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Reviews

Evolution of C_2B_4 Carborane Chemistry: from Early Years to the Present

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A review of the chemistry of polyhedral cluster complexes in which s-, p-, d- and f-block metals are incorporated mainly into C_{cage}-trimethylsilyl-substituted C_2B_4 carborane cages is presented. While the main thrust of this review is on the results obtained in authors' laboratories, comparisons are made to similar systems and to those involving both large- and small-cage carboranes. In this way we hope to demonstrate the unique chemistry of the small-C_2B_4-cage systems that has emerged over the last 40 years. However, a full picture of the chemistry of these systems cannot be presented without heavy reference to the larger, more stable 11- and 12-vertex cages, which in many ways preceded their more diminutive cousins. The focus of much of the current research is directed toward systematizing the chemistry of metallacarboranes with the aim of promoting their use as possible electronic, ceramic, and/or catalytic materials. However, such endeavors are based on our knowledge about the fundamental interactions that are at work in determining the structures and properties of these cluster complexes. This review attempts to provide such an overview of small-cage heterocarborane chemistry.

I. Introduction

Carboranes, or carbaboranes, are mixed hydride clusters of carbon and boron in which these elements occupy the vertices of "electron deficient" cages. These clusters can be expanded by incoprating other atoms into the cage structures to give heterocarboranes. When the heteroatom is a metal, the compounds are referred to as metallacarboranes. These compounds have been the subject of a number of reviews that adequately cover the general literature up to 1997, while later mini-reviews exemplify the rapid expansion of the area.[1−5] This review will focus specifically on the most promising research that has been published in recent years on the complexes in which s-, p-, d- and f-block metals are incorporated into C_2B_4 carborane cages to form the respective metallacarboranes.

The structures of the heterocarboranes can be rationalized using a series of electron-counting rules, collectively called "Wade's rules".[6] Two polyhedral structures will be commonly encountered in this review: one in which the cage atoms occupy all the vertices of a closed polyhedron to give a closo structure, while in the other one of the vertices is removed to give an open

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basket like, nido structure. More open geometries, such as arachno and hypho, can be obtained by successively removing other vertices from the nido structure. The electron-counting rules give a simple relationship between the geometry and the number of skeletal electron pairs. In a cluster having n skeletal atoms, a closo structure is found when the number of skeletal electron pairs is equal to $n + 1$, while a nido structure is stabilized by $n + 2$ electron pairs, an arachno structure by $n + 3$ pairs, and a hypho structure by $n + 4$ pairs.[6b] While these rules offer a simple and elegant electron structure−geometry relationship for boranes and carboranes, they cannot be as easily applied to rationalize the structures of many metallacarboranes where distortions caused by size and other ligands can complicate such relationships.[1a,3b,4]

The chemistry of the metallacarboranes originated with the recognition that the *nido*-dicarbollide ion, $C_2B_9H_{11}^{2-}$, was similar to the cyclopentadienide ligand (Cp^-) in that both could bond to metals using a set of six electrons in delocalized π-type orbitals directed above the pentagonal face of the ligand.[7,8] This has ultimately led to the syntheses of metallacarboranes of two general structural types: half-sandwich complexes, in which a metal moiety occupies the missing vertex of a *nido*-carborane, to form a *closo*-metallacarborane, or full-sandwich compounds, in which a metal occupies a common vertex of two carboranes, to give *commo*-metallacarboranes. In general, the greater polarizability of boron compared to that of carbon and the higher ligand charge make the carboranes better ligands than the Cp derivatives, especially for the higher oxidation state metals.[10,11] Consequently, a wide variety of metal complexes of the carborane ligand systems have been synthesized and characterized.

The chemistry of the smaller C_2B_4 carborane ligand system has been much less studied than that of the larger cages. One of the main constraints on the development of these smaller carborane ligands has been their synthetic procedures, which involve the gas-phase reactions of alkynes with volatile pentaborane(9) at very high temperatures; these are hazardous reactions.[9a−c] Also, more times than not, the products were complex mixtures of carboranes and organoboranes, obtained in only millimolar quantities, which required tedious separation by gas chromatography. Unlike the icosahedral $C_2B_{10}H_{12}$ precursors, none of the smaller carborane compounds are available commercially.[9a−c] The second stumbling block for the development of the smaller carborane cage system has been the difficulty in generating its most demanding dianion, $[R_2C_2B_4H_4]^{2-}$ (R = H or substituent group), even though the corresponding monoanion has been known since 1966.[9d] A major breakthrough in the smaller cage chemistry was the development of new and safer methods for the multigram-scale production of reasonably air-stable carborane derivatives[9e−h] and their ready conversion to the desired dilithium or sodium/lithium salt of the C_2B_4 carborane dianion.[9h] There are two isomeric arrangements of the atoms on the C_2B_3 bonding face, one in which the two carbon atoms occupy adjacent positions, the "carbons adjacent" isomer, and the "carbons apart" isomer, in which the carbons are separated by a boron atom. Both form metallacarboranes and will be discussed together.

The potential applications of boron cluster compounds have been reviewed recently.[1−5,12] In general, metallacarboranes are finding increased applications in catalysis,[13−18] boron neutron capture therapy (BNCT),[19,20] siloxane-linked polymers,[21] solvent extraction of radionuclides,[12] and ceramics.[22,23] The transition-metal metallacarboranes are also used to catalyze polyhedral borane reactions: e.g., syntheses of multicage compounds and alkenylcarboranes and ring closures.[24]

Because this review is restricted to results published within the past few years, when the chemistry of the d- and f-block metallacarboranes has experienced an upsurge, these metal complexes will be discussed before the main-group metallacarboranes.

II. Metallacarboranes of d-Block Elements

Our discussion is restricted to metallacarboranes in which the d-block metal is incorporated into the polyhedral framework of the carborane. No attempt will be made to cover those compounds where the transition-metal atom is in a bridging group linking several carborane polyhedra together or is involved solely as a member of a substituent group. Also, since we have restricted our discussion to C_2B_4 cage systems, other metallacarboranes, especially those involving C_2B_9 cages, will be discussed only in the context of the smaller cage systems. In this regard, the reader should be aware that

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both the C_2B_4 and C_2B_9 systems are developing along remarkably parallel lines. Since much of the insight into the chemistry of the metallacarboranes is obtained from structural and bonding studies, this section will place as much emphasis on these aspects as on their reaction chemistry. Because of chemical similarities and related interests, the discussion will be divided into four sections, dealing with the early transition metals (groups 3−7), the later transition metals (groups 8−12), linked cage and mulitdecker complexes, and alkene, alkyne aryl-linked polymetallacarborane clusters.

A. Early-Transition-Metal Complexes. During the past few years there have been reports on the syntheses and structures of sandwich compounds of metals in groups 3, 4, 6, and 7. The first three groups have similar structures and potential uses and will be discussed together.

The first known examples of metallacarboranes of early transition metals were contained in the 1975 report by Salentine and Hawthorne of the syntheses of the π complexes of Ti, Zr, and V with the dianion $[1,2\text{-}C_2B_{10}H_{12}]^{2-}$ or its *C,C′*-dimethyl derivative.[25] Soon after this initial publication, these investigators reported the synthesis of the series $[M^{II}(C_2B_{10}H_{10}R_2)_2]^{2-}$ (M = Ti, V, Cr, Mn, R = H; M = Ti, Zr, Hf, V, R = CH_3), as well as the mixed-ligand titanacarboranes of the formula $[C_xH_xTiC_2B_nH_{n+2}]^{m-}$ ($x = 5$, $n = 10$, $m = 1$; $x = 8$, $n = 9, 10$, $m = 0, 1$).[26] The crystal structure of $\{4,4'\text{-Ti}[1,6\text{-}(CH_3)_2\text{-}1,6\text{-}C_2B_{10}H_{10}]_2\}^{2-}$, as its tetraethylammonium salt, showed that the titanium metal, in a formal oxidation state of 2+, was sandwiched between two dinegative C_2B_{10} carborane cages.[27] Similarities in the spectra of this titanium complex and those of the other $[M^{II}(C_2B_{10}H_{10}R_2)_2]^{2-}$ complexes indicated that all had similar structures. It was found that the *commo*-metallacarboranes were much more stable than their metallocene analogues; this has been found generally to be the case when comparing the carborane and the Cp ligand systems. In addition, unlike titanocene and pentamethyltitanocene, the metallacarboranes showed no tendency to expand their coordination spheres and go from 14-electron configurations to 16-electron ones.[26] Despite the rather interesting initial results, the area of early-transition-metal metallacarborane chemistry has remained somewhat dormant until the past few years.

The first carborane analogues of yttrocene, $[\text{Li(THF)}_4]\text{-}\{1\text{-Cl-}1\text{-(THF)-}2,2'\text{-}(SiMe_3)_2\text{-}3,3'\text{-(R)}_2\text{-}4,4',5,5'\text{-Li(THF)-}[1,1'\text{-}\textit{commo}\text{-Y}(2,3\text{-}C_2B_4H_4)_2]\}$ (R = $SiMe_3$ (Figure 1), Me) and $\{\text{Na(THF)}_3\}_2\{[1\text{-(THF)-}1\text{-}(\mu\text{-H})_2\text{-}2,2',4,4'\text{-}(SiMe_3)_4\text{-}1,1'\text{-}\textit{commo}\text{-Y}(2,4\text{-}C_2B_4H_4)_2]_2\}$ (Figure 2) were synthesized in 74−83% yields by the reactions of YCl_3 with the respective carborane dianions in 1:2 stoichiometries, as shown in Scheme 1.[28] The yttracarboranes differ from their zirconium analogues in that, while the Cl and THF ligands in the latter complexes were substitutionally inert, both could be removed from the former complexes by reaction with NaH, to give the hydrido complex $1\text{-H-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}[4,4',5\text{-Li(THF)}]_2\text{-}[1,1'\text{-}\textit{commo}\text{-Y}(2,3\text{-}C_2B_4H_4)_2]$ (see Scheme 1). Although the structure of the hydride was not determined, it most likely exists as a dimer with two Y−H−Y bridge bonds and might be better formulated as $\{1\text{-H-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}[4,4',5\text{-Li(THF)}]_2\text{-}[1,1'\text{-}\textit{commo}\text{-Y}(2,3\text{-}C_2B_4H_4)_2]\}_2$. Dimer formation was also found in the carbons-apart yttracarborane $\{\text{Na(THF)}_3\}_2\{[1\text{-(THF)-}1\text{-}(\mu\text{-H})_2\text{-}2,2',4,4'\text{-}(SiMe_3)_4\text{-}1,1'\text{-}\textit{commo}\text{-Y}(2,4\text{-}C_2B_4H_4)_2]_2\}$ (Scheme 1). However, the direct synthesis of an alkyl-substituted yttracarborane proved unsuccessful. Scheme 1 shows the result of an

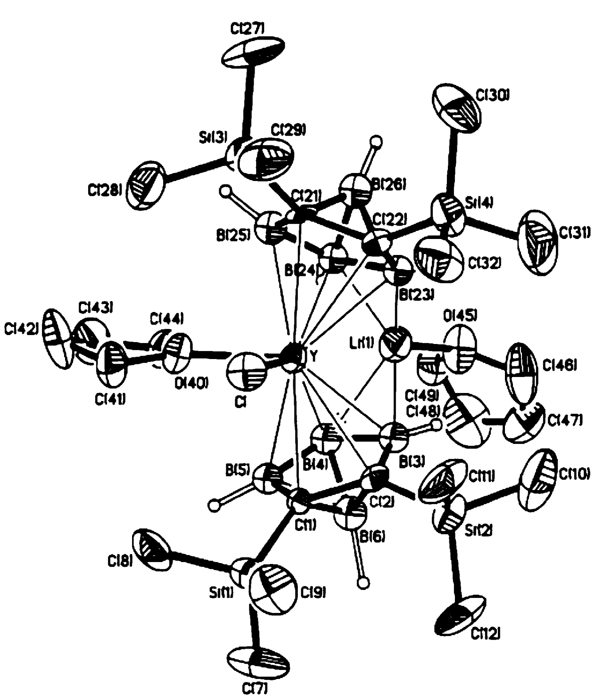

Figure 1. Crystal structure of a monomeric haloyttracarborane sandwich complex.

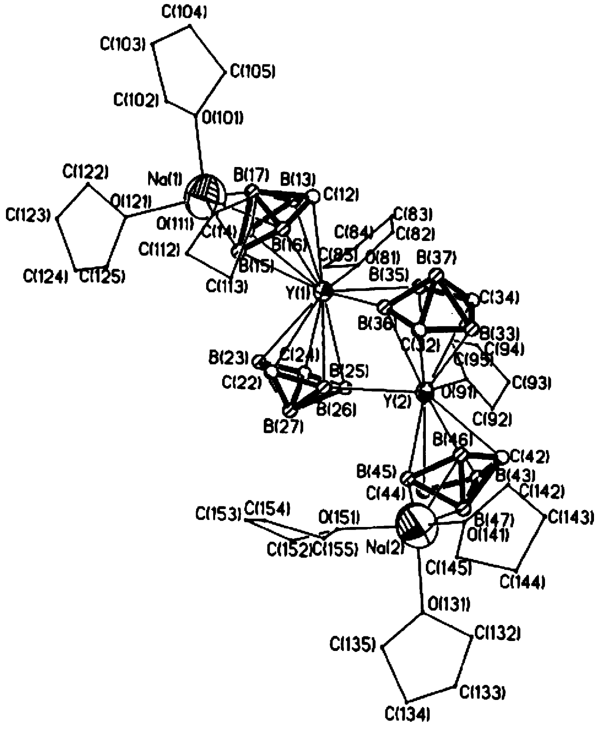

Figure 2. Crystal structure of a dimeric yttracarborane sandwich complex.

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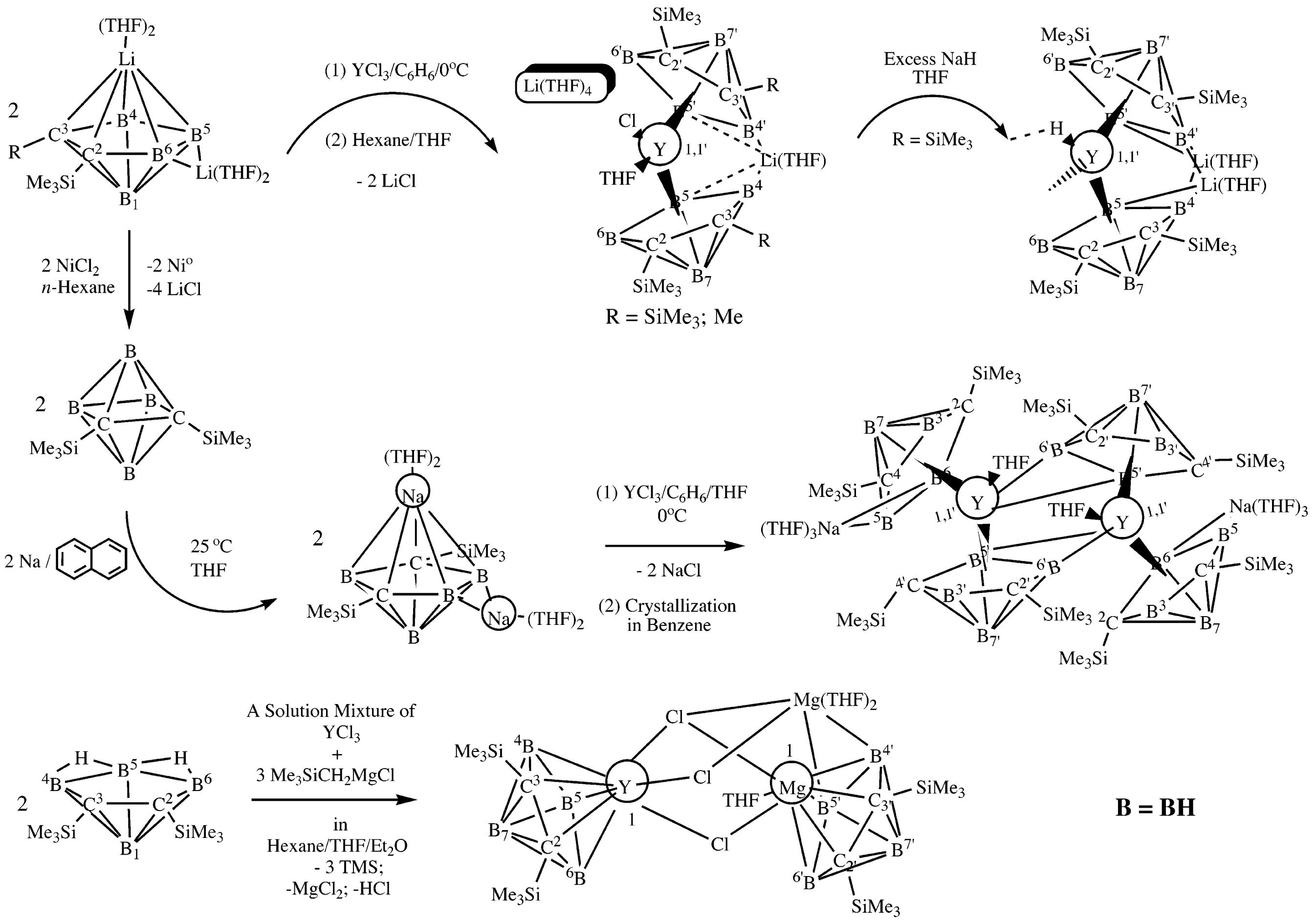
Scheme 1. Syntheses of the "Carbons Adjacent" and "Carbons Apart" Yttracarboranes



B = BH

attempted synthesis of such a complex by an initial reaction of YCl_3 with the Grignard reagent Me_3SiCH_2MgCl, followed by reaction with the neutral carborane *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$, in a 1:2 molar ratio. The synthetic strategy was to first form the trialkyl compound $Y(CH_2SiMe_3)_3$, which would then form *closo*-1-$Y(CH_2SiMe_3)$-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$, with the elimination of 2 equiv of Me_3SiCH_3 (TMS). Instead of the anticipated *closo*-yttracarborane, the novel mixed magnesa-/yttracarborane *closo*-1-Y-{1,1′-(μ-Cl)$_2$-*exo*-[5,6-(μ-H)$_2$-Mg(THF)$_2$]-1,1′-(μ-Cl)$_2$-[*closo*-1-Mg(THF)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]}-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ was obtained (see Figure 3). The lower Y−Cnt distance in the mixed magnesa-/yttracarborane (2.308 Å; Figure 3), compared to that in the carbons-adjacent (2.376 ± 0.013 Å; Figure 1) and the "carbons apart" (2.580 ± 0.036 Å; Figure 2) yttracarboranes could be the result of steric factors. On the other hand, the Mg−Cnt distance of 2.032 Å found in the mixed complex is similar to the analogous Mg−Cnt distances in the half-sandwich complex *closo*-1-(TMEDA)-1-Mg-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (2.132 Å) and the full-sandwich complex {*commo*-1,1′-Mg[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]$_2$}$^{2-}$ (2.018 Å).[29]

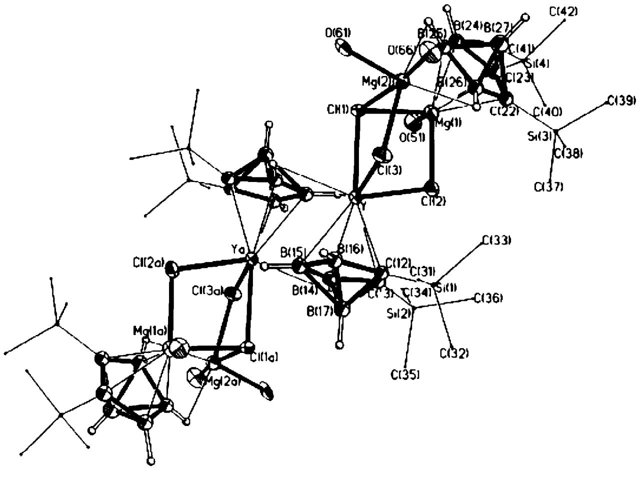


Figure 3. Crystal structure of a magnesium salt of a mixed half-sandwich chloroyttra-/chloromagnesacarborane complex.

The only other group 3 metallacarborane structural report was that of $[Li(THF)_3]Li[Sc(C_2B_9H_{11})(Cp^*)(CH\{Si(CH_3)_3\}_2]_2$ ($Cp^* = [C_5(CH_3)_5]^-$), which showed that the Sc was bonded to three centers: the Cp* centroid, the dicarbollide C_2B_3 face centroid, and the C atom of the $CH[Si(CH_3)_3]_2$ group.[30] The dimeric structure arose from the fact that two $[Sc(C_2B_9H_{11})(Cp^*)(CH\{Si(CH_3)_3\}_2)]^-$ units were loosely connected by one Li atom. It seems that the large coordinating ligands effectively prevented the Sc from increasing its coordination number to 4. One of the limitations of using carborane

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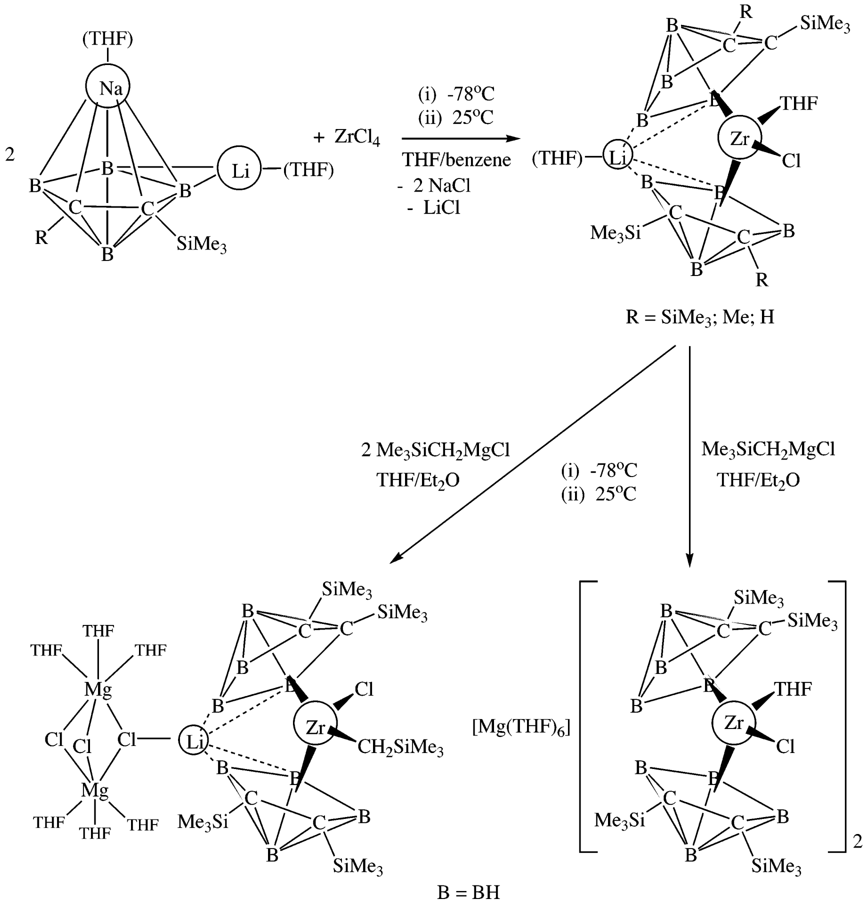
Scheme 2. Syntheses of Zirconacarborane Sandwich Complexes



ligands with group 3 metals as the basis for catalytic processes is that, with two dianionic ligands and a 3+ charge on the metal, the complexes are anionic, so that there is little possibility of adding reactive anionic ligands, such as alkyls. Such an addition would be the first step in the potential use of these d^0 complexes as Ziegler−Natta type catalysts. Therefore, the mixed complexes offer a convenient solution to that problem and it would be anticipated that mixed carborane/Cp complexes, such as the Sc species, or the purely carborane-based complexes, such as the yttrium bent sandwich, should support α-olefin polymerization or oligomerization catalytic activity, as is found in many of the bent d^0 cyclopentadienyl complexes.[31]

Because of their potential as homogeneous olefin polymerization catalysts, the group 4 metallacarboranes, where the transition metal is in a formal 4+ oxidation state, should prove to be especially interesting compounds. The first such complex was a zirconium(IV) carborane sandwich, reported in the C_2B_4 cage system, as outlined in Scheme 2.[32] One of the characteristics of these compounds was their ability and tendency to incorporate varying numbers of THF molecules of solvation, depending on the complex and conditions. The crystal structure of one of the zwitterionic zirconacarboranes (Figure 4) shows three THF molecules: two solvating the lithium and one coordinated to the zirconium. The most surprising and, from a practical standpoint, disappointing results were the products obtained by the reactions of chlorozirconacarborane with Me_3SiCH_2MgCl (see Scheme 2). A 1:1 molar ratio of the complex and the Grignard reagent resulted in the replacement of two Li^+ atoms by Mg^{2+}, giving

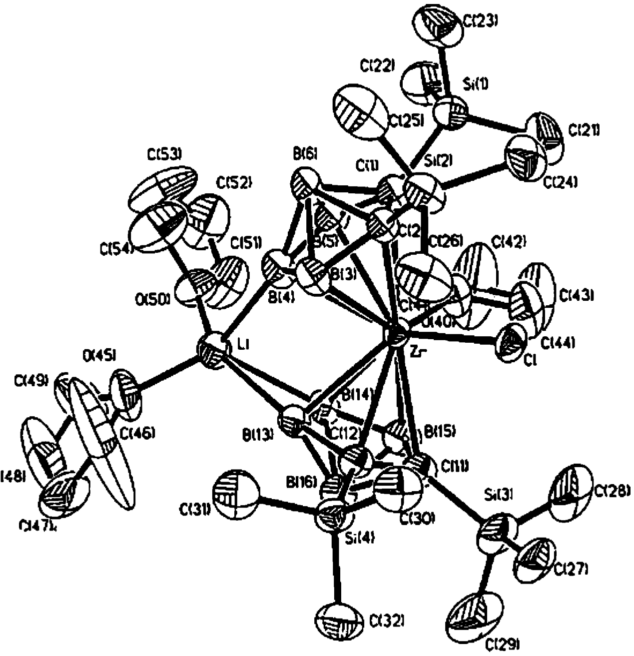


Figure 4. Crystal structure of a zwitterionic chlorozirconacarborane sandwich complex.

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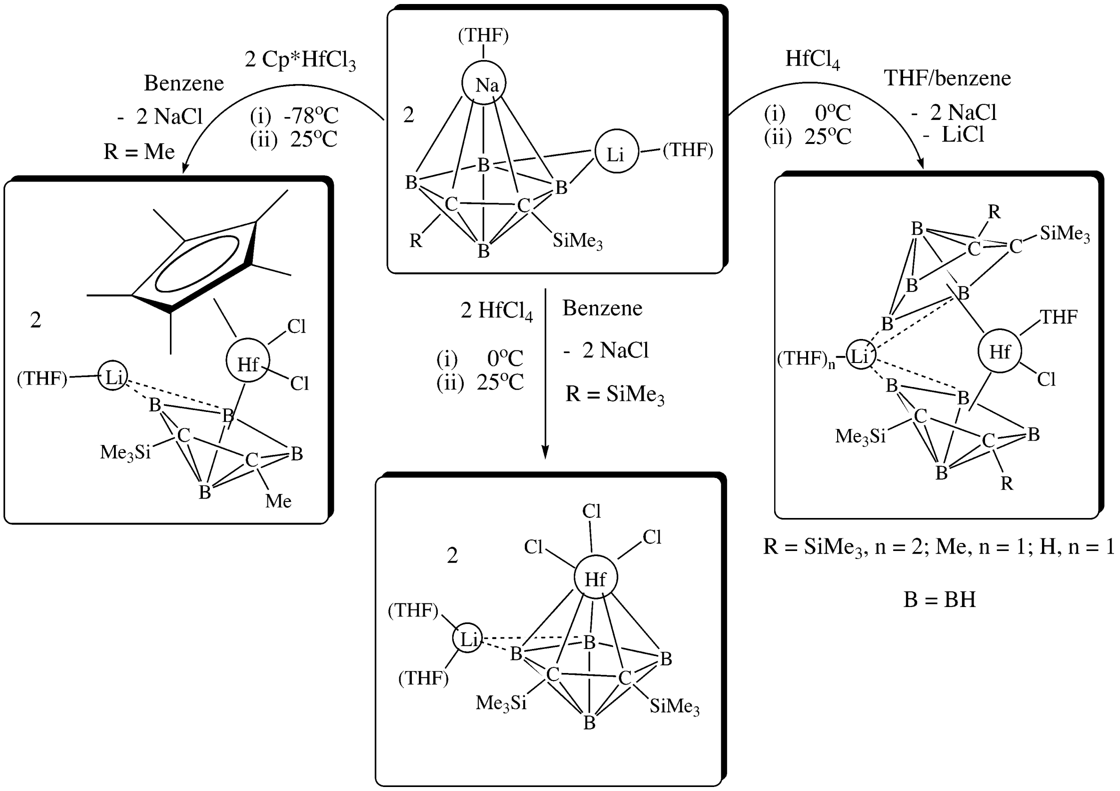
Scheme 3. Syntheses of Hafnacarborane Complexes



R = $SiMe_3$, n = 2; Me, n = 1; H, n = 1

B = BH

the ionic zirconacarborane. The only major alteration in the metallacarboranes is that a cation no longer occupies a bridging position on the zirconacarborane anions (see Figure 4). The same reaction with excess Me_3SiCH_2MgCl resulted in the formation of a complex double salt in which a $Mg_2Cl_3(THF)_6$ moiety is associated with the bridging Li, with the zirconacarborane structure being little affected (see Scheme 2). The high (65%) yield of this compound indicates that it is the major product of the reaction of the chlorozirconacarborane with the Grignard reagent. The fact that $[Me_3SiCH_2]^-$ replaced the THF in the primary coordination sphere of the zirconium demonstrates the inertness of the Cl that is coordinated to the zirconium; this is quite different from the behavior of corresponding chlorozirconocenes.[33] The corresponding *commo*-chlorohafnacarboranes, formed by the reaction of $HfCl_4$ and carborane in a 1:2 molar ratio, were found to have structures similar to that of the chlorozirconacarborane shown in Figure 4 (see Scheme 3).[34] A 1:1 ratio fo $HfCl_2$ to carborane produced the half-sandwich $[Li(THF)_2]$-$[1,1,1\text{-}(Cl)_3\text{-}\textit{closo}\text{-}1\text{-}Hf\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]$. On the other hand, both 2:1 and 1:1 molar ratios of carborane to Cp^*HfCl_3 produced exclusively the mixed-sandwich complex $1,1'\text{-}(Cl)_2\text{-}2\text{-}(SiMe_3)\text{-}3\text{-}(Me)\text{-}4,5\text{-}Li(THF)\text{-}1,1'$-*commo*-$Hf[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}2,3\text{-}C_2B_4H_4)]$ in 82% yield. While the formation of an alkali-metal chloride is an important component of the driving force in these reactions, the stability (or inertness) of the resulting hafnacarboranes must also be considered. The formulas of all these compounds show that they all contain the elements of LiCl, with the Cl atoms coordinated to the Hf metals and the Li atoms being present as exopolyhedrally bound $Li(THF)_n^+$ cations; however, they show little inclination to eliminate LiCl. It is an open question as to whether the three chlorides in the half-sandwich complex are equally coordinated to the hafnium to give a trichlorohafnium capping group, similar to those found in the MCl_3Cp^* (M = Zr, Hf) complexes,[35] or whether one Cl is more loosely bound to give an aggregate of a dichlorohafnacarborane and a LiCl. Since the X-ray-quality crystals of this could not be obtained and spectroscopic analysis could not resolve this question, there is no way at present to ascertain the exact nature of the capping group; the formulation as shown in Scheme 3 must be considered as tentative. The ease of preparation of both the full- and half-sandwich hafnacarboranes should allow a systematic investigation of the effects of changing the other ligands or pendant groups on the substitution reactions of these d^0 metallacarboranes. In the same way, a number of other Zr(IV) and Hf(IV) sandwich complexes in the C_2B_9 carborane system have been synthesized.[36] It is of interest to note that these syntheses proceeded quite cleanly, while the reaction of $ZrCl_4$ with $Na_2C_2Me_2B_{10}H_{10}$ yielded only the $[Zr(C_2Me_2B_{10}H_{10})_2]^{2-}$ anionic complex, in which the Zr was in a formal 2+ state. Moreover, cyclic voltammetry of this Zr(II) complex showed no reversible oxidation or reduction waves.[25] Mixed $Cp^*/C_2B_9H_{11}$ bent-sandwich compounds of the form $(Cp^*)(C_2B_9H_{11})M(R)$ (M = Hf, Zr), where the metals are in 4+ states, have also been recently synthesized and characterized.[36]

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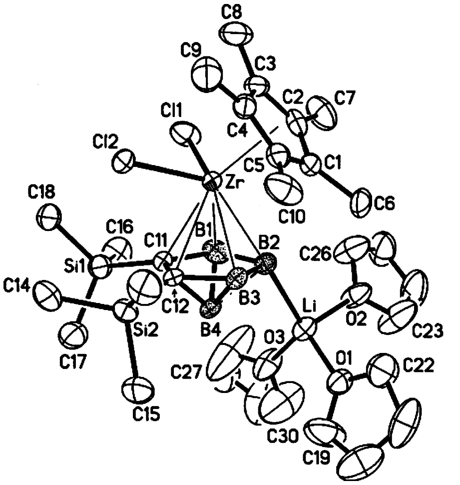

Figure 5. Crystal structure of a dichlorozirconacarborane derived from pentamethylcyclopentadiene and C_2B_4 carborane ligands.

The complex $[Li(THF)_3]\{[\eta^5\text{-}C_2B_4H_4(SiMe_3)_2](\eta^5\text{-}C_5Me_5)ZrCl_2\}$ was synthesized via reaction of $(C_5Me_5)ZrCl_3$ with the dianion $[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$.[37] This metallocene derivative can be described as an anionic bent-sandwich complex associated with a $[Li(THF)_3]^+$ cation via interaction with a B atom of the $[C_2B_4H_4(SiMe_3)_2]^{2-}$ cage, as observed in its crystal structure analysis (Figure 5). The dianionic carborane and pentamethylcyclopentadienide ligands are coordinated to the zirconium in an η^5 fashion, and the coordination geometry about the Zr atom is that of a distorted tetrahedron defined by the two chlorides and the centroids of the pentamethylcyclopentadienyl and carborane ligands. The Cl−Zr−Cl angle is 94.6(1)°, and the (C_2B_3 centroid)−Zr−(C_5Me_5 centroid) angle is 131.3°. Attempts to synthesize zirconium silyl and alkyl complexes incorporating this carborane ligand have so far proved unsuccessful.[37] Grimes and co-workers have synthesized bent-sandwich complexes of the mixed C_2B_4 carborane and cyclopentadienide ligands, $Cp'MXY(R_2C_2B_4H_4)$ (M = Nb, Ta, R = $SiMe_3$, Me, Et, Cp′ = Cp, Cp*, X, Y = Cl; M = Zr, R = Et, X = Cl, Y = THF, Cp′ = Cp, Cp*).[38] Crystal structures of several of the niobium and tantalum species showed bent-sandwich geometries, similar to that shown in Figure 5. Of particular interest are the reactions of $CpMCl_4$ with the cobaltacarborane anion $Cp^*Co(Et_2C_2B_3H_4)^-$, which gave the bent triple-decker sandwich complexes $Cp^*Co(Et_2C_2B_3H_3)M(Cl)_2Cp'$.[38]

Somewhat different results were observed in the *C*-trimethylsilyl-substituted titanacarborane systems. The reaction of Cp_2TiCl_2 with the unsolvated "carbons adjacent" dilithium compounds *closo-exo*-Li-1-Li-2-(R)-3-($SiMe_3$)-2,3-$C_2B_4H_4$ (R = $SiMe_3$, Me, H) produced the corresponding mixed-ligand sandwich titanacarboranes [*commo*-1-Cp-1-Ti^{III}-2-(R)-3-($SiMe_3$)-2,3-$C_2B_4H_4$]$_2$ (R = $SiMe_3$ (Figure 6), Me, H).[39] Scheme 4 outlines the syntheses of the mixed-ligand sandwich Ti(III) complexes and their subsequent oxidation to the corresponding Ti(IV) complexes. The reactions represent an interesting series in that a reaction of the carborane dianion with Cp_2TiCl_2 in a 1:1 molar ratio produced the Ti(III) complex [*commo*-1-Cp-1-Ti^{III}-2-(R)-3-($SiMe_3$)-2,3-$C_2B_4H_4$]$_2$ and dihydrofulvalene; the Ti(IV) could only be obtained by displacing the Ti(III) in the mixed-sandwich compounds with Ti(IV) to give [*commo*-1-Cp-1-Cl-1-(THF)-1-Ti^{IV}-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$], with a structure similar to that shown in Figure 4. The driving force for this last reaction was thought to be the formation of the stable $TiCl_3(THF)_3$. However, it is not known whether this reaction proceeds by an electron transfer or a substitution mechanism. Attempts to synthesize directly a Ti(IV) mixed-ligand sandwich complex by the reaction of the neutral *nido*-carboranes and Cp^*TiMe_3, following the method of Jordan,[40] gave complex mixtures of products that could be neither separated nor characterized. Therefore, most of the synthetic efforts have involved the direct syntheses of Ti(III) complexes using $TiCl_3$ as the metalating agent.[39] Scheme 4 shows that the products of the reactions of $TiCl_3$ with the different dilithiacarborane compounds depended on steric factors arising from the nature of the cage carbon substituents and the location of the cage carbons in the C_2B_3 bonding face of the carborane ligand. The structures of the different titanacarboranes have all been verified by single-crystal X-ray diffraction studies.[39]

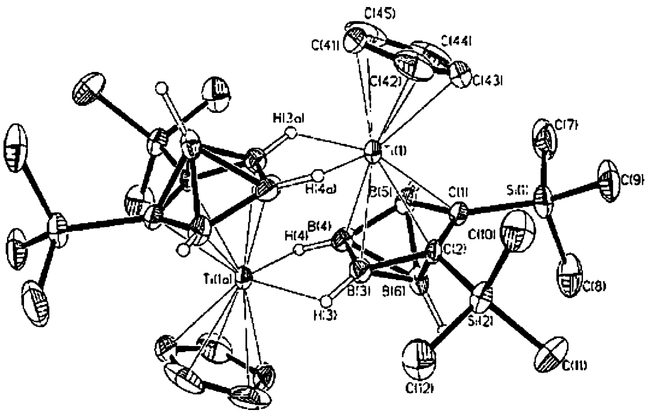

Figure 6. Crystal structure of the mixed-ligand neutral metallacarboranes of titanium(III).

The only half-sandwich titanacarborane that could be formed was that of the "carbons apart" isomer, shown in Figure 7.[39b] At present, it is not known exactly why the "carbons apart" and "carbons adjacent" carboranes should give such different products when reacted with $TiCl_3$. It could be that, because of the intervening boron atom, the steric restrictions on additional coordination at the titanium imposed by the cage carbon substituents would be somewhat tempered, allowing for the coordination of a chlorine atom and the large TMEDA molecule. Grimes and co-workers have recently reported the synthesis and reactivity of a series of 14-electron titanium complexes of the types $L_2Cl_2Ti(Et_2C_2B_4H_4)$ (L_2 = 2 PMe_3, $Me_2P(CH_2)_xPMe_2$; x = 2, 3) and $[Me_2P(CH_2)_3PMe_2]_2Me_2Ti(Et_2C_2B_4H_4)$ and a related zirconium com-

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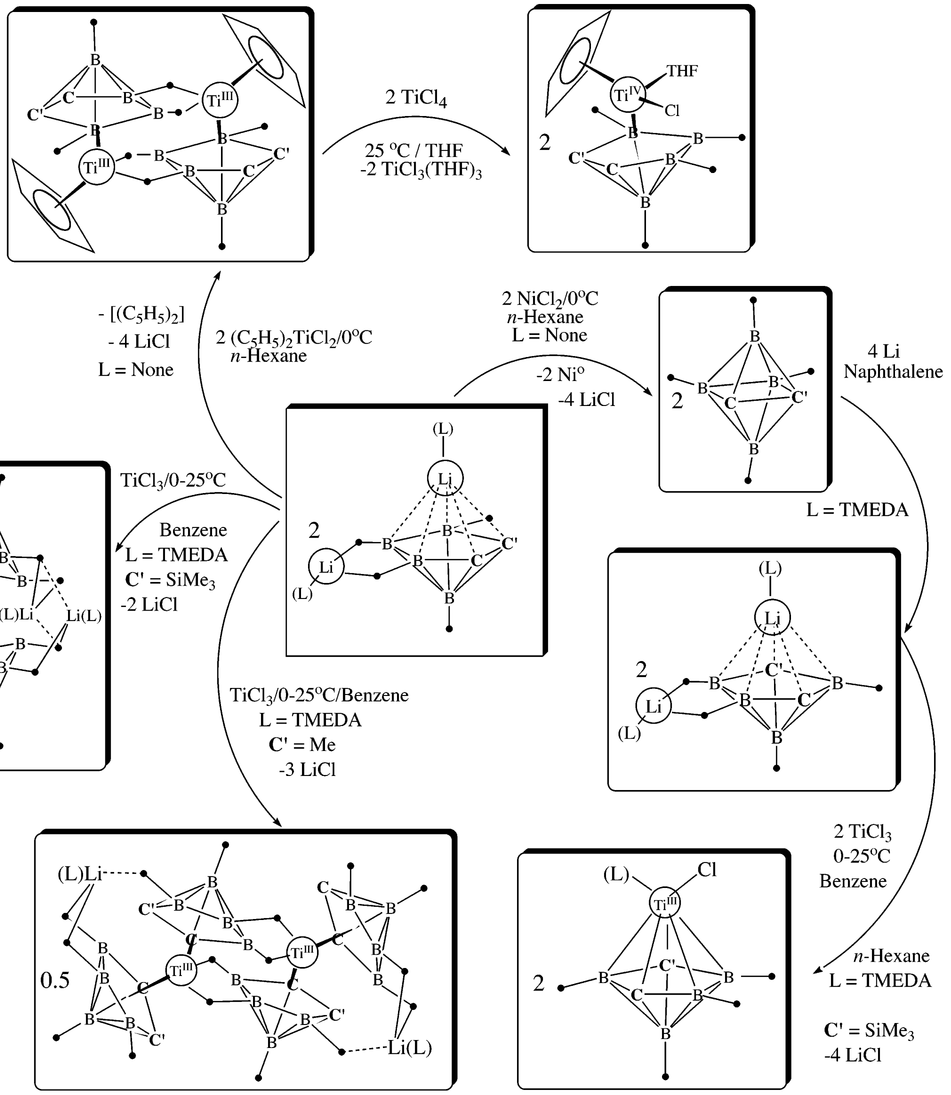
Scheme 4. Syntheses of the "Carbons Adjacent" and "Carbons Apart" Titanacarboranes



C = C-SiMe$_3$; **C'** = C-SiMe$_3$, Me, H; ● = H

plex, $L_2Cl_2Zr(Et_2C_2B_4H_4)$ (L_2 = 2 PMe_3, $Me_2P(CH_2)_3PMe_2$).[41] These compounds were reported to be catalyst precursors for the polymerization of ethylene at 1 atm of pressure in the presence of methylaluminoxane. It was observed that the choice of phosphine ligand had a significant effect on catalytic activity.[41] Some of the titanium species $L_2X_2Ti(Et_2C_2B_4H_4)$ (L_2 = 2 PMe_3, X = Cl; L_2 = dmpp, X = Cl, Me) have also been characterized by X-ray crystallography.[41] The general structural features are similar to those shown in Figure 7, except that the Ti has an extra Cl coordinated. Thus, these compounds, plus the bent Y, Zr, and Hf C_2B_4 carborane sandwich compounds discussed earlier, represent the initial phases of the syntheses of a class of 14-electron, d^0 bent-metallocene analogues, which could prove to be effective Ziegler−Natta type olefin polymerization catalysts.[33b] It is clear from the above discussion that this fascinating area of research is only in its formative stages.

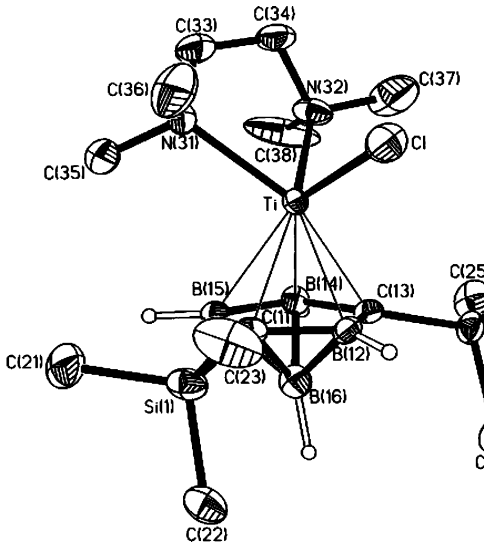


Figure 7. Crystal structure of a half-sandwich chlorotitanacarborane.

Grimes and co-workers have extended their initial study on group 5 metallacarboranes[38] by derivatizing the sandwich complexes of tantalum and niobium, $CpCl_2M(2,3\text{-}Et_2C_2B_4H_4)$ (M = Ta, Nb).[42] This was ac-

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(41) Dodge, T.; Curtis, M. A.; Russell, J. M.; Sabat, M.; Finn, M. G.; Grimes, R. N. *J. Am. Chem. Soc.* **2000**, *122,* 10573.

complished by the treatment of the parent species with elemental halogens or *N*-halosuccinimides to produce B_{unique}- or B_{basal}-substituted halo derivatives, and in some cases, all of the ring boron atoms were halogenated. These compounds in turn reacted with Grignard reagents to yield the corresponding B-alkyl- and B-aryl-substituted complexes.[42] Similarly, the heterodinuclear bent triple-decker sandwich complex $Cp^*Co(Et_2C_2B_3H_3)Cl_2Ta(Et_2C_2B_4H_4)$, discussed above, could be converted to the corresponding *B*-tribromo derivative.[42] While the alkyl- and aryl-substituted tantalacarboranes $(Et_2C_2B_4H_4)CpTaR_2$ (R = Me_3, Ph) undergo insertion reactions with nitriles and isonitriles, the dimethyltantalacarborane undergoes clean photochemical insertion of alkynes to give vinyltantalum species, unlike their metallocene analogues, which are known to produce methylidyne intermediates.[43] The analogous diphenyltantalacarborane is thermally reactive, eliminating benzene and undergoing trapping reactions of the derived benzyne intermediate with alkynes. The structures of the resulting tantalaindene species have been confirmed by X-ray crystallography, protonolysis, and spectroscopy.[43c] The authors have hypothesized that a Ta−C fragment can undergo intramolecular insertion into a carborane B−H bond, a step unknown for cyclopentadienyl C−H bonds and one that is potentially relevant to the use of metallacarborane complexes as catalysts for olefin polymerization and related processes.[43c] On the other hand, the dichlorotantalacarborane $(Et_2C_2B_4H_4)CpTaCl_2$ was converted to the corresponding hydridotantalacarborane dimer $[(Et_2C_2B_4H_4)CpTa(H)]_2(\mu\text{-}Cl)_2$ by treatment with $LiAlH_4$ in THF, which in turn undergoes alkyne insertion with *p*-tolylacetylene to generate exclusively *trans*-$CpCl(p\text{-}MeC_6H_4CH{=}CH)Ta(Et_2C_2B_4H_4)$. This product undergoes reaction with anhydrous HCl to produce *p*-tolylstyrene with recovery of the original dichlorotantalacarborane catalyst.[43b]

In group 6, the first anionic chromium sandwich complex, $[3,3'\text{-}Cr\{1,2\text{-}(Me)_2\text{-}1,2\text{-}C_2B_9H_9\}_2]^-$, along with the corresponding mixed Cp/carborane analogue, $(\eta^5\text{-}Cp)Cr(C_2B_9H_{11})$, were synthesized nearly 35 years ago by Ruhle and Hawthorne.[44] The crystal structure of the sandwich complex consisted of two icosahedral cages joined at the formal Cr(III) metal ion center.[45] Unlike the chromocenium analogue and the mixed-ligand complex, both of which were extremely moisture sensitive, the *commo*-chromacarborane was found to be so stable to hydrolysis that it was not affected even by hot, concentrated sulfuric acid.[44] Moreover, the complex showed no tendency to undergo either oxidation or reduction without cluster demolition.[44] On the other hand, it was reported that the Cr(III) sandwich complex of a C_2B_4 carborane system could easily be oxidized to the corresponding neutral Cr(IV) complex.[10,46] The anionic Cr(III) sandwich complexes, of the type $[1,1'$-*commo*-$Cr\{2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4\}_2]^-$ (R = $SiMe_3$, Me, H), having either $Li(THF)_4^+$ or $Li(TMEDA)_2^+$ counterions, could be synthesized by the reactions of $CrCl_3$ and the corresponding THF-solvated lithium/sodium carborane double salts, followed by extraction and crystallization from solutions of benzene and THF or TMEDA.[46] Chemical oxidation of the anionic Cr(III) sandwich species with $PbCl_2$ produced a novel, diamagnetic, neutral Cr(IV) sandwich complex as a dark red, air-sensitive, crystalline solid in 63% yield. Structures of the Cr(III) and Cr(IV) metallacarboranes, where R = $SiMe_3$, were essentially the same, indicating that the complexes are isostructural (see Figure 8). The effective magnetic moment of 3.93 μ_B at room temperature was consistent with a high-spin d^3 system.[46] The observation that the oxidized Cr(IV) complex gave well-resolved ^1H, ^{11}B, and ^{13}C NMR spectra is consistent with a spin singlet state for the complex.[4,10] The Cr−C(cage) bond distances are shorter than those found in the corresponding icosahedral analogue,[45] and about the same as those in the mixed-ligand complex, $1\text{-}Cr(\eta^7\text{-}C_7H_7)\text{-}2,3\text{-}(Et)_2\text{-}2,3\text{-}C_2B_4H_4$,[47] and in chromocene.[48]

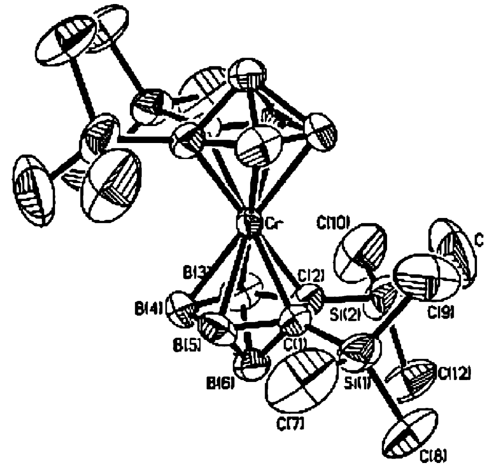

Figure 8. Crystal structure of an anionic chromium(III)−carborane sandwich complex.

The dianionic molybda- and tungstacarboranes of the C_2B_4 cage systems have been reported by Grimes and co-workers, who have shown that the carborane dianion undergoes reactions with $(RCN)_3M(CO)_3$ (M = Mo, W; R = Me, Et) to produce the lithium salts of the corresponding metallacarboranes $[(Et_2C_2B_4H_4)M(CO)_3]^{2-}$.[49] When it is treated with Ph_4PX in the presence of triflic acid, the molybdenum species subsequently forms the dimeric complex $[(Et_2C_2B_4H_4)M(CO)_2]_2(\mu\text{-}X)_2$ (X = Cl, Br, I). The dimeric nature of the product was confirmed by X-ray crystallography, which shows the two MC_2B_4 pentagonal-pyramidal clusters that are linked via an intercluster metal−metal bond (see Figure 9).[49] Both the molybdenum and tungsten carbonyl species have also been incorporated into a cobalt metal complex to form the mixed-metal multidecker sandwich species (see Figure 10).[49]

The manganese or rhenium (group 7) complexes of a number of carborane ligand systems have been known

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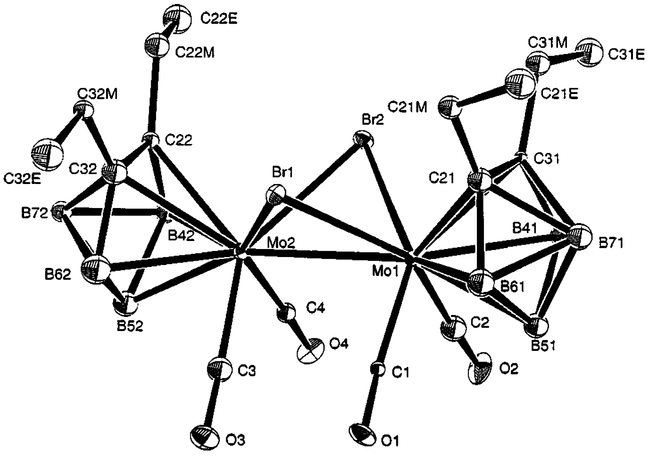

Figure 9. Crystal structure of a dimeric molybdacarborane complex.

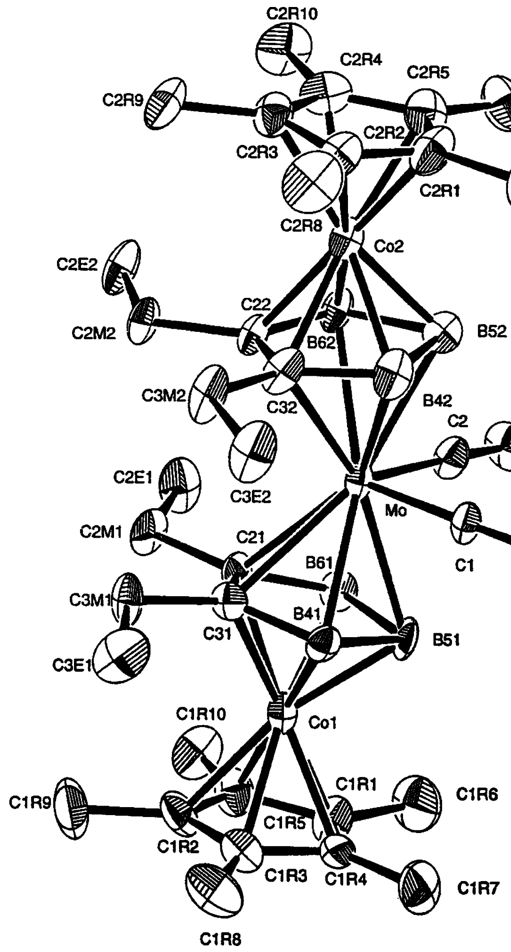

Figure 10. Crystal structure of a mixed molybda/cobalta multidecker sandwich complex.

since the original report on $Cs[(C_2B_9H_{11})M(CO)_3]$ (M = Mn(I), Re(I)) by Hawthorne and Andrews in 1965.[50] However, most of the reported manganacarborane complexes are the half-sandwich *closo* species with a $Mn(R_3P)_x(CO)_{3-x}$ (R = alkyl or aryl group; $x = 0-2$) unit occupying a vertex of either an icosahedron or one of its lower homologues.[51] Until recently, the only known *commo*-manganacarboranes have been the anionic complexes of the types $[4,4'\text{-}Mn^{II}(1,6\text{-}C_2B_{10}H_{12})_2]^{2-}$ and $[Mn^{IV}(CB_{10}H_{11})_2]^{2-}$, whose geometries could not be confirmed by X-ray crystallography.[26,52] The synthesis and crystal structure of a novel zwitterionic and paramagnetic manganese sandwich complex, $\{[Li(THF)][Li(TMEDA)]_2\}\{commo\text{-}Mn_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_4\}$, was reported in 1991.[53] The synthetic pathway to this compound is given in eq 1, and its structure is shown in Figure 11.

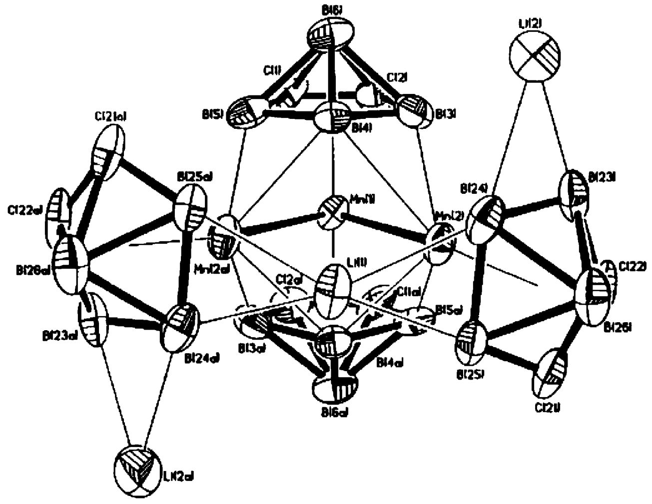

Figure 11. Crystal structure of a trinuclear, mixed-valence, zwitterionic manganacarborane.

$$9\text{Na(THF)Li}[2,3\text{-}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4] + 6\text{MnCl}_2 \xrightarrow[\text{(2) hexane/THF/TMEDA}]{\text{(1) THF; 0 °C, 1 h and 25 °C, 24 h}} 3\text{LiCl} + 9\,\text{NaCl} + 2\{[\text{Li(THF)}][\text{Li(TMEDA)}]_2\}\{commo\text{-Mn}_3[2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4]_4\} + closo\text{-}1,2\text{-}(\text{SiMe}_3)_2\text{-}1,2\text{-C}_2\text{B}_4\text{H}_4 \tag{1}$$

Figure 11 shows that the complex has a "butterfly" structure, in which the three Mn atoms are coordinated by the carborane ligands and form a central trigonal plane. There seems to be no direct interaction between the two terminal Mn atoms, and all metal−metal interactions take place through the central Mn atom. The relevant bond lengths are $Mn_{central}-Mn_{terminal}$ = 2.68 Å and $Mn_{terminal}-Mn_{terminal}$ = 3.28 Å, with a $Mn_{terminal}-Mn_{central}-Mn_{terminal}$ bond angle of 75.5°.[53] The central Mn atom is essentially η^5-bonded to two parallel C_2B_3 carborane faces, with metal to cage atom distances ranging from 2.155 to 2.249 Å. These are significantly shorter than the Mn−C bond distances of 2.42 Å found in the corresponding high-spin Cp analogue.[54] The "butterfly" geometry of the complex is presumably stabilized by direct Mn−Mn bonding and by the additional interaction of the terminal Mn atoms with the unique and basal borons on the central manganese sandwich (the Mn(2)−B(4) and Mn(2)−B(3) bond dis-

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tances of 2.518 and 2.445 Å are not too different from the Mn(2)−B(24) and Mn(2)−B(25) bond distances of 2.398 and 2.507 Å, respectively (see Figure 11)). In a formal sense, the Mn complex is a cluster composed of both a sandwich (commo) and two-half-sandwich (closo) geometries. The presence of three loosely boron bound $[Li(solv)]^+$ units within the coordination sphere makes the complex a zwitterionic cluster.[53] The effective magnetic moment of the complex (8.3 μ_B at 298 K) decreases monotonically with decreasing temperature and reaches 6.2 μ_B at 15 K, indicating a significant antiferromagnetic coupling between the central and terminal Mn atoms. The shorter central Mn−centroid distance (1.708 Å), when compared to the terminal Mn−centroid distance of 2.125 Å, is consistent with a high-spin Mn(I)−Mn(III)−Mn(I) trinuclear system. Unfortunately, there was no signal in the X-band EPR spectrum of the complex at 25 °C.[53]

An entirely different result was obtained by the reaction of the trinuclear half-sandwich gadolinacarborane cluster {*closo*-$Gd_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_3(\mu$-*closo*-$Li_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_3)[\mu\text{-}Li(THF)]_3(\mu_3\text{-}OMe)(\mu_3\text{-}O)$},[55,56] with $MnCl_2$. The product of this reaction was a simpler manganacarborane, 3,3′,4,4′-Mn(TMEDA)-*commo*-$Mn[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$ (see Figure 12).[56] The crystal structure of the cluster clearly shows that a Mn atom, formally in a 2+ oxidation state, is coordinated to two somewhat parallel carborane cages (Mn−C = 2.167 Å, Mn−B = 2.243 Å, and Cnt−Mn−Cnt = 175.5°).[56] For charge balance, an additional exo-polyhedral Mn^{II}(TMEDA) unit is present within the coordination sphere and interacts strongly with two borons of each cage as well as with the central Mn atom (Mn−Mn = 2.665 Å). The incorporation of a second metal atom into the structure of a sandwich complex as a counterion has been observed previously in the carborane complexes of Sc, Y, Zr, and Hf.[5a,c] The room-temperature effective magnetic moment (7.6 μ_B) of the dimanganese complex decreases monotonically with decreasing temperature and reaches 5.6 μ_B at 80 K, indicating that a significant antiferromagnetic coupling exists between the two Mn atoms.[56]

B. Later Transition Metal Complexes. A variety of late (group 8−12)-transition-metal carborane complexes encompassing both large and small carborane ligands have been described, beginning with the initial report on the metallocene-type metallacarborane sandwich complexes, such as dianionic $[Fe^{II}(C_2B_9H_{11})_2]^{2-}$ and monoanionic $[Fe^{III}(C_2B_9H_{11})_2]^-$.[8] There are a number of review articles, monographs, and chapters in books that adequately cover most of the published work in this area up to 2000.[1−5,57] Therefore, our discussions in this part of the review will attempt to summarize the work reported since that time on the sandwich and half-sandwich complexes of the group 8−12 metals.

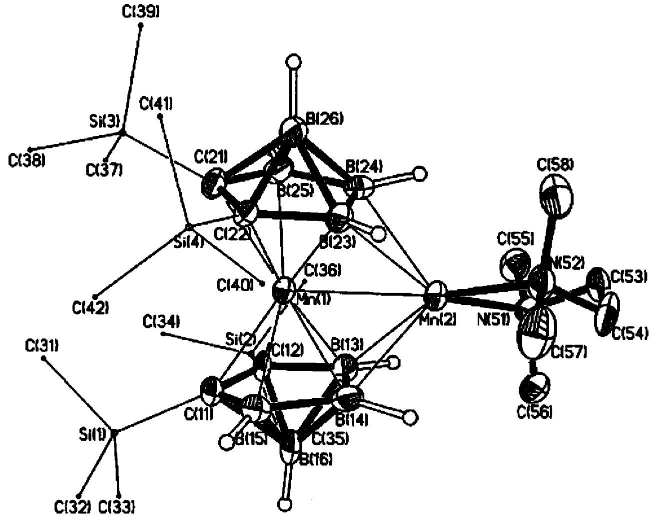

Figure 12. Crystal structure of a “wedge-bridged” dimanganacarborane sandwich complex.

In a series of papers on the metal-promoted face-to-face fusion of carborane cages, Grimes and co-workers have reported the results of investigations of the formation of single polyhedral C_4B_8 clusters from the iron sandwich precursor $(R_2C_2B_4H_4)_2FeH_2$ or its cobalt analogue $(R_2C_2B_4H_4)_2CoH$ (R = Me, Et, *n*-propyl).[58−60] In a systematic study of this fusion process, these authors concluded that the reaction is intramolecular with respect to the carborane ligands. No evidence was found of ligand exchange when the fusion reaction was carried out in a mixture containing two different $(R_2C_2B_4H_4)_2FeH_2$ complexes, one in which R = CH_3 and another where R = C_2H_5. One of the interesting findings of this study was that of a slow conversion of the diamagnetic $(R_2C_2B_4H_4)_2FeH_2$ in THF, $(C_2H_5)_2O$, or $CH_3OC_2H_4OCH_3$ (DME) to a paramagnetic diiron complex. This diiron complex was identified as a mixed high-spin Fe(II)−low-spin Fe(II) complex of the form $(R_2C_2B_4H_4)_2Fe^{II}$(low spin)Fe^{II}(high spin)L_2, where L_2 = 2THF, $2(C_2H_5)_2O$, DME. An X-ray diffraction study of this complex when L_2 = DME showed that one iron, presumably the low-spin one, was sandwiched between two parallel carborane ligands with the second iron, in an FeL_2 unit, occupying a wedging position between the two carborane ligands and coordinated to these ligands via four Fe−B bonds.[61] Since the structure of the diiron species is similar to that of the previously described dimanganese complex (see Figure 12),[56] it can also be regarded as a formal zwitterionic sandwich complex whose coordination sphere contains both the cation and the anion. Although the two Fe atoms are within the normal bonding distance (2.414 Å), the ^{57}Fe Mössbauer spectra indicate that there is very little direct Fe−Fe interaction. Presumably, the two carborane faces fuse at the B−B edges to form the corresponding C_4B_8 species.[61] The bonding in this “wedge” bridged dinuclear sandwich, as well as in its monoiron precursor, $(R_2C_2B_4H_4)_2Fe^{II}H_2$, have been investigated theoretically using extended Hückel molecular orbital calculations. The results

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show that a wedged configuration, rather than a bent-sandwich structure, is favored by the stronger Fe−carborane bonding, compared to Fe−Cp bonding, and the larger size of the carborane ligand.[62]

In the small-cage system the behavior of the late-transition-metal carborane complexes depends on the thermodynamic stabilities of the two isomeric C_2B_4 carboranes.[63] In general, both the "carbons adjacent" and the "carbons apart" isomers seem to bind metals equally well, but the latter isomer is the more stable one. For example, it was found that the reactions of anhydrous $NiCl_2$ with the dilithium-complexed "carbons adjacent" *nido*-carborane dianions $[2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ (R = $SiMe_3$, Me) in *n*-hexane, THF, or TMEDA produced the corresponding *closo*-1,2-carborane derivatives in 40−59% yields along with small quantities of C_4B_8 carborane derivatives, with no evidence of a persisting nickelacarborane.[9i] The formation of the face-to-face fused C_4B_8 cages reported by Grimes and co-workers proceeded from the less thermodynamically stable "carbons adjacent" metallacarboranes (vide supra).[58−60,64] On the other hand, the reaction of $NiCl_2$ with the dilithium-complexed "carbons apart" *nido*-carborane dianion $[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]^{2-}$ produced a Ni(IV) complex, *commo*-1,1′-Ni$[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]_2$, and Ni^0 when the THF-solvated dilithium compound of $[2,4\text{-}(SiMe_3)_2$-*nido*-$2,4\text{-}C_2B_4H_4]^{2-}$ was used.[65] In the presence of TMEDA, the Ni(II) half-sandwich 1-(TMEDA)-*closo*-Ni$[2,3\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4$ could be obtained.[65] Thus, in the presence of good coordinating solvents the half-sandwich *closo*-metallacarboranes can be stabilized.[65−67] Another example is seen in the fact that a full-sandwich Co(III) complex, $\{1,1'$-*commo*-Co-$[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2\}^-$, was formed by the reaction of $CoCl_2$ with the THF-solvated trinuclear *closo*-samaracarborane precursor,[56] while the TMEDA-solvated dilithiacarborane reacted with $CoCl_2$ to give the half-sandwich 1-Co(TMEDA)-$2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4$.[67] Since there are many examples in which changes in oxidation numbers accompany the metalation reactions, the sequence of reactions leading to the various products is not clear-cut. Hawthorne and co-workers reported that the reaction of Co(II) with $[C_2B_9H_{11}]^{2-}$ led to the isolation of the monoanionic cobalt(III) sandwich complex $[(1,2\text{-}C_2B_9H_{11})_2Co]^-$ or, in the presence of NaC_5H_5, the Co(III) mixed-sandwich complex $(C_5H_5)Co(1,2\text{-}C_2B_9H_{11})$, both with the concomitant formation of metallic cobalt.[68] This suggests a rapid oxidation, or disproportionation, of an initially formed Co(II) complex. Additionally, the results with the C_2B_4 cage systems also point to a similar disproportionation sequence. In a systematic study of the syntheses, structures, and reactivities of the metallacarboranes of iron, cobalt, and nickel, *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe$[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$, M^+[*commo*-1,1′-Co$\{2,3\text{-}(SiMe_3)_2\text{-}(2,3\text{-}C_2B_4H_4)\}_2]^-$ (M = CoCl, $Co_3(TMEDA)_3Cl_5$), *commo*-1,1′-M$[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]_2$ (M = FeH, CoH, Ni), and 1-(TMEDA)-*closo*-$2,4\text{-}(SiMe_3)_2\text{-}1,2,4\text{-}MC_2B_4H_4$ (M = Co, Ni) were synthesized by the 1:1 molar ratio reactions of the respective MCl_2 salts with *closo*-*exo*-4,5-Li$(THF)_2$-1-Li$(THF)_2$-$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4$, *closo*-*exo*-4,5-Li(TMEDA)-1-Li(TMEDA)-$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4$, *closo*-*exo*-5,6-$[(\mu\text{-}H)_2Li(THF)_2]$-1-Li$(THF)_2$-$2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4$, and *closo*-*exo*-5,6-$[(\mu\text{-}H)_2Li(TMEDA)]$-1-Li(TMEDA)-$2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4$. The reactions are outlined in Schemes 5 and 6.[69]

Reference to Schemes 5 and 6 shows that, with the exception of *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe$[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$, all *commo*-metallacarboranes were the results of a redox process, in addition to a ligation reaction; the coproduct in all these reactions was the respective zerovalent metal. The only two redox-free ligation reactions were found in the formations of the "carbons apart" metallacarboranes 1-(TMEDA)-*closo*-$2,4\text{-}(SiMe_3)_2\text{-}1,2,4\text{-}MC_2B_4H_4$ (M = Co, Ni). In both complexes the metal ions are coordinated to the bidentate TMEDA molecules, in addition to the more oxidation-resistant "carbons apart" carborane ligand. On the other hand, the "carbons apart" carborane ligands favored a disproportionation of Fe(II) in the formation of *commo*-1,1′-FeH$[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]_2$ and Fe(0), even in the presence and absence of TMEDA. As Schemes 5 and 6 show, two full-sandwich ferracarboranes were produced, *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe$[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$ (Scheme 5) and *commo*-1,1′-FeH$[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]_2$ (Scheme 6). It is tempting to describe the wedged ferracarborane *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe$[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$ as being similar to the diiron complex $[2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2Fe\cdot Fe(L)_2$ (L = TMEDA, THF), identified by Grimes and co-workers as an intermediate in the oxidative cage fusion to give $(CH_3)_4C_4B_8H_8$.[61] However, the diiron complex shown in Scheme 5 was isolated in 90% yield and showed no tendency to react further in the absence of air.[69]

The results of the reaction of the late-transition-metal halides with the "carbons adjacent" and "carbons apart" *nido*-C_2B_4 carboranes can be understood on the basis of an initial formation of a *closo*-MC_2B_4 complex, which could be sufficiently stable to be isolated or undergo further reactions, yielding either the full-sandwich *commo*-carborane and/or redox products. Since these reactions are run in nonpolar solvents (hexane, benzene), they are most likely between clusters and aggregates rather than isolated ions. Under such conditions metal proximity would be likely facilitating metal-to-metal electron transfer. Thus, the relatively large number of disproportionation reactions found in this chemistry should not be surprising. The exception seems to be that the "carbons adjacent" nickelacarborane decomposes directly to give predominately Ni(0) and the oxidative closure product, *closo*-$1,2\text{-}(SiMe_3)_2\text{-}1,2\text{-}$

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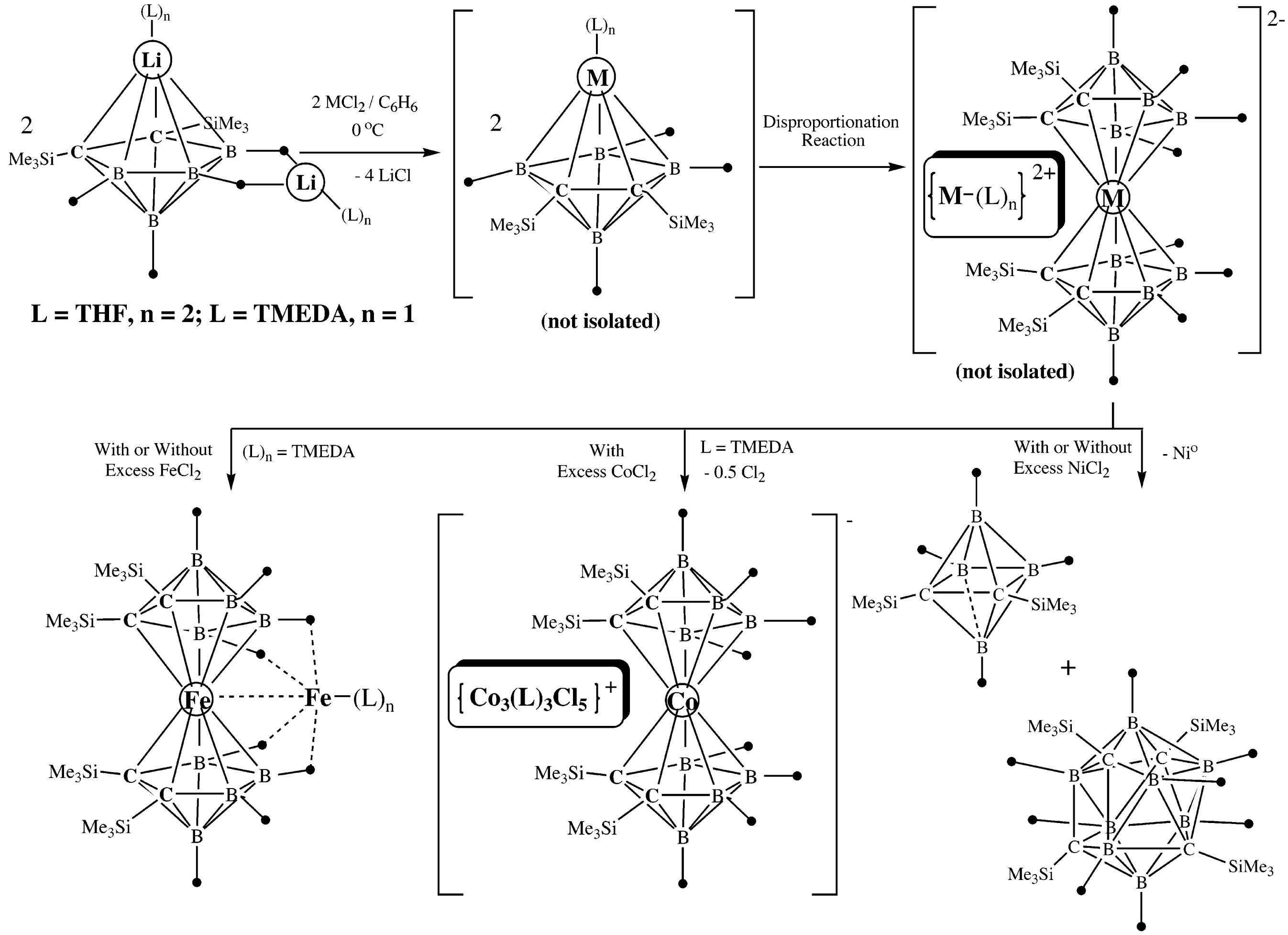
Scheme 5. Synthetic Pathways to "Carbons Adjacent" Metallacarboranes of Fe, Co, and Ni



$C_2B_4H_4$.[9i,70,71] On the other hand, the formation of the face-to-face fused C_4B_8 cages reported by Grimes and co-workers proceeded from oxidation of a full-sandwich metallacarborane (vide supra).[58−60,64]

The metallacarboranes of the late transition metals illustrate a factor that is prevalent in metallacarborane chemistry: that is, the relationship between the metal's oxidation state and cluster structure. When different oxidation states are available to the metal, the higher states are found in the full-sandwich (commo) compounds, while the half-sandwich (closo) compound supports lower states. This is true for both transition metals and main-group metals. The nickelacarboranes nicely illustrate this oxidation state/structure correlation. The metallacarboranes of Ni^{II}, Ni^{III}, and Ni^{IV} have been reported in both the small, C_2B_4, and the larger, C_2B_9,[72,73] cage systems, with the Ni^{II} involved in *closo*-metallacarboranes and the two higher oxidation states in sandwiched commo complexes. The unusual charge-compensated nickelacarborane *commo*-1,1′-Ni^{III}-[(2,4-$(SiMe_3)_2$-5,6-B_2-{σ-N(Me)$(CH_2)_2$N$(Me)_2$}-2,4-$C_2B_2H_2$)-(2′,4′-$(SiMe_3)_2$-2′,4′-$C_2B_4H_4$)] (see Figure 13) was the unexpected product of the reaction of the Ni^{IV} complex (see Scheme 6) with carefully dried TMEDA. The high yield (89%) indicates that the charge-compensated nickel(III) complex was the main product of the reaction, rather than the result of an interesting side reaction. It is of interest to note that when the reaction was carried out in the presence of moisture, 1-(TMEDA)-*closo*-2,4-$(SiMe_3)_2$-1,2,4-$NiC_2B_4H_4$ was formed, in addition to *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$; this is the only example known to date of an oxidative cage closure reaction of the small-cage "carbons apart" carboranes.[65] Hawthorne has recently proposed that the geometric changes accompanying the *commo*-Ni^{III}/Ni^{IV}-carborane interconversions be used as the basis for constructing molecular gates.[74]

Metal atom synthesis has been used widely in organometallic chemistry and can be used in metallacarborane syntheses. This methodology has been profitably exploited by Sneddon and co-workers in the syntheses of a number of unusual metallacarboranes.[75−77] The reaction of thermally generated cobalt atoms with hexaborane(10), bis(trimethylsilyl)acetylene, and cyclopentadiene gave a mixed-ligand complex, 5,1′,2′-[1-(η-

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(70) Hosmane, N. S.; Zhang, H.; Maguire, J. A.; Wang, Y.; Colacot, T. J.; Gray, T. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1000−1002.

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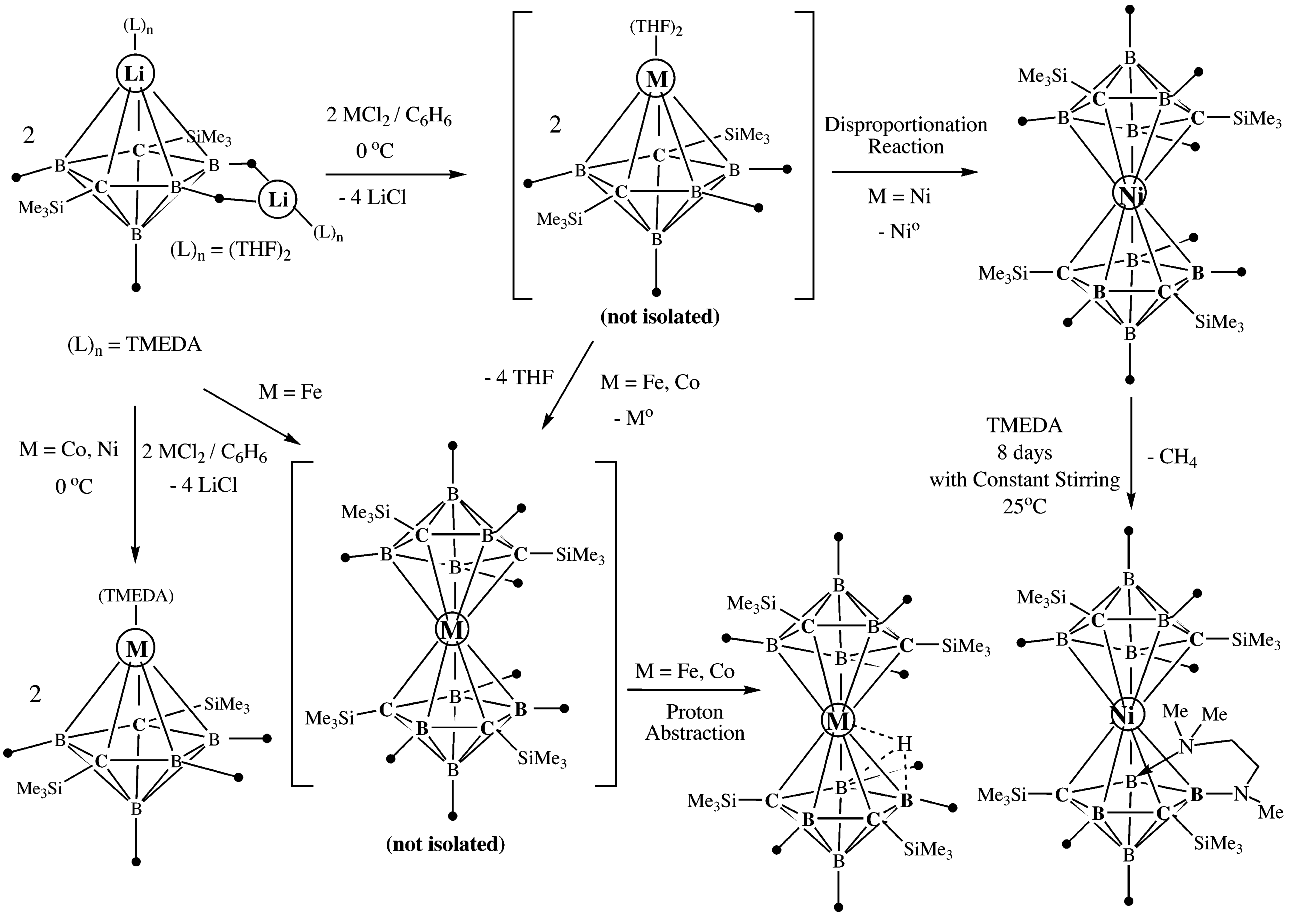
Scheme 6. Synthetic Pathways to "Carbons Apart" Metallacarboranes of Fe, Co, and Ni



C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5], as the major product.[76] This unusual complex consists of a unique bridged structure of a [1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$] sandwich in which the terminal hydrogen on the unique boron is replaced by a B_2H_5 moiety via a three-center B−B−B bond. Alternatively, the complex can be viewed as a metallacarborane-bridged diborane derivative.[76] From these results it is apparent that the use of highly reactive metal atoms can produce not only traditional types of metallacarboranes but also new and unusual organometallic/metallaborane clusters. Unfortunately, not many experimental results using this technique are available in the literature and very little is known about the mechanisms of these metal atom reactions. The method itself, while producing exciting results, is not as yet practical for targeted metallacarborane synthesis.

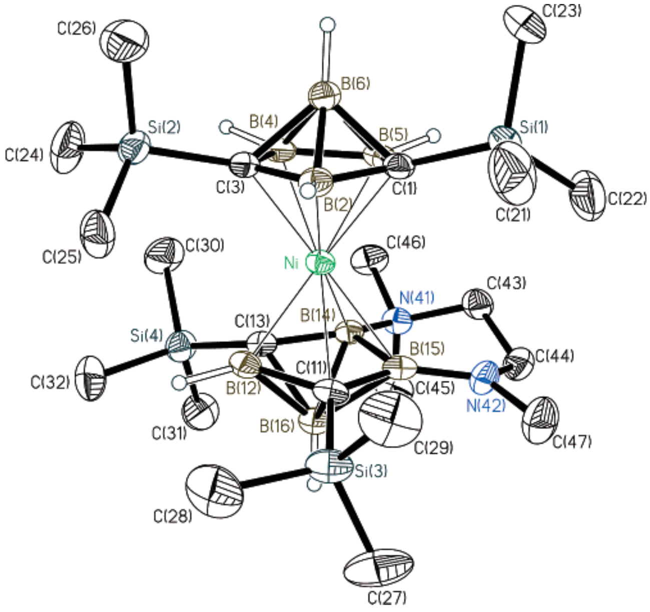


Figure 13. Crystal structure of a charge-compensated, Ni(III)-sandwiched nickelacarborane complex.

Metallacarborane derivatives, formed by the addition of organic functional groups to parent carborane or metallacarborane precursors, have been used as synthons in the preparation of multidecker sandwich complexes. The chemical reactivity of $(C_5Me_5)Co(Et_2C_2B_3H_5)$ toward electrophilic reagents has been exploited successfully by Grimes and co-workers to prepare a number of functionalized metallacarborane derivatives.[78−80] In this method, the unique boron-substituted chloro, bromo, and iodo derivatives were prepared by the reactions of $[(C_5Me_5)Co(Et_2C_2B_3H_4)]^-$ with $MeSO_2Cl$, $BrCH_2CN$, and CF_3I.[79] On the other hand, reaction with $CF_3C(O)Cl$ produced exclusively a *B*(nonunique)-C(O)CF_3 derivative, while monohalo *B*(nonunique)-X derivatives were obtained by the reaction of $(C_5Me_5)Co(Et_2C_2B_3H_5)$ with *N*-halosuccinimides.[79] The reaction of $[(C_5Me_5)Co(Et_2C_2B_3H_4)]^-$ with acetyl chloride gave a B(unique)-substituted 2-vinyl acetate derivative instead of the expected acetyl one. The base-catalyzed

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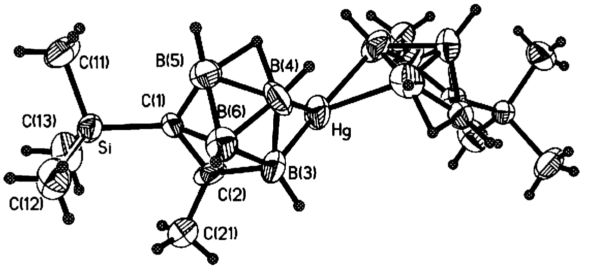

Figure 14. Crystal structure of a mercuracarborane complex.

cleavage of this complex produced a B(unique)-substituted acetyl complex.[78]

There are no examples where group 11 metals have been incorporated into smaller carborane cages, and only a few examples of the group 12 metallacarboranes exist. These include mercuracarboranes of the larger C_2B_9 cage system, in which Hg occupies an apical position above an open face of the carborane.[81,82] In these compounds, the Hg atom is slip-distorted toward the unique boron on the C_2B_3 pentagonal face of the carborane, giving an η^3 (or η^1)-carborane−metal interaction. This slip distortion is commonly found in the later d-block metallacarboranes.[81] Another mode of Hg−carborane interaction is when an HgX group bonds equally, or almost equally, to two adjacent borons on the open face of the carborane, thereby formally replacing a bridge hydrogen. These are encountered mainly in the small-cage systems. The first report was of μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$,[83] followed by those of the cobaltacarboranes μ,μ'-$[(\eta^5$-$C_5R_5)Co(CH_3)_2C_2B_3H_4]_2Hg$ and μ-$[(\eta^5$-$C_5R_5)Co$−$(CH_3)_2C_2B_3H_4]HgCl$ (R = H, CH_3).[84] Since $(\eta^5$-$C_5R_5)Co(CH_3)_2C_2B_3H_5$ is a direct analogue of $(CH_3)_2C_2B_4H_6$ in which a $(\eta^5$-$C_5R_5)Co$ moiety replaces the apical B−H vertex, their behavior should parallel the unsubstituted mercuracarboranes. In addition to μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$,[83] a bridged trimethylsilyl-substituted mercuracarborane, μ,μ'-$[2$-$(Si(CH_3)_3)$-3-(CH_3)-$2,3$-$C_2B_4H_5]_2Hg$,[85] has also been reported (see Figure 14). The most surprising aspect of the structure is in the arrangement of the ligands around the Hg. In both μ-$[(\eta^5$-$C_5(CH_3)_5)Co(CH_3)_2C_2B_3H_4]HgCl$ and μ,μ'-$[(\eta^5$-$C_5(CH_3)_5)Co(CH_3)_2C_2B_3H_4]_2Hg$ the geometry around each Hg atom is essentially linear, indicating sp hybridization of the Hg, which is reasonable for a d^{10} metal.[84] In the bis(cobaltacarborane) this leads to a structure in which the two cages are directly across the metal center from one another but point in opposite directions, giving a trans, “stair-step” type configuration; this is not the case in μ,μ'-$[2$-$(Si(CH_3)_3)$-3-(CH_3)-$2,3$-$C_2B_4H_5]_2Hg$. Reference to Figure 14 shows that the two carborane cages are not arranged opposite one another around the metal but, rather, are localized to one side of the metal (the B(4)−Hg−B(4)#1 bond angle is 92.8(7)° and the B(3)−Hg−B(3)#1 angle is 151.5(8)°). This leads to a structure in which the faces of the carboranes are twisted with respect to one another, giving rise to a dihedral angle of 76.0(6)° between the B(3)−Hg−B(4) plane and the B(3)#1−Hg−B(4)#1 plane. An inspection of the unit cell of the mercuracarborane did not reveal any particular interaction that could lead to one side of the Hg being uncovered. Whatever the reason for this orientation, it is apparent that the local geometry about the Hg cannot be rationalized on the basis of an sp-hybridized metal atom. Additional structural information on μ,μ'-metal-bridged complexes is clearly necessary.

It is apparent from the above discussions that recent synthetic, structural, bonding, and reactivity studies have established transition-metal-containing metallacarborane complexes as an important area of study in organometallic chemistry.

C. Linked Cage and Multidecker Complexes. The synthesis of new materials having novel electronic or optical properties is of great current interest. One approach to the synthesis of such materials is to systematically link small sandwich units together to form an extended multidecker sandwich system. Immediately following the discovery of the triple-decker structure of the $Cp_3Ni_2^+$ complex in the early 1970s,[86] Grimes and co-workers synthesized the first neutral triple-decker metallacarborane sandwich compound.[87] Most of the subsequent research in this field has been dominated by Grimes and co-workers, who have repeatedly demonstrated how small metallacarboranes can be stacked and then linked systematically to give extended arrays. A number of reviews by both Grimes[3a,57b,c,d,88−90] and Siebert[91−93] have adequately described the latest developments in this area of research. Therefore, our discussions in this section will cover only the highlights of the results in this area.

The key breakthrough reaction leading to the production of multidecker metallacarboranes involves the removal of an apical BH unit in metallacarboranes by treatment of a particular metallacarborane with TMEDA and H_2O or methanol at elevated temperatures, in a so-called “decapitation” reaction.[94−97] For example, the reaction of TMEDA and $[\eta^6$-$C_{13}H_{10}FeEt_2C_2B_4H_5]$ pro-

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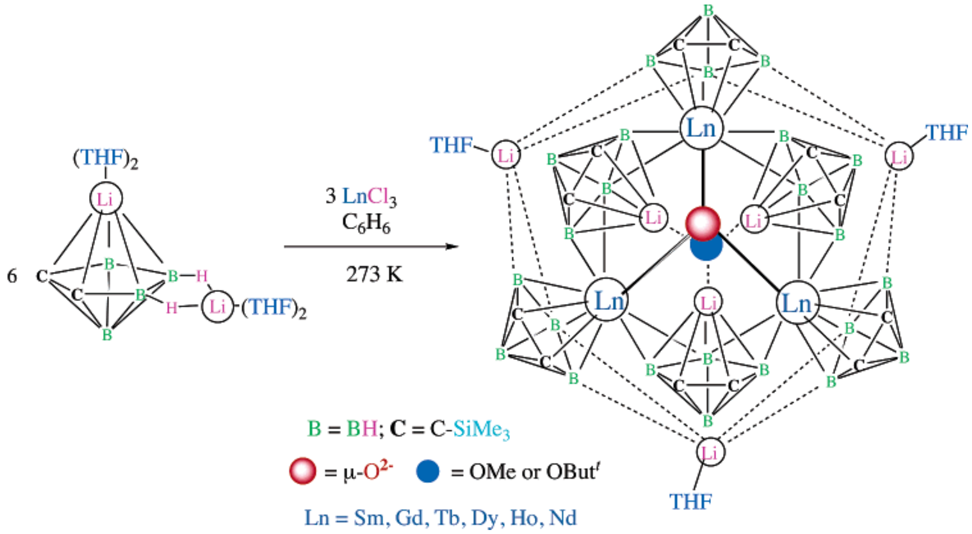
Scheme 7. Synthesis of Trinuclear Oxolanthanacarborane Clusters



duced the corresponding *nido*-1-[(η^6-$C_{13}H_{10}$)$FeEt_2C_2B_3H_5$], in which the apical B−H unit was removed and replaced by two B−H−B hydrogen bridges.[95] Removal of the bridge H atoms with appropriate reagents afforded the key anionic intermediate that was used to construct a number of desired multidecker species.[88,89,94,96,98,99] A general synthetic procedure, which can be applied to a number of different stacked systems, can be found in refs 57b−d, 89, and 90. In this way, the synthesis of large families of isolable, electrically neutral multidecker sandwich complexes having three, four, five, or six decks and incorporating C_2B_3 or C_3B_2 planar rings have been prepared and structurally characterized. This gives rise to an area of carborane chemistry that has no parallel in the larger C_2B_9, C_2B_{10}, and C_3B_8 carborane systems.[3a,57b−d,89,90,100−102] Since the retirements of Professors Grimes and Siebert from active laboratory research, an enormous burden has been transmitted to the younger scientists, who have been trained in their laboratories, to extend and develop these species into electronic materials.

D. Alkene-, Alkyne-, and Aryl-Linked Polymetallacarborane Clusters. During the past decade there has been an upsurge in reports dealing with the syntheses and characterizations of the polymetalla species of the C_2B_4 carborane ligands that are linked to aliphatic and aromatic unsaturated hydrocarbons. These substances have the potential of being the precursors for conducting or semiconducting nanoscale electronic materials. The electron-delocalized “super-aromatic” bonding environment of these cluster systems along with their thermal and oxidative stability, as well as their synthetic viability, make the smaller C_2B_4 carboranes attractive ligands for further investigation. Readers are advised to consult the recently published review and journal articles of Grimes that adequately described these developments.[3a,101−106]

III. Metallacarboranes of f-Block Elements

During the past decade or so, the chemistry of the lanthanide elements has increased in scope such that it is no longer limited to the formation of purely ionic compounds. New classes of lanthanide complexes with unusual structures and novel reactivities have emerged.[107] Although a variety of ligands have been reported in different organolanthanide systems, the cyclopentadienide anion and its C-substituted derivatives are most often utilized.[108] The first report of the synthesis and structural characterization of an f-block metallacarborane was that of the uranacarborane $[U(C_2B_9H_{11})_2Cl_2]^{2-}$ in 1977,[109] followed, in 1988, by those of the compounds *closo*-3-Yb(DMF)$_4$-1,2-$C_2B_9H_{11}$ and [3,3′-(THF)$_2$-*commo*-3,3′-Sm($C_2B_9H_{11}$)$_2$]$^-$.[110] Since these initial reports, a number of lanthanide complexes, mainly in the C_2B_{10} and C_2B_9 cage systems, have been described.[5c,111] Our interest has been in the lanthanide

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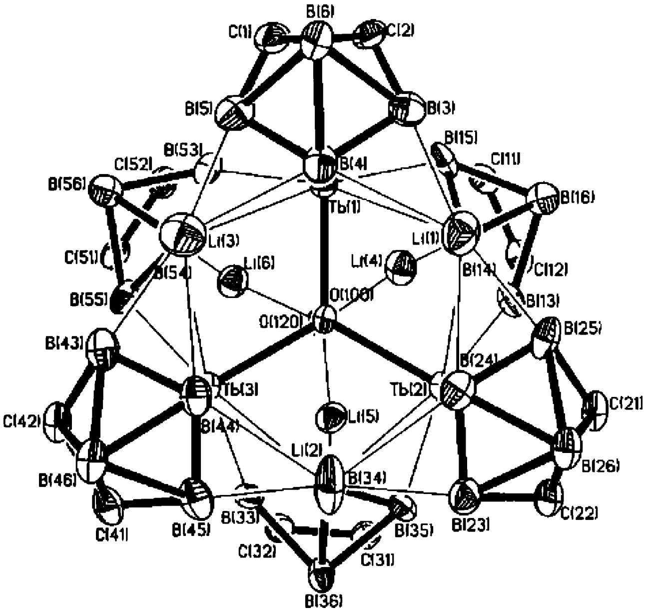

Figure 15. Crystal structure of the trinuclear oxolanthanacarborane cluster complex.

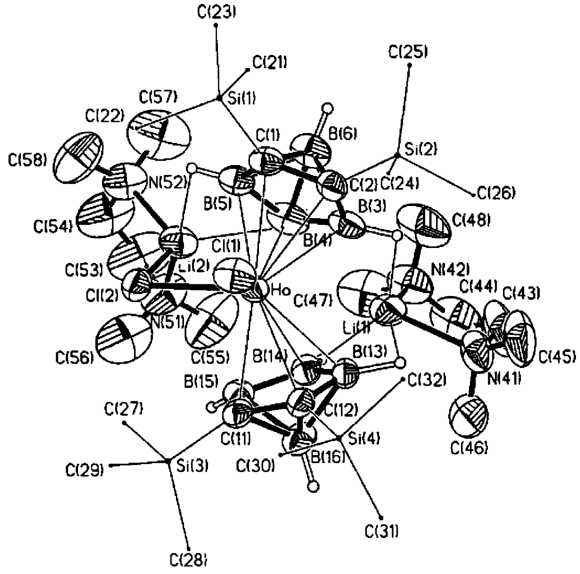

Figure 16. Crystal structure of the haloholmacarborane sandwich complex.

complexes of the C_2B_4 cage systems,[112] which exhibit reaction characteristics that are not found in the larger cages. For example, the reaction of the THF-solvated dilithium salt of the $[2,3\text{-}(SiMe_3)_2C_2B_4H_4]^{2-}$ dianion with anhydrous $LnCl_3$ in a molar ratio of 2:1 in dry benzene and THF produced trinuclear Ln(III) carboranes of the form $\{[\eta^5\text{-}1\text{-}Ln\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_3[(\mu\text{-}1\text{-}Li\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4)_3(\mu_3\text{-}OMe)][\mu\text{-}Li(THF)]_3(\mu_3\text{-}O)\}$ (Ln = Sm, Gd, Tb, Dy, Ho, Nd), instead of the expected full-sandwich lanthacarboranes (see Scheme 7).[112a,d,g,k] These clusters, shown in Figure 15, are composed of three half-sandwich lanthanacarboranes and three lithiacarboranes arranged around an oxide ion and a methoxide ion, respectively.[112g] These unexpected products were believed to arise from the initial formation of a half-sandwich lanthanacarborane, which reacts further with the THF solvent or its decomposition product, to form the final trinuclear cluster. On the other hand, the reaction of the TMEDA-solvated dilithium salt of the $[2,3\text{-}(SiMe_3)_2C_2B_4H_4]^{2-}$ dianion with anhydrous $LnCl_3$ at equivalent 2:1 molar ratios produced the full-sandwich species $[1\text{-}Cl\text{-}1\text{-}(\mu\text{-}Cl)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}5,6\text{-}[(\mu\text{-}H)_2Li(TMEDA)]\text{-}4,4',5,5'\text{-}[(\mu\text{-}H_3)Li(TMEDA)\text{-}\mathit{commo}\text{-}Ln\text{-}(2,3\text{-}C_2B_4H_4)_2]^-$ (Ln = Sm, Gd, Dy, Ho, Er; see Figure 16 for example).[112e,h] In addition, several half-sandwich complexes have been reported.[112j,m,n] Most of the small-cage lanthanacarboranes have involved the use of the “carbons adjacent” ($2,3\text{-}C_2B_4$) isomer. There is also a “carbons apart” ($2,4\text{-}C_2B_4$) isomer in which the two carbon atoms on the face are separated by a boron atom; these also form metallacarboranes.[5c,112m,113] Although isolated full- and half-sandwich lanthanacarboranes in the “carbons apart” cage system had been reported,[113,114] these lanthanacarboranes had not been studied systematically, until recently. The reactions of *closo-exo*-$5,6\text{-}Na(THF)_2\text{-}1\text{-}Na(THF)_2\text{-}2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4$ with anhydrous $LnCl_3$ (Ln = Nd, Gd, Dy, Ho, Er, Tb, Lu), in molar ratios of 2:1 in dry benzene (C_6H_6), produced the full-sandwich lanthanacarborane complexes $2,2',4,4'\text{-}(SiMe_3)_4\text{-}3,5',6'\text{-}[(\mu\text{-}H)_3Na[(X)_n(Y)_m]\text{-}1,1'\text{-}\mathit{commo}\text{-}Ln(\eta^5\text{-}2,4\text{-}C_2B_4H_4)_2$ (Ln = Nd, X = THF, $n = 2$, Y = none; Ln = Gd, X = THF, $n = 3$, Y = none; Ln = Dy, X = THF, $n = 1$; Y = TMEDA, $m = 1$; Ln = Ho, X = DME, $n = 1$, Y = none; Ln = Er, X = THF, $n = 1$, Y = none; Ln = Tb, X, Y = none; Ln = Lu, X = THF, $n = 2$, Y = none) in 70−93% yields.[115] A general synthetic procedure is outlined in Scheme 8. While the solid-state structures of the dimeric Nd, Gd, Dy, Ho, and Lu sandwich metallacarboranes were determined by X-ray crystallography, only one of them (when Ln = Gd) is shown in Figure 17.[115] These results differ markedly from those obtained in the “carbons adjacent” system, where a very similar procedure gave exclusively the trinuclear clusters of the half-sandwich lanthanacarboranes and lithi-

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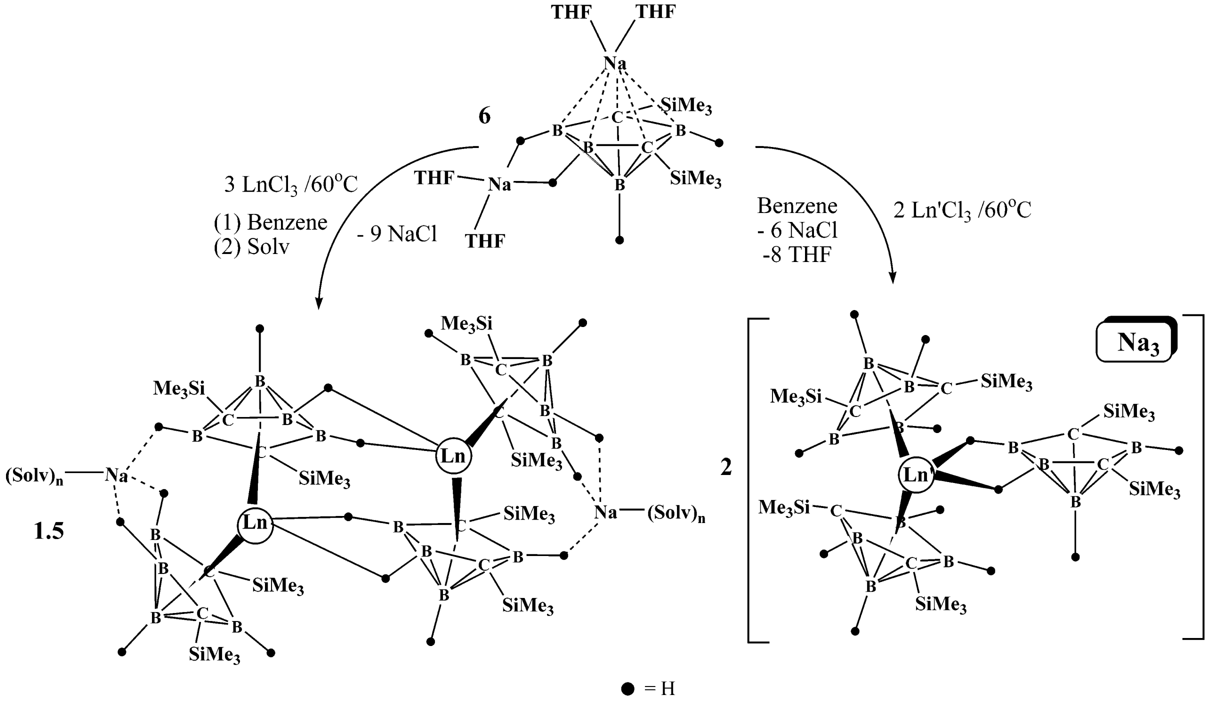
Scheme 8. Syntheses of "Carbons Apart" Lanthanacarborane Complexes



Ln = Nd, Gd, Tb, Dy, Ho, Er, Lu; Ln' = Dy, Er; Solv = THF and/or TMEDA; n = 1-3

acarboranes at room temperature.[112a−d,g,k] It is difficult to understand why the very different products were obtained. However, the "carbons adjacent" carborane requires the use of *t*-BuLi as a deprotonating agent. Since both *t*-BuLi and lanthanide compounds are known to degrade THF and other oxygen-containing compounds,[116,117] it could well be that such degradation reactions produce the methoxide and oxide products that effectively prevented the formation of the expected full-sandwich compounds.[112g] The results described in Scheme 8, in which the full-sandwich complexes were formed under similar conditions, but in the absence of *t*-BuLi, further supports this contention. This is consistent with the fact that when the TMEDA-solvated dilithiacarborane *closo-exo*-5,6-[(μ-H)$_2$Li(TMEDA)-1-Li(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$ was reacted with LnCl$_3$, only the full-sandwich complexes were formed.[112h] The reactions of the larger *nido*-C_2B_9 carborane anion with LnCl$_3$ in a 2:1 molar ratio produced only the expected full-sandwich lanthanacarboranes.[109,110,118]

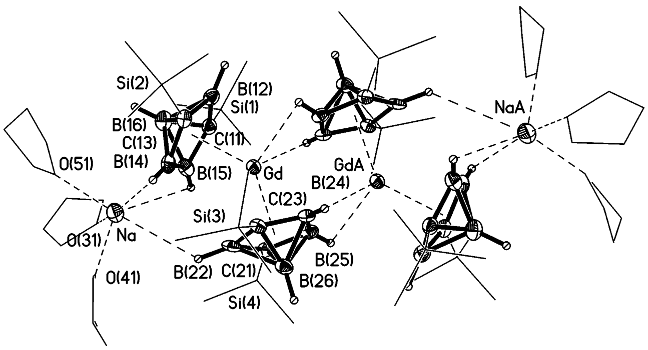


Figure 17. Crystal structure of the dimeric gadolinacarborane sandwich complex.

Most of the metalation reactions were run using either a 1:1 or 2:1 molar ratio of carborane to LnCl$_3$; the consequences of using higher reaction ratios have not been investigated. The effect of the reaction stoichiometry on the nature of the products was probed by studying the reactions of *closo-exo*-5,6-Na(THF)$_2$-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$ with anhydrous LnCl$_3$ (Ln = Dy, Er), in molar ratios of 3:1, under the same experimental conditions used in the preparation of "carbons apart" lanthanacarborane sandwich complexes. In the Cp system, a 3:1 ligand to metal ratio produced LnCp$_3$ complexes in which the three Cp$^-$ ligands were η^5-bonded to a lanthanide metal.[119] However, the products were the mixed metallacarborane complexes [Na$_3$]-[1,1′-{5,6-(μ-H)$_2$-*nido*-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$}-2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Ln-(2,4-$C_2B_4H_4$)$_2$] (Ln = Dy, Er).[114a,115] In these compounds three carborane ligands were found to be associated with each lanthanide metal center, two through η^5-bonding modes and one through a set of two Ln-H−B bonding interactions (see Figure 18). Although these are stoichiometric analogues of tris(cyclopentadienyl) lanthanide complexes, their structures and bonding modes are quite different.[120] It may be that, even with the presence of the three Na$^+$ counterions, the high total negative charge due to the three carborane ligands (6−) prevents a (tris) η^5-bonding interaction. Steric considerations may also be important in such cases.

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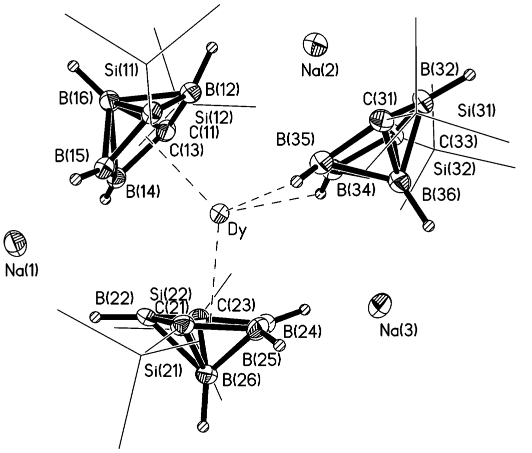

Figure 18. Crystal structure of a dysprosacarborane complex comprising three C_2B_4 carborane ligands.

However, a number of sterically crowded $(C_5Me_4R)_3La$ (R = Me, Et, ^{i}Pr, $SiMe_3$) complexes have been synthesized and structurally characterized;[121] therefore, it is difficult to assess the relative importance of the size of the carborane ligands in destabilizing tris complexes. Thus, the reactions of the "carbons-apart" C_2B_4 carborane ligands with a number of $LnCl_3$ salts, in molar ratios of 2:1 and 3:1, produced full-sandwich lanthanacarborane complexes in which each Ln(III) occupies the apical positions above the open faces of two carborane dianions and is bonded to a third by two Ln-H−B bridges. If excess carborane is not available, this bonding pattern is satisfied by dimerization (see Figure 17).[115b]

Our interest in oxo−lanthanide compounds stems from the observation that, unlike the larger cage (C_2B_9 and C_2B_{10}) analogues, the small-cage carboranes can form unusual oxolanthanacarboranes of the type $\{[\eta^5\text{-}1\text{-Ln-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_3[(\mu\text{-}1\text{-Li-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4)_3(\mu_3\text{-OMe})][\mu\text{-Li(THF)}]_3(\mu_3\text{-O})\}$ (Ln = Nd, Sm, Gd, Tb, Dy, Ho).[112g,k] The extension of this chemistry is limited by the use of THF as an oxygen source. Therefore, the synthetic route for the trinuclear oxolanthanacarboranes has several disadvantages. It greatly complicates the development of any general synthetic scheme, it is difficult to control the stoichiometry of the synthesis, and it introduces a number of other degradation products such as MeO^- that can then influence the reaction. These complications could be countered by the direct use of an oxide donor, such as water, in the reactions. It was found that when anhydrous $LnCl_3$ (Ln = La, Nd, Gd, Tb, Ho, Lu) was treated with stoichiometric quantities of freshly distilled H_2O under reflux conditions in THF and the resulting mixtures were reacted with *closo-exo*-5,6-$Na(THF)_2$-1-$Na(THF)_2$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ in an overall carborane to $LnCl_3$ to H_2O molar ratio of 5:4:1, a series of oxide-encapsulated complexes, $\{[\eta^5\text{-}1\text{-Ln(THF)}_n\text{-}2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]_4(\mu\text{-Cl})_2(\mu_4\text{-O})\}\cdot y\text{THF}$ (Ln = La, $n = 0$, $y = 1$; Ln = Nd, $n = 1$, $y = 0$; Ln = Gd, $n = 0$, $y = 1$; Ln = Tb, $n = 1$, $y = 0$; Ln = Ho, $n = 0$, $y = 1$; Ln = Lu, $n = 1$, $y = 0$), are produced in 73−86% yields.[122] A general synthetic procedure is outlined in Scheme 9, and the general molecular geometry of the complexes, when Ln = Tb, is shown in Figure 19. The reactions are very sensitive to both stoichiometry and procedure: the $LnCl_3/H_2O$/THF mixture must be refluxed until a homogeneous solution is obtained, and the reactions must be carried out initially at −78 °C and then completed at reflux temperatures. If $LnCl_3$ and H_2O were added to a solution of the carborane ligand without prior refluxing, the water directly attacked and rapidly decomposed the carborane ligand.[122] The best yields were obtained from "exact" stoichiometric mixtures, assuming one carborane dianion acts as a proton scavenger; there is NMR evidence for the formation of a neutral *nido*-carborane in the final reaction mixture. A 1:1 molar ratio of carborane to Ln led to the same products, but in lower yields. In addition, reactions in which the Ln to H_2O ratios were less than 4:1 resulted in the formation of inseparable product mixtures, while higher ratios produced the tetralanthanide clusters and the unreacted carborane precursor.[122] The ionic nature of the bonding is also seen in the DFT results on the model compound $La_4OCl_2(2,4\text{-}C_2B_4H_6)_4(OH_2)_4$.[122b] Thus, the results of this work demonstrated the systematic synthetic approach of using water as one of the controlled reagents to construct hitherto unexplored lanthanacarborane clusters comprising a $[(C_2B_4Ln)_4Cl_2O]$ core. Although oxygen coordination numbers ranging from 3 to 6 have been observed for f-block metal complexes,[123,124] there does not seem to be any consistency in either the precursor or the synthetic procedures. Clusters with a similar tetrahedral Ln_4O core were found for $[Ln_4(\mu_4\text{-O})(NHPh)_3(OSiMe_2NPh)_6\cdot Na_6(THF)_7]$ (Ln = Gd, Yb), which were obtained in low yields (8.9%) by the reaction of $LnBr_3$, NaNHPh, and $(Me_2SiO)_3$ in THF,[125] while the planar Ln_4O core in $Na_6\{[(C_6H_5SiO_2)_8]_2Nd_4(\mu_4\text{-O})\}$ was obtained in 16% yield by the reaction of anhydrous $NdCl_3$ and sodium oligo(phenylsiloxanolate) in an *n*-butanol solution.[126a] The planar Ln_4O core cluster in $[Tb_4L_2(NO_3)_4(MeOH)_2(\mu_4\text{-O})]$ (H_3L = 1,3-bis(2-hydroxy-3-methoxybenzylamino)propan-2-ol) was obtained by the reaction of hydrated $Tb(NO_3)_3\cdot 5H_2O$ with H_3L in a 2:1 ratio in methanol.[126b] On the other hand, the butterfly form of Ce_4O in the cerium complex $Ce_4O(O^iPr)_{13}(^iPrOH)$ was obtained from the photoreduction of $Ce_2(O^iPr)_8(^iPrOH)$ in a 2:1 mixture of $MeOC_2H_4OMe$/*i*-PrOH.[124] The complexity is illustrated in the reactions of YCl_3 and $LaCl_3$ with $NaOCMe_3$ under different conditions.[123] While a 1:3 molar reaction of YCl_3 and $NaOCMe_3$ in THF produced the trinuclear $Y_3(\mu_3\text{-OCMe}_3)(\mu_3\text{-Cl})(\mu\text{-OCMe}_3)(OCMe_3)_4(THF)_2$, in which the metals form a triangular core, the same reaction, when carried out in the presence of Me_3COH, produced an isomeric compound

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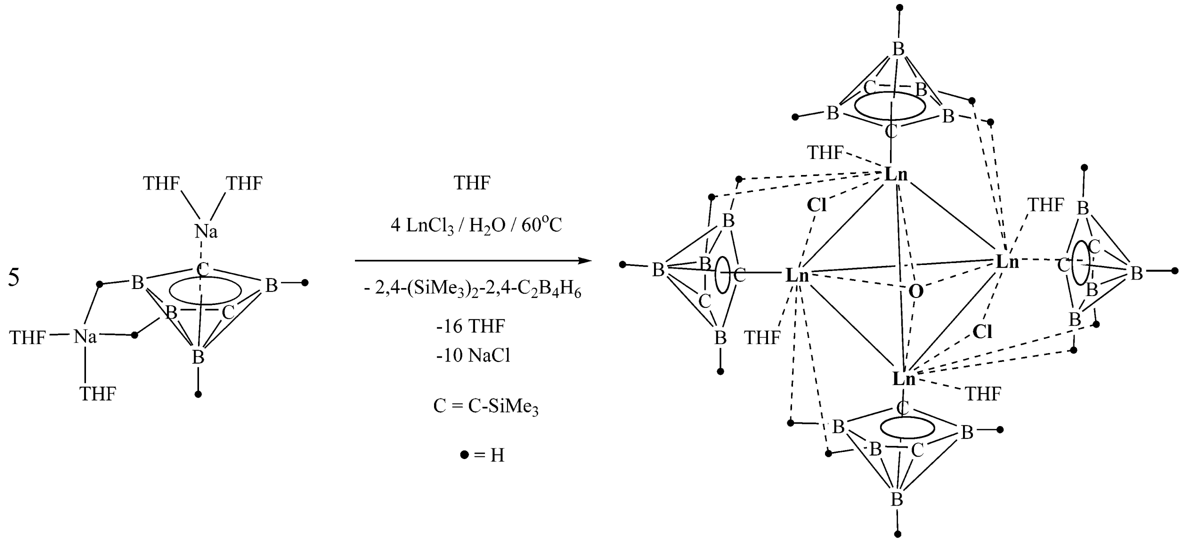
Scheme 9. Synthesis of an Oxide Ion Encapsulating Tetralanthanide Tetrahedron, Surrounded by "Carbons Apart" Carborane Cages



Ln = La, Nd, Gd, Tb, Ho, Lu

differing in the placement of the two THF molecules. The reaction of $LaCl_3$ with 3 equiv of $NaOCMe_3$ in THF produced the compound $La_3(\mu_3\text{-}OCMe_3)_2(\mu\text{-}OCMe_3)(OCMe_3)_4(THF)_2$, which is similar to the trinuclear Y complex except that $OCMe_3$ now occupies both triply bridging positions. On the other hand, the reaction of a 1:2 molar ratio of YCl_3 and $LiOCMe_3$ produced the dimer $[Y_4(\mu_3\text{-}OCMe_3)(\mu\text{-}OCMe_3)_4(OCMe_3)_4(\mu_4\text{-}O)(\mu\text{-}Cl)_2Li_4(\mu\text{-}OCMe_3)_2]_2$, in which the Y_4 cores are arranged in a butterfly arrangement about an oxide ion. Some of this same complexity can be inferred for the lanthanacarboranes.

In the "carbons apart" 2,4-C_2B_4 cage system, only the full-sandwich lanthanacarboranes of Nd, Gd, Dy, Ho, Er, Tb, and Lu were obtained, and the preparation of the corresponding half-sandwich complexes has proved to be very difficult, irrespective of the reaction stoichiometry.[115] Although advantage can be taken of the propensity of the 2,4-C_2B_4 cages to form oxide-encapsulated lanthanacarborane clusters,[122] no simple and discrete half-sandwich halolanthanacarboranes have beeen isolated. The only way to obtain the simple half-sandwich complex was by reacting the monosodium compound *nido*-1-Na(THF)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ (**1**)[9h,i] with anhydrous LnX_3 in a molar ratio of 2:1, in dry THF.[112n] This reaction produced the dimeric half-sandwich species [1-(X)-1,1-$(THF)_2$-2,3-$(SiMe_3)_2$-1-Ln(η^5-2,3-$C_2B_4H_4$)$]_2$ (**2**, Ln = Ce, X = Br; **3**, Ln = Gd, X = Cl; **4**, Ln = Lu, X = Cl), in high yields, along with 1 equiv of the neutral *nido*-carborane precursor 2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$.[112n] Although the exact mechanism is not known, the method covers the syntheses involving metals of the lanthanide series at the beginning, in the middle, and at the end within the group. Therefore, it should be generally applicable to all lanthanide metals, and most likely the actinides as well. The method also has the advantage that it protects against the complications of THF decomposition found in other synthetic methods.[112a–d,g,k]

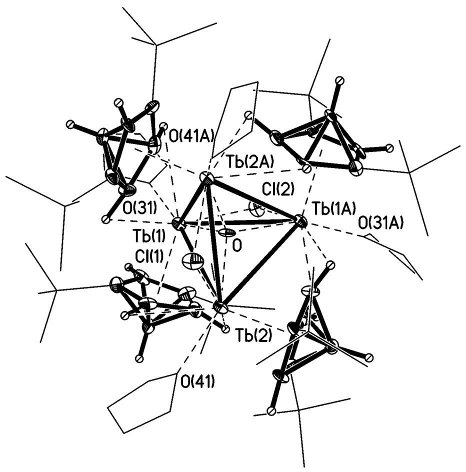


Figure 19. Crystal structure of an oxide ion encapsulating a tetraterbium tetrahedron, surrounded by "carbons apart" carborane cages.

In a reactivity study of the sandwiched lanthanacarborane complexes, a mixed half- and full-sandwich lanthanacarborane complex was synthesized. Thus, the reaction of the "carbons apart" carborane dianion with anhydrous $NdCl_3$, in a molar ratio of 2:1, produced, in 80% yield, the full-sandwich neodymacarborane 2,2′,4,4′-$(SiMe_3)_4$-5,6-[$(\mu\text{-}H)_2$Na$(THF)_2$]-1,1′-*commo*-Nd(η^5-2,4-$C_2B_4H_4)_2$, which was reacted further with $NdCl_3$ in a 3:1 molar ratio to give the novel dimeric ion pair {[*closo*-1-Nd$(\mu\text{-}H)_6$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$^+$[1,1′-$(THF)_2$-2,2′,4,4′-$(SiMe_3)_4$-5,5′,6,6′-$(\mu\text{-}H)_4$-1,1′-*commo*-Nd(η^5-2,4-$C_2B_4H_4)_2$]$^-$·C_4H_8O·$2C_6H_6$}$_2$.[127] The compound, shown in Figure 20, consists of a half-sandwich cationic neodymacarborane that is coordinated to an anionic full-sandwich neodymacarborane. This work exemplifies the dual role of metallacarboranes as both the cation and the anion in a single species.[127]

The two-electron reductive cage openings of the *closo*-carboranes have been well-documented in the literature.[63b,128] In a series of papers Stone and co-workers

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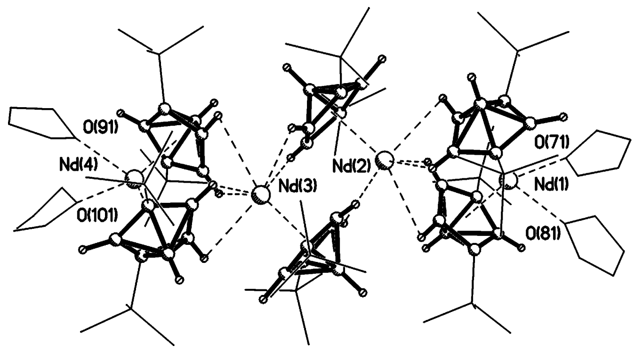

Figure 20. Crystal structure of the sandwiched neodymacarborane ion pair comprising a half-sandwich cation and full-sandwich anion.

reported the simultaneous cage reduction and metalation of *closo*-carboranes in the C_2B_n (n = 6, 8, 9) cage systems using a number of zerovalent nickel, platinum, and palladium complexes.[129] While the monocarbon carborane [*closo*-$CB_{10}H_{11}$]$^-$ was also found to react in a similar manner,[130] the icosahedral *closo*-$(RC)_2B_{10}H_{10}$ cage has been opened by the reaction of a group 1 metal, in the presence and absence of catalysts, to give the corresponding *nido*-carboranes.[131,132] The group 2 element Mg was also found to react with *closo*-1,2-$C_2B_{10}H_{12}$ in the presence of catalytic amounts of 1,2-dibromoethane.[133] In addition, Xie and co-workers have reported the uncatalyzed reduction of Na[1-($Me_2C(C_5H_5)$-*closo*-1,2-$C_2B_{10}H_{11}$] by Na metal to form the ansa ligand Na_3-[1-($Me_2C(C_5H_5)$-*nido*-1,2-$C_2B_{10}H_{11}$], in which a Cp^- group is tethered to a dianionic *nido*-$C_2B_{10}H_{11}$ moiety via an Me_2C bridge; metal complexes of this ligand were also described.[134] In all of the reductive cage-opening processes, the resulting *nido*-carborane products have a "carbons apart" geometry where the two cage carbons are separated by at least one boron atom on the open faces of the carboranes. When the two cage carbons are bridged, by either an organic group or a metal complex, cage reduction produced the "carbons adjacent" *nido*-C_2B_{10} cage, which seem to be susceptible to further reduction to give the respective *arachno*-carboranes.[135]

In comparison to the large number of catalyzed and uncatalyzed approaches to reduction/opening processes that have been described for the large-cage *closo*-carboranes, the methods applicable to the small C_2B_4 cage system are quite limited. Although there have been some very interesting, but isolated, reports of the reductive cage openings of *closo*-$C_2B_4H_6$ by Lewis bases, such as $(CH_3)_3N$,[136] and low-valent metal compounds,[137] the only general, high-yield method of transforming either *closo*-1,6-$(CR)_2B_4H_4$ (R = H or a cage carbon substituent) or its 1,2-isomer to the corresponding [*nido*-2,4-$(CR)_2B_4H_4$]$^{2-}$ species is by naphthalene-catalyzed group 1 metal reduction.[63b] The use of naphthalene in the traditional two-electron reductive cage-opening reactions has several disadvantages. It introduces an additional reagent that must be removed from the reaction mixture before the *nido*-carborane products can be reacted further. In addition, naphthalene also has a tendency to cocrystallize with any product or to substitute for a terminal B−H hydrogen, which often interferes with the reactivity of these dianionic ligands. The inability of the *closo*-C_2B_4 carboranes to undergo two-electron reduction in the absence of naphthalene led to the question of whether such carborane cages could be reductively opened and simultaneously metalated by an in situ generation of activated metal atoms, similar to that reported for the larger *closo*-$(CR)_2B_{10}H_{10}$.[129,130,134,135,138] This possibility was tested by the reaction of anhydrous $ErCl_3$ with 4 equiv of freshly cut potassium metal, under reflux conditions in THF, followed by direct addition of the *closo*-carborane 1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ to produce the "carbons apart" erbacarborane sandwich 2,2′,4,4′-$(SiMe_3)_4$-3,6′-[(μ-H)$_2$K-(THF)$_2$]-1,1′-*commo*-Er(η^5-2,4-$C_2B_4H_4$)$_2$ in 82% yield (see Scheme 10).[114b] It is of interest to note that under equivalent conditions neither one of the metals alone reacted with the *closo*-carborane, nor did a reaction mixture of K and $ErCl_3$ in a 3:1 molar ratio; in both cases the *closo*-carborane precursor was recovered unchanged. The sequence is also important; if the carborane, $ErCl_3$, and K are mixed in a 2:1:4 molar ratio as in eq 2, a mixture is obtained in which the products are

$$ErCl_3 + 4K + 2\ closo\text{-}(CSiMe_3)_2B_4H_4 \xrightarrow{THF} [K(THF)_2]Er(CSiMe_3)_2B_4H_{42} + 3KCl \quad (2)$$

inseparable, and product analysis was not possible. The net reaction in Scheme 10 and given in eq 2 is the same as that for the naphthalene-catalyzed reduction of the *closo*-carborane, followed by isolation and purification of the K salt of the corresponding dianion and then its reaction with $ErCl_3$; this is the normal synthetic route.[114a] Therefore, the same driving forces are at work in both methods. Viewed from this perspective, the method outlined in Scheme 10 just substitutes Er^{3+} for naphthalene as an electron-transfer agent. The fact that the reaction of *closo*-carborane with the 1:3 molar mixture of $ErCl_3$ and K produced no lanthanacarborane shows that even finely divided (atomic) Er metal is not a strong enough reducing agent to bring about the reaction. The reaction shown in Scheme 10 seems to be an unprecedented example of a new two-electron reductive cage opening process in which the capping metal acts as the

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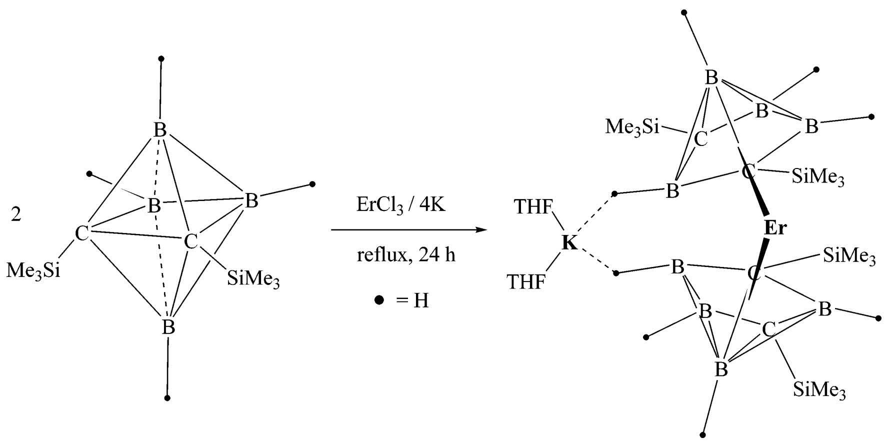
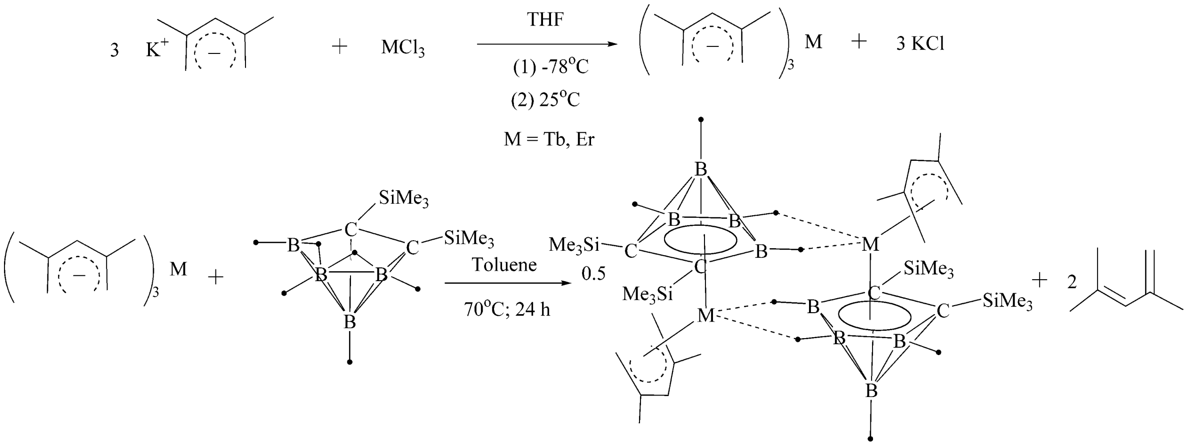
Scheme 10. One-Pot, Two-Electron Reductive Cage Opening with Concomitant Metalation



Scheme 11. Synthesis of Lanthanacarboranes of Mixed Open-Pentadienyl and Carborane Ligands



electron-transfer catalyst. Since there is nothing unique about Er, the method should prove to be a general route to the formation of a number of diverse metallacarboranes in the sub-icosahedral cage systems. However, this remains to be demonstrated.

In addition to the well-studied cyclopentadienyl ligand, there is another π-electron donor, the open pentadienyl ligand R_7C_5 (R = H or an alkyl derivative). A number of so-called “open metallocenes” where the pentadienyl group replaces one or more cyclopentadienyl ligands have been synthesized and characterized.[139] The pentadienyls have been shown to be similar to their cyclic analogues in some respects but possess a unique chemistry that has led to a number of unusual compounds, such as the metallabenzenes and their π complexes.[140,141] While both the metal−pentadienyls and the metallacarboranes have often been compared to the metallocenes, there is only one report of combining open-metallocene and metallacarborane chemistry. This involved the syntheses and structural determinations of two open-sandwich lanthanacarboranes, $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$ (Ln = Tb, Er). The compounds were synthesized in a two-step process, as outlined in Scheme 11.[142] The tris(pentadienyl)lanthanide complex was first synthesized by the reaction of a 3:1 molar ratio of $K[2,4\text{-}(Me)_2C_5H_5]$ and $LnCl_3$ (Ln = Tb, Er) in THF following the published procedures.[143,144] The $Ln(2,4\text{-}(Me)_2C_5H_5)_3$ compounds were then treated immediately with $2,3\text{-}(SiMe_3)_2$-*nido*-$2,3\text{-}C_2B_4H_6$ in a 1:1 molar ratio in toluene to give $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$ (Ln = Tb, Er) dimers, in yields of 76 and 82%, respectively. The pentadienyl group can potentially act as an η^1-, η^3- or η^5-bonding ligand. The crystal structures show that each compound crystallizes as $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$ (Ln = Tb (see Figure 21), Er), a dimer in which a planar pentadienyl ligand and a carborane ligand are η^5-bonded to a metal atom. In addition, each carborane is η^2-bonded to the neighboring metal in the dimer.[142] The synthesis outlined in Scheme 11 is based on the acidity of the bridged hydrogens in *nido*-$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_6$ being higher than that of the methylene hydrogens on the neutral pentadiene, $2,4\text{-}(Me)_2C_5H_6$. The “diprotic” *nido*-$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_6$ removes two $[2,4\text{-}(Me)_2C_5H_5]^-$ ligands by protonation on the tris(pentadienyl)lanthanide, leading to the mixed-

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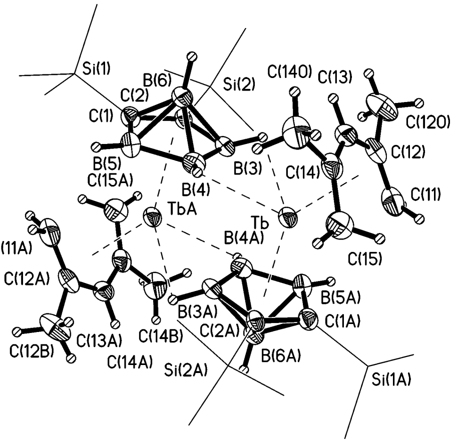

Figure 21. Crystal structure of the dimeric terbacarboranes derived from mixed open-pentadienyl and carborane ligands.

ligand products. Since the metal plays somewhat of a passive role, it should be possible to expand the scope of these reactions to other metal−pentadienyl systems and *nido*-carboranes.

IV. Metallacarboranes of Main-Group Elements

As pointed out in the Introduction to this review, the structure and chemistry of the main-group metallacarboranes have been the subject of a number of recent extensive reviews, including several dated 2002,[5,145] and a brief reference to the latest work in the area has also been made.[146] Therefore, just an overview of the most recent results will be presented. For convenience, the discussion will be in increasing order of group number.

A. Complexes of Group 1 Elements. The group 1 metallacarboranes are probably the most synthesized and the least thought about of the metallacarboranes; they are commonly used as precursors for other, “more interesting”, compounds. The most used synthetic route to metallacarboranes is through the reactions of open-faced carborane anions with metal reagents, usually metal halides. This procedure was used in the syntheses of the initially reported metallacarboranes having the general formula 3,1,2-M$(CR)_2B_9H_9$ (M = metal moiety; R = H or an alkyl group).[7,63a,68] The carborane fragments were synthesized by an initial degradation of *closo*-1,2-$(CR)_2B_{10}H_{10}$ by alcoholic KOH, to produce the monoanions $[(3),1,2\text{-}(CR)_2B_9H_{10}]^-$, which were assumed to be *nido*-carboranes having a single bridged hydrogen. The bridged hydrogen was then removed by the reaction with NaH, to give the dianionic ligands *nido*-$[(3),1,2\text{-}(CR)_2B_9H_9]^{2-}$. Since equivalent results were obtained with different alkali metals or when tetralkylammonium cations were used,[68] the alkali metals were assumed to be innocent spectator ions. The situation in the smaller C_2B_4 cage system is not so straightforward. The dianionic ligands of the type *nido*-$[2,3\text{-}(CR)_2B_4H_4]^{2-}$ should normally be made by removing the two bridging hydrogens from the corresponding *nido*-2,3-$(CR)_2B_4H_6$. Onak and Dunks found that the reaction of *nido*-2,3-$C_2B_4H_8$ with the strong base NaH produced the monosodium compound, according to eq 3.[9d] The most interesting aspect of this reaction is its stoichiometry; the monoanion is the exclusive product formed, even in the presence of excess NaH and at elevated temperatures. Grimes and co-workers studied the kinetics of this deprotonation reaction with various substituted carboranes of the type *nido*-2,3-R,R′-$C_2B_4H_6$ (where R = alkyl, arylmethyl, phenyl; R′ = R, H), using both NaH and KH in THF (C_4H_8O).[147] Their results were consistent with a mechanism involving a direct reaction of the carborane with a hydride site on the solid MH base. As was found for the unsubstituted carboranes, only a single bridging hydrogen was removed in these heterogeneous reactions. This lack of reactivity of the monoanion toward the metal hydride bases was somewhat surprising, in view of the fact that the monoanions react readily with bases such as *n*-BuLi to give mixed Na/Li salts. These mixed salts have proved to be useful synthons in the preparation of a number of heterocarboranes (vide infra).[148] A possible explanation of the reaction preference of the monoanions was provided by the crystal structure of the sodium salt of the trimethylsilyl-substituted carborane monoanion $[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5]^-$.[149] The solid-state structure is that of an extended network of dimeric $(C_4H_8ONa^+)_2[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5^-]_2$ clusters that are layered symmetrically on top of one another. The remaining bridge hydrogen on each carborane cage in the dimer is well shielded by the surrounding groups. In much the same way, the reaction of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ with NaH in tetramethylethylenediamine (TMEDA) resulted in the exclusive formation of the monosodium salt, which crystallized as a $[(TMEDA)Na^+]_2[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5^-]_2$ dimer (see Figure 22).[9i] It was argued that the monosodium carboranes would exist in THF or TMEDA solutions as intimate ion-pair clusters, with structures similar to those shown in Figure 22, and that the steric shielding of the bridging hydrogens (H(34)) in such clusters would effectively prevent reaction of the monoanion with a surface H^- site on the solid NaH. Support for this argument was furnished by the synthesis of the more extensively solvated *nido-exo*-4,5-$[(\mu\text{-}H)_2Na(TMEDA)_2\text{-}2\text{-}(SiMe_3)\text{-}3\text{-}Me\text{-}2,3\text{-}C_2B_4H_5]$, in which the $[Na(TMEDA)_2]^+$ does not act as a capping group but is exo-polyhedrally bound, leaving the bridge hydrogen unprotected.[150] It was found that this less sterically protected bridge hydrogen could easily be removed by NaH, to give the corresponding disodium compound.[150] The bridge hydrogen in the highly solvated $[Li(TMEDA)_2{}^+][nido\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5^-]$ was also found to be unprotected and to react readily with NaH

$$nido\text{-}C_2B_4H_8 + \text{excess NaH} \xrightarrow[0-150\ °C]{THF} Na[nido\text{-}C_2B_4H_7] + H_2 \quad (3)$$

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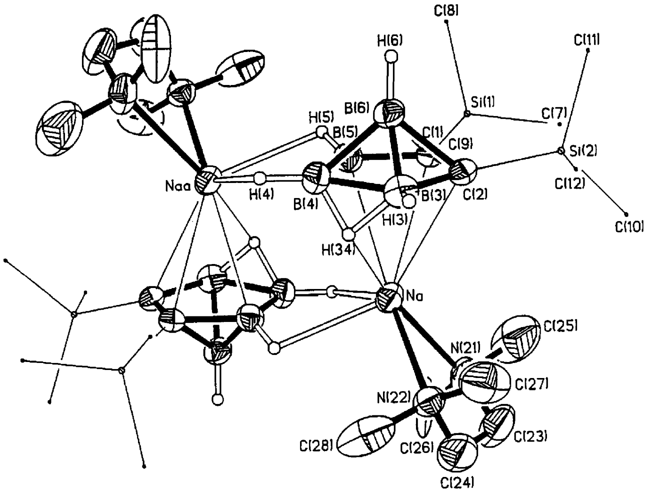

Figure 22. Crystal structure of the dimeric form of 1-Na-(THF)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$.

to give the corresponding Na/Li carborane.[151] Therefore, the stoichiometry of eq 3 seems to be dictated more by the heterogeneous nature of the reaction and steric factors than by the acidities of the monoanions.

The structures of several of the dianionic group 1 half-sandwich carboranes have been determined.[9i,63b,65,152] In these bimetallic compounds the two metal ions occupy nonequivalent positions in the cluster: one is exo-polyhedrally bound to two adjacent borons on the C_2B_3 face of the carborane, while the other occupies the apical position above the bonding face. The results show that the metal replacing the first removed bridging hydrogen occupies the apical position. It is of interest to note that while the neutral and monoanionic compounds of the "carbons adjacent" *nido*-carboranes were the first ones synthesized, with further deprotonation being reported some 25 years later, the opposite is true for the "carbons apart" carboranes; the bimetalated *nido*-carborane dianions are the ones produced directly from the cage-opening reactions of *closo*-C_2B_4 carboranes. Careful reaction of the disodium compound of the "carbons apart" carborane dianion with anhydrous HCl results in the protonation of the two adjacent borons to give a monosodium compound, whose overall geometry is similar to that shown in Figure 22; attempts at more extensive protonation lead to the decomposition of the carborane.[152]

Slow sublimation of the TMEDA-solvated monolithium carborane complex produced the full-sandwich lithiacarborane complex $[Li(TMEDA)_2]$[*commo*-1,1′-Li$\{2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5\}_2$], as a transparent crystalline solid.[153] The exact nature of the subliming species is not known. Since alkyllithiums have been shown to be sublimable, the monolithium compound could be the subliming species, which then disproportionates to give the ionic full-sandwich lithiacarborane complex. The spectroscopic data of this compound are consistent with its solid-state structure, shown in Figure 23.[153] The distances from lithium to the ring centroids in the complex (2.047 and 2.071 Å) are longer than the value of 1.906 Å found in the half-sandwich dilithiacarborane[9i] but are comparable to the corresponding metal−centroid distance of 2.008 Å found in the $[Cp_2Li]^-$ sandwich complex.[154] The sensitivity of the metal-to-ligand distance to the ligand charge is consistent with a predominantly ionic interaction between the group 1 metal and the carborane cages. So far, only the lithium was found to form such sandwich compounds.

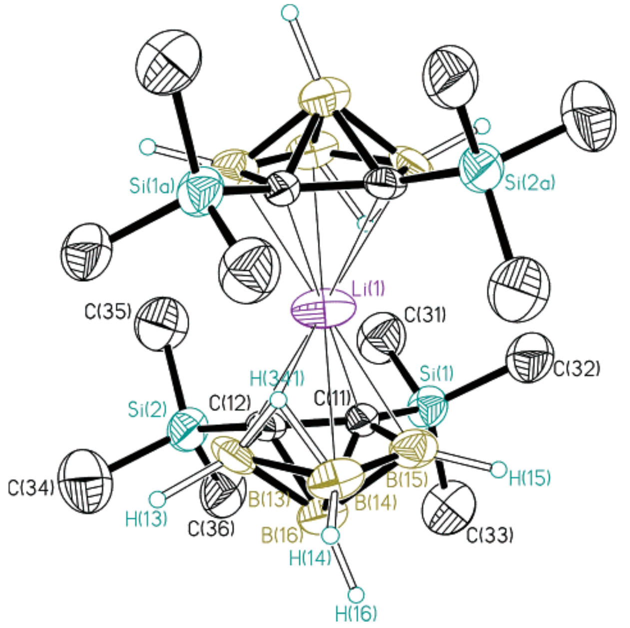

Figure 23. Crystal structure of the full-sandwich lithiacarborane complex $[Li(TMEDA)_2]$[*commo*-1,1′-Li$\{2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5\}_2$].

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.[155] The first step produced a paramagnetic intermediate which reacted slowly with another 1 equiv 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.[155] With Cs, protonation of the carborane dianion did not occur; instead, a polymeric [*exo*-Cs(TMEDA)-1-Cs-$(SiMe_3)_4$-$C_4B_8H_8]_n$ was obtained. The structure of the dicesiacarborane, which is given in Figure 24, shows that one Cs occupies an apical position above an open six-membered 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).

B. Complexes of Group 2 Elements. Although the organometallic chemistry of group 2 elements has

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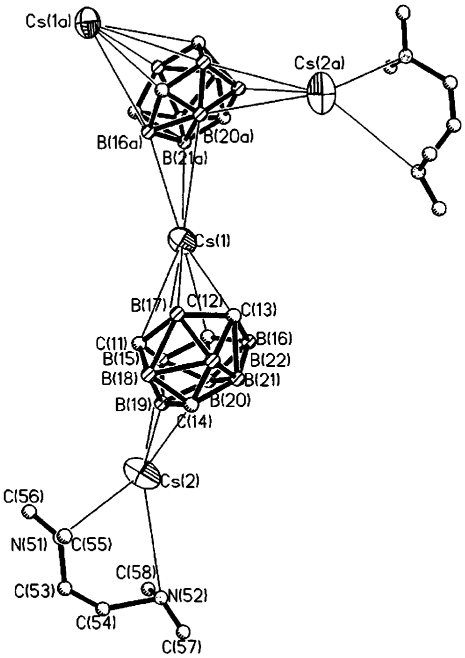

Figure 24. Crystal structure of [*exo*-Cs(TMEDA)-1-Cs-$(SiMe_3)_4C_4B_8H_8]_n$. For clarity, all H atoms and the $SiMe_3$ groups are omitted.

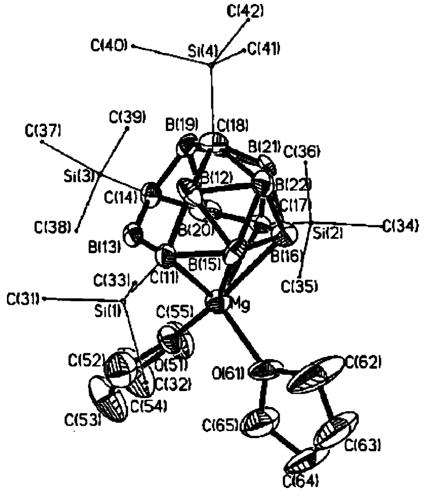

Figure 25. Crystal structure of $(THF)_2Mg(SiMe_3)_4C_4B_8H_8$.

received special attention in recent years and a large number of novel cyclopentadienyl complexes have been synthesized and crystallographically characterized,[156] structural reports on the metallacarborane complexes of group 2 elements are limited. Over 35 years ago, the first group 2 metallacarborane, the beryllacarborane $(CH_3)_3NBeC_2B_9H_{11}$, was synthesized from the reaction of a benzene solution of (3)-1,2-$C_2B_9H_{13}$ with a diethyl ether solution of dimethylberyllium and isolated as its trimethylamine adduct.[157,158] Although the structure of this compound could not be obtained, NMR spectroscopy suggested the closo geometry. It was only in 1990 that the studies of the group 2 metallacarboranes were extended to the syntheses and structural characterizations of the calca- and strontacarboranes *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$ and [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$.[159,160] These complexes formed readily from the reaction of the corresponding metal iodides with Na_2[*nido*-7,9-$C_2B_{10}H_{12}$]. The crystal structure showed that in *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$ the calcium ion, solvated by four acetonitrile molecules, was coordinated above the hexagonal C_2B_4 face of the carborane.[159] While the calcium complex is essentially monomeric, the structure of the corresponding strontacarborane is more complex.[160] This species crystallizes as a polymeric spiral chain, in which a $Sr(MeCN)_3$ group resides above the C_2B_4 open face of the carborane, in a manner similar to that found in the calcacarborane. However, each Sr is also bonded to a neighboring $C_2B_{10}H_{12}$ cage through two Sr−H−X bonds, where X is one of the cage carbons on the upper tier six-membered ring and a boron on the lower pentagonal ring. It is unusual to find cage carbon atoms involved in such bridges, even though such an example is known in the lanthanacarborane system.[161]

The barium−carborane complex is known only in the small-cage system. The baracarborane 1-[Ba$(THF)_2$(4,5-$(\mu\text{-}H)_2$-2,3-$(SiMe_3)_2$-$C_2B_4H_5$)]-2,3-$(SiMe_3)_2C_2B_4H_5$ was synthesized in almost quantitative yield by the reaction of tetrakis(tetrahydrofuran)barium tetrakis[tris(trimethylsilylmethyl)zincate] with 2,3-bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane in THF.[162] The crystal structure is that of a $[(THF)_2Ba(2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5)_2]_2$ dimer in which the THF-solvated barium is coordinated above the C_2B_3 face of one carborane and is bonded to another by two Ba−H−B bonds. The two baracarboranes are held in the dimer by Ba−H−B bonds to the apical borons of each of the former carborane ligands.

In the C_2B_4 cage system both the half-sandwich and full-sandwich magnesacarboranes *closo*-1-Mg(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ and {*commo*-1,1′-Mg[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2\}^{2-}$ have been synthesized and structurally characterized.[163] The structure of the half-sandwich compound is that of a dimeric [*closo*-1-Mg(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2$ unit in which the solvated Mg atoms occupy apical positions above the C_2B_3 face of the carborane and are also bonded to the unique borons of the adjacent carborane cages by single Mg−H−B bridges.[164] The carboranes are η^5-bonded to the Mg in the full sandwich complex, in a structure similar to that shown in Figure 13. The magnesium complex of the tetracarbon carborane $(THF)_2Mg(SiMe_3)_4C_4B_8H_8$ has been prepared and structurally characterized.[155a] The structure, shown in Figure 25, is a rather complex one that can be thought of as being composed of an electron-precise three-coordinate boron atom (B(13)), a four-

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[164] When referring to the different borons on the pentagonal faces of *nido*-carboranes in the C_2B_4 and C_2B_9 cage systems, the B atom that resides in the mirror plane of the C_2B_3 face is sometimes called the unique boron, while those off this plane are the basal borons.

coordinate carbon atom (C(14)), a $(THF)_2Mg$ unit, and an electron-deficient fragment. In this way the compound is interesting in that it is one of the few examples of a cluster that contains both electron-precise and electron-deficient molecular units. It is not known whether this magnesacarborane is an isolated example or the first of a series of structurally new metallacarboranes.

A half-sandwich "carbons apart" magnesacarborane, *closo*-1-Mg(THF)$_3$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$, has been reported. It was synthesized by the reaction of MeMgBr with the corresponding sodium-complexed monoanionic carborane precursor *nido*-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_5$ in THF.[165] The single-crystal X-ray diffraction analysis showed it to have a closo structure in which a THF-solvated Mg occupies the apical position above the bonding face of the carborane cage.[165]

C. Complexes of Group 13 Elements. There have been reports on the syntheses, structures, and reactivities of the metallacarboranes involving all the group 13 metals.[166] The insertion of aluminum into a carborane cage was first reported in 1968 by Mikhailov and Potapova from the reaction of ethylaluminum dichloride with (3)-1,2-dicarbollide ion, as shown in eq 4; unfortunately, the product was not structurally characterized.[167] Soon after this report, detailed studies of the syntheses and structures of the aluminacarboranes, derived from the reaction of (3)-1,2-$C_2B_9H_{13}$ with trialkylaluminums, R_3Al (R = Me, Et), were carried out.[168,169] The reactions were found to go through two distinct steps, the first being the formation of a bridged compound, 7,8-μ-Al(R)$_2$-1,2-$C_2B_9H_{12}$, which, on being heated, eliminated an RH molecule to produce the half-sandwich aluminacarborane *closo*-3-Al(R)-1,2-$C_2B_9H_{11}$.[170,171]

$$\text{(3)-1,2-}C_2B_9H_{11}{}^{2-} + EtAlCl_2 \xrightarrow[-40\ °C]{THF} 2Cl^- + C_2B_9H_{11}AlEt{\cdot}2THF \quad (4)$$

Two examples of full-sandwich aluminacarboranes have also been reported.[172,173] In the presence of CO(g), *closo*-3-Al(Et)-1,2-$C_2B_9H_{11}$ was found to decompose to give a zwitterionic aluminacarborane in which one Al was sandwiched between two dicarbollide ligands, while the second Al was involved in an exo-polyhedral Al(Et)$_2$ group which was attached to the sandwich through two Al−H−B bridges.[172] On the other hand, the reaction of a number of different aluminum alkyl reagents with the thallacarborane precursor $Tl_2[7,8\text{-}C_2B_9H_{11}]$ produced the isolated aluminacarborane sandwich [*commo*-3,3′-Al-(3,1,2-$AlC_2B_9H_{11}$)$_2$]$^-$ as its Tl$^+$ salt.[173] The geometries of the full-sandwich aluminacarboranes were quite regular; the Al atoms were found to be symmetrically bonded to the planar C_2B_3 faces of the carboranes, and the two metal-bonding carborane faces were essentially parallel and oriented directly opposite to one another.[170−174] The aluminum−carborane atom distances found in the zwitterionic and Tl$^+$ aluminacarboranes are essentially the same, indicating that the bridging aluminum group does not materially perturb the internal bonding of the commo complexes. The aluminum atoms in the *closo*-aluminacarboranes were also found to be symmetrically bonded to the cage. The capping metals act as Lewis acid centers and formed donor−acceptor complexes with Lewis bases.[174,175] Adduct formation leads to a decrease in the hapticity of the carborane, from η^5 to η^3 (or η^1). Extreme slip distortions of the capping metal on complexation with a base is a common observation in main-group metallacarborane chemistry. In addition to having interesting structures, the *closo*-aluminacarboranes have been found to be versatile dicarbollyl transfer reagents in the syntheses of other metallacarboranes.[176]

There are much fewer data on the aluminacarboranes in the C_2B_4 cage system. The synthesis of the smaller cage aluminacarborane was first reported by Grimes and co-workers as part of an extended study of the reactions of M[2,3-$C_2B_4H_7$] (M = Na, Li) with a series of organometallic reagents of Al, Ga, Rh, Au, and Hg.[177] The reaction of the carborane monoanion with (CH$_3$)$_2$AlCl produced a highly unstable liquid that was described as the bridged aluminacarborane [(CH$_3$)$_2$Al]-$C_2B_4H_7$. When the bridged compound was pyrolyzed in the gas phase at 100 °C, small amounts of a more volatile compound were produced. Although structural verification of this product was not possible, the infrared and mass spectra of this new product were consistent with the formula *closo*-1,2,3-$AlC_2B_4H_6$.[177] Sneddon and Beck were able to synthesize better characterizable aluminacarboranes from the reaction of *nido*-2,3-(Et)$_2$-2,3-$C_2B_4H_6$ with Et$_3$N and AlH$_3$.[178] The initial formation of a bridged complex, 4,5-μ-AlH$_2$NEt$_3$-2,3-Et$_2C_2B_4H_5$, and its subsequent thermal decomposition to the seven-vertex aluminacarborane 6-AlHNEt$_3$-3,4-Et$_2C_2B_4H_4$ were consistent with the earlier work of Grimes.[177] However, further pyrolysis at higher temperatures produced the novel complex *commo*-AlNEt$_3$-[(6-AlNEt$_3$-3,4-Et$_2C_2B_4H_4$)-(4′,5′-μ-AlNEt$_3$-2′,3′-Et$_2C_2B_4H_5$)], which had no precedent in earlier work. To date, there have been no reported X-ray crystal structures on any of the small-cage aluminacarboranes.

Several aluminacarboranes derived from $C_2B_6H_8$ and $C_2B_8H_{10}$ cage systems have also been reported. The complex [μ-6,9-AlEt(OEt$_2$)-6,9-$C_2B_8H_{10}$] was prepared by the equimolar reaction of Na[5,6-$C_2B_8H_{11}$] with diethylaluminum chloride−diethyl etherate in refluxing tolu-

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[165] Zheng, C.; Wang, J. Q.; Maguire, J. A.; Hosmane, N. S. *Main Group Met. Chem.* **1999**, *22*, 361.

[166] For obvious reasons, only those elements below boron in group 13 and those below carbon in group 14 will be discussed.

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[174] (a) Schubert, D. M.; Bandman, M. A.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046. (b) Bandman, M. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 1204.

[175] Whenever the average value of a parameter is quoted, the uncertainty given is the average deviation.

[176] Jutzi, P.; Galow, P. *J. Organomet. Chem.* **1987**, *319*, 139.

[177] Magee, C. P.; Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Organomet. Chem.* **1975**, *86*, 159.

[178] Beck, J. S.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 3467.

ene,[179] while a 2-fold excess of the carborane yielded the sandwich compound $[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2]^-$ as its sodium salt.[180] The structures of the two aluminacarboranes show a tetrahedral arrangement around the Al atoms, which are more strongly bonded to the two cage carbon atoms of the carborane than to the boron atoms. In view of the uneven bonding and the nonplanarity of the carborane bonding faces, the aluminum atoms are best described as participating in 2e−2c bonds with essentially sp^3-hybridized cage carbons, giving a completely classical metal−carborane bonding interaction. The reaction of $Na[1,3\text{-}C_2B_7H_{12}]\cdot OEt_2$ with Et_2AlCl was found to produce an unusual bis(carboranyl)aluminum complex, $Na[Al(\eta^2\text{-}2,7\text{-}C_2B_6H_8)_2]$.[181]

There are much more structural data available on the heavier group 13 metallacarboranes, especially in the smaller cage C_2B_4 system. The half-sandwich complexes *closo*-1-CH_3-1,2,3-$MC_2B_4H_6$ (M = Ga, In) were synthesized by Grimes and co-workers by the reaction of *nido*-2,3-$C_2B_4H_8$ with $M(CH_3)_3$ under pyrolytic conditions.[182] The structure of the gallacarborane could be determined by X-ray crystallography.[182b] The complex is a distorted-pentagonal-bipyramidal cage, in which the Ga is bonded above the C_2B_3 face of the carborane but is slipped toward the boron side of the face; the Ga−C(2,3) bond distances are about 0.1 Å greater than the Ga−B(4,5,6) distances. Also, the gallium-bound CH_3 group is not oriented directly opposite the carborane ligand but is tilted toward the cage carbons. An analysis using extended Hückel molecular orbital (EHMO) theory explained these distortions by noting that slippage and tilting would enhance bonding between the gallium orbital that is radially directed toward the center of the C_2B_4 cage and the π-type carborane MO's that are localized more heavily on the boron side of the C_2B_3 bonding face.[183] These same distortions were also present in the trimethylsilyl-substituted gallacarborane *closo*-1-(t-C_4H_9)-2,3-$(SiMe_3)_2$-1,2,3-$GaC_2B_4H_4$[184] and the indacarborane *closo*-1-(Me_2CH)-2,3-$(SiMe_3)_2$-1,2,3-$InC_2B_4H_4$.[185] The group 13 metals were found to act as Lewis acid sites and formed complexes with a number of Lewis bases, such as bipyridine (2,2′-$C_{10}H_8N_2$) and bipyrimidine (2,2′-$C_8H_6N_4$).[184,186−188] Structural studies show that, on coordination with the base, the slip distortion of the metal increases and the base is oriented over the boron side of the C_2B_3 bonding face. The increased slip distortion observed on base complexation in the gallacarboranes has been explained using the molecular orbital calculations.[187] The main base−gallium bonding is through MO's that result from the interaction of the nitrogen "lone pair" bipyrimidine orbital with the LUMO of the gallacarborane fragment. The MO that involves antibonding interactions between the gallium and the cage carbons that are opposite the base is stabilized by movement of the metal away from the carbon atoms. In addition, slippage of the metal allows the base molecule to align itself more parallel to the C_2B_3 face of the carborane, which permits a stronger interaction between the base and the gallacarborane orbitals. These same factors have been shown to be important in determining the extent of slip distortions in the stannacarboranes and their base complexes[186] and are probably responsible for the large slip distortion found in the triethylphosphine−aluminacarborane complex. When the gallacarborane to bipyrimidine molar ratio was increased to 2:1, the bridged complex 1,1′-(2,2′-$C_8H_6N_4$)-[1-(t-C_4H_9)-Ga-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2$ was obtained in high yield.[184] The two gallacarboranes occupy trans positions across the bipyrimidine base, and the local geometry around each base−metallacarborane unit is that of a slip-distorted bipyridine−gallacarborane complex.

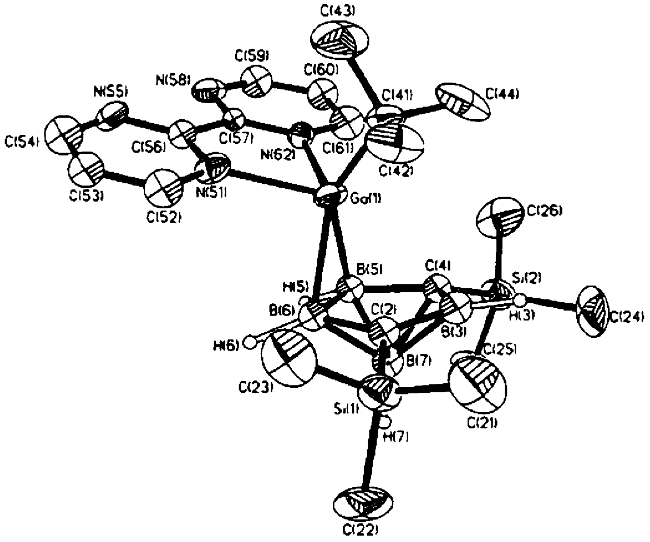

Figure 26. Crystal structure of the "carbons apart" gallacarborane 1-(2,2′-$C_8H_6N_4$)-1-(t-C_4H_9)-1-Ga-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$.

There have been several donor−acceptor complexes reported between the isomeric "carbons apart" gallacarboranes and bidentate and tridentate bases, to give adducts of the type 1-(L)-1-(t-C_4H_9)-2,4-$(SiMe_3)_2$-1,2,4-$GaC_2B_4H_4$ (L = 2,2′-$C_8H_6N_4$, 2,2′-$C_{10}H_8N_2$, and 2,2′:6′,2″-$C_{15}H_{11}N_3$).[188] The structure of the complex where L = 2,2′-$C_8H_6N_4$ is shown in Figure 26; the bipyridine (L = 2,2′-$C_{10}H_8N_2$) analogue is quite similar, while no structure for the terpyridine complex was reported.[188] Just as with the corresponding "carbons adjacent" complexes, the structure shows that the base is coordinated to the metal and that the metal group is slipped away from the cage carbons. What is unusual is the extent of the metal slippage. For example, in Figure 26, the slippage is such that the gallium atom is directly above the B(5)−B(6) bond so that the carborane participates in η^2 bonding with the metal.[188] Unfortunately, no structural data are available on the uncomplexed "carbons apart"

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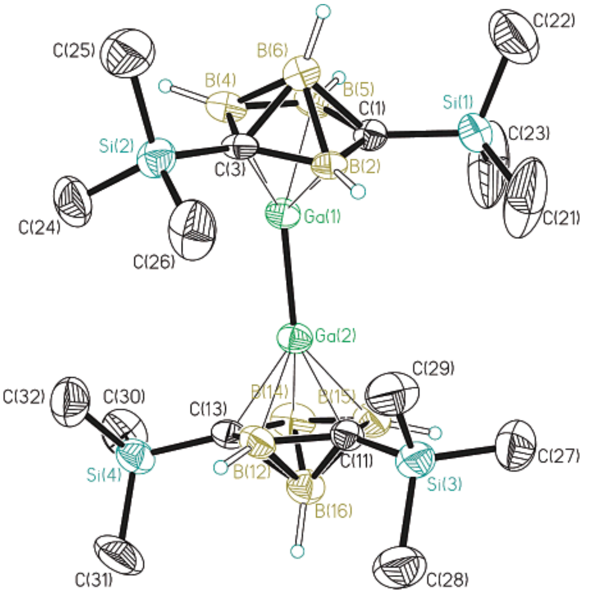

Figure 27. Crystal structure of the digallacarborane *closo*-1-Ga[σ-*closo*-1-Ga-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$.

gallacarborane; therefore, the exact extent to which base bonding enhances, or causes, metal slippage cannot be assessed. However, quantum-mechanical calculations[189] along with the structure of the novel digallacarborane *closo*-1-Ga[σ-*closo*-1-Ga-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$, shown in Figure 27,[190] indicate that the uncomplexed *closo*-gallacarborane is probably only slightly slip distorted.

The digallane is of interest, in that the Ga−Ga single bond is unusually short (2.340 Å);[190] it is essentially the same as the Ga−Ga distance of 2.343 Å found in the anion radical $[Ga_2(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_4]^{\bullet-}$, where strong evidence was found for the existence of Ga−Ga multiple bonding.[191]

Much of the structural work on the half-sandwich gallacarboranes, and their base complexes, has been duplicated in the indacarboranes, with similar results.[186,188] The same arguments used in rationalizing the geometries of the gallacarboranes have been applied to the corresponding indacarboranes. The observed differences can be attributed to the fact that the metal−carborane interactions in the indacarboranes are more ionic than those found in the corresponding gallacarboranes.[186]

Much less information is available on the syntheses and structures of the heavier group 13 metallacarboranes in the larger cage icosahedral system. The half-sandwich gallacarborane 3-(C_2H_5)Ga-1,2-$C_2B_9H_{11}$ has been synthesized and spectroscopically characterized,[169] but no half-sandwich complexes having indium have been reported in this system. Hawthorne and co-workers have found that the reaction of the dicarbollide transfer reagent Tl[*closo*-3,1,2-$TlC_2B_9H_{11}$] with excess $GaCl_3$ in toluene gave exclusively the full-sandwich gallacarborane Tl[*commo*-3,3′-Ga(3,1,2-$GaC_2B_9H_{11})_2$] in 55% yield.[174] The structure shows that a Ga^{III} is sandwiched between two $[C_2B_9H_{11}]^{2-}$ ligands and that the Ga is slightly slipped toward the boron side of the C_2B_3 carborane face.[173,174] It is of interest to note the divergence of the reaction products in the C_2B_4 and C_2B_9 cage systems: the former cage system contains only half-sandwich complexes, while the latter system yields predominantly the full-sandwich metallacarboranes. This is probably due to the nature of the gallium reagent used in the syntheses, rather than a difference in bonding preferences in the two cage systems. The half-sandwich complexes were obtained from metal alkyl reagents, such as $Ga(CH_3)_3$,[182] $[(t\text{-}C_4H_9)GaCl_2]_2$,[184] and $(Me_2CH)InI_2$,[188] while the full-sandwich complex resulted when $GaCl_3$ was used as the gallium source.[174] When $GaCl_3$ is substituted for $[(t\text{-}C_4H_9)GaCl_2]_2$ in the reaction with the dilithium complexed $[2,n\text{-}(SiMe_3)_2\text{-}2,n\text{-}C_2B_4H_4]^{2-}$ dianion in a 1:2 stoichiometry in TMEDA, the full-sandwich compound [*commo*-1,1′-Ga(2,*n*-$(SiMe_3)_2$-1,2,*n*-$GaC_2B_4H_4)_2]^-$ ($n = 3, 4$) was obtained, while the same reaction in 1:1 toichiometry resulted, in high yields, in the formation of a half-sandwich chlorogallacarborane, *closo*-1-(TMEDA)-1-(Cl)-2,*n*-$(SiMe_3)_2$-1,2,*n*-$GaC_2B_4H_4$.[192] The structures of the gallacarboranes show that the gallium atoms are not equally bonded to the atoms in the C_2B_3 faces of the carboranes but are slipped toward the more boron-rich sides of the faces. The distortions were much larger in the half-sandwich complexes, such that the carboranes are better described as being η^3- or η^2-bonded to the apical gallium metal.[192]

The half-sandwich thallacarborane $[3,1,2\text{-}Tl(CR)_2B_9H_9]^-$ was first synthesized by Green and Stone in 1972 by the reaction of thallium(I) acetate with an aqueous alkaline solution of $[(3)\text{-}1,2\text{-}(CR)_2B_9H_{10}]^-$.[193] The thallacarboranes, precipitated as their Tl^+ salts, were found to be both air and water stable and have been used extensively as synthons in the production of both transition-metal[193] and main-group[161,174] metallacarboranes. The structures of $[3,1,2\text{-}TlC_2B_9H_{11}]^-$, as its $[PPh_3Me]^+$ [194] and $[PPN]^+$ salts,[195,196] and the complex $Tl[3,1,2\text{-}Tl(CMe)_2B_9H_9]$[197] have been reported. As in the galla- and indacarboranes, the Tl(I) occupies the apical position above the C_2B_3 bonding face but is slipped toward the boron side of the ring. The large Tl−carborane distances, coupled with the ease of thallium replacement, have been taken as an indication of predominantly ionic metal−carborane bonding.

D. Complexes of Group 14 Elements. The carborane complexes of group 14 elements are the most studied complexes among the main-group metallacarboranes, and their chemistry has been extensively reviewed.[5,145,146,198] All carboranes containing more than one cage carbon atom can formally be thought of as

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(195) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F.; Do, Y. *Inorg. Chem.* **1991**, *30*, 3589.

(196) $[PPN]^+$ = bis(triphenylphosphoranylidene)ammonium cation.

(197) Jutzi, P.; Wegener, D.; Hursthouse, M. B. *Chem. Ber.* **1991**, *124*, 295.

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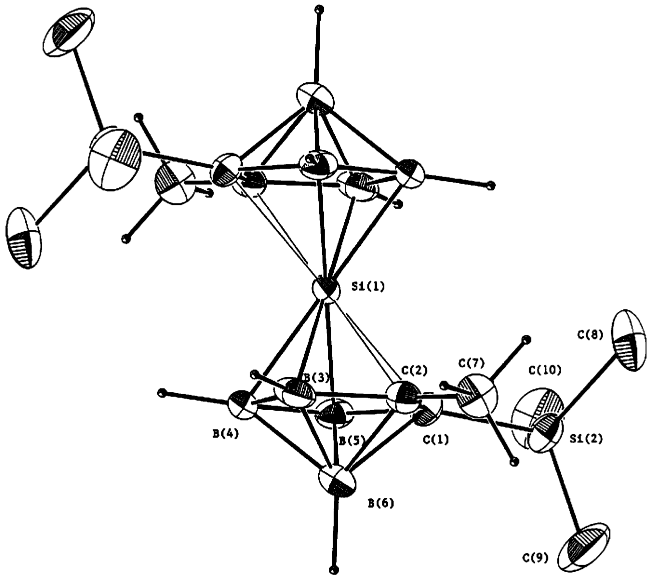

Figure 28. Crystal structure of *commo*-1,1′-Si[2,3-$(SiMe_3)_2$-1,2,3-$SiC_2B_4H_4$]$_2$.

arising from a "cage expansion" of a less carbon rich carborane. However, a more restricted definition will be taken, so that this section will cover those heterocarboranes containing group 14 elements heavier than carbon. Except for lead, examples are known where the group 14 metals or metalloids are present in both their +2 and +4 oxidation states; normally the +2 states are found in the half-sandwich complexes, with the full-sandwich complexes supporting the +4 states. Rudolph and co-workers prepared the first group 14 metallacarboranes by treating 7,8-$C_2B_9H_{11}^{2-}$ with MX_2 (M = Ge, Sn, Pb).[199,200] On the basis of IR, NMR, and Mössbauer spectroscopy and mass spectrometry, the products were assigned a *closo*-3-M-1,2-$C_2B_9H_{11}$ structure, in which the cage carbons occupied adjacent positions. The study was later expanded to include the "carbons apart" germacarborane 3-Ge-1,7-$C_2B_9H_{11}$, which was spectroscopically characterized.[201] The syntheses are of interest in that, while the 3,1,7-germacarborane was prepared in good yield by the reaction of GeI_2 with 7,9-$C_2B_9H_{11}^{2-}$, the use of $SnCl_2$ in place of GeI_2 did not lead to the expected stannacarborane; instead, the reaction produced, in 78% yield, the oxidative cage closure product *closo*-2,3-$C_2B_9H_{11}$ and Sn metal. When it was heated to 450 °C, 3-Sn-1,2-$C_2B_9H_{11}$ underwent disproportionation to give *closo*-2,3-$C_2B_9H_{11}$.[201] The apparent increased tendency of the "carbons apart" carborane to undergo oxidative cage closure, in comparison to its "carbons adjacent" isomer, is surprising in view of the fact that the former isomers are thought to be thermodynamically more stable.[202] It is also contrary to observations in the smaller cage C_2B_4 system, in that the "carbons adjacent" carboranes are the more easily oxidized of the two isomers.[65] Since these initial reports, a large number of group 14 metallacarboranes have been synthesized and spectroscopically and structurally characterized, and their reaction chemistry has also been explored.

The insertion of silicon was reported in 1986 for both the large- and small-cage carborane systems. Hawthorne and co-workers reported the structure of a silacarborane, *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$, prepared in 78% yield from the reaction of $SiCl_4$ with the dicarbollide dianion in refluxing benzene.[203] A concurrent report described the synthesis of full-sandwich silacarboranes of the C_2B_4 cage system, *commo*-1,1′-Si-(2-$(SiMe_3)$-3-(R)-1,2,3-$SiC_2B_4H_4$)$_2$ (R = $SiMe_3$,[204] H,[205] and Me[205]), according to eq 5. The structure of the small-

$$2[\mathrm{NaLi}][(\mathrm{Me_3Si})(\mathrm{R})\mathrm{C_2B_4H_4}] + \mathrm{SiCl_4} \rightarrow [(\mathrm{Me_3Si})(\mathrm{R})\mathrm{C_2B_4H_4}]\mathrm{Si^{IV}} + [(\mathrm{Me_3Si})(\mathrm{R})\mathrm{C_2B_4H_4}]\mathrm{Si^{II}} + \mathrm{NaCl} + \mathrm{LiCl} \quad (5)$$

cage silacarborane is shown in Figure 28. The crystal structure shows that in the complex the silicon, in a formal +4 oxidation state, is sandwiched between the planar and parallel C_2B_3 faces of the carborane ligands, with the cage carbons occuping trans positions across the silicon. At least in the case of the smaller cage system, the course of the reactions is quite dependent on both the nature of the starting carborane and the silylating reagent. For example, the Na/Li compounds of the dianion [2-$(SiMe_3)$-3-(R)-2,3-$C_2B_4H_4$]$^{2-}$ reacted, in a 2-fold molar excess, with $SiCl_4$ to give the full-sandwich silacarboranes, with yields ranging from 18% (R = $SiMe_3$) to 57% (R = Me).[205] When R = $SiMe_3$, a small amount (~1%) of another compound was also obtained, which was tentatively identified as the half-sandwich Si^{II} complex 1-Si-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$.[205] On the other hand, no reaction was found when the [2-$(SiMe_3)$-3-(R)-2,3-$C_2B_4H_5$]$^-$ monoanion, as either its Na or Li compound, was used.[205] Use of SiH_2Cl_2 in place of $SiCl_4$ in the reaction of the Na/Li compound of the R = Me carborane resulted in the formation of the Si^{IV} half-sandwich complex [2-$(SiMe_3)$-3-Me-2,3-$C_2B_4H_4$]SiH-(Cl) (see eq 6). The chloride ligand could be replaced by

$$2[\mathrm{NaLi}][(\mathrm{Me_3Si})(\mathrm{R})\mathrm{C_2B_4H_4}] + \mathrm{SiH_2Cl_2} \rightarrow [(\mathrm{Me_3Si})(\mathrm{R})\mathrm{C_2B_4H_4}]\mathrm{SiH(Cl)} + \mathrm{NaCl} + \mathrm{LiCl} \quad (6)$$

reaction with NaH, to give [2-$(SiMe_3)$-3-Me-2,3-$C_2B_4H_4$]-SiH_2, as shown in eq 7; the ^{29}Si NMR spectrum of this complex gave a splitting pattern that suggested the presence of B−H−Si bridges.[205]

$$[(\mathrm{Me_3Si})(\mathrm{R})\mathrm{C_2B_4H_4}]\mathrm{SiH(Cl)} + \mathrm{NaH} \rightarrow [(\mathrm{Me_3Si})(\mathrm{R})\mathrm{C_2B_4H_4}]\mathrm{SiH_2} + \mathrm{NaCl} \quad (7)$$

Detailed studies of the reactivity of the air- and moisture-stable bis(η^5-dicarbollide)silicon sandwich complex *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ with Lewis bases, such as pyridine and trimethylphosphine, have been

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reported.[203b] Structures of the products formed from the reaction with pyridine, (10-*exo*-η^1-7,8-$C_2B_9H_{11}$)(10-*endo*-η^1-7,8-$C_2B_9H_{11}$)Si(C_5H_5N)$_2$, and Me_3P, [η^5-10-{$(Me_3P)_2$-BH}$C_2B_8H_{10}$]Si(η^1-$C_2B_9H_{11}$), were determined by X-ray diffraction.[203b] The latter complex represents a unique example of the partial removal of a BH vertex of a carborane cage by a Lewis base. These results are quite different from those found when the small-cage group 13 and group 14 metallacarboranes react with monodentate Lewis bases (see below).

The full-sandwich silacarborane complexes have been investigated theoretically using both semiempirical[206] and ab initio[207] molecular orbital theory. The molecular orbital energies and heavy-atom atomic orbital contributions for the compounds *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ and *commo*-1,1′-Si(1,2,3-$SiC_2B_4H_6$)$_2$ were obtained from MNDO calculations.[206] The main Si−carborane bonding was found to be through the interactions of the Si 3p orbitals with π-type orbitals on the C_2B_3 bonding faces of the carboranes. In this regard the bonding is similar to that found in the silicocenes $(C_5R_5)_2Si$.[208] However, one striking difference between carborane and cyclopentadienyl ligand systems is the difference in oxidation states supported by the two ligands; in the full-sandwich silacarboranes, Si^{IV} entities occupy the commo positions, while in the silicocenes, Si^{II} is found.[208] The LUMO's for both the icosahedral and pentagonal-bipyrimidal silacarboranes involve strongly antibonding interactions between the silicons and their respective cages. These are the orbitals that would be populated if the silicons were in +2 states. On the other hand, the HOMO's in $(C_5H_5)_2Si$, which would be partially depopulated in $[(C_5H_5)_2Si]^{2+}$, are involved in a doubly degenerate E_{1g} state that, while having very little silicon−Cp interaction, accounts for some of the strongest C−C π bonding in the Cp rings.[206] Therefore, a Si^{IV} state would not be expected in the silicocenes.

There is ample evidence of a structure−oxidation state preference in the heavier group 14 metallacarboranes, in that the half-sandwich complexes are associated with the lower, +2, oxidation state, with the +4 state being found in the full-sandwich complexes. This is best demonstrated by the germacarboranes, where it was found that the reaction of $Li^+[2,3\text{-}(CSiMe_3)_2B_4H_5]^-$ with $GeCl_4$ produced a mixture of the full sandwich $[2,3\text{-}(CSiMe_3)_2B_4H_4]_2Ge^{IV}$ and the half sandwich $[2,3\text{-}(CSiMe_3)_2B_4H_4]Ge^{II}$, in yields of 20% and 27%, respectively.[209] When *closo*-1-Sn-2-($SiMe_3$)-3-(R)-2,3-$C_2B_4H_4$ was used as the carborane transfer reagent, the only product was the full-sandwich germacarborane.[210] The structure of the full-sandwich complex is quite similar to that of the corresponding silacarborane in that the Ge^{IV} is sandwiched between two carborane ligands such that the GeC_4B_8 cluster has C_{2h} symmetry.[209] Aside from differences that are directly attributable to atom size, the germacarboranes are more slip distorted than the corresponding silacarboranes. While the structure of the half-sandwich germacarborane could not be determined, X-ray diffraction studies have been reported for the $GeCl_3$-substituted "carbons adjacent" germacarborane *closo*-1-Ge-2-($SiMe_3$)-3-(R)-5-($GeCl_3$)-2,3-$C_2B_4H_3$ (R = $SiMe_3$, Me, H).[211] In this complex, a Ge^{II} is symmetrically bonded to the C_2B_3 face of the carborane, with little indication of a slip distortion, while another germanium, in a formal +4 state, is involved in an exo-polyhedral $GeCl_3$. The lack of slip distortion of the capping Ge was rationalized on the basis that the replacement of the H on the unique boron with the more electron withdrawing $GeCl_3$ group would favor a centrally located capping metal.[211b] There are two Lewis acid sites in *closo*-germacarboranes, the apical Ge(II) and the exo-polyhedral Ge(IV). Even though two germanium atoms are present, no evidence has been found to indicate that the Ge(IV) atoms in these compounds act as Lewis acids sites. It seems that the Ge(IV) atoms in the mixed-valence *closo*-germacarboranes have their valences well satisfied through bonding to the three chlorine atoms and the unique borons; even strong nucleophiles displace, rather than disrupt, the $GeCl_3$ moiety.[211b]

The direct reaction of the mono- or dianionic salts of the C_2B_9 and C_2B_4 *nido*-carboranes with $SnCl_2$,[212−214] $SnCl_4$,[210] and $PbCl_2$[215] produced only the half-sandwich metallacarboranes. These methods follow the general procedure used by Rudolph and co-workers in their original reports of the syntheses of the *closo*-3-M-1,2-$C_2B_9H_{11}$ (M = Ge, Sn, Pb) series.[199,200] The *C*-methyl-substituted icosahedral stannacarborane *closo*-3-Sn-1,2-$(Me)_2$-1,2-$C_2B_9H_9$ was also prepared using this method.[212,213] However, crystal structures have been determined only for the smaller cage stannacarboranes. The structure of *closo*-1-Sn-2-($SiMe_3$)-3-(R)-2,3-$C_2B_4H_4$ (R = Me) shows that a bare Sn(II) occupies an apical position above the C_2B_3 open face of the carborane but is slip distorted away from the cage carbons.[213] The structures of the stannacarboranes where R = H,[216] $SiMe_3$[215b,217] are similar. Except for the fact that the half-sandwich lead complex *closo*-1-Pb-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ crystallizes as a dimer, its structure is essentially the same as that of the stannacarborane.[215a] The carbons-apart plumbacarborane *closo*-1-Pb(TMEDA)-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ was also found to have a similar structure.[215b] It is of interest to note that the heavier group 14 full-sandwich complexes could not be synthesized by the direct carborane−metal halide reaction, when $SnCl_4$ was used with $[2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_5]^-$; only reductive insertion of the metal occurred, yielding *closo*-1-Sn-2-($SiMe_3$)-3-(R)-2,3-$C_2B_4H_4$.[210] The inability

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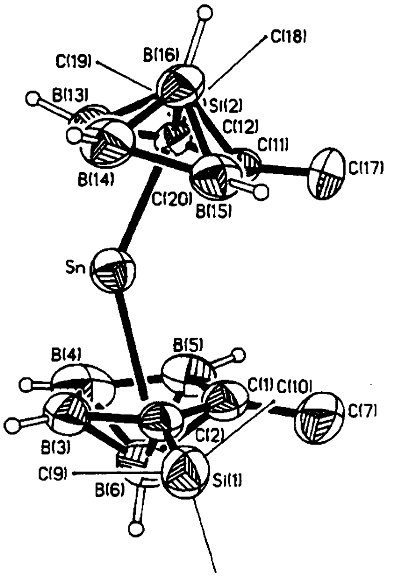

Figure 29. Crystal structure of *commo*-1,1′-Sn[2-($SiMe_3$)-3-(CH_3)-1,2,3-$SnC_2B_4H_4$]$_2$.

to obtain the full-sandwich complexes was explained on the basis of the decreasing tendency of the heavier main-group metals to form high oxidation states. This oxidation state preference was also demonstrated in the larger cage system by Voorhees and Rudolph, who reported that reaction of bis(organo)tin dichlorides with $[C_2B_9H_{11}]^{2-}$ gave only the Sn^{II} stannacarborane.[200] A half-sandwich Sn^{IV} carborane, 1,1-$(Me)_2$-1,2,3-$SnC_2B_8H_{10}$, was reported by Kennedy and co-workers from the reaction of Me_2SnCl_2 with [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$.[218] The similarity of the ^{11}B NMR spectrum of this stannacarborane with that of [μ-6,9-AlEt(OEt_2)-6,9-$C_2B_8H_{10}$], in which the metal bridges the carborane through two Al−C_{cage} bonds, prompted the authors to describe the Sn^{IV} complex as a classically bridged *nido*-stannacarborane.[218a] Exposure of this compound to air led to decomposition, giving a product thought to be 1,2,3-$SnC_2B_8H_{10}$.[218] The [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ ligand is of interest in that its half-sandwich complexes can be described as either bridged *nido*- or true *closo*-metallacarboranes, depending on the compactness of the complexes.[218b] Even though there is a demonstrated reluctance of Sn in a +4 oxidation state to form carborane complexes, there is one report of a full-sandwich Sn^{IV} carborane π complex, *commo*-1,1′-Sn[2-($SiMe_3$)-3-(Me)-1,2,3-$SnC_2B_4H_4$]$_2$. This compound was obtained from the reaction of *closo*-1-Sn-2-($SiMe_3$)-3-(Me)-2,3-$C_2B_4H_4$ and $TiCl_4$, according to eq 8.[219] The

$$\begin{gathered}2[\textit{closo}\text{-1-Sn-2-}(SiMe_3)\text{-3-(Me)-2,3-}C_2B_4H_4] + \\ 2TiCl_4 \xrightarrow[THF/C_6H_6]{25\ °C} 2TiCl_3(THF)_3 + SnCl_2 + \\ \textit{commo}\text{-1,1}'\text{-Sn}[2\text{-}(SiMe_3)\text{-3-(Me)-1,2,3-}SnC_2B_4H_4]_2\end{gathered} \tag{8}$$

structure, shown in Figure 29, is unlike those of its silicon and germanium analogues in that the stannacarborane complex is bent, such that the (ring centroid 1)−Sn−(ring centroid 2) angle is 142.5°. This is similar to the corresponding angles of 145.8 and 144.1° found for (η^5-C_5H_5)$_2$Sn and (η^5-C_5Me_5)$_2$Sn complexes.[220,221] Bending in the stannocenes and several other divalent group 14 metallocenes is well-known and has been explained in terms of the stereochemical influence of the metal's "lone pair" of electrons,[222] which may be offset by the presence of large groups, such as C_6H_5, on the Cp ring.[223] However, the similar bending shown in Figure 29, where the tin is in a formal +4 state with no "lone pairs", indicates that other factors are important in determining the geometries of the sandwich compounds of the heavier group 14 elements.

Despite the presence of an exo-polyhedral lone pair of electrons on the M^{II} capping metals of the group 14 half-sandwich complexes, they show no tendency to function as a Lewis base. On the contrary, their chemistry is dominated by Lewis acid behavior. All of the half-sandwich metallacarboranes of germanium, tin, and lead have been found to form donor−acceptor complexes with monodentate,[215,224−226] bidentate,[212,213,215,217,228−232] bis(bidentate),[233,234] and tridentate[235,236] bases. The bonding in these complexes has been the subject of several theoretical studies.[189,227,237] Figure 30 shows the structure of the 1-(2,2′-$C_{10}H_8N_2$)-2,3-$(SiMe_3)_2$-1,2,3-$SnC_2B_4H_4$ complex.[216] The 1-(2,2′:6′,2″-$C_{15}H_{11}N_3$)-2,3-$(SiMe_3)_2$-1,2,3-$SnC_2B_4H_4$ complex has a similar structure.[236] The structures are quite similar to those of the group 13 base−metallacarborane complexes in that the base is oriented over the unique boron, B(4) in Figure 30, and the metals are highly slip distorted. In the structures of the bis(bidentate) base complexes 1,1′-(2,2′-$C_8H_6N_4$)[2,3-$(SiMe_3)_2$-1,2,3-$MC_2B_4H_4$]$_2$ (M = Sn,[233] Pb[234]) the two metallacarborane fragments occupy trans positions with respect to the bipyrimidine base, similar to that found for 1,1′-(2,2′−$C_8H_6N_4$)[1-(*t*-C_4H_9)-1-Ga-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]$_2$. The local sym-

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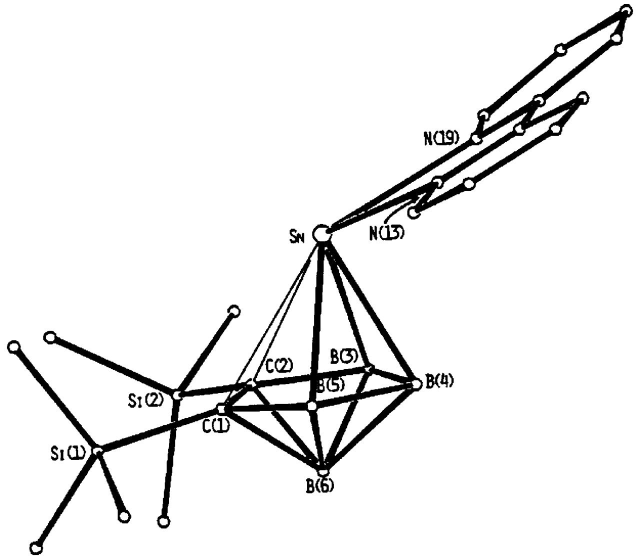

Figure 30. Crystal structure of 1-(2,2′-$C_{10}H_8N_2$)-2,3-$(SiMe_3)_2$-1,2,3-$SnC_2B_4H_4$.

metries around each metal atom in the bridged complexes are the same as that shown in Figure 30. Studies of the bipyridine−stannacarborane complexes in both the pentagonal-bipyramidal and icosahedral systems show that base orientation and metal slippage are the results of a weakening of the metal−cage carbon bonds opposite the base and the relief of electron−electron repulsion between the base and the carborane ligands so that the base can orient for maximum overlap with the metal. The same types of distortions are also found in the base−SnCp system. While the tin in the $[(\eta^5\text{-}C_5Me_5)Sn]^+$ half-sandwich complex is centered over the pentagonal face of the Cp* ligand,[238] in the $[(2,2'\text{-}C_{10}H_8N_2)Sn(C_5Me_5)]^+$ complex, the tin is slip distorted and the bipyridine molecule is oriented over one side of the Cp ring, much like the orientation shown in Figure 30.[239] The complexes formed by the group 14 metallacarboranes with monodentate bases are also similar to that shown in Figure 30.[224,225] As with their polydentate analogues, the bases reside over the boron side of the C_2B_3 bonding face of the carborane and the metals are slip distorted in the direction of base orientation. The same explanations used in rationalizing these distortions in the bidentate bases are operable in monodentate base complexes. There is good evidence that the potential energy surfaces governing the geometries of these complexes are fairly shallow, so that other factors, such as crystal-packing forces, may assume higher than normal importance. For example, there are two crystallographically independent molecules of 1-$[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2(Me)_2N)]$-2,3-$(SiMe_3)_2$-1,2,3-$SnC_2B_4H_4$, one in which the ferrocenylamine nitrogen is directly over the unique boron and another in which the base is rotated about 10° out of the mirror plane of the metallacarborane.[224] However, it is interesting that, in both molecules, the ferrocenyl group is not in a position of minimum steric interaction with the stannacarborane but is oriented in such a way that the lower half of the Cp ring is within the van der Waals distances to the MC_2B_4 cage. Similar ferrocene amine orientation and additional interaction between the capping metals and one of the Cp rings were observed in the structures of both the plumba- and germacarborane complexes. It was argued that such interactions might compensate for the less than ideal steric arrangement of the ligands.[225]

While most of the structural studies have been carried out on the “carbons adjacent” metallacarboranes, there are several “carbons apart” base−stannacarborane complexes whose structures have been reported.[225] The structures bear the same relationship to their “carbons adjacent” analogues as was found in the group 13 metallacarborane−base complexes: that is, the base molecules were found to be oriented opposite the cage carbons and tin atoms were displaced in the direction of base orientation.[226]

Several full-sandwich tin complexes in the azoboronyl and diborolenyl systems have also been described. Schmid, Zaika, and Boese reported the synthesis and structure of $[1\text{-}t\text{-}C_4H_9\text{-}2,3\text{-}(Me)_2\text{-}1,2\text{-}NBC_3H_2]_2Sn$.[240] The structure of this complex is that of a bent sandwich, similar to that found in the isoelectronic Cp system.[238] Siebert and co-workers have reported the synthesis and structure of the bent tetradecker sandwich complex $[(C_5H_5)Co(C_2B_2C)]_2Sn$ (C_2B_2C = 4,5-$(Et)_2$-1,3-$(Me)_2$-1,3-B_2C_3H), obtained from the reaction of the $[(C_5H_5)Co(C_2B_2C)]^-$ anion with $SnCl_2$.[241]

In the above examples the group 13 or 14 heteroatom (a metal or a metalloid) was found to occupy an apical position above a mixed carbon−boron or nitrogen−carbon−boron bonding face, and the analogy of such complexes with the corresponding cyclopentadienyl compounds was stressed as providing a useful basis for the discussion of structures and properties. An alternative approach is to recognize the isoelectronic and isolobal relationships that exist between the group 13 and 14 elements with the HC and HB^- units and view these compounds as substituted borane analogues. For example, Seyferth and co-workers have reported the synthesis and structural determination of the silicon analogue of *o*-carborane, 1,2-$(Me)_2$-1,2-$Si_2B_{10}H_{10}$.[242] Its structure is much better discussed in terms of a one-to-one substitution of Si for C atoms in the “parent” carborane 1,2-$(Me)_2$-1,2-$C_2B_{10}H_{10}$. This approach will prove especially useful in the discussions concerning the incorporation of group 15 and 16 heteroatoms into carborane cages. Recently, the synthesis and characterization of constrained-geometry half-sandwich sila- and germacarboranes in the large-cage system was reported.[243] According to this report, the reaction of the $[nido\text{-}7\text{-}(OCH_2)\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_9]^{3-}$ trianion with anhydrous $MeMCl_3$ (M = Si, Ge) gives *closo*-1-M(Me)-2-$(1\text{-}\eta^1(\sigma)\text{-}OCH_2)$-3-Me-$\eta^5$-2,3-$C_2B_9H_9$ (M = Si, Ge).[243]

E. Complexes of Group 15 Elements. A group 15 atom is isoelectronic and isolobal with a CH group. Therefore, substitution of group 15 elements for one or more CH or BH^- units in a carborane cage should yield

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compounds with similar structures and comparable reactivities. This has been found to be the case; a number of overview articles on mono and poly aza, phospha, arsa, and stiba boranes and carboranes have been published by Todd.[244,245] In keeping with the restrictions outlined at the beginning of this section, only those group 15 heterocarboranes that are derived from the smaller C_2B_4 carborane ligands will be stressed.

The dicarboranes have been found to react with phosphorus and arsenic di- and trihalides, but the reactions seem to be quite sensitive to the nature of the carborane precursor. In 1974, Smith and Hawthorne found that, while the reaction of the monoanion $[7,8\text{-}C_2B_9H_{12}]^-$ or the dilithium salt $Li_2[7,8\text{-}C_2B_9H_{11}]$ with CH_3AsBr_2 produced mainly uncharacterizable polymeric materials, the use of $Tl_2[7,8\text{-}C_2B_9H_{11}]$ afforded the icosahedral *closo*-arsacarborane 3-Me-3-As-1,2-$C_2B_9H_{11}$ in 30% yield.[246] In like manner the dithallium salt was found to react with the series $RAsX_2$ (R = CH_3, X = Br; R = Ph, *n*-C_4H_9, X = Cl) to give the corresponding 3-R-3-As-1,2-$C_2B_9H_{11}$ in varying yields.[246] A closo-icosahedral structure for these compounds was assigned on the basis of ^{11}B and ^1H NMR spectra. This structural assignment was supported by the later work of Jutzi and co-workers, who found that both PCl_3 and $AsCl_3$ reacted with $Li_2[Me_2C_2B_9H_9]$ to give $ClE[Me_2C_2B_9H_9]$ (E = P, As).[247] The structure of the complex where E = As was determined by X-ray crystallography and was found to have a distorted-icosahedral structure.[247] The arsenic was not symmetrically bound to the C_2B_3 open face of the carborane but was slipped toward the boron side of the ring such that the carborane was η^3-bonded to the capping arsenic atom. This structure was quite similar to that of the THF−stannacarborane complex and also to that of the $[(C_5Me_5)_2As]^+$.[212,248] The similarities in the structures of all three complexes led the authors to conclude that the AsCl group was functioning as a two-electron donor with both the Cl and a lone pair of electrons on the As being exo-polyhedral. This view was supported by the fact that the $ClE[Me_2C_2B_9H_9]$ (E = P, As) heterocarboranes reacted with $AlCl_3$ to give a neutral adduct of the form $ClE[Me_2C_2B_9H_9]\cdot AlCl_3$, in which the $AlCl_3$ group was coordinated to E.[247] Both $ClP[Me_2C_2B_9H_9]$ and $ClAs[Me_2C_2B_9H_9]$ were found to react with *i*-PrMgCl to give the isopropyl derivatives *i*-PrE$[Me_2C_2B_9H_9]$. At least in the case of the phosphacarborane the method was found to be superior to the direct reaction of $Li_2[Me_2C_2B_9H_9]$ with *i*-$PrPCl_2$. The reaction of $ClP[Me_2C_2B_9H_9]$ with $AgBF_4$ resulted in the replacement of the Cl by a F atom to give $FP[Me_2C_2B_9H_9]$. All were assumed to have the slip-distorted closo structure.[247] Phosphine fragments have also been inserted into the smaller C_2B_4 cages, but the structures of the resulting phosphacarboranes are open to question. The double salt Na/Li$[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]$ was found to react with $[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]PCl_2$ to give a phosphacarborane formulated by the authors as *closo*-1-$[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]$-1-P-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$.[249] A slip-distorted closo designation was given on the basis of the similarity of the ^{13}C and ^{11}B NMR spectra of the compound to those of the known group 13 and group 14 *closo*-heterocarboranes. The observation that the ^{31}P NMR resonance of the capping phosphorus at δ −129.7 ppm, which was shifted upfield by about 283 ppm from its precursor, $[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]PCl_2$, was taken as further evidence of a π-type complex. On the other hand, Sneddon and co-workers found very different results from the reaction of $NaLi[2,3\text{-}(R)_2\text{-}2,3\text{-}C_2B_4H_4]$ (R = Et, Bz) and $R'PCl_2$ (R′ = Ph, *t*-Bu, Me).[250] The ^{11}B NMR spectra, combined with an ab initio/IGLO/NMR study, indicated that the resulting phosphacarboranes were 7-vertex cages, best formulated as *nido*-6-R′-3,4-$(R)_2$-6,3,4-$PC_2B_4H_4$.[250] The ^{31}P NMR resonances of the products were in the δ +16.4 to +112.9 ppm range, which are significantly downfield from that found for the bis(trimethylsilyl)-substituted phosphacarborane. At present there is no ready explanation as to why such seemingly similar reactants should give such different products.

It is clear that our understanding of the nature and consequences of the incorporation of group 15 elements into carborane cages is incomplete. All structural evidence indicates that an underivatized (bare) group 15 element (E) is isoelectronic and isolobal with a CH or BH^- unit and functions as a three-electron cage donor possessing an exo-polyhedral lone pair of electrons. Under certain conditions these lone pairs can be made to react with R^+ moieties to give the electronically equivalent RE^+ units, as found in the reaction of *nido*-$PCB_9H_{11}^-$ with MeI to give *nido*-P(Me)CB_9H_{11}.[251] However, there seems to be no clear consistent picture of the interaction of a “neutral” RE unit with carborane cages; in some cases they seem to act as two-electron donors,[247,249,252] while in others a four-electron-donor model seems to be more useful.[250] In this regard it should be noted that “the number of electrons donated to cage bonding” is more a function of one’s a priori assumptions about the system than it is the final results. For example, the *nido*-P(Me)CB_9H_{11} was described as arising from the coordination of a lone pair of P electrons with Me^+, giving a three-electron-donor MeP^+ moiety that associates with a 23-cage-electron $[CB_9H_{11}]^-$ fragment, to generate the required 13 electron pairs for a stable 11-vertex nido structure. Alternatively, the *nido*-P(Me)CB_9H_{11} could be viewed as being composed of a four-electron-donor MeP group that is incorporated into a 22-cage-electron fragment, to give the 13 electron pairs; the former description was used because of the method of preparation. Another point worth mentioning is that the terms closo, nido, arachno, etc. carry both structural and electronic connotations; for simple systems both meanings apply and the geometry can be nicely correlated with the number of cage

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electrons. However, in many of the heterocarboranes neither the geometry nor the number of cage electrons is simply described. In the group 13 and 14 metallacarboranes the capping metals are slip distorted, and when the metals react with Lewis bases to form adducts, slip distortion increases. In such adducts it is not apparent how to assign the extra electron pairs brought by the base. It has been suggested that the terms closo, nido, etc. be used exclusively to denote skeletal electron pairs;[253] to this end we have used the theory of neutral descriptive terms such as half-sandwich, slipped sandwich, etc. in many places in this review. However, we have also used the same prefixes and numbering systems that were found in the original literature; the confusion thus introduced by these multiple descriptors mirrors that which currently exists in the literature.

V. Current and Future Directions

Our discussion summarizes the most promising research published during the past few years in the area of small-cage metallacarboranes following two main thrusts. Although each individual report has its own individual focus, one thrust is directed toward systematizing the chemistry of these compounds in order to promote their use as possible electronic, ceramic, and catalytic materials. Another is to provide information on which we can test, and expand, our knowledge about the fundamental interactions that are at work in determining the structures and properties of these fascinating clusters. The results of these studies are establishing a unique and useful area of organometallic chemistry that will continue to grow and bear fruit in the 21st century.

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