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Recent Advances in the Chemistry of Heterocarborane Complexes Incorporating s- and p-Block Elements

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Contents

I. Introduction

Carboranes are mixed hydrides of carbon and boron in which these elements are members of electron-deficient cages. The cages can be expanded by incorporating into them other atoms, to give heterocarboranes; if the heteroatom is a metal, the resulting compound is called a metallacarborane. This review will cover recent developments in these cage expansions when the heteroatom is one of the main group elements. There have been a large number of reviews and monographs that cover earlier work on these compounds,[1,2] and such work will be discussed only as background to current results or for purposes of comparison. The cage geometries can range from completely closed polyhedra (*closo*-), to more open ones, derived by removing one (*nido*-), two (*arachno*-), or more vertices from the closed structures. The structures of heterocarboranes composed of fused deltahedra can be predicted from the number of electron pairs involved in cage bonding, using a set of rules embodied in the Polyhedral Skeletal Electron Pair Theory.[3] The number of electrons involved in cage bonding can be obtained by assuming that one valence electron of each cage carbon or boron atom is involved in a classical two-center–two-electron bond with an *exo* polyhedral hydrogen (or other group), leaving the remaining valence electrons (three from each C and two from each boron) for cage bonding. In addition to the cage and terminal atoms, bridged hydrogens can also be present; these bridging atoms will each contribute one electron to the cage. If the cluster is anionic, the electrons imparting the overall charge to the cage are also assumed to be involved in cage bonding. These cage electrons are delocalized in a set of molecular orbitals (MO's) constructed from three atom-based orbitals of each cage atom, one radially directed into the center of the cluster and the other two tangentially oriented.

Using this approach, it is easily seen that, a carborane with the general formula $[(CH)_a(BH)_{n-a}H_b]^{c-}$ having n vertices and b bridged hydrogens would have $^1/_2[2n + a + b + c]$ skeletal electron pairs (P). If $P = n + 1$, a *closo* structure is expected; when $P = n + 2$, a *nido* structure should be the most stable; $P = n + 3$, an *arachno* structure, etc., can be predicted.[3,4] Replacement of a BH unit by a moiety that could supply three correctly oriented orbitals and two electrons for cage bonding should not materially affect intracage bonding or cluster geometry; such groups would include the heavier group 14 elements (Ge, Sn, and Pb) as well as R–M moieties, where M is a heavy group 13 metal. Such extensions form the bases for the rationale of the structures of many other heterocarboranes. It should also be noted that the *exo* polyhedral hydrogens could be replaced by any single bonding group without changing any of the above arguments. Using such isolobal and isoelectronic arguments, these electron counting rules can be extended to heterocarboranes and to other clusters, including transition metal clusters.[4,5]

An alternative approach to rationalizing the formation, structures, and reactivities of heterocarboranes, especially the metallacarboranes, is to consider them as organometallic complexes formed between metals and open-cage carborane π-bonding ligands. The most often cited metallacarboranes in this review are those in which metal groups occupy the apical positions above the C_2B_3 open faces of the *nido* carborane dianions, $[7,8-R_2C_2B_9H_9]^{2-}$ and $[2,3-R_2C_2B_4H_4]^{2-}$ (R = H or a cage carbon substituent). The principal metal-bonding orbitals of these carboranes should be those filled orbitals that extend above the C_2B_3 open faces of the dianions.

When viewed from the metal's perspective above the open C_2B_3 faces of the carboranes, these MO's bear striking resemblances to the primary metal-bonding orbitals of the cyclopentadienide ion, (Cp), $[C_5H_5]^-$ (see Figure 1).[6] One of the most important differences is that, in going from the homonuclear C_5 ring to the heteronuclear C_2B_3 one, the degeneracy of the HOMO is lifted with the higher energy MO's being richer in the less electronegative boron atoms. Therefore, the high-energy metal bonding MO's in the carboranes will be more localized on the borons with the carbon centered ones lying lower in energy. The similarities between the Cp and the $[7,8-R_2C_2B_9H_9]^{2-}$ ligands were first recognized by Hawthorne[9] and have proven to be a useful guide for the syntheses of metallacarboranes that parallel those of the metallocenes. In this way one can view the metallacarboranes as having half- or full-sandwich structures.

Anil Saxena is employed at the Dow Corning Corporation as an Associate Chemical Specialist. He was born in 1958 in India and studied at the Universities of Agra and Rajasthan and obtained his Ph.D. degree in 1982. His postdoctoral experience was in organosilicon chemistry with Colin Eaborn at the University of Sussex and with Adrian Brook at the University of Toronto, and in carborane chemistry with Narayan Hosmane at Southern Methodist University and with Josef Michl at University of Colorado at Boulder. He was a recipient of the Alexander von Humboldt fellowship and worked with Friedo Huber at the University of Dortmund. He was employed at the Tata Institute of Fundamental Research and the Indian Institute of Chemical Technology for brief period of time. In his present position, he is working in the Silicon Modified Organic KCI at the corporate headquarters of Dow Corning Corporation in Midland, MI. He has coauthored more than 50 research publications including five reviews and monographs. His current research interests are in the area of organosilicon chemistry, emulsion polymerization, cationic polymerization, and finding new applications for silicon polymers.

John Maguire is Professor of Chemistry at Southern Methodist University. He was born in Alabama in 1936, received his B.S. Degree in Chemistry from Birmingham Southern College in 1958 and his Ph.D. Degree in Physical Chemistry in 1963 from Northwestern University under the direction of Ralph G. Pearson. He joined the faculty of Southern Methodist University as an Assistant Professor of Chemistry and is now Professor of Chemistry. From 1976 to 1979 he was Associate Dean of University College at SMU and from 1979 to 1981 he was Dean of University College and General Education at SMU. His research interests are in the structure and properties of intercalation compounds and in the bonding, structure, and reactivity in carborane cage compounds.

This terminology has some advantages over the alternate *closo* and *commo* notations, which carry both a structural and an electronic connotation. It turns out that many of the metallacarboranes have distorted geometries so that the structures are not regular and many times it is not obvious which electrons are to be included as cage bonding. In order to avoid confusion, and unwarranted consternation, we will use terms such as half-, full-, bent-, and slipped-sandwich when describing the structures of many of the metallacarboranes.

Narayan S. Hosmane was born in Gokarn, Southern India, in 1948. He is a B.S. and M.S. graduate of Karnatak University, located in the state of Karnataka, India. He obtained a Ph.D. degree in Inorganic Chemistry in 1974 from the University of Edinburgh, Scotland, under the supervision of Professor Evelyn Ebsworth who is currently Vice Chancellor of University of Durham. After a brief postdoctoral research training in Professor Frank Glockling's laboratory at the Queen's University of Belfast, he joined Lambeg Research Institute in Northern Ireland, and then moved to the United States to do research in the area of carboranes and metallacarboranes. After postdoctoral work with Professors W. E. Hill and F. A. Johnson at Auburn University and Russell Grimes at the University of Virginia, in 1979 he joined the faculty at the Virginia Polytechnic Institute and State University. In 1982, he joined the faculty at Southern Methodist University, where he is currently Professor of Chemistry. In 1985, he was a Visiting Professor at The Ohio State University and worked with Professor Sheldon Shore. He was the organizer and co-founder of the first Boron in the USA (BUSA) workshop which was hosted in Dallas in April 1988. He received the 1994 Camille and Henry Dreyfus Scholar Award and has been honored with the Mother India International Award for his contribution to education and BUSA Award for his achievements in Boron Science. A fellow of the Royal Society of Chemistry and the American Institute of Chemists, he has been listed in *Who's Who in the World*. His research interests are in the synthesis and structure of carboranes, metallacarborane sandwich compounds, and organosilicon compounds, with particular emphasis on the Ziegler–Natta catalysis.

II. Heterocarboranes of Main Group Elements

A large number of main group elements have been incorporated into polyhedral carborane cages. This discussion will focus on the carborane cages that have expanded to incorporate elements in the s-block groups (groups 1 and 2), excluding hydrogen, and certain of the p-block group elements (groups 13−16), excluding carbon and boron. The halogen group has also been excluded; although halogens have been substituted for terminal hydrogens, there are no reports of the incorporation of a halogen into the polyhedral structure of a carborane or borane cage. Since most of the elements to be discussed are metals or metalloids, vast majority of the compounds will be metallacarboranes, in which the main group element functions as a capping group. No attempt will be made to cover those compounds where the heteroatom is in a bridging group linking several carborane polyhedra together, or when it is involved solely as a member of an *exo* polyhedral substituent group. Also, this review will not cover the heteroboranes; all cages discussed will contain both carbon and boron atoms, as well as the heteroatoms. Much of the insight into the bonding and reactivity of main group heterocarboranes has been derived directly from structural data, mainly solid state X-ray diffraction analyses, thus, a great deal of emphasis will be placed on the results of structural studies. Despite
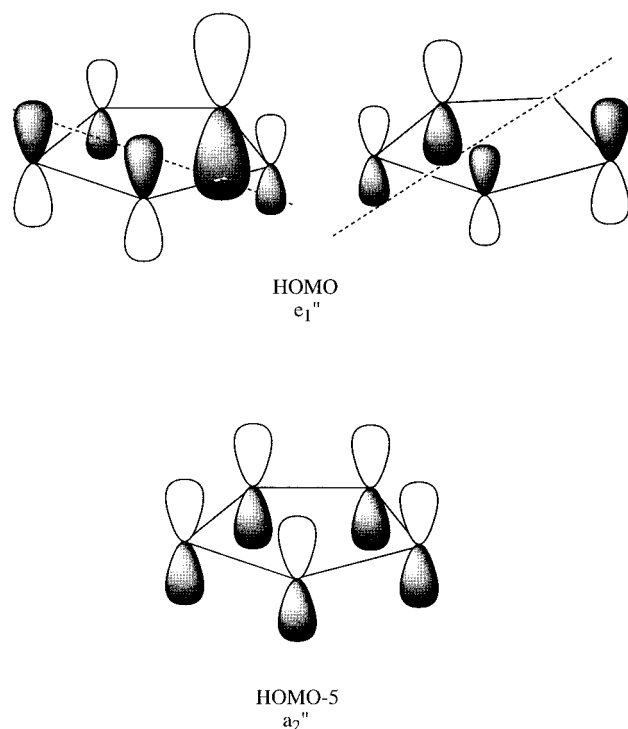
HOMO
e_1''

HOMO-5
a_2''

Figure 1. High-energy filled molecular orbitals of $[C_5H_5]^-$ in terms of their input p_π atomic orbitals.

this emphasis, the structures of only a small percentage of the complexes will actually be discussed. A listing of selected crystallographic parameters of all the structurally characterized heterocarboranes is given in Table 1.

A. Complexes of Group 1 Elements

The group 1 metallacarboranes are probably the most synthesized and, until recently, the least thought about of the metallacarboranes, in that they are commonly used as precursors for other, "more interesting", compounds. The most used synthetic route to metallacarboranes is through the reactions of open face carborane anions with metal reagents, usually metal halides. This procedure was used by Hawthorne and co-workers in the syntheses of the initially reported metallacarboranes having the general formulas, $3,1,2$-$M(CR)_2B_9H_9$ (M = metal moiety; R = H or an alkyl group).[9,10] 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, $[(3),1,2$-$(CR)_2B_9H_{10}]^-$, 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*-$[(3),1,2$-$(CR)_2B_9H_{11}]^{2-}$. Since equivalent results were obtained with different alkali metals or when tetralkylammonium cations were used,[10b] 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*-$[2,3$-$(CR)_2B_4H_4]^{2-}$ should normally be made by removing the two bridged hydrogens from the corresponding *nido*-2,3-$(CR)_2B_4H_6$. However, Onak and Dunks found that the reaction of *nido*-2,3-$C_2B_4H_8$ with NaH produced the monosodium compound, according to eq 1.[11] The most interesting, and least

$$nido\text{-}C_2B_4H_8 + \text{excess NaH} \xrightarrow[0-150\,°C]{\text{THF}}$$
$$\text{Na}[nido\text{-}C_2B_4H_7] + H_2 \quad (1)$$
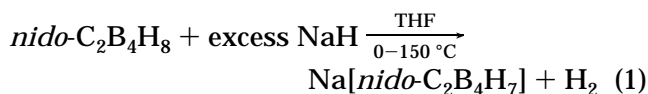
understood aspect of this reaction was its stoichiometry; the monoanion was the exclusive product formed, even in the presence of excess NaH and at elevated temperatures. Grimes and co-workers studied the kinetics of this deprotonation reaction with various substituted carboranes of the type, *nido*-2,3-R,R'-$C_2B_4H_6$ (where R = alkyl, arylmethyl and phenyl; R' = R, H), using both NaH and KH in THF (C_4H_8O).[12] 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*).[13] 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, $[2,3$-$(SiMe_3)_2$-$2,3$-$C_2B_4H_5]^-$.[14] The solid state structure, shown in Figure 2, is that of an extended network of dimeric $(C_4H_8ONa^+)_2[2,3$-$(SiMe_3)_2$-$2,3$-$C_2B_4H_5^-]_2$ clusters that are layered symmetrically on top of one another. The remaining bridge hydrogen on each carborane cage in the dimer [H(34) in Figure 2] is well shielded by the surrounding groups. This shielding is even more apparent in the space-filling model of the cluster, shown in Figure 3. 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 $[(\text{TMEDA})Na^+]_2[2,3$-$(SiMe_3)_2$-$2,3$-$C_2B_4H_5^-]_2$ dimer, with a structure similar to that shown in Figure 2, with the THF molecules replaced by TMEDA's. The major effect of the solvent substitution is that the larger TMEDA molecules tend to break up the chain structure found in THF, leading to isolated dimeric clusters.[15] 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 2, and that the steric shielding of the bridging hydrogens 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-$[(\mu\text{-}H)_2$Na-$(\text{TMEDA})_2$-2-$(SiMe_3)$-3-Me-$2,3$-$C_2B_4H_5]$, shown in Figure 4.[16] The $[Na(\text{TMEDA})_2]^+$ does not act as a capping group, but is *exo* polyhedrally bound, leaving the bridge hydrogen unprotected. It was found that this less sterically protected bridge hydrogen could easily be removed by NaH, to give the corresponding disodium compound.[16] The bridge hydrogen in the highly solvated $[Li(\text{TMEDA})_2^+][nido$-2,3-$(SiMe_3)_2$-$2,3$-$C_2B_4H_5^-]$ was also found to be unprotected and to react readily with NaH to give the corresponding Na/Li carborane.[17] Therefore, the stoichiometry of eq 1

Table 1. Selected Crystallographic Parameters for Heterocarboranes of Main Group Elements[a]

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
Heterocarboranes of Group 1 Elements			
1. Lithium Complexes			
exo-4,5-[(μ-H)$_2$Li(TMEDA)-1-Li(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$	Li(1)−Cnt(3) = 1.906 Li(1)−C(1) = 2.367(9) Li(1)−C(2) = 2.296(9) Li(1)−B(3) = 2.291(9) Li(1)−B(4) = 2.371(9) Li(1)−B(5) = 2.337(10) Li(1)−N(21) = 2.192(9) Li(1)−N(22) = 2.159(9)	Cnt(3)−Li(1)−N(21) = 137.2 Cnt(3)−Li(1)−N(22) = 141.7 N(21)−Li(1)−N(22) = 81.0(3) N(31)−Li(2)−N(32) = 88.1(3) N(31)−Li(2)−H(4) = 124(1) N(31)−Li(2)−H(5) = 111(1) N(32)−Li(2)−H(4) = 117(1) N(32)−Li(2)−H(5) = 115(1)	15
[Li(TMEDA)$_2$]$^+$[2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_5$]$^-$	Li···Cnt = 5.27 Li−N(21) = 2.120(16) Li−N(22) = 2.065(15) Li−N(31) = 2.090(15) Li−N(32) = 1.103(14) C(1)−C(2) = 1.468(12) B(3)−H(34) = 1.22 B(4)−H(34) = 1.23	N(21)−Li−N(22) = 88.8(6) N(21)−Li−N(31) = 116.3(7) N(22)−Li−N(31) = 124.8(7) N(21)−Li−N(32) = 123.1(7) N(22)−Li−N(32) = 119.3(7) N(31)−Li−N(32) = 88.3(6) B(3)−H(34)−B(4) = 87.0	17
closo-exo-5,6-[(μ-H)$_2$Li(TMEDA)]-1-Li(TMEDA)-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$	Li(1)−Cnt(2) = 1.908 Li(1)−C(1) = 2.295(9) Li(1)−B(2) = 2.318(10) Li(1)−C(3) = 2.374(9) Li(1)−B(4) = 2.344(9) Li(1)−B(5) = 2.299(10)	Cnt(2)−Li(1)−N(21) = 135.5 Cnt(2)−Li(1)−N(22) = 143.0 N(21)−Li(1)−N(22) = 81.4(3)	18
closo-exo-5,6-[(μ-H)$_2$Li(THF)](μ-THF)-1-Li-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$	Li(1)−Cnt(1) = 1.891 Li(1)−C(1) = 2.275(11) Li(1)−B(2) = 2.289(12) Li(1)−C(3) = 2.344(12) Li(1)−B(4) = 2.349(12) Li(1)−B(5) = 2.327(12) Li(1)···Li(1a) = 2.709(22) Li(1)−O(20a) = 2.288(11)	Cnt(1)−Li(1)−Li(1a) = 87.9 Cnt(1)−Li(1)−O(20a) = 134.8 O(20)−Li(2)−O(25) = 115.6(7) Li(1a)−Li(1)−Li(2a) = 95.0(5) Cnt(1)−Li(1)−Li(2a) = 174.8	18
[Li(TMEDA)$_2$][*commo*-1,1′-Li{2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_5$}$_2$]	Li(1)−Cnt(1) = 2.047 Li(1)−C(11) = 2.20(1) Li(1)−C(12) = 2.29(1) Li(1)−B(3) = 2.55(1) Li(1)−B(4) = 2.74(1) Li(1)−B(5) = 2.47(2) Li(4)−N(61) = 2.10(2) Li(4)−N(62) = 2.12(2)	Cnt(1)−Li(1)−Cnt(1a) = 180.0	21
2. Sodium Complexes			
[*nido*-1-Na(THF)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_5$]$_2$	Na−Cnt(1) = 2.778 Na−C(1) = 2.832(10) Na−C(2) = 3.071(11) Na−B(3) = 3.307(11) Na−B(4) = 3.290(10) Na−B(5) = 2.920(11) Na−H(34) = 2.57(8) Na−O = 2.346(9) Na−B(4a) = 2.995(12) Na−B(6b) = 3.179(12)	Cnt(1)−Na−O = 100.5 H(5a)−Na−H(4b) = 94.2(3) B(4a)−Na−B(6b) = 96.2(3) B(6b)−Na−H(5a) = 124(2) B(4a)−Na−H(4b) = 69(2) O−Na−B(4a) = 127.2(2) O−Na−H(5a) = 76(2) O−Na−H(4b) = 83(2) O−Na−B(6b) = 100.9(3)	14,15
[*nido*-1-Na(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_5$]$_2$	Na−Cnt(2) = 2.774 Na−C(1) = 2.846(5) Na−C(2) = 3.199(5) Na−B(3) = 3.360(7) Na−B(4) = 3.191(7) Na−B(5) = 2.799(6) Na−N(21) = 2.509(5) Na−N(22) = 2.556(4) Na−H(34) = 2.58(4)	Cnt(2)−Na−N(21) = 142.8 Cnt(2)−Na−N(22) = 106.5 Cnt(2)−Na−B(4d) = 110.6 Cnt(2)−Na−H(5d) = 108 N(21)−Na−N(22) = 73.5(1) N(21)−Na−B(4d) = 94.6(2) N(22)−Na−B(4d) = 130.2(2) N(21)−Na−H(5d) = 109(1) N(22)−Na−H(5d) = 85(1) B(4d)−Na−H(5d) = 53(1)	15
nido-exo-4,5-[(μ-H)$_2$Na(TMEDA)$_2$]-2-(SiMe$_3$)-3-(Me)-2,3-C$_2$B$_4$H$_5$	Na−B(4) = 2.792(7) Na−B(5) = 2.869(7) Na−N(11) = 2.541(5) Na−N(12) = 2.577(5) Na−N(21) = 2.559(5) Na−N(22) = 2.641(6) C(2)−C(3) = 1.451(7)	B(4)−Na−B(5) = 33.0(2) B(4)−Na−N(11) = 119.1(2) B(5)−Na−N(11) = 143.0(2) B(4)−Na−N(12) = 98.7(2) B(5)−Na−N(12) = 87.6(2) N(11)−Na−N(12) = 71.6(2)	16

Table 1 (Continued)

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
[*closo-exo*-5,6-Na(THF)$_2$-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]$_2$	Na(1)−C(1) = 2.667(15) Na(1)−Cnt(1) = 2.38 Na(1)−O(40) = 2.299(13) Na(1)−O(45) = 2.354(14) Na(1)−O(50) = 2.530(12) Na(1)−C(3) = 2.796(15) Na(1)−B(4) = 2.795(18) Na(1)−B(5) = 2.708(17)	Cnt(1)−Na(1)−O(40) = 125.5 Cnt(1)−Na(1)−O(45) = 126.7 Cnt(1)−Na(1)−O(50) = 113.6 Cnt(2)−Na(2)−O(50) = 132.5	19
nido-1-(THF)-1-(TMEDA)-1-Na-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_5$	Na−C(11) = 2.925(8) Na−B(12) = 2.662(17) Na−O(31) = 2.347(7) Na−N(34) = 2.469(9) Na−C(11A) = 2.925(8) Na−N(34A) = 2.469(9)	C(11)−Na−B(12) = 31.8(2) C(11)−Na−O(31) = 105.8(3) C(11)−Na−N(34) = 106.3(3) B(12)−Na−O(31) = 88.0(4) B(12)−Na−N(34) = 138.0(3)	20

Heterocarboranes of Group 2 Elements

1. Magnesium Complexes

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
[*closo*-1-Mg(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_2$	Mg(1)−Cnt(1) = 2.139 Mg(2)−Cnt(2) = 2.124 Mg(1)−C(11) = 2.649(3) Mg(1)−C(12) = 2.635(3) Mg(1)−B(13) = 2.493(3) Mg(1)−B(14) = 2.393(3) Mg(1)−B(15) = 2.472(4) Mg(1)−B(24) = 2.540(5) Mg(2)−B(14) = 2.534(5) Mg(1)−N(51) = 2.327(2) Mg(1)−N(52) = 2.252(2)	Cnt(1)−Mg−N(51) = 119.6 Cnt(1)−Mg−N(52) = 127.5 Cnt(2)−Mg−N(61) = 120.1 Cnt(2)−Mg−N(62) = 127.2	30
{[Na(THF)$_2$]$_2$}{*commo*-1,1′-Mg[2,3-(SiMe$_3$)$_2$-1,2,3-MgC$_2$B$_4$H$_4$]$_2$}	Mg−Cnt(1,2) = 2.018 Mg−C(11) = 2.446(13) Mg−C(12) = 2.461(14) Mg−B(13) = 2.420(16) Mg−B(14) = 2.398(16) Mg−B(15) = 2.405(18) B(13)−Na = 2.976(17) B(14)−Na = 2.867(17) B(16)−Na = 3.055(18)	Cnt−Mg−Cnt = 176.7	30
(THF)$_2$Mg(SiMe$_3$)$_4$C$_4$B$_8$H$_8$	Mg−C(11) = 2.315(10) Mg−C(17) = 2.326(9) Mg−B(13) = 2.644(12) Mg−B(15) = 2.393(12) Mg−B(16) = 2.402(11) Mg−B(20) = 2.687(14) Mg−O(51) = 2.034(7) Mg−O(61) = 2.027(8) C(11)−B(13) = 1.550(15)	B(13)−C(14)−B(19) = 111.7(8) B(13)−C(14)−B(20) = 112.4(8)	32

2. Calcium Complexes

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
closo-1,1,1,1-(MeCN)$_4$-1,2,4-CaC$_2$B$_{10}$H$_{12}$	Ca(1)−N(10) = 2.471(5) Ca(1)−N(20) = 2.431(5) Ca(1)−N(30) = 2.476(5) Ca(1)−N(40 = 2.508(5) Ca(1)−C(2) = 2.701(5) Ca(1)−B(3) = 2.879(6) Ca(1)−C(4) = 2.895(5) Ca(1)−B(5) = 2.649(6) Ca(1)−B(6) = 2.828(6) Ca(1)−B(7) = 2.935(6)	Cnt−Ca(1)−N(10) = NR Cnt−Ca(1)−N(20) = NR Cnt−Ca(1)−N(40) = NR	27

3. Strontium Complexes

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
[*closo*-1,1,1-(MeCN)$_3$-1,2,4-SrC$_2$B$_{10}$H$_{12}$]$_n$	Sr(1)−N(1A) = 2.630(9) Sr(1)−N(2A) = 2.777(10) Sr(1)−N(3A) = 2.682(8) Sr(1)−C(2) = 2.997(10) Sr(1)−B(3) = 2.873(10) Sr(1)−C(4) = 3.176(10) Sr(1)−B(5) = 3.129(10) Sr(1)−B(6) = 2.909(10) Sr(1)−B(7) = 3.082(10) Sr(1)−H(2) = 2.62(9) Sr(1)−H(12) = 2.56(9)	Cnt−Sr(1)−N(1A) = NR Cnt−Sr(1)−N(2A) = NR Cnt−Sr(1)−N(3A) = NR H(2)−Sr(1)−H(12) = NR	28

Table 1 (Continued)

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
Heterocarboranes of Group 13 Elements			
1. Aluminum Complexes			
nido-7,8-μ-Al(Me)$_2$-1,2-C$_2$B$_9$H$_{12}$	Al−B(7) = 2.33(2)	B(7)−Al−B(8) = 47(1)	36, 38
	Al−B(8) = 2.28(2)	H−Al−H = 109	
	Al−C(1) = 4.36(2)		
	Al−C(2) = 3.65(2)		
	Al−B(4) = 3.90(2)		
	Al−Me(1) = 1.93(2)		
	Al−Me(2) = 1.94(2)		
	Al−H = 1.34		
	B−H = 1.34		
closo-3-(Et)-3,1,2-AlC$_2$B$_9$H$_{11}$	Al−Cl(1) = 2.173(7)	C(1)−Al−C(2) = 42.1(.3)	37
	Al−Cl(3) = 1.930(4)	C(1)−Al−B(4) = 46.2(0.3)	
	Al−B(4) = 2.138(8)	B(4)−Al−B(6) = 49.6(0.3)	
	Al−B(8) = 2.136(9)	C(1)−Al−B(7) = 77.5(0.3)	
		C(1)−Al−B(8) = 80.3(0.3)	
		B(4)−Al−B(7) = 83.0(0.3)	
		C(1)−Al−C(3) = 119.9(0.4)	
		B(4)−Al−C(3) = 137.8(0.4)	
		B(8)−Al−C(3) = 158.1(0.5)	
commo-3,3′-Al[(*exo*-8,9-(μ-H)$_2$Al(C$_2$H$_5$)$_2$-3,1,2-AlC$_2$B$_9$H$_9$)-(3′,1′,2′-AlC$_2$B$_9$H$_{11}$)]	Al−C(1) = 2.288(5)	C(21)−Al(20)−C(23) = 130.3(3)	39, 41
	Al−C(1′) = 2.240(4)	H(8)−Al(20)−H(9) = 98.72	
	Al−C(2) = 2.272(5)		
	Al−C(2′) = 2.254(5)		
	Al−B(4) = 2.237(5)		
	Al−B(4′) = 2.174(5)		
	Al−B(7) = 2.230(5)		
	Al−B(7′) = 2.164(5)		
	Al−B(8) = 2.177(5)		
	Al−B(8′) = 2.130(5)		
[Tl$^+$][*commo*-3,3′-Al(3,1,2-AlC$_2$B$_9$H$_{11}$)$_2$]$^-$	Al(3)−C(1) = 2.30(2)	Cnt−Al(3A)−Cnt′ = NR	40, 41
	Al(3)−C(2) = 2.29(2)		
	Al(3)−B(4) = 2.22(2)		
	Al(3)−B(7) = 2.24(2)		
	Al(3)−B(8) = 2.14(2)		
endo-10-[AlEt(PEt$_3$)$_2$]-7,8-C$_2$B$_9$H$_{11}$	Al(12)−C(1) = 1.974(4)	C(1)−Al(12)−B(10) = 141.23(19)	41
	Al(12)−B(10) = 2.128(5)	P(1)−Al(12)−C(1) = 97.65(14)	
	Al(12)−C(7) = 2.942(4)	P(2)−Al(12)−B(10) = 101.66(13)	
	Al(12)−P(2) = 2.554(2)	P(1)−Al(12)−P(2) = 95.25(5)	
	Al(12)−P(1) = 2.567(2)	P(2)−Al(12)−C(1) = 105.57(14)	
nido-[μ-6,9-AlEt(OEt$_2$)-6,9-C$_2$B$_8$H$_{10}$]	Al−C(6) = 2.030(3)	C(6)−Al−C(9) = 99.44(12)	41, 46
	Al−C(9) = 2.025(3)	C(11)−Al−O() = 99.87(13)	
	Al−B(5) = 2.500(4)		
	Al−B(7) = 2.509(4)		
	Al−B(8) = 2.499(4)		
	Al−B(10) = 2.514(4)		
	Al−C(1) = 1.966(3)		
	Al−O(1) = 1.909(2)		
[PPN$^+$][Al(η^2-6,9-C$_2$B$_8$H$_{10}$)$_2$]$^-$	Al−C(6) = 2.06(2)	C(6)−Al−C(9) = 98.7(9)	41,47
	Al−C(6′) = 2.07(2)	C(6′)−Al−C(9′) = 102.1(9)	
	Al−C(9) = 2.05(2)	C(6)−Al−C(6′) = 114.2(9)	
	Al−C(9′) = 2.08(2)	C(9)−Al−C(9′) = 113.6(9)	
	Al−B(ave) = 2.53(2)	C(6)−Al−C(9′) = 114.5(9)	
Na[Al(η^2-2,7-C$_2$B$_6$H$_8$)$_2$]	Al−C(2a) = 2.018(5)	C(2a)−Al−C(7a) = 82.40(2)	41,48
	Al−C(2b) = 2.018(5)	C(2b)−Al−C(7b) = 81.88(2)	
	Al−C(7a) = 2.017(5)		
	Al−C(7b) = 2.020(5)		
	Al−B(3a) = 2.282(6)		
	Al−B(3b) = 2.276(6)		
	Al−B(6a) = 2.517(6)		
	Al−B(6b) = 2.517(6)		
	Al−B(8a) = 2.517(6)		
	Al−B(8b) = 2.511(6)		
2. Gallium Complexes			
Tl[*commo*-3,3′-Ga(3,1,2-GaC$_2$B$_9$H$_{11}$)$_2$]	Ga−C(1) = 2.565(7)	B(10)−Ga−B(10′) = 170.5(2)	41
	Ga−C(2) = 2.591(8)		
	Ga−B(4) = 2.265(8)		
	Ga−B(7) = 2.297(8)		

Table 1 (Continued)

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
	Ga−B(8) = 2.083(8) Ga−C(1′) = 2.481(7) Ga−C(2′) = 2.492(7) Ga−B(4′) = 2.253(8) Ga−B(7′) = 2.251(8) Ga−B(8′) = 2.095(8)		
[Li(TMEDA)$_2$][*commo*-1,1′-Ga{2,3-(SiMe$_3$)$_2$-1,2,3-GaC$_2$B$_4$H$_4$}$_2$]	Ga−Cnt(1,1A) = 1.878 Ga−C(11) = 2.489(11) Ga−C(12) = 2.468(11) Ga−B(13) = 2.243(14) Ga−B(14) = 2.141(13) Ga−B(15) = 2.249(13) Li−N(31) = 2.095(17) Li−N(32) = 2.086(17) C(11)−C(12) = 1.527(16)	Cnt(1)−Ga−Cnt(1A) = 180.0	63
[Na(TMEDA)$_2$][*commo*-1,1′-Ga{2,4-(SiMe$_3$)$_2$-1,2,4-GaC$_2$B$_4$H$_4$}$_2$]	Ga−Cnt(21) = 1.920 Ga−Cnt(22) = 1.929 Ga−C(11) = 2.431(21) Ga−B(12) = 2.605(25) Ga−C(13) = 2.390(21) Ga−B(14) = 2.119(30) Ga−B(15) = 2.190(30) Ga−C(21) = 2.483(23) Ga−B(22) = 2.544(31) Ga−C(23) = 2.418(20) Ga−B(24) = 2.159(27) Ga−B(25) = 2.141(26) Na−N(51) = 2.488(25) Na−N(52) = 2.522(25) Na−N(61) = 2.432(29) Na−N(62) = 2.491(25)	Cnt(21)−Ga−Cnt(22) = 178.2	63
closo-1-(TMEDA)-1-(Cl)-2,3-(SiMe$_3$)$_2$-1,2,3-GaC$_2$B$_4$H$_4$	Ga−Cnt = 2.126 Ga−Cl = 2.237(5) Ga−B(13) = 2.334(20) Ga−B(14) = 2.073(18) Ga−C(11) = 2.833(17) Ga−N(31) = 2.121(15)	Cnt−Ga−Cl = 102.7 Cnt−Ga−N(31A) = 134.6	63
closo-1-(TMEDA)-1-(Cl)-2,4-(SiMe$_3$)$_2$-1,2,4-GaC$_2$B$_4$H$_4$	Ga−Cnt = 2.273 Ga−Cl = 2.193(2) Ga−C(11) = 2.747(6) Ga−B(12) = 3.078(7) Ga−C(13) = 2.877(6) Ga−B(14) = 2.248(7) Ga−B(15) = 2.157(8) Ga−N(31) = 2.166(5) Ga−N(32) = 2.099(5)	Cnt−Ga−Cl = 98.9 Cnt−Ga−N(31) = 130.7 Cnt−Ga−N(32) = 136.7 Cl−Ga−N(31) = 99.1(2) Cl−Ga−N(32) = 99.9(2) N(31)−Ga−N(32) = 83.9(2)	63
closo-1-(TMEDA)-1-(H)-2,3-(SiMe$_3$)$_2$-1,2,3-GaC$_2$B$_4$H$_4$	Ga−Cnt = 2.116 Ga−H(1) = 1.30(6) Ga−C(11) = 2.790(7) Ga−C(12) = 2.833(7) Ga−B(13) = 2.399(9) Ga−B(14) = 2.100(10) Ga−B(15) = 2.345(9) Ga−N(31) = 2.212(6) Ga−N(32) = 2.192(6) C(11)−C(12) = 1.481(10)	Cnt−Ga−H(1) = 104.2 Cnt−Ga−N(31) = 131.7 Cnt−Ga−N(32) = 132.3 H(1)−Ga−N(31) = 106.0(3) H(1)−Ga−N(32) = 95.0(3) N(31)−Ga−N(32) = 80.7(2)	63
closo-1-(TMEDA)-1-(Me)-2,3-(SiMe$_3$)$_2$-1,2,3-GaC$_2$B$_4$H$_4$	Ga−Cnt = 2.108 Ga−C$_{(Me)}$(1) = 2.098(8) Ga−C(11) = 2.804(7) Ga−C(12) = 2.832(7) Ga−B(13) = 2.381(9) Ga−B(14) = 2.065(9) Ga−B(15) = 2.351(9) Ga−N(31) = 2.209(7) Ga−N(32) = 2.175(6) C(11)−C(12) = 1.486(10)	Cnt−Ga−C$_{(Me)}$(1) = 104.8 Cnt−Ga−N(31) = 132.0 Cnt−Ga−N(32) = 132.3 C$_{(Me)}$(1)−Ga−N(31) = 98.4(3) C$_{(Me)}$(1)−Ga−N(32) = 101.2(3) N(31)−Ga−N(32) = 81.4(2)	63
1-CH$_3$GaC$_2$B$_4$H$_6$	Ga−B(5) = 2.11(3) Ga−C(2) = 2.32(3) C(2)−C(3) = 1.47(4)	B(4)−Ga−B(5) = 46(2) B(4)−Ga−B(6) = 75(2) B(5)−Ga−CH$_3$ = 166(2)	49

Table 1 (Continued)

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
	Ga−B(4) = 2.22(3)	B(4)−B(5)−B(6) = 105(3)	
	Ga−CH$_3$ = 1.91(3)	B(4)−C(3)−C(2) = 113(3)	
	B(4)−B(5) = 1.70(3)	B(4)−Ga−C(3) = 40(2)	
	C(3)−B(4) = 1.57(4)	C(2)−Ga−C(3) = 37(2)	
	C(2)−Ga−CH$_3$ = 122(3)		
	B(5)−B(4)−C(3) = 104(3)		
closo-1-(*t*-C$_4$H$_9$)-1-Ga-2,3-(SiMe$_3$)-2,3-C$_2$B$_4$H$_4$	Ga−Cnt = 1.748	C(7)−Ga−Cnt = 155.8	51
	Ga−C(2) = 2.282(5)	Ga−Cnt−B(6) = 171.2	
	Ga−B(4) = 2.131(7)		
	Ga−C(7) = 1.970(5)		
	Ga−C(1) = 2.291(5)		
	Ga−B(3) = 2.171(5)		
	Ga−B(5) = 2.199(8)		
1,1′-(2,2′-C$_8$H$_6$N$_4$)[1-(*t*-C$_4$H$_9$)-1-Ga-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_2$	Ga−Cnt = 2.067	N(1)−Ga−Cnt = 123.7	51
	Ga−C(2) = 2.781(10)	C(7)−Ga−N(1) = 99.2(4)	
	Ga−B(4) = 2.062(11)	C(7)−Ga−Cnt = 123.7	
	Ga−C(7) = 1.984(10)	N(2)−Ga−Cnt = 124.8	
	Ga−N(2) = 2.321(8)		
	Ga−C(1) = 2.804(10)		
	Ga−B(3) = 2.314(10)		
	Ga−B(5) = 2.341(12)		
	Ga−N(1) = 2.332(8)		
1-(2,2′-C$_8$H$_6$N$_4$)-1-(*t*-C$_4$H$_9$)-1-Ga-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$	Ga−Cnt[a] = 2.142	N(1)−Ga−Cnt = 132.0	54
	Ga−C(1) = 2.860(3)	N(3)−Ga−Cnt = 129.2	
	Ga−B(3) = 2.426(5)	N(1)−Ga−N(3) = 73.4(1)	
	Ga−B(5) = 2.332(5)		
	Ga−N(1) = 2.174(3)		
	Ga−C(2) = 2.907(4)		
	Ga−B(4) = 2.077(4)		
	Ga−C(7) = 2.019(5)		
	Ga−N(3) = 2.178(4)		
1-(2,2′-C$_{10}$H$_8$N$_2$)-1-(*t*-C$_4$H$_9$)-1-Ga-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$	Ga−Cnt = 2.204	Cnt−Ga−C(13) = 114.8	55
	Ga−C(1) = 2.938	Cnt−Ga−N(17) = 128.2	
	Ga−B(3) = 2.437	Cnt−Ga−N(24) = 130.0	
	Ga−B(4) = 2.069		
	Ga−B(5) = 2.400		
	Ga−N(17) = 2.152		
1-(2,2′-C$_{10}$H$_8$N$_2$)-1-(*t*-C$_4$H$_9$)-1-Ga-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$	Ga−Cnt = 2.297	Cnt−Ga−C(13) = 110.0	55
	Ga−C = 2.840	Cnt−Ga−N() = 130.9	
	Ga−B(2) = 3.120	N(17)−Ga−N(24) = 76.9	
	Ga−B(4) = 2.198		
	Ga−B(5) = 2.195		
	Ga−N = 2.094		
1-(2,2′-C$_8$H$_6$N$_4$)-1-(*t*-C$_4$H$_9$)-1-Ga-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$ (molecule A)	Ga−Cnt = 2.244	Cnt−Ga−C(13) = 113.0	55,62
	Ga−C(1) = 2.808(13)	Cnt−Ga−N(24) = 130.1	
	Ga−B(2) = 3.019(17)	Cnt−Ga−N(17) = 125.4	
	Ga−C(3) = 2.771(13)	C(13)−Ga−N(24) = 103.6	
	Ga−B(4) = 2.185(19)	C(13)−Ga−N(17) = 103.4	
	Ga−B(5) = 2.198(17)	N(17)−Ga−N(24) = 73.9	
	Ga−C(13) = 1.988(22)		
	Ga−N(17) = 2.153(12)		
	Ga−N(24) = 2.152(11)		
1-(2,2′-C$_8$H$_6$N$_4$)-1-(*t*-C$_4$H$_9$)-1-Ga-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$ (molecule B)	Ga−Cnt = 2.432	Cnt−Ga−C(43) = 147.5	55,62
	Ga−C(31) = 2.974(13)	Cnt−Ga−N(54) = 108.3	
	Ga−B(32) = 3.309(18)	Cnt−Ga−N(47) = 87.9	
	Ga−C(33) = 2.987(13)	C(43)−Ga−N(54) = 103.7	
	Ga−B(34) = 2.226(16)	C(43)−Ga−N(47) = 105.1	
	Ga−B(35) = 2.225(17)	N(47)−Ga−N(54) = 77.2	
	Ga−C(43) = 1.943(17)		
	Ga−N(47) = 2.064(14)		
	Ga−N(54) = 2.116(10)		
closo-1-Ga[*σ*-*closo*-1-Ga-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$	Ga(1)−Ga(2) = 2.340(2)	Cnt(1)−Ga(1)−Ga(2) = 159.6	57
	Ga(1)−Cnt(1) = 1.679	Cnt(2)−Ga(2)−Ga(1) = 164.4	
	Ga(1)−C(1) = 2.164(8)		
	Ga(1)−B(2) = 2,232(11)		
	Ga(1)−C(3) = 2.146(10)		
	Ga(1)−B(4) = 2.145(11)		
	Ga(1)−B(5) = 2.125(10)		
	Ga(2)−Cnt(2) = 1.679		

Table 1 (Continued)

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
3. Indium Complexes			
[*closo*-1-(Me$_2$CH)-2,3-(SiMe$_3$)$_2$-1,2,3-InC$_2$B$_4$H$_4$]$_2$	In(1)−C(1) = 2.676(5) In(1)−C(2) = 2.660(4) In(1)−B(3) = 2.425(6) In(1)−B(4) = 2.297(5) In(1)−B(5) = 2.431(6) In(1)−B(10) = 2.847(5) In(1)−B(11) = 3.014(6) In(1)−C(13) = 2.143 In(1)−(Cnt)= 2.100 In(2)−In(1) = 3.696(1)	Cnt(1)−In(1)−C(13) = 134.9	52,53
1-(2,2′-C$_8$H$_6$N$_4$)-1-[(Me)$_2$CH]-1-In-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$	In−Cnt = 2.219 In−C(1) = 2.849(6) In−C(2) = 2.888(4) In−B(3) = 2.487(7) In−B(4) = 2.250(6) In−B(5) = 2.480(7) In−C(21) = 2.141(8) In−N(31) = 2.424(5) In−N(37) = 2.391(4)	Cnt−In−C(21) = 119.9 Cnt−In−N(31) = 128.9 Cnt−In−N(37) = 133.8 C(21)−In−N(37) = 96.9(2) N(31)−In−N(37) = 66.8(1)	53
[*closo*-1-(Me$_2$CH)-2,4-(SiMe$_3$)$_2$-1,2,4-InC$_2$B$_4$H$_4$]$_2$	In(1)−C(2) = 2.440(4) In(1)−B(3) = 2.524(5) In(1)−C(4) = 2.449(4) In(1)−B(5) = 2.320(5) In(1)−B(6) = 2.318(5) In(1)−(Cnt) = 1.989 In(1)⋯In(1a) = 3.696(1)	Cnt(1)−In(1)−C(21) = 150.3 Cnt(1)−In(1)−H(6a) = 126 Cnt(1)−In(1)−H(5a) = 127 In(1)−C(21) = 2.133(5)	55
1-(2,2′-C$_{10}$H$_8$N$_2$)-1-[(Me)$_2$CH]-1-In-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$	In(1)−C(2) = 2.746(15) In(1)−B(3) = 2.918(16) In(1)−C(4) = 2.737(15) In(1)−B(5) = 2.338(14) In(1)−B(6) = 2.336(14) In(1)−C(21) = 2.091(13) In(1)−N(51) = 2.357(13) In(1)−N(58) = 2.386(13) B(6)−B(7) = 1.731(16) B(5)−B(7) = 1.741(16) B(3)−B(7) = 1.785(13)	B(5)−In(1)−C(21) = 142.5(5) B(6)−In(1)−C(21) = 139.9(5) B(5)−In(1)−N(51) = 96.7(4) B(6)−In(1)−N(51) = 124.3(4) C(21)−In(1)−N(51) = 95.8(4) B(5)−In(1)−N(58) = 119.7(4) B(6)−In(1)−N(58) = 97.8(4) C(21)−In(1)−N(58) = 97.8(4) N(51)−In(1)−N(58) = 68.5(3)	55
4. Thallium Complexes			
[PPh$_3$Me]$^+$[*closo*-3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$	Tl−B(unique) = 2.664(7) Tl−B(basal) = 2.744(8) Tl−B(basal) = 2.741(7) Tl−C(1) = 2.915(6) Tl−C(2) = 2.923(6) Tl⋯Tl = 7.967(1)	Tl−Cnt−B(apical) = NR	65
{[PPN]$^+$[*closo*-3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$}$_2$	Tl(3)−B(8) = 2.664(7) Tl(3)−B(4) = 2.744(8) Tl(3)−B(7) = 2.741(7) Tl(3)−C(1) = 2.915(6) Tl(3)−C(2) = 2.923(6) Tl(3)⋯Tl(3′) = 4.241(1) Tl(3)−H(8) = 2.62(11) Tl(3)−H(7) = 2.83(11)	B(10)−Tl(3)−Tl(3′) = 76.2	66
[Tl]$^+$[*closo*-2,3-(Me)$_2$-1,2,3-TlC$_2$B$_9$H$_9$]$^-$	Tl(1)−B(1a) = 2.739(82) Tl(1)−B(1b) = 2.682(72) Tl(1)−B(1c) = 2.969(73) Tl(1)−C(1a) = 3.173(73) Tl(1)−C(1b) = 3.278(25) C(1a)−C(1b) = 1.571(100) Tl(4b)⋯Tl(4c) = 3.67	B(1b)−Tl(1)−B(1a) = 37.4(22) B(1c)−Tl(1)−B(1a) = 56.7(23) B(1c)−Tl(1)−B(1b) = 36.5(21)	68

Heterocarboranes of Group 14 Elements

1. Silicon Complexes			
commo-1,l′-Si(2,3-(SiMe$_3$)$_2$-1,2,3-SiC$_2$B$_4$H$_4$)$_2$	Si−C(1) = 2.23(1) Si−C(2) = 2.25(1) Si−B(3) = 2.10(1) Si−B(4) = 2.03(1) Si−B(5) = 2.10(1)	Cnt(1)−Si−Cnt(2) = NR	75
commo-1,l′-Si(2-(SiMe$_3$)-3-(Me)-1,2,3-SiC$_2$B$_4$H$_4$)$_2$	Si(1)−C(1) = 2.236(6) Si(1)−C(2) = 2.228(7)	Si(1)−B(3)−C(2) = 73.1(5) Si(1)−B(3)−B(4) = 64.0(5)	76

Table 1 (Continued)

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
	Si(1)−B(3) = 2.108(12)	Si(1)−B(3)−B(6) = 90.8(6)	
	Si(1)−B(4) = 2.037(10)	Si(1)−B(5)−C(1) = 73.0(4)	
	Si(1)−B(5) = 2.117(9)	Si(1)−B(5)−B(4) = 63.5(5)	
	Si(2)−C(1) = 1.861(7)	Si(1)−B(5)−B(6) = 93.0(5)	
	Si(2)−C(8) = 1.899(13)	Si(1)−B(4)−B(3) = 68.5(5)	
	Si(2)−C(9) = 1.770(20)	Si(1)−B(4)−B(5) = 68.5(5)	
	Si(2)−C(10) = 1.872(14)	Si(1)−B(4)−B(6) = 93.0(6)	
		C(1)−Si(1)−C(2) = 38.9(2)	
commo-3,3′-Si(3,1,2-SiC$_2$B$_9$H$_{11}$)$_2$	Si−C(1,2) = 2.22(1)	Cnt(1)−Si−Cnt(2) = NR	74
	Si−B(4,7) = 2.14(1)		
	Si−B(8) = 2.05(1)		
(10-*exo*-η^1-7,8-C$_2$B$_9$H$_{11}$)(10-*endo*-η^1-7,8-C$_2$B$_9$H$_{11}$)Si(C$_5$H$_5$N)$_2$	Si(1)−N(1A) = 1.923(3)	N(1A)−Si(1)−N(1B) = 89.67(11)	74(b)
	Si(1)−N(1B) = 1.923(3)	B(10)−Si(1)−B(10′) = 140.44(15)	
	Si(1)−B(10) = 2.020(4)	B(9′)−B(10′)−Si(1) = 80.43(19)	
	Si(1)−B(10′) = 2.008(4)	B(9)−B(10)−Si(1) = 126.64(23)	
	Si(1)−B(9′) = 2.475(4)	B(11′)−B(10′)−Si(1) = 78.07(19)	
	Si(1)−B(11′) = 2.416(4)	B(11)−B(10)−Si(1) = 125.79(22)	
	Si(1)−C(7′) = 2.943(4)		
	Si(1)−C(8′) = 2.972(4)		
	C(7)−C(8) = 1.592(4)		
[η^5-10-{(Me$_3$P)$_2$BH}C$_2$B$_8$H$_{10}$]Si(η^1-C$_2$B$_9$H$_{11}$)	Si(3)−C(7) = 2.054(4)	Cnt−Si(3)−Cnt' = 159.7(2)	74(b)
	Si(3)−C(8) = 2.042(4)	B(10)−B(12)−P(1) = 112.9(2)	
	Si(3)−B(1) = 2.045(4)	B(10)−B(12)−P(2) = 111.7(2)	
	Si(3)−B(2) = 2.036(4)	P(1)−B(12)−P(2) = 113.2(2)	
	Si(3)−B(4) = 2.063(4)		
	Si(3)−C(7′) = 2.673(4)		
	Si(3)−C(8′) = 2.692(4)		
	Si(3)−B(9′) = 2.325(4)		
	Si(3)−B(10′) = 2.004(4)		
	Si(3)−B(11′) = 2.311(4)		
	C(7)−C(8) = 1.562(5)		
	C(7′)−C(8′) = 1.560(5)		
closo-1,2-(Me)$_2$-1,2-Si$_2$B$_{10}$H$_{10}$	Si−C(1) = 1.827(3)	C(1)−Si(1)−B(5) = 129.5(1)	113
	Si−B(5) = 2.017(3)	C(1)−Si(1)−B(4) = 129.1(2)	
	Si−B(4) = 2.018(3)	C(1)−Si(1)−B(6) = 129.8(1)	
	Si−B(6) = 2.113(4)	C(1)−Si(1)−B(3) = 128.9(1)	
	Si−B(3) = 2.116(3)	C(1)−Si(1)−Si(2) = 124.3(1)	
	Si(1)−Si(2) = 2.308(2)	B(3)−Si(1)−Si(2) = 56.9(1)	
		B(11)−B(6)−Si(1) = 112.2(2)	
		B(11)−B(6)−Si(2) = 60.7(1)	
		Si(1)−B(6)−Si(2) = 66.1(1)	
	2. Germanium Complexes		
commo-1,1′-Ge(2,3-(SiMe$_3$)$_2$-1,2,3-GeC$_2$B$_4$H$_4$)$_2$	Ge−C(1) = 2.38(2)	C(1)−Ge−C(2) = 34.9(6)	80,81
	Ge−C(2) = 2.39(2)	C(1)−Ge−B(3) = 66.7(9)	
	Ge−B(3) = 2.14(3)	C(1)−Ge−B(4) = 70.1(8)	
	Ge−B(4) = 2.08(3)	C(1)−Ge−B(5) = 41.2(7)	
	Ge−B(5) = 2.15(2)	C(2)−Ge−B(3) = 41.8(9)	
	C(1)−C(2) = 1.43(3)	C(2)−Ge−B(4) = 70.1(9)	
	C(1)−B(6) = 1.72(3)	C(2)−Ge−B(5) = 66.0(8)	
	C(2)−B(6) = 1.72(3)	B(3)−Ge−B(4) = 43.5(11)	
	B(3)−B(6) = 1.73(4)	B(3)−Ge−B(5) = 70.9(10)	
	B(4)−B(6) = 1.72(3)	B(4)−Ge−B(5) = 43.4(9)	
	B(5)−B(6) = 1.71(3)		
closo-1-Ge-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$	Ge(1)−C(1) = 2.221(3)	B(3)−Ge(1)−B(2) = 45.06(14)	82(a)
	Ge(1)−C(2) = 2.219(3)	B(3)−Ge(1)−C(2) = 71.36(13)	
	Ge(1)−B(1) = 2.279(4)	B(2)−Ge(1)−C(2) = 41.92(13)	
	Ge(1)−B(2) = 2.211(4)	B(3)−Ge(1)−C(1) = 41.70(13)	
	Ge(1)−B(3) = 2.209(4)	C(2)−Ge(1)−C(1) = 67.99(11)	
closo-1-Ge-2,3-(SiMe$_3$)$_2$-5-(GeCl$_3$)-2,3-C$_2$B$_4$H$_3$	Ge(1)−C(1) = 2.251(4)	C(1)−Ge(1)−C(2) = 38.9(2)	82(b)
	Ge(1)−C(2) = 2.244(4)	C(1)−Ge(1)−B(3) = 68.7(2)	
	Ge(1)−B(3) = 2.265(6)	C(2)−Ge(1)−B(3) = 41.1(2)	
	Ge(1)−B(4) = 2.243(6)	C(1)−Ge(1)−B(4) = 69.4(2)	
	Ge(1)−B(5) = 2.250(6)	C(2)−Ge(1)−B(4) = 69.6(2)	
	Ge(2)−B(4) = 1.995(6)	B(3)−Ge(1)−B(4) = 43.0(2)	
	Ge(2)−Cl(1−3) = 2.145(2)	Cl(1)−Ge(2)−Cl(2) = 103.4(1)	
	C(1)−C(2) = 1.496(7)	Ge(1)−B(4)−Ge(2) = 130.1(3)	
1-Ge[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$CH$_2$(Me)$_2$N)]-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$	Ge(1)−Cnt(1) = 1.893	Cnt(1)−Ge(1)−N(1) = 130.0	95
	Ge(1)−C(12) = 2.443(6)	Cnt(2)−Ge(2)−N(2) = 128.0	
	Ge(1)−B(14) = 2.208(8)		

Table 1 (Continued)

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
	Ge(1)−N(1) = 2.496(6)		
	Ge(1)−C(11) = 2.452(6)		
	Ge(1)−B(13) = 2.272(7)		
	Ge(1)− B(15) = 2.260(8)		
1-Ge-($C_{10}H_8N_2$)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$	Ge−N(9) = 2.321(4)	B(3)−Ge−B(5) = 69.0(2)	97,99
	Ge−N(10) = 2.474(4)	B(3)−Ge−N(9) = 110.4(2)	
	Ge−B(3) = 2.255(7)	B(3)−Ge−N(10) = 84.0(2)	
	Ge−B(4) = 2.208(7)	B(4)−Ge−B(5) = 42.2(2)	
	Ge−B(5) = 2.371(7)	B(4)−Ge−N(9) = 84.1(2)	
	Ge−C(1) = 2.579(5)	B(4)−Ge−N(10) = 105.0(2)	
	Ge−C(2) = 2.510(5)	B(5)−Ge−N(9) = 104.7(2)	
	C(1)−C(2) = 1.480(6)	B(5)−Ge−N(10) = 147.1(2)	
		N(9)−Ge−N(10) = 66.7(1)	
1-Ge(2,2′-C$_8$H$_6$N$_4$)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$	Ge−Cnt = 1.964	N(1)−Ge−Cnt = 124.9	103
	Ge−N(4) = 2.315(11)	N(1)−Ge−B(3) = 88.8(5)	
	Ge−B(4) = 2.189(15)	N(1)−Ge−B(5) = 147.1(5)	
	Ge−C(1) = 1.858(13)	N(4)−Ge−B(4) = 86.7(5)	
	Ge−N(1) = 2.572(11)	N(4)−Ge−B(5) = 103.7(5)	
	Ge−B(3) = 2.269(17)	N(1)−Ge−B(4) = 105.0(5)	
	Ge−B(5) = 2.330(16)	N(4)−Ge−B(3) = 116.2(5)	
	Ge−C(2) = 2.528(12)	B(3)−Ge−B(4) = 43.9(6)	
	C(1)−C(2) = 1.468(16)	B(3)−Ge−B(5) = 68.6(6)	
	C(6)−C(7) = 1.463(18)	Ge−N(4)−C(7) = 124.2(9)	
	N(4)−C(7) = 1.353(15)	Ge−B(3)−B(4) = 65.5(8)	
	N(1)−C(7) = 1.289(16)		
3. Tin Complexes			
closo-1-Sn-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$	Sn(1)−C(2) = 2.499(5)	C(2)−Sn(1)−C(3) = 34.9(2)	87
	Sn(1)−C(3) = 2.481(6)	C(2)−Sn(1)−B(4) = 62.3(2)	
	Sn(1)−B(4) = 2.422(6)	C(2)−Sn(1)−B(5) = 64.6(2)	
	Sn(1)−B(5) = 2.418(8)	C(3)−Sn(1)−B(4) = 37.6(2)	
	Sn(1)−B(6) = 2.431(7)	C(3)−Sn(1)−B(5) = 64.5(2)	
	C(2)−C(3) = 1.494(7)	C(3)−Sn(1)−B(6) = 62.3(2)	
closo-1-Sn-2-(SiMe$_3$)-3-(Me)-2,3-C$_2$B$_4$H$_4$	Sn−C(1) = 2.476(3)	C(1)−Sn−C(2) = NR	83
	Sn−C(2) = 2.489(4)	B(2)−Sn−C(1) = NR	
	Sn−B(1) = 2.402(5)	B(2)−Sn−C(2) = NR	
	Sn−B(2) = 2.378(6)		
	Sn−B(3) = 2.426(6)		
closo-1-Sn-2-(SiMe$_3$)-3-(H)-2,3-C$_2$B$_4$H$_4$	Sn−C(1) = 2.518(5)	C(1)−Sn−C(2) = 34.7(2)	86
	Sn−C(2) = 2.475(6)	C(1)−Sn−B(5) = 35.3(2)	
	Sn−B(3) = 2.432(7)	C(2)−Sn−B(3) = 37.9(2)	
	Sn−B(4) = 2.397(8)	B(3)−Sn−B(4) = 39.9(3)	
	Sn−B(5) = 2.431(7)	B(4)−Sn−B(5) = 39.8(3)	
	C(1)−C(2) = 1.490(8)		
commo-1,1′-Sn-[(η^5-C$_5$H$_5$)Co(η^5-C$_2$B$_2$C)]$_2$ (C$_2$B$_2$C = 4,5-diethyl-1,3-dimethyl-1,3-diborolenyl)	Sn−B(1a,b) = 2.59	Cnt−Sn−Cnt′ = 112−114	112
	Sn−B(3a,b) = 2.71		
	Sn−C(2) = 2.43		
	Sn−C(4) = 2.96		
	Sn−C(5) = 2.89		
[1-*t*-C$_4$H$_9$-2,3-(Me)$_2$-1,2-NBC$_3$H$_2$]$_2$Sn	Sn−C(3) = 2.489(9)	Cnt(1)−Sn−Cnt(2) = 133.5	110
	Sn−C(4) = 2.592(10)		
	Sn−B(2) = 2.742(10)		
	Sn−C(5) = 2.810(10)		
	Sn−N(1) = 2.917(9)		
	N(1)−B(2) = 1.480(7)		
	B(2)−C(3) = 1.511(7)		
	N(1)−C(5) = 1.399(4)		
commo-1,1′-Sn[2-(SiMe$_3$)-3-(Me)-1,2,3-SnC$_2$B$_4$H$_4$]$_2$	Sn−C(1) = 2.719(6)	Cnt(1)−Sn−Cnt(2) = 142.5	89
	Sn−C(2) = 2.716(5)		
	Sn−B(3) = 2.429(8)		
	Sn−B(4) = 2.234(9)		
	Sn−B(5) = 2.421(8)		
	Sn−C(11) = 2.675(6)		
	Sn−C(12) = 2.721(6)		
	Sn−B(13) = 2.425(7)		
	Sn−B(14) = 2.234(7)		
	Sn−B(15) = 2.388(7)		
	Sn−Cnt(1) = 2.105		
	Sn−Cnt(2) = 2.087		
	C(1)−C(2) = 1.453(8)		
	C(11)−C(12) = 1.478(7)		

Table 1 (Continued)

compound	E–X (length, Å)	X–Y–Z (angle, deg)	ref(s)
1-(C_4H_8O)-2,3-(Me)$_2$-1,2,3-SnC$_2$B$_9$H$_9$	Sn–O(1) = 2.430(2) Sn–C(1) = 2.653(3) Sn–C(2) = 2.699(3) Sn–B(1) = 2.425(4) Sn–B(2) = 2.375(4) Sn–B(3) = 2.479(4) C(1)–C(2) = 1.575(4)	O(1)–Sn–C(1) = 129.63(9) O(1)–Sn–C(2) = 152.9(1) O(1)–Sn–B(1) = 93.5(1) O(1)–Sn–B(2) = 87.4(1) O(1)–Sn–B(3) = 124.6(1) C(1)–Sn–C(2) = 34.22(9)	60
1-[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$CH$_2$(Me)$_2$N)]-2,3-(SiMe$_3$)$_2$-1,2,3-SnC$_2$B$_4$H$_4$	Sn(1)–N(1) = 2.557(7) Sn(1)–C(12) = 2.664(8) Sn(1)–B(14) = 2.388(12) Sn(1)–C(11) = 2.635(8) Sn(1)–B(13) = 2.451(12) Sn(1)–B(15) = 2.439(10) C(11)–C(12) = 1.490(9)	N(1)–Sn(1)–C(11) = 138.6(2) N(1)–Sn(1)–C(12) = 149.0(3) C(11)–Sn(1)–C(12) = 32.7(2) N(1)–Sn(1)–B(13) = 115.9(4) N(1)–Sn(1)–B(14) = 87.5(3) N(1)–Sn(1)–B(15) = 102.9(3)	94
1-[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$CH$_2$(Me)$_2$N)]-2,4-(SiMe$_3$)$_2$-1,2,4-SnC$_2$B$_4$H$_4$	Sn–Cnt(5) = 2.060 Sn–C(1) = 2.440(7) Sn–B(2) = 2.520(8) Sn–C(3) = 2.533(6) Sn–B(4) = 2.440(8) Sn–B(5) = 2.415(8) Sn–N(13) = 2.723(5) Fe–Cnt(c1) = 1.637 Fe–Cnt(c2) = 1.646 N(13)–C(14) = 1.455(8) C(14)–C(20) = 1.500(9)	Cnt(5)–Sn–N(13) = 119.3 Sn–N(13)–C(14) = 113.0(4) Sn–N(13)–C(15) = 101.0(4) Sn–N(13)–C(16) = 107.2(4) Cnt(c1)–Fe–Cnt(c2) = 178.5	96
1-(2,2′-C$_{10}$H$_8$N$_2$)-2,3-(Me)$_2$-1,2,3-SnC$_2$B$_9$H$_9$	Sn(1)–N(1) = 2.412(14) Sn(1)–N(2) = 2.374(15) Sn(1)–B(1) = 2.56(2) Sn(1)–B(2) = 2.35(3) Sn(1)–B(3) = 2.55(2)	N(1)–Sn(1)–N(2) = 68.1(5) N(1)–Sn(1)–B(1) = 89.1(6) N(1)–Sn(1)–B(2) = 88.3(7) N(1)–Sn(1)–B(3) = 128.4(7) N(2)–Sn(1)–B(1) = 130.1(6) N(2)–Sn(1)–B(2) = 90.9(7) N(2)–Sn(1)–B(3) = 92.2(7)	60
1-(2,2′-C$_{10}$H$_8$N$_2$)-2,3-(SiMe$_3$)$_2$-1,2,3-SnC$_2$B$_4$H$_4$	Sn–N(13) = 2.49(1) Sn–N(19) = 2.54(1) Sn–B(3) = 2.44(2) Sn–B(4) = 2.37(2) Sn–B(5) = 2.52(1) Sn–C(1) = 2.75(1) Sn–C(2) = 2.70(1) C(1)–C(2) = 1.44(2)	N(13)–Sn–N(19) = 64.0(4) B(3)–Sn–N(13) = 120.2(4) B(3)–Sn–N(19) = 90.7(5) B(4)–Sn–N(13) = 85.4(5) B(4)–Sn–N(19) = 91.8(5) B(5)–Sn–N(13) = 91.5(4) B(5)–Sn–N(19) = 129.4(4)	86
1-(2,2′-C$_{10}$H$_8$N$_2$)-2-(Me)-3-(SiMe$_3$)-1,2,3-SnC$_2$B$_4$H$_4$	Sn–C(1) = 2.817(5) Sn–C(2) = 2.819(6) Sn–B(3) = 2.541(7) Sn–B(4) = 2.359(7) Sn–B(5) = 2.489(7) Sn–N(11) = 2.474(4) Sn–N(17) = 2.476(4)	C(1)–Sn–C(2) = 30.0(2) C(1)–Sn–B(4) = 59.5(2) C(1)–Sn–N(11) = 143.4(1) C(1)–Sn–N(17) = 119.7(2) C(2)–Sn–N(11) = 123.6(2) C(2)–Sn–N(17) = 142.6(2) B(4)–Sn–N(11) = 85.4(2) B(4)–Sn–N(17) = 87.8(2)	98
1-(2,2′-C$_{10}$H$_8$N$_2$)-2,4-(SiMe$_3$)$_2$-1,2,4-SnC$_2$B$_4$H$_4$	Sn–Cnt = 2.152 Sn–N(13) = 2.614(4) Sn–N(20) = 2.625(4) Sn–C(1) = 2.573(5) Sn–B(2) = 2.683(6) Sn–C(3) = 2.640(5) Sn–B(4) = 2.405(6) Sn–B(5) = 2.393(5) C(18)–C(19) = 1.478(6)	Cnt–Sn–N(13) = 121.8 Cnt–Sn–N(20) = 116.1 N(13)–Sn–N(20) = 61.5(1) Sn–N(13)–C(14) = 118.5(3) Sn–N(20)–C(19) = 122.0(3) Sn–N(13)–C(18) = 122.8(3) Sn–N(20)–C(21) = 119.3(3)	96
1-(1,10-C$_{12}$H$_8$N$_2$)-2,3-(SiMe$_3$)$_2$-1,2,3-SnC$_2$B$_4$H$_4$	Sn–C(1) = 2.838(9) Sn–C(2) = 2.763(9) Sn–B(3) = 2.466(9) Sn–B(4) = 2.379(8) Sn–B(5) = 2.575(8) Sn–N(1) = 2.464(6) Sn–N(2) = 2.536(7) C(1)–C(2) = 1.470(10)	N(1)–Sn–N(2) = 66.0(2) N(2)–Sn–B(3) = 85.8(3) N(2)–Sn–B(4) = 95.2(3) N(1)–Sn–B(5) = 93.4(2) B(3)–Sn–B(5) = 63.5(3) N(1)–Sn–B(3) = 111.1(3) N(1)–Sn–B(4) = 79.7(3) N(2)–Sn–B(5) = 134.5(2)	59
1,1′-(2,2′-C$_8$H$_6$N$_4$)-[2,3-(SiMe$_3$)$_2$-1,2,3-SnC$_2$B$_4$H$_4$]$_2$	Sn–C(1)–2.640(7) Sn–C(2) = 2.653(7) Sn–N(1) = 2.638(6) Sn–N(2a) = 2.589(6)	B(3)–Sn–B(4) = 40.9(3) B(4)–Sn–B(5) = 40.7(3) B(3)–Sn–N(1) = 88.3(2) B(4)–Sn–N(1) = 91.2(2)	94,102

Table 1 (Continued)

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
	Sn−B(3) = 2.436(9)	B(5)−Sn−N(1) = 129.2(2)	
	Sn−B(4) = 2.380(8)		
	Sn−B(5) = 2.468(8)		
1-(2,2′-C$_8$H$_6$N$_4$)-2,4-(SiMe$_3$)$_2$-1,2,4-SnC$_2$B$_4$H$_4$	Sn−Cnt = 2.076	Cnt−Sn−N(13) = 116.1	96
	Sn−C(1) = 2.552(5)	Cnt−Sn−N(20) = 116.7	
	Sn−B(2) = 2.499(6)	N(13)−Sn−N(20) = 58.6(1)	
	Sn−C(3) = 2.438(5)	Sn−N(13)−C(14) = 117.3(3)	
	Sn−B(4) = 2.439(6)	Sn−N(13)−C(18) = 124.8(3)	
	Sn−B(5) = 2.479(6)	Sn−N(20)−C(19) = 116.7(3)	
	Sn−N(13) = 2.640(4)	Sn−N(20)−C(21) = 121.8(4)	
	Sn−N(20) = 2.832(4)		
1-(2,2′:6′,2″-C$_{15}$H$_{11}$N$_3$)-2,3-(SiMe$_3$)$_2$-1,2,3-SnC$_2$B$_4$H$_4$	Sn−C(1) = 2.740(12)	B(3)−Sn−B(4) = 39.3(5)	105
	Sn−C(2) = 2.775(13)	B(4)−Sn−B(5) = 39.4(5)	
	Sn−B(3) = 2.549(14)	B(3)−Sn−B(5) = 62.2(5)	
	Sn−B(4) = 2.367(17)	N(1)−Sn−B(3) = 132.0(5)	
	Sn−B(5) = 2.461(16)	N(1)−Sn−B(4) = 92.9(5)	
	Sn−N(1) = 2.648(13)	N(2)−Sn−B(4) = 78.6(4)	
	Sn−N(2) = 2.593(11)	N(3)−Sn−B(4) = 95.5(5)	
	Sn−N(3) = 2.564(12)	N(3)−Sn−B(5) = 132.2(5)	
1-(2,2′:6′,2″-C$_{15}$H$_{11}$N$_3$)-2-(Me)-3-(SiMe$_3$)-1,2,3-SnC$_2$B$_4$H$_4$	Sn−C(1) = 2.832(3)	C(2)−Sn−C(1) = 30.1(1)	104,105
	Sn−C(2) = 2.825(4)	B(5)−Sn−B(3) = 62.4(1)	
	Sn−B(3) = 2.570(4)	B(4)−Sn−C(2) = 58.2(1)	
	Sn−B(4) = 2.396(4)	N(12)−Sn−B(4) = 78.9(1)	
	Sn−B(5) = 2.559(4)	N(13)−Sn−B(4) = 91.5(1)	
	Sn−N(11) = 2.687(3)	N(11)−Sn−B(4) = 95.5(1)	
	Sn−N(12) = 2.573(3)	N(12)−Sn−N(11) = 61.1(1)	
	Sn−N(13) = 2.560(3)	N(13)−Sn−N(11) = 121.5(1)	
	C(1)−C(2) = 1.471(5)	N(13)−Sn−N(12) = 63.6(1)	

4. Lead Complexes

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
[closo-2,3-(SiMe$_3$)$_2$-1,2,3-PbC$_2$B$_4$H$_4$]$_2$	Pb−C(1) = 2.582(17)	C(1)−Pb−C(2) = 33.6(4)	85,100
	Pb−C(2) = 2.634(14)	C(2)−Pb−B(3) = 35.4(5)	
	Pb−B(3) = 2.601(16)	C(2)−Pb−B(4) = 60.1(5)	
	Pb−B(4) = 2.579(17)	C(1)−Pb−B(5) = 36.6(5)	
	Pb−B(5) = 2.520(20)	B(3)−Pb−B(5) = 62.9(5)	
	Pb(a)···Pb(d) = 4.165(14)	C(1)−Pb−B(4) = 61.6(5)	
	C(1)−C(2) = 1.510(19)		
[closo-2-(SiMe$_3$)-3-(Me)-1,2,3-PbC$_2$B$_4$H$_4$]$_2$	Pb(1)−C(11) = 2.690(16)	C(11)−Pb(1)−C(12) = 32.3(6)	100
	Pb(1)−B(13) = 2.531(20)	C(12)−Pb(1)−B(14) = 59.8(5)	
	Pb−(1)−B(15) = 2.555(20)	B(13)−Pb(1)−B(15) = 63.0(8)	
	Pb(1)−B(24) = 3.128(22)	C(11)−Pb(1)−B(14) = 60.6(6)	
	Pb(1b)−B(13a) = 3.813(23)		
	Pb(1)−C(12) = 2.636(15)		
	Pb(1)−B(14) = 2.494(19)		
	Pb(1)−B(23) = 3.247(22)		
	Pb(1)−Pb(2) = 4.236(14)		
1-[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$CH$_2$(Me)$_2$N)]- 2,3-(SiMe$_3$)$_2$-1,2,3-PbC$_2$B$_4$H$_4$	Pb−Cnt = 2.209	Cnt−Pb−N = 124.3	95
	Pb−C(1) = 2.712(7)	Pb−N−C(23) = 108.6(4)	
	Pb−C(2) = 2.730(8)	Pb−N−C(24) = 114.3(5)	
	Pb−B(3) = 2.532(12)	Pb−N−C(25) = 103.2(4)	
	Pb−B(4) = 2.451(10)		
	Pb−B(5) = 2.537(8)		
	Pb−N = 2.682(6)		
	C(1)−C(2) = 1.494(12)		
1-(2,2′-C$_{10}$H$_8$N$_2$)-2,3-(SiMe$_3$)$_2$-1,2,3-PbC$_2$B$_4$H$_4$	Pb−N(1) = 2.674(9)	N(1)−Pb−N(2) = 60.6(3)	100
	Pb−N(2) = 2.581(9)	N(2)−Pb−C(1) = 139.5(3)	
	Pb−C(1) = 2.706(10)	N(2)−Pb−C(2) = 139.8(3)	
	Pb−C(2) = 2.787(10)	N(1)−Pb−B(4) = 102.9(4)	
	Pb−B(3) = 2.643(12)	N(2)−Pb−B(5) = 104.4(4)	
	Pb−B(4) = 2.504(13)	N(1)−Pb−C(1) = 106.8(3)	
	Pb−B(5) = 2.521(15)	N(1)−Pb−C(2) = 137.7(3)	
		N(2)−Pb−B(4) = 85.0(4)	
1-(2,2′-C$_{10}$H$_8$N$_2$)-2-(Me)-3-(SiMe$_3$)-1,2,3-PbC$_2$B$_4$H$_4$	Pb−N(1) = 2.615(7)	N(1)−Pb−N(2) = 60.9(2) 101	
	Pb−N(2) = 2.663(7)	N(2)−Pb−C(1) = 141.6(2)	
	Pb−C(1) = 2.835(8)	N(2)−Pb−C(2) = 111.5(2)	
	Pb−C(2) = 2.770(8)	N(1)−Pb−B(4) = 80.8(3)	
	Pb−B(3) = 2.566(10)	B(4)−Pb−B(5) = 38.8(3)	
	Pb−B(4) = 2.466(8)		
	Pb−B(5) = 2.601(9)		
	C(1)−C(2) = 1.481(11)		

Table 1 (Continued)

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
1,1′-(2,2′-C$_8$H$_6$N$_4$)-[2,3-(SiMe$_3$)$_2$-1,2,3-PbC$_2$B$_4$H$_4$]$_2$	Pb−Cnt = 2.203 Pb−C(1) = 2.711(10) Pb−C(2) = 2.729(10) Pb−B(3) = 2.527(12) Pb−B(4) = 2.473(13) Pb−B(5) = 2.503(13) Pb−N(1) = 2.748(9) Pb−N(2a) = 2.737(8) N(2)−Pba = 2.737(8) C(1)−C(2) = 1.486(14)	N(1)−Pb−Cnt = 117.5 N(2a)−Pb−Cnt = 113.4 N(1)−Pb−C(1) = 122.4(3) N(1)−Pb−C(2) = 145.7(3) C(1)−Pb−C(2) = 31.7(3) N(1)−Pb−N(2a) = 58.6(2)	103

Heterocarboranes of Group 15 Elements

1. Nitrogen Complexes

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
10-(C$_6$H$_5$CH$_2$)-*nido*-10,7,8-NC$_2$B$_8$H$_{10}$	N(10)−B(5) = NR N(10)−B(6) = NR N(10)−B(9) = NR N(10)−B(11) = NR N(10)−C(9) = NR	C(1)−C(9)−N(10) = NR plane 3[C(1)−C(6)]−plane 2[B(9)−C(8)] = 101.9	116
5-(η^6-C$_6$Me$_6$)-7-(MeO)-*arachno*-5-RuN(Me)C(H)B$_9$H$_{11}$	B(6)−N(67) = 1.488(10) B(7)−N(67) = 1.528(12) C(89)−N(67) = 1.570(12) C(67)−N(67) = 1.484(10) Ru(5)−C = 2.183(6)−2.259(6) Ru−B = 2.221(11)−2.352(9) B(9)−H$_\mu$(89a) = 1.502(11) C(89)−H$_\mu$(89a) = 1.330(11)	B(6)−N(67)−B(7) = 104.4(7) C(89)−N(67)−C(67) = 113.3(7)	117
hypo-5-(Me)-5,11,7,14-CNS$_2$B$_7$H$_9$	N(11)−B(12) = 1.490(6) N(11)−C(5) = 1.298(5) N(11)−H(11) = 0.78(4) S(7)−B(12) = 1.958(5) S(14)−B(12) = 1.951(5) S(7)−B(1) = 1.876(5) S(7)−B(2) = 1.900(6) S(14)−B(8) = 1.924(6) S(14)−B(9) = 1.882(5) B(4)−C(5) = 1.555(6) C(5)−C(5A) = 1.488(5)	B(12)−N(11)−H(11) = 122(3) C(5)−N(11)−H(11) = 114(3) B(12)−N(11)−C(5) = 123.4(4) N(11)−C(5)−B(4) = 123.9(3) N(11)−C(5)−C(5A) = 118.0(4) B(4)−C(5)−C(5A) = 118.1(3) S(7)−B(12)−S(14) = 111.8(3) S(7)−B(12)−N(11) = 104.9(3) S(14)−B(12)−N(11) = 105.9(2)	122

2. Phosphorus Complexes

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
closo-9,10-(Cl)$_2$-1,7-CHPB$_{10}$H$_8$	P−B(2) = 2.01(1) P−B(3) = 2.02(1) P−B(8) = 2.03(1) P−B(11) = 2.01(1) P−B(12) = 2.04(1) B(2)−C = 1.72(1) B(3)−C = 1.70(2) B(6)−C = 1.73(2) B(5)−C = 1.75(1) B(4)−C = 1.74(2) Cl(1)−B(9) = 1.803(9) Cl(2)−B(10) = 1.772(10)	B(2)−P−B(3) = 54.5(6) B(2)−P−B(8) = 94.5(6) B(2)−P−B(11) = 53.0(6) B(2)−P−B(12) = 93.7(6) B(3)−P−B(8) = 53.5(6) B(3)−P−B(11) = 93.5(6) B(3)−P−B(12) = 93.4(6) B(8)−P−B(11) = 93.7(6) B(8)−P−B(12) = 53.5(6) B(11)−P−B(12) = 53.7(6) B(2)−C−B(3) = 65.5(8) B(3)−C−B(6) = 114.5(9)	128
[(3)-7-(CH$_3$)-1,7-PCB$_9$H$_{10}$]$_2$Fe	Fe−Cnt = 1.47 P−C(av) =1.80 P−B(av) = 1.90 B−B(av) = 1.81 B−C(av) = 1.71	Cnt(1)−Fe−Cnt(2) = 178	133
nido-(CNMe$_3$)B$_{10}$H$_{10}$P(C$_6$H$_5$)	P(12)−C(17) = 1.845(4) P(12)−B(8) = 2.347(5) P(12)−B(9) = 1.998(5) P(12)−B(10) = 2.018(5) P(12)−B(11) = 2.381(5) N(13)−C(7) = 1.545(5)	C(17)−P(12)−B(9) = 99.0(2) C(17)−P(12)−B(10) = 102.0(2) B(9)−P(12)−B(10) = 54.5(2)	134

3. Arsenic Complexes

compound	E−X (length, Å)	X−Y−Z (angle, deg)	ref(s)
1-(Cl)-2,3-(Me)$_2$-1,2,3-AsC$_2$B$_9$H$_9$	As−Cl(1) = 2.213(6) As−B(1a) = 2.179(19) As−B(1b) = 2.149(19) As−B(1c) = 2.243(21) As−C(1a) = 2.51 As−C(1b) = 2.55 Cl(1)−H(1b) = 2.95	B(1a)−As−Cl(1) = 115.0(6) B(1b)−As−Cl(1) = 92.0(6) B(1b)−As−B(1a) = 50.2(7) B(1c)−As−Cl(1) = 116.5(6) B(1c)−As−B(1a) = 81.7(8) B(1c)−As−B(1b) = 51.1(7)	137

Table 1 (Continued)

compound	E–X (length, Å)	X–Y–Z (angle, deg)	ref(s)
	4. Bismuth Complexes		
$1,2\text{-}Bi_2B_{10}H_{10}$	Bi(1)–Bi(2) = 2.956(4)		132
	Bi(1)–B(3) = 2.63(8)		
	Bi(1)–B(4) = 2.39(8)		
	Bi(1)–B(5) = 2.44(8)		
	Bi(1)–B(6) = 2.62(8)		
	Bi(2)–B(3) = 2.51(8)		
	Bi(2)–B(6) = 2.66(8)		
	Bi(2)–B(7) = 2.42(8)		
	Bi(2)–B(11) = 2.41(9)		
	Heterocarboranes of Group 16 Elements		
	1. Sulfur Complexes		
$nido\text{-}8,8\text{-}(PPh_3)_2\text{-}8\text{-}H\text{-}8,7,9\text{-}RhCSB_8H_{10}$	S(9)–Rh(8) = 2.447(3)	P(1)–Rh(8)–P(2) = NR	148
	S(9)–B(4) = 2.054(9)	S(9)–Rh(8)–C(7) = NR	
	S(9)–B(5) = 1.968(9)	B(5)–S(9)–Rh(8) = NR	
	S(9)–B(10) = 1.941(10)	B(4)–S(9)–B(10) = NR	
	Rh(8)–P(1) = 2.331(3)	B(10)–H(bridge)–B(11) = NR	
	Rh(8)–P(2) = 2.336(3)		
	Rh(8)–H(8) = 1.47(6)		
	Rh(8)–C(7) = 2.175(7)		
	Rh(8)–B(3) = 2.188(8)		
	Rh(8)–B(4) = 2.237(8)		
$closo\text{-}[1,1\text{-}(PPh_3)_2\text{-}1,2,3\text{-}RhCSB_8H_9$	S(3)–Rh(1) = 2.348(3)	P(1)–Rh(1)–P(2) = NR	148
	S(3)–B(6) = 1.912(5)	C(2)–Rh(1)–S(3) = NR	
	S(3)–B(7) = 1.927(5)	Rh(1)–S(3)–B(9) = NR	
	S(3)–B(9) = 2.002(5)	B(6)–S(3)–B(7) = NR	
	Rh(1)–P(1) = 2.354(3)		
	Rh(1)–P(2) = 2.315(3)		
	Rh(1)–C(2) = 2.118(5)		
	Rh(1)–B(4) = 2.321(5)		
	Rh(1)–B(5) = 2.385(5)		
	Rh(1)–B(6) = 2.461(5)		
	Rh(1)–B(7) = 2.364(5)		

[a] Absence of parentheses indicates a mean value for given bond lengths and bond angles. Cnt denotes the centroid of the bonding face. NR means not reported.
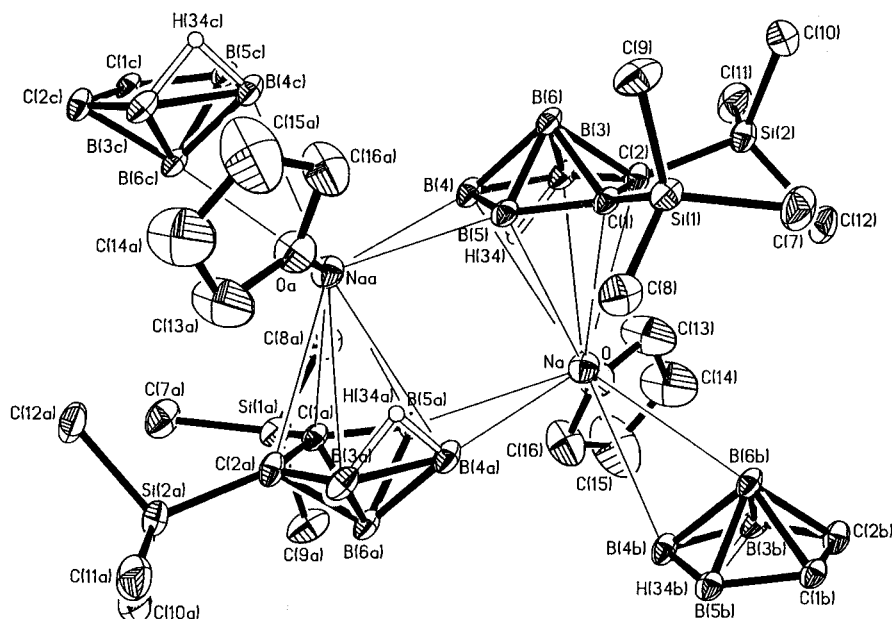
Figure 2. Perspective view of the dimeric form of $1\text{-}Na(THF)\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5$. (Reprinted with permission from ref 14. Copyright 1989 Royal Society of Chemistry.)

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 carboranes have also been determined.[15,18] Figure 5 shows the structure of $exo\text{-}4,5\text{-}[(\mu\text{-}H)_2Li(TMEDA)\text{-}1\text{-}$ $Li(TMEDA)\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4$, which is probably typical for these bimetallic compounds.[15] The two lithiums 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
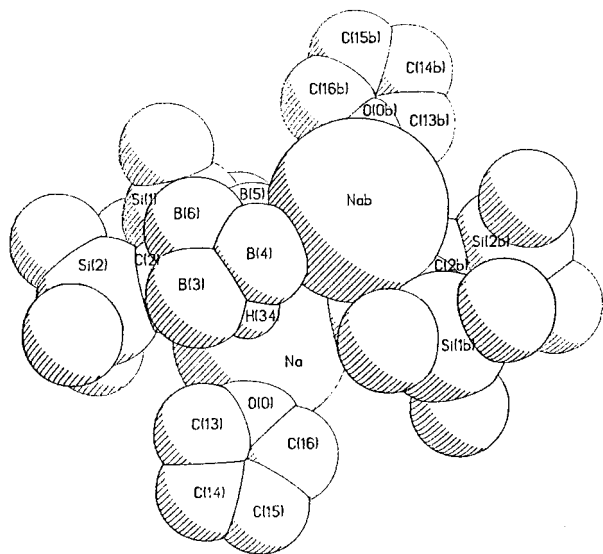
Figure 3. Space-filling model of 1-Na(THF)-2,3-(SiMe₃)₂-2,3-C₂B₄H₅. (Reprinted with permission from ref 14. Copyright 1989 Royal Society of Chemistry.)
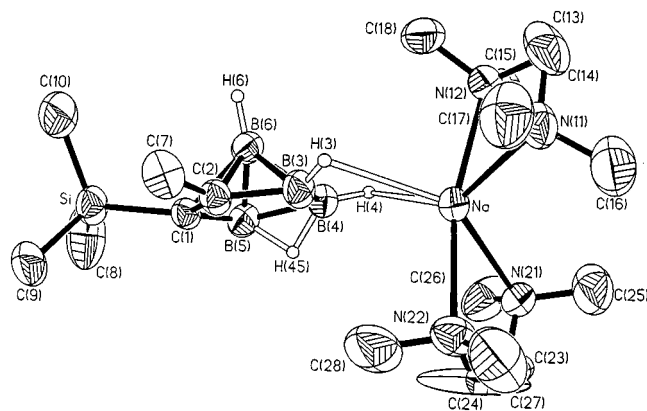
Figure 4. Perspective view of *nido-exo*-4,5-[(μ-H)₂Na-(TMEDA)₂-2-(SiMe₃)-3-Me-2,3-C₂B₄H₅]. (Reprinted from ref 16. Copyright 1994 American Chemical Society.)
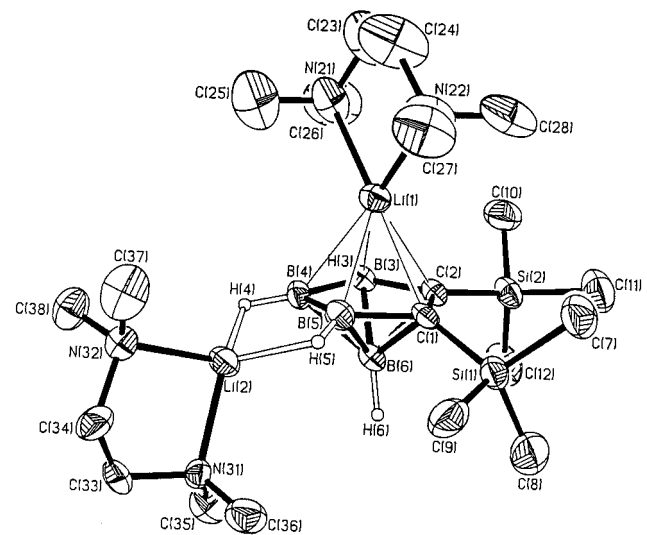
Figure 5. Perspective view of *closo-exo*-4,5-(μ-H)₂Li-(TMEDA)-1-Li(TMEDA)-2,3-(SiMe₃)₂-2,3-C₂B₄H₄]. (Reprinted from ref 15. Copyright 1993 American Chemical Society.)

face. The ⁷Li NMR spectrum of this complex in C₆D₆ shows two resonances, one at δ −1.60 ppm, due to the *exo* polyhedral Li, and another at δ −6.03 ppm,
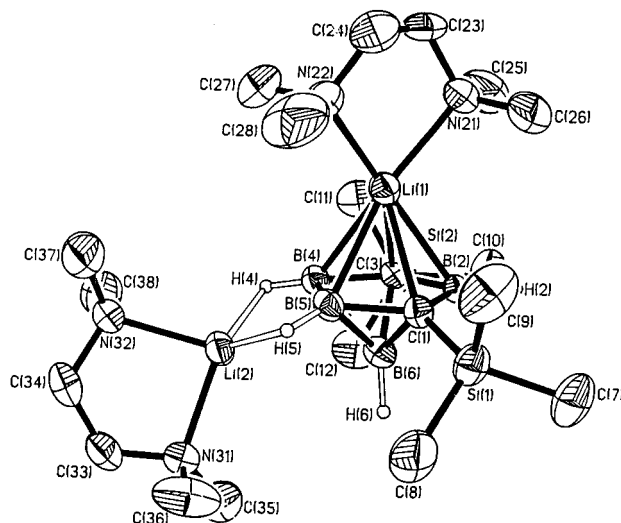
Figure 6. Perspective view of *closo-exo*-5,6-(μ-H)₂Li-(TMEDA)-1-Li(TMEDA)-2,4-(SiMe₃)₂-2,4-C₂B₄H₄]. (Reprinted from ref 18. Copyright 1993 American Chemical Society.)

ascribed to the apical Li, (relative to external aqueous LiNO₃).[15] This indicates that the ion cluster is quite stable in solution, with little ion exchange. The ⁷Li NMR spectrum of the corresponding mixed Na/Li salt showed a single resonance at δ −1.82 ppm, indicating that the Li occupied the *exo* polyhedral position with the Na in an apical position.[15] Most of the structural data on the group 1 and other main group metalla-carboranes in the C₂B₄ system have been collected on isomers in which the two cage carbons were adjacent to one another in the pentagonal C₂B₃ face of the carborane, to give the so-called "carbons adjacent" complexes. There is another isomeric structure in which the two carbon atoms are separated by a boron to produce the "carbons apart" metallacarboranes. Both the disodium and dilithium salts of this isomer can be obtained from the two-electron reduction of either the 1,2- or 1,6-C₂B₄ *closo* carboranes with the corresponding metal naphthalenides.[18,19] The structure of the TMEDA-solvated dilithiacarborane in this system is shown in Figure 6. It is similar to that of its "carbons adjacent" isomer (Figure 5) in that one Li is attached to two adjacent borons through Li−H−B bridges, with the other Li being in an apical position.[18] The observance of two ⁷Li NMR resonances suggests that the cluster shown in Figure 6 is also present in solution. The two isomeric systems are also similar in that the TMEDA-solvated complexes are monomeric in nature, while in THF, more extended clusters are formed.[18] 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 20 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* C₂B₄ carboranes. Careful reaction of the disodium compound with anhydrous HCl results in the protonation of the two adjacent borons (similar to B(4) and B(5) in Figure 6) to give a monosodium compound, whose overall geometry is similar to that shown in Figure 2. However, attempts at more
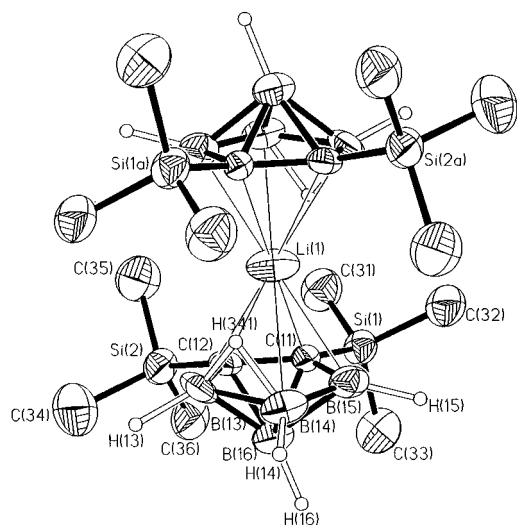
Figure 7. Crystal structure of the anionic full-sandwich lithiacarborane complex, [*commo*-1,1′-Li{2,3-(SiMe₃)₂-2,3-C₂B₄H₅}₂]⁻. (Reprinted from ref 21. Copyright 1996 American Chemical Society.)

extensive protonation led to the decomposition of the carborane.[20]

Slow sublimation of the TMEDA-solvated monolithium carborane complex[17] at 160−170 °C over a period of 6−7 h *in vacuo* produced the full-sandwich lithiacarborane complex, [Li(TMEDA)₂][*commo*-1,1′-Li{2,3-(SiMe₃)₂-2,3-C₂B₄H₅}₂], as a transparent crystalline solid.[21] The mechanism of the formation of this complex 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 7.[21] 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,[15] but are comparable to the corresponding metal−centroid distance of 2.008 Å found in the [Cp₂Li]⁻ sandwich complex.[22] 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. Careful inspection of Figure 7 shows that the lithium atom is displaced toward the cage carbons and one of the basal borons. This slip distortion is most probably due to the presence of B−H−B bridging hydrogens on the bonding faces. The high yield for this reaction indicates that it may prove to be a general method for the selective synthesis of a number of hitherto unknown full-sandwich metallacarboranes of group 1 and other metals.

B. Complexes of Group 2 Elements

Although the organometallic chemistry of group 2 elements has received special attention in recent years and a large number of novel cyclopentadienyl complexes have been synthesized and crystallographically characterized,[23,24] structural reports on the metallacarborane complexes of group 2 elements are limited. Over 25 years ago, Hawthorne and Popp
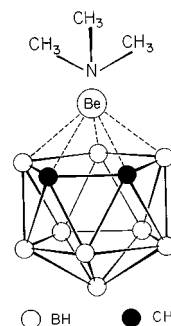
Figure 8. Proposed structure of the beryllacarborane, (Me₃NBeC₂B₉H₁₁). (Reprinted from ref 26. Copyright 1968 American Chemical Society.)
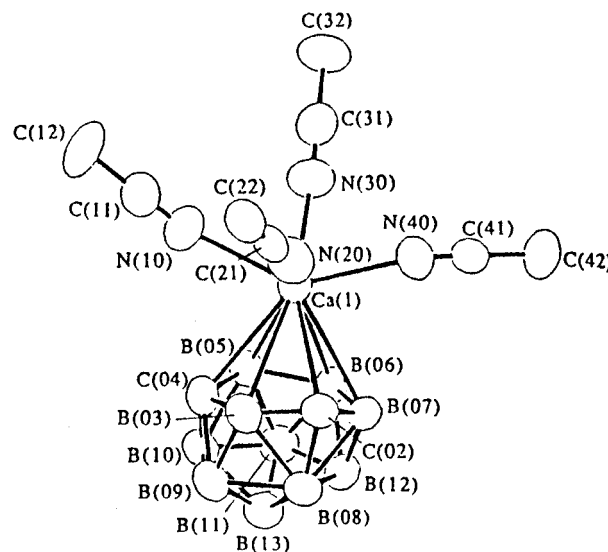
Figure 9. Crystal structure of the calcacarborane complex, *closo*-1,1,1,1-(MeCN)₄-1,2,4-CaC₂B₁₀H₁₂. (Reprinted from ref 27. Copyright 1990 American Chemical Society.)
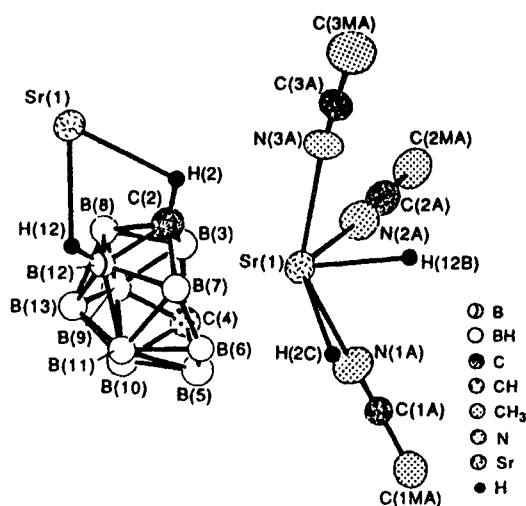
Figure 10. Crystal structure of the strontacarborane complex, *closo*-1,1,1-(MeCN)₃-1,2,4-SrC₂B₁₀H₁₂]ₙ. (Reprinted from ref 28. Copyright 1990 American Chemical Society.)

reported the first group 2 metallacarborane, the beryllacarborane, (CH₃)₃NBeC₂B₉H₁₁, obtained from the reaction of a benzene solution of (3),1,2-C₂B₉H₁₃ with a diethyl ether solution of dimethylberyllium, and isolated as its trimethylamine adduct.[25,26] Although the structure of this compound could not be obtained, NMR spectroscopy suggested the *closo*
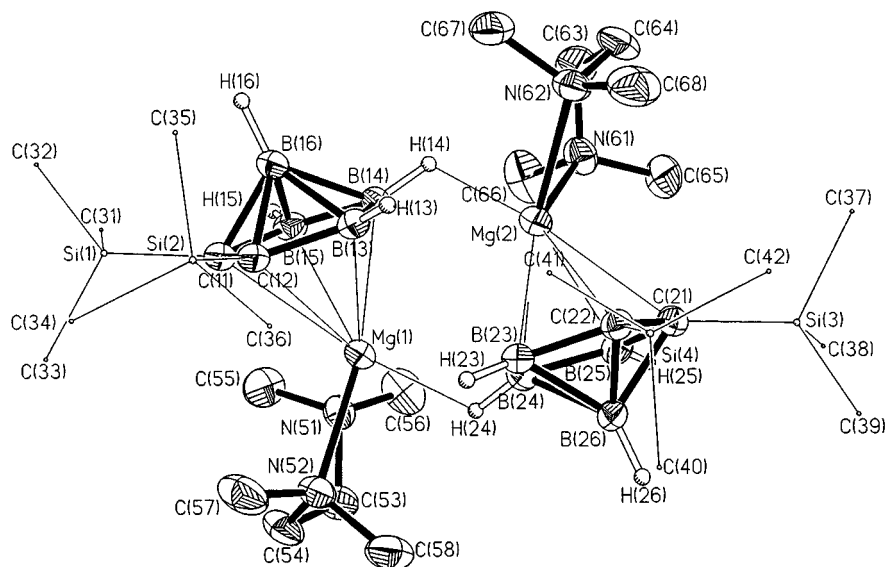
Figure 11. Crystal structure of the [*closo*-1-Mg(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_2$ dimer. (Reprinted from ref 30. Copyright 1995 American Chemical Society.)

structure shown in Figure 8. It was only fairly recently 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$_2$B$_{10}$H$_{12}$ and [*closo*-1,1,1-(MeCN)$_3$-1,2,4-SrC$_2$B$_{10}$H$_{12}$]$_n$.[27,28] These complexes, whose structures are shown in Figures 9 and 10, formed readily from the reaction of the corresponding metal iodides with Na$_2$[*nido*-7,9-C$_2$B$_{10}$H$_{12}$]. Figure 9 shows that in *closo*-1,1,1,1-(MeCN)$_4$-1,2,4-CaC$_2$B$_{10}$H$_{12}$ the calcium ion, solvated by four acetonitrile molecules, is coordinated above the hexagonal C$_2$B$_4$ face of the carborane.[27] The Ca−ring−atom distances range from 2.649 Å, for B(5), to 2.935 Å for B(7), with no systematic differences between the Ca−C and Ca−B distances being evident; any difference in metal−carborane distances seems to be as much a function on the nonplanarity of the C$_2$B$_4$ bonding face than any difference in metal bonding preferences. While the calcium complex is essentially monomeric, the structure of the corresponding strontacarborane, shown in Figure 10 is more complex.[28] This species crystallizes as a polymeric spiral chain, in which Sr(MeCN)$_3$ groups reside above the C$_2$B$_4$ open faces of the carboranes, in a manner similar to that found in the calcacarborane (Figure 9). However, each Sr is also bonded to a neighboring C$_2$B$_{10}$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 B on the lower pentagonal ring. It is unusual to find cage carbon atoms involved in such bridges. The IR spectra of both complexes exhibit splitting of the B−H stretching bands, which have been rationalized in terms of an essentially ionic metal−carborane compound, with the M^{2+} interacting more strongly with the proximal hydrogens in the upper carborane face than with those in the lower pentagonal ring. This uneven interaction causes the B−H force constants to differ enough so that splitting is observed.[27] Such an explanation had been used earlier in rationalizing similar B−H splitting in the IR spectra of the icosahedral lanthanacarboranes.[29]
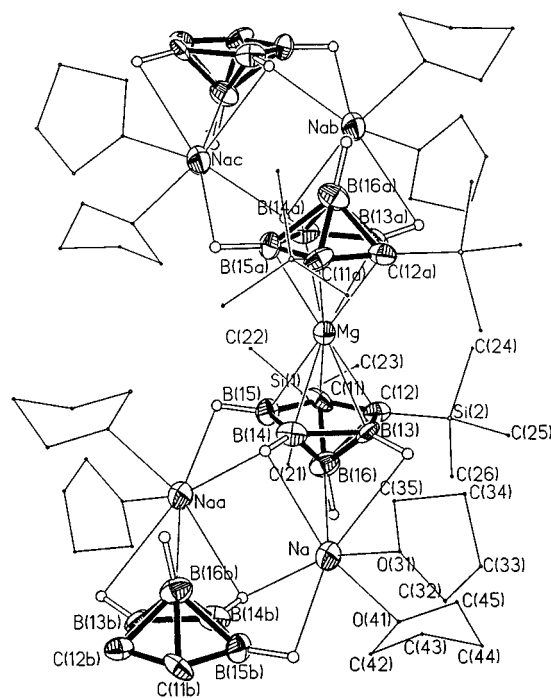
Figure 12. Crystal structure of the disodium salt of {*commo*-1,1'-Mg[2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_2$}$^{2-}$ dianion. (Reprinted from ref 30. Copyright 1995 American Chemical Society.)

In the C$_2$B$_4$ cage system both the half-sandwich and full-sandwich magnesacarboranes, *closo*-1-Mg(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ and {*commo*-1,1'-Mg[2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_2$}$^{2-}$, have been synthesized and structurally characterized (see Figures 11 and 12).[30] The structure of the half-sandwich compound is that of a dimeric [*closo*-1-Mg(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_2$ unit in which the solvated Mg atoms occupy apical positions above the C$_2$B$_3$ face of the carborane and are also bonded to the unique borons [B(14)] of the adjacent carborane cages by single Mg−H−B bridges.[31] In each half-sandwich complex, the Mg atom is not symmetrically bonded to the C$_2$B$_3$ face but is dislocated, or slipped, toward
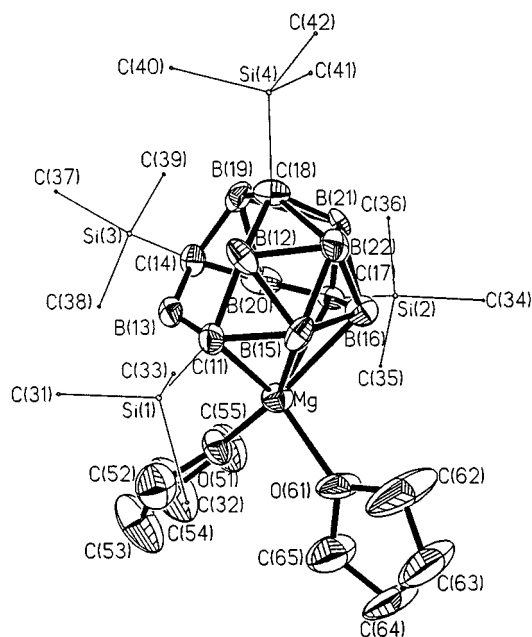
Figure 13. Crystal structure of $(THF)_2Mg(SiMe_3)_4C_4B_8H_8$. (Reprinted from ref 32. Copyright 1996 American Chemical Society.)

the unique boron, B(14 or 24) in Figure 11. Since the carboranes are η^5-bonded to the Mg in the full sandwich complex, shown in Figure 12, this slip distortion could be the result of the dimeric nature of the cluster. Assuming that the interaction is essentially ionic, there is no reason to expect slip distortions. Quite recently, the magnesium complex of the tetracarbon carborane, $(THF)_2Mg(SiMe_3)_4C_4B_8H_8$, has been prepared and structurally characterized.[32] The structure, shown in Figure 13, 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-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.

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.[33] 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 2; unfortunately, the product was not structurally characterized.[34]

$$(3),1,2\text{-}C_2B_9H_{11}{}^{2-} + EtAlCl_2 \xrightarrow[-40\ °C]{THF}$$
$$2Cl^- + C_2B_9H_{11}AlEt\cdot2THF \quad (2)$$
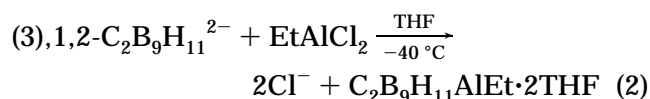
Hawthorne and co-workers conducted detailed studies of the syntheses and structures of the aluminacarboranes derived from the reaction of (3),1,2-$C_2B_9H_{13}$ with trialkyl aluminums, R_3Al (R = Me, and Et).[35,36] The reactions were found to go through two
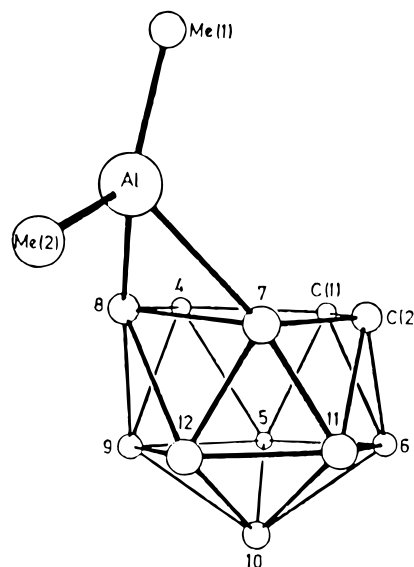
Figure 14. Crystal structure of 7,8-μ-Al(Me)$_2$-1,2-$C_2B_9H_{12}$. (Reprinted with permission from ref 38. Copyright 1971 Royal Society of Chemistry.)
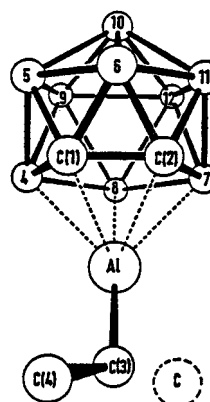
Figure 15. Crystal structure of *closo*-3-Al(Et)-1,2-$C_2B_9H_{11}$. (Reprinted with permission from ref 37. Copyright 1972 Royal Society of Chemistry.)

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 heating, eliminated an RH molecule to produce the half-sandwich aluminacarborane, *closo*-3-Al(R)-1,2-$C_2B_9H_{11}$. The structures of the bridged and *closo* aluminacarboranes are shown in Figures 14 and 15, respectively.[37,38] Two examples of the full-sandwiched aluminacarboranes have also been reported.[39,40] 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, as shown in Figure 16.[39] On the other hand, the reaction of a number of different aluminum alkyl reagents with the thallacarborane precursor, $Tl_2[7,8$-$C_2B_9H_{11}]$, produced the isolated aluminacarborane sandwich, [*commo*-3,3'-Al(3,1,2-AlC$_2B_9H_{11})_2]^-$, as its Tl^+ salt (Figure 17).[40] 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
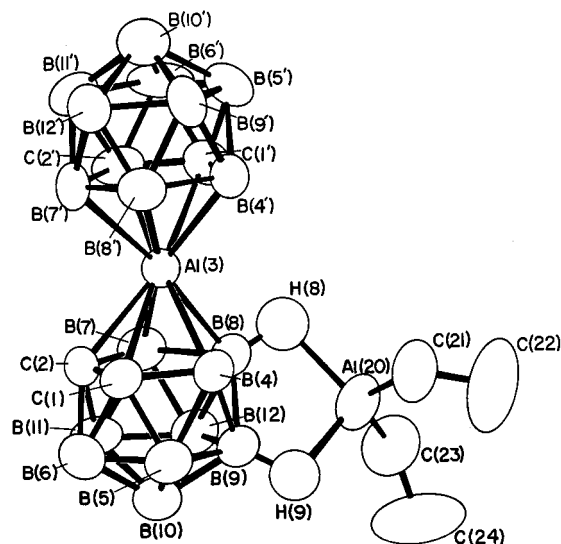
Figure 16. Crystal structure of the aluminacarborane, *commo*-3,3′-Al[(*exo*-8,9-(μ-H)$_2$Al(C$_2$H$_5$)$_2$-3,1,2-AlC$_2$B$_9$H$_9$)-(3′,1′,2′,-AlC$_2$B$_9$H$_{11}$)]. (Reprinted from ref 39. Copyright 1986 American Chemical Society.)

Figure 18. Crystal structure of *endo*-10-{AlEt(PEt$_3$)$_2$}-7,8-C$_2$B$_9$H$_{11}$. (Reprinted from ref 41. Copyright 1990 American Chemical Society.)

Scheme 1

Figure 17. Crystal structure of {*commo*-3,3′-Al(3,1,2-AlC$_2$B$_9$H$_{11}$)$_2$}$^-$. (Reprinted from ref 40. Copyright 1988 American Chemical Society.)

another.[37−41] The aluminum−carborane atom distances found in the zwitterionic and the 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.[41] Figure 18 shows the structure of one such adduct, that of *endo*-10-{AlEt(PEt$_3$)$_2$}-7,8-C$_2$B$_9$H$_{11}$.[41] As can be seen from the figure, coordination leads to a slip distortion of the Al; in the uncomplexed aluminacarborane the Al−C$_2$B$_3$ atom distances were equivalent and equal to 2.17 ± 0.02 Å,[37] while the relevant distances in Figure 18 are Al−C(7,8) = 2.959 ± 0.017 Å, Al−B(9,11) = 2.480 ± 0.032 Å, and Al−B(10) = 2.128 Å.[42] 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.[2] In addition to having interesting structures, the *closo* aluminacarboranes have been found to be versatile dicarbollyl transfer reagents in the syntheses of other metallacarboranes, as outlined in Scheme 1.[43]

Scheme 2

Figure 19. Crystal structure of $[\mu\text{-}6,9\text{-}AlEt(OEt_2)\text{-}6,9\text{-}C_2B_8H_{10}]$. (Reprinted from ref 46. Copyright 1987 American Chemical Society.)
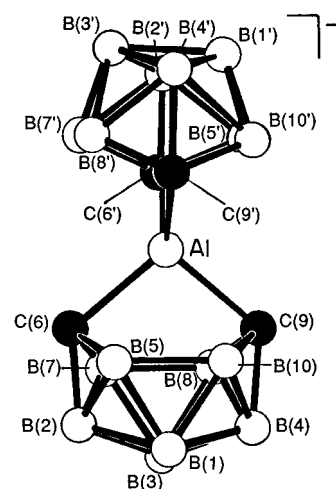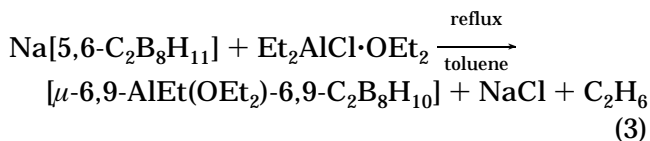

Figure 20. Crystal structure of $Na[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2]$. (Reprinted from ref 47. Copyright 1987 American Chemical Society.)
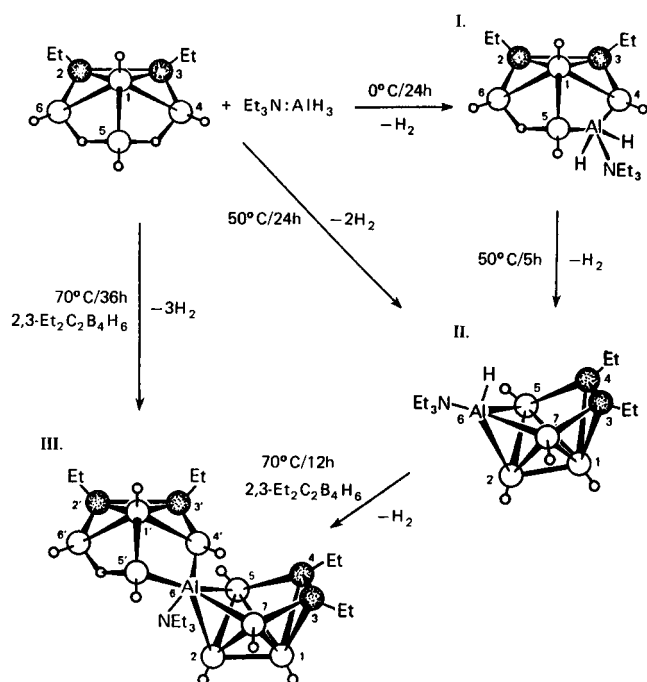
There is much less data on the aluminacarboranes in the C_2B_4 cage system. The synthesis of the smaller cage aluminacarborane was first reported by Grimes and co-workers as part of an extended study of the reactions of $M[2,3\text{-}C_2B_4H_7]$ (M = Na, Li) with a series of organometallic reagents of Al, Ga, Rh, Au, and Hg.[44] The reaction of the carborane monoanion with $(CH_3)_2AlCl$ produced a highly unstable liquid that was described as the bridged aluminacarborane, $[(CH_3)_2Al]C_2B_4H_7$. Characterization was very difficult and the formulation of the product was based primarily on analogy with the better characterized products of the analogous Ga reactions. 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 was consistent with the formula, $closo\text{-}1,2,3\text{-}Al(Me)C_2B_4H_6$.[44] Sneddon and Beck were able to synthesize better characterizable aluminacarboranes from the reaction of $nido\text{-}2,3\text{-}(Et)_2\text{-}2,3\text{-}C_2B_4H_6$ with $Et_3N:AlH_3$, as outlined in Scheme 2.[45] The initial formation of a bridged complex, $4,5\text{-}\mu\text{-}AlH_2NEt_3\text{-}2,3\text{-}Et_2C_2B_4H_5$, and its subsequent thermal decomposition to the seven-vertex aluminacarborane, $6\text{-}AlHNEt_3\text{-}3,4\text{-}Et_2C_2B_4H_4$, was consistent with the earlier work of Grimes.[44] However, further pyrolysis at higher temperatures produced the novel complex, $commo\text{-}AlNEt_3\text{-}[(6\text{-}AlNEt_3\text{-}3,4\text{-}Et_2C_2B_4H_4)(4',5',\text{-}\mu\text{-}AlNEt_3\text{-}2',3'\text{-}Et_2C_2B_4H_5)]$, which had no precedent in earlier work (see Scheme 2). To date, there has been no reported X-ray crystal structures on any small cage aluminacarborane.

Hawthorne and co-workers have reported the syntheses and structures of several aluminacarboranes derived from $C_2B_6H_8$ and $C_2B_8H_{10}$ cage systems. The complex, $[\mu\text{-}6,9\text{-}AlEt(OEt_2)\text{-}6,9\text{-}C_2B_8H_{10}]$, was prepared by the equimolar reaction of $Na[5,6\text{-}C_2B_8H_{11}]$ with diethylaluminum chloride−diethyl etherate in refluxing toluene (eq 3),[46] 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.[47] The structures of
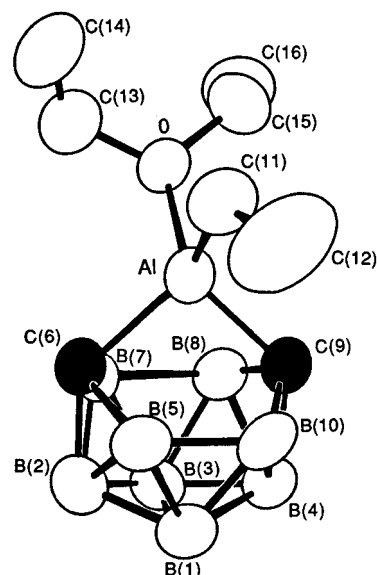
$$Na[5,6\text{-}C_2B_8H_{11}] + Et_2AlCl\cdot OEt_2 \xrightarrow[\text{toluene}]{\text{reflux}}$$
$$[\mu\text{-}6,9\text{-}AlEt(OEt_2)\text{-}6,9\text{-}C_2B_8H_{10}] + NaCl + C_2H_6$$
$$(3)$$

the two aluminacarboranes, given in Figures 19 and 20, 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 two-electron−two-center 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, $Na[Al(\eta^2\text{-}2,7\text{-}C_2B_6H_8)_2]$, whose structure is shown in Figure 21.[48]
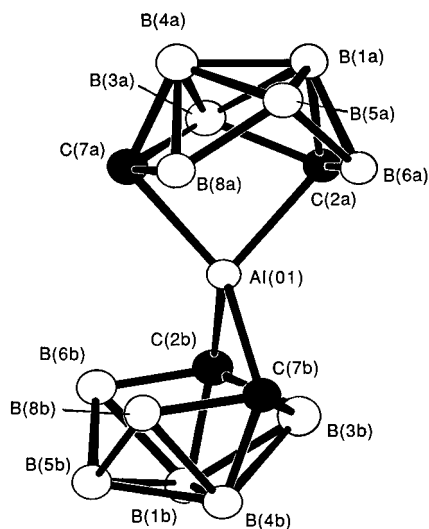
Figure 21. Crystal structure of Na[Al(η^2-2,7-C$_2$B$_6$H$_8$)$_2$]. (Reprinted from ref 48. Copyright 1987 American Chemical Society.)

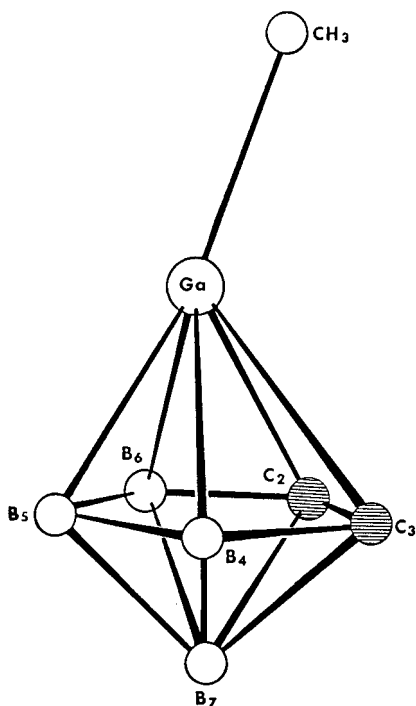**Figure 22.** Crystal structure of *closo*-1-CH$_3$-1,2,3-GaC$_2$B$_4$H$_6$. (Reprinted from ref 49. Copyright 1972 American Chemical Society.)

There is much more structural data available on the heavier group 13 metallacarboranes, especially in the smaller cage C$_2$B$_4$ system. The half-sandwich complexes, *closo*-1-CH$_3$-1,2,3-MC$_2$B$_4$H$_6$ (M = Ga and In), were synthesized by Grimes and co-workers by the reaction of *nido*-2,3-C$_2$B$_4$H$_8$ with M(CH$_3$)$_3$ under pyrolytic conditions.[49] The structure of the gallacarborane could be determined by X-ray crystallography and the results are shown in Figure 22.[49b] The complex is a distorted pentagonal-bipyramidal cage, in which the Ga is bonded above the C$_2$B$_3$ 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
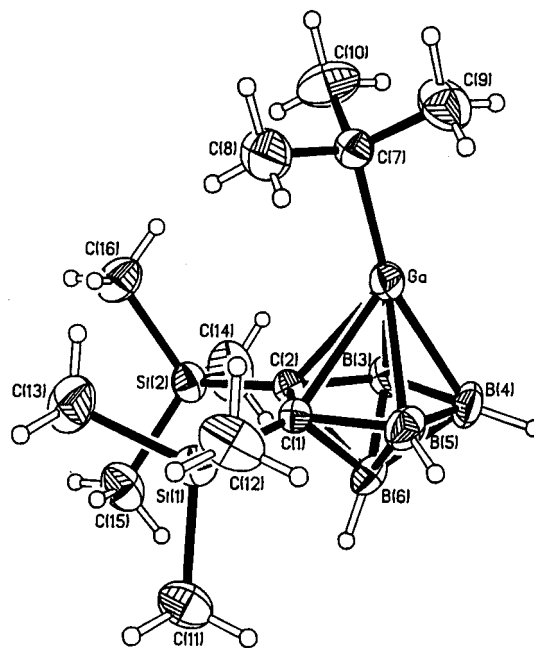
Figure 23. Crystal structure of *closo*-1-(*t*-C$_4$H$_9$)-2,3-(SiMe$_3$)$_2$-1,2,3-GaC$_2$B$_4$H$_4$. (Reprinted from ref 51. Copyright 1991 American Chemical Society.)

cage carbons. The extent of this tilt can be noted from the angle made by the Ga–CH$_3$ bond and the normal drawn from the average C$_2$B$_3$ plane through the Ga; in *closo*-1-CH$_3$-1,2,3-C$_2$B$_4$H$_6$ the tilt angle is 9.8°. 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$_2$B$_4$ cage and the π-type carborane MO's that are localized more heavily on the boron side of the C$_2$B$_3$ bonding face (see Figure 1).[50] These same distortions were also present in the trimethylsilyl-substituted gallacarborane, *closo*-1-(*t*-C$_4$H$_9$)-2,3-(SiMe$_3$)$_2$-1,2,3-GaC$_2$B$_4$H$_4$,[51] and the indacarborane, *closo*-1-(Me$_2$CH)-2,3-(SiMe$_3$)$_2$-1,2,3-InC$_2$B$_4$H$_4$.[52] The complexes were synthesized directly from the reaction of the metal alkyl halide, [(*t*-C$_4$H$_9$)-GaCl$_2$]$_2$ or (Me$_2$CH)InI$_2$, with the alkali metal-complexed dianion, [2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$^{2-}$, and were the sole metallacarborane products, irrespective of the metal-to-carborane molar ratios used. The structure of the gallacarborane is shown in Figure 23; the structure of the indacarborane is quite similar.[52] The group 13 metals in both the galla- and indacarboranes 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$_8$N$_2$) and bipyrimidine (2,2'-C$_8$H$_6$N$_4$).[51,53-55] Figure 24 gives the structure of the bipyrimidine–gallacarborane complex, 1-(2,2'-C$_8$H$_6$N$_4$)-1-(*t*-C$_4$H$_9$)-2,3-(SiMe$_3$)$_2$-1,2,3-GaC$_2$B$_4$H$_4$,[54] the structure of the corresponding bipyridine complex was also determined and found to be quite similar to the one shown in Figure 24.[55] Therefore, this structure is probably typical of the base–gallacarborane adducts. A comparison of the complexed and uncomplexed gallacarborane complexes, shown in Figures 23 and 24, respectively, show that on coordination with the base, the slip distortion of the metal increases and that the base is oriented over the boron side of the C$_2$B$_3$ bonding face. The average Ga–
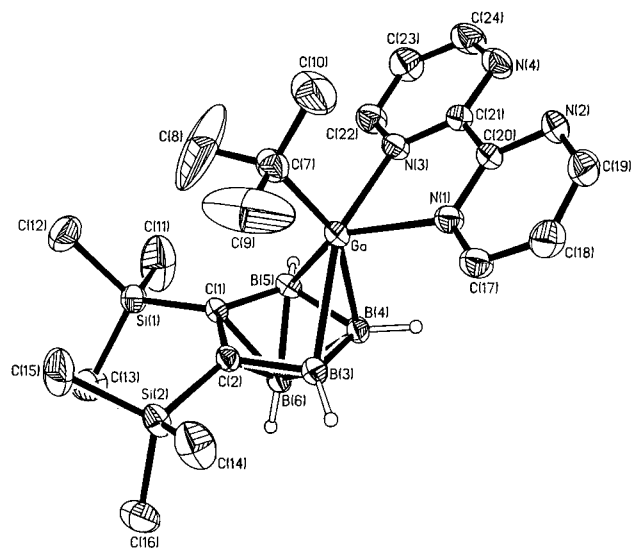
Figure 24. Crystal structure of 1-(2,2′-$C_8H_6N_4$)-1-(t-C_4H_9)-1-Ga-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$. (Reprinted with permission from ref 54. Copyright 1992 Plenum Publishing Co.)

C(1,2), Ga−B(3,5), and Ga−B(4) distances found for the uncomplexed gallacarborane were, 2.29, 2.18, and

2.13 Å, respectively,[51] compared to 2.88, 2.38, and 2.08 Å, respectively, found for the equivalent distances in the bipyrimidine complex.[54] The angle between the plane of the bipyrimidine and the C_2B_3 face is 41°, and the Ga−t-C_4H_9 tilt angle in the bipyrimidine-complexed gallacarborane was reported as 40.5°, compared to a value of 18.0° for the uncomplexed gallacarborane. The increased slip distortion observed on base complexation in the gallacarboranes has been explained using the molecular orbital correlation diagram shown in Figure 25 and the orbital energy diagram given in Figure 26.[54] As can be seen in Figure 25 the main base−gallium bonding is through MO 57s, which results from the interaction of the nitrogen "lone pair" bipyrimidine orbital (27s) with the LUMO of the gallacarborane fragment (33s). Figure 26 shows that this MO, which 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
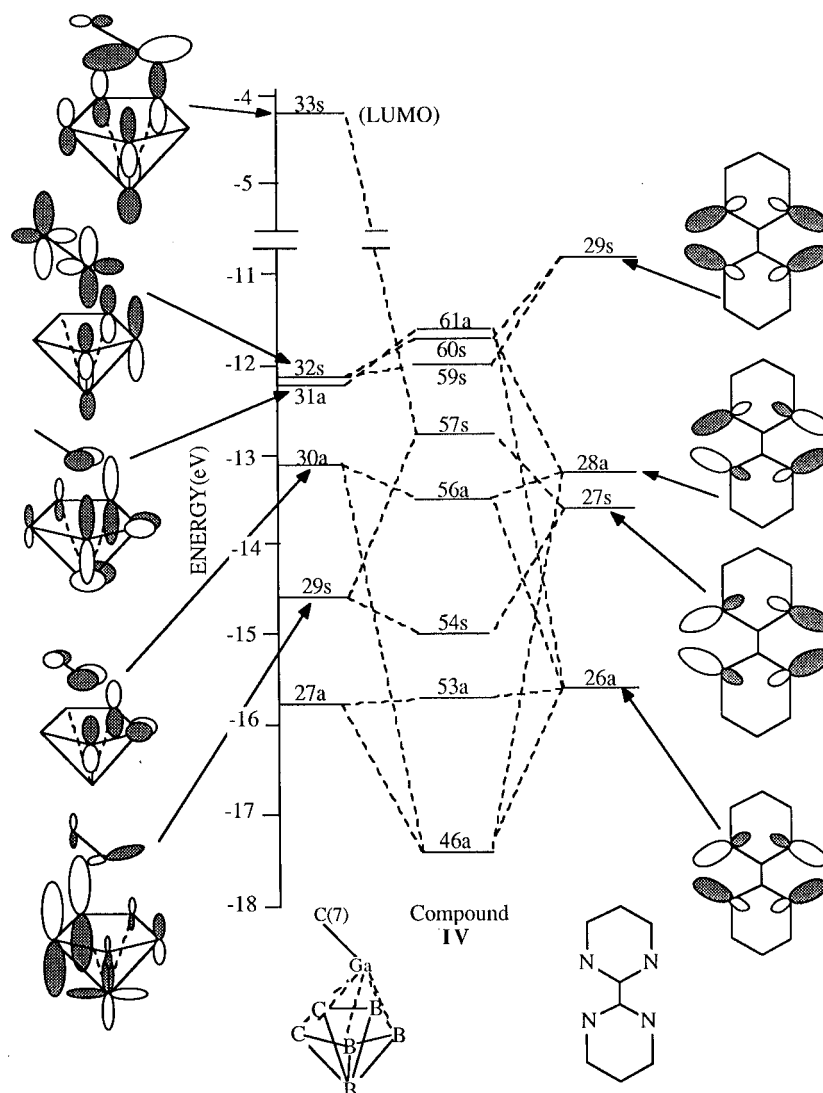
Figure 25. Molecular orbital correlation diagram for the formation of 1-($C_8H_6N_4$)-1-(t-C_4H_9)-1,2,3-Ga$C_2B_4H_6$ from its gallacarborane and bipyrimidine fragments. (Reprinted with permission from ref 54. Copyright 1992 Plenum Publishing Co.)
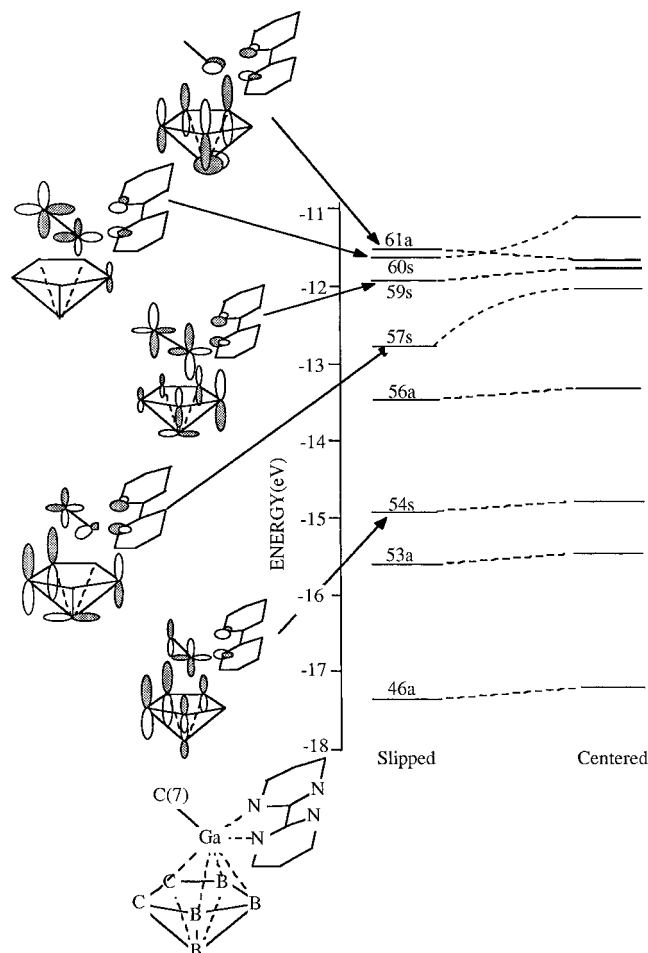
Figure 26. Energies of the molecular orbitals of 1-($C_8H_6N_4$)-1-(t-C_4H_9)-1,2,3-GaC$_2$B$_4$H$_6$ as a function of metal slippage. (Reprinted with permission from ref 54. Copyright 1992 Plenum Publishing Co.)

Figure 27. Crystal structure of the bridged complex, 1,1′-(2,2′-$C_8H_6N_4$)[1-(t-C_4H_9)-1-Ga-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$]$_2$. (Reprinted from ref 51. Copyright 1991 American Chemical Society.)
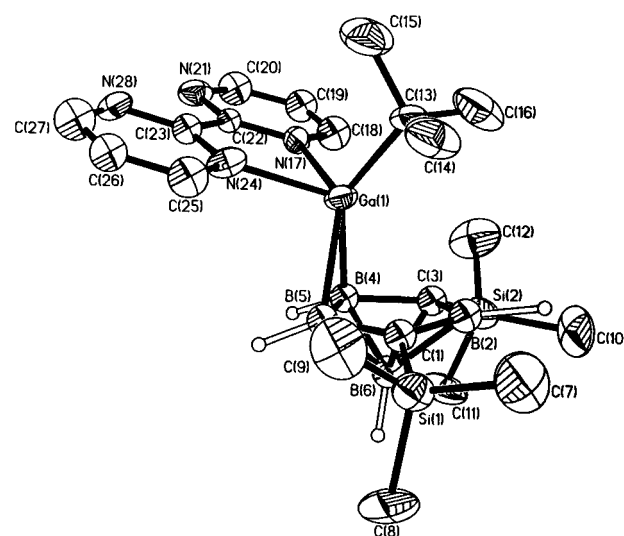
Figure 28. Crystal structure of the "carbons apart" gallacarborane, 1-(2,2′-$C_8H_6N_4$)-1-(t-C_4H_9)-1-Ga-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$. (Reprinted from ref 55. Copyright 1995 American Chemical Society.)

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 (see below) and are probably responsible for the large slip distortion found in the triethylphosphine−aluminacarborane complex shown in Figure 18.[56] 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, the structure of this complex is shown in Figure 27.[51] The two gallacarboranes occupy trans positions across the bipyrimidine base and the local geometries around each base−metallacarborane units are similar to that shown in Figure 24.

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$_2$B$_4$H$_4$ (L = 2,2′-$C_8H_6N_4$, 2,2′-$C_{10}H_8N_2$, and 2,2′:6′,2″-$C_{15}H_{11}N_3$).[55] The structure of the complex where L = 2,2′-$C_8H_6N_4$ is shown in Figure 28, the bipyridine (L = 2,2′-$C_{10}H_8N_2$) analogue is quite similar, while no structure for the terpyridine complex was reported.[55] 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. There were two crystallographically independent molecules in the unit cell of the bipyrimidine−gallacarborane complex. The first one given in Figure 28 shows that the t-C_4H_9 group is situated directly over the cage with the base oriented almost directly opposite to the unique boron, [B(2)], the angle subtended by the Ga−t-C_4H_9 bond and the pseudo mirror plane of the GaC$_2$B$_4$ cage was reported to be 8.5°. In the second molecule the two groups are rotated by almost 180°, so that the base is over the open face of the carborane. This adduct is not as symmetric as the molecule shown in Figure 28, in that the Ga−t-C_4H_9 bond is rotated out of the mirror plane by 28.9°.[55] What is unusual about both complexes is the extent of the metal slippage. For example, in Figure 28, 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, the metal−carborane bond distances of interest in Figure 28 are Ga−B(5,6) = 2.193 ± 0.001 Å, Ga−C(2,4) = 2.789 ± 0.018 Å, Ga−B(3) = 3.018 Å.[55] Unfortunately, no structural data are available
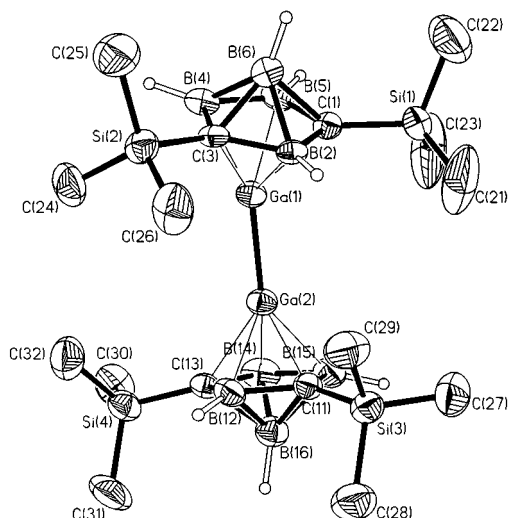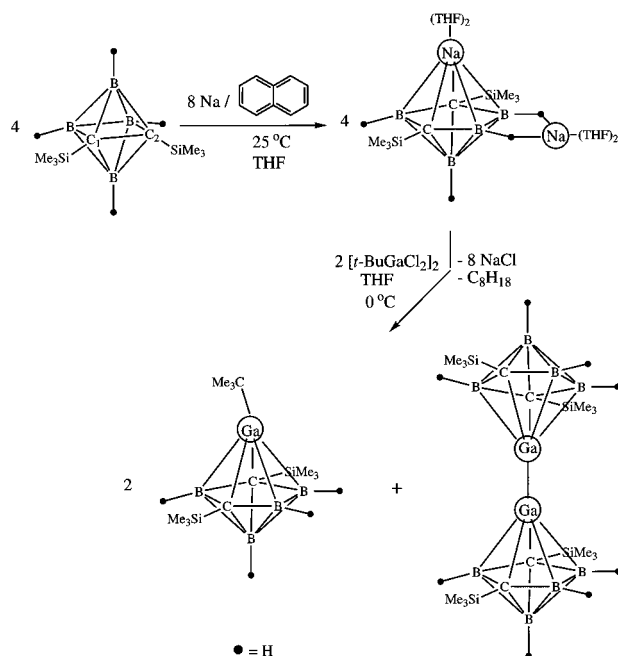
Figure 29. Crystal structure of the digallacarborane, *closo*-1-Ga[*o-closo*-1-Ga-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$. (Reprinted with permission from ref 57. Copyright 1995 VCH Verlagsgesellschaft mbH.)

Scheme 3

● = H

on the uncomplexed "carbons apart" gallacarborane so the exact extent to which base bonding enhances, or causes, metal slippage cannot be assessed. However, quantum mechanical calculations,[55] along with the structure of the novel digallacarborane, *closo*-1-Ga[*o-closo*-1-Ga-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$, shown in Figure 29,[57] indicate that the uncomplexed *closo*-gallacarborane is probably only slightly slip distorted. The digallane, whose synthesis is outlined in Scheme 3, is of interest in that the Ga–Ga single bond is unusually short (2.340 Å);[57] it is essentially the same as the Ga–Ga distance of 2.343 Å found in the anion radical, [Ga$_2$(2,4,6-*t*-Bu$_3$C$_6$H$_2$)$_4$]$^{\cdot -}$, where strong evidence was found for the existence of Ga–Ga multiple bonding.[58]

The C$_2$B$_3$ bonding faces of the carboranes in the base–gallacarborane complexes are not planar, but are folded such that the unique boron is out of the plane formed by the cage carbons and the basal

Table 2. Slip Distortion and Cage-Folding Parameters of Some Group 13 Pentagonal Bipyramidal Metallacarboranes

M	R	$\Delta^{b,c}$	folding angle^d	ref(s)
1-M-2,4-(CR)$_2$B$_4$H$_4$^{a}				
LGa^e	SiMe$_3$	−0.09	1.22	57
Ga(CMe$_3$)	H	−0.05	0.0	(3-21G*)[57]
(C$_{10}$H$_8$N$_2$)Ga(CMe$_3$)	SiMe$_3$	−1.10	6.95	55
(C$_8$H$_6$N$_4$)Ga(CMe$_3$)	SiMe$_3$	−1.01	8.85	55
(C$_8$H$_6$N$_4$)Ga(CMe$_3$)	SiMe$_3$	−1.36	7.70	55
In(CHMe$_2$)	SiMe$_3$	−0.25	3.64	55
(C$_{10}$H$_8$N$_2$)In(CHMe$_2$)	SiMe$_3$	−0.75	6.87	55
1-M-2,3-(CR)$_2$B$_4$H$_4$^{a}				
Ga(Me)	H	0.20	−0.63	49b
Ga(CMe$_3$)	SiMe$_3$	0.19	−2.68	51
(C$_8$H$_6$N$_4$)Ga(CMe$_3$)	SiMe$_3$	1.01	−8.67	54
(C$_{10}$H$_8$N$_2$)Ga(CMe$_3$)	SiMe$_3$	1.10	−8.49	55
In(CHMe$_2$)	SiMe$_3$	0.50	−4.42	53
(C$_{10}$H$_8$N$_2$)In(CHMe$_2$)	SiMe$_3$	0.78	−5.34	53

^{a} Atom numbering systems given in Figures 24 and 28. ^{b} In angstroms, see text for definition. ^{c} For 1-M-2,4-(CR)$_2$B$_4$H$_4$, Δ [B(5,6)] = −1.05 ± 0.03 Å, Δ [C(2,4)] = 0.46 ± 0.01 Å, Δ [B(3)] = 1.38 ± 0.02 Å; for 1-M-2,3-(CR)$_2$B$_4$H$_4$, Δ [C(1,2)] = −1.08 ± 0.03 Å, [B(3,5)] = 0.36 ± 0.02 Å, Δ [B(4)] = 1.41 ± 0.04 Å. ^{d} The acute dihedral angle between the planes B(3)−C(2)−C(1)−B(5) and B(3)−B(4)−B(5) (Figure 24) or C(2)−B(6)−B(5)−C(4) and C(1)−B(2)−C(3) (Figure 28); an angle of 0 indicates a planar C$_2$B$_3$ face, a positive angle indicates ring folding toward the metal. ^{e} L = 1-Ga-2,4-(CSiMe$_3$)$_2$B$_4$H$_4$.

borons. The extent and direction of the folding seems to be a function of slip distortion of the metallacarborane. Table 2 gives the acute dihedral angle between the plane formed by the unique boron and its two adjacently bound facial atoms and that formed by the other four facial atoms [B(3)−B(4)−B(5) and B(3)−C(2)−C(1)−B(5) in Figure 24, or C(1)−B(2)−C(3) and C(3)−B(4)−B(5)−C(1) in Figure 28] for a number of group 13 metallacarboranes. A positive folding angle indicates that the unique boron is above the plane defined by the other four facial atoms, and a folding angle of zero would indicate a planar C$_2$B$_3$ face. The extent and direction of slippage in the table is given by the parameter Δ, which is the lateral distance, in angstroms, of the metal from an extension of the normal drawn from the apical boron to the C$_2$B$_3$ facial plane, a positive value of Δ denotes slippage toward the unique boron. The results summarized in this table demonstrate that a correlation between slip distortion and ring folding exists. Similar conclusions were reached in other main group and transition metal carborane complexes.[59−61] Theoretical studies on the stannacarboranes indicated that enhanced bonding between the metal and the basal borons result from negative folding angles, while increased metal−B(unique) bonding resulted from ring folding in the opposite direction.[62] However, in the "carbons apart" base−gallacarborane complexes, the gallium and the unique boron are separated by more than 3 Å, and it would be surprising if a direct through-space interaction between a gallium and a boron separated by such large distances would be strong enough to produce the folding angles shown in Table 2.

Much of the structural work on the half-sandwich gallacarboranes, and their base complexes, have been duplicated in the indacarboranes.[53,55] Except that it crystallizes as a dimer, the structure of the uncomplexed "carbons adjacent" indacarborane, 1-[Me$_2$CH]-
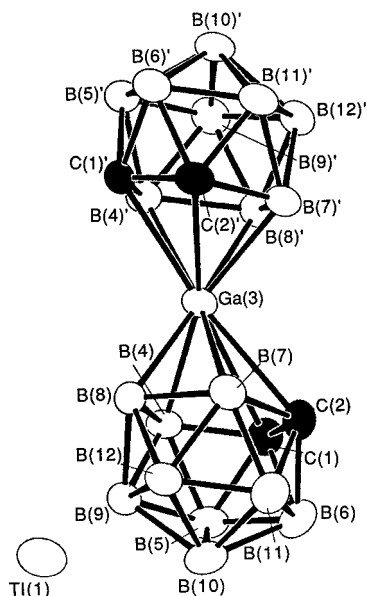
Figure 30. Crystal structure of [*commo*-3,3′-Ga(3,1,2-GaC$_2$B$_9$H$_{11}$)$_2$]$^-$ as its Tl$^+$ salt. (Reprinted from ref 41. Copyright 1990 American Chemical Society.)

2,3-(SiMe$_3$)$_2$-1,2,3-InC$_2$B$_4$H$_4$ is very similar to the structure shown in Figure 23, in that the metal occupies the apical position above the C$_2$B$_3$ bonding face and is slightly slip distorted toward the unique boron (see Table 2); this slip distortion is also greatly enhanced by coordination of the indium with a base, giving adduct geometries similar to that shown in Figure 24.[53] The same arguments used in rationalizing the geometries of the gallacarboranes can be applied to the corresponding indacarboranes. The observed differences can be attributed to the fact that the metal−carborane interactions are more ionic in the indacarboranes than those found in the corresponding gallacarboranes.[53]

Much less information is available on the syntheses and structures of the heavier group 13 metallacarboranes in the larger cage, icosahedral system. No half-sandwich complexes having either gallium or indium have been reported in this system. However, Hawthorne and co-workers have found that the reaction of the dicarbollide transfer reagent, Tl[*closo*-3,1,2-TlC$_2$B$_9$H$_{11}$] with excess GaCl$_3$ in toluene gave exclusively the full-sandwich gallacarborane, Tl-[*commo*-3,3′-Ga(3,1,2-GaC$_2$B$_9$H$_{11}$)$_2$], in 55% yield.[41] The structure, given in Figure 30, shows that a Ga^{III} is sandwiched between two [C$_2$B$_9$H$_{11}$]$^{2-}$ ligands and that the Ga is slightly slipped toward the boron side of the C$_2$B$_3$ carborane face, the bond distances are Ga−C(1,2) = 2.532 ± 0.046 Å, Ga−B(4,7) = 2.266 ± 0.015 Å, and Ga−B(8) = 2.089 ± 0.006 Å.[40,41] It is of interest to note the divergence of the reaction products in the C$_2$B$_4$ and C$_2$B$_9$ cage systems, the former cage system containing only half-sandwich complexes, while the latter system yields only 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$_3$)$_3$,[49] [(*t*-C$_4$H$_9$)GaCl$_2$]$_2$,[51] or (Me$_2$CH)-InI$_2$,[55] while the full-sandwich complex resulted when
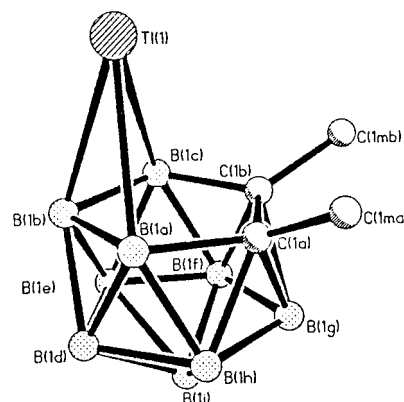
Figure 31. Crystal structure of [1,2-(Me)$_2$-3,1,2-TlC$_2$B$_9$H$_9$]$^-$ as its Tl$^+$ salt. (Reprinted with permission from ref 68. Copyright 1991 VCH Verlagsgesellschaft mbH.)

GaCl$_3$ as the metalating agent.[41] When GaCl$_3$ is substituted for [(*t*-C$_4$H$_9$)GaCl$_2$]$_2$ in the reaction with the dilithium complexed [2,3(4)-(SiMe$_3$)$_2$-2,3(4)-C$_2$B$_4$H$_4$]$^{2-}$ carborane dianion in 1:2 stoichiometry in TMEDA, the full-sandwich compound, [*commo*-1,1′-Ga(2,3(4)-(SiMe$_3$)$_2$-1,2,3(4)-GaC$_2$B$_4$H$_4$)$_2$]$^-$, was obtained, while the same reaction in 1:1 stoichiometry resulted, in high yields, in the formation of a half-sandwich chlorogallacarborane, *closo*-1-(TMEDA)-1-(Cl)-2,3(4)-(SiMe$_3$)$_2$-1,2,3(4)-GaC$_2$B$_4$H$_4$, which was further converted to the corresponding *closo* gallacarborane hydride and alkyl derivatives.[63]

The half-sandwich thallacarborane, [3,1,2-Tl-(CR)$_2$B$_9$H$_9$]$^-$, was first synthesized by Green and Stone in 1972 by the reaction of thallium(I) acetate with an aqueous alkaline solution of [(3),1,2-(CR)$_2$B$_9$H$_{10}$]$^-$.[64] 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[64] and main group[29,41] metallacarboranes. The structures of [3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$, as its [PPh$_3$Me]$^+$,[65] or [PPN]$^+$ salts,[66,67] and Tl[3,1,2-Tl(CMe)$_2$B$_9$H$_9$][68] have been reported. Figure 31 shows the structure of the [3,1,2-Tl-(CMe)$_2$B$_9$H$_9$]$^-$ anion, which is typical of the thallacarboranes.[68] Like the galla- and indacarboranes, the Tl^I occupies the apical position above the C$_2$B$_3$ 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.[1,2,69] All carboranes containing more than one cage carbon atom can formally be thought of as arising from a "cage expansion" of a less carbon rich carborane. However, a more restricted definition will be taken so that this review will cover those heterocarboranes containing the 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
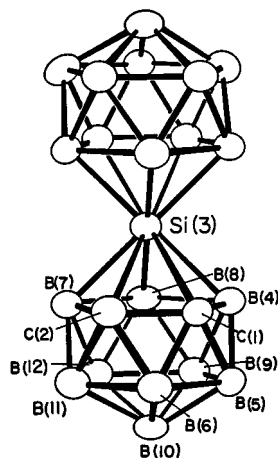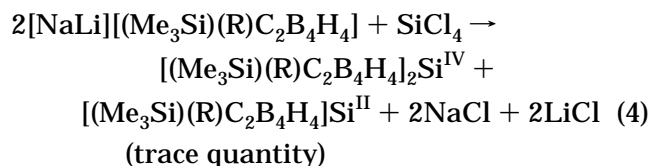
Figure 32. Crystal structure of *commo*-3,3'-Si(3,1,2-SiC$_2$B$_9$H$_{11}$)$_2$. (Reprinted from ref 74. Copyright 1986 American Chemical Society.)

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$_2$B$_9$H$_{11}$$^{2-}$ with MX$_2$ (M = Ge, Sn, and Pb).[70,71] On the basis of IR, NMR, Mössbauer spectroscopy, and mass spectrometry, the products were assigned to be a *closo*-3-M-1,2-C$_2$B$_9$H$_{11}$ structure, in which the cage carbons occupied adjacent positions. The study was later expanded to include the "carbons apart" germacarborane, 3-Ge-1,7-C$_2$B$_9$H$_{11}$, that was spectroscopically characterized.[72] The syntheses are of interest in that, while the 3,1,7-germacarborane was prepared in good yield by the reaction of GeI$_2$ with 7,9-C$_2$B$_9$H$_{11}$$^{2-}$, the use of SnCl$_2$ in place of the GeI$_2$ did not lead to the expected stannacarborane, but the reaction produced, in 78% yield, the oxidative cage closure product, *closo*-2,3-C$_2$B$_9$H$_{11}$ and Sn metal. When heated to 450 °C, 3-Sn-1,2-C$_2$B$_9$H$_{11}$ underwent disproportionation to

give *closo*-2,3-C$_2$B$_9$H$_{11}$.[72] The apparent increased tendency of the "carbons apart" carborane to undergo oxidative cage closure, compared to its "carbons adjacent" isomer, is surprising in view of the fact that the former isomers are thought to be the thermodynamically more stable.[73] It is also contrary to observations in the smaller cage C$_2$B$_4$ system, in that the "carbons adjacent" carboranes are the more easily oxidized of the two isomers.[18] Since these initial reports, a large number of group 14 metallacarboranes have been synthesized, spectroscopically and structurally characterized, and their reaction chemistry has also been explored.

The insertion of silicon has been 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$_2$B$_9$H$_{11}$)$_2$, prepared in 78% yield from the reaction of SiCl$_4$ with the dicarbollide dianion in refluxing benzene.[74] A concurrent report described the synthesis of the full-sandwich silacarboranes of the C$_2$B$_4$ cage system, *commo*-1,1'-Si(2-(SiMe$_3$)-3-(R)-1,2,3-SiC$_2$B$_4$H$_4$)$_2$ (R = SiMe$_3$,[75] H,[76] and Me[76]), according to the eq 4. The

$$2[NaLi][(Me_3Si)(R)C_2B_4H_4] + SiCl_4 \rightarrow$$
$$[(Me_3Si)(R)C_2B_4H_4]_2Si^{IV} +$$
$$[(Me_3Si)(R)C_2B_4H_4]Si^{II} + 2NaCl + 2LiCl \quad (4)$$
$$\text{(trace quantity)}$$

structures of the large and small cage silicarboranes are shown in Figures 32 and 33, respectively. The crystal structures show that in each complex the silicon, in a formal +4 oxidation state, is sandwiched between the planar and parallel C$_2$B$_3$ faces of the carborane ligands, with the cage carbons occupy 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
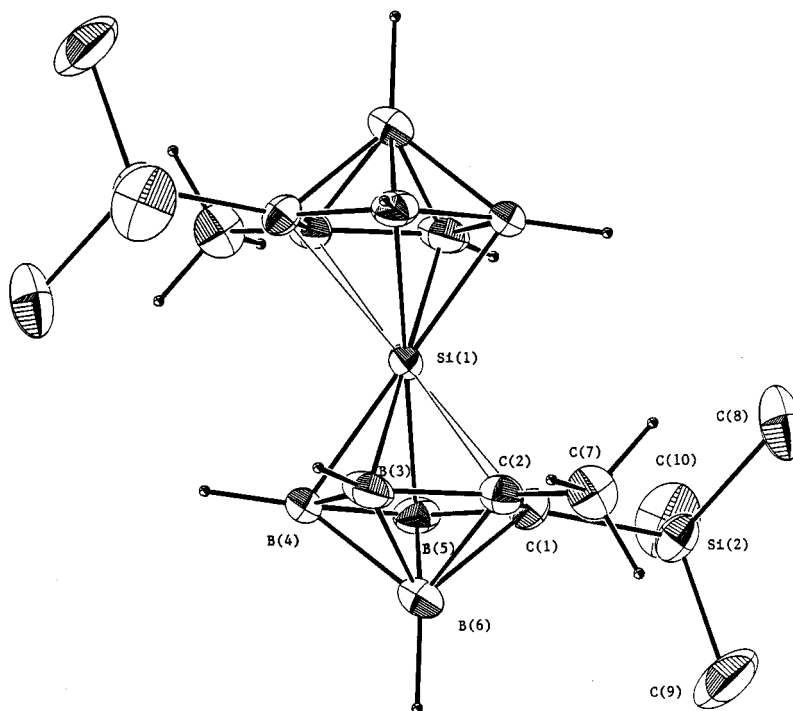

Figure 33. Crystal structure of *commo*-1,1'-Si[2,3-(SiMe$_3$)$_2$-1,2,3-SiC$_2$B$_4$H$_4$]$_2$. (Reprinted with permission from ref 75. Copyright 1986 Royal Society of Chemistry.)
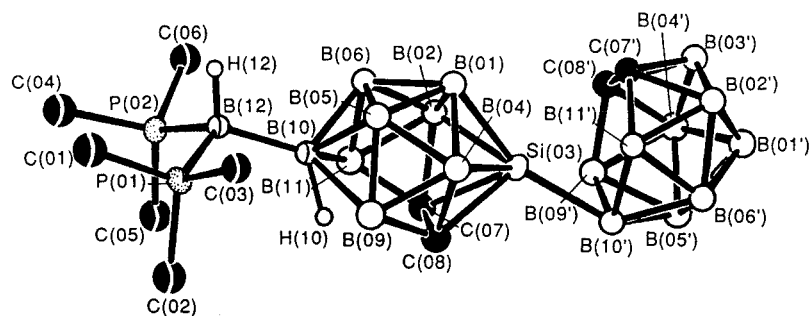
Figure 34. Crystal structure of $[\eta^5\text{-}10\text{-}\{(Me_3P)_2BH\}C_2B_8H_{10}]Si(\eta^1\text{-}C_2B_9H_{11})$. (Reprinted from ref 74b. Copyright 1990 American Chemical Society.)

carborane and the silylating reagent. For example, the Na/Li compounds of the $[2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ dianion reacted, in a 2-fold molar excess, with $SiCl_4$ to give the full-sandwich silacarboranes, yields ranging from 18% (R = $SiMe_3$) to 57% (R = Me).[76] When R = $SiMe_3$, a small amount (~1%) of another compound was also obtained that was tentatively identified as the half-sandwich Si^{II} complex, $1\text{-}Si\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4$.[76] On the other hand, no reaction was found when the $[2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_5]^-$ monoanion, as either its Na or Li compound, was used.[76] 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, $[2\text{-}(SiMe_3)\text{-}3\text{-}Me\text{-}2,3\text{-}C_2B_4H_4]SiH(Cl)$ (see eq 5). The chloride ligand could be replaced by reaction with NaH to give $[2\text{-}(SiMe_3)\text{-}3\text{-}Me\text{-}2,3\text{-}C_2B_4H_4]SiH_2$, as shown in eq 6; the ^{29}Si NMR spectrum of this complex gave a splitting that suggested the presence of B−H−Si bridges.[76]

$$[NaLi][(Me_3Si)(R)C_2B_4H_4] + SiH_2Cl_2 \text{ (excess)} \rightarrow$$
$$[(Me_3Si)(R)C_2B_4H_4]SiH(Cl) + NaCl + LiCl \quad (5)$$

$$[(Me_3Si)(R)C_2B_4H_4]SiH(Cl) + NaH \rightarrow$$
$$[(Me_3Si)(R)C_2B_4H_4]SiH_2 + NaCl \quad (6)$$
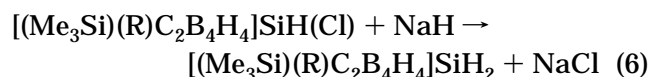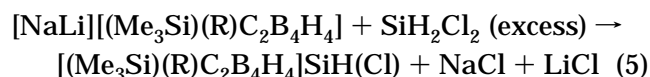
Detailed reactivity studies between the air- and moisture-stable bis(η^5-dicarbollide)silicon sandwich complex, $commo\text{-}3,3'\text{-}Si(3,1,2\text{-}SiC_2B_9H_{11})_2$, and Lewis bases, such as pyridine and trimethylphosphine, have been reported.[74b] Structures of the products formed from the reaction with pyridine, $(10\text{-}exo\text{-}\eta^1\text{-}7,8\text{-}C_2B_9H_{11})(10\text{-}endo\text{-}\eta^1\text{-}7,8\text{-}C_2B_9H_{11})Si(C_5H_5N)_2$, and Me_3P, $[\eta^5\text{-}10\text{-}\{(Me_3P)_2BH\}C_2B_8H_{10}]Si(\eta^1\text{-}C_2B_9H_{11})$, were determined by X-ray diffraction.[74b] The latter complex, shown in Figure 34, 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[77] and *ab initio*[78] molecular orbital theory. Figure 35 shows the molecular orbital energies and heavy atom atomic orbital contributions for the compounds $commo\text{-}3,3'\text{-}Si(3,1,2\text{-}SiC_2B_9H_{11})_2$ and $commo\text{-}1,1'\text{-}Si(1,2,3\text{-}SiC_2B_4H_6)_2$ obtained from MNDO calculations.[77] As can be seen in the figure, the main Si−carborane bonding is 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, $(C_5R_5)_2Si$.[79] 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.[79] This oxidation state preference can be understood from the diagrams shown in Figure 35. Note that 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 the $(C_5H_5)_2Si$, 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 interactions, account for some of the strongest C−C π-bonding in the Cp rings.[77] 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.[80] When $closo\text{-}1\text{-}Sn\text{-}2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4$ was used as the carborane transfer reagent, the only product was the full-sandwich germacarboranes.[81] 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.[80] Aside from differences that are directly attributable to atom size, the germacarboranes show a greater slip distortion than was found in the corresponding silacarboranes (the differences between the M−C(1,2) and M−B(4) distances are 0.17 and 0.38 Å, respectively, for the sila- and germacarboranes, see Figure 33 for atom numbering). While the structure of the half-sandwich germacarborane could be determined only for an "carbons apart" isomer,[82a] X-ray diffraction studies have been reported for the $GeCl_3$-substituted "car-
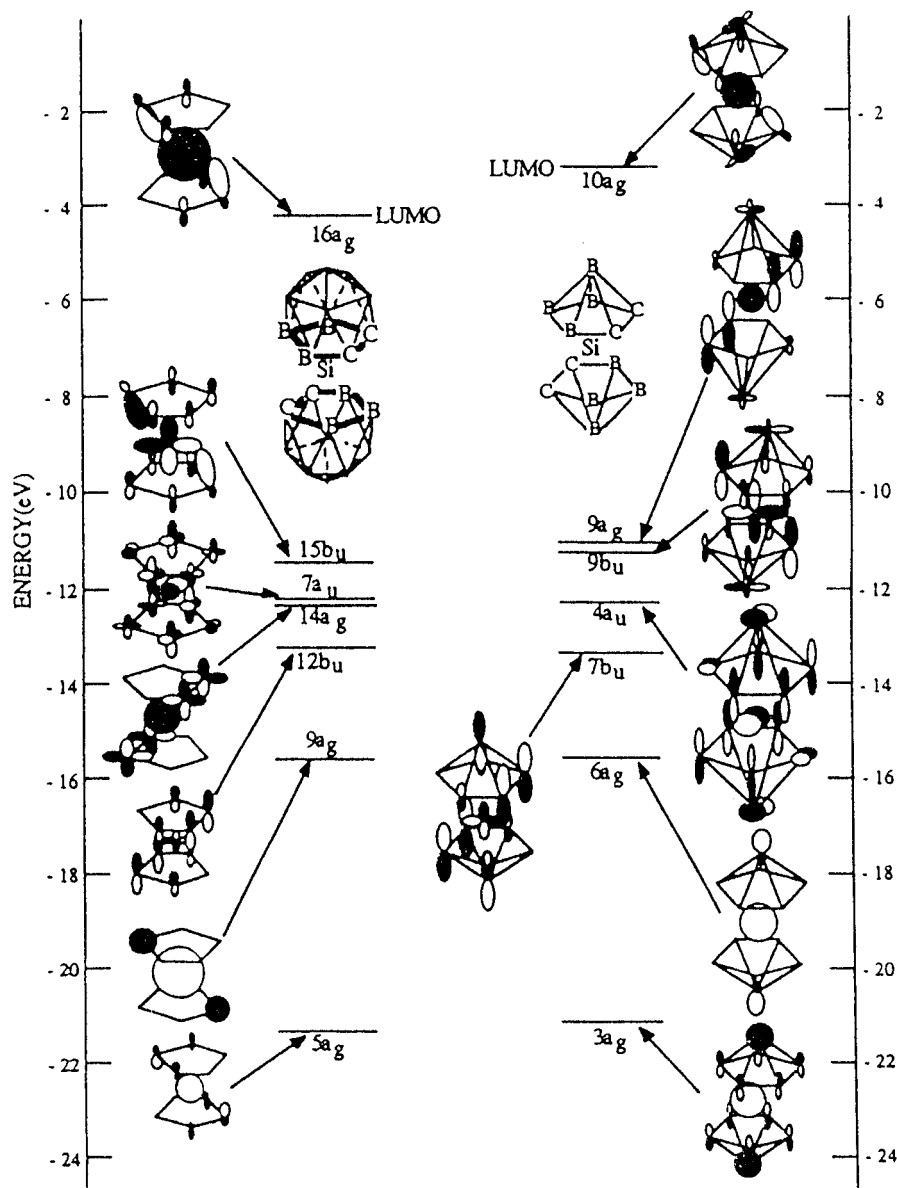
Figure 35. Molecular orbital energies and composition of $Si(C_2B_9H_{11})_2$ and $Si(C_2B_4H_6)_2$. (Reprinted from ref 77. Copyright 1991 American Chemical Society.)

bons adjacent" germacarborane, *closo*-1-Ge^{II}-2,3-(SiMe$_3$)$_2$-5-(GeCl$_3$)-2,3-C$_2$B$_4$H$_3$, which is shown in Figure 36.[82b] In this complex, a Ge^{II} is symmetrically bonded to the C$_2$B$_3$ face of the carborane, with little indication of a slip distortion (the Ge−C(1,2) and the Ge−B(4) distances are 2.248 ± 0.004 Å and 2.243 Å, respectively), while another germanium, in a formal +4 state, is involved in an *exo*-polyhedral GeCl$_3$ group that is bonded to the unique boron [B(4) in Figure 36]. 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 a more electron-withdrawing group, such as GeCl$_3$, would favor a centrally located capping metal.[82]

The direct reaction of the mono- or dianionic salts of the C$_2$B$_9$ and C$_2$B$_4$ *nido* carboranes with SnCl$_2$,[60,83,84] SnCl$_4$,[81] or PbCl$_2$[85] 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$_2$B$_9$H$_{11}$ (M = Ge, Sn, Pb) series.[70,71] The

C-methyl-substituted icosahedral stannacarborane, *closo*-3-Sn-1,2-(Me)$_2$-1,2-C$_2$B$_9$H$_9$, was also prepared using this method.[60,83] 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$_2$B$_4$H$_4$ (R = Me) is given in Figure 37.[83] The structures of the stannacarboranes where R = H[86] and SiMe$_3$[87] are similar to that in Figure 37. Except for the fact that the half-sandwich lead complex, *closo*-1-Pb-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$, crystallizes as a dimer, this figure also provides a good representation of the geometry of the plumbacarboranes.[85] 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-(SiMe$_3$)-3-(R)-2,3-C$_2$B$_4$H$_5$]$^-$, only reductive insertion of the metal occurred yielding *closo*-1-Sn-2-(SiMe$_3$)-3-(R)-2,3-C$_2$B$_4$H$_4$.[81] The inability to obtain the full-sandwich complexes was explained on the basis of the decreasing tendency of the heavier main group metals to
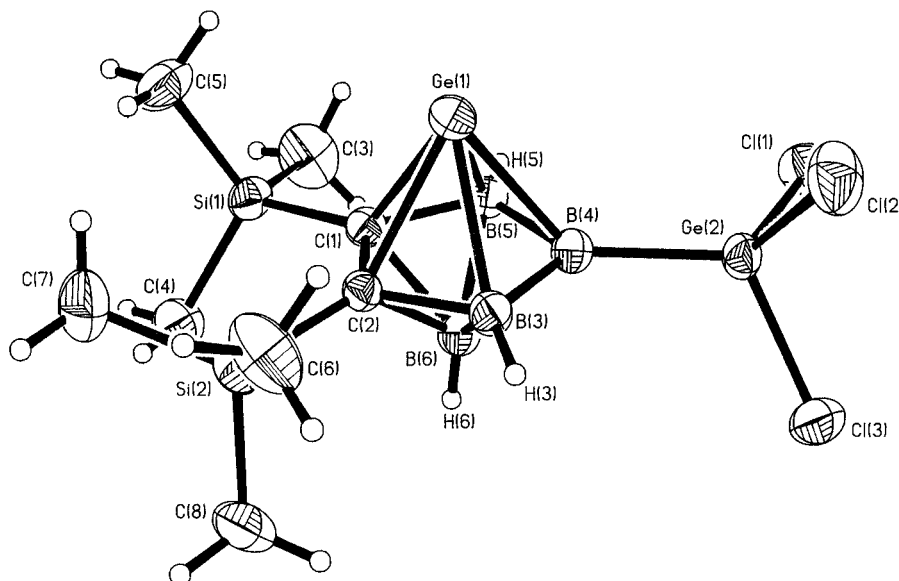
Figure 36. Crystal structure of *closo*-1-Ge^{II}-2,3-(SiMe$_3$)$_2$-5-(GeCl$_3$)-2,3-C$_2$B$_4$H$_3$. (Reprinted from ref 82. Copyright 1988 American Chemical Society.)
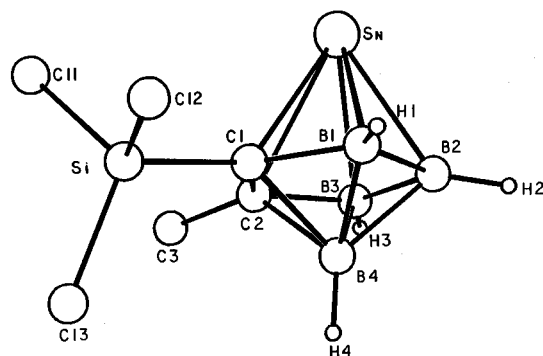

Figure 37. Crystal structure of *closo*-1-Sn-2-(SiMe$_3$)-3-(CH$_3$)-2,3-C$_2$B$_4$H$_4$. (Reprinted with permission from ref 83. Copyright 1984 Royal Society of Chemistry.)

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$_2$B$_9$H$_{11}$]$^{2-}$ gave only the Sn^{II} stannacarborane.[71] A half-sandwich Sn^{IV} carborane, 1,1-(Me)$_2$-1,2,3-SnC$_2$B$_8$H$_{10}$, was reported by Kennedy and co-workers from the reaction of Me$_2$SnCl$_2$ with [*nido*-6,9-C$_2$B$_8$H$_{10}$]$^{2-}$.[88] However, the similarity of the ^{11}B NMR spectra of this stannacarborane with that of [μ-6,9-AlEt(OEt$_2$)-6,9-C$_2$B$_8$H$_{10}$], in which the metal bridges the carborane through two Al–C$_{cage}$ bonds (see Figure 19), prompted the authors to describe the Sn^{IV} complex as a classically bridged *nido*-stannacarborane.[88a] Exposure of this compound to air led to decomposition, giving a product thought to be 1,2,3-SnC$_2$B$_8$H$_{10}$.[88] The [*nido*-6,9-C$_2$B$_8$H$_{10}$]$^{2-}$ ligand is of interest in that its half-sandwich complexes can be described as either bridged *nido* or true *closo* metallacarboranes, depending on compactness of the complexes.[88b] 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$_2$B$_4$H$_4$]$_2$. This compound was obtained from the
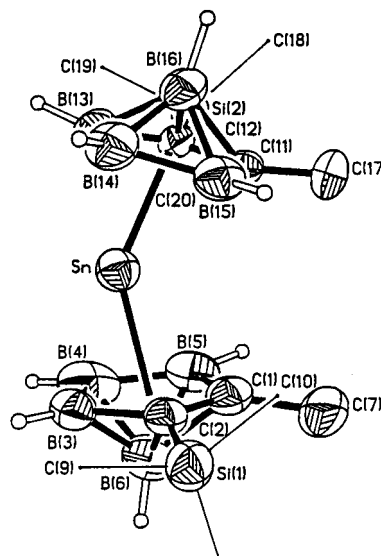
Figure 38. Crystal structure of *commo*-1,1'-Sn[2-(SiMe$_3$)-3-(CH$_3$)-1,2,3-SnC$_2$B$_4$H$_4$]$_2$. (Reprinted from ref 89. Copyright 1992 American Chemical Society.)

reaction of *closo*-1-Sn-2-(SiMe$_3$)-3-(Me)-2,3-C$_2$B$_4$H$_4$ and TiCl$_4$, according to eq 7. The structure, shown

$$2[closo\text{-}1\text{-}Sn\text{-}2\text{-}(SiMe_3)\text{-}3\text{-}(Me)\text{-}2,3\text{-}C_2B_4H_4] +$$

$$2TiCl_4 \xrightarrow[25\ °C]{THF/C_6H_6} 2TiCl_3(THF)_3 + SnCl_2 +$$

$$commo\text{-}1,1'\text{-}Sn[2\text{-}(SiMe_3)\text{-}3\text{-}(Me)\text{-}1,2,3\text{-}SnC_2B_4H_4]_2 \tag{7}$$
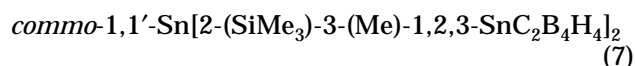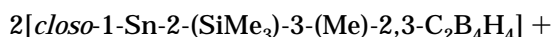
in Figure 38,[89] is unlike those of its silicon and germanium analogues in that the stannacarborane complex is bent, such that the (ring centroid 1)–Sn–(ring centroid 2) angle is 142.5°. This is similar to the corresponding angles of 145.8° and 144.1° found for (η^5-C$_5$H$_5$)$_2$Sn and (η^5-C$_5$Me$_5$)$_2$Sn complexes.[90,91] Bending in the stannocenes, and several other divalent group 14 metallocenes are well known and have been explained in terms of the stereochemical influ-
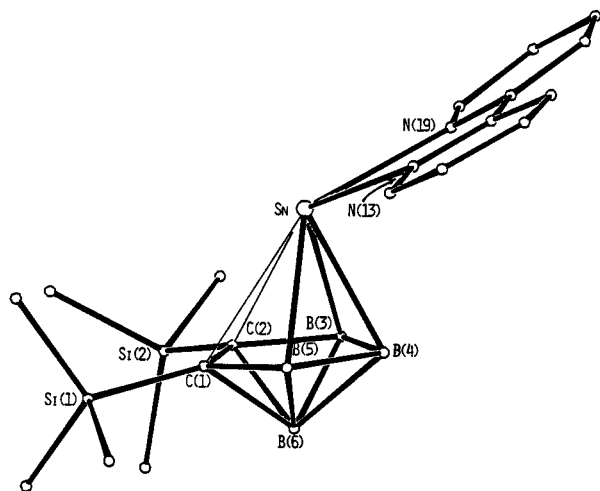
Figure 39. Crystal structure of 1-(2,2′-$C_{10}H_8N_2$)-2,3-(SiMe₃)₂-1,2,3-SnC₂B₄H₄. (Reprinted from ref 86. Copyright 1986 American Chemical Society.)
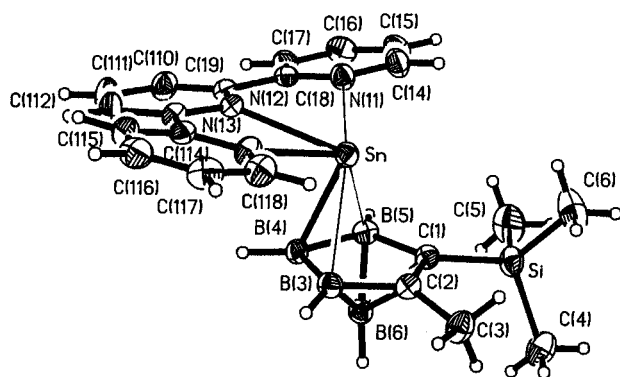

Figure 40. Crystal structure of 1-($C_{15}H_{11}N_3$)-2,3-(SiMe₃)₂-1,2,3-SnC₂B₄H₄. (Reprinted from ref 105. Copyright 1989 American Chemical Society.)

ence of the metal's "lone pair" of electrons,[92] which may be offset by the presence of large groups, such as C_6H_5, on the Cp ring.[93] However, the similar bending shown in Figure 38, 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,[85,94−96] bidentate,[59,83,85,87,97−101] bis(bidentate)[102,103] and tridentate[104,105] bases. The bonding in these complexes have been the subject of several theoretical studies.[56,59,106] Figure 39 shows the structure of the 1-(2,2′-$C_{10}H_8N_2$)-2,3-(SiMe₃)₂-1,2,3-SnC₂B₄H₄ complex;[86] Figure 40, the 1-(2,2′:6′,2″-$C_{15}H_{11}N_3$)-2,3-(SiMe₃)₂-1,2,3-SnC₂B₄H₄;[105] and Figure 41, that of 1-(THF)-2,3-(Me)₂-1,2,3-SnC₂B₉H₉.[60] 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 39, and the metals are highly slip distorted. In the
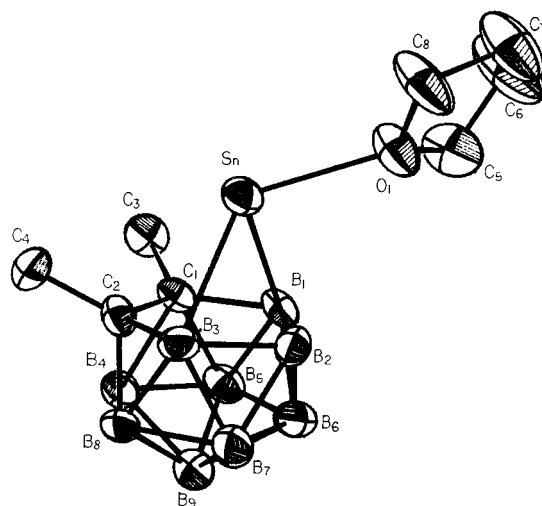

Figure 41. Crystal structure of 1-(C_4H_8O)-2,3-(Me)₂-1,2,3-SnC₂B₉H₉. (Reprinted from ref 60. Copyright 1987 American Chemical Society.)

structures of the bis(bidentate) base complexes, 1,1′-(2,2′-$C_8H_6N_4$)[2,3-(SiMe₃)₂-1,2,3-MC₂B₄H₄]₂ (M = Sn[102] and Pb[103]), 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-(SiMe₃)₂-2,3-$C_2B_4H_4$]₂ (see Figure 27). The local symmetries around each metal atom in the bridged complexes are the same as that shown in Figure 39. 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. These same types of distortions are also found in the base−SnCp system. While the tin in the [(η^5-C_5Me_5)Sn]$^+$ half-sandwich complex is centered over the pentagonal face of the Cp* ligand,[107] in the [(2,2′-$C_{10}H_8N_2$)-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 39.[108] While the pseudo mirror plane of the original stannacarborane was preserved in the bipyridine−stannacarborane adduct, shown in Figure 39,[109] considerably more asymmetry was found in some of the other base-metallacarborane complexes. This can be seen in Figure 42, which shows the structure of 1-(2,2′-$C_{10}H_8N_2$)-2,3-(SiMe₃)₂-1,2,3-PbC₂B₄H₄,[100] where the base is rotated such that one nitrogen, N(2) in Figure 42, was almost directly over the unique boron, giving a N(2)−Pb−B(4)−B(6) torsion angle of 176.7°, and was more strongly bonded to the metal than was the other nitrogen atom. This unequal bonding gives rise to a nonplanarity of the bipyridine molecule, such that the dihedral angle between the two NC₅ rings is 9.2°, rather than the expected 0°.[100] Unsymmetrical base bonding is even more evident in 1-(2,2′:6′,2″-$C_{15}H_{11}N_3$)-2,3-(SiMe₃)₂-1,2,3-SnC₂B₄H₄, shown in Figure 40, where one of the Sn−N bonds is significantly longer than the other two.[105] In this complex, it is an open question whether the base would be better described as functioning as a bidentate rather than a tridentate ligand. The complexes
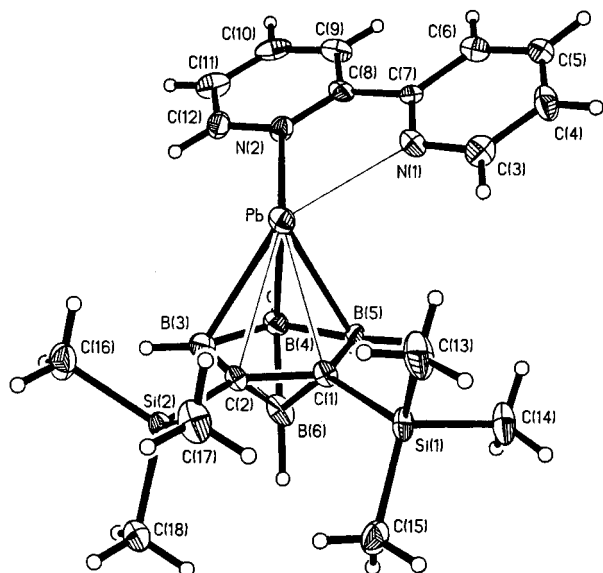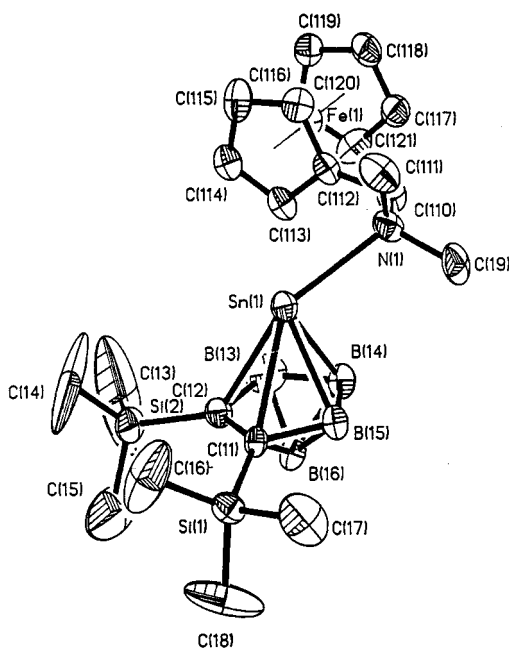
Figure 42. Crystal structure of 1-(2,2′-C$_{10}$H$_8$N$_2$)-2,3-(SiMe$_3$)$_2$-1,2,3-PbC$_2$B$_4$H$_4$. (Reprinted from ref 100. Copyright 1990 American Chemical Society.)

Figure 43. Crystal structure of 1-[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$-CH$_2$(Me)$_2$N)]-2,3-(SiMe$_3$)$_2$-1,2,3-SnC$_2$B$_4$H$_4$. (Reprinted from ref 94. Copyright 1989 American Chemical Society.)

formed by the group 14 metallacarboranes with monodentate bases are shown in Figures 41, 43, and 44.[60,94,95] As with their polydentate analogues, the bases reside over the boron side of the C$_2$B$_3$ 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-[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$CH$_2$(Me)$_2$N)]-2,3-(SiMe$_3$)$_2$-1,2,3-SnC$_2$B$_4$H$_4$, the one in which the ferrocenyl amine nitrogen is directly over the unique boron,
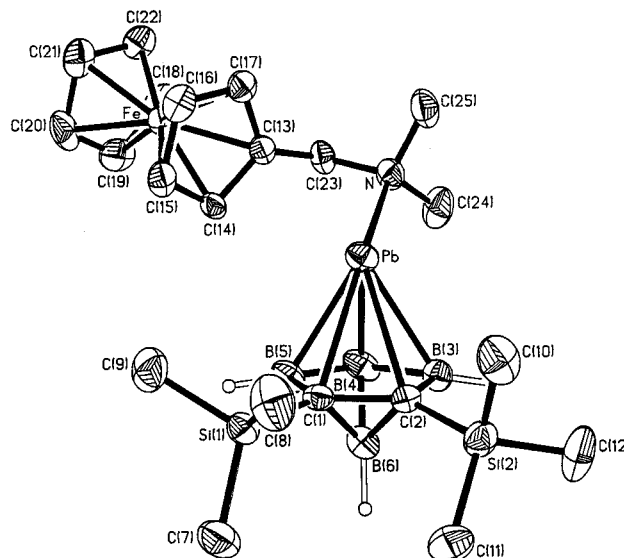
Figure 44. Crystal structure of 1-[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$-CH$_2$(Me)$_2$N)]-2,3-(SiMe$_3$)$_2$-1,2,3-PbC$_2$B$_4$H$_4$. (Reprinted from ref 95. Copyright 1992 American Chemical Society.)

B(14) in Figure 43, and another in which the base is rotated about 10° out of the mirror plane of the metallacarborane, similar to the base orientation found in Figure 41.[94] However, it is interesting that in both molecules, the ferrocenyl group is not in a position of minimum steric interactions 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$_2$B$_4$ 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 (see Figure 44). It was argued that such interactions might compensate for the less than ideal steric arrangement of the ligands.[95]

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.[96] 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. The main difference is that the extent of the slippages in the stannacarboranes are less than those found in the corresponding gallacarboranes.[96] In addition, it was found that in the isomeric ferrocenyl amine−stannacarborane complex, the ferrocene group was rotated away from the metallacarborane and assumed a position of minimum ligand−ligand repulsion (see Figure 45). This is quite different from the situation found in the analogous "carbons adjacent" ferrocene amine−group 14 metallacarborane adducts. The added repulsion due to the nearer presence of the C$_{(cage)}$−SiMe$_3$ groups resulting from a closer ferrocene−Sn distance would be more than enough to overcome any stabilizing effect that might result from direct tin−Cp interactions, so that the geometry shown in Figure 45 would be the expected lowest energy structure for the adduct.[96]
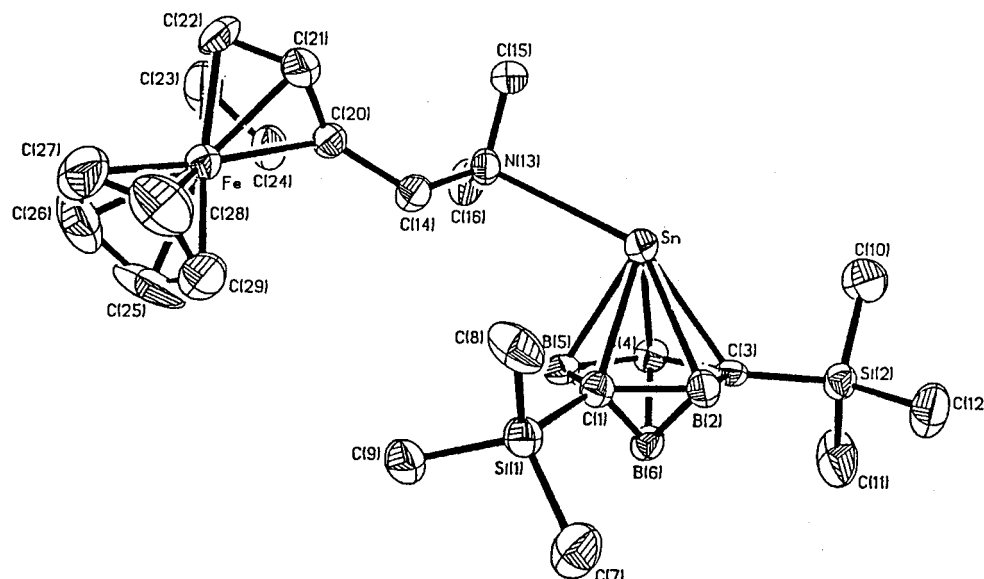
Figure 45. Crystal structure of 1-[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$CH$_2$(Me)$_2$N)]-2,4-(SiMe$_3$)$_2$-1,2,4-SnC$_2$B$_4$H$_4$. (Reprinted from ref 96. Copyright 1994 American Chemical Society.)
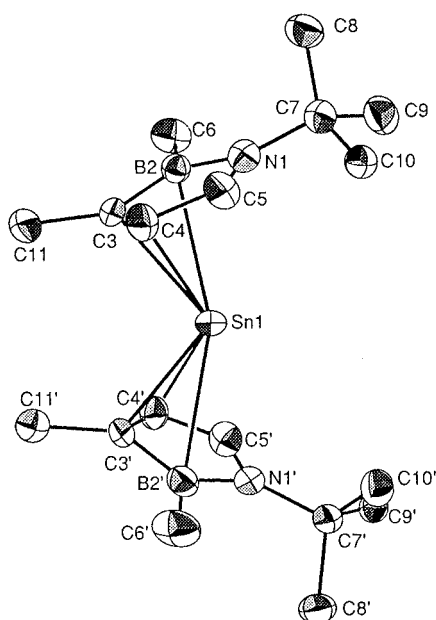
Figure 46. Crystal structure of [1-t-C$_4$H$_9$-2,3-(Me)$_2$-1,2-NBC$_3$H$_2$]$_2$Sn. (Reprinted with permission from ref 110. Copyright 1985 VCH Verlagsgesellschaft mbH.)

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-t-C$_4$H$_9$-2,3-(Me)$_2$-1,2-NBC$_3$H$_2$]$_2$Sn.[110] The structure of this complex, shown in Figure 46, is that of a bent sandwich, similar to that found in the isoelectronic Cp system; the dihedral angle between the two planar NBC$_3$ rings is 46.5°, which is smaller than the 55° found in (C$_5$H$_5$)$_2$Sn,[111] but larger than the 36° reported for (C$_5$Me$_5$)$_2$Sn.[107] Siebert and co-workers have reported the synthesis and structure of the bent tetradecker sandwich complex, [(C$_5$H$_5$)Co(C$_2$B$_2$C)]$_2$Sn (C$_2$B$_2$C = 4,5-(Et)$_2$-1,3-(Me)$_2$-1,3-B$_2$C$_3$H), obtained from the reaction of the [(C$_5$H$_5$)Co(C$_2$B$_2$C)]$^-$ anion with SnCl$_2$; the structure of the complex is shown in Figure 47.[112] Coordination to the tin was through the C$_2$B$_2$C rings, and the dihedral angle between these rings was 67°,

which was larger than those found for the other Sn(II) sandwich complexes.

In the above examples the group 13 or 14 heteroatom (a metal or a metalloid) was found to occupy apical positions 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$_2$B$_{10}$H$_{10}$.[113] Its structure, shown in Figure 48, 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$_2$B$_{10}$H$_{10}$. This approach will prove especially useful in the discussions concerning the incorporation of group 15 and 16 heteroatoms into carborane cages.

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 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 stibaboranes have been published.[114,115] In keeping with the restrictions outlined at the beginning of this review, only those group 15 heterocarboranes that still retain at least one cage carbon will be considered here.

There have been only a few reports of the incorporation of nitrogen into the carborane cages. When cage expansion does occur, the nitrogen is invariably present in an R—N unit, where R is usually H or an alkyl group. The unit acts as a four-electron donor,
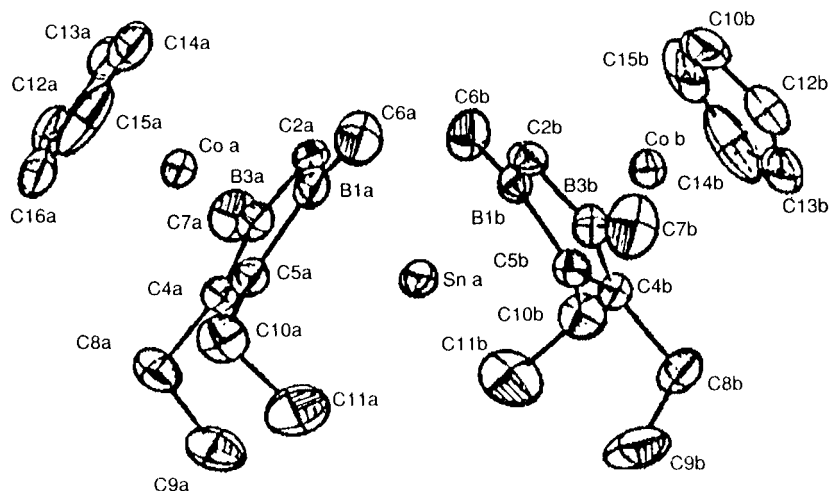
Figure 47. Crystal structure of $[(C_5H_5)Co(4,5-(Et)_2-1,3-(Me)_2-1,2-B_2C_3H)]_2Sn$. (Reprinted from ref 112. Copyright 1983 American Chemical Society.)
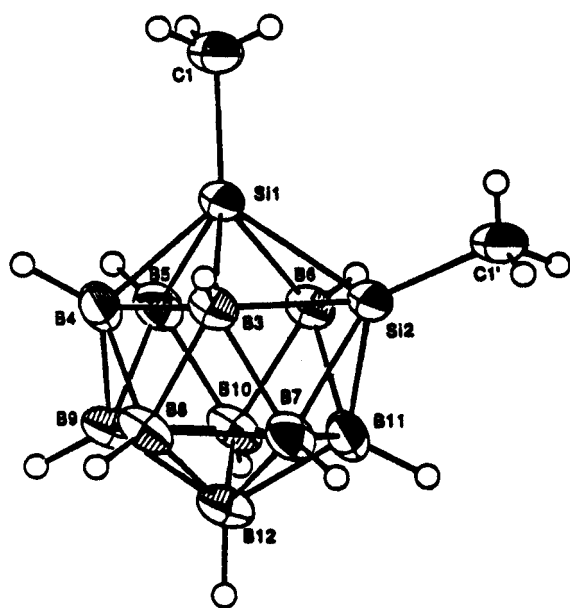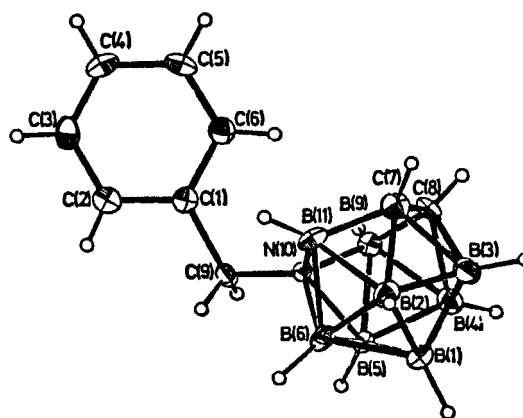

Figure 48. Crystal structure of $1,2-(Me)_2-1,2-Si_2B_{10}H_{10}$. (Reprinted from ref 113. Copyright 1993 American Chemical Society.)

Figure 49. Crystal structure of $10-(C_6H_5CH_2)-nido-10,7,8-NC_2B_8H_{10}$. (Reprinted with permission from ref 116. Copyright 1975 Royal Society of Chemistry.)

Figure 50. Crystal structure of $5-(\eta^6-C_6Me_6)-7-(MeO)-arachno-5-RuN(Me)C(H)B_9H_{11}$. (Reprinted with permission from ref 117. Copyright 1990 Royal Society of Chemistry.)

similar to CH_2. This is best illustrated by the structure of $10-(C_6H_5CH_2)-nido-10,7,8-NC_2B_8H_{10}$, shown in Figure 49, in which the nitrogen resides between the two boron atoms of the planar C_2B_2N of the *nido*-NC_2B_8 cage, which is consistent with a skeletal electron pair count of 13 for an 11-vertex *nido* structure.[116] Reaction of MeN≡C with the methoxy-substituted ruthenaborane, $6-(\eta^6-C_6Me_6)-8-(MeO)-nido-6-RuB_9H_{12}$, gave a 12-vertex *isoarachno*-RuC-NB_9 cluster, $5-(\eta^6-C_6Me_6)-7-(MeO)-arachno-5-RuN-(Me)C(H)B_9H_{11}$, whose structure is shown in Figure 50.[117] This product, which arises from the incorporation of a N≡C unit into the borane cage, is quite different from that obtained from the analogous reactions of RN≡C with the isoelectronic ruthenaborane, $6-(\eta^6-C_6Me_6)-nido-6-RuB_9H_{13}$, where it was found that only the carbon atoms from one or two isocyanides were incorporated into the cage structures to give 11-vertex *closo*-type metallacarborane products. Since carbon insertion by the reaction of isocyanides with boranes and heteroboranes had been known for some time, the ruthenacarborane product
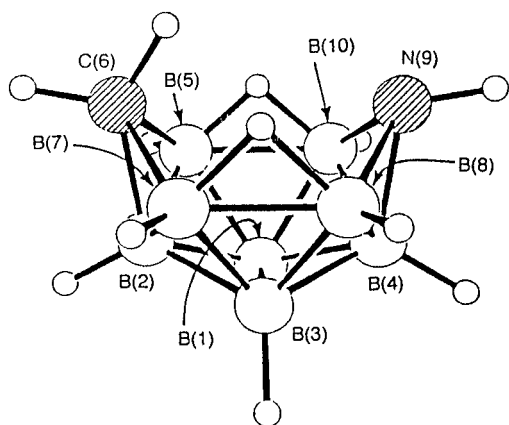
shown in Figure 50 was unexpected.[118] Irrespective of the mechanism for its formation, it is clear that the nitrogen atom in this compound is incorporated into the cage structure in much the same way as is the one in Figure 49. A similar situation is found in the monocarbon azaborane, $arachno-6,9-CNB_8H_{13}$, shown in Figure 51.[119] This compound, formed in 15% yield from the reaction of $arachno-4-CB_8H_{14}$ with excess sodium nitrite, is structurally related to the *arachno* heteroboranes, $6,9-C_2B_8H_{14}$ and $6,9-N_2B_8H_{12}$.[120,121] Use of sulfur in place of sodium nitrite

Figure 51. Proposed structure of *arachno*-6,9-CNB$_8$H$_{13}$. (Reprinted from ref 119. Copyright 1991 Royal Society of Chemistry.)
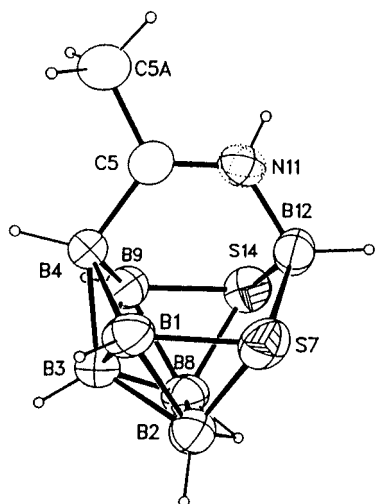

Figure 52. Crystal structure of *hypo*-5-(Me)-5,11,7,14-CNS$_2$B$_7$H$_9$. (Reprinted from ref 122. Copyright 1989 American Chemical Society.)

resulted in the thiacarborane, *arachno*-6,9-CSB$_8$H$_{12}$, whose structure is the same as that shown in Figure 51, except that a S replaces the N–H unit.[119] The reactions of nitriles with boranes and heteroboranes have also been found to proceed through different paths, depending on the exact nature of the reactants. Sneddon and co-workers have studied the reaction of acetonitrile with the isoelectronic anions, *arachno*-S$_2$B$_7$H$_8^-$ and *arachno*-C$_2$B$_7$H$_{12}$.[122] They found that the carborane anion gave carbon insertion, leading to the tricarbon carborane, *nido*-6-(Me)-5,6,9-C$_3$B$_7$H$_{10}$. Its proposed molecular geometry is similar to the one shown in Figure 51, except that a C–Me is substituted for the N–H group, a neighboring boron [B(8)] is replaced by a carbon, and the two bridging hydrogens are deleted. The *nido* designation reflects the skeletal electron pair count of 12 (*n* + 2). On the other hand, the isoelectronic thiaborane underwent a nitrile insertion to give the air stable cluster, *hypo*-5-(Me)-5,11,7,14-CNS$_2$B$_7$H$_9$, shown in Figure 52.[122] In this compound a CN unit is inserted across opposing boron atoms on the S$_2$B$_4$ hexagonal face of the original *arachno* thiaborane, to give a cluster with a planar five member and two puckered six-membered rings. The CN group could either be considered as part of the cage system, with 15 cage electron pairs involving in an 11-vertex, *n* + 4,
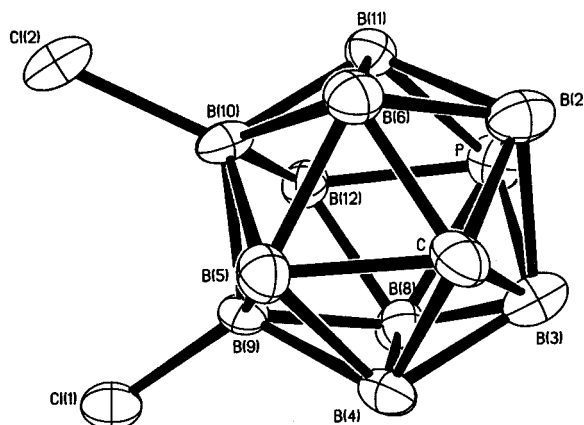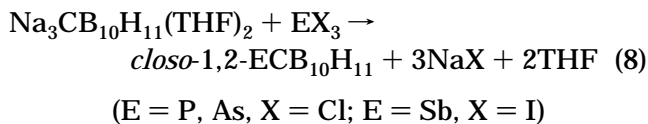

Figure 53. Crystal structure of *closo*-9,10-(Cl)$_2$-1,7-CHPB$_{10}$H$_8$. (Reprinted from ref 128. Copyright 1975 American Chemical Society.)

structure, alternatively, the cluster could be viewed as consisting of an electron deficient S$_2$B$_7$H$_8$ fragment bridged by an exopolyhedral imine group; the authors cite evidence supporting both views, as well as a justification of the *hypo* designation in either view. Cage expansion was also found in the reaction of *closo*-C$_2$B$_8$H$_{10}$ with *t*-BuNH$_2$ to give 11-*t*-C$_4$H$_9$-*arachno*-5,10,11-C$_2$NB$_8$H$_{12}$, in which the *t*-BuNH was formally acting as a five-electron donor group.[123] Theoretical calculations on several mixed group 15 heteroboranes and carboranes of the type *closo*-XYB$_n$H$_n$ (*n* = 3−5; X, Y = N, CH, P, and SiH) indicate that their relative stabilities depend on both the nature of the heteroatom groups and the size of the cluster.[124]

While examples of nitrogen incorporation are limited to those in which the nitrogen is also bonded to one or two *exo* polyhedral groups, underivatized (bare) heavier group 15 elements have been inserted into both borane and carborane cages. The most studied group 15 carboranes are those of the form *closo*-1,2-ECB$_{10}$H$_{11}$ (E = P, As, and Sb), obtained from the reaction of the monocarbon carborane with the appropriate group 15 halide, as shown in eq (8).[125−127]

$$Na_3CB_{10}H_{11}(THF)_2 + EX_3 \rightarrow$$
$$closo\text{-}1,2\text{-}ECB_{10}H_{11} + 3NaX + 2THF \quad (8)$$

$$(E = P, As, X = Cl; E = Sb, X = I)$$

All of these compounds had distorted icosahedral structures that are formally obtained by replacing a CH unit in *closo*-1,2-C$_2$B$_{10}$H$_{12}$ with an isoelectronic and isolobal group 15 element. The 1,7 and 1,12 isomers could be obtained, in varying yields, from the thermal rearrangements of the respective 1,2 isomers.[126−128] Figure 53 shows the crystal structure of one of the thermally rearranged icosahedral phosphacarboranes, *closo*-9,10-(Cl)$_2$-1,7-CHPB$_{10}$H$_8$.[128] Like their analogous dicarbacarboranes, the group 15 *closo* carboranes were found to undergo boron abstraction reactions with bases such as piperidine, to give the corresponding *nido*-ECB$_9$H$_{11}^-$, in which both heteroatoms were on the open pentagonal faces of the compounds.[126,127] These *nido* anions were found to react with both transition metal[127,129] and main group metal[130] halides to give the respective half- and full-sandwich metallacarboranes. Although the monocarbon heterocarboranes are the most studied, there
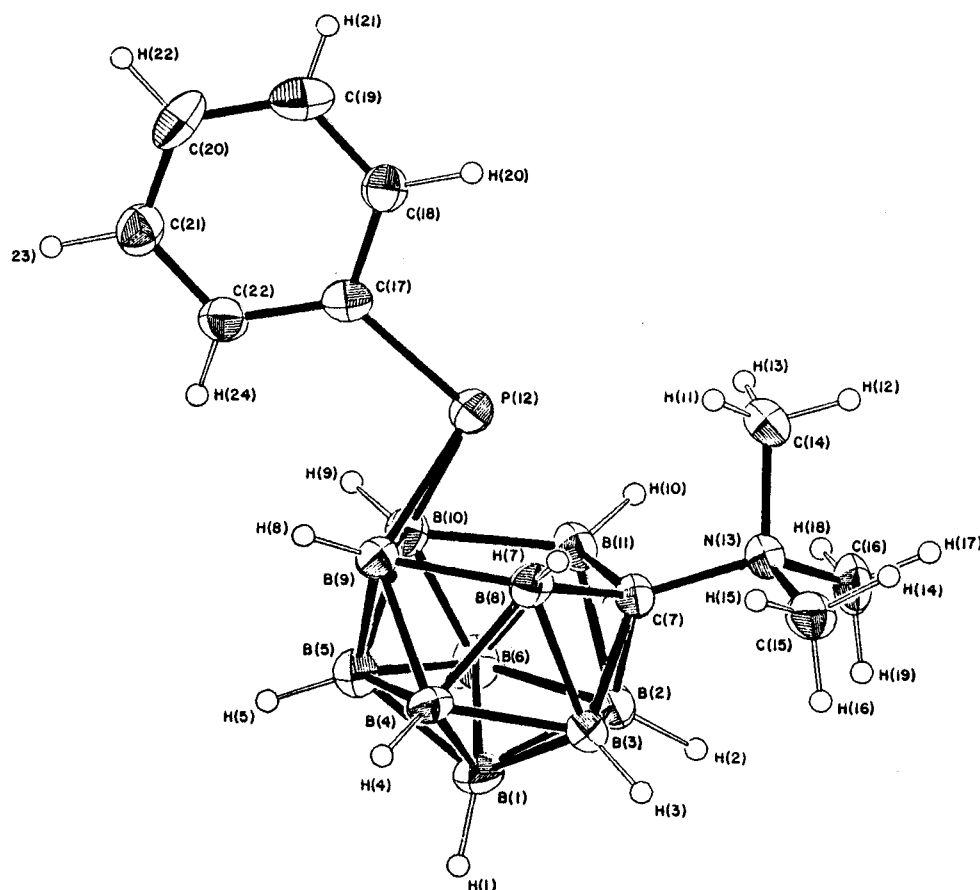
Figure 54. Crystal structure of *nido*-(CNMe₃)B₁₀H₁₀(PC₆H₅). (Reprinted with permission from ref 134. Copyright 1978 Elsevier Sequoia.)

are some examples of more extensive heteroatom substitution, such as $As_2C_2B_7H_9$, which has been described by Todd and co-workers.[131] On the basis of its ¹¹B NMR spectrum, the structure was postulated to be that of an 11-vertex *nido* cage possessing an open As_2C_2B pentagonal face in which the two As atoms occupy adjacent positions and the C's are separated by a B atom; the *nido* structure would be expected from its cage electron−pair count of 13 for $n + 2$ pairs. There are no examples of Bi substitution into carborane cages, however, complexes of the type *closo*-1,2-EBiB₁₀H₁₀ (E = P, As, Sb, Bi) are known.[132] The structure of the compound where E = Bi was found to be that of a very distorted icosahedron with the Bi atoms occupying adjacent positions. The distortion in its geometry would be expected from the large size difference between the cage atoms. (The average bond distances are Bi−Bi = 2.957 Å, Bi−B = 2.48 Å, B−B = 1.80 Å.)[132]

There is a varied and interesting chemistry involving the syntheses, structures, and reactivities of the heteroboranes arising from the insertion of group 15 elements into borane cages; the interested reader is referred to Todd's recent overview on main group heteroboranes.[115b]

While there seems to be little doubt that the unsubstituted group 15 elements function as isolobal and isoelectronic replacements of CH units, there is some question regarding the functioning of the heavier group 15 atoms having *exo* polyhedral substituents. It was found that *nido*-PCB₉H₁₁⁻, formed by the action of base on *closo*-1,2-PCB₁₀H₁₁ (see

above), reacted quantitatively with MeI in THF to give P(CH₃)CB₉H₁₁.[126] Although the structure of this phosphacarborane was not determined directly, a *nido* structure in which both the cage carbon and the phosphorus occupy nonadjacent positions on the open pentagonal face the carborane was assigned, on the basis of the crystal structure of its iron sandwich compound, [(3)-7-(CH₃)-1,7-PCB₉H₁₀]₂Fe.[133] Since the Me group was found to be *exo* polyhedrally bound to the phosphorous, the P(CH₃)CB₉H₁₁ could formally be described as being derived from [*nido*-C₂B₉H₁₂]⁻ by the replacement of a CH unit by the isoelectronic and isolobal (CH₃)P⁺ group. The charge-compensated monocarbon *nido* carborane, (CNMe₃)B₁₀H₁₂, was found to react with RPCl₂ (R = Me, Et or Ph) to give *nido*-(CNMe₃)B₁₀H₁₀PR.[134] The low temperature X-ray crystal structure of the compound where R = Ph is shown in Figure 54.[134] In this compound the P atom resides above the open pentagonal face of the carborane but is severely slipped toward the two boron atoms that are opposite the cage carbon atom, the average P−B(9,10) distance is 2.008 ± 0.010 Å which is significantly shorter than the 2.364 ± 0.017 Å found for the P−B(8,11) distance. Thus, the compound was viewed as a *nido*-(CNMe₃)B₁₀H₁₀ fragment with a PPh unit bridging two adjacent boron atoms. Its structure was quite similar to that reported by Tolpin and Lipscomb for the anion, [(CHPh)B₁₀H₁₀(CPh)]⁻,[135] upon replacement of the PPh by CHPh and CNMe₃ by CPh.

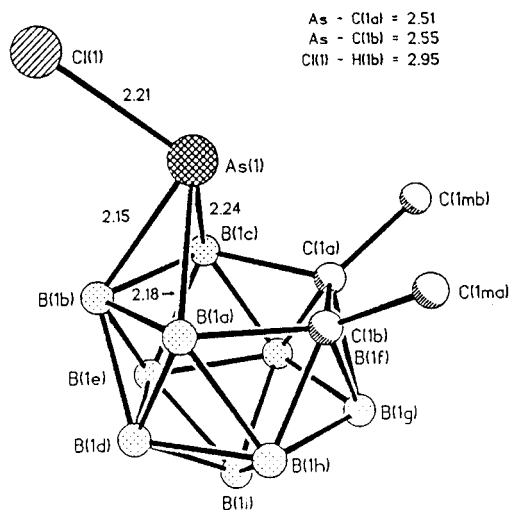The dicarbacarboranes have been found to react with phosphorous and arsenic di- and trihalides, but
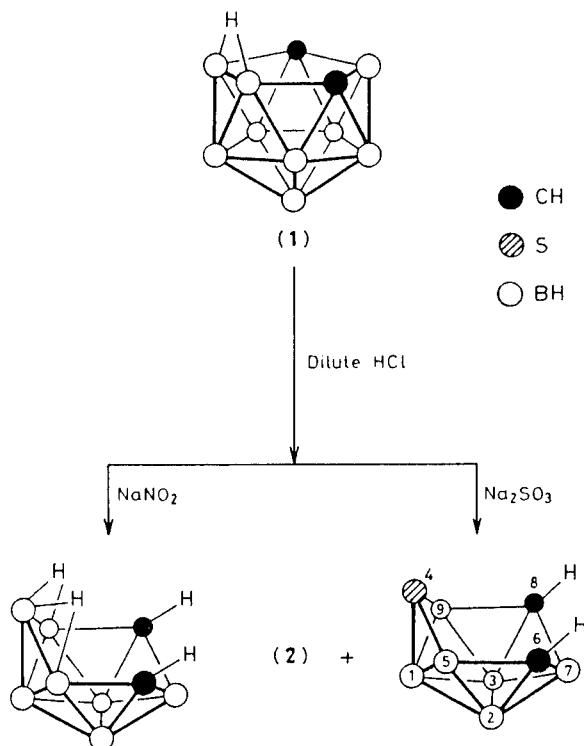
As – C(1a) = 2.51
As – C(1b) = 2.55
Cl(1) – H(1b) = 2.95

Figure 55. Crystal structure of 1-Cl-2,3-(Me)$_2$-1,2,3-AsC$_2$B$_9$H$_{11}$. (Reprinted with permission from ref 137. Copyright 1991 Elsevier Sequoia.)

the reactions seem to be quite sensitive to the nature of the starting carborane. In 1974, Smith and Hawthorne found that while the reaction of the monoanion, [7,8-C$_2$B$_9$H$_{12}$]$^-$, or the dilithium salt, Li$_2$[7,8-C$_2$B$_9$H$_{11}$], with CH$_3$AsBr$_2$ produced mainly uncharacterizable polymeric materials, the use of Tl$_2$[7,8-C$_2$B$_9$H$_{11}$] afforded the icosahedral *closo* arsa-carborane, 3-Me-3-As-1,2-C$_2$B$_9$H$_{11}$, in 30% yield.[136] In like manner the dithallium salt was found to react with the series RAsX$_2$ (R = CH$_3$, X = Br; R = Ph, *n*-C$_4$H$_9$, X = Cl) to give the corresponding 3-R-3-As-1,2-C$_2$B$_9$H$_{11}$ in varying yields.[136] A *closo* icosahedral structure for these compounds was assigned on the basis of ^{11}B and ^{1}H NMR spectra. This structural assignment was supported by the later work of Jutzi and co-workers who found both PCl$_3$ and AsCl$_3$ reacted with Li$_2$[Me$_2$C$_2$B$_9$H$_9$] to give ClE[Me$_2$C$_2$B$_9$H$_9$] (E = P, As).[137] The structure of the complex where E = As was determined by X-ray crystallography and was found to have a distorted icosahedral structure, as shown in Figure 55.[137] The arsenic was not symmetrically bound to the C$_2$B$_3$ open face of the carborane but was slipped toward the boron side of the ring such that the carborane was η^3-bonded to capping arsenic atom. The relevant distances reported were As−B(1b) = 2.15 Å, As−B(1a,c) = 2.21 ± 0.03 Å, and As−C(a,b) = 2.53 ± 0.02 Å. This structure was quite similar to that of the THF−stannacarborane complex, shown in Figure 41, and also to that of the [(C$_5$Me$_5$)$_2$As]$^+$; the equivalent distances are 2.38 Å, 2.46 ± 0.02 Å, and 2.78 ± 0.08 Å for the THF−stannacarborane complex[60] and 2.19 Å, 2.38 ± 0.01 Å, and 2.66 ± 0.01 Å for the [(C$_5$Me$_5$)$_2$As]$^+$.[138] 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 exopolyhedral. This view was supported by the fact that the ClE[Me$_2$C$_2$B$_9$H$_9$] (E = P, As) heterocarboranes reacted with AlCl$_3$ to give a neutral adduct of the form ClE[Me$_2$C$_2$B$_9$H$_9$]·AlCl$_3$, in which the AlCl$_3$ group was coordinated to E.[137] Both ClP[Me$_2$C$_2$B$_9$H$_9$] and ClAs[Me$_2$C$_2$B$_9$H$_9$] were found to react with *i*-PrMgCl to give the isopropyl derivatives, *i*-PrE[Me$_2$C$_2$B$_9$H$_9$]. At least in the case of the phos-

phacarborane the method was found to be superior to the direct reaction of Li$_2$[Me$_2$C$_2$B$_9$H$_9$] with *i*-PrPCl$_2$. The reaction of ClP[Me$_2$C$_2$B$_9$H$_9$] with AgBF$_4$ resulted in the replacement of the Cl by a F atom to give FP[Me$_2$C$_2$B$_9$H$_9$]. All were assumed to have the slip-distorted *closo* structure shown in Figure 55.[137] Phosphine fragments have also been inserted into the smaller C$_2$B$_4$ cages, but the structures of the resulting phosphacarboranes are open to question. The double salt Na/Li[2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$] was found to react with [2,4,6-(*t*-C$_4$H$_9$)$_3$C$_6$H$_2$]PCl$_2$ to give the phosphacarborane formulated by the authors as *closo*-1-[2,4,6-(*t*-C$_4$H$_9$)$_3$C$_6$H$_2$]-1-P-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ in 38% yield.[139] 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 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 was shifted upfield by about 283 ppm from its precursor, [2,4,6-(*t*-C$_4$H$_9$)$_3$C$_6$H$_2$]PCl$_2$, was taken as further evidence of π-type complex. On the other hand, Sneddon and co-workers found very different results from the reaction of NaLi[2,3-(R)$_2$-2,3-C$_2$B$_4$H$_4$] (R = Et, Bz) and R′PCl$_2$ (R′ = Ph, *t*-Bu, Me).[140] The ^{11}B NMR spectra, combined with an *ab initio*/IGLO/NMR study indicated that the resulting phosphacarboranes were 7-vetex cages, best formulated as *nido*-6-R′-3,4-(R)$_2$-6,3,4-PC$_2$B$_4$H$_4$. The ^{31}P NMR resonances of the products were in the δ +16.4 ppm to δ +112.9 ppm range, which are significantly downfield from that found for 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 exopolyhedral 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$_9$H$_{11}$$^-$ with MeI to give *nido*-P(Me)CB$_9$H$_{11}$.[126] 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,[137,139] while in others a four-electron donor model seems to be more useful.[140] 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$_9$H$_{11}$ discussed above was described as arising from the coordination of a lone pair of P electrons with a Me$^+$, giving a three-electron donor MeP$^+$ moiety that associates with a 23-cage-electron [CB$_9$H$_{11}$]$^-$ fragment, to generate the required 13 electron pairs for a stable 11-vertex *nido* structure. Alternatively, the *nido*-P(Me)CB$_9$H$_{11}$ 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

Scheme 4

(1)

● CH
⊘ S
○ BH

Dilute HCl

NaNO₂   Na₂SO₃

(2)   +

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 electrons.[3] However, in many of the heterocarboranes neither the geometry nor the number of cage electrons are simply described. In the groups 13 and 14 metallacarboranes the capping metals are slip distorted (see Figures 22, 23, and 37) and when the metals react with Lewis bases to form adducts, slip distortion increases (see Figures 24−28 and 39−45). 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,[141] to this end we have used the theory 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 was found in the original literature; the confusion thus introduced by these multiple descriptors mirrors those that are currently existing in the literature.

F. Complexes of the Group 16 Elements

The only group 16 element to be discussed is sulfur. Although there are reports of the incorporation of oxygen, selenium, and tellurium atoms into borane cages,[115,142,143] the studies on carboranes concern only the insertion of sulfur atoms. The most general synthetic methods involve the reaction of a carborane anion with either a sulfite ion or with elemental sulfur. For example, the reaction of the "carbons apart", *nido*-[7,9-$C_2B_9H_{12}$]⁻, with NaNO₂ or Na₂SO₃ in dilute HCl produced the cage degradation products, *arachno*-6,8-$C_2B_7H_{13}$ or *arachno*-4,6,8-$SC_2B_6H_{10}$,
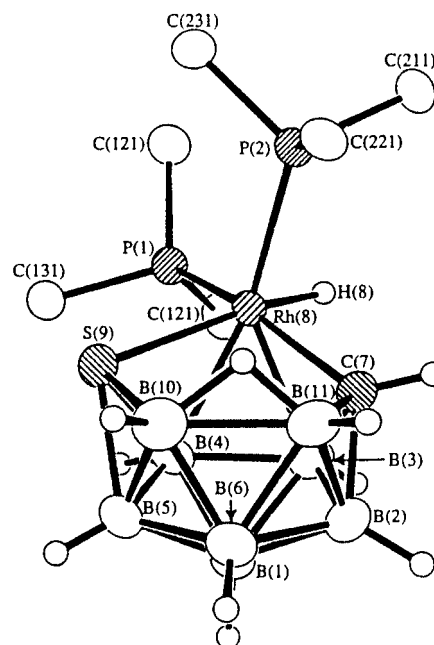

Figure 56. Crystal structure of *nido*-[8,8-(PPh₃)₂-8-H-8,7,9-RhCSB₈H₁₀]. (Reprinted from ref 148. Copyright 1992 American Chemical Society.)

according to Scheme 4.[144] Similar reactions with the "carbons adjacent" *nido*-7,8-[$C_2B_9H_{12}$]⁻ resulted in the formation of less cage degradation product *nido*-7,8,10-$C_2SB_8H_{10}$.[145] The *nido* structures, which were assigned on the basis of their ¹H and ¹¹B NMR spectra, illustrate that the S is acting as a four-electron donor in that it "replaces" the four-electron group of a BH unit and two bridging hydrogens in a *nido*-7,8-$C_2B_9H_{12}$ molecule. A *nido* structure was also supported by combined UV photoelectron/MNDO studies.[146] Selective degradation of [$C_2B_{10}H_{13}$]⁻, with KHSO₃ with concomitant insertion of sulfur atom produced the monocarbon thiacarborane, *arachno*-4,6-CSB_7H_{11}.[147] The reaction of *arachno*-4-CB_8H_{14} with excess sulfur resulted in the direct insertion of a sulfur atom to give *arachno*-6,9-CSB_8H_{12}, whose structure is that of the *arachno*-6,9-CNB_8H_{13}, shown in Figure 51, with the replacement of the NH by a S atom.[119] The *arachno* carborane was found to react with [RhCl(PPh₃)₃] in the presence of base to give the metallacarborane, 8,8-(PPh₃)₂-8-H-8,7,9-RhCSB₈H₁₀ as shown in eq 9.[148] The structure of this metalla-

$$[RhCl(PPh_3)_3] + [CSB_8H_{12}] + base \rightarrow$$
$$[(PPh_3)_2HRhCSB_8H_{10}] + PPh_3 + baseH^+Cl^- \quad (9)$$
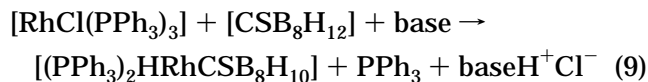
carborane, shown in Figure 56, is that of a *nido* cluster containing a bridging hydrogen and a metal-bound hydride;[148] the *nido* structure is also the one expected on the basis of the electron-counting rules. Thermolysis of the rhodathiacarborane resulted in a two-electron loss, via the elimination of an H₂ molecule, to form *closo*-[1,1-(PPh₃)₂-1,2,3-RhCSB₈H₉, whose structure is shown in Figure 57.[148] Subsequent work has shown the *arachno*-6,9-CSB_8H_{12} to be a versatile ligand that can add metal groups directly or after the directed elimination of one or two boron vertices.[149] Group 16 heterocarboranes have also been obtained by carbon insertion into the het-
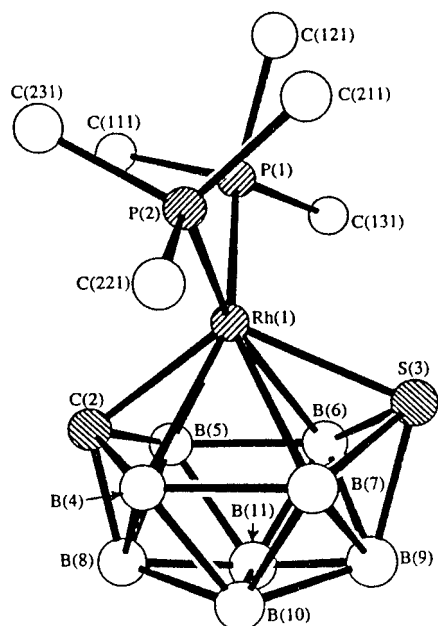
Figure 57. Crystal structure of *closo*-[1,1-(PPh₃)₂-1,2,3-RhCSB₈H₉]. (Reprinted from ref 148. Copyright 1992 American Chemical Society.)

eroboranes. Todd and co-workers have reported the syntheses of several $B_9H_9SCNH_2R$ compounds from the reactions of $B_9H_{11}S$ with the appropriate isocyanide, $C≡NR$.[150] The ^1H and ^{11}B NMR spectra of the compounds indicated an 11-vertex *nido* structure with the S and C atoms from the isocyanide occupying adjacent positions on the open face of the thiacarborane. It was reported that the selenacarboranes could be prepared using this same general procedure.[150]

III. Current and Future Directions

The above discussion clearly demonstrates that main group heterocarboranes possess unique synthetic and structural properties. The group 1 metallacarboranes are not only versatile synthons for the production of a variety of full- and half-sandwich complexes containing main group, *d*-block and *f*-block elements, they have also been shown to possess a rich structural chemistry of their own. The development of convenient synthetic routes to heterocarboranes having both group 13 and group 15 elements offers the possibility of using such compounds as precursors in the formation of semiconducting materials. In this regard, recent work by Hawthorne[74b] on the thermal decomposition of silacarboranes to give silicon mirrors offers the hope that the metallacarboranes will find use as MOCVD sources for thin-film production.

In addition to these potential practical uses of the main group metallacarboranes, a number of fundamental questions have been raised that have yet to be adequately explored. The polyhedral electron-counting rules offer a simple and elegant basis for rationalizing the structures of a number of metallacarboranes clusters.[3–5] However, in the more complex clusters where several different heteroatoms may have been inserted, the structures do not follow a simple pattern. A rule that holds for one heterocarborane may be totally inadequate when applied

to a seemingly similar system. A great deal more structural and theoretical work needs to be done in order to define the limits in which such rules can be safely applied. The syntheses and reactivities of many of the metallacarboranes also offer a intriguing mixture of the boringly obvious and the inexplicable. For example, the general synthesis of many of the half- and full-sandwich metallacarboranes seems to involve a straightforward double displacement reaction between a labile salt of the carborane ligand and the respective heteroatom halide. Yet in some cases, such as with $SnCl_4$, reductive insertion takes place to give the half-sandwich stannacarborane.[81] This was originally rationalized on the basis of the inherent stability of Sn(II) vs Sn(IV); however, it was found that these same carborane ligands gave stable Sn(IV) full-sandwich complexes that could be structurally characterized.[89] The results of the analogous reactions with $GeCl_4$ are even more complex. Depending on the starting conditions and stoichiomertries, three different germacarboranes, a reductively inserted half-sandwich complex,[80] a full-sandwich compound,[81] or a mixed-valence digermanium heterocarborane,[82] have been obtained as the major products for the same carborane.

The relative importance of thermodynamic stability vs kinetic trapping in determining the structures and reaction products of the heterocarboranes have just begun to be explored.

IV. Acknowledgments

V. References

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