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Synthesis, Structure, and Reactivity of 13- and 14-Vertex Carboranes

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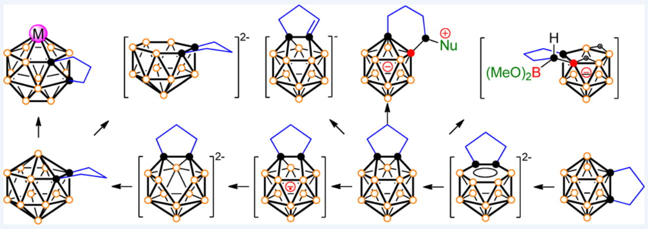

CONSPECTUS: Carboranes are a class of polyhedral boron hydride clusters in which one or more of the BH vertices are replaced by CH units. Their chemistry has been dominated by 12-vertex carboranes for over half a century. In contrast, knowledge regarding supercarboranes (carboranes with more than 12 vertices) had been limited merely to possible cage geometries predicted by theoretical work before 2003. Only in recent years has significant progress been made in synthesizing supercarboranes. Such a breakthrough relied on the use of Carbon-Atoms-Adjacent (CAd) nido-carborane dianions or arachno-carborane tetraanions as starting materials. In this Account, we describe our work on constructing and elucidating the chemistry of supercarboranes.

Earlier attempted insertions of the formal $[BR]^{2+}$ unit into Carbon-Atoms-Apart (CAp) 12-vertex *nido*-$[7,9\text{-}C_2B_{10}H_{12}]^{2-}$ did not produce the desired 13-vertex carboranes. Such failure is often attributed to the extraordinary stability of the B_{12} icosahedron (the "icosahedral barrier"). However, the difference in reducing power between CAp and CAd 12-vertex *nido*-carborane dianions had been overlooked. Our results have shown that CAd nido-carborane dianions are weaker reducing agents than the CAp isomers, allowing a capitation to prevail over a redox reactivity. This finding provides an entry point to the synthesis of supercarboranes and a series of 13- and 14-vertex *closo*-carboranes have been prepared and structurally characterized. They share some chemical properties with those of 12-vertex carboranes; on the other hand, they have their own unique characteristics. For example, a 13-vertex *closo*-carborane can undergo single electron reduction to give a stable carborane radical anion with $[2n + 3]$ framework electrons, which can accept one additional electron to form a 13-vertex CAd *nido*-carborane dianion. 13-Vertex *closo*-carborane can also react with various nucleophiles to afford the cage carbon and/or boron extrusion products *closo*-CB_{11}^{-}, *nido*-CB_{10}^{-}, *closo*-CB_{10}^{-}, and *closo*-C_2B_{10}, depending on the nature of the nucleophiles.

Studies of supercarboranes remain a relative young research area, particularly in comparison to the rich literature of icosahedral carboranes with 12-vertices. Other supercarboranes are expected to be prepared and structurally characterized as the field progresses, and the results detailed here will further these efforts.

■ INTRODUCTION

Carboranes are a class of polyhedral boron hydride clusters in which one or more of the BH vertices are replaced by CH units. They constitute a class of structurally unique molecules with exceptionally thermal and chemical stabilities and the ability to hold various substituents. These properties have made them useful basic units in supramolecular design, medicine, catalysts and materials.[1] Their chemistry has been dominated by icosahedral carboranes with 12 vertices for over half a century.[1] On the other hand, carboranes with more than 12 vertices (supercarboranes), although studied theoretically, were experimentally unknown until 2003.[2]

Many attempts to prepare 13-vertex carboranes using "polyhedral expansion" methodology[3] by insertion of $[BR]^{2+}$ (R = alkyl, H, halide) into a 12-vertex Carbon-Atoms-Apart (CAp) *nido*-$[7,9\text{-}C_2B_{10}H_{12}]^{2-}$ failed,[2] although this method works well in the reconstruction of *o*-carboranes via reaction of 11-vertex Carbon-Atoms-Adjacent (CAd) *nido*-$[7,8\text{-}C_2B_9H_{11}]^{2-}$ with RBX_2.[1a] It also works well in the synthesis of a series of 13-vertex metallacarboranes via the insertion of a metal fragment into a 12-vertex CAp *nido*-$[7,9\text{-}C_2B_{10}H_{12}]^{2-}$.[1a] The failure to insert boron is often attributed to "icosahedral barrier" (the extraordinary stability of the B_{12} icosahedron).[2]

We revisited the aforementioned reactions and found that 12-vertex CAp *nido*-$[7,9\text{-}C_2B_{10}H_{12}]^{2-}$ is a very strong reducing agent, whereas 11-vertex CAd *nido*-$[7,8\text{-}C_2B_9H_{11}]^{2-}$ is almost redox inactive, which is supported by literature work.[4] Such a dramatic difference in reducing power between isomers of *nido*-carborane dianions had been largely overlooked. With this in mind, we speculated that there are two competitive reactions between CAp *nido*-$[7,9\text{-}C_2B_{10}H_{12}]^{2-}$ and RBX_2: capitation versus redox reaction. The former leads to the formation of a 13-vertex carborane $C_2B_{11}H_{12}(R)$, while the latter gives *o*-$C_2B_{10}H_{12}$, the starting material. In other words, the experimentally observed *o*-$C_2B_{10}H_{12}$ in the above reactions appears to be the result of a redox reaction, rather than the degradation of the expected 13-vertex carborane by losing a BH vertex.[2] If this is true, lowering the reducing power of *nido*-$[R_2C_2B_{10}H_{10}]^{2-}$ dianions should promote the capitation, leading to the formation of the desired supercarboranes.

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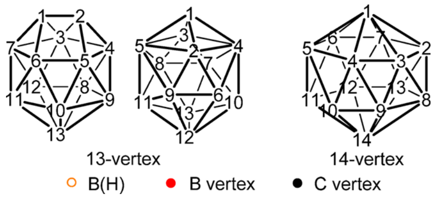
Electrochemical studies show that the redox potentials of carboranes depend upon the relative positions of the two cage carbons atoms.[5] The easiest way to control the relative positions of such cage carbons during the cage-opening process is to introduce an appropriate linker between two cage carbon atoms. To this end, we developed a method to prepare three regioisomers of *nido*-$[R_2C_2B_{10}H_{10}]^{2-}$ in a controlled manner, in which the two cage carbons are in 7,8-, 7,9-, and 7,10-positions, respectively.[6] Reactivity studies on these isomers show that CAd *nido*-$[7,8\text{-}R_2C_2B_{10}H_{10}]^{2-}$ has the weakest reducing power among them. This finding offered a critical entry point into the synthesis of supercarboranes.[7] Since then, significant progress has been made in this research area.[7,8] This Account summarizes these recent developments in the synthesis, structure, and reactivity of 13- and 14-vertex carboranes. Their numbering systems and color codes are illustrated in Chart 1.

Chart 1. Numbering System and Color Code in 13- and 14-Vertex *closo*-Clusters

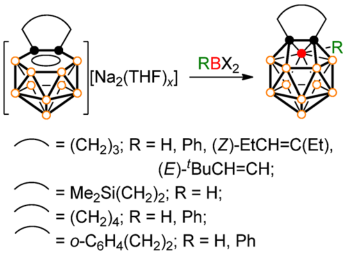


13-VERTEX CARBORANES

Synthesis and Characterization

13-Vertex *closo*-carboranes can be prepared by reaction of CAd 12-vertex *nido*-carborane dianions with dihaloboranes via a [12 + 1] protocol. Treatment of $[7,8\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_{10}H_{10}][Na_2(THF)_x]$, $[7,8\text{-}Me_2Si(CH_2)_2\text{-}7,8\text{-}C_2B_{10}H_{10}][Na_2(THF)_x]$, or $[7,8\text{-}(CH_2)_4\text{-}7,8\text{-}C_2B_{10}H_{10}][Na_2(THF)_x]$ with $HBBr_2\cdot SMe_2$ in toluene afforded CAd 13-vertex *closo*-carboranes $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$,[9] $1,2\text{-}Me_2Si(CH_2)_2\text{–}1,2\text{-}C_2B_{11}H_{11}$,[10] or $1,2\text{-}(CH_2)_4\text{-}1,2\text{-}C_2B_{11}H_{11}$[11] in about 40% isolated yields (Scheme 1).

Scheme 1. Synthesis of CAd 13-Vertex *closo*-Carboranes



Mono-B-substituted 13-vertex *closo*-carboranes $3\text{-R-}1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{10}$ [R = Ph, (*Z*)-EtCH═C(Et), (*E*)-^{t}BuCH═CH],[9] $3\text{-Ph-}1,2\text{-}(CH_2)_4\text{-}1,2\text{-}C_2B_{11}H_{10}$,[11] and $3\text{-Ph-}1,2\text{-}o\text{-}C_6H_4(CH_2)_2\text{-}1,2\text{-}C_2B_{11}H_{10}$[12] were synthesized in the same manner using RBX_2 (X = Cl, Br) as capping agents.

CAd 13-vertex *closo*-carboranes have a henicosahedral cage geometry with one trapezoidal C_2B_2 open face, and thus, the cage C atoms are less connected. A typical structure is shown in Figure 1. The $C_{cage}–C_{cage}$ distances are much shorter than those observed in other carboranes (Table 1), and diagnostically, the ^{13}C NMR signals of cage carbons are significantly downfield shifted to about 140 ppm (Table 2). Most of CAd 13-vertex *closo*-carboranes without B-substituents exhibit similar ^{11}B NMR spectra spanning a narrow range 5 to −2 ppm in a 1:5:5 pattern (Figure 2).

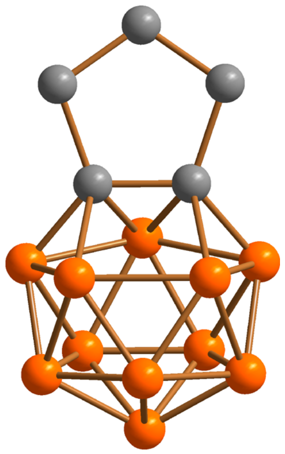


Figure 1. Molecular structure of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$.

13-Vertex *closo*-carboranes without a C,C′-linkage were also prepared. $1,2\text{-}Me_2Si(CH_2)_2\text{-}1,2\text{-}C_2B_{11}H_{11}$ undergoes facile desilylation on silica gel to afford $1,2\text{-}Me_2\text{-}1,2\text{-}C_2B_{11}H_{11}$.[10] It does not degrade to a 12-vertex carborane in solution but isomerizes upon heating to its CAp isomer, $1,6\text{-}Me_2\text{-}1,6\text{-}C_2B_{11}H_{11}$ (Scheme 2). This result suggests that the C,C′-linkage does not have any obvious effects on the stability of 13-vertex *closo*-carboranes and that the CAp isomer is thermodynamically more stable than its CAd one. These results support our earlier assumption that the reducing power of *nido*-carborane dianions plays a critical role in the synthesis of supercarboranes. The role of C,C′-linkage is to lock the two cage carbon atoms in *ortho*-positions during the reduction, leading to the formation of CAd *nido*-carborane dianions with lower reducing power, which facilitates the capitation reaction to yield 13-vertex *closo*-carboranes.

Electrophilic Substitution

Treatment of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$ with excess MeI, Br_2, or I_2 in the presence of $AlCl_3$ generated hexa-substituted 13-vertex *closo*-carboranes $8,9,10,11,12,13\text{-}X_6\text{-}1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_5$ (X = Me, Br, I; Scheme 3).[9] Similar to the 12-vertex carboranes, the substituted B(H) vertices are those farthest from the cage carbons, that is, the most electron-rich. These B-substituted species have similar structural features to the parent 13-vertex *closo*-carborane, but the substituents significantly influence the cage boron chemical shifts due to electronic effects (Figure 3).

One-Electron Reduction

Carboranes with odd skeletal electron counts are very rare. The only characterized example is neutral radical $CB_{11}Me_{12}\cdot$ with [2*n* + 1] framework electrons.[13] We found that 13-vertex carborane radical anion $[\{1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}\}\cdot][Na(18\text{-}crown\text{-}6)(THF)_2]$ could be isolated in 80% yield as brown crystals from the reaction of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$ with 1 equiv of Na metal in THF, followed by recrystallization in the presence of 18-crown-6 (Scheme 4).[14] It has a very similar cage structure to that of its parent species but with elongated bond lengths. This radical species exhibits an EPR signal with g = 1.994 at room temperature, which is similar to that observed in

Table 1. Cage C−C Bond Lengths (Å) in CAd Carboranes $R_2C_2B_nH_n$ (n = 11, 12)

R_2	13-vertex *closo-*	13-vertex *nido-*	14-vertex *closo-*	
			2,3-isomer	2,8-isomer
$(CH_2)_3$	1.421(3)	1.529(8)	1.608(4)	1.599(3)
$Me_2Si(CH_2)_2$	1.439(3)	1.568(6)	1.648(3)	1.663(5)
$(CH_2)_4$	1.425(4)			1.622(3)
o-$C_6H_4(CH_2)_2$	1.427(2)	1.553(5)	1.594(4)	
Me_2	1.421(5)	1.556(11)		

Table 2. ^{13}C Chemical Shifts of Cage Carbons in Carboranes $R_2C_2B_nH_n$ (n = 10−12)[a]

R_2	12-vertex *closo-*	13-vertex *closo-*	13-vertex *nido*[b]	14-vertex *closo-*	
$(CH_2)_3$	84.0	136.4	16.0	72.3 (2,3-)	90.0 (2,8-)
$Me_2Si(CH_2)_2$	87.5	144.5	11.2	76.2 (2,3-)	90.9 (2,8-)
$(CH_2)_4$	73.2	142.5	10.3	66.0 (2,3-)	78.4 (2,8-)
o-$C_6H_4(CH_2)_2$	71.2	138.9	9.2	65.0 (2,3-)	
Me_2	73.5	140.7 (1,2-)	7.3 (1,2-)		77.7 (2,8-)[c]
		120.6, 83.2 (1,6-)	44.4, 35.7 (1,6-)	63.7 (2,4-)	78.6 (2,9-)

[a] In $CDCl_3$, in units of ppm. Numbers in parentheses refer to the cage carbon positions of the compounds. [b] In d_5-pyridine. [c] In CD_2Cl_2.

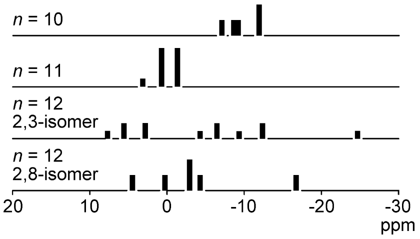
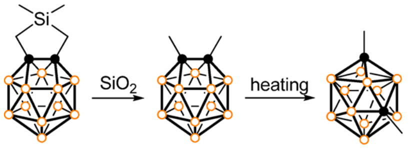
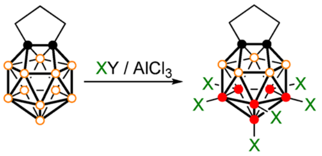


Figure 2. Stick presentation of chemical shifts and relative intensities of $^{11}B\{^1H\}$ spectra of $(CH_2)_3C_2B_nH_n$ (n = 10−12).

Scheme 2. Synthesis of CAd and CAp 13-Vertex *closo*-Carboranes without C,C′-Linkage



Scheme 3. Electrophilic Substitution Reaction of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$



X = Me, Y = I; X = Y = Br or I

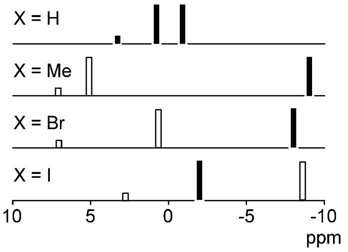
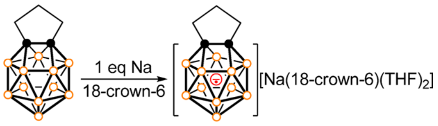


Figure 3. Stick presentation of chemical shifts and relative intensities of $^{11}B\{^1H\}$ spectra of $8,9,10,11,12,13\text{-}X_6\text{-}1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_5$. The solid and hollow lines represent the BH and BX vertices, respectively.

Scheme 4. One-Electron Reduction of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$



$CB_{11}Me_{12}\cdot$.[13] It can be viewed as [2n + 3] system that is an intermediate between the two well-established and abundant [2n + 2] and [2n + 4] systems. Cyclic voltammetry of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$ shows stepwise two-electron reduction, with the first wave reversible and the second quasi-reversible (Figure 4). It is noteworthy that the corresponding 12-vertex carborane $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{10}H_{10}$ only undergoes a simultaneous two-electron reduction to give *nido*-$[(CH_2)_3C_2B_{10}H_{10}]^{2-}$.[15] These results suggest that larger cages may enhance the stability of clusters with [2n+3] framework electrons.

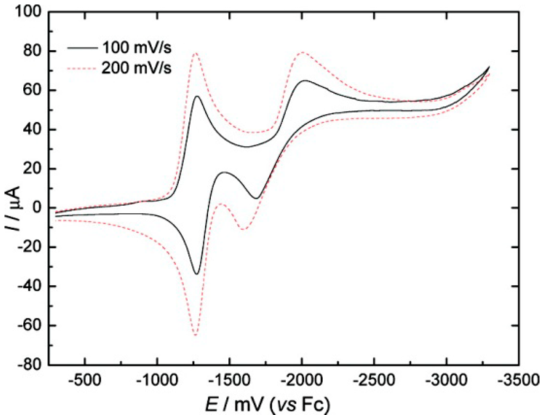
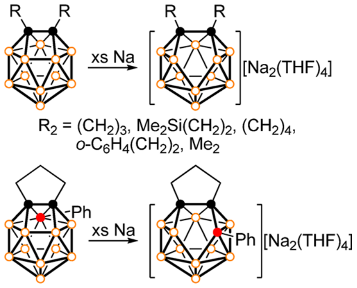


Figure 4. Cyclic voltammetry of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$. Reproduced with permission from ref 14. Copyright 2007 American Chemical Society

Two-Electron Reduction

13-Vertex *closo*-carboranes are readily reduced to the corresponding *nido*-carborane dianions by excess group 1 metals. Treatment of 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$, 3-Ph-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{10}$, 1,2-$Me_2Si(CH_2)_2$-1,2-$C_2B_{11}H_{11}$, 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$, 1,2-*o*-$C_6H_4(CH_2)_2$-1,2-$C_2B_{11}H_{11}$, or 1,2-Me_2-1,2-$C_2B_{11}H_{11}$ with excess Na metal in THF afforded 13-vertex [1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$],[9] [3-Ph-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{10}$][$Na_2(THF)_4$],[9] [1,2-$Me_2Si(CH_2)_2$-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$],[16] [1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$]-[$Na_2(THF)_4$],[16] [1,2-*o*-$C_6H_4(CH_2)_2$−1,2-$C_2B_{11}H_{11}$]-[$Na_2(THF)_4$],[9] or [1,2-Me_2-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$],[16] respectively, in high yields (Scheme 5).

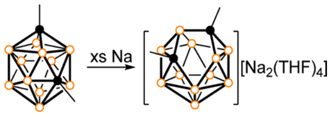
Scheme 5. Reduction of CAd 13-Vertex Carboranes by Na Metal



These complexes have structures related to one-dimensional coordination polymers inasmuch as Na^+ ions link the carborane cages via Na···H−B interactions. The cages all have a bent five-membered C_2B_3 open face, which is generated by formally breaking the B−B bond in the trapezoidal face of the parent *closo*-carboranes. The cage C−C bonds are elongated by about 0.1 Å (Table 1). It is noteworthy that the two cage carbons remain in adjacent positions during the reduction of 1,2-Me_2-1,2-$C_2B_{11}H_{11}$, forming [1,2-Me_2-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$], which is significantly different from that of 12-vertex analogues.[1a]

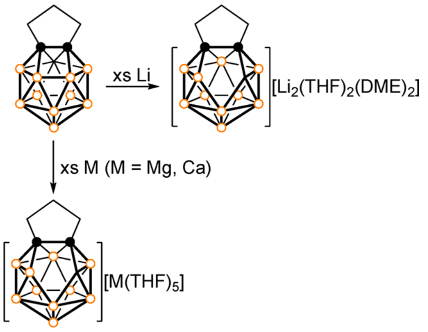
The CAp 13-vertex *closo*-carborane 1,6-Me_2-1,6-$C_2B_{11}H_{11}$ also reacted quickly with excess Na metal in THF to afford CAp *nido*-[1,3-Me_2-1,3-$C_2B_{11}H_{11}$][$Na_2(THF)_4$] (Scheme 6). The geometry of the anion is similar to those of CAd ones, however, in this case the two cage carbons have become separated, as confirmed by X-ray analyses.[16]

Scheme 6. Reduction of CAp 1,6-Me_2-1,6-$C_2B_{11}H_{11}$ by Na Metal



13-Vertex *closo*-carboranes can be reduced by other alkali or alkali earth metals. Treatment of 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with excess Li or activated Mg or Ca powder in THF, gave [1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$][$Li_2(THF)_2(DME)_2$] or [1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$][$M(THF)_5$] (M = Mg, Ca) (Scheme 7).[9] No 13-vertex *arachno*-carborane tetraanion has ever been observed even under forced reaction conditions. In sharp contrast, 12-vertex *closo*-carborane 1,2-$(CH_2)_3$-1,2-$C_2B_{10}H_{10}$ was readily reduced by excess Li metal to form CAd [*arachno*-$(CH_2)_3C_2B_{10}H_{10}$]$^{4-}$ via [*nido*-$(CH_2)_3C_2B_{10}H_{10}$]$^{2-}$.[6] All CAd 13-vertex *nido*-carborane salts without boron substituents exhibit very similar ^{11}B NMR spectra with peaks at about −10, −15, and −26 ppm in an intensity ratio of 1:5:5. These high-field shifted signals indicate the increased charge density of the cage after taking up two electrons. This phenomenon is also reflected in the upfield-shifted cage-carbon signals (<20 ppm) observed in the ^{13}C NMR spectra (Table 2).

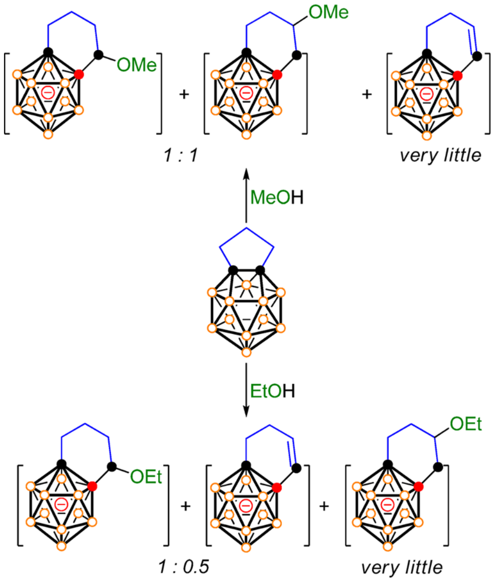
Scheme 7. Reduction of 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ by Li, Mg and Ca Metal



Cage Carbon Extrusion

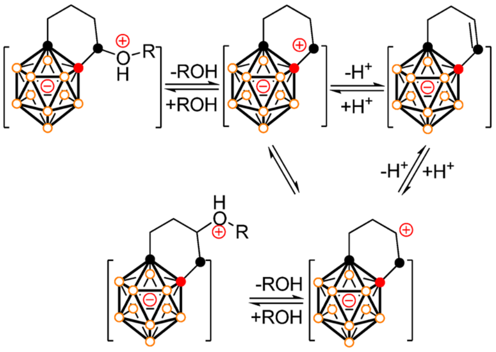
CAd 13-vertex *closo*-carborane 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ reacts with a variety of nucleophiles to give the cage carbon extrusion products, that is, 12-vertex *closo*-CB_{11}^--type anions.[17,18] Reaction of 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with ROH gave a mixture of CB_{11}^- anions [1,2-$(CH_2)_3CH(OR)$-1-$CB_{11}H_{10}$]$^-$, [1,2-$(CH_2)_2CH(OR)CH_2$-1-$CB_{11}H_{10}$]$^-$ (R = Me, Et), and [1,2-$(CH_2)_2CH{=}CH$-1-$CB_{11}H_{10}$]$^-$ (Scheme 8). The product ratio was influenced by nucleophilicity of the alcohol. Control experiments indicated that [1,2-$(CH_2)_3CH(OMe)$-1-$CB_{11}H_{10}$]$^-$ was initially formed, which was stable in a basic MeOH solution but led to a mixture of products under acidic conditions. Thus, an acid-promoted elimination/isomerization pathway is proposed to account for the formation of these CB_{11}^- mixtures (Scheme 9).

Scheme 8. Reaction of 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with Alcohols



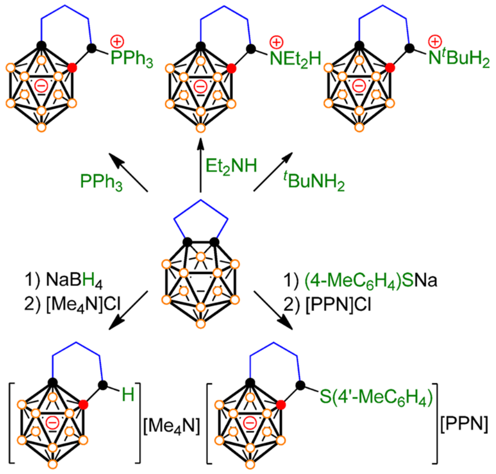
1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ reacted with PPh_3, ^{t}BuNH$_2$, or Et_2NH in toluene to give zwitterionic complex 1,2-$(CH_2)_3CH$-(PPh_3)-1-$CB_{11}H_{10}$, 1,2-$(CH_2)_3CH(N^tBuH_2)$-1-$CB_{11}H_{10}$, or 1,2-

Scheme 9. Acid Promoted Elimination/Isomerization Pathway



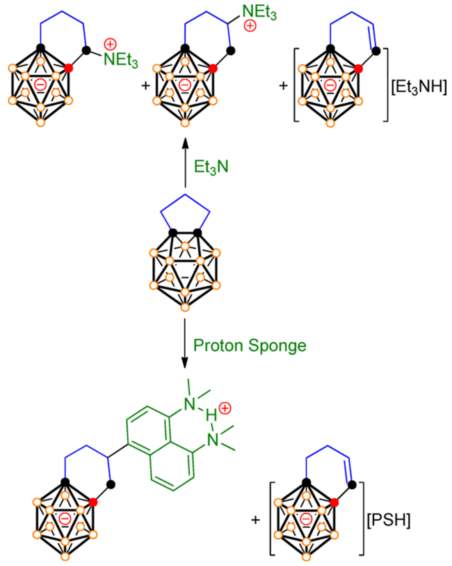
$(CH_2)_3CH(NEt_2H)\text{-}1\text{-}CB_{11}H_{10}$, respectively, in high yields.[17,18] It also interacted with soft nucleophiles $(4\text{-}MeC_6H_4)SNa$ or $NaBH_4$ in THF to afford, after cation exchange with [PPN]Cl (PPN = bis(triphenylphosphoranylidene)ammonium cation) or $[Me_4N]Cl$, $[1,2\text{-}(CH_2)_3CHS(4'\text{-}MeC_6H_4)\text{-}1\text{-}CB_{11}H_{10}][PPN]$ or $[1,2\text{-}(CH_2)_4\text{-}1\text{-}CB_{11}H_{10}][Me_4N]$ in moderate yields (Scheme 10).[18]

Scheme 10. Reaction of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$ with Nucleophiles



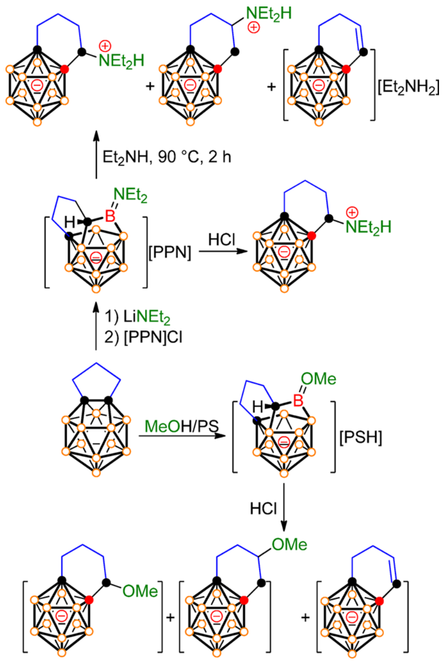
In sharp contrast, the reaction of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$ with tertiary amines proceeds only at elevated temperatures to afford a mixture of CB_{11}^- products. A solution of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$ in pure Et_3N was refluxed for 2 days to give $1,2\text{-}(CH_2)_3CH(NEt_3)\text{-}1\text{-}CB_{11}H_{10}$, $1,2\text{-}(CH_2)_2CH(NEt_3)CH_2\text{-}1\text{-}CB_{11}H_{10}$, and $[1,2\text{-}(CH_2)_2CH{=}CH\text{-}1\text{-}CB_{11}H_{10}][Et_3NH]$ in 75%, 5%, and 5% yields, respectively.[18] The reaction with PS (proton sponge) in THF at 90 °C was much slower and did not complete even in 28 days, leading to the isolation of $1,2\text{-}(CH_2)_2CH(4'\text{-}C_{10}H_5\text{-}1',8'\text{-}(NMe_2)_2H)CH_2\text{-}1\text{-}CB_{11}H_{10}$ and $[1,2\text{-}(CH_2)_2CH{=}CH\text{-}1\text{-}CB_{11}H_{10}][PSH]$ in 20% and 50% yields, respectively.[18] α-Isomer $1,2\text{-}(CH_2)_3CH(4'\text{-}C_{10}H_5\text{-}1',8'\text{-}(NMe_2)_2H)\text{-}1\text{-}CB_{11}H_{10}$ was not detected. These reactions are summarized in Scheme 11. Control experiments showed that these products were not interchangeable under the corresponding reaction conditions, indicating that the reaction was unlikely to proceed via the acid promoted elimination/isomerization pathway shown in Scheme 9.

Scheme 11. Reaction of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$ with Et_3N and Proton Sponge



An intermediate $[7,8,10\text{-}(CH_2)_3CHB(NEt_2)\text{-}7\text{-}CB_{10}H_{10}][PPN]$ was isolated by treatment of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$ with $LiNEt_2$ in THF followed by cation exchange with [PPN]Cl.[18] Another intermediate $[7,8,10\text{-}(CH_2)_3CHB(OMe)\text{-}7\text{-}CB_{10}H_{10}][PSH]$ was prepared by addition of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}$ to a MeOH solution containing PS (Scheme 12).[19] Both were structurally characterized, showing B=X (X = N, O) double bond characters. Protonation with HCl resulted in the formation of CB_{11}^- anion $1,2\text{-}(CH_2)_3CH(NEt_2H)\text{-}1\text{-}CB_{11}H_{10}$, or a mixture of $[1,2\text{-}(CH_2)_3CH(OMe)\text{-}1\text{-}CB_{11}H_{10}]^-$, $[1,2\text{-}(CH_2)_2CH(OMe)CH_2\text{-}1\text{-}CB_{11}H_{10}]^-$, and $[1,2\text{-}(CH_2)_2CH{=}CH\text{-}1\text{-}CB_{11}H_{10}]^-$. On the other hand, heating a toluene solution of $[7,8,10\text{-}(CH_2)_3CHB(NEt_2)\text{-}7\text{-}CB_{10}H_{10}]$-

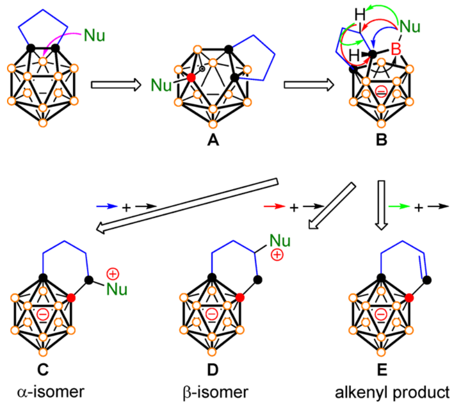
Scheme 12. Synthesis of Intermediates and Their Transformation to CB_{11}^- Anions



[PPN] and Et_2NH at 90 °C gave directly a mixture of 1,2-$(CH_2)_3CH(NEt_2H)$-1-$CB_{11}H_{10}$, 1,2-$(CH_2)_2CH(NEt_2H)CH_2$-1-$CB_{11}H_{10}$, and [1,2-$(CH_2)_2CH{=}CH$-1-$CB_{11}H_{10}$][Et_2NH_2] (Scheme 12). It was noted that, under the reaction conditions, 1,2-$(CH_2)_3CH(NEt_2H)$-1-$CB_{11}H_{10}$ was stable and not isomerized to 1,2-$(CH_2)_2CH(NEt_2H)CH_2$-1-$CB_{11}H_{10}$.

A plausible mechanism to account for the above experimental observations is pictured in Scheme 13. Nucleophilic attack on the most electron-deficient seven-coordinate cage boron gives the intermediate **A** (vide infra). Acceptance of lone-pair electrons from the nucleophile (Nu) coupled with H-migration from cage B to cage C leads to the formation of intermediate **B**. Migration of the Nu group in **B** induces the reconstruction of the cage to afford the α-substituted CB_{11}^- anion **C**. In the basic media, the Nu may attack the β-C in **B**, resulting in the H-migration and cage reconstruction to yield the β-substituted CB_{11}^- anion **D**. Alternatively, Nu may attack β-H in **B**, leading to the formation of C=C double bond and cage-closure to afford alkenyl-substituted CB_{11}^- anion **E**.[18]

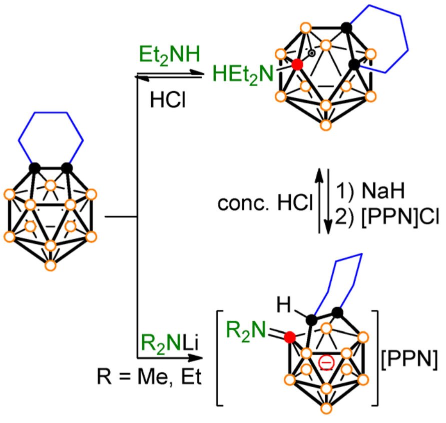
Scheme 13. Proposed Reaction Mechanism



The C,C′-linkage between two cage carbon atoms plays a role in the cage carbon extrusion reactions of 13-vertex *closo*-carboranes. In general, 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$ is less reactive than 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$.[20] Reaction of 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$ with MeOH proceeded very slowly at room temperature with the formation of a mixture of CB_{11}^- anions as indicated by ^{11}B NMR spectroscopy. Its reaction with excess Et_2NH at room temperature afforded 3-NEt_2H-1,7-$(CH_2)_4$-1,7-$C_2B_{11}H_{11}$ in 90% isolated yield (Scheme 14), which gave a mixture of CB_{11}^- anions upon heating. This 13-vertex *nido*-carborane has a similar cage geometry to that of [1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$], but the cage carbons are at different positions. X-ray analyses reveal that the NEt_2H group is bonded to the central boron atom (*meta* position) of the C_2B_3 open face with a B−N bond distance of 1.580(2) Å. It represents the first intermediate **A** in the cage carbon extrusion reaction of 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with nucleophiles shown in Scheme 13.

Treatment of 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$ with $LiNR_2$ in THF gave, after cation exchange with [PPN]Cl, ionic salts [9-NR_2-7,8,10-$(CH_2)_4CCH$-$B_{11}H_{10}$][PPN] (R = Me, Et).[20] This anion was also prepared via the deprotonation of 3-NEt_2H-1,7-$(CH_2)_4$-1,7-$C_2B_{11}H_{11}$ by NaH. The process is reversible: addition of conc. HCl regenerated 3-NEt_2H-1,7-$(CH_2)_4$-1,7-$C_2B_{11}H_{11}$ and finally 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$, rather than *closo*-CB_{11}^- anions (Scheme 14). X-ray analyses revealed that this 13-vertex *nido*-carborane anion has a different cage structure from that of [7,8,10-$(CH_2)_3CHB(Nu)$-7-$CB_{10}H_{10}$]$^-$ (Nu = OMe, NEt_2) although it also bears a B=N multiple bond. The differences observed in the reactions of 1,2-$(CH_2)_n$-1,2-$C_2B_{11}H_{11}$ (n = 3, 4) may be associated with the cage rearrangement that is restricted by carbon-chain length as the ring expansion process would be easier from a 5- to 6- than from a 6- to 7-membered ring.

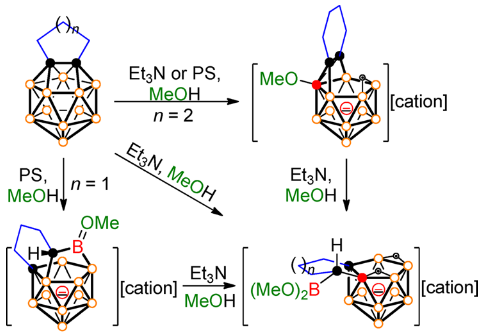
Scheme 14. Reaction of 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$ with Amine and Amide



Cage Boron and Carbon Extrusion

13-Vertex *closo*-carboranes show nucleophile-dependent reactivity. Reaction of 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with MeOH/PS at room temperature gave [7,8,10-$(CH_2)_3CHB(OMe)$-7-$CB_{10}H_{10}$][PSH] which was converted to an 11-vertex *nido*-CB_{10}^- salt, [7,8-$(CH_2)_3CHB(OMe)_2$-7-$CB_{10}H_{11}$][PSH], after treatment with Et_3N/MeOH (Scheme 15).[19] Another intermediate 13-vertex *nido*-[3-OMe-1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$]$^-$ was obtained in 90% yield from the reaction of 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$ with Et_3N/MeOH. It was converted to *nido*-[7,8-$(CH_2)_4CHB(OMe)_2$-7-$CB_{10}H_{11}$]$^-$ upon heating in Et_3N/MeOH (Scheme 15).[20] These results indicate that different $(CH_2)_n$ linkages can stabilize different intermediates of the reactions, offering valuable information on the reaction mechanisms.

Scheme 15. Reaction of 13-Vertex Carboranes with Basic MeOH

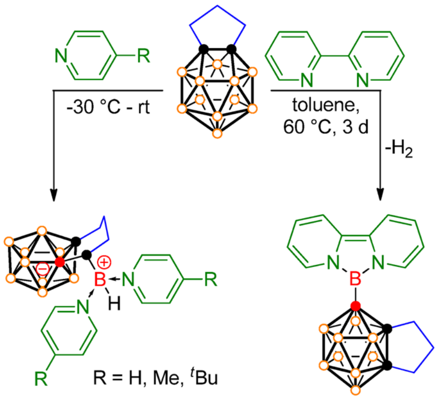


n =1, 2; [cation] = [Et_3NH] or [PSH]

X-ray analyses reveal that the B−O distance of 1.437(5) Å in *nido*-[3-OMe-1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$]$^-$ is much longer than that of 1.377(5) Å observed in *nido*-[7,8,10-$(CH_2)_3CHB(OMe)$-7-$CB_{10}H_{10}$]$^-$, suggesting that the former is a single bond whereas the latter is a double bond. It shows that the MeO group is bonded to a seven-coordinate cage boron in *nido*-[3-OMe-1,2-(CH$_2$)$_4$-1,2-C$_2$B$_{11}$H$_{11}$]$^-$ which may be the first intermediate. Back donation of electrons from the oxygen to cage boron results in the formation of the second intermediate [7,8,10-(CH$_2$)$_4$CHB(OMe)-7-CB$_{10}$H$_{10}$]$^-$, which is converted to the final product *nido*-CB$_{10}$$^-$ salt upon heating.

Reaction of 1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_{11}$ with pyridines 4-RC$_5$H$_4$N at −30 °C gave zwitterionic salts, 11-vertex *closo*-CB$_{10}$$^-$ complexes, 2,4-(CH$_2$)$_3$CHBH(RC$_5$H$_4$N)$_2$-2-CB$_{10}$H$_9$ (R = H, Me, ^{t}Bu; Scheme 16), in which a boronium fragment is attached to the carbon linkage, as confirmed by X-ray analyses.[18,19] These reactions became very complex as the reaction temperature was increased to room temperature, giving a mixture of CB$_{11}$$^-$ and CB$_{10}$$^-$ anions.

Scheme 16. Reaction of 1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_{11}$ with Pyridines



On the other hand, treatment of 1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_{11}$ with 1 equiv of bipyridine (bipy) at 60 °C did not give *closo*-CB$_{10}$$^-$ anion. Rather, it afforded a cage boron extrusion species, 12-vertex *closo*-C$_2$B$_{10}$ compound, 4-B(bipy)-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_9$ in 59% isolated yield (Scheme 16).[19] At least formally, elimination of H$_2$ from BH vertices generates two electrons that are taken by bipy. The resulting [bipy]$^{2-}$ binds to *exo*-[B]$^{2+}$ fragment to yield the final product.

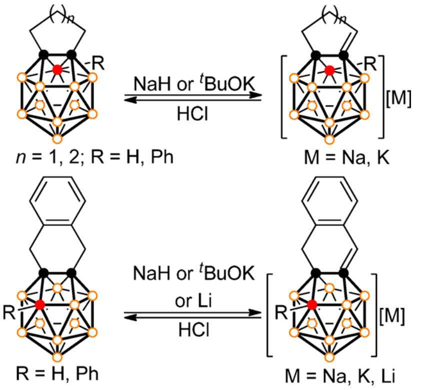
The above results clearly show that 13-vertex carboranes have diverse reactivity patterns which are dependent on the nature of nucleophiles and significantly different from that of 12-vertex carboranes.

Deprotonation

The α-CH$_2$ proton of the linkage in 13-vertex *closo*-carboranes can be deprotonated by strong bases to form 13-vertex carborane monoanions. Treatment of 3-R-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_{10}$, 3-R-1,2-(CH$_2$)$_4$-1,2-C$_2$B$_{11}$H$_{10}$, or 3-R-1,2-*o*-C$_6$H$_4$(CH$_2$)$_2$-1,2-C$_2$B$_{11}$H$_{10}$ (R = H, Ph) with NaH or ^{t}BuOK in THF afforded, after cation exchange with [PPN]Cl, [3-R-1,2-(CH$_2$)$_2$CH-1,2-C$_2$B$_{11}$H$_{10}$][PPN], [3-R-1,2-(CH$_2$)$_3$CH-1,2-C$_2$B$_{11}$H$_{10}$][PPN], or [3-R-1,2-*o*-C$_6$H$_4$(CH$_2$)CH-1,2-C$_2$B$_{11}$H$_{10}$][PPN] in moderate to high yields (Scheme 17).[11] Compound 1,2-*o*-C$_6$H$_4$(CH$_2$)$_2$-1,2-C$_2$B$_{11}$H$_{11}$ also reacted with 1 equiv of Li metal in THF to give [1,2-*o*-C$_6$H$_4$(CH$_2$)CH-1,2-C$_2$B$_{11}$H$_{11}$][Li(THF)$_4$]. Protonation of these anions by 3 M HCl regenerated the neutral 13-vertex *closo*-carboranes.

X-ray analyses showed that the geometry of the anions is similar to that of the parent *closo*-carboranes, but with elongated cage-atom−cage-atom distances. One of the cage C−B bonds is broken, leading to the formation of two trapezoidal open faces, which is very close to that of the radical anion [{1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_{11}$}•]$^-$.[14] The *exo* C═C bond distances fall in a range 1.352(4)−1.446(7) Å, suggesting the existence of significant double bond character. These observations are supported by NMR data with the chemical shifts of α-*CH* units being found at 5.27−6.15 ppm in ^{1}H NMR and at 140.1−150.1 ppm in ^{13}C NMR spectra. As a result of *exo* C═C double bond formation, the negative charge is partially delocalized into the carborane cage. It is noteworthy that the α-methylene hydrogen atom in 12-vertex *closo*-carborane 1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_{10}$ cannot be deprotonated by strong bases, implying that 13-vertex *closo*-carboranes are stronger electron-withdrawing units than the 12-vertex ones.

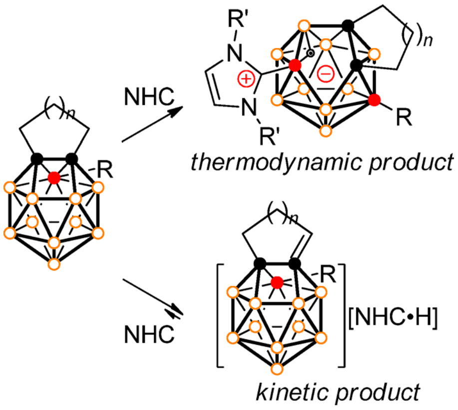
Scheme 17. Deprotonation of 13-Vertex Carboranes



Reaction with *N*-Heterocyclic Carbenes

12-Vertex *o*-carboranes react with *N*-heterocyclic carbenes (NHCs) to give either imidazolium carboranyl salts[21] or carborane-carbene adducts,[21,22] in which NHC acts as a base or nucleophile, respectively. Treatment of 13-vertex carboranes 3-R-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_{10}$ or 3-R-1,2-(CH$_2$)$_4$-1,2-C$_2$B$_{11}$H$_{10}$ (R = H, Ph) with IPr [1,3-bis(2′,6′-diisopropylphenyl)-imidazol-2-ylidene] or IMes [1,3-bis(2′,4′,6′-trimethylphenyl)-imidazol-2-ylidene] gave zwitterionic salts 13-vertex *nido*-[11-*R*-3-NHC-1,7-(CH$_2$)$_n$-1,7-C$_2$B$_{11}$H$_{10}$] (n = 3, 4; R = H, Ph; NHC = IPr, IMes) in 55−81% isolated yields, respectively (Scheme 18).[23] No 1:2 adducts were isolated even in the presence of excess NHCs, probably due to steric reasons. Careful analyses of NMR data reveal that NHCs initially deprotonate the α-CH$_2$

Scheme 18. Reaction of 13-Vertex Carboranes with NHCs



n = 1, 2; R = H, Ph; NHC = IPr, IMes

proton of 13-vertex carborane 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$, giving an imidazolium salt [1,2-$(CH_2)_2$CH-1,2-$C_2B_{11}H_{11}$][IPrH] as a kinetic product. The resulting salt is then slowly converted to the NHC adduct 3-IPr-1,7-$(CH_2)_3$-1,7-$C_2B_{11}H_{11}$ as a thermodynamic species within 12 h. The results suggest that the deprotonation is very fast and reversible whereas the nucleophilic addition is slow. It is interesting to note that the final products are air- and moisture-stable.

Single-crystal X-ray analyses reveal that these carborane-carbene adducts bear a similar cage geometry to that of 3-NEt_2H-1,7-$(CH_2)_4$-1,7-$C_2B_{11}H_{11}$ generated from the reaction of 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$ with Et_2NH.[20] The $C_{carbene}$−B_{cage} bond lengths range from 1.58 to 1.61 Å, which is close to those observed in NHC-borane complexes.

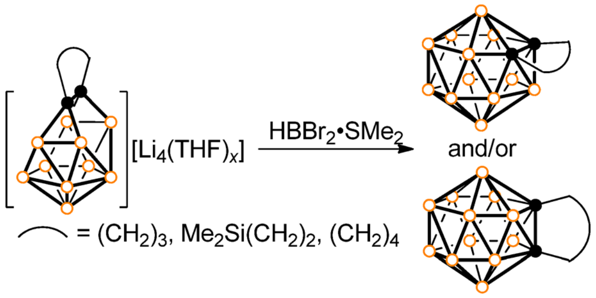
14-VERTEX CARBORANES

Synthesis and Characterization

14-Vertex *closo*-carboranes can be prepared by polyhedral expansion methodology via [12 + 2] or [13 + 1] protocols. The former adds two BH vertices to two open faces of a CAd 12-vertex *arachno*-carborane tetraanion. The latter incorporates one BH vertex to the open face of a 13-vertex *nido*-carborane dianion.

Reaction of *arachno*-[1,2-$(CH_2)_3$-1,2-$C_2B_{10}H_{10}$][$Li_4(THF)_5$], *arachno*-[1,2-$Me_2Si(CH_2)_2$-1,2-$C_2B_{10}H_{10}$][$Li_4(THF)_x$], or *arachno*-[1,2-$(CH_2)_4$-1,2-$C_2B_{10}H_{10}$][$Li_4(THF)_5$] with 5 equiv of $HBBr_2{\cdot}SMe_2$ in toluene gave 14-vertex *closo*-carboranes 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$,[24] 2,3-$Me_2Si(CH_2)_2$-2,3-$C_2B_{12}H_{12}$ and 2,8-$Me_2Si(CH_2)_2$-2,8-$C_2B_{12}H_{12}$,[16] or 2,8-$(CH_2)_4$-2,8-$C_2B_{12}H_{12}$ in <7% yields (Scheme 19).[16] It was noted that the corresponding 13-vertex *closo*-carboranes and 12-vertex *closo*-carboranes were also isolated in each case, as a result of redox reactions.

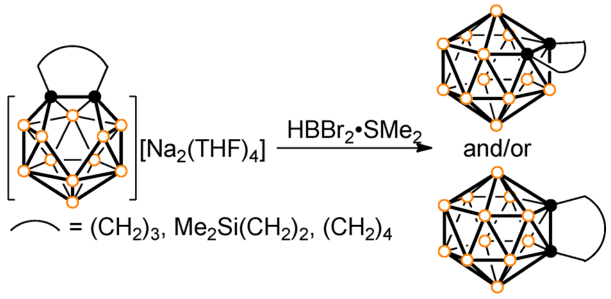
Scheme 19. Synthesis of 14-Vertex Carboranes via a [12 + 2] Protocol



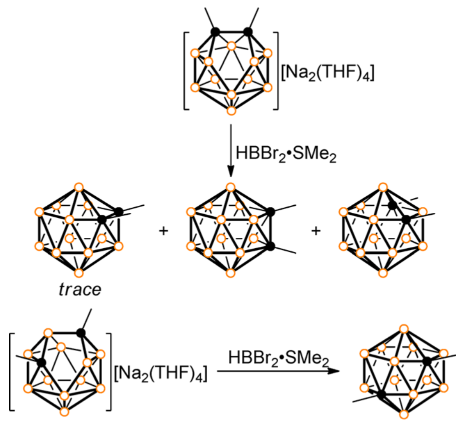
Treatment of *nido*-[1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$], *nido*-[1,2-$Me_2Si(CH_2)_2$-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$], or *nido*-[1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$] with 2 equiv of $HBBr_2{\cdot}SMe_2$ in toluene afforded 14-vertex *closo*-carboranes 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$,[24] 2,3-$Me_2Si(CH_2)_2$-2,3-$C_2B_{12}H_{12}$ and 2,8-$Me_2Si(CH_2)_2$-2,8-$C_2B_{12}H_{12}$, or 2,3-$(CH_2)_4$-2,3-$C_2B_{12}H_{12}$ and 2,8-$(CH_2)_4$-2,8-$C_2B_{12}H_{12}$ in 10−30% yields (Scheme 20).[16]

CAd and CAp 14-vertex *closo*-carboranes without a linkage can also be prepared in a similar manner. Reaction of CAd *nido*-[1,2-Me_2-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$] or CAp *nido*-[1,3-Me_2-1,3-$C_2B_{11}H_{11}$][$Na_2(THF)_4$] with 2 equiv of $HBBr_2{\cdot}SMe_2$ in toluene resulted in the isolation of 2,8-Me_2-2,8-$C_2B_{12}H_{12}$ and 2,4-Me_2-2,4-$C_2B_{12}H_{12}$, or 2,9-Me_2-2,9-$C_2B_{12}H_{12}$ in <1% isolated yields (Scheme 21).[16] 2,8-Me_2-2,8-$C_2B_{12}H_{12}$ was slowly isomerized to the 2,4-isomer in solution at room temperature.

Scheme 20. Synthesis of 14-Vertex Carboranes via a [13 + 1] Protocol



Scheme 21. Synthesis of 14-Vertex Carboranes without C,C′-Linkage via a [13 + 1] Protocol

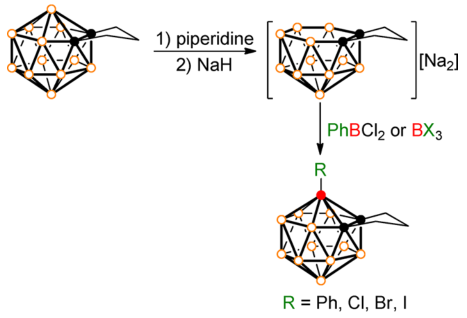


It was noted that the above reactions generated a mixture of highly polar carboranes as major products which were inseparable.

Cage-B-substituted 14-vertex *closo*-carboranes are synthesized using a redox inactive synthon 13-vertex *nido*-[8,9-$(CH_2)_3$-8,9-$C_2B_{11}H_{12}$]$^{2-}$ as a starting material, which is prepared via deboration of 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$.[25] Treatment of [8,9-$(CH_2)_3$-8,9-$C_2B_{11}H_{11}$]Na_2 with 2 equiv of $PhBCl_2$ or BX_3 (X = Cl, Br, I) in toluene afforded 1-R-2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{11}$ (R = Ph, Cl, Br, I) in 8−49% isolated yields (Scheme 22).[16]

X-ray analyses show that all 14-vertex *closo*-carboranes adopt a bicapped hexagonal antiprism geometry. A representative

Scheme 22. Synthesis of B-substituted 14-Vertex Carboranes via a [13 + 1] Protocol



example of 2,8-$(CH_2)_3$-2,8-$C_2B_{12}H_{12}$ is displayed in Figure 5.[24] The cage C−C bond lengths are longer than those observed in 13-vertex analogues (Table 1). The ^{11}B NMR spectra indicate that the nature of substituents at 1 position has obvious effects on the chemical shifts (Figure 6).[9,16,24] The signals of the cage carbons are generally observed at high field (Table 2). Moreover, the ^{13}C chemical shifts of two cage carbons in 2,3- and 2,4-isomers (in which the two cage carbons are on the same 6-membered belt) are always shifted upfield by 10−20 ppm in comparison to those in 2,8- and 2,9-isomers (in which the two cage carbons are on the different 6-membered belts).

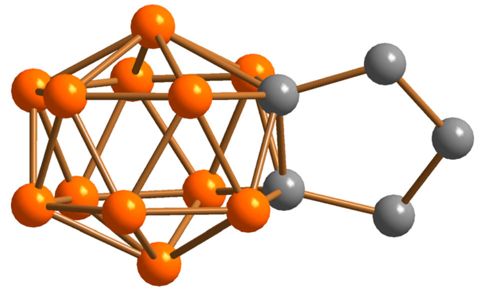


Figure 5. Molecular structure of 2,8-$(CH_2)_3$-2,8-$C_2B_{12}H_{12}$.

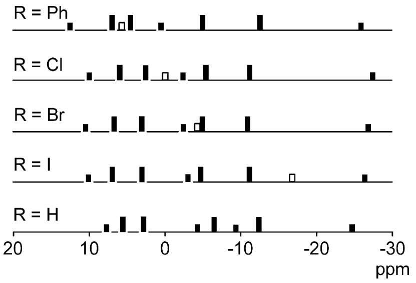
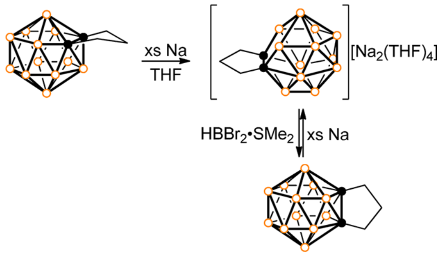


Figure 6. Stick presentation of chemical shifts and relative intensities of $^{11}B\{^1H\}$ NMR spectra of 14-vertex *closo*-carboranes 1-R-2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{11}$ (R = H, Ph, Cl, Br, I). The solid and hollow lines represent the BH and BR vertices, respectively.

Two-Electron Reduction

The 14-vertex *closo*-carborane 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ readily undergoes two-electron reduction with Na metal in THF to give a 14-vertex *nido*-carborane salt $[(CH_2)_3C_2B_{12}H_{12}][Na_2(THF)_4]$ (Scheme 23).[26] As indicated by X-ray analyses, its cage structure can be viewed as a result of removal of a degree-five vertex from a 15-vertex *closo*-cluster. The resulting bent pentagonal open face is larger and flatter than that observed in the 13-vertex *nido*-carborane dianions.

Scheme 23. Reduction of CAd 14-Vertex *closo*-Carboranes

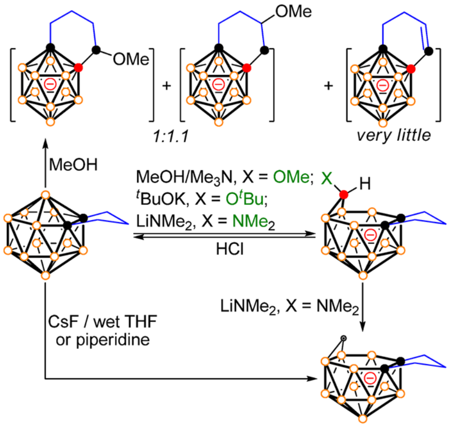


This salt is resistant to further reduction by Li metal. Such a high reducing power leads to the failure in synthesizing 15-vertex carborane(s) via its capping reaction with $RBBr_2 \cdot SMe_2$. Only a redox reaction is observed, which gives 2,8-$(CH_2)_3$-2,8-$C_2B_{12}H_{12}$. Reduction of 2,8-$(CH_2)_3$-2,8-$C_2B_{12}H_{12}$ with excess Na metal affords the same *nido*-carborane salt (Scheme 23).[26]

Reaction with Nucleophiles

14-Vertex *closo*-carboranes are generally less reactive than the 13-vertex ones. Reaction of 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ with MeOH proceeded very slowly at ambient temperature, but heating the solution at 70 °C led to the completion of the reaction in 2 days to give a mixture of CB_{11}^- anions $[1,2\text{-}(CH_2)_3CH(OMe)\text{-}1\text{-}CB_{11}H_{10}]^-$, $[1,2\text{-}(CH_2)_2CH(OMe)CH_2\text{-}1\text{-}CB_{11}H_{10}]^-$, and $[1,2\text{-}(CH_2)_2CH{=}CH\text{-}1\text{-}CB_{11}H_{10}]^-$ (Scheme 24).[25] Apparently, both cage carbon and boron extrusion reactions take place. Unlike that of 13-vertex *closo*-carboranes, 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ does not react with PPh_3 even under forced reaction conditions.

Scheme 24. Reaction of 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ with Nucleophiles



On the other hand, treatment of 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ with $MeOH/Me_3N$, ^tBuOK, or $LiNMe_2$ produced 14-vertex *nido*-$[8,9\text{-}(CH_2)_3\text{-}\mu\text{-}11,12\text{-}(X)BH\text{-}8,9\text{-}C_2B_{11}H_{11}]^-$ (X = OMe, O^tBu, NMe_2).[25] Protonation of these monoanions by conc. HCl generated 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$. In the presence of excess $LiNMe_2$, $[8,9\text{-}(CH_2)_3\text{-}\mu\text{-}11,12\text{-}(NMe_2)BH\text{-}8,9\text{-}C_2B_{11}H_{11}]^-$ underwent deboration to give 13-vertex *nido*-$[8,9\text{-}(CH_2)_3\text{-}8,9\text{-}C_2B_{11}H_{12}]^-$. The same anion was also obtained from the reaction of 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ with an excess amount of CsF or piperidine (Scheme 24). This anion was stable in refluxing MeOH, suggesting that the formation of the 12-vertex *closo*-CB_{11}^- and 13-vertex *nido*-$C_2B_{11}^-$ may result from two parallel pathways.

■ CONCLUSION AND SUMMARY

Recognition of the lower reducing power of CAd carborane anions over that of CAp isomers has led to significant progress in the chemistry of supercarboranes over the past decade. Subsequently, a series of 13- and 14-verex CAd *closo*-carboranes have been prepared via [12 + 1], [12 + 2], and [13 + 1] protocols using CAd 12-vertex *nido*-$[R_2C_2B_{10}H_{10}]^{2-}$, *arachno*-$[R_2C_2B_{10}H_{10}]^{4-}$, and CAd 13-vertex *nido*-$[R_2C_2B_{11}H_{11}]^{2-}$ as synthons, respectively. CAp 13-vertex *closo*-carborane has also been synthesized via thermal isomerization of CAd *closo*-species 1,2-Me_2-1,2-$C_2B_{11}H_{11}$, thus suggesting that CAp isomer is more thermodynamically stable than the CAd one. These results are in line with those observed in the thermal isomerization of 12-vertex carboranes, which also indicates that the C,C′-linkages between the two cage carbon atoms have no obvious effect on the stabilization of 13-vertex *closo*-carboranes. The role of these linkages is to lock the two cage carbons in adjacent positions during reduction process, ensuring the formation of the desired CAd carborane anions. In a similar manner, CAp 14-vertex *closo*-carboranes are prepared from the thermal isomerization of non-C,C′-linked CAd 14-vertex isomers. It is noteworthy that the capping efficiency between CAp 12-vertex or 13-vertex *nido*-carborane dianion and dihaloborane is rather low, resulting in the formation of only trace amount of corresponding CAp 13- or 14-vertex *closo*-carboranes.

Both 13- and 14-vertex *closo*-carboranes are readily reduced by group 1 metals to generate the corresponding 13- and 14-vertex *nido*-carborane dianions, which are, however, resistant to further reduction. Thus, both 13- and 14-vertex *arachno*-carborane tetraanions remain elusive though 12-vertex *arachno*-carborane tetraanions are well-known. On the other hand, 13-vertex carborane radical monoanions with $[2n+3]$ framework electrons have been synthesized and structurally characterized while 12- and 14-vertex analogues are unknown.

Reactivity studies indicate that the reducing power of CAd *nido*-carborane dianions increases as the cluster size gets bigger and follows the trend: 12-vertex < 13-vertex < 14-vertex. Accordingly, the capping efficiency of these anions with dihaloboranes decreases as the cluster size increases. As a result, attempted insertion of a $[BR]^{2+}$ unit into a CAd 14-vertex *nido*-carborane dianion has not produced the desired 15-vertex *closo*-carborane. Instead, it affords a structural isomer of CAd 14-vertex *closo*-carborane. On the other hand, both 13- and 14-vertex *nido*-carborane dianions are a class of useful synthons for the preparation of 14- and 15-vertex metallacarboranes via polyhedral expansion methodology.[26−28] Thus, 14-vertex *closo*-carboranes and 15-vertex metallacarboranes represent the largest carboranes and metallacarboranes known so far.

13-Vertex *closo*-carboranes undergo electrophilic substitution reaction to give the corresponding hexa-substituted species with the furthest BH vertices away from the cage carbons being substituted. Such a substitution pattern is consistent with that observed in 12-vertex *closo*-carboranes. On the other hand, 13-vertex *closo*-carboranes show nucleophile-dependent reactivities, which is different from that of 12-vertex species. Depending upon the nature of nucleophiles, 13-vertex *closo*-carboranes can undergo either cage carbon extrusion reaction to give 12-vertex *closo*-CB_{11}^- monoanions, or cage boron extrusion reaction to produce 12-vertex *closo*-C_2B_{10} neutral molecules, or cage carbon and boron extrusion reaction to generate 11-vertex *closo*-CB_{10}^- or *nido*-CB_{10}^- monoanions. In contrast, 14-vertex *closo*-carboranes are less reactive than 13-vertex species. They react with nucleophiles in acidic media to afford 12-vertex *closo*-CB_{11}^- monoanions or 14-vertex/13-vertex *nido*-carboranes in basic media. In general, supercarboranes have more diverse reactivity patterns than their icosahedral cousins.

In comparison to the rich literature of 12-vertex carboranes, studies of supercarboranes remain a relative young research area. Their reaction scope and mechanism need to be further explored. The synthetic yields of 14-vertex *closo*-carboranes need to be improved. On the other hand, supercarboranes $C_2B_nH_{n+2}$ with $n > 12$ have become new synthetic targets. To achieve this goal, new borane reagents with lower oxidizing ability are required to prevent the redox reaction between *nido*-carborane dianions and borane reagents, thus facilitating the capping reactions. New synthetic methodologies such as $[14 + n]$ or $[12 + n]$ $(n > 2)$ protocols await development. It is envisaged that a new class of boron clusters of extraordinary size will be prepared as research in this area proceeds. The search for applications of supercarboranes in many disciplines such as BNCT, electronics, catalysis, polymers, and nanomaterials is anticipated in the future.[8]

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Notes

The authors declare no competing financial interest.

Biographies

Jian Zhang received a B.Sc. in 2004 from Peking University. In 2005, he moved to The Chinese University of Hong Kong (CUHK), and he earned his Ph.D. degree in 2011 under the supervision of Professor Zuowei Xie. He is currently working as a Postdoctoral Fellow in the laboratory of Prof. Xie. His research interests include the synthesis and reactivity of supercarboranes.

Zuowei Xie obtained a B.Sc. from Hangzhou University in 1983, a M.Sc. from Shanghai Institute of Organic Chemistry (SIOC), the Chinese Academy of Sciences in 1986, and his Ph.D. in 1990, working in a joint program between SIOC and the Technische Universität Berlin. After serving as a Research Associate in SIOC and as a Postdoctoral Fellow at the University of Southern California, he joined the chemistry faculty of CUHK in 1995, where he is now a Choh-Ming Li Professor of Chemistry. He has coauthored over 215 papers and received several prestigious awards including the State Natural Science Prizes in 1997 and 2008, the Chinese Chemical Society Yao-Zeng Huang Award in Organometallic Chemistry in 2010, and the Croucher Award from the Croucher Foundation (Hong Kong) in 2003.

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