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Synthesis and Reactivity Studies of the Small Carborane *closo*-2,3-$Et_2C_2B_5H_5$

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Three new viable synthetic routes to the small *closo*-carborane 2,3-$Et_2C_2B_5H_5$ (I) are reported based on cluster expansion reactions of the small *nido*-carborane 2,3-$Et_2C_2B_4H_6$ utilizing Lewis base–borane adducts. Thus, reaction of *nido*-2,3-$Et_2C_2B_4H_6$ with $Et_3N{\cdot}BH_3$ at 140 °C resulted in the capping of the open face of the *nido*-carborane by a BH group derived from the amine–borane and produced I in 50–60% yield. Reactions employing $Et_3N{\cdot}{}^{10}BH_3$ confirmed that the inserted BH group is derived from the amine–borane. Reactions of *nido*-2,3-$Et_2C_2B_4H_6$ with $Et_3N{\cdot}BH_3$ at higher temperature (170 °C) resulted in the isolation of a mixture of *closo*-carboranes including I, *closo*-1,7-$Et_2C_2B_6H_6$ (II), and *closo*-1,7-$Et_2C_2B_7H_7$ (III). II and III were also formed by reaction of I with $Et_3N{\cdot}BH_3$ at 190 °C. Alternatively, I may be prepared by the reaction of Li^+[*nido*-2,3-$Et_2C_2B_4H_5$]$^-$ with $(CH_3)_2S{\cdot}BH_3$ or reaction of Na^+Li^+[*nido*-2,3-$Et_2C_2B_4H_4$]$^{2-}$ with $(CH_3)_2S{\cdot}BHBr_2$ in yields of of 44% and 49%, respectively. Reaction of Na^+Li^+[*nido*-2,3-$Et_2C_2B_4H_4$]$^{2-}$ with $PhBCl_2$ or $MeBBr_2$ produced the mono-B-substituted compounds *closo*-1-Ph-2,3-$Et_2C_2B_5H_4$ (IV) (41%), and *closo*-1-Me-2,3-$Et_2C_2B_5H_4$ (V) (46%). Thermolysis of I at ~320 °C in the gas phase resulted in the high-yield (81%) isomerization of the carborane to *closo*-2,4-$Et_2C_2B_5H_5$ (VI). Halogenation of I with elemental bromine or with $Br_2/AlBr_3$ at room temperature results in the exclusive formation of *closo*-5-Br-2,3-$Et_2C_2B_5H_4$ (VII). Reaction of I with 1 equiv of $Li(BEt_3)H$ resulted in the formation of the first seven-vertex *nido*-carborane anion [*nido*-3,4-$Et_2C_2B_5H_6$]$^-$ (VIII), which was shown to have a structure based on a dodecahedron missing one five-connected vertex, and is thus the first 18-electron, seven-vertex nido polyhedral borane for which this geometry has been confirmed. The analogous *neutral*, seven-vertex 18-electron species *nido*-6-Me_3P-3,4-$Et_2C_2B_5H_5$ (IX) was formed in the reaction between I and Me_3P at temperatures above −40 °C.

Introduction

Studies of the closo-$R_2C_2B_5H_5$ cage system have focused largely on the nonadjacent-carbon isomer *closo*-2,4-$R_2C_2B_5H_5$. This isomer is one of several *closo*-carboranes formed in the complex pyrolytic reactions of pentaborane(9) with alkynes[1] and is also obtained in the thermolytic decomposition of *nido*-2,3-$R_2C_2B_4H_6$.[2] Although these methods produce *closo*-2,4-$R_2C_2B_5H_5$ in good yield, they exhibit poor selectivity and result in the formation of several other carborane systems.

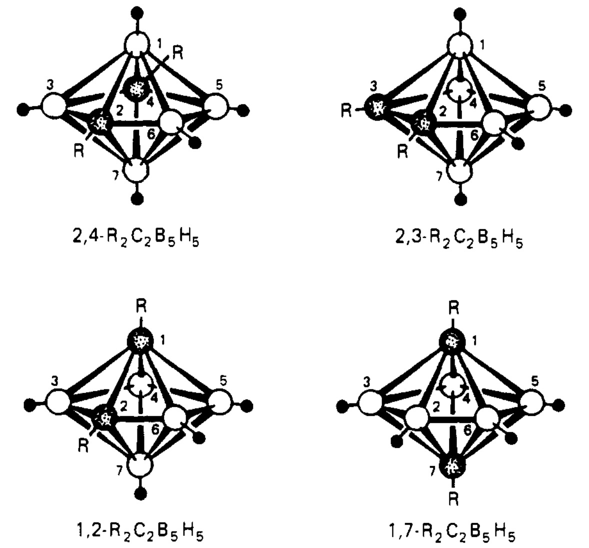
As shown in Chart I, there are four possible isomers for the *closo*-$R_2C_2B_5H_5$ cage system. Theoretical calculations[3] have shown that the tendency of carbon atoms to occupy positions of low coordination in the pentagonal bipyramidal framework is more important than their tendency to keep apart. The 1,2- and 1,7-isomers are therefore predicted to be high-energy structures, and indeed, neither of these isomers has been observed. By contrast, the adjacent-carbon isomer *closo*-2,3-$R_2C_2B_5H_5$ is predicted to be only approximately 15–25 kcal/mol less stable than the 2,4-isomer;[3] however, the compound has been isolated only as a byproduct in the reaction between B_6H_{12} and alkynes, and its chemistry has not been explored.[4]

In a recent communication,[5] we reported a simple cage-capping reaction resulting in the high-yield, selective formation of *closo*-2,3-$Et_2C_2B_5H_5$. Herein we report a detailed study of this thermal expansion, as well as two new pathways to the 2,3-isomer and a route to its mono-B-substituted derivatives. In addition, we describe the first chemical studies of this compound, including isomerization, halogenation, cage-opening, and cage-expansion reactions.

Experimental Section

All manipulations were carried out by standard high-vacuum or inert-atmosphere techniques as described by Shriver.[6]

Chart I



2,4-$R_2C_2B_5H_5$ 2,3-$R_2C_2B_5H_5$

1,2-$R_2C_2B_5H_5$ 1,7-$R_2C_2B_5H_5$

Materials. The carborane *nido*-2,3-$Et_2C_2B_4H_6$ was prepared by a literature method.[7] Triethylamine-borane, tributylphosphine–borane, dimethyl sulfide–borane and dimethyl sulfide–dibromoborane were purchased from Aldrich and used as received. The $^{10}BF_3{\cdot}CaF_2$ (^{10}B = 92.24%) was obtained from Eagle-Picher. The complex $Et_3N{\cdot}{}^{10}BH_3$ was prepared on the basis of a literature method.[8] Methylboron dibromide and phenylboron dichloride were obtained from Alfa. Sodium hydride (dry, 97%), $Li(BEt_3)H$, butyllithium (1.6 M and 2.5 M in hexanes), trimethylamine, triethylamine, and pyridine were obtained from Aldrich and used as received. Trimethylphosphine (Aldrich) was freed from $[(CH_3)_3P{\cdot}AgI]_4$ by heating it in vacuo to >200 °C. All solvents were reagent grade and freshly distilled from either sodium–benzophenone or $LiAlH_4$.

Physical Measurements and Instrumentation. ^1H NMR spectra at 200.1 MHz, ^{11}B NMR spectra at 64.2 MHz, and ^{10}B NMR spectra at 21.5 MHz were obtained on a Bruker AF-200 Fourier transform spectrometer. ^{11}B NMR spectra at 160.5 MHz were obtained on a Bruker AM-500 Fourier transform spectrometer. Chemical shifts for ^{11}B NMR spectra are relative to external $BF_3{\cdot}O(C_2H_5)_2$ (0.00 ppm), with a negative sign indicating an upfield shift. Chemical shifts for ^1H NMR spectra (ppm) are based on 7.15 ppm for C_6D_6 (relative to Me_4Si at 0.00 ppm). The two-dimensional COSY ^{11}B–^{11}B NMR[9] experiments were conducted

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Table I. ^{11}B and ^{1}H NMR Data

compd	nucleus	δ (m, assgnt, *J*, rel area)
closo-2,3-$Et_2C_2B_5H_5$ (I)[a]	^{11}B	7.0 (d, B4,6, J_{BH} = 170 Hz, 2), 2.5 (d, B5, J_{BH} = 150 Hz, 1), −14.2 (d, B1,7, J_{BH} = 170 Hz, 2)
	2D (^{11}B–^{11}B)	cross-peaks: B5–B1,7, B4,6–B1,7, B4,6–B5
	^{1}H	2.13 (q, CH_2, J_{HH} = 7.2 Hz, 4), 0.94 (t, CH_3, J_{HH} = 7.7 Hz, 6)
	$^{1}H\{^{11}B\}$	4.5 (s, BH4,6 and BH5, 3), 0.2 (s, BH1,7, 2)
closo-1,7-$Et_2C_2B_6H_6$ (II)[a]	^{11}B	5.9 (d, B2,5,6,8, J_{BH} = 165 Hz, 4), −5.6 (d, B3,4, J_{BH} = 170 Hz, 2)
	^{1}H	2.23 (q, CH_2, J_{HH} = 7.6 Hz, 4), 1.02 (t, CH_3, J_{HH} = 7.6 Hz, 6)
closo-1,7-$Et_2C_2B_7H_7$ (III)[a]	^{11}B	27.0 (d, B9, J_{BH} = 150 Hz, 1), −5.5 (d, B3,4, J_{BH} = 175 Hz, 2), −9.3 (d, B2,5,6,8, J_{BH} = 165 Hz, 4)
	^{1}H	2.51 (q, CH_2, J_{HH} = 7.4 Hz, 4), 1.09 (t, CH_3, J_{HH} = 7.5 Hz, 6)
closo-1-Ph-2,3-$Et_2C_2B_5H_4$ (IV)[a]	^{11}B	6.6 (d, B4,6, J_{BH} = 170 Hz, 2), 2.1 (d, B5, J_{BH} = 175 Hz, 1), −5.1 (s, B1, 1), −21.0 (d, B7, J_{BH} = 170 Hz, 1)
	^{1}H	6.96 (m, C_6H_5, 5), 2.12 (m, CH_2, J_{HH} = 7.5 Hz, 4), 1.01 (t, CH_3, J_{HH} = 7.7 Hz, 6)
closo-1-Me-2,3-$Et_2C_2B_5H_4$ (V)[a]	^{11}B	6.6 (d, B4,6, J_{BH} = 165 Hz, 2), 2.0 (d, B5, J_{BH} = 160 Hz, 1), −5.2 (s, B1, 1), −21.1 (d, B7, J_{BH} = 175 Hz, 1)
	2D (^{11}B–^{11}B)	cross-peaks: B4,6–B5, B4,6–B1, B4,6–B7, B5–B1, B5–B7
	^{1}H	2.10 (q, CH_2, J_{HH} = 7.4 Hz, 4), 1.01 (t, CH_3, J_{HH} = 7.5 Hz, 6), −0.59 (s, B1–CH_3)
closo-2,4-$Et_2C_2B_5H_5$ (VI)[a]	^{11}B	8.0 (d, B3, J_{BH} = 165 Hz, 1), 5.8 (d, B5,6, J_{BH} = 170 Hz, 2), −17.7 (d, B1,7, J_{BH} = 175 Hz, 2)
	2D (^{11}B–^{11}B)	cross-peaks: B5,6–B1,7
	^{1}H	2.26 (q, CH_2, J_{HH} = 7.7 Hz, 4), 0.93 (t, CH_3, J_{HH} = 7.7 Hz, 6)
	$^{1}H\{^{11}B\}$	4.6 (s, BH3, 1), 4.3 (s, BH5,6, 2), 0.5 (s, BH1,7, 2)
closo-5-Br-2,3-$Et_2C_2B_5H_4$ (VII)[a]	^{11}B	7.0 (s, B5, 1), 5.4 (d, B4,6, J_{BH} = 175 Hz, 2), −16.1 (d, B1,7, J_{BH} = 180 Hz, 2)
	^{1}H	2.10 (q, CH_2, J_{HH} = 7.5 Hz, 4), 0.91 (t, CH_3, J_{HH} = 7.7 Hz, 6)
$(CH_3)_4N^+$[*nido*-3,4-$Et_2C_2B_5H_6$]$^-$ (VIII)[b]	^{11}B	24.1 (d, B2, J_{BH} = 140 Hz, 1), 19.3 (t, B6, J_{BH} = 110 Hz, 1), 4.8 (d, B5,7, J_{BH} = 130 Hz, 2), −21.3 (d of q, B1, J_{BH} = 155 Hz, J_{BB} = 26 Hz, 1)
	2D (^{11}B–^{11}B)	cross-peaks: B1–B2, B1–B5,7, B2–B5,7, B2–B6, B6–B5,7
	^{1}H	3.27 (s, $(CH_3)_4N^+$, 12), 2.31 (m, CH_2, J_{HH} = 7.5 Hz, 4), 1.11 (t, CH_3, J_{HH} = 7.5 Hz, 6)
	$^{1}H\{^{11}B\}$	4.6 (s, BH, 1), 2.7 (s, BH, 1), 2.3 (s, BH, 2), −0.3 (s, BH, 1)
nido-6-Me_3P-3,4-$Et_2C_2B_5H_5$ (IX)[c]	^{11}B	20.8 (d, B2, J_{BH} = 145 Hz, 1), 0.0 (d of d, B6, J_{BP} = 43 Hz, J_{BH} = 126 Hz, 1), −2.4 (d, B5,7, J_{BH} = 145 Hz, 2), −21.1 (d, B1, J_{BH} = 150 Hz, 1)
	2D (^{11}B–^{11}B)	cross-peaks: B1–B2, B1–B5,7, B2–B5,7, B2–B6 (weak), B6–B5,7
	^{1}H	2.71 (m, CH_2, J_{HH} = 7.5 Hz, 4), 1.47 (t, CH_3, J_{HH} = 7.6 Hz, 6), 0.46 (d, $(CH_3)_3P$, J_{PH} = 11.3 Hz, 9)[d]

[a] ^{11}B NMR, 64.2 MHz; ^{1}H NMR, 200.1 MHz; C_6D_6 solvent. [b] ^{11}B NMR, 160.5 MHz, acetone-d_6; ^{1}H NMR, 200.1 MHz, methylene-d_2 chloride. [c] ^{11}B NMR, 160.5 MHz; ^{1}H NMR, 200.1 MHz; C_6D_6. [d] Spectrum also contained a resonance for free Me_3P at 0.79 ppm.

with s-type selection parameters at 64.2 MHz. Unit and high-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer. Gas chromatography–mass spectrometry was performed on a Hewlett-Packard 5890A gas chromatograph (equipped with a cross-linked methylsilicone column) interfaced to a Hewlett Packard 5970 mass selective detector. Gas–liquid chromatography was conducted on a Varian Aerograph Model 1400 gas chromatograph. Infrared spectra were recorded on a Perkin-Elmer 1430 infrared spectrophotometer. ^{11}B and ^{1}H NMR data are given in Table I, while IR data are given in Table II.

Syntheses of *closo*-2,3-$Et_2C_2B_5H_5$. Reactions of *nido*-2,3-$Et_2C_2B_4H_6$ with $Et_3N{\cdot}BH_3$. At 140 °C. Into a 100-mL one-piece flask was syringed 2.12 mL (14.3 mmol) of $Et_3N{\cdot}BH_3$. The flask was then degassed, and 0.378 g (2.88 mmol) of *nido*-2,3-$Et_2C_2B_4H_6$ was condensed in at −196 °C. The flask was then placed in an oil bath and stirred while the temperature of the bath was increased gradually to 140 °C. (Mixtures heated at temperatures lower than 130 °C gave no indication of reaction.) The reaction was maintained at this temperature for 48 h with periodic (approximately every 8 h) removal of evolved hydrogen and triethylamine (removal of these materials was accomplished by maintaining the reaction flask at ∼−50 °C while pumping dynamically through a −196 °C trap). The volatile components of the reaction were then separated by vacuum-line fractionation through a 0, −45, and −196 °C trap series. Stopping in the −45 °C trap was 0.265 g of a clear liquid material. The ^{11}B NMR spectrum of this material showed it to be *closo*-2,3-$Et_2C_2B_5H_5$ (I)[5] with additional small peaks corresponding to the starting material *nido*-2,3-$Et_2C_2B_4H_6$.

The *nido*-carborane was then removed by reacting the carborane mixture with ∼5 mmol of NaH in 5 mL of THF. The reactants were allowed to warm to 0 °C and stirred for 1 h. Fractionation of the volatile materials through a −45 and −196 °C trap series afforded 0.210 g (1.49 mmol, 51.7% yield) of pure I, stopping at −45 °C. Exact mass measurement for $^{12}C_6{}^{11}B_5{}^{1}H_{15}$: calcd, 142.1639; found, 142.1610. The total amount of Et_3N recovered in the reaction was 0.165 g (1.63 mmol).

Table II. Infrared Data

compd	ν, cm^{-1}
I[a]	2970 (s), 2950 (w), 2880 (w), 2600 (s), 1080 (w), 920 (w), 840 (w), 800 (w)
IV[b]	3070 (m), 3045 (m), 3010 (m), 2970 (s), 2935 (m), 2875 (m), 2590 (s), 1950 (w), 1880 (w), 1810 (w), 1720 (w), 1665 (w), 1595 (m), 1455 (m), 1430 (m), 1380 (m), 1260 (m, br), 1180 (w), 1150 (w), 1090 (w), 1065 (m), 1025 (w), 1000 (m), 970 (w), 950 (m), 915 (w), 870 (m), 820 (w), 790 (w), 750 (m), 740 (w), 700 (s), 635 (w)
V[b]	2965 (s), 2940 (s), 2880 (m), 2590 (s), 1455 (m), 1380 (w), 1320 (s), 1260 (w), 1155 (m), 1135 (w), 1070 (w), 970 (w), 920 (w), 900 (m), 845 (w), 825 (w), 790 (w), 740 (w), 720 (w)
VI[a]	2970 (s), 2935 (m), 2883 (m), 2600 (s), 2335 (w), 1460 (w), 1335 (w), 1165 (w), 890 (m), 780 (w), 735 (w), 660 (w)
VII[b]	2970 (s), 2930 (s), 2880 (m), 2610 (s), 1455 (s), 1380 (m), 1360 (w), 1310 (w), 1155 (w), 1140 (w), 1110 (s), 1070 (w), 1040 (w), 1030 (w), 900 (s), 870 (w), 855 (s), 790 (w), 770 (w), 760 (m), 735 (m)
VIII[c]	3020 (m), 2960 (s), 2930 (m), 2900 (w), 2870 (w), 2530 (s), 2520 (s), 2500 (m), 2460 (s), 2440 (s), 2360 (m), 2310 (s), 1485 (s), 1455 (m), 1445 (w), 1420 (w), 1370 (w), 1360 (w), 1310 (w), 1285 (w), 1180 (m), 1150 (w), 1060 (w), 1030 (w), 1000 (w), 980 (w), 950 (s), 920 (w), 880 (w), 850 (w), 810 (w), 750 (w), 710 (w)

[a] Gas phase, NaCl windows. [b] Neat liquid, NaCl windows. [c] KBr pellet.

At 170 °C. In a similar procedure, 0.312 g (2.37 mmol) of *nido*-2,3-$Et_2C_2B_4H_6$ and 1.44 g (12.5 mmol) of $Et_3N{\cdot}BH_3$ were reacted at 170 °C for 36 h. Fractionation of the volatile materials through a 0, −45, −196 °C trap series afforded 0.297 g of material stopping at −45 °C. GC/MS of the carborane mixture on a 25-ft cross-linked methylsilicone column (initial temperature 40 °C, ramped at 10 °C/min) showed mass

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cutoffs at *m/e* 154, 142 and 166, displaying characteristic six, five-, and seven-boron envelopes, respectively. Pure samples of these compounds were obtained by preparative GLC of the carborane mixture on a 4.5-ft, 6% tricresyl phosphate on Chromasorb P, 60/80 mesh column at 100 °C. The compounds *closo*-1,7-$Et_2C_2B_6H_6$ (II), R_v = 0.9; *closo*-2,3-$Et_2C_2B_5H_5$ (I), R_v = 2.5; and *closo*-1,7-$Et_2C_2B_7H_7$ (III), R_v = 3.3 (reference *nido*-2,3-$Et_2C_2B_4H_6$, R_v = 1.0) were obtained in a 1:0.6:0.3 ratio and their identities confirmed by a comparison of their ^{11}B NMR spectral data with literature values.[10]

Reaction of *nido*-2,3-$Et_2C_2B_4H_6$ with $Et_3N\cdot{}^{10}BH_3$ at 140 °C. Under conditions identical with those described above, 0.298 g (2.27 mmol) of *nido*-2,3-$Et_2C_2B_4H_6$ and 1.57 g (13.6 mmol) of $Et_3N\cdot{}^{10}BH_3$ were reacted at 140 °C. After a similar workup, 0.153 g (1.09 mmol, 48.0%) of *closo*-[1-^{10}B]-2,3-$Et_2C_2B_5H_5$ was isolated. Exact mass measurement for $^{12}C_6{}^{11}B_4{}^{10}B_1H_{15}$: calcd, 141.168; found, 141.170.

Thermolysis of *nido*-2,3-$Et_2C_2B_4H_6$ at 140 °C. Into a 25-mL break-seal tube equipped with a vacuum stopcock was condensed 0.073 g (0.55 mmol) of *nido*-2,3-$Et_2C_2B_4H_6$. The tube was sealed and heated at 140 °C for ~48 h. The tube was then opened (only a trace amount of H_2 was produced), and the contents were fractionated through a -45 and -196 °C trap series. Stopping at -45 °C was 0.064 g (0.49 mmol, 89.1%) of *nido*-2,3-$Et_2C_2B_4H_6$. Analysis of the material by ^{11}B and ^1H NMR showed only resonances associated with *nido*-2,3-$Et_2C_2B_4H_6$.

Reaction of *nido*-2,3-$Et_2C_2B_4H_6$ with Et_3N at 140 °C. Into a 25-mL break-seal tube were condensed 0.190 g (1.45 mmol) of *nido*-2,3-$Et_2C_2B_4H_6$ and 0.168 g (1.66 mmol) of Et_3N. The tube was sealed and then heated in an oven at 140 °C for 36 h. The tube was transferred to the vacuum line, and the volatile materials fractionated through a -45 and -196 °C trap series. The material stopping at -45 °C was determined to be pure *nido*-2,3-$Et_2C_2B_4H_6$, 0.183 g (1.39 mmol, 95.9%), by comparison of its ^{11}B and ^1H NMR spectra with those of an authentic sample.

Reaction of Li^+[*nido*-2,3-$Et_2C_2B_4H_5$]$^-$ with $(CH_3)_2S\cdot BH_3$. In a typical reaction, 1.26 mL of a 2.5 M solution of butyllithium in hexanes (3.2 mmol of BuLi) was charged into a 100-mL two-neck reaction flask equipped with a vacuum stopcock and stirbar. The flask was evacuated at -196 °C and charged with 0.406 g (3.09 mmol) of *nido*-2,3-$Et_2C_2B_4H_6$ and ~3 mL of dry hexanes. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 2 h. At this point, a 10-mL addition funnel containing 0.47 g (6.2 mmol) of $(CH_3)_2S\cdot BH_3$ in 3 mL of hexanes was exchanged under N_2 for the ground-glass stopper. The $(CH_3)_2S\cdot BH_3$ solution was then added dropwise at 0 °C over 1 h. The reaction mixture was allowed to stir for 4 h at room temperature and then for an additional 2 h at ~45 °C. The reaction flask was attached to a vacuum line, and the volatile components were fractionated through a -45 and -196 °C trap series (a ^{11}B NMR spectrum of the involatile reaction residues in diethyl ether showed the presence of $LiBH_4$). Stopping at -45 °C was a mixture of I, $(CH_3)_2S\cdot BH_3$, and a small amount of *nido*-2,3-$Et_2C_2B_4H_6$. The mixture was then condensed into a 25-mL flask containing ~10 mmol of NaH in 5 mL of THF. The contents of the flask were allowed to warm slowly to 0 °C and then stirred for ~2 h. Vacuum fractionation of the material through a -45 and -196 °C trap series afforded 0.191 g (1.35 mmol, 43.7%) of pure I at -45 °C and $(CH_3)_2S$ and THF at -196 °C. Similar reactions between Na^+[*nido*-2,3-$Et_2C_2B_4H_5$]$^-$ and $(CH_3)_2S\cdot BH_3$ in THF yielded only trace quantities of I.

Reaction of Na^+[*nido*-2,3-$Et_2C_2B_4H_5$]$^-$ with BuLi and $(CH_3)_2S\cdot BHBr_2$. The Na^+Li^+[*nido*-2,3-$Et_2C_2B_4H_4$]$^{2-}$ was prepared by using a procedure similar to that described by Hosmane.[11] To a 100-mL round-bottom two-neck flask equipped with a stirbar, a high vacuum stopcock on one neck, and a rubber septum on the other was added 2.4 mL of a 1.6 M solution of BuLi in hexanes. The flask was attached to the vacuum line, and hexanes were removed at 0 °C. Tetrahydrofuran, ~10 mL, was then condensed into the flask at -196 °C, and the contents were allowed to warm to 0 °C. Through the septum was then syringed a solution of Na^+[*nido*-2,3-$Et_2C_2B_4H_5$]$^-$ in THF (3.89 mmol in 5 mL of THF). After being stirred for 2 h at 0 °C, the solution turned an opaque greenish color. At this point, the reaction mixture was cooled at -45 °C and 0.910 g (3.89 mmol) of $(CH_3)_2S\cdot BHBr_2$ syringed into the flask. The reaction was then warmed slowly to room temperature and allowed to stir for 2 h. The flask was attached to the vacuum line, and the volatile components were fractionated through a 0, -45, and -196 °C trap series. The material stopping at -45 °C was purified by reaction with NaH as described above to give 0.269 g (1.90 mmol, 49%) of pure I.

Reaction of Na^+[*nido*-2,3-$Et_2C_2B_4H_5$]$^-$ with BuLi and $PhBCl_2$. In a similar fashion 3.5 mmol of BuLi were reacted with 3.5 mmol of Na^+[*nido*-2,3-$Et_2C_2B_4H_5$]$^-$ in THF. After being stirred for 2 h at 0 °C, the solution exhibited a clear, dark olive color indicative of the formation of Na^+Li^+[*nido*-2,3-$Et_2C_2B_4H_4$]$^{2-}$. At this point 0.572, g (3.60 mmol) of $PhBCl_2$ was added to the reaction flask via syringe. The reaction mixture was maintained at 0 °C for an additional 2 h and subsequently warmed to room temperature for a 12-h period. The flask was then opened under a blanket of N_2 and 10 mL of cold pentane added. The reaction mixture was filtered to remove NaCl and LiCl, and the filtrate was transferred to a 100-mL one-piece flask. This flask was then attached to a U-trap on the vacuum line. After removal of volatiles at room temperature for ~2 h, the U-trap was cooled at -196 °C and the flask heated at 80 °C. Over a 3-h period, 0.313 g (1.44 mmol, 41.1%) of pure liquid 1-Ph-2,3-$Et_2C_2B_5H_4$ (IV) was collected in the U-trap. Exact mass measurement for $^{12}C_{12}{}^{11}B_5{}^1H_{19}$: calcd, 218.195; found, 218.198.

Reaction of Na^+[*nido*-2,3-$Et_2C_2B_4H_5$]$^-$ with BuLi and $MeBBr_2$. In an identical procedure, 4.2 mmol of BuLi and 4.19 mmol of Na^+[*nido*-2,3-$Et_2C_2B_4H_5$]$^-$ were reacted in vacuo. After being stirred for 2 h at 0 °C, the solution exhibited a clear dark olive color. At this point, the flask was attached to the vacuum line and 0.764 g (4.12 mmol) of $MeBBr_2$ was condensed in at -196 °C. The reaction mixture was warmed immediately to -78 °C and then gradually warmed to room temperature over a 2-h period while stirring was continued. After an additional 4 h, the reaction mixture was milky white, indicating the formation of NaBr/LiBr. The flask was then attached to the vacuum line, and the volatile components were fractionated through a -15, -45, and -196 °C series. Stopping at -20 °C was 0.300 g (1.93 mmol, 46.1%) of *closo*-1-CH_3-2,3-$Et_2C_2B_5H_4$ (V). Exact mass measurement for $^{12}C_7{}^{11}B_5{}^1H_{17}$: calcd, 156.180; found, 156.178. The -45 °C trap contained a mixture of unreacted $MeBBr_2$ and the starting *nido*-2,3-$Et_2C_2B_4H_6$, as determined by ^{11}B NMR.

Reactions of *closo*-2,3-$Et_2C_2B_5H_5$. Thermolysis of *closo*-2,3-$Et_2C_2B_5H_5$ at 320 °C. A 25-mL break-seal tube charged with 0.114 g (0.81 mmol) of *closo*-2,3-$Et_2C_2B_5H_5$ was placed in an oven at 320 °C for 47.5 h. The tube was then attached to the vacuum line, and the volatile materials were fractionated through a 0, -45, and -196 °C trap series. Stopping at -45 °C was 0.093 g (0.66 mmol) of pure *closo*-2,4-$Et_2C_2B_5H_5$ (VI), corresponding to a yield of 81%. Exact mass measurement for $^{12}C_6{}^{11}B_5{}^1H_{15}$: calcd, 142.1639; found, 142.1644.

Reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with Aluminum Powder and Bromine. To a 25-mL flask containing 0.036 g (1.33 mmol) of aluminum powder at -196 °C were added 0.527 g (3.30 mmol) of elemental bromine, 0.183 g (1.30 mmol) of I, and ~3 mL of dry CS_2. The mixture was allowed to warm slowly to room temperature and then stirred overnight. Removal of the volatile materials at room temperature left an oily residue in the reaction flask, which was then extracted with 5 mL of methylene chloride and filtered through a short plug (~5 cm) of silica gel. Solvent was removed under high vacuum to afford 0.196 g (0.89 mmol, 68.4%) of a slightly yellow, viscous oily liquid, *closo*-5-Br-2,3-$Et_2C_2B_5H_4$ (VII). Exact mass measurement for $^{12}C_6{}^{11}B_5{}^{81}Br_1{}^1H_{14}$: calcd, 222.072; found, 222.076.

Reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with Bromine. In a similar experiment, 0.162 g (1.15 mmol) of I and 0.342 g (2.14 mmol) of Br_2 were combined in 3 mL of CS_2 in vacuo. After the mixture was stirred for 20 h at room temperature, the flask was attached to the vacuum line and the volatile materials were removed. Workup similar to that described above yielded 0.134 g (0.609 mmol, 53.0%) of VII.

Reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with $Li(BEt_3)H$ and $(CH_3)_4NCl$. In a typical reaction, 0.171 g (1.21 mmol) of I, ~1.4 mmol of $Li(BEt_3)H$ (1.4 mL of a 1 M THF solution), and 0.136 g (1.24 mmol) of $(CH_3)_4NCl$ were combined in 5 mL of THF in vacuo. The reaction mixture was warmed slowly to room temperature and was allowed to stir for 24 h. The resulting solution was then filtered under a blanket of argon and LiCl removed. Solvent and Et_3B were evaporated from the filtrate under high vacuum to give a white powdery solid. Recrystallization from methylene chloride/octane at -10 °C afforded 0.143 g (0.66 mmol, 54.5%) of pure $(CH_3)_4N^+$[*nido*-3,4-$Et_2C_2B_5H_6$]$^-$ [$(CH_3)_4N$(VIII)]. Anal. Calcd for $C_{10}N_1B_5H_{28}$: C, 55.51; H, 13.04; N, 6.47. Found: C, 55.15; H, 13.09; N, 6.09. Similar reactions utilizing NaH did not result in hydride addition, and only starting materials were recovered.

Attempted Protonation of *nido*-3,4-$Et_2C_2B_5H_6^-$. All attempts to protonate the anion were unsuccessful. For example, reaction of 0.229 g (1.06 mmol) of $(CH_3)_4N$(VIII) with 1.5 mmol of anhydrous HCl in methylene chloride at -45 °C yielded only the neutral carborane I, 0.126 g (0.89 mmol, 84.0%). Similar reactions with anhydrous HCl in a number of solvents at temperatures as low as -78 °C carried out directly in the NMR probe gave no indication of products other than I.

Reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with Me_3P. Into an NMR tube equipped with a vacuum stopcock were charged 0.072 g (0.51 mmol) of

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I, 0.040 g (0.55 mmol) of Me_3P, and ~1 mL of C_6D_6. The tube was sealed, warmed to room temperature, and placed in the NMR instrument. The ^{11}B NMR spectrum of the reaction mixture clearly showed that a reaction had occurred by the appearance of four new doublets in a 1:1:2:1 pattern attributed to the *nido*-6-Me_3P-3,4-$Et_2C_2B_5H_5$ (IX) adduct. Removal of the volatile materials from the reaction tube resulted in conversion of the new species back to I. It was additionally noted that the resonances associated with the spectrum of I were always present in the ^{11}B NMR spectrum of IX at approximately a 5% level. This was true even in the presence of a 50-fold excess of Me_3P.

In low-temperature experiments carried out in the NMR instrument, it was found that reaction between Me_3P and I in THF occurred at temperatures as low as -40 °C. Other Lewis bases were examined for their ability to form similar adducts with I, and it was found that pyridine formed an adduct with I at low temperature but that this species decomposed on warming to room temperature. Trimethylamine gave no reaction with I at temperatures below 100 °C, and at higher temperatures, >140 °C, cage degradation and the formation of $(CH_3)_3N\cdot BH_3$ was observed.

Reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with Et_3N. In a similar reaction, a sealed NMR tube containing 0.049 g (0.35 mmol) of I and 0.5 mL of Et_3N was monitored by ^{11}B NMR spectroscopy. No reaction was observed below 140 °C. After the tube was heated in an oven at 140–150 °C for 8 h, a small amount of white solid had formed in the tube. The ^{11}B NMR spectrum exhibited, in addition to peaks associated with I, new peaks corresponding to the degradation products *nido*-2,3-$Et_2C_2B_4H_6$ and $Et_3N\cdot BH_3$. After ~1 week of heating at 160–190 °C, most of the *closo*-2,3-$Et_2C_2B_5H_5$ had been consumed and the ^{11}B NMR spectrum showed mainly degradation products.

Reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with $Et_3N\cdot BH_3$ at 190 °C. Into a 25-mL break-seal tube was syringed 1.43 g (12.4 mmol) of $Et_3N\cdot BH_3$. The tube was frozen at -196 °C, and 0.295 g (2.09 mmol) of I was condensed in. The tube was then sealed and heated in an oven at ~190 °C for 12 h. Fractionation of the volatile materials through -5, -45, and -196 °C trap series afforded 0.290 g of clear liquid stopping at -45 °C. GC/MS of this material showed the mixture to consist of I, II, and III in a 1:0.8:0.7 ratio. The -5 °C trap contained, in addition to unreacted $Et_3N\cdot BH_3$, small amounts of higher carboranes including $Et_2C_2B_8H_8$, *m/e* 178, and $Et_2C_2B_{10}H_{10}$, *m/e* 202, as determined by GC/MS.

Reaction of *closo*-2,4-$Et_2C_2B_5H_5$ with $Et_3N\cdot BH_3$. An NMR tube containing 0.022 g (0.16 mmol) of VI and 0.047 g (0.41 mmol) of $Et_3N\cdot BH_3$ was placed in an oven and the ^{11}B NMR spectrum monitored periodically as the temperature was increased. It was found that at <300 °C no reaction was observed. VI was recovered quantitatively after heating at 250 °C for 2 days.

Results and Discussion

Synthetic Routes to *closo*-2,3-$Et_2C_2B_5H_5$. An attractive starting material for the synthesis of *closo*-2,3-$R_2C_2B_5H_5$ is the small *nido*-carborane 2,3-$R_2C_2B_4H_6$. The compound can be synthesized in large amounts and in reasonable yields.[7] It has a pentagonal-pyramidal structure containing an open face with adjacent carbons; therefore, a BH insertion into this open face would yield the *closo*-carborane directly. As presented in the Experimental Section, we have now developed three synthetic methods for the preparation of *closo*-2,3-$Et_2C_2B_5H_5$, starting with either the neutral carborane *nido*-2,3-$Et_2C_2B_4H_6$ or its mono- or dianions, $Et_2C_2B_4H_5^-$ or $Et_2C_2B_4H_4^{2-}$.

Thermal Expansions. As shown in eq 1–3, thermally induced capping reactions of neutral polyhedral boranes, carboranes and heteroboranes employing either Lewis base-borane adducts or diborane(6) as expansion reagents, have previously been shown to be an effective route to cage-expanded species.

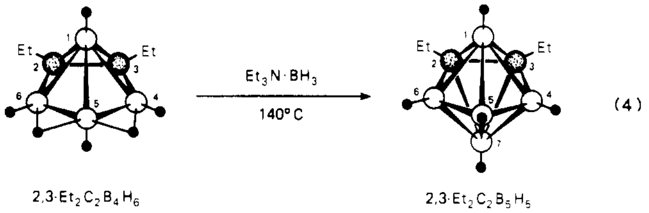
$$B_{10}H_{14} + 2Et_3N\cdot BH_3 \rightarrow [(Et_3NH)_2]^{2+}[closo\text{-}B_{12}H_{12}]^{2-} \quad (1)^{12}$$

$$closo\text{-}1,7\text{-}C_2B_6H_8 + 0.5B_2H_6 \rightarrow closo\text{-}1,6\text{-}C_2B_7H_9 + H_2 \quad (2)^{13}$$

$$arachno\text{-}9\text{-}L\text{-}6\text{-}SB_9H_{11} + Et_3N\cdot BH_3 \rightarrow [Et_3NH]^+[nido\text{-}SB_{10}H_{11}]^- \quad (3)^{14}$$

Similar reactions of diborane(6) with *nido*-2,3-$Et_2C_2B_4H_6$ could also be envisioned as a pathway to I; however, Onak[15] has previously examined the reaction of *nido*-2,3-$C_2B_4H_8$ with B_2H_6 at 220 °C and found that, due to the rapid decomposition of diborane(6) at these temperatures, no cage-expanded species are produced. These results suggested that a base–borane that could provide a stabilized source of borane at elevated temperatures might be a more suitable expansion reagent.

The reaction of *nido*-2,3-$Et_2C_2B_4H_6$ with $Et_3N\cdot BH_3$ at 140 °C was found to result in a one-boron expansion, producing, as the only cage expanded product, *closo*-2,3-$Et_2C_2B_5H_5$ (I). The reaction, as shown in eq 4, results in the capping of the open pentagonal face of the *nido*-carborane by a BH group derived from the amine–borane.



(4)

In a typical experiment, reaction 2.88 mmol of *nido*-2,3-$Et_2C_2B_4H_6$ with 14.3 mmol of $Et_3N\cdot BH_3$ for 48 h produced 1.49 mmol (51.7% yield) of I. The pure carborane is obtained by reaction of the product mixture, which typically contains unreacted *nido*-2,3-$Et_2C_2B_4H_6$, with NaH. I is then isolated from the involatile salt, Na^+[*nido*-2,3-$Et_2C_2B_4H_5$]$^-$ by vacuum distillation and purified by simple fractionation.

It was found that sharply decreased yields of *closo*-2,3-$Et_2C_2B_5H_5$ were obtained when reactions were continued for longer times (~10 days) or when liberated Et_3N was not removed from the reaction flask. These results suggested that the closo system was somewhat unstable in the presence of Et_3N under the reaction of conditions. A control experiment showed that continuous heating of a sample of I with Et_3N at 140–190 °C resulted in complete cage degradation and formation of *nido*-2,3-$Et_2C_2B_4H_6$, $Et_3N\cdot BH_3$, and other unidentified degradation products. Therefore, it is necessary to periodically (typically every 8 h) remove the triethylamine that is evolved during the reaction in order to achieve good yields.

A variety of different Lewis base borane adducts were examined for use as expansion reagents. It was found that weak adducts such as $(CH_3)_2S\cdot BH_3$ decomposed at lower temperatures than are needed to effect cage expansion.[16] When stronger Lewis base adducts than $Et_3N\cdot BH_3$ were used, e.g. $(n\text{-}Bu)_3P\cdot BH_3$, small amounts of I could be isolated but reaction rates were extremely slow. Thus, it appears that the $Et_3N\cdot BH_3$ adduct supplies the correct balance of stability and enhancement of hydridic character of the borane hydrogens to effect cage expansion.

Confirmation of the amine–borane as the source of a BH-capping unit was obtained from reactions employing $Et_3N\cdot ^{10}BH_3$. The boron NMR data for the product clearly indicate ^{10}B enrichment exclusively at the apical positions. Thus, as shown in Figure 1a, the ^{11}B NMR spectrum of an isotopically normal sample of I gives the expected three resonances in a 2:1:2 ratio for the B4,6, B5, and B1,7 borons, respectively, while the isotopically enriched species (Figure 1b) gives a 2:1:1.2 intensity pattern consistent with an ^{11}B content of ~15–20% for one of the apical positions. Similarly the ^{10}B spectrum (Figure 1c) for the enriched species exhibits a 2:1:5.1 pattern, consistent with the presence of ~75–80% of ^{10}B at one apical position.

Since the ^{10}B enrichment is highly concentrated at the apical positions and the carbon atoms remain in adjacent positions, the insertion process occurs with no major rearrangement of the carborane framework. This is probably a consequence of the mild

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(14) Hertler, W. R.; Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1967**, *6*, 1696–1706.

(15) Fung, A. P.; DiStefano, E. W.; Fuller, K.; Siwapinyoyos, G.; Onak, T.; Williams, R. E. *Inorg. Chem.* **1979**, *18*, 372–376.

(16) Pyrolysis of $(CH_3)_2S\cdot BH_3$ at temperatures above 70 °C results in the formation of higher cage species, including $B_{12}H_{10}(SMe_2)_2$. See, for example, Miller et al. (Miller, H. C.; Miller, N. E.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1456–1463) for the pyrolysis of $(CH_3)_2S$ with B_2H_6.

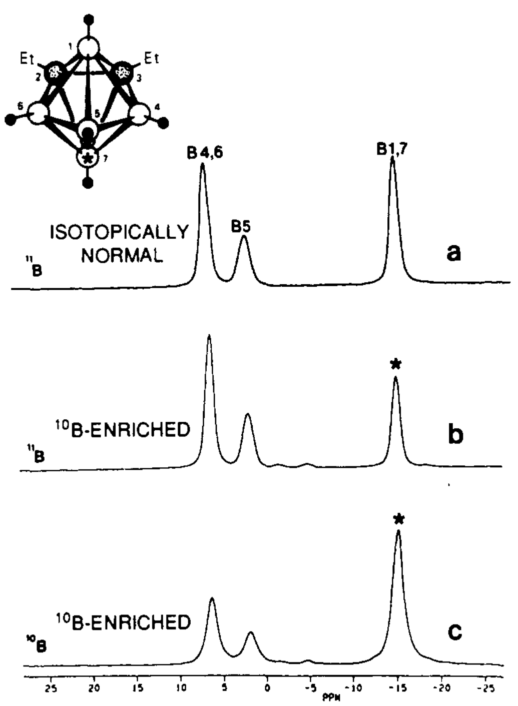

Figure 1. (a) 64.2-MHz $^{11}B\{^1H\}$ NMR spectrum of *closo*-2,3-$Et_2C_2B_5H_5$ (I). (b) 64.2-MHz $^{11}B\{^1H\}$ NMR spectrum of [1-^{10}B]-*closo*-2,3-$Et_2C_2B_5H_5$. (c) 21.5-MHz $^{10}B\{^1H\}$ NMR spectrum of [1-^{10}B]-*closo*-2,3-$Et_2C_2B_5H_5$.

reaction conditions, and indeed, Onak[15] has previously shown that the reaction of *nido*-2,3-$C_2B_4H_8$ with $^{10}BMe_3$ at significantly higher temperatures, ~244 °C, results in formation of the permethylated species *closo*-1,3,5,6,7-2,4-$Me_5C_2B_5H_2$, in which the incorporation of ^{10}B is only slightly enhanced at the 1,7-positions. Thus, the temperatures required for expansion with $^{10}BMe_3$ are in the vicinity of those needed to cause separation of the cage carbon atoms, as well as apical/equatorial boron exchange, and this results in the isolation of a ^{10}B scrambled compound. We also found, as discussed below, that I undergoes cage rearrangement at higher temperature (320 °C) to produce the nonadjacent-carbon isomer, VI. Likewise, thermolysis of a ^{10}B-enriched sample of I at 320 °C led to the formation of an isotopically scrambled 2,4-molecule with little evidence of localization of ^{10}B at any particular position. Extensive scrambling of an inserted boron during isomerization is consistent with a complex mechanism of isomerization. A model for the cage rearrangement process in the *closo*-$C_2B_5H_7$ carborane has recently been proposed by McKee.[3e] This model predicts that the isomerization of I to VI proceeds over two square-capped-prism transition states, necessitating two 90° local bond rotations.

Although there are now several known examples of cage expansion with Lewis base–borane complexes or diborane(6), there are little mechanistic data for the expansion process. Expansion of *nido*-2,3-$Et_2C_2B_4H_6$ with $Et_3N{\cdot}BH_3$ could occur, as shown in Figure 2, through initial bridge substitution of a $Et_3N{\cdot}BH_2$ unit with the evolution of 1 equiv of hydrogen, followed by subsequent loss of an additional 1 equiv of H_2 and dissociation of Et_3N to effect cage closure. Indeed, Wallbridge[17] has shown that the boron-bridged compound *nido*-μ-4,5-Me_2B-2,3-$Me_2C_2B_4H_5$ is thermally unstable above 0 °C decomposing to Me_3B and various carborane species including a B–Me derivative of *closo*-2,3-$Me_2C_2B_5H_5$. Likewise, we have demonstrated a similar bridge-insertion cage-expansion pathway in the reactions of *nido*-2,3-$Et_2C_2B_4H_6$ with $Et_3N{\cdot}AlH_3$,[18] in which the initially isolated bridging species *nido*-4,5-μ-$AlH_2{\cdot}NEt_3$-2,3-$Et_2C_2B_4H_5$, analogous to the proposed boron-bridging intermediate *nido*-4,5-μ-$BH_2{\cdot}NEt_3$-2,3-$Et_2C_2B_4H_5$ (Figure 2), was subsequently found to eliminate H_2 to produce the cage-expanded seven-vertex species *nido*-6-$AlH{\cdot}NEt_3$-3,4-$Et_2C_2B_4H_4$. Both the mild reaction conditions and the Lewis acidity of the cage-inserted aluminum atom result in the retention of the Et_3N substituent at the aluminum center. In contrast, the higher reaction temperatures and lower acidity of the cage-inserted boron atom results in dissociation of the amine and effects complete cage closure to produce *closo*-2,3-$Et_2C_2B_5H_5$.

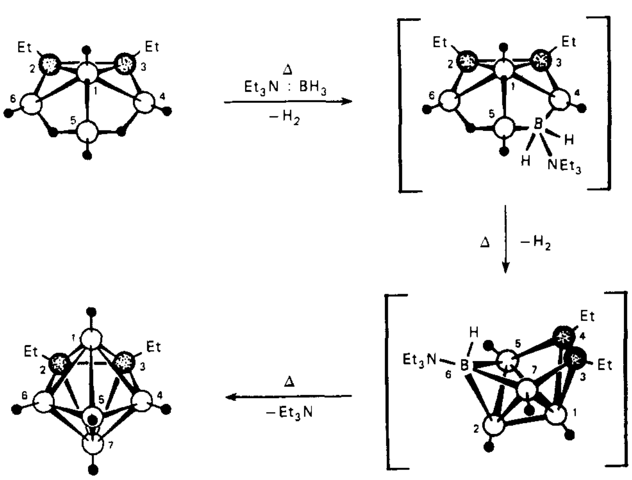

Figure 2. Possible mechanism of thermal cage-expansion of *nido*-2,3-$Et_2C_2B_4H_6$ with $Et_3N{\cdot}BH_3$.

Reaction of *nido*-2,3-$Et_2C_2B_4H_6$ with $Et_3N{\cdot}BH_3$ at 170 °C resulted in the isolation of *closo*-2,3-$Et_2C_2B_5H_5$ and two additional expansion products, *closo*-1,7-$Et_2C_2B_6H_6$ and *closo*-1,7-$Et_2C_2B_7H_7$, corresponding to a two-boron and a three-boron expansion, respectively. Since it is known, for example, that *closo*-1,7-$C_2B_6H_8$ reacts with B_2H_6 to form *closo*-1,7-$C_2B_7H_9$,[13] it is possible that expansion with base–boranes also follows a sequential insertion process. However, the possibility that Lewis base degradation of the *closo*-2,3-$Et_2C_2B_5H_5$ framework at these temperatures results in the formation of reactive lower carborane fragments, which can subsequently add one or more BH units, cannot be ruled out.

Anionic Expansions. The thermal reactions of Lewis base–boranes with *nido*-2,3-$Et_2C_2B_4H_6$ afford a viable pathway to the *closo*-2,3-$Et_2C_2B_5H_5$ cage system; however, the problems associated with attack of free amine on the closo product suggested that milder reaction conditions for the expansion process should be explored. Shore[19] has previously shown that a *nido*-borane anion can react with diborane(6) to afford cage-expanded species. As shown in eq 5, the reaction of LiB_5H_8 with B_2H_6 results in

$$LiB_5H_8 + B_2H_6 \xrightarrow{Me_2O} B_6H_{10} + LiBH_4 \qquad (5)$$

a one-boron expansion and production of hexaborane(10).[19b] Thus, bridge deprotonation of the *nido*-borane creates a basic site into which the electrophilic BH_3 group may insert. This type of reaction has recently been extended to the *nido*-2,3-$R_2C_2B_4H_6$ cage system where Shore has shown that the reaction of [*nido*-2,3-$(Si(CH_3)_3)_2$-2,3-$C_2B_4H_5]^-$ with pentaborane(9) results in a four-boron expansion, producing the carborane *arachno*-6-Si-$(CH_3)_3$-6,9-$C_2B_8H_{13}$.[20]

In a similar manner, the reaction of Li^+[*nido*-2,3-$Et_2C_2B_4H_5]^-$ with 2 equiv of $(CH_3)_2S{\cdot}BH_3$ in hexane solvent was found to result in the formation of I in approximately 40% yield.

$$Li^+[nido\text{-}2,3\text{-}Et_2C_2B_4H_5]^- + 2(CH_3)_2S{\cdot}BH_3 \rightarrow closo\text{-}2,3\text{-}Et_2C_2B_5H_5 + LiBH_4 + 2(CH_3)_2S \qquad (6)$$

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(17) (a) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc. D* **1971**, 622–623. (b) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1972**, 918–923.

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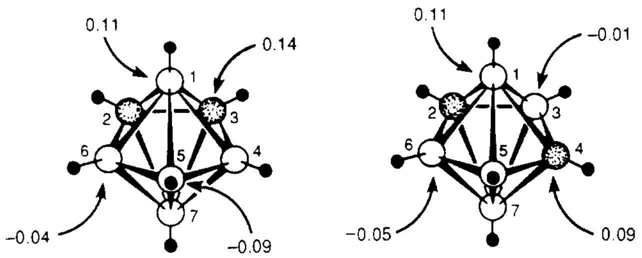
Chart II



We also found that similar reactions between $Na^+[nido\text{-}2,3\text{-}Et_2C_2B_4H_5]^-$ and BH_3·THF produced only trace amounts of I and resulted in the formation of neutral *nido*-2,3-$Et_2C_2B_4H_6$; thus, the nature of the base–borane adduct, as noted for the thermal expansions, plays a crucial role in effecting BH insertion. Although the yields of this reaction are lower than those obtained in the thermal expansions, the experimental procedure is more convenient in that reaction times are faster and, since I is unreactive toward $(CH_3)_2S$ under these conditions, removal of free $(CH_3)_2S$ is unnecessary.[21]

Several recent reports by Hosmane[11] have shown that the dianion of *nido*-2,3-$R_2C_2B_4H_6$ can be reacted with a variety of dihalogenated main-group complexes resulting in simple metathesis and formation of cage-inserted species. These results suggested that reaction of the dianion $Na^+Li^+[nido\text{-}2,3\text{-}Et_2C_2B_4H_4]^{2-}$ with dihaloboranes might be a useful pathway for the synthesis of I. Hawthorne has in fact previously reported a cage expansion of this type for the dianion of the C_2B_9 cage system:[22]

$$1,2\text{-}C_2B_9H_{11}^{2-} + PhBCl_2 \rightarrow 3\text{-}Ph\text{-}1,2\text{-}C_2B_{10}H_{11} + 2NaCl \quad (7)$$

As shown in eq 8 and 9, the reaction of $Na^+Li^+[nido\text{-}2,3\text{-}Et_2C_2B_4H_4]^{2-}$ with $(CH_3)_2S$·$BHBr_2$ or RBX_2 (R = Ph, Me; X = Br, Cl) resulted in the formation of the corresponding cage expansion products, I, *closo*-1-Ph-2,3-$Et_2C_2B_5H_4$ (IV), and *closo*-1-Me-2,3-$Et_2C_2B_5H_4$ (V), in yields of 49%, 41%, and 46%, respectively. In all cases, the pure compounds were obtained by vacuum fractionation. The ^{11}B NMR spectra of the B-substituted compounds IV and V each contain four resonances in a 2:1:1:1 pattern, with the singlets centered at ~5 ppm, consistent with the compounds being apically substituted derivatives of I. In addition to resonances assigned to the equivalent carborane ethyl groups, the ^1H NMR spectra of both compounds display appropriate resonances for their B-substituted substituents (IV, BPh, 6.95 ppm; V, BMe, -0.59 ppm).

$$Na^+Li^+[nido\text{-}2,3\text{-}Et_2C_2B_4H_4]^{2-} + (CH_3)_2S\cdot BHBr_2 \xrightarrow{THF} closo\text{-}2,3\text{-}Et_2C_2B_5H_5 + NaBr + LiBr + (CH_3)_2S \quad (8)$$

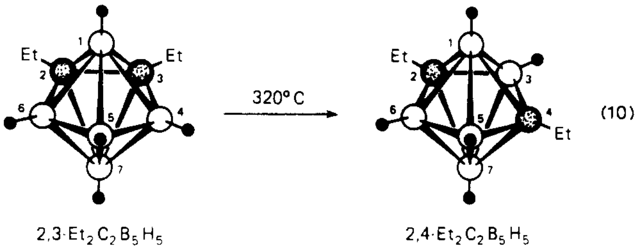
$$Na^+Li^+[nido\text{-}2,3\text{-}Et_2C_2B_4H_4]^{2-} + RBX_2 \xrightarrow{THF} closo\text{-}1\text{-}R\text{-}2,3\text{-}Et_2C_2B_5H_4 + NaX + LiX \quad (9)$$

$$R = Ph,\ Me;\ X = Br,\ Cl$$

Reactivity of *closo*-2,3-$Et_2C_2B_5H_5$. The chemistry of the nonadjacent-carbon isomer *closo*-2,4-$R_2C_2B_5H_5$ has previously been explored in detail, including studies of its reactivity toward electrophilic and nucleophilic reagents, as well as framework rearrangement and polymerization reactions.[23] Although both the 2,3- and 2,4-isomers of *closo*-$R_2C_2B_5H_5$ are expected to exhibit similar pentagonal-bypyramidal geometries, the location of the cage carbon atoms, in either adjacent or nonadjacent equatorial positions, influences the electronic density distribution in these molecules. As shown in Chart II, population analysis calculations[3] for these carboranes indicate that the equatorial positions have the highest electron densities, while the apical borons are positively charged.

These calculations predict that electrophilic attacks should occur at the equivalent 5,6-positions of the 2,4-isomer, consistent with the observed formation of *closo*-5-Br-2,4-$C_2B_5H_6$ upon reaction of *closo*-2,4-$C_2B_5H_7$ with either Br_2 or $Br_2/AlBr_3$.[23,24] In *closo*-2,3-$C_2B_5H_7$, the unique boron, B5, on the equatorial plane is predicted to be the preferential site for electrophilic attack,[3] and indeed it was found that halogenation with either Br_2 or $Br_2/AlBr_3$ resulted in the isolation of a single product that was identified on the basis of its spectral data as *closo*-5-Br-2,3-$Et_2C_2B_5H_4$ (VII).

The electronic density distributions in these cage systems also influence their thermodynamic stabilities. Molecular orbital studies predict that the nonadjacent-carbon isomer *closo*-2,4-$C_2B_5H_7$, having greater charge delocalization, should be energetically preferred with respect to the 2,3-isomer.[3] Indeed, thermolysis (Eq 10) of the 2,3-isomer at 320 °C in the gas phase resulted in the production of *closo*-2,4-$Et_2C_2B_5H_5$ in high yield (81%). The 2,3-isomer is completely consumed in this reaction, and the resulting 2,4-product is purified by vacuum line fractionation. Thus, the isomerization reaction provides a convenient, selective synthetic route to the 2,4-isomer.



(10)

The *closo*-2,3-$C_2B_5H_7$ isomer is also predicted to have a significantly higher dipole moment than the *closo*-2,4-isomer (2,4-isomer, μ_{calcd} (D) = 2.36,[3b] 1.24,[3c] 1.77,[3f] μ_{obsd} = 1.32;[25] 2,3-isomer, μ_{calcd} = 6.32,[3b] 3.04[3c]) and, therefore, should be particularly susceptible to attack by polar reagents. Addition of a two-electron nucleophile to the *closo*-$R_2C_2B_5H_5$ cage system should result in the production of an 18-electron, $n + 2$, open-cage nido species. The use of nucleophilic reagents to effect cage opening of small *closo*-carboranes has previously been reported by Onak.[23,26] It was shown, for example, that *closo*-1,6-$C_2B_4H_6$ slowly reacts with NaH or LiH to produce the nido species 2,4-$C_2B_4H_7^-$ or with $(CH_3)_3N$ to form the dipolar adduct 5-$(CH_3)_3N^+[nido\text{-}2,4\text{-}C_2B_4H_6]^-$. However, the reaction of *closo*-2,4-$R_2C_2B_5H_5$ with nucleophilic reagents such as Me_3N or $Li(BEt_3)H$ failed to yield any isolable cage opened products.[27] By contrast, we have found that the adjacent 2,3-isomer is highly susceptible to polar attack. As shown in eq 11, reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with a slight molar excess of $Li(BEt_3)H$ and 1 equiv of $(CH_3)_4NCl$ results in the formation of $(CH_3)_4N^+[nido\text{-}3,4\text{-}Et_2C_2B_5H_6]^-$ [$(CH_3)_4N$(VIII)].

$$closo\text{-}2,3\text{-}Et_2C_2B_5H_5 + Li(BEt_3)H + (CH_3)_4NCl \xrightarrow[\text{room temp}]{THF} (CH_3)_4N^+[nido\text{-}3,4\text{-}Et_2C_2B_5H_6]^- + LiCl + BEt_3 \quad (11)$$

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(21) We have found that *closo*-2,3-$Et_2C_2B_5H_5$ is unreactive toward $(CH_3)_2S$ at temperatures up to 150 °C.

(22) (a) Hawthorne, M. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 4392–4393. (b) Hawthorne, M. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 896–901.

(23) For a review of the chemistry of *closo*-2,4-$R_2C_2B_5H_5$ see: (a) Onak, T. *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: Deerfield Beach, FL, 1988; Chapter 7. (b) Onak, T. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 1, Chapter 5.4. (c) Onak, T. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; Chapter 10.

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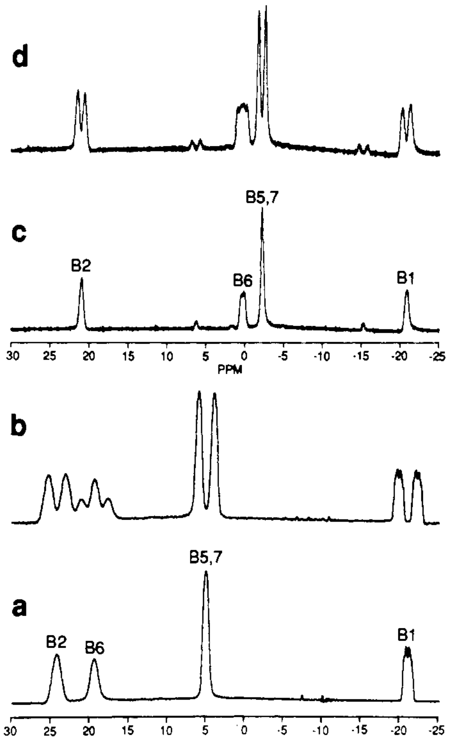

Figure 3. (a) 64.2-MHz $^{11}B\{^1H\}$ NMR spectrum of [*nido*-3,4-$Et_2C_2B_5H_6]^-$ (VIII). (b) ^1H-coupled spectrum of VIII. (c) 160.5 MHz $^{11}B\{^1H\}$ NMR spectrum of *nido*-6-Me_3P-3,4-$Et_2C_2B_5H_5$ (IX). (d) ^1H-coupled spectrum of IX.

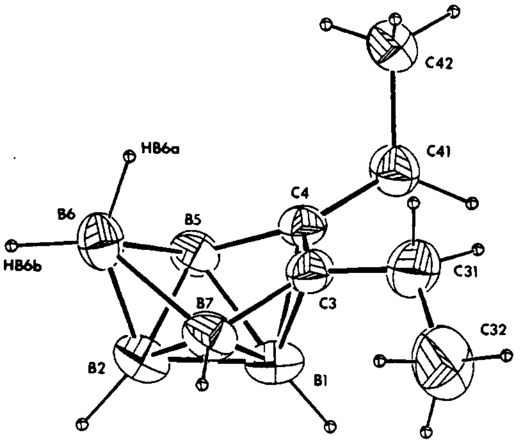

Figure 4. ORTEP drawing of the molecular structure of [*nido*-3,4-$Et_2C_2B_5H_6]^-$ (VIII).

The 64.2-MHz ^{11}B NMR spectrum (Figure 3a) of VIII shows four resonances in a 1:1:2:1 area ratio consistent with the existence of a molecular mirror plane. Furthermore, the peak at 19.3 ppm appears as a triplet in the ^1H-coupled spectrum (Figure 3b) indicating that the addition of hydride has produced a $-BH_2$ group rather than a more commonly observed B–H–B bridging-hydrogen structure. It should also be noted that the peak assigned to B1 shows quartet coupling (J_{BB} = 26 Hz) resulting from strong interaction with another boron (B2) in the cage. A single-crystal X-ray structural determination[28] of the compound has confirmed these structural features and demonstrated that the anion adopts a nido geometry consistent with its 18 skeletal-electron count. Thus, as shown in the ORTEP drawing in Figure 4, the structure of the anion is based on a dodecahedron missing one five-connected vertex and is the first 18-electron seven-vertex nido boron cluster for which this geometry has been conclusively demonstrated. VIII is additionally one of the few examples of a polyhedral borane containing an isolated $-BH_2$ group with no proximal bridging hydrogens. Shore has also established the presence of a $-BH_2$ moiety of this type in the recently determined structure of $B_{11}H_{14}^-$.[29]

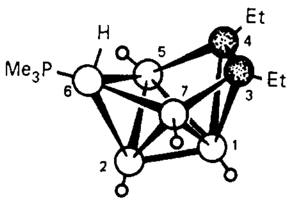

Figure 5. Proposed structure of *nido*-6-Me_3P-3,4-$Et_2C_2B_5H_5$ (IX).

Seven-vertex nido-cage systems are known for borazine (e.g. $(\eta^6\text{-}B_3N_3Et_6)Cr(CO)_3)$[30,31] and boracycle transition-metal complexes (e.g. $(\eta^6\text{-}C_5H_5BPh)Mn(CO)_3)$[30,32] as well as for isoelectronic π-arene systems (e.g. $(\eta^6\text{-}C_6H_6)Cr(CO)_3)$.[33] In contrast to the structure observed for VIII, these metal complexes exhibit structures based on a hexagonal pyramid. A limited number of 18-electron seven-vertex clusters have also been found among boranes and carboranes containing heteroatoms, and these have been shown or predicted to exhibit a variety of structures.[34] The dimetallaheptaborane *nido*-$(\eta^5\text{-}C_5Me_5)_2Co_2B_5H_9$[35] has been proposed to exhibit a structure based on a dodecahedron missing one four-connected vertex, while the aluminacarborane *nido*-6-$AlH\cdot NEt_3$-3,4-$Et_2C_2B_4H_4$[18] and silacarborane $(Me_3Si)(Me)C_2B_4H_4SiH_2$[11] are predicted to have gross geometries similar to that observed for VIII. Other variations in this geometry may be possible. Indeed, Onak[23,36] has reported that reaction of the 3-Cl or 5-Cl derivatives of *closo*-2,4-$C_2B_5H_7$ with tertiary amines leads to the formation of 1:1 adducts, i.e. $(CH_3)_3N\cdot ClC_2B_5H_6$, which are proposed, on the basis of NMR data, to exhibit some degree of both closo and nido character.

It is also important to note that several seven-vertex heteroboranes and carboranes having *formal* 16-electron closo electron counts have been found to exhibit structures closely related to that observed for VIII. Examples of such molecules include the osmaplatinaborane $[(Ph_3P)_2(CO)\overline{Os(PhMe_2Ph)(ClHPt}B_5H_7)]$ reported by Bould[37] and the isoelectronic platinacarborane 1,2,3-$(Et_3P)_2PtMe_2C_2B_4H_4$ prepared by Stone.[38] Hosmane has also reported several examples of distorted closo seven-vertex systems, including 1-Sn-2-$[Si(CH_3)_3]$-2,3-$C_2B_4H_5$[39] and 1-Sn-$[C_{10}H_8N_2]$-2,3-$[Si(CH_3)_3]_2$-2,3-$C_2B_4H_4$[39,40] and has recently re-

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(34) Several review articles have discussed nido seven-vertex cage systems. See, for example: (a) Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, *32*, 519–679. (b) Greenwood, N. N. *Chem. Soc. Rev.* **1984**, *13*, 353–374. (c) Greenwood, N. N. *Pure Appl. Chem.* **1983**, *55*, 1415–1430. (d) Grimes, R. N. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 1, Chapter 5.5. (e) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987; Chapters 3 and 4.

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viewed the structures and bonding in these and related carboranes containing group 13 and 14 heteroatoms.[41]

The X-ray results for *nido*-3,4-$Et_2C_2B_5H_6^-$, which confirm that the cage carbons remain adjacent, in conjunction with the mild reaction conditions leading to the formation of the anion support a cage-opening process involving no major rearrangement of the *closo*-2,3-$Et_2C_2B_5H_5$ skeletal framework. Such a process resulting in the formation of the five-membered open face requires that hydride add exclusively at one of the apical (B1,7) positions and be accompanied by the opening of a triangular C–B–C face. These conclusions are also consistent with calculations[3a-d] of the ground-state charges in *closo*-2,3-$C_2B_5H_7$ which indicate that the apical borons are the only positively charged borons in the molecule and would, therefore, be the sites of nucleophilic attack.

A similar cage opening can be effected with a strong nucleophile such as Me_3P. Thus, as shown in eq 12, reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with Me_3P results in cage opening and production of

$$\text{excess } Me_3P + closo\text{-}2,3\text{-}Et_2C_2B_5H_5 \rightarrow \underset{\text{IX}}{nido\text{-}6\text{-}Me_3P\text{-}3,4\text{-}Et_2C_2B_5H_5} \quad (12)$$

the *neutral* seven-vertex species *nido*-6-Me_3P-3,4-$Et_2C_2B_5H_5$ (IX). The 64.2-MHz ^{11}B NMR spectrum (Figure 3d) of IX is similar to that of VIII, consisting of four doublets in a 1:1:2:1 area ratio. Upon ^1H decoupling (Figure 3c), the resonance at 0.0 ppm shows ^{31}P coupling (J_{BP} = 43 Hz), consistent with previous measurements of ^{31}P–^{11}B coupling in phosphine–borane adducts.[42] The ^{11}B–^{11}B two-dimensional NMR spectrum of IX exhibits all cross-peaks expected for the proposed seven-vertex nido geometry shown in Figure 5. The ^1H NMR spectrum in excess Me_3P shows, in addition to the equivalent cage ethyl resonances, a doublet at 0.79 ppm (J_{PH} = 2.9 Hz) for free Me_3P and an additional doublet at 0.46 ppm (J_{PH} = 11.2 Hz) for cage-bound Me_3P. As indicated in the Experimental Section, attempts to isolate IX as a discreet species resulted in loss of the Me_3P ligand and reversion to I, suggesting that a base-mediated closo–nido equilibrium exists. Additionally, I could not be completely converted to IX even in the presence of a large excess of Me_3P. Several other nucleophilic reagents were examined for their ability to effect cage-opening of the *closo*-2,3-$Et_2C_2B_5H_5$ framework. Amine bases such as Me_3N or C_5H_5N caused extensive cage degradation as evidenced by the appearance of an amine–borane resonance in the ^{11}B NMR spectrum of product mixtures.

In summary, we have reported new, viable synthetic routes to the *closo*-2,3-$R_2C_2B_5H_5$ cage system based on cluster expansion reactions of *nido*-2,3-$Et_2C_2B_4H_6$ utilizing Lewis base–borane adducts. These routes have allowed the production of *closo*-2,3-$Et_2C_2B_5H_5$ in sufficient quantities to begin an examination of its chemistry. In view of the unusual susceptibility of this closo system to attack by polar reagents, a wide range of further cage-opening and cage-expansion chemistry should be possible. We are currently exploring these possibilities as well as examining the extension of cluster growth reactions employing Lewis acid–base adducts to a variety of borane, carborane, and heteroatom systems.

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Synthesis and Characterization of Amine–Alkylcyanoboranes

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Synthetic methods for the conversion of alkyltrihydroborates to amine–alkylcyanoboranes have been developed. The most efficient of these is cyanation of the alkyltrihydroborates with mercuric cyanide to give the corresponding alkylcyanodihydroborates. These stable salts, when treated with 1 equiv of HCl in diethyl ether, followed by addition of an amine, produce the amine–alkylcyanoboranes (amine = Me_3N, py, TMED, quinuclidine; alkyl = methyl, benzyl, *sec*-butyl, isobutyl) in moderate yield. The new amine–alkylcyanoboranes are thermally, oxidatively, and hydrolytically stable and can be purified by using standard chromatographic methods.

Introduction

Amine-cyanoboranes (**1**, Figure 1) are useful precursors to boron-centered amino acid analogues (**2**). Many of these analogues have been prepared in the last decade.[1] Uppal and Kelly reported the first amine–cyanoboranes in 1970 with the synthesis of the trimethylamine, *p*-methylpyridine, morpholine, and TMED adducts of "BH_2CN".[2] They treated $NaBH_3CN$ with acidified THF to produce "THF·BH_2CN" and then added the desired amine to displace solvent. In 1978, Spielvogel combined their syntheses with the Schaefer and Anderson method for making amine–boranes[3] to produce the cyanoboranes **1** (amine = Me_3N, Me_2NH, $MeNH_2$, NH_3) in a single, high-yield step (eq 1).[4] Another

$$\text{amine}\cdot HCl + NaBH_3CN \rightarrow \mathbf{1} + NaCl + H_2 \quad (1)$$

$$Me_3N\cdot BH_2I + NaCN \rightarrow Me_3N\cdot BH_2CN + NaI \quad (2)$$

$$Na[BH_3CN] \xrightarrow{I_2} [BH_2CH]_n \xrightarrow{\text{amine}} \text{amine}\cdot BH_2CN + NaI \quad (3)$$

method was published in 1974 by Bratt, in which cyanide was introduced by the displacement of iodide (eq 2).[5] Martin et al.

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