{10}]$, $Cs_2[B_{12}H_{12}]$, and $CsBH_4$ (95). The sensitivity of polyhedral expansion reactions to solvent, temperature, and pressure is further exemplified by the results in dioxane at 120°C under pressure. To obtain the *closo* borane, $Na[B_{11}H_{14}]$ is first converted to $Cs_2[B_{11}H_{13}]$, which can be pyrolyzed to give $Cs_2[B_{11}H_{11}]$ (91).

$$NaBH_4 + 5\,B_2H_6 \xrightarrow{120^\circ C} Na[B_{11}H_{14}] + 10\,H_2 \qquad (37)$$

Pyrolysis of $[(C_2H_5)_4N][BH_4]$ at 185°C gives a 90% yield of $[(C_2H_5)_4N]_2[B_{10}H_{10}]$ (96). The $[B_{12}H_{12}]^{2-}$ anion can be prepared by the reaction of $(C_2H_5)_3N\cdot BH_3$ with decaborane in an inert high boiling hydrocarbon solvent at 190°C (94).

$$2[(C_2H_5)_3N\cdot BH_3 + B_{10}H_{14} \xrightarrow{190^\circ C} [(C_2H_5)_3NH]_2\,[B_{12}H_{12}] + 3\,H_2 \qquad (38)$$

The $[B_6H_6]^{2-}$, $[B_7H_7]^{2-}$, $[B_8H_8]^{2-}$, $[B_9H_9]^{2-}$, and $[B_{11}H_{11}]^{2-}$, *closo* anions are hydrolytically less stable than the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ *closo* anions. All of these anions are more stable in basic than in acidic solution. The $[B_7H_7]^{2-}$ ion is the least stable hydrolytically and is degraded even in basic media. The $[B_6H_6]^{2-}$, $[B_8H_8]^{2-}$, and $[B_9H_9]^{2-}$ *closo* anions are stable in neutral and alkaline solutions but react rapidly with aqueous acid. Strongly acidic solutions (>2*N* HCl) are necessary for the hydrolysis of $[B_{11}H_{11}]^{2-}$. The $[B_{12}H_{12}]^{2-}$ anion is the most hydrolytically stable borane anion, withstanding even 3 *N* HCl at 95°C, conditions that slowly degrade $[B_{10}H_{10}]^{2-}$ (17,90). A salt of the $[B_{12}H_{12}]^{2-}$ anion, produced by Callery Chemical Co., currently finds commercial application in the fuse of the passenger-side automotive airbag.

Much work has been done on the functionalization of *closo* polyborane anions. Both nucleophilic and electrophilic substitution routes have been explored. Most acid-catalyzed nucleophilic substitutions of $[B_{10}H_{10}]^{2-}$ with, eg, amides, ethers, and sulfones, give products having equatorial substituents (97).

$$(B_nH_n)^{2-} + 2\,R_2O^+ \longrightarrow \left[B_nH_{n-2}(OR)_2\right]^{2-} + RH \qquad (39)$$

$$[B_nH_n]^{2-} + H^+ + HCON(CH_3)_2 \longrightarrow \left[B_nH_{n-1}\left(OCH{=}N(CH_3)_2\right)\right]^- + H_2 \qquad (40)$$

$$[B_nH_n]^{2-} + H^+ + R_2SO_2 \longrightarrow [B_nH_{n-1}OS(O)R_2]^- + H_2 \qquad (41)$$

These *O*-bonded substituents are easily cleaved with hydroxide ion to give the corresponding hydroxyl derivative, $[B_nH_n\text{-}1(OH)]^{2-}$ or $[B_nH_n\text{-}2(OH)_2]^{2-}$, n = 10,12. It was initially shown that reaction of $[B_{12}H_{12}]^{2-}$ with H_2S leads to thiolation of the dodecaborate cage (98). The product $[HSB_{12}H_{11}]^{2-}$, known as "BSH", was found to be a promising reagent for boron neutron capture therapy (BNCT) of cancer, discussed below. The acid-catalyzed nucleophilic substitution of $[B_{12}H_{12}]^{2-}$ using *N*-methylthiopyrrolidone or *N*-methylbenzothiazole provides thioethers that undergo alkaline hydrolysis to give the BSH thiolate (99). Sulfur can also be introduced to the dodecaborate cage by electrophilic substitution using acetlysulfenyl chloride (100). The isomeric inner sulfonium salts $[Me_2SB_{12}H_{11}]^-$ and $(Me_2S)_2B_{12}H_{10}$ have been prepared and can be converted to the $[MeSB_{12}H_{11}]^-$ and $[(MeS)_2B_{12}H_{10}]^{2-}$ thioether anions by reduction with excess sodium or potassium (101). Further reduction of these methyl thioethers using lithium in methylamine results in cleavage to BSH (102).

Highly or persubstituted *closo* polyhedral borane anions have been dubbed "camouflaged" boranes since substantial subtitution of vertex hydrogens by larger groups results in a substituent shell enclosing and chemically concealing the boron polyhedron. The persubstituted compounds technically are not boron hydrides but fit decidedly within this class. The [*closo*-$B_{12}H_{12}$]$^{2-}$ anion can be perhydroxylated to [*closo*-$B_{12}(OH)_{12}$]$^{2-}$ by treatment with hydrogen peroxide(103,104). This compound serves as a useful reagent for the further functionalization of borane cages. For example, reaction of a [*closo*-$B_{12}(OH)_{12}$]$^{2-}$ salt with benyl chloride in the presence of ethyldiisopropylamine results in the per-*O*-benzylated compound [*closo*-$B_{12}(OCH_2Ph)_{12}$] (105). This large spherical anion undergoes reversible one-electron oxidation to give the radical anion [*hypercloso*-$B_{12}(OCH_2Ph)_{12}$]$^{-\cdot}$, where the *hypercloso* designation is used for compounds having an apparent *closo* structure that possess $<2n+2$ skeletal electrons. Although the subject of computational studies, the parent *hypercloso*-$B_{12}H_{12}$ has not been synthesized.

The [*closo*-$B_{12}H_{12}$]$^{2-}$ anion can also be peralkylated. For example, prolonged reaction of tetraalkylammonium salts of [*closo*-$B_{12}H_{12}$]$^{2-}$ with methyl iodide in trimethylaluminum solvent yields the corresponding [*closo*-$B_{12}(CH_3)_{12}$]$^{2-}$ salts, which can be cation exchanged to give salts of a variety of other cations (106). The [*closo*-$B_{12}(CH_3)_{12}$]$^{2-}$ anion is a unique large symmetrical and hydrophobic anion that, like the *O*-benzylated B_{12} compound above, undergoes reversible one-electron oxidation to give a paramagnetic radical anion.

The reaction of [$B_{10}H_{10}$]$^{2-}$ with excess nitrous acid gives an explosive intermediate that can be reduced to the nonexplosive bis inner-diazonium salt 1,10-$(N_2)_2B_{10}H_8$[66750-86-5] (eq. 42). This diazonium species is a useful synthetic intermediate.

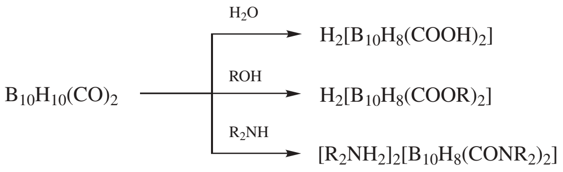
$$[B_{10}H_{10}]^{2-} \xrightarrow{HNO_2} [\text{explosive intermediate}] \xrightarrow{NaBH_4} 1,10-(N_2)_2B_{10}H_8 \qquad (42)$$

Unfortunately, [$B_{12}H_{12}$]$^{2-}$ does not undergo the corresponding reaction. The N_2 group is the only moiety that can be displaced readily from the B_{10}-cluster by a variety of nucleophiles (107).

$$1,10-(N_2)_2B_{10}H_8 + 2\,L \longrightarrow 1,10-L_2B_{10}H_8 + 2\,N_2 \qquad (43)$$

where L = ammonia, amines, nitriles, hydrogen sulfide, azide ion, hydroxide ion, and carbon monoxide.

The dicarbonyl [12539-66-1] available from 1,10-$(N_2)_2B_{10}H_8$ is another important species because of the scope of its chemistry. Carbonyls of [$B_{12}H_{12}$]$^{2-}$ can be formed from CO and the conjugate acid of [$B_{12}H_{12}$]$^{2-}$. The B_{10}- and B_{12}-carbonyls exhibit very similar reactivity (108). The carbonyls can be considered anhydrides of carboxylic acids and accordingly react with alcohols and amines to give esters and amides:



$$B_{10}H_{10}(CO)_2 \xrightarrow{H_2O} H_2[B_{10}H_8(COOH)_2] \qquad (44)$$

$$B_{10}H_{10}(CO)_2 \xrightarrow{ROH} H_2[B_{10}H_8(COOR)_2] \qquad (45)$$

$$B_{10}H_{10}(CO)_2 \xrightarrow{R_2NH} [R_2NH_2]_2[B_{10}H_8(CONR_2)_2] \qquad (46)$$

Halogenation of *closo*-boranes has been studied extensively. The exhaustive fluorination of *closo*-boranes leads to compounds such as [*closo*-$B_{12}F_{12}$]$^{2-}$ (109). Halogenation of [$B_{12}H_{12}$]$^{2-}$ and [$B_{10}H_{10}$]$^{2-}$ occurs using elemental halogen in solvents such as water, alcohols, or tetrachloroethane. Initial rates are extremely high in all cases with $[B_{10}H_{10}]^{2>}$($[B_{12}H_{12}]^{2-}$. The kinetic order is F ≥ Cl > Br > I (110). Typical products are $[B_{10}Cl_{10}]^{2-}$ [12430-33-0],$[B_{10}H_3Br_7]^{2-}$ [12360-16-6]$[B_{10}I_{10}]^{2-}$ [12430-43-2], $[B_{12}Cl_6H_6]^{2-}$ [12430-46-5], $[B_{12}H_3Br_6Cl_3]^{2-}$ [12536-79-7], and $[B_{12}I_{12}]^{2-}$ [12587-25-6]. In general, the alkali and alkaline earth metal salts of the B_{10}- and B_{12}-halogenated derivatives have excellent thermal, oxidative, and hydrolytic stabilities.

Due to their extreme kinetic stabilities, oxidative degradation of $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ to boric acid is extremely difficult and requires Kjeldahl digestion or neutral permanganate. Degradation is catalyzed by crown ethers under milder conditions. The heat of reaction obtained from the permanganate degradation leads to a calculated heat of formation for $[B_{10}H_{10}]^{2-}$ (aq) of 92.5±21.1 kJ/mol (22.1±5.0 kcal/mol) (108).

The oxidative coupling of both $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ has been studied in some detail (112–116). The $[B_{10}H_{10}]^{2-}$ anion can be oxidized chemically or electrochemically to give $[B_{20}H_{19}]^{3-}$ and $[B_{20}H_{18}]^{2-}$[59724-35-5] (eqs.47–49).

$$(B_{10}H_{10})^{2-} \rightleftarrows (B_{10}H_{10})^{-} + e^{-} \tag{47}$$

$$2[B_{10}H_{10}]^{2-} \longrightarrow [B_{20}H_{19}]^{3-} + H^{+} \tag{48}$$

$$[B_{20}H_{19}]^{3-} \longrightarrow [B_{20}H_{18}]^{2-} + H^{+} + 2e^{-} \tag{49}$$

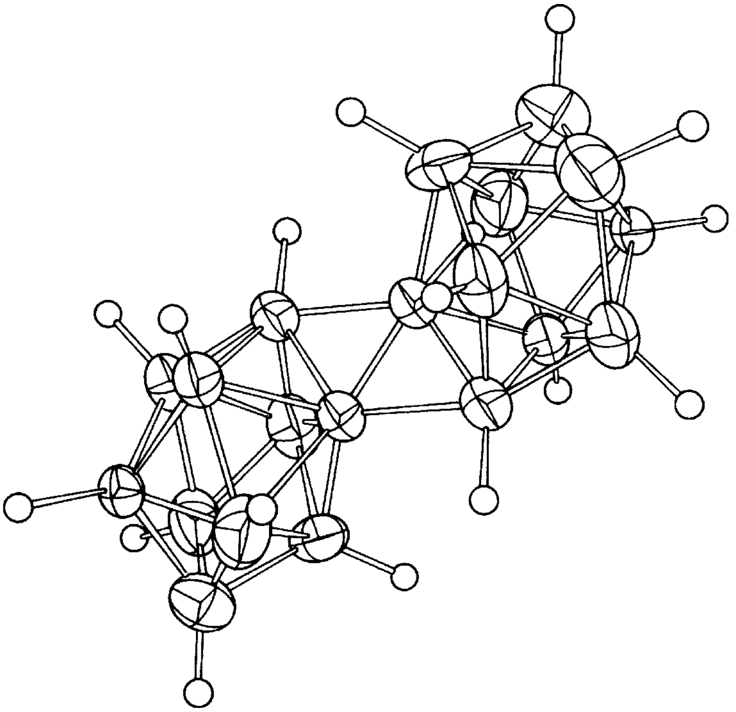


Fig. 7. The structure of one isomer of $[B_{20}H_{18}]^{2-}$ where ○ and ⊗ represents BH and B. Courtesy of the American Chemical Society (114).

These are conjuncto-boranes consisting of two B_{10}-clusters linked via a double three-center B−B−B bond as originally proposed (112) and later confirmed by X-ray crystallography (113). The oxidation of $[B_{10}H_{10}]^{2-}$ with aqueous ferric ion at room temperature was more recently shown to yield $[\mathit{cis}\text{-}B_{20}H_{18}]^{2-}$, an isomer in the which the two B_{10}-cages are bound together in a cisoid configuration (114). The structures of the isomeric $[\mathit{cis}\text{-}B_{20}H_{18}]^{2-}$ and $[\mathit{trans}\text{-}B_{20}H_{18}]^{2-}$ anions are shown in Figure 7. Reduction of $[B_{20}H_{18}]^{2-}$ by sodium metal in liquid ammonia gives $[B_{20}H_{18}]^{4-}$ [59724-36-6], in which the two B_{10}-clusters are joined by a single two-center B−B bond through the apical or equatorial positions. The nondestructive electrochemical oxidation of $[B_{12}H_{12}]^{2-}$ leads to the $[B_{24}H_{23}]^{2-}$ anion (115).

5.7. Tetrahydroborates. The tetrahydroborates constitute the most commercially important group of boron hydride compounds. Tetrahydroborates of most of the metals have been characterized and their preparations have been reviewed (46). The most important commercial tetrahydroborates are those of the alkali metals. Some properties are given in Table 4.

Sodium tetrahydroborate, also called sodium borohydride, is the single most important industrial boron hydride material in terms of tonnage produced. It is manufactured by Rohm & Haas and Finnish Chemicals (Nokia) using boric acid as the source of boron. Treatment of trimethyl borate with a metal hydride, eg, NaH, in the absence of a solvent yields sodium hydrotrimethoxyborate [16940-17-3], $Na[HB(OCH_3)_3]$, (eq. 50) which disproportionates in the presence of solvents such as tetrahydrofuran (THF) at 60–70°C (eq. 51) (123).

$$MH + B(OCH_3)_3 \longrightarrow M\big[BH(OCH_3)_3\big] \quad M = Li,\ Na,\ K \tag{50}$$

$$4\,M\big[BH(OCH_3)_3\big] \longrightarrow MBH_4 + 3\,M\big[B(OCH_3)_4\big] \tag{51}$$

Addition of diborane (eq. 52) under the latter conditions renders the production of MBH_4 essentially continuous until consumption of the metal hydride is complete because trimethyl borate is regenerated.

$$3\,M\big[BH(OCH_3)_4\big] + 2\,B_2H_6 \longrightarrow 3\,MBH_4 + 4\,B(OCH_3)_3 \tag{52}$$

Variations on this method are used for the commercial production of $NaBH_4$, but are less satisfactory for the manufacture of $LiBH_4$ and KBH_4. Some metathetical conversions are shown in equations 53–58.

$$TiNO_3 + KBH_4 \xrightarrow{H_2O} TiBH_4 + KNO_3 \tag{53}$$

$$NaBH_4 + KOH \xrightarrow{H_2O} KBH_4 + NaOH \tag{54}$$

$$[(C_6H_5)_4P]F + KBH_4 \xrightarrow{H_2O} [(C_6H_5)_4P]\,[BH_4] + KF \tag{55}$$

$$NaBH_4 + LiCl \xrightarrow{\text{isopropylamine}} LiBH_4 + 2\,LiCl \tag{56}$$

$$MgCl_2 + 2\,NaBH_4 \longrightarrow Mg[BH_4]_2 + 2\,NaCl \tag{57}$$

$$NH_4F + NaBH_4 \longrightarrow NH_4[BH_4] + NaF \tag{58}$$

Table 4. **Properties of Alkali Metal Tetrahydroborates**

	Compound					
Property	$LiBH_4$	$NaBH_4$	KBH_4	$RbBH_4$	$CsBH_4$	References
CAS Registry Number	[16949-15-8]	[16940-66-2]	[13762-51-1]	[20346-99-0]	[19193-36-3]	
mp, °C	268	505	585			(116–118)
decomp. temp., °C	380	315	584	600	600	(116–118)
density, g/mL	0.68	1.08	1.17	1.71	2.40	(117, 119, 120)
refractive index	1.547	1.490	1.487	1.498	122	
lattice energy, kJ/mol[a]	792.0	697.5	657	648	630.1	117
ΔH_f°, kJ/mol[a]	−184	−183	−243	−246	−264	120, 121
ΔS_{298}°, J/(mol·K)[a]	−128.7	−126.3	−161	−179	−192	122

[a] To convert J to cal, divide by 4.184.

There is considerable interest in sodium borohydride for the safe and efficient storage and transportation of energy. Although concentrated aqueous solutions of sodium borohydride with the addition of ~1% sodium hydroxide are stable and nonflammable, they are readily decomposed catalytically by metals such as ruthenium, nickel, cobalt, and platinum with the evolution of substantial quantities of H_2 gas. This

$$NaBH_4 + 4\ H_2O \xrightarrow{\text{catalyst}} NaB(OH)_4 + 4\ H_2 \tag{59}$$

provides a method of producing "hydrogen on demand" for fuel cells or combustion engines. It is notable that half of the hydrogen generated in this reaction comes from water. Thus the deliverable hydrogen content of a concentrated sodium borohydride solution is quite high, and competitive with other known technologies for mobile H_2 storage applications in terms of energy content per unit weight requirement.

Sodium borohydride can also be used in "direct" fuel cells (essentially batteries) since H_2 can be generated directly at a platinum anode. In this case the decomposition of $NaBH_4$ can be expressed by the following anode half reaction, where each mole of $NaBH_4$ provides eight electrons.

$$NaBH_4 + 8\ OH^- \longrightarrow NaB(OH)_4 + 4\ H_2O + 8\ e^- \tag{60}$$

As a result, 20 mg of $NaBH_4$ is sufficient to operate a cell at 100 mA for ~1 h. Millennium Cell Corp. in the United States is developing a variety of commercial power sources that utilize sodium borohydride as fuel, including borohydride powered automobiles that run on either H_2-powered internal combustion engines or fuel cell powered electric motors. Prototype borohydride vehicles have demonstrated similar range and performance characteristics to conventional automobiles. The current barrier to the commercial use sodium borohydride in such large-scale power applications is the need for an efficient method of recycling the by-product sodium metaborate back to sodium borohydride.

With a hydrogen economy predicted for the future of energy management it is likely that sodium borohydide will play an increasingly important role in the storage and transport of hydrogen, if not for mass transportion then at least for small-scale or portable power sources.

The physical and chemical properties of the tetrahydroborates show more contrasts than the salts of nearly any other anion, ranging from highly ionic compounds such as $CsBH_4$ and $Ba(BH_4)_2$ to covalent volatile species such as $Al(BH_4)_2$ and $Zr(BH_4)_4$. The alkali metal salts are the most stable. In dry air, $NaBH_4$ is stable to 300°C and in vacuo to 400°C with only partial decomposition. In contrast, several tetrahydroborates, including the titanium, thallium, gallium, copper, and silver salts, are unstable at or slightly above ambient temperatures. The chemical and physical properties of the tetrahydroborates are closely related to molecular structure. Sodium tetrahydroborate, which is typical of the alkali metal tetrahydroborates except for the lithium salt, has a face-centered cubic (fcc) crystal lattice that is essentially ionic and contains the tetrahedral $[BH_4]^-$ anion. The tetrahydroborates of the polyvalent metals are in many cases the

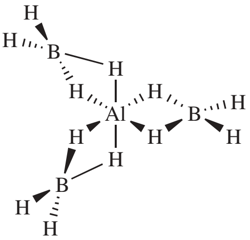


Fig. 8. The structure of Al(BH_4)$_3$.

most volatile derivatives of these metals known. Aluminum tris(tetrahydroborate)[16963-07-5], Al[BH_4]$_3$, has a normal boiling point of 44.5°C and uranium bis(tetrahydroborate) [33725-14-3], U[BH_4]$_2$, has a vapor pressure of 530 Pa (4 torr) at 61°C. Other covalent tetrahydroborates include Be[BH_4]$_2$, Zr[BH_4]$_4$, Hf[BH_4]$_4$, and U[BH_4]$_4$. These compounds contain M–H–B-type bonds. The structure of Al[BH_4]$_3$ is shown in Figure 8. The alkali metal tetrahydroborates are stable in dry air, and the sodium and potassium salts can be crystallized from aqueous solution. Alternatively, Al[BH_4]$_3$ is hydrolyzed explosively and is pyrophoric in air.

Sodium tetrahydroborate is quite soluble in liquid ammonia and soluble to some extent in a variety of other solvents. It is appreciably soluble only in polar solvents of high dielectric constant and those that can solvate the metal ion, such as water, amines, *N,N*-diethylformamide (DMF), and glyme ethers. The rate of hydrolysis of $NaBH_4$ in water is increased by either lowering the pH or by increasing the temperature. It can be recrystallized from alkaline solutions. Dissolution in water results in a slow hydrolysis until the solution becomes alkaline. A 0.01 M solution of $NaBH_4$ gives initial pH 9.6. Only very slow hydrolysis occurs at pH values >12.9. Thus aq $NaBH_4$ solutions can be rendered stable by addition of $\sim1\%$ NaOH.

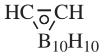
The tetrahydroborates have been used as reducing agents for a variety of inorganic reductions. Many metal cations are reduced by borohydrides in protic or aprotic solvents. The products of these reductions may be lower valent cations, free elements, volatile hydrides, or metal borides. For example, Sn, Ge, As, Sb, and Bi salts or oxides can be reduced to SnH_4, GeH_4, AsH_3, SbH_3, and BiH_3. Several of these reactions are utilized in quantitative analytical procedures. Reactive metal powder can be prepared by borohydride reduction of metal compounds such as cobalt chloride, chromium oxide, tungsten oxide, and molybdenum oxide or chloride. Sodium tetrahydroborate, as well as amine boranes, are used in electroless plating (qv), particularly of nickel, palladium, and platinum, on both metallic and nonmetallic substrates. Many transition metal hydride complexes have been prepared by reactions utilizing borohydrides. Borohydrides also find use in the bleaching of paper pulp and clays, purification of organic chemicals and pharmaceuticals, the recovery of valuable metals, and the treatment of wastewater from industrial process streams. Covalent metal tetrahydroborates derived from Ti, Zr, Co, Ni, and Rh have shown catalytic activity in hydrogenation, polymerization, and isomerization reactions (47). An important industrial use of sodium tetrahydroborate is in the production of the dithionite anion by reduction of the bisulfite anion (124).

The use of tetrahydroborates, as well as the boranes and organoboranes, for organic transformations has proven to be even more significant because these reduction reactions are highly selective and nearly quantitative (125). The reducing characteristics of borohydrides may be varied by changing the associated cation and by changing the solvent. Borohydrides are often the reagents of choice for the reduction of aldehydes and ketones to the corresponding alcohols, especially when selective reduction in the presence of other functional groups is required. Many other functional groups, such as acid chlorides, imines, and peroxides, can also be reduced using borohydrides.

6. Heteroboranes

Heteroboranes contain heteroelements classified as nonmetals. The heteroatoms known to form part of a borane polyhedron include C, N, O, Si, P, Ge, As, S, Se, Sb, and Te either alone or in combination (126). In principle, heteroboranes containing a variety of heteroatoms could have a wide range of skeletal sizes. Of these, the carboranes have by far the greatest demonstrated scope of chemistry.

6.1. Carboranes. The term carborane is widely used as a contraction of the IUPAC approved nomenclature carbaborane. The first carboranes, including isomers of $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$, were prepared in the mid-1950s. These carboranes were obtained as mixtures in low yield from the reaction of smaller boranes such as pentaborane(9) with acetylene in a silent electric discharge. The discovery of the icosahedral *closo*-1,2-dicarbadodecaborane(12) [16872-09-6], 1,2-$C_2B_{10}H_{12}$, came soon after and led to a rapid development of carborane chemistry (127). This latter carborane, usually called *ortho*-carborane, is prepared in good yields by the reaction of acetylene and one of the 6,9-$L_2B_{10}H_{12}$ species such as $[(C_2H_5)_2S]_2B_{10}H_{12}$[28377-92-6] or 6,9-$(H_3CCN)_2B_{10}H_{12}$, where L is a Lewis base (Fig. 9). A variety of *C*-substituted *ortho*-carboranes isobtained by utilizing substituted acetylenes, RC≡CR′. The symbols



$$\begin{array}{c}HC\overset{-}{}CH\\ \diagdown O\diagup\\ \quad B_{10}H_{10}\end{array}$$

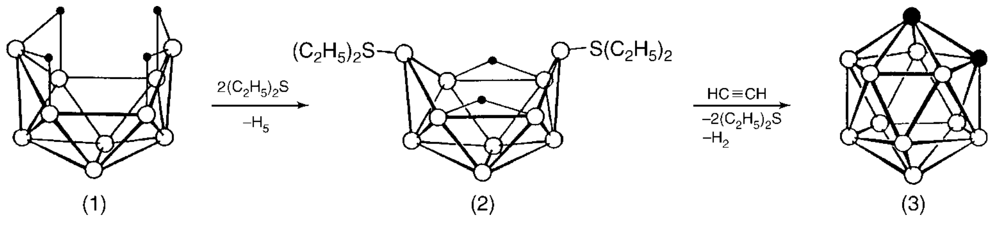


Fig. 9. The synthesis of *closo*-1,2-$C_2B_{10}H_{12}$ (3) from *nido*-$B_{10}H_{14}$ (1) via *arachno*-$[(C_2H_5)_2S]_2B_{10}H_{12}$ (2) where ○ represents BH; ● CH; and ● H.

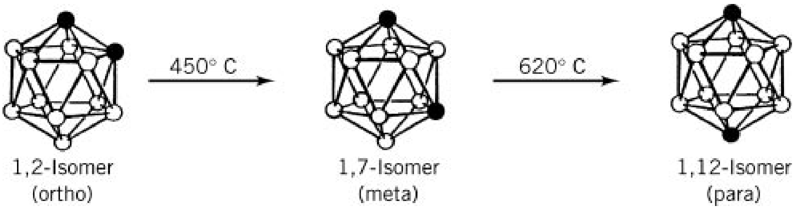


Fig. 10. Thermal rearrangement of *closo*-$C_2B_{10}H_{12}$, where ○ represents BH; ● CH.

$RCB_{10}H_{10}CR'$, and

$$\mathrm{H\overline{CB_{10}H_{10}C}H}$$

are used in the literature to represent substituted *closo*-carboranes. The carbons-apart isomers, called *meta*-carborane [16986-21-6], and *para*-carborane [20644-12-6], respectively, are obtained by thermal isomerization (Fig. 10) of 1,12-$C_2B_{10}H_{12}$ (see Fig. 10 for numbering conventions). The C–H vertices in the carboranes are acidic and *C*-substituted carboranes can be obtained conveniently through the intermediacy of lithium reagents such as 1,2-dilithium-*o*-carborane [22220-85-5], 1,2-Li_2-1,2-$C_2B_{10}H_{10}$, and 1,7-dilithium-*meta*-carborane [17217-89-9], 1,7-Li_2-1,7-$C_2B_{10}H_{10}$, which are readily prepared by treatment of *o*- or *m*-carborane with *n*-C_4H_9Li. Furthermore, it has been shown (128) that 1,2-dehydro-*o*-carborane, $C_2B_{10}H_{10}$, which can be generated through loss of lithium bromide from the lithium salt of the 2-bromo-*o*-carboranyl anion, $C_2B_{10}H_{11}Br$, exhibits chemistry similar to 1,2-dehydrobenzene [462-80-1] (benzyne), C_6H_4. This reactivity was demonstrated through 2 + 2, 4 + 2, and related cycloaddition reactions with dienes, leading to *C*-substituted organocyclic carboranes.

The discovery (129) of the base-promoted degradation of the isomeric *closo*-$C_2B_{10}H_{12}$ cages provided one of the most important carborane anion systems, the isomeric [*nido*-$C_2B_9H_{12}$]$^-$ anions,

$$\mathit{closo} - \mathrm{C_2B_{10}H_{12}} + \mathrm{RO^-} + 2\,\mathrm{ROH} \longrightarrow [\mathit{nido} - \mathrm{C_2B_9H_{12}}]^- + \mathrm{B(OR)_3} + \mathrm{H_2} \tag{61}$$

where R = CH_3, C_2H_5, etc. The [*nido*-$C_2B_8H_{12}$]$^-$ cages, and their *C*-substituted derivatives, are commonly referred to as dicarbollide ions, derived from the Spanish *olla*, meaning a bowl. Note that the rules governing the numbering of heteroborane cages calls for different systems for *closo* and *nido* cages (7). Thus the base-promoted degradation of 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ cages leads to 7,8-, 7,9-, and 2,9-*nido* 11-vertex cages, respectively. The [*nido*-7,8-$C_2B_9H_{12}$]$^-$ features a five-membered C_2B_3 open face having a perpendicular plane of symmetry passing between the two adjacent carbon atoms and through the unique boron atom of the open face. In addition to 11 terminal B–H and C–H hydrogens in [*nido*-7,8-$C_2B_9H_{12}$]$^-$ there is a twelfth hydrogen atom associated with the open face, that is referred to as an *endo*-hydrogen. Although the subject of some controversy, the position of this hydrogen atom was shown to reside in the solid-state structures of at least some of its salts in an unsymmetrical bridging position between the unique boron of the open face (B10) and an adjacent boron atom (B9/B11) (130–132). Deprotonation of this extra hydrogen of [*nido*-$C_2B_9H_{12}$]$^-$ leads to the [*nido*-$C_2B_9H_{11}$]$^{2-}$ dianion. Protonation of the [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion with strong acids leads to the neutral highly acidic $C_2B_9H_{13}$ molecule.

Aside from their extensive use in metallacarborane chemistry, the dicarbollide anions are important intermediates in the synthesis of other carborane compounds. For example, aqueous ferric chloride oxidation of the [7,8-$C_2B_9H_{11}$]$^-$ anion results in the 10-vertex cage *nido*-5,6-$C_2B_8H_{12}$ (133) and the aqueous chromic acid oxidation of [7,9-$C_2B_9H_{11}$]$^-$ yields *arachno*-1,3-$C_2B_7H_{13}$ [17653-38-2] (29).

Nonicosahedral carboranes can be prepared from the icosahedral species by similar degradation procedures or by reactions between boranes such as B_4H_{10} and B_5H_9 with acetylenes. The degradative reactions for intermediate $C_2B_nH^{n+2}$ species ($n = 6–9$) have been described in detail (134). The small *closo*-$C_2B_nH_n + 2$ species ($n = 3–5$ are obtained by the direct thermal reaction (500–600°C) of B_5H_9 using acetylene in a continuous-flow system. The combined yields approach 70% and the product distribution is ~5:5:1 of 2,4-$C_2B_5H_7$ [20693-69-0] to 1,6-$C_2B_4H_6$ [20693-67-8] to 1,5-$C_2B_3H_5$ [20693-66-7] (135). A similar reaction (eq. 62) employing base catalysts, such as 2,6-dimethylpyridine, at ambient temperature gives *nido*-2,3-$C_2B_4H_8$ [21445-77-2] (136). The *C*-substituted derivatives, *nido*-$(CR)_2C_2B_4H_6$, can be prepared conveniently. The trimethylsilyl-substituted derivatives, *nido*-2,3-$[(CH_3)_3Si]_2$-2,3-$C_2B_4H_6$, with carbon atoms adjacent in the five-membered open face, and *nido*-2,4-$[(CH_3)_3Si]_2$-2,4-$C_2B_4H_6$, with carbon atoms apart in the open face, have been used extensively in research studies (137). The [*nido*-$C_2B_4H_7$]$^-$ anion can be prepared by deprotonation of *closo*-$C_2B_4H_8$.

$$B_5H_9 + HC{\equiv}CH \xrightarrow{L} 2,3 - C_{24}H_8 + L \cdot BH_3 \; (L = \text{base}) \qquad (62)$$

The *arachno* carboranes 1,3-$C_2B_7H_{13}$ (29) and 6,9-$C_2B_8H_{14}$ [38670-58-5] (138) are unusual in that two of the extra hydrogens occur in CH_2 groups. The other two extra hydrogens are present as B–H–B bridges. The compound *arachno*-CB_8H_{14} contains one CH_2 group and four bridging hydrogens. The CH_2 groups in these *arachno* carboranes are quite acidic and can be deprotonated readily to give the corresponding carborane mono- and dianions, where are useful synthetic reagents.

As with the simple boranes, the *closo* carboranes are generally more thermally stable than the corresponding *nido* and *arachno* species. Thermal decomposition of *nido* and *arachno* carboranes often leads to one or more *closo* carborane. For example, pyrolysis of 2,3-$C_2B_4H_8$ is another route to 2,3-$C_2B_5H_7$ [30347-95-6], 1,2-$C_2B_4H_6$ [20693-68-9],1,6-$C_2B_4H_6$ [20693-67-8], and 1,5-$C_2B_3H_5$ [20693-66-7] (139).

A readily accessible carborane is *nido*-7-(NH_3)-7-$CB_{10}H_{12}$ [12539-44-5], a zwitterionic species formally derived from [$CB_{10}H_{13}$]$^-$ by replacement of a H^- by NH_3. It has been shown (140) that this monocarbaborane can be obtained in excellent yield by treatment of $B_{10}H_{14}$ with CN^- followed by passage through an acidic ion-exchange column (eq. 63).

$$B_{10}H_{14} + 2NaCN \xrightarrow[-HCN]{H_2O} Na_2[B_{10}H_{13}CN] \xrightarrow{H_2} CB_{10}H_{12}(NH_3) \tag{63}$$

The related mono-*N*-alkylated carboranes, 7-(NH_2R)-7-$CB_{10}H_{12}$, can be prepared by treatment of decaborane(14) with alkyl isocyanides (141).

$$B_{10}H_{14} + RNC \longrightarrow (H_2NR)\ CB_{10}H_{12} \tag{64}$$

The nitrogen of these aminocarboranes can be alkylated to give, eg, 7-$[N(CH_3)_3]$-7-$CB_{10}H_{12}$ [31117-16-5]. These compounds give [*closo*-2-$CB_{10}H_{11}]^-$ [38102-45-0] upon treatment with Na in THF followed by iodine oxidation (eq. 65) (142).

$$[CB_{10}H_9(Nr_3)] \xrightarrow[THF]{Na} [CB_{10}H_{11}]^{3-} \xrightarrow{I_2} [CB_{10}H_{11}]^- + 2\,I^- \tag{65}$$

Other large monocarbaboranes include *nido*-6-(NR_3)-6-CB_9H_{11}[*closo*-1-$CB_9H_{10}]^-$; [38192-43-7] and [*closo*-$CB_{11}H_{12}]^-$; [39102-46-0]. The *closo* monocarbaboranes can be functionalized at carbon via lithiation using reagents such as *n*-butyl lithium in a manner similar to the two-carbon carboranes. The small monocarbaboranes *closo*-1-CB_5H_7 [25301-90-0], *nido*-2-CB_5H_9 [12385-35-2], and a variety of their alkylated derivatives are also known (143,144).

Synthetic methods have been developed to prepare a variety of tricarbaboranes that contain three carbons in their polyhedral skeletons. The isomeric 11-vertex *nido*-$C_3B_8H_{12}$ and its *C*-substituted derivatives form a family analogous to the dicarbollides discussed above, with the [*nido*-$C_3B_8H_{12}]^-$ anion behaving as a strong base having no extra hydrogens about its open five-membered face (145). Other tricarbaboranes include *nido*-$C_3B_7H_{10}$, and *arachno*-$C_3B_7H_{12}$, for which various isomers and *C*-substituted derivatives are known (146). Tetracarbaboranes, containing four carbon atoms in a single polyhedral skeleton, were rare until the discovery (147) of the metallacarborane-mediated synthesis of $(CH_3)_4C_4B_8H_8$ [58815-26-2].

$$[2,3-(CH_3)_2-2,3-C_2B_4H_5]^- \xrightarrow{CoCl} [(CH_3)_2C_2B_4H_4]_2CoH \xrightarrow{[O]} (CH_3)_4C_4B_8H_8 \tag{66}$$

As the $C_4B_n{-}4H_n$ series of tetracarbaboranes is classified in the electron-counting formalism as *nido*, these molecules can have more open structures even though extra hydrogens are absent, as shown for the isomers of 2,3,4,5-$C_4B_2H_6$ [28323-17-3] and $(CH_3)_4C_4B_8H_8$, at least one isomer of the latter having an open nonicosahedal structure (148). Other tetracarbaboranes include isomers of *nido*-$C_4B_8H_{10}$, *nido*-$C_4B_7H_{11}$, and *arachno*-8-$[CH_3OC(O)]$-7,8,9,10-$C_4B_8H_{13}$ (149).

Cage rearrangements in polyhedral carboranes are well known. Although most carborane cages are stable at room temperature, many undergo rearrangements at elevated temperatures. Carborane isomers obtained by conventional synthetic routes are often kinetic products and not the thermodynamically most stable isomers. When subjected to elevated temperatures below the ultimate decomposition temperatures, carboranes often undergo rearrangements to the more stable isomers. This process may involve the sequential formation of a series of successively more stable isomers. Isomerization of the *closo*-1,2-$C_2B_{n\text{-}2}H_n$ ($5 \leq n \leq 12$) carboranes and their *C*-substituted derivatives has attracted considerable interest. Perhaps most intensely studied is the rearrangement of *closo*-$C_2B_{10}H_{12}$ (see Fig. 10). This rearrangement reflects a progression toward greater stability as a result of increasing carbon atom separation within the cage. The mechanisms for this cage rearrangement, as well as the rearrangements of other carboranes, heterocarboranes, and metallacarboranes, has been a topic of much controversy (150). Several mechanisms have been proposed including most notably the diamond–square–diamond, modified diamond–square–diamond, triangular face rotation, pentagonal rotation, and opening closure processes, among others. In addition to thermal cage rearrangements, a number of carborane species are believed to undergo reversible rearrangements in solution at or near room temperature. For example, ^{11}B nmr spectral data indicates that the $[CB_{10}H_{11}]^-$ ion (151) and *closo*-$C_2B_6H_8$ (152) may be fluxional in solution.

Considerable effort has been devoted to the synthesis of novel materials using carborane building blocks that may find application as components for nano technology (153,154). Icosahedral carboranes can be linked together by direct C–C bond formation to produce concatented compounds having geometrically distinct structures that may depend on the isomeric carbon configuration of the carborane cages. Carborane molecules can be linked together either by direct C–C bonds or via variety of linking group to form a “carboracycles” or chains. Linking together *p*-carborane molecules by direct C–C bonds leads to rigid rod-shaped molecules referred to as “carborods” (155). A carborod tetramer is shown in Figure 11. These cylindrical molecules have van der Waals diameters of ~7 Å, which is relatively thick compared to other known rigid-rod molecules, such as staffanes, rodanes, and cubanes. Related carborods can be prepared by connecting the carbon atoms of a series of *p*-carborane molecules with various linker groups, eg, biphenyl.

As with the *closo*-boranes discussed above, a family of highly substituted (camouflaged) *closo*-carboranes also exists. For example, exhaustive fluorination of icosahedral two-carbon carboranes provides *closo*-1,2-$(H)_2$-1,2-$C_2B_{10}F_{10}$ (156), *closo*-1,7-$C_2B_{10}F_{12}$ (156, 157) and *closo*-1,12-$(H)_2$-1,12-$C_2B_{10}F_{10}$ (156), all of which are air stable. In aqueous media, they hydrolyze to boric acid. The fluorinated one-carborane monoanion 1-$[HCB_{11}F_{12}]^-$ has also been prepared and shown to undergo nucleophilic substitution by OH^- at B–F vertices in basic aqueous media (158). *Closo*-carboranes can also be peralkylated carboranes. For example, 1,12-$C_2B_{10}(CH_3)_{12}$ (159), $[CB_{11}(CH_3)_{12}]^-$ (160), *closo*-1,12-$(H)_2$-1,12-$C_2B_{10}(CH_3)_{10}$ (161) and related compounds have been prepared. Oxidation of $[CB_{11}(CH_3)_{12}]^-$ leads to the stable free radical $[CB_{11}(CH_3)_{12}]^-$ (162), which is a moderately air-stable strong oxidizing agent. Smaller carboranes may be highly substituted as well, as illustrated by the preparation of [*closo*-1-H-$CB_9X_9]^-$, [*closo*-1-NH_2-$CB_9X_9]^-$ [*closo*-1-H-$CB_9X_9]^-$ anions, which X is chlorine, bromine, and iodine (163) and related compounds.

Subsequent halogenation of the alkyl camouflaged carboranes leads to halogenoalkylcarboranes. For example, chlorination of 1,12-$C_2B_{10}(CH_3)_{12}$ provides

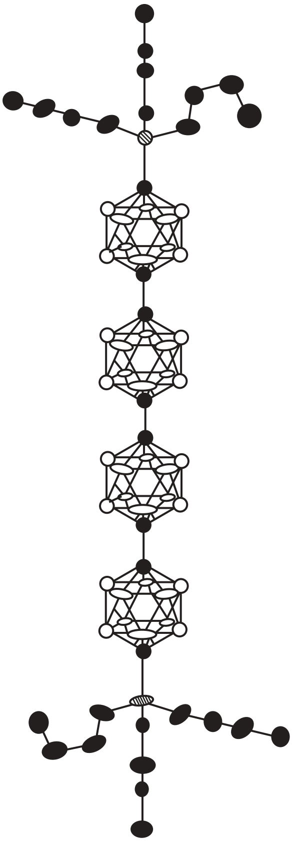


Fig. 11. A carborane rigid rod (carborod) containing four *p*-carborane units terminated by tri-*n*-butylsilyl groups, where ○, ●, ◎, and ○ represents BH; C, CH_2, and CH_3; (Si, and hydrogen is omitted.)

1,12-$C_2B_{10}(CHCl_2)_{12}$, where the steric bulk of chloride prevents full complete substitution of methyl hydrogens (164). This spherical molecule is comparable in size the fullerene C_{60}. Fluorination of $Cs[CB_{11}(CH_3)_{12}]$ using F_2 and K_2NiF_6 provides $Cs[CB_{11}(CF_3)_{12}]^-$, the anion of which has been described as simultaneously explosive and "inert" (165). Salts of the $[CB_{11}(CF_3)_{12}]^-$ anion are flammable and percussion sensitive, exploding upon scraping with a metal spatula. However, this compound is chemically inert and resists attack by 20% KOH in ethanol, concentrated H_2SO_4, anhydrous CF_3SO_3H, and BF_3/HF mixtures. The anion likely remains unprotonated in aqueous solution. Prolonged treatment of *closo*-1,12-$(H)_2$-1,12-$C_2B_{10}(CH_3)_{10}$ with F_2 at temperatures >35°C leads to quantitative conversion to *closo*-1,12-$(F)_2$-1,12-$C_2B_{10}(CF_3)_{10}$ (166). This air-stable compound is unchanged in acidic solution but is slowly degraded in basic media. It is stable to 300°C, however, mixture of this and related fluoromethylcarborane were reported to detonate upon scraping with a spatula. *Extreme care should be taken when handling any of the fluoroalkylcarboranes*.

6.2. Weakest Anions and Strongest Acids. Carborane anions have received much attention as robust anions that have very low nucleophilicity and weak coordination to metal ions anions. For example, [*closo*-$CB_{11}H_{12}$]$^-$ and [*closo*-CB_9H_{10}]$^-$ have been studied as members of a class described as the weakest coordinating anions (167). Such anions are important as counterions in catalytic metal complexes, where their lack of significant coordination results in the stabilization of highly reactive cationic metal centers (168–172). Such catalyst systems are especially useful in stereochemically controlled olefin polymerizations (173). The functionalization of carborane anions can be used to enhance or fine tune their properties for specific applications (174). For example, the halogenated anions [$CB_{11}H_6X_6$] (X = Cl, Br), are extremely weak nucleophiles and are chemically unreactive. The weakest anion character of these carborane anions has led to a counterpart chemistry, the strongest acids (175). Carboranes such as *closo*-$CB_{11}H_{13}$, the conjugate acid of [*closo*-$CB_{11}H_{12}$]$^-$, and especially its halogenated derivative are superacids (those acids stronger than 100% sulfuric acid). For example, the superacids H[$CB_{11}H_6X_6$] (X = Cl, Br), halogenated at the cage positions farthest from the carbon, are among the strongest acids known, having acid strength strong enough to protonate any arenes. The chlorine-containing derivative is shown in Figure 12. Most strong acids have serious limitations because they are too nucleophilic and have oxidizing capacity. Thus their protonation reactions are usually accompanied by oxidative degradation. Hence, very strong acids are generally associated with highly corrosive liquids. The lack of significant nucleophilicity in the carboranyl anions, however, allows their conjugate acids to participate in pure protonation reactions without the destructive effects usual found with other superacids. Moreover, these are perhaps the only superacidic reagents that are easily weighed and delivered in stoichiometric quantities. The carborane superacids should prove useful in many acid-catalyzed chemical processes, including industrial polymerizations.

A diversity of polyhedral carborane cage-containing polymers has been prepared. The best known of these are elastomeric polycarboranylsiloxanes which were developed by Olin Corp. (176) and Union Carbide Corp. (177) in the 1970s. These are based on *m*-carborane cages linked by polysiloxane groups with direct C–Si bonds. The properties of these materials can be varied by

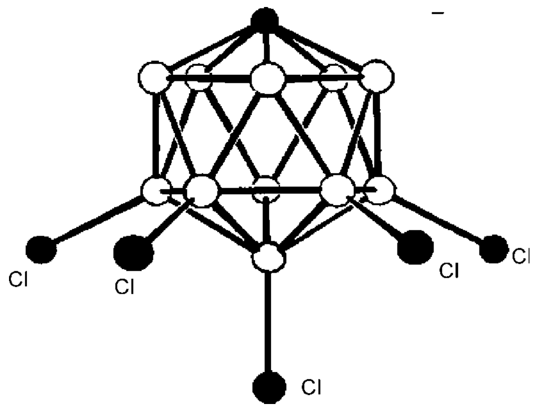


Fig. 12. The highly robust [$CB_{11}H_6Cl_6$]$^-$ anion is the conjugate base of one of the strongest known superacids, where ○ represents B; ○ C ; ● Cl and hydrogen is omitted.

Table 5. **Heteroboranes**

Heteroborane[a]	CAS Registry Number	References
	Group 15 (V) heteroatoms	
arachno-6-NB_8H_{13}	[58920-21-1]	179
nido-10-$C_6H_5CH_2$-7,8,10-$C_2NB_8H_{10}$	[58614-34-9]	179
nido-7-CH_3-7-$PB_{10}H_{12}$	[57108-87-9]	180
closo-$C_6H_5PB_{11}H_{11}$	[57139-68-1]	181
closo-$CPB_{10}H_{11}$	[17398-92-4]	181
[*nido*-7,8-$CPB_9H_{11}]^-$	[52110-38-0]	24
closo-1,2-$As_2B_{10}H_{10}$	[51292-90-1]	182
[*nido*-7-$AsB_{10}H_{12}]^-$	[51292-97-8]	182
[*nido*-7,8-$As_2B_9H_{10}]^-$	[51358-26-0]	183
[*closo*-$AsB_{11}H_{11}]^-$	[51898-88-5]	182
closo-1,2-$CAsB_{10}H_{11}$	[23231-66-5]	184
	Group 16 (VI) heteroatoms	
closo-$SB_{11}H_{11}$	[56464-75-6]	22
[*arachno*-6-$SB_{11}H_{12}]^-$	[51358-27-1]	185
nido-4-SB_8H_{10}	[59351-07-4]	22
closo-1-SB_9H_9	[41646-56-4]	22
nido-7-$SB_{10}H_{12}$	[58984-44-4]	186
arachno-6,8-$S_2B_7H_9$	[63115-77-5]	187
arachno-6,8-CSB_7H_{11}	[63115-78-6]	187
nido-7-$SeB_{10}H_{12}$	[61649-90-9]	188
nido-7,8-$Se_2B_9H_9$	[61618-06-2]	188
nido-7-$TeB_{10}H_{12}$	[61649-91-0]	188

[a] The *closo, nido, arachno* classifications are given on the basis of framework electron count and not structure.

changing the length and substituents of the polysiloxane linkages as well as their overall molecular weights. Some of these materials have excellent thermal stabilities, chemical resistance, and high temperature elastomeric properties. Polymers of this type, known under the trade name Dexsil, were commercial materials, useful as high temperature stationary phases in gas chromatography among other applications. These compounds, however, have not been produced commercially for many years. The organic and organometallic chemistry of *closo* carborane derivatives has been reviewed (5,178).

6.3. Other Heteroboranes. Other well-documented families of heteroboranes include the azaboranes, thiaboranes, phosphaboranes, arsenaboranes, stibaboranes, selenaboranes, and telluraboranes (126). Table 5 lists representative examples of heteroboranes from Groups 15 (V) and 16 (VI). The thiaboranes are the most extensively developed class of heteroboranes after the carboranes. The thiaboranes [*arachno*-6-$SB_9H_{12}]^-$ [45979-10-0] and *nido*-6-SB_6H_{11} [59120-72-8] (185) can be converted (eq. 67) to 1-SB_9H_9 [41646-56-4], which has a nonicosahedral fragment structure (22).

$$B_{10}H_{14} \xrightarrow[H_2O]{S_x^{2-}} [arachno\text{-}6\text{-}SB_9H_{12}]^- \xrightarrow[C_6H_6]{I_2}$$

$$nido\text{-}6\text{-}SB_9H_{11} \xrightarrow{\Delta} closo\text{-}1\text{-}SB_9H_9 \qquad (67)$$

Preparation of the smaller thiaboranes, 4-SB_8H_{10}, occurs via the thiaboranes [*arachno*-6-$SB_9H_{12}]^-$ and larger species are attainable by expansion reactions.

$$closo\text{-}1\text{-}SB_9H_9 \xrightarrow[CH_3OH]{KOH} [4\text{-}SB_8H_9]^- \underset{-H^+}{\overset{+H^+}{\rightleftarrows}} 4\text{-}SB_8H_{10} \qquad (68)$$

Closo-1-SB_9H_9 and *closo*-$SB_{11}H_{11}$, unlike most other thiaboranes, are resistant to moisture and air oxidation. Other thiaboranes include the nine-vertex clusters *arachno*-$S_2B_7H_9$ (187) and *arachno*-SB_8H_9 (22), which are isostructural with *arachno*-$C_2B_7H_{13}$. These can be prepared in high yield.

$$[6-SB_9H_{12}]^- \xrightarrow{\Delta,H^+} 7-SB_{10}H_{12} \xrightarrow{R_3NBH_3} SB_{11}H_{11} \qquad (69)$$

7. Metallaboranes

7.1. Transition-Element Metallaboranes. The transition-metal hydroborate cluster, $HMn_3(CO)_{10}(BH_3)_2$, containing a B_2H_6 moiety, which is multiplied bridging between three manganese carbonyl and manganese carbonyl hydride centers via M−H−B bridges, might be regarded as the first structurally characterized metallaborane cluster (189). This and similar clusters were isolated in the 1960s as by-products in the synthesis of transition-metal carbonyl hydrides by sodium borohydride reduction of metal carbonyls, a standard method for the preparation of transition-metal hydride complexes and clusters since the 1970s (190). Indeed, the $[BH_4]^-$ anion acts as a ligand in a wide variety of metal complexes in which from one to all four hydrogen atoms are involved in bonding to metals (191). However, the chemistry of stable metallaboranes that incorporate metals in vertex positions of polyhedral borane clusters was developed somewhat later. To date a great many metallaborane clusters have been characterized covering a wide range of metals, sizes, and polyhedral fragment geometries.

One of the most extensive classes of metallaboranes are those derived from decaborane, which in most cases produces 11-vertex metallaborane products. The $[B_{10}H_{12}]^-$ [12430-37-4] anion can also be considered as a bidentate ligand that coordinates metals between boron atoms 2,11 and 3,8, the metal at position 7 (Fig. 1**n**) such that the metal in effect occupies the position of a bridge hydrogen of the conjugate acid borane. Situations in which a metal vertex may be regarded as equivalent to an H^+, BH^{2+}, or the $BH_2{}^+$ moiety have also been discussed (192,193). In the case of the $[B_{10}H_{12}]^-$ ligand, the bridge hydrogens lie in positions 8,9 and 10,11. Typical complexes containing $[B_{10}H_{12}]^{2-}$ include $[M(B_{10}H_{12})_2]^{2-}$, where M = Zn, Cd, Hg (194), Co, Ni, Pd, Pt (195); $L_2M(B_{10}H_{12})$, where M = Pd, Pt; L = PR_3 (195); and $[L_3M(B_{10}H_{12})]^-$ where M = Co, Rh, Ir; L = CO, PR_3 (195). The X-ray structure of $[Ni(B_{10}H_{12})_2]^{2-}$ [31388-28-0] is shown in Figure 13 (196). If the $[B_{10}H_{12}]^{2-}$ ligand in the Ni complex is considered to be bidentate, coordination about the metal is effectively square planar. The geometry of the metal in analogous complexes varies according to the requirements of the

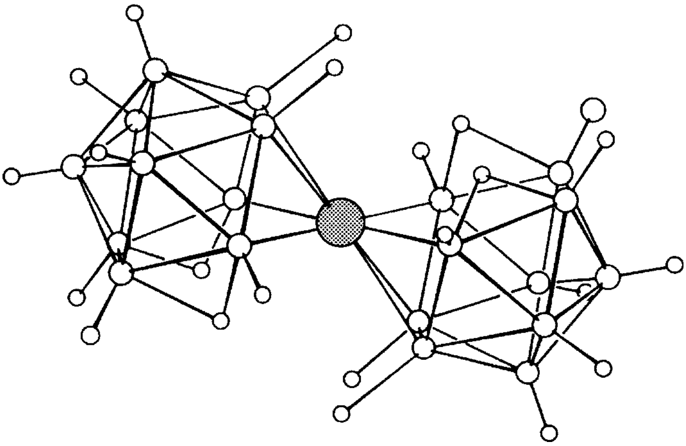
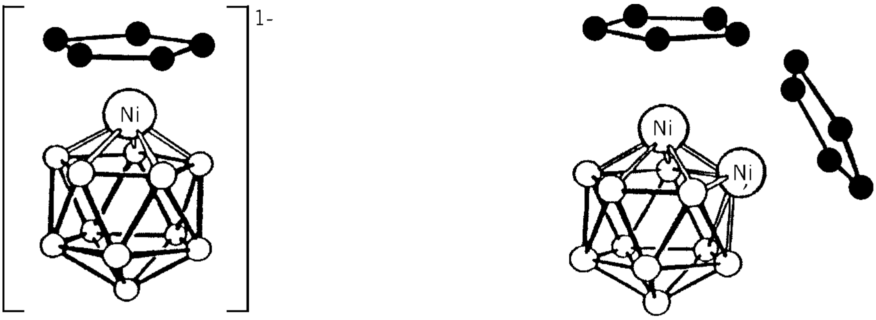


Fig. 13. The structure of $[Ni(B_{10}H_{12})_2]^{2-}$ (196) where ◍ represents the Ni; ○ B; and ○ H.

metal. For example, $[Zn(B_{10}H_{12})_2]^{2-}$ [19154-53-1] is tetrahedral (197). The $[B_{10}H_{13}]^-$ ion [36928-50-4] (198) is especially useful for the synthesis of 11-vertex *nido* metallaboranes. These syntheses are influenced by (*1*) the cation of the $[B_{10}H_{13}]^-$ salt; (*2*) the nature of other ligands about the metal; and (*3*) the availability of a proton trap for the reaction (195,199).

The first *closo* metallaborane complexes prepared (200) were the nickelaboranes [*closo*-(η^5-C_5H_5)Ni($B_{11}H_{11}$)]$^-$ and *closo*-1,2-(η^5-C_5H_5)$_2$-1,2-$Ni_2B_{10}H_{10}$ [55266-88-1] (Fig. 14). These species are equivalent to [*closo*-$CB_{11}H_{12}$]$^-$ and *closo*-$C_2B_{10}H_{12}$ by the electron-counting formalism. The mixed-bimetallic anion [*closo*-(η^5-C_5H_5)$_2$CoNi($B_{10}H_{10}$)]$^-$ and other related species were reported later (201). These metallaboranes display remarkable hydrolytic, oxidative, and thermal stability.



(a) (b)

Fig. 14. The structures of *closo* metallaboranes where ○ represents BH; ● CH: (**a**) [*closo*-(η^5-C_5H_5)Ni($B_{11}H_{11}$)]$^-$; (**b**) *closo*-1,2-(η^5-C_5H_5)$_2$-1,2-$Ni_2B_{10}H_{10}$.

Closo metallaboranes can also be formed by the direct interaction of polyborane and metal carbonyl clusters. For example,

$$\begin{aligned}&\textit{arachno}\text{–}B_{10}H_{12}[S(C_2H_5)_2]_2 + Co_2(CO)_5 \xrightarrow[\textit{reflux}^{\circ}C]{\text{toluene}} \\ &\textit{closo}\text{–}(CO)_5Co_2B_{10}H_8[S(C_2H_5)_2] + 3\ CO + 2\ H_2 \qquad (70)\end{aligned}$$

yields two isomers of this 12-vertex *closo* compound in good yield (202). Both air-stable isomers contain a $Co_2(CO)_8$ cobalt carbonyl cluster fragment, which can be considered a four framework electron-donor group. The retention of two $S(C_2H_5)_2$ substituents allows these clusters to comply with electron-counting rules for a *closo* compound. The B–SR_2 groups each donate three framework electrons. The structure of one isomer of *closo*-$(CO)_5Co_2B_{10}H_8[S(C_2H_5)_2]_2$ is shown in Figure 15.

A number of novel products have been isolated from the reaction of $[B_5H_8]^-$ [31426-87-6] and $CoCl_2$ and $[C_5H_5]^-$ in THF (203,204). The predominant product is *nido*-2-(CpCo)-B_4H_8 [43061-99-0]. Also obtained are isomeric clusters containing up to four cobalt atoms, eg, $(\eta^5\text{-}C_5H_5Co)_4B_4H_8$[59370-82-0]. Characterization of these clusters indicates an unusual 2*n* framework electron count having geometries reminiscent of strictly metallic clusters (11,205). Other metallaboranes, particularly those containing early transition metals, such as the series $(Cp^*Re)_2B_nH_n$, where $n = 8\text{–}10$, have structural characteristics that are borderline between the classical polyhedral boranes and metal borides (206). These have structures that exhibit nondeltahedral geometries and cross-cluster bonds.

7.2. Main Group Element Metallaboranes. A variety of metallaborane clusters, which incorporate main group metals in vertex positions of polyhedral metallaborane clusters, have been reported. Examples are $(BH_4)BeB_5H_{10}$

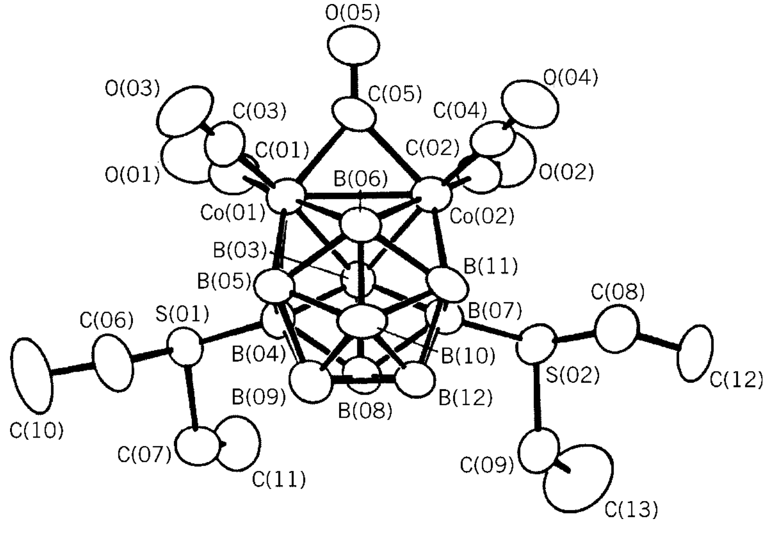


Fig. 15. The structure of one isomer of *closo*-$(CO)_5Co_2B_{10}H_8[S(C_2H_5)_2]_2$ without the hydrogens. Courtesy of the American Chemical Society (202).

(207), $MgB_{10}H_{12} \cdot 2O(C_2H_5)_2$ (208), $[(CH_3)HgB_{10}H_{12}]^-$ (209), $[AlB_{10}H_{14} \cdot 2O(C_2H_5)_2]^-$ (210), $[(CH_3)AlB_{11}H_{11}]^{2-}$ (211), $(CH_3)InB_{10}H_{12}$ (209), $[(CH_3)_2TlB_{10}H_{12}]^-$ (209), and $(CH_3)_2MB_{10}H_{12}$, where, M = Si (212), Ge (213), or Sn (213). A number of main group metal complexes have been reported that incorporate borane moieties via M–H–B bridges, such as those found in $Al(BH_4)_3$ (Fig. 8). Examples of other compounds in this class include the octahydrotriborate complexes $Be(B_3H_8)_2$ (214), $(C_5H_5)BeB_3H_8$ (214), $[(CH_3)BeB_3H_8]_2$ (214), $(CH_3)_2AlB_3H_8$ (215), $H_2GaB_3H_8$ (216), $(CH_3)_2GaB_3H_8$ (216), $Mg(B_3H_8)_2 \cdot 6THF$ (217), and $(BH_4)MgB_3H_8 \cdot 5THF$ (217). Complexes containing the $[B_3H_8]$ unit are generally fluxional in solution. The low temperature static structure of $Be(B_3H_8)_2$ exhibits C_{2v} symmetry and features a tetrahedral beryllium center covalently linked via four Be–H–B bonds to two B_3H_8 units (218). The nmr spectral data for $[(CH_3)Be(B_3H_8)]_2$ indicates a methyl bridged dimer structure.

Several complexes containing the $B_5H_{10}Be$ unit, such as $(BH_4)BeB_5H_{10}$ and $Be(B_5H_{10})_2$ (207) have been characterized. X-ray diffraction studies (219) of these compounds show pentagonal pyramid structures having the beryllium atom in a basal position with three of the five bridging hydrogen atoms at the open face taking part in Be–H–B bonds. In $(BH_4)BeB_5H_{10}$, the BH_4 moiety is linked to the beryllium center by two Be–H–B bonds. The structure of $Be(B_5H_{10})_2$ consists of two pyramidal $B_5H_{10}Be$ units linked at a common basal position beryllium atom.

The volatile, air-sensitive liquid species $(CH_3)_2AlB_3H_8$ and $(CH_3)_2GaB_3H_8$ are prepared by the direct reaction of the corresponding main group metal halide and salts of the $[B_3H_8]^-$ ion, in the absence of solvent (220). The reaction of $(CH_3)_2AlB_3H_8$ and $Al(BH_4)_3$ results in the species $(BH_4)_2AlB_3H_8$. These small metallaboranes are fluxional in solution and have limited thermal stability at room temperature. The high yield preparation of the *closo*-aluminaborane anion $[(CH_3)AlB_{11}H_{11}]^{2-}$ has been described (211).

$$Na_2[B_{11}H_{13}] + Al(CH_3)_3 \longrightarrow Na_2[(CH_3)AlB_{11}H_{11}] + 2\ CH_4 \ >90\% \qquad (71)$$

Similar synthetic strategies involving the elimination of alkyl groups from organometallic reagents and acidic B–H–B groups have been used to prepare a number of other metallaboranes and metallacarboranes. The $[(CH_3)AlB_{11}H_{11}]^{2-}$ anion is isostructural with *closo*-$[B_{12}H_{12}]^{2-}$. The methyl group is attached to aluminum projecting radially from the icosahedral AlB_{11} cage.

The silacarborane analogue of C,C-dimethyl-*ortho*-carborane, *closo*-1,2-$(CH_3)_2$-1,2-$Si_2B_9H_{11}$ [128270-48-4] has been reported (221). This *o*-silacarborane, which has an icosahedral framework much like *o*-carborane and is reported to be stable to air and moisture, was obtained in low yield from the reaction of decaborane and bis(dimethylamino)methylsilane in refluxing benzene.

$$B_{10}H_4 + CH_3(H)Si\left[N(CH_3)_2\right]_2 \longrightarrow \textit{closo} - 1,2 - (CH_3)_2{-}1,2 - Si_2B_9H_{11}$$

$$+ 6,9 - \left[(CH_3)_2NH\right]_2B_{10}H_{12} + \text{other products} \qquad (72)$$

7.3. Exopolyhedral Metallaboranes. Polyboranes may bind exopolyhedral metals in a variety of ways. Most commonly metals are bound via

M–H–B interactions. In other cases, metals may formally replace bridging hydrogen atoms at edge positions to give B–M–B interactions. Metals may also be attached to polyborane cages by direct M–B σ-bonds. The M–H–B bonds are found in $Cu[B_{10}H_{10}]$ (222) and in $\{[(C_6H_5)_3P]_2Cu\}_2$-μ-$B_{10}H_{10}$ [54020-26-7] (193). In both cases, the metal centers are bound through a bidentate interaction with two adjacent B–H groups.

A series of divalent lanthanide metal metallaborane derivatives has been prepared by the redox reaction of metallic lanthanides and boron hydrides and by the metathesis reaction of boron hydride salts with $LnCl_2$ where Ln = Sm, Eu, Yb (223,224). The species $(CH_3CN)_6Yb[(\mu\text{-}H)_2B_{10}H_{12}]$, $(CH_3CN)_4Yb[(\mu\text{-}H)_3BH]_2$, and $(C_6H_5N)_4Yb[(\mu\text{-}H)_3BH_4]_2$ have been structurally characterized by X-ray crystallography and shown to contain ytterbium to boron hydride Yb–H–B linkages. Thermal decomposition of lanthanaboranes can be used to generate lanthanide metal borides.

Metallaboranes containing M–B σ-bonds can be prepared by nucleophilic displacement reactions (225) and oxidative addition (226) of B–H and B–Br bonds to metal centers. For example, the reaction of $IrCl(CO)[P(CH_3)_3]_2$ and 1- or 2-BrB_5H_8 results in 2-$[IrBr_2(CO)\text{-}[P(CH_3)_3]_2B_5H_8]$ in which the B_5H_8 polyhedron serves as ligand for the metal.

Boranes also form derivatives in which main group elements occupy a bridging position between two boron atoms, rather than a polyhedral vertex. An extensively studied system is μ-$R_3MB_5H_8$, where R = H, CH_3, C_2H_5, halogen, and M = Si, Ge, Sn, Pb (227). The structure of 1-Br-μ-$[(CH_3)_3Si]$-B_5H_7 [28323-19-5] is shown in Figure 16 (228).

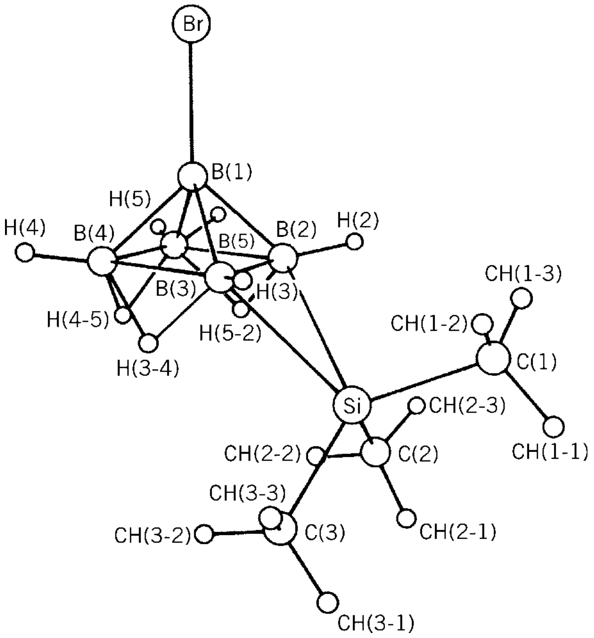


Fig. 16. Structure of 1-Br-μ-$[(CH_3)_3Si]B_5H_7$. Courtesy of the American Chemical Society (228).

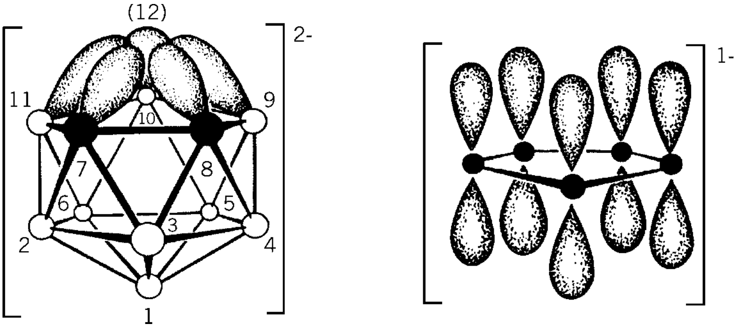


Fig. 17. Structural analogy between the $[7,8\text{-}C_2B_9H_{11}]^{2-}$ dicarbollide dianion and the $[C_5H_5]^-$ anion (6), where ○ represents BH; ● CH; showing *p* orbital lobes.

7.4. Metallacarboranes. In the early 1960s, M. F. Hawthorne recognized (6,299) the bonding similarities between the pentagonal face of the isomeric [*nido*-$C_2B_9H_{11}]^{2-}$ ions and the well-known cyclopentadienide ion $[C_5H_5]^-$ (Cp^-) (Fig. 17). The isomeric [*nido*-$C_2B_9H_{11}]^{2-}$ anions and their *C*-substituted derivative, which are commonly known as dicarbollide ions, form stable complexes with most of the metallic elements. An extensive chemistry also exists for the isomeric *C*-substituted derivatives of the smaller carborane anion [*nido*-$R_2C_2B_4H_6]^{2-}$. Many other carboranes are also known to form metal complexes. Indeed nearly all metals can be combined with polyboron hydride clusters to produce an apparently limitless variety of cluster compounds. The chemistry of metallacarboranes incorporating *d*-block metals has been reviewed (230).

7.5. Transition-Metal Metallacarboranes. The first demonstration of the insertion of a transition metal into an open face of a carborane cage was with the iron sandwich compound [*commo*-$Fe(C_2B_9H_{11})_{12}]^{2-}$ [12541-50-3] (231). This product is readily air oxidized to [*commo*-$(C_2B_9H_{11})_2Fe]^-$ [12547-76-1], a complex containing a formal Fe^{3+} center. These complexes, as well as those formed from a variety of formally d^3, d^5, d^6, and d^7 transition metals (Table 6),

Table 6. **Structure of $[(C_2B_9H_{11})_2M^{n+}]^{n-4}$ Complexes as a Function of Electronic Configuration**

Electronic configuration					
d^3	d^5	d^6	d^7	d^8	d^9
		Unslipped sandwich[a]			
Cr^{3+}	Fe^{3+}	Fe^{2+} Co^{2+} Ni^{4+} Pd^{2+}	Co^{2+} Ni^{3+} Pd^{2+}		
		Slipped sandwich[b]			
				Cu^{3+} Ni^{2+} Pd^{2+} Au^{3+}	Cu^{2+} Au^{2+}

[a] See Figure 18**a**.

[b] See Figure 18**b**.

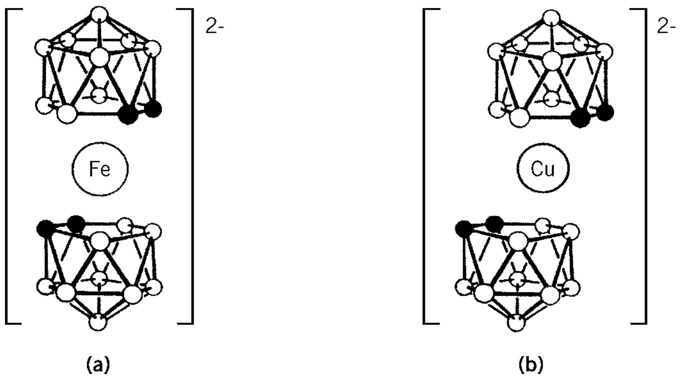


Fig. 18. Exemplary structures of (**a**) unslipped and (**b**) slipped metallacarborane dicarbollide sandwich derivatives where ○ represents BH; ● CH.

have symmetrical sandwich structures (232) of the type shown in Figure 18**a**. By contrast, d^8 and d^9 metals form slipped sandwich structures as shown in Figure 18**b** (6,233). A great many icosahedral complexes have been produced by incorporating transition metals into clusters based on the dicarbollide cage. (233,234). Examples are

$$\begin{tikzcd} {[nido\text{-}C_2B_9H_{11}]^{2-} + [C_5H_5]^- + M^{2+}} \arrow[r] & {[closo\text{-}\eta^5\text{-}C_5H_5)MC_2B_9H_{11}]^-} \arrow[d, "{[O]}"] \\ & closo\text{-}(\eta^5\text{-}C_5H_5)MC_2B_9H_{11} \end{tikzcd} \qquad (73)$$

where M = Fe, Co, Ni, Cr.

Metallacarborane dicarbollide complexes are generally more robust than the corresponding cyclopentadiene complexes. The bis(dicarbollide) sandwich complexes of general formula $[M(C_2B_9H_{11})_2]^-$, where M is Fe^{3+}, Co^{3+}, and Ni^{3+}, exhibit great thermal, chemical, redox, and radiolytic stability. These species are also unusual in that they are extremely hydrophobic anions that form very strong conjugate acids. This unique combination of features leads to a number of potential uses such as the extraction of organic compounds from extremely dilute solutions and the isolation of metal cations, including the quantitative separation of radionuclides, eg, ^{137}Cs (235).

Representative icosahedral metallacarborane carbonyl complexes are prepared as shown (236).

$$[nido{-}C_2B_9H_{11}]^{2-} + M(CO)_6 \xrightarrow[M=Cr,\ Mo,\ W]{h\nu} [closo - (C_2B_9H_{11})M(CO)_3]^- + 3\,CO \qquad (74)$$

$$[nido{-}C_2B_9H_{11}]^{2-} + BrM(CO)_5 \xrightarrow[M=Mn,\ Re]{\Delta} [closo - (C_2B_9H_{11})M(CO)_3]^- + Br^- + 2\,CO \qquad (75)$$

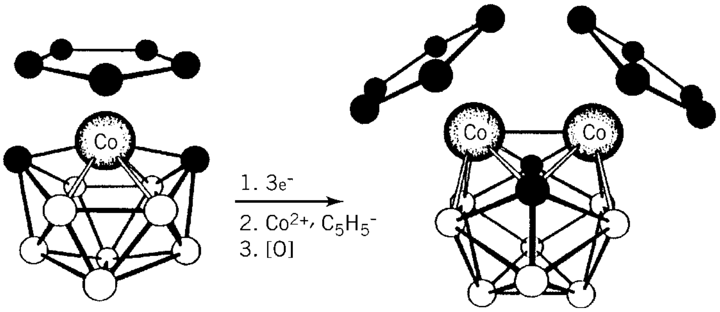


Fig. 19. A characteristic polyhedral expansion reaction leading to isomeric $[(\eta^5\text{-}C_5H_5)Co]_2C_2B_8H_{10}$ clusters where represents ○ BH; ● CH. The 2,9-$(\eta^5\text{-}C_5H_5)$-2,9-Co_2-1,12-$C_2B_8H_{10}$ isomer is shown. Courtesy of the American Chemical Society (245).

Fundamental methodologies for the synthesis and transformation of metallacarboranes(6) include polyhedral expansion (237–242), contraction (243), subrogation (244), and related reactions. Many carboranes are readily reduced from *closo* to *nido* molecules with a concomitant opening of the cage structures (see Fig. 2). The open, nontriangular faces of the resulting *nido* anions are generally capable of coordination to metals. The polyhedral expansion reaction (237–242), also called metal insertion, is most general for two-carbon carboranes.

$$closo - C_2B_nH_{n+2} + 2e^- \longrightarrow [nido - C_2B_nH_{n+2}]^{2-} \tag{76}$$

$$M^x \longrightarrow [commo - M(C_2B_nH_{n+2})_2]^{n-4} \tag{77}$$

Multiple polyhedral expansion reactions, carried out either simultaneously or sequentially, have been used to prepare metallacarboranes having multiple metal centers (245). An example is given in Figure 19.

In most cases, the prolonged treatment of a *closo* carborane or borane with strong base results in the removal of a single boron vertex to yield a *nido* cluster, inert to further degradation. This principle is exploited in the polyhedral contraction and subrogation synthetic strategies. In the prototypical case, the polyhedral contraction reaction (243) involves the degradative removal of a formal $[BH]^{2+}$ vertex from a *closo n* vertex metallacarborane followed by a two-electron oxidation of the *nido* intermediate to produce the corresponding *closo n*-1 vertex metallacarborane. An example of the polyhedral contraction reaction is given in Figure 20 (243). Polyhedral subrogation (244) is similar to the polyhedral contraction except that instead of oxidation of the *nido* metallacarborane intermediate, this intermediate is trapped by insertion of a metal atom to provide a bimetallacarborane framework. In practice, this procedure often leads to polymetallacarboranes as shown in Figure 21 (245).

Application of the polyhedral expansion methodology to $C_2B_{10}H_{12}$ leads to supraicosahedral metallacarboranes such as *closo*-$(\eta^5\text{-}C_5H_5)CoC_2B_{10}H_{12}$ [33340-90-8] (237–242). Further expansion of 13-vertex species or thermal metal transfer reactions leads to the 14-vertex cluster $[(\eta^5\text{-}C_5H_5)Co]_2C_2B_{10}H_{12}$ [52649-56-6] and [52649-57-7] (242). Similar 14-vertex species have been obtained from

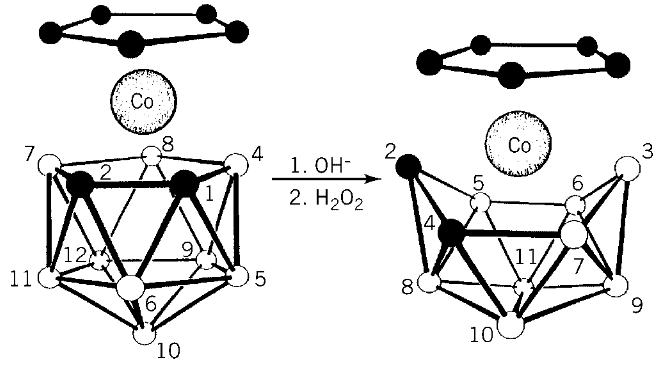


Fig. 20. A characteristic polyhedral contraction reaction leading to $(\eta^5\text{-}C_5H_5)CoC_2B_8H_{10}$ where represents BH; CH. Courtesy of the American Chemical Society (243).

tetracarbaboranes (246) and show unusual structures. The isomeric bimetallic cobaltacarborane complexes *closo*-$(\eta^5\text{-}CpCo)_2C_2B_8H_{10}$ can be formed by either polyhedral expansion or contraction reactions. Six isomers of this cluster are formed in the thermally induced intermolecular metal transfer and polyhedral expansion of the 11-vertex *closo*-$(\eta^5\text{-}Cp)CoC_2B_8H_{10}$.

Metallacarboranes are subject to thermal rearrangement reactions similar to those of carboranes and heteroboranes (247–249). In a study of the *closo* metallacarboranes $(\eta^5\text{-}C_5H_5)CoC_2B_nH_{n+2}$, $n = 6\text{–}10$ (202), it was concluded that the empirical rules governing thermal rearrangements are (*1*) the transition-metal atom preferentially occupies the highest order vertex; (*2*) the carbon atoms do not decrease their mutual separation; (*3*) carbon atoms migrate to the lowest order vertices; and (*4*) carbon atoms migrate away from the transition metal providing rules (*2*) and (*3*) are not violated. Exceptions have been found, but at least some exceptions result from kinetic rather than thermodynamic control of the rearrangement (246).

The highly robust nickelacarborane system [*commo*-3,3′-Ni(3,1,2-$C_2B_9H_{12})_2]^{n-}$ ($n = 0 - 2$) is particularly illustrative of the electronic effects associated with metallacarboranes (50,250). The monoanion, containing a formal Ni^{3+} center, is a symmetrical sandwich compound with the metal bound in η^5-fashion to

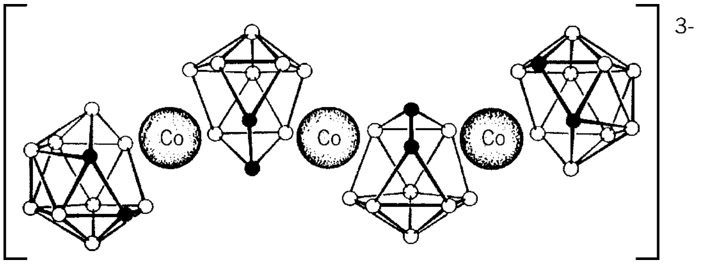


Fig. 21. A polymetallacarborane anion resulting from the polyhedral subrogation reaction where represents BH; CH Courtesy of the American Chemical Society (245).

each dicarbollide cage face and the carbon of the two dicarbollide cage of opposite sides in a transoid configuration. Reduction of this monoanion results in a dianionic sandwich compound containing a formal Ni^{2+} center in which the two dicarbollide cages are symmetrically slipped such that the metal is closer to the three boron atoms of each cage face. Alternatively, oxidation of the monoanion gives an unslipped, but distorted, neutral sandwich having a cisoid configuration with the carbon atoms of the dicarollide cages lying on the same side. This bright yellow, air-stable compound is a rare example of a complex containing a formal Ni^{4+} center, and illustrates the ability of the dicarbollide cage to stabilize high or otherwise unusual oxidation states of metals. This neutral nickelacarborane sandwich [*commo*-3,3′-Ni(3,1,2-$C_2B_9H_{12})_2$], forms intensely colored charge-transfer complexes in the presence of excess electron donor species such as *N,N*-dimethylaniline, naphthalene, and pyrene, accompanied by dramatic color changes (251).

Another example of the relationship between metallacarborane structure and the electronics of the metal center is found in the "pinwheel cluster" shown in Figure 22 (252). In this trimeric cupracarborane three *nido* dicarbollide ligands, each charge compensated by substitution of an $H:^-$ by methyl nicotinate, are η^3-bonded to a Cu^+ ion and to a neighboring copper center via B−H−Cu bonds. This cluster, which has crystallographic C_3 symmetry and three

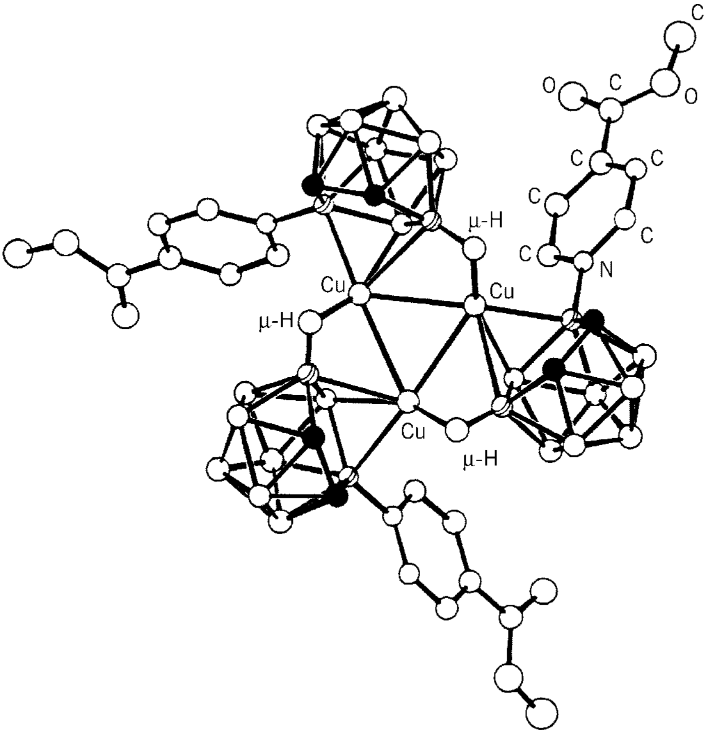


Fig. 22. Molecular structure of the metallacarborane pinwheel cupracarborane complex $Cu_3(\mu\text{-}H)_3C_2B_9H_9[4\text{-}(C_5H_4N)CO_2CH_3]_3$ where ⊘ within the cage structure represents ○ B; ◯ BH; and ● carboranyl CH. Courtesy of the American Chemical Society (252).

equivalent Cu–Cu bonds, is stabilized by M–H–B bonding in much the same way that metal carbonyl clusters are stabilized by bridging CO groups.

Metallacarboranes containing early transition metals including Ti, V, Cr, Mn, Zr, and Hf in a variety of oxidation states are especially unique (253). For example, the titanium 2+, 3+, and 4+ compounds [*commo*-$Ti(C_2B_{10}H_{12})_2]^{2-}$, *closo*-($\eta^5$-$C_5H_5)TiC_2B_{10}H_{12}$, *closo*-$(C_8H_8)TiC_2B_{10}H_{12}$, and *closo*-$(C_8H_8)TiC_2B_9H_{11}$ have no counterparts in traditional organometallic chemistry (254). These compounds exhibit remarkable thermal stability.

A precursor to several *closo* 10-vertex cobaltacarboranes is *arachno*-$[C_2B_7H_{11}]^{2-}$ [42319-46-0], which is obtained by the deprotonation of 6,8-$C_2B_7H_{13}$ [17653-38-2]. When treated with excess $CoCl_2$ and cyclopentadienide ion [12127-83-2], $[C_2B_7H_{11}]^{2-}$ gives *closo*-(η^5-$C_5H_5)Co(C_2B_7H_9)$ [37381-23-0] and [51539-00-5] (eq. 78), which occurs as two isomers, *closo*-2-[(η^5-C_5H_5)Co]-1,6-$C_2B_7H_9$ [41348-11-2], and *closo*-2-[(η^5-C_5H_5)Co]-1,10-$C_2B_7H_9$ [42808-86-6] (29).

$$[C_2B_7H_{11}]^{2-} + [C_5H_5]^- + \frac{3}{2}\,Co^{2+} \longrightarrow H_2 + \frac{1}{2}\,Co + (C_5H_5)Co(C_2B_7H_9) \qquad (78)$$

An interesting *closo* 10-vertex monocarbon metallacarborane species is *closo*-10-[(C_5H_5)Ni]-1-CB_8H_9 [52540-76-8] (255), which contains a metal atom bound to a B_4-face. *Nido* 10-vertex metallaboranes frequently have boatlike frameworks where the metal is at the 6- or 9-position; however, the nature of the bonding depends on the metal. Examples of nine-vertex metallacarboranes include [*closo*-2-$(CO)_3$-2,1,6-$MnC_2B_6H_8]^-$ [41267-49-6] (256), which has the expected tricapped trigonal prism structure, and the clusters $[(C_5H_5)Ni]_2C_2B_5H_7$ [51108-05-5] (257) and 6,8-$(CH_3)_2$-1,1-$[P(CH_3)_3]_2$-1,6,8-$PtC_2B_6H_6$ (258).

Many structures are possible for the smaller metallacarboranes, and various synthetic strategies are available. Especially noteworthy is the occurrence of triple- and tetradecker sandwich compounds (259,260). The polyhedral expansion synthetic strategy can also be used with small carboranes (257). For example, the small metallacarborane *closo*-1,1,1-$(CO)_3$-1,2,3-$FeC_2B_4H_6$ [32761-40-3] (257) is obtained from $C_2B_4H_8$ upon treatment with $Fe(CO)_5$.

7.6. Exopolyhedral Metallacarboranes. Many metallacarboranes are known that exhibit exopolyhedral bonding to metals. Most commonly in these compounds metals are bound via M–H–B interactions in which the B–H group can be regarded as a two-electron donor to the metal center. In other cases, M–B, M–C, or M–M bonding may be involved. For example, electron-rich transition-metal complexes are capable of activating carboranyl B–H bonds leading to B-metalated metallacarboranes. Thus the d^8 Ir^+ complex $[Ir(C_8H_{14})_2Cl]_2$ reacts with 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ carboranes in the presence of triphenylphosphine to give regiospecific B-metalated oxidative addition products of the type $[(C_6H_5)_3P]_2IrHCl$-*closo*-$C_2B_{10}H_{11}$ (261,262). Similarly, the *C*-substituted phosphinacarborane 1-$[(CH_3)_3P]$-*closo*-$C_2B_{10}H_{11}$ reacts with $[Ir(C_8H_{14})_2Cl]_2$ to give a metallacycle containing an Ir–B bond (262, 263). An example of exopolyhedral metal binding by a combination of M–M and M–H–B bonding is given in Figure 23. This complex is formed in the reaction of copper(I) chloride, $(C_6H_5)_3P$, and [*closo*-3,1,2-$TlC_2B_9H_{11}]^-$ (264). A variety of

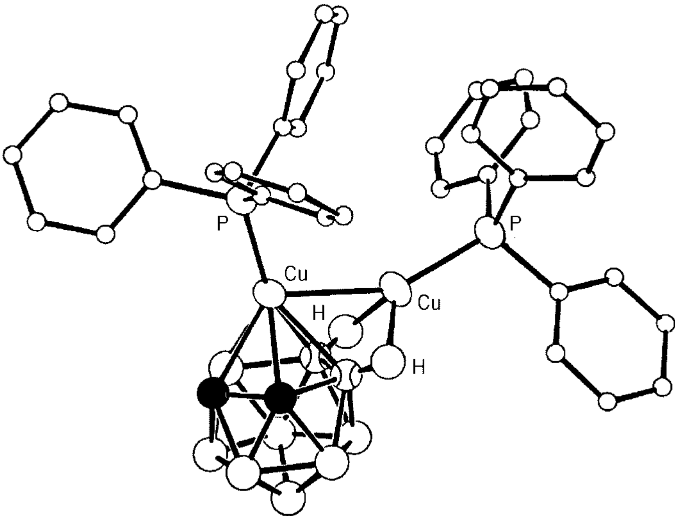


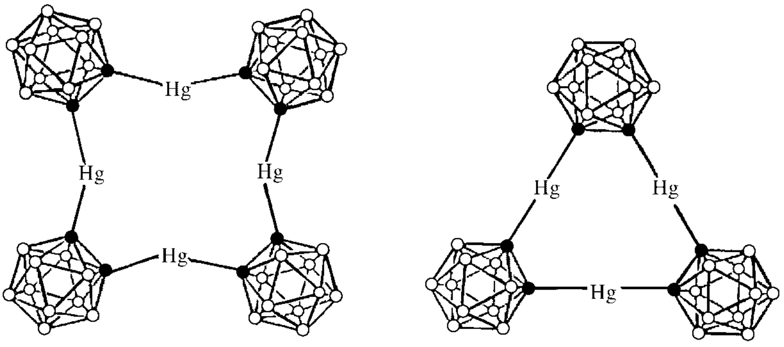
Fig. 23. The molecular structure of [*closo-exo*-4,8-((-H)$_2$Cu[P(C$_6$H$_5$)$_3$]-3-[(C$_6$H$_5$)$_3$P]-3,1,2-CuC$_2$B$_9$H$_9$, where ⊘ within the cage structure represents B; ○ BH; and ● carboranyl CH. Courtesy of the American Chemical Society (264).

metallacarborane complexes containing metal–metal bonds between cage framework metal centers and exopolyhedral metal centers have also been prepared (265).

Carborane cages can also be B-metalated by direct mercuration. The strongly electrophilic reagent $(CF_3CO_2)_2Hg$ in CF_3CO_2H reacts *closo*-$C_2B_9H_{12}$ to give the B-mercuricarborane, $C_2B_{10}H_{11}$-Hg-O_2CCF_3. Disproportionate of this compound leads to the bis(B-carbonyl)mercury compound, $Hg(C_2B_{10}H_{11})_2$, containing B–Hg σ-bonds (266). Mercuration primarily occurs at the 9-position, which is most remote from the carbon atoms of *o*- and *m*- carborane. These compounds have significant preparative value since they can be used as reagents for the synthesis of many B-substituted carborane derivatives. For example, reaction of $Hg(C_2B_{10}H_{11})_2$ with MX_3, where M is Ga, In, Tl, P, As, or Sb, and X is a halide, provides a range of B-substituted carboranes of the type $C_2B_8H_{11}MX_2$. Mercuration can also be done on carborane cages of metallacarboranes (267).

Metallation of carborane cages at carbon also provides useful synthetic agents. Lithiation at carbon using butyllithium is often employed to form intermediates to *C*-functionalized carboranes. Also, the copper *C*-metallated compound $Cu_2C_2B_{10}H_{10}$ is a convenient reagent, particularly for the C-arylation to the carborane cage, since this compound reacts with aryl halides in the presence of pyridine (268).

7.7. Host–Guest Chemistry-Carborane Anticrowns. An extensive literature exists for compounds that complex cations, including the crown ethers and more complex host–guest chemistries. However, compounds that display selective anion complexation are more unusual. Anion complexation has received increasing attention recently because of its importance to biology and analytical chemistry (269). A class of macrocyclic metallacarboranes has been developed that act as unique multidentate Lewis acid hosts (270). Macrocyclic

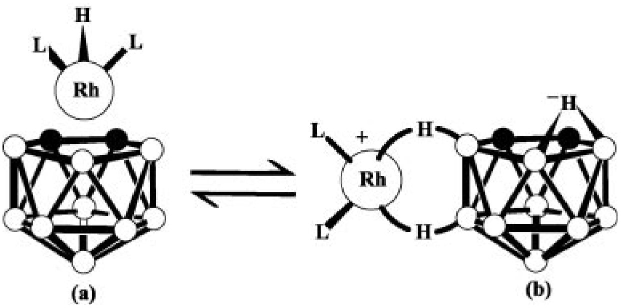


(a) (b)

Fig. 24. Macrocyclic mercuracarborands, [9]mercurand-3 (**a**) and [12]mercurand-4 (**b**), where represents BH; C.

mercuracarboranes have been prepared involving three or four *closo*-1,2-$C_2B_{10}H_{10}$ cages linked into cycles by an equal number of bridging mercury(II) atoms that are σ-bonded to the carborane carbons. These cycles are termed mercurands, where a numerical suffix indicates the cycle size and prefix in brackets indicated the total number of atoms completing the cycle, ie, [9] mercurand-3 (Fig. 24**a**) and [12] mercurand-4 (Fig. 24**b**). The mercury atoms in these compounds contain two empty p orbitals and exhibit Lewis acidity toward a variety of nucleophiles. For example, the trimer [9] mercurand-3 will sequester I^-, Br^-, Cl^-, SCN^-, NO_3^-, and ClO_4^-, in which the anions lie at the center of the cycles and are coordinated symmetrically to the mercury atoms. The [9] mercurand-3 cycle has also been incorporated as the active component in chloride-selective membrane electrodes. The tetrameric cyclic [12] mercurand-4 can sequester I^-, Br^-, Cl^-, CN^-, NO_3^-, and O_2^{2-}, $CH_3CO_2^-$, $C_6H_5S^-$, OH^-, and *closo*-$B_{10}H_{10}^{2-}$. The formation constant for [12] mercurand-4 can sequester Cl^- has been estimated at 10^7.

7.8. Metallacarboranes in Catalysis. Perhaps the most intensely studied of all metallacarborane complexes is the exopolyhedral metallacarborane *closo*-3,3-$[P(C_6H_5)_3]_2$-3-H-3,1,2-$RhC_2B_9H_{11}$[61250-52-0], shown in Figure 25**a**,



(a) (b)

Fig. 25. (**a**) The structure of *closo*-3,3-$[(C_6H_5)_3P]_2$-3-H-3,1,2-$RhC_2B_9H_{11}$, and (**b**) one isomer of its tautomer *exo–nido*-$(L_2Rh)_2$-$(\mu\text{-}H)_2$-7,8-$C_2B_9H_{12}$, where L is $(C_6H_5)_3P$.

and its cage *C*-substituted derivatives. The three available isomers of *closo*-$[P(C_6H_5)_3]_2(H)Rh{-}C_2B_9H_{11}$ are synthesized in high yield by the oxidative addition of $[P(C_6H_5)_3]_2RhCl$ with the appropriate [*nido*-$C_2B_9H_{12}]^-$ ion (271), which may also be made chiral by the attachment of a single-alkyl or -aryl group at a carbon position (272). The resulting hydridorhodacarboranes are quite robust and catalyze a number of reactions including the isomerization and hydrogenation of olefins, the deuteration of B–H groups, and the hydrosilanolysis of alkenyl acetates. These species function as homogeneous catalyst precursors for the isomerization and hydrogenation of olefins as well as other reactions (273). Extensive investigations of rhodacarborane catalysts and the mechanisms responsible for their activity revealed the novel *closo–nido* tautomerism illustrated in Figure 25**a** and **b**. When alkyl or aryl substituents are present at the carborane carbon atoms, the usual rhodacarborane complex isolated is not the *closo* species, but rather an *exo–nido* complex in which the $[P(C_6H_5)_3]_3$ Rh^+ center is bonded to the [*nido*-7,8-$(R)_2$-7,8-$C_2B_9H_{12}]^-$, (R = alkyl, aryl), ions by a pair of Rh–H–B three-center, two-electron bridge bonds (274). The formation of *exo–nido* tautomers in this rhodacarborane system has been attributed primarily to steric factors. The isolation of *closo* structures for *C*-substituted isomers, which carry their substituent steric bulk removed from the metal center, such as *closo*-2,2-$[P(C_6H_5)_3]$-2-H-1-(CH_3)-7-(C_6H_5)-2,1,7-$RhC_2B_9H_{11}$, supports this contention.

The generality of *closo–exo–nido* redox equilibria in solution for these rhodacarborane species was demonstrated by labeling studies using derivatives of the *nido*-carborane precursor anion having a bridging B–D–B group. The deuterium is specifically transferred to the rhodium vertex of the *closo* tautomer (275). Retention of the D-label at the rhodium center during catalytic reactions proves that the H- (or D-) ligand attached to the $[P(C_6H_5)_3]_2RhH$ vertex does not participate in the catalytic processes, but is sequestered in the B–D–B bridge of the catalytically active *exo–nido* tautomer or related structure. The contention that the rhodacarborane *exo–nido* tautomer is the actual catalyst in solution is further supported by the observation that the catalytic hydrogenation and isomerization of alkenes exhibits the same characteristics and reaction rate law regardless of whether these reactions are conducted using a *closo* species or one of its *exo–nido* counterparts (276). In addition, the occurrence of facile carborane cage exchange reactions coupled with rate data obtained for such processes also implicates a reactive *exo–nido* intermediate (277).

Rhodacarborane catalysts have been immobilized by attachment to polystyrene beads with appreciable retention of catalytic activity (278). A 13-vertex *closo*-hydridorhodacarborane has also been synthesized and demonstrated to possess catalytic activity similar to that of the icosahedral species (279). Air-oxidation of *closo*-3,3-$[P(C_6H_5)_3]_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ results in a brilliant purple dimer. This compound contains two formal Rh^{2+} centers linked by a sigma bond and a pair of Rh–H–B bridge bonds. A number of similar dimer complexes have been characterized, and the mechanism of dimer formation in these rhodacarborane clusters has been studied in detail (280).

The exopolyhedral metallacarborane complex $Ti(C_2B_{10}H_{11})_4$, which is prepared by the reaction of $TiCl_4$ and 1-Li-1,2-$C_2B_{10}H_{11}$, has also been reported to be an active heterogeneous catalyst for the polymerization of olefins when supported on alumina and in the presence of $(C_2H_5)_2AlCl$ cocatalyst (281).

7.9. Main Group Element Carborane Derivatives. Main group element carborane derivatives have been reviewed (282). Although Group 1 (IA) metallacarboranes were prepared before other metallacarboranes, representatives of this class were only studied in detail in the past decade. For example, degradation of *o*-carborane (*closo*-$C_2B_{10}H_{12}$) in alcoholic KOH leads to the potassium salt of the dicarbollide monoanion ([*nido*-$C_2B_9H_{11}]^-$) in high yield. This monoanion salt is either used as a synthetic reagent or further deprotonated with potassium or sodium hydride or *n*-butyllithium to give salts of the dicarbollide dianion ([*nido*-$C_2B_9H_{11}]^{2-}$), which are often used in the preparation of other metallacarboranes. Similar methods are used in the preparation of other Group 1 (IA) metallacarborane derivatives, which are generally treated as intermediate synthetic reagents. The carborane *nido*-$C_2B_4H_8$, which has two bridging hydrogens associated with its pentagonal open face, can be deprotonated with NaH to give $Na[C_2B_4H_7]$. Further deprotonation to the dianion does not occur even in the presence of excess NaH (283), but can be effected using solution bases such as n-butyllithium. This behavior was perplexing until the X-ray crystal structure was determined for the THF solvated sodium salt of the *C*-trimethylsilyl-substituted carborane monoanion $\{2,3\text{-}[(CH_3)_3Si]\text{-}2,3\text{-}C_2B_4H_5\}^-$ (284). This compound, which exists as a dimer in the solid state, has a THF solvated sodium atom capping its open face and apparently shielding the extra-hydrogen from heterogeneous reaction with solid bases. An analogous compound was prepared having tetramethylenediamine (TMEDA) solvent in place of THF and shown to have a similar structure and reactivity. However, a more extensively solvated variation with two TMEDA molecules per sodium atom has an *exo–nido* structure with a $(TMEDA)_2Na$ moiety is not capping but bound to the carborane cage via a pair of Na–H–B bridges (285). This compound is readily deprotonated by NaH. Structures have now been determined for a number of other Group 1 (IA) metallacarboranes, which often contain metals complexed by the carborane cage and thus participating in the polyhedral framework (282).

Structures have been determined for TMEDA solvated dilithium salts of isomericdianions $\{2,3\text{-}[(CH_3)_3Si]\text{-}2,3\text{-}C_2B_4H_4\}^{2-}$ and $\{2,4\text{-}[(CH_3)_3Si]\text{-}2,4\text{-}C_2B_4H_4\}^{2-}$. These contain one TMEDA solvated lithium atom capping the pentagonal open face and another TMED–Li moiety bound in *exo*-polyhedral fashion via a pair of Li–H–B bridges to two borons of the five-membered face (286). Solution nmr data shows little or no exchange of the lithiums in solution indicating that the solution structure is similar to that seen in the solid state. This type of structure is probably typical of many Group 1 (IA) salts of carboranyl dianions. A TMEDA solvated monolithium salt of the $\{2,3\text{-}[(CH_3)_3Si]\text{-}2,3\text{-}C_2B_4H_5\}^-$anion has also been prepared (287). Slow vacuum sublimation of this compound at 160–170°C results in formation of the lithiacarborane anionic sandwich $\{$*commo*-$1\text{-}1'\text{-}Li\text{-}2,3\text{-}[(CH_3)_3Si]_2\text{-}2,3\text{-}C_2B_4H_5\}^-$ (288). The lithium atom in this complex is displaced toward the carbon atoms and one of the face boron atoms due to the presence of the *exo*-hydrogen atom bridging between the remaining two boron atoms. It is unclear if the Group 1 (IA) metals exhibit covalent bond character in their interactions with the open faces of carborane cages or if bonding to the cage faces is merely electrostatically preferred.

A number of alkaline earth element metallacarborane derivatives have been characterized. The icosahedral beryllacarborane, *closo*-$3\text{-}[(CH_3)_3N]\text{-}3,1,$

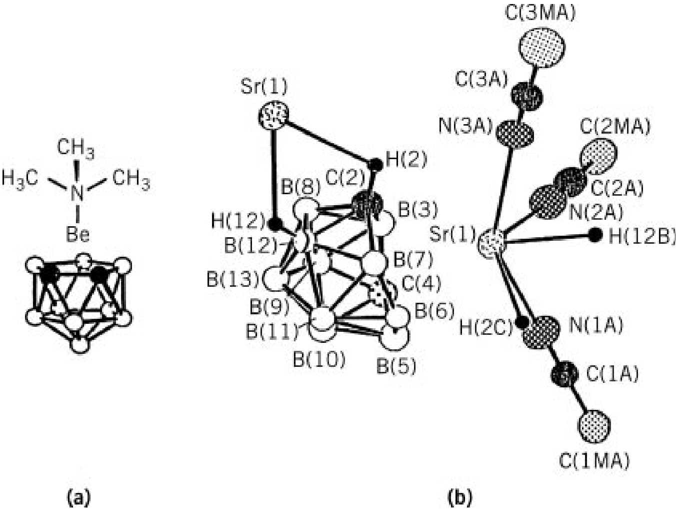


Fig. 26. (**a**) The proposed structure of *closo*-3-$(CH_3)_3N$-3,1,2-$BeC_2B_9H_{11}$, where ○ represents BH; ● CH; and (**b**) the X-ray structure of the polymeric [*closo*-1,1,1-$(CH_3CN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$ showing the metal-to-carborane interaction with the metal of the adjacent monomer unit. A indicates an atom on the CH_3CN ligand; MA is the methyl group; H(12B) is the hydrogen bound to the boron at position 12; H(2C) is the hydrogen bound to the carbon at position 2. Courtesy of the American Chemical Society (289,291).

2-$BeC_2B_9H_{11}$, shown in Figure 26**a**, was prepared via the reaction of *nido*-7,8-$C_2B_9H_{13}$ and $Be(CH_3)_2 \cdot [O(C_2H_5)_2]_2$ followed by reaction of the diethyletherate product and trimethylamine (289).

The reaction of calcium iodide and strontium iodide and the [*nido*-$C_2B_{10}H_{12}]^{2-}$ ion in THF followed by treatment with acetonitrile provides the 13-vertex metallacarboranes [*closo*-1,1,1,1-$(CH_3CN)_4$-1,2,4-$CaC_2B_{10}H_{12}$ (290) and [*closo*-1,1,1-$(CH_3CN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$ (291), respectively. Both of these highly air-sensitive compounds have been structurally characterized by X-ray crystallography. The calcium complex contains a $[Ca(CH_3CN)_4]^{2+}$ moiety that caps the hexagonal C_2B_4 face of the [*nido*-$C_2B_{10}H_{12}]^{2-}$ cage to complete the 13-vertex polyhedron. The strontium compound, shown in Figure 26**b**, is polymeric and features a $Sr(CH_3CN)_3H_2$ capping moiety, the hydrogen atoms of which are involved in Sr−H−C and Sr−H−B bridging interactions with terminal hydrogen atoms of the carborane cage of adjacent strontium carborane repeating units, producing a spiral polymer chain. Bridging M−H−C interactions are rare in metallacarborane chemistry because B−H groups are generally more basic than C−H groups. A barium carborane complex was reported that contains a barium center solvated by two tetrahydrofuran molecules and bonded to three 2,3-bis(trimethylsilyl)-2,3-*nido*-$C_2B_4H_5$ cages. Two of the carborane cages coordinate to barium via a pair of Ba−H−B three-center bonds involving two boron atoms of the C_2B_3 pentagonal face and, the third cage is coordinated by two carbons of the open face and a bridging hydrogen lying between two of the borons of open face to form a four-center $BaHB_2$ bond (292).

The cogener relationship between boron and aluminum has prompted considerable interest in the aluminacarboranes. The Lewis acid–base adduct

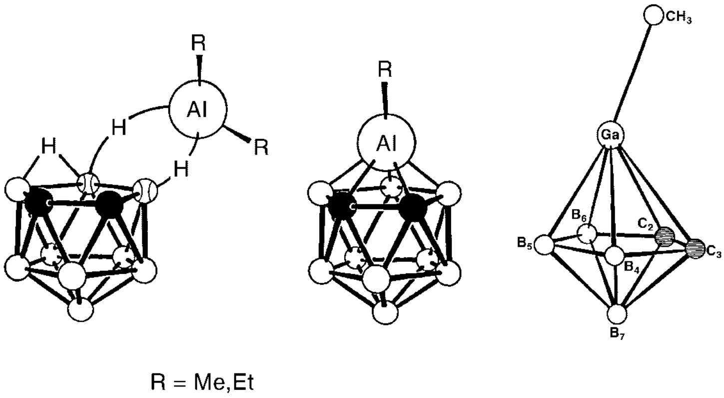


Fig. 27. The molecular structures of (**a**) 3-R-3,1,2-$AlC_2B_9H_{11}$, and (**b**) *exo–nido*-9,10-(μ-AlR_2)(μ-H)$_2$-7,8-$C_2B_9H_{10}$ where ○ represents BH; ● CH; ⊘ B; and R = CH_3, C_2H_5, and (**c**) 1-CH_3-1,2,3-$GaC_2B_4H_6$. Courtesy of the American Chemical Society (296).

3-(C_2H_5)-3,1,2-$AlC_2B_9H_{11}\cdot$2THF was first prepared by the reaction of Na_2[7,8-$C_2B_9H_{11}$] and (C_2H_5)$AlCl_2$ in THF solution (293). The reaction of the acidic species *nido*-$C_2B_9H_{13}$ and trialkylaluminum reagents (294) results in loss of 1 equiv of alkane and formation of *nido* aluminacarborane species of the type *exo–nido*-9,10-(μ-AlR_2)(μ-H)$_2$-7,8-$C_2B_9H_{10}$ (Fig. 27**b**). Upon heating these species, a second equivalent of alkane is lost with the formation of 12-vertex *closo* aluminacarboranes of the type *closo*-3-R-3,1,2-$AlC_2B_9H_{11}$ (Fig. 27**a**). These two steps can be combined to produce the *closo* aluminacarboranes in a single step:

$$\textit{nido} - 7,8 - C_2B_9H_{13} + MR_3 \longrightarrow \textit{closo} - 3 - R - 3,1,2 - MC_2B_9H_{11} \qquad (79)$$

for M = Al; R = CH_3, C_2H_5; for M = Ga; R = C_2H_5. The same methodology can be applied to the preparation of the corresponding gallacarborane (294). In the absence of Lewis bases, these clusters contain a main group element bound in η^5-fashion to the five-membered face of the dicarbollide cage. The X-ray crystal structure (295) of *closo*-3-(C_2H_5)-3,1,2-$AlC_2B_9H_{11}$ reveals an undistorted icosahedral cluster; however, the ethyl group on aluminum is tilted away from the normal to the plane of the cage bonding face in the direction of the carbon atoms at an angle of 19.4°. This aluminacarborane and its *C*-substituted derivatives form adducts with Lewis bases in which the aluminum atom is slipped dramatically with respect to the dicarbollide cage face in a direction away from the two-carbon atoms (296).

The *closo*-3-(C_2H_5)-3,1,2-$AlC_2B_9H_{11}$ complex is especially interesting because in aromatic solvents it exists in temperature-dependent equilibrium with a unique highly fluxional dimer molecule consisting of the [*commo*-Al($C_2B_9H_{11}$)$_2$]$^-$ sandwich ion complexed with a [(C_2H_5)$_2$Al]$^+$ moiety via two Al–H–B interactions (296). The free [Al($C_2B_9H_{11}$)$_2$]$^-$ sandwich ion (Fig. 28**a**), in which the aluminum atom is bound in η^5-fashion to the pentagonal faces of two dicarbollide cages, has been prepared independently and structurally

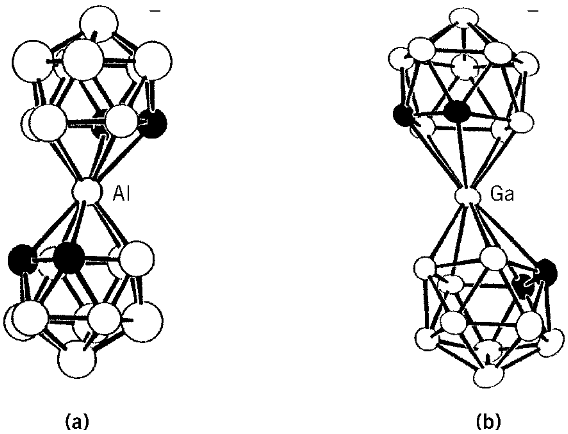


Fig. 28. The X-ray structures of (**a**) [*commo*-3,3′-Al(3,1,2-AlC$_2$B$_9$H$_{11}$)$_2$]$^-$, and (**b**) [*commo*-3,3′-Ga(3,1,2-GaC$_2$B$_9$H$_{11}$)$_2$]$^-$. Courtesy of the American Chemical Society (296).

characterized (296,297). The analogous gallacarborane sandwich anion [Ga(C$_2$B$_9$H$_{11}$)$_2$]$^-$ (Fig. 28**b**) has also been characterized and found to possess a significantly distorted structure (296,298). Various aluminacarboranes have been prepared based on the [C$_2$B$_4$H$_6$]$^{2-}$ anion and its *C*-substituted derivatives (299,300), which contain aluminum atoms that either participate in the polyhedral framework of carborane cages or bridge between boron atoms in the polyhedral frameworks. In addition, the aluminacarboranes [Al(C$_2$B$_6$H$_8$)$_2$]$^-$, C$_2$H$_5$ AlC$_2$B$_8$H$_{10}$, and [Al(C$_2$B$_8$H$_{10}$)$_2$]$^-$ (296) contain aluminum atoms that are σ-bound to carbon atoms in the carborane frameworks.

Other smaller Group 13 (III A) element metallacarboranes include the isomeric seven-vertex gallacarborane cluster *closo*-CH$_3$GaC$_2$B$_4$H$_6$ (18), shown in Figure 27c, which exhibits a tilt distortion of the Ga–CH$_3$ group similar to that observed for *closo*-3-(C$_2$H$_5$)-3,1,2-AlC$_2$B$_9$H$_{11}$. The alkylaluminum and alkylgallium *closo*-metallacarboranes react with Lewis bases to give product having two two-electron donor bases coordinated to the metal accompanied by slippage of the metal toward the side or edge of the pentagonal face (301). A novel gallacarborane complex of the *C*-substituted 2,4-[Si(CH$_3$)$_3$]$_2$-2,4-*nido*-C$_2$B$_4$H$_4$ cage was prepared under conditions permitting loss of the sustituent at gallium to provide a seven-vertex *closo*-gallacarborane dimer (Fig. 31) in which the cage-capping gallium atoms link two seven-vertex clusters together via a gallium–gallium bond, as shown in Figure 29 (302). This complex exhibits an unusually short Ga–Ga bond (2.340 Å).

The thallacarborane anion [*closo*-3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$ and its *C*-methyl derivatives are often used as synthetic reagents since they are air-stable and have excellent shelf life (303). The parent anion is prepared by the reaction of [*nido*-C$_2$B$_9$H$_{12}$]$^-$ and thallium(I) acetate [563-68-8] in aqueous base to give the salt Tl[TlC$_2$B$_9$H$_{11}$], in which one thallium atom caps the dicarbollide cage and the second thallium atom serves as a counterion to the 12-vertex anion. This compound, a yellow, air-stable, insoluble powder, is a convenient synthetic reagent for the preparation of other metallacarboranes. A variety of other thallacarborane

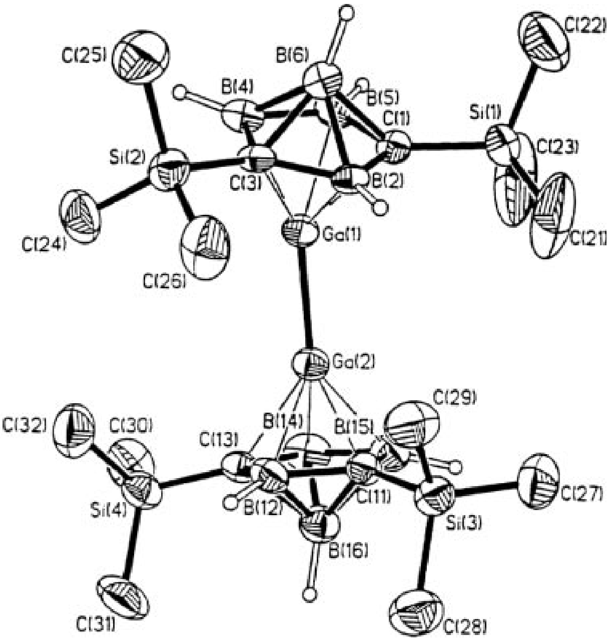


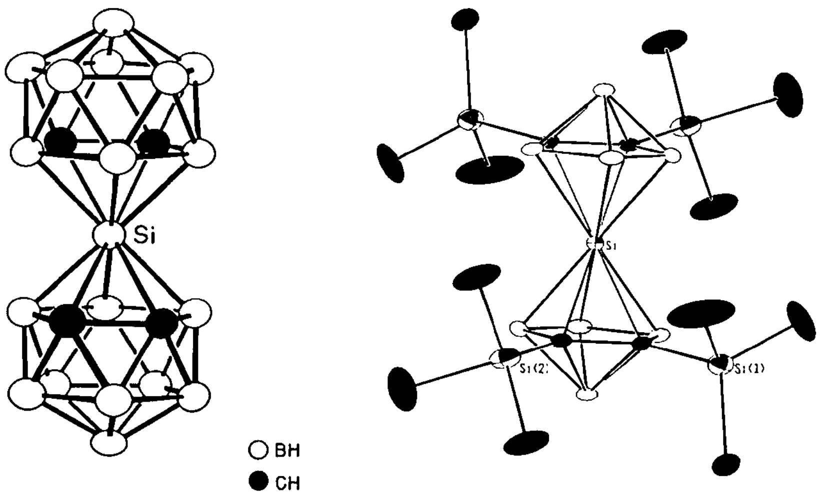
Fig. 29. The X-ray structure of [*closo*-Ga-2,4-[Si(CH$_3$)$_3$]$_2$-2,4-C$_2$B$_4$H$_4$]$_2$, containing a Ga–Ga bond.

salts, eg, [(C$_6$H$_5$)$_3$PCH$_3$][3,1,2-TlC$_2$B$_9$H$_{11}$] and [PPN][3,1,2-TlC$_2$B$_9$H$_{11}$], where PPN=[(C$_6$H$_5$)$_3$P]$_2$N$^+$, can be prepared by cation-exchange reactions using the dithallium compound. The [PPN]$^+$ salt is a useful reagent because of its enhanced solubility in organic solvents. Several of these salts have been characterized by X-ray crystallography. The thallium atom of [*closo*-3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$ is positioned at the open five-membered face of the dicarbollide cage and is slipped slightly toward the unique boron atom of the cage face. Metal–cage bonding in this anion and its *C*-substituted derivatives has been the subject of some controversy. On one hand the thallium cage atom distances are relatively long, suggesting an ionic interaction. On the other hand, ^{1}H and ^{11}B nmr spectra show strong coupling between thallium and the cage atoms, indicative of a covalent interaction. The yellow color of the *closo*-[3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$ anion has been attributed to metal–cage charge transfer. In some salts, including that of the [(C$_6$H$_5$)$_3$P]$_2$N$^+$ cation, the solid-state structure of this anion is that of a dimer linked by four Tl–H–B bridging interactions (304).

A series of compounds of the type *closo*-MC$_2$B$_9$H$_{11}$ in which M is divalent Ge, Sn, and Pb, have been prepared (305).

$$[nido-7,8-\mathrm{C_2B_9H_{11}}]^{2-} + \mathrm{MX_2} \longrightarrow closo-3,1,2-\mathrm{MC_2B_9H_{11}} + 2\mathrm{X}^- \qquad (80)$$

As the B–H group, the 2+ main group atoms act as two-electron donors to the *closo*-MC$_2$B$_9$H$_{11}$ cage system. Bonding considerations suggest that these compounds should possess an unshared lone pair of electrons available for bonding at the metal center. However, the complexes do not exhibit Lewis base



(a) (b)

Fig. 30. The X-ray structures (**a**) *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11})_2$, where ○ represents BH; ● CH, and (**b**) *commo*-2,2(,3,3′-$[(CH_3)_2Si]_4$-*commo*-1,1′-Si(1,2,3-$C_2B_4H_4$). Courtesy of the American Chemical Society (308).

properties and actually act primarily as Lewis acids, forming donor–acceptor complexes with a variety of donor molecules. The analogous seven-vertex cluster *closo*-$SnC_2B_4H_6$ and its *C*-substituted derivatives form similar donor complexes with Lewis bases. The cluster *closo*-$CH_3GeCB_{10}H_{11}$ (306) has been described. In this compound a Ge–CH_3 moiety, which may be regarded as a three-electron donor, caps a monocarbon carborane cage, to give a 12-vertex, 26-electron *closo* system. The methyl group on germanium in this compound is reversibly removed by reaction with pyridine to yield the $[GeCB_{10}H_{11}]^-$ anion.

The X-ray structure of the bis(dicarbollide) sandwich compound *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11})_2$ (Fig. 30**a**) contains a silicon atom in a highly unusual bonding mode (307). This compound, which has good thermal stablity, is prepared in good yield.

$$2\,Li_2[7,8-C_2B_9H_{11}] + SiCl_4 \longrightarrow commo-3,1,2-SiC_2B_9H_{112} + 4\,LiCl \quad 80\% \tag{81}$$

It is isoelectronic and isostructural with the aluminum sandwich ion [*commo*-3,3′-Al(3,1,2-$AlC_2B_9H_{11})_2]^-$ shown in Figure 28**a**. The silicon is η^5-bonded in unslipped fashion to the C_2B_3 faces of two dicarbollide cages. This bis (dicarbollide) silicon sandwich also forms adducts of a variety of structural types with Lewis bases such as pyridine and trimethylphosphine.

A series of sandwich compounds of the type *commo*-$[(CH_3)_3Si(R)$-$C_2B_4H_4]_2M$, where M is Si, Ge, Sn, and Pb, and R is variously $(CH_3)_3Si$, CH_3, and H, have also been prepared (308). These compounds, formed by reactions between salts of the $[(CH_3)_3Si(R)C_2B_4H_4]^{2-}$ and $[(CH_3)_3Si(R)C_2B_4H_5]^-$ ions and

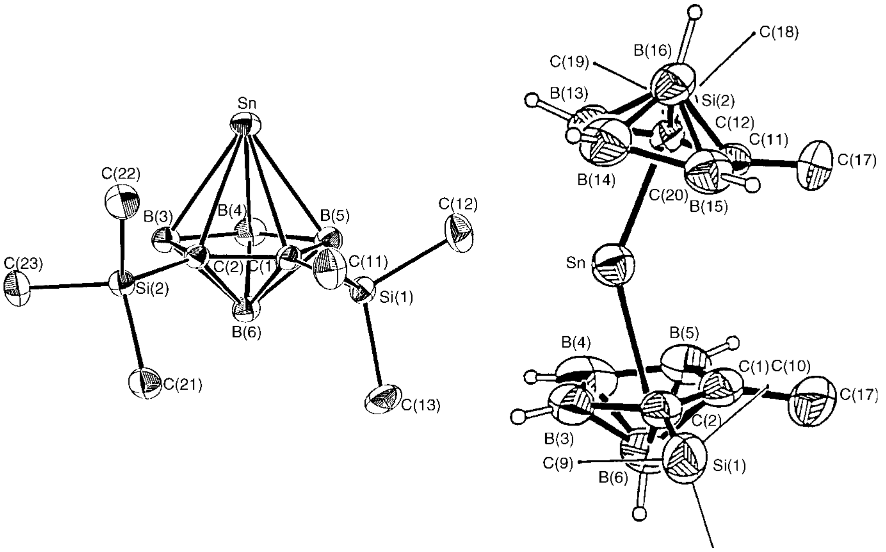


Fig. 31. The X-ray structure of (**a**) 2,3-$[(CH_3)_2Si]_2$-1,2,3-$SnC_2B_4H_4$ and (**b**) *commo*-1,1′-Sn-{2-$[Si(CH_3)_3]$-3-(CH_3)-1,2,3-$SnC_2B_4H_4\}_2$. Courtesy of the American Chemical Society (18,310312).

appropriate main group element halides, have structures containing central main group elements in the 4+ oxidation states similar to the bis(dicarbollide) silicon sandwich compound. The structure of the silicon sandwich compound *commo*-$[(CH_3)_3Si_2C_2B_4H_4]_2Si$ is shown in Figure 30**b**.

In compounds of the type *closo*-$MC_2B_4H_6$, where M is Ge, Sn, and Pb, the main group elements complete one apex of a pentagonal bipyramid (309). As in the case of the analogous icosahedral clusters, the lone pair of electrons at the divalent main group element center has no tendency to form donor–acceptor complexes with Lewis acids. A number of *C*-substituted compounds of the type *closo*-$MC_2(R)_2B_4H_4$, where M is Si, Ge, Sn, Pb and R is variously H, CH_3, $Si(CH_3)_3$, have also been characterized (310). The X-ray crystal structure of one of the tin-containing members of this series is shown in Figure 31. The compounds in this group react with Lewis bases to form adducts having a variety of intriguing structures, a number of which have been characterized by X-ray crystallography (311). The formal Sn^{4+} sandwich compound *commo*-1,1′-Sn-{2-[Si $(CH_3)_3]$-3-(CH_3)-1,2,3-$SnC_2B_4H_4\}_2$, shown in Figure 31**b**, has been prepared and shown to exhibit a bent configuration (312). The (ring centroid 1)-Sn-(ring centroid 2) angle is142.5°, which is similar to those found for $(\eta^5\text{-}C_5H_5)_2Sn$ and $[\eta_5\text{-}C_5(CH_3)_5]_2Sn$, 145.8° and 144.1°, respectively (313).

A number of related clusters has been prepared based on other heterocarborane cages with faces analogous to $[C_5H_5]^-$. Some of these include the [*nido*-$ECB_9H_{10}]^{2-}$ anions where E = P, As, which form metal complexes with many transition and main group elements. *Closo*-$GePCB_9H_{10}$ and *closo*-$GeAsCB_9H_{10}$ are examples (314).

7.10. f-Block Element Metallacarborane Derivatives. The chemistry of metallacarboranes containing *f*-block elements has been reviewed (230). The first actinide metallacarborane complex, *commo*-($C_2B_9H_{11}$)UCl_2, was prepared in 1977 (315). The coordination geometry of this complex can be described as distorted tetrahedral with the four positions occupied by two η^5-bound [7,8-$C_2B_9H_{11}]^-$ cages and two chloride ions. Complexes of this type are often referred to as bent sandwiches because of the configuration of the two-dicarbollide cage about the metal center, which is analogous to the corresponding pentamethyl cyclopentadiene–metal complexes.

The synthesis of lanthanacarboranes has been described (316). The metathetical reaction of [*nido*-$C_2B_9H_{11}]^{2-}$ salts with LnI_2, where Ln = Sm or Yb, in THF leads to Ln^{2+} complexes of the type ($C_2B_9H_{11}$)Ln(thf)$_4$. These complexes, which are stable to temperatures >200°C, undergo ligand exchange reactions in a variety of donor solvents. The reaction in DMF (solvent) gives the corresponding ($C_2B_9H_{11}$)Ln(dmf)$_4$ complexes. The structure of the ytterbium complex has been determined to be a *closo* icosahedral cluster consisting of a $C_2B_9H_{11}$ cage capped by an ytterbium atom to which four dmf ligands are coordinated via oxygen. These reactions are similar to those for calcium and strontium metallacarboranes. The reaction of ($C_2B_9H_{11}$)Sm(thf)$_4$ in THF (solvent) with a soluble salt of the [*closo*-3,1,2-$TlC_2B_9H_{11}]^-$ anion affords the bent samarium sandwich anion, [*commo*-($C_2B_9H_{11})_2$Sm(thf)$_2]^-$ (Fig. 32). The two η^5-dicarbollide cages and two thf ligands are in the coordination sphere of samarium and the average dicarbollide–Sm–dicarbollide angle is 132°. The metal–dicarbollide cage distances found in structurally characterized lanthanacarboranes are similar to the metal–carbon distances observed for the corresponding lanthanum–pentamethylcyclopentadiene complexes. Neutral monocage complexes of Sm and Yb have also been prepared using the 12-vertex [*nido*-$C_2B_{10}H_{12}]^{2-}$ cage.

7.11. Boron Neutron Capture Therapy. There is great interest in the use of polyboron hydride compounds for boron neutron capture therapy (BNCT) for the treatment of cancers (315–320) and other diseases. Boron-10 is unique

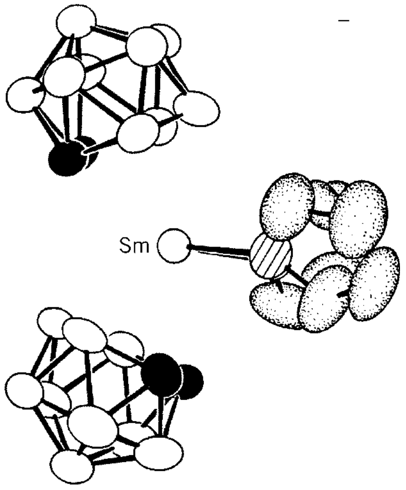
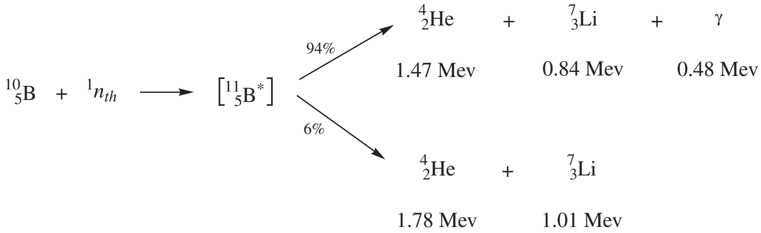


Fig. 32. The X-ray structure of [3,3-($C_4H_8O)_2$-*commo*-3,3′-Sm(3,1,2-$SmC_2B_9H_{11})_2]^-$, where ○ represents BH; ● CH; ▨ O ; ◍ CH_2. Courtesy of the American Chemical Society (316).

among the light elements in that it possesses an unusually high neutron capture nuclear cross-section ($3.8 \times (10^{-25}$ m^2), 0.02–0.05 eV neutron). The nuclear reaction between ^{10}B and low energy thermal neutrons yields alpha particles and recoiling lithium-7 nuclei:



(82)

2.28 M eV is released as kinetic energy.

Because the cytotoxic effects of the energetic lithium-7 and α particles are spacially limited to a range of only about one-cell diameter, the destructive effects are confined to only one or two cells near the site of the event. Thus BNCT involves the selective delivery of sufficiently high concentrations of ^{10}B-containing compounds to tumor sites followed by the irradiation of these sites with a beam of relatively nondestructive thermal neutrons. The resulting cytotoxic reaction can then in theory destroy the tumor cells that are intimately associated with ^{10}B target. The great advantage of BNCT is its cell level selectivity for destroying tumor cells without significant damage to healthy tissue. This attribute makes BNCT particularly valuable in the treatment of tumors that are difficult or impossible to remove by surgical methods, including malignant brain tumors such as glioblastoma and astrocyctoma.

It has been estimated that using available neutron intensities, such as 10^{10} neutrons/cm$^2 \cdot$ s, concentrations of ^{10}B from 10–30 μg/g of tumor with a tumor cell to normal cell selectivity of at least five are necessary for BNCT to be practical. Hence, the challenge of BNCT lies in the development of practical means for the selective delivery of approximately 10^9 ^{10}B atoms to each tumor cell for effective therapy using short neutron irradiation times. Indeed, many experimental ^{10}B delivery systems have been developed (315–317). Derivatives of ^{10}B-enriched *closo*-borane anions and carboranes appear to be especially suitable for BNCT because of their high concentration of ^{10}B and favorable hydrolytic stabilities under physiological conditions. To date, the most extensively studied polyboron hydride compounds in BNCT research have been the icosahedral mercaptoborane derivatives $Na_2[B_{12}H_{11}SH]$ (called BSH) and $Na_4[(B_{12}H_{11}S)_2]$, which have been used in human trials, particularly in Japan, with some success. New generations of tumor-localizing boronated compounds are being developed. The dose-selectivity problem of BNCT has been approached using boron hydride compounds in combination with a variety of delivery vehicles including boronated polyclonal and monoclonal antibodies, porphyrins, amino acids, nucleotides, carbohydrates, and liposomes. BNCT has also been proposed as a treatment for other diseases such as arthritis.

7.12. Boranes as Pharmacophores. The unique properties of polyhedral boranes, such as hydrophobicity, steric bulk, stability under physiological conditions, and ease of functionalization, have been exploited in the design of new pharmaceutical agents. For example, the dicarba-*closo*-dodocaborane moiety has been studied as hydrophobic pharmacophores in the modulation of tumor necrosis factor (321) and the design of estrogen antagonists (322) Carboranes have also been used as pharmacophores in retinoid antagonists (323) and other biologically active molecules of therapeutic interest.

A related potential medical application of metallacarboranes is based on the highly favorable kinetic stability of many metallacarborane complexes under physiological conditions and ability to form stable complexes with a wide range of metals. These features make certain functionalized metallacarboranes containing radiometals ideal choices for use as medical imaging reagents. The use of antibody-conjugated bridged dicarbollide metallacarborane (venus fly trap) chelate complexes incorporating γ-emitting $^{57}Co^{3+}$ in the imaging tumors has been reported (324,325).

8. Economic Aspects

Despite the fact that many boron hydride compounds possess unique chemical and physical properties, very few of these compounds have yet undergone significant commercial exploitation. This is largely owing to the extremely high cost of most boron hydride materials, which has discouraged development of all but the most exotic applications. Nevertheless, considerable commercial potential is foreseen for boron hydride materials if and when economical and reliable sources become available. Only the simplest of boron hydride compounds, most notably sodium tetrahydroborate, $NaBH_4$, diborane(6), B_2H_6, and some of the borane adducts, eg, amine boranes, are now produced in significant commercial quantities.

8.1. Sodium Tetrahydroborate, Na[BH_4].

This air-stable white powder, commonly referred to as sodium borohydride, is the most important commercial boron hydride material. It is used in a variety of industrial processes including bleaching of paper pulp and clays, preparation and purification of organic chemicals and pharmaceuticals, textile dye reduction, recovery of valuable metals, wastewater treatment, and production of dithionite compounds. Sodium borohydride is produced by Rohm & Haas Co., in manufacturing plants in the Netherlands and the state of Washington, and in Scandinavia by Finnish Chemicals (Nokia), with Rohm & Haas supplying most of the market. More than 6 million lb of this material supplied as powder, pellets, and aqueous solution (called Borol solution), were produced in 2001.

8.2. Diborane(6), B_2H_6.

This spontaneously flammable gas is consumed primarily by the electronics industry as a dopant in the production of silicon wafers for use in semiconductors. It is also used to produce amine boranes and the higher boron hydrides. Callery Chemical Co., a division of Mine Safety Appliances Co., and Voltaix, Inc., are the main U.S. producers of this substance. Several hundred tons were manufactured worldwide in 2001.

8.3. Borane Adducts.

Trialkylamine and dialkylamine boranes, such as tri-*tert*-butylamine borane and dimethylamine borane, are mainly used in electroless plating processes. Other borane adducts, such as THF−borane and dimethyl sulfide–borane are used for specialized reduction reactions. These are produced by Callery Chemical Co. and Aldrich Chemical Co.

8.4. Organoboron Hydrides. A variety of organoboron hydrides produced by hydroboration of olefins is commercially available. These are widely used in organic synthesis and the manufacture of pharmaceuticals. Examples include 9-borabicyclo[3.3.1]nonane (9-BBN), obtained by hydroboration of 1,5-cyclooctene, and diispinocampheylborane (DIP_2BH), produced by hydroboration of α-pinene. The latter is useful for asymmetric syntheses. A wide variety of borane reducing agents and hydroborating agents is available from Aldrich Chemical Co., Inc. and Callery Chemical Co.

8.5. Polyhedral Boron Hydrides. Although relatively large quantities of polyhedral boron hydrides and carboranes have been produced under various government contracts, these materials are not currently produced on large-scale commercial basis. Decaborane(14) (*nido*-$B_{10}H_{14}$), and carborane isomers, such as the *o*, *m*-, and *p*-carborane (*closo*-1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$), as well as various other derivatives, are available in experimental quantities. Prices for these compounds range, according to purity, composition, and quantity purchased, from $30 to 500 or more per gram. Callery Chemical Co. has the capability to produce some of these materials on demand.

Demonstrated areas of potential commercial applications for other boron hydride-based materials are listed according to the classes of these materials.

Polyhedral Boron Hydrides. These are used as experimental agents in neutron capture therapy of cancers (317–320), and as burn rate modifiers (accelerants) in gun and rocket propellant compositions. A salt of the $[B_{12}H_{12}]^{2-}$ anion is used in the fuse system of the passenger-side automotive airbag.

Carboranes. These are used as experimental agents in neutron capture therapy (317–320), and as burn rate modifiers in gun and rocket propellants. They have been used as high temperature elastomers and high temperature gas–liquid chromatography stationary phases and have potential for use in other unique materials, optical switching devices (326), and gasoline additives (327).

Metallacarboranes. These have potential for use in homogeneous catalysis (273), including hydrogenation, hydrosilylation, isomerization, hydrosilanolysis, phase-transfer, burn rate modifiers in gun and rocket propellants, neutron capture therapy (317–320), medical imaging (324,325), processing of radioactive waste (327), analytical reagents, and as ceramic precursors.

BIBLIOGRAPHY

"Boron Hydrides" under "Boron Compounds" in *ECT* 1st ed., Vol. 2, pp. 593–600, by S. H. Bauer, Cornell University; "Boron Hydrides and Related Compounds" under "Boron Compounds," Suppl. 1, pp. 103–130, by S. H. Bauer, Cornell University; "Diborane and Higher Boron Hydrides" under "Boron Compounds," Suppl. 2, pp. 109–113, by W. J. Shepherd and E. B. Ayres, Callery Chemical Company; "Boron Hydrides" under "Boron Compounds" in *ECT* 2nd ed., Vol. 3, pp. 684–706, by G. W. Campbell, Jr., U.S. Borax Research Corporation; "Boron Hydrides and their Metalla Derivatives" under "Boron Compounds," in *ECT* 3rd ed., Vol. 4, pp. 135–183, by R. W. Rudolph, The University of Michigan; "Boron Hydrides and their Metalla Derivatives" under "Boron Compounds," in *ECT* 4th ed., Vol. 4,

pp. 439–500, by D. M. Schubert, U.S. Borax Inc.; "Boron Hydrides, Heteroboranes, and their Metalla Derivatives" in *ECT* (online), posting date: December 4, 2000, by David M. Schubert, U.S. Borax Inc.

CITED PUBLICATIONS

1. A. Stock, *Hydrides of Boron and Silicon*, Cornell University Press, Ithaca, N. Y., 1933.
2. H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.* **78**, 5694 (1956); H. C. Brown, *Hydroboration*, W. A. Benjamin, Inc., New York, 1962; S. E. Thomas, *Organic Synthesis, The role of Boron and Silicon*, Oxford University Press, Oxford, 1991; H. C. Brown and P. V. Ramachandran, in W. Siebert, ed., *Advances in Boron Chemistry*, The Royal Society of Chemistry, Cambridge, U.K., 1997, p. 151.
3. R. T. Holtzmann, ed., *Production of Boranes and Related Research*, Academic Press, New York, 1967.
4. W. N. Lipscomb, *Science* **196**, 1047 (1977).
5. T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.* **2**, 1089 (1963); M. M. Fein, J. Bobinski, N. Meyers, N. Schartz, and M. S. Cohen, *Inorg. Chem.* **2**, 111 (1963); L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Y. A. Struchkov, *Izw. Akad. Nauk. SSSR, Ser. Khim.* 2069 (1963).
6. M. F. Hawthorne, *Acc. Chem. Res.* **1**, 281 (1968); M. F. Hawthorne, *Pure Appl. Chem.* **29**, 547 (1972); **33**, 475 (1973); K. P. Callahan and M. F. Hawthorne, *Pure Appl. Chem.* **39**, 475 (1974); R. N. Grimes, ed., *Metal Interactions with Boron Clusters*, Plenum Press, New York, 1982.
7. G. L. Leigh, ed., *Nomenclature of Inorganic Chemistry, Recommendations 1990*, IUPAC, Oxford, UK, 1990, Chapt. I-11.
8. J. B. Casey, W. J. Evans, W. H. Powell, and T. E. Sloan, "A Structural Definitive Descriptor and Numbering System for Cluster Compound Nomenclature," Chemical Abstract Service, presented at the *198th National Meeting of the American Chemical Society*, Miami Beach, Fl., Sept. 1989.
9. R. E. Williams, *Inorg. Chem.* **10**, 210 (1971); K. Wade, *J. Chem. Soc. Chem. Commun.* 792 (1971); R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.* **11**, 1974 (1971).
10. R. E. Williams, *Adv. Inorg. Chem. Radiochem.* **18**, 67 (1976).
11. R. W. Rudolph, *Acc. Chem. Res.* **9**, 446 (1976).
12. H. Hogenveen and P. W. Kwant, *Acc. Chem. Res.* **8**, 413 (1975).
13. E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.* **79**, 91 (1979).
14. K. Wade, *Adv. Inorg. Chem. Radiochem.* **18**, 1 (1976).
15. R. E. Williams, in G. A. Olah, R. E. Williams, and K. Wade, eds., *Electron Deficient Compounds of Boron and Carbon*, John Wiley & Sons, Inc., New York, 1991, Chapt. 2.
16. I. Shapiro, C. D. Good, and R. E. Williams, *J. Am. Chem. Soc.* **84**, 3837 (1962).
17. F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.* **6**, 1271 (1967).
18. R. N. Grimes and W. J. Rademaker, *J. Am. Chem. Soc.* **91**, 6498 (1969).
19. P. M. Garrett, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.* **8**, 1907 (1969).
20. W. H. Knoth, *J. Am. Chem. Soc.* **89**, 1274 (1967).
21. F. N. Tebbe, P. M. Barret, and M. F. Hawthorne, *J. Am. Chem. Soc.* **86**, 4222 (1964).

22. W. R. Pretzer and R. W. Rudolph, *J. Am. Chem. Soc.* **98**, 1441 (1976).
23. R. L. Voorhees and R. W. Rudolph, *J. Am. Chem. Soc.* **91**, 2173 (1969).
24. L. J. Todd, J. L. Little, and H. T. Silverstein, *Inorg. Chem.* **8**, 1698 (1969).
25. D. A. Franz and R. N. Grimes, *J. Am. Chem. Soc.* **92**, 1438 (1970).
26. R. N. Grimes, C. L. Bramlett, and R. L. Vance, *Inorg. Chem.* **7**, 1066 (1968).
27. P. Binger, *Tetrahedron Lett.*, 2675 (1966).
28. K. Borer, A. B. Littlewood, and C. S. G. Phillips, *J. Inorg. Nucl. Chem.* **15**, 316 (1960).
29. P. M. Garrett, T. A. George, and M. F. Hawthorne, *Inorg. Chem.* **8**, 2008 (1969).
30. W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.* **95**, 4565 (1973); V. Chowdhry and co-workers, *J. Am. Chem. Soc.* **95**, 4560 (1973).
31. B. Lockman and T. Onak, *J. Am. Chem. Soc.* **94**, 7923 (1972).
32. T. E. Berry, F. N. Tebbe, and M. F. Hawthorne, *Tetrahedron Lett*. **12**, 715 (1965).
33. W. N. Lipscomb and co-workers, *J. Chem. Phys.* **27**, 200 (1957).
34. P. C. Keller, *Inorg. Chem.* **9**, 75 (1970).
35. M. Mangion and co-workers, *J. Am. Chem. Soc.* **98**, 449 (1976); A. V. Fratini, G. W. Sullivan, M. L. Denniston, R. K. Hertz, and S. G. Shore, *J. Am. Chem. Soc.* **96**, 3013 (1974).
36. G. Kodama and A. R. Dodds, paper presented at meeting, *Imeboron III*, Ettal, Germany, July 6, 1976.
37. R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Am. Chem. Soc.* **92**, 3351 (1970).
38. R. W. Rudolph and V. Chowdhry, *Inorg. Chem.* **13**, 248 (1974).
39. D. M. P. Mingos, *Nature Phys. Sci.* **236**, 99 (1972).
40. M. Hofmann, M. A. Fox, R. Greatrex, P. v. R. Schleyer, and R. E. Williams, *Inorg. Chem.* **40**, 1790 (2001).
41. L. G. Sneddon, J. C. Huffman, R. O. Schaeffer, and W. E. Streib, *J. Chem. Soc., Chem. Commun.* **474** (1972).
42. A. R. Siedel, G. M. Bodner, and L. J. Todd, *J. Inorg. Nucl. Chem.* **33**, 3671 (1971).
43. V. T. Brice, H. D. Johnson II, and S. G. Shore, *J. Am. Chem. Soc.* **95**, 6629 (1973).
44. G. L. McKnown, B. P. Don, R. A. Beaudet, P. J. Vergamini, and L. H. Jones, *J. Chem. Soc., Chem. Commun.*, 765 (1974).
45. D. A. Franz, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.* **94**, 412 (1972).
46. B. J. Meneghelli and R. W. Rudolph, *Inorg. Chem.* **14**, 1429 (1975).
47. M. G. H. Wallbridge, *Prog. Inorg. Chem.* **11**, 99 (1970).
48. T. J. Marks and J. R. Kolb, *Chem. Rev.* **77**, 263 (1977).
49. P. L. Timms, *J. Am. Chem. Soc.* **90**, 4585 (1968); N. S. Hosmane, in W. Siebert, ed., *Advances in Boron Chemistry*, The Royal Society of Chemistry, Cambridge, U.K. 1997, p. 350.
50. M. F. Hawthorne and co-workers, *J. Am. Chem. Soc.* **90**, 879 (1968); R. M. Wing, *J. Am. Chem. Soc.* **90**, 4828 (1968).
51. L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.* **90**, 4823 (1968).
52. C. Glidewell, *J. Organometal. Chem.* **102**, 339 (1975).
53. K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *J. Am. Chem. Soc.* **97**, 296 (1975).
54. L. J. Guggenberger, *J. Am. Chem. Soc.* **94**, 114 (1972).
55. H. E. Ruhle and M. F. Hawthorne, *Inorg. Chem.* **7**, 2279 (1968); D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.* **10**, 2587 (1971).
56. H. M. Colquhoun, T. J. Greenhough, and M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 1019 (1976).
57. G. K. Barker and co-workers, *J. Chem. Soc., Chem. Commun.*, 804 (1975).
58. S. G. Shore, in E. L. Muetterties, ed., *Boron Hydride Chemistry*, Academic Press, New York, 1975, Chapt. 3.; E. L. Muetterties and W. H. Knoth, *Polyhedral Boranes*, Marcel Dekker, Inc., New York, 1968.

59. H. C. Longuet-Higgins, *Q. Rev. Chem. Soc.* **11**, 121 (1957).
60. W. H. Eberhardt, B. L. Crawford Jr., and W. N. Lipscomb, *J. Chem. Phys.* **22**, 989 (1954).
61. R. W. Rudolph and D. A. Thompson, *Inorg. Chem.* **13**, 2779 (1974).
62. R. G. Pearson, *J. Am. Chem. Soc.* **91**, 4947 (1969).
63. R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.* **11**, 1974 (1972).
64. W. Kutzelnigg, *Isr. J. Chem.* **19**, 193 (1980); W. Kutzelnigg, *J. Phys. Chem.* **76**, 1919 (1982).
65. J. W. Bausch, G. K. Prakash, and R. E. Williams, paper presented at the 2nd Boron USA Workshop (BUSA II), Research Triangle Park, N. C., June 1990.
66. N. N. Greenwood and R. Greatrex, *Pure Appl. Chem.* **59**, 857 (1987), and references cited therein.
67. C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc.* **82**, 5757 (1960).
68. S. Hermanek and J. Plesek, *Coll. Czech. Chem. Commun.* **31**, 177 (1966); R. E. Enrione and R. Schaeffer, *J. Inorg. Nucl. Chem.* **18**, 103 (1961).
69. M. A. Toft, J. B. Leach, F. L. Himpsl, and S. G. Shore, *Inorg. Chem.* **21**, 1952 (1982); *J. Am. Chem. Soc.* **103**, 988 (1981); S. H. Lawrence and co-workers, *Inorg. Chem.* **25**, 367 (1986); N. S. Hosmane, J. R. Wermer, Z. Hong, T. D. Getman, and S. G. Shore, *Inorg. Chem.* **26**, 3638 (1987), and references cited therein.
70. R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.* **81**, 3554 (1959).
71. R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961).
72. G. A. Guter and G. W. Schaeffer, *J. Am. Chem. Soc.* **78**, 3546 (1956); M. F. Hawthorne, A. R. Pitochelli, R. D. Strahm, and J. J. Miller, *J. Am. Chem. Soc.* **82**, 1825 (1960).
73. M. F. Hawthorne and J. J. Miller, *J. Am. Chem. Soc.* **80**, 754 (1958).
74. M. F. Hawthorne, *J. Am. Chem. Soc.* **80**, 3480 (1958).
75. J. J. Miller and M. F. Hawthorne, *J. Am. Chem. Soc.* **81**, 4501 (1959).
76. M. F. Hawthorne, A. R. Pitochelli, R. D. Strahm, and J. J. Miller, *J. Am. Chem. Soc.* **82**, 1825 (1960).
77. B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.* **1**, 622 (1966).
78. J. A. DuPont and M. F. Hawthorne, *Chem. Ind.*, 405 (1962).
79. V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.* **1**, 734 (1962).
80. H. D. Johnson, II and S. G. Shore, *J. Am. Chem. Soc.* **93**, 3798 (1971).
81. D. Gaines and T. V. Iorns, *J. Am. Chem. Soc.* **92**, 4571 (1970).
82. J. A. DuPont and M. F. Hawthorne, *J. Am. Chem. Soc.* **84**, 1804 (1962).
83. D. F. Gaines, H. Beall *Inorg. Chem.* **39**, 1812 (2000).
84. L. I. Zakharkin and V. N. Kalinin, *J. Gen. Chem. USSR* **36**, 2154 (1966); R. L. Williams, I. Dunstan, and N. J. Blay, *J. Chem. Soc.*, 5006 (1960).
85. D. Gaines and J. A. Martens, *Inorg. Chem.* **7**, 704 (1968).
86. H. D. Johnson, II, V. T. Brice, G. L. Brubaker, and S. G. Shore, *J. Am. Chem. Soc.* **94**, 6711 (1972).
87. M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.* **81**, 5519 (1959); A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.* **82**, 3228 (1960).
88. W. H. Knoth and co-workers, *J. Am. Chem. Soc.* **84**, 1056 (1962).
89. E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.* **3**, 444 (1964).
90. F. Klanberg and E. L. Muetterties, *Inorg. Chem.* **5**, 1955 (1966).
91. J. L. Boone, *J. Am. Chem. Soc.* **86**, 5036 (1964).
92. S. Y. Tyree, Jr., ed., *Inorg. Synth.* **9**, 16 (1967).
93. H. C. Miller, M. E. Miller, and E. L. Muetterties, *Inorg. Chem.* **3**, 1456 (1964).
94. E. L. Muetterties, *Inorg. Synth.* **10**, 82 (1967).

95. W. L. Jolly, *Inorg. Synth.* **11**, 27 (1968).
96. J. M. Makhlouf, W. V. Hough, and G. T. Hefferan, *Inorg. Chem.* **6**, 1196 (1967).
97. E. L. Muetterties and W. H. Knoth, Polyhedral Boranes, Marcel Dekker, Inc. New York, 1968, p. 1
98. W. H. Knoth, J. C. Sauer, D. C. English, W. R. Hertler, E. L. Muetterties, *J. Am. Chem. Soc.* **86**, 3973 (1964).
99. E. I. Tolpin, G. R. Wellum, S. A. Berley, *Inorg. Chem.* **24**, 2934, (1976); T. Nakagawa, T. Nagai, *Chem. Pharm. Bull.* **98**, 1515 (1998).
100. E. I. Tolpin, G. R. Wellum, and S. A. Berley, *Inorg. Chem.* **17**, 2867, (1978).
101. E. J. M. Hamilton, G. T. Jordan IV, E. A. Meyers, and S. G. Shore, *Inorg. Chem.* **35**, 5335 (1996); R. G. Kultyshev, J. Meyers, and S. G. Shore, *Inorg. Chem.* **38**, 4913 (1999); R. G. Kultyshev, J. Meyers, and S. G. Shore, *Inorg. Chem.* **39**, 3333 (2000).
102. R. G. Kultyshev, S. Liu, and S. G. Shore, *Inorg. Chem.* **39**, 6094 (2000).
103. T. Peymann, A. Herzog, C. B. Knobler, and M. F. Hawthorne *Angew. Chem., Int. Ed. Engl.* **38**, 1062 (1999).
104. M. Andreas, C. B. Knobler, and M. F. Hawthorne *Angew. Chem., Int. Ed. Engl.* **40**(9), 1662 (2001).
105. T. Peymann, C. B. Knobler, S. I. Khan, and M. F. Hawthorne, *Angew. Chem. Int. Ed. Engl.* **40**, 1664 (2001).
106. T. Peymann, C. B. Knobler, S. I. Khan, and M. F. Hawthorne, *Inorg. Chem.* **40**, 1291 (2001).
107. W. H. Knoth, *J. Am. Chem. Soc.* **88**, 935 (1966).
108. A. Kaczmarczyk, W. C. Nichols, W. H. Stockmayer, and T. B. Eames, *Inorg. Chem.* **7**, 1057 (1968).
109. W. H. Knoth, J. C. Sauer, J. H. Balthis, and H. C. Miller, *J. Am. Chem. Soc.* **89**, 4842 (1967).
110. W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, and E. L. Muetterties, *J. Am. Chem. Soc.* **84**, 1056 (1962).
111. W. H. Knoth, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.* **3**, 159 (1964).
112. M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *J. Am. Chem. Soc.* **85**, 3704 (1963); M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, *J. Am. Chem. Soc.* **87**, 1893 (1965).
113. R. L. Pilling, M. F. Hawthorne, and E. A. Pier, *J. Am. Chem. Soc.* **86**, 3568 (1964).
114. C. H. Schwalbe and W. N. Lipscomb, *Inorg. Chem.* **10**, 151 (1971).
115. F. Li, K. Shelly, C. B. Knobler, and M. F. Hawthorne, *Angew. Chem. Int. Ed. Engl.* **37**, 1868 (1998).
116. R. J. Wiersema and R. L. Middaugh, *J. Am. Chem. Soc.* **85**, 3704 (1963); R. L. Middaugh and F. Farha, Jr., *J. Am. Chem. Soc.* **88**, 4147 (1966).
117. E. M. Fedneva, V. I. Alpatova, and V. I. Mikheeva, *Russ. J. Inorg. Chem.* **9**, 826 (1964).
118. V. I. Mikheeva and S. M. Arkhipev, *Russ. J. Inorg. Chem.* **11**, 805 (1966).
119. V. I. Mikheeva, M. S. Selivokhina, and G. N. Kryukova, *Russ. J. Inorg. Chem.* **1**, 838 (1962).
120. S. C. Abrahams and J. Kalnajs, *J. Chem. Phys.* **22**, 434 (1954).
121. W. D. Davis, L. S. Mason, and G. Stegman, *J. Am. Chem. Soc.* **71**, 2775 (1949).
122. M. D. Banus, R. W. Bragdon, and A. A. Hinckley, *J. Am. Chem. Soc.* **76**, 3848 (1954).
123. A. P. Altschuler, *J. Am. Chem. Soc.* **77**, 5455 (1955).
124. M. B. Smith and G. E. Bass, *J. Chem. Eng. Data* **8**, 342 (1963).
125. H. I. Schlesinger and co-workers, *J. Am. Chem. Soc.* **75**, 199 (1953).
126. G. S. Panson and C. E. Weill, *J. Inorg. Nucl. Chem.* **15**, 184 (1960).

127. A. Pelter, K. Smith, and H. C. Brown, *Borane Reagents*, Academic Press, London, 1988.
128. J. Plesek, S. Hermanek, J. C. Huffman, P. Ragatz, and R. Schaeffer, *J. Chem. Soc. Commun.* 935 (1975); B. Stibr, J. Plesek, and S. Hermanek, in J. F. Liebman, A. Greenberg, and R. E. Williams, eds., *Molecular Structure and Energetics, Vol. 5, Advances in Boron and Boranes*, VCH Publishers, New York, p. 35 (1988). P. Paetzold, J. Muller, F. Meyer, H.-P. Hansen, and L. Schneider, p. 337; J. Holub, T. Jelinek, B. Stibr, J. D. Kennedy, and M. Thornton-Pett, p. 359, A. Ouassas, B. Fenet, H. Mongeot, and B. Frange, in G. W. Kalbalka, ed., *Current Topics in The Chemistry of Boron*, The Royal Society of Chemistry, Cambridge, 1994, p. 363; A. E. Willie, K. Su, P. J. Carroll, and L. G. Sneddon.
129. R. N. Grimes, *Carboranes*, Academic Press, New York, 1970.
130. H. L. Gingrich, T. Ghosh, Q. Huang, and M. Jones, Jr., *J. Am. Chem. Soc.* **112**, 4082 (1990).
131. M. F. Hawthorne and R. A. Wiesboeck, *J. Am. Chem. Soc.* **86**, 1642 (1964); M. F. Hawthorne and co-workers, *J. Am. Chem. Soc.* **90**, 862 (1968).
132. J. Buchanan, E. J. M. Hamilton, D. Reed, and A. J. Welch, *J. Chem. Soc. Dalton Trans.*, 677 (1990).
133. M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. MacKinnon, I. S. Neretin, K. Wade *Chem. Commun.*, 1649 (1999).
134. M. A. Fox, A. E. Goeta, J. A. K. Howard, A. K. Hughes, A. L. Johnson, D. A. Keen, K. Wade, C. C. Wilson, *Inorg. Chem.* **40**, 173 (2001).
135. J. Plesek and S. Hermanek, *Collect. Czech. Chem. Commun.* **38**, 338 (1973).
136. G. B. Dunks and M. F. Hawthorne, *Acc. Chem. Res.* **6**, 124 (1973).
137. J. F. Ditter, E. B. Klusmann, J. D. Oates, and R. E. Williams, *Inorg. Chem.* **9**, 889 (1970).
138. T. Onak, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.* **85**, 3378 (1963).
139. U. Siriwardane, M. S. Uslam, T. A. West, N. S. Hosmane, J. A. Maguire, A. H. Cowley, *J. Am. Chem. Soc.* **109**, 4600 (1987).
140. B. Stibr, J. Plesek, and S. Hermanek, *Coll. Czech. Chem. Commun.* **39**, 1805 (1974).
141. T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.* **3**, 1686 (1964).
142. W. H. Knoth, *Inorg. Chem.* **10**, 598 (1971).
143. D. E. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *Inorg. Chem.* **6**, 2229 (1967).
144. R. J. Wiersema and M. F. Hawthorne, *Inorg. Chem.* **12**, 785 (1973).
145. G. B. Dunks and M. F. Hawthorne, *Inorg. Chem.* **8**, 2667 (1969).
146. E. Groszek, J. R. Leach, G. T. F. Wong, C. Ungermann, and T. Onak, *Inorg. Chem.* **10**, 2770 (1971).
147. B. Stibr, J. Holub, and F. Teixidor, in W. Siebert, ed., *Advances in Boron Chemistry*, The Royal Society of Chemistry, Cambridge, 1997 p. 331.
148. K. Su, B. Barnum, P. J. Carroll, and L. G. Sneddon, *J. Am. Chem. Soc.* **114**, 2730 (1992); K. Su, P. J. Carroll, and L. G. Sneddon, *J. Am. Chem. Soc.*, **115**, 10004 (1993).
149. W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.* **96**, 7116 (1974); K. K. Fonda and R. N. Grimes, *Polyhedron* **9**, 949 (1990), and references cited therein.
150. J. P. Pasinski and R. A. Beaudet, *J. Chem. Phys.* **61**, 683 (1974); D. P. Freyberg, R. Weiss, E. Sinn, and R. N. Grimes, *Inorg. Chem.* **16**, 1847 (1977).
151. B. Stibr, T. Jelinek, E. Drdakova, S. Hermanek, and J. Plesek, *Polyhedron* **7**, 669 (1988); K. Su, P. J. Carroll, and L. G. Sneddon, *J. Am. Chem. Soc.* **115**, 10004 (1993).
152. S. Wu and M. Jones Jr., *J. Am. Chem. Soc.* **111**, 5373 (1989), and references cited therein; B. M. Gimarc and J. J. Ott, *Main Group Met. Chem.* **12**, 77 (1989).
153. R. J. Wiersema and M. F. Hawthorne, *Inorg. Chem.* **12**, 785 (1973).
154. M. L. Thompson and R. N. Grimes, *J. Am. Chem. Soc.* **93**, 6677 (1971).

155. M. F. Hawthorne, in W. Siebert, ed., *Advances in Boron Chemistry*, The Royal Society of Chemistry, Cambridge, U.K. 1997, p. 261.
156. P. Kaszynski, D. Lipiak, K. A. Bairamov, E. Brady, M. K. Patel, and J. Laska, in W. Siebert, ed., *Advances in Boron Chemistry*, The Royal Society of Chemistry, Cambridge, U.K. 1997, p. 508.
157. X. Yang, W. Jiang, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.* **114**, 9719 (1992); J. Muller, K. Base, T. F. Magnera, and J. Michl, *J. Am. Chem. Soc.* **114**, 9721 (1992).
158. S. Kongpricha, and H. Schroeder *Inorg. Chem.* **8**, 2449 (1969).
159. R. J. Lagow, and J. L. Margave, *J. Inorg. Nucl. Chem.* **35**, 2084 (1973).
160. S. V. Ivanov, J. J. Rockwell, O. G. Polyakov, C. M. Gaudinski, O. P. Anderson, K. A. Solntsev, and S. H. Strauss, *Angew. J. Am. Chem. Soc.* **120**, 4224 (1998).
161. W. Jiang, D. E. Harwell, M. D. Mortimer, C. B. Knobler, and M. F. Hawthorne, *Inorg, Chem.* **25**, 4355 (1996).
162. B. T. King, Z. Janousek, B. Gruner, M. Trammell, B. C. Noll, J. Michl, *J. Am. Chem. Soc.* **118**, 3313 (1996); I. Zharov, B. T. King, Z. Havlas, A. Pardi, and J. Michl, *J. Am. Chem. Soc.* **122**, 10253 (2000).
163. W. Jiang, C. B. Knobler, M. D. Mortimer, and M. F. Hawthorne, *Angew. Chem.* **107**, 1470 (1995).
164. B. T. King, B. C. Noll, A. J. McKinley, and J. Michl, *J. Am. Chem. Soc.* **118**, 10902 (1996).
165. C.-W. Tsang, Q. Yang, E. T.-P. Sze, T. C. W. Mak, D. T. W. Chan, and Z. Xie, *Inorg. Chem.* **39**, 3582 (2000); C.-W. Tsang, Q. Yang, E. T.-P. Sze, T. C. W. Mak, D. T. W. Chan, and Z. Xie, *Inorg. Chem.* **39**, 5851 (2000).
166. W. Jiang, C. B. Knobler, and M. F. Hawthorne, *Angew. Chem. Int. Ed. Engl.* **35**, 2536 (1996); W. Jiang, C. B. Knobler, and M. F. Hawthorne, *Angew. Chem. Int. Ed. Engl.* **108**, 2653 (1996).
167. B. T. King, J. Michl, *J. Am. Chem. Soc.* **122**, 10255 (2000).
168. A. Herzog, R. P. Callahan, C. L. B. Macdonald, V. M. Lynch, M. F. Hawthorne, and R. J. Lagow, *Angew. Chem. Int. Ed. Engl.* **40**, 2121 (2001).
169. C. A. Reed, *Acc. Chem. Res.* **31**, 133 (1998).
170. S. M. Ivanova, S. V. Ivanova, S. M. Miller, O. P. Andersen, K. A. Solntsev, S. H. Strauss, *Inorg. Chem.* **38**, 3756 (1999).
171. A. J. Lupinetti, M. D. Havighurst, S. M. Miller, O. P. Andersen, S. H. Strauss *J. Am. Chem. Soc.* **121**, 11920 (1999).
172. C. A. Reed, Z. Bau, R. Bau, A. Bernesi, *Science*, **262**, 402 (1993).
173. Z. Xie, R. Bau, C. A. Reed *Angew. Chem., Int. Ed. Engl.* **33**, 2433 (1994).
174. Z. Xie, R. Bau, C. A. Reed *Inorg. Chem.* **34**, 5403 (1995).
175. C. A. Reed, N. L. P. Fackler, K.-C. Kim, D. Stasko, D. R. Evans *J. Am. Chem. Soc.* **121**, 8466 (1999)
176. Eur. Pat. Appl. 88,300,698, 88,300,699 (1998), H. W. Turner.
177. C. A. Reed, K-C Kim, R. D. Bolskar, and L. J. Mueller, *Science*, **289**, 101 (2000).
178. S. Papetti, B. B. Schaeffer, A. P. Gray, and T. L. Heying, *J. Polymer. Sci.* **4** (A-1), 1623 (1966); U. S. Pats. 3,388,090 (1968); 3,388,091 (1968); 3,388,092 (1968), T. L. Heying, S. Papetti, and O. G. Shaffling.
179. E. Hedaya and co-workers, *J. Polym. Sci., Polym. Chem. Ed.* **15**, 2229 (1977), and references cited therein.
180. S. Bresadola, in R. N. Grimes, ed., *Metal Interactions with Boron Clusters*, Plenum Press, New York, 1982.
181. K. Base and co-workers, *J. Chem. Soc., Chem. Commun.*, 934 (1975).
182. J. L. Little and A. C. Wong, *J. Am. Chem. Soc.* **93**, 522 (1971).
183. J. L. Little, J. T. Moran, and L. J. Todd, *J. Am. Chem. Soc.* **89**, 5495 (1967).

184. J. L. Little, S. S. Pao, and K. K. Sugathan, *Inorg. Chem.* **13**, 1752 (1974).
185. J. L. Little, *Inorg. Chem.* **18**, 1598 (1979).
186. L. J. Todd, A. R. Burke, H. T. Silverstein, J. L. Little, and G. S. Wilkholm, *J. Am. Chem. Soc.* **91**, 3376 (1969).
187. W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.* **6**, 1696 (1967).
188. W. R. Pretzer and R. W. Rudolph, *J. Am. Chem. Soc.* **95**, 931 (1973).
189. J. Plesek, S. Hermanek, and Z. Janousek, *Coll. Czech. Chem. Commun.* **42**, 785 (1977).
190. J. L. Little, G. D. Friesen, and L. J. Todd, *Inorg. Chem.* **16**, 869 (1977).
191. H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.* **87**, 2753 (1965).
192. H. D. Kaesz and R. B. Saillant, *Chem. Rev.* **72**, 344 (1972).
193. H. Nöth, M. Thomann, M. Bremer, and G. Wagner, in G. W. Kabalka, ed., *Advances in Boron Chemistry*, The Royal Society of Chemistry, Cambridge, U.K. 1994, p. 387.
194. P. Wegner, in E. L. Muetterties, ed., *Boron Hydride Chemistry*, Academic Press, New York, 1975, Chapt. 12.
195. J. T. Gill and S. Lippard, *Inorg. Chem.* **14**, 751 (1975).
196. N. N. Greenwood and N. F. Travers, *J. Chem. Soc. A*, 3257 (1971).
197. F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.* **7**, 2072 (1968).
198. L. J. Guggenberger, *J. Am. Chem. Soc.* **94**, 114 (1972).
199. N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J. Chem. Soc. A*, 809 (1971).
200. B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.* **1**, 622 (1962).
201. N. N. Greenwood and D. N. Sharrocks, *J. Chem. Soc. A*, 2334 (1969).
202. B. P. Sullivan, R. N. Leyden, and M. F. Hawthorne, *J. Am. Chem. Soc.* **97**, 455 (1975).
203. R. N. Leyden, B. P. Sullivan, R. T. Baker, and M. F. Hawthorne, *J. Am. Chem. Soc.* **100**, 3758 (1978); R. N. Leyden and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 310 (1975); C. G. Salentine, R. R. Rietz, and M. F. Hawthorne, *Inorg. Chem.* **12**, 3025 (1975).
204. D. M. Schubert, C. B. Knobler, P. A. Wegner, and M. F. Hawthorne, *J. Am. Chem. Soc.* **110**, 5219 (1988).
205. V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.* **95**, 5078 (1973).
206. *Ibid.* **98** 1600 (1976).
207. D. F. Gaines and J. L. Walsh, *Inorg. Chem.* **17**, 1238 (1978).
208. S. Ghosh, M. Shang, Y. Li, and T. P. Fehlner, *Angew. Chem. Int. Ed. Engl.* **40**, 1125 (2001).
209. D. L. Denton, W. R. Clayton, M. Mangion, S. G. Shore, and E. A. Meyers, *Inorg. Chem.* **15**, 541 (1976).
210. N. N. Greenwood and N. F. Travers, *J. Chem. Soc. A*, 15 (1968).
211. N. N. Greenwood, B. S. Thomas, and D. W. Waite, *J. Chem. Soc., Dalton Trans.*, 299 (1975).
212. N. N. Greenwood and J. A. McGinnety, *J. Chem. Soc. A*, 1090 (1966).
213. T. D. Getman and S. G. Shore, *Inorg. Chem.* **27**, 3439 (1988).
214. R. E. Loffredo and A. D. Norman, *Inorg. Nucl. Chem. Lett.* **13**, 599 (1977).
215. R. E. Loffredo and A. D. Norman, *J. Am. Chem. Soc.* **93**, 5587 (1971).
216. D. F. Gaines, J. Morris, D. Hillenbrand, and J. L. Walsh, *Inorg. Chem.* **17**, 1516 (1978).
217. J. Borlin and D. F. Gaines, *J. Am. Chem. Soc.* **94**, 1367 (1972).
218. S. Hermanek and J. Plesek, *Coll. Czech. Chem. Commun.* **31**, 177 (1966).
219. W. V. Hough, L. J. Edwards, and A. J. McElroy, *J. Am. Chem. Soc.* **80**, 1828 (1958).
220. J. C. Calabrese, D. F. Gaines, S. J. Hildebrandt, and J. H. Morris, *J. Am. Chem. Soc.* **98**, 5489 (1976).

221. D. F. Gaines and J. L. Walsh, *Chem. Commun.*, 482 (1976); D. F. Gaines, J. L. Walsh, and J. C. Calabrese, *Inorg. Chem.* **17**, 1242 (1978).
222. J. Borlin and D. F. Gaines, *J. Am. Chem. Soc.* **94**, 1367 (1972).
223. D. Seyferth, K. Büchner, W. S. Rees, Jr., and W. M. Davis, *Angew. Chem. Int. Ed. Engl.* **29**, 918 (1990).
224. T. E. Paxson, M. F. Hawthorne, L. D. Brown, and W. N. Lipscomb, *Inorg. Chem.* **13**, 2772 (1974).
225. J. P. White, III, H.-B. Deng, and S. G. Shore, *J. Am. Chem. Soc.* **111**, 8946 (1989).
226. J. P. White, III, and S. G. Shore, paper presented at the the *2nd Boron USA Workshop (BUSA II)b*, Research Triangle Park, N. C., June 1990.
227. D. F. Gaines and T. V. Iorns, *Inorg. Chem.* **7**, 1041 (1968).
228. M. R. Churchill, J. J. Hackbarth, A. Davison, D. D. Traficante, and S. S. Wreford, *J. Am. Chem. Soc.* **96**, 4041 (1974).
229. D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.* **90**, 6617 (1968).
230. J. C. Calabrese and L. F. Dahl, *J. Am. Chem. Soc.* **93**, 6042 (1971).
231. M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.* **87**, 1818 (1965); M. F. Hawthorne, D. C. Young, and co-workers, *J. Am. Chem. Soc.* **90**, 879 (1968).
232. A. K. Saxena and N. S. Hosmane, *Chem. Rev.* **93**, 1081 (1993).
233. M. F. Hawthorne and T. D. Andrews, *J. Chem. Soc., Chem. Commun.*, 443 (1965); R. J. Wilson, L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.* **91**, 758 (1969); L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.* **89**, 470 (1967).
234. M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.* **87**, 3987 (1965).
235. L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.* **90**, 4823 (1968).
236. R. J. Wilson, L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.* **91**, 758 (1969).
237. J. Plesek and co-workers, *Collec. Czech. Chem. Commun.* **49**, 2776 (1984).
238. M. F. Hawthorne and T. D. Andrews, *J. Am. Chem. Soc.* **87**, 2496 (1965); M. F. Hawthorne and H. W. Ruhle, *Inorg. Chem.* **8**, 176 (1969).
239. G. B. Dunks and M. F. Hawthorne, *J. Am. Chem. Soc.* **92**, 7213 (1970).
240. W. J. Evans and M. F. Hawthorne, *J. Am. Chem. Soc.* **93**, 3063 (1971).
241. D. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.* **95**, 1109 (1973).
242. W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.* **95**, 4565 (1973).
243. W. J. Evans and M. F. Hawthorne, *Inorg. Chem.* **13**, 869 (1974).
244. W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 38 (1974).
245. C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Am. Chem. Soc.* **94**, 8391 (1972); C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 900 (1972); J. N. Francis and M. F. Hawthorne, *Inorg. Chem.* **10**, 863 (1971); D. F. Dustin, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 805 (1973).
246. D. F. Dustin and M. F. Hawthorne, *J. Am. Chem. Soc.* **96**, 3462 (1974).
247. M. R. Churchill, A. H. Reis, Jr., J. N. Francis, and M. F. Hawthorne, *J. Am. Chem. Soc.* **92**, 4993 (1970).
248. W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.* **99**, 4016 (1977).
249. M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, *J. Am. Chem. Soc.* **94**, 6679 (1972).
250. D. F. Dustin, C. J. Jones, and R. J. Wiersema, *J. Am. Chem. Soc.* **96**, 3085 (1974).
251. W. J. Evans, C. J. Jones, B. Stibr, R. A. Grey, and M. F. Hawthorne, *J. Am. Chem. Soc.* **96**, 7405 (1974); C. G. Salentine and M. F. Hawthorne, *J. Am. Chem. Soc.* **97**, 6382 (1975).
252. R. J. Wilson, L. F. Warren, Jr., M. F. Hawthorne, *J. Am. Chem. Soc.* **92**, 1157 (1970).
253. D. M. Schubert, D. E. Harwell, C. B. Knobler, and M. F. Hawthorne, *Acta Chem. Scand.* **53**, 721 (1999).

254. H. C. Kang, Y. Do, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.* **109**, 6530 (1988); H. C. Kang, Y. Do, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.* **27**, 1716 (1988).
255. C. G. Salentine and M. F. Hawthorne, *Inorg. Chem.* **15**, 2872 (1976).
256. C. G. Salentine and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 848 (1975).
257. W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.* **98**, 4818 (1976).
258. M. F. Hawthorne and A. D. Pitts, *J. Am. Chem. Soc.* **89**, 7115 (1967); A. D. George and M. F. Hawthorne, *Inorg. Chem.* **8**, 1801 (1969); F. J. Hollander, D. H. Templeton, and A. Zalkin, *Inorg. Chem.* **12**, 2262 (1973).
259. R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.* **13**, 1138 (1974).
260. A. J. Welch, *J. Chem. Soc. Dalton Trans.*, 225 (1976).
261. R. N. Grimes, *J. Am. Chem. Soc.* **93**, 261 (1971); R. N. Grimes, *Coord. Chem. Rev.* **28**, 47 (1979); A. Fassenbecker, M. D. Attwood, R. N. Grimes, M. Stephan, H. Pritzkow, U. Zenneck, and W. Siebert, *Inorg. Chem.* **29**, 5164 (1990), and references cited therein.
262. R. N. Grimes, *Chem. Rev.* **92**, 251 (1992).
263. E. L. Hoel and M. F. Hawthorne, *J. Am. Chem. Soc.* **96**, 6770 (1974).
264. *Ibid.* **97**, 6388 (1975).
265. *Ibid.* **95**, 2712 (1973).
266. H. C. Kang, Y. Do, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.* **27**, 1716 (1988).
267. S. J. Dossett, I. J. Hart, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 3481 (1990); S. J. Dossett, I. J. Hart, M. U. Pilotti, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 3489 (1990), and references cited therein.
268. V. I. Bregadze, V. Ts. Kampel, and N. N. Godovikov, *J. Organometal. Chem.* **136**, 281 (1976); V. I. Bregadze, V. Ts. Kampel, A. Ya. Usiatinsky, and N. N. Godovikov, *Pure Appl Chem.* **63**, 835 (1991); V. I. Bregadze, *Chem. Rev.* **92**, 209, (1992).
269. V. I. Bregadze, A. Ya. Usiatinsky, O. B. Zhidlova, O. M. Khitrova, P. V. Petrovskii, F. M. Dolgushin, A. I. Yanovsky, and Yu. T. Struchkov, in W. Siebert, ed., *Advances in Boron Chemistry*, The Royal Society of Chemistry, Cambridge, U.K., 1997, p. 341.
270. W. Clegg, H. M. Colquhoun, R. Coult, M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride, and K. Wade, in G. W. Kabalka, ed., *Advances in Boron Chemistry*, The Royal Society of Chemistry, Cambridge, U.K., 1994, p. 232.
271. A. Muller, H. Reuter, S. Dillinger, *Angew. Chem. Int. Ed. Engl.* **34**, 2328 (1995).
272. M. F. Hawthorne, Z. Zheng, *Acc. Chem. Res.* **30**, 267 (1997).
273. T. E. Paxson and M. F. Hawthorne, *J. Am. Chem. Soc.* **96**, 4674 (1974); D. C. Busby and M. F. Hawthorne, *Inorg. Chem.* **21**, 4101 (1982).
274. R. T. Baker, M. S. Delaney, R. E. King III, C. B. Knobler, J. A. Long, T. B. Marder, T. E. Paxson, R. G. Teller, and M. F. Hawthorne, *J. Am. Chem. Soc.* **106**, 2965 (1984).
275. P. M. Garrett, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.* **9**, 1947 (1970); P. M. Garrett, G. S. Ditta, and M. F. Hawthorne, *J. Am. Chem. Soc.* **93**, 1265 (1971).
276. J. A. Long, T. B. Marder, P. E. Behnken, and M. F. Hawthorne, *J. Am. Chem. Soc.* **106**, 2979 (1984); C. B. Knobler and co-workers, *J. Am. Chem. Soc.* **106**, 2990 (1984).
277. J. A. Long, T. B. Marder, P. E. Behnken, and M. F. Hawthorne, *J. Am. Chem. Soc.* **106**, 2979 (1984).
278. P. E. Behnken and co-workers, *J. Am. Chem. Soc.* **106**, 3011 (1984); P. E. Behnken and co-workers, *J. Am. Chem. Soc.* **106**, 7444 (1984).
279. J. A. Long, T. B. Marder, and M. F. Hawthorne, *J. Am. Chem. Soc.* **106**, 3004 (1984).
280. B. A. Sosinsky, W. C. Kalb, R. A. Grey, V. A. Uski, and M. F. Hawthorne, *J. Am. Chem. Soc.* **99**, 6768 (1977).

281. J. D. Hewes, C. B. Knobler, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 206 (1981).
282. P. E. Behnken and co-workers, *J. Am. Chem. Soc.* **107**, 932 (1985).
283. *Res. Discl.* **292**, 588 (1988).
284. N. S. Hosmane and J. A. Maguire, *Adv. Organometal. Chem.* **30**, 99 (1990); A. K. Saxena, J. A. Maguire, and N. S. Hosmane, *Chem. Rev.* **97**, 2421 (1997).
285. T. Onak and G. B. Dunks, *Inorg. Chem.* **5**, 439 (1966).
286. N. S. Hosmane, U. Siriwardane, G. Zhang, H. Zhu, and J. A. Maguire, *J. Chem. Soc. Chem. Commun.* 1128 (1989).
287. N. S. Hosmane, L. Jia, Y. Wang, A. K. Saxena, H. Zhang, and J. A. Maguire, *Organometallics* **13**, 4113 (1994).
288. N. S. Hosmane, A. K. Saxena, R. D. Barreto, H. Zhang, J. A. Maguire, L. Jia, Y. Wang, A. R. Oki, K. V. Grover, S. J. Whitten, K. Dawson, M. A. Tolle, U. Siridawardane, U. Demissie, and J. S. Fagner, *Organometallics* **12**, 3001 (1993); H. Zhang, Y. Wang, A. K. Saxena, A. R. Oki, J. A. Maguire, and N. S. Hosmane, *Organometallics* **12**, 3933 (1993).
289. Y. Wang, H. Zhang, J. A. Maguire, and N. S. Hosmane, *Organometallics* **12**, 3781 (1993).
290. N. S. Hosmane, J. Yang, H. Zhang, and J. A. Maguire, *J. Am. Chem. Soc.* **118**, 5150 (1996).
291. R. Khattar, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.* **112**, 4962 (1990).
292. R. Khatter, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.* **29**, 2191 (1990).
293. G. Popp and M. F. Hawthorne, *Inorg. Chem.* **10**, 391 (1971).
294. M. Westerhausen, C. Gückel, S. Schneiderbauer, H. Nöth, and N. S. Hosmane, *Angew. Chemie Int. Ed. Engl.* **40**, 1902 (2001).
295. B. M. Mikhailov and T. V. Potapova, *Izv. Akad. Nauk. SSSR, Ser. Khim.* **5**, 1153 (1968).
296. D. A. T. Young, R. J. Wiersema, and M. F. Hawthorne, *J. Am. Chem. Soc.* **93**, 5687 (1971).
297. M. R. Churchill, A. H. Reis, Jr., D. A. T. Young, G. R. Willey, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 298 (1971); M. Churchill and A. H. Reis, *J. Chem. Soc., Dalton Trans.*, 1317 (1972).
298. D. M. Schubert, M. A. Bandman, W. S. Rees, Jr., C. B. Knobler, P. Lu, W. Nam, and M. F. Hawthorne, *Organometallics* **9**, 2046 (1990).
299. M. A. Bandman, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.* **27**, 2399 (1988).
300. *Ibid.* **28**, 1204 (1989).
301. C. P. Magee, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Organomet. Chem.* **86**, 159 (1975).
302. J. S. Beck, L. G. Sneddon, *J. Am. Chem. Soc.* **110**, 3467 (1988).
303. N. S. Hosmane, A. K. Saxena, K.-J. Lu, J. A. Maguire, H. Zhang, Y. Wang, C. J. Thomas, D. Zhu, B. R. Grover, T. G. Gray, J. F. Eintracht, H. Isom, and A. H. Cowley, *Organometallics* **14**, 5104 (1995).
304. A. K. Saxena, H. Zhang, J. A. Maguire, N. S. Hosmane, and A. H. Cowley, *Angew. Chem. Int. Ed. Engl.* **34**, 332 (1995).
305. J. L. Spencer, M. Green, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1178 (1972).
306. M. J. Manning, C. B. Knobler, M. F. Hawthorne, and Y. Do, *Inorg. Chem.* **30**, 3589 (1991).
307. R. L. Voorhees and R. W. Rudolph, *J. Am. Chem. Soc.* **91**, 2173 (1969); R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Am. Chem. Soc.* **92**, 3351 (1970);

V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, *J. Am. Chem. Soc.* **95**, 4560 (1973).
308. L. J. Todd, A. R. Burke, H. T. Silverstein, J. L. Little, and G. S. Wilkholm, *J. Organomet. Chem.* **91**, 3376 (1969).
309. D. M. Schubert, W. S. Rees, Jr., C. B. Knobler, and M. F. Hawthorne, *Organometallics* **9**, 2938 (1990).
310. U. Siriwardane and co-workers, *J. Am. Chem. Soc.* **109**, 4600 (1987); N. S. Hosmane, P. de Meester, U. Siriwardane, M. S. Islam, and S. S. C. Chu, *J. Chem. Soc., Chem. Commun.*, 1421 (1986).
311. K.-S. Wong and R. N. Grimes, *Inorg. Chem.* **16**, 2053 (1977).
312. N. S. Hosmane, N. N. Sirmokadam, and R. H. Herber, *Organometallics* **3**, 1665 (1984); N. S. Hosmane and co-workers, *Organometallics* **5**, 772 (1986); A. H. Cowley, P. Galow, N. S. Hosmane, P. Jutzi, and N. C. Norman, *J. Chem. Soc., Chem. Commun.*, 1564 (1984).
313. A. K. Saxena, H. Zhang, J. A. McGuire, N. S. Hosmane, and A. H. Cowley, *Angew, Chem. Int. Ed. Engl.* **34**, 332–334 (1995).
314. L. Jia, H. Zhang, N. S. Hosmane, *Organometallic* **11**, 2957 (1992).
315. J. L. Atwood, W. E. Hunter, A. H. Cowley, R. A. Jones, C. A. Stewart, *J. Chem. Soc., Chem. Commun.* 925 (1981); P. Jutzi, *Adv. Organomet. Chem.* **26**, 217 (1986).
316. N. S. Hosmane and co-workers, *Organometallics* **7**, 1893 (1988); N. S. Hosmane, K. J. Lu, U. Siriwardane, and M. S. Shet, *Organometallics* **9**, 2798 (1990).
317. D. C. Beer and L. J. Todd, *Organometal. Chem.* **50**, 93 (1973).
318. F. R. Fronczek, G. W. Halstead, and K. N. Raymond, *J. Am. Chem. Soc.* **99**, 1769 (1977).
319. M. J. Manning, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.* **110**, 4458 (1988).
320. D. A. Feakes, in M. F. Hawthorne, and co−workers, eds, *Frontiers in Neutron Capture Therapy*, Vol. 1, Kluwer Academic/Plenum Publishers, New York, 1998, Chapter 3, p. 23.
321. G. L. Locker, *Am. J. Roentgenol.* **36**, 1 (1936); R. F. Barth, A. H. Soloway, and R. G. Fairchild, *Sci. Am.*, Oct. (1990).
322. F. Alam, R. F. Barth, and A. H. Soloway, *Antibodies, Immunoconjugates, Radiopharmaceut.* **2**, 145 (1989); R. F. Barth, A. H. Soloway, and R. G. Fairchild, *Cancer Res.* **50**, 1061 (1990).
323. Y. Endo, et al. *Biol. Pharm. Bull.* **23**, 513 (2000).
324. Y. Endo, et al. *Chem. Pharm. Bull.* **48**, 314 (2000); Y. Endo and co−workers, *Biomed. Chem. Lett.* **9**, 3701 (1999); *Biomed. Chem. Lett.* **9**, 3313 (1999).
325. Y. Endo, and co-workers *Biomed. Chem. Lett.* **10**, 1733 (2000); Y. Endo, et al. *Chem. Pharm. Bull.*, **47**, 585 (1999).
326. M. F. Hawthorne, A. Varadarajan, C. B. Knobler, J. D. Beatty, and S. Chakrabarti, *J. Am. Chem. Soc.* **112**, 5365 (1990).
327. M. F. Hawthorne and A. Maderna, *Chem. Rev.* **99**, 3421 (1999).
328. U.S. Pat. 3,711,180 (1973), T. J. Klingen and J. R. Wright (to the University of Mississippi).
329. U.S. Pat. 3,539,330 (1970), D. C. Young (to Union Oil Co.).

DAVID M. SCHUBERT
U.S. Borax Inc.