Recent Advances in the Chemistry of Metallacarboranes

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Most carborane derivatives of the icosahedral (C_2B_{10}) or small cage (C_2B_4) systems are formed by varying the groups on the cage carbon atoms. This is usually accomplished in the original carborane synthesis by treating substituted acetylenes with either the decaborane(14) or pentaborane(9) precursors to give directly carboranes that have adjacent carbon atoms in the cage ("carbon atoms adjacent"). The larger cages are obtained as *closo*-icosahedra, while the small-cage C_2B_4 carboranes have *nido* structures as well as a cage geometry in which the carbon atoms are separated by a boron atom. Although these "carbon atoms apart" or *nido*-2,4-$(CR)_2B_4H_6$ carboranes are thermodynamically more stable and are more symmetric than the "carbon atoms adjacent" isomers, they have not been as well studied, mainly because they must be synthesized from their "carbon atoms adjacent" analogues through a sequential series of oxidative cage-closure/reductive cage-opening reactions. We have concentrated much of our recent research on the reactivity patterns of $C_{(cage)}$-appended alkyl- and silylamido, alkyloxo, alkylphosphido, and alkylthio derivatives of the "carbon atoms apart" carboranes. We have also sought to develop a safe, bench-scale preparation of small-cage carboranes that does not require isolating and handling dangerous and toxic carborane precursors such as pentaborane(9). This microreview discusses the latest developments towards such a process and the subsequent reaction chemistry of the "carbon atoms apart" carboranes.

Introduction

Extensive research has been reported on the chemical and structural properties of metallacarboranes in pentagonal-bipyramidal (MC_2B_4) and icosahedral (MC_2B_9) cage systems.[1] They are generally synthesized by the reaction of the mono- or dianions of their respective *nido*-C_2B_4 or C_2B_9

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carboranes with suitable metal reagents. Much of the interest in them stems from the fact that three primary metal-binding carborane π-type molecular orbitals that are localized on the C_2B_3 open pentagonal faces, which are quite similar to those in cyclopentadienide $[C_5R_5]^-$ ligands. Our research has involved synthetic, structural, reactivity and theoretical studies on the full- and half-sandwich metallacarboranes derived from the interactions of $[nido\text{-}2\text{-}(SiMe_3)\text{-}n\text{-}(R)\text{-}2,n\text{-}C_2B_4H_4]^{2-}$ (n = 3, 4; R = SiMe$_3$, *n*Bu, *t*Bu, Me, H) with main-group,[2] d-group,[3] and f-group metals.[4] Originally, pentaborane(9) (B_5H_9), which reacts with various alkynes to furnish small-cage C_2B_4 carboranes, could be obtained from an extensive US-government surplus. However, at present, that source is no longer available, and no commercial source has taken its place.[5] Thus, a new, convenient and safe method of producing pentaborane(9) is needed − ideally a one-pot method from a readily available starting material so that the pentaborane(9) can then further react with the appropriate alkyne to generate, in situ, the corresponding small-cage carborane; such a method is described herein. With a steady source of starting materials available, we have extended our studies of the "carbon atoms apart" metallacarboranes. We have also embarked on the construction of $C_{(cage)}$-appended alkyl- and silylamido and alkyloxo derivatives of the larger C_2B_9 cage systems and have investigated their reactivity toward group-4 and -14 metals so as to prepare metallacarboranes with new geometries that could function as precursors to catalysts or possibly exhibit intrinsic catalytic activity. We hope that the reader will realize that there is still a wealth of fascinating research to be explored in this area.

1. Synthesis of Boron-10 Enriched Pentaborane(9) from Boric Acid and Its Conversion into *nido*-$^{10}B_{10}H_{14}$ and *anti*-$^{10}B_{18}H_{22}$

Pentaborane(9) is an important synthon for several higher polyhedral borane cages, including $[B_9H_{14}]^-$,[6] $[B_{11}H_{14}]^-$,[7] $[B_{12}H_{12}]^{2-}$ as well as other cage-expanded borane anions,[8] and the neutral decaborane, $B_{10}H_{14}$.[9] The corresponding ^{10}B-enriched species could function as precursors for several boron-based drugs for use in boron neutron capture therapy (BNCT). With the exception of the expensive $^{10}B_{10}H_{14}$,[10] there is no commercial supplier for any of these boranes. Therefore, a convenient synthesis for ^{10}B-enriched pentaborane(9) has an obvious appeal. It was this incentive that led us to explore alternative routes to ^{10}B-enriched polyhedral boranes, starting from the readily available ^{10}B-enriched boric acid, $H_3{}^{10}BO_3$. Specifically, $H_3{}^{10}BO_3$, was converted into the corresponding sodium borohydride, $Na^{10}BH_4$, in essentially quantitative yields, by using a slightly modified literature method, involving the formation of butyl borate, $(nBuO)_3{}^{10}B$, and then treating it with NaH in mineral oil at 250 °C.[11,12] Subsequent oxidation of $Na^{10}BH_4$ with I_2 in diglyme, followed by the addition of dioxane during the purification step, gave the dioxane-complexed sodium salt of octahydrotriborate(−1), $Na[^{10}B_3H_8]\cdot 3C_4H_8O_2$, in almost quantitative yields [Equation (1)].[13]

$$3\,Na^{10}BH_4 + I_2\,(\text{in diglyme/dioxane}) \rightarrow 2\,H_2 + 2\,NaI + Na[^{10}B_3H_8]\cdot 3C_4H_8O_2 \tag{1}$$

Treatment of $Na[^{10}B_3H_8]\cdot 3C_4H_8O_2$ with $NiCl_2$ in anhydrous benzene or heavy mineral oil at 110 °C [Equation (2)] gave the corresponding $^{10}B_5H_9$ as the first isolated ^{10}B-enriched pentaborane(9) in a laboratory environment.[14]

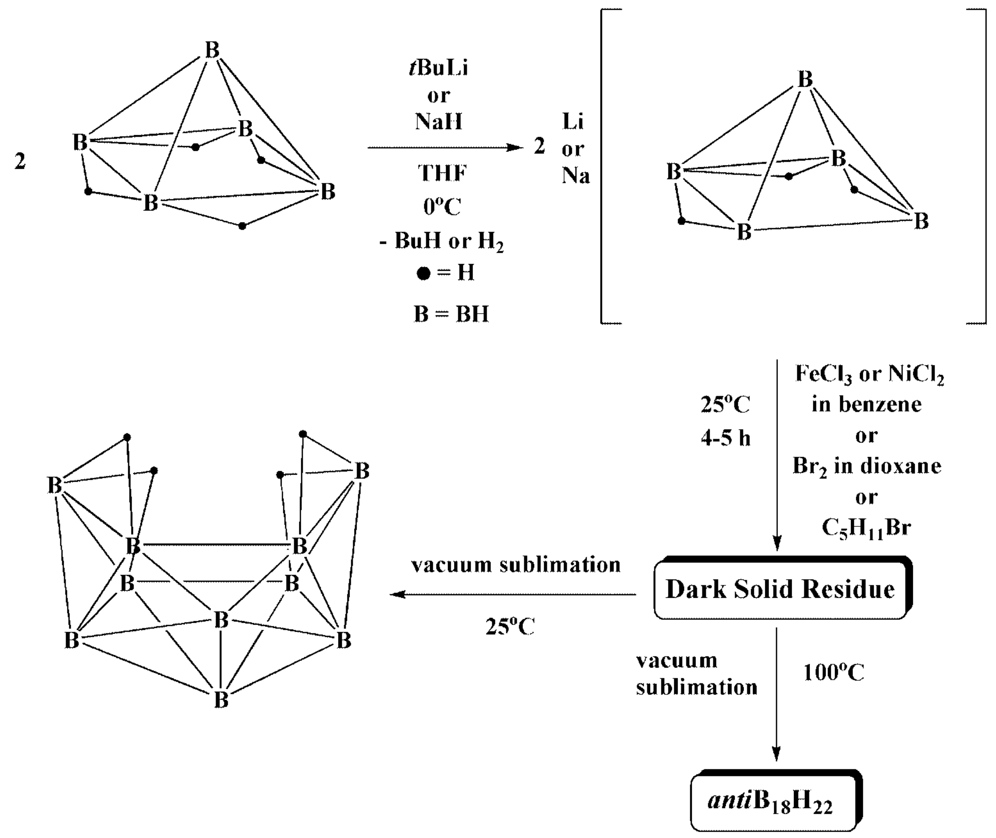
$$2\,Na[^{10}B_3H_8]\cdot 3C_4H_8O_2 + NiCl_2 \xrightarrow[\substack{-\,2\,NaCl/-\,Ni^0\\ -\,2\,C_4H_8O_2}]{\substack{\text{Benzene or}\\ \text{heavy mineral oil}\\ 110^{\circ}\text{C}/12\text{ h}}} {}^{10}B_5H_9 + 2\,H_2 + C_4H_8O_2\cdot{}^{10}BH_3 \tag{2}$$

Of the various reported methods of preparing natural B_5H_9,[15,16] that in Equation (2) is by far the most convenient and straightforward. Since the ^{10}B-enriched pentaborane is the only borane product of high volatility, its safe production, easy isolation and storage in heavy mineral oil make this method most attractive, to both those who work with small-cage (C_2B_4) carboranes and to researchers who did not have previous access to these materials. Boron-10 enriched decaborane, $^{10}B_{10}H_{14}$, is the key chemical in preparing almost all of the $C_{(cage)}$-substituted bio-boron molecules that are currently undergoing clinical trials as boron drugs for BNCT.[17] We therefore devised an alternative synthesis that started with the $^{10}B_5H_9$ prepared as described previously to afford, with slight modifications, using different oxidizing agents and reaction temperatures, either $^{10}B_{10}H_{14}$ or *anti*-$^{10}B_{18}H_{22}$ (Scheme 1).[18a] The conversion of natural pentaborane(9) to decaborane(14) has been previously demonstrated by Brewer and Grimes using the iron(II) and iron(III) chloride mediated cage fusion reactions.[18b]

This procedure constitutes the first systematic synthetic approach to pentaborane(9) and decaborane(14) of both natural and ^{10}B-enriched analogues and to their cage-expanded neutral and anionic borane species.[14,18]

2. Reductive Cage-Opening Process with Concomitant Metalation of the Resulting Carborane Ligand: A Novel Route to Metallacarborane Synthesis

The two-electron reductive cage-opening of the *closo*-carboranes has been well-documented.[19−21] In a series of papers Stone and co-workers reported the simultaneous cage reduction and metalation of *closo*-carboranes in the C_2B_n (n = 6, 8, 9) cage systems, using a number of zero-valent nickel, platinum, and palladium complexes.[22] The mono-carbon carbaborane $[closo\text{-}CB_{10}H_{11}]^-$ reacts in a similar manner,[23] and the icosahedral *closo*-$(RC)_2B_{10}H_{10}$ cage has been opened by reaction with a group-1 metal, in both the



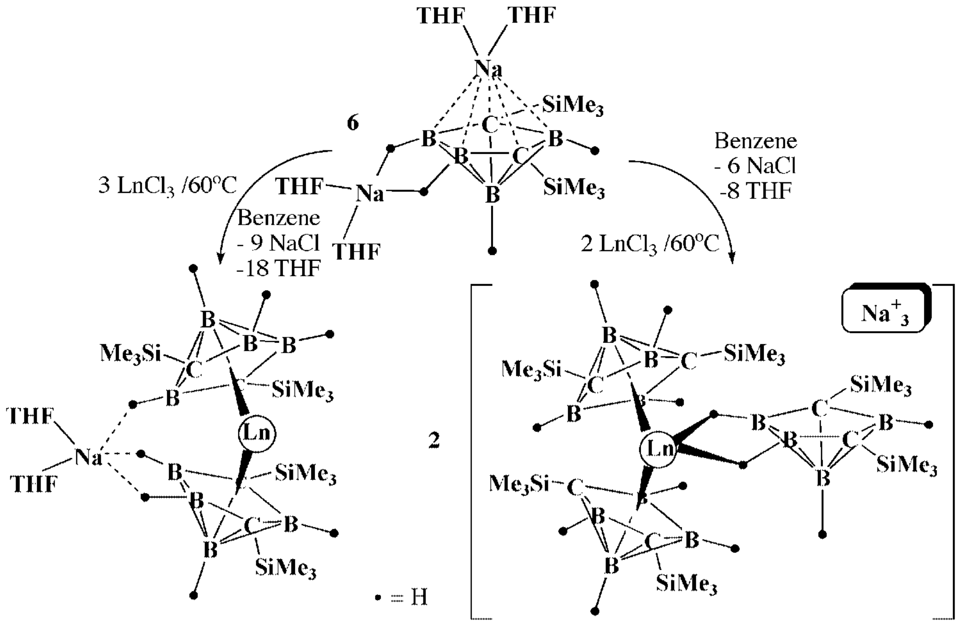
Scheme 1. Synthesis of *nido*-$^{10}B_{10}H_{14}$ and *anti*-$^{10}B_{18}H_{22}$ from $^{10}B_5H_9$

presence and absence of catalysts, to give the corresponding *nido*-carboranes.[24,25] In addition, Mg (group 2) reacts with *closo*-1,2-$C_2B_{10}H_{12}$ in the presence of catalytic amounts of 1,2-dibromomethane.[26] Conversely, Xie and co-workers have reported a noncatalyzed reduction of Na[1-$Me_2C(C_5H_5)$-*closo*-1,2-$C_2B_{10}H_{11}$] by Na metal to give the *ansa*-ligand Na_3[1-$Me_2C(C_5H_5)$-*nido*-1,2-$C_2B_{10}H_{11}$], in which a Cp^- group is tethered to a dianionic *nido*-$C_2B_{10}H_{11}$ moiety via an Me_2C bridge; metal complexes of this ligand were also described.[27] All such reductive cage opening processes yield *nido*-carborane products with a "carbon atoms apart" geometry in which the two cage carbon atoms are separated by at least one boron atom on the open faces of the carboranes. When the two-cage carbon atoms are bridged, by either an organic group or a metal complex, cage reduction produced the "carbon atoms adjacent" *nido*-C_2B_{10} cage, which seems to be susceptible to further reduction to give the respective *arachno*-carboranes.[28] There are a number of catalyzed and noncatalyzed approaches to cage reduction/opening processes for large-cage *closo*-carboranes, but only a few for small C_2B_4 cage systems. Despite some very interesting, but isolated, reports of reductive cage openings of *closo*-$C_2B_4H_6$ by Lewis bases, such as $(CH_3)_3N$,[29] and low-valent metal compounds,[30] the only general, high-yield method of transforming either *closo*-1,6-$(CR)_2B_4H_4$ (R = H or a cage carbon substituent) or its 1,2-isomer to the corresponding [*nido*-2,4-$(CR)_2B_4H_4]^{2-}$ species is by naphthalene-catalyzed group-1 metal reduction.[20]

The use of naphthalene in these traditional two-electron reductive cage-opening reactions has several disadvantages. It introduces an additional reagent that must be removed from the reaction mixture before the *nido*-carborane products can be treated further. In addition, naphthalene also has a tendency to co-crystallize with any product or to substitute for a terminal B−H hydrogen atom, which often interferes with the reactivity of these dianionic ligands. The subsequent metalations of these ligands, in the conventional synthetic procedure (Scheme 2) produce metallacarboranes of different geometries depending on the ratios of reactants involved.[31−40] The structures of some recently reported representative compounds are depicted in Figures 1 and 2.[39,40]

The seeming inability of the *closo*-carboranes to undergo reduction in the absence of naphthalene led us to question whether such carboranes could be reductively opened by the in situ generation of reactive metal atoms whose cations are good coordinators of the carborane. To explore this possibility, anhydrous $ErCl_3$ was treated with 4 equiv. of freshly cut potassium metal, under refluxing conditions in THF, to produce what we believe to be an active erbium metal alloy of the form of Er/K* (Scheme 3).

The alloy was immediately treated with the *closo*-carborane 1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ which, after refluxing overnight with constant stirring, produced a light-orange crystalline solid, identified as the "carbon atoms apart" erbacarborane sandwich, 2,2′,4,4′-$(SiMe_3)_4$-3,6′-[(μ-H)$_2$K(THF)$_2$]-1,1′-*commo*-Er(η^5-2,4-$C_2B_4H_4$)$_2$, in 82%



Ln = Nd, Gd, Dy, Er, Lu

Scheme 2. Conventional synthetic route for lanthanacarboranes

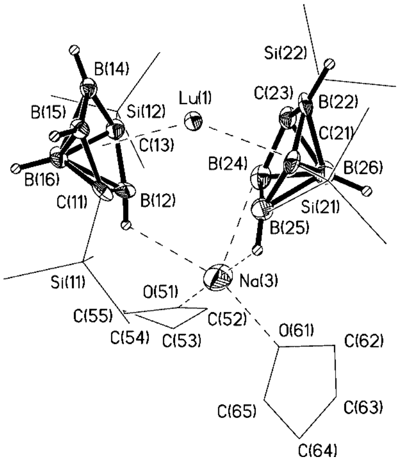


Figure 1. Crystal structure of a full-sandwiched lutetiacarborane complex

yield (Scheme 3 and Figure 3).[41] It is noteworthy that, under the same reaction conditions, neither the Er or K metals alone, nor the one generated in situ by treating K with $ErCl_3$ in a 3:1 ratio, underwent reductive cage opening; in both cases the *closo*-carborane precursor was recovered. Although the Na/Hg alloy has been widely used in coupling reactions of many organometallic species,[42] there have been no reports of its use either in the reductive cage opening of the carboranes or in the synthesis of mercuracarborane complexes. Therefore, the reaction shown in Scheme 3 is an unprecedented example of a new reductive cage-opening process that could prove applicable to the *closo*-carboranes in both the icosahedral and sub-icosahedral cage systems, thus affording hitherto unknown metallacarborane species.

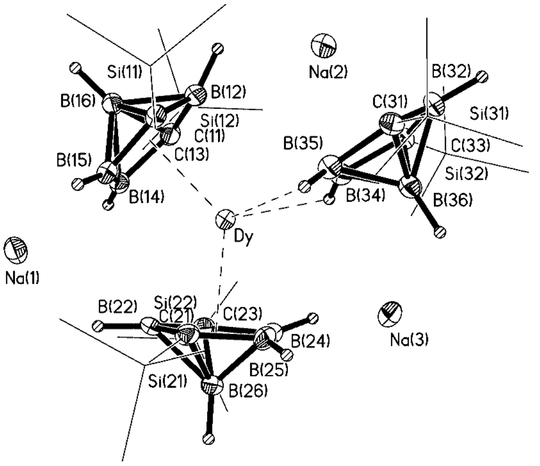
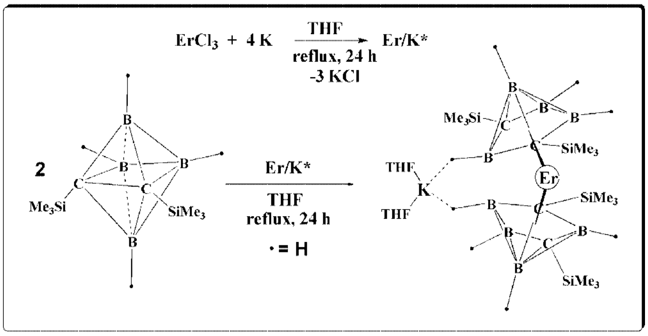


Figure 2. Crystal structure of a full-sandwiched dysprosacarborane complex



Scheme 3. One-pot two-electron reductive cage opening with concomitant metalation of the carborane ligand

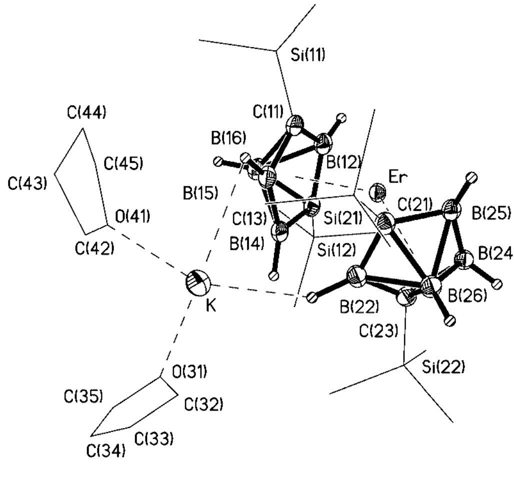
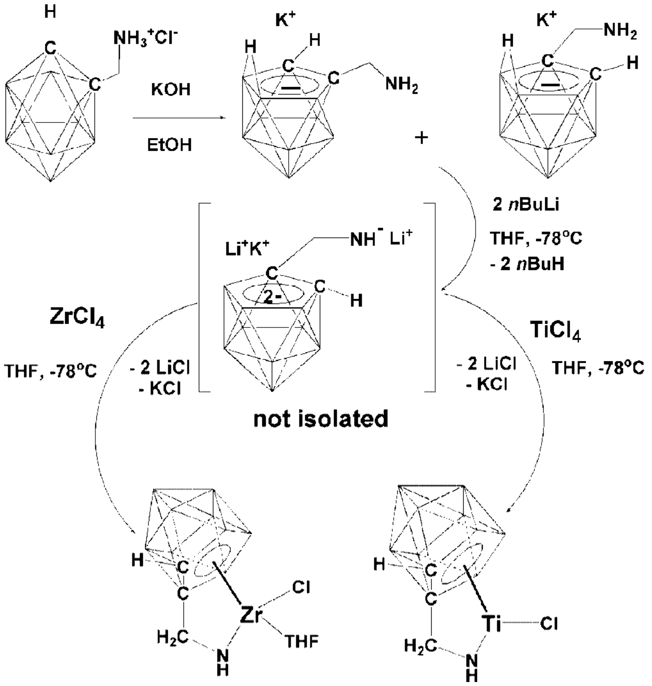


Figure 3. Crystal structure of a full-sandwiched erbacarborane complex

3. Chemistry of Half-Sandwich, Constrained-Geometry C_2B_9 Metallacarboranes

The potential applications of functionalized carborane clusters in catalytic organic reactions have resulted in reports of the syntheses and reactivities of several new metallacarboranes.[43] Our preliminary research has shown that the trianionic ligand [*nido*-7-(CH_2NH)-7,8-$C_2B_9H_{10}$]$^{3-}$, prepared from the reaction of [*nido*-7-(CH_2NH_2)-7,8-$C_2B_9H_{11}$]$^-$ with 2 equiv. of *n*BuLi, reacts with MCl_4 (M = Ti, Zr) to give the corresponding half-sandwich metallacarboranes (Scheme 4).[44]

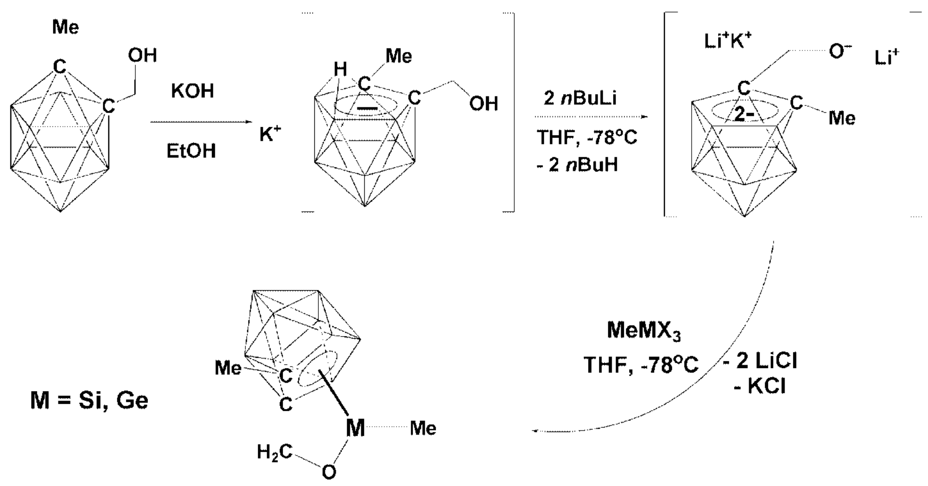


Scheme 4. Synthesis of *ansa*-alkylamidometallacarboranes; unlabelled vertices are BH groups

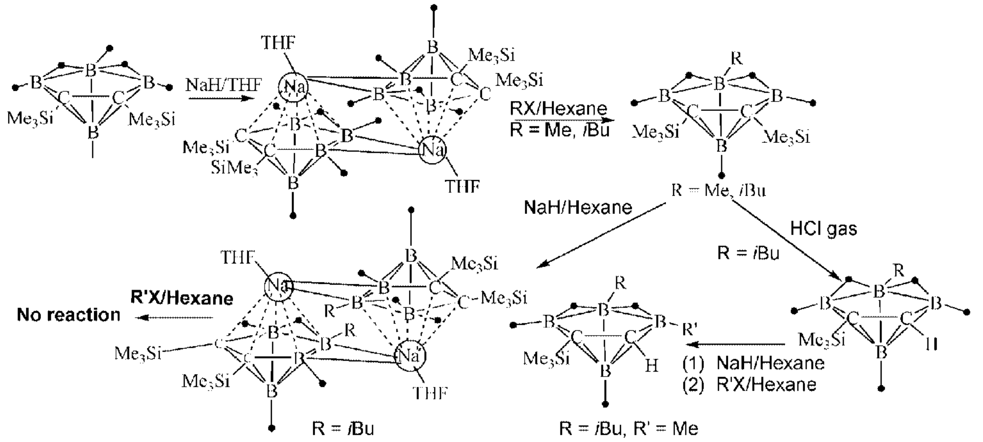
Of the handful of reports in which the appended moiety forms either a coordinate covalent bond or another delocalized π-bond with the metal atom *exo*-polyhedrally, none have demonstrated the additional stabilization of the metal atom by σ-bonding to the $C_{(cage)}$-appended moiety.[43] Therefore, our results are the first examples of half-sandwiched group-4 metallacarboranes in which the nitrogen atom of the *exo*-polyhedral $C_{(cage)}$-alkylamido unit is $\eta^1(\sigma)$-bonded to the metal atom that is complexed with the open C_2B_3-bonding face of the carborane ligand (Scheme 4). Other constrained-geometry ligands, such as the *ansa*-alkyloxocarborane, can thus be used to prepare a series of $C_{(cage)}$-appended half-sandwich alkyloxometallacarboranes (Scheme 5)[45] In these syntheses, the in situ generated trianionic ligand is treated with anhydrous $MeMCl_3$ (M = Si, Ge), followed by re-crystallization from a toluene/heptane solution to form the corresponding half-sandwich group-14 metallacarboranes, *closo*-1-M(Me)-2-[1-$\eta^1(\sigma)$-OCH_2]-3-Me-η^5-2,3-$C_2B_9H_9$ (M = Si, Ge), in 48 and 56% yields, respectively. The NMR spectra, IR spectra and the microanalytical data for these species confirmed the formulations shown in Scheme 5.[45]

4. Syntheses and Reactivities of $B_{(cage)}$-Alkyl- and -Silylamido C_2B_4 Carborane Ligands

The usefulness of the carborane ligands would be extended if substituents could be systematically introduced on the boron atoms of both 2,3- and 2,4-C_2B_4 carboranes. While there have been several isolated reports of the syntheses of such derivatives,[46–48] only Davis and Grimes have reported a systematic study of the *B*-alkylation of the *nido*-C_2B_4 cage.[49] They found that the reactions of the [*nido*-2,3-$R_2C_2B_4H_5$]$^-$ (R = Et, CH_2Ph) anion with the organic halides R′X [R′ = Me, Et, CH_2Ph, $(CH_2)_3Ph$ and $CH_2C_6H_4Me$; X = Cl or Br] gave exclusively *nido*-4-(R′)-2,3-$(R)_2$-2,3-$C_2B_4H_5$ products. The triethyl- and tribenzyl-alkylated carboranes undergo both metalation and cage-fusion reactions. However, this study was not systematically extended to further alkylation reactions. To investigate the reactivities of alkylated and polyalkylated carboranes, we examined the regiospecific alkylation of the *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ carborane and investigated the chemical behavior of any *B*-alkylated products. The following questions were addressed: (1) Is it possible to systematically alkylate and/or polyalkylate carboranes having such bulky substituents as the $SiMe_3$ groups? (2) If so, what is the effect of the $SiMe_3$ groups in determining the distribution of products? (3) Could any alkylated product undergo standard deprotonation and oxidation reactions preparatory to the formation of metallacarboranes and the "carbon atoms apart" analogues, respectively? (4) How effective are the standard techniques of ^1H, ^{11}B, and ^{13}C NMR spectroscopy in identifying the structures of any alkylated products? To address these concerns, the sodium compound of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ was treated with standard alkylating agents, MeI and *i*BuBr, to produce the corresponding neutral monoalkylated carboranes, *nido*-5-(*R*)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ (R = Me and *i*Bu) in 75% yields (see Scheme 6).[50]



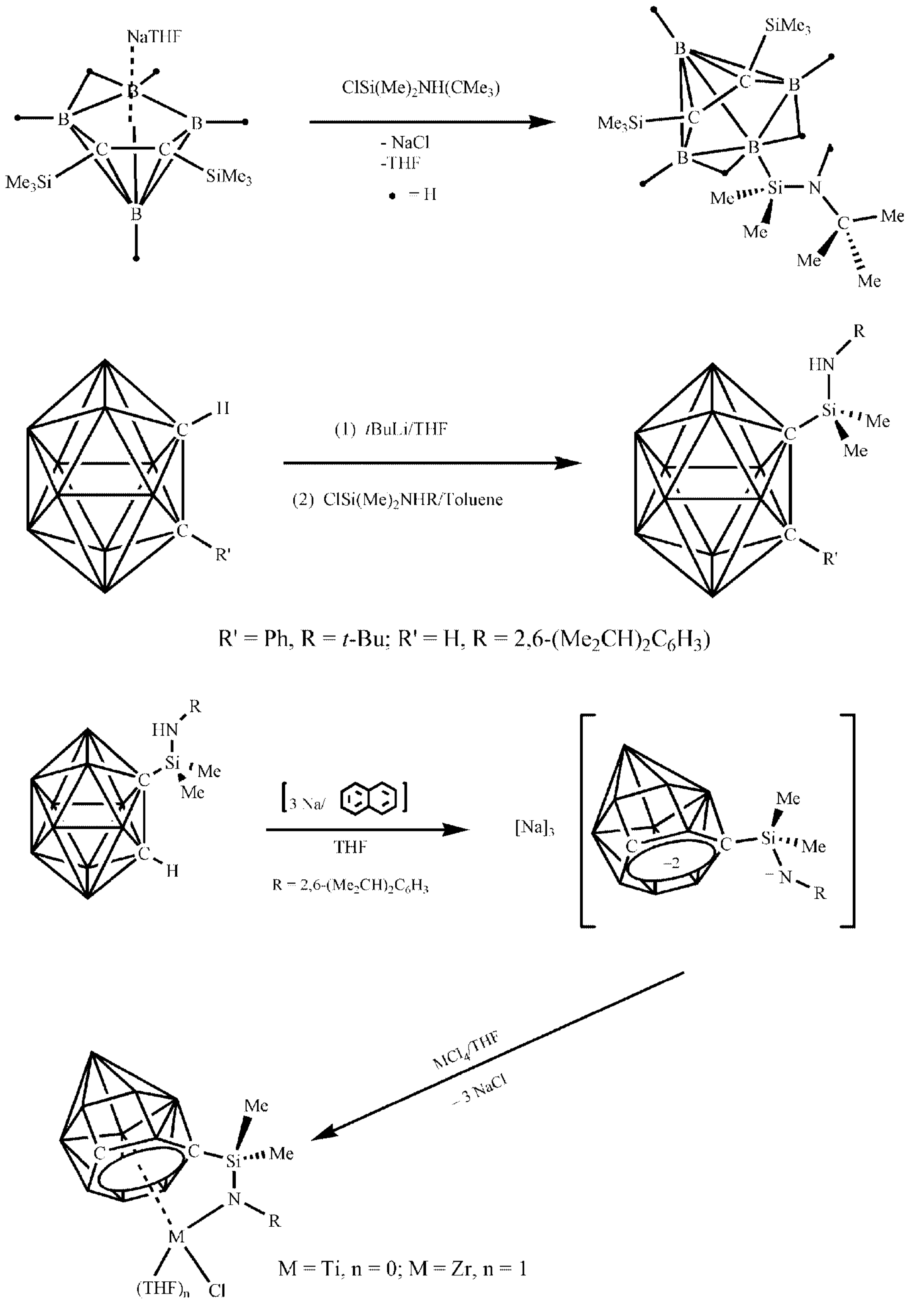
Scheme 5. Synthesis of *ansa*-alkyloxometallacarboranes; unlabelled vertices are BH groups



Scheme 6. Systematic $B_{(\mathrm{cage})}$-alkylation of *nido*-2,3-$(\mathrm{SiMe_3})_2$-2,3-$\mathrm{C_2B_4H_6}$

The alkylation reaction seems to be a general one that leads exclusively to $B_{(\mathrm{unique})}$-alkylated products. These reactions presumably proceed through an intermediate in which the incoming alkyl unit is bridged between the unique boron atom and one of its neighboring basal boron atoms. The intermediate then collapses with the alkyl group migrating to the terminal position of one of the two boron atoms, changing places with its terminal hydrogen atom. The difference in the directing ability of $\mathrm{SiMe_3}$ compared with *C*-alkyl groups is probably due to the steric bulk of the former. This unique directive property of the $\mathrm{SiMe_3}$ group was profitably exploited in the synthesis of the corresponding $B_{(\mathrm{cage})}$-silylamido-substituted carborane derivatives. The reactions of $\mathrm{RNHSi(Me)_2Cl}$ [R = *t*Bu, 2,6-$(\mathrm{Me_2CH})_2\mathrm{C_6H_3}$] with the carborane ligands *nido*-1-Na-$(\mathrm{C_4H_8O})$-2,3-$(\mathrm{SiMe_3})_2$-2,3-$\mathrm{C_2B_4H_5}$ and Li[*closo*-1-R′-1,2-$\mathrm{C_2B_{10}H_{10}}$] produced two kinds of neutral ligand precursors, *nido*-5-[$\mathrm{Si(Me)_2N(H)R}$]-2,3-$(\mathrm{SiMe_3})_2$-2,3-$\mathrm{C_2B_4H_5}$ (R = *t*Bu) and *closo*-1-R′-2-[$\mathrm{Si(Me)_2N(H)R}$]-1,2-$\mathrm{C_2B_{10}H_{10}}$ [R = *t*Bu, R′ = Ph; R = 2,6-$(\mathrm{Me_2CH})_2\mathrm{C_6H_3}$, R′ = H], in 85, 92, and 95% yields, respectively (Scheme 7).[51] Treatment of *closo*-2-[$\mathrm{Si(Me)_2NH}$(2,6-$(\mathrm{Me_2CH})_2\mathrm{C_6H_3}$)]-1,2-$\mathrm{C_2B_{10}H_{11}}$ with 3 equiv. of freshly cut sodium metal in the presence of naphthalene produced, in almost quantitative yield, the corresponding cage-opened sodium salt of the "carbon atoms apart" carborane trianion, [*nido*-3-{$\mathrm{Si(Me)_2N}$(2,6-$(\mathrm{Me_2CH})_2\mathrm{C_6H_3}$)}-1,3-$\mathrm{C_2B_{10}H_{11}}$]$^{3-}$, whose reaction with anhydrous $\mathrm{MCl_4}$ (M = Ti and Zr) in 1:1 molar ratios gave the corresponding half-sandwich neutral d^0-metallacarboranes, *closo*-1-M[(Cl)(THF)$_n$]-2-{1′-η^1,σ-N[2,6-$(\mathrm{Me_2CH})_2$-$\mathrm{C_6H_3}$]$\mathrm{(Me)_2Si}$}-2,4-η^6-$\mathrm{C_2B_{10}H_{11}}$ (M = Ti, *n* = 0; M = Zr, *n* = 1) in 47 and 36% yields, respectively (Scheme 7).[51] Conversely, the small-cage species 5-*t*$\mathrm{BuNHSi(Me)_2}$-2,3-$(\mathrm{SiMe_3})_2$-2,3-$\mathrm{C_2B_4H_5}$ had limited use as a ligand since it could not withstand deprotonation with a strong base. Therefore, the reactivity of the neutral carborane with $\mathrm{M(NMe_2)_4}$ (M = Zr and Ti) was studied. However, while possible metalation occurred, no characterizable products could be isolated.[51] All compounds were characterized by elemental analysis, ^{1}H, ^{11}B, and ^{13}C NMR spectra and IR spectra, and the ligand processor, *closo*-2-[$\mathrm{Si(Me)_2NH}${2,6-$(\mathrm{Me_2CH})_2\mathrm{C_6H_3}$}]-1,2-$\mathrm{C_2B_{10}H_{11}}$, was also characterized by single-crystal X-ray diffraction.

The crystal structure (Figure 4) of this *ansa* ligand shows that it consists of a closed $\mathrm{C_2B_{10}}$ polyhedron with a distorted icosahedral cage geometry. The intracage bond



Scheme 7. Syntheses, cage-opening and concomitant metalation of the *B*$_{(cage)}$- and *C*$_{(cage)}$-substituted silylamidocarborane ligands; unlabelled vertices are BH groups

lengths are quite similar to those reported for *closo*-1-(methyl)-2-(phthalimidomethyl)-1,2-$C_2B_{10}H_{10}$.[52] The *exo*-polyhedral $Si(Me)_2NH[2,6-(Me_2CH)_2C_6H_3]$ group is attached to a cage carbon atom by a standard 2*c*2*e* bond, and the Si−C(02) bond of 1.911(3) Å is longer than the Si−C bonds in $(C_5Me_4SiMe_2N$*t*Bu)Ti(prone-2,4-hexadiene) [1.869(6) Å],[53] and η^5:σ-$Me_2Si(C_9H_6)$-η^6-$(C_2B_{10}H_{10}$-$CH_2NMe)Zr(NC_5H_5)]$ [1.861(6) Å].[54] The four groups on the silicon atom are in a distorted tetrahedral arrangement, with X−Si−Y angles ranging from 103.53° for N−Si−C(02) to 114° for N−Si−C(03/04). The most interesting aspect of this structure is the large C(1)−N−Si angle of 125.5(2)°.[51] This is probably due to repulsion between the Si−Me groups and the large diisopropylphenyl moiety. Such an angle indicates that the lone pair on the nitrogen atom would not be particularly available for bonding. However, from its conversion to the corresponding half-sandwich neutral d^0-metallacarborane, *closo*-1-M[(Cl)(THF)$_n$]-2-{1′-η^1,σ-N[2,6-($Me_2CH)_2C_6H_3$](Me)$_2$Si}-2,4-η^6-$C_2B_{10}H_{11}$ (M = Ti, *n* = 0; M = Zr, *n* = 1), it seems that η^1-coordination of the N atom is possible after removal of its H atom to form the amido group.

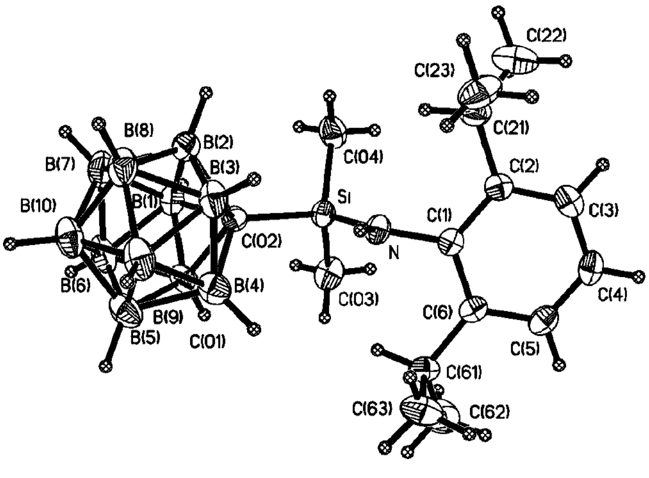


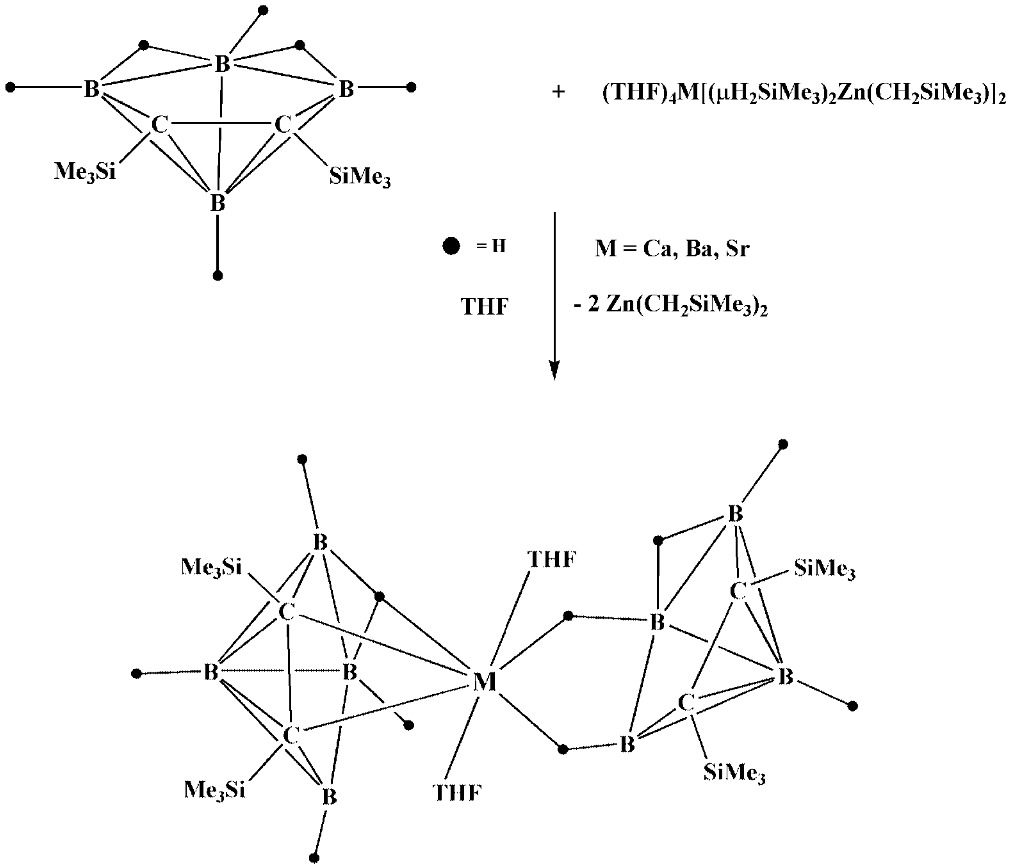
Figure 4. Crystal structure of the *ansa*-carborane ligand, *closo*-2-[Si(Me)$_2$NH{2,6-($Me_2CH)_2C_6H_3$}]-1,2-$C_2B_{10}H_{11}$

5. Novel Synthetic Approach to Heavier Group-2 Metallacarboranes

The reaction of tetrakis(tetrahydrofuran)barium bis[tris(trimethylsilylmethyl)zincate] with 2,3-bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane in THF yielded nearly quantitatively the bis(carborane)barium complex (Scheme 8).[55]

Only one of the trimethylsilylmethyl groups of the zincate is active in this metalation. The formed bis(trimethylsilylmethyl)zinc neither reacts with the carborane nor with the bis(carborane)barium complex. Each barium atom in the dimeric complex shows a coordination number of nine (Figure 5).[55]

The Ba−O bond lengths (ca. 2.74 Å) lie in the expected range. Furthermore, two carborane ligands are bonded via hydride bridges with Ba−H distances of approximately 2.90 Å, which were refined isotropically and can be interpreted as Ba−H−B three-center bonds. A third carborane ligand is coordinated with Ba−C distances of 3.16 Å and a bridging hydrogen atom [Ba1−H356 = 2.93(4) Å]. This corre-



Scheme 8. Synthesis of heavier group-2 metallacarboranes of the C_2B_4 cage systems

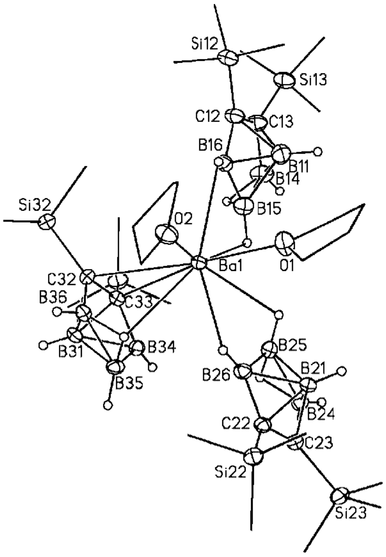


Figure 5. Crystal structure of a baracarborane complex

sponds to a four-center $BaHB_2$ bond. In the highly ionic solvated $Ba(BH_4)_2$ the boranate anions coordinate via three H atoms to the alkaline earth metal atom, thus forming three-center Ba−H−B bonds.[56] The Ba−C distances are similar to those of barium bis[tris(trimethylsilylmethyl)zincates][57] where bridging trimethylsilylmethyl moieties between barium and zinc atoms were found. The Ba−C distances of substituted barocenes vary between 2.90 and 3.00 Å.[58] This coordination of the carborane to the barium center is quite different from that of (carborane)magnesium and -calcium complexes.[31,59−61] In the magnesacarborane complex the metal center bonds to the hydride substituents but not to the carbon atoms. With the doubly deprotonated carborane ligands the metal centers show shorter contacts to the boron atoms than to the carbon atoms. The barium complex has very long Ba−B bonds due to the coordination geometry about the metal center. Nevertheless, this baracarborane was the first example of the heaviest group-2 metallacarborane. Similarly, the corresponding calca- and strontacarboranes have been synthesized and structurally characterized.[62]

Conclusions

Our recent work on carborane chemistry has concentrated on developing synthetic routes to new carborane ligands in both large and small cage systems. The aim is to establish general procedures for the systematic production of specific metallacarboranes that have potentially useful and interesting properties. We have also developed synthetic routes to precursor boranes that might otherwise be unavailable. Such routes invite chemists to explore the properties of these fascinating molecules.

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