Supercarboranes: Achievements and perspectives*

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Abstract: This article highlights the achievements in the chemistry of supercarboranes (carboranes with more than 12 vertices) in the past decade and the future perspectives. The chemistry of boron clusters has been dominated by 12-vertex carboranes for several decades. Only in recent years has significant progress been made in the chemistry of supercarboranes. Such a breakthrough relies on the use of CAd (carbon-atoms-adjacent) 12-vertex *nido*-carborane anions as starting materials. A series of 13- and 14-vertex carboranes as well as their corresponding 14- and 15-vertex metallacarboranes have been prepared and structurally characterized. Reactions of supercarboranes with reducing agents, electrophiles, and nucleophiles are studied, which reveal a more diverse and richer reaction chemistry than their icosahedral cousins.

Keywords: cage compounds; carboranes; boron clusters; metallacarboranes; supercarboranes.

INTRODUCTION

Supercarboranes are carboranes with more than 12 vertices. Compared to the well-established chemistry of icosahedral carboranes ($R_2C_2B_{10}H_{10}$) [1,2], that of supercarboranes had been elusive until 2003 [3]. On the other hand, a series of supermetallacarboranes with 13- [4] and 14-vertex [5] have been prepared and structurally characterized, due to the stabilization of borane frameworks by metal atoms [6]. They are generally synthesized by "polyhedral expansion", a method originally developed by Hawthorne [7], which constructs an $(n + 1)$-vertex framework from an n-vertex cluster. This method works well in the reconstruction of *ortho*-carboranes from the *nido*-C_2B_9 species and dihaloboranes [8]. However, it had never produced a 13-vertex carborane in the attempted insertion from a carbon-atoms-apart (CAp) *nido*-7,9-$C_2B_{10}H_{12}$ dianion [9]. This failure is often attributed to the "icosahedral barrier" [9b,10], as indicated by theoretical calculations that the icosahedral $[B_{12}H_{12}]^{2-}$ is the most stable one among *closo*-boranes $[B_nH_n]^{2-}$ [3a].

The breakthrough in the synthesis of supercarboranes relies on the use of carbon-atoms-adjacent (CAd) *nido*-[7,8-$R_2C_2B_{10}H_{10}$]$^{2-}$ anions [11]. We believe that redox reactions between CAp *nido*-[7,9-$R_2C_2B_{10}H_{10}$]$^{2-}$ and R'BX$_2$ may be superior to the capitation reactions, leading to the formation of *closo*-$R_2C_2B_{10}H_{10}$ (Scheme 1). On the other hand, CAd 12-vertex *nido*-carborane dianions, which are relatively weaker reducing reagents and stronger nucleophiles compared to the CAp analogues [12], offer a very valuable entry point in the synthesis of 13-vertex carboranes [13]. This article summarizes the achievements in the study of supercarboranes and offers some future perspectives in this field.
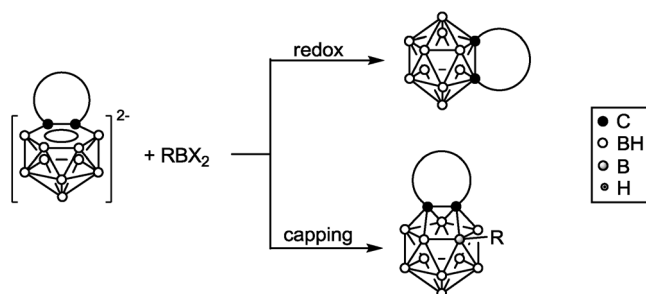

**Scheme 1** Competitive reactions of 12-vertex *nido*-carborane dianion with RBX$_2$.

SYNTHESIS OF 13-VERTEX CARBORANES

CAd 13-vertex carboranes are generally synthesized via a [12 + 1] protocol from CAd *nido*-[7,8-R$_2$C$_2$B$_{10}$H$_{10}$]$^{2-}$ dianions and RBX$_2$ reagents. For example, treatment of the CAd *nido*-[μ-7,8-*o*-C$_6$H$_4$(CH$_2$)$_2$-7,8-C$_2$B$_{10}$H$_{10}$][Na$_2$(THF)$_4$], or [μ-7,8-(CH$_2$)$_3$-7,8-C$_2$B$_{10}$H$_{10}$][Na$_2$(THF)$_x$], which are prepared by the reactions of corresponding 12-vertex *closo*-carboranes with excess sodium metal in tetrahydrofuran (THF) [11b,c,14], with different dihaloborane reagents produces a series of CAd 13-vertex carboranes μ-1,2-*o*-C$_6$H$_4$(CH$_2$)$_2$-5-R-1,2-C$_2$B$_{11}$H$_{10}$ (R = Ph, H) [9b,14], or μ-1,2-(CH$_2$)$_3$-3-R-1,2-C$_2$B$_{11}$H$_{10}$ [R = H, Ph, *Z*-EtCH=C(Et), *E*-*t*BuCH=CH] [14] (Scheme 2). The results suggest that the less sterically demanding C,C'-linkage and more electrophilic borane reagents lead to the higher yields of supercarboranes. On the other hand, donor solvents, such as THF, 1,2-dimethoxyethane (DME), and Et$_2$O, result in much lower yields.
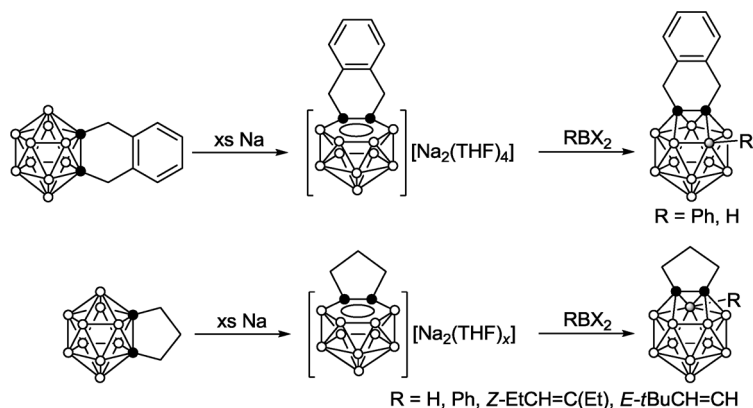
Scheme 2 Synthesis of CAd 13-vertex carboranes.

It is believed that the CAd *nido*-carborane dianions are weaker reducing agents or stronger nucleophiles, than the corresponding CAp counterparts, facilitating the capping reactions. Do the C,C'-linkages play a role in the stabilization of supercarboranes? To address this issue, a CAd 13-vertex carborane with a removable linkage μ-1,2-Me$_2$Si(CH$_2$)$_2$-1,2-C$_2$B$_{11}$H$_{11}$ is prepared in a similar manner from μ-1,2-Me$_2$Si(CH$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (Scheme 3) [15]. This species undergoes facile desilylation reaction at ambient temperature over silica gel to give the CAd 1,2-Me$_2$-1,2-C$_2$B$_{11}$H$_{11}$ without linkage, which can be quantitatively converted to its CAp isomer 1,6-Me$_2$-1,6-C$_2$B$_{11}$H$_{11}$ upon heating (Scheme 3). These experimental results clearly illustrate that the C,C'-linkages do not have any obvious
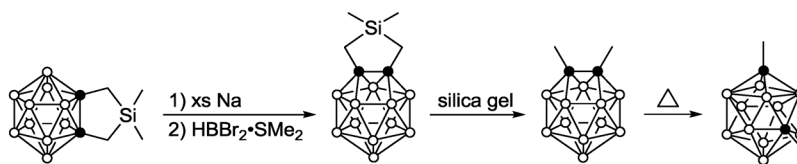
Scheme 3 Synthesis of CAd and CAp 13-vertex carboranes without C,C'-linkage.

effect on the stability of 13-vertex carboranes. In fact, similarly to the 12-vertex carborane system [16], the CAp isomer is thermodynamically more stable than the CAd 13-vertex carborane.

All structurally characterized CAd 13-vertex carboranes have a common henicosahedral geometry bearing one or two trapezoidal open faces constructed by the two cage carbons and boron atoms of the B_5 belt. The cage C–C bond distances in CAd 13-vertex carboranes are remarkably shorter, ranging from 1.42 to 1.46 Å, than those found in *o*-carboranes. The structure of CAp 13-vertex carborane $1,6$-Me$_2$-$1,6$-C$_2$B$_{11}$H$_{11}$ has not yet been confirmed by X-ray analyses.

SYNTHESIS OF 14-VERTEX CARBORANES

Two approaches to 14-vertex carboranes have been developed [17a]. One is the [12 + 2] protocol in which two [BH]$^{2+}$ vertices are added to one open hexagonal face and one open pentagonal face of a CAd 12-vertex *arachno*-carborane tetraanion. The other is the [13 + 1] protocol in which a [BH]$^{2+}$ fragment is incorporated into an open pentagonal face of a CAd 13-vertex *nido*-carborane dianion.

Reaction of CAd 12-vertex carborane μ-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_{10}$ with an excess amount of finely cut lithium metal in THF gives a CAd 12-vertex *arachno*-[μ-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_{10}$][Li$_4$(THF)$_5$], which consists of two adjacent hexagonal and pentagonal bonding faces [11a,17]. Treatment of this salt with 5 equiv of HBBr$_2$·SMe$_2$ in toluene affords a CAd 14-vertex carborane μ-2,3-(CH$_2$)$_3$-2,3-C$_2$B$_{12}$H$_{12}$ in 7 % yield along with a CAd 13-vertex carborane μ-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_{11}$ (isolated in 32 % yield) and a CAd 12-vertex carborane μ-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_{10}$ (isolated in 2 % yield; Scheme 4) [17a]. The formation of the 14-vertex carborane indicates that two [BH]$^{2+}$ moieties can be added into the pentagonal and hexagonal faces of a CAd 12-vertex *arachno*-carborane in one reaction. On the other hand, the isolation of CAd 12-vertex *closo*-carborane suggests that HBBr$_2$ can oxidize *arachno*-[μ-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_{10}$]$^{4-}$ to *nido*-[μ-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_{10}$]$^{2-}$, and finally to *closo* μ-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_{10}$. The 13-vertex carborane may be formed either from the
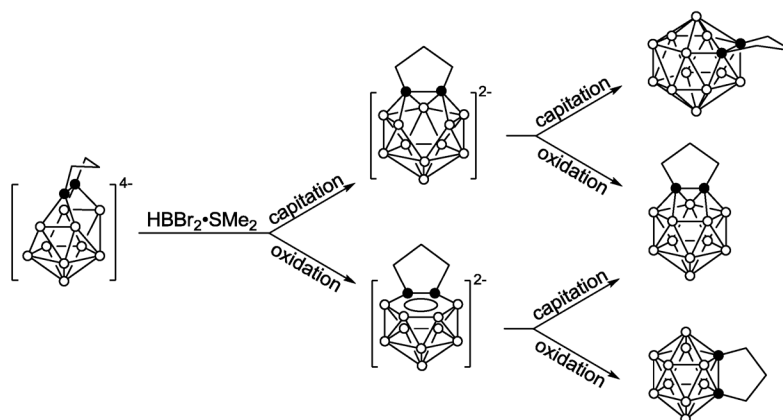
Scheme 4 Reaction of *arachno*-[μ-1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_{10}$]$^{4-}$ with HBBr$_2$.

capitation reaction of $HBBr_2$ with *nido*-[μ-1,2-$(CH_2)_3$-1,2-$C_2B_{10}H_{10}$]$^{2-}$ or oxidation of a CAd 13-vertex *nido*-[μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$]$^{2-}$.

This CAd 14-vertex carborane can also be prepared from the reaction of CAd 13-vertex *nido*-carborane salt [μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$][$Na_2(THF)_4$] [synthesized by the reduction of 13-vertex carborane μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with excess Na metal in THF] with 1.5 equiv of $HBBr_2$·SMe_2 in 30 % yield [17a].

SYNTHESIS OF 15-VERTEX RUTHENACARBORANES

The CAd 14-vertex *closo*-carborane μ-2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ or μ-2,8-$(CH_2)_3$-2,8-$C_2B_{12}H_{12}$ reacts readily with an excess amount of sodium metal in THF to afford the same CAd 14-vertex *nido*-carborane salt [μ-1,2-$(CH_2)_3$-1,2-$C_2B_{12}H_{12}$][$Na_2(THF)_4$] (Scheme 5) [18]. Its solid-state structure as revealed by single-crystal X-ray analyses shows the presence of a bent pentagonal open face that is constructed by formally breaking a B–B bond in the B5 belt after two-electron uptake from the sodium metal, and is larger and flatter than those observed in the CAd 13-vertex *nido*-carboranes. It is rational to assume that addition of a [BH]$^{2+}$ unit to the open five-membered ring would result in the formation of a 15-vertex species. However, treatment of [μ-1,2-$(CH_2)_3$-1,2-$C_2B_{12}H_{12}$][$Na_2(THF)_4$] with 2 equiv of $HBBr_2$·SMe_2 does not give the desired 15-vertex carborane, rather affords an isomer of CAd 14-vertex carborane μ-2,8-$(CH_2)_3$-2,8-$C_2B_{12}H_{12}$ [17a]. These results show that polyhedral expansion methodology, which works well in the preparation of 13- and 14-vertex carboranes, has been unsuccessful when applied to the synthesis of 15-vertex carboranes. This may be ascribed to the stronger reducing power of 14-vertex *nido*-carborane dianions over the 12- and 13-vertex species, facilitating the redox reactions. On the other hand, a metal fragment can be incorporated into a 14-vertex *nido*-carborane to form a 15-vertex metallacarborane. Reaction of [μ-1,2-$(CH_2)_3$-1,2-$C_2B_{12}H_{12}$][$Na_2(THF)_4$] with 0.5 equiv of [(*p*-cymene)$RuCl_2$]$_2$ in THF produces a CAd 15-vertex ruthenacarborane μ-1,4-$(CH_2)_3$-7-*p*-cymene-7,1,4-$RuC_2B_{12}H_{12}$ in 62 % yield (Scheme 5) [18]. It adopts a *closo* structure containing 26 triangulated faces similar to that predicted for [$B_{15}H_{15}$]$^{2-}$ [3a].

It is noted that an isomer of CAd 15-vertex ruthenacarborane μ-1,6-$(CH_2)_3$-7-*p*-cymene-7,1,6-$RuC_2B_{12}H_{12}$ is isolated from the thermolysis of a CAd 14-vertex ruthenacarborane μ-2,8-$(CH_2)_3$-1-*p*-cymene-1,2,8-$RuC_2B_{11}H_{11}$ [19].
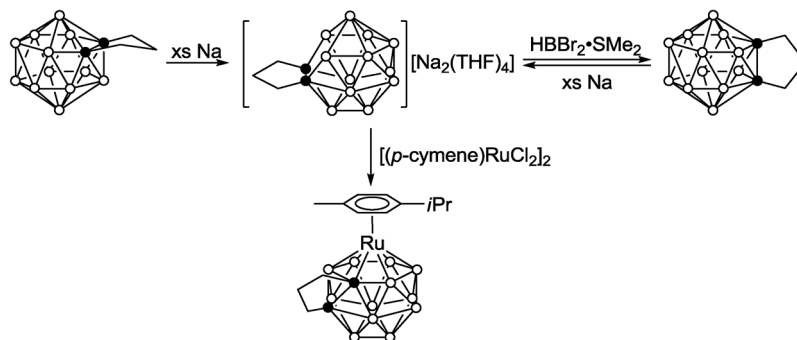

Scheme 5 Synthesis of a 15-vertex ruthenacarborane.

SINGLE-ELECTRON REDUCTION OF 13-VERTEX CARBORANE

13-Vertex *closo*-carborane can undergo single-electron reduction to generate a stable carborane radical anion, which is an intermediate in the two-electron reduction process leading to the *nido* species.

Treatment of μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with 1 equiv of sodium metal in THF at room temperature, followed by recrystallization from a THF/hexane mixed-solvent solution in the presence of 18-crown-6, gives brown crystals identified as a monoanionic salt [μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$][Na(18-crown-6)(THF)$_2$] (Scheme 6) [20]. Further reduction with an excess amount of sodium metal in THF generates the CAd 13-vertex *nido*-carborane dianionic salt [μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$][Na$_2$(THF)$_4$] as colorless crystals. Cyclic voltammetry of μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ confirms this stepwise reduction process, which is shown by one reversible and one quasi-reversible peaks.
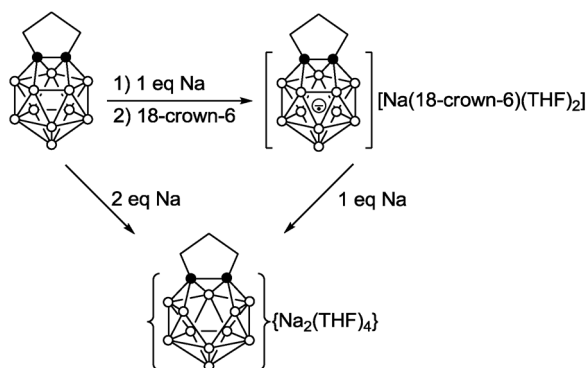
Scheme 6 Reduction of CAd 13-vertex carborane μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$.

This paramagnetic species exhibits an electron paramagnetic resonance (EPR) signal with $g = 1.994$ (line width = 23G in solution and 5.5G in the solid state) at room temperature, which is similar to those observed in $CB_{11}Me_{12}{}^{\bullet}$ [21] and $[B_{12}R_{12}]^{-\bullet}$ [22]. Single-crystal X-ray analyses reveal that this radical monoanion has a geometry similar to that of its parent CAd 13-vertex *closo* species with elongated C–B/B–B distances, which is significantly different from that of CAd 13-vertex *nido*-carborane dianions. This represents the first example of a fully characterized carborane radical anion with [$2n + 3$] framework electrons.

## ELECTROPHILIC SUBSTITUTION REACTION OF 13-VERTEX CARBORANE

Like 12-vertex carboranes, 13-vertex *closo*-carboranes can undergo electrophilic substitution reactions. Treatment of CAd μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with an excess amount of MeI, Br_2, or I_2 in the presence of a catalytic amount of $AlCl_3$ in CH_2Cl_2 at room temperature affords the hexasubstituted CAd 13-vertex *closo*-carboranes 8,9,10,11,12,13-X_6-μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_5$ (X = Me, Br, I; Scheme 7) [14]. The results indicate that the BH vertices which are the farthest to the cage carbons (B8 to B13) are the most electron-rich and the easiest to be attacked by electrophiles. On the other hand, interaction of μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with H_2O_2 leads to complete degradation of the cage, resulting in the formation of $B(OH)_3$, which differs significantly from its icosahedral cousins [23]. These substitution reactions can be closely monitored by ^{11}B NMR spectroscopy as the resultant hexasubstituted CAd 13-vertex carboranes have distinctive ^{11}B chemical shifts.
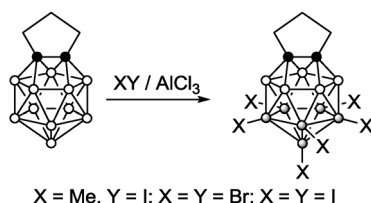
Scheme 7 Electrophilic substitution reactions of CAd 13-vertex carborane.
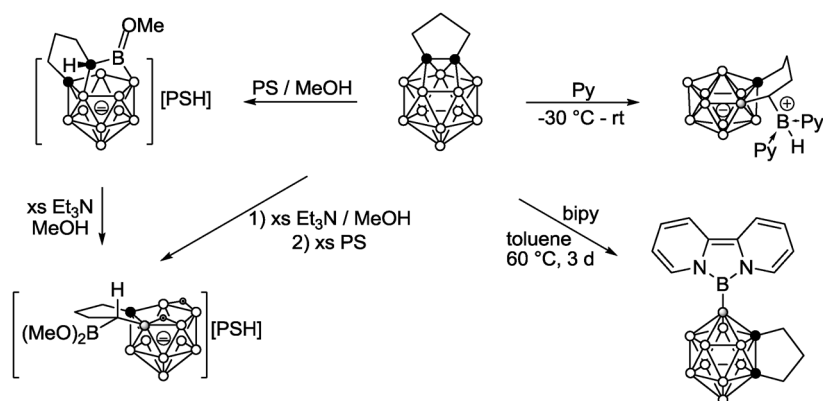
NUCLEOPHILIC REACTION OF 13-VERTEX CARBORANE

13-Vertex carboranes are generally more reactive toward nucleophiles compared to their 12-vertex analogues and show distinctive reactivity patterns. While 12-vertex *closo* o-$R_2C_2B_{10}H_{10}$ undergo deboration to generate the corresponding 11-vertex *nido*-$[R_2C_2B_9H_9]^{2-}$ in the presence of nucleophiles such as MeOH/KOH [24], the CAd 13-vertex carborane μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ reacts readily with MeOH at room temperature to give a cage-carbon-extrusion product, 12-vertex monocarbado-decaborate salt $[μ-1,2-(CH_2)_3CH(OMe)-1-CB_{11}H_{10}][Me_3NH]$ after recrystallization from an aqueous solution of $[Me_3NH]Cl$ (Scheme 8). Reaction with PPh_3 affords a zwitterionic compound 12-vertex μ-1,2-$(CH_2)_3CH(PPh_3)$-1-$CB_{11}H_{10}$. In a similar manner, treatment of CAp 13-vertex carborane 1,6-Me_2-1,6-$C_2B_{11}H_{11}$ with MeOH produces a 12-vertex species $[1-Me-2-CH_3CH(OMe)-1-CB_{11}H_{10}]^-$ [25].
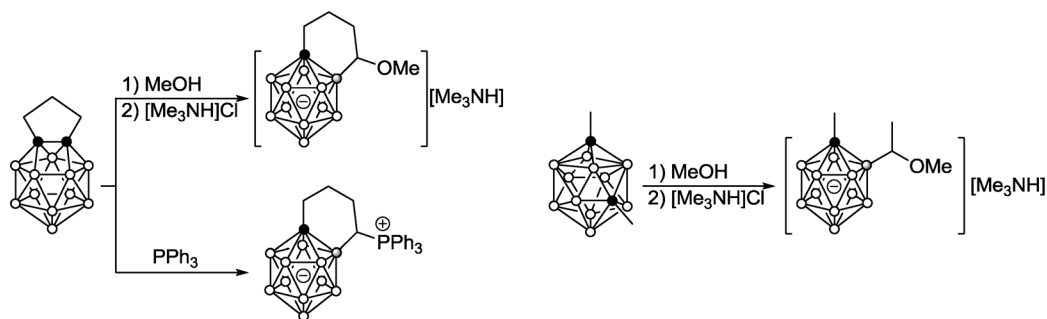
**Scheme 8** Cage-carbon extrusion reactions of CAd and CAp 13-vertex carboranes with nucleophiles.

Cage boron atom of a CAd 13-vertex carborane μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ can also be extruded from the cluster. Treatment of μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with Et_3N/MeOH at room temperature, followed by cation exchange with proton sponge (PS) gives an 11-vertex *nido*-CB_{10} complex [μ-7,8-$(CH_2)_3CHB(OMe)_2$-7-$CB_{10}H_{11}$][PSH] as colorless crystals in 90 % yield. The intermediate of the reaction is isolated by mixing μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with an excess amount of PS in MeOH, which is identified as [*nido*-μ-η:η:η-7,8,10-$(CH_2)_3CHB(OMe)$-7-$CB_{10}H_{10}$][PSH]. It can be quantitatively converted to [μ-7,8-$(CH_2)_3CHB(OMe)_2$-7-$CB_{10}H_{11}$][PSH] in Et_3N/MeOH solution at room temperature (Scheme 9). On the other hand, reaction of μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with pyridine (Py) at −30 °C gives another 11-vertex *closo* complex μ-2,4-$(CH_2)_3CHBH(Py)_2$-2-$CB_{10}H_9$ in 56 % isolated yield. Interestingly, treatment of μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with 1 equiv of bipyridine (bipy) at 60 °C affords a 12-vertex carborane 4-B(bipy)-μ-1,2-$(CH_2)_3$-1,2-$C_2B_{10}H_9$ in 59 % isolated yield (Scheme 9) [26]. These results show that 13-vertex carboranes have a very diverse reactivity pattern, depending upon the nature of nucleophiles.

Scheme 9 Cage-boron extrusion reactions of a CAd 13-vertex carborane with nucleophiles.
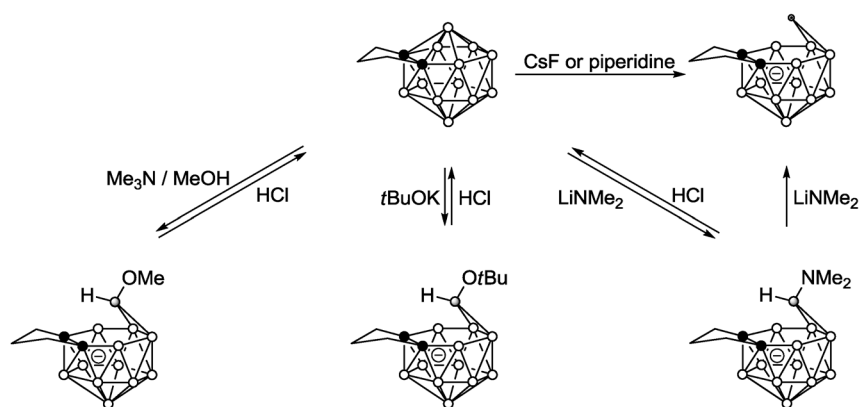
NUCLEOPHILIC REACTION OF 14-VERTEX CARBORANE

14-Vertex *closo*-carboranes are less reactive than 13-vertex *closo*-carboranes. Reaction of μ-2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ with MeOH proceeds extremely sluggishly at ambient temperature, and is incomplete after one month. This reaction can be accelerated by heating at 70 °C and completed in 2 d, affording the 12-vertex CB_{11}^- anions $[\mu$-1,2-$(CH_2)_3CH(OMe)$-1-$CB_{11}H_{10}]^-$, $[\mu$-1,2-$(CH_2)_2CH(OMe)CH_2$-1-$CB_{11}H_{10}]^-$, and $[\mu$-1,2-$(CH_2)_2CH=CH$-1-$CB_{11}H_{10}]^-$ (Scheme 10) [27]. NMR experiments suggest that $[\mu$-1,2-$(CH_2)_3CH(OMe)$-1-$CB_{11}H_{10}]^-$ is initially formed and isomerized to $[\mu$-1,2-$(CH_2)_2CH(OMe)CH_2$-1-$CB_{11}H_{10}]^-$ upon heating probably via a $[\mu$-1,2-$(CH_2)_2CH=CH$-1-$CB_{11}H_{10}]^-$ intermediate.
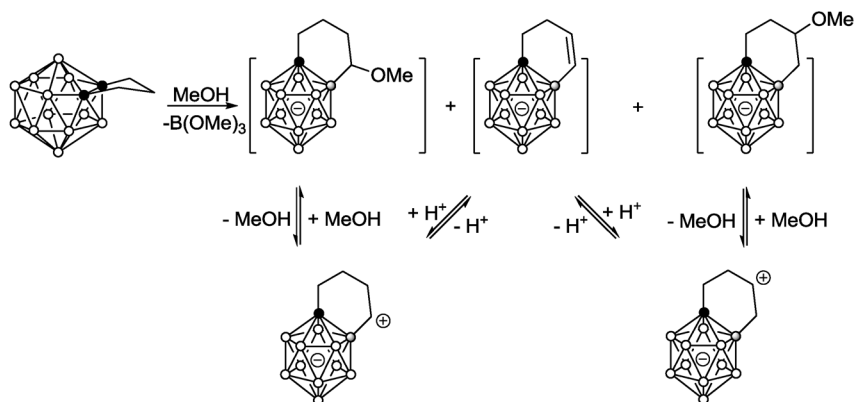
Scheme 10 Reaction of a 14-vertex carborane with MeOH.

Addition of Me_3N to the MeOH solution of a 14-vertex carborane μ-2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ at room temperature gives the salt of the *nido*-C_2B_{12} anion $[\mu$-8,9-$(CH_2)_3$-μ-11,12-(MeO)BH-8,9-$C_2B_{11}H_{11}][Me_3NH]$ in quantitative yield. In a very similar manner, treatment of 14-vertex μ-2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ with *t*BuOK or LiNMe$_2$ in THF affords the 14-vertex *nido*-C_2B_{12} monoanion $[\mu$-8,9-$(CH_2)_3$-μ-11,12-(Nu)BH-8,9-$C_2B_{11}H_{11}]^-$ (Nu = *t*BuO or Me_2N) (Scheme 11). These complexes have very similar structural features with the nucleophiles bound to the bridging boron atom, which is the most electrophilic site in the 14-vertex *closo*-carborane. Treatment of the 14-vertex *nido*-C_2B_{12}

Scheme 11 Reaction of a 14-vertex carborane with nucleophiles.

monoanions [μ-8,9-(CH$_2$)$_3$-μ-11,12-(Nu)BH-8,9-C$_2$B$_{11}$H$_{11}$]$^-$ (Nu = MeO, tBuO, or Me$_2$N) with HCl regenerates the CAd 14-vertex *closo*-carborane μ-2,3-(CH$_2$)$_3$-2,3-C$_2$B$_{12}$H$_{12}$ [27].

In the presence of an excess amount of LiNMe$_2$ in THF, the 14-vertex *nido*-C$_2$B$_{12}$$^-$ monoanion [μ-8,9-(CH$_2$)$_3$-μ-11,12-(Me$_2$N)BH-8,9-C$_2$B$_{11}$H$_{11}$]$^-$ undergoes deboration to give a 13-vertex *nido*-C$_2$B$_{11}$$^-$ anion [μ-8,9-(CH$_2$)$_3$-8,9-C$_2$B$_{11}$H$_{12}$]$^-$. This *nido*-C$_2$B$_{11}$$^-$ monoanion is also prepared from the reaction of a CAd 14-vertex *closo*-carborane μ-2,3-(CH$_2$)$_3$-2,3-C$_2$B$_{12}$H$_{12}$ with a wet piperidine or an excess amount of cesium fluoride in THF (Scheme 11). The geometry of the CAd *nido*-C$_2$B$_{11}$$^-$ anion [μ-8,9-(CH$_2$)$_3$-8,9-C$_2$B$_{11}$H$_{12}$]$^-$ is different from that of CAd *nido* 13-vertex carborane anions in the group 1 metal salts that are generated by the reduction of CAd 13-vertex *closo*-carboranes with group 1 metals.

CONCLUSIONS AND FUTURE PERSPECTIVES

The breakthrough in the synthesis of supercarboranes relies on the use of CAd carborane anions that are weaker reducing agents and stronger nucleophiles than their CAp counterparts. The results show that CAd 12-vertex *nido*-[R$_2$C$_2$B$_{10}$H$_{10}$]$^{2-}$, *arachno*-[R$_2$C$_2$B$_{10}$H$_{10}$]$^{4-}$, and 13-vertex *nido*-[R$_2$C$_2$B$_{11}$H$_{11}$]$^{2-}$ are useful synthons for the preparation of CAd 13- and 14-vertex carboranes via polyhedral expansion methodology. CAp 13-vertex carborane can be synthesized from the thermal isomerization of non-C,C'-bridged CAd 13-vertex isomers, suggesting that CAp isomers are more thermodynamically stable than the CAd ones.

13-Vertex and 14-vertex *closo*-carboranes can be readily reduced to the corresponding *nido*-carborane anions by group 1 metals. Single-electron reduction is also achieved for 13-vertex carboranes, leading to the formation of stable carborane radical anion with [2n + 3] framework electrons. However, unlike 12-vertex carboranes, they are resistant to further reduction to the *arachno*-species by lithium metal. These *nido* salts are good synthons for the synthesis of 14- and 15-vertex metallacarboranes [28].

13-Vertex *closo*-carborane undergoes electrophilic substitution with the furthest B(H) vertices away from the cage-carbons being substituted, generating the corresponding hexasubstituted species. On the other hand, they react with nucleophiles to give cage-carbon and/or cage-boron extrusion products, depending on the nature of nucleophiles. The 14-vertex *closo*-carborane also undergoes nucleophile-dependent reactions to afford different products. These results suggest that supercarboranes have more diverse reactivity patterns than their icosahedral cousins.

Although significant progress has been made in supercarborane chemistry in the past 10 years, the studies on the reaction and coordination chemistry of superclusters remain a relatively young

research area, particularly in comparison to the rich literature of 12-vertex carboranes. Higher-vertex (≥15) carboranes are expected to be prepared as the field progresses. To achieve this goal, new methodologies and reagents need to be developed. Understanding of the reaction mechanisms also helps to design new synthetic routes to superclusters. It is anticipated that supercarboranes may find applications in many disciplines such as electronics, catalysis, boron neutron capture therapy (BNCT), and nanomaterials. The achievements in this field in the past decade have laid a solid ground for further studies.

ACKNOWLEDGMENTS

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