After 7 days of reaction time, an infrared spectrum of another aliquot exhibited strong absorption bands characteristic of **6e** and additional bands of medium intensity characteristic of **1**. A GLC analysis gave results identical with those described above.

After 28 days, an infrared spectrum of another aliquot was nearly superimposable with that of **1** in the region of 2400–1600 cm^{-1}. No absorption bands characteristic of **6e** were discernible. Biallyl was apparently formed in the hot (~280 °C) GLC injection port.

(B) Experiment No. 2. To a solution of **4** (190 mg, 0.180 mmol) in 0.50 mL of Me_2SO-d_6, in a 5-mm NMR tube equipped with a rubber septum, was added via syringe benzyl bromide (20 μL, 0.17 mmol). The ^{1}H NMR spectrum of the resulting red solution was identical with that of **6e**. An infrared spectrum of an aliquot of the reaction mixture in THF was identical with that of **6e** in the region of 2400–1600 cm^{-1}.

A second portion of benzyl bromide (24 μL, 0.20 mmol) was added to the tube through the septum, via syringe. The tube was then sealed under an atmosphere of nitrogen. The ^{1}H NMR spectrum of the resulting sample indicated the presence of **6e** and $PhCH_2Br$ in a molar ratio of approximately 1:1. No change was discernible by ^{1}H NMR after 20 h at room temperature. The sample was then heated in the dark at 80–100 °C. Over a period of 2 h, ^{1}H NMR spectra showed a gradual decrease in the intensities of singlets at δ 3.97 and 4.63, resonances characteristic of **6e** and $PhCH_2Br$, respectively. Concurrently, singlets appeared at δ 2.13 and 2.72 (resonances characteristic of toluene and bibenzyl, respectively) and gradually increased in intensity. After 2 h at 80–100 °C, no resonances characteristic of **6e** were detectable above noise, and only a trace of $PhCH_2Br$ was evident. Integration of the spectrum indicated the formation of bibenzyl in ~30% yield and toluene-$d_{0,1}$ in 35–50% yield.

The sealed tube was opened under a nitrogen atmosphere, and its contents were transferred to a second 5-mm tube. An infrared spectrum of 1 aliquot of the crude reaction mixture in THF was essentially superimposable with that of **1**. An analytical TLC analysis of the crude reaction mixture revealed the presence of **1**. The second NMR tube containing the bulk of the reaction mixture was equipped with a rubber septum. The presence of bibenzyl and toluene in the solution was confirmed by measuring ^{1}H NMR spectra before and after addition of authentic samples of the two.

Reaction of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]{\cdot}2THF$ (6a) with Dimethylphenylphosphine. A solution of **6a** (110 mg, 0.132 mmol) and $P(CH_3)_2Ph$ (25 μL, 0.17 mmol) in 250 μL of Me_2SO-d_6 was sealed under a nitrogen atmosphere in a 5-mm NMR tube. The ^{1}H NMR spectrum of the resulting mixture exhibited only reasonances characteristic of the two individual components. After the tube was heated in the dark for 1 h at 100 °C, the spectrum was devoid of a doublet at δ 1.25, a resonance characteristic of free $P(CH_3)_2Ph$. In addition, the singlet at δ 2.22, characteristic of **6a**, had significantly decreased in intensity. Several new resonances had appeared in the region δ 1.3–1.6.

In an inert-atmosphere glovebox, the sample was removed from the tube. An infrared spectrum of 1 aliquot of the crude reaction mixture in THF exhibited several absorption bands in the region of 2400–1400 cm^{-1}. Bands characteristic of unreacted **6a** were evident. The sample was filtered. Addition of 0.5 mL of THF to the filtrate resulted in red crystals of **3b** [20 mg, 27%, based on $P(CH_3)_2Ph$]. Infrared spectra (KBr pellet and THF solution) of the product were identical with those of **3b**. Anal. Calcd for $C_{44}H_{42}Fe_2O_4P_4$: C, 60.71; H, 4.86; Fe, 12.83. Found: C, 60.88; H, 5.21; Fe, 12.45.

The filtrate from the crystallization above was chromatographed in air on a 20 × 20 cm, 250-μ silica gel plate with an eluant of 1:1 benzene:hexane. The major red band was scraped from the plate, washed free of the silica with benzene, and filtered. The solvent of the resulting red filtrate was removed under reduced pressure, affording **2b** (8 mg, 8%, based on **6a**): ^{1}H NMR ($CDCl_3$) δ 1.56 (d, J = 8 Hz, 6 H), 6.4–7.8 (m, 25 H). The infrared spectrum of the product in THF was identical with that of **2b**.

Reaction of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]{\cdot}2THF$ (6a) with Carbon Monoxide. A 0.02 M solution of **6a** was stirred at room temperature under carbon monoxide at 40 psig. Infrared spectra of the crude reaction mixture, taken periodically over a period of 2 weeks, showed a gradual increase in the intensities of absorption bands characteristic of **1** and a gradual decrease in the intensities of absorption bands characteristic of **6a**.

Reaction of $NaFe_2(PPh_2)_2(CO)_5[C(O)CH_3]{\cdot}2THF$ (6a) with Sodium. To a solution of **6a** (50 mg, 0.060 mmol) in 3 mL of THF was added 50% sodium dispersion (8 mg, 0.2 mmol). After 2 h of stirring, the red mixture was filtered. Diffusion of hexane vapor into the filtrate resulted in crystals of **4**, which were washed with hexane and dried in vacuo (41 mg, 65%). The solution infrared spectra of the product and an authentic sample of **4** were identical. Treatment of a THF solution of the product with dioxygen (air) resulted in the formation of **1**.

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Registry No. **1**, 19599-68-9; **2a**, 79190-80-0; **2b**, 79172-57-9; **2d**, 79172-58-0; **3a**, 79172-59-1; **3b**, 79172-60-4; **3c**, 79200-24-1; **4**, 79172-61-5; **5**, 72124-56-2; **6a**, 72275-07-1; **6b**, 79172-63-7; **6c**, 79172-82-0; **6d**, 79172-84-2; **6e**, 79172-86-4; **6f**, 79172-88-6; **6g**, 79172-90-0; **6h**, 79172-92-2; **7**, 72275-03-7; **8a**, 79200-26-3; **8b**, 72275-05-9; **9**, 79172-93-3; **10**, 79172-95-5; **11**, 79172-96-6; **12**, 79391-51-8; **13**, 79172-64-8; $Na_2Fe(CO)_4$, 14878-31-0; $Fe(CO)_5$, 13463-40-6; Ph_2PCl, 1079-66-9; Cf_3CO_2H, 76-05-1; benzoyl chloride, 98-88-4; CCl_4, 56-23-5; $ICH_2CH_2CH_2I$, 627-31-6; allyl bromide, 106-95-6; benzyl bromide, 100-39-0.

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Reaction of $(CH_3)_3L$ (L = N, P) with Chlorinated Compounds of *closo*-2,4-$C_2B_5H_7$: Net Displacement Reactions at Boron Atoms of *closo*-Carboranes

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Unlike the parent pentagonal-pyramidal *closo*-2,4-$C_2B_5H_7$, both 3-Cl-*closo*-2,4-$C_2B_5H_6$ and 5-Cl-*closo*-2,4-$C_2B_5H_6$ readily react with $(CH_3)_3L$ (L = N, P) to form 1:1 adducts. Removal of Cl^- from these two adducts, using BCl_3, produces the unique [3-$(CH_3)_3L$-*closo*-2,4-$C_2B_5H_6$]$^+$ and [5-$(CH_3)_3L$-*closo*-2,4-$C_2B_5H_6$]$^+$ cations, respectively. The reaction of $(CH_3)_3N$ with 1-Cl-*closo*-2,4-$C_2B_5H_6$ proceeds with more difficulty than with the other two B–Cl isomers, but once formed, the 1:1 adduct combines with BCl_3 to give the rearrangement product [3-$(CH_3)_3N$-*closo*-2,4-$C_2B_5H_6$]$^+$[BCl_4]$^-$.

Introduction

Reactivities of the small *closo*-carboranes toward $(CH_3)_3L$ (L = P or N) are known to follow the order 1,5-$C_2B_3H_5$ > 1,6-$C_2B_4H_6$ > 2,4-$C_2B_5H_7$. The smallest cage compound forms unstable adducts whereas 1,6-$C_2B_4H_6$ gives the well-characterized open cage dipolar 5-$(CH_3)_3L^+$-*nido*-2,4-$C_2B_4H_6^-$; the largest of the three, 2,4-$C_2B_5H_7$, does not react with $(CH_3)_3L$ at temperatures below the decomposition of either reagent but is readily cleaved by many secondary amines, R_2NH, to products such as $R_2NH{\cdot}BH_3$ and $[R_2NBHCH_3]_x$, x = 1, 2.[1-3]

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In a recent communication[4] we reported a marked enhancement of *closo*-2,4-$C_2B_5H_7$ reactivity with $(CH_3)_3L$ upon placing a chlorine atom in the 5-position of this carborane cage. Further, the resulting 1:1 adduct was converted, with use of BCl_3, to the first reported nitrogen- and phosphorus-attached derivatives of a nonicosahedral *closo*-carborane cation, $[5\text{-}(CH_3)_3L\text{-}2,4\text{-}C_2B_5H_6]^+$. The chemistry of this and related compounds is expanded and detailed in the present study.

Experimental Section

Materials. The small *closo*-carborane 2,4-$C_2B_5H_7$ was obtained from Chemical Systems, Inc., Irvine, CA. Methyl chloride (J. T. Baker) was used without further purification; aluminum trichloride (Matheson Coleman and Bell) was sublimed before using. $(CH_3)_3N$ (J. T. Baker) was used without further purification. Chlorine (Matheson) was passed through −78, −140, and −190 °C traps in a high-vacuum line to remove traces of HCl and water. The purity of monoglyme, $CH_3OCH_2CH_2OCH_3$ (Matheson, Coleman & Bell), was confirmed by infrared and ^1H NMR studies before before using. BCl_3 was obtained from Matheson and $NaBH_4$ and NaH from Metal Hydrides, Inc. Trimethylphosphine was a gift from Harold Goldwhite, and an additional quantity of the compound was obtained from Alfa Chemical Co. The deuterated solvents $CDCl_3$, $CD_3OCD_2CD_2OCD_3$, and CD_2Cl_2 were acquired from Norrell Chemical Co.

Instrumentation and Apparatus. Boron-11 and proton NMR spectra were obtained with use of a Varian HA-100 spectrometer operated at 32.1 and 100 MHz, respectively. The ^{11}B NMR spectra (proton decoupled) were recorded while irradiating at 100.08 MHz with a General Radio Model 1061 frequency synthesizer with a power booster provided by an Electronic Navigation Industries Model 320L RD power amplifier and a locally constructed broad-band unit. The ^1H NMR spectra were recorded while irradiating at 32.1 MHz. In addition, proton spectra were recorded on a FT Bruker WP-60 instrument equipped with a Fluke 6061b frequency synthesizer operated at 19.25 MHz and an ENI-320L amplifier used for ^{11}B decoupling. The boron-11 NMR chemical shift data are reported relative to boron trifluoride–ethyl etherate, δ 0.0, and were obtained by using boron trichloride, δ +46.8 (downfield from $(C_2H_5)_2O\cdot BF_3$), as a secondary external standard. The proton chemical shifts are reported relative to internal tetramethylsilane, δ 0.00.

Standard high-vacuum apparatus was used to transfer all chemical reagents and products.

5-Cl-*closo*-2,4-$C_2B_5H_6$. A catalytic amount (approximately 0.5 mmol) of $AlCl_3$ was sublimed into a clean, dry 25-mL flask. Pure *closo*-2,4-$C_2B_5H_7$ (3.5 mmol) was added and condensed into the flask at −196 °C, followed by the addition of the same quantity of chlorine gas. Upon warming of the mixture to room temperature, the disappearance of Cl_2 was complete within 30 min. The reaction mixture was fractionated through −140 and −190 °C traps to remove HCl (a very small amount of noncondensable gas was also observed). The material in the −140 °C trap was further separated by cold-column fractionation,[5] and the collected fractions were as follows: (a) a 2.75-mmol portion, which distilled at −100 °C (the ^{11}B NMR of the sample exhibited resonances at δ +60 and +46.8 corresponding to CH_3BCl_2 and BCl_3, respectively); (b) a 0.65-mmol portion, which distilled at −73 °C (the ^{11}B and ^1H NMR of the sample showed the spectrum of unreacted $C_2B_5H_7$); (c) 2.2 mmol (77% yield based on consumed $C_2B_5H_7$) of 5-Cl-*closo*-2,4-$C_2B_5H_6$,[6,7] which emerged from the column between −73 and −47 °C; (d) a small fraction (0.1 mmol) of $Cl_2C_2B_5H_5$, which was removed from the column upon warming to room temperature.

5-Cl-6-CH_3-2,4-$C_2B_5H_5$. Into a 25-mL flask that was partially coated with a small amount of freshly sublimed $AlCl_3$ was added CH_3Cl (1.9 mmol) and 5-Cl-2,4-$C_2B_5H_6$ (1.9 mmol). The flask was sealed while the contents were kept at −196 °C. No reaction occurred after warming the mixture to room temperature as evidenced by NMR monitoring. The sample was then heated for 2-h increments, with an increase in the temperature of 5–10 °C each time. There was no noticeable change in the NMR spectra until the temperature reached 100 °C. The temperature was then raised to 130 °C for a 2-h period, and subsequently it was determined from NMR data that more than 50% of the starting carborane had reacted. Additional changes in the spectrum occurred after another 2 h of heating at the same temperature, but after an additional 3 h of heating there was no further change in the NMR pattern of the reaction mixture. The flask was opened to the vacuum line, and some noncondensable gas (~1 mmol) was observed. The volatile fractions separated by cold-column fractionation are as follows: (a) material that distilled at −107 °C (0.75 mmol) (this fraction exhibited a boron-11 NMR spectrum having peaks at δ +46.8 and +60 assigned to BCl_3 and CH_3BCl_2, respectively);[8] (b) unreacted 5-Cl-2,4-$C_2B_5H_6$ (0.75 mmol) distilled at −80 to −60 °C; (c) a fraction (0.95 mmol, 83% based on $ClC_2B_5H_6$ consumed) that was a mixture of 5-Cl-6-CH_3-2,4-$C_2B_5H_5$ (~95%) and of 1-CH_3-5-Cl-$C_2B_5H_5$ (~5%) distilled at −60 to −40 °C. The ^{11}B and ^1H NMR data for 5-Cl-6-CH_3-2,4-$C_2B_5H_5$ are given in Table I. For 1-CH_3-5-Cl-2,4-$C_2B_5H_5$, the only NMR peaks that were clearly seen were the B(1)CH_3 resonance at δ −9.4 and the upper member of the B(7)H doublet centered at δ −24.6 in the ^{11}B NMR and the CH_3 resonance at δ −0.264 in the ^1H NMR. An alternate approach to the synthesis of 5-Cl-6-Me-2,4-$C_2B_5H_5$ involved the chlorination of 5-Me-2,4-$C_2B_5H_6$. The products from this reaction, however, were a very complicated mixture of compounds, making the desired product(s) difficult to isolate.

Reaction of 5-Cl-2,4-$C_2B_5H_6$ with Trimethylamine. (A) Use of $CDCl_3$ or $CHCl_3$ as a Solvent. A quantity of 5-Cl-2,4-$C_2B_5H_6$ (2.0 mmol) was added to a mixture of $(CH_3)_3N$ (2.0 mmol) and dry $CDCl_3$ (~1.5 mL) while the solution was kept near −196 °C. Subsequently, the sample was allowed to come to room temperature by which time only one liquid phase was observed. After 1 h had elaspsed, a portion of the solution was divided into three aliquots (under a dry nitrogen atmosphere) and added to NMR tubes for the following determinations.

(a) The volatile portion of one aliquot of solution (~0.20 mL) in a 4-mm NMR tube was distilled away in vacuo at room temperature. Both ^{11}B and ^1H NMR spectra show the volatile fraction to consist of a very small quantity of 5-Cl-2,4-$C_2B_5H_6$ (and presumably $CDCl_3$). The nonvolatile white solid residue was dissolved in an amount of fresh $CDCl_3$ to attain the original volume (~0.2 mL) of solution in the NMR tube. The ^{11}B NMR spectra of the adduct (with and without ^1H decoupling) and the ^1H NMR spectra (^{11}B decoupled) show broad peaks with approximate NMR shift data given in Table I. At various low temperatures, −10, −20, and −50 °C, the resolution of the spectra did not improve nor was additional line broadening noted.

(b) Another 0.2-mL (containing approximately 0.27 mmol of the $(CH_3)_3N\cdot ClC_2B_5H_6$ adduct) aliquot of the original solution was transferred to a 4-mm NMR tube, and the volatile portion was removed as above. To the remaining nonvolatile residue was added excess BCl_3 (0.4 mmol) and $CDCl_3$ (1.5 mmol). After all the reactants were mixed by tapping and inverting the sample tube several times, the solution separated into two liquid layers; the ratio of liquid height, in a comparison of top to bottom layer, was 3:4, respectively. A ^{11}B NMR spectrum of the bottom layer showed the resonances of BCl_3, δ +47, a trace quantity of 5-Cl-2,4-$C_2B_5H_6$, and minor unidentified impurities. The ^{11}B (Figure 1) and ^1H NMR spectra of the clear colorless top layer were consistent with $[5\text{-}(CH_3)_3N\text{-}closo\text{-}2,4\text{-}C_2B_5H_6]^+[BCl_4]^-$; for data see Table I.

(c) Another aliquot (~0.12 mL) was transferred into a 3-mm NMR tube and the volatile portion subsequently removed as above. The residue was gradually heated from 40 to 90 °C, in vacuo, over a 2-h period to insure the removal of all volatile material; the solid sample did not melt over this temperature range. The sample was then cooled to −196 °C and $CHCl_3$ was added, reestablishing the original liquid level (~0.12 mL). A quantity of BCl_3 (0.30 mmol) was also added to the mixture, and then the tube was subsequently sealed. After the sample was mixed well at room temperature, two liquid layers were again observed. Peak integration of the ^1H (with and without ^{11}B decoupling) NMR spectra for the top layer showed a 2:1 ratio (±2%)

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Table I. NMR Parameters

compd	nucleus	δ $^{11}B^{a,b}$ (J/Hz) [δ ^{11}B, calcd]^d	nucleus	δ $^1H^c$ (J/Hz)^b
$(CH_3)_3N{\cdot}5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$	2 B	−19.4 d (179)	1 HC	5.68
	1 B	+6.3 d (157)	1 HC	7.63
	1 B	+17.4 s	2 HB	0.36
	1 B	+2.3 d (130)	1 HB	4.57
			1 HB	3.77
			$(H_3C)_3N$	3.40
$[5\text{-}(CH_3)_3N\text{-}2,4\text{-}C_2B_5H_6]^+[BCl_4]^-$	B(1, 7)	−19.3 d (190)	HB(1, 7)	0.66 s
	B(3)	+6.3 d (183)	HC(2)	5.86 m
	B(5)	+16.8 s	HB(3)	4.88 t (6.5)
	B(6)	+1.7 d (156)	HC(4)	6.27 m
	BCl_4^-	+10.3 s	HB(6)	4.21 d (9.0)
			$(H_3C)_3N$	3.41 s
$[3\text{-}(CH_3)_3N\text{-}2,4\text{-}C_2B_5H_6]^+[BCl_4]^-$	B(1, 7)	−17.8 (184)	HB(1, 7)	0.45 s
	B(3)	+17.1 s	HC(2, 4)	5.85 d (9.9)
	B(5, 6)	+3.9 d (160)	HB(5, 6)	3.82 d (9.7)
	BCl_4^-	+7.7 s	$(H_3C)_3N$	3.40 s
$[5\text{-}(CH_3)_3N\text{-}6\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_5]^+$	B(1, 7)	−18.0 d (189) [−18.7]^d	HB(1, 7)	0.8 s [0.72]^d
	B(3)	+5.8 d (200) [+5.5]	HC(2)	5.43 dd (7.0, 3.6) [5.44]
	B(5)	+14.0 s [+15.4]	HB(3)	4.75 t (7.1) [4.74]
	B(6)	+9.9 s [+8.9]	HC(4)	6.00 dd (7.1, 3.6) [6.05]
			CH_3B	0.89 s
			$(H_3C)_3N$	3.40 s
$5\text{-}Cl\text{-}6\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_5$	B(1, 7)	−19.0 d (180) [−19.2]^d	HB(1, 7)	0.6 [0.61]
	B(3)	+4.3 d (180) [+4.1]	HC(2)	5.1 [5.01]
	B(5)	+12.0 s [+11.4]	HB(3)	4.68 t (6.8) [4.70]
	B(6)	+9.8 s [+8.0]	HC(4)	5.3 [5.21]
			$CH_3B(6)$	0.68
$1\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$	B(1)	−15.8 s	HC(2, 4)	5.93 dd (6.8, 9.7)
	B(3)	+8.8 d (167)	HB(3)	5.10 t (6.8)
	B(5, 6)	+3.5 d (173)	HB(5, 6)	4.29 d (9.7)
	B(7)	−32.8 d (190)	HB(7)	−0.06 s

[a] Referenced to BCl_3, δ +46.8 ppm, a secondary external standard. [b] Abbreviations: s = singlet, d = doublet, t = triplet. [c] ^{11}B-decoupled ^1H data referenced to internal $(CH_3)_4Si$, δ 0.00. [d] See text and Tables II and III.

of $CHCl_3$ to $[5\text{-}(CH_3)_3N\text{-}$*closo*$\text{-}2,4\text{-}C_2B_5H_6][BCl_4]$.

(B) Use of CD_2Cl_2 or CH_2Cl_2 as the Solvent. The formation of the 1:1 $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6{\cdot}(CH_3)_3N$ adduct in methylene chloride gave essentially the same results as described above when $CDCl_3$ or $CHCl_3$ was used. But several sharp impurity peaks were also observed in the region of δ 2.2–3.0 in the ^1H NMR spectra. After addition of BCl_3, the solution remained as one liquid layer. Both ^{11}B and ^1H NMR spectra are consistent with the salt $[5\text{-}(CH_3)_3N\text{-}2,4\text{-}C_2B_5H_6][BCl_4]$. Upon addition of excess BCl_3 to the solution, the BCl_4^- resonance in the ^{11}B NMR spectrum at δ +10.3 shifted downfield to δ +33.2. This is a reversible process as was observed by removing the excess BCl_3 upon which the BCl_4^- peak shifted to δ +10.

(C) Reaction of $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ with Excess $(CH_3)_3N$. Trimethylamine (10 mmol) was condensed over $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ (2.5 mmol) in a 250-mL glass bulb. After the mixture was allowed to react at room temperature for 2 h, a substantial quantity of white solid had formed. No noncondensable gas was detected. The volatile portion was removed and identified as trimethylamine (7.0 mmol).

Attempt To Release $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ from the 1:1 $(CH_3)_3N$ Adduct Using HCl. The adduct from part C above was treated with dry HCl (1.75 mmol) at ambient temperature. No $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ was released during a 2-h treatment with the HCl, as evidenced by the absence of any carborane material in the volatile portion after high-vacuum fractionation. However, small amounts of cleavage products such as BCl_3, CH_3BCl_2, and $CH_2(BCl_2)_2$ were detected in the volatile portion. After removal of the HCl, BCl_3 (2.0 mmol) was subsequently added to the residue. Upon dissolution of the resulting mixture in $CDCl_3$ (~2 mmol), the formation of $[5\text{-}(CH_3)_3N\text{-}$*closo*$\text{-}2,4\text{-}C_2B_5H_6][BCl_4]$ resulted.

Reactions of $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ with Other Reagents. At ambient conditions, $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ did not react either with BCl_3 or with Lewis bases such as $(C_2H_5)_3N$, $(C_6H_5)_3P$, and $(C_6H_5)N(CH_3)_2$. However, $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ (0.5 mmol) did react with $(CH_3)_3P$ (0.6 mmol) to afford a 1:1 solid adduct, and when this adduct was subsequently treated with excess BCl_3, $[5\text{-}(CH_3)_3P\text{-}2,4\text{-}C_2B_5H_6]^+[BCl_4]^-$ was obtained, which exhibits the following ^{11}B NMR chemical shifts (δ, CD_2Cl_2): −18.9 (d, J(BH) = 189 Hz), B(1,7); +7, broad, B(3,6); +3.8 (d, J(PB) = 158 Hz), B(5); +30.6 ($BCl_4^- \rightleftharpoons BCl_3$).

Reaction of a 1- and $3\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ Mixture with $(CH_3)_3N$. To a mixture (0.40 mmol) of $1\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ (80%) and $3\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ (20%) was added $(CH_3)_3N$ (0.15 mmol). A white precipitate formed when the sample was warmed to room temperature. After the sample had remained at room temperature for approximately 2 h, the volatile portion (0.30 mmol) was removed in vacuo, and except for a small amount of $(CH_3)_3N$, the volatile fraction contained nearly pure $1\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ (from ^{11}B and ^1H NMR analyses). To the solid residue (containing 1:1 $3\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6\text{–}(CH_3)_3N$) was added BCl_3 (0.25 mmol) followed by $CDCl_3$ (1 mmol). The solids did not dissolve well in the $CDCl_3$, and the ^{11}B NMR of the solution exhibited only a BCl_3 resonance. The volatile portion was removed, and the solid was dissolved in CD_2Cl_2 (1.0 mmol). Fresh BCl_3 (0.25 mmol) was then added before sealing the tube. Upon being warmed to room temperature, the entire contents of the tube became a single liquid phase. The NMR data, Table I, were consistent with a CD_2Cl_2 solution of $[3\text{-}(CH_3)_3N\text{-}2,4\text{-}C_2B_5H_6]^+[BCl_4]^-$, formed in quantitative yield.

Reaction of $1\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ with $(CH_3)_3N$. To pure $1\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ (0.30 mmol) kept at 196 °C in a NMR tube was added $(CH_3)_3N$ (0.5 mmol). The tube with its contents was then sealed, allowed to come to room temperature, and mixed well by shaking. The sample was monitored by both ^1H and ^{11}B NMR at 1–2-day intervals. After 1 day some solid had formed, but the ^1H NMR of the liquid phase showed only the resonances of both $(CH_3)_3N$ and unreacted $1\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$. After 3 days, additional solid was formed with a concomitant reduction of the liquid phase. Again the liquid phase was found to contain only $1\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ and $(CH_3)_3N$. Most of the liquid disappeared within a 7-day period. The sample tube was subsequently opened into the high-vacuum apparatus, and volatile material was removed. Both $CDCl_3$ (2.0 mmol) and BCl_3 (0.5 mmol) were added to the solid residue before sealing the sample tube again. The sample was warmed slowly from −196 °C to room temperature upon which two distinct layers were formed. The ^{11}B NMR spectrum corresponded to that found for $[3\text{-}(CH_3)_3N\text{-}$*closo*$\text{-}2,4\text{-}C_2B_5H_6]^+[BCl_4]^-$ formed in quantitative yield, with shifts found at δ −17.6 (d, area 2, 180 Hz), +4 (d, area 2, 157 Hz), +17.4 (s, area 1), and +7.9 (s, area 1) corresponding to B(1,7), B(5,6), B(3), and $[BCl_4]^-$, respectively. The ^{11}B-decoupled ^1H NMR resonances are found at δ 3.4, 5.90 (d, 10 Hz), 3.83, and 0.41 and assigned to $Me_3NB(3)$, HC(2,4), HB(5,6), and HB(1,7), respectively.

Reaction of $5\text{-}Cl\text{-}6\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_5$ with $(CH_3)_3N$. A sample of $5\text{-}Cl\text{-}6\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_5$ (0.50 mmol), containing 5% $5\text{-}Cl\text{-}1\text{-}CH_3\text{-}$

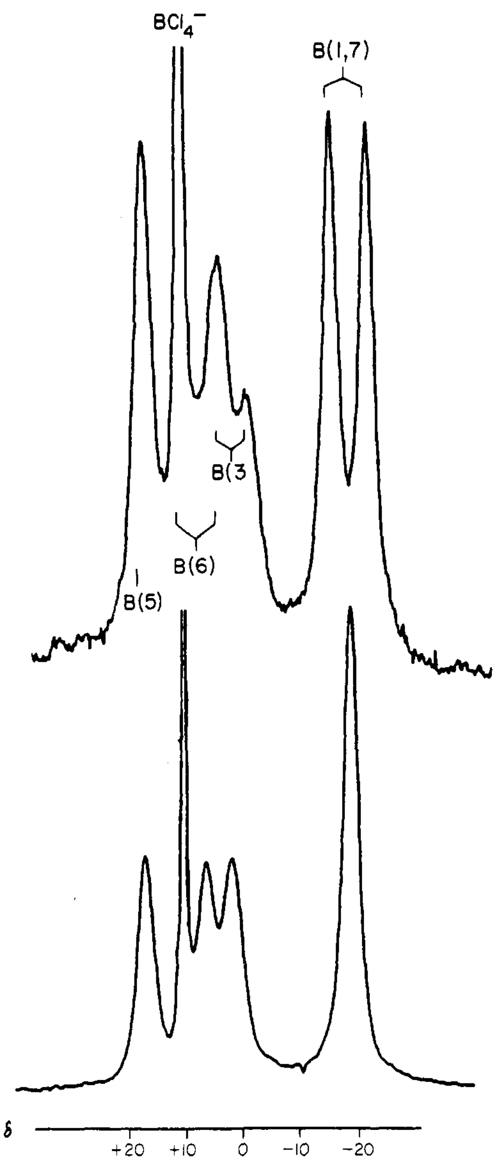

Figure 1. Undecoupled (top) and ^{1}H-decoupled (bottom) ^{11}B NMR of $[5\text{-}(CH_3)_3N\text{-}closo\text{-}2,4\text{-}C_2B_5H_6][BCl_4]$.

$2,4\text{-}C_2B_5H_5$ impurity, and $(CH_3)_3N$ (1.0 mmol) was added to a 4-mm NMR tube kept at −196 °C, and the sample tube was subsequently sealed. The mixture was warmed to room temperature, and after 1 h of standing white solids began to precipitate from the liquid solution. After an overnight period had elapsed, the liquid portion was reduced in volume to approximately half the original quantity. After the tube was inverted, the liquid portion drained to the opposite end, leaving white solids adhering to the other end of the tube; no additional solids formed in the liquid layer with additional time (1 day) at room temperature. The sample tube was opened, and excess $(CH_3)_3N$ (~0.4 mmol) was removed. To the white solid residue was added BCl_3 (0.50 mmol) and $CDCl_3$ (2.0 mmol), but because the solids did not dissolve in $CDCl_3$, the solvent was changed to CD_2Cl_2 (2 mmol). A fresh portion of BCl_3 (0.5 mmol) was also added upon changing solvents. All solids dissolved in CD_2Cl_2, and the ^{11}B resonances observed for the solution were found at δ −17.9 (d, area 2, 189 Hz), +5.7 (d, area 1, 200 Hz), +14.0 (s, area 1), +9.9 (s, area 1) and +39 (s) and assigned to B(1,7), B(3), B(5), B(6), and BCl_4^- (in exchange process with BCl_3), respectively, for the salt $[5\text{-}(CH_3)_3N\text{-}6\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_5]^+[BCl_4]^-$. The ^{1}H NMR shifts are found at δ 6.00 (HC(4)), 5.43 (HC(2)), 4.75 (HB(3)), 3.40 ($(CH_3)_3N$–B), 0.89 (CH_3B), and 0.86 (HB(1,7)). In addition to the above, weak ^{11}B NMR absorptions were found at δ −8.8 (CH_3B(1)) and −26.2 (high-field member of HB(7) doublet) and a weak ^{1}H absorption at δ −0.2 ± 0.1 was observed. These are attributed to those resonances of $[5\text{-}(CH_3)_3N\text{-}1\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_5]^+[BCl_4]^-$ that are not overlapped with the main product.

Reactions of Trimethylamine with Chloroform and Methylene Chloride. A control experiment indicated that at ambient temperature CH_2Cl_2 reacted with $(CH_3)_3N$ slowly over a period of 1–2 days. The resulting solid complex did not dissolve very well in CH_2Cl_2 but was soluble in CD_3CD_2OD. The ^{1}H NMR spectrum of the solution exhibited resonances at δ 5.69, relative area 2, and δ 3.00, relative area 9, consistent with $[(CH_3)_3NCH_2Cl]^+[Cl]^-$.[9] A mixture of $(CH_3)_3N$ (0.5 mmol) and $CHCl_3$ (0.5 mmol) was mixed at room temperature. No reaction was observed over a period of 2 weeks.

Reaction of $5\text{-}Cl\text{-}C_2B_5H_6$ with Sodium Tetrahydroborate. Into a 3-mm tube was added $NaBH_4$ (0.0039 g, 0.1 mmol) and $CD_3OCD_2CD_2OCD_3$ (0.5 mmol, dried over $LiAlH_4$). $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ (0.075 mmol) was subsequently added to the mixture, and the tube and contents were then sealed. At room temperature the ^{11}B NMR spectrum of the resulting mixture did not exhibit peaks other than those for $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$. The sample was then heated at 70 °C for 1 h, but no reaction occurred, as assessed by NMR monitoring. After the sample was heated at 100 °C for 15 h, the ^{11}B NMR spectrum indicated that approximately 50% of the starting $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ had reacted and new peaks appeared at δ −20.9 (B(1,7), J(HB) = 184 Hz), +4.6 (B(5,6), J(HB) = 183 Hz), and +7.9 (B(3), J(HB) = 187 Hz) corresponding to $2,4\text{-}C_2B_5H_7$.[8] The sample was subsequently heated at the same temperature (100 °C) for an additional period of 2 days. The spectrum of $2,4\text{-}C_2B_5H_7$ significantly gained in intensity relative to that assigned to $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$.

Results and Discussion

Although the parent $closo\text{-}2,4\text{-}C_2B_5H_7$ does not react with tertiary amines nor with tertiary phosphines, below 300 °C we have found that placement of a chlorine atom at certain boron sites of this pentagonal-bipyramidal carborane can result in facile adduct formation with Lewis bases. Both 5- and $3\text{-}Cl\text{-}closo\text{-}2,4\text{-}C_2B_5H_6$ form 1:1 adducts with $(CH_3)_3N$ in the course of warming frozen 1:1 mixtures of the reagents to room temperature. Analogously, $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ reacts rapidly with $(CH_3)_3P$ to give a solid product, which analyzes for the 1:1 adduct, $(CH_3)_3P\cdot ClC_2B_5H_6$. All three of these adducts react with BCl_3 to form the salts $[L\text{-}closo\text{-}2,4\text{-}C_2B_5H_6]^+[BCl_4]^-$, where L = R_3N or R_3P (Figure 2). Nuclear magnetic resonance data (Table I) provide firm evidence to show that the same boron atom to which the chlorine was originally bound is the site of Lewis base attachment in the salts. Thus, the net effect of adduct formation, and subsequent reaction of these adducts with BCl_3, is a two-step displacement of a boron-substituted chlorine by the amine (or phosphine). It is significant to note that there is no evidence to indicate that any portion of the second step in this sequence involves the abstraction of L from the adduct to give $L\cdot BCl_3$ and $ClC_2B_5H_6$. Moreover, treatment of the $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6\cdot(CH_3)_3N$ adduct with dry HCl does not release the chlorocarborane from the amine; both this and the results of the BCl_3 reaction suggest a strong B–N bond in the adduct.

In contrast to the above *B*-chloro isomers, $1\text{-}Cl\text{-}closo\text{-}2,4\text{-}C_2B_5H_6$ reacts much more slowly with trimethylamine to form an adduct, which, after BCl_3 is added, gives *not* the anticipated $[1\text{-}(CH_3)_3N\text{-}closo\text{-}2,4\text{-}C_2B_5H_6]^+[BCl_4]^-$ salt but instead the same isomer, $[3\text{-}(CH_3)_3N\text{-}closo\text{-}2,4\text{-}C_2B_5H_6]^+[BCl_4]^-$, as experienced when the reaction sequence is started with $3\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$ (Figure 2).

By the drawing of an analogy to products obtained from the reactions of $closo\text{-}1,6\text{-}C_2B_4H_6$ with tertiary amines and phosphines,[1-3] it is to be expected that the Lewis base adducts of the $closo\text{-}ClC_2B_5H_6$ isomers should all adopt nido skeletal arrangements of cage carbon and boron atoms. An appropriate nido structure can be formally derived by removing a high-coordination vertex from an 8-vertex closo polyhedron,[10,11] as

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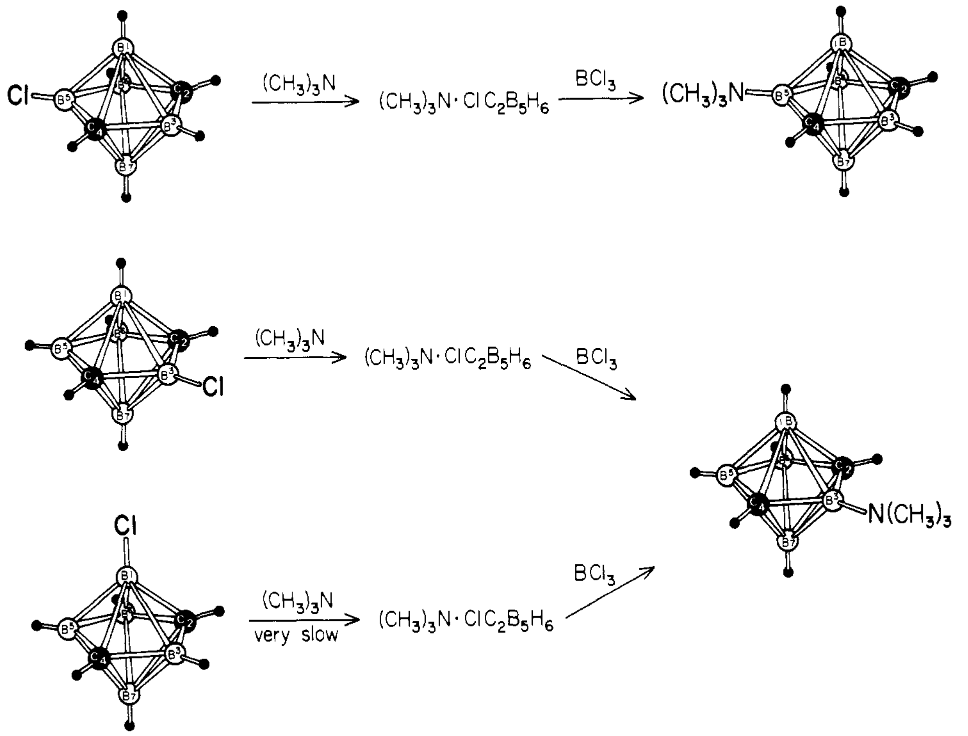
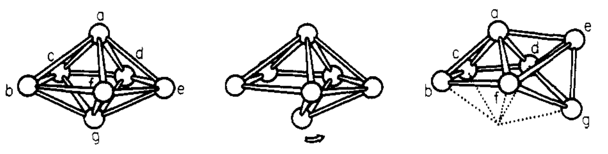


Figure 2. Reaction of *B*-chloro derivatives of *closo*-2,4-$C_2B_5H_7$ with $(CH_3)_3N$ and subsequently with BCl_3. The two $(CH_3)_3NC_2B_5H_6$ structures depicted on the far right are cations; BCl_4^- is the counterion.



(I) (II)

Figure 3. Conversion of closo to nido Geometry for a 7-atom polyhedron.

depicted in II, Figure 3. In the present instance, the accessibility of a 7-atom nido compound from the 7-atom closo polyhedron is realized by separating an axial atom from two (adjacent) equatorial atoms (of I, Figure 3) in such a manner as to minimize changes in bond distances within the remainder of the framework. The resulting nido structure, II (or hybrid of I and II, see below), allows for numerous isomeric possibilities when placement of Cl and $(CH_3)_3N$ substituents as well as positioning of cage carbon atoms is considered. On the basis of structural knowledge of the starting closo cage material as well as of the eventual closo product salt obtained after BCl_3 is added (and on the assumption that no extraordinary rearrangements are occurring with the reactions that utilize 5- and 3-Cl-2,4-$C_2B_5H_6$ isomers as the starting materials), the following considerations are plausible for the 5- and 3-$ClC_2B_5H_6$ adducts: (1) Position g of II, originally one of the two axial positions of the closo structure, should be occupied neither by a cage carbon atom nor by the $(CH_3)_3N$ substituent group in the adduct when the reaction starts with 5- or 3-Cl-2,4-$C_2B_5H_6$. (2) The approach of the $(CH_3)_3N$ toward the closo cage in the case of the 5-Cl and 3-Cl derivatives of $C_2B_5H_7$ is expected to decrease the need of the halogen-bound boron for cage electrons; thus it is tempting to assign this cage boron atom to one of the two equatorial positions (position b or c of II), which separates from axial position g. Consequently, both the Cl and $(CH_3)_3N$ groups in the adducts are probably bound to either b or c in II. (3) From the above statements 1 and 2, the cage carbons for the adduct derived from 5-Cl-2,4-$C_2B_5H_6$ are consequently located at d and f or at c and e, should the Cl and $(CH_3)_3N$ groups both be situated at b, or at the related mirror image positions, b and e (or d and f), should the substituents be located at position c. For the 3-Cl-2,4-$C_2B_5H_6$ adduct the cage carbons can only be positioned at c and f should the substituents be at b (consider also the mirror image possibility here, as well). It is not possible to arrive at any satisfactory orientation of the Cl and $(CH_3)_3N$ groups with respect to exo or endo locations relative to the open face.

An important feature of 5-$(CH_3)_3L$-*nido*-2,4-$C_2B_4H_6$ formation from *closo*-1,6-$C_2B_4H_6$ and $L(CH_3)_3$ (L = N, P) is the net movement of a hydrogen from a terminal (originally attached to a *closo*-1,6-$C_2B_4H_6$ boron) to a bridging position (μ-5,6 of the nido product) adjacent to the $(CH_3)_3L$-attached boron.[1-3] An analogous net movement of a terminal hydrogen to a bridging position as a result of R_3L: attack at the chlorine-attached boron of either 5- or 3-Cl-*closo*-2,4-$C_2B_5H_6$ (forming the respective adducts) is not immediately obvious nor indicated by NMR data. And the movement of the chlorine into a stable bridging position is not likely when we acknowledge that stable boron compounds with bridging chlorine atoms are unknown (e.g., BCl_3 is a monomer; *cf.* BH_3, which is manifested as B_2H_6. Also, chloropolyboranes are rather common but none are known to contain a bridging chlorine atom although bridging hydrogen atoms are often found in such molecules[12]). It is significant to note that the boron-attached terminal hydrogen of the smaller (octahedral) $C_2B_4H_6$ carborane, upon moving to a bridging site in the (pentagonal-pyramidal) adduct can be considered an electron-donating "prop" assisting the cage to retain a (open-face) nido structure. And because such simple terminal to bridging hydrogen movement cannot occur upon R_3L: attack of *B*-Cl-*closo*-2,4-$C_2B_5H_6$ at a BCl site, the adduct product in this instance may not prove to be very stable in a formal open-cage

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(nido) form, II (Figure 3), and may adopt some closo-framework character. The tendency of the cage to close, or open, should also be a function of the ease with which the halogen atom can depart as halide ion. Such ionic character is promoted by the addition of boron trichloride to the adduct, whereby BCl_3 is observed to combine with the incipient Cl^- ion to form BCl_4^- (vide supra). It may well be that a significant degree of B–Cl bond ionization is present in the adduct, implicating a proportionate amount of closo character for the carborane cage. In this regard, it is interesting to note the ^{11}B NMR of the 5-Cl-2,4-$C_2B_5H_6$·$(CH_3)_3N$ adduct is somewhat similar (Table I) to that of its closo precursor as well as to that of the final closo product ion. However, the ^{11}B NMR pattern of this adduct is broad, making it difficult to ascertain whether the resonance of relative area 2 at δ −19.4 (Table I) represents two equivalent (consistent with a closo cage framework of proper symmetry) or two nonequivalent boron atoms (consistent with a nido structure, e.g., II (Figure 3), or a closo cage in which the two axial positions are not symmetrically disposed toward an equatorial B(Cl)(NMe_3) group). The broadness of the peaks could suggest a degree of fluxional behavior, perhaps involving positions a and g (Figure 3) taking turns breaking away from positions b and c. A variable-temperature NMR study conducted on a solution of this adduct molecule unfortunately did not illuminate this matter.

The $(CH_3)_3N$·5-Cl-2,4-$C_2B_5H_6$ adduct appears to be very stable, even when in solution, with no tendency to dissociate into the starting materials. In contrast, the $(CH_3)_3N$·3-Cl-2,4-$C_2B_5H_6$ adduct, upon dissolving in $HCCl_3$ or H_2CCl_2, shows NMR spectroscopic properties very similar to those of 3-Cl-2,4-$C_2B_5H_6$. Only upon addition of BCl_3 directly to the solid $(CH_3)_3N$·3-$ClC_2B_5H_6$ adduct, before dissolution in solvent, is [3-$(CH_3)_3N$-2,4-$C_2B_5H_6$]$^+$[BCl_4]$^-$ formed in excellent yield. Otherwise, some dissociation of the adduct appears to take place in $HCCl_3$ solution, consequently allowing dissociated R_3L to form R_3L·BCl_3 when BCl_3 is subsequently added, or in the case of CH_2Cl_2 as the diluent, the Lewis base reacts with the solvent to eventually form products such as [$(CH_3)_3NCH_2Cl$]$^+Cl^-$ (when R = CH_3, L = N).[9]

When 5-Cl-6-CH_3-*closo*-2,4-$C_2B_5H_5$ is employed as the starting material in the $(CH_3)_3N/BCl_3$ reaction sequence, the *B*-methyl group of the product, [5-$(CH_3)_3N$-6-CH_3-*closo*-2,4-$C_2B_5H_5$][BCl_4], is in the same type (5,6) of cage equatorial position as in the starting material. This suggests that cage rearrangements during the course of the 5-Cl-2,4-$C_2B_5H_6$·N$(CH_3)_3$ amine adduct formation, and subsequent BCl_3 addition, are highly unlikely (unless, of course, an interchange occurs between the 5- and 6-positions). This is in contrast to the reaction sequence involving 1-Cl-*closo*-2,4-$C_2B_5H_6$, which produces [3-$(CH_3)_3N$-*closo*-2,4-$C_2B_5H_6$][BCl_4] (vide supra). It has been earlier suggested that *dsd* and/or triangle-rotation mechanisms can account for certain thermal rearrangements involving closed polyhedra.[12-21] If products or intermediates are restricted to those without adjacent cage carbon atoms or without cage carbon atoms at the high-coordination axial positions,[21,22] the following equilibria result between B-substituted compounds of *closo*-$C_2B_5H_7$:

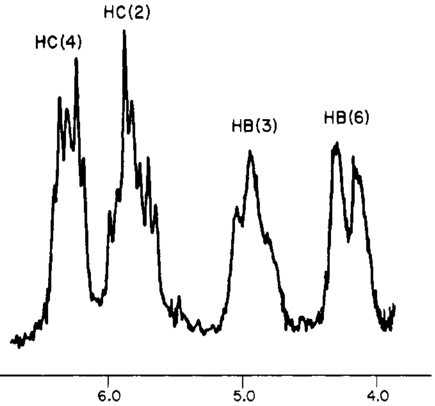

Figure 4. Low-field region of the ^1H NMR (^{11}B-decoupled) spectrum of [5-$(CH_3)_3N$-*closo*-2,4-$C_2B_5H_6$][BCl_4].

$$(dsd)\quad 5\text{-X-2,4-}C_2B_5H_6 \rightleftharpoons 1\text{-X-2,4-}C_2B_5H_6 \rightleftharpoons 3\text{-X-2,4-}C_2B_5H_6$$

$$(\text{triangle-rotation})\quad 1\text{-X-2,4-}C_2B_5H_6 \rightleftharpoons 5\text{-X-2,4-}C_2B_5H_6 \rightleftharpoons 3\text{-X-2,4-}C_2B_5H_6$$

On application of a triangle-rotation scheme, the route to a 3-substituted from a 1-substituted compound of *closo*-2,4-$C_2B_5H_7$ must involve a 5-substituted intermediate. But a triangle-rotation mechanism seems inconsistent with the rearrangement observed in the present study in that (a) 1-Cl-2,4-$C_2B_5H_6$ leads to the rearranged product [3-$(CH_3)_3N$-2,4-$C_2B_5H_6$]$^+$ only and (b) both 5-Cl-2,4-$C_2B_5H_6$ and 5-Cl-6-CH_3-2,4-$C_2B_5H_5$ both show, upon reaction with $(CH_3)_3N$ and subsequently BCl_3, no indication of rearranged (1- or 3-substituted) products. In contrast, a *dsd*-related scheme allows a direct conversion of 1-substituted to a 3-substituted 7-atom closo cage without requiring an intermediate 5-substituted closo cage. Earlier *dsd* mechanistic schemes suggest pseudo-"C_{2v}" or -"C_{3v}" intermediates (or transition states) during the rearrangement of a 7-atom closo cage to another such polyhedron.[12,13,22,23] The role that $(CH_3)_3N$ could play in promoting these schemes is not entirely clear; previous studies do not address a situation involving the role of a Lewis base in this type of cage rearrangement. A C_{3v} related intermediate, with all triangular faces, can be considered a high-energy closo system with acute bond angles. (The C_{3v} framework may better be considered hyper-closo when viewed as a capped octahedron.)[24] The C_{2v} related intermediate is essentially an unstable arachno 7-atom cage system derived by uncapping two of the square faces of a 9-vertex closo tricapped trigonal prism. The more open C_{2v} should be favored over a C_{3v} intermediate (or transition state) when a Lewis base with its pair of electrons is attached, as in the adducts of the present study. But an arachno C_{2v} intermediate even seems suspect when it is acknowledged that the stable Lewis base adduct of *closo*-$ClC_2B_5H_6$ may not be as open (nido) as might originally be expected, owing to factors mentioned earlier in this discussion section. More attractive is a *dsd*-related rearrangement process, which does not involve the simultaneous creation of two square "open" faces (as in the C_{2v} intermediate) but forms sequentially one square face followed by *dsd* closing

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Table II. Proton NMR Additivity Constants[a]

position and type of substitution	σ (^{1}H) for each hydrogen type, ppm[b]						
	1	2	3	4	5	6	7
1-Cl		+0.40	+0.15	+0.40	+0.16	+0.16	−0.17
3-CH_3	+0.06	−0.30		−0.30	−0.13	−0.13	+0.06
-Cl	+0.44	−0.17		−0.17	−0.18	−0.18	+0.44
-$(CH_3)_3N$	+0.34	+0.27		+0.27	−0.31	−0.31	+0.34
5-CH_3	+0.06	−0.22	−0.14	−0.42		−0.25	+0.06
-Cl	+0.44	~-0.1	~-0.11	−0.1		−0.25	+0.44
-$(CH_3)_3N$	+0.55	+0.33	−0.07	+0.74		+0.08	+0.55
6-CH_3	+0.06	−0.42	−0.14	−0.22	−0.25		+0.06
-Cl	+0.44	−0.1	−0.11	−0.1	−0.25		+0.44
-$(CH_3)_3N$	+0.55	+0.74	−0.07	+0.33	+0.08		+0.55
7-Cl	−0.17	+0.40	+0.15	+0.40	+0.16	+0.16	

[a] Values for the groups were derived from data in the following references: 3-CH_3-2,4-$C_2B_5H_6$, ref 22; 3- and 5-Cl-2,4-$C_2B_5H_6$, ref 7; 1-Cl-2,4-$C_2B_5H_6$, the present study. [b] Based on δ(substituted compound) − (parent compound).

Table III. ^{11}B NMR Additivity Constants[a]

position and type of substitution	σ (^{11}B) for each boron type, ppm[b]				
	1	3	5	6	7
1-CH_3	+9.4	+1.1	0.0	0.0	−5.3
-Cl	+5.4	+1.6	−0.5	−0.5	−11.6
3-CH_3	+0.9	+6.7	−0.1	−0.1	+0.9
-Cl	+2.8	+7.6	−1.1	−1.1	+2.8
-$(CH_3)_3N$	+3.1	+9.9	−0.1	−0.1	+3.1
5-CH_3	+0.6	−0.8	+7.2	−1.4	+0.6
-Cl	+1.4	−2.3	+8.8	−3.2	+1.4
-$(CH_3)_3N$	+1.9	−0.9	+12.8	−2.3	+1.9
6-CH_3	+0.6	−0.8	−1.4	+7.2	+0.6
-Cl	+1.4	−2.3	−3.2	+8.8	+1.4
-$(CH_3)_3N$	+1.9	−0.9	−2.3	+12.8	+1.9
7-CH_3	−5.3	+1.1	0.0	0.0	+9.4
-Cl	−11.6	+1.6	−0.5	−0.5	+5.4

[a] Values for the groups were derived from data in the following references: methyl derivatives, ref 22; 3- and 5-Cl-2,4-$C_2B_5H_6$, ref 7; 1-Cl-2,4-$C_2B_5H_6$ and 3- and 5-Me_3N-2,4-$C_2B_5H_6$, the present study. [b] Based on δ(substituted compound) − δ(parent compound).

of this face within the same time interval that another square face is forming. Closing the second square face in an appropriate *dsd* fashion then gives rise to the observed rearrangement product.

No reaction is observed between 5-Cl-2,4-$C_2B_5H_6$ and Lewis bases such as triethylamine, triphenylphosphine, and phenyldimethylamine; however, an apparent hydride displacement of the halogen takes place upon reacting this carborane derivative with $NaBH_4$, giving the parent *closo*-2,4-$C_2B_5H_7$.

Nuclear Magnetic Resonance

Most of the ^{11}B and ^{1}H NMR resonances of the new *closo*-2,4-$C_2B_5H_7$ derivatives (Table I) were assigned upon making comparisons to closely related systems reported in past literature.[6–8,22,25] The HC(2) and HC(4) proton resonances (Figure 4) of the $[5\text{-}(CH_3)_3N\text{-}closo\text{-}2,4\text{-}C_2B_5H_6]^+$ ion are assigned on the basis of nearest-neighbor H,H coupling patterns; normally, values of 6–10 Hz are found for J(H H) between HC(cage) and HB(3) or HB(5).[7,22,25–27] The low-field multiplet at δ 6.27 stretching across a region of 13 Hz is assigned to HC(4), comprising a combination of J[H(4)H(3)] = 6.5 Hz and J[H(4)H(2)] $\cong$ 4 Hz, whereas the multiplet at δ 5.86, stretching across a region of 20 Hz, is assigned to HC(2), comprising a combination of J[H(2)H(3)] = 6.5 Hz, J[H(2)H(6)] = 9.0 Hz, and J[H(2)H(4)] $\cong$ 4 Hz. A long-range HC(2)HC(4) coupling of 3.6 Hz is clearly observed in the ^{11}B-decoupled HC resonances of the $[5\text{-}(CH_3)_3N\text{-}6\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_5]^+$ ion. This is the first instance in which long-range coupling of this type has been observed as an easily assigned "first-order" pattern and is made possible by the large chemical shift difference between the two HC(cage) types. This situation is created by the combined opposite substituent shift effects of the 5-$(CH_3)_3N^+$– and 6-CH_3– groups. Such substituent effects can be independently numerically determined by comparing the NMR data for appropriate monosubstituted compounds with that for the parent 2,4-$C_2B_5H_7$ (Table II). Combining both the individual effects of the 5-$(CH_3)_3N^+$– and 6-CH_3– groups predicts a chemical shift difference of 0.61 ppm between HC(4) (nearer the positively charged $(CH_3)_3N$– group) and HC(2); this is very close to the observed difference of 0.57 ppm (in both cases the HC(4) resonance is at lower field than that of HC(2)). A similar comparison can be made between the calculated HC(2)···HC(4) chemical shift difference (with use of Table II) and the experimentally observed value (obtained from Table I) for the precursor 5-Cl-6-CH_3-2,4-$C_2B_5H_5$, which in both cases are 0.20 ppm. Further, all observed chemical shift values, ^{11}B as well as ^{1}H, for both of the disubstituted compounds are very nearly those (correlation coefficient $r = 0.997$) calculated on the basis of additivity effects (Tables II and III) derived from the comparison monosubstituted compounds. The calculated ^{11}B and ^{1}H δ values for both 5-Cl-6-CH_3-2,4-$C_2B_5H_5$ and $[5\text{-}(CH_3)_3N\text{-}6\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_5]^+$ are given in brackets in Table I beside the experimental values for comparison.

The presence of trimethylamine in 1-Cl-2,4-$C_2B_5H_6$ (in an approximate mole ratio of 1:1, and before reaction takes place) significantly shifts (0.19 ppm) the HC(cage) proton resonances downfield without greatly affecting the other cage resonances; one explanation of this observation may involve HC(cage) hydrogen bonding to the trimethylamine solvent. This is consistent with the known cage carbon attached hydrogen (weak) acidity for this compound[28–30] and proposed hydrogen bonding observed in other carborane cage systems.[31,32]

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Registry No. 5-Cl-*closo*-2,4-$C_2B_5H_6$, 79534-16-0; 5-Cl-6-CH_3-*closo*-2,4-$C_2B_5H_5$, 79550-11-1; 1-CH_3-5-Cl-*closo*-2,4-$C_2B_5H_5$,

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A New Approach to the Structures and Rearrangements in *closo*-Boron Hydrides

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A new approach to bonding in *closo*-boron hydrides, $B_nH_n^{2-}$, has been developed in which each boron atom is considered to bond directly to all other boron atoms. A simple bireciprocal interaction is used to relate energy u to internuclear distance d: $u = 1/d^x - 1/d^y$. A good fit with experimental structures is found for low values of x and y, typical values being $x = 2$ and $y = 1$. This simple expression allows the assessment of a large number of complex molecular polyhedra in which the geometric parameters are allowed to vary freely in order to reach a minimum energy. For example, in $B_{12}H_{12}^{2-}$ no less than 10 structures are found between the most stable stereochemistry, the regular icosahedron, and the cuboctahedron.

Two basic approaches have been used to describe the bonding in *closo*-boron hydrides, $B_nH_n^{2-}$, and related compounds.[1] The first is a topological description of localized bonds. Each boron atom participates in four tetrahedrally arranged bonds, which may be B–H, B–B, or three-center B_3, the three boron atoms being in a triangular arrangement. A large number of resonance structures must be considered for any molecule. For example, each resonance form in the highly symmetrical structure of $B_{12}H_{12}^{2-}$ has four different types of boron atoms, while in $B_8H_8^{2-}$ all boron atoms must be different in any one resonance structure. One result from this approach to bonding is the prediction that the stable molecular polyhedra will be those that contain only triangular faces, but this may arise directly from the assumption of triangular three-center B_3 bonding.

The second approach is a molecular orbital treatment. Each boron atom uses one sp hybrid pointing out from the boron cluster for B–H bonding, the other pointing inward for bonding within the cluster. The single most bonding molecular orbital is that formed by the in-phase interaction of *all* these radial sp-hybrid orbitals at the center of the cluster, in an *n*-center bond that directly bonds each boron atom to every other boron atom. The two remaining p orbitals tangential to the surface of the cluster interact with similar orbitals on other boron atoms, and with the inwardly directed sp hybrids, to form very complicated molecular orbital schemes.

It is very difficult to use either of these approaches to accurately predict structural parameters such as bond lengths and bond angles or to assess the relative stability of the large number of transition states that can be visualized in intramolecular rearrangements.

In this work we explore an alternative bonding approach. Each boron atom is considered to interact simultaneously with *all* other boron atoms, the interactions depending *only* on the interatomic distances. A simple bireciprocal relation is used to describe the energy u_{ij} between two boron atoms i and j separated by a distance d_{ij}:

$$u_{ij} = \frac{1}{d^x} - \frac{1}{d^y} \qquad \text{where } x > y$$

The total bonding energy is then

$$U = \sum_{ij} u_{ij}$$

where d and U are in arbitrary units. Values of x and y are obtained by fitting the resulting calculated structures against the known crystal structures of $B_8H_8^{2-}$ and $B_9H_9^{2-}$, which are the only simple compounds known with sufficient precision for this purpose. Some implications to the intramolecular rearrangements of $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{12}H_{12}^{2-}$ are then discussed.

Structure of $B_8H_8^{2-}$

The anion in $[Zn(NH_3)_4][B_8H_8]$ is dodecahedral (Figure 1), with a crystallographic S_4 axis.[2] The four B_a atoms are 1.508 Å from the center of the cluster O, the O–B_a vectors making an angle of 31.1 ± 0.6° to the S_4 axis. The four B_b atoms are 1.315 Å from O, the O–B_b vectors making an angle of 105.7° to the same axis. The distance ratio $(O–B_a)/(O–B_b) = 1.15 \pm 0.02$, which is intermediate between the dodecahedron constructed by making all boron–boron edge lengths equal, $(O–B_a)/(O–B_b) = 1.374$, and the dodecahedron formed by placing all boron atoms equidistant from the center.

Calculations based on the above energy expressions confirm that this dodecahedral structure is the only minimum on the potential energy surface, at all values of x and y. This is in contrast to eight-coordinate metal complexes where the square antiprism is the most stable structure,[3] although the general forms of the potential energy surfaces are similar. The angular parameters are relatively insensitive to the values chosen for x and y, compared with the sharp dependence of the distance ratio, $(O–B_a)/(O–B_b)$. The variation of $(O–B_a)/(O–B_b)$ with x and y is shown in Figure 2, the shaded area corresponding to the value obtained from the crystal structure determination. A satisfactory fit between calculation and experiment is obtained, for example, for $x = 2.0$, $y = 1.0$, or $x = 1.5$, $y = 1.2_5$. Potentials of this type are very shallow and allow all boron–boron interactions to be significantly bonding.

Structure of $B_9H_9^{2-}$

The structure of $Rb_2[B_9H_9]$ is disordered, due to two different orientations of the tricapped trigonal-prismatic anion within the crystal.[4] The ratio between the distance from the center of the cluster O to the capping atoms B_c and the distance between O and the prism atoms B_p is $(O–B_c)/(O–B_p) = 1.14 \pm 0.02$. The angle six O–$B_p$ vectors make to the threefold axis is 50.1 ± 1.0°. The distance ratio is again

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