long-range bridgefoot interference, the better the balance between the HOMO and the NUMO contaminations of LUMO, and therefore the less pronounced is the LUMO steering of the entering donor. This could become of paramount importance in sterically hindered bridge structures.

(9) The *relative electronegativities of the bridgefoot groups* determine the *magnitude* of the polarization, for it is this electronic asymmetry that drives the HOMO and NUMO mixings with the LUMO. Chemically, the greater the electron donation of the substituent ligand to the substituted bridgefoot atom, the less pronounced is the orbital steering. Whether the kinetically favored asymmetric product is actually observed depends on the temperature at which the product is isolated and on the steric congestion present during the nucleophile entry in the second interchange step.

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Appendix

From the 2×2 secular determinant for the bridge/bridgefoot interference, the bridge orbital energies are

$$\text{S, two-node} \quad \epsilon_2 = (\alpha_b + \alpha_{bf} + \beta_{bf})/2 - 2^{1/2}\beta + ...$$

$$\text{A, one-node} \quad \epsilon_1 = \alpha_{bf} - \beta_{bf}$$

$$\text{S, no-node} \quad \epsilon_0 = (\alpha_b + \alpha_{bf} + \beta_{bf})/2 + 2^{1/2}\beta + ...$$

The higher order terms in ϵ_2 and ϵ_0 may be ignored if

$$-(4 + f) < \Delta\alpha/|\beta| < 4 - f$$

which becomes the validity condition for the following analysis.

The conditions for the SAS and ASS sequences are

	SAS	ASS
$\Delta\alpha/|\beta|$	$>-2(2^{1/2}) + 3f$	$<-2(2^{1/2}) + 3f$

For each of these two possibilities for bridge MO sequence, there are the two possibilities for LUMO polarization by either the HOMO or the NUMO. Quantitatively, these four possibilities are distinguished by the conditions on $\Delta\alpha/|\beta|$

	SAS	ASS
LUMO polarized by NUMO	$<3f$	$>-6(2^{1/2}) + 3f$
LUMO polarized by HOMO	$>3f$	$<-6(2^{1/2}) + 3f$

Construction of Figure 5A for an S bridge atomic orbital is as follows. $\Delta\alpha/|\beta|$, f space is divided into two regions corresponding to the SAS and ASS sequences by the line $\Delta\alpha/|\beta| = -2(2^{1/2}) + 3f$ in the center of Figure 5A. These two regions are subdivided by the NUMO, HOMO dominance conditions: $\Delta\alpha/|\beta| = 3f$ (SAS case) and $\Delta\alpha/|\beta| = -6(2^{1/2}) + 3f$ (ASS case). The validity condition $-(4 - f) < \Delta\alpha/|\beta| < 4 - f$ truncates the full space as shown by the upper solid diagonal line of negative slope (the lower limit is parallel to the upper but falls off scale in Figure 5A). The dashed line is included to distinguish the high- and low-bridge cases. The shaded areas denote LUMO polarization by the HOMO.

Replacement of the S bridge atom atomic orbital with an A orbital has the effects of changing S to A and A to S in the sequence codes (SAS, ASS → ASA, SAA) and of replacing f with $-f$ in all the conditions derived above for the S bridge orbital (because it is now the one-node A bridgefoot MO of normalized energy shift f that interferes with the bridge atom orbital). The change in sign of f provides a convenient relationship between the region divider lines in parts A and B of Figure 5: the dividers in Figure 5B are rotated from their positions in Figure 5A by an angle equal to twice that which its Figure 5A analogue makes with the f axis. Construction of Figure 5B is analogous to that of Figure 5A with the simple modification that the signs of the slopes of the space-dividing lines in Figure 5A are reversed.

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Reaction of the Small Closo Carboranes 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ with BX_3 (X = Halogen, Phenyl): A Method of Preparing "3"-Substituted 2,4-$C_2B_5H_7$ Derivatives and Preparation of 2-Br_2B-*closo*-1,6-$C_2B_4H_5$

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The reaction of *closo*-2,4-$C_2B_5H_7$ with BX_3 (X = Cl, Br, I, C_6H_5) at elevated temperatures (270 °C for BCl_3, 160 °C for BBr_3, 120 °C for BI_3, 160 °C for $B(C_6H_5)_3$) results in halogen, or phenyl, substitution primarily at the 3-position of the carborane (i.e. 3-X-*closo*-2,4-$C_2B_5H_6$). *closo*-2,4-$C_2B_5H_7$ also reacts with $(CH_3)_3CCl$ at 270 °C to give 3-Cl-*closo*-2,4-$C_2B_5H_6$. A closo carborane containing a trigonal boron σ-bonded to a cage carborane, 2-Br_2B-*closo*-1,6-$C_2B_4H_5$, is prepared from *closo*-1,6-$C_2B_4H_6$ and BBr_3 at 265 °C.

Introduction

Halogenations of *closo*-2,4-$C_2B_5H_7$ utilizing X_2 (X = Cl, Br, I) and Friedel-Crafts type catalysts have been found to result in the formation of the 5-substituted isomer 5-X-*closo*-2,4-$C_2B_5H_6$, followed by the formation of 5,6-X_2-*closo*-2,4-$C_2B_5H_5$ (X = Cl,[1-3] Br,[4,5] I[5]). Further chlorination[6] of 5,6-Cl_2-2,4-$C_2B_5H_5$ in the presence of $AlCl_3$ gives nearly equal amounts of 1,5,6-Cl_3-*closo*-2,4-$C_2B_5H_4$ and 3,5,6-Cl_3-*closo*-2,4-$C_2B_5H_4$. Chlorination of *closo*-2,4-$C_2B_5H_7$ in a light-initiated reaction[1] produces a mixture of 1-Cl-, 3-Cl-, and 5-Cl-2,4-$C_2B_5H_6$, but mostly the last isomer. Equilibrium amounts of 3-X-2,4-$C_2B_5H_6$ (X = Cl, Br, I) isomer are found from the thermal rearrangement of 5-X-$C_2B_5H_6$,[3,5,6] but the separation of the "3"-isomer from the other *B*-X-*closo*-2,4-$C_2B_5H_6$ isomers is often very tedious. In the present study, a new way of preparaing 3-X-*closo*-2,4-$C_2B_5H_6$ (X = Cl, Br, I, C_6H_5) is presented. In addition, 2-Br_2B-*closo*-1,6-$C_2B_4H_5$, a

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compound with an exo-cage B–B bond, is synthesized by way of a reaction between BBr_3 and *closo*-1,6-$C_2B_4H_6$.

Experimental Section

Materials and Handling of Chemicals. The parent carboranes *closo*-2,4-$C_2B_5H_7$ and *closo*-1,6-$C_2B_4H_6$ were obtained from R. E. Williams. *closo*-2,4-$C_2B_5H_7$ was used without further purification. *closo*-1,6-$C_2B_4H_6$ was purified by complexing the impurity 2-CH_3-*closo*-1,5-$C_2B_3H_4$ with tetramethylethylenediamine over a period of several minutes under ambient conditions. Pure 1,6-$C_2B_4H_6$ was obtained by passing the volatile material through a trap at −75 °C and collecting the carborane at −190 °C. Tribromoborane (Alrich Chemical) was placed in a storage tube over molecular sieves prior to use. Triiodoborane was sublimed directly into the reaction vessel or added directly into the vessel under dry nitrogen. Triphenylborane (Aldrich Chemical), trifluoroborane (Union Carbide), trichloroborane (Matheson), chloromethane (J. T. Baker), CD_2Cl_2 (Aldrich Chemical), C_6D_6 (Norrell Chemical), C_6H_6 (Eastman Kodak), and CH_2Cl_2 (Aldrich Chemical) were used without further purification. 5-Cl-*closo*-2,4-$C_2B_5H_6$ was prepared and purified by literature methods.[3,6] All materials were handled in a standard high-vacuum line or under nitrogen in a drybox. Purification of volatile compounds was accomplished by either cold-column separation[7] or trap-to-trap fractionation.

Nuclear Magnetic Resonance. Proton (60-MHz) NMR spectra were obtained by using a Bruker WP-60 FT spectrometer equipped with Fluke 6160B ^{11}B and General Radio 1062 ^{10}B decoupler units. The ^{11}B decoupling frequencies used for the *closo*-2,4-$C_2B_5H_7$ derivatives were 19.25525 MHz for both HB(3,5,6) and HC(2,4) proton regions and 19.25485 MHz for the HB(1,7) apex region; the ^{10}B decoupler frequencies were 6.44785 MHz for the HB(3,5,6) and HC(2,4) regions and 6.447693 MHz for the HB(1,7) apex region. Application of a modified NMRENIT iterative computer program[8,9] to the data from the more complex proton NMR spectra provided a more accurate assessment of chemical shifts and coupling constants.

Boron-11 (160.44-MHz) NMR spectra were obtained by use of a Bruker WM-500 FT spectrometer available at California Institute of Technology, Pasadena, CA. 2-D boron NMR spectra were obtained by using a standard ^{11}B/^{11}B-COSY program. All ^{11}B NMR chemical shift data are based on $\delta(BF_3{\cdot}OEt_2) = 0.00$, with the parent 2,4-$C_2B_5H_7$ used as a secondary standard: δ(1,7) −21.73, δ(3) +7.02, δ(5,6) +3.83.

Reaction between *closo*-2,4-$C_2B_5H_7$ and BCl_3 To Give 3-Cl-2,4-$C_2B_5H_6$ and Other Chlorinated Carboranes. *closo*-2,4-$C_2B_5H_7$ (0.4 mmol) and BCl_3 (0.6 mmol) were sealed in a 3-mm NMR tube equipped with a 1.5-mL glass expansion bulb, and the mixture was heated at 270 °C for 5 days. The formation of 3-Cl-2,4-$C_2B_5H_6$ (15%) was detected by ^{1}H NMR.[3,6] The sample was further heated at 270 °C for a total of 27 days. ^{11}B NMR analysis indicated the presence of 2,4-$C_2B_5H_7$ (31 mol %), 3-Cl-2,4-$C_2B_5H_6$ (43%) [^{11}B NMR δ −18.35 (d, 2 B, B(1,7), J(BH) = 182.5 Hz), +14.97 (s, 1 B, B(3)), +3.25 (d, 2 B, B(5,6), J(BH) = 172.3 Hz); ^{1}H NMR δ 0.548 (H(1,7))],[3,6] 5-Cl-2,4-$C_2B_5H_6$ (10%) [^{11}B NMR δ −20.04 (d, 2 B, B(1,7), J(BH) = 183.9 Hz), NMR (d, 1 B, B(3), J(BH) = 188.7 Hz), +13.81 (s, 1 B, B(5)), +1.05 (d, 1 B, B(6), J(BH) = 176.4 Hz); ^{1}H NMR δ 0.550 (H(1,7))],[3,6] 1-Cl-2,4-$C_2B_5H_6$ (1%) [^{11}B NMR δ −16.10 (s, 1 B, B(1)), +8.17 (d, 1 B, B(3), J(BH) = 189.0 Hz), +3.35 (d, 2 B, B(5,6), J(BH) = 173.3 Hz), −33.07 (d, 1 B, B(7), J(BH) = 186.4 Hz); ^{1}H NMR δ −0.064 (H(1,7))],[6] 1,3-Cl_2-2,4-$C_2B_5H_5$ (2%),[6] 3,5-Cl_2-2,4-$C_2B_5H_5$ (2%) [^{11}B NMR δ 17.05 (d, 2 B, B(1,7)), +12.58 (s, 1 B, B(3)), +12.31 (s, 1 B, B(5)), −0.07 (d, 1 B, B(6)); ^{1}H NMR δ 0.979 (H(1,7))],[6] 1,5-Cl_2-2,4-$C_2B_5H_5$ (1%) [^{11}B NMR δ −14.69 (s, 1 B, B(1)), +6.46 (d, 1 B, B(3)), +12.89 (s, 1 B, B(5)), +0.64 (d, 1 B, B(6)), −31.22 (d, 1 B, B(7)); ^{1}H NMR δ 0.450 (H(1,7))],[6] 1,3,5-Cl_3-2,4-$C_2B_5H_4$ (1%),[6] two unknown carborane compounds [with B(1,7) peaks at δ −20.95, ca. 4%, and δ −17.04, ca. 4%, respectively], and cleavage products [totaling 1%; CH_3BCl_2 (δ 62.30), $CH_2(BCl_2)_2$ (δ 59.12),[3,10] and one unidentified compound with a small ^{11}B NMR doublet resonance at δ 57.60]. Some colorless glassy solids also were present at the bottom and along the interior wall of the NMR tube.

Reaction between *closo*-2,4-$C_2B_5H_7$ and *tert*-Butyl Chloride To Give 3-Cl-2,4-$C_2B_5H_6$ and Other Chlorinated Carboranes. *closo*-2,4-$C_2B_5H_7$ (0.3 mmol) and *tert*-butyl chloride (0.4 mmol) were condensed into a 3-mm NMR tube, equipped with an attached 1.5-mL bulb, at −196 °C. The NMR tube was sealed and subsequently heated at various temperatures. ^{1}H NMR gave no evidence that reaction had occurred after heating the sample at temperatures up to 130 °C for 48 h. The sample was further heated at 265–270 °C for 10 days. More than 50% of the $(CH_3)_3CCl$ disappeared, and there was NMR evidence that several chlorinated carboranes had formed. Further heating at 270 °C for 30 days gave the following chlorinated products: 3-Cl-2,4-$C_2B_5H_6$ (18%), 5-Cl-2,4-$C_2B_5H_6$ (3%), and 1-Cl-2,4-$C_2B_5H_6$ (2%). The mixture was heated at 265–270 °C for an additional 28 days, after which both ^{1}H and ^{11}B NMR showed the presence of 2,4-$C_2B_5H_7$ (49 mol %), 3-Cl-2,4-$C_2B_5H_6$ (34%), 5-Cl-2,4-$C_2B_5H_6$ (5%), 1-Cl-2,4-$C_2B_5H_6$ (4%), 1,3-Cl_2-2,4-$C_2B_5H_5$ (3%), 3,5-Cl_2-2,4-$C_2B_5H_5$ (1%),[3,6] and cleavage products [total of 4%; the ratio of BCl_3, $CH_2(BCl_2)_2$, CH_3BCl_2,[3,10] singlet at 63.37 ppm (which is perhaps $RBCl_2$, R = C_4H_9) is 6:1:5:4].

Reaction of *closo*-2,4-$C_2B_5H_7$, BCl_3, and *tert*-Butyl Chloride. Into a 3-mm NMR tube equipped with a 1.5-mL expansion bulb were condensed *closo*-2,4-$C_2B_5H_7$ (0.4 mmol), BCl_3 (0.3 mmol), and $(CH_3)_3CCl$ (0.9 mmol). The NMR tube, with its contents, was sealed and heated at 90 °C for 47 h, after which a ^{1}H NMR spectrum indicated that the amount of $(CH_3)_3CCl$ decreased to 0.7 mmol and new signals (multiplets) appeared at ca. 0.9 ppm. A ^{11}B NMR spectrum gave no evidence for the formation of any 2,4-$C_2B_5H_7$ derivatives. The mixture was subsequently heated at 150 °C for 21 h and then at 170 °C for 48 h. Most (80%) of the $(CH_3)_3CCl$ had then disappeared and the intensity of the multiplets increased, but no new carborane product was detected by either ^{1}H or ^{11}B NMR. The temperature was then raised to 270 °C for 24 h. A ^{1}H NMR spectrum of the sample taken at the end of this heating period exhibited a HB(1,7) resonance attributed to 3-Cl-2,4-$C_2B_5H_6$ and/or 5-Cl-2,4-$C_2B_5H_6$ (the ^{1}H NMR chemical shifts of HB(1,7) of 3-Cl-2,4-$C_2B_5H_6$ and 5-Cl-2,4-$C_2B_5H_6$ are δ 0.548 and 0.550, respectively.[9] The sample was further heated at 270 °C for a total of 15 days. The products and unreacted starting materials, as analyzed by ^{11}B NMR, were as follows: 2,4-$C_2B_5H_7$ (21.3 mol %), 3-Cl-2,4-$C_2B_5H_6$ (56.7%), 5-Cl-2,4-$C_2B_5H_6$ (6.3%), 1-Cl-2,4-$C_2B_5H_6$ (1.5%), 3,5-Cl_2-2,4-$C_2B_5H_5$ (3.5%), 1,3-Cl_2-2,4-$C_2B_5H_5$ (2.3%), 1,5-Cl_2-2,4-$C_2B_5H_5$ (1.0%), 1,3,5-Cl_3-2,4-$C_2B_5H_4$ (1.2%),[3,6] and cleavage products (total 6.2%, ratio of CH_3BCl_2, $CH_2(BCl_2)_2$, and $(Cl_2BCH_2\text{–})_2$[3,10] is 1.5:1.5:1.0); the ratio of BCl_3 to carborane compounds was 1.0:1.1. The contents of the NMR tube were subsequently heated at 270 °C for an additional 12 days. The calculated mole percentages of the unreacted starting materials and products were as follows: 2,4-$C_2B_5H_7$ (5.2%), 3-Cl-2,4-$C_2B_5H_6$ (63.4%), 5-Cl-2,4-$C_2B_5H_6$ (5.6%), 1-Cl-2,4-$C_2B_5H_6$ (1.3%), 3,5-Cl_2-2,4-$C_2B_5H_5$ (4.1%), 1,3-Cl_2-2,4-$C_2B_5H_5$ (7.8%), 1,5-Cl_2-2,4-$C_2B_5H_5$ (2.2%), 1,3,5-Cl_3-2,4-$C_2B_5H_4$ (3.6%),[3,6] and cleavage products (total 7.0%; ratio of CH_3BCl_2, $CH_2(BCl_2)_2$, and $(Cl_2BCH_2\text{–})_2$[3,10] is 2.8:3.7:1.0). The methyl peak of $(CH_3)_3CCl$ in the ^{1}H NMR spectrum completely disappeared and was replaced by a combination of broad and sharp peaks between δ 0.7 and 1.7 (probably polymerized butyl chloride derived compounds). The ratio of BCl_3 to carborane compounds remained at 1.0:1.1.

Reaction of *closo*-2,4-$C_2B_5H_7$ and *closo*-5-Cl-2,4-$C_2B_5H_6$ with BCl_3/CH_3Cl. Into a 3-mm NMR tube equipped with a 1.5-mL expansion bulb were introduced *closo*-2,4-$C_2B_5H_7$ (0.4 mmol), *closo*-5-Cl-2,4-$C_2B_5H_6$ (0.15 mmol), BCl_3 (0.17 mmol), and CH_3Cl (0.16 mmol). The NMR tube, with its contents, was sealed and heated at 150 °C for 7 days. A ^{1}H NMR spectrum of the sample gave no evidence that a reaction had occurred. The mixture was further heated at 270 °C for a total of 21 days. Both ^{1}H and ^{11}B NMR spectra indicated the chlorination of 2,4-$C_2B_5H_7$ and of 5-Cl-2,4-$C_2B_5H_6$ had taken place at the B(3) position of each reactant. The mole ratio of CH_3Cl to carborane compounds was not changed after the reaction, implying that CH_3Cl was not involved in the reaction (see the following control experiment between 2,4-$C_2B_5H_7$ and CH_3Cl). Analysis of the contents in the NMR tube by ^{11}B NMR showed the presence of 2,4-$C_2B_5H_7$ (43 mol %), 3-Cl-2,4-$C_2B_5H_6$ (25%), 5-Cl-2,4-$C_2B_5H_6$ (21%), 3,5-Cl_2-2,4-$C_2B_5H_5$ (4%), an unidentified 2,4-$C_2B_5H_7$ derivative (4%, B(1,7) peak at δ −20.96), and trace amounts of 1-Cl-2,4-$C_2B_5H_6$, 1,5-Cl_2-2,4-$C_2B_5H_5$, 1,3-Cl_2-2,4-$C_2B_5H_5$, and 1,3,5-Cl_3-2,4-$C_2B_5H_4$.[3,6] Also, cleavage products (total 1%; CH_3BCl_2, $CH_2(BCl_2)_2$,[3,10] and a compound with a doublet at δ 57.6) were formed. At this point in the reaction the ratio of BCl_3 to all carborane compounds was 1.0:3.4.

Attempted Reaction between *closo*-2,4-$C_2B_5H_7$ and CH_3Cl. Both *closo*-2,4-$C_2B_5H_7$ (0.4 mmol) and CH_3Cl (0.6 mmol) were sealed in a 3-mm NMR tube and heated at 160 °C for 24 h and at 270 °C for 15 days. ^{1}H NMR gave no evidence that a reaction had occurred. Further heating at 295 °C for 6 days revealed the presence of boron-boron-coupled products [e.g. 1,3′-(2,4-$C_2B_5H_6)_2$ and 1,1′-(2,4-$C_2B_5H_6)_2$] from the analyses of both ^{1}H and ^{11}B NMR spectra.[11] The results of the

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2,4-$C_2B_5H_7/CH_3Cl$ control experiment indicate that CH_3Cl is not the immediate source of chlorine in the chlorinated 2,4-$C_2B_5H_7$ product obtained from the carborane/BCl_3/CH_3Cl experiment described above.

Chlorination of *closo*-5,6-$(C_5H_5)_2$-2,4-$C_2B_5H_5$ with BCl_3 To Give *closo*-3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$. *closo*-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ (0.23 mmol, containing 8% of 1,5-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ and 1.5% of 3,5-$(C_2H_5)_2$-2,4-$C_2B_5H_5$)[12] was added to a 3-mm NMR tube, followed by the addition of BCl_3 (0.8 mmol). The NMR tube was sealed and heated at 160 °C for 2.5 days. A ^{11}B NMR spectrum of the sample indicated that 8% of the starting carborane had been converted to 3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$. Additional heating of the sample at 190 °C for 10 days increased the yield of 3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$ to 11%. The sample was further heated at 236 °C for 9 days. A ^{11}B NMR analysis indicated the presence of 5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ (50%) [^{11}B NMR δ −20.92 (d, 2 B, B(1,7), J(BH) = 175.9 Hz), +5.26 (d, 1 B, B(3), J(BH) = 179.2 Hz)), +10.99 (s, 2 B, B(5,6))], 3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$ (31%) [^{11}B NMR δ −17.55 (d, 2 B, B(1,7), J(BH) = 178.1 Hz), +13.17 (s, 1 B, B(3)), +10.52 (s, 2 B, B(5,6))], 1,5-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ (11%) [^{11}B NMR δ −9.46 (s, 1 B, B(1)), +7.09 (d, 1 B, B(3), J(BH) = 180.8 Hz)), +13.15 (s, 1 B, B(5)), +1.69 (d, 1 B, B(6), J(BH) = 164.9 Hz), −26.95 (d, 1 B, B(7), J(BH) = 177.1 Hz))], 3,5-$(C_2H_5)_2$-2,4-$C_2B_2H_5$ (3%) [^{11}B NMR δ −20.16 (d, 2 B, B(1,7), J(BH) = 174.6 Hz), +15.00 (s, 1 B, B(3)), +13.2 (s, 1 B, B(5)), 1.23 (d, 1 B, B(6), J(BH) = 164.5 Hz)], and 3-Cl-1,5-$(C_2H_5)_2$-2,4-$C_2B_5H_4$ (4%) [^{11}B NMR δ −6.77 (s, 1 B, B(1)), +14.59 (s, 1 B, B(3)), +12.5 (s, 1 B, B(5)), +0.94 (d, 1 B, B(6), J(BH) = 174.4 Hz), −23.48 (d, 1 B, B(7), J(BH) = 181.1 Hz))].

Reaction between *closo*-2,4-$C_2B_5H_7$ and BBr_3 To Give 3-Br-2,4-$C_2B_5H_6$ and Other Brominated Carboranes. *closo*-2,4-$C_2B_5H_7$ (0.35 mmol) and BBr_3 (0.60 mmol) were condensed into a 3-mm NMR tube equipped with a 1.5-L bulb at −196 °C. The NMR tube was sealed and heated at 120 °C for 2 days; subsequently a ^1H NMR spectrum gave no evidence that a reaction had occurred. The mixture was heated at 160 °C for 3 days, and both ^1H and ^{11}B NMR spectra were taken. Both the ^1H NMR and ^{11}B NMR spectra showed that monobromination of 2,4-$C_2B_5H_7$ occurred at both the B(3) position (20%) and the B(5) position (4%); dibromination (1%), to give 3,5-Br_2-2,4-$C_2B_5H_5$,[5] also occured. Further heating at 160 °C for the total of 12 days gave the following results: 2,4-$C_2B_5H_7$ (13%), 3-Br-2,4-$C_2B_5H_6$ (49%), 5-Br-2,4-$C_2B_5H_6$ (7%), and 3,5-Br_2-2,4-$C_2B_5H_5$ (31%).[5] The ratio of BBr_3 to carborane compounds increased to 3.5:1.0 from the original 1.8:1.0.

Reaction between *closo*-2,4-$C_2B_5H_7$ and 1,2-Dibromoethane. Both *closo*-2,4-$C_2B_5H_7$ (0.4 mmol) and 1,2-dibromoethane (0.4 mmol) were sealed in a 3-m NMR tube and heated at 270 °C for 9 days. Both ^{11}B and ^1H NMR gave no evidence that a reaction had occurred. Subsequently, the mixture was heated at 320 °C for 22 h. Analysis of the contents in the NMR tube by ^{11}B NMR showed the presence of 2,4-$C_2B_5H_7$ (77%), 3-Br-2,4-$C_2B_5H_6$ (14%), 5-Br-2,4-$C_2B_5H_6$ (6%), and 1-Br-2,4-$C_2B_5H_6$ (3%).[5]

Reaction of *closo*-2,4-$C_2B_5H_7$ and BI_3. Triiodoborane (0.8 mmol) was added to a 3-mm NMR tube equipped with a 1.5-mL bulb in a nitrogen drybag. The NMR tube was attached to a vacuum line, and 2,4-$C_2B_5H_7$ (0.4 mmol) was subsequently added. The NMR tube with its contents was sealed and warmed from −190 °C to room temperature. Heating the sample at 120 °C for 19 h caused a color change of the sample from pink to yellow. ^1H and ^{11}B NMR analyses of the sample indicated that 88% of the starting material had reacted to give 3-I-2,4-$C_2B_5H_6$ (52%), 5-I-2,4-$C_2B_5H_6$ (5%), 3,5-I_2-2,4-$C_2B_5H_5$ (7%),[5] unidentified carborane compounds (21%), and CH_3BI_2[10] (10%, δ(^{11}B) 49.4). The NMR tube was opened to the vacuum line, and some noncondensable gas (ca. 0.15 mmol) was observed. When all volatile materials were pumped through a liquid-nitrogen trap, nonvolatile liquid and solid materials remained in the NMR tube. A ^{11}B NMR spectrum of the volatile materials (0.5 mmol) indicated the presence of 2,4-$C_2B_5H_7$, 3-I-2,4-$C_2B_5H_6$, 5-I-2,4-$C_2B_5H_6$,[5] and a small amount of an unidentified compound (^{11}B NMR doublet, δ −17.8). To separate the nonvolatile liquid and solid materials from one another, the liquid portion was syringed into a "new" NMR tube, and C_6D_6 (as solvent) was added to both the "new" (containing the "liquid") and "old" (containing the "solid") NMR tubes. Boron-11 NMR spectra of both tubes were similar; both contained BI_3, but the "solid" protion (dissolved in C_6D_6) contained a larger amount of BI_3 than the "liquid" portion, and there was some 1,10-$C_2B_8H_{10}$[13] present in the "solid" portion. Unidentified carborane compounds in both of the NMR tubes exhibited the following ^{11}B NMR chemical shifts: δ −21.0 (d), −19.5 (d), −17.8 (d), −7.6 (s), −6.3 (s), −3.9 (s), +6.2 (d), and +7.7 (s).

Reaction of *closo*-2,4-$C_2B_5H_7$ and Triiodoborane in C_6H_6. A solution of triiodoborane in C_6H_6 was syringed into a 3-mm NMR tube in a dry bag containing nitrogen. The NMR tube was attached to a vacuum line, and 2,4-$C_2B_5H_7$ (0.5 mmol) was subsequently added. The NMR tube was sealed and warmed to room temperature. When the sample was heated at 115 °C for 18 h, the color of the sample changed from pink to yellow. A ^1H NMR spectrum of the sample indicated that only 11% of the 2,4-$C_2B_5H_7$ remained and two new HB(1,7) peaks of carborane derivatives appeared at δ 0.39 and (81%) and δ 0.72 (7%). Also, two sets of multiplets appeared at δ 8.1 and 7.3. After the sample was allowed to stand at room temperature for 5 days, a ^{11}B NMR spectrum was taken. It was observed that the amount of 2,4-$C_2B_5H_7$ increased to 39% of the total carboranes. The relative amounts of carborane products were as follows: 3-I-2,4-$C_2B_5H_6$ (37%), 5-I-2,4-$C_2B_5H_6$ (5%),[5] and unidentified dicarbaheptaboranes with resonances at δ −17.8 (broad, doublet, 6%) and at δ −20.9 (doublet, 2%). The sample was heated at 118 °C for additional 19 h. When the sample was cooled to room temperature, a large quantity of yellow crystals formed. The NMR tube was opened to a vacuum line, and volatile materials were vacuum-pumped out of the NMR tube into a −190 °C trap. The materials in the −190 °C trap were found to be 2,4-$C_2B_5H_7$, 3-I-2,4-$C_2B_5H_6$, 5-I-2,4-$C_2B_5H_6$, an unidentified compound (δ(^{11}B) −17.8), and CH_3BI_2 (δ 49.4).[10] CD_2Cl_2 (2 mmol) was added to the NMR tube containing nonvolatile materials. A ^{11}B NMR spectrum of the sample was taken and analyzed: small amounts of 2,4-$C_2B_5H_7$, 3-I-2,4-$C_2B_5H_6$, 5-I-2,4-$C_2B_5H_6$,[5] and unidentified 2,4-$C_2B_5H_7$ derivatives [^{11}B(1,7)H peaks at δ −21.0, −19.5, −17.8, −17.2, and −16.3] were found; also, a relatively sharp single peak appeared at δ −68.

Attempted Reaction between *closo*-2,4-$C_2B_5H_7$ and BF_3. Into a 3-mm NMR tube equipped with a 1.5-mL bulb were condensed *closo*-2,4-$C_2B_5H_7$ (0.4 mmol) and BF_3 (0.4 mmol). The NMR tube was sealed and heated at 260 °C for 6 days and at 320 °C for 1 day. The ^1H NMR spectra gave no evidence for the formation of fluoro derivatives of 2,4-$C_2B_5H_7$. Further heating at 370 °C for 1 day revealed the presence of boron–boron-coupled products [e.g. 1,3′-(2,4-$C_2B_5H_6)_2$, 1,1′-(2,4-$C_2B_5H_6)_2$][11] by analyses of both ^{11}H and ^{11}B NMR spectrum. Also, it was observed that some white solid matter formed inside the NMR tube.

Reaction of *closo*-2,4-$C_2B_5H_7$ and Triphenylborane. A solution of triphenylborane in benzene was syringed into a 3-mm NMR tube in a dry bag containing nitrogen. The NMR tube was opened to a vacuum line, and 2,4-$C_2B_5H_7$ (0.4 mmol) was added to the same NMR tube. The NMR tube was sealed and warmed to room temperature. After the sample was heated at 160 °C for 2 days, new peaks appeared at δ −19.14 and 13.51 in the ^{11}B NMR spectrum. The ^1H NMR spectrum disclosed that a multiplet at δ 8.07 had disappeared and a singlet at δ 0.39 (presumed to be the HB(1,7) peak of a new product) and a multiplet at δ 8.33 had appeared. Further heating of the sample at 160 °C for additional 3 days gave 21% of the product "A". After the sample was heated at 160 °C for a total of 8 days, a large amount of yellow-brown solid was formed. ^{11}B and ^1H NMR analyses of the sample indicated the following compounds were present: 2,4-$C_2B_5H_7$, product A with a B(1,7) peak at −19.15, and product B, which exhibited a B(1,7) peak at δ −20.90. The NMR tube was opened to a vacuum line, and some noncondensable gas (ca. 0.1 mmol) was observed. The volatile materials from the reaction were vacuum-pumped out of the NMR tube into a trap at −190 °C. CD_2Cl_2 was added into the reaction NMR tube to dissolve the nonvolatile materials. The materials in the −190 °C trap were identified as 2,4-$C_2B_5H_7$ and C_6H_6. The materials remaining in the reaction NMR tube were found to be 2,4-$C_2B_5H_7$ (28%), compound A (64%), and compound B (8%) as analyzed by ^{11}B NMR. ^{11}B and ^1H NMR data [^{11}B NMR δ −19.15 (d, 2 B, B(1,7), J(BH) = 177.8 Hz), +13.59 (s, 1 B, B(3)), +3.65 (d, 2 B, B(5,6), J(BH) = 167.7 Hz); ^1H NMR δ 0.39 (H(1,7)), 5.78 (H(2,4)), 4.09 (H(5,6))] for compound A were consistent with that expected for 3-C_6H_5-*closo*-2,4-$C_2B_5H_6$. Compound B [^{11}B NMR δ −20.90 (d, 2 B, B(1,7), J(BH) = 181 Hz), +4.97 (d, 1 B, B(3)), ca. +11.8 (s, 1 B, B(5)), +1.5 (d, 1 B, B(6))] is most probably 5-C_6H_5-*closo*-2,4-$C_2B_5H_6$. A second NMR tube containing 2,4-$C_2B_5H_7$ (0.6 mmol), triphenylborane, and C_6H_6 was prepared. After the NMR tube was heated at 165 °C for 2.5 days, the tube was opened to the vacuum line. Some noncondensable gas (ca. 0.3 mmol) was observed. The volatile materials were condensed into a −190 °C trap and were identified as unreacted 2,4-$C_2B_2H_7$ and C_6H_6. A 3-cm length of the reaction NMR tube, which contained nonvolatile material, was inserted into a new NMR tube under dry nitrogen. CD_2Cl_2 was added to the new NMR tube, and a ^{11}B spectrum of the sample indicated that a 2,4-$C_2B_5H_7$ derivative, most probably 3-C_6H_5-2,4-$C_2B_5H_6$, was present as the only carborane material.

Attempted Reaction of *closo*-1,6-$C_2B_4H_6$, BCl_3, and CH_3Cl. *closo*-1,6-$C_2B_4H_6$ (0.55 mmol), BCl_3 (0.55 mmol), and dichloromethane (0.9 mmol) were sealed in a 3-mm NMR tube, and the sample was then heated at 295 °C for 28 h. A proton NMR spectrum of the sample gave no evidence that a reaction occurred. Further heating of the sample at 350 °C for 3 days caused the disappearance of *closo*-1,6-$C_2B_4H_6$ and the formation of both CH_3BCl_2 and BCl_3.[3]

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Reaction of *closo*-1,6-$C_2B_4H_6$ and BBr_3 To Give 2-Br_2B-*closo*-1,6-$C_2B_4H_5$. Both *closo*-1,6-$C_2B_4H_6$ (0.4 mmol) and BBr_3 (0.65 mmol) were added into a 3-mm NMR tube equipped with a 1.5-mL bulb. The NMR tube was sealed and the sample heated at 120 °C for 2 days, at 160 °C for 3 days, and 200 °C for 1 day. Proton NMR spectra taken after each heating period indicated that no reaction had occurred. However, the color of the sample changed from pink to colorless after heating to 160 °C. Further heating at 265 °C, for 2 days resulted in some new peaks in the ^1H and ^{11}B NMR spectra. The mole percent of the new boron-containing product(s) was less than 10% of the starting carborane as analyzed by the ^{11}B NMR spectrum. After the sample was heated at 265 °C for a total of 4 days, the ratio of the starting material, *closo*-1,6-$C_2B_4H_6$, to the new boron-containing product(s) was 2:1. When the sample was heated at the same temperature for another 4 days, three layers were formed in the NMR tube: the bottom layer was intractable solid matter; the middle layer was a powderlike solid matter, and the top layer was a colorless liquid. ^{11}B NMR analysis of the liquid portion of the sample indicated that 2-Br_2B-*closo*-1,6-$C_2B_4H_5$ and trace amounts of various diboranes were present. One of the diboranes was identified as bromodiborane,[14] but two others, with ^{11}B NMR doublets (and further split into triplets) at δ 14.52 and 13.75, respectively, could not be positively identified although a *cis*- and *trans*-1,2-$Br_2B_2H_4$ mixture may well be implicated. The tube was opened to the vacuum line, and some noncondensable gas (ca. 0.3 mmol) was measured. All volatile condensable materials were transferred to a "new" 3-mm NMR tube. CD_2Cl_2 was added into the "old" reaction NMR tube in an unsuccessful attempt to dissolve the nonvolatile solid matter. ^{11}B NMR and ^1H NMR spectra of the two tubes indicated that the volatile portion was composed of unreacted *closo*-1,6-$C_2B_4H_6$ (10%),[13] 2-Br_2B-*closo*-1,6-$C_2B_4H_5$ (7%), CH_3BBr_2 (8%; ^1H and ^{11}B NMR chemical shifts at δ 1.344 and 62.72, respectively),[10] BBr_3 (75%),[10] and trace amounts of the diboranes mentioned above. The nonvolatile portion was composed of a large quantity of an apparent cage-cleavage product (^{11}B resonance at δ 57.2) and small amount of *closo*-1,6-$C_2B_4H_6$, 2-Br_2B-*closo*-1,6-$C_2B_4H_5$, and BBr_3. When the volatile fraction was subjected to cold-column fractionation, a portion that distilled from −190 to −85 °C was identified as a mixture of *closo*-1,6-$C_2B_4H_6$, CH_3BBr_2, and an unidentified cleavage product (^{11}B resonance at δ 62.27). A second fraction distilled between −84 and −64 °C and was composed to cleavage products: BBr_3, CH_3BBr_2, and an unidentified compound (^{11}B resonance at δ 42.39). A third fraction distilled between −64 and −50 °C and was determined to be a mixture of 2-Br_2B-*closo*-1,6-$C_2B_4H_5$ (3%) and BBr_3 (97%). A fourth fraction that distilled between −50 and −27 °C consisted of a mixture of 2-Br_2B-*closo*-1,6-$C_2B_4H_5$ (69%), *closo*-1,6-$C_2B_4H_6$ (18%), and BBr_3 (13%). The last fraction trapped with an ice bath contained 2-Br_2B-*closo*-1,6-$C_2B_4H_5$ [^{11}B NMR δ −14.79 (d, B(3,5)H, J = 192.8 Hz), −12 (s, B(2), broad), −10.64 (d, B(4), J = 189.5 Hz), +70.7 (1:1:1:1 quartet with resolution enhancement, BBr_2, $J(BB')$ = 123 Hz); ^1H NMR δ 3.30 (H(1,6)C), 2.11 (H(3,5)B), 2.22 (H(4)B)].

Reaction of *closo*-1,6-$C_2B_4H_6$ and BI_3 in C_6H_6. Triiodoborane (0.15 mmol) was dissolved in C_6H_6 (0.8 mmol), and the solution was transferred into an NMR tube. *closo*-1,6-$C_2B_4H_6$ (0.5 mmol) was subsequently added, and the tube was sealed and subsequently warmed to room temperature. After the sample was heated at 160 °C for 1 day, the color of the solution changed from blood red to burgundy. When the sample was started at −20 °C for 1 day and subsequently warmed to room temperature, it was observed that crystals had formed in the NMR tube. A ^1H NMR spectrum showed new peaks at δ 8.29 (triplet with J = 7.9 Hz, each member of which was further split into doublet with J = 1.6 Hz) and at δ 7.4 (multiplet). A ^{11}B NMR spectrum showed no new peaks, but the relative amount of BI_3 decreased. Further heating of the sample of 160 °C for 19 h produced a yellow solid material, which formed in the bottom of the tube. When the sample was heated at 250 °C for 3 h, all BI_3 disappeared, but no new peaks appeared in the ^{11}B NMR spectrum.

Reaction of *closo*-1,6-$C_2B_4H_6$ and BI_3 in the Absence of a Solvent. After BI_3 was sublimed into a 3-mm NMR tube, *closo*-1,6-$C_2B_4H_6$ (1.0 mmol) was added. The NMR tube and its contents were sealed and heated at 114 °C for 26 h. A ^{11}B NMR spectrum indicated that no reaction had occurred. Further heating of the sample at 160 °C for 27 h caused the color to change from purple to yellow. Also, a yellow solid material formed in the bottom of the NMR tube. The NMR tube was opened to the vacuum line, and all volatile material (0.65 mmol of recovered *closo*-1,6-$C_2B_4H_6$ and a trace amount of BI_3) was removed. When the remaining contents of the NMR tube were heated with a heat gun under vacuum, a second fraction (additional *closo*-1,6-$C_2B_4H_6$, BI_3, and a cleavage product, CH_3BI_2, at $\delta(^{11}B)$ 49.4)[10] was removed. Solid material remained in the NMR tube that did not dissolve in C_6D_6.

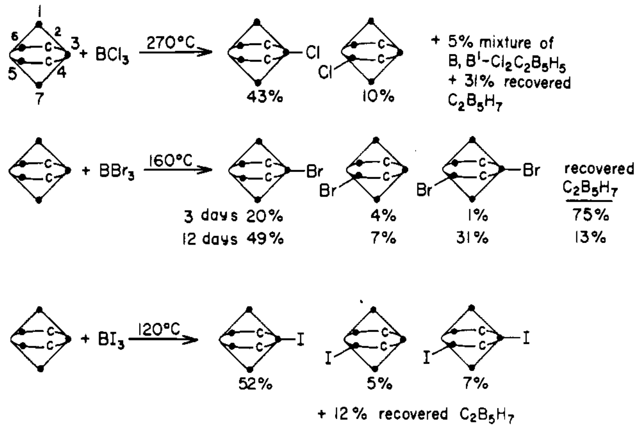

Figure 1. Summary of reactions between *closo*-2,4-$C_2B_5H_7$ and BX_3 (X = Cl, Br, I).

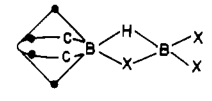

Figure 2. Possible bridging intermediate (or transition state) during the reaction between *closo*-2,4-$C_2B_5H_7$ and BX_3.

Reaction of C_6H_6 and BI_3. Triiodoborane was dissolved in C_6H_6, and the solution was added to a 3-mm NMR tube under dry nitrogen. The NMR tube and its contents were cooled to liquid-nitrogen temperature, evacuated, and sealed. After the sample was heated at 119 °C for 19 h, a new ^{11}B NMR peak appeared at δ 47.7 ($C_6H_5BI_2$).[10,15] The ratio of BI_3 to $C_6H_5BI_2$ was found to be 2.1:1.0. A ^1H NMR spectrum showed new peaks at δ 8.31 (a triplet further divided into doublets) and at δ 7.4 (a multiplet). Further heating of the sample of 119 °C for an additional 48 h did not change the ratio of BI_3 and $C_6H_5BI_2$.

Results and Discussion

Halogenation of *closo*-2,4-$C_2B_5H_7$ with BX_3 (X = Cl, Br, I) yields, as the principal product, a derivative of 2,4-$C_2B_5H_7$ containing a substituent, X, on the B(3) site (Figure 1). The simultaneous formation of 5-X-2,4-$C_2B_5H_6$, in minor amounts, is also observed. The parent *closo*-2,4-$C_2B_5H_7$ reacts (at reasonable rates) with BCl_3, BBr_3, and BI_3 utilizing minimum temperatures of 270, 160, and 120 °C, respectively. At temperatures up to 370 °C a reaction of 2,4-$C_2B_5H_7$ with BF_3 does not give rise to fluoro-substituted carboranes but instead yields some carborane-coupled products, $(C_2B_5H_6)_2$.[11] Thus, the ease of *closo*-2,4-$C_2B_5H_7$ halogenation with BX_3 follows the order I > Br > Cl >> F.

It is known that three-coordinate boron compounds, such as BR_3 (R = alkyl, alkenyl, or aryl) and BX_3 (X = F, Cl, Br, I), are known[16] to undergo redistribution reactions, e.g. $BR_3 + BX_3 \rightleftharpoons RBX_2 + R_2BX$, etc. Similarly, the thermal rearrangement of the monochloro and the dichloro derivatives of *closo*-2,4-$C_2B_5H_7$ are known to be accompanied by a very slow chlorine exchange between cage molecules.[6] The postulated mechanisms for these redistribution reactions all involve a bridging transition state (or intermediate)[16,17] in which an available boron orbital of the starting material(s) is employed. The halogenation reaction of *closo*-2,4-$C_2B_5H_7$ with BX_3 may occur via a similar bridging transition state (or intermediate), as shown in Figure 2. The rate-determining step of this halogen transfer could well be the breaking of the BX_3 boron–halogen bond in such a bridging intermediate. In this regard it is interesting to note that boron–halogen bond energies for B–F, B–Cl, B–Br, and B–I are estimated to be 613, 456, 377, and 272 kJ/mol,[18,19] respectively. This trend is a rea-

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sonable qualitative reflection of the various minimum temperatures required (vide supra) for $C_2B_5H_7$ halogenation.

It is also found in the present study that *closo*-2,4-$C_2B_5H_7$ reacts with $(CH_3)_3CCl$ to give 3-Cl-2,4-$C_2B_5H_6$ at 295 °C, but the rate of formation of 3-Cl-$C_2B_5H_6$ from 2,4-$C_2B_5H_7$ and $(CH_3)_3CCl$ is less facile than from the reaction of 2,4-$C_2B_5H_7$ and BCl_3. When CH_3Cl is used as the alkyl halide and when temperatures as high as 270 °C are used, no chlorine transfer from this reagent to the carborane is observed; instead, evidence for the formation of boron–boron-coupled cage products, $(C_2B_5H_6)_2$,[11] is found only. 3-Br-2,4-$C_2B_5H_6$ is formed from the reaction of 2,4-$C_2B_5H_7$ and $BrCH_2CH_2Br$ at temperatures higher than 300 °C. This is considerably higher than that required (160 °C) for the formation of 3-Br-2,4-$C_2B_5H_6$ from BBr_3 and 2,4-$C_2B_5H_7$. It is possible that the reaction of alkyl halides with the carborane to give *B*-halo derivatives of the cage compound involves a radical pathway. This may explain why $(CH_3)_3Cl$ is much more effective than CH_3Cl for carborane chlorination.

Trace amounts of the apically substituted 1-X-2,4-$C_2B_5H_6$ isomer are found from the BX_3/2,4-$C_2B_5H_7$ reaction, but the percentage of this isomer increases upon the use of alkyl halides as the halogen source. This may be a reflection of the higher temperatures required with the use of the alkyl halides and the suspicion that if a radical process is operating it is expected to be less selective; however, it has been established that temperatures close to 300 °C promote *B*-X-2,4-$C_2B_5H_6$ isomer rearrangement[3,5,6] and that the small amounts of observed 1-X-2,4-$C_2B_5H_6$ (in the present study) may well be formed by the rearrangement of the initially produced 3-X-2,4-$C_2B_5H_6$ and/or 5-X-2,4-$C_2B_5H_6$.

The reluctance of B(1), or the chemically equivalent B(7), of *closo*-2,4-$C_2B_5H_7$ to undergo exchange with BX_3 may be explained by a consideration of the boron atom coordination number: B(1,7) has a coordination number of 6, whereas B(3) and B(5,6) have coordination numbers of 5. Therefore, it is anticipated that it should be more difficult for the apical B(1,7) to increase its coordination, as compared to equatorial B(3) and/or B(5,6), should a bridging intermediate (or transition state) be considered during the reaction of the carborane with BX_3. Among the two "low coordination" equatorial positions, B(3) and B(5,6), halogenation of $C_2B_5H_7$ prefers to take place at B(3). From previous studies[20,21] it has been suggested that B(3) is more electropositive than B(5,6), and it can be speculated that this enhances the B(3) susceptibility toward accetance of an electron-donating bridging atom, such as a halogen of

$B(:\ddot{\underset{..}{X}}:)_3$

Also it is known from *B*-X-2,4-$C_2B_5H_6$ rearrangement studies[5,6] that the most stable isomer among the three *B*-substituted isomers is 3-X-2,4-$C_2B_5H_6$ (X = Cl, Br). Therefore, 2,4-$C_2B_5H_7$ may be more stabilized when a halogen is attached to B(3) via a bridging bond[16,17] than when a halogen is attached (in the same fashion) to B(5). It is to be noted that B(3) appears to be involved in weaker bonding to B(1) and B(7) than is B(5,6) [as assessed by 2-D NMR of 2,4-$C_2B_5H_7$ and its derivatives; B(3) shows very weak cross peaks with B(1) and B(7), implying weak coupling and weak bonding between the two boron types, while B(5) (or B(6)) shows strong cross peaks (presumably stronger bonding) with B(1) and B(7)]. This supports the notion that B(3) may be in a better position than is B(5,6) to help contribute an "empty" orbital for the purpose of bridge bonding with an external halogen. Unfortunately no detailed LUMO calculations are available for a critical correlation in this regard.

The net outcome of the $C_2B_5H_7/BX_3$ halogenation reaction appears to parallel that observed for $B_5H_9/BCl_3/FeCl_3$, which results in the formation of 1-Cl-B_5H_9;[22] however, the primary pentaborane derivative obtained is that in which the halogen ends up at the most negatively charged boron site whereas in the $C_2B_5H_7$ case, as mentioned above, the halogen becomes attached to the most positively charged boron. It is of some interest to note that the order of reactivity between some $C_2B_5H_7$ compounds and BCl_3 is 5,6-$(C_2H_5)_2C_2B_5H_5$ > 2,4-$C_2B_5H_7$ > 5-Cl-$C_2B_5H_6$; the implication of this reactivity order as regards the stability of the proposed bridging intermediates (or transition state) (Figure 2) is not immediately obvious.

An attempt to place an alkoxy group on 2,4-$C_2B_5H_7$, by use of $B[OCH(CH_3)_2]_3$ as the reagent, was unsuccessful; however, reaction of 2,4-$C_2B_5H_7$ with $B(C_6H_5)_3$ at 160–165 °C produces a compound that is analyzed by both ^1H and ^{11}B NMR as 3-C_6H_5-2,4-$C_2B_5H_6$. In contrast, reaction of triphenylborane with the smaller carborane 1,6-$C_2B_4H_6$ at elevated temperatures does not appear to give a *B*-phenyl derivative of this octahedral carborane.

A closo carborane containing a trigonal boron σ-bonded to a cage carborane has been isolated from the reaction of *closo*-1,6-$C_2B_4H_6$ and BBr_3 (eq 1).

$$closo\text{-}1,6\text{-}C_2B_4H_6 + BBr_3 \rightarrow 2\text{-}Br_2B\text{-}1,6\text{-}C_2B_4H_5 \qquad (1)$$

The result of this reaction is analogous to the $BCl_3/B_5H_9/AlCl_3$ reaction that produces 1-$(Cl_2B)B_5H_8$.[22] The BBr_2 ^{11}B NMR resonance of 2-Br_2B-1,6-$C_2B_4H_5$ is far downfield, δ +70.7; this is in the region reminiscent of that associated with the BCl_2 boron of 1-$(Cl_2B)B_5H_8$.[22] Also, the ^{11}B–^{11}B coupling constant of the B–BBr_2 group (123 Hz) is nearly the same as that of the B–BCl_2 group (124 Hz) of 1-$(Cl_2B)B_5H_8$[22] and is within the range (100–151 Hz) found for boron–boron intercage bonds of the coupled compounds $(2,4\text{-}C_2B_5H_6)_2$.[11] The reaction of *closo*-1,6-$C_2B_4H_6$ with BI_3 at 120 °C produces some solid material; the product may be 2-I_2B-*closo*-1,6-$C_2B_4H_5$, but this could not be substantiated. An attempted reaction of *closo*-1,6-$C_2B_4H_6$ and BI_3 in the presence of C_6H_6 gave $I_2BC_6H_5$ instead, which is obviously produced directly from C_6H_6 and BI_3.[15]

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