METALLABORANES AND METALLACARBORANES OF s-BLOCK ELEMENTS

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ABSTRACT

The syntheses, structures and reactivity of the compounds formed by the incorporation of a group 1 or group 2 element into a borane or carborane cage have been reviewed. The group 1 boranes were generally found to comprise compounds in which lithium ions replace bridged hydrogens in a borane cage. Some of these lithiated compounds were found to crystallize from solution as oligomers. The carboranes showed much more variations in which a number of group 1 metals occupied both bridging, apical or *commo*-positions of the *nido*-carborane anions. The group 2 boranes were restricted to those of beryllium and magnesium. Examples of compounds were described where the beryllium ions occupy both bridging and apical positions, while only bridging magnesiums were reported. As with the group 1 compounds, the group 2 carboranes were more numerous, with examples of beryllium, magnesium, calcium and strontium metals being incorporated into the electron deficient cages.

INTRODUCTION

This review will cover the published work on the compounds in which an s-block (group 1 or 2) metal is incorporated into the polyhedral borane or carborane cage; it will not cover those compounds where the metal is a member of an exopolyhedral, spectator group. A quick review of the some of the nomenclature and electronic structure conventions used in these cage compounds will be helpful in our discussions. To start, consider two of the simplest hydrides of carbon and boron, ethane (C_2H_6) and diborane (B_2H_6). Although they have similar formulas, their internal bonding and chemical properties are quite different. Both molecules possess six hydrogen atoms that can each furnish one orbital and one electron for bonding and two second period main group elements, each contributing one *s* and three *p* valence orbitals, giving a total of 14 orbitals to be used in bonding. The two molecules differ in the number of electrons that are delocalized in bonding; ethane has 14, one for every orbital, while diborane has only 12. Therefore, ethane can be classified as an "electron precise" compound and its formula can be rationalized in terms of a series of two-center-two-electron (*2c-2e*) bonds holding the molecule together. On the other hand, in B_2H_6, the number of electrons (12) is less than the number of orbitals (14), such compounds are said to be "electron deficient", and one must resort to multi-centered bonds in order to rationalize their formulas. For example, diborane can be described as being held together by two *3c-2e* B-H-B bridge bonds and four *2c-2e* B-H terminal bonds. Multicentered bonds, bridged hydrogens, as well as *2c-2e* terminal B-H bonds are all characteristics of the borane cages. Many of the compounds in the following sections will be pictured using line formulas and ORTEP diagrams. In electron precise compounds, such as ethane, it is understood that each line connecting adjacent nuclei represents a *2c-2e* electron pair bond. However, in an electron deficient compound, this is not always the case. In interpreting these formulas it is convenient to separate the atoms into two groups: the boron atoms that define the vertices of the polyhedral cage and the exo-polyhedral hydrogen (or other) atoms. The lines joining cage boron atoms to one another show only the connectivity within in the polyhedron, while those joining the terminal atoms to the cage not only show connectivity but also represent *2c-2e* electron pair bonds. For example, in the octahedral $[B_6H_6]^{2-}$ the boron atoms occupy the apices of a regular octahedron, as shown in **Figure 1**.

The lines connecting these atoms serve only to delineate the cage. On the other hand, the line joining each terminal hydrogen to a boron represents a *2c-2e* electron pair bond. In the same way, the valence orbitals and electrons in the $[B_6H_6]^{2-}$ can be apportioned into a set that is involved in cage bonding and another group involved with bonding to the terminal hydrogens.

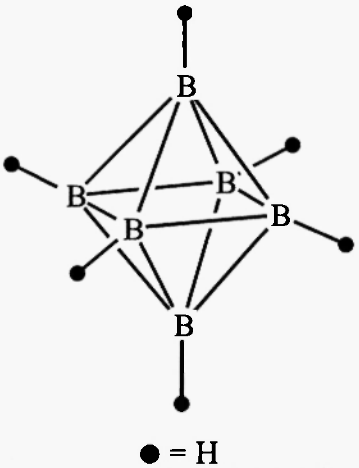


Figure 1. Line drawing of $[B_6H_6]^{2-}$ dianion.

Using this formalism, each boron utilizes one orbital and one electron for bonding to the terminal hydrogen, leaving two electrons and three orbitals (one directed radially towards the center of the cage and two directed tangentially) available for cage bonding. For an *n* vertex polyhedron made up of fused triangular faces (deltahedra), similar to those shown in **Figure 2**, there is a simple and elegant relation between the number of electron pairs used for cage bonding (P) and the cage geometry [1-3]. Namely, if $P = n + 1$, the cage has a closed structure (*closo*); structures *i, iv, vii* and *x* in **Figure 2** are examples of closo-structures. On the other hand, if $P = n + 2$, the cage opens to give a *nido* structure, which can be visualized as arising from the removal of a vertex from an n+1 closo-cage (see *ii, v, viii* and *xi* in **Figure 1**); if $P = n + 3$, the cage opens further to give an *arachno* structure, usually formed by the removal of two adjacent vertices from an n + 2 closo-cage (see *iii, vi, ix* and *xii* in **Figure 2**). The process can continue giving more open structures, referred to as *hypo* ($P = n + 4$), *fisco* ($P = n + 5$), and *reticulo* ($P = n + 6$) [2]. The electrons from bridged hydrogens and those arising from the overall charge also contribute to P. Using these rules, it is easy to see that the closo-boranes all have the general formula, $[B_nH_n]^{2-}$, while a compound such as pentaborane(9), B_5H_9, with $n = 5$ and $P = 7$ ($n + 2$) has a square pyramidal, nido-structure, with four bridged hydrogens located between adjacent borons on the open square planar face [4]. The electronic/structure rules can be extended to the heteroboranes by noting that any atom, or group of atoms, that are isoelectronic and isolobal with a B-H, or a $[B\text{-}H]^-$ unit can be substituted into a borane without a gross change of cage geometry [2,5,6]. An especially important group of these heteroboranes are the carboranes, in which R-C groups (R = single bonded substituent) replace one or more $[B\text{-}H]^-$ units in a cage. For example the neutral n-vertex closo-carboranes have the formulas $C_2B_{n-2}H_n$. When metals are incorporated into borane or carborane cages, the resulting compounds are called metallaboranes or metallacarboranes. In some cases, the heteroatom may form a common vertex with two cages, giving the so called *commo*-complexes. It should also be noted that the replacement of a terminal hydrogen by some other atom or group that interacts through a single 2*c*-2*e* bond will not change the cage electron pair count and should not greatly effect the cage geometry.

An alternate way of viewing the metallaboranes or metallacarboranes is as organometallic compounds in which the electron deficient cage is treated as a ligand which bonds to the metal center. Following such a formalism, one could refer to a closo-metallacarborane as a half-sandwich and the commo-complexes as full-sandwich compounds. These have the advantage of being purely geometric terms without any implications as to the number of cage electrons.

In reviewing the s-block, compounds, the group 1 metals will be discussed first, starting with the simplest boranes and ending with the metallacarboranes having the highest cage carbon content, then the group 2 metals will be treated in a similar fashion.

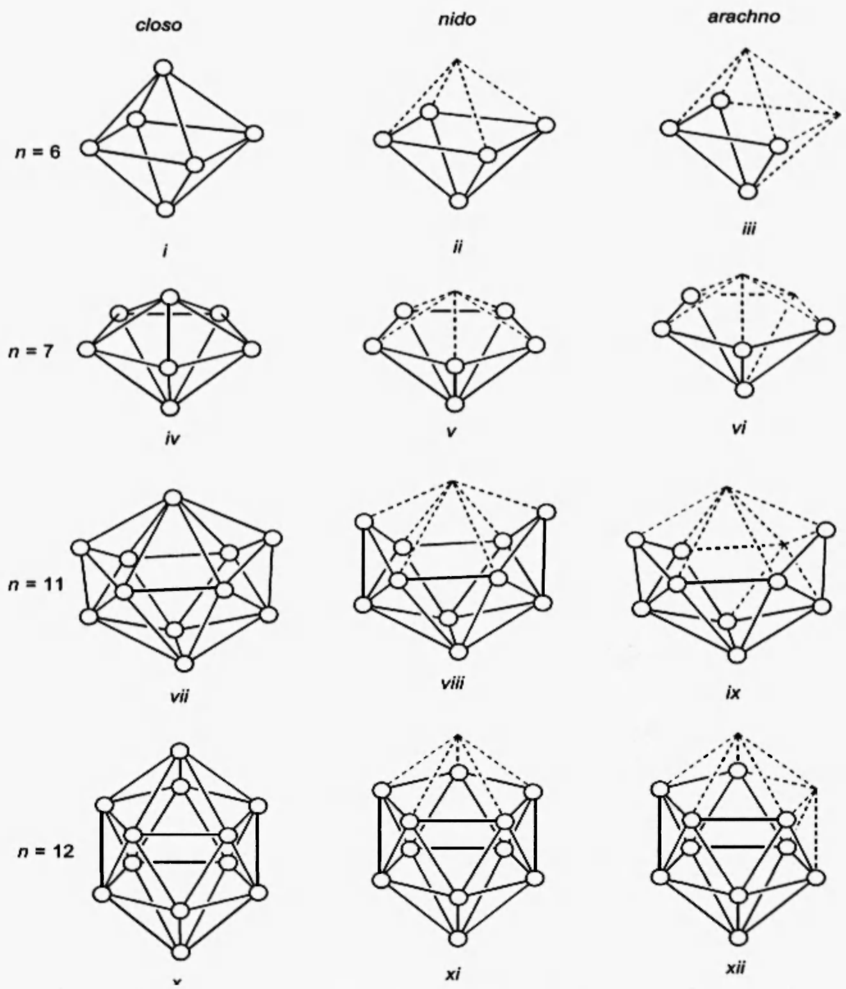


Figure 2. Some idealized deltahedra and deltahedral fragments.
Dash lines delineate the positions of missing vertices.

In all cases, the structural chemistry of the compounds will be emphasized. Because of space restrictions, the chemistry of the tetrahydroborates (MBH_4) or diborane(6) will not be discussed. The uses of these compounds are too widespread for inclusion in a review such as this; they are the starting materials for the syntheses of the higher boranes and heteroboranes and their use in hydroboration reactions has generated a whole family of organic reagents [7].

Group 1 Metallaboranes and Metallacarboranes

Of all the metallaboranes and metallacarboranes the group 1 compounds are some of the most often encountered, in that they are common starting materials in the syntheses of higher order heteroborane clusters. For example, one of the standard methods of cage synthesis is the high temperature reaction of tetrahydroborates with smaller cage compounds, an example of which is shown in eq. 1 [8]. Since, under different conditions the same two reactants produce other cages [8], eq. 1 is one example of the product of a series of fusion reactions of sodium hydroborate cages.

$$2\,NaBH_4 + 5\ B_2H_6 \xrightarrow[(C_2H_5)_3N]{180\ °C} Na_2[B_{12}H_{12}] + 13\ H_2 \qquad (1)$$

There is no evidence as to the role of the group 1 element in such reactions, but it has generally been assumed that they do not play an active role. Any influence that M^+ has on the physical and chemical properties of the $M_2[B_nH_n]$ salts can be rationalized on the basis of general electrostatic interactions of the [*closo*-B_nH_n]$^{2-}$ with exo-polyhedral M^+ ions [9]. However, when bridged hydrogens are present more specific metal-cage interactions are possible. **Figure 3** shows the structure of [$(thp)_2Li$]$B_4H(CH_3)_4$, (thp = tetrahydropyran, $C_5H_{10}O$), reported by Paetzold and coworkers from the reaction of $B_4H_2(CH_3)_4$ with Li in the presence of thp [10].

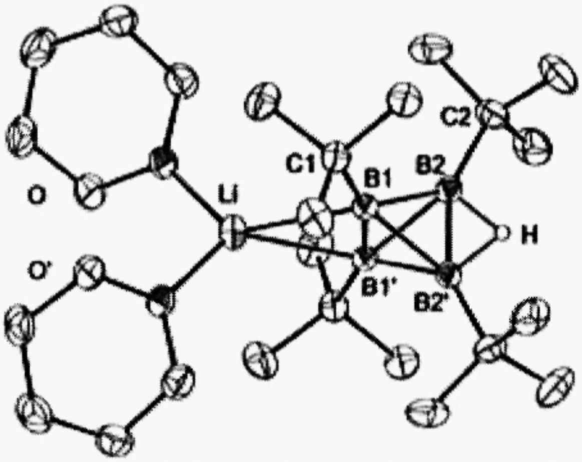


Figure 3. Perspective view of $(C_5H_{10}O)_2Li[B_4H(CH_3)_4$. Terminal hydrogens omitted for clarity. Reprinted with permission from reference 10.

The structure can be understood in terms of a $(thp)_2Li$ unit replacing one of the bridged hydrogens in $B_4H_2(CH_3)_4$. Since the $(thp)_2Li$ group is isoelectronic and isolobal with a H, such a replacement should not alter the geometry of the borane. Therefore, the structure of [$(thp)_2Li$]$B_4H(CH_3)_4$ confirms the structure of the parent $B_4H_2(CH_3)_4$, which could not be determined by X-ray crystallography [10]. Bridging Li atoms were also reported in the tetrameric [Li(12-crown-4)]$_4$[$(MeCH)_3(BMe)_3Li$]$_4$ and [$(MeCH)_3(BMe)_3Li_2(thp)_2$]$_4$ shown in **Figure 4** [11]. The former compound consists of four [$(MeCH)_3(BMe)_3$]$^{2-}$cages held together by Li bridging centers, while in the latter, each cage contains an additional $Li(thp)_2$ unit. In both cages the electron pair count is that for a *hypo* structure. An alternate view of the tetrameric units would be that of cyclic *commo*-lithiacarboranes.

The group 1 metallacarboranes are the most common precursors in the syntheses of the *p*-, *d*- and *f*-block carboranes. Their first widespread use was by Hawthorne in the preparation of the icosahedral MC_2B_9 metallacarboranes. The carborane anions were initially produced by the degradation of orthocarborane, *closo*-1,2-$(CR)_2B_{10}H_{10}$ (R = H or a singly bonded substituent), with alcoholic KOH, as shown in eq. 2 [12]. The monoanion could be further deprotonated with a strong base such as NaH to give the [$(CR)_2B_9H_9$]$^{2-}$, which acts as a versatile 6-π electron donor ligand for a variety of metals, [13,14]. Equation (2) involves a multiple ethoxide attack on one of the cage borons of the orthocarborane, with apparently little active participation of the K^+ ion [12].

$$1,2\text{-}(CR)_2B_{10}H_{10} + KOCH_2CH_3 + 2CH_3CH_2OH \xrightarrow[\text{KOH}]{\text{Reflux}} K[(CR)_2B_9H_{10}] + B(OC_2H_5)_3 + H_2 \quad (2)$$

Since the reactivity of [$(CR)_2B_9H_{10}$]$^-$ and [$(CR)_2B_9H_9$]$^{2-}$ was the same for a number of different univalent cations, the group 1 metals were considered to be spectators whose main function was to maintain charge neutrality and were not considered as integral parts of the cages or active participants in their ensuing reactions [13]. Direct evidence of the exo-polyhedral locations of the group 1 metals has recently been furnished by Oki and coworkers who determined the solid state structure of the cesium salt of the [$C_2B_9H_{12}$]$^-$ monoanion, views of which are shown in **Figures 5** and **6** [15].

As can be seen, the structure consists of four $CsC_2B_9H_{12}$ arranged about a CsCl ion pair (Figure 5), with the [$Cs_5(C_2B_9H_{12})_4Cl$] units further associated through Cs-H-B bridges to give an extended polymeric network. It is of interest to note that none of the cesium ions occupy the apical positions above the open C_2B_3 faces of the carboranes.

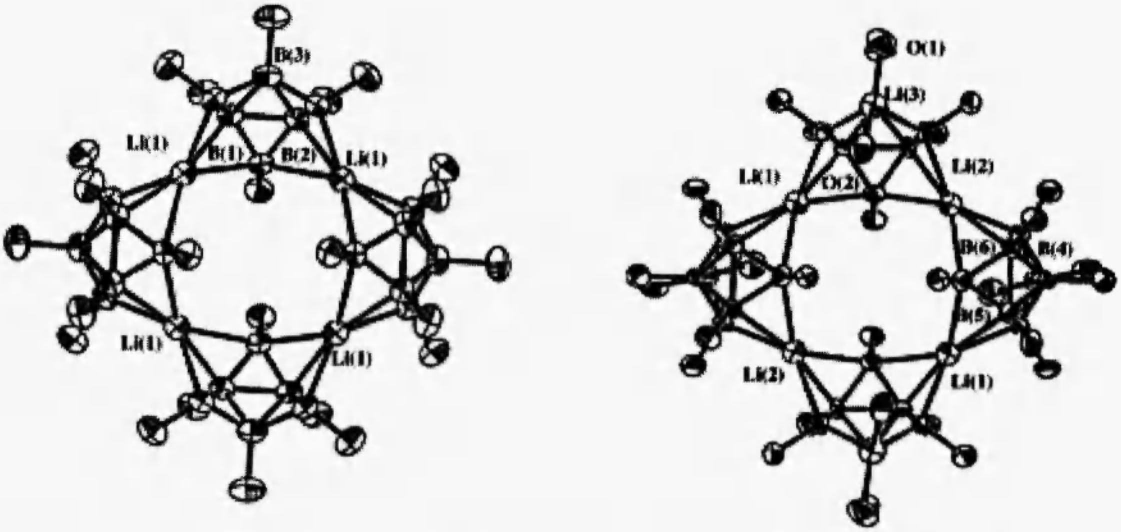


Figure 4. Perspective view of (A) [Li(12-crown-4)]$_4$[(MeCH)$_3$(BMe)$_3$Li]$_4$ and (B) [MeCH)$_3$(BMe)$_3$Li$_2$(C$_5$H$_{10}$O)$_2$]$_4$. For clarity, The [Li(12-crown-4)]$^+$ and the hydrogen atoms are omitted and only the O's in C$_5$H$_{10}$O are shown. Reprinted with permission from reference 11.

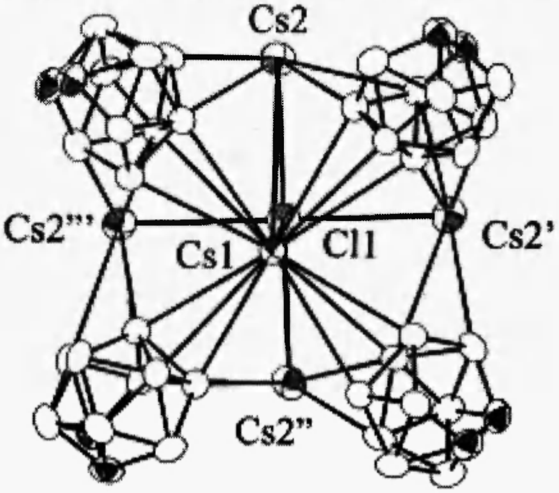


Figure 5. Perspective view of [Cs$_5$(C$_2$B$_9$H$_{12}$)$_4$Cl]. Terminal hydrogens omitted for clarity. Reprinted with permission from reference 15.

The authors report that the 12th hydrogen undergoes fast tautomerization between the two bridging positions between the adjacent boron atoms on the C_2B_3 open face (see **Figure 6**). At present, it is not known whether the bridging hydrogen effectively blocks the apical position or if preferential metal-carborane attractions favor the exo-polyhedral positions of the cesium ions.

Direct reaction of *closo*-1,2-$C_2B_{10}H_{12}$ with strong bases such as C_4H_9Li results in the deprotonation of the cage carbons, to give 1,2-$(CLi)_2B_{10}H_{10}$, which allows for the introduction of a number of different derivative groups, producing materials with interesting and useful properties [16]. Other metalating agents, including Grignard reagents, have also been used to remove the terminal C-H bonds [17]. While these metals are exo-polyhedral and are technically outside the range of this review, their importance as starting materials warrants their mention.

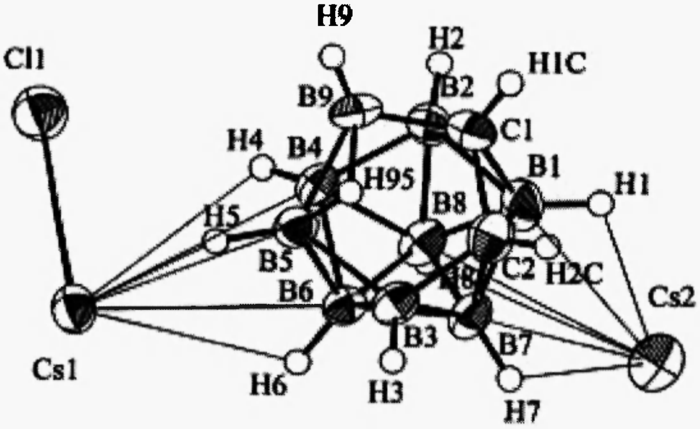


Figure 6. Perspective view of $[Cs_5(C_2B_9H_{12})_4Cl]$ showing the Cs-cage interactions. Terminal hydrogens omitted for clarity. Reprinted with permission from reference 15.

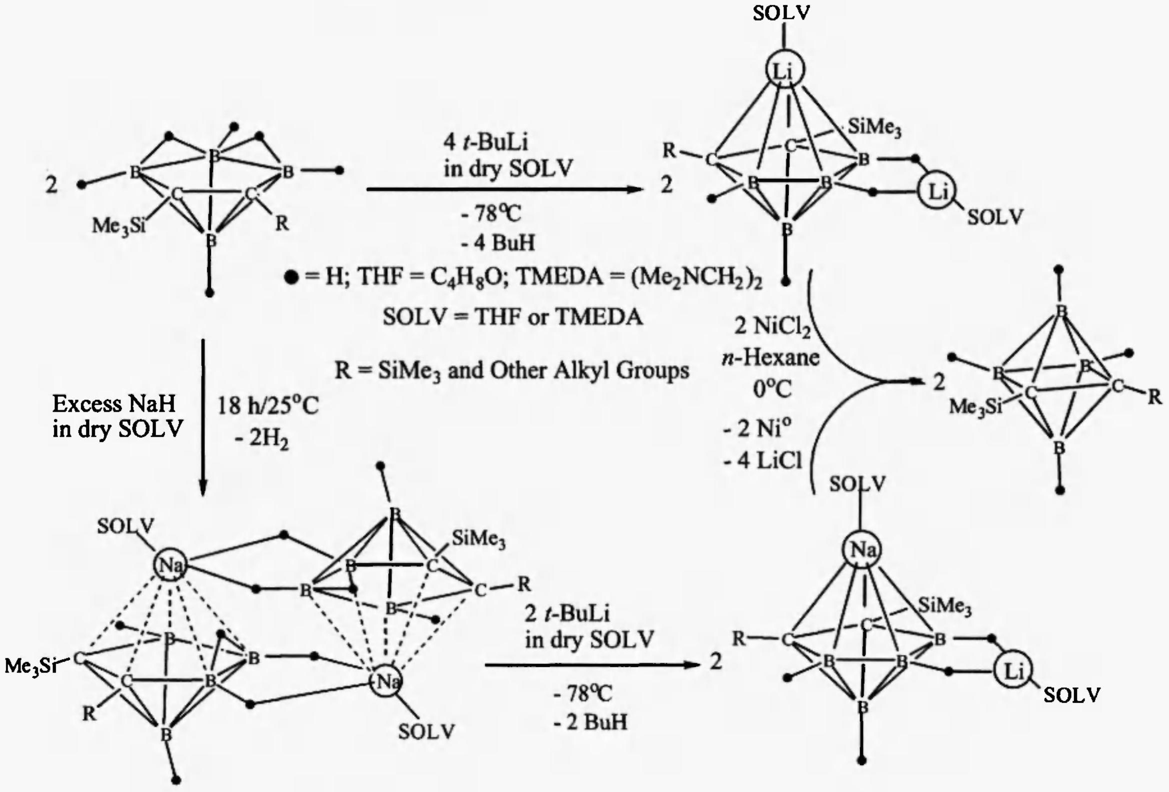
There seems to be a more direct metal involvement with the smaller, C_2B_4 cages. As with the larger $[C_2B_9H_{11}]^{2-}$ carboranes, the $[nido\text{-}(CR)_2B_4H_4]^{2-}$ dianions has been found to be excellent 6 π- electron donor ligands [14]. However, unlike $[C_2B_9H_{11}]^{2-}$, their formation requires two distinctly different base reactions. It has been repeatedly demonstrated that a base such as NaH removes only a single proton from *nido*-2,3-$(CR)_2B_4H_6$, even at elevated temperatures and with stronger bases such as KH (see eq. 3) [18,19]. This result is surprising since other bases, such as C_4H_9Li, deprotonate the monoanion and can easily remove two protons from *nido*-2,3-$(CR)_2B_4H_6$, as snown in **Scheme 1**.

$$nido\text{-}2,3\text{-}(CR)_2B_4H_6 + \text{NaH (excess)} \xrightarrow[0-150\ ^\circ C]{THF} Na[nido\text{-}2,3\text{-}(CR)_2B_4H_5] + H_2 \qquad (3)$$

Terminal hydrogens omitted for clarity. Reprinted with permission from reference 20. Insight into the reason for the stoichiometry of eq. 3 was furnished by the solid state structure of the sodium compound of the monoanion, $[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5]^-$, shown in **Figure 7**. The crystal structure is that of an extended chain of $[(THF)Na]_2[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5]_2$ dimers that are layered on top of one another [20]. Structurally, each cluster is composed of two 1-(THF)-1-Na-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ units that are associated in a head-to-tail dimer through the interaction of the apical Na in one unit with the B(4,6)-H groups on a neighboring carborane. The structure of the TMEDA solvated sodium salt of this carborane anion showed similar dimer formation [21]. It is quite apparent that the bridge hydrogens in such dimers are well protected within the clusters. The kinetics of eq. 3, studied by Grimes and coworkers [19], was consistent with a mechanism in which the carborane reacts directly with a hydride site on the solid base. Considering the high solubility of the sodium compounds in low dielectric solvents such as THF, TMEDA and C_6H_6, it is quite likely that the dimers shown in **Figure 7** persist in solution, resulting in a monoanionic species that sterically cannot react with the solid hydride base.

The fact that the more extensively solvated [*exo*-4,5-$\{(\mu\text{-}H)_2Na(TMEDA)_2\}$-2-$(SiMe_3)$-3-Me- *nido*-2,3-$C_2B_4H_5$], in which the $[(TMEDA)_2Na]^+$ is well removed from the carborane cage (see **Figure 8**), reacts readily with NaH to give the dianion is further support for this steric argument [22].

Scheme 1. Synthetic Route for Group 1 Metal -Complexed Carboranes



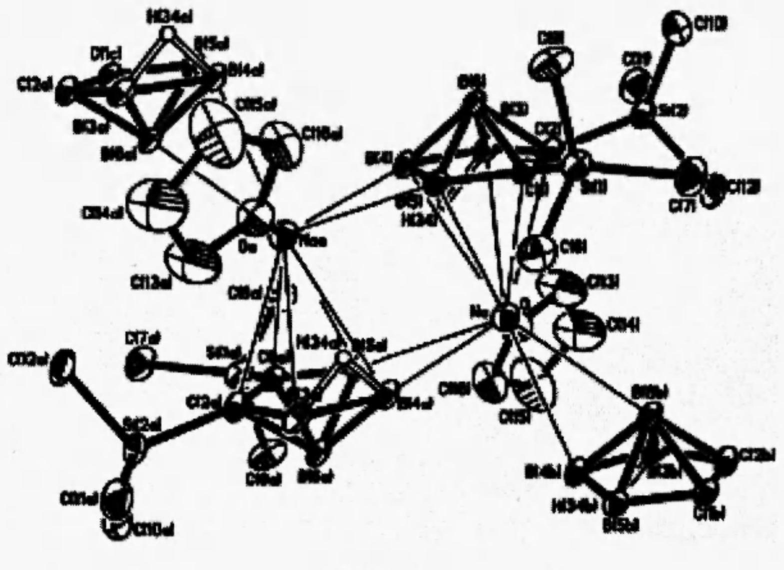


Figure 7. Perspective view of the $[(THF)Na]_2[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5]_2$ dimer.

The unprotected bridged hydrogen in the similarly solvated lithium compound, $[Li(TMEDA)_2^+][$*nido*$\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5^-]$, was also found to be reactive towards NaH [23]. It is of interest to note that, unlike the cesium compound of the C_2B_9 cage shown in **Figure 5**, the presence of a bridge hydrogen in the smaller, C_2B_4 cage system does not seem to block the metal from the apical position.

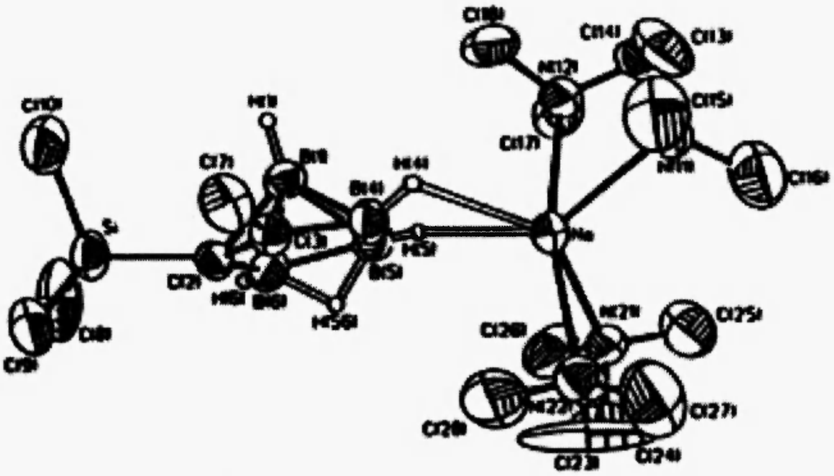


Figure 8. Perspective view of the *exo*-4,5-[(μ-H)$_2$Na(TMEDA)$_2$]-2-(SiMe$_3$)-3-(Me)-*nido*-2,3-$C_2B_4H_5$. Terminal hydrogens omitted for clarity. Reprinted with permission from reference 22.

The structure of the group 1 dianionic compound, [*exo*-4,5-{(μ-H)$_2$Li(TMEDA)}-1-Li(TMEDA)-2,3-(SiMe$_3$)$_2$-*closo*-2,3-$C_2B_4H_4$], given in **Figure 9**, shows that one [(TMEDA)Li] unit occupies the apical position above the C_2B_3 face of the carborane, with the other solvated Li being exo-polyhedrally bound through B(4,5)-H bridges [21]. While the closo designation is consistent with both the structure and the cage electron pair count of 8, it is not apparent that the [(TMEDA)Li]$^+$ ion is in any way isolobal with a B-H group; the apical position might simply be that favored by electrostatic interactions.

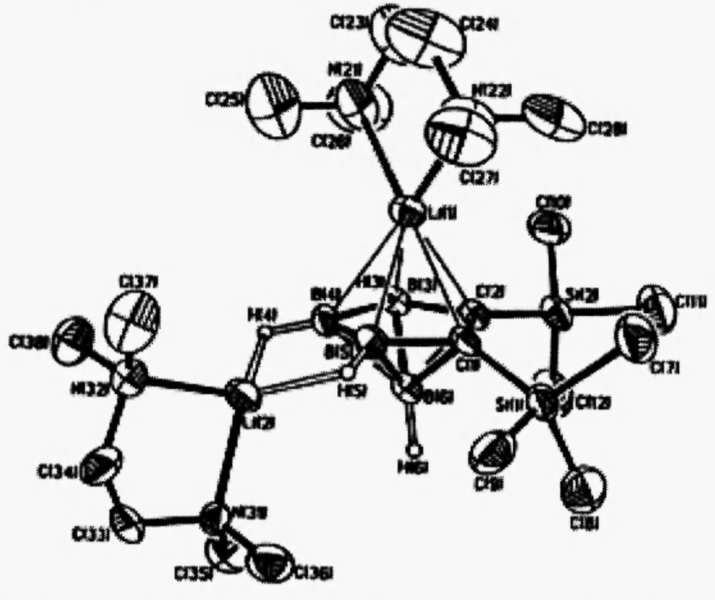


Figure 9. Perspective view of the *exo*-4,5-[(μ-H)$_2$Li(TMEDA)]-1-Li(TMEDA)-2,3-(SiMe$_3$)$_2$-*closo*-2,3-$C_2B_4H_4$. For clarity only the cage H's are shown. Reprinted with permission from reference 21.

The compound could alternately described as a half sandwich lithium complex in which the nido-carborane dianion is η^5– bonded to the capping Li. The compound exhibits two ^{7}Li NMR resonances, one at δ –1.60 ppm and another at –6.08 ppm (relative to $LiNO_3$(*aq*)), the former was ascribed to the exo-polyhedrally bound Li, with the latter assigned to the capping atom [21]. The ^{7}Li NMR of the mixed Na/Li salt, *closo-exo*-Li(THF)-1-Na(THF)-2-(SiMe$_3$)-3-Me-2,3-$C_2B_4H_4$, formed by the sequential reaction of NaH and BuLi, shows only a peak at −1.82 ppm, indicating only an exo-polyhedral lithium. The absence of an apical lithium shows that the locations of the group 1 metals are determined by the order of reaction, the first one occupies the apical position while the second one is relegated to a position outside of the cage. In the solvents studied, C_6H_6, THF and TMEDA, there seems to be no evidence of metals exchanging positions. In view of the low dielectric constants of these solvents, this is not surprising.

Figure 10 shows the crystal structure of [Li$^+$(TMEDA)$_2$]$^+$[*commo*-1,1'-Li{2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_5$}$_2$]$^-$, which was obtained in 61% yield from the slow sublimation of a TMEDA solution of the monolithium carborane at 160-170 °C [24]. The synthesis is of interest in that the Li sandwich compound was a fairly high yield sublimation product, meaning that either it or, more likely, the monolithium compound was volatilized. The structure of the sandwich compound shows that a lithium, Li(1) in **Figure 10**, is symmetrically bound to two [*nido*-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_5$]$^-$ monoanions, with the other lithium, Li(4), being involved in a well separated [Li$^+$(TMEDA)$_2$]$^+$ cation (not shown). The Li(1)-Cnt (Cnt = C_2B_3 centroid) distances average 2.059 Å, which is somewhat longer than the 1.906 Å of the monolithium precursor, but close to the Li-Cp$_{(cnt)}$ value of 2.008 Å found in [Cp_2Li]$^-$ (Cp = $C_5H_5^-$) [25]. The ^{7}Li NMR of the lithiacarborane sandwich shows resonances for both the exo-polyhedral Li (δ 0.29 ppm) and the commo-lithium (δ−2.60 ppm), indicating that the sandwich structure persists in solution [24]. To date, no other group 1 metallacarborane full-sandwich compounds have been reported.

There is another isomeric form of the nido-C_2B_4 cage in which the two cage carbons are not adjacent to one another, but are separated by a boron atom. The "carbons apart" dianions of the type [2,4-$(CR)_2B_4H_4$]$^{2-}$ have also been shown to be excellent ligands for metals [14(b), 26,27].

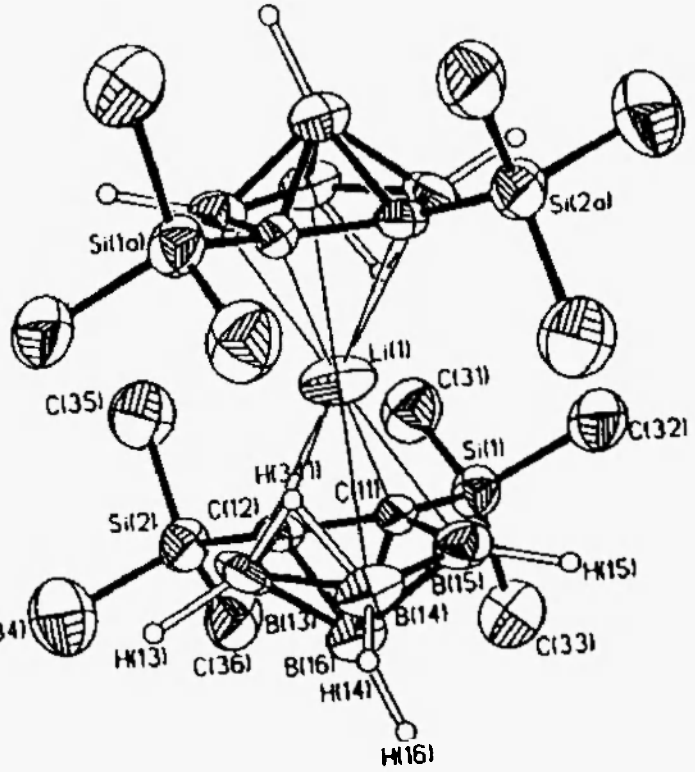


Figure 10. Perspective view of the [Li(TMEDA)$_2$]$^+$[*commo*-1,1'-Li{2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_5$}$_2$]$^-$. For clarity only the cage hydrogens are shown. Reprinted with permission from reference 24.

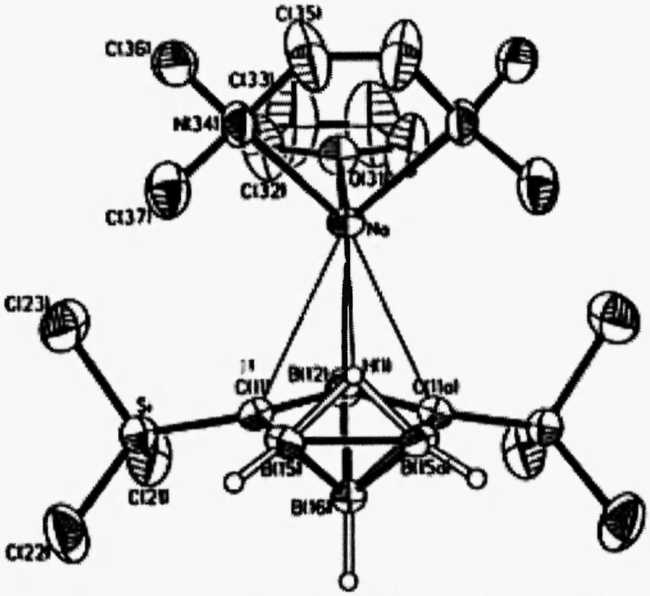
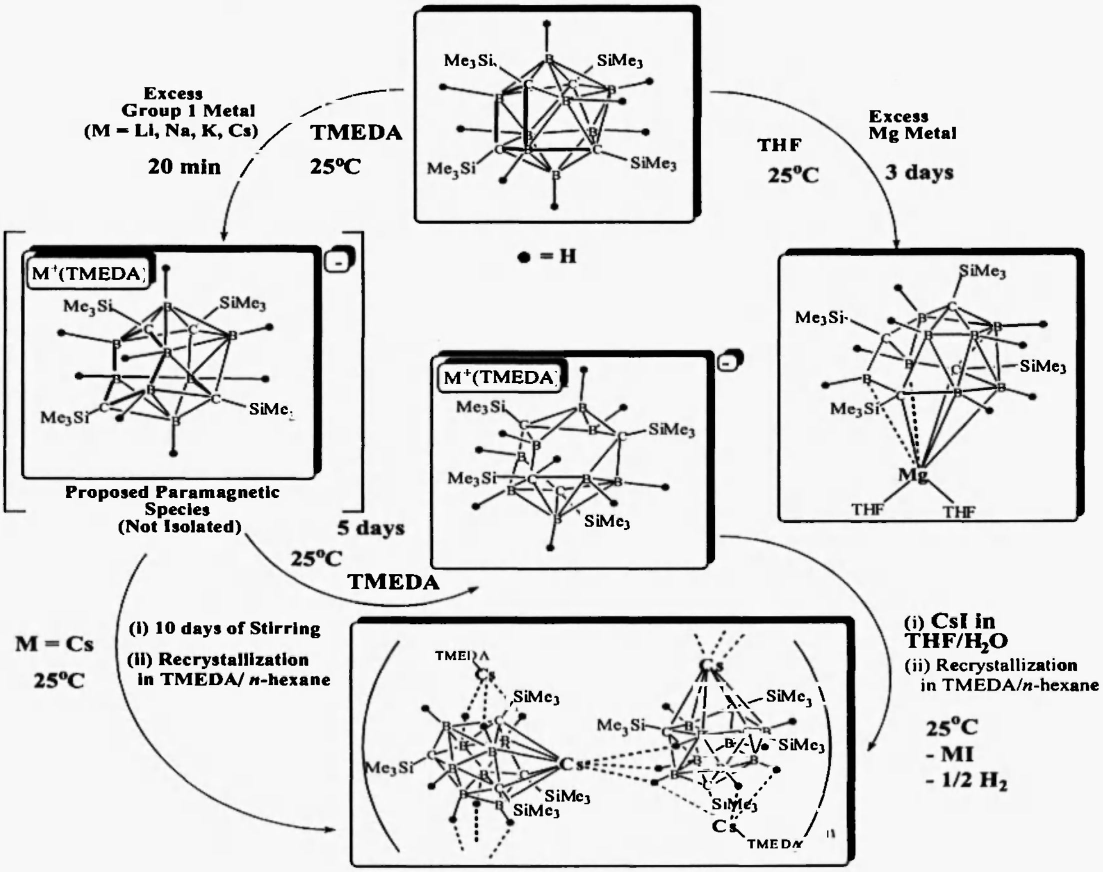


Figure 11. Perspective view of 1-(THF)-1-(TMEDA)-1-Na-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_5$. For clarity only the cage hydrogens are shown. Reprinted with permission from reference 25.

Scheme 2. Syntheses of Tetracarbon-carborane Compounds of Group 1 and Group 2 Metals



The structures of the group 1 compounds of both the mono- and dianionic salts of the "carbons apart" carboranes are similar to that of their "carbons adjacent" analogues in that in the monoanionic compound of the metal occupies the apical position above the C_2B_3 face, as shown in the structure of 1-(THF)-1-(TMEDA)-1-Na-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_5$ given in **Figure 11** [28], while in the dianionic compounds both apically and exo-polyhedrally bound metal groups are present [29].

The structures of several group 1 compounds in the C_4B_8 system have been reported [301. The tetracarbon carborane, *nido*-2,4,6,12-$(SiMe_3)_4$-2,4,6,12-$C_4B_8H_8$ was found to react with the group 1 metals, Li, Na, K, and Cs, in a two-step process, as shown in **Scheme 2**. The first step produced a paramagnetic intermediate which reacted slowly with another equivalent of metal to form a diamagnetic dianion, $[(SiMe_3)_4C_4B_8H_8]^{2-}$. For all metals except Cs, the dianion picked up a proton to form $[(THF)_4M][(SiMe_3)_4C_4B_8H_9]$, in which the solvated group 1 metal was well removed from the cage; the yields ranged from 35-45% [30]. In the case of Cs, protonation of the carborane dianion did not occur, instead the polymeric [*exo*-Cs(TMEDA)-1-Cs-$(SiMe_3)_4C_4B_8H_8]_n$ was obtained in 41% yield. The structure of the dicesiacarborane, which is given in **Figure 12**, shows that one Cs occupies an apical position above an open six member C_3B_3 face and also bonds to a B_3 face of a neighboring carborane. The net effect is a staggered $-C_4B_8-Cs-C_4B_8-Cs-$ polymeric structure. The second Cs, is not part of the chain but is attached to each cage through upper and lower belt Cs–H–E bonds (E = B,C) [30].

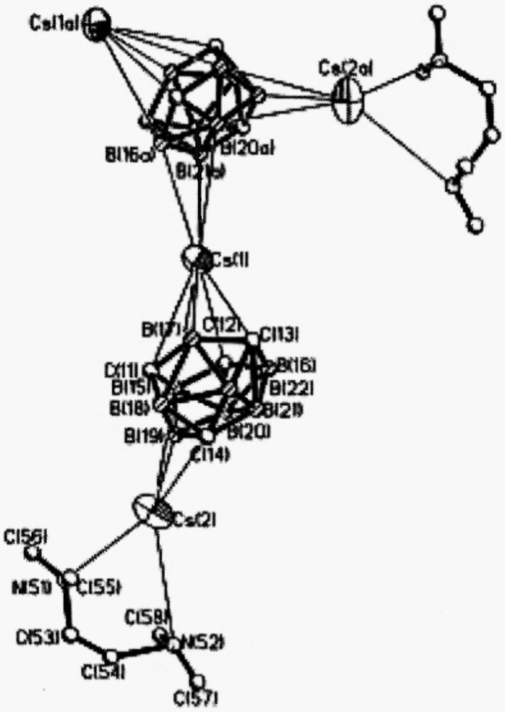
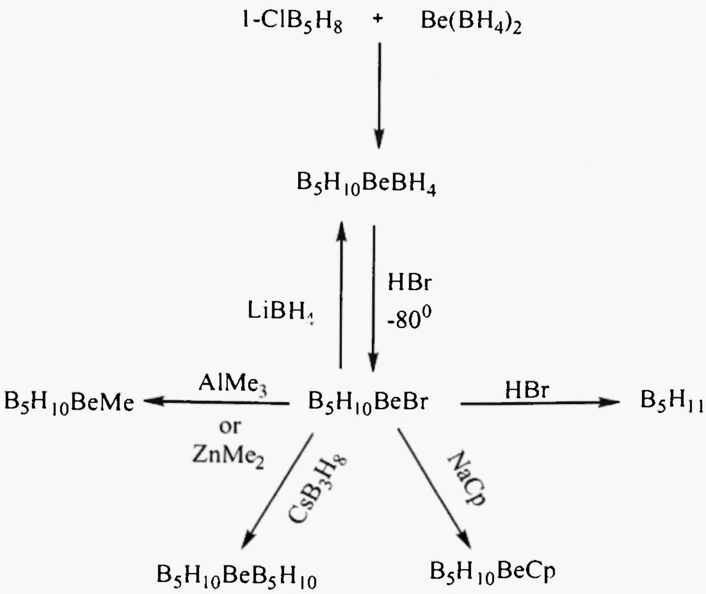


Figure 12. Crystal structure of [*exo*-Cs(TMEDA)-1-Cs-$(SiMe_3)_4C_4B_8H_8]_n$. For clarity, all H atoms and the $SiMe_3$ groups are omitted. Reprinted with permission from reference 30.

Group 2 Metallaboranes and Metallacarboranes

The structural information available on the group 2 metals is not plentiful, and, with several notable exceptions, seems to be limited to the two smallest members of that group, beryllium and magnesium. Gaines and coworkers reported the synthesis and structure of beryllium bis(octahydrotriborate), $Be(B_3H_8)_2$ from the reaction of $BeCl_2$ and CsB_3H_8 [31]. The structure showed that the beryllium was associated with each B_3H_8 cage through two B-H-Be bonds, resulting in an essentially tetrahedral coordination of the Be atom. All the beryllium atoms are exo- to the B_3H_8 cages and their interactions are similar to those found in the metal tetrahydroborates.

Scheme 3. Summary of the reaction chemistry of $B_5H_{10}BeX$ compounds



The $Be(B_3H_8)_2$ molecule was found to react with NaC_5H_5 and $Zn(CH_3)_2$ to give $(C_5H_5)BeB_3H_8$ and $(CH_3BeB_3H_8)_2$, respectively [31]. A number of beryllaboranes of the general type, $B_5H_{10}BeX$ (X = BH_4, B_5H_{10}, Cl, Br, CH_3, and C_5H_5) were synthesized as shown in **Scheme 3** [32]. The structure of $B_5H_{10}BeBH_4$, given in **Figure 13**, is that of a distorted nido-B_5Be pentagonal pyramidal cage in which a Be atom occupies one of the basal positions [33]. Even though it is distorted, the Be seems to be fully incorporated into the cluster; the relevant bond distance are: Be-B(1) = 2.033Å, Be-B(3) = 1.967Å and Be-B(6) = 1.983Å. The $B_5H_{10}Be$ cage is similar to that of B_6H_{10} except that a Be has replaced one of the borons and an extra bridged hydrogen is present. The compound is of special interest in that it contains two B-H-Be bridges.

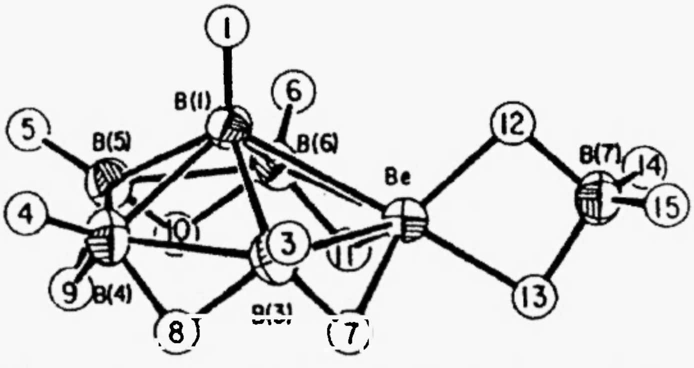


Figure 13. Crystal structure of $B_5H_{10}BeBH_4$. Reprinted with permission from reference 33.

The cage electron count of 16 (10 from the B's + 5 from the bridge H's + 1 from the Be) is consistent with the nido- structure.

The structures of the other $B_5H_{10}BeX$ compounds were not determined, but the similarities in their stoichiometries and their ^{11}B NMR spectra argue for structures similar to that given in **Figure 13** with different substituents on the Be atom [33]. The reaction of $B_5H_{10}BeBr$ with CsB_3H_8 led to the formation $B_5H_{10}BeB_5H_{10}$, a commo-beryllaborane in which the Be atom occupies a basal position in two nido-cages, with the dihedral angle between the basal planes of tne cages being 66° (see **Figure 14**) [33].

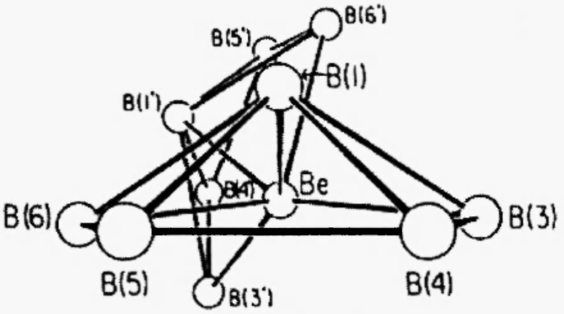


Figure 14. Perspective view of 2,2'-*commo*-Be$(B_5H_{10})_2$ showing the relative orientations of the B_5H_{10} cages. Reprinted with permission from reference 33.

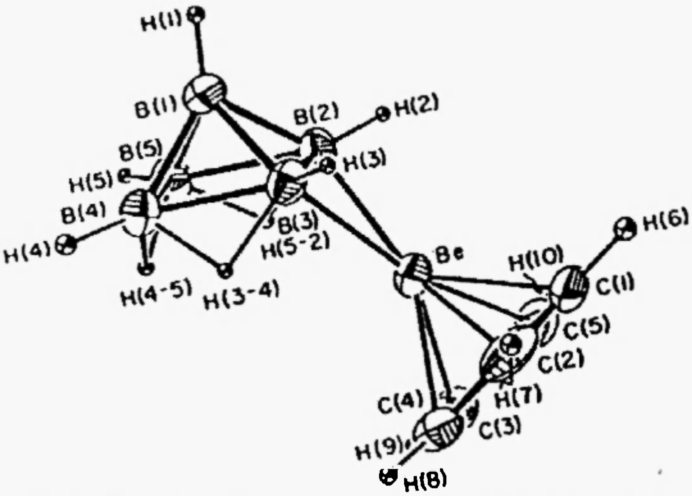


Figure 15. Crystal structure of $[\mu\text{-}(\eta^5\text{-}C_5H_5)Be]B_5H_8$. Reprinted with permission from reference 34.

A different beryllaborane, $[\mu\text{-}(\eta^5\text{-}C_5H_5)Be]B_5H_8$, was obtained from the reaction of $(\eta^5\text{-}C_5H_5)BeCl$ and the pentaborane salt, KB_5H_8 [34]. The structure is that of pentaborane(9), with a $[(\eta^5\text{-}C_5H_5)Be]$ group replacing a bridging hydrogen (see **Figure 15**). The bridging beryllium group can be removed by reaction with a Brönsted acid, HX, to regenerate the B_5H_9 and $(\eta^5\text{-}C_5H_5)BeX$ [34]. Several magnesaboranes have been reported in which the Mg occupies bridging positions, among these are $Mg(THF)_2(B_6H_9)_2$ [35] and $Mg(THF)_2(2\text{-}CH_3B_6H_8)_2$ [36]. The compounds were formed by the deprotonation of B_6H_{10} or $2\text{-}CH_3B_6H_9$ by either CH_3MgBr or $Mg(CH_3)_2$ in THF. The structure of $Mg(THF)_2(B_6H_9)_2$, given in **Figure 16**, shows that a $(THF)_2Mg$ group replaces a bridged hydrogen on the open pentagonal face of each borane [35]. Both the proton and ^{11}B NMR spectra show the compounds to be fluxional. Diethyl magnesium and MeMgI have also been found to react at low temperature with decaborane(14) to give $(Et_2O)_2MgB_{10}H_{12}$ [37], and $B_{10}H_{14-n}(MgI)_n$ (n = 1 and 2) [38], respectively. The latter compounds reacted with water to give MgIOH and $B_{10}H_{14}$, while the former decomposed in water with the evolution of hydrogen.

In contrast to the boranes, there has been a number of reports on the group 2 metallacarboranes, one reason being that a carbon + a group 2 element combination is isoelectronic with two boron atoms. This isoelectronic relationship lead Popp and Hawthorne to explore the syntheses and properties of the beryllacarboranes in the MC_2B_9 cage systems [39,40]. These investigators report that a benzene solution of $(3)\text{-}1,2\text{-}C_2B_9H_{13}$ reacted with a diethyl ether solution of dimethylberyllium to give a beryllacarborane, as outlined in eq. (4).

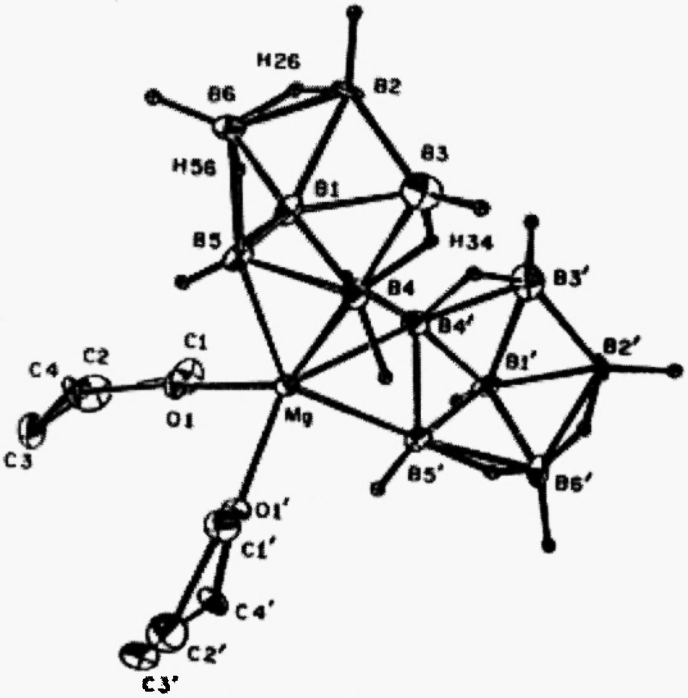


Figure 16. Crystal structure of $(THF)_2Mg(B_6H_9)_2$. Fro clarity thr THF H's are omitted. Reprinted with permission from reference 35.

$$C_2B_9H_{13} + Be(CH_3)_2{\cdot}(OEt_2)_2 \longrightarrow BeC_2B_9H_{11}{\cdot}OEt_2 + OEt_2 + 2\,CH_4 \qquad (4)$$

The $BeC_2B_9H_{11}{\cdot}OEt_2$ was isolated as an extremely air and water sensitive solid that could not be fully characterized; the formulation of the product as $BeC_2B_9H_{11}{\cdot}OEt_2$ was inferred by its proton NMR spectra and the identity of the other products. However, when anhydrous $(CH_3)_3N$ was passed through a solution of the beryllacarborane product in dry CH_2Cl_2, the more stable adduct, $BeC_2B_9H_{11}{\cdot}N(CH_3)_3$ was isolated and characterized. Elemental analysis, mass spectra and proton and ^{11}B NMR data were consistent with the structure shown in **Figure 17** [39].

It was further reported that the reaction of $BeCl_2$ with the $[(3)\text{-}1,2\text{-}C_2B_9H_{11}]^{2-}$ failed to product Be insertion, irrespective of the presence or absence of donor solvents [40]. This is of interest in that the reaction of a metal halide with a carborane dianion is a standard metallation procedure. When eq. (4) was attempted using only one mole equivalent of OEt_2 per mole of the beryllium alkyl, a highly insoluble product, thought to be a $[BeC_2B_9H_{11}]_n$ polymer was produced; when this solid was treated with liquid $N(CH_3)_3$ for an extended period of time, the $BeC_2B_9H_{11}{\cdot}N(CH_3)_3$ adduct, shown in **Figure 17**, was formed [40]. Reaction of the base-stabilized beryllacarborane with alcoholic KOH regenerated the $[(3)\text{-}1,2\text{-}C_2B_9H_{12}]^-$ monoanion in about 79% yield [40]. While the structures of the beryllacarboranes could not be determined, the heavier group 2 metals form structurally known metallacarboranes with the [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ ligand [41,42]. Reaction of a THF solution of Na_2[*nido*-7,9-$C_2B_{10}H_{12}$] with CaI_2 produced an insoluble, colorless complex which, on recrystallization from a CH_3CN/Et_2O mixture afforded the calcacarborane, *closo*-1,1,1,1-$(CH_3CN)_4$-1,2,4-$CaC_2B_{10}H_{12}$, whose structure is shown in **Figure 18** [41].

This was the first structurally characterized group 2 metallacarborane. The structure shows that the calcium ion, coordinated the four CH_3CN molecules resides above the C_2B_4 face of the carborane. The Ca-ring-atom distances range from 2.649 Å for B(5) to 2.935 Å for B(7), with an average of 2.814 Å.

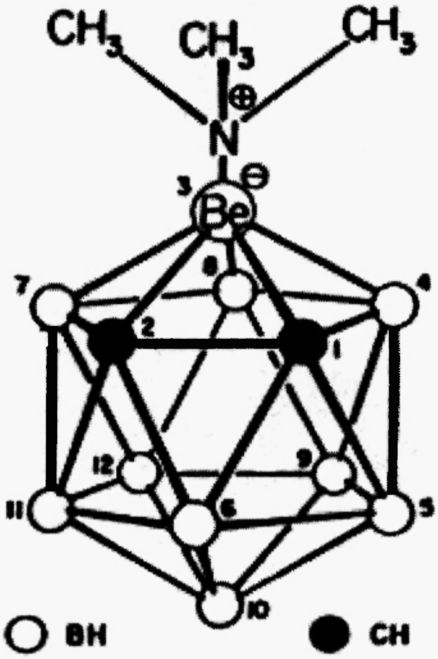


Figure 17. Proposed structure of $[(CH_3)_3N]BeC_2B_9H_{11}$. Reprinted with permission from reference 39.

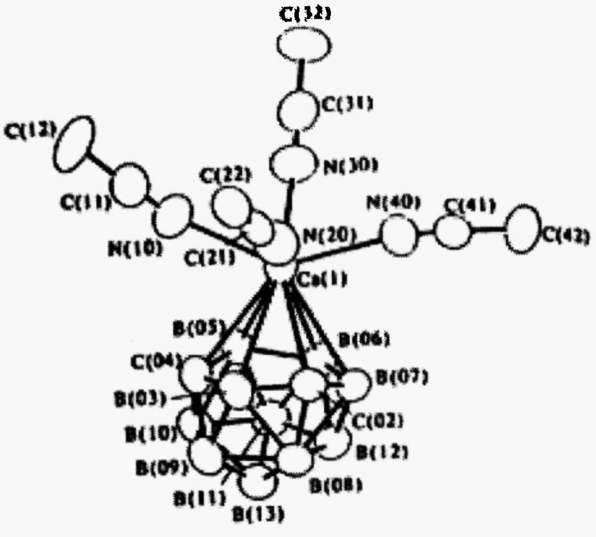


Figure 18. Crystal structure of *closo*-1,1,1,1-$(CH_3CN)_4$-1,2,4-$CaC_2B_{10}H_{12}$. Hydrogens not shown for clarity. Reprinted with permission from reference 41.

Any differences in metal-carborane distances seem to be more a function of the nonplanarity of the C_2B_4 ring rather than a differential bonding preference of the metal. The reaction of SrI_2 and Na_2[*nido*-7,9-$C_2B_{10}H_{12}$] under conditions similar to those used for the calcium carborane, produced the novel polymeric strontium carborane, [*closo*-1,1,1-$(CH_3CN)_3$-1,2,4-$C_2B_{10}H_{12}]_n$, a unit of which is shown in **Figure 19** [42].

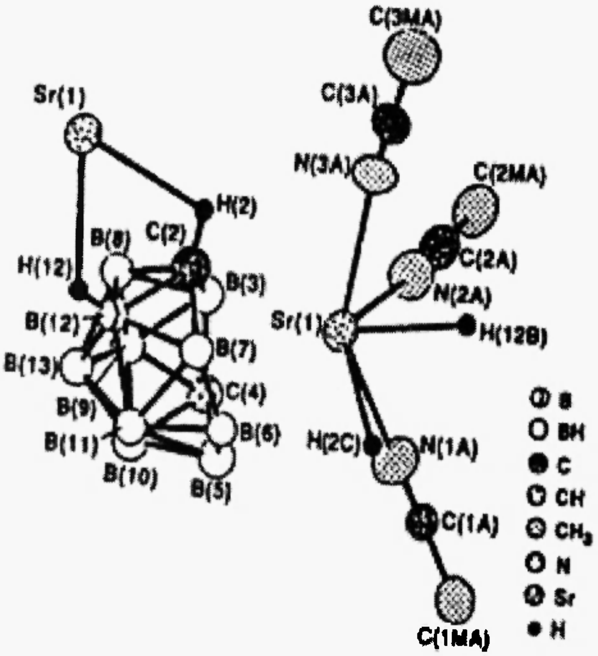
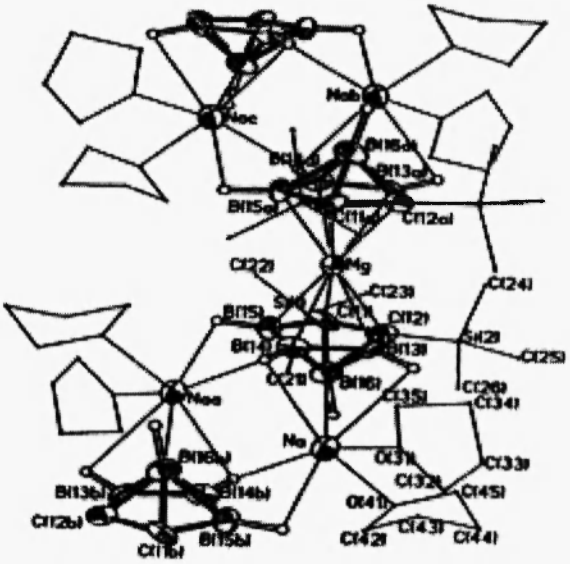


Figure 19. Crystal structure of a section of [*closo*-1,1,1-(CH_3CN)-1,2,4-$SrC_2B_{10}H_{12}]_n$ showing the metal-cage interactions Hydrogens not shown for clarity. Reprinted with permission from reference 42.

The structure shows a cage geometry similar to that of the calcium carborane, except that one of the solvating CH_3CN molecules is replaced by a set of Sr-H-X bridge bonds to a neighboring carborane, where X is a boron on the lower belt of the carborane and a carbon on its C_2B_4 upper ring. The preference for the carbon over one of the four available upper ring borons is unusual. Since the ^{11}B NMR of both the group 2 carboranes are quite similar, it was thought that the strontium complex was momomeric in solution; the authors reported evidence that at high temperatures the calcium carborane may lose a molecule of CH_3CN to form a polymeric ($CaC_2B_{10}H_{12}$)(CH_3CN)$_3$ complex [42].

The reactions of the mono- and dianions in the 2,3-C_2B_4 and 2,4-C_2B_4 cage systems with various magnesium reagents have been studied and are summarized in **Scheme 4** [43,44]. The magnesium reagents used were Mg(*n*-C_4H_9)$_2$, $MgBr_2$ and Mg(CH_3)Br, which are standard metallating precursors. However, **Scheme 4** demonstrates that contrasting results can be obtained from slight changes in the carborane and magnesium reagents. The magnesium dialkyl reacted with 2 mole equivalents of *nido*-1-Na(L)$_n$-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_5$ (n = 1, L = TMEDA; n = 2, L = THF) to give the corresponding full- sandwich magnesacarborane, [Na(L)$_n$]$_2$[*commo*-1,1'-Mg{2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$}$_2$] (n = 2, L = THF; n = 1, L = TMEDA), the structure of the THF solvated compound is shown in **Figure 20**.

In these complexes the two carborane cages are η^5-coordinated to the commo-magnesium atom, with an average Mg–C_2B_3 bond distances being 2.426±0.022 Å. In like manner, the reaction of $MgBr_2$ with the carbons apart *closo-exo*-5,6-[(μ-H)$_2$Li(TMEDA)]-1-Li(TMEDA)-2,4-($SiMe_3$)$_2$-2,4-$C_2B_4H_4$ in a 1:1 molar ratio produced the half-sandwich complex (see **Scheme 4**), while a 2:1 carborane-to-$MgBr_2$ molar ratio afforded the full-sandwich, [Li(TMEDA)]$_2$[[*commo*-1,1'-Mg{2,4-($SiMe_3$)$_2$-2,4-$C_2B_4H_4$}$_2$], the THF solvated dilithium carboranes reacted similarly [44].



L = THF [n = 2, (IV)] or TMEDA [n = 1, (V)] L = TMEDA (VI) or THF (VII)

Figure 20. A perspective view of the polymeric full-sandwich magnesacarborane, $[Na(THF)_2]_2$[*commo*-1,1'-Mg{2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$}$_2$]. For clarity, the solvated THF molecules and the *exo*-polyhedral $SiMe_3$ units are drawn with circles of arbitrary radii. Reprinted with permission from reference 44.

While the reactions with either the dialkyl- or dihalo-magnesium compounds seem to be straightforward, use of $(CH_3)MgBr$ as the metallating agent initiated a more complex reaction sequence. When *nido*-1-Na(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ was reacted with the Grignard reagent in a 1:1 molar ratio, the expected half-sandwich complex, *closo*-1-Mg(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ was formed in 87% yield [44]. The compound, shown in **Figure 21**, crystallized as a dimer of two opposing MgC_2B_4 cages, with each magnesium occupying an apical position above the C_2B_3 face of one carborane and bonded to the unique boron of the other carborane unit *via* a Mg-H-B bridge [44].

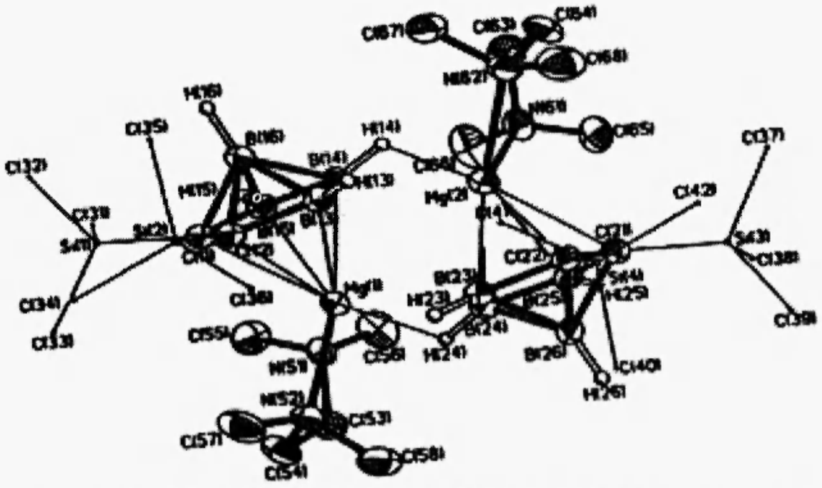


Figure 21. A perspective view of the dimeric magnesacarborane, *closo*-1-Mg(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$. For clarity, the *exo*-polyhedral $SiMe_3$ groups were drawn with circles of arbitrary radii and the methyl and methylene H's are omitted. Reprinted with permission from reference 44.

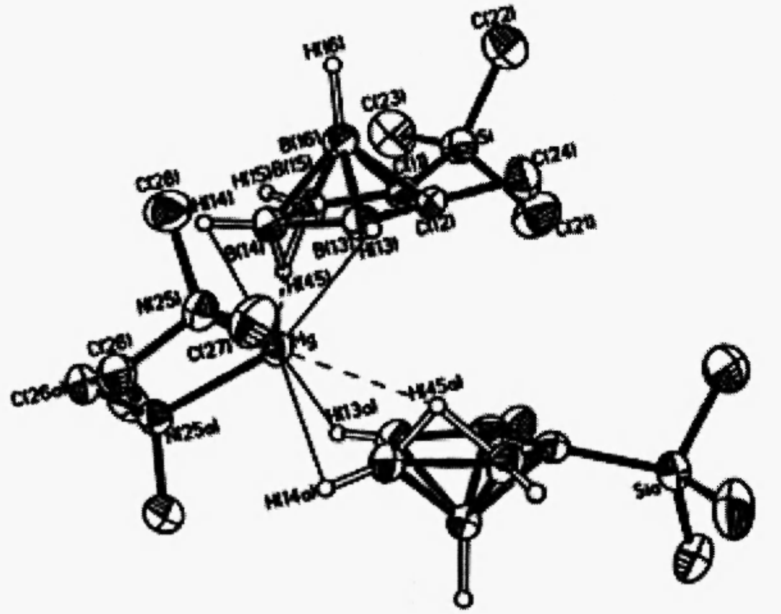


Figure 22. A perspective view of *commo-exo*-4,4',5,5'-Mg(TMEDA)$_2$[2-(SiMe$_3$)-3-(Me)-2,3-$C_2B_4H_5$]$_2$. For clarity, the methyl and methylene H's are omitted. Reprinted with permission from reference 44.

On the other hand, when *nido*-1-Na(TMEDA)-2-(SiMe$_3$)-3-(Me)-2,3-$C_2B_4H_5$ was used, a 2:1 carborane-to-Grignard molar ratio produced the unusual full-sandwich exo-complex, *commo-exo*-4,4',5,5'-Mg(TMEDA)[2-(SiMe$_3$)-3-Me-2,3-$C_2B_4H_5$]$_2$ in 94% yield.

On the other hand, when *nido*-1-Na(TMEDA)-2-(SiMe$_3$)-3-(Me)-2,3-$C_2B_4H_5$ was used, a 2:1 carborane-to-Grignard molar ratio produced the unusual full-sandwich exo-complex, *commo-exo*-4,4',5,5'-Mg(TMEDA)[2-(SiMe$_3$)-3-Me-2,3-$C_2B_4H_5$]$_2$ in 94% yield.

Although the mechanism for this reaction is not known, it was speculated to involve an initial formation of a half-sandwich intermediate of the form 1-(TMEDA)-1-Me-2-(SiMe$_3$)-3-(Me)-1,2,3-$MgC_2B_4H_5$ which would disproportionate *via* a Schlenk-type equilibrium to give the commo-exo-product and (Me)$_2$Mg(TMEDA), as shown in **Scheme 4**. Such an equilibrium was suggested by Wade and coworkers in the dioxane-induced disproportion of the Grignard, (2-Me-1,2-$C_2B_{10}H_{10}$)MgBr to give $MgBr_2$ and (2-Me-1,2-$C_2B_{10}H_{10}$)$_2$Mg, which was thought to favor the dicarboranyl magnesium [45]. Irrespective of the mechanism, the 94% yield for the production of the exo-sandwich magnesium compound suggests a major mechanistic pathway. It is of interest to note that the carbons apart carborane, *nido*-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_5$ reacts with MeMgBr in a 1:1 molar ratio to give the half-sandwich, *closo*-1-Mg(THF)$_3$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$ in 89%yield, with seemingly no complications such as those depicted in **Scheme 4** [40]. At this point it is not known what role the substitution of an Me for an SiMe$_3$ group in the precursor carborane played in determining the course of these reactions; if it turns out to be a significant one, it would constitute one of the few examples of a cage carbon substituent materially effecting the course of a metallation reaction.

The reactions of the tetracarbon carborane, *nido*-2,4,6,12-(SiMe$_3$)$_4$-2,4,6,12-$C_4B_8H_8$ with a variety of group 1 metals have already been discussed (vide supra). This carborane, and several of its B-alkylated derivaties, can also be reductively opened with magnesium metal, as was shown in **Scheme 2**. Two different cage structures were isolated, one found in (THF)$_2$Mg(SiMe$_3$)$_4$(B-Me)$C_4B_7H_7$ (see **Figure 23**) and another in the (L)$_2$Mg(SiMe$_3$)$_2$(R)$_2$(B-Y)$C_4B_7H_7$ (L = THF, R = SiMe$_3$, Y = *t*-Bu; L = THF, R = SiMe$_3$, Y = H; (L)$_2$ = TMEDA, R = *n*-Bu, Y = H) series, which have the general cage structure exemplified by that of (THF)$_2$Mg(SiMe$_3$)$_4$(B–*t*-Bu)$C_4B_7H_7$ shown in **Figure 24** [30].

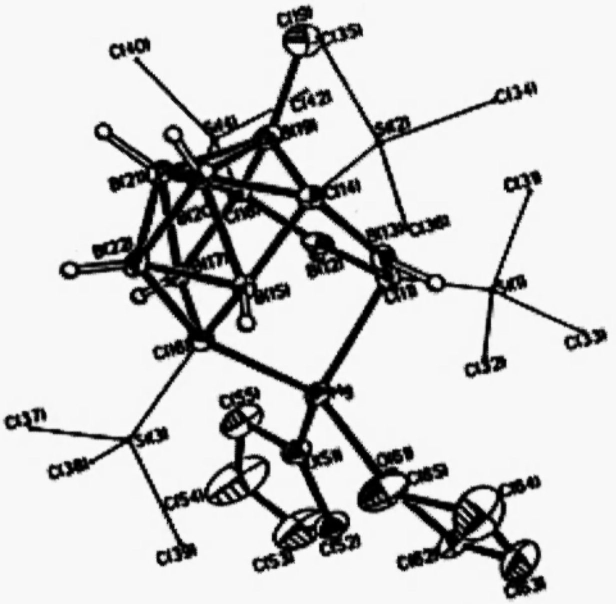


Figure 23. Crystal structure of (THF)$_2$Mg(SiMe$_3$)$_4$(B-Me)C$_4$B$_7$H$_7$. For clarity, the H atoms of the methyl and methylene moieties are omitted and the SiMe$_3$ groups are drawn with circles of arbitrary radii. Reprinted with permission from reference 30.

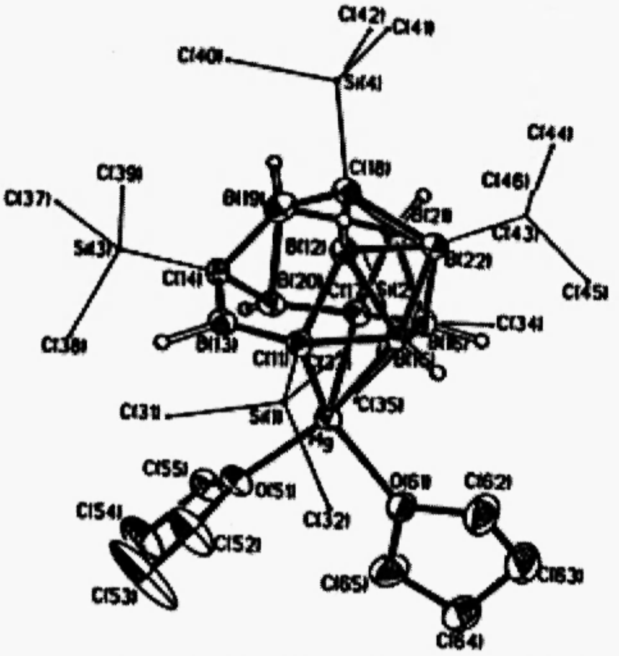


Figure 24. A perspective view of (THF)$_2$Mg(SiMe$_3$)$_4$(B-*t*-Bu)C$_4$B$_7$H$_7$. For clarity, the $B_{(cage)}$-bound *tert*-butyl group and the $C_{(cage)}$-bound SiMe$_3$ groups are drawn with circles of arbitrary radii, and the THF H's are omitted. Reprinted with permission from reference 30.

Both compounds show the presence of electron precise boron and carbon atoms as well as electron deficient cages. At present, there is no ready explanation as to why different structures are produced from essentially equivalent reaction conditions. GIAO ab initio molecular orbital calculation show that the observed ^{11}B NMR chemical shifts of these magnesacarboranes are not consistent with either of the solid state structures [30], indicating rapid isomerization of the species in solution. Thus, those structures shown in **Figures 23** and **24** could represent two kinetically trapped examples of a number of different structures that coexist in equilibrium in solution. Solution fluxionality was proposed by Grimes and coworkers to account for the structures and spectroscopic properties of some transition metal metallacarboranes obtained from the related $(CH_3)_4C_4B_8H_8^{2-}$ carborane dianion [47].

Conclusions

The group 1 and group 2 metals are generally ignored in most discussions of main group metallaboranes and carboranes. However, it is apparent from the above discussions that there is a rich collection of structural and chemical information about these organometallic compounds available. Many of the structures found are those that are easily rationalized by our current descriptions of the electronic structures of the metals and the cages with which they are associated. However, there are just as many that are surprising in view of those same descriptions. One thing that is very well demonstrated is that, at least for the main group metallaboranes and carboranes, there is life before group 13.

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