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Reaction of a 14-Vertex Carborane with Nucleophiles: Formation of *nido*-C_2B_{12}, *nido*-C_2B_{11}, and *closo*-CB_{11} Carborane Anions

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Nucleophilic reactions of a 14-vertex *closo*-carborane are reported. 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ (**1**) reacts with MeOH at 70 °C to give *closo*-CB_{11} anions [1,2-$(CH_2)_3$CH(OMe)-1-$CB_{11}H_{10}]^-$ ([**2a**]$^-$), [1,2-$(CH_2)_2$CH(OMe)CH_2-1-$CB_{11}H_{10}]^-$ ([**2b**]$^-$), and [1,2-$(CH_2)_2$CH=CH-1-$CB_{11}H_{10}]^-$ ([**2c**]$^-$). It is suggested that [**2c**]$^-$ is an intermediate for the isomerization from [**2a**]$^-$ to [**2b**]$^-$. Treatment of **1** with MeOH/Me_3N, ^{t}BuOK or $LiNMe_2$ affords *nido*-C_2B_{12} species [8,9-$(CH_2)_3$-μ-11,12-(Nu)BH-8,9-$C_2B_{11}H_{11}]^-$ (Nu = MeO ([**3a**]$^-$), ^{t}BuO ([**3b**]$^-$), and Me_2N ([**3c**]$^-$)). In the presence of acid such as HCl, anions [**3**]$^-$ are converted to **1**. However, [**3**]$^-$ undergo deboration reaction, in the presence of bases, to generate a *nido*-C_2B_{11} anion [8,9-$(CH_2)_3$-8,9-$C_2B_{11}H_{12}]^-$ ([**4**]$^-$) that can also be formed directly from the reaction of **1** with excess CsF or piperidine. Mechanistic studies show that [**3a**]$^-$ is the first intermediate in the reaction of **1** with MeOH and [**4**]$^-$ is unlikely an intermediate.

Introduction

Icosahedral carboranes $C_2B_{10}H_{10}R_2$ have dominated the research activities in carborane chemistry for almost half a century.[1] They can react with nucleophiles to selectively remove one BH vertex to give *nido*-$C_2B_9H_9R_2^{2-}$ dianions,[2] initiating the chemistry of metallacarboranes.[3] Carboranes can be reduced by group 1 metals to afford *nido*-$C_2B_{10}H_{10}R_2^{2-}$ dianions[4] and *arachno*-$C_2B_{10}H_{10}R_2^{4-}$ tetraanions,[5] which are good π ligands for transition metals.[3] They can undergo electrophilic substitution reactions to generate multisubstituted carboranes.[6] Carboranes are also finding many applications in BNCT (Boron Neutron Capture Therapy)[7] and materials science.[8]

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In sharp contrast, supercarboranes (carboranes with more than 12 vertices) are much less explored although a number of 13- and 14-vertex carboranes have been prepared and structurally characterized since 2003.[9−15] Like 12-vertex carboranes, they can be reduced by group 1 metals to give the corresponding *nido*-supercarborane dianions,[10−15] and react with electrophiles to yield multisubstituted supercarboranes.[12] On the other hand, 13-vertex carboranes exhibit some interesting properties of their own. For example, 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ can undergo single-electron reduction to generate a stable carborane radical anion with $2n + 3$ framework electrons,[16] and react with nucleophiles to afford monocarba-*closo*-dodecaborate anions via a cage-carbon extrusion process.[17] The latter is significantly different from 12-vertex carboranes.[18] We wondered if this is a unique chemical property of supercarboranes. In this connection, we examined the reactions of a 14-vertex carborane with various nucleophiles and discovered that it has a richer reaction chemistry than the 13-vertex carboranes. The results are reported in this article.

Results and Discussion

To make a comparison between 13- and 14-vertex carboranes in reactions with nucleophiles, the reaction of 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ (**1**)[11] with MeOH was first attempted and closely monitored by ^{11}B NMR spectroscopy. It was found that this reaction proceeded very slowly at room temperature and was not completed in one month. However, the ^{11}B NMR spectra clearly showed the formation of $B(OMe)_3$ and *closo*-$CB_{11}H_{10}R_2^-$ with the gradual disappearance of **1**. This reaction was accelerated by heating to reflux at 70 °C in a closed vessel and completed in 48 h. Addition of $[Me_3NH]Cl$ to the reaction solution gave a mixture of $[Me_3NH][1,2\text{-}(CH_2)_3CH(OMe)\text{-}1\text{-}CB_{11}H_{10}]$ ($[Me_3NH][\mathbf{2a}]$) and $[Me_3NH][1,2\text{-}(CH_2)_2CH(OMe)CH_2\text{-}1\text{-}CB_{11}H_{10}]$ ($[Me_3NH][\mathbf{2b}]$) in a molar ratio of about 1:1.1 as measured by ^{1}H NMR spectroscopy (Scheme 1). $[Me_3NH][\mathbf{2b}]$ was isolated as a pure compound in 35% yield by fractional recrystallization from acetone although the conversion of **1** is 100%. $[Me_3NH][\mathbf{2a}]$ is a known compound.[17] Two isomers have similar ^{11}B NMR spectra, but have different ^{1}H NMR spectra. The molecular structure of $[Me_3NH][\mathbf{2b}]$ was further confirmed by single-crystal X-ray analyses and shown in Figure 1. The icosahedral cage of $[\mathbf{2b}]^-$ bears the same structural features of monocarba-*closo*-dodecaborate anions.[17,19]

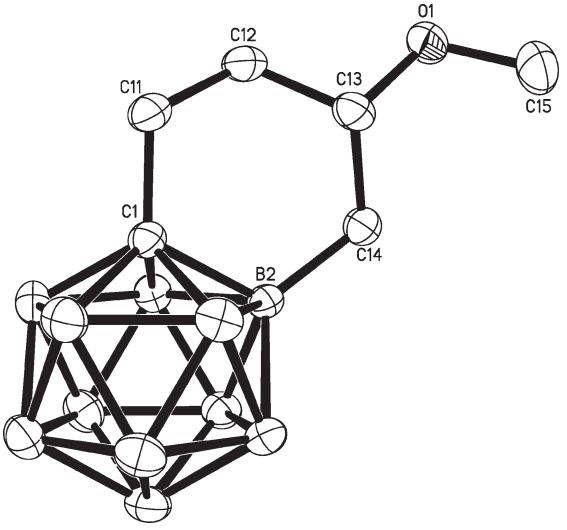
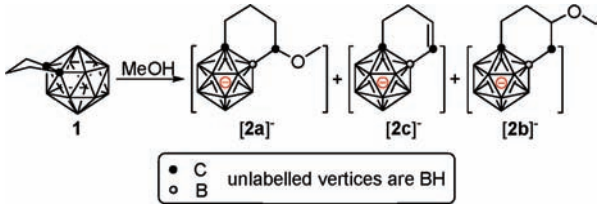


Figure 1. Molecular structure of the anion $[1,2\text{-}(CH_2)_2CH(OCH_3)CH_2\text{-}1\text{-}CB_{11}H_{10}]^-$ in $[Me_3NH][\mathbf{2b}]$ (all H atoms are omitted for clarity). Selected bond lengths [Å]: C1−C11 1.528(3), C11−C12 1.520(3), C12−C13 1.510(4), C13−C14 1.517(3), C14−B2 1.594(3), B2−C1 1.718(3), and C13−O1 1.455(3).

Scheme 1. Reaction of 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ (**1**) with MeOH



We also found few nice crystals among crystalline materials after the concentration of the above mother liquor, which was identified as $[Me_3NH][1,2\text{-}(CH_2)_2CH{=}CH\text{-}1\text{-}CB_{11}H_{10}]$ ($[Me_3NH][\mathbf{2c}]$) by single-crystal X-ray analyses. As shown in Figure 2, the C(13)−C(14) bond length of 1.319(7) Å clearly indicates a C=C double bond. Unfortunately, its spectroscopic data were not able to be collected because of an insufficient amount of sample. Nevertheless, the structural characterization of $[\mathbf{2c}]^-$ offers some hints about the isomerization between $[\mathbf{2a}]^-$ and $[\mathbf{2b}]^-$ as shown in Scheme 2. This process is promoted by heating in MeOH solution, which is supported by NMR experiments. This is the reason why only $[\mathbf{2a}]^-$ is initially isolated from the reaction of 13-vertex carboranes with MeOH at room temperature.[17] It is noteworthy that **1** does not react with PPh_3 even in refluxing toluene whereas the 13-vertex one reacts readily with PPh_3 to give the zwitterionic compound 1,2-$(CH_2)_3CH(PPh_3)$-1-$CB_{11}H_{10}$.[17] These results indicate that 13-vertex carborane is more reactive than 14-vertex one, which can be ascribed to the presence of a trapezoidal face in the 13-vertex carborane while the 14-vertex carboranes have only triangulated faces.

The aforementioned results raise a question on the mechanism by which the *closo*-CB_{11} anions **2** are formed. The formation of $B(OMe)_3$ suggests that MeOH must attack the

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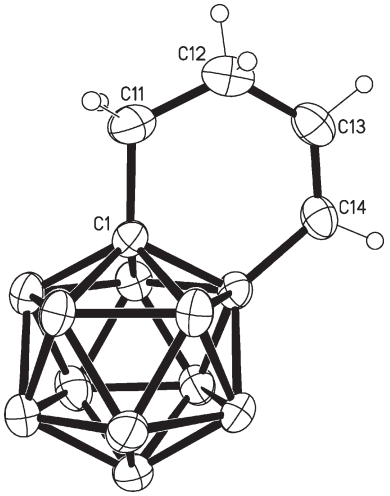
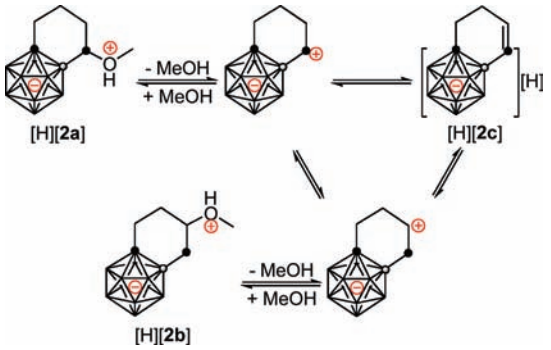


Figure 2. Molecular structure of the anion $[1,2\text{-}(CH_2)_2CH{=}CH\text{-}1\text{-}CB_{11}H_{10}]^-$ in $[Me_3NH][\mathbf{2c}]$ (the H atoms of all BH vertices are omitted for clarity). Selected bond lengths [Å]: C1−C11 1.537(6), C11−C12 1.445(8), C12−C13 1.498(9), C13−C14 1.319(7), C14−B2 1.572(6), and B2−C1 1.690(6).

Scheme 2. Possible Mechanism for the Interchange among $[\mathbf{2a}]^-$, $[\mathbf{2b}]^-$, and $[\mathbf{2c}]^-$



cage boron atom. We tried to trap the intermediates. After many attempts, the salt of the *nido*-C_2B_{12} anion $[Me_3NH][8,9\text{-}(CH_2)_3\text{-}\mu\text{-}11,12\text{-}(MeO)BH\text{-}8,9\text{-}C_2B_{11}H_{11}]$ ($[Me_3NH][\mathbf{3a}]$) was obtained as a white solid in almost quantitative yield by mixing **1** with MeOH and Me_3N aqueous solution at room temperature. The reaction was complete in 1 min as indicated by ^{11}B NMR spectroscopy. Compound $[Me_3NH][\mathbf{3a}]$ was fully characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy as well as elemental analyses. Despite of poor resolution of single-crystal X-ray analyses for $[Me_3NH][\mathbf{3a}]$, the preliminary diffraction results together with NMR data are enough to confirm the connectivity pattern for $[\mathbf{3a}]^-$.[20] The ^{11}B NMR experiments showed that $[Me_3NH][\mathbf{3a}]$ can be converted to **1** after the addition of concentrated HCl to its MeOH solution at room temperature. Heating a MeOH solution of $[Me_3NH][\mathbf{3a}]$ gave *closo*-CB_{11} anions and $B(OMe)_3$.

Reaction of **1** with 1.5−2 equiv of ^{t}BuOK or $LiNMe_2$ in tetrahydrofuran (THF) afforded $\{K(THF)\}\{8,9\text{-}(CH_2)_3\text{-}\mu\text{-}11,12\text{-}(^t\text{BuO})BH\text{-}8,9\text{-}C_2B_{11}H_{11}\}$ ($\{K(THF)\}\{\mathbf{3b}\}$) in 55% isolated yield or $[PPN][8,9\text{-}(CH_2)_3\text{-}\mu\text{-}11,12\text{-}(Me_2N)BH\text{-}8,9\text{-}C_2B_{11}H_{11}]$ ($[PPN][\mathbf{3c}]$) in 80% isolated yield after addition of [PPN]Cl (PPN = bis(triphenylphosphine)iminium cation), respectively (Scheme 3). It is noted that both reactions are complete in 1 min. They are more stable in solution than $[Me_3NH][\mathbf{3a}]$ probably because of the bulky substituents on the boron atom. Both were fully characterized by various spectroscopic techniques, elemental analyses, and single-crystal X-ray diffraction studies. Figures 3 and 4 show the molecular structures of $\{K(THF)\}\{\mathbf{3b}\}$ and $[\mathbf{3c}]^-$, respectively. Anions $[\mathbf{3a}]^-$, $[\mathbf{3b}]^-$, and $[\mathbf{3c}]^-$ have very similar structural features with the nucleophiles bound to the bridging boron atom which is the most electrophilic site in **1**. The B−O distance of 1.390(5) Å in $[\mathbf{3b}]^-$ falls in the range 1.37−1.41 Å normally observed in alkoxy-substituted

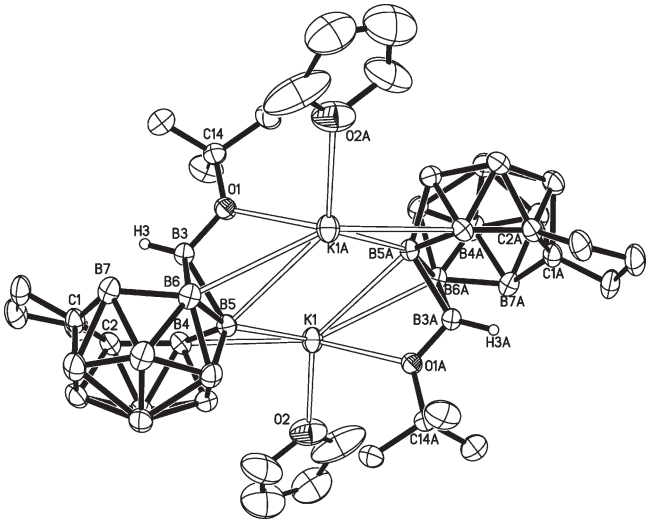
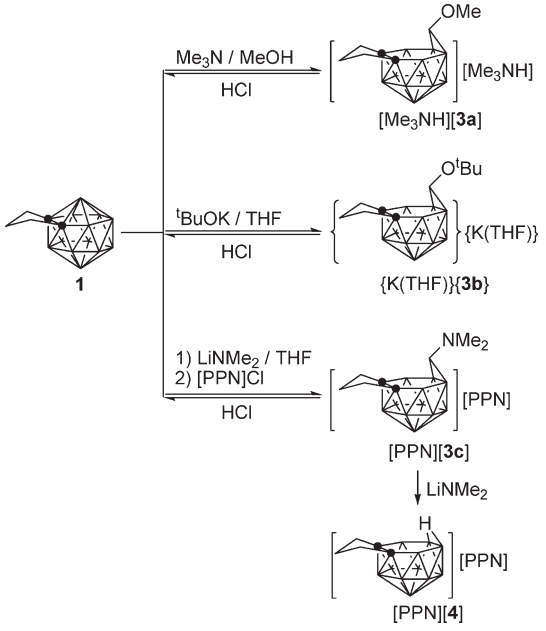


Figure 3. Molecular structure of $\{K(THF)\}\{8,9\text{-}(CH_2)_3\text{-}\mu\text{-}11,12\text{-}(^t\text{BuO})BH\text{-}8,9\text{-}C_2B_{11}H_{11}\}$ ($\{K(THF)\}\{\mathbf{3b}\}$) (all H atoms are omitted for clarity). Selected bond lengths [Å]: B3−O1 1.390(5), B3−B5 1.879(5), B3−B6 1.879(5), C1−C2 1.529(5), C2−B4 1.647(5), B4−B5 1.774(5), B5−B6 1.779(5), B6−B7 1.770(6), and B7−C1 1.655(6).

Scheme 3. Reaction of **1** with Nucleophiles



(20) Crystal data for $[Me_3NH][\mathbf{3a}]$: $C_9H_{31}B_{12}NO$, M_r = 299.1, monoclinic, $P2_1/n$, a = 22.267(5), b = 7.914(2), c = 22.267(5) Å, β = 93.30°, V = 3917(1) Å^3, T = 296 K, Z = 8, μ = 0.052 mm^{-1}, R_1 = 0.193, wR_2 (F^2) = 0.509, see Supporting Information for details.

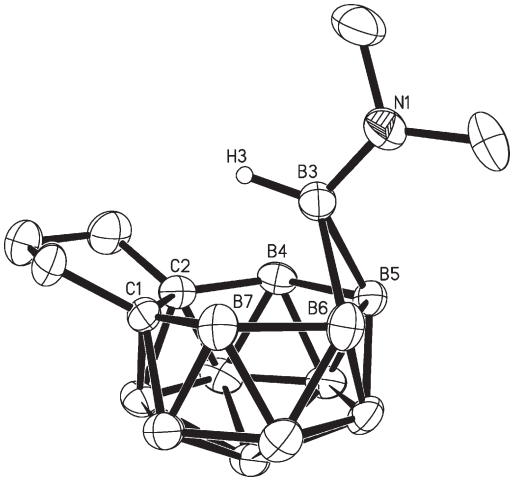
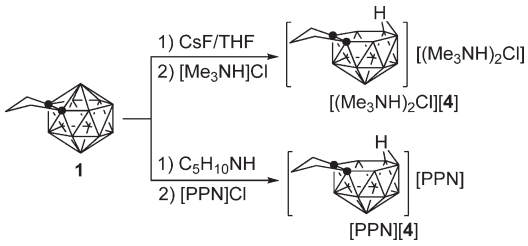


Figure 4. Molecular structure of the anion [8,9-$(CH_2)_3$-μ-11,12-(Me_2N)BH-8,9-$C_2B_{11}H_{11}]^-$ in [PPN][**3c**] (all H atoms are omitted for clarity). Selected bond lengths [Å]: N1−B3 1.414(4), B3−B5 1.888(4), B3−B6 1.891(5), C1−C2 1.547(3), C2−B4 1.628(4), B4−B5 1.786(5), B5−B6 1.783(4), B6−B7 1.781(4), and B7−C1 1.627(4).

Scheme 4. Synthesis of *nido* 13-Vertex Carborane Anions $[\mathbf{4}]^-$



carboranes.[21] The B−N distance of 1.414(4) Å in $[\mathbf{3c}]^-$ is shorter than that of 1.506(6) Å observed in *nido*-$C_2B_{10}H_{12}$-$[HNP(NMe_2)_3]$.[22]

Like [Me_3NH][**3a**], both {K(THF)}{**3b**} and [PPN][**3c**] can react with excess concentrated HCl in acetone to produce **1**. Heating their MeOH solution in the presence of concentrated HCl afforded the *closo*-CB_{11} anions **2** whereas a mixture of products was observed in the absence of HCl. These results indicate that a strong acidic media can promote the formation of CB_{11} anions **2**.

{K(THF)}{**3b**} did not show any activity toward an excess amount of ^{t}BuOK in THF probably because of steric reasons. On the other hand, [PPN][**3c**] reacted with excess $LiNMe_2$ in THF after prolonged stirring to give a deborated product [PPN][8,9-$(CH_2)_3$-8,9-$C_2B_{11}H_{12}$] ([PPN][**4**]). When a large excess amount of CsF was used as a reagent,[23] a *nido*-C_2B_{11} anionic salt [$(Me_3NH)_2Cl$][**4**] was isolated in 60% yield after

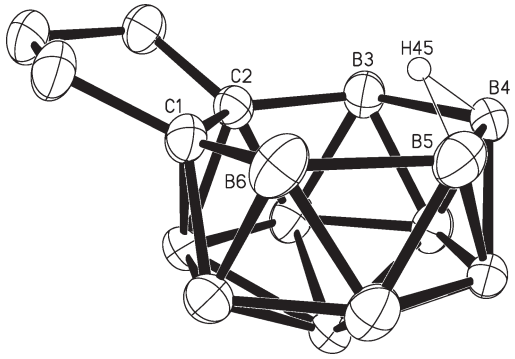


Figure 5. Molecular structure of the anion [8,9-$(CH_2)_3$-8,9-$C_2B_{11}H_{12}]^-$ in [PPN][**4**] (all H atoms are omitted for clarity). Selected bond lengths [Å]: C1−C2 1.557(3), C2−B3 1.603(4), B3−B4 1.788(4), B4−B5 1.817(5), B5−B6 1.795(5), and B6−C1 1.607(4).

treatment with [Me_3NH]Cl. A [PPN] salt of $[\mathbf{4}]^-$ was also prepared in 85% yield from the reaction of **1** with piperidine[24] followed by the addition of [PPN]Cl (Scheme 4). It is surprising that these salts are very stable in refluxing MeOH even in the presence of concentrated HCl, suggesting that $[\mathbf{4}]^-$ is unlikely as an intermediate in the transformation from a *closo*-C_2B_{12} species to CB_{11} anions. Figure 5 shows the molecular structure of the anion $[\mathbf{4}]^-$ in [PPN][**4**] derived from single-crystal X-ray analyses. Despite of poor resolution of single-crystal X-ray analyses for [$(Me_3NH)_2Cl$][**4**], the preliminary diffraction results together with NMR and elemental analyses data are enough to confirm the connectivity pattern for [$(Me_3NH)_2Cl$][**4**].[25] The geometry of $[\mathbf{4}]^-$ is different from that of *nido* 13-vertex carboranes generated by the reduction of *closo* species with group 1 metals,[11,12] but is very similar to that observed in 14-vertex metallacarboranes.[13,14]

The above experimental data offer a clue to the reaction mechanism for the formation of *closo*-CB_{11} anions **2**: (1) a strong acidic media is essential, (2) the anion $[\mathbf{3a}]^-$ is the first intermediate, and (3) the *nido*-13-vertex carborane anion $[\mathbf{4}]^-$ is not an intermediate. Having these results, we may propose a possible reaction pathway for the formation of the CB_{11} anion $[\mathbf{2a}]^-$ as shown in Scheme 5. Other possibilities can not, however, be ruled out at this stage. Nucleophilic attack on the seven-coordinate boron atom adjacent to the two cage carbons gives the first intermediate [H][**3a**]. Migration of the H^+ from the oxygen atom to one of the cage carbon atoms, which may be coupled with the nucleophilic attack of MeOH on another cage boron adjacent to two cage carbons as well as on the bridging boron atom, affords the final product [H][**2a**]. On the other hand, in the presence of base, $[\mathbf{3a}]^-$ undergoes deboration to generate $[\mathbf{4}]^-$. It is noteworthy that if CD_3OD was used as a reagent, the H/D exchange on cage BH vertices was also observed,[26] which does not offer useful information on proton transfer process.

In conclusion, 14-vertex carborane shows a diverse reactivity pattern toward various nucleophiles, leading to the

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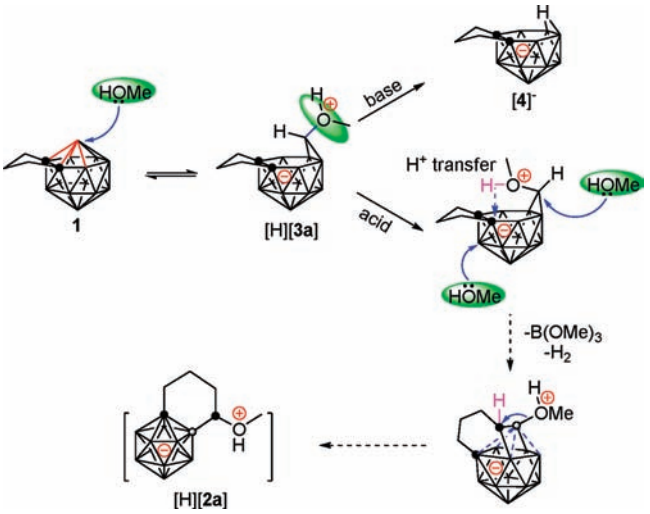
(25) Crystal data for [$(Me_3NH)_2Cl$][**4**]: $C_{33}H_{114}B_{33}Cl_3N_6$, M_r = 1058.4, orthorhombic, *Pnma*, a = 11.839(2), b = 34.882(4), c = 16.429(2) Å, V = 6785(2) Å^3, T = 173 K, Z = 4, μ = 0.166 mm^{-1}, R_1 = 0.106, wR_2 (F^2) = 0.262, see Supporting Information for details.

(26) It has been documented that carboranes can undergo H/D exchange in acidic media, see: (a) Setkina, V. N.; Malakhova, I. G.; Stanko, V. I.; Klimova, A. I.; Zakharkin, L. I. *Izvestiya Akad. Nauk SSSR Seriya Khim.* **1966**, 1678. (b) Jelínek, T.; Plešek, J.; Mareš, F.; Hemánek, S.; tíbr, B. *Polydedron* **1987**, *6*, 1981–1986.

Scheme 5. Possible Reaction Pathways for the Formation of *nido*-C_2B_{11} and *closo*-CB_{11} Anions



formation of *nido*-C_2B_{12}, *nido*-C_2B_{11}, and *closo*-CB_{11} carborane anions dependent upon the nature of the nucleophiles. It is more reactive than 12-vertex carboranes but is less reactive than 13-vertex ones.

Experimental Section

General Procedures. Unless otherwise noted, all experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ was prepared according to literature method.[11] THF was refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 1600 Fourier transform spectrometer. ^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400.0 MHz. ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 75.5 MHz or a Bruker DPX 400 spectrometer at 100.6 MHz. ^{11}B NMR spectra were recorded on a Bruker DPX 300 spectrometer at 96.3 MHz. ^{31}P NMR spectra were recorded on a Bruker DPX 300 spectrometer at 121.5 MHz. All chemical shifts were reported in δ units with reference to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3\cdot OEt_2$ (0.00 ppm) for boron chemical shifts, and to external 85% H_3PO_4 (0.00 ppm) for phosphorus chemical shifts. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences, China.

Reaction of 1 with MeOH. A MeOH solution (5 mL) of **1** (78 mg, 0.38 mmol) in a closed Schlenk flask was heated to reflux at 70 °C for 48 h. After addition of [Me_3NH]Cl (72 mg, 0.75 mmol), the mixture was stirred for another 1 h at room temperature. Removal of the volatile materials gave a white solid that was washed with water to remove the excess amount of [Me_3NH]Cl. The ^{1}H NMR of the crude product showed the molar ratio of [**2a**]$^-$/[**2b**]$^-$ was about 1:1.1. Fractional recrystallization from acetone afforded [Me_3NH][**2b**] as colorless crystals (38 mg, 35%). ^{1}H NMR (acetone-d_6): δ 6.70 (brs, 1H, N*H*), 3.21 (m, 1H, OC*H*), 3.18 (s, 12H, NCH_3 + OCH_3), 2.01 (m, 1H, CH_2), 1.92 (m, 1H, CH_2), 1.55 (m, 1H, CH_2), 1.48 (m, 1H, CH_2), 1.28 (m, 1H, CH_2), 0.74 (m, 1H, CH_2). ^{13}C{^{1}H} NMR (acetone-d_6): δ 79.9 (O*C*H), 67.7 (cage *C*), 54.7 (OCH_3), 46.0 (NCH_3), 36.1 (*C*H_2), 31.9 (*C*H_2), 21.4 (br, B*C*H_2). ^{11}B NMR (acetone-d_6): δ −7.0 (s, 1B), −9.9 (d, J_{BH} = 130 Hz, 1B), −12.1 (d, J_{BH} = 122 Hz, 7B), −13.5 (d, J_{BH} = 171 Hz, 1B), −15.6 (d, J_{BH} = 136 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2522 (vs). Anal. Calcd for $C_9H_{30}B_{11}NO$: C, 37.63; H, 10.53; N, 4.88. Found: C, 38.10; H, 10.77; N, 4.68.

Concentration of the mother liquor yielded few colorless X-ray-quality-crystals identified as [Me_3NH][**2c**].

Preparation of [Me_3NH][8,9-$(CH_2)_3$-μ-11,12-(MeO)BH-8,9-$C_2B_{11}H_{11}$] ([Me_3NH][3a]). To a MeOH solution (5 mL) of **1** (54 mg, 0.26 mmol) was added an aqueous solution of Me_3N (45%, 0.5 mL, 7.00 mmol), and the reaction mixture was stirred at room temperature for 1 min. After removal of solvents under vacuum, the solid residue was thoroughly washed with hexane and Et_2O to give [Me_3NH][**3a**] as a white solid (75 mg, 96%). Recrystallization from a CH_2Cl_2 solution afforded colorless crystals. ^{1}H NMR (CD_2Cl_2): δ 9.04 (brs, 1H, N*H*), 3.35 (s, 3H, OCH_3), 2.97 (s, 9H, NCH_3), 2.58 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 1.88 (m, 1H, CH_2), 1.60 (m, 1H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 86.1 (br, cage *C*), 60.3 (OCH_3), 46.8 (NCH_3), 41.1 (*C*H_2), 25.1 (*C*H_2). ^{11}B NMR (CD_2Cl_2): δ 22.3 (d, J_{BH} = 138 Hz, 1B), 9.8 (d, J_{BH} = 149 Hz, 2B), 4.5 (d, J_{BH} = 133 Hz, 1B), −1.2 (d, J_{BH} = 136 Hz, 2B), −4.1 (d, J_{BH} = 148 Hz, 2B), −8.5 (d, J_{BH} = 120 Hz, 3B), −28.3 (d, J_{BH} = 138 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2517 (vs). Anal. Calcd for $C_9H_{31}B_{12}NO$: C, 36.14; H, 10.45; N, 4.68. Found: C, 36.41; H, 10.53; N, 4.77.

Preparation of {K(THF)}{8,9-$(CH_2)_3$-μ-11,12-(^{t}BuO)BH-8,9-$C_2B_{11}H_{11}$} ({K(THF)}{3b}). To a THF solution (10 mL) of **1** (104 mg, 0.50 mmol) was added ^{t}BuOK (84 mg, 0.75 mmol) under stirring at room temperature The reaction was complete in 1 min. Removal of THF gave a yellow solid, which was extracted with Et_2O (3 × 10 mL). Slow evaporation at room temperature afforded {K(THF)}{**3b**} as colorless needle crystals (88 mg, 55%). Single-crystals suitable for X-ray analyses were grown from a THF/hexane solution at room temperature. ^{1}H NMR (acetone-d_6): δ 3.62 (m, OC_4H_8), 2.48 (m, 2H, CH_2), 1.98 (m, 2H, CH_2), 1.78 (m, 5H, CH_2 + OC_4H_8), 1.56 (m, 1H, CH_2), 0.99 (s, 9H, OC(CH_3)$_3$). ^{13}C{^{1}H}NMR (acetone-d_6): δ 83.6 (br, cage *C*), 74.0 (O*C*(CH$_3$)$_3$), 67.8 (OC_4H_8), 41.2 (*C*H_2), 30.4 (OC(*C*H$_3$)$_3$), 25.8 (OC_4H_8), 25.0 (*C*H_2). ^{11}B NMR (acetone-d_6): δ 24.3 (d, J_{BH} = 132 Hz, 1B), 7.5 (d, J_{BH} = 145 Hz, 2B), 3.5 (d, J_{BH} = 142 Hz, 1B), 0.8 (d, J_{BH} = 139 Hz, 2B), −1.5 (d, J_{BH} = 145 Hz, 2B), −4.8 (d, J_{BH} = 132 Hz, 2B), −7.4 (d, J_{BH} = 169 Hz, 1B), −28.0 (d, J_{BH} = 132 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2519 (vs). Anal. Calcd for $C_{11}H_{31}B_{12}KO_{1.5}$ (M − 0.5THF): C, 37.09; H, 8.77. Found: C, 37.64; H, 8.43.

Preparation of [PPN][8,9-$(CH_2)_3$-μ-11,12-(Me_2N)BH-8,9-$C_2B_{11}H_{11}$] ([PPN][3c]). To a THF solution of **1** (52 mg, 0.25 mmol) was added $LiNMe_2$ (26 mg, 0.50 mmol) under stirring at room temperature. The reaction was finished in 1 min. A saturated MeOH solution of [PPN]Cl was then added until the precipitation was complete. An orange-yellow solid was collected and washed with MeOH (3 × 2 mL). Recrystallization from acetone gave [PPN][**3c**] as orange-yellow crystals (158 mg, 80%). ^{1}H NMR (acetone-d_6): δ 7.71 (m, 18H, C_6H_5), 7.58 (m, 12H, C_6H_5), 2.59 (s, 6H, NCH_3), 2.37 (m, 2H, CH_2), 1.89 (m, 2H, CH_2), 1.75 (m, 1H, CH_2), 1.47 (m, 1H, CH_2). ^{13}C-{^{1}H}NMR (acetone-d_6): δ 134.6, 133.3, 130.5, 129.0, 127.5 (C_6H_5), 41.2 (*C*H_2), 25.3 (*C*H_2). ^{11}B NMR (acetone-d_6): δ 25.7 (d, J_{BH} = 140 Hz, 1B), 4.5 (d, J_{BH} = 154 Hz, 2B), 1.6 (d, J_{BH} = 140 Hz, 2B), −0.2 (d, J_{BH} = 138 Hz, 3B), −6.9 (d, J_{BH} = 103 Hz, 3B), −28.5 (d, J_{BH} = 137 Hz, 1B). ^{31}P NMR (acetone-d_6): δ 38.5. IR (KBr, cm^{-1}): ν_{BH} 2504 (vs). Anal. Calcd for $C_{43}H_{54}B_{12}N_2P_2$: C, 65.33; H, 6.88. Found: C, 65.52; H, 6.46.

Preparation of [PPN][8,9-$(CH_2)_3$-8,9-$C_2B_{11}H_{12}$] ([PPN][4]). A piperidine solution (2 mL) of **1** (52 mg, 0.25 mmol) was stirred at room temperature for 8 h. After removal of piperidine under vacuum, the residue was dissolved in MeOH (2 mL). A saturated MeOH solution of [PPN]Cl was added to the above solution until the precipitation was complete. The white solid was collected by filtration and washed with MeOH (3 × 2 mL). Recrystallization from acetone gave [PPN][**4**] as colorless

Table 1. Crystal Data and Summary of Data Collection and Refinement for $[Me_3NH][\mathbf{2b}]$, $[Me_3NH][\mathbf{2c}]$, $\{K(THF)\}\{\mathbf{3b}\}$, [PPN][**3c**], and [PPN][**4**]

	$[Me_3NH][\mathbf{2b}]$	$[Me_3NH][\mathbf{2c}]$	$\{K(THF)\}\{\mathbf{3b}\}$	[PPN][**3c**]	[PPN][**4**]
formula	$C_9H_{30}B_{11}NO$	$C_8H_{26}B_{11}N$	$C_{13}H_{35}B_{12}KO_2$	$C_{43}H_{54}B_{12}N_2P_2$	$C_{41}H_{48}B_{11}NP_2$
fw	287.25	255.21	392.23	790.54	735.65
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$P2_1$	$P\bar{1}$
a, Å	11.706(3)	7.849(1)	7.999(1)	22.362(1)	9.370(1)
b, Å	12.298(3)	10.415(1)	14.476(1)	9.241(1)	14.283(2)
c, Å	13.143(3)	20.184(1)	21.580(1)	23.662(1)	15.939(2)
α, deg	90	90	90	90	93.98(1)
β, deg	109.85(1)	90	100.30(1)	112.68(1)	102.22(1)
γ, deg	90	90	90	90	90.32(1)
V, Å^3	1780(1)	1650(1)	2459(1)	4511(1)	2079(1)
Z	4	4	4	4	2
T, K	293	296	296	296	296
λ, Å	Mo Kα (0.71073)	Cu Kα (1.54178)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
D_{calcd}, Mg/m^3	1.072	1.027	1.060	1.164	1.175
μ, mm^{-1}	0.056	0.331	0.222	0.130	0.136
no. of obsd reflns	3127	2592	4339	21390	7237
no. of params refnd	199	182	257	1071	500
goodness of fit	1.022	1.054	1.020	1.044	1.004
R1[a]	0.068	0.099	0.078	0.049	0.044
wR2[a]	0.177	0.273	0.219	0.120	0.123

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

crystals (156 mg, 85%). ^{1}H NMR (acetone-d_6): δ 7.71 (m, 18H, C_6H_5), 7.58 (m, 12H, C_6H_5), 2.34 (m, 2H, CH_2), 2.05 (m, 2H, CH_2), 1.68 (m, 1H, CH_2), 1.49 (m, 1H, CH_2). ^{13}C{^{1}H}NMR (acetone-d_6): δ 134.6, 133.3, 130.5, 129.0, 127.5 (C_6H_5), 40.3 (CH_2), 26.5 (CH_2). ^{11}B NMR (acetone-d_6): δ 0.6 (d, J_{BH} = 134 Hz, 2B), −0.9 (d, J_{BH} = 139 Hz, 3B), −7.9 (d, J_{BH} = 152 Hz, 2B), −11.1 (d, J_{BH} = 127 Hz, 2B), −14.8 (d, J_{BH} = 136 Hz, 1B), −33.0 (d, J_{BH} = 138 Hz, 1B). ^{31}P NMR (acetone-d_6): δ 38.6. IR (KBr, cm^{-1}): ν_{BH} 2511 (vs). Anal. Calcd for $C_{41}H_{48}B_{11}NP_2$: C, 66.94; H, 6.58; N, 1.90. Found: C, 66.89; H, 6.60; N, 1.56.

Preparation of $[(Me_3NH)_2Cl][8,9\text{-}(CH_2)_3\text{-}8,9\text{-}C_2B_{11}H_{12}]$ ($[(Me_3NH)_2Cl][\mathbf{4}]$). To a THF solution (5 mL) of **1** (50 mg, 0.24 mmol) was added CsF (185 mg, 1.22 mmol), and the mixture was stirred at room temperature for 7 d. After addition of $[Me_3NH]Cl$ (120 mg, 1.25 mmol), the mixture was stirred for another 1 h at room temperature. Removal of the precipitate and the solvent gave a white solid that was recrystallized from acetone to afford $[(Me_3NH)_2Cl][\mathbf{4}]$ as colorless crystals (51 mg, 60%). ^{1}H NMR (acetone-d_6): δ 7.18 (brs, 2H, NH), 3.02 (s, 18H, NCH_3), 2.34 (m, 2H, CH_2), 2.07 (m, 2H, CH_2), 1.69 (m, 1H, CH_2), 1.48 (m, 1H, CH_2). ^{13}C{^{1}H} NMR (acetone-d_6): δ 82.3 (cage C), 45.2 (NCH_3), 40.2 (CH_2), 26.4 (CH_2). ^{11}B NMR (acetone-d_6): δ 0.5 (d, J_{BH} = 133 Hz, 2B), −1.1 (d, J_{BH} = 160 Hz, 3B), −8.2 (d, J_{BH} = 148 Hz, 2B), −11.5 (d, J_{BH} = 138 Hz, 2B), −15.0 (d, J_{BH} = 126 Hz, 1B), −33.3 (d, J_{BH} = 133 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2507 (vs). Anal. Calcd for $C_{11}H_{38}B_{11}ClN_2$: C, 37.45; H, 10.86; N, 7.94. Found: C, 37.59; H, 10.32; N, 7.50.

X-ray Structure Determination. Data were collected at 296 K on a Bruker AXS kappa Apex II Duo diffractometer using Mo−Kα or Cu−Kα radiation. An empirical absorption correction was applied using the multiscan method. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.[27] For the non-centrosymmetric structure of [PPN][**3c**], the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[28] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 1.

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Supporting Information Available: Crystallographic data in CIF format for complexes $[Me_3NH][\mathbf{2b}]$, $[Me_3NH][\mathbf{2c}]$, $[Me_3NH][\mathbf{3a}]$, $\{K(THF)\}\{\mathbf{3b}\}$, [PPN][**3c**], [PPN][**4**], and $[(Me_3NH)_2Cl][\mathbf{4}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881.