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Reaction of 13-Vertex Carborane μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ with Nucleophiles: Scope and Mechanism

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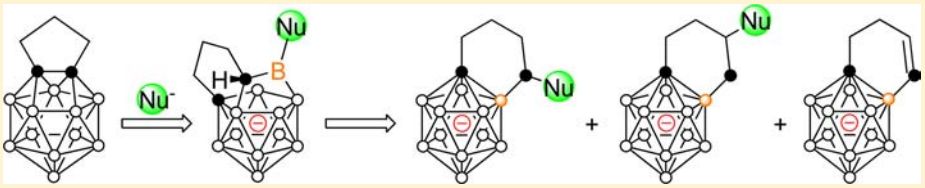
Supporting Information



ABSTRACT: 13-Vertex carborane, μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ (**1**), reacted with a series of nucleophiles (Nu) to give the cage carbon extrusion products $[\mu$-1,2-$(CH_2)_3$CH(Nu)-1-$CB_{11}H_{10}]^-$, $[\mu$-1,2-$(CH_2)_2$CH(Nu)CH_2-1-$CB_{11}H_{10}]^-$, and/or $[\mu$-1,2-$(CH_2)_2$CH=CH-1-$CB_{11}H_{10}]^-$, depending on the nature of Nu and the reaction conditions. The key intermediates for the formation of CB_{11}^- anions were isolated and structurally characterized as $[\mu$–η:η:η-7,8,10-$(CH_2)_3$CHB(Nu)-7-$CB_{10}H_{10}]^-$ (Nu = OMe, NEt_2). The reaction mechanism is thus proposed, which involves the attack of Nu at the most electron-deficient cage boron, followed by H-migration to one of the cage carbons, leading to the formation of the intermediate. Nu-migration gives the products.

INTRODUCTION

Icosahedral carboranes are a class of carbon/boron clusters with exceptionally thermal and chemical stabilities, which have received much attention for more than half a century.[1] The chemistry of subicosahedral carboranes has also been well developed.[1,2] In contrast, studies of supercarboranes (carboranes with more than 12 vertices) remain a young research area.[3] Only in recent years, several 13- and 14-vertex carboranes have been synthesized,[4] which rely on the use of CAd (Carbon-Atoms-Adjacent) carborane anions.[5]

Chemical properties of these supercarboranes have been documented. For example, μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ (**1**) can undergo electrophilic substitution to give 8,9,10,11,12,13-X_6-μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_5$ (X = Me, Br or I),[4c] single-electron reduction to generate a stable carborane radical anion with [2*n* +3] framework electrons,[6] and two-electron reduction to produce *nido* 13-vertex carborane dianion.[4b,c] Compound **1** reacts with MeOH or PPh_3 to afford the unexpected cage carbon extrusion products 12-vertex monocarba-*closo*-dodecaborate anions[7] and with Me_3N/MeOH or pyridine to yield the cage carbon/boron extrusion species CB_{10}^- anions.[8] Such a nucleophile-dependent reactivity prompts us to further investigate the effects of nucleophiles on the formation of the products and to understand the reaction mechanism. We report in this article the reaction scope of 13-vetex carborane and related reaction pathways upon the isolation of the key intermediates.

RESULTS AND DISCUSSION

Reaction of 1 with Alcohols. Reaction of μ-1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ (**1**) with pure MeOH at room temperature for 12 h gave, after addition of $[Me_3NH]Cl$, $[\mu$-1,2-$(CH_2)_3$CH-(OMe)-1-$CB_{11}H_{10}][Me_3NH]$ ([**2a**][Me_3NH]) in 75% isolated yield.[7] It was noted that heating led to the formation of a mixture of products containing [**2a**][Me_3NH] and $[\mu$-1,2-$(CH_2)_2$CH(OMe)CH_2-1-$CB_{11}H_{10}][Me_3NH]$ ([**2b**][Me_3NH]) in a molar ratio of about 1:1 together with the observation of a very small amount of $[\mu$-1,2-$(CH_2)_2$CH=CH-1-$CB_{11}H_{10}]$-$[Me_3NH]$ ([**3**][Me_3NH]) (Scheme 1).

Compound **1** also reacted with EtOH in a similar manner, but the ratio of the products varied, which might be related to different nucleophilicity of alcohols.[9] An EtOH solution of **1** was heated at 70 °C for 24 h to give, after addition of $[Me_3NH]Cl$, a mixture of $[\mu$-1,2-$(CH_2)_3$CH(OEt)-1-$CB_{11}H_{10}]$-$[Me_3NH]$ ([**4a**][Me_3NH]) and [**3**][Me_3NH] in a molar ratio of about 1:0.5 in 70% isolated yield with the observation of a very small amount of $[\mu$-1,2-$(CH_2)_2$CH(OEt)CH_2-1-$CB_{11}H_{10}]$-$[Me_3NH]$ ([**4b**][Me_3NH]) (Scheme 1). However, these complexes were inseparable. The NMR spectra of the mixture were recorded and the corresponding signals of [**4a**][Me_3NH], [**3**][Me_3NH], and [**4b**][Me_3NH] were assigned using COSY, HSQC, and HMBC techniques. The peaks at 5.85 ppm in the ^1H NMR spectrum, a sharp signal at 131.8, and a broad one at 132.7 ppm in the ^{13}C NMR spectrum confirmed the formation of the alkenyl product, $[\mathbf{3}]^-$.[10] The characteristic NMR data of

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Scheme 1. Reaction of 1 with ROH (R = Me, Et)

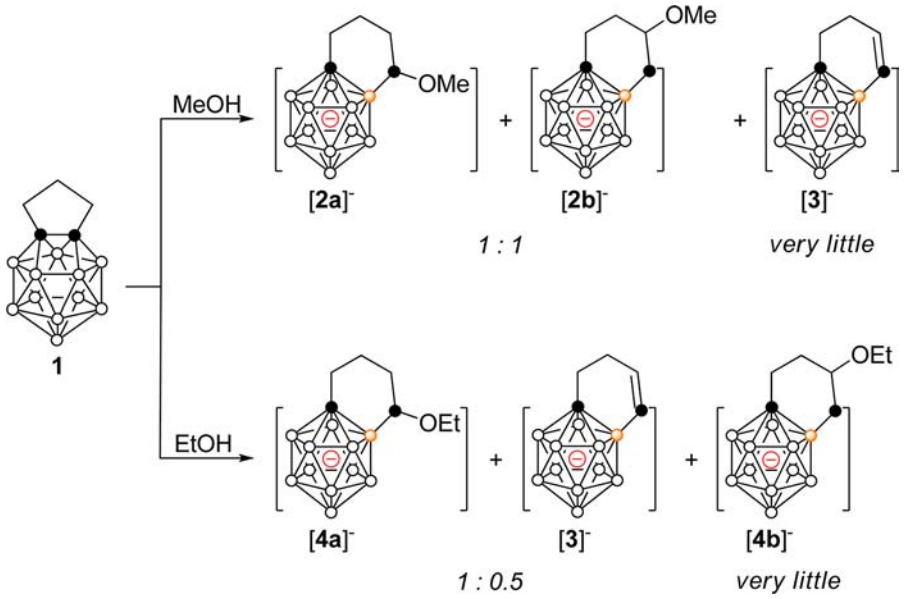

Table 1. Characteristic Chemical Shifts of $[\mu$-1,2-$(CH_2)_3CH(Nu)$-1-$CB_{11}H_{10}]^-$ Anions[a]

compd (Nu)	B2	α-CH	β-CH_2	γ-CH_2	δ-CH_2	α-CH	β-CH_2	γ-CH_2	δ-CH_2	cage C
$[\mathbf{2a}]^-$ (OMe)[b]	−7.7	3.11	1.68, 1.39	1.46, 1.21	1.81	74.2	29.6	23.2	36.7	69.2
$[\mathbf{4a}]^-$ (OEt)[b]	−7.7	3.19	1.68, 1.29	1.43, 1.17	1.77	71.5	29.9	23.1	36.1	69.2
5a (PPh_3)	−[e]	3.73	2.14, 1.47	1.64, 1.56	1.98, 1.64	17.2	24.9	25.3	36.2	67.7
6a (N^tBuH_2)	−9.4	3.36	2.01, 1.63	1.51, 1.39	1.85	44.5	29.3	23.2	35.1	68.9
7a (NEt_2H)	−[e]	3.40	2.00, 1.53	1.68, 1.38	1.98, 1.79	54.4	24.7	24.5	35.5	69.1
$[\mathbf{8a}]^-$ ($S(4\text{-}MeC_6H_4)$)[c]	−7.9	3.12	1.71, 1.38	1.55, 1.20	1.86	31.7	29.5	23.5	36.5	68.2
$[\mathbf{9}]^-$ (H)[d]	−7.2	0.89	1.35	1.29	1.83	14.2	22.8	26.0	36.5	67.9
10a (NEt_3)	−[e]	3.54	2.17, 1.63	1.72, 1.38	2.00, 1.81	66.0	24.5	25.5	36.3	69.4
15a (NC_5H_5)	−8.7	4.73	2.30, 2.07	1.80, 1.54	2.08, 1.95	65.6	29.9	24.7	35.4	68.8

[a]The solution was in d_6-acetone and is given in ppm. [b]The cation is $[Me_3NH]^+$. [c]The cation is $[PPN]^+$. [d]The cation is $[Me_4N]^+$. [e]There was an overlap with other cage B signals.

Table 2. Characteristic Chemical Shifts of $[\mu$-1,2-$(CH_2)_2CH(Nu)CH_2$-1-$CB_{11}H_{10}]^-$ Anions[a]

compd (Nu)	B2	α-CH_2	β-CH	γ-CH_2	δ-CH_2	α-CH_2	β-CH	γ-CH_2	δ-CH_2	cage C
$[\mathbf{2b}]^-$ (OMe)[b]	−7.0	1.48, 0.74	3.21	1.55, 1.28	2.01, 1.92	21.4	79.9	31.9	36.1	67.7
$[\mathbf{4b}]^-$ (OEt)[b]	−[d]	1.41, 0.74	3.27	1.52, 1.24	1.97, 1.88	22.2	77.7	32.0	35.8	67.6
7b (NEt_2H)	−8.2	1.39, 1.23	3.59	1.80, 1.70	2.16, 2.03	14.7	63.4	27.5	35.8	66.4
10b (NEt_3)	−8.0	1.50, 1.37	3.54	2.07, 1.69	2.19, 2.03	15.5	72.7	27.0	36.8	66.3
11b ($C_{14}H_{18}N_2$)[c]	−[d]	1.28, 1.07	3.34	1.68, 1.53	2.10	22.6	35.3	32.3	36.0	66.8
15b (NC_5H_5)	−8.1	1.74, 1.65	4.87	2.22, 1.96	2.24	24.6	73.6	33.1	36.2	66.2

[a]The solution was in d_6-acetone and is given in ppm. [b]The cation is $[Me_3NH]^+$. [c]The solution was in d_6-DMSO. [d]There was an overlap with other cage B signals.

these CB_{11}^- anions were summarized in Tables 1 and 2, respectively.

Fractional recrystallization from acetone gave few crystals of $[\mathbf{4a}][Me_3NH]$ as identified by single-crystal X-ray analyses (Figure 1). The icosahedral cage has the same structural features of monocarba-*closo*-dodecaborate anions.[11] The key structural parameters of some related CB_{11}^- anions are summarized in Table 3. The C11-C1-B2-C14 atoms are almost coplanar, and the exo 6-membered ring adopts a cyclohexene conformation with the OEt substituent taking up the *e* position.

A possible reaction mechanism for the formation of $[\mathbf{2a}]^-$/$[\mathbf{4a}]^-$, $[\mathbf{2b}]^-$/$[\mathbf{4b}]^-$ and $[\mathbf{3}]^-$ is proposed in Scheme 2. This hypothesis is supported by the following NMR experiments. The ^1H and ^{13}C NMR spectra clearly showed the initial formation of $[\mathbf{2a}]^-$ with disappearance of **1** in CD_3OD. The corresponding peaks of $[\mathbf{2b}]^-$ and $[\mathbf{3}]^-$ were observed after several hours, and the mixture finally arrived at an equilibrium with a molar ratio of about 1:1 for $[\mathbf{2a}]^-$:$[\mathbf{2b}]^-$ at room temperature. After heating the solution for 24 h at 70 °C, no obvious changes were observed. On the other hand, $[\mathbf{2a}][Na]$, prepared by treatment of $[\mathbf{2a}][Me_3NH]$ with an excess of NaOH, was stable for weeks in refluxing CD_3OD without any detectable change in the ^1H NMR spectrum. However, addition of drops of concentrated HCl to the above solution led to the formation of $[\mathbf{2b}]^-$, and the molar ratio of $[\mathbf{2a}]^-$:$[\mathbf{2b}]^-$ reached

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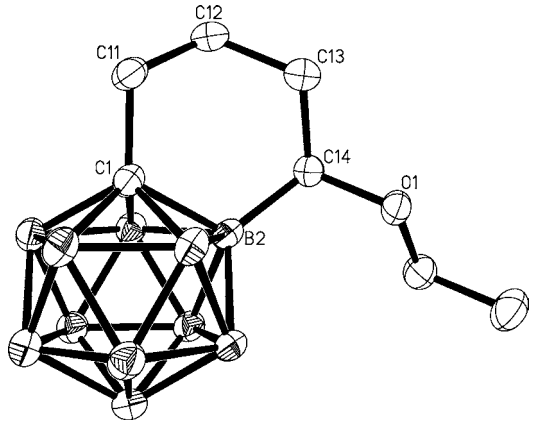


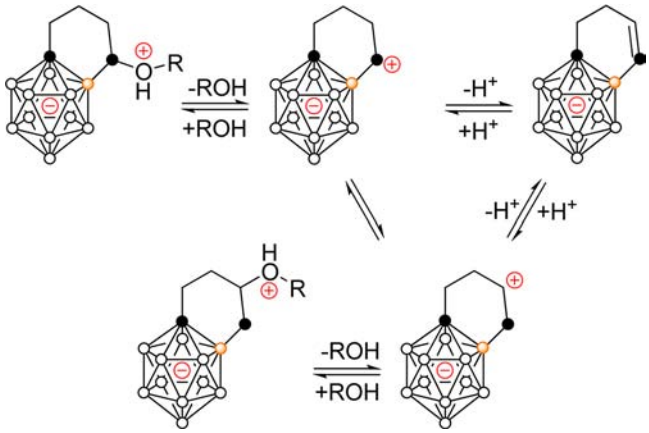
Figure 1. Molecular structure of $[\mu\text{-}1,2\text{-}(CH_2)_3CH(OEt)\text{-}1\text{-}CB_{11}H_{10}]^-$ ($[\mathbf{4a}]^-$) in $[\mathbf{4a}][Me_3NH]$.

about 1:1 after refluxing for 24 h. These results suggest that the isomerization process does not proceed in the absence of H^+.

Reaction of 1 with PPh_3, $^tBuNH_2$, Et_2NH, (4-MeC_6H_4)SNa, and $NaBH_4$. Compound **1** reacted with PPh_3 in toluene to give a zwitterionic compound μ-1,2-$(CH_2)_3CH(PPh_3)$-1-$CB_{11}H_{10}$ (**5a**) in 80% isolated yield.[7] It also reacted with $^tBuNH_2$ or Et_2NH in toluene at room temperature to afford the zwitterionic species μ-1,2-$(CH_2)_3CH(N^tBuH_2)$-1-$CB_{11}H_{10}$ (**6a**) or μ-1,2-$(CH_2)_3CH(NEt_2H)$-1-$CB_{11}H_{10}$ (**7a**) in 90% isolated yields. Reaction of **1** with (4-MeC_6H_4)SNa in refluxing THF gave, after addition of [PPN]Cl (PPN = bis(triphenylphosphoranylidene)ammonium chloride), an ionic salt $[\mu$-1,2-$(CH_2)_3CHS(4\text{-}MeC_6H_4)$-1-$CB_{11}H_{10}][PPN]$ ($[\mathbf{8a}]$-[PPN]) in 80% yield. Treatment of **1** with $NaBH_4$ in refluxing THF afforded, after addition of $[Me_4N]Cl$, $[\mu$-1,2-$(CH_2)_4$-1-$CB_{11}H_{10}][Me_4N]$ ($[\mathbf{9}][Me_4N]$) in 85% isolated yield. The above reactions were summarized in Scheme 3.

Complexes **6a**, **7a**, $[\mathbf{8a}]$[PPN], and $[\mathbf{9}][Me_4N]$ were characterized by various spectroscopic techniques. The substituted cage B(2) atoms were observed as singlets in the ^1H coupled ^{11}B NMR spectra at −9.4 ppm in **6a**, −7.9 ppm in $[\mathbf{8a}]^-$, and −7.2 ppm in $[\mathbf{9}]^-$. The solid-state structures of **6a**, **7a**, and $[\mathbf{9}][Me_4N]$ were further confirmed by single-crystal X-ray analyses, and the corresponding anions are shown in Figures 2, 3, and 4.

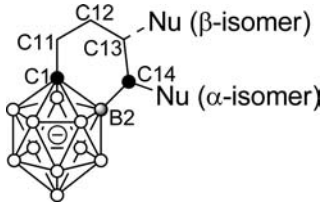
Scheme 2. Acid Promoted Elimination/Isomerization Pathway



Reaction of 1 with Tertiary Amines. Reactions of **1** with tertiary amines were not as facile as those with primary or secondary amines. Almost no reaction took place at room temperature, but it proceeded and completed within 48 h when **1** was heated in refluxing Et_3N. Column chromatographic separation on silica gel gave the zwitterionic compounds μ-1,2-$(CH_2)_3CH(NEt_3)$-1-$CB_{11}H_{10}$ (**10a**) and μ-1,2-$(CH_2)_2CH(NEt_3)CH_2$-1-$CB_{11}H_{10}$ (**10b**) in 75% and 5% yields, respectively. $[\mathbf{3}][Et_3NH]$ was observed in the reaction mixture (about 5%) but was unable to be isolated (Scheme 4).

Complexes **10a** and **10b** were characterized by various spectroscopic techniques as well as HRMS. The characteristic

Table 3. Selected Bond Lengths (Å) in $[\mu$-1,2-$(CH_2)_3CH(Nu)$-1-$CB_{11}H_{10}]^-$ and $[\mu$-1,2-$(CH_2)_2CH(Nu)CH_2$-1-$CB_{11}H_{10}]^-$ Anions



compd (Nu)	C1−B2	C1−C11	C11−C12	C12−C13	C13−C14	C14−B2	C14/C13-Nu	av C−B	av B−B
$[\mathbf{2a}]^-$ (OMe)[a]	1.721(4)	1.527(4)	1.519(5)	1.520(5)	1.527(4)	1.603(4)	1.459(4)	1.714(4)	1.771(5)
$[\mathbf{4a}]^-$ (OEt)	1.725(2)	1.532(2)	1.524(3)	1.527(2)	1.527(3)	1.599(3)	1.464(2)	1.721(3)	1.780(3)
5a (PPh_3)[a]	1.724(4)	1.517(4)	1.532(5)	1.523(5)	1.560(4)	1.625(4)	1.815(3)	1.717(5)	1.773(5)
6a (N^tBuH_2)	1.709(2)	1.526(2)	1.526(3)	1.518(3)	1.534(2)	1.601(2)	1.531(2)	1.715(3)	1.773(3)
7a (NEt_2H)	1.695(3)	1.515(3)	1.540(4)	1.504(5)	1.526(3)	1.601(3)	1.521(3)	1.715(4)	1.770(4)
$[\mathbf{9}]^-$ (H)	1.700(6)	1.507(9)	1.528(8)	1.517(9)	1.527(9)	1.681(10)	/	1.718(7)	1.740(11)
10a (NEt_3)	1.729(5)	1.519(5)	1.527(6)	1.603(7)	1.581(6)	1.679(6)	1.573(5)	1.705(5)	1.758(10)
15a (NC_5H_5)	1.714(3)	1.525(3)	1.520(4)	1.541(3)	1.536(3)	1.612(3)	1.507(2)	1.717(3)	1.774(4)
16a (NC_5H_4Me)	1.716(5)	1.525(5)	1.534(6)	1.522(6)	1.517(5)	1.610(4)	1.502(4)	1.714(6)	1.777(7)
$[\mathbf{2b}]^-$ (OMe)[b]	1.718(3)	1.528(3)	1.520(3)	1.510(4)	1.517(3)	1.594(3)	1.455(3)	1.714(4)	1.774(4)
10b (NEt_3)	1.704(4)	1.519(4)	1.528(4)	1.530(4)	1.517(3)	1.597(4)	1.561(3)	1.712(5)	1.771(5)
11b ($C_{14}H_{18}N_2$)	1.715(11)	1.521(10)	1.509(10)	1.516(11)	1.519(9)	1.597(11)	1.521(11)	1.702(12)	1.767(14)

[a]See ref 7. [b]See ref 10.

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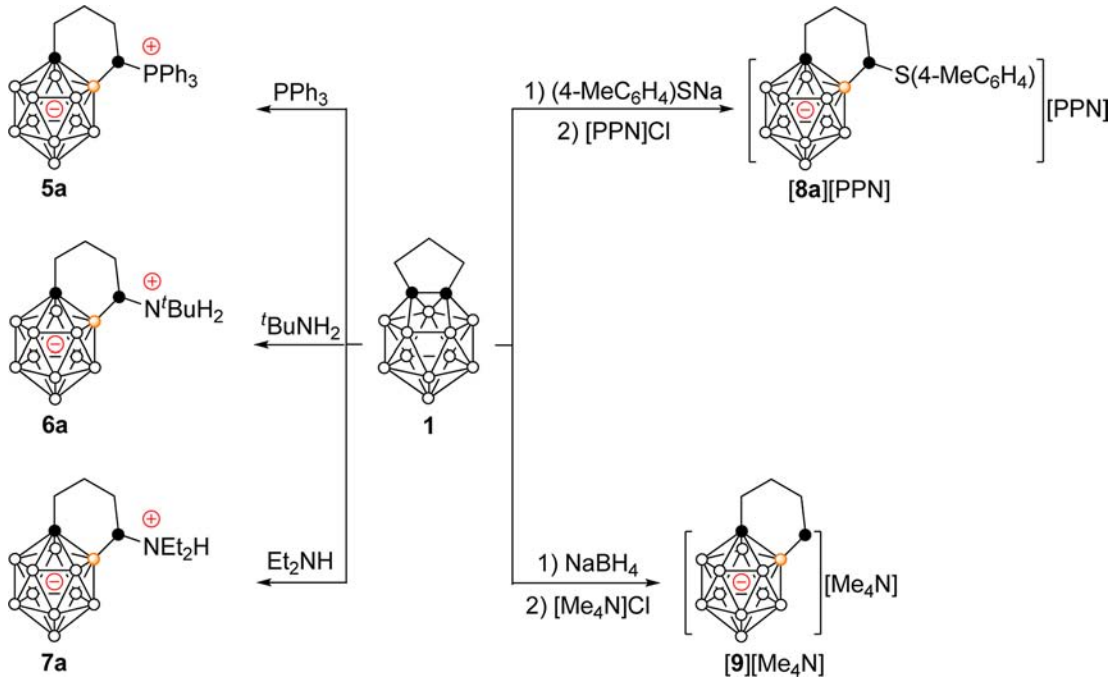
Scheme 3. Reaction of 1 with PPh_3, $^tBuNH_2$, Et_2NH, $(4\text{-}MeC_6H_4)SNa$, and $NaBH_4$



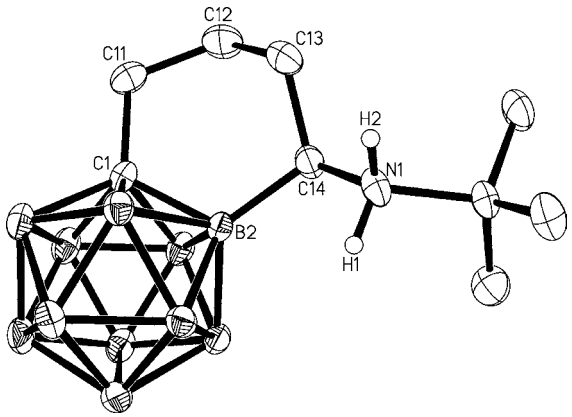


Figure 2. Molecular structure of μ-1,2-$(CH_2)_3CH(N^tBuH_2)$-1-$CB_{11}H_{10}$ (**6a**) (only H atoms on N are shown for clarity).

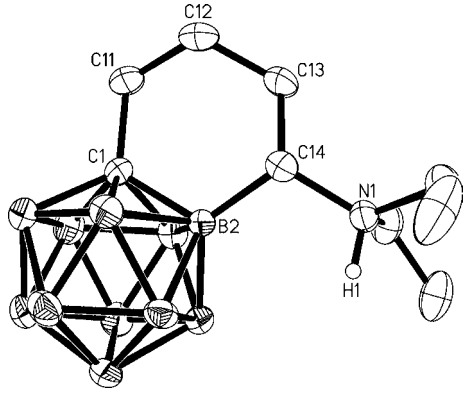


Figure 3. Molecular structure of μ-1,2-$(CH_2)_3CH(NEt_2H)$-1-$CB_{11}H_{10}$ (**7a**) (only H atom on N is shown for clarity).

substituted cage B(2) atom was observed at −8.0 ppm for **10b**, but it was overlapped with other B resonances in **10a** in the ^{11}B NMR spectra. The unique broad peaks of α-*C* at 66.0 ppm in

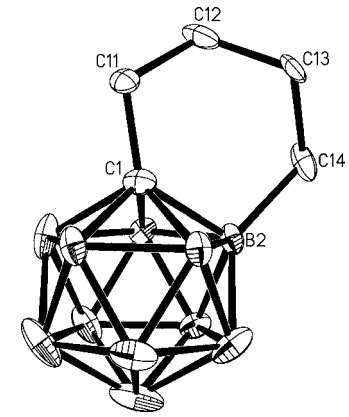


Figure 4. Molecular structure of $[\mu$-1,2-$(CH_2)_4$-1-$CB_{11}H_{10}]^-$ ($[\mathbf{9}]^-$) in $[\mathbf{9}][Me_4N]$.

10a and 15.5 ppm in **10b** in the ^{13}C NMR spectra indicated that the NEt_3 group is bound to different carbon atoms. The molecular structures of **10a** and **10b** were further confirmed by single-crystal X-ray analyses and shown in Figures 5 and 6, which are consistent with the spectroscopic features.

Treatment of **1** with PS (Proton Sponge) afforded μ-1,2-$(CH_2)_2CH[4'\text{-}C_{10}H_5\text{-}1',8'\text{-}(NMe_2)_2H]CH_2$-1-$CB_{11}H_{10}$ (**11b**) in 24% gross yield and [**3**][PSH] in 58% gross yield. Recrystallization from MeCN or MeOH gave **11b** or [**3**][PSH] as colorless crystals, respectively. It was noted that the reaction was not completed even after 28 d and no α-isomer μ-1,2-$(CH_2)_3CH[4'\text{-}C_{10}H_5\text{-}1',8'\text{-}(NMe_2)_2H]$-1-$CB_{11}H_{10}$ was observed. The above result suggests that PS acts as a C-nucleophile[12] rather than N-nucleophile in the reaction.

Complex **11b** has a very poor solubility in d_6-acetone and other common organic solvents. NMR spectra were then taken in d_6-DMSO. Its distortionless enhancement by polarization transfer (DEPT) ^{13}C NMR spectrum indicated 5 CH and 5 tertiary carbon atoms in the aromatic region. The feature of the

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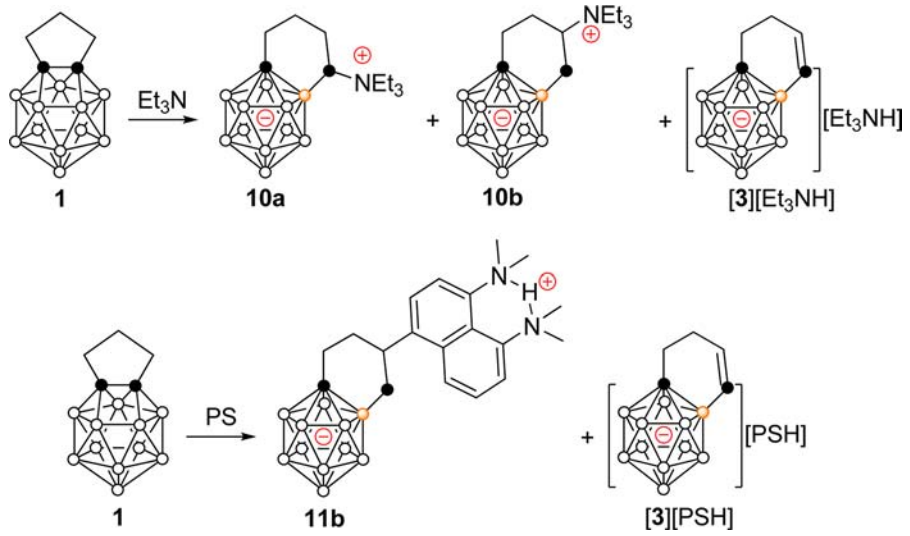
Scheme 4. Reaction of 1 with Et_3N and Proton Sponge (PS)



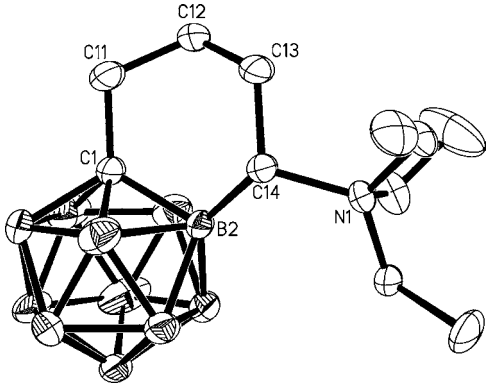


Figure 5. Molecular structure of μ-1,2-$(CH_2)_3CH(NEt_3)$-1-$CB_{11}H_{10}$ (**10a**).

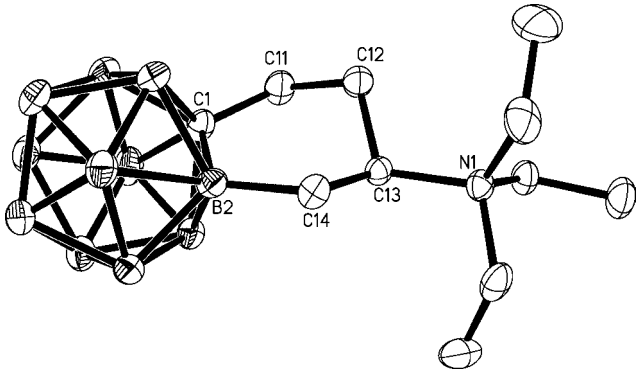


Figure 6. Molecular structure of μ-1,2-$(CH_2)_2CH(NEt_3)CH_2$-1-$CB_{11}H_{10}$ (**10b**).

NMR spectra of [**3**][PSH] in d_6-acetone was in accordance with that of [**3**][Me_3NH]. The molecular structures of both **11b** and [**3**][PSH] were further confirmed by single-crystal X-ray analyses and that of **11b** is shown in Figure 7. The structure of [**3**][PSH] is shown in Figure S1 in the Supporting Information owing to its poor resolution.

The formation of $[\mathbf{3}]^-$, **10a** and **10b** seemed very similar to that of the reaction of **1** with primary alcohol. We initially speculated that they were formed from a similar elimination/addition process via $[\mathbf{3}]^-$ as shown in Scheme 2. On the other hand, we noted that the reaction was performed in a basic media, in which **10a** should be stable. To gain some insight into the reaction mechanism, the following NMR experiments were carried out. Compound **10a** was heated to reflux in acetone, Et_3N/C_6D_6, or pyridine in a closed vessel at 90 °C for 48 h. In all cases, no obvious change was observed in the ^1H NMR spectra. Under the same conditions, **10b** was also stable. These results strongly suggest that **10a** and **10b** are not interchangeable under the reaction conditions, which is significantly different from that observed in the reaction of **1** with alcohols. A different reaction mechanism is anticipated (vide infra).

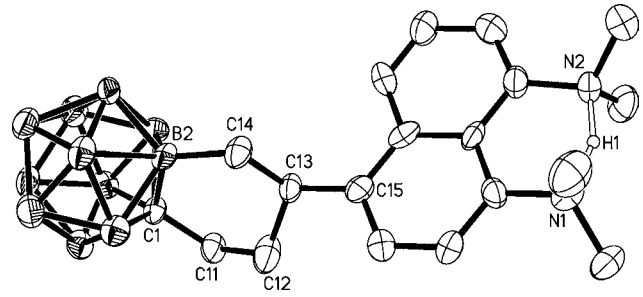


Figure 7. Molecular structure of μ-1,2-$(CH_2)_2CH$[4′-$C_{10}H_5$-1′,8′-$(NMe_2)_2H$]CH_2-1-$CB_{11}H_{10}$ (**11b**) (only the bridging H atom is shown for clarity).

Reaction of 1 with Pyridines. We communicated earlier that **1** reacted with pyridine (Py) at low temperature to generate a zwitterionic salt 11-vertex monocarba-*closo*-undecaborate complex, μ-2,4-$(CH_2)_3CHBH(C_5H_5N)_2$-2-$CB_{10}H_9$ (**12**).[8] Under the same reaction conditions, reaction of **1** with 4-MeC_5H_4N or 4-^{t}BuC_5H_4N afforded a similar zwitterionic salt μ-2,4-$(CH_2)_3CHBH(MeC_5H_4N)_2$-2-$CB_{10}H_9$ (**13**) or μ-2,4-$(CH_2)_3CHBH(^tBuC_5H_4N)_2$-2-$CB_{10}H_9$ (**14**) in 52% or 30% isolated yield (Scheme 5). These three complexes exhibited very similar spectroscopic features in d_6-DMSO. Single crystals of **13** and **14** were grown via vapor diffusion of MeOH into a DMSO solution. X-ray diffraction studies indicate that they bear the same cage (Figures 8 and 9), which is similar to that of **12** and other monocarba-*closo*-undecaborate anions.[13]

The above reactions were sensitive to temperature. Compound **1** reacted very vigorously with pyridine at room

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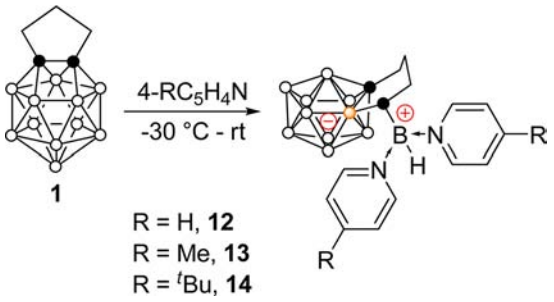
Scheme 5. Reaction of 1 with Pyridines at Low Temperature



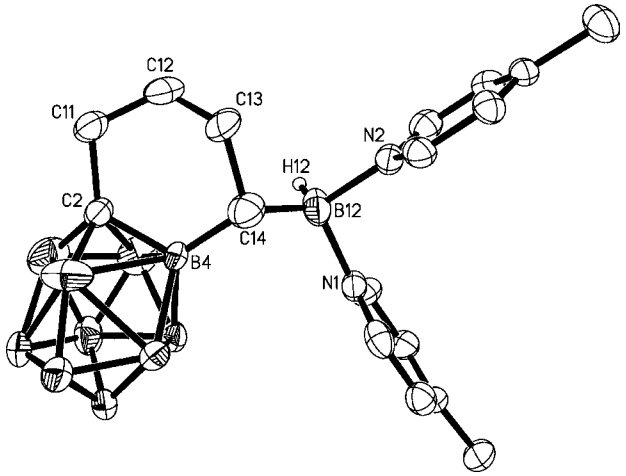


Figure 8. Molecular structure of μ-2,4-$(CH_2)_3$CHBH$(MeC_5H_4N)_2$-2-$CB_{10}H_9$ (**13**) (only exo-BH hydrogen atom is shown for clarity).

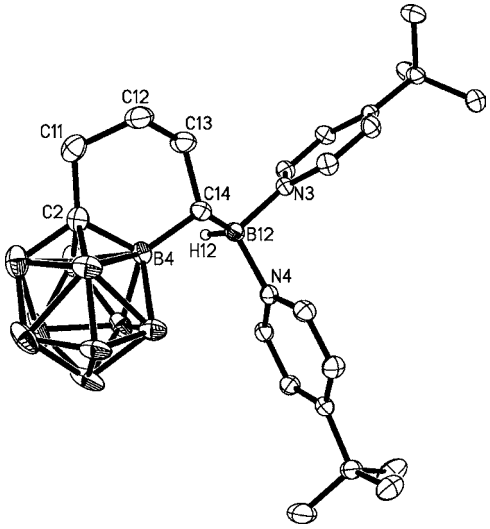


Figure 9. Molecular structure of μ-2,4-$(CH_2)_3$CHBH$(^tBuC_5H_4N)_2$-2-$CB_{10}H_9$ (**14**) (only exo-BH hydrogen atom is shown for clarity).

temperature to give a mixture of products. The NMR spectra of the crude product mixture showed the presence of a small amount of **12** and $[\mathbf{3}]^-$ with other CB_{11}^- anions as major products. Column chromatographic separation, followed by fractional recrystallization, afforded zwitterionic salts μ-1,2-$(CH_2)_3$CH(NC_5H_5)-1-$CB_{11}H_{10}$ (**15a**) and μ-1,2-$(CH_2)_2$CH-$(NC_5H_5)CH_2$-1-$CB_{11}H_{10}$ (**15b**) in 36% and 4% yields, respectively (Scheme 6). The molecular structure of **15a** was further confirmed by single-crystal X-ray analyses and is shown in Figure 10.

Similarly, reactions of **1** with 4-MeC_5H_4N also gave a mixture of products at room temperature as evidenced from the ^{1}H NMR spectrum, from which complex μ-1,2-$(CH_2)_3$CH-(MeC_5H_4N)-1-$CB_{11}H_{10}$ (**16a**) was crystallized out from a CH_2Cl_2 solution and confirmed by single-crystal X-ray analyses (Figure 11).

Characterization of Reaction Intermediates. The above experimental results indicated that one of the cage carbons is extruded from **1**, in which the nucleophile is attached to the extruded carbon atom. To the best of our knowledge, cage carbon extrusion from carborane clusters is very rare. A *closo*-to-*closo* example is the transformation of $[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]^-$ to $[3\text{-}NC\text{-}closo\text{-}B_{11}F_{10}]^{2-}$ via deprotonation, which is limited to highly fluorinated boron clusters.[14] Another example is the conversion of $[7\text{-}R\text{-}\mu\text{-}(9,10\text{-}HR'C)\text{-}7\text{-}nido\text{-}CB_{10}H_{11}]^-$ to $[1\text{-}R\text{-}6\text{-}CH_2R'\text{-}1\text{-}closo\text{-}CB_9H_8]^-$, in which the cage carbon extrusion is suggested to proceed after the removal of one BH vertex.[15] On the other hand, it is well documented that reaction of *o*-carboranes with nucleophiles gives deboration products.[16] Such reaction involves the attack of nucleophiles on the most electron-deficient cage boron that bonded to both cage carbon atoms. Several reaction intermediates, such as 1:1 adducts, μ-9,10,11-BH$[NH{=}P(NMe_2)_3]$-7,8-$C_2B_9H_{11}$[17a] and μ-9,10,11-BH(NHC)-7,8-$C_2B_9H_{11}$ [N-heterocyclic carbenes (NHC)],[17b] as well as 1:2 adducts, 10-$BH(NHC)_2$-7,8-$C_2B_9H_{11}$[18] and 10-$BH(py)_2$-7-Br-7,8-$C_2B_9H_{10}$,[19] have been structurally characterized.

In order to get some insight into the reaction of **13**-vertex carboranes with nucleophiles, we did NMR studies. Mixing **1** and excess Et_2NH in C_6D_6 at −30 °C to room temperature for 10 min gave a stable intermediate that showed a distinct ^{11}B NMR spectrum from that of the product **7a**. This intermediate was stable for a day and then slowly converted to the final product **7a** as evidenced by NMR spectra, which makes the spectroscopical characterization possible.

The ^{1}H−^{13}C HSQC (see Figure S2 in the Supporting Information) and ^{1}H−^{1}H COSY experiments clearly illustrated the formation of a $(CH_2)_3$CH unit, suggesting that a H atom had migrated to one cage carbon. This CH group exhibited a characteristic signal at 1.87 ppm in the ^{1}H NMR spectrum and a peak at 12.7 ppm in the ^{13}C NMR spectrum, indicating that it was not attached to the N atom; that is, the reaction should not be initiated by the attack of a nucleophile on the cage carbon atom. A downfield signal at 39.8 ppm in the ^{11}B NMR spectrum suggested there was a low-coordinate boron atom that might be bound to the N atom (see Figure S3 in the Supporting Information). Similar NMR features were observed in the reaction with $^tBuNH_2$, but the reaction was much faster. After many attempts, it was found that treatment of **1** with 1 equiv of $LiNEt_2$ in THF afforded a species with the same NMR characteristics as those with Et_2NH. Accordingly, intermediate $[\mu\text{-}\eta\text{:}\eta\text{:}\eta\text{-}7,8,10\text{-}(CH_2)_3CHB(NEt_2)\text{-}7\text{-}CB_{10}H_{10}][PPN]$ ($[\mathbf{7i}]$-[PPN]) was isolated in 90% yield from an equimolar reaction of **1** and $LiNEt_2$ in THF, followed by cation exchange with [PPN]Cl (Scheme 7). It has the same NMR features as described before. Its molecular structure was further confirmed by single-crystal X-ray analyses and is shown in Figure 12. The anion $[\mathbf{7i}]^-$ is composed of a *nido*-CB_{10} cage with a $(CH_2)_3CHB(NEt_2)$ linkage that sits above the open five-membered CB_4 face. The pseudo three-coordinate B is in a trigonal planar geometry with a sum of bond angles around the

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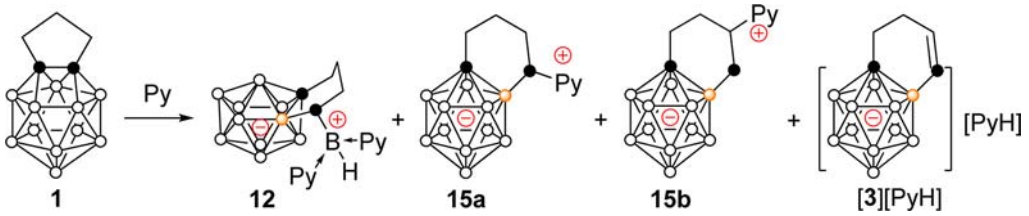
Scheme 6. Reaction of 1 with Pyridine at Room Temperature



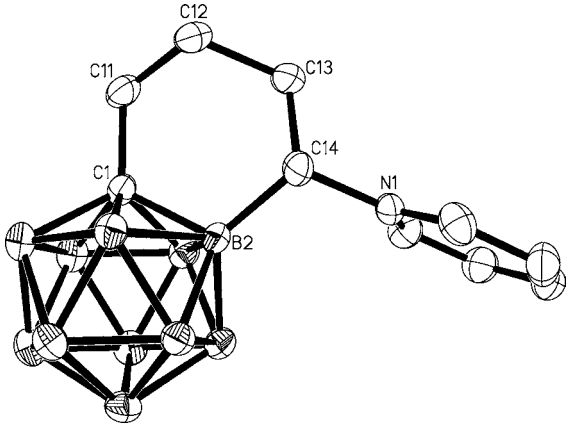


Figure 10. Molecular structure of μ-1,2-$(CH_2)_3CH(NC_5H_5)$-1-$CB_{11}H_{10}$ (**15a**).

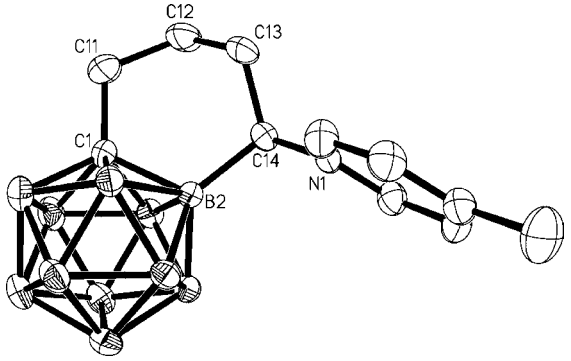


Figure 11. Molecular structure of μ-1,2-$(CH_2)_3CH(MeC_5H_4N)$-1-$CB_{11}H_{10}$ (**16a**).

boron atom of 359.8(8) °. This result is consistent with the downfield shifted ^{11}B NMR chemical shift (38.8 ppm) and the very short B–N bond length of 1.414(11) Å.[20]

We noted that the NMR and structural features of [**7i**][PPN] were very similar to those of [μ–η:η:η-7,8,10-$(CH_2)_3CHB(OMe)$-7-$CB_{10}H_{10}]^-$ ([**2i**]$^-$), which was prepared from the reaction of **1** with MeOH in the presence of PS in 95% yield (Scheme 7).[8]

Reaction Pathways. The aforementioned two structurally characterized intermediates were stable in CD_2Cl_2 solutions for several weeks at room temperature. However, addition of concentrated HCl led to the immediate formation of the corresponding CB_{11}^- species. Treatment of a CH_2Cl_2 solution of [**7i**]Li, prepared directly from **1** and an equimolar amount of $LiNEt_2$, with concentrated HCl at 0 °C gave **7a** in 80% isolated yield. In a similar manner, addition of concentrated HCl to a CD_2Cl_2 solution of [**2i**][PSH] afforded a mixture of [**2a**]$^-$ and [**2b**]$^-$ as evidenced by the ^{1}H NMR spectrum (Scheme 7). It is clear that a proton can promote the transformation of [**2i**]$^-$ or [**7i**]$^-$ to the corresponding CB_{11}^- anions. This may be ascribed to the fact that the protonation of hetero atoms (O or N) can weaken B═X (X = O, N) interactions and facilitate the migration of a Et_2N or MeO group from B to C atom in the intermediates.

As mentioned in the previous section, experimental results showed that **10a** and **10b** were not interconvertible. We wondered if they were directly produced from the intermediate. In this regard, we reexamined the reaction of **1** with Et_2NH in C_6D_6 at 90 °C. The ^{11}B NMR spectrum showed the initial formation of the intermediate [**7i**]$^-$ that disappeared upon heating. After removal of C_6D_6 and Et_2NH, the ^{1}H and ^{13}C NMR spectra were recorded in d_6-acetone, clearly showing the formation of **7a** and [**3**]$^-$. The reaction was then scaled up using toluene as the solvent. Column chromatographic separation on silica gel gave **7a** and μ-1,2-$(CH_2)_2CH(NEt_2H)$-CH_2-1-$CB_{11}H_{10}$ (**7b**) in 80% and 3.7% isolated yields, respectively (Scheme 8). Under the same reaction condition, **7a** was stable and did not convert to **7b**.

These experimental results clearly indicated that CB_{11}^- isomers could be directly generated from the intermediated [**7i**]$^-$ upon heating. The reaction of [**7i**]$^-$ with pyridine was also examined by NMR, which did not show any characteristic peaks of **12** except for those of CB_{11}^- anions. It was suggested that the formation of **12** may be via a different intermediate, which is not clear at this stage.

On the basis of the above mechanistic studies, the reaction pathways for the formation of CB_{11}^- anions are proposed in Scheme 9. Nucleophilic attack on the most electron-deficient seven-coordinate cage boron atom that is bound to both cage carbon atoms in 13-vertex carborane gives the intermediate **C**. Acceptance of 2e$^-$ from the nucleophile and H-migration from the cage B to cage C atom results in the cleavage of C–C/B and B–B bonds, leading to the formation of intermediate **D**. The B═X p_π–p_π interactions between the B and heteroatom X can enhance the stability of **D**, allowing the isolation and structural characterization of [**2i**]$^-$ and [**7i**]$^-$. 1,2-Migration of the Nu group in **D** induces the cleavage of the CH-B(cage) bond and the formation of B–B bonds affording the α-substituted CB_{11}^- anion **E**. In the basic media, the nucleophile may attack the β-H in **D**, leading to the formation of the C═C double bond and the cleavage of CH-B (cage)/formation of B–B bonds, which yields the alkenyl-substituted CB_{11}^- anion **F**. Alternatively, the nucleophile may attack β-C, resulting in the 1,2-migration of an H atom and the cleavage of the CH-B(cage)/formation of B–B bonds, which produces the β-substituted CB_{11}^- anion **G**.

■ CONCLUSION

13-Vertex carborane can react with many kinds of nucleophiles including very weak ones to give generally the cage carbon extrusion products CB_{11}^- anions via a common intermediate, [μ–η:η:η-7,8,10-$(CH_2)_3CHB(Nu)$-7-$CB_{10}H_{10}]^-$. The reaction

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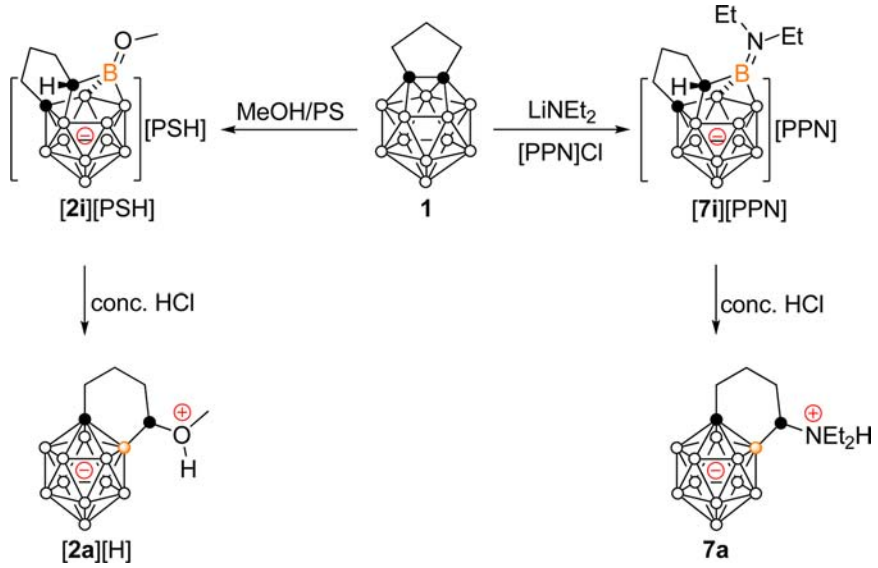
Scheme 7. Preparation of Reaction Intermediates



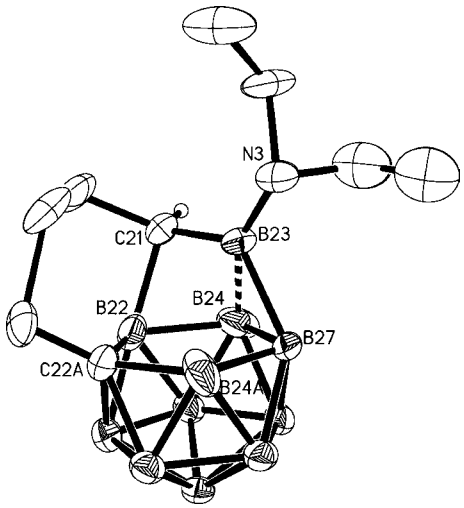


Figure 12. Molecular structure of $[\mu\text{–}\eta\text{:}\eta\text{:}\eta\text{-}7,8,10\text{-}(CH_2)_3CHB(NEt_2)\text{-}7\text{-}CB_{10}H_{10}]^-$ ($[\mathbf{7i}]^-$) in [**7i**][PPN] (only CH hydrogen is shown for clarity).

rates depend upon the nature and bulkiness of nucleophiles. In case of pyridines, however, the reaction temperature can alter the reaction pathways, leading to the formation of CB_{10}^- anions at low temperatures and of CB_{11}^- anions at high temperatures. These results are significantly different from those reported for the 12-vertex carboranes, which enhances our understanding of supercarborane chemistry.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, all experiments were performed under an atmosphere of dry dinitrogen or argon with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques or in a glovebox. CH_2Cl_2 was refluxed over CaH_2 for several days and distilled immediately prior to use. Other organic solvents were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. μ-1,2-$(CH_2)_3$-1,2-$C_2B_{10}H_{10}$ (**1**),[4c] [**2a**][Me_3NH],[7] **5a**,[7] [**2i**][PSH][8], and **12**[8] were prepared according to the respective literature methods. All other chemicals were purchased from either Aldrich or Acros Chemical Company and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 1600 Fourier transform spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 spectrometer or a Bruker DPX 400Q spectrometer at 400 and 100 MHz, respectively. The ^{11}B NMR spectra were recorded on a Bruker DPX 300 spectrometer at 96 MHz or a Varian Inova 400 spectrometer, a Bruker DPX 400 spectrometer, or a Bruker DPX 400Q spectrometer at 128 MHz. All chemical shifts were reported in δ units with references to the residual protons or carbons of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3{\cdot}OEt_2$ (0.0 ppm) for boron chemical shifts. Mass spectra were recorded on a Thermo Finnigan MAT 95 XL spectrometer. Elemental analyses were performed by MEDAC Ltd. (Brunel University, Middlesex, U.K.) or Shanghai Institute of Organic Chemistry, CAS, Shanghai, China.

Reaction of 1 with MeOH. Method A: Compound **1** (196 mg, 1.00 mmol) was dissolved in MeOH (10 mL), and the solution was stirred at room temperature for 12 h. After addition of [Me_3NH]Cl (191 mg, 2.00 mmol), the mixture was further stirred for 1 h. MeOH was then pumped off, and the residue was thoroughly washed with water to give a white solid. Recrystallization from acetone gave [μ-1,2-$(CH_2)_3$CH(OMe)-1-$CB_{11}H_{10}$][Me_3NH] ([**2a**][Me_3NH]) as colorless crystals (215 mg, 0.75 mmol, 75%). **Method B**: Compound **1** (196 mg, 1.00 mmol) was dissolved in MeOH (10 mL) in a sealed tube, and the solution was heated at 70 °C for 24 h. After the addition of [Me_3NH]Cl (191 mg, 2.00 mmol), the mixture was further stirred for 1 h. Removal of the solvent gave a white solid that was washed with cold water to remove the excess amount of [Me_3NH]Cl. The ^1H NMR spectrum of the crude product mixture showed a molar ratio of [**2a**][Me_3NH]/[μ-1,2-$(CH_2)_2$CH(OMe)CH_2-1-$CB_{11}H_{10}$][Me_3NH] ([**2b**][Me_3NH]) of about 1:1, together with the observation of a small amount (<5%) of [μ-1,2-$(CH_2)_2$CH=CH-1-$CB_{11}H_{10}$][Me_3NH] ([**3**][Me_3NH]). Thoroughly washing with water followed by recrystallization from acetone afforded [**2b**][Me_3NH] as colorless crystals (100 mg, 0.35 mmol, 35%). [**2a**][Me_3NH]: ^1H NMR (400 MHz, acetone-d_6) δ 3.34 (s, 3H, OCH_3), 3.20 (s, 9H, NCH_3), 3.11 (t, J = 6.9 Hz, 1H, α-C*H*), 1.81 (m, 2H, δ-CH_2), 1.68 (m, 1H, β-CH_2), 1.46 (m, 1H, γ-CH_2), 1.39 (m, 1H, β-CH_2), 1.21 (m, 1H, γ-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 74.2 (br, α-CH), 69.2 (cage *C*), 57.7 (OCH_3), 46.2 (NCH_3), 36.7 (δ-CH_2), 29.6 (β-CH_2), 23.2 (γ-CH_2). ^{11}B NMR (96 MHz, acetone-d_6) δ −7.7 (s, 1B), −9.3 (d, J_{BH} = 145 Hz, 1B), −12.3 (d, J_{BH} = 113 Hz, 6B), −13.5 (overlapping, 1B), −13.9 (overlapping, 2B). IR (KBr) ν_{max} (cm^{-1}) 2539 (vs, BH). These data are consistent with those reported.[7] [**2b**][Me_3NH]: ^1H NMR (400 MHz, acetone-d_6) δ 3.21 (m, 1H, β-C*H*), 3.185 (s, 9H, NCH_3), 3.177 (s, 3H, OCH_3), 2.01 (m, 1H, δ-CH_2), 1.92 (m, 1H, δ-CH_2), 1.55 (m, 1H, γ-CH_2), 1.48 (m, 1H, α-CH_2), 1.28 (m, 1H, γ-CH_2), 0.74 (m,

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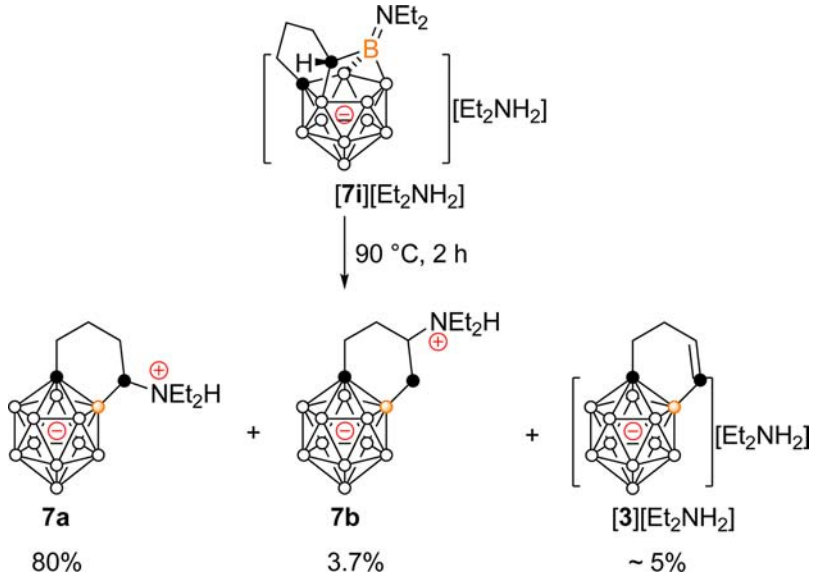
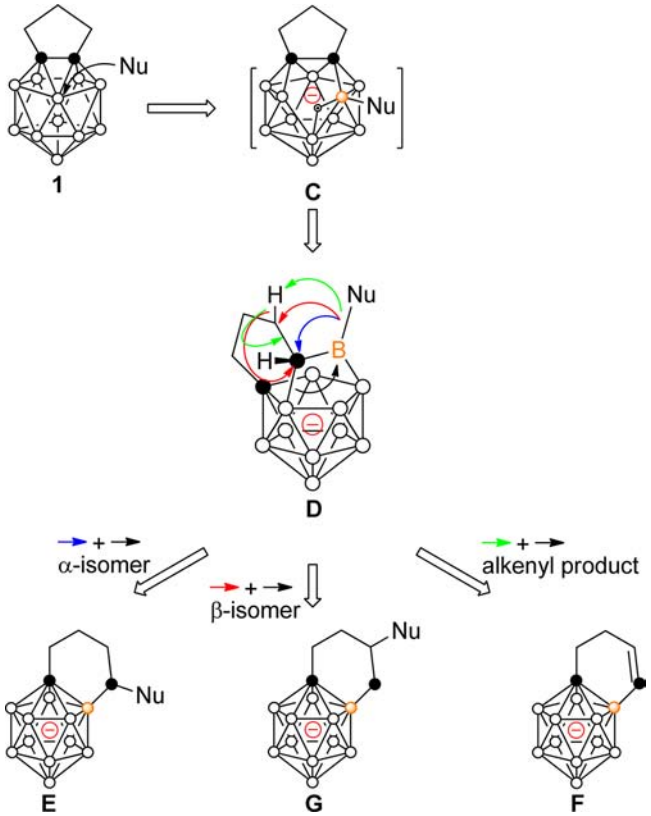
Scheme 8. Thermolysis of [7i][Et_2NH_2]



Scheme 9. Proposed Reaction Pathways for the Formation of CB_{11}^- Anions



1H, α-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 79.9 (β-CH), 67.7 (cage *C*), 54.7 (OCH_3), 46.0 (NCH_3), 36.1 (δ-CH_2), 31.9 (γ-CH_2), 21.4 (br, α-CH_2). ^{11}B NMR (96 MHz, 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) ν_{max} (cm^{-1}) 2522 (vs, BH). These data are consistent with those reported.[10]

Reaction of 1 with EtOH. Compound **1** (196 mg, 1.00 mmol) was dissolved in EtOH (10 mL) in a sealed tube, and the solution was heated at 70 °C for 24 h. After the addition of [Me_3NH]Cl (191 mg, 2.00 mmol), the mixture was further stirred for 1 h. Removal of the volatile materials gave a white solid that was washed with cold water to remove an excess amount of [Me_3NH]Cl. The ^1H NMR spectrum of the crude product mixture showed a molar ratio of [μ-1,2-$(CH_2)_3$CH(OEt)-1-$CB_{11}H_{10}$][Me_3NH] ([**4a**][Me_3NH])/[**3**]-[Me_3NH] of ca. 1:0.5, together with a very small amount (<5%) of [μ-1,2-$(CH_2)_2$CH(OEt)CH_2-1-$CB_{11}H_{10}$][Me_3NH] ([**4b**][Me_3NH]). They were inseparable and characterized by COSY, HSQC, and HMBC NMR techniques. Fractional recrystallization from acetone afforded few crystals of [**4a**][Me_3NH]. [**3**][Me_3NH]: ^1H NMR (400 MHz, acetone-d_6) δ 5.85 (m, 2H, *CH*═*CH*), 3.13 (s, 9H, NCH_3), 1.98 (dt, J_1 = 2.9 Hz, J_2 = 6.4 Hz, 2H, γ-CH_2), 1.87 (t, *J* = 6.7 Hz, 2H, δ-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 132.7 (br, α-CH), 131.8 (β-CH), 66.7 (cage *C*), 45.9 (NCH_3), 33.0 (δ-CH_2), 26.0 (γ-CH_2). [**4a**][Me_3NH]: ^1H NMR (400 MHz, acetone-d_6) δ 3.69 (dq, J_1 = 9.5 Hz, J_2 = 7.0 Hz, 1H, OCH_2), 3.44 (dq, J_1 = 9.5 Hz, J_2 = 7.0 Hz, 1H, OCH_2), 3.19 (dd, J_1 = 6.1 Hz, J_2 = 9.1 Hz, 1H, α-*CH*), 3.13 (s, 9H, NCH_3), 1.77 (m, 2H, δ-CH_2), 1.68 (m, 1H, β-CH_2), 1.43 (m, 1H, γ-CH_2), 1.29 (m, 1H, β-CH_2), 1.17 (m, 1H, γ-CH_2), 1.07 (t, *J* = 7.0 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 71.5 (br, α-CH_2), 69.2 (cage *C*), 64.7 (OCH_2), 45.9 (NCH_3), 36.1 (δ-CH_2), 29.9 (β-CH_2), 23.1 (γ-CH_2), 15.9 (CH_2CH_3). [**4b**][Me_3NH]: ^1H NMR (400 MHz, acetone-d_6) δ 3.41 (1H, OCH_2), 3.31 (1H, OCH_2), 3.27 (1H, β-*CH*), 3.13 (9H, NCH_3), 1.97 (1H, δ-CH_2), 1.88 (1H, δ-CH_2), 1.52 (1H, γ-CH_2), 1.41 (1H, α-CH_2), 1.24 (1H, γ-CH_2), 1.05 (t, *J* = 7.0 Hz, 3H, CH_2CH_3), 0.74 (1H, α-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 77.7 (β-CH), 67.6 (cage *C*), 62.3 (OCH_2), 45.9 (NCH_3), 35.8 (δ-CH_2), 32.0 (γ-CH_2), 22.2 (br, α-CH_2), 15.9 (CH_2CH_3).

Preparation of μ-1,2-$(CH_2)_3$CH(N^tBuH_2)-1-$CB_{11}H_{10}$ (6a). To a toluene (10 mL) solution of **1** (98 mg, 0.50 mmol) was added $^tBuNH_2$ (1.0 mL, 696 mg, 9.5 mmol) at 0 °C, and the mixture was stirred overnight. Removal of the volatile materials gave a pale yellow solid. Recrystallization from CH_2Cl_2 afforded **6a** as colorless crystals (121 mg, 0.45 mmol, 90%). ^1H NMR (400 MHz, acetone-d_6) δ 3.36 (t, *J* = 7.3 Hz, 1H, α-*CH*), 2.01 (m, 1H, β-CH_2), 1.85 (m, 2H, δ-CH_2), 1.63 (m, 1H, β-CH_2), 1.57 (s, 9H, CCH_3), 1.51 (m, 1H, γ-CH_2), 1.39 (m, 1H, γ-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 68.9 (cage *C*), 60.7 (CCH_3), 44.5 (br, α-CH), 35.1 (δ-CH_2), 29.3 (β-CH_2), 26.4 (CCH_3), 23.2 (γ-CH_2). ^{11}B NMR (96 MHz, acetone-d_6) δ −8.9 (d, J_{BH} = 137 Hz, 1B), −9.4 (s, 1B), −11.6 (d, J_{BH} = 159 Hz, 5B), −13.8 (d, J_{BH} = 170 Hz, 4B). IR (KBr) ν_{max} (cm^{-1}) 2546 (vs, BH). HRMS (EI) calcd for $C_9H_{28}{}^{11}B_9{}^{10}B_2N$ $[M]^+$ *m*/*z* 269.3312, found *m*/*z* 269.3312.

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Preparation of μ-1,2-$(CH_2)_3CH(NEt_2H)$-1-$CB_{11}H_{10}$ (7a). To a toluene (10 mL) solution of **1** (98 mg, 0.50 mmol) was added Et_2NH (1.0 mL, 707 mg, 9.7 mmol) at 0 °C, and the mixture was stirred overnight. Removal of the volatile materials gave a pale yellow solid. Recrystallization from CH_2Cl_2 afforded **7a** as colorless crystals (121 mg, 0.45 mmol, 90%). ^{1}H NMR (400 MHz, acetone-d_6) δ 3.78 (m, 2H, NCH_2), 3.52 (m, 1H, NCH_2), 3.40 (m, 2H, NCH_2 + α-CH), 2.00 (m, 1H, β-CH_2), 1.98 (m, 1H, δ-CH_2), 1.79 (m, 1H, δ-CH_2), 1.68 (m, 1H, γ-CH_2), 1.53 (m, 1H, β-CH_2), 1.43 (t, J = 7.3 Hz, 6H, CH_3), 1.38 (m, 1H, γ-CH_2). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ 69.1 (cage C), 54.4 (br, α-CH), 47.1 (NCH_2), 35.5 (δ-CH_2), 24.7 (β-CH_2), 24.5 (γ-CH_2), 11.2, 10.0 (CH_3). ^{11}B NMR (96 MHz, acetone-d_6) δ −8.5 (d, J_{BH} = 153 Hz, 1B), −10.8 (d, J_{BH} = 159 Hz, 2B), −11.8 (d, J_{BH} = 146 Hz, 4B), −13.0 (d, J_{BH} = 124 Hz, 4B). IR (KBr) ν_{max} (cm^{-1}) 2549 (vs, BH). HRMS (EI) calcd for $C_9H_{28}{}^{11}B_9{}^{10}B_2N$ [M]$^+$ m/z 269.3312, found m/z 269.3310.

Preparation of [μ-1,2-$(CH_2)_3CHS(4\text{-}MeC_6H_4)$-1-$CB_{11}H_{10}$][PPN] ([8a][PPN]). To a THF (10 mL) solution of **1** (98 mg, 0.50 mmol) was added (4-MeC_6H_4)SNa (76 mg, 0.52 mmol). The reaction vessel was closed and heated at 70 °C for 48 h. [PPN]Cl (287 mg, 0.50 mmol) was added, and the mixture was further stirred for 6 h. After filtration and removal of THF, the residue was recrystallized from MeOH to give [**8a**][PPN] as a white solid (343 mg, 0.40 mmol, 80%). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.70 (m, 18H, PPN), 7.56 (m, 12H, PPN), 7.19 (d, J = 8.1 Hz, 2H, C_6H_4), 7.03 (d, J = 8.0 Hz, 2H, C_6H_4), 3.12 (t, J = 5.8 Hz, 1H, α-CH), 2.23 (s, 3H, CH_3), 1.86 (m, 2H, δ-CH_2), 1.71 (m, 1H, β-CH_2), 1.55 (m, 1H, γ-CH_2), 1.38 (m, 1H, β-CH_2), 1.20 (m, 1H, γ-CH_2). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 137.0, 134.9 (C_6H_4), 134.4, 133.0, 130.3 (PPN), 129.9 (C_6H_4), 128.0 (PPN), 68.2 (cage C), 36.5 (δ-CH_2), 31.7 (br, α-CH_2), 29.5 (β-CH_2), 23.5 (γ-CH_2), 20.9 (CH_3). ^{11}B NMR (128 MHz, acetone-d_6) δ −7.9 (s, 1B), −9.7 (d, J_{BH} = 142 Hz, 2B), −12.1 (d, J_{BH} = 129 Hz, 6B), −14.4 (d, J_{BH} = 202 Hz, 2B). IR (KBr) ν_{max} (cm^{-1}) 2532 (vs, BH). Anal. Calcd for $C_{48}H_{54}B_{11}NP_2S$ (M): C, 67.20; H, 6.34; N, 1.63. Found: C, 67.21; H, 6.32; N, 1.52.

Preparation of [μ-1,2-$(CH_2)_4$-1-$CB_{11}H_{10}$][NMe_4] ([9][NMe_4]). To a THF (10 mL) solution of **1** (98 mg, 0.50 mmol) was added $NaBH_4$ (38 mg, 1.0 mmol). The reaction vessel was closed and heated at 70 °C overnight. After filtration, to the clear solution was added [NMe_4]Cl (110 mg, 1.0 mmol). Removal of the solvent gave a residue that was washed with water and recrystallization from acetone to give [**9**][NMe_4] as colorless crystals (115 mg, 0.42 mmol, 85%). ^{1}H NMR (400 MHz, acetone-d_6) δ 3.41 (s, 12H, CH_3), 1.83 (t, J = 6.2 Hz, 2H, δ-CH_2), 1.35 (br, 2H, β-CH_2), 1.29 (m, 2H, γ-CH_2), 0.89 (br, 2H, α-CH_2). ^{13}C{^{1}H} NMR (128 MHz, acetone-d_6) δ 67.9 (cage C), 55.9 (CH_3), 36.5 (δ-CH_2), 26.0 (γ-CH_2), 22.8 (β-CH_2), 14.2 (br, α-CH_2). ^{11}B NMR (96 MHz, acetone-d_6) δ −7.2 (s, 1B), −9.7 (d, J_{BH} = 177 Hz, 1B), −11.6 (d, J_{BH} = 140 Hz, 4B), −12.9 (d, J_{BH} = 135 Hz, 4B), −15.9 (d, J_{BH} = 137 Hz, 1B). IR (KBr) ν_{max} (cm^{-1}) 2512 (vs, BH). Anal. Calcd for $C_9H_{30}B_{11}N$ [M]: C, 39.85; H, 11.15; N, 5.16. Found: C, 40.09; H, 11.32; N. 4.93.

Reaction of 1 with Et_3N. A Et_3N (10 mL) solution of **1** (196 mg, 1.00 mmol) was heated at 90 °C in a sealed vessel for 48 h to give a pale yellow suspension. Removal of Et_3N gave a solid. Column chromatographic separation (SiO_2, 300−400 mesh, CH_2Cl_2), followed by recrystallization from CH_2Cl_2 afforded μ-1,2-$(CH_2)_3CH(NEt_3)$-1-$CB_{11}H_{10}$ (**10a**) (223 mg, 0.75 mmol, 75%) and μ-1,2-$(CH_2)_2CH(NEt_3)CH_2$-1-$CB_{11}H_{10}$ (**10b**) (15 mg, 0.05 mmol, 5%) as colorless crystals. **10a**: ^{1}H NMR (400 MHz, acetone-d_6) δ 3.89 (m, 3H, NCH_2), 3.74 (m, 3H, NCH_2), 3.54 (d, J = 10.5 Hz, 1H, α-CH), 2.17 (br, 1H, β-CH_2), 2.00 (m, 1H, δ-CH_2), 1.81 (m, 1H, δ-CH_2), 1.72 (m, 1H, γ-CH_2), 1.63 (m, 1H, β-CH_2), 1.44 (m, 9H, CH_3), 1.38 (m, 1H, γ-CH_2). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 69.4 (cage C), 66.0 (α-CH), 54.1 (NCH_2), 36.3 (δ-CH_2), 25.5 (γ-CH_2), 24.5 (β-CH_2), 10.1 (CH_3). ^{11}B NMR (96 MHz, acetone-d_6) δ −8.1 (d, J_{BH} = 152 Hz, 1B), −10.0 (d, J_{BH} = 195 Hz, 1B), −11.0 (d, J_{BH} = 141 Hz, 2B), −12.0 (d, J_{BH} = 141 Hz, 6B), −13.8 (d, J_{BH} = 163 Hz, 1B). IR (KBr) ν_{max} (cm^{-1}) 2544, 2521 (vs, BH). HRMS (EI) calcd for $C_{11}H_{32}{}^{11}B_9{}^{10}B_2N$ [M]$^+$ m/z 297.3626, found m/z 297.3617. **10b**: ^{1}H NMR (400 MHz, acetone-d_6) δ 3.54 (m, 7H, NCH_2 + β-CH), 2.19 (m, 1H, δ-CH_2), 2.07 (m, 1H, γ-CH_2), 2.03 (m, 1H, δ-CH_2), 1.69 (m, 1H, γ-CH_2), 1.50 (m, 1H, α-CH_2), 1.41 (m, 9H, CH_3), 1.37 (m, 1H, α-CH_2). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 72.7 (β-CH), 66.3 (cage C), 53.1 (NCH_2), 36.8 (δ-CH_2), 27.0 (γ-CH_2), 15.5 (α-CH_2), 9.5 (CH_3). ^{11}B NMR (96 MHz, acetone-d_6) δ −8.0 (s, 1B), −9.3 (d, J_{BH} = 140 Hz, 1B), −11.5 (d, J_{BH} = 127 Hz, 5B), −12.7 (d, J_{BH} = 119 Hz, 2B), −13.8 (d, J_{BH} = 94 Hz, 1B), −14.9 (d, J_{BH} = 129 Hz, 1B). IR (KBr) ν_{max} (cm^{-1}) 2537 (vs, BH). HRMS (EI) calcd for $C_{11}H_{32}{}^{11}B_9{}^{10}B_2N$ [M]$^+$ m/z 297.3626, found m/z 297.3620.

Reaction of 1 with PS. To a THF (10 mL) solution of **1** (196 mg, 1.00 mmol) was added PS (1.072 g, 5.00 mmol), and the mixture was heated at 90 °C in a sealed vessel for 28 d to give a pale yellow suspension. After filtration, the pale yellow solid was thoroughly washed with CH_2Cl_2 to give a crude product μ-1,2-$(CH_2)_2CH[4'\text{-}C_{10}H_5\text{-}1',8'\text{-}(NMe_2)_2]CH_2$-1-$CB_{11}H_{10}$ (**11b**) (100 mg, 0.24 mmol, 24%). Recrystallization from MeCN afforded **11b** as colorless crystals (50 mg, 0.12 mmol, 12%). Removal of the solvent from the filtrate and thoroughly washing with Et_2O gave a crude product [μ-1,2-$(CH_2)_2CH{=}CH$-1-$CB_{11}H_{10}$][PSH] ([**3**][PSH]) as a pale yellow solid (240 mg, 0.58 mmol, 58%). Recrystallization from CH_2Cl_2 afforded [**3**][PSH] as colorless crystals (220 mg, 0.54 mmol, 54%). [**3**][PSH]: ^{1}H NMR (400 MHz, acetone-d_6) δ 8.12 (m, 4H, $C_{10}H_6$), 7.77 (t, J = 7.9 Hz, 2H, $C_{10}H_6$), 5.90 (brm, 2H, CH=CH), 3.34 (d, J = 2.6 Hz, 12H, NCH_3), 2.01 (m, 2H, δ-CH_2), 1.92 (t, J = 6.6 Hz, γ-CH_2). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 145.3, 136.2 ($C_{10}H_6$), 133.2 (br, α-CH), 131.8 (β-CH), 130.1, 127.9, 122.5, 120.0 ($C_{10}H_6$), 66.9 (cage C), 46.6 (NCH_3), 33.4 (δ-CH_2), 26.4 (γ-CH_2). ^{11}B NMR (96 MHz, acetone-d_6) δ −9.1 (d, J_{BH} = 168 Hz, 1B), −10.9 (d, J_{BH} = 146 Hz, 3B), −12.2 (d, J_{BH} = 121 Hz, 4B), −13.6 (d, J_{BH} = 133 Hz, 3B). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.04 (d, J = 8.2 Hz, 2H, $C_{10}H_6$), 7.80 (d, J = 7.4 Hz, 2H, $C_{10}H_6$), 7.73 (t, J = 7.9 Hz, 2H, $C_{10}H_6$), 5.99 (br, 1H, β-CH), 5.93 (d, J = 12.7 Hz, 1H, α-CH), 3.18 (d, J = 2.7 Hz, 12H, NCH_3), 2.05 (m, 2H, δ-CH_2), 1.96 (t, J = 6.6 Hz, γ-CH_2). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ 144.0, 136.1 ($C_{10}H_6$), 133.1 (β-CH), 131.9 (br, α-CH), 130.4, 127.8, 121.8, 119.1 ($C_{10}H_6$), 67.7 (cage C), 47.1 (NCH_3), 33.0 (δ-CH_2), 26.3 (γ-CH_2). ^{11}B NMR (96 MHz, CD_2Cl_2) δ −10.3 (d, J_{BH} = 132 Hz, 1B), −11.5 (d, J_{BH} = 150 Hz, 2B), −12.8 (d, J_{BH} = 167 Hz, 2B), −13.5 (d, J_{BH} = 130 Hz, 2B), −14.6 (d, J_{BH} = 129 Hz, 3B). IR (KBr) ν_{max} (cm^{-1}) 2534, 2516 (vs, BH). Anal. Calcd for $C_{19}H_{35}B_{11}N_2$ [M]: C, 55.60; H, 8.60; N, 6.83. Found: C, 55.13; H, 8.30; N, 7.33. **11b**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 (d, J = 8.7 Hz, 1H, $C_{10}H_5$), 8.07 (d, J = 7.5 Hz, 1H, $C_{10}H_5$), 8.00 (d, J = 8.1 Hz, 1H, $C_{10}H_5$), 7.80 (t, J = 8.1 Hz, 1H, $C_{10}H_5$), 7.58 (d, J = 8.0 Hz, 1H, $C_{10}H_5$), 3.34 (m, 1H, β-CH), 3.14 (d, J = 2.2 Hz, 3H, CH_3), 3.12 (m, 6H, CH_3), 3.10 (d, J = 1.7 Hz, 3H, CH_3), 2.10 (m, 2H, δ-CH_2), 1.68 (m, 1H, γ-CH_2), 1.53 (m, 1H, γ-CH_2), 1.28 (m, 1H, α-CH_2), 1.07 (m, 1H, α-CH_2). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 147.4, 145.6, 141.9, 132.3, 126.9, 123.7, 123.1, 121.5, 121.4, 119.2 ($C_{10}H_5$), 66.8 (cage C), 45.7, 45.6 (CH_3), 36.0 (δ-CH_2), 35.3 (β-CH_2), 32.3 (γ-CH_2), 22.6 (α-CH_2). ^{11}B NMR (96 MHz, DMSO-d_6) δ −12.5 (br, 11B). IR (KBr) ν_{max} (cm^{-1}) 2536 (vs, BH). HRMS (EI) calcd for $C_{19}H_{35}{}^{11}B_9{}^{10}B_2N_2$ [M]$^+$ m/z 410.3891, found m/z 410.3886.

Reaction of 1 with C_5H_5N. Method A: To C_5H_5N (5 mL) was slowly added **1** (98 mg, 0.50 mmol) in batches at −30 °C. The resulting dark blue solution was stirred at room temperature overnight and gradually turned to a clear brown solution. After removal of the solvent, the residue was washed with THF to give μ-2,4-$(CH_2)_3CHBH(C_5H_5N)_2$-2-$CB_{10}H_9$ (**12**) as a white powder (100 mg, 0.28 mmol, 56%). X-ray-quality crystals were obtained by recrystallization from DMSO/MeOH. **Method B**: C_5H_5N (5 mL) was slowly added to **1** (196 mg, 1.00 mmol) at room temperature. The reaction was very vigorous. After removal of the solvent, column chromatographic separation (SiO_2, 300−400 mesh, CH_2Cl_2) gave crude μ-1,2-$(CH_2)_3CH(NC_5H_5)$-1-$CB_{11}H_{10}$ (**15a**) (139 mg, 0.50 mmol, 50%) and crude μ-1,2-$(CH_2)_2CH(NC_5H_5)CH_2$-1-$CB_{11}H_{10}$ (**15b**) (24 mg, 0.09 mmol, 9%). Repeated recrystallization from CH_2Cl_2 and acetone afforded **15a** (100 mg, 0.36 mmol, 36%) and **15b** (12 mg, 0.04 mmol, 4%) as white solids. X-ray quality crystals of **15a** were grown from slow evaporation of an acetone solution. **12**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (d, J = 5.4 Hz, 2H, C_5H_5N), 9.00

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(d, J = 5.4 Hz, 2H, C_5H_5N), 8.35 (t, J = 7.6 Hz, 1H, C_5H_5N), 8.32 (t, J = 7.7 Hz, 1H, C_5H_5N), 7.90 (t, J = 7.0 Hz, 2H, C_5H_5N), 7.84 (t, J = 7.0 Hz, 2H, C_5H_5N), 2.53 (m, 1H, δ-CH_2), 2.28 (m, 1H, δ-CH_2), 1.69 (m, 1H, γ-CH_2), 1.28 (m, 1H, γ-CH_2), 0.94 (m, 2H, β-CH_2), 0.52 (m, 1H, α-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 147.7, 146.3, 143.9, 143.7, 127.3, 126.4 (C_5H_5N), 72.8 (cage C), 34.8 (δ-CH_2), 27.1 (β-CH_2), 26.5 (γ-CH_2), 14.9 (α-CH). ^{11}B NMR (128 MHz, DMSO-d_6) δ 1.9 (br, 1B), −10.2 (br, 9B), −15.5 (br, 1B). These data are consistent with those reported.[8] **15a**: ^1H NMR (400 MHz, acetone-d_6) δ 9.11 (d, J = 5.7 Hz, 2H, C_5H_5N), 8.63 (t, J = 7.8 Hz, 1H, C_5H_5N), 8.22 (d, J = 6.7 Hz, 2H, C_5H_5N), 4.73 (d, J = 6.3 Hz, 1H, α-CH), 2.30 (br, 1H, β-CH_2), 2.08 (m, 1H, δ-CH_2), 2.07 (m, 1H, β-CH_2), 1.95 (m, 1H, δ-CH_2), 1.80 (m, 1H, γ-CH_2), 1.54 (m, 1H, γ-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 145.2, 144.5, 128.9 (C_5H_5N), 68.8 (cage C), 65.6 (br, α-CH), 35.4 (δ-CH_2), 29.9 (β-CH_2), 24.7 (γ-CH_2). ^{11}B NMR (128 MHz, acetone-d_6) δ −8.7 (s, 1B), −8.8 (d, J_{BH} = 139 Hz, 1B), −10.5 (d, J_{BH} = 174 Hz, 1B), −11.8 (d, J_{BH} = 161 Hz, 4B), −13.6 (br, 4B). HRMS (EI) calcd for $C_{10}H_{20}{}^{11}B_9{}^{10}B_2N$ $[M - 2H]^+$ m/z 273.2692, found m/z 273.2691. **15b**: ^1H NMR (400 MHz, acetone-d_6) δ 9.29 (d, J = 5.8 Hz, 2H, C_5H_5N), 8.70 (t, J = 7.7 Hz, 1H, C_5H_5N), 8.25 (t, J = 6.7 Hz, 2H, C_5H_5N), 4.87 (m, 1H, β-CH), 2.24 (m, 2H, δ-CH_2), 2.22 (m, 1H, γ-CH_2), 1.96 (m, 1H, γ-CH_2), 1.74 (m, 1H, α-CH_2), 1.65 (m, 1H, α-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 146.4, 144.1, 129.3 (C_5H_5N), 73.6 (β-CH), 66.2 (cage C), 36.2 (δ-CH_2), 33.1 (γ-CH_2), 24.6 (br, α-CH_2). ^{11}B NMR (128 MHz, acetone-d_6) δ −8.1 (s, 1B), −9.0 (d, J_{BH} = 193 Hz, 1B), −10.3 (d, J_{BH} = 155 Hz, 1B), −11.4 (d, J_{BH} = 128 Hz, 4B), −12.3 (d, J_{BH} = 134 Hz, 2B), −13.5 (d, J_{BH} = 150 Hz, 1B), −14.7 (d, J_{BH} = 150 Hz, 1B). HRMS (ESI) calcd for $C_{10}H_{22}{}^{11}B_9{}^{10}B_2NNa$ $[M + Na]^+$ m/z 298.2741, found m/z 298.2742.

Reaction of 1 with 4-MeC$_5$H$_4$N. Method A: To 4-MeC_5H_4N (5 mL) was slowly added **1** (98 mg, 0.50 mmol) in batches at −30 °C. The resulting dark blue solution was stirred at room temperature overnight, and it gradually turned to a clear brown solution. After removal of the solvent, the residue was washed with THF to give μ-2,4-$(CH_2)_3CHBH(MeC_5H_4N)_2$-2-$CB_{10}H_9$ (**13**) as a white powder (100 mg, 0.26 mmol, 52%). X-ray-quality crystals were obtained by recrystallization from DMSO/MeOH. **Method B**: To a C_6D_6 (0.5 mL) solution of **1** (10 mg, 0.05 mmol) was slowly added 4-MeC_5H_4N (0.1 mL, 1.03 mmol) at room temperature. NMR spectra indicated the formation of a mixture of **13**, μ-1,2-$(CH_2)_3CH(MeC_5H_4N)$-1-$CB_{11}H_{10}$ (**16a**), μ-1,2-$(CH_2)_2CH(MeC_5H_4N)CH_2$-1-$CB_{11}H_{10}$, and [**3**][4-$MeC_5H_4NH$]. Few crystals were grown from a CH_2Cl_2 solution and structurally identified as **16a**·CH_2Cl_2. **13**: ^1H NMR (400 MHz, DMSO-d_6) δ 8.87 (d, J = 5.7 Hz, 2H, C_4H_5N), 8.80 (d, J = 5.7 Hz, 2H, C_4H_5N), 7.69 (d, J = 5.4 Hz, 2H, C_4H_5N), 7.64 (d, J = 5.6 Hz, 2H, C_4H_5N), 2.52 (m, 1H, δ-CH_2), 2.47 (s, 6H, CH_3), 2.28 (m, 1H, δ-CH_2), 1.68 (m, 1H, γ-CH_2), 1.27 (m, 1H, γ-CH_2), 0.94 (m, 2H, β-CH_2), 0.47 (m, 1H, α-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 156.3, 146.8, 145.4, 127.6, 126.7 (C_4H_5N), 72.7 (cage C), 34.8 (δ-CH_2), 27.2 (β-CH_2), 26.4 (γ-CH_2), 21.0 (CH_3), 14.8 (α-CH). ^{11}B NMR (128 MHz, DMSO-d_6) δ 2.7 (br, 1B), −10.2 (br, 8B), −15.9 (br, 2B). Anal. Calcd for $C_{17}H_{31}B_{11}N_2$ [M]: C, 53.40; H, 8.17; N, 7.33. Found: C, 53.29; H, 8.44; N, 7.22.

Reaction of 1 with 4-^{t}BuC$_5$H$_4$N. Method A: To 4-^{t}BuC$_5$H$_4$N (5 mL) was slowly added **1** (98 mg, 0.50 mmol) in batches at −30 °C. The dark blue solution was stirred at room temperature overnight and gradually turned to a clear brown solution. After removal of the solvent, the residue was washed with THF to give μ-2,4-$(CH_2)_3CHBH(^tBuC_5H_4N)_2$-2-$CB_{10}H_9$ (**14**) as a white powder (70 mg, 0.15 mmol, 30%). X-ray-quality crystals were obtained by recrystallization from DMSO/MeOH. **Method B**: To a C_6D_6 (0.5 mL) solution of **1** (10 mg, 0.05 mmol) was slowly added 4-^{t}BuC$_5$H$_4$N (0.1 mL, 6.8 mmol) at room temperature. NMR spectra indicated the formation of a mixture of **14**, μ-1,2-$(CH_2)_3CH(^tBuC_5H_4N)$-1-$CB_{11}H_{10}$, μ-1,2-$(CH_2)_2CH(^tBuC_5H_4N)CH_2$-1-$CB_{11}H_{10}$, and [**3**]-[^{t}BuC$_5H_4$NH]. **14**: ^1H NMR (400 MHz, DMSO-d_6) δ 8.93 (d, J = 5.8 Hz, 2H, C_4H_5N), 8.87 (d, J = 5.8 Hz, 2H, C_4H_5N), 7.87 (d, J = 5.8 Hz, 2H, C_4H_5N), 7.81 (d, J = 5.8 Hz, 2H, C_4H_5N), 2.52 (m, 1H, δ-CH_2), 2.28 (m, 1H, δ-CH_2), 1.69 (m, 1H, γ-CH_2), 1.30 (s, 9H, CH_3), 1.28 (m, 10H, CH_3 + γ-CH_2), 0.94 (m, 2H, β-CH_2), 0.51 (m, 1H, α-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 167.8, 167.6, 147.2, 145.8, 124.1, 123.1 (C_4H_5N), 72.7 (cage C), 67.0 (THF), 35.63, 35.59 (CCH_3), 34.8 (δ-CH_2), 29.64, 29.59 (CH_3), 27.2 (β-CH_2), 26.4 (γ-CH_2), 25.1 (THF), 15.1 (α-CH). ^{11}B NMR (128 MHz, DMSO-d_6) δ 3.2 (br, 1B), −10.2 (br, 8B), −15.9 (br, 2B). Anal. Calcd for $C_{23}H_{43}B_{11}N_2$ [M]: C, 59.21; H, 9.29; N, 6.00. Found: C, 59.13; H, 9.26; N, 5.55.

NMR Characterization of [μ−η:η:η-7,8,10-$(CH_2)_3$CHB(NEt_2)-7-$CB_{10}H_{10}$][Et_2NH_2] ([7i][Et_2NH_2]). To a C_6D_6 (0.5 mL) solution of **1** (9.8 mg, 0.05 mmol) was added Et_2NH (35 mg, 0.48 mmol) at −30 °C, and the solution was slowly warmed to room temperature. ^1H NMR (400 MHz, C_6D_6) δ 3.61 (m, 2H, NCH_2), 3.26 (m, 1H, NCH_2), 3.13 (m, 1H, NCH_2), 2.82 (m, 1H, δ-CH_2), 2.62 (m, 1H, β-CH_2), 2.16 (m, 1H, δ-CH_2), 1.87 (m, 2H, α-CH + γ-CH_2), 1.82 (m, 1H, γ-CH_2), 1.67 (m, 1H, β-CH_2), 1.26 (t, J = 6.9 Hz, 3H, CH_3), 1.11 (t, J = 6.9 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 93.6 (cage C), 43.6 (NCH_2), 38.4 (δ-CH_2), 33.4 (β-CH_2), 27.6 (γ-CH_2), 15.1, 14.3 (CH_3), 12.7 (α-CH). ^{11}B NMR (128 MHz, C_6D_6) δ 39.8 (s, 1B), 21.1 (br, 1B), 0.5 (d, J_{BH} = 113 Hz, 1B), −6.0 (d, J_{BH} = 97 Hz, 2B), −11.6 (d, J_{BH} = 131 Hz, 1B), −15.4 (d, J_{BH} = 191 Hz, 2B), −17.7 (d, J_{BH} = 148 Hz, 1B), −19.4 (d, J_{BH} = 192 Hz, 1B), −23.8 (d, J_{BH} = 115 Hz, 1B).

Preparation of [μ−η:η:η-7,8,10-$(CH_2)_3$CHB(NEt_2)-7-$CB_{10}H_{10}$]-[PPN] ([7i][PPN]). To a THF (10 mL) solution of **1** (98 mg, 0.50 mmol) was added Et_2NLi (40 mg, 0.50 mmol) at room temperature, and the mixture was stirred overnight. After addition of [PPN]Cl (287 mg, 0.50 mmol), the mixture was further stirred for 6 h. Removal of the solvent gave a solid. Recrystallization from CH_2Cl_2 afforded [**7i**][PPN] as pale yellow crystals (363 mg, 0.45 mmol, 90%). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.69 (m, 12H, PPN), 7.53 (m, 18H, PPN), 3.46 (m, 1H, NCH_2), 3.33 (m, 1H, NCH_2), 3.09 (m, 2H, NCH_2), 2.35 (m, 1H, δ-CH_2), 2.33 (m, 1H, β-CH_2), 1.66 (m, 1H, δ-CH_2), 1.56 (m, 1H, γ-CH_2), 1.43 (m, 1H, γ-CH_2), 1.41 (m, 1H, α-CH), 1.24 (m, 1H, β-CH_2), 1.09 (t, J = 7.0 Hz, 3H, CH_3), 1.06 (t, J = 7.1 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 134.2, 132.6, 129.9, 127.4 (PPN), 92.9 (cage C), 43.4, 43.3 (NCH_2), 38.0 (δ-CH_2), 33.0 (β-CH_2), 27.3 (γ-CH_2), 15.0, 14.1 (CH_3), 12.2 (α-CH). ^{11}B NMR (128 MHz, CD_2Cl_2) δ 38.8 (s, 1B), 20.2 (br, 1B), −0.4 (d, J_{BH} = 141 Hz, 1B), −6.9 (d, J_{BH} = 127 Hz, 2B), −12.2 (d, J_{BH} = 128 Hz, 1B), −16.3 (d, J_{BH} = 123 Hz, 2B), −18.5 (d, J_{BH} = 141 Hz, 1B), −20.4 (d, J_{BH} = 113 Hz, 1B), −24.6 (d, J_{BH} = 118 Hz, 1B). IR (KBr) ν_{max} (cm^{-1}) 2510 (vs, BH). Anal. Calcd for $C_{45}H_{57}B_{11}N_2P_2$ [M]: C, 66.99; H, 7.12; N, 3.47. Found: C, 67.18; H, 7.08; N. 3.50.

Alternative Method for the Preparation of μ-1,2-$(CH_2)_3$CH-(NEt_2H)-1-$CB_{11}H_{10}$ (7a). To a THF (10 mL) solution of **1** (196 mg, 1.00 mmol) was added Et_2NLi (80 mg, 1.00 mmol) at room temperature, and the mixture was stirred overnight. After removal of THF, CH_2Cl_2 (10 mL) was added, and the solution was cooled to 0 °C. A 1.0 M solution of HCl (5 mL, 5.0 mmol) was added, and the mixture was stirred at room temperature for 30 min. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The organic portions were combined and dried over Na_2SO_4. Concentration of the CH_2Cl_2 solution afforded **7a** as colorless crystals (215 mg, 0.80 mmol, 80%).

Thermolysis of [7i][Et_2NH_2]. To a toluene (20 mL) solution of **1** (196 mg, 1.00 mmol) was added Et_2NH (2 mL, 1.414 g, 19.2 mmol) at −30 °C. The solution was slowly warmed to room temperature and heated at 90 °C for 2 h in a closed vessel. Column chromatographic separation (SiO_2, 300−400 mesh, CH_2Cl_2) followed by recrystallization from CH_2Cl_2 afforded **7a** (215 mg, 0.80 mmol, 80%) as colorless crystals and μ-1,2-$(CH_2)_2CH(NEt_2H)CH_2$-1-$CB_{11}H_{10}$ (**7b**) as a white solid (10 mg, 0.037 mmol, 3.7%). **7b**: ^1H NMR (400 MHz, acetone-d_6) δ 3.59 (m, 1H, β-CH), 3.40 (m, 4H, NCH_2), 2.16 (m, 1H, δ-CH_2), 2.03 (m, 1H, δ-CH_2), 1.80 (m, 1H, γ-CH_2), 1.70 (m, 1H, γ-CH_2), 1.42 (t, J = 7.3 Hz, 6H, CH_3), 1.39 (m, 1H, α-CH_2), 1.23 (m, 1H, α-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 66.4 (cage C), 63.4 (β-CH), 46.1 (NCH_2), 35.8 (δ-CH_2), 27.5 (γ-CH_2), 14.7 (br, α-CH_2), 11.0 (CH_3). ^{11}B NMR (128 MHz, acetone-d_6) δ −8.2 (s, 1B), −9.3 (d, J_{BH} = 151 Hz, 1B), −11.6 (d, J_{BH} = 131 Hz, 7B), −13.8 (d, J_{BH} = 165 Hz, 1B), −15.0 (d, J_{BH} = 142 Hz, 1B). IR (KBr) ν_{max} (cm^{-1}) 2534 (vs,

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BH). HRMS (EI) calcd for $C_9H_{26}{}^{11}B_9{}^{10}B_2N$ $[M - 2H]^+$ m/z 267.3156, found m/z 269.3152.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected on a Bruker SMART 1000 CCD diffractometer or a Bruker AXS kappa Apex II Duo diffractometer using Mo $K\alpha$ radiation. An empirical absorption correction was applied using the SADABS program.[21] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F^2 using SHELXTL.[22] The hydrogen atoms were geometrically fixed using the riding model. Noted that $[\mathbf{7i}]^-$ in [**7i**][PPN], the $(CH_2)_4$ chain and Me_4N^+ in [**9**][Me_4N], and Et_3N in **10a** are disordered over two sets of positions with equal occupancies. **16a** showed one CH_2Cl_2 of solvation. Crystal data and details of data collection and structure refinements are included in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format for complexes [**4a**]-[Me_3NH], **6a**, **7a**, [**9**][Me_4N], **10a**, **10b**, **11b**, **13**, **14**, **15a**, **16a**·CH_2Cl_2, and [**7i**][PPN], molecular structure of [**3**][PSH], and ^{11}B NMR spectra of some structurally characterized or observed intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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