

# Reactions of *nido*-2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> with Triethylamine-Alane: Syntheses of New Small Aluminacarboranes

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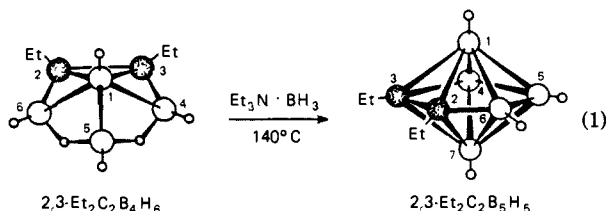
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**Abstract:** The reaction of *nido*-2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> with triethylamine-alane has been studied under various conditions and found to produce three new small cage aluminacarboranes. At 0 °C the reaction results in the elimination of 1 equiv of H<sub>2</sub> and the insertion of a Et<sub>3</sub>NAlH<sub>2</sub> unit into a bridging position at the base of the carborane, producing the *nido*-carborane 4,5- $\mu$ -AlH<sub>2</sub>NEt<sub>3</sub>-2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (I) in high yield. Subsequent heating of I at 50 °C results in the loss of an additional 1 equiv of H<sub>2</sub> and produces the *nido* seven-vertex species 6-AlHNEt<sub>3</sub>-3,4-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (II). Compound II may also be prepared by direct reaction of 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> and Et<sub>3</sub>N·AlH<sub>3</sub> at 50 °C. Reaction of 2 equiv of 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> with Et<sub>3</sub>N·AlH<sub>3</sub> at 70 °C results in the elimination of 3 equiv of H<sub>2</sub> and produces the bis(carboranyl)aluminum species *commo*-AlNEt<sub>3</sub>-[(6-AlNEt<sub>3</sub>-3,4-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)(4',5'- $\mu$ -AlNEt<sub>3</sub>-2',3'-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>)] (III) in good yield. Compound III may also be formed by reaction of II with 1 equiv of 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> at 70 °C.

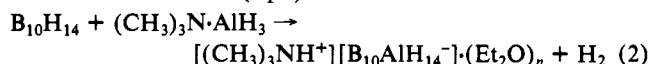
Although the first aluminacarboranes were reported nearly 20 years ago,<sup>1a-d</sup> only recently has there been a systematic attempt<sup>2-6</sup> to develop general synthetic pathways to these molecules. In an ongoing study of main-group heterocarboranes, Hawthorne et al. have synthesized aluminacarborane derivatives of both the C<sub>2</sub>B<sub>6</sub><sup>3</sup> and C<sub>2</sub>B<sub>8</sub><sup>4a,b</sup> cage systems, as well as a bimetallic bis( $\eta^5$ -dicarbollide)aluminum sandwich complex.<sup>5</sup> As a developing class of heteroatom systems, the aluminacarboranes exhibit both unusual structures and bonding modes as well as diverse patterns of reactivity.<sup>1-6</sup> In view of the emerging chemistry of the larger cage systems, aluminum analogues of the smaller carboranes would be expected to be highly reactive, synthetically useful species. However, general synthetic pathways to small aluminacarboranes have not yet been developed. Previous attempts to synthesize such molecules have met with limited success, yielding only the partially characterized, bridge-bound species  $\mu$ -(CH<sub>3</sub>)<sub>2</sub>Al-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>7</sub>.<sup>7</sup>

In a recent communication,<sup>8</sup> we have shown that Et<sub>3</sub>N·BH<sub>3</sub> is an effective reagent for cage expansion of the small *nido*-carborane 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (eq 1). The reaction results in the capping of the



open pentagonal face of the *nido*-carborane by a BH group derived from the amine-borane. The above reaction presumably occurs through an initial bridge substitution<sup>9</sup> of a Et<sub>3</sub>NBH<sub>2</sub> unit with

the evolution of 1 equiv of H<sub>2</sub>, followed by subsequent loss of an additional 1 equiv of H<sub>2</sub> and dissociation of triethylamine to effect cage closure. This result suggested that an aluminum analogue of the base-borane system might effect a similar cage expansion with 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>. Indeed,<sup>10a,b</sup> Greenwood has shown that Me<sub>3</sub>N·AlH<sub>3</sub> is an effective cage-expansion reagent for decarborane(14), forming the aluminaborane anion B<sub>10</sub>AlH<sub>14</sub><sup>-n</sup>Et<sub>2</sub>O under mild conditions (eq 2).



The reactions described herein explore the utility of Et<sub>3</sub>N·AlH<sub>3</sub> as a cage expansion reagent for the small *nido*-carborane 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> and have resulted in the syntheses of three new small aluminacarboranes.

## Experimental Section

All manipulations were carried out by standard high-vacuum or inert-atmosphere techniques as described by Shriver.<sup>11</sup>

**Materials.** Triethylamine-alane (Et<sub>3</sub>N·AlH<sub>3</sub>) and trimethylamine-alane (Me<sub>3</sub>N·AlH<sub>3</sub>) were prepared by the method of Ruff and Hawthorne.<sup>12</sup> The small *nido*-carborane 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> was prepared by a standard literature method.<sup>13</sup> Pentane was dried over P<sub>2</sub>O<sub>5</sub>. Toluene, benzene, and diethyl ether were dried over and distilled from sodium metal.

**Physical Measurements.** <sup>11</sup>B NMR spectra at 160.5 MHz were obtained on a Bruker AM-500 Fourier transform spectrometer. <sup>1</sup>H NMR spectra at 200.1 MHz were obtained on an IBM AF-200 Fourier transform spectrometer. Chemical shifts for <sup>11</sup>B NMR spectra are relative to external BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, with a negative sign indicating an upfield shift. Chemical shifts for <sup>1</sup>H NMR spectra (ppm) are based on 7.15 ppm for C<sub>6</sub>D<sub>6</sub> (relative to Me<sub>4</sub>Si at 0.00 ppm). Unit and high-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1430 infrared spectrophotometer. Elemental analyses were obtained from Schwarzkopf Laboratories, Woodside, NY.

**Synthesis of 4,5- $\mu$ -AlH<sub>2</sub>NEt<sub>3</sub>-2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (I).** In a typical reaction, 211 mg (1.61 mmol) of Et<sub>3</sub>N·AlH<sub>3</sub> was syringed into a 100-mL round-bottomed reaction flask containing a magnetic stirring bar. The flask

(9) The boron-bridged compound  $\mu$ -4,5-Me<sub>2</sub>B-2,3-Me<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> has been shown to be thermally unstable above 0 °C, decomposing to Me<sub>3</sub>B and various carborane species including Me<sub>3</sub>C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>. The latter compound was proposed to be a BMe derivative of *closo*-2,3-Me<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>. See: Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* 1972, 918-923.

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Table I.  $^{11}\text{B}^a$  and  $^1\text{H}^b$  NMR Data

compd	nucleus	$\delta$ (m, $J$ (Hz), relative area, assignment)
I	$^{11}\text{B}^c$	2.5 (d, 110, 1, B4 or B5 or B6), 1.3 (d, $\sim$ 220, 1, B4 or B5 or B6), -0.2 (d, $\sim$ 130, 1, B4 or B5 or B6), -43.6 (d, 175, 1, B1)
	$^1\text{H}^c$	2.47 (m, 4, $\text{CH}_2$ (cage Et)), 2.35 (q, 7.3, 6, $\text{CH}_2$ ( $\text{Et}_3\text{N}$ )), 1.32 (t, 7.8, 3, $\text{CH}_3$ (cage Et)), 1.31 (t, 7.8, 3, $\text{CH}_3$ (cage Et)), 0.65 (t, 7.3, 9, $\text{CH}_3$ ( $\text{Et}_3\text{N}$ )) $^f$
	$^1\text{H}\{^{11}\text{B}\}^c$	4.1 (s, 1, BH4 or BH5 or BH6), 4.0 (s, 1, BH4 or BH5 or BH6), 3.9 (s, 1, BH4 or BH5 or BH6), -0.3 (s, 1, BH1), -2.5 (s, BHB)
II	$^{11}\text{B}^c$	8.2 (d, $\sim$ 125, 1, B2), 6.6 (d, $\sim$ 130, 2, B5,7), -37.1 (d, 168, 1, B1)
	$^1\text{H}^c$	2.70 (q, 7.5, 4, $\text{CH}_2$ (cage Et)), 2.07 (q, 7.3, 6, $\text{CH}_2$ ( $\text{Et}_3\text{N}$ )), 1.43 (t, 7.6, 6, $\text{CH}_3$ (cage Et)), 0.52 (t, 7.3, 9, $\text{CH}_3$ ( $\text{Et}_3\text{N}$ )) $^f$
	$^1\text{H}\{^{11}\text{B}\}^c$	4.3 (s, 1, BH2), 4.1 (s, 2, BH5,7), -0.2 (s, 1, BH1)
III	$^{11}\text{B}^d$	9.0 (d, $\sim$ 2, 120 $^\circ$ ), -1.3 (d, $\sim$ 1, 115 $^\circ$ ), -47.8 (d, $\sim$ 1, 165 $^\circ$ )
	$^1\text{H}^e$	2.66 (m, 7.5, 8, $\text{CH}_2$ (cage Et)), 2.37 (q, 7.2, 6, $\text{CH}_2$ ( $\text{Et}_3\text{N}$ )), 1.53 (t, 7.5, 12, $\text{CH}_3$ (cage Et)), 0.73 (t, 7.4, 9, $\text{CH}_3$ ( $\text{Et}_3\text{N}$ )) $^f$
	$^1\text{H}\{^{11}\text{B}\}^c$	4.1 (s, BH), 3.0 (s, BH), -1.2 (s, BH), -2.3 (s, BHB)

$^a$  160.5 MHz.  $^b$  200.1 MHz.  $^c$   $\text{C}_6\text{D}_6$  solvent.  $^d$  Toluene- $d_8$  solvent.  $^e$  Coupling constants measured at 80  $^\circ\text{C}$  on a 64.2-MHz instrument.  $^f$  For reference:  $^1\text{H}$  NMR spectrum of triethylamine-alane in  $\text{C}_6\text{D}_6$  [2.28 (q, 7.3,  $\text{CH}_2$ ), 0.79 (t, 7.3,  $\text{CH}_3$ )].

Table II. Infrared Spectra $^a$  of the Aluminum Complexes

compd	absorptions, $\text{cm}^{-1}$
I	2960 (s), 2930 (m), 2870 (m), 2570 (s, B-H str), 2520 (m, B-H str), 1810 (s, br, Al-H str), 1455 (s), 1395 (m), 1385 (m), 1330 (w), 1295 (w), 1180 (w), 1170 (w, sh), 1160 (m), 1085 (m), 1065 (w), 1040 (m), 1020 (w), 1005 (m), 950 (w), 930 (w), 895 (w), 860 (w), 835 (w), 765 (s, br), 715 (s)
II	3080 (w), 2965 (s), 2930 (s), 2870 (m), 2560 (m, sh, B-H str), 2510 (s, B-H str), 1845 (m, br, Al-H str), 1470 (m), 1455 (m, br), 1390 (m), 1180 (w), 1155 (m), 1085 (m), 1025 (m), 800 (m, br), 730 (m)
III	3080 (m, br), 2960 (s), 2920 (m), 2860 (m), 2550 (sh, B-H str), 2500 (s, br, B-H str), 1455 (s), 1395 (m), 1370 (m), 1260 (m), 1170 (w), 1155 (m), 1085 (w), 1065 (w), 1025 (m), 960 (w), 800 (m), 725 (w)

$^a$  Neat films between NaCl plates.

was evacuated at  $-196$   $^\circ\text{C}$  and charged with 251 mg (1.91 mmol) of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$ . The reaction mixture was allowed to warm slowly to  $0$   $^\circ\text{C}$  at which point it was placed in an ice bath and then stirred continuously for 24 h. Periodic measurement (every  $\sim$ 6 h) of noncondensibles with a Toepler pump revealed that a total of 1.6 mmol of  $\text{H}_2$  had been produced during the 24-h period. The reaction flask was then attached to a vacuum line and maintained at  $0$   $^\circ\text{C}$  while the volatile components were fractionated through a  $-45$ ,  $-196$   $^\circ\text{C}$  trap series. After fractionation for 3 h, the  $-45$   $^\circ\text{C}$  trap was found to contain 34 mg (0.26 mmol) of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$ . Remaining in the reaction flask was 383 mg (1.47 mmol) (91.3% yield based on  $\text{Et}_3\text{N}\cdot\text{AlH}_3$ ) of an extremely air-sensitive and thermally unstable, clear, oily liquid determined to be  $4,5\text{-}\mu\text{-AlH}_2\text{NET}_3\text{-}2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_5$  (I) by its  $^{11}\text{B}$  and  $^1\text{H}$  NMR (Table I) and IR (Table II) data. Attempts to further purify this material resulted in the formation of compound II and starting materials.

A similar reaction to that described above was attempted with a 2:1 ratio of  $\text{Et}_3\text{N}\cdot\text{AlH}_3$  to  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$ . No species containing two bridging Al units were isolated. The reaction products consisted of I and excess  $\text{Et}_3\text{N}\cdot\text{AlH}_3$  in an approximately 1:1 ratio as determined by  $^1\text{H}$  and  $^{11}\text{B}$  NMR.

**Synthesis of  $6\text{-AlHNET}_3\text{-}3,4\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4$  (II).** In a typical reaction, 183 mg (1.40 mmol) of  $\text{Et}_3\text{N}\cdot\text{AlH}_3$  was syringed into a 50-mL one-piece flask containing a magnetic stirring bar. The flask was evacuated at  $-196$   $^\circ\text{C}$  and charged with 186 mg (1.42 mmol) of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$ . The reaction mixture was slowly warmed to  $50$   $^\circ\text{C}$  and then stirred continuously for 24 h. A total of 2.7 mmol of  $\text{H}_2$  was evolved during this period as measured by the Toepler pump. At this point  $\text{H}_2$  production had ceased, and the reaction flask was transferred to a vacuum line. The volatile materials were then fractionated through a  $0$ ,  $-45$ ,  $-196$   $^\circ\text{C}$  trap series. Stopping in the  $0$   $^\circ\text{C}$  trap was 5 mg (0.04 mmol) of  $\text{Et}_3\text{N}\cdot\text{BH}_3$ . The  $-45$   $^\circ\text{C}$  trap contained 24 mg (0.18 mmol) of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$ . A trace amount of  $\text{Et}_3\text{N}$  was stopped at  $-196$   $^\circ\text{C}$ . Remaining in the reaction flask was 329 mg of an air-sensitive, clear, oily liquid. The material was dissolved in 5 mL of dry benzene and filtered through a fine frit, which retained a small amount of pyrophoric, insoluble white solid. The filtrate was then transferred to a clean, dry flask and attached to the vacuum line. Removal of benzene afforded 258 mg (1.00 mmol) (71.4% yield) of pure, liquid  $6\text{-AlHNET}_3\text{-}3,4\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4$  (II) as characterized by its  $^{11}\text{B}$  and  $^1\text{H}$  NMR (Table I) and IR (Table II) data. Anal. Calcd for  $\text{C}_{12}\text{B}_4\text{N}_1\text{Al}_1\text{H}_{30}$ : C, 55.74; B, 16.72; N, 5.42; Al, 10.43; H, 11.69. Found: C, 54.77; B, 14.35; N, 4.87; Al, 11.73; H, 12.80. Exact mass measurement for  $^{12}\text{C}_{12}\text{B}_4\text{N}_1\text{Al}_1\text{H}_{30}$ : calcd 259.2566; found 259.2592.

**Synthesis of  $\text{commo-AlNEt}_3\text{-}[(6\text{-AlNEt}_3\text{-}3,4\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)(4',5'\text{-}\mu\text{-AlNEt}_3\text{-}2',3'\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6)]$  (III).** Into a 100-mL reaction flask charged with a magnetic stirring bar and 186 mg (1.42 mmol) of  $\text{Et}_3\text{N}\cdot\text{AlH}_3$  was condensed 407 mg (3.10 mmol) of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$ . The mixture was slowly warmed to  $70$   $^\circ\text{C}$  and then stirred continuously for 36 h. A total of 4.4 mmol of  $\text{H}_2$  was evolved during this period as measured by the Toepler pump. The flask was then attached to a vacuum line, and the volatile materials were fractionated through a  $0$ ,  $-45$ ,  $-196$   $^\circ\text{C}$  trap series.

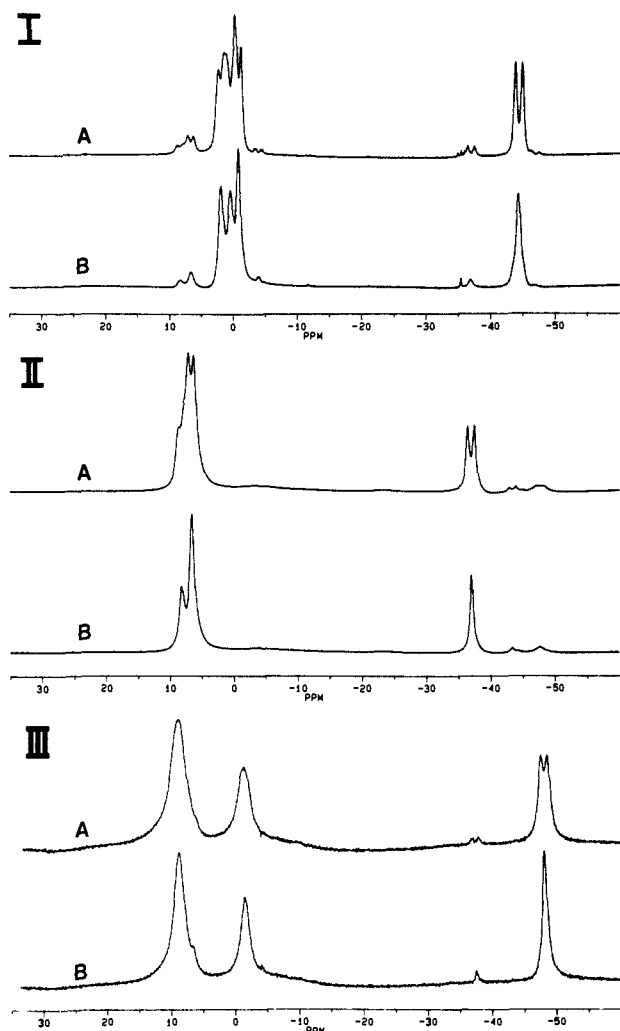
Stopping in the  $0$   $^\circ\text{C}$  trap was 24 mg (0.21 mmol) of  $\text{Et}_3\text{N}\cdot\text{BH}_3$ . The  $-45$   $^\circ\text{C}$  trap contained 37 mg (0.28 mmol) of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$ . Triethylamine, in trace amounts, was stopped at  $-196$   $^\circ\text{C}$ . Remaining in the reaction flask was 483 mg of an air-sensitive, oily, opaque solid. The material was dissolved in 5 mL of dry benzene and filtered through a fine frit, which retained a trace amount of insoluble material. Addition of  $\sim$ 30 mL of cold, dry pentane to the filtrate caused precipitation of a white solid, which was removed to a frit, washed with an additional 10-mL portion of cold pentane, and then dried under high vacuum. The above procedure afforded 338 mg (0.87 mmol) (61.3% based on  $\text{Et}_3\text{N}\cdot\text{AlH}_3$ ) of pure *commo-AlNEt}\_3\text{-}[(6\text{-AlNEt}\_3\text{-}3,4\text{-Et}\_2\text{C}\_2\text{B}\_4\text{H}\_4)(4',5'\text{-}\mu\text{-AlNEt}\_3\text{-}2',3'\text{-Et}\_2\text{C}\_2\text{B}\_4\text{H}\_6)] (III). The material was characterized by its  $^{11}\text{B}$  and  $^1\text{H}$  NMR (Table I) and IR (Table II) data. Anal. Calcd for  $\text{C}_{18}\text{B}_8\text{N}_1\text{Al}_1\text{H}_{44}$ : C, 55.72; B, 22.29; N, 3.61; Al, 6.95; H, 11.43. Found: C, 54.66; B, 23.34; N, 4.43; Al, 6.43; H, 11.31. Exact mass measurement for  $^{12}\text{C}_{18}\text{B}_8\text{N}_1\text{Al}_1\text{H}_{44}$ : calcd 288.2829; found 288.2789.*

**Reaction of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$  with  $\text{Et}_3\text{N}\cdot\text{AlH}_3$  in Benzene, Pentane, Toluene, or Diethyl Ether.** Reactions similar to those described above were carried out in each of the above solvents. In all cases it was found that the reaction rate was appreciably slower than when  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$  and  $\text{Et}_3\text{N}\cdot\text{AlH}_3$  are reacted in neat form. For example, reaction of 1.62 mmol of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$  with 1.58 mmol of  $\text{Et}_3\text{N}\cdot\text{AlH}_3$  in 10 mL of benzene at  $50$   $^\circ\text{C}$  was less than 50% complete (by  $^1\text{H}$  and  $^{11}\text{B}$  NMR) after 2 days.

**Conversion of I to II.** A 50-mL reaction flask was charged with 273 mg (1.05 mmol) of I and  $\sim$ 5 mL of dry toluene. The contents were stirred at  $50$   $^\circ\text{C}$  for  $\sim$ 5 h. The flask was then removed to the Toepler pump, and the evolved  $\text{H}_2$  was measured (1.3 mmol). Fractionation through a  $0$ ,  $-196$   $^\circ\text{C}$  trap series afforded no volatile materials. Remaining in the reaction flask was an oily liquid, which was then purified in a manner similar to that described in the synthesis of II. This procedure afforded 210 mg (0.81 mmol) (77.1% yield) of II. The purity of the product was confirmed by comparison of its  $^{11}\text{B}$  and  $^1\text{H}$  NMR and IR data with those of an authentic sample.

**Conversion of II to III.** A 50-mL reaction flask was charged with 164 mg (0.63 mmol) of II and a magnetic stirring bar. The flask was evacuated, and 81 mg (0.62 mmol) of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$  and 10 mL of dry toluene were condensed in. The contents were then stirred at  $70$   $^\circ\text{C}$  for  $\sim$ 12 h. The flask was removed to the Toepler pump, and the evolved  $\text{H}_2$  was measured (0.8 mmol). The volatile material was then fractionated through a  $0$ ,  $-45$ ,  $-196$   $^\circ\text{C}$  trap series where 9.2 mg (0.08 mmol) of  $\text{Et}_3\text{N}\cdot\text{BH}_3$  was stopped at  $0$   $^\circ\text{C}$ , 14 mg (0.11 mmol) of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$  was stopped at  $-45$   $^\circ\text{C}$ , and a trace amount of  $\text{Et}_3\text{N}$  was retained at  $-196$   $^\circ\text{C}$ . The reaction flask contained a crude, white oily solid. Purification as described in the synthesis of III yielded 140 mg (0.36 mmol) (58.1%) of pure white solid determined to be III by comparison of its  $^{11}\text{B}$  and  $^1\text{H}$  NMR and IR spectra with those of an authentic sample.

**Reactions of  $2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_6$  with  $\text{Me}_3\text{N}\cdot\text{AlH}_3$ .** Reactions similar to those described in the syntheses of I–III were performed with  $\text{Me}_3\text{N}\cdot\text{AlH}_3$  as the expansion reagent. It was found that there was no reaction



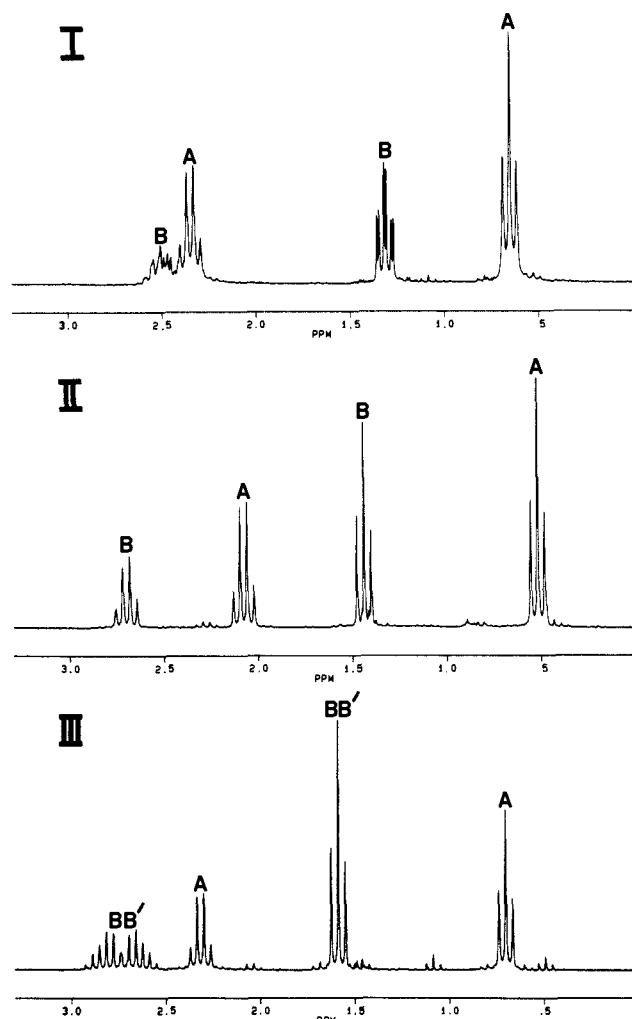
**Figure 1.** 160.5-MHz  $^{11}\text{B}$  NMR spectra of 4,5- $\mu\text{-AlH}_2\text{NEt}_3$ -2,3- $\text{Et}_2\text{C}_2\text{B}_4\text{H}_5$  (I), 6- $\text{AlHNEt}_3$ -3,4- $\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$  (II), and *commo*- $\text{AlNEt}_3$ -[(6- $\text{AlNEt}_3$ -3,4- $\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$ )(4',5'- $\mu\text{-AlNEt}_3$ -2',3'- $\text{Et}_2\text{C}_2\text{B}_4\text{H}_5$ )] (III). A spectra are proton spin-coupled; B spectra are proton spin-decoupled.

of 2,3- $\text{Et}_2\text{C}_2\text{B}_4\text{H}_6$  and  $\text{Me}_3\text{N}\cdot\text{AlH}_3$  either in neat form or in pentane, benzene, toluene, or diethyl ether solvent below 50 °C. At higher temperatures only trace amounts of cage-expansion products were obtained, and the  $^{11}\text{B}$  and  $^1\text{H}$  NMR spectra of the product mixtures revealed large amounts of 2,3- $\text{Et}_2\text{C}_2\text{B}_4\text{H}_6$ , as well as numerous degradation products, the major one of which was  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_3$ .

### Results and Discussion

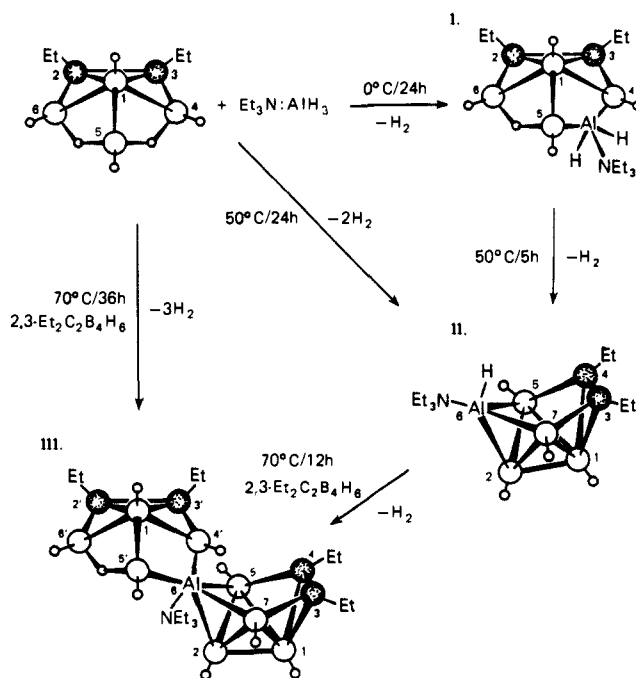
The reaction of  $\text{Et}_3\text{N}\cdot\text{AlH}_3$  with 2,3- $\text{Et}_2\text{C}_2\text{B}_4\text{H}_6$  at 0 °C was found to produce exclusively the Al-bridged species 4,5- $\mu\text{-AlH}_2\text{NEt}_3$ -2,3- $\text{Et}_2\text{C}_2\text{B}_4\text{H}_5$  (I) as shown in Scheme I. The spectral data for I indicate that bridge substitution has occurred, resulting in the replacement of one bridging hydrogen of the *nido*-carborane by a  $\text{Et}_3\text{NAlH}_2$  unit derived from the amine-alane. Thus, as shown in Figure 1, the 160.5-MHz  $^{11}\text{B}$  NMR spectrum of I exhibits three low-field doublets, resulting from the inequivalence of three BH units in the basal plane, and a high-field doublet, denoting an apical BH environment. These data are consistent with those reported for other heteroatom bridge-substituted derivatives of 2,3- $\text{R}_2\text{C}_2\text{B}_4\text{H}_6$ .<sup>7,9,14</sup>

The  $^1\text{H}$  NMR spectrum (Figure 2) shows the presence of both amine and carborane ethyl groups in a 3:2 ratio. The carborane



**Figure 2.** 200.1-MHz  $^1\text{H}$  NMR spectra of I-III. In each spectrum, A indicates resonances arising from triethylamine protons and B (B') indicates resonances due to cage-ethyl protons.

### Scheme I



ethyl groups are, in fact, resolved into two sets, denoting a lack of mirror symmetry in the basal plane. The  $^1\text{H}\{^{11}\text{B}\}$  spectrum (Table I) shows the expected basal and apical B-H resonances,

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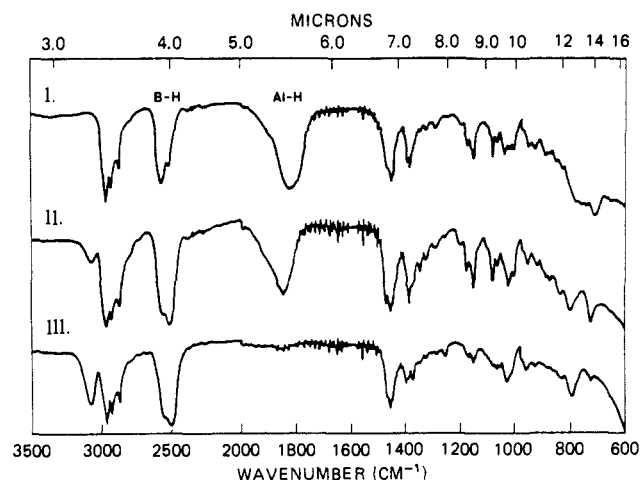


Figure 3. Infrared spectra of I-III.

as well as the BHB resonance for the remaining bridge hydrogen.

As shown in Figure 3, the IR spectrum exhibits a split B-H stretching band in the 2500–2600-cm<sup>-1</sup> region, as is observed in nearly all known heteroatom-bridged 2,3-R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> derivatives.<sup>7,9,14b,c,e,15</sup> The most significant feature of the IR spectrum is the presence of a characteristic strong band at 1810 cm<sup>-1</sup> due to Al-H stretching.<sup>10a,b,16</sup> Both electron impact (EI) and chemical ionization (CI) mass spectra failed to exhibit groupings corresponding to the molecular ion of I, although the CI spectrum exhibited a cutoff at *m/e* 132, with a characteristic 4-boron pattern corresponding to Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub><sup>+</sup>.

Compound I is reactive above 0 °C, whereupon hydrogen is evolved and conversion to II occurs. The thermal instability of I is consistent with Grimes' earlier report<sup>7</sup> of the aluminum-bridged species  $\mu$ -(CH<sub>3</sub>)<sub>2</sub>Al-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>7</sub>, which was found to be too unstable to characterize completely.

Upon warming I to 50 °C in toluene or by reacting Et<sub>3</sub>N·AlH<sub>3</sub> with 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> at 50 °C without solvent, the nido seven-vertex species 6-AIHNEt<sub>3</sub>-3,4-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (II) is formed in good yield as shown in Scheme I.

The composition of II was established by elemental analysis and exact-mass measurements. The compound is an example of an *n* + 2 nido skeletal-electron system (seven cage atoms and nine skeletal-electron pairs) and would be expected to adopt an open-cage geometry based on a dodecahedron missing one vertex as shown in Scheme I.

Seven-vertex nido cage systems are rare in polyhedral borane and carborane chemistry. For example, the parent heptaborane B<sub>7</sub>H<sub>11</sub> has never been isolated.<sup>17</sup> Although no neutral carborane of this class has been reported, recent work in our laboratories has resulted in the synthesis and structural characterization of the isoelectronic carborane anion 3,4-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub><sup>-</sup><sup>18</sup> and confirmed a seven-vertex, open-faced structure based on a dodecahedron missing one five-connected vertex. The only reported examples of neutral seven-vertex nido cage systems are found among boranes and carboranes containing heteroatoms.<sup>19</sup> Although limited in number, these species have been shown to exhibit a variety of structures. The dimetallaheptaborane *nido*-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>B<sub>5</sub>H<sub>9</sub><sup>20</sup>

for example, has been proposed to exhibit a structure based on a dodecahedron missing one four-connected vertex. A completely different geometry has been observed for several borazene and boracycle transition-metal complexes. These species, including ( $\eta^6$ -B<sub>3</sub>N<sub>3</sub>Et<sub>6</sub>)Cr(CO)<sub>3</sub><sup>21</sup> and ( $\eta^6$ -C<sub>5</sub>H<sub>5</sub>BPh)Mn(CO)<sub>3</sub><sup>22</sup> as well as isoelectronic  $\pi$ -arene complexes, such as ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>3</sub>,<sup>19a,23</sup> are known to adopt structures based on a hexagonal pyramid. More recently, the silacarborane (Me<sub>3</sub>Si)(Me)C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>SiH<sub>2</sub><sup>24</sup> has been synthesized and proposed, on the basis of the spectral data, to exhibit a gross geometry similar to that found for 3,4-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub><sup>-</sup> and proposed for II.

It should also be noted that several formally *closo* seven-vertex heteroboranes and carboranes have been found to exhibit distorted *closo* structures approximating a dodecahedron missing one vertex. Examples of such molecules include the osmaplatinaborane

[(Ph<sub>3</sub>P)<sub>2</sub>(CO)Os(PhMe<sub>2</sub>P)(ClHPtB<sub>5</sub>H<sub>7</sub>)] reported by Kennedy<sup>25</sup> and the isoelectronic platinumacarborane 1,2,3-(Et<sub>3</sub>P)<sub>2</sub>PtMe<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> prepared by Stone.<sup>26</sup> Hosmane has also reported several other examples of "slipped" *closo* seven-vertex systems, including 1-Sn-2-[Si(CH<sub>3</sub>)<sub>3</sub>]-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub><sup>27</sup> and 1-Sn[C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>]-2,3-[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>,<sup>28</sup> and has recently discussed the structures and bonding in these and related carboranes which contain group 13 and 14 heteroatoms.<sup>29</sup>

The physical data obtained for II clearly indicate that the formal Et<sub>3</sub>NAlH<sub>2</sub><sup>2+</sup> unit is not located in a bridging position but is instead inserted into the Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub><sup>2-</sup> carborane cage, resulting in a five-coordinate Al(III) center. The retention of the Et<sub>3</sub>N ligand bound to the aluminum is consistent with previous reports concerning the acidic nature of cage-inserted aluminum atoms. For example, the *closo*-aluminacarborane 3-AlEt-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> has been shown<sup>1a,b,d,2</sup> to form a bis(tetrahydrofuran) adduct, 3-(THF)<sub>2</sub>AlEt-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>. Furthermore, an X-ray structural determination<sup>2,4a</sup> of *nido*- $\mu$ -6,9-AlEt(OEt)<sub>2</sub>-6,9-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> has demonstrated that a diethyl ether moiety is bound directly to the aluminum center.

The 160.5-MHz <sup>11</sup>B NMR spectrum of II (Figure 1) consists of two low-field doublets (area 1:2) and a high-field doublet (area 1) assignable to the basal and apical boron atoms, respectively. The <sup>1</sup>H NMR spectrum (Figure 2) indicates the presence of both amine and carborane ethyl groups in a 3:2 ratio. The cage ethyl groups are equivalent, indicating mirror symmetry. The <sup>1</sup>H(<sup>11</sup>B) spectrum (Table I) exhibits three B-H resonances in the expected 1:2:1 ratio and shows no bridging hydrogen resonances. The IR spectrum of II (Figure 3) exhibits the expected B-H and Al-H stretching bands, although the Al-H stretch is not as intense as that for I.

The fact that II can be obtained from thermolysis of I or by direct reaction of 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> and Et<sub>3</sub>N·AlH<sub>3</sub> at 50 °C suggests that the heteroatom cage expansion with Et<sub>3</sub>N·AlH<sub>3</sub> is a two-step process involving the loss of 1 equiv of hydrogen at each step. The hydrogen loss apparently arises from association of the hydridic H atoms on the AlH<sub>3</sub> unit with the protonic bridging hydrogens on the carborane.

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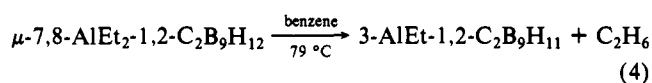
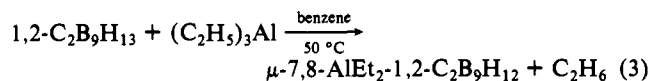
(17) Although B<sub>7</sub>H<sub>11</sub> has never been isolated, there is mass spectral evidence that supports its existence as a transient species. See: McLaughlin, E.; Rozett, R. W. *Inorg. Chem.* **1972**, *11*, 2567–2568, and references therein.

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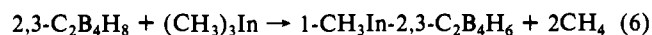
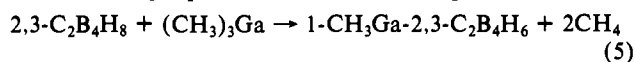
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Elimination of hydrogen or an alkane to effect heteroatom insertion into a neutral *nido*-carborane has been well-documented in a number of studies. Hawthorne<sup>1b-d,2</sup> has shown, for example, that 1,2-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub> can undergo a two-step expansion process with triethylaluminum as shown in eq 3 and 4, in which 1 mol equiv of ethane is liberated at each step.



Likewise, the first reported gallacarborane<sup>30,31</sup> and the only indacarborane<sup>31</sup> were prepared by the thermal elimination of methane in the gas-phase reactions shown in eq 5 and 6. Indeed,



our previous work<sup>8</sup> with Et<sub>3</sub>N·BH<sub>3</sub> has shown that a BH unit may be inserted into 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> with the elimination of hydrogen. The above results clearly indicate that intermolecular elimination of an alkane or hydrogen is a useful synthetic pathway for homo/heteroatom insertion into a *nido*-carborane and support the stepwise insertion process outlined in Scheme I.

The reaction of 2 mol equiv of 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> with 1 equiv of Et<sub>3</sub>N·AlH<sub>3</sub> at 70 °C results in the formation of the bis(carboranyl) compound *commo*-AlNEt<sub>3</sub>-[(6-AlNEt<sub>3</sub>-3,4-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>)(4',5'-μ-AlNEt<sub>3</sub>-2',3'-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>)] (III) as shown in Scheme I. The fact that II retains an Al-H bond suggests its role as a possible intermediate in the formation of III. This hypothesis was confirmed by reacting II with 1 equiv of 2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> at 70 °C as shown in Scheme I.

The composition of III was established by elemental analysis. The chemical ionization mass spectrum of III gave no grouping corresponding to the molecular ion but exhibited a characteristic 8-boron pattern at *m/e* 288 corresponding to a P-Et<sub>3</sub>N fragment. The infrared spectrum of III (Figure 3) exhibits a strong, broad B-H stretching band at 2500 cm<sup>-1</sup>. There are no bands present in the 1800-1900-cm<sup>-1</sup> region, thus confirming that there are no remaining Al-H bonds on the Et<sub>3</sub>NAl unit.

The reaction stoichiometry leading to the formation of III, in conjunction with its chemical composition, suggests that the compound has a structure in which two carborane units are joined by a Et<sub>3</sub>NAl unit. As shown in the proposed structure (Scheme I), the aluminum atom is bound in an η<sup>2</sup>-fashion to the Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub><sup>-</sup> cage and in an η<sup>3</sup>-mode to the Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub><sup>2-</sup> ligand. The aluminum atom is thus six-coordinate and in a formal 3+ oxidation state. In such a structure the aluminum-bridged component of III may be considered an analogue of I and the aluminum-inserted component an analogue of II. Both cages are therefore *n* + 2 *nido* skeletal-electron systems displaying open-cage geometries.

It would be expected, given the asymmetry of the proposed structure, that III would exhibit complex <sup>11</sup>B and <sup>1</sup>H NMR spectra. Surprisingly, both spectra of III are quite simple. As shown in Figure 1, the 160.5-MHz <sup>11</sup>B spectrum of III exhibits two very broad resonances at low field, and a doublet at high field, indicating an apical BH environment. The <sup>1</sup>H NMR spectrum (Figure 2) shows the presence of both amine and carborane ethyl groups in the expected 3:4 ratio. Although the carborane ethyl groups display a complex pattern for the CH<sub>2</sub> protons, the CH<sub>3</sub> protons appear as a single triplet. Symmetry considerations indicate that at least two and possibly four carborane CH<sub>3</sub> resonances might be observable. The <sup>1</sup>H{<sup>11</sup>B} spectrum gives broad BH resonances at low field and an apical BH at high field. An additional, broad resonance at -2.3 ppm confirms the presence

of the remaining bridge hydrogen on the bridge-substituted cage.

The simplicity of both the <sup>11</sup>B and <sup>1</sup>H NMR spectra suggests that III may exhibit dynamic behavior in solution. Hawthorne's previous studies of aluminacarboranes have shown that several of these systems, including μ-7,8-AlR<sub>2</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>,<sup>1b-d,2</sup> *nido*-[μ-6,9-AlEt(OEt<sub>2</sub>)-6,9-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub>],<sup>2,4a</sup> Na<sup>+</sup>[Al(η<sup>2</sup>-2,7-C<sub>2</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>]<sup>-2,3</sup> and *commo*-3,3'-Al[(*exo*-8,9-(μ-H)<sub>2</sub>AlEt<sub>2</sub>-3,1,2-AlC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)-(3',1',2'-AlC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]<sup>-2,3</sup> are fluxional and, as in the case of III, exhibit room-temperature NMR spectra, which are too simple on the basis of their established molecular symmetries. In an attempt to verify fluxional behavior in III, a variable-temperature NMR study was undertaken.

The high-temperature (80 °C) <sup>11</sup>B NMR spectrum of III exhibited sharpening of all three resonances and the appearance of <sup>1</sup>H coupling for the downfield peaks. Similar effects were noted by Hawthorne in the high-temperature spectra of Na<sup>+</sup>[Al(η<sup>2</sup>-2,7-C<sub>2</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>]<sup>-2,3</sup>. The <sup>1</sup>H NMR spectrum of III at this temperature revealed sharper, although otherwise unchanged, resonances. Low-temperature <sup>11</sup>B spectra between 27 and -95 °C revealed only increasingly broadened resonances. Similarly, <sup>1</sup>H spectra over the same temperature range showed only broadening of the amine ethyl resonances. Thus, in contrast to Hawthorne's studies of the μ-7,8-AlR<sub>2</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub><sup>1b-d,2</sup> and Na<sup>+</sup>[Al(η<sup>2</sup>-2,7-C<sub>2</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>]<sup>-2,3</sup> systems, no new resonances were observed in either spectra at low temperatures.

Fluxional behavior in III could conceivably involve several different types of interconversions. For example, the Et<sub>3</sub>NAlEt<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> unit and the neighboring bridge proton may be involved in an exchange process at room temperature. This type of behavior, however, is not observed for the Et<sub>3</sub>NAl unit in I nor would it account for the high degree of symmetry observed in the spectral data. Perhaps a more likely situation involves the movement of the two carborane ligands about the Et<sub>3</sub>NAl unit in a μ-η<sup>2</sup> to η<sup>3</sup> conversion. Thus, the Et<sub>3</sub>NAl unit is alternately bridge-bound to one cage and inserted into the other. Such a process would also involve the migration of the bridging hydrogen from one cage to another, possibly involving B-H-Al intermediates, as proposed by Hawthorne for the μ-7,8-AlEt<sub>2</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub> system.<sup>1c</sup> Rearrangements about the *commo*-Al center would seem a likely prospect in view of the highly fluxional nature of known π-type complexes of aluminum. Jutzi has pointed out, for example, that known dialkyl(cyclopentadienyl)aluminum compounds are so highly fluxional that low-temperature NMR experiments are inadequate in ascertaining their mechanisms of rearrangements.<sup>32a,b</sup> Indeed, while providing evidence of fluxional behavior, previous variable-temperature NMR studies of aluminacarboranes have in no case conclusively elucidated the mechanism of rearrangement. For example, low-temperature studies of *nido*-μ-6,9-AlEt(OEt<sub>2</sub>)-6,9-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub><sup>2,4a</sup> failed to reveal any reduction in symmetry. In view of the above considerations, it is likely that III may exhibit either of the fluxional processes previously discussed or perhaps other processes in which rearrangement of the carborane ligand skeletal systems is involved. Further analysis of the structural elements of III that would support any fluxional process will have to await an X-ray crystallographic study of this molecule. As yet no crystals of III suitable for structural study have been obtained.

The effectiveness of Et<sub>3</sub>N·AlH<sub>3</sub> as a cage-expansion reagent suggested that other base-alanes might also exhibit this capability. All attempts to effect analogous insertion/expansion reactions with Me<sub>3</sub>N·AlH<sub>3</sub>, however, resulted only in the isolation of degradation products and starting materials. Since *nido*-2,3-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> is stable to attack by Me<sub>3</sub>N<sup>33</sup> in the temperature range of these reactions (<100 °C), it is probable that the formation of large amounts of (CH<sub>3</sub>)<sub>3</sub>N·BH<sub>3</sub> results from attack of free Me<sub>3</sub>N on the expansion products. In contrast, when Et<sub>3</sub>N·AlH<sub>3</sub> is the expansion reagent, only trace amounts of Et<sub>3</sub>N·BH<sub>3</sub> are isolated.

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High yields of expansion products are thus dependent on the preservation of the Al-N bond during the reaction and may therefore be related to the Lewis base strength in the base-alane complex.

In summary, the results presented herein have demonstrated that triethylamine-alane is a useful reagent for the synthesis of a variety of new types of aluminacarboranes, including the only examples of group 13 heterocarboranes in which the heteroatom retains active M-H bonds. The base-alane provides a convenient source of highly reactive Al-H bonds under mild reaction conditions and thus should be a useful expansion reagent for other

borane, carborane, and metal cluster systems. Studies aimed at exploring such reactions, as well as examining the reactivity and synthetic utility of the small aluminacarboranes reported herein, are now in progress.

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**Registry No.** I, 113859-97-5; II, 113859-98-6; III, 113859-99-7; Et<sub>3</sub>N·AlH<sub>3</sub>, 12076-08-3; 2,2-Et<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, 80583-48-8; Et<sub>3</sub>N·BH<sub>3</sub>, 1722-26-5; Me<sub>3</sub>N·AlH<sub>3</sub>, 16842-00-5; Me<sub>3</sub>BH<sub>3</sub>, 75-22-9.

## Magnetic Field Effects on the Catalytic Oxidation of 2,6-Di-*tert*-butylphenol by CoSMDPT: <sup>2</sup>H and <sup>17</sup>O Magnetic Isotope Effects

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**Abstract:** The effect of a magnetic field between 0 and 70 kG on the catalytic oxidation rate of 2,6-di-*tert*-butylphenol, DTBP, to form 2,6-di-*tert*-butylquinone, BQ, by cobalt(II) bis(3-(salicylideneamino)propyl)methylamine, CoSMDPT, in the presence of O<sub>2</sub> is reported. No kinetic <sup>2</sup>H isotope effect is observed with DTBP-OD, and DTBP-4-*d*<sub>1</sub>-OD exhibits mass and magnetic kinetic isotope effects of 1.25 and 1.22, respectively. In the presence of additive phenol, CoSMDPT catalyzes the formation of 2,2',6,6'-tetra-*tert*-butyldiphenoquinone, DPQ. The mass and magnetic isotope effects in DPQ formation are negligible for the deuteration of the phenolic position. DTBP-4-*d*<sub>1</sub>-OD in the presence of phenol-OD exhibits kinetic mass and magnetic <sup>2</sup>H isotope effects in DPQ formation of 1.73 and 1.31, respectively. These results are compared to the oxidation rate of DTBP by Pb(OAc)<sub>4</sub>, which is unaffected by a 0-70-kG magnetic field and has a <sup>2</sup>H kinetic isotope effect of 1.28 for DTBP-4-*d*<sub>1</sub>-OD. A significant <sup>17</sup>O magnetic isotope effect is observed only for BQ production. The <sup>17</sup>O enrichment of BQ given has an overall enrichment factor, *S*(*f*) = 1.76, at 9% DTBP conversion. These results are discussed in terms of a proposed mechanism.

Very weak magnetic fields have been linked to human health hazards ranging from an elevated incidence of cancer<sup>1</sup> to miscarriages.<sup>2</sup> This suggests the widespread commercial application of superconducting devices<sup>3</sup> could or might constitute a health risk. However, evidence to link magnetic fields with health hazards remains inconclusive because of the lack of a clear chemical understanding of how magnetic fields can affect biological systems. Without this understanding it is difficult to identify the biological chemistry most likely to exhibit magnetic effects.<sup>4</sup> Most investigations of magnetochemistry have focused on the reactivity of excited-state molecules, which occur in the photochemical production of radical pairs<sup>5</sup> or electrogenerated chemiluminescence.<sup>6</sup> Although the existence of magnetic field effects in chemical reactions that proceed thermally remains controversial,<sup>5,7</sup>

a few magnetochemical studies exist of established radical-pair reactions such as alkyl lithium-alkyl halide exchange reactions.<sup>8</sup> The magnetic field effect depends on a number of experimental variables such as magnetic field strength, the presence of magnetic isotopes, solvent viscosity, and the nature of the alkyl group.<sup>8</sup> The observation of magnetochemistry in these thermal reactions has generated only limited interest to date. The magnetic field induced change in each product is no greater than 10-15% and is comparable to the reproducibility of these exothermic heterogeneous reactions.<sup>9</sup>

In contrast to the relatively small effects observed in stoichiometric radical-pair reactions, larger magnetochemical effects were observed in catalytic reactions that produce a single product. In a recent study we describe a magnetic field induced threefold change in the rate of the transition-metal-catalyzed O<sub>2</sub> oxidation of 2,6-di-*tert*-butylphenol, DTBP.<sup>10</sup> We have extended our initial observations on the catalyst cobalt(II) bis(3-(salicylidene-

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