

# Recent advances in the chemistry of small cage Main Group metallacarboranes

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## Abstract

This overview presents our significant recent findings in the area of small cage Main Group metallacarboranes during the past several years. The highlights of these findings are as follows. (1) The study on the  $C_4B_8$ -carborane led to the introduction of an unusual 'carbons-apart' carborane species that acts as a restricted electron-acceptor by removing only the valence electrons of a Group 1 or Group 2 metal thus forming the corresponding alkali and alkaline earth metal compounds. Further reactivity studies of these species in solvent extraction of radioactive cesium ion ( $^{137}Cs^+$ ) from nuclear wastes has rekindled our interest to explore new avenues in this area of Main Group metallocarborane research. (2) The syntheses and structures of fully sandwiched anionic lithia- and magnesacarboranes and half-sandwich lithia-, cesia- and magnesacarboranes have exemplified their rich structural and coordination chemistry beyond their existence as versatile synthons for the production of other metallacarboranes of d-block and f-block elements. (3) Synthesis and reactivity studies on half- and full-sandwich gallacarboranes opened up the possibility of using such compounds as precursors in the formation of conducting materials. (4) Even though two germanium atoms are present, the reactivity study on the mixed-valence digermacarboranes with Lewis bases shows no indication of *exo*-polyhedral Ge(IV) atoms being the Lewis acid site. On the contrary, the donor N atoms of the Lewis bases bond exclusively with the apical Ge(II) atom. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Metallacarboranes; Main Group complexes; Half- and full-sandwich

## 1. Background

A rapidly expanding field of cluster chemistry is one involving the construction of polyhedral carborane cages through the incorporation of heteroatoms to form heterocarboranes. When the heteroatom is a metal, the compounds are referred to as metallacarboranes. The chemistry of these species originated with the recognition that the *nido*-carborane dianions,  $C_2B_9H_{11}^{2-}$  and  $C_2B_4H_6^{2-}$ , were similar to the cyclopentadienide ligand ( $Cp^-$ ) in that both could bond to metals using a set of six electrons in delocalized  $\pi$ -type orbitals directed perpendicular to the pentagonal face of the ligand (see Fig. 1) [1–6]. This has ultimately led to the syntheses of metallacarboranes of two general structural types. Half-sandwich complexes in which a metal moiety occupies the missing vertex of a *nido*-car-

borane, to form a *closo*-metallacarborane, or full-sandwich compounds in which a metal occupies a common vertex of two carboranes, to give *commo*-metallacarboranes. Although the  $Cp$ -carborane analogy has proven very useful as a synthetic guide, a number of important features of carborane dianions, such as their dinegative charge and the presence of different kinds of atoms (boron and carbon) in the bonding faces, cause the two ligand systems to exhibit significantly different properties. Consequently, a wide variety of metal complexes of the icosahedral and subicosahedral carborane ligand systems have been synthesized and characterized [2–9]. It is of interest to note that the carborane ligands tend to stabilize high formal oxidation states of the metals; therefore,  $\pi$  complexes with metals such as Cr(IV), Ni(IV) and Sn(IV) have recently been synthesized and structurally characterized. Such oxidation states are not common in other  $\pi$  systems [10,11]. Metallacarboranes are also finding increased applications in catalysis [12–17], boron neutron capture therapy (BNCT) [18,19],

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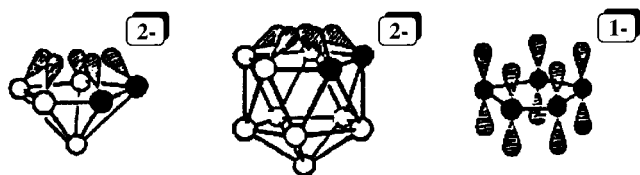


Fig. 1. Relative  $\pi$  overlap with metal:  $C_2B_4H_6^- \geq C_2B_9H_{11}^{2-} > C_5H_5^-$

solvent extraction of radionuclides [20] and ceramics [21,22]. Recent findings in our laboratory (described in the following section) and elsewhere clearly demonstrate that  $C_2B_4$ -carborane-based organometallic chemistry is an emerging area of very considerable scope and versatility [7–11]. Although the metal– $C_2B_4$  carborane ligand interactions are similar to those of the 12-vertex (icosahedral) metallacarboranes, and some of the reactivities are likewise related, the stereochemistry is markedly different. Moreover, oxidative face-to-face ligand fusion, construction of multidecker metal sandwich complexes, formation and isolation of stable Ge(IV), Sn(IV) and Cr(IV) sandwiched species, trinuclear half-sandwich lanthanacarborane and ‘butterfly’ manganacarborane clusters have no known parallel in the icosahedral systems [1–11]. Although the chemistry of  $C_2B_4$ -metallacarboranes has relationships to other areas of organometallic chemistry, it possesses a number of distinct characteristics. Consequently, new frontiers of organometallics have begun to be investigated.

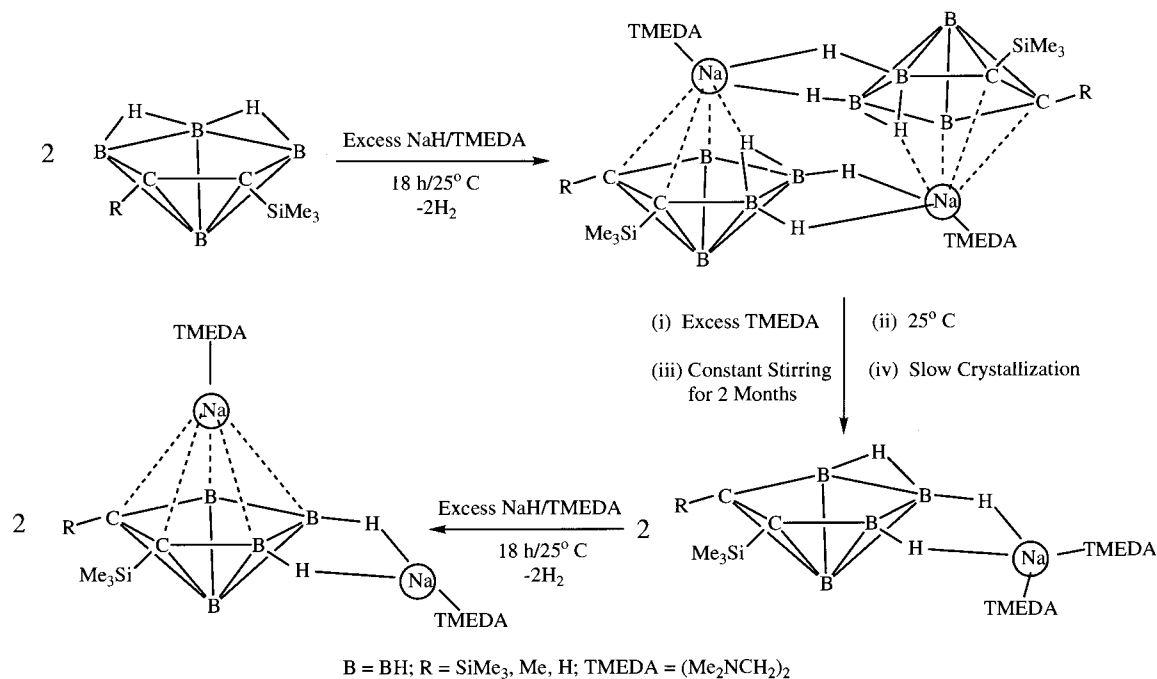
Metallacarboranes are commonly synthesized by the reaction of a halide of the selected metal atom with either the mono- or dianion of a *nido*-carborane. There are two types of arrangements of the facial atoms, one in which the two carbon atoms are directly bonded to one another is called a ‘carbons-adjacent’ isomer, and another in which the carbons are separated by a boron atom is known as a ‘carbons-apart’ isomer. Since the ‘carbons-adjacent’ carborane precursors can be prepared more easily than the ‘carbons-apart’ isomers, most of the published results have been on metallacarboranes formed from the former ligands. However, recent results indicate that, not only are the latter carborane ligands just as effective as the former in bonding to metals, they also have the added advantage of being less susceptible to oxidative cage closure [10,11]. In this overview, highlights of our recent studies in the field of Main Group metallacarborane research will be presented.

## 2. Metallacarboranes 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 have been used mainly as precursors for other metallacarborane

complexes of p, d, and f-block elements and no studies were conducted about their unique structural patterns and coordination chemistry. The carborane fragments of the larger cage systems were synthesized by an initial degradation of *closo*-1,2-(CR) $_2$ B $_{10}$ H $_{10}$  by alcoholic KOH, to produce the monoanions, [(3),1,2-(CR) $_2$ B $_9$ H $_{10}$ ] $^-$ , 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) $_2$ B $_9$ H $_{11}$ ] $^{2-}$  [1b,c]. Since similar results were obtained with different alkali metals or when tetralkylammonium cations were used [1c], the alkali metals were assumed to be innocent spectator ions. The situation in the smaller,  $C_2B_4$  cage system is not so straightforward. For example, the carborane monoanion, can be obtained by the heterogeneous reaction of *nido*-(CR) $_2$ B $_4$ H $_6$  with NaH in THF as shown in Scheme 1.

The main point of interest in this reaction is that the stoichiometry is 1:1, even with the use of excess NaH or a stronger KH base, and at elevated temperatures [23]. A possible explanation for this behavior was provided by the structures of the monosodium compounds, 1-Na(L)-2,3-(SiMe $_3$ ) $_2$ -2,3-C $_2$ B $_4$ H $_5$  (L = THF or TMEDA) [24]. When L = THF, the structure is that of an extended array of Na $_2$ (C $_2$ B $_4$ ) $_2$  dimers that are stacked on top of one another to give a series of –(carborane) $^-$ –Na $^+$ –(carborane) $^-$ – chains, while L = TMEDA the chain structure is broken but the ion cluster dimers remain (see Fig. 2). These compounds are all fairly soluble in nonpolar and low dielectric constant solvents, indicating that the isolated ion clusters are quite stable in solution. Grimes and coworkers have suggested that the deprotonation of *nido*-2,3-RR’C $_2$ B $_4$ H $_6$  (where R = alkyl, aryl, methyl and phenyl; R’ = R, H) with NaH or KH in THF occurred at the surface of MH through the direct reaction of the bridged H with a H $^-$  ion in the hydride lattice [25]. From Fig. 2 it is apparent that the second bridge hydrogen in an ion pair formed by the carborane monoanion and a solvated sodium ion would be effectively blocked from a direct reaction with a second hydride lattice site, thus preventing a second deprotonation. On the other hand, soluble bases, such as BuLi, react readily with either the monosodium compound or the neutral *nido*-carborane to form the mixed sodium/lithium or dilithium complexed dianion [24]. Direct Group 1 metal–cage interaction was found in the TMEDA-solvated dilithium species, *closo-exo*-4,5-[( $\mu$ -H) $_2$ Li(TMEDA)]-1-Li(TMEDA)-2,3-(SiMe $_3$ ) $_2$ -2,3-C $_2$ B $_4$ H $_4$ . The crystal structure of this compound shows that the two lithiums occupy quite different positions relative to the carborane face, with one lithium occupying an apical position above the C $_2$ B $_3$  face, and the other located exopolyhedrally and about halfway between B(4) and

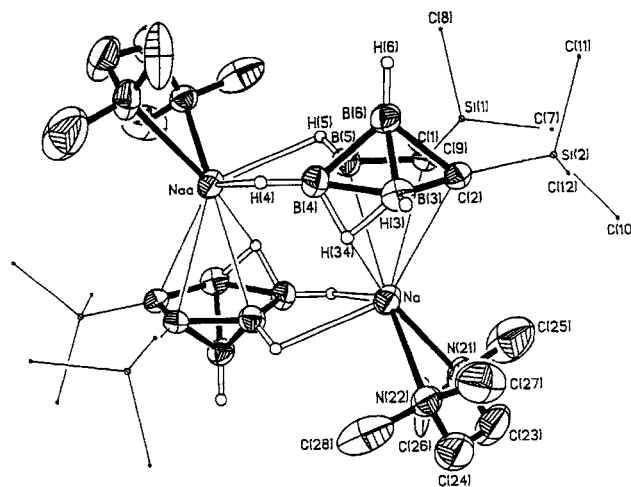


Scheme 1.

B(5) and directed down below the plane of the C<sub>2</sub>B<sub>3</sub> face (the Li(2)–B(4) and Li(2)–B(5) bond distances are 2.226 and 2.241 Å, respectively (see Fig. 3)). In contrast to the structures of the sodium species shown in Fig. 2, there is not extensive association between metallacarborane units. In an effort to ascertain the extent to which these lithium arrangements are dictated by interactions within the dilithiacarborane itself rather than crystal lattice forces, MNDO-SCF calculations were carried out on the model compound *closo-exo*-4,5-[(μ-H)<sub>2</sub>Li(TMEDA)]-1-Li(TMEDA)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> which showed that the structure shown in Fig. 3 can be assumed to be a minimum energy structure arising from interactions among the carborane and its two Li(TMEDA) groups [24]. The orientations of the TMEDA molecules in Fig. 3 seem to be governed more by electrostatic rather than metal-ligand covalent interactions. Although crystal structures could not be obtained for the mixed sodium/lithium compounds, the <sup>7</sup>Li-NMR spectrum is consistent with a structure in which the Li is *exo*-polyhedral and the Na occupies the apical position. The structures of the extensively solvated species, [Li(TMEDA)<sub>2</sub>]<sup>+</sup>[*nido*-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>]<sup>-</sup> and *nido-exo*-4,5-[(μ-H)<sub>2</sub>Na(TMEDA)]<sub>2</sub>-2-(SiMe<sub>3</sub>)-3-(Me)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (Fig. 4), show that they are composed of discrete, well separated cation and anion units within the unit cell [7]. It is significant that these monoanions react readily with NaH to give either the mixed-lithium/sodium or disodium compounds of the dianion (Scheme 1). Therefore, it seems that steric effects are as important as inherent acid/base strength

in determining the reactivity of the *nido*-carborane anions. 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 carboranes are the ones produced directly from the cage-opening reactions of *closo*-C<sub>2</sub>B<sub>4</sub>-carboranes (Scheme 2 and Fig. 5) [27a,b].

Careful reaction of either the disodium or dilithium-complexed carborane dianion with HCl results in the protonation of the two adjacent borons (similar to B(4) and B(5) in Fig. 5) to give the monometallated species,

Fig. 2. Perspective view of a discrete dimeric unit of *nido*-1-Na(TMEDA)-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>.

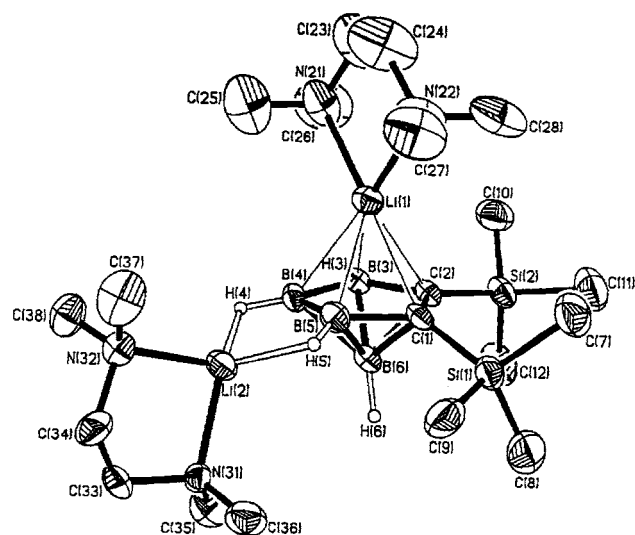


Fig. 3. Perspective view of the TMEDA-solvated 'carbons-adjacent' dilithiacarborane.

whose structure is similar to that of the monosodium compound (see Fig. 6) [27c]. However, attempts at further protonation led to the decomposition of the carborane.

Slow sublimation of the TMEDA-solvated monolithium carborane complex at 160–170°C over a period of 6–7 h in vacuo produced the full-sandwich lithiacarborane complex,  $[\text{Li}(\text{TMEDA})_2][\text{compro-1,1}'\text{-Li}\{2,3\text{-}(\text{SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_5\}_2]$ , as a colorless crystalline solid [28]. The mechanism of the formation of this complex is not known. Since alkylolithiums 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 crystal structure, shown in Fig. 7 [28]. 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

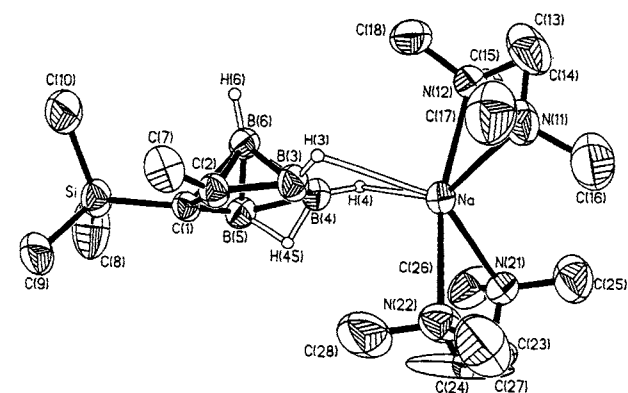
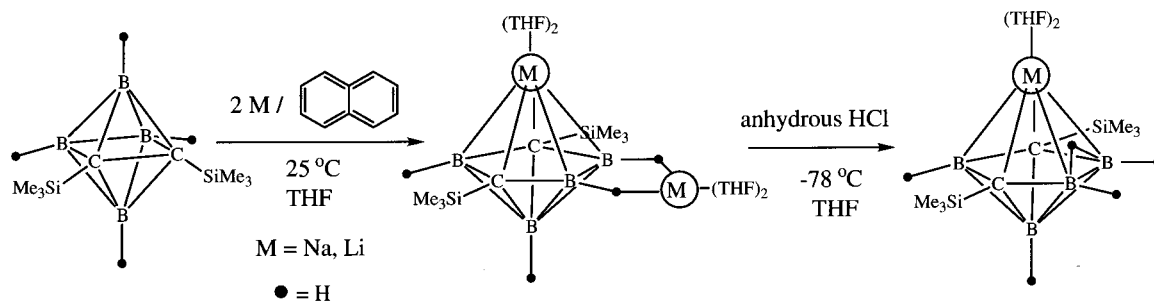


Fig. 4. X-ray structure of a discrete monomeric monosodium salt of 2,3-dicarba-*nido*-hexaborate(1-).

[24], but are comparable to the corresponding metal-centroid distance of 2.008 Å found in the  $[\text{Cp}_2\text{Li}]^-$  sandwich complex [29]. 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 Fig. 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 H's on the bonding faces.

Further investigation of the oxidative cage closure reactions of the bis(trimethylsilyl)-substituted *nido*-2,3- $\text{C}_2\text{B}_4$ -carboranes revealed that there is an accompanying oxidative cage fusion process that leads to the formation of a novel tetracarbon-carborane isomer, 2,4,7,9- $(\text{SiMe}_3)_4\text{C}_4\text{B}_8\text{H}_8$ , whose structure is based more on the cuboctahedron than on the icosahedron [30]. This new geometry is of interest in that a cuboctahedral structure was proposed by Lipscomb for the key intermediate in the diamond-square-diamond (DSD) mechanism of the thermal conversion of *closo*-1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$  to *closo*-1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$  [31]. The 'carbons-apart' tetracarbon-carborane was found to be thermally unstable, but did not isomerize to either of Grimes' 'carbons-adjacent' isomers, moreover, the use of Grimes' method for the oxidative ligand fusion, involving the reaction of  $\text{FeCl}_2$  with the monosodium salt of *nido*-2,3- $(\text{SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_6$ , failed to produce the carbons-adjacent analogues of  $(\text{SiMe}_3)_4\text{C}_4\text{B}_8\text{H}_8$  [30]. The most surprising observation of all was its reactivity toward alkali and alkaline-earth metals where the 2,4,7,9- $(\text{SiMe}_3)_4\text{C}_4\text{B}_8\text{H}_8$ -cage acts as a restricted electron-acceptor by removing only the valence electrons of a Group 1 or Group 2 metal [32]. For example, the room temperature reaction between a TMEDA solution of 2,4,7,9-tetracarba-*nido*-dodecaborane (12),  $(\text{SiMe}_3)_4\text{C}_4\text{B}_8\text{H}_8$ , and excess cesium metal, in the absence of naphthalene and aromatic solvents, produced the novel EPR-silent species,  $[\text{exo}-(\mu\text{-H})_2\text{Cs}(\text{TMEDA})]\text{-1-Cs-2,4,7,9-}(\text{SiMe}_3)_4\text{-2,4,7,9-C}_4\text{-B}_8\text{H}_8]_n$ , which is the first example of a cesium compound in which the metal interacts with the carborane cage sequentially to form repeating metal-carborane units [33]. It has been demonstrated that the formation of the final diamagnetic dicesiacarborane product involves a paramagnetic monocesiacarborane intermediate as in the analogous reaction [32] of the  $\text{C}_4\text{B}_8$ -carborane with the lithium metal. The X-ray diffraction study on the cesium complex confirmed its polymeric structure in which each  $\text{C}_4\text{B}_8$ -carborane fragment serves as a ligand to two Cs atoms, bonded to one through an open six-membered face and to the other via upper- and lower-belt M–H–E (where E = B or C) interactions (Fig. 8) [33]. This structural feature is somewhat similar to that of the Sr complex of the  $[\text{C}_2\text{B}_{10}\text{H}_{12}]^{2-}$  ligand, reported by Hawthorne and coworkers [34]. However, the interatomic distances of



Scheme 2.

Cs to the carborane cages are such that it could be regarded as a cesium–carborane complex in which some degree of interaction exists between the metal and the  $\pi$ -electron density on the carborane cage. Since this cesium compound can also be prepared by an ion-exchange reaction directly from lithium, sodium or potassium salts of the  $C_4B_8$ -cage (see Fig. 8(b)), further study of this and related compounds in solvent extraction of radioactive cesium metal ( $^{137}\text{Cs}$ ) from nuclear waste is envisioned.

### 3. Metallacarboranes of Group 2 elements

The half- and full-sandwich magnesium complexes in the  $C_2B_4$  cage system have been recently synthesized and structurally characterized [35]. The magnesacarboranes were prepared by the reactions of either the ‘carbons-adjacent’ monosodium carboranes or the ‘carbons-apart’ dilithium compounds with various metallating reagents, as outlined in Scheme 3. As can be seen from this scheme, the products of these reactions are complex functions of the stoichiometries of the reactions, the nature of the carborane precursors and the nature of the metallating reagents. The most straightforward results are those obtained from the reactions of the TMEDA-solvated dilithiacarborane,  $[\text{Li}(\text{TMEDA})]_2[2,4-(\text{SiMe}_3)_2-2,4-C_2B_4H_4]$ , and  $\text{MgBr}_2$ , where the products were determined by the stoichiometry of the reactions. A 1:1  $\text{MgBr}_2$ -to-carborane molar ratio produced the half-sandwich magnesacarborane, *closo*-1-Mg(TMEDA)-2,4-( $\text{SiMe}_3$ )<sub>2</sub>-2,4- $C_2B_4H_4$ , while a 1:2  $\text{MgBr}_2$ -to-carborane molar ratio gave the full-sandwich compound,  $[\textit{commo}$ -1,1'-Mg- $\{2,4-(\text{SiMe}_3)_2-2,4-C_2B_4H_4\}_2]^{2-}$  [35]. Similarly, the full-sandwich carbons-adjacent *commo*-magnesacarboranes (Scheme 3) were produced in high yields from the 1:2 stoichiometry of the dialkyl magnesium with either the THF or the TMEDA-solvated monosodium compounds of the *nido*-carborane precursors [35]. One of the most surprising results in this study was the formation of the *exo*-sandwich magnesacarborane, *commo*-

*exo*-4,4',5,5'-Mg(TMEDA)[2-( $\text{SiMe}_3$ )-3-(Me)-2,3- $C_2B_4H_5$ ]<sub>2</sub> (Scheme 3), from the reaction of  $\text{MeMgBr}$  with  $[\text{Na}(\text{TMEDA})][2-(\text{SiMe}_3)-3-(\text{Me})-2,3-C_2B_4H_5]$  under conditions identical to those used in the synthesis of the *closo*-magnesacarborane. This compound was produced in 94% yield, the highest for any magnesacarborane, from a 1:1 Grignard-to-carborane molar ratio. Scheme 3 also outlines a tentative rationalization for this reaction. As in the formation of half-sandwich magnesacarborane, it has been postulated that the initial product in the reaction is the methylmagnesacarborane, *closo*-1-(TMEDA)Mg( $\text{CH}_3$ )-2-( $\text{SiMe}_3$ )-3-(Me)-2,3- $C_2B_4H_5$ . This intermediate, instead of dimerizing with the loss of methane, undergoes a disproportionation reaction to give *exo*-sandwich magnesacarborane and a dialkyl magnesium compound, through a Schlenk-type equilibrium [36]. Irrespective of the mechanism, the almost quantitative formation of this species shows that it is an extremely stable compound. The formation of the *exo*-sandwich magnesacarborane instead of a more conventional *closo*-product could be the result of less steric crowding in the initially formed *closo*-methylmagnesacarborane intermediate,

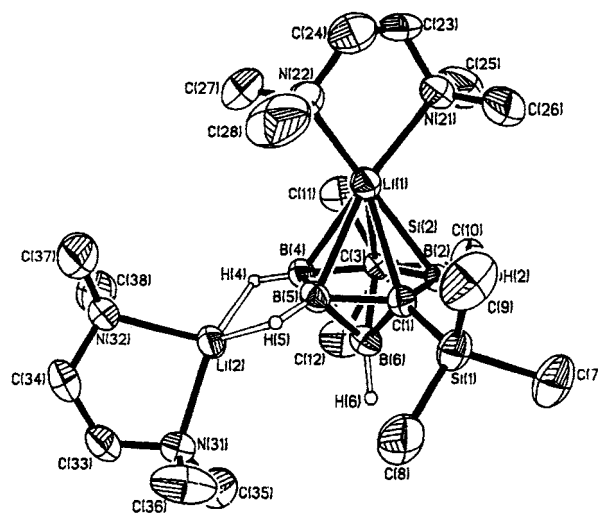


Fig. 5. Perspective view of the TMEDA-solvated ‘carbons-apart’ dilithiacarborane.

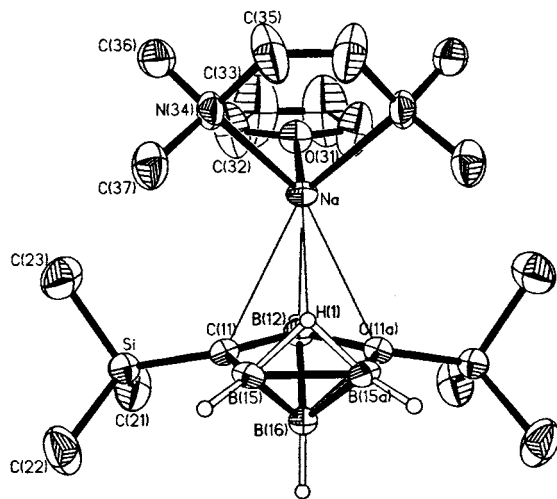


Fig. 6. X-ray structure of the discrete monomeric unit of *nido*-1-Na[(TMEDA)(THF)]-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>.

which in turn would allow dimerization directly between the two capping magnesium atoms via a double Me and carborane bridge. Such doubly bridged structures have been proposed as transition states in the ligand exchange processes that proceed through Schlenk equilibria [37]. In the formation of *closo*-magnesiumcarborane, the presence of the second, bulky SiMe<sub>3</sub> group could prevent such bridging and restrict interaction of the two methylmagnesiumcarborane intermediate to the sides opposite the cage carbons as found in Fig. 9. The structure of the half-sandwich compound is that of a dimeric [*closo*-1-Mg(TMEDA)-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub> unit in which the solvated Mg atoms occupy apical positions above the C<sub>2</sub>B<sub>3</sub> 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

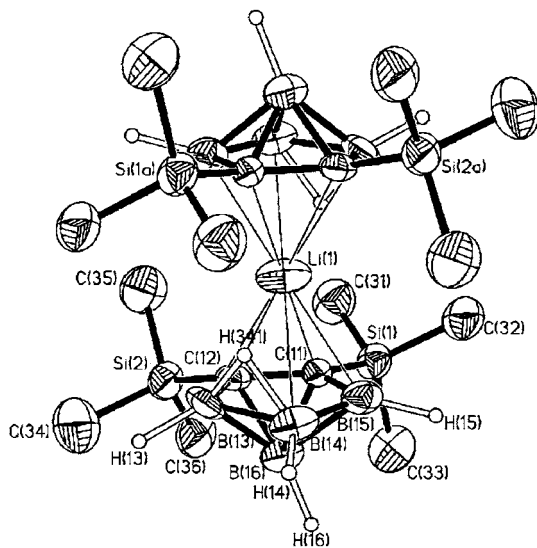


Fig. 7. Perspective view of the anionic full-sandwich lithiacarborane complex.

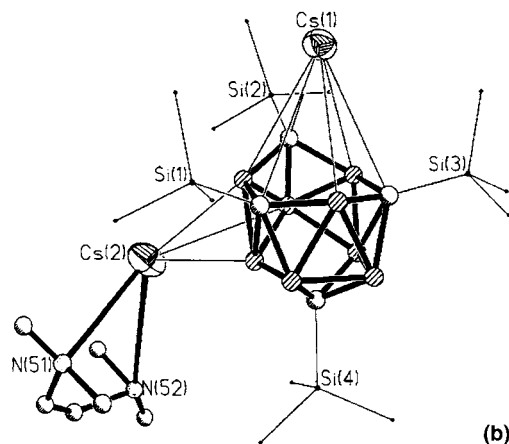
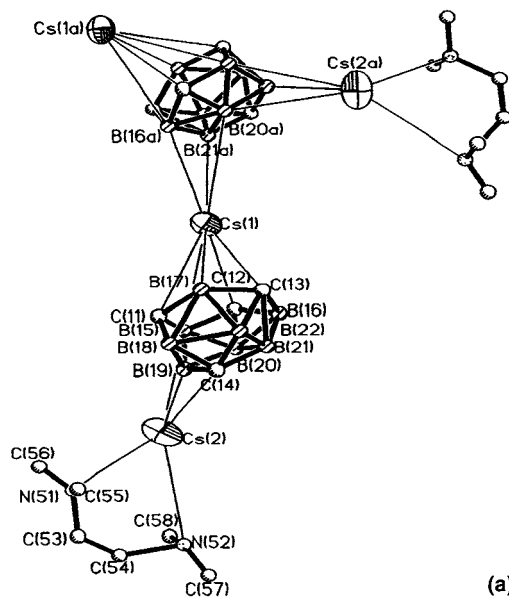


Fig. 8. X-ray structure of the dicesiacarborane complex (a) a cesiacarborane dimer in a polymeric chain (b) perspective view of a single unit of the dicesiacarborane.

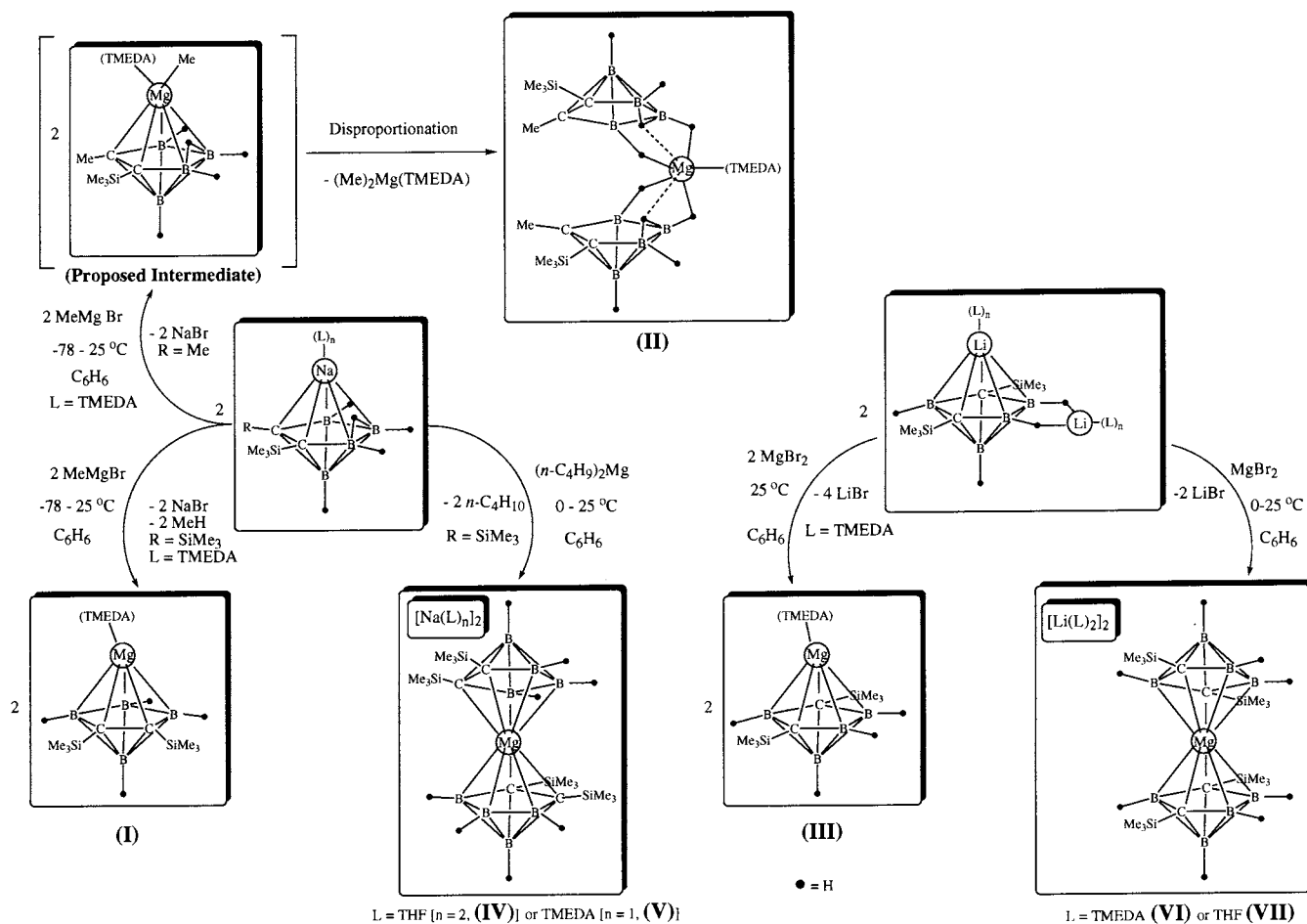
(see Fig. 9). In each half-sandwich complex, the Mg atom is not symmetrically bonded to the C<sub>2</sub>B<sub>3</sub> face but is dislocated, or slipped, towards the unique boron, B(14 or 24). Since the carboranes are η<sup>5</sup>-bonded to the Mg in the full sandwich complex, shown in Fig. 10, this 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. In contrast to the very symmetric bonding in the sandwich complex, shown in Fig. 10, the *exo*-sandwich magnesiumcarborane shows such extreme slippage that the compound is better described as one in which a TMEDA-solvated magnesium is exopolyhedrally bound to the two cages through a pair of Mg–H–B bridges of unequal strength (see Fig. 11). The bond distances in this compound are comparable to the shorter metal–carborane atom distances in compounds shown in Figs. 9 and 10 [35b].

Recently, the Mg complex of the tetracarbon carborane,  $(\text{THF})_2\text{Mg}(\text{SiMe}_3)_4\text{C}_4\text{B}_8\text{H}_8$ , has been prepared and structurally characterized (Scheme 4) [32]. The structure, shown in Fig. 12, 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  $(\text{THF})_2\text{Mg}$  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 [32]. It is not known whether this magnesacarborane is an isolated example or the first of a series of structurally new metallocarboranes. Nonetheless, the results suggest that the ‘carbons-apart’  $\text{C}_4\text{B}_8$ -carborane can be effectively used to oxidize a single metal-atom species, thus facilitating the formation of the corresponding 1:1 ionic or predominantly ionic products without the loss of any metal- or cage-bound moieties. If this is proven correct, the present methodology would constitute a general approach to the oxidative synthesis of a series of ionic (noncoordinating) or predominantly ionic (weakly coordinating) metallocarborane species, that would be of

both theoretical and practical interest. Thus, this work exemplifies a potentially useful application of a carborane cage system in the production of unique non- or least-coordinating anions for use in Ziegler–Natta catalysis.

#### 4. Metallocarboranes of Group 13 elements

There has been a number of reports on the syntheses, structures and reactivities of half-sandwich alkylgal-lacarboranes that incorporated both the ‘carbons-adjacent’ and ‘carbons-apart’  $\text{C}_2\text{B}_4$ -carborane ligands [38]. These reports described that the reactive site of the molecule is the apical gallium metal which acts as a Lewis acid by complexing with Lewis bases, such as 2,2'-bipyridine, 2,2'-bipyrimidine, and 2,2':6',2'-terpyridine. In each complex, the apical gallium is slip-distorted away from the cage carbons and, in the case of the  $1,2,4\text{-Ga}(\text{CR})_2\text{B}_4\text{H}_4$ , the metal is away from the unique boron above the  $\text{C}_2\text{B}_3$  bonding face. Thus, these reports exemplified the pattern of reactivities that are not only inherent in these half-sandwich *t*-butylgal-



Scheme 3.

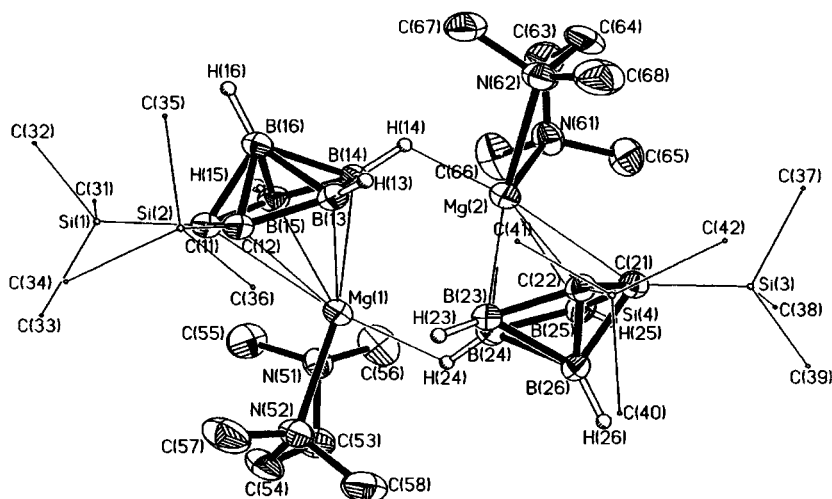


Fig. 9. Perspective view of the dimeric half-sandwich magnesacarborane.

laccarboranes, but also identical to those of the other Group 13 and Group 14 half-sandwich metallocarboranes in both the  $C_2B_4$  and  $C_2B_9$ -carborane ligand systems [38]. It is of interest to note the divergence of the reaction products in the  $C_2B_4$  and  $C_2B_9$  cage systems; the former cage system has produced only half-sandwich complexes, while the latter system yielded only the full-sandwich metallocarboranes. This is probably due to the nature of the metal reagent used in the syntheses, rather than a difference in bonding preferences in the two cage systems. Thus, the half-sandwich complexes were obtained from metal alkyl reagents [38], such as  $Ga(CH_3)_3$ ,  $[(t-C_4H_9)_2GaCl_2]_2$ , or  $(Me_2CH)InI_2$ , while the full-sandwich complex resulted when  $GaCl_3$  as the metallating agent [39]. When  $GaCl_3$  is substituted for  $[(t-C_4H_9)_2GaCl_2]_2$  in the reaction with the dilithium complexed  $[2,n-(SiMe_3)_2-2,n-C_2B_4H_4]^{2-}$  dianion in 1:2 stoichiometry in TMEDA, the full-sandwich compound,  $[commo-1,1'-Ga(2,n-(SiMe_3)_2-1,2,n-GaC_2B_4H_4)_2]^-$ , ( $n = 3, 4$ ) was obtained (see Scheme 5 and Figs. 13 and 14) 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,*n*-( $SiMe_3$ )<sub>2</sub>-1,2,*n*- $GaC_2B_4H_4$  (Fig. 15) [40], which was further converted to the corresponding *closo*-gallacarborane hydride (Fig. 16) and alkyl derivatives [41]. The structures of the gallacarboranes show that the gallium atoms are not equally bonded to the atoms in the  $C_2B_3$  faces of the carboranes but are slipped toward the more boron rich sides of the faces. Perhaps, slippages in the full-sandwich gallacarboranes are such that maximum differences in the Ga– $C_2B_3$  distances were 0.34 Å in the structure depicted in Fig. 13 and 0.45 Å in the other isomer shown in Fig. 14. The distortions were much larger in the half-sandwich complexes such that the carboranes are better described as being  $\eta^3$ - or  $\eta^2$ -bonded to the apical gallium metal [40].

A surprising formation of Ga(II)–Ga(II)-linked digallacarborane was observed in the reaction of  $[Ga(t-Bu)Cl_2]_2$  with the disodium compound of the ‘carbons-apart’ carborane dianion, in 1:2 stoichiometry [42]. The two major products were half-sandwich gallacarborane and a novel digallacarborane, which could be separated by fractional distillation and sublimation. The crystal structure of the digallacarborane (Fig. 17) exhibits the shortest Ga–Ga bond distances known to date. All evidence shows that there is no multiple metal–metal bonding. While the mechanism for the formation of this species is not known, the dependence on the nature of the Group 1 metal in the precursor indicates that this compound is probably not the result of a simple elimination of *t*-Bu groups during the isolation of the half-sandwich gallacarborane via vacuum distillation [42].

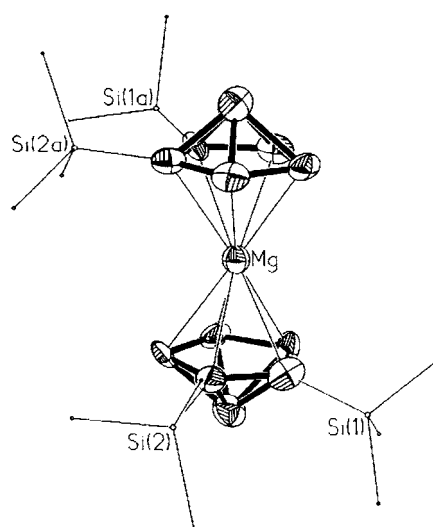
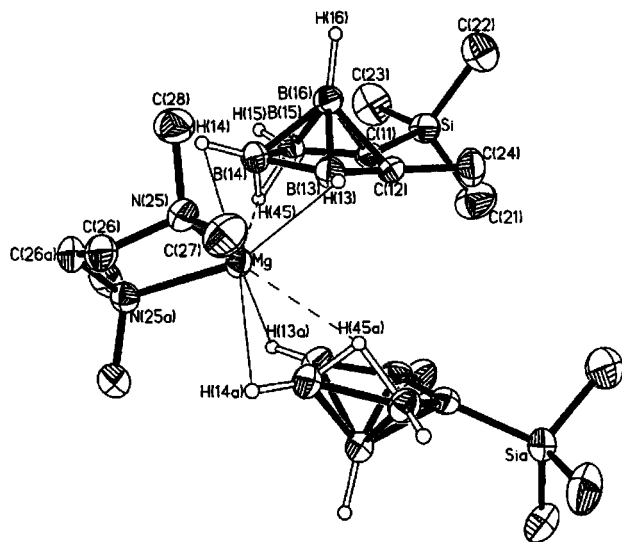
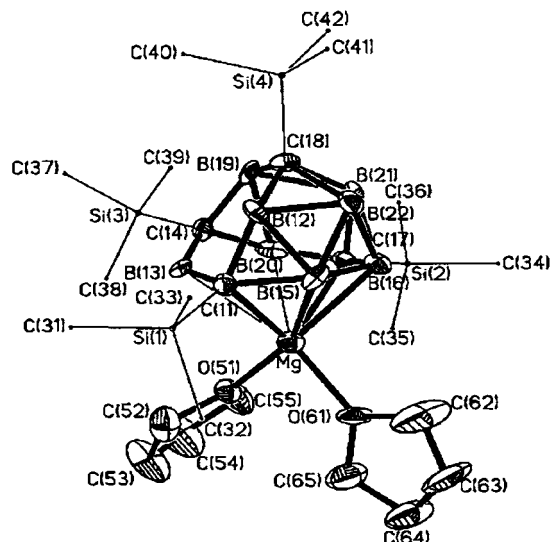


Fig. 10. ORTEP drawing of the anionic full-sandwich magnesacarborane.

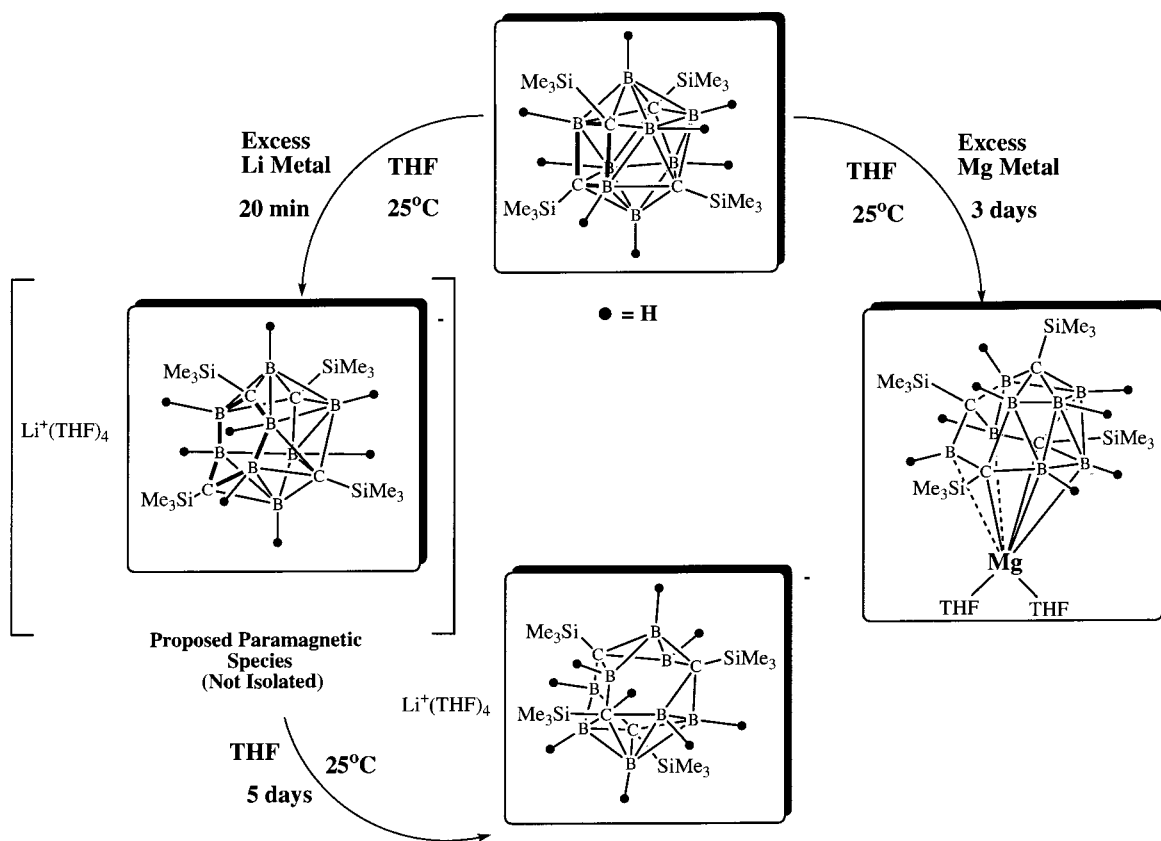


Fig. 11. ORTEP drawing of the *exo*-sandwich magnesacarborane.Fig. 12. Perspective view of the  $(\text{THF})_2\text{Mg}(\text{SiMe}_3)_4\text{C}_4\text{B}_8\text{H}_8$ .

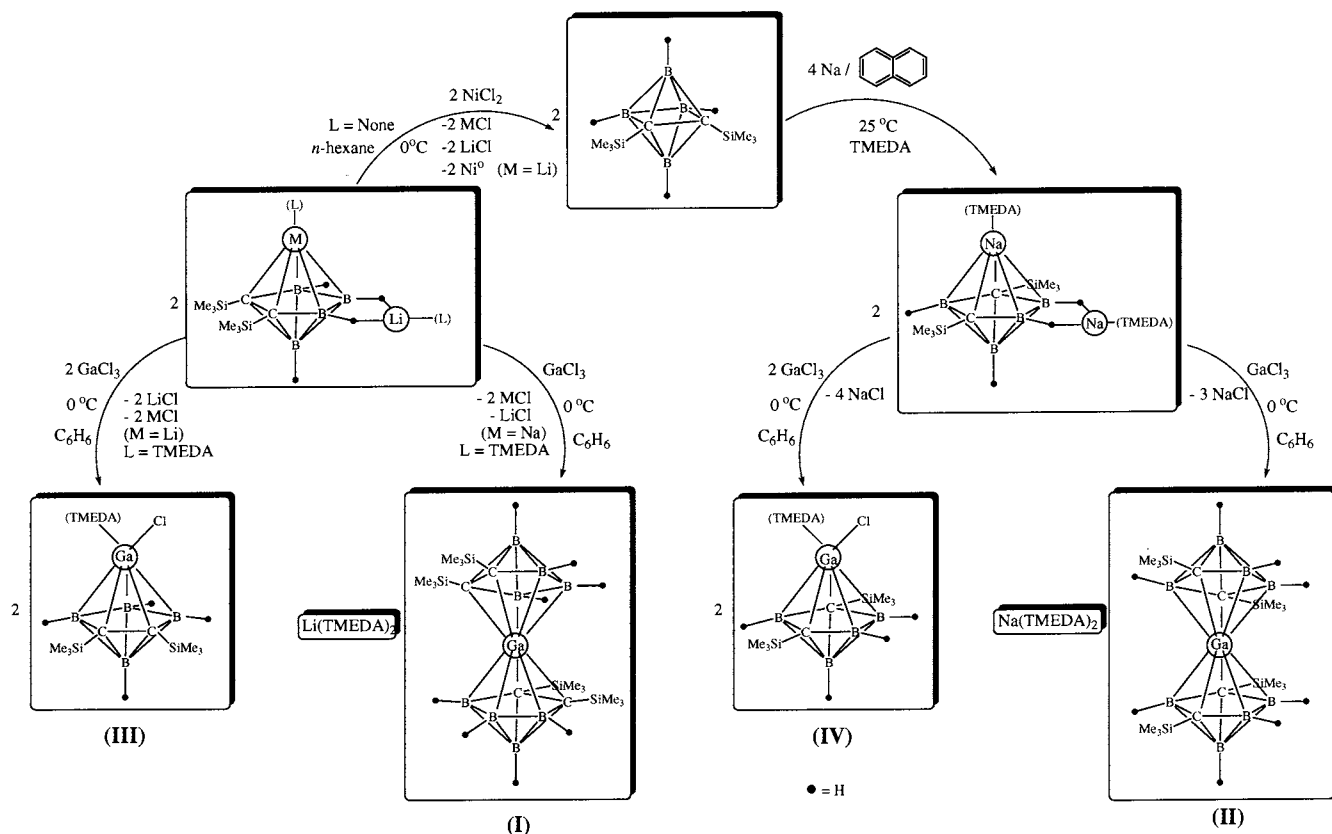
### 5. Metallocarboranes of Group 14 elements

Research in the area of Group 14 metallocarboranes has been quite active in recent years [7,8,10,11b,38]. All elements in that group have been inserted into carbo-

rane cages and a wealth of structural information is available on a number of half-sandwich, *closo*-carboranes of germanium, tin and lead as well as the full-sandwich, *commo*-complexes of silicon, germanium and tin [38]. These studies show that a definite structure-oxi-



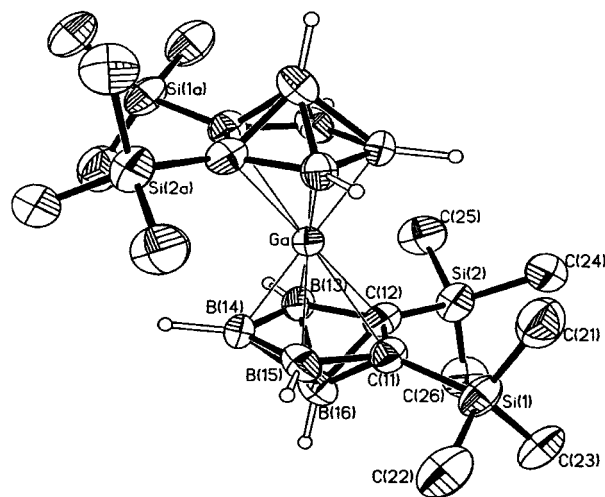
Scheme 4.



Scheme 5.

dation state relationship exists in these systems; in the *closo*-complexes the capping Group 14 elements are in formal +2 oxidation states, while the *commo*-complexes contain the elements in their +4 states. The coordination chemistry of *closo*- $M^{II}C_2B_4$  metallacarboranes has also been investigated and the structures of the resulting donor–acceptor complexes involving Lewis bases such as 2,2'-bipyridine ( $C_{10}H_8N_2$ ), 2,2'-bipyrimidine ( $C_8H_6N_4$ ), (ferrocenylmethyl)-*N,N*-dimethylamine,  $[(\eta^5-C_5H_5)-Fe(\eta^5-C_5H_4CH_2N\{Me\}_2)]$ , and 2,2':6',2'-terpyridine ( $C_{15}H_{11}N_3$ ) have been reported [8,38]. The structures of these adducts show that, despite having a 'lone pair' of electrons, the Group 14 element acts as a Lewis acid and bonds to the base. Coordination by the base leads to a distortion of the  $MC_2B_4$  cage in that the metal atom is dislocated, or slipped toward the boron side of the  $C_2B_3$  face of the carborane ligand; in all cases the base molecules are oriented opposite the cage carbons. These results raised the general question as to what would be the outcome of the reactions between Lewis bases and metallacarboranes possessing two potential acid sites, an  $M^{II}$  and an  $M^{IV}$  metal. In an effort to ascertain which metal atom would be the preferred acid site and to obtain more information regarding the structure, bonding and reactivity pattern of the new class of mixed-valence metal-

lacarboranes, we have synthesized several B–GeCl<sub>3</sub>-substituted *closo*-germacarboranes,  $[1-Ge-2-(SiMe_3)-3-(R)-5-(GeCl_3)-2,3-C_2B_4H_3]$  ( $R = SiMe_3, Me$  and  $H$ ), as outlined in Scheme 6. A representative structure, when  $R = SiMe_3$ , is shown in Fig. 18 [43a,b]. This scheme summarizes the reactions leading to the formation of the mixed valence germacarboranes. No

Fig. 13. Perspective view of the anionic 'carbon-adjacent' *commo*-gallacarborane.

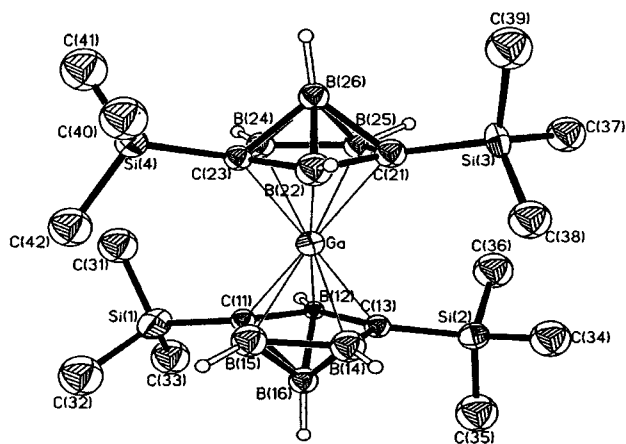
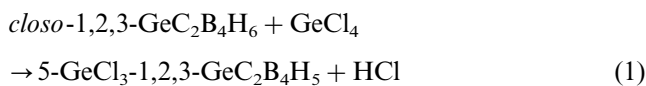


Fig. 14. Perspective view of the anionic 'carbon-apart' *commo*-gallacarborane.

neutral  $\text{GeCl}_3$  substituted carborane was found in the reaction products, indicating that the initial step in the reaction sequence is the reductive insertion of germanium to form a *closo*-germacarborane, which then reacts with a second  $\text{GeCl}_4$  molecule to give the mixed valence complex and  $\text{HCl}$ . Such a substitution is not unreasonable from an energy standpoint. For example, ab initio molecular orbital calculations at the B3LYP/6-31G\* level showed that  $\Delta E$  for Eq. (1) would be  $-20.83 \text{ kJ mol}^{-1}$  [43b]. Although



this value is only approximate and is for the gas phase, it does indicate that the substitution of a  $\text{GeCl}_3$  unit for

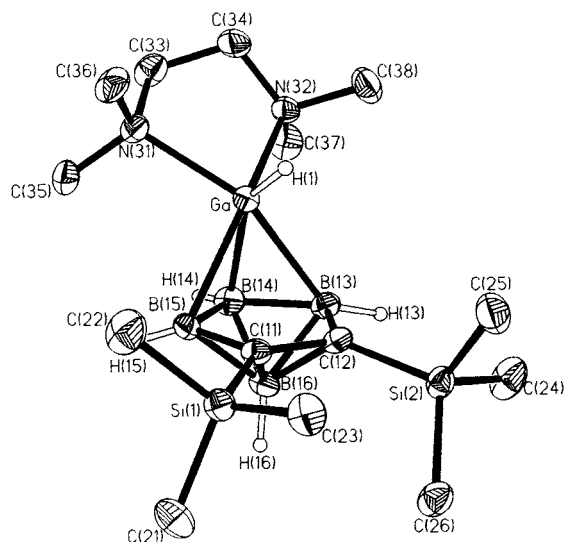


Fig. 16. ORTEP drawing of the 'carbon-adjacent' *closo*-gallacarborane hydride.

a terminal hydrogen would be an energetically favorable reaction.

There are two Lewis acid sites in *closo*-germacarboranes (see Fig. 18), the apical  $\text{Ge(II)}$  and the *exo*-polyhedral  $\text{Ge(IV)}$ . While one would qualitatively expect the higher oxidation state  $\text{Ge}$  to be the site for base coordination, just the opposite was found with all Lewis bases studied (2,2'-bipyridine, 2,2'-bipyrimidine and 2,2':6':2'-terpyridine) in which the donor N atoms bond exclusively with the apical  $\text{Ge(II)}$  (see Figs. 19 and 20, for example) [43b].

It is of interest to note that the reaction of the underivatized germacarboranes with the bis(bidentate)

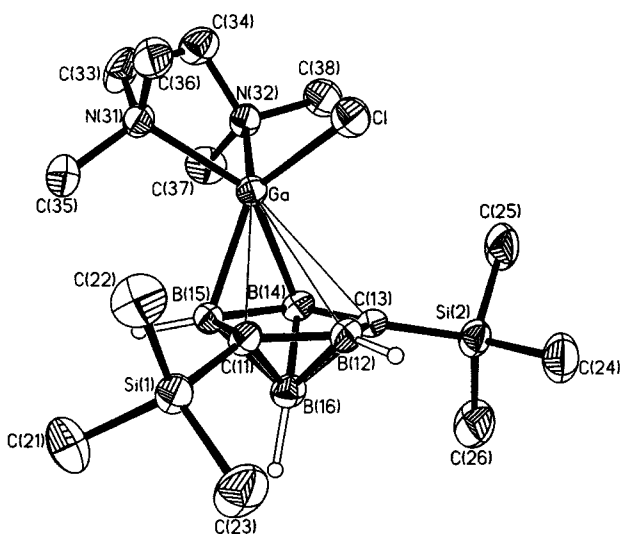


Fig. 15. Perspective view of the 'carbon-apart' *closo*-chlorogallacarborane.

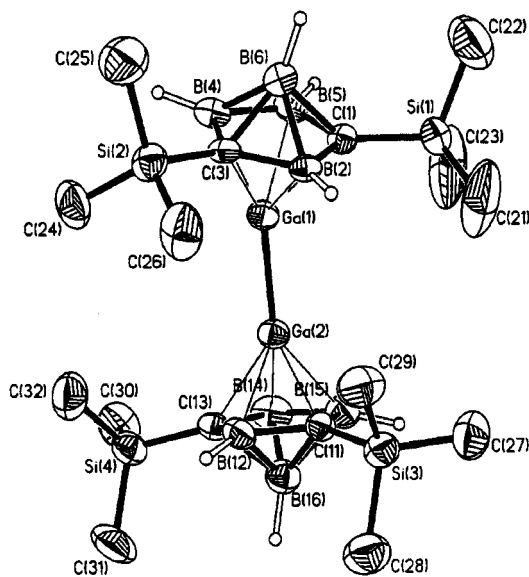
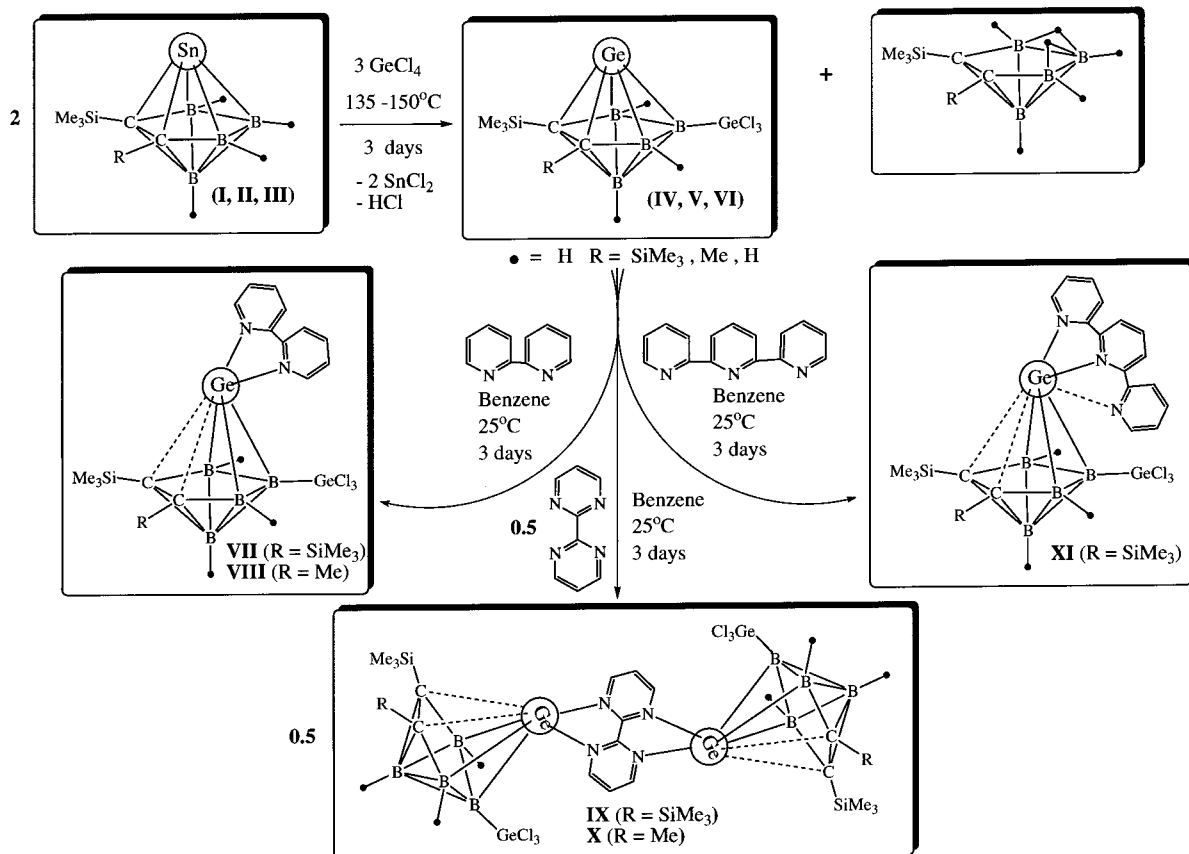


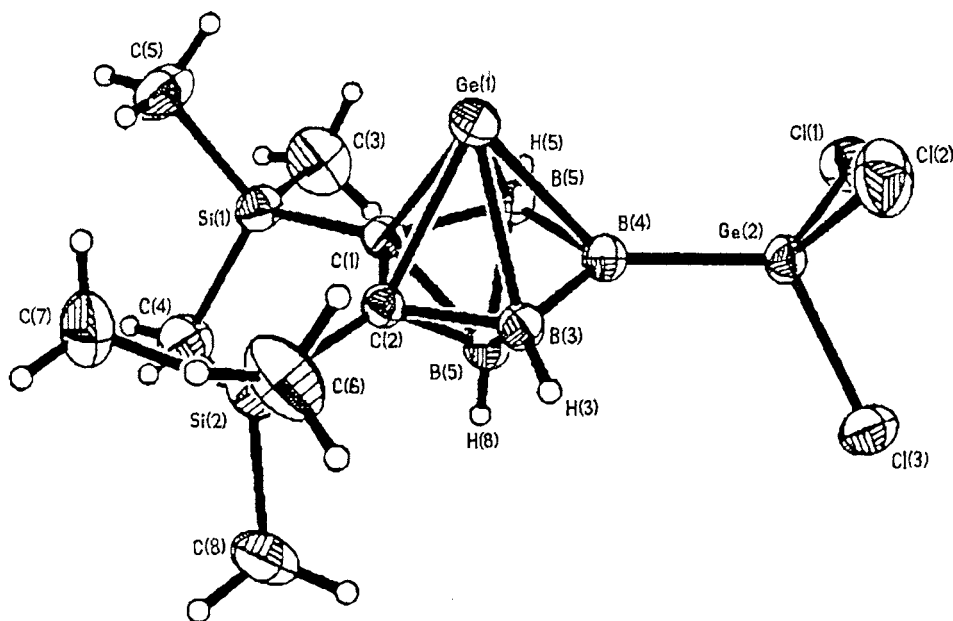
Fig. 17. Perspective view of the neutral  $\text{Ga(II)}\text{-Ga(II)}$ -linked digal-lacarborane complex.



Scheme 6.

ligand  $\text{C}_8\text{H}_6\text{N}_4$  resulted in 1:1 donor–acceptor complexes [8,38], rather than the bridged compound shown in Fig. 20 [43b]. In this regard, the mixed valence

*closo*-germacarboranes are more analogous to the stannacarboranes which react with  $\text{C}_8\text{H}_6\text{N}_4$  to give bridged 2:1 complexes [8,38]. Thus, even though two germa-

Fig. 18. Structure of the mixed valence *closo*-germacarborane.

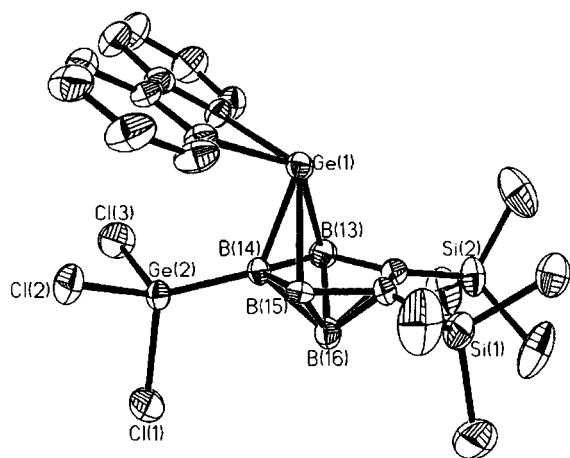


Fig. 19. Structure of the 2,2'-bipyridine adduct of the mixed valence germacarborane.

nium atoms are present, no evidence has been found to indicate that the Ge(IV) atoms in these compounds act as Lewis acid sites. An inspection of the LUMO and LUMO + 1 molecular orbitals obtained from *ab initio* calculations at the HF/3-21G\* level of theory shows localization only on the apical Ge(II) and carborane cage. Therefore, from frontier orbital considerations one would predict that the lower valence apical germanium would be the preferred reaction site for a nucleophile. It seems that the Ge(IV) atoms in the mixed valence *closo*-germacarboranes have their valences well-satisfied through bonding to the three chlorine atoms and the unique borons; even strong nucleophiles displace, rather than disrupt, the GeCl<sub>3</sub> moiety [43b].

## 6. Current and future directions

This overview summarizes the most promising research published during the past few years in the area of Main Group metallacarboranes following two main thrusts. Although each individual report has its own focus, one thrust is directed toward systematizing the chemistry of these compounds in order to promote their use in the selective recovery of radionuclides from nuclear wastes, as possible non- and/or weakly coordinating species in Ziegler–Natta catalysis, and as precursors to electronic, ceramic and catalytic materials. Another is to provide information on which we can test, and expand, our knowledge about the fundamental interactions that are at work in determining the structures and properties of these fascinating cage molecules. The results of these studies are establishing a unique and useful area of organometallic chemistry that will continue to grow and bear fruit in 21st century. For example, the Group 1 metallacarboranes [11,24,26–28] 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 also have been shown to possess a rich structural and coordination chemistry of their own. The development of convenient synthetic routes to Main Group metallacarboranes having both Group 13 [40,41] and Group 15 elements offers the possibility of using such compounds as precursors in the formation of semiconducting materials. The preliminary report on the polymeric cesium–carborane compound [33] give every indication that such compounds may be developed as better reagents

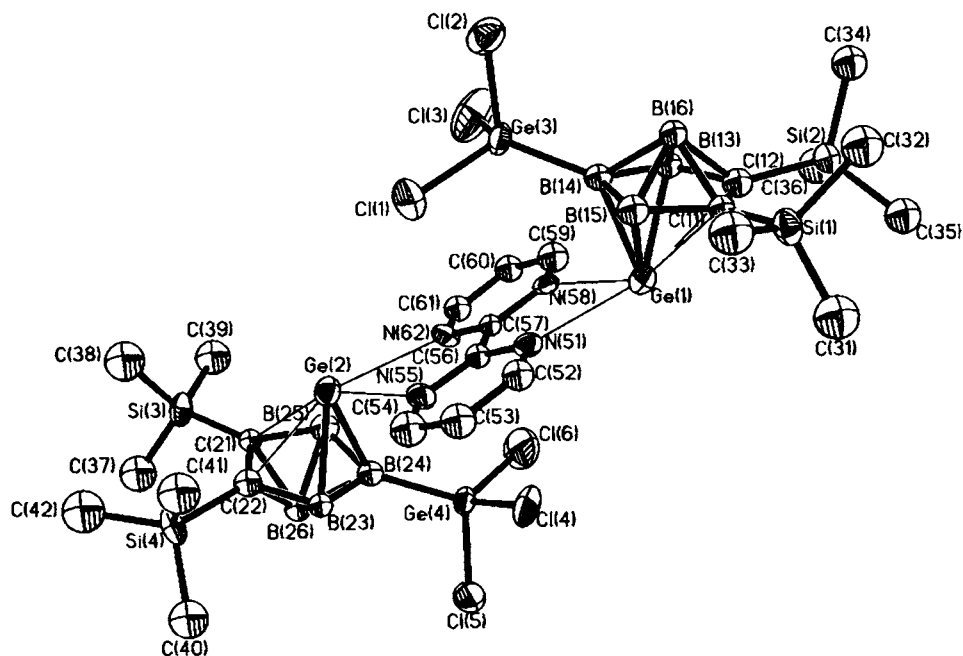


Fig. 20. X-ray structure of the 2,2'-bipyrimidine adduct of a mixed valence *closo*-germacarborane complex.

for removal of radioactive cesium metal ( $^{137}\text{Cs}$ ) from nuclear wastes in the presence of high concentrations of other Group 1 cations. Such speculation has aroused the interest of researchers outside the field of traditional carborane chemistry [44]. These recent findings presage a wealth of useful chemistry that awaits further exploration in this fascinating area of carborane chemistry.

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