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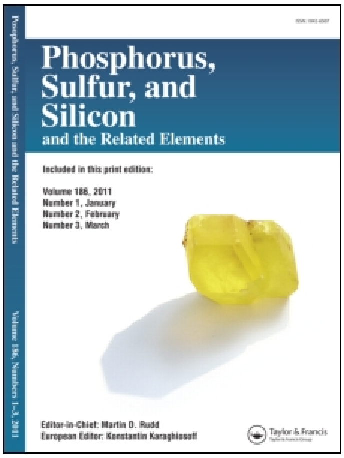

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HETEROATOM INCORPORATED CAGES AND CLUSTERS

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The significant recent findings in our laboratory are as following: (1) The synthesis and crystal structure of the first *"carbons apart"* C_4B_8-carborane provided an indirect evidence for the existence of a carborane cuboctahedron, a geometry that was proposed by Lipscomb in 1960 as an intermediate in his classic DSD mechanism for the thermal rearrangement of *ortho*-carborane to *meta*-carborane. (2) The first examples of fully sandwiched anionic lithia- and magnesacarboranes and half-sandwich cesia- and magnesacarboranes have been synthesized and structurally characterized. (3) A number of half- and full-sandwich galla- and indacarboranes were synthesized and their reactivities at the metal center for further complexation were explored. (4) The lanthanide metal reagents exhibited a different reactivity pattern with the *"carbons apart"* carborane ligands than with the corresponding *"carbons adjacent"* counterparts and further exemplify the role of solvents in determining the course of reactions in these systems.

Key Words: Heterocarboranes, Main Group Metal Complexes, Sandwich Complexes

INTRODUCTION

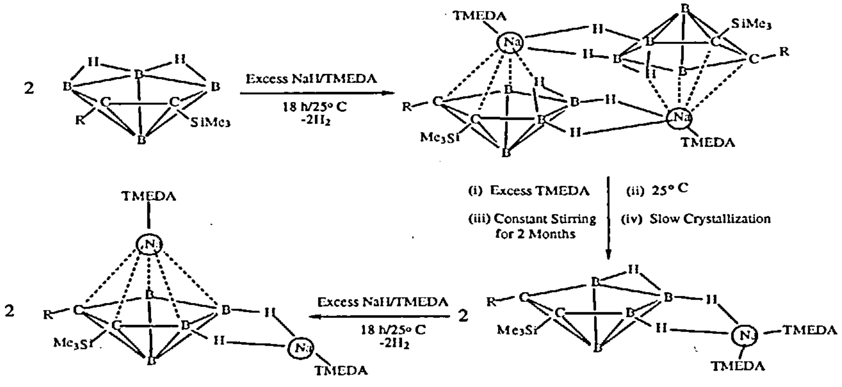
Heterocarboranes are those in which a polyhedral carborane cage is expanded through the incorporation of a heteroatom or a heteroatom group. When the heteroatom is a metal, the clusters are referred to as metallacarboranes. Small carboranes, such as *nido*-dicarbahexaborane(8) and its *C*-trimethylsilyl-, alkyl-, and aryl- substituted derivatives, are not only important precursors to larger cages such as *nido-*, *arachno-*, and *closo*-carboranes, *commo*-bis(metallacarborane) complexes, and di- and tetra-carbon metallacarboranes, they also can act as building blocks for the construction of multiple-decked sandwich complexes.[1] These extended sandwich systems have novel structures and possess unusual spectroscopic properties. The carborane anions, $[R_2C_2B_4H_4]^{2-}$ and $[R_2C_2B_3H_3]^{4-}$, can be considered to be isolobal with $[C_5R_5]^-$ (R = alkyl, aryl or $SiMe_3$) anion in that they all have six electrons delocalized in π-type orbitals on an open pentagonal face. The metal orbitals tend to overlap more efficiently with carborane orbitals than with those of the cyclopentadienyl anion on formation of η^5-metal complexes.[2] Thus, together with the lower electronegativity and higher polarizability of boron versus carbon and the higher ligand charge of the carborane often times leads to stronger, more covalent interactions between the carborane ligands and the capping metal atom in metallacarborane systems than in the corresponding cyclopentadienyl metal complexes.[3] An added advantage of the carborane ligand is that nearly all of the characterized metallacarborane complexes are neutral and are soluble in organic media.

Heterocarboranes are commonly synthesized by the reaction of a halide of the selective heteroatom with either the mono- or dianion of a *nido*-carborane. The most common metallacarboranes are those in which the metal bonds to a pentagonal C_2B_3 face. There are two types of arrangements of the facial atoms, one in which the two carbons atoms are directly bonded to one another in the so called "carbons adjacent" isomer, and another in which the carbons are separated by a boron atom, 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, results indicate that, not only are the carbons apart ligands just as effective in bonding to metals, they also have the advantage of being less susceptible to oxidative cage closure.

RESULTS AND DISCUSSION

HETEROCARBORANES OF GROUP 1 ELEMENTS

The carborane monoanion, can be obtained by the heterogeneous reaction of *nido*-$(CR)_2B_4H_6$ with NaH in THF as shown in **Scheme I**. The main point of interest in this reaction is that the stoichiometry is 1:1, even with the use of excess NaH and elevated temperatures.[4] A possible



B = BH; R = $SiMe_3$, Me, H; TMEDA = $(Me_2NCH_2)_2$

Scheme I. Reactivity of *nido*-C_2B_4-carboranes with NaH

explanation for this behavior was provided by the structures of the monosodium compounds, 1-Na(L)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ (L = THF or TMEDA).[5] When L = THF the structure is that of an extended array of $Na_2(C_2B_4)_2$ dimers that are stacked on top of one another to give a series of -(carborane)$^-$-Na^+-(carborane)$^-$- chains, with L = TMEDA the chain structure is broken, but the ion cluster dimers remain (see **Figure 1**). 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 shown that the deprotonation of *nido*-2,3-RR'$C_2B_4H_6$ (where R = alkyl, arylmethyl 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.[6] From **Figure 1** 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.[5] Direct group 1 metal-cage interaction was found in the TMEDA-solvated dilithium species, *closo*-*exo*-4,5-[(μ-H)$_2$Li(TMEDA)]-1-Li(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$. The crystal structure of this compound showed that the two lithiums occupied quite different positions relative to the carborane face, with one lithium being in an apical position above the C_2B_3 face, and the other located exopolyhedrally, about halfway between the unique and a basal boron and directed down below the plane of the C_2B_3 face as shown in **Figure 2**. In contrast to the structures of the monosodium species shown in **Figure 1**, there is not extensive association between metalla-carborane units. In an effort to ascertain the extent to which these

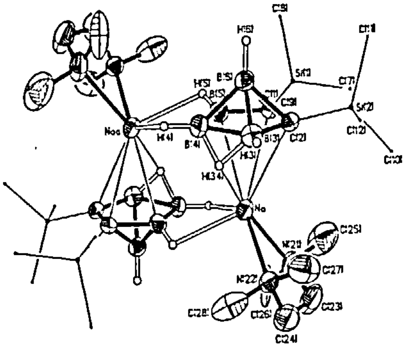


FIGURE 1 Perspective view of a discrete dimeric unit of *nido*-1-Na(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$.

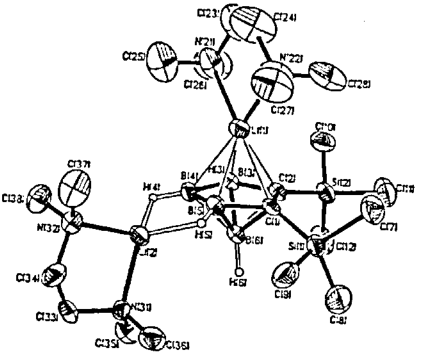


FIGURE 2 Perspective view of the TMEDA-solvated "carbons adjacent" dilithiacarborane.

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)$_2$Li(TMEDA)]-1-Li(TMEDA)-2,3-$C_2B_4H_6$ which showed that the structure shown in **Figure 2** was a minimum energy structure arising from interactions among the carborane and its two Li(TMEDA) groups.[5] As expected, the orientations of the TMEDA molecules in **Figure 2** 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 ^{7}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 more extensively solvated species, [Li(TMEDA)$_2$]$^+$ [*nido*-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_5$]$^-$ and *nido*-*exo*-4,5-[(μ-H)$_2$Na(TMEDA)$_2$]-2-(SiMe$_3$)-3-(Me)-2,3-$C_2B_4H_5$ (**Figure 3**), show that they are composed of discrete, well separated cations and anions 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 I**). 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, just the opposite is true for the "carbons apart" carboranes; the bimetallated carboranes are the ones produced directly by the cage-opening reactions of *closo*-C_2B_4-carboranes (**Scheme II** and **Figure 4**).[8(a,b)] Careful reaction of either the

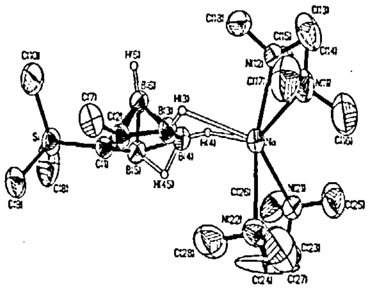


FIGURE 3 Crystal structure of a discrete monomeric monosodium salt of 2,3-dicarba-*nido*-hexaborate(1-).

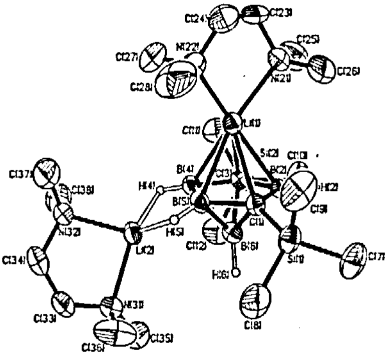
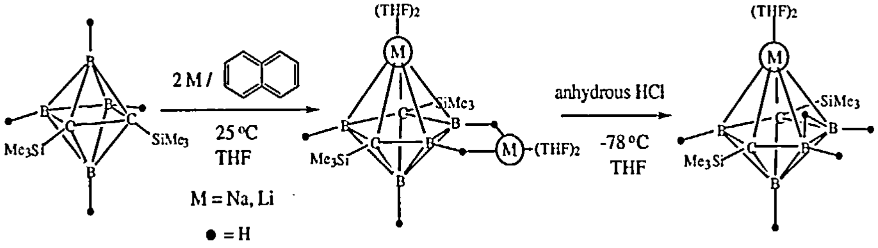


FIGURE 4 Crystal structure of the TMEDA-solvated "carbons apart" dilithiacarborane.

dinatra or dilithiacarborane with HCl results in the protonation of the two adjacent borons (similar to B(4) and B(5) in **Figure 4**) to give the monometallated species, whose overall geometry is similar to that shown in **Figure 1.** However, attempts at further protonation led to the decomposition of the carborane.[8(c)]



Scheme II. Syntheses of "*C*-Apart" C_2B_4-Carborane Di- and Monoanions

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, $[Li(TMEDA)_2][$*commo*-$1,1'-Li\{2,3-(SiMe_3)_2-2,3-C_2B_4H_5\}_2]$, as a colorless crystalline solid.[9] The mechanism of the formation of this complex is yet to be determined. Since alkyllithiums have been shown to be sublimable, a 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 5.**[9] 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,[5] but

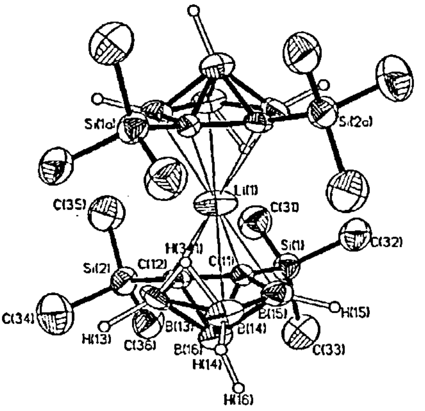


FIGURE 5 Crystal structure of the anionic full-sandwich lithiacarborane complex.

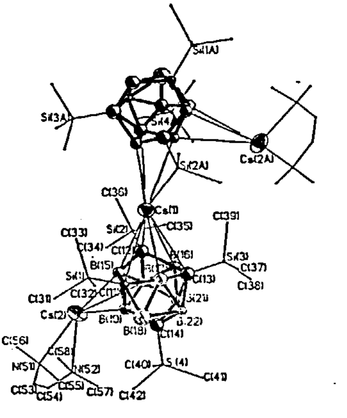


FIGURE 6 Crystal structure of the polymeric cesiacarborane complex.

are comparable to the corresponding metal-centroid distance of 2.008 Å found in the $[Cp_2Li]^-$ sandwich complex.[10] 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. Inspection of **Figure 5** shows that the Li atom is displaced toward the cage C's and one of the basal B's. This slip distortion is most probably due to the presence of B-H-B bridging H's on the bonding faces.

The room temperature reaction between a TMEDA solution of 2,4,7,9-tetracarba-*nido*-dodecaborane (12), $(SiMe_3)_4C_4B_8H_8$, and finely cut excess cesium metal, in the absence of either naphthalene or aromatic solvents, produced the polymeric cesiacarborane complex, [*exo*-[(μ-H)$_2$Cs(TMEDA)]-1-Cs-2,4,7,9-$(SiMe_3)_4$-2,4,7,9-$C_4B_8H_8]_n$, which is the first organometallic π-complex of the cesium metal ever to be reported.[11] It is believed that the formation of this cesiacarborane product involves the initial formation of a paramagnetic monocesiacarborane intermediate as was found in the analogous reaction of the C_4B_8-carborane with the lithium metal.[12] The X-ray diffraction study on the cesium complex confirmed its polymeric structure in which each C_4B_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 (**Figure 6**).[11] This structural feature is somewhat similar to that of the Sr complex of the $[C_2B_{10}H_{12}]^{2-}$ ligand, reported by Hawthorne and coworkers.[13]

HETEROCARBORANES OF GROUP 2 ELEMENTS

The half- and full-sandwich magnesium complexes in the C_2B_4 cage system, *closo*-1-Mg(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ and {*commo*-1,1'-Mg[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2\}^{2-}$, have been recently synthesized and structurally characterized.[14] The structure of the half-

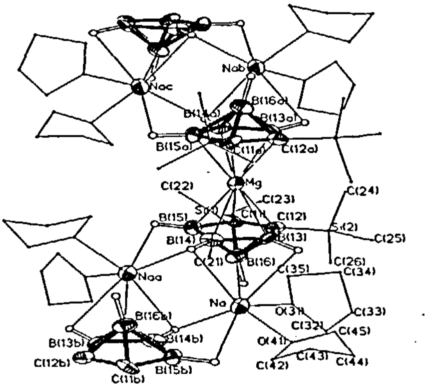


FIGURE 7 Crystal structure of the full-sandwich magnesacarborane complex.

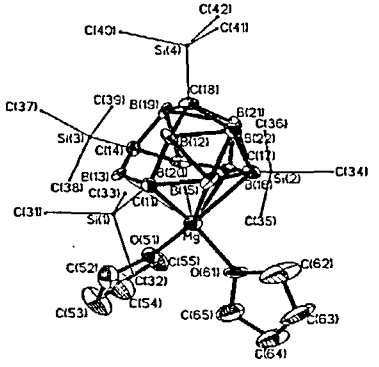
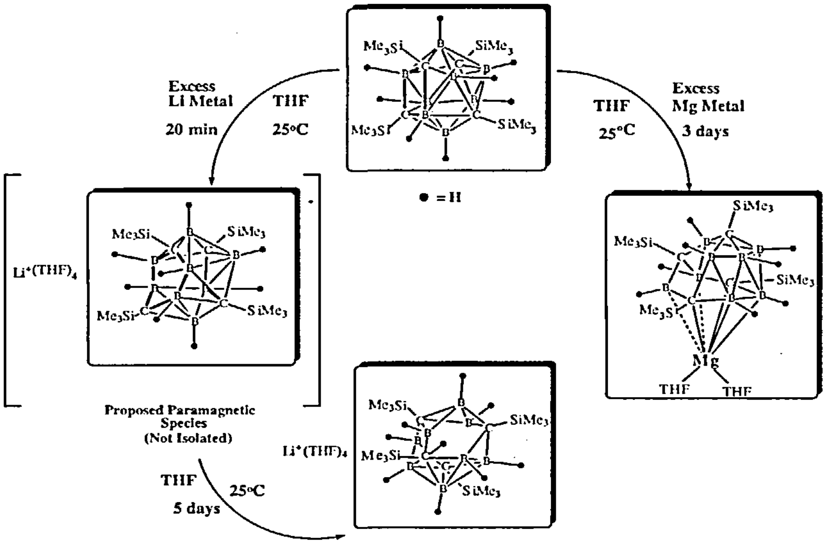


FIGURE 8 Crystal structure of $(THF)_2Mg(SiMe_3)_4C_4B_8H_8$.

sandwich compound is that of a dimeric [*closo*-1-Mg(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2$ unit in which the solvated Mg atoms occupy apical positions above the C_2B_3 face of the carborane and are also bonded to the unique borons [B(14)] of the adjacent carborane cages by single Mg-H-B bridges.[14] In each half-sandwich complex, the Mg atom is not symmetrically bonded to the C_2B_3 face but is dislocated, or slipped, towards the unique boron, B(14 or 24). Since the carboranes are η^5-bonded to the Mg in the full sandwich complex, shown in **Figure 7**, 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 (**Scheme III**).[12] The structure, shown in **Figure 8**, 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.



Scheme III. Reactivity of the "*C*-Apart" $(Me_3Si)_4C_4B_8H_8$ With Li and Mg Metals

HETEROCARBORANES OF GROUP 13 ELEMENTS

There has been a number of reports on the syntheses, structures and reactivities of half-sandwich alkylgallacarboranes of both the carbons adjacent (2,3-) and carbons apart (2,4-) C_2B_4-carborane systems.[15] These reports collectively demonstrate that the reactive site of the molecule is the apical gallium atom that acts as a Lewis acid site and forms donor-acceptor complexes with 2,2'-bipyridine, 2,2'-bipyrimidine, and 2,2':6',2"-terpyridine. In the 1,2,3-$Ga(CR)_2B_4H_4$ complex, the gallium is slipped toward the unique boron, while in the case of the 1,2,4-$Ga(CR)_2B_4H_4$, the metal slipped in the opposite direction. These reports exemplified a pattern of reactivities that are not only inherent in these half-sandwich *t*-butylgallacarboranes, but are also identical to those found in other group 13 and group 14 half-sandwich metallacarboranes in both the C_2B_4 and C_2B_9 carborane syatems.[15] It is of interest to note that there is a divergence of the reaction products in the C_2B_4 and C_2B_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 metal reagent used in the syntheses and their stoichiometries, rather than a difference in bonding preferences in the two cage systems. The half-sandwich complexes were obtained from metal alkyl reagents,[15] such as $Ga(CH_3)_3$, $[(t\text{-}C_4H_9)GaCl_2]_2$, or $(Me_2CH)InI_2$, while the full-sandwich complex resulted when $GaCl_3$ as the metallating agent.[16] When $GaCl_3$ is substituted for $[(t\text{-}C_4H_9)GaCl_2]_2$ in the reaction with the dilithium complexed $[2,3(4)\text{-}(SiMe_3)_2\text{-}2,3(4)\text{-}C_2B_4H_4]^{2-}$ 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)-$GaC_2B_4H_4$}$_2$]$^-$, was obtained (see **Figures 9** and **10**), while the same reaction in 1:1 stoichiometry resulted, in high yields, in the formation of a half-sandwich chlorogallacarborane, *closo-*

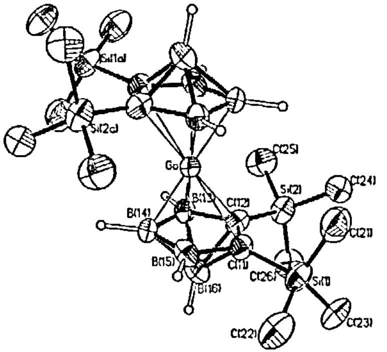


FIGURE 9 Crystal structure of the anionic "*c*-adjacent" *commo*-gallacarborane.

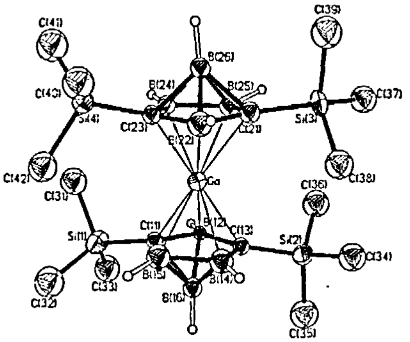


FIGURE 10 Crystal structure of the "*c*-apart" *commo*-gallacarborane anion.

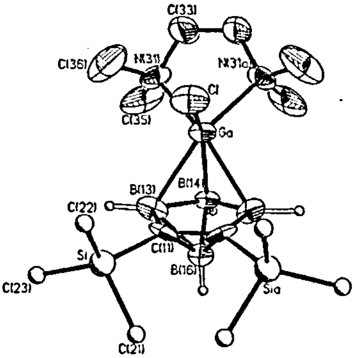


FIGURE 11 Crystal structure of the "*c*-adjacent" *closo*-chlorogallacarborane.

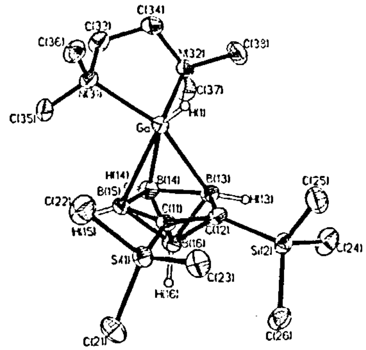


FIGURE 12 Crystal structure of the "*c*-adjacent"*closo*-gallacarborane hydride.

1-(TMEDA)-1-(Cl)-2,3(4)-($SiMe_3$)$_2$-1,2,3(4)-$GaC_2B_4H_4$ **(Figure 11)**,[17] which can be further converted to the corresponding *closo*-gallacarborane hydride **(Figure 12)** and alkyl derivatives.[18]

HETEROCARBORANES OF LANTHANIDES

The synthetic utility of the mononuclear full-sandwich lanthanacarborane was demonstrated in the reaction summarized in **Scheme IV**. This reaction produced the first mixed carborane sandwich complex in high yield and it could prove to be a general synthetic route to mixed-carborane metal complexes **(Scheme IV and Figure 13)**.[19]

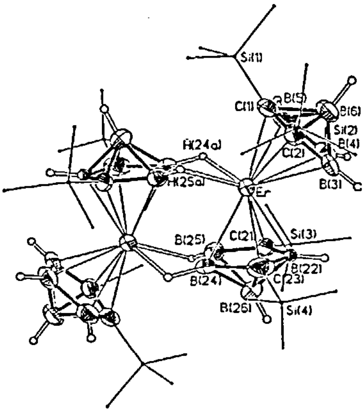


FIGURE 13 Crystal structure of the mixed-ligand dimeric erbacarborane.

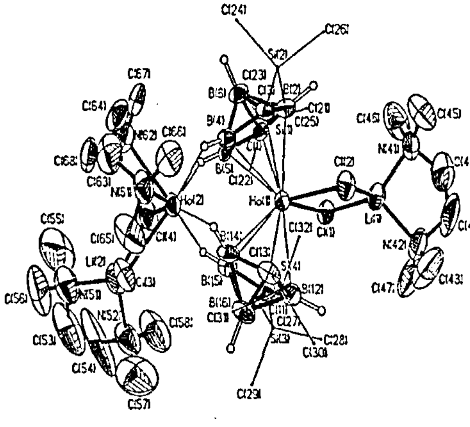
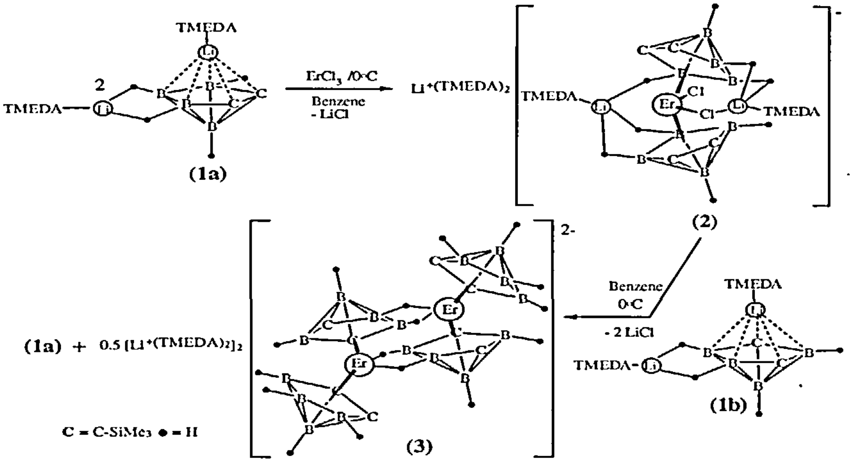


FIGURE 14 Crystal structure of the "*C*-apart" dinuclear holmacarborane.

When TMEDA-solvated **1b (Scheme IV)** was reacted with $LnCl_3$, the resulting lanthanacarborane was exclusively the "*C*-apart" dinuclear complex (**Figure 14**, Ln = Ho),[20(a)] while dimeric sandwiches were formed with the THF-solvated precursors (**Figure 15**, Ln = Dy).[20(b)] Thus the role of the metal-solvating molecules on the syntheses of lanthanacarboranes was exemplified.



Scheme IV. Syntheses of Mixed-Ligand Lanthanacarboranes

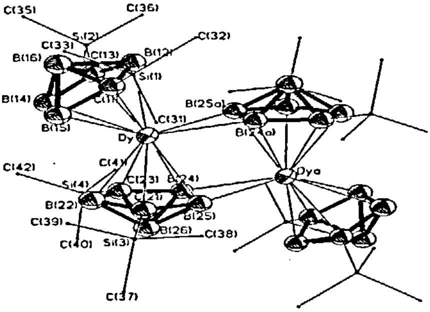


FIGURE 15 Crystal structure of the dianionic dimeric dysprosacarborane complex.

ACKNOWLEDGMENTS

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