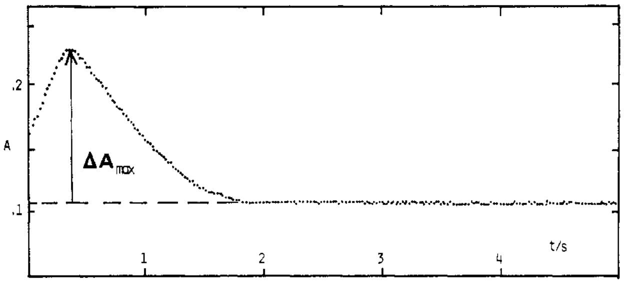

Figure 11. Absorbance–time plot for reaction in the absence of added NaI. ($[I_2]_0$ = 0.2 mM, $[Cr^{II}{}_2]_0$ = 3.6 mM, λ = 410 nm, path length 2 mm, T = 25 °C). The maximum in the absorbance is attributed to a maximum in the concentration of I_3^- ion, occuring when $[I_2]_T = [I^-]_T = {}^2/_3[I_2]_0$ = 0.4 mM. From $K = 2.2 \times 10^4$ M^{-1} and measured extinction coefficients of the components, the value of ΔA_{max} is calculated as 0.116 compared with the measured value of 0.123.

where $k_1 = Kk'_1$. Presumably, the iodide ions are coordinated in the two axial positions, but the positions of the two sodium ions cannot be specified. The limiting first-order iodide dependence of $k_2{}^*$ is consistent with these steps, assuming that the subsequent reaction of the monomer is not catalyzed by iodide.

$$Na[Cr(OAc)_2I] + NaI_3 \xrightarrow{k'_2} Cr(OAc)_2I + NaI + NaI_2 \quad (24)$$

$$Na[Cr_2(OAc)_2I] + NaI_2 \twoheadrightarrow Cr_2(OAc)_2I + 2NaI \quad (25)$$

$$Cr(OAc)_2I \twoheadrightarrow \text{products} \quad (26)$$

Here, "NaI_2" denotes the sodium ion pair of the radical ion I_2^-, so that eq 24 and 25 together constitute the two-step mechanism that is usually postulated for reactions of one-electron reductants with I_2.[14,15] Equation 26 covers a number of steps, but in particular it involves the early release of iodide ion and polymerization of chromium(III) monomer to form a derivative of the oxo-centered trimer, such as $[Cr_3O(OAc)_6(HOAc)_3](OAc)$.

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Registry No. $Cr_2(OOCCH_3)_4$, 15020-15-2; I_2, 7553-56-2.

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Net Front-Side Displacement Reactions in a Carborane System: Halide-Exchange Reactions among Derivatives of *closo*-2,4-Dicarbaheptaborane, 2,4-$C_2B_5H_7$

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Halogen exchange is observed between *B*-halo derivatives of *closo*-2,4-$C_2B_5H_7$ and tetraalkylammonium halides and appears possible only when the "reagent" halide ion is smaller than the "leaving" halide. Thus, both 3- and 5-$IC_2B_5H_6$ react with bromide ion to give quantitative amounts of the respective 3- and 5-$BrC_2B_5H_6$ isomers. Similarly, 5-$BrC_2B_5H_6$ is converted to 5-$ClC_2B_5H_6$ in the presence of Cl^-. This same halide ion reacts with the carborane adduct $(CH_3)_3N{\cdot}5,6\text{-}Br_2C_2B_5H_5$ to give both 5-Cl-6-$BrC_2B_5H_5$ and 5,6-$Cl_2C_2B_5H_5$. Fluoride ion reacts with 5-$BrC_2B_5H_6$ or with the trimethylamine adduct of 5-$ClC_2B_5H_6$ to give 5-$FC_2B_5H_6$. Two other fluorine-substituted carboranes, 3-$FC_2B_5H_6$ and 3,5-$F_2C_2B_5H_5$, are produced in yields exceeding 90% from tetrabutylammonium fluoride and 3-I and 3,5-I_2 derivatives of $C_2B_5H_7$, respectively. All indications point to an increase in (cage)-boron–halogen bond energy as the primary driving force behind the displacement reactions. The rate of substitution, as the halide ion is varied, is in correspondence with the expected nucleophilicity trend $F^- > Cl^- > Br^-$ in nonaqueous solvents. Halogen exchange in a few instances results in rearrangement products; i.e., both $(CH_3)_3N{\cdot}5\text{-}IC_2B_5H_6$/benzyltriethylammonium bromide/CH_2Cl_2 and $(CH_3)_3N{\cdot}5IC_2B_5H_6$/benzyltriethylammonium chloride/CH_2Cl_2 mixtures produce substantial quantities of 3-$ClC_2B_5H_6$ below 100 °C.

Introduction

Synthetic routes to B-substituted compounds of *closo*-2,4-$C_2B_5H_7$ have often involved the use of a Lewis acid to catalyze the introduction of the substituent[1-5] in a manner that is reminiscent of a Friedel-Crafts type of reaction. Several other reactions leading to *B*-X-2,4-$C_2B_5H_6$ compounds from the parent 2,4-$C_2B_5H_7$ are thermally induced or light-induced.[1,4-8] In addition, trace yields of three mono- and some difluoro derivatives of 2,4-$C_2B_5H_7$ are obtained from the direct action of F_2 on the parent carborane.[9] Also, another type of reaction leading to B-substituted dicarbaheptaboranes involves the removal of Cl^- from 1:1 trimethylamine adducts of both 3-Cl- or 5-Cl-2,4-$C_2B_5H_6$, producing the respective $[B\text{-}(CH_3)_3N{\cdot}closo\text{-}2,4\text{-}C_2B_5H_6]^+$ cation isomers.[10]

A previous study,[11] describing the surprising quantitative conversion of the trimethylamine adduct of 5-Br-2,4-$C_2B_5H_6$ in dichloromethane solution to the halogen exchange product, 5-Cl-2,4-$C_2B_5H_6$, provided the motivation for the present study. A mechanism was proposed in which a $[5\text{-}(CH_3)_3N{\cdot}closo\text{-}2,4\text{-}C_2B_5H_6]^+$ intermediate combined with chloride ion (available from

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a reaction of a small equilibrium amount of "free" trimethylamine with the methylene chloride) to give, after an amine extraction step, the observed chlorocarborane. This suggested to us the possibility of producing numerous other substituted carboranes by anion/halocarborane exchange reactions. The present study concentrates on interconversions of *B*-halo derivatives of the *closo*-dicarbaheptaborane 2,4-$C_2B_5H_7$, in both the presence and absence of trimethylamine.

Experimental Section

Materials and Handling of Chemicals. The parent *closo*-2,4-$C_2B_5H_7$ was obtained from R. E. Williams, Chemical Systems Inc., Irvine, CA, and used without further purification. Benzyltrethylammonium chloride, benzyltriethylammonium bromide, and tetrabutylammonium fluoride were obtained from the Aldrich Chemical Co. The first two compounds were anhydrous crystalline salts and were used as received. The latter compound came as a 1 M solution in tetrahydrofuran (THF) containing less than 5% water; the fluoride salt was purified by removing the THF over a steam bath and removing the water by heating to approximately 110 °C under reduced pressure. A method for removing only the water involved placing the THF–tetrabutylammonium fluoride solution over calcium hydride drying agent and subsequently decanting the solution from the resulting solids prior to use. Another sample of tetrabutylammonium fluoride was received in a trihydrated form and was heated to 110 °C under reduced pressure to remove the water. Trimethylamine (J. T. Baker), methylene bromide (Aldrich Chemical), methylene chloride (Eastman Kodak), chloroform (Fisher Scientific), acetone (MCB Reagents), methylene-d_2 chloride and chloroform-*d* (Wilmad Glass Co.) were used as received.

Nuclear Magnetic Resonance Spectroscopy. Boron-11 NMR spectra were obtained by using both Varian HA-100 CW (32.1 MHz) and Bruker WM-500 FT (160.44 MHz) spectrometers. Proton-decoupled boron spectra were also recorded for all compounds in order to confirm assignments. Variation of the delay times between FID pulses minimized saturation effects for the purpose of determining of compound mixture concentrations by FT-NMR area measurements. The boron chemical shift data were referenced relative to $BF_3{\cdot}Et_2O$, $\delta = 0.00$, with the parent 2,4-$C_2B_5H_7$ used as a secondary standard: $\delta(1,7) = -21.73$, $J(^{11}BH) = 180$ Hz; $\delta(3) = +7.02$, 183 Hz; $\delta(5,6) = +3.83$ ppm, 170 Hz. Negative chemical shift values are upfield of the $BF_3{\cdot}Et_2O$ resonance. Approximate chemical shift and coupling constant errors for all dicarbaheptaboranes (parent and derivatives) are as follows: ±0.02 ppm and ±3 Hz for the cage 1-, 3-, and 7-positions of the carborane; ±0.06 ppm and ±10 Hz for the cage 5- and 6-positions.

Halogen Exchange between $(CH_3)_3N{\cdot}3\text{-}IC_2B_5H_6$ and Benzyltriethylammonium Bromide in CH_2Br_2. 3-$IC_2B_5H_6$,[12] (0.1 mmol), containing 10% 5-$IC_2B_5H_6$, was combined with an equimolar amount of trimethylamine and subsequently with benzyltriethylammonium bromide (ca. 0.25 mmol) in 0.25 mL of CH_2Br_2 as solvent. The mixture was allowed to stand at room temperature for 45 days with periodic ^{11}B NMR monitoring. Evidence of 3-$BrC_2B_5H_6$ began to appear after 27 days, in a yield of approximately 30%. In order to increase the rate of formation, the sample was warmed to 40 °C for 18 days, showing an increase in the amount of 3-$BrC_2B_5H_6$ to ca. 80% of the total carborane concentration. A final heating of the mixture at 90 °C for 1 day gave a 90% yield of 3-$BrC_2B_5H_6$ [^{11}B NMR: −19.0 (d, 2 B, B(1,7), *J*(BH) = 184 Hz), +9.0 (s, 1 B, B(3)), +3.2 (d, 2 B, B(5,6), *J*(BH) = 176 Hz) ppm][12] and a 10% yield of 5-$BrC_2B_5H_6$ [^{11}B NMR: −20.7 (d, 2 B, B(1,7), *J*(BH) = 185 Hz), +6.4 (d, 1 B, B(3), *J*(BH) = 189 Hz), +8.1 (s, 1 B, B(5)), +1.6 (d, 1 B, B(6), *J*(BH) = 174 Hz) ppm].[2,11,12] Trace quantities of compound(s) with very weak ^{11}B NMR resonances at $\delta = -14.2$ (s) and +14.1 (s) were also noted.

Halogen Exchange between 5-$IC_2B_5H_6$ and Benzyltriethylammonium Bromide in CH_2Br_2. 5-$IC_2B_5H_6$[12] (0.25 mmol) was combined with benzyltriethylammonium bromide (ca. 0.18 mmol) in CH_2Br_2 (ca. 0.4 mL) as solvent. The sample was allowed to stand at room temperature for 24 days after which a ^{11}B NMR (160.44 MHz) spectrum of the mixture showed that no reaction had occurred. The sample was allowed to stand for another 22 days and heated at 75 °C for 24 h, upon which 5-$BrC_2B_5H_6$ and 5-$IC_2B_5H_6$ were both observed in nearly equal quantities. A third heating period of an additional 65 h at 70 °C gave 5-$BrC_2B_5H_6$[2,11,12] [^{11}B NMR: −20.8 (d, 2 B, B(1,7), *J*(BH) = 186 Hz), +6.2 (d, 1 B, B(3), *J*(BH) = 190 Hz), +8.0 (s, 1 B, B(5)), +1.7 (d, 1 B, B(6), J(BH) = 183 Hz) ppm] and 5-$IC_2B_5H_6$ [^{11}B NMR: −20.7 (d, 2 B, B(1,7), *J*(BH) = 186 Hz), +6.6 (d, 1 B, B(3), *J*(BH) = 190 Hz), +7.9 (s, 1 B, B(5)), +3.9 (d, 1 B B(6)) ppm][12] in a 3:1 ratio. Trace quantities of compound(s) with very weak ^{11}B NMR resonances at $\delta = 0.0$ (s) and −2.8 (s) were also noted. A final heating period of 29 h at 75 °C showed no further change. The yield of 5-$BrC_2B_5H_6$ is nearly quantitative based on available benzyltriethylammonium bromide at the start of the reaction.

Attempted I/Br Exchange between Benzyltriethylammonium Bromide and a 3:1 $(CH_3)_3N{\cdot}3\text{-}IC_2B_5H_6/(CH_3)_3N{\cdot}5\text{-}IC_2B_5H_6$ Mixture in CD_2Cl_2. 3-$IC_2B_5H_6$,[12] containing 25% 5-$IC_2B_5H_6$, (0.1 mmol) was combined with a slight excess of trimethylamine and subsequently with benzyltriethylammonium bromide (0.25 mmol) in approximately 0.25 mL of CD_2Cl_2 as solvent. Periodic ^{11}B NMR monitoring of the sample at 4, 22, 43, and finally 57 days (under ambient conditions) showed increasing amounts of 3-$ClC_2B_5H_6$ [^{11}B NMR: −18.6 (d, 2 B, B(1,7), *J*(BH) = 185 Hz), +14.8 (s, 1 B, B(3)), +2.9 (d, 2 B, B(5,6), *J*(BH) = 173 Hz) ppm] and 5-$ClC_2B_5H_6$ [^{11}B NMR: −20.2 (d, 2 B, B(1,7)), +5.1 (d, 1 B, B(3)), +13.6 (s, 1 B, B(5)), +0.9 (d, 1 B, B(6)) ppm][4,5] with yields of 60% and 20%, respectively, observed at the end of 57 days. In addition to the above, weak ^{11}B NMR absorptions were found at $\delta = -8.4$ (q, probably $(CH_3)_3N{\cdot}BH_3$),[13] −50.0 (s), +7.6 (s), +16.9 (s), and +25.5 (s); all of these resonances together accounted for ca. 15% of the total boron content. The formation of a white precipitate in small quantity was also observed.

Attempted I/Br Exchange between Benzyltriethylammonium Bromide and a 3:1 $(CH_3)_3N{\cdot}5\text{-}IC_2B_5H_6$–$(CH_3)_3N{\cdot}3\text{-}IC_2B_5H_6$ Mixture in CD_2Cl_2. A mixture of 5-$IC_2B_5H_6$ (75%) and 3-$IC_2B_5H_6$[12] (25%) (0.25 mmol total) was combined with an equimolar quantity of trimethylamine and subsequently with benzyltriethylammonium bromide (ca. 0.25 mmol) in CD_2Cl_2 (ca. 0.25 mL) as solvent. The mixture was allowed to stand at room temperature for 26 days, upon which a large amount of crystalline material had formed. The volatile portion of the mixture was transferred to another NMR tube for ^{11}B NMR (160.44 MHz) analysis. The spectrum showed the presence of 3-$ClC_2B_5H_6$ (ca. 85% yield) [^{11}B NMR: −18.2 (d, 2 B, B(1,7), *J*(BH) = 184 Hz), +15.1 (s, 1 B, B(3)), +3.2 (d, 2 B, B(5,6), *J*(BH) = 176 Hz) ppm] and 5-$ClC_2B_5H_6$ (ca. 15% yield) [^{11}B NMR: −19.9 (d, 2 B, B(1,7)), +5.3 (d, 1 B, B(3)), +13.2 (s, 1 B, B(5)), +1.1 (d, 1 B, B(6)) ppm].[4,5]

I/Cl Halogen Exchange between 3-$IC_2B_5H_6$ and Benzyltriethylammonium Chloride in CH_2Cl_2. 3-$IC_2B_5H_6$[12] (0.2 mmol) was mixed with benzyltriethylammonium chloride (0.22 mmol) in methylene chloride (0.25 mL) as solvent. A ^{11}B NMR (160.44 MHz) spectrum taken after 9 days at room temperature showed a 78% conversion to 3-$ClC_2B_5H_6$ [^{11}B NMR: −17.8 ppm (d, 2 B, B(1,7), *J*(BH) = 180 Hz), +15.5 (s, 1 B, B(3)), +3.6 (d, 2 B, B(5,6), *J*(BH) = 168 Hz) ppm][4,5] with the remaining 22% represented by unassigned NMR peaks observed at $\delta = +15.74$ (s), +10.2 (s), +4.8 (d), +19.5 (d), and +16.3 (d).

I/Cl Halogen Exchange between $(CH_3)_3N{\cdot}3\text{-}IC_2B_5H_6$ and Benzyltriethylammonium Chloride in CD_2Cl_2. 3-$IC_2B_5H_5$[12] (0.1 mmol) was added to an equimolar amount of trimethylamine and an excess of benzyltriethylammonium chloride (0.23 mmol) in CD_2Cl_2. The reaction was allowed to stand at room temperature for 43 days, upon which a ca. 95% yield of 3-$ClC_2B_5H_5$ had formed [^{11}B NMR: −19.0 (d, 2 B, B(1,7)), +15.1 (s, 1 B, B(3)), +1.1 (d, 2 B, B(5,6)) ppm].[4,5] In addition to the above, a very weak ^{11}B NMR absorption was found at $\delta = -8.3$ (q, probably $(CH_3)_3N{\cdot}BH_3$).[13] A white precipitate, $[(CH_3)_3N{\cdot}CH_2Cl]^+X^-$,[14] was also observed.

I/Cl Halogen Exchange between 5-$IC_2B_5H_6$ and Benzyltriethylammonium Chloride in CH_2Cl_2. Benzyltriethylammonium chloride (0.22 mmol) was combined with 5-$IC_2B_5H_6$[12] (0.25 mmol) in methylene chloride as solvent. The mixture was allowed to stand at room temperature for 2 days upon which a ^{11}B NMR (160.44 MHz) spectrum showed the pattern expected for a 45% yield of 5-$ClC_2B_5H_6$[4,5] with the remainder as unreacted 5-$IC_2B_5H_6$. After 23 days at room temperature, the yield of 5-$ClC_2B_5H_6$ increased to 84% with a corresponding reduction of the amount of the iodocarborane. A spectrum [^{11}B NMR: −20.1 (d, 2 B, B(1,7), *J*(BH) = 183 Hz), +5.1 (d, 1 B, B(3), *J*(BH) = 189 Hz), +13.5 (s, 1 B, B(5)), +1.1 (d, 1 B, B(6), *J*(BH) = 173 Hz) ppm] taken after a total of 29 days at room temperature and 44 h at 75 °C indicated that 5-$ClC_2B_5H_6$[4,5] formed in 90–95% yield.

I/Cl Halogen Exchange between $(CH_3)_3N{\cdot}5\text{-}C_2B_5H_6$ and Benzyltriethylammonium Chloride in CH_2Cl_2. 5-$IC_2B_5H_6$[12] (0.25 mmol) was combined with an equivalent amount of trimethylamine, 50–60 mg of benzyltriethylammonium chloride, and ca. 0.4 mL of CH_2Cl_2 solvent. The reaction was allowed to stand to room temperature for 33 days after which ^{11}B NMR analysis (160.44 MHz) showed that 5-$ClC_2B_5H_6$ [^{11}B NMR: −20.2 (d, 2 B, B(1,7), *J*(BH) = 184 Hz), +5.3 (d, 1 B, B(3),

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J(BH) = 184 Hz), +13.7 (s, 1 B, B(5)), +1.1 (d, 1 B, B(6)) ppm][4,5] formed in a 25–30% yield; other resonances observed were an intense peak at $\delta = -8.21$ (q, assigned to $(CH_3)_3N{\cdot}BH_3$),[13] a peak at $\delta = +12.95$ (s), and large and broad peaks at $\delta = -50.5$ and +26.3. The latter three peaks were identical with those observed for a sample of 5-$IC_2B_5H_6$ (0.1 mmol) combined with an excess of $(CH_3)_3N$ (0.3 mmol) in $CDCl_3$ (0.8 mmol) as solvent; therefore, these peaks were assigned to a species of the type $y(CH_3)_3N{\cdot}IC_2B_5H_6$ in which y = 2 or 3. The carborane sample containing benzyltriethylammonium chloride was heated at 90 °C for 24 h; ^{11}B NMR analysis indicated that 3-$ClC_2B_5H_6$ (50%) [^{11}B NMR: −18.5 (d, 2 B, B(1,7), J(BH) = 184 Hz), +14.8 (s, 1 B, B(3)), +3.1 (d, 2 B, B(5,6), J(BH) = 174 Hz) ppm] was formed as the major product, along with 5-$ClC_2B_5H_6$ (20%) [^{11}B NMR: = −20.2 (d, 2 B, B(1,7), J(BH) = 184 Hz), +5.1 (d, 1 B, B(3), J(BH) = 184 Hz), +13.6 (s, 1 B, B(5)), +0.9 (d, 1 B, B(6)) ppm][4,5] and a small amount of the polyamine–carborane species. A large amount of white precipitate (most probably $[(CH_3)_3N{\cdot}CH_2X]Y$, X and Y = halogen)[11,14] was also observed after the heating period.

I/F Halogen Exchange between 3-$IC_2B_5H_6$ and Tetrabutylammonium Fluoride in Tetrahydrofuran. 3-$IC_2B_5H_6$[12] (ca. 0.25 mmol) was combined with tetrabutylammonium fluoride (0.25 mmol, as a 1 M solution in THF). The sample was allowed to stand at room temperature for 13 days upon which 3-$FC_2B_5H_6$ [^{11}B NMR: −18.2 (d, 2 B, B(1,7), J(BH) = 178 Hz), +16.1 (s, 1 B, B(3)), +1.0 (d, 2 B, B(5,6), J(BH) = 169 Hz) ppm][9] was formed in 90% yield. The other 10% was represented by a doublet at $\delta = +1.3$ ($HBF_2{\cdot}$THF?).

I/F Halogen Exchange between 3,5-$I_2C_2B_5H_5$ and Tetrabutylammonium Fluoride in THF. A solution of tetrabutylammonium fluoride in THF (ca. 0.50 mL of a 1 M solution) was syringed into a 3-mm NMR tube equipped with a 1-mL glass expansion bulb. To this was added a solution of 3,5-$I_2C_2B_5H_5$[12] (0.25 mmol) in pentane (0.5 mL). The sample tube was cooled to −190 °C, evacuated, sealed, and allowed to stand at room temperature for a period of 13 days. A ^{11}B NMR (160.44 MHz) spectrum of the sample showed only peaks corresponding to 3,5-$F_2C_2B_5H_5$ [^{11}B NMR: −17.0 (d, 2 B, B(1,7), J(BH) = 173 Hz), +13.0 (s, 1 B, B(3)), +15.3 (s, 1 B, B(5)), −10.6 (d, 1 B, B(6), J(BH) = 148 Hz) ppm]; these chemical shift values agree well with those calculated by using substituent additivity parameters obtained from ref 12: δ = −17.4 for B(1,7), +13.9 for B(3), +15.1 for B(5), and −8.1 for B(6).

Br/Cl Halogen Exchange between 5-$BrC_2B_5H_6$ and Benzyltriethylammonium Chloride in CH_2Cl_2. 5-$BrC_2H_5B_6$[2,12] (0.2 mmol) was combined with benzyltriethylammonium chloride (0.22 mmol) in CH_2Cl_2 (0.3 mL) as solvent. The reaction mixture was allowed to stand for 9 days at room temperature after which a ^{11}B NMR (160.44 MHz) spectrum of the sample contents showed the presence of 5-$BrC_2B_5H_6$ (61%) and 5-$ClC_2B_5H_6$[4,5] (39%) respectively. A second spectrum taken after the sample remained at room temperature for a total of 30 days showed 5-$ClC_2B_5H_6$ and 5-$BrC_2B_5H_6$ to be roughly equal in quantity. A third spectrum, taken after the sample was kept for a total of 50 days at room temperature and subsequently heated at 50 °C for 24 h showed that the 5-$ClC_2B_5H_6$ yield had increased to 66% and 5-$BrC_2B_5H_6$ was present in 34% yield. After the sample was heated for 44 h at 75 °C, the ^{11}B NMR showed 5-$ClC_2B_5H_6$ [^{11}B NMR: −20.1 (d, 2 B, B(1,7), J(BH) = 183 Hz), +5.1 (d, 1 B, B(3), J(BH) = 188 Hz), +13.6 (s, 1 B, B(5)), +0.9 (d, 1 B, B(6), J(BH) = 177 Hz) ppm] present in nearly quantitative yield.

Br/Cl Halogen Exchange between $(CH_3)_3N{\cdot}5\text{-}BrC_2B_5H_6$ and Benzyltriethylammonium Chloride in CD_2Cl_2. The $(CH_3)_3N$ adduct of 5-$BrC_2B_5H_6$[11] (0.23 mmol) was combined with benzyltriethylammonium chloride (0.23 mmol) and CD_2Cl_2 (0.5 mL) as solvent. The mixture was allowed to stand at room temperature and monitored by periodic ^{11}B NMR spectra. These spectra showed a steady buildup of 5-$ClC_2B_5H_6$ [^{11}B NMR: −20.0 (d, 2 B, B(1,7)), +5.3 (d, 1 B, B(3)), +13.8 (s, 1 B, B(5)), +1.1 (d, 1 B, B(6)) ppm][4,5] to a yield of >90% after 30 days. The appearance of a white crystalline precipitate (most probably $[(CH_3)_3N{\cdot}CH_2Cl]^+X^-$, $X^- = Cl^-$ or Br^-)[11,14] was also observed.

Br/Cl Halogen Exchange between $(CH_3)_3N{\cdot}5\text{-}BrC_2B_5H_6$ and Benzyltriethylammonium Chloride in $CDCl_3$. The $(CH_3)_3N$ adduct of 5-$BrC_2C_5H_6$[11] (0.15 mmol) was added to benzyltriethylammonium chloride (0.16 mmol) in approximately 0.25 mL of $CDCl_3$ as solvent. The mixture was allowed to stand at room temperature with periodic monitoring of the solution with ^{11}B NMR (160.44 MHz). These spectra showed a slow buildup of 5-$ClC_2B_5H_6$,[4,5] giving a maximum yield of 50% of this compound after 30 days. (Note: no precipitate is formed, vide infra.)

Br/Cl Halogen Exchange between $(CH_3)_3N{\cdot}5,6\text{-}Br_2C_2B_5H_5$ and Benzyltriethylammonium Chloride in CD_2Cl_2. $(CH_3)_3N$ (0.25 mmol) was added to 5,6-$Br_2C_2B_5H_5$,[12] (0.25 mmol); to this sample was added a 2-fold excess of benzyltriethylammonium chloride in 1.0 mL of CD_2Cl_2 as solvent. The sample was allowed to stand at room temperature for 4 h after which a ^{11}B NMR (160.44 MHz) spectrum showed 5,6-$Cl_2C_2B_5H_5$ [^{11}B NMR: −18.6 (d, 2 B, B(1,7), J(BH) = 192 Hz), +2.0 (d, 1 B, B(3), J(BH) = 192 Hz), +10.3 ppm (s, 2 B, B(5,6)) ppm][4,5] and what is believed to be 5-Cl-6-$BrC_2B_5H_5$ [^{11}B NMR: −18.7 (d, 2B, B-(1,7)), +2.9 (d, 1 B, B(3)), +11.4 (s, 1 B, B(5)), +4.7 (s, 1 B, B(6)) ppm]; these chemical shift values agree well with those calculated by using substituent additivity parameters obtained from ref 12: δ = −18.1 for B(1,7), +4.2 for B(3), +12.7 for B(5), and 5.8 for B(6)] in a ratio of approximately 4:1. A second ^{11}B NMR spectrum taken after 4.5 days showed an approximately 90% conversion to 5,6-$Cl_2C_2B_5H_5$ with no observable precipitate. Other peaks were observed in the ^{11}B NMR at δ = −13.5 (s) and −51.0 (s), bis- or tris(trimethylamine) adduct of a halocarborane?), both very minor intensities.

Br/Cl Halogen Exchange between $2(CH_3)_3N{\cdot}5,6\text{-}Br_2C_2B_5H_5$ and Benzyltriethylammonium Chloride in CD_2Cl_2. 5,6-$Br_2C_2B_5H_5$[12] (0.37 mmol) was combined with $(CH_3)_3N$ (ca. 0.75 mmol) and subsequently with an excess of benzyltriethylammonium chloride in ca. 1 mL of CD_2Cl_2. The reaction was allowed to stand at room temperature for 4 h after which ^{11}B NMR analysis showed an approximately 90% yield of 5,6-$Cl_2C_2B_5H_5$ [^{11}B NMR −18.9 (d, 2 B, B(1,7), J(BH) = 192 Hz), +1.7 (d, 1 B, B(3), J(BH) = 192 Hz), +10.1 (s, 2 B, B(5,6)) ppm][4,5] and a white precipitate (most probably $[(CH_3)_3N{\cdot}CH_2X]Y$, X, Y = halogen).[11,14] Other peaks were observed in the ^{11}B NMR at δ = −13.8 (s) and −51.0 (s), both very weak.

Adduct Formation between 5,6-$Br_2C_2B_5H_5$ and Two $(CH_3)_3N$ Molecules in CD_2Cl_2. 5,6-$Br_2C_2B_5H_5$[12] (ca. 0.7 mmol) was combined with trimethylamine (6 mmol) and allowed to stand at room temperature for 4 days. A ^{11}B NMR (160.44 MHz) spectrum of the mixture showed peaks at δ = −50.4, −8.0, +6.5 +13.2, and +26.1; all of these peaks are very broad.

Br/F Halogen Exchange between 5-$BrC_2B_5H_6$ and Tetrabutylammonium Fluoride in Tetrahydrofuran (THF). 5-$BrC_2B_5H_6$[2,12] (ca. 0.3 mmol) was combined with tetrabutylammonium fluoride (0.5 mmol) as a 1 M solution in THF. The reactions were sealed into an NMR tube equipped with a 3-mL glass bulb and allowed to stand at room temperature for 2 days. A ^{11}B NMR (160.44 MHz) spectrum showed the presence of 5-$FC_2B_5H_6$ and 5-$BrC_2B_5H_6$ in nearly equal quantities. The sample was allowed to stand at room temperature for another 14 days after which time only 5-$FC_2B_5H_6$ [^{11}B NMR; −20.8 (d, 2 B, B(1,7), J(BH) = 176 Hz), +2.7 (d, 1 B, B(3), J(BH) = 175 Hz), +17.2 (s, 1 B, B(5)), −6.0 (d, 1 B, B(6), J(BH) = 160 Hz) ppm][9,15] was observed in the ^{11}B NMR spectrum. Cold-column vacuum fractionation[16] of the volatile portion of the mixture gives 5-$FC_2B_5H_6$ in the −90 °C fraction.

Br/F Halogen Exchange between $(CH_3)_3N{\cdot}5\text{-}BrC_2B_5H_6$ and Tetrabutylammonium Fluoride in CH_2Cl_2. 5-$BrC_2B_5H_6$[2,12] (0.02 mol) was combined with an approximately equal amount of $(CH_3)_3N$ and subsequently with an excess of tetrabutylammonium fluoride in CH_2Cl_2 as solvent. The reaction was left at room temperature for 43 days after which an equimolar mixture of 5-$FC_2B_5H_6$ [^{11}B NMR: −20.9 (d, 2 B, B(1,7), J(BH) = 180 Hz), +3.2 (d, 1 B, B(3), J(BH) = 188 Hz), +19.1 (s, 1 B, B(5)), −3.8 (d, 1 B, B(6), J(BH) = 163 Hz) ppm][9,15] and $C_2B_5H_7$ [^{11}B NMR: −21.8 (d, 2 B, B(1,7), J(BH) = 180 Hz), +7.1 (d, 1 B, B(3), J(BH) = 184 Hz), +3.7 (d, 2 B, B(5,6), J(BH) = 161 Hz) ppm][13] was formed. Other peaks in the ^{11}B NMR are at δ = −1.19 (s, probably $(CH_3)_3N{\cdot}BF_3$ or THF$\cdot BF_3$),[17] −8.4 (q, most probably $(CH_3)_3N{\cdot}BH_3$),[17] and +0.02 (s), in a boron ratio of 58:4:5; however, these side products amount to only ca. 7% of the 5-$FC_2B_5H_6$. The sample was separated by cold-column fractionation[16] with the 5-$FC_2B_5H_6$ compound isolated at −90 °C.

Attempted Br/F Halogen Exchange between 5-$BrC_2B_5H_6$ and Tetrabutylammonium Fluoride in CH_2Cl_2. 5-$BrC_2B_5H_6$[2,12] (0.12 mmol) was combined with an excess tetrabutylammonium fluoride (ca. 0.25 mmol) in CH_2Cl_2 as the solvent. (Note: traces of THF and water were present as determined by proton NMR; see Materials section.) The mixture was allowed to stand at room temperature for 19 days after which time a quantitative yield of 5-$ClC_2Br_5H_6$ [^{11}B NMR: −20.5 (d, 2 B, B(1,7), J(BH) = 187 Hz), +5.7 (d, 1 B, B(3), J(BH) = 184 Hz), +13.5 (s, 1 B, B(5)), +1.3 (d, 1 B, B(6), J(BH) = 167 Hz) ppm][4,5] was observed. The reaction was repeated with 0.25 mmol of 5-$BrC_2B_5H_6$ with the same result observed after only 3 days at room temperature.

Attempted Cl/F Halogen Exchange between 5-$ClC_2B_5H_6$ and Tetrabutylammonium Fluoride in CH_2Br_2. 5-$ClC_2B_5H_6$[4,5] (0.3 mmol) was combined with tetrabutylammonium fluoride (ca. 0.25 mmol, as a 1 M solution in CH_2Br_2). The sample was allowed to stand at room temperature for 28 days and heated for a total of 68 h at 70–75 °C after which time no reaction was observed, as monitored by ^{11}B NMR.

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Table I. Summary of Halogen Exchange Reaction Data[a]

reagents	conditions	carborane product(s)
9:1 $3\text{-}IC_2B_5H_6{:}5\text{-}IC_2B_5H_6 + Br^- + CH_2Br_2$	rt, 45 days	$3\text{-}BrC_2B_5H_6$ (30%)
	40 °C, 18 days	$3\text{-}BrC_2B_5H_6$ (80%)
	90 °C, 24 h	$3\text{-}BrC_2B_5H_6$ (90%), $5\text{-}BrC_2B_5H_6$ (10%)
$5\text{-}IC_2B_5H_6 + Br^- + CH_2Br_2$	70 °C, 24 h	$5\text{-}BrC_2B_5H_6$ (67%)
	70 °C, 89 h	$5\text{-}BrC_2H_5H_6$ (100%)
3:1 $3\text{-}IC_2B_5H_6{:}5\text{-}IC_2B_5H_6 + Me_3N + Br^- + CD_2Cl_2$	rt, 22 days	$3\text{-}ClC_2B_5H_6$ (50%), $5\text{-}ClC_2B_5H_6$ (15%)
	rt, 43 days	$3\text{-}ClC_2B_5H_6$ (60%), $5\text{-}ClC_2B_5H_6$ (20%)
	rt, 57 days	$3\text{-}ClC_2B_5H_6$ (60%), $5\text{-}ClC_2B_5H_6$ (20%)
3:1 $5\text{-}IC_2B_5H_6{:}3\text{-}IC_2B_5H_6 + Me_3N + Br^- + CH_2Cl_2$	rt, 26 days	$5\text{-}ClC_2B_5H_6$ (15%), $3\text{-}ClC_2B_5H_6$ (85%)
$3\text{-}IC_2B_5H_6 + Cl^- + CH_2Cl_2$	rt, 9 days	$3\text{-}ClC_2B_5H_6$ (78%)
$3\text{-}IC_2B_5H_6 + Me_3N + Cl^- + CD_2Cl_2$	rt, 43 days	$3\text{-}ClC_2B_5H_6$ (ca. 95%)
$5\text{-}IC_2B_5H_6 + Cl^- + CH_2Cl_2$	rt, 23 days	$5\text{-}ClC_2B_5H_6$ (84%)
	75 °C, 44 h	$5\text{-}ClC_2B_5H_6$ (>90%)
$5\text{-}IC_2B_5H_6 + Me_3N + Cl^- + CH_2Cl_2$	rt, 33 days	$5\text{-}ClC_2B_5H_6$ (30%)
	90 °C, 24 h	$5\text{-}ClC_2B_5H_6$ (20%), $3\text{-}ClC_2B_5H_6$ (50%)
$3\text{-}IC_2B_5H_6 + F^- + THF$	rt, 13 days	$3\text{-}FC_2B_5H_6$ (ca. 90%)
$3,5\text{-}I_2C_2B_5H_5 + F^- + THF$ + pentane	rt, 13 days	$3,5\text{-}F_2C_2B_5H_5$ (>95%)
$5\text{-}BrC_2B_5H_6 + Cl^- + CH_2Cl_2$	rt, 9 days	$5\text{-}ClC_2B_5H_6$ (39%)
	rt, 30 days	$5\text{-}ClC_2B_5H_6$ (50%)
	50 °C, 24 h	$5\text{-}ClC_2B_5H_6$ (66%)
	75 °C, 44 h	$5\text{-}ClC_2B_5H_6$ (>95%)
$Me_3N{\cdot}5\text{-}BrC_2B_5H_6 + Cl^- + CD_2Cl_2$	rt, 7 days	$5\text{-}ClC_2B_5H_6$ (50%)
	rt, 30 days	$5\text{-}ClC_2B_5H_6$ (>90%)
$Me_3N{\cdot}5\text{-}BrC_2B_5H_6 + Cl^- + CDCl_3$	rt, 30 days	$5\text{-}ClC_2B_5H_6$ (50%)
$5,6\text{-}Br_2C_2B_5H_5 + Me_3N + Cl^- + CD_2Cl_2$	rt, 4 h	$5,6\text{-}Cl_2C_2B_5H_5$ (75%), $5\text{-}Cl\text{-}6\text{-}BrC_2B_5H_5$ (20%)
	rt, 4.5 days	$5,6\text{-}Cl_2C_2B_5H_5$ (90%)
$5,6\text{-}Br_2C_2B_5H_6 + 2\ Me_3N + Cl^- + CD_2Cl_2$	rt, 4 h	$5,6\text{-}Cl_2C_iB_5H_5$ (90%)
$5\text{-}BrC_2B_5H_6 + F^- + THF$	rt, 2 days	$5\text{-}FC_2B_5H_6$ (50%)
	rt, 16 days	$5\text{-}FC_2B_5H_6$ (100%)
$5\text{-}BrC_2B_5H_6 + Me_3N + CH_2Cl_2 + F^-$	rt, 43 days	$5\text{-}FC_2B_5H_6$ (45%), $C_2B_5H_7$ (45%)
$5\text{-}BrC_2B_5H_6 + F^- + CH_2Cl_2$	rt, 3 days	$5\text{-}ClC_2B_5H_6$ (100%)
$Me_3N{\cdot}5\text{-}ClC_2B_5H_6 + F^- + CH_2Cl_2$	rt, 47 days	$5\text{-}FC_2B_5H_6$ (50%), $5\text{-}ClC_2B_5H_6$ (25%), $C_2B_5H_7$ (20%)
$Me_3N{\cdot}5\text{-}ClC_2B_5H_6 + Br^- + CD_2Cl_2$	rt, 103 days	$5\text{-}ClC_2B_5H_6$ (100%)

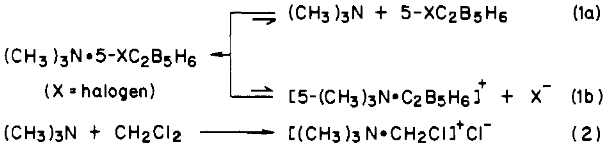
[a] Key: Cl^- = benzyltriethylammonium chloride, Br^- = benzyltriethylammonium bromide, F^- = tetrabutylammonium fluoride; rt = room temperature.

Cl/F Halogen Exchange between $(CH_3)_3N{\cdot}5\text{-}ClC_2B_5H_6$ and Tetrabutylammonium Fluoride in CH_2Cl_2. $(CH_3)_3N{\cdot}5\text{-}ClB_5H_6$[10] (0.4 mmol) was added to approximately 1 mL of a 1 M solution of tetrabutylammonium fluoride in CH_2Cl_2. The sample was kept at room temperature for 33 days after which a complex set of peaks were observed in the ^{11}B NMR spectrum. A second spectrum taken 14 days later showed no further change. The volatile fraction was separated from the remainder of the solution; a ^{11}B NMR spectrum of the volatiles indicated the presence of $5\text{-}FC_2B_5H_6$ (50% yield) [^{11}B NMR: −20.7 (d, 2 B, B(1,7)), +3.9 (d, 1 B, B(3)), +19.4 (s, 1 B, B(5)), −3.8 (d, 1 B, B(6)) ppm],[9,15] $5\text{-}Cl\text{-}C_2B_5H_6$ (25%) [^{11}B NMR: −19.9 (d, 2 B, B(1,7)), +5.4 (d, 1 B, B(3)), +14.0 (s, 1 B, B(5)), +1.3 (d, 1 B, B(6)) ppm],[4,5] and $C_2B_5H_7$ (20%) [^{11}B NMR: −21.7 (d, 2 B, B(1,7)), +7.3 (d, 1 B, B(3)), +3.4 (d, 2 B, B(5,6)) ppm];[13] in addition, the presence of a very weak quartet resonance centered at $\delta = -8.1$ (most probably $(CH_3)_3N{\cdot}BH_3$)[17] was noted.

Attempted Cl/Br Halogen Exchange between $(CH_3)_3N{\cdot}5\text{-}ClC_2B_5H_6$ and Benzyltriethylammonium Bromide in CD_2Cl_2. $(CH_3)_3N{\cdot}5\text{-}ClC_2B_5H_6$[10] (0.04 mmol), was added to approximately 0.25 mL of benzyltriethylammonium bromide in CD_2Cl_2 as solvent. The reaction was kept at room temperature for 103 days after which time unreacted $5\text{-}C_2B_5H_6$[4,5] was the only boron-containing material observed in the ^{11}B NMR spectrum.

Discussion

A recent study described the slow but quantitative conversion of the trimethylamine adduct of $5\text{-}Br\text{-}2,4\text{-}C_2B_5H_6$, in the presence of dichloromethane, to the halogen-exchange product, $5\text{-}Cl\text{-}2,4\text{-}C_2B_5H_6$.[11] A mechanism proposed to account for this exchange is shown in eq 1 and 2.[11] This presented the possibility that halide ion was responsible for the observed exchange, and suggested that a source of halide ion other than that available from the rather slow reaction between trimethylamine and the dihalomethane solvent could serve better in the cage substituent exchange reaction. In the present work (Figure 1, Table I), we amply illustrate the ability of smaller halide ions to displace larger halogens from $B\text{-}XC_2B_5H_6$ compounds. Furthermore, our studies show that often there is no need to prepare an amine adduct prior to carrying out most exchange reactions. It is found, though, that the amine adducts of the halocarboranes can in some instances react faster, or give a higher halogen-exchanged carborane product yield, than can the halocarbonanes themselves. This may imply that eq 1 can provide for a species more prone toward substituent exchange than in those cases in which the trialkylamine is not used.



Net halogen exchange between many B-halo derivatives of *closo*-2,4-$C_2B_5H_7$ and tetraalkylammonium halides is possible only when the "reagent" halide ion is smaller than the "leaving" halide. Thus, both 3- and $5\text{-}IC_2B_5H_6$ react with benzyltriethylammonium bromide to give quantitative amounts of the respective 3- and $5\text{-}BrC_2B_5H_6$ isomers. Similarly, $5\text{-}BrC_2B_5H_6$ is converted to $5\text{-}ClC_2B_5H_6$ in the presence of Cl^-. We have been unable to observe halogen exchange between $5\text{-}ClC_2B_5H_6$ and F^-, but use of the trimethylamine adduct of $5\text{-}ClC_2B_5H_6$ as the carborane starting material does give, in the presence of tetrabutylammonium fluoride, usable quantities of $5\text{-}FC_2B_5H_6$. A nearly quantitative yield of this fluorocarborane is obtained from the ambient reaction of $5\text{-}BrC_2B_5H_6$ with fluoride ion. Two other fluorine-substituted carboranes, $3\text{-}FC_2B_5H_6$ and $3,5\text{-}F_2C_2B_5H_5$,[15] are produced in yields exceeding 90% from tetrabutylammonium fluoride and 3-I and 3,5-I_2 derivatives of $C_2B_5H_7$, respectively. The overall result of these halogen/halogen exchange reactions is a net front-side displacement at the cage boron site containing the functional atom.

Because the halocarboranes are generally unstable in the presence of hydroxyl groups it is necessary to avoid water and alcohols as solvents; tetrahydrofuran is convenient for some of the fluorocarborane preparations, and dihalomethanes work well as solvents for most all halogen/halogen exchange reactions. It is highly desirable to avoid the use of a CH_2X_2 solvent in which X

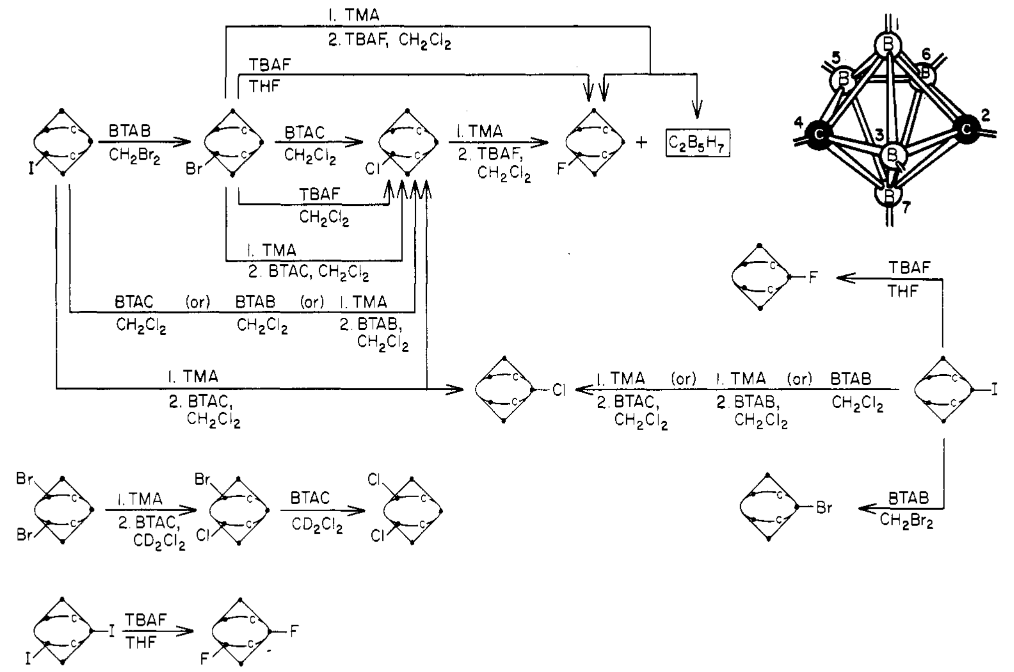


Figure 1. Halogen-exchange schematic for *closo*-2,4-$C_2B_5H_7$ derivatives: TMA = $(CH_3)_3N$, TBAF = $[(C_4H_9)_4N]F$, BTAC = $[C_6H_5CH_2(C_2H_5)_3N]Cl$, BTAB = $[C_6H_5CH_2(C_2H_5)_3N]Br$.

is a smaller halogen than the halogen of the halide reagent. For example, the reaction of $(CH_3)_3N{\cdot}3IC_2B_5H_6$ with benzyltriethylammonium bromide using CH_2Cl_2 as the solvent produces $3\text{-}ClC_2B_5H_6$, whereas, when the solvent is changed to CH_2Br_2, the desired $3\text{-}BrC_2B_5H_6$ is obtained. In the experiment in which CH_2Cl_2 is used as the solvent the expected bromocarborane product is bypassed in favor of a chlorocarborane even though bromide ion is initially the only halide ion present. If chloride ion is responsible for the observed exchange, it may have been introduced into the reaction mixture from the very slow reaction of CH_2Cl_2 with $(CH_3)_3N$ (the latter available in small quantity from the carborane adduct, eq 1a) to give the $[(CH_3)_3N{\cdot}CH_2Cl]^+Cl^-$ salt.[11,14] Alternately, the chloride ion may become available through halogen/halogen exchange between dihalomethane solvent and halide reagent. Apparently the smaller halide ion reacts faster than the large halides with the carborane derivative or, alternately, the carborane derivative with the smaller halogen to boron bond is kinetically accessible and more stable than halocarborane product(s) with (larger) halogen to boron bond(s). Because moderately polar aprotic organic solvents are found to be more useful than hydroxyl-containing solvents, a good general halide source compatible with the selected solvents are compounds such as the tetralkylammonium halides, e.g. benzyltriethylammonium bromide, benzyltriethylammonium chloride, and tetrabutylammonium fluoride.

Several unsuccessful attempts were made with the intent to replace a smaller (carboranyl) halogen with a larger halogen; for example, a $(CH_3)_3N{\cdot}5\text{-}ClC_2B_5H_6$/benzyltriethylammonium bromide mixture does not show any indication of providing a bromocarborane. And because the halocarborane formed in each of the exchange reactions strongly favors the compound with the (presumed) strongest[18,19] B–X (X = halogen) bond, this consideration may well be the overriding thermodynamic factor in deciding the outcome of the exchange product(s).

The relative rate of substitution, as the halide ion is varied, corresponds to the expected nucleophilicity trend $F^- > Cl^- > Br^-$ in aprotic solvents.[20,21] For example, the formation of $3\text{-}ClC_2B_5H_6$ from a $3\text{-}IC_2B_5H_6/Cl^-$ mixture is faster than the formation of $3\text{-}BrC_2B_5H_6$ from a $3\text{-}IC_2B_5H_6/Br^-$ mixture.

Halogen exchange in a few instances results in rearrangement products; i.e., both $(CH_3)_3N{\cdot}5\text{-}IC_2B_5H_6$/benzyltriethylammonium bromide/CH_2Cl_2 and $(CH_3)_3N{\cdot}5IC_2B_5H_6$/benzyltriethylammonium chloride/CH_2Cl_2 mixtures can be encouraged to produce substantial quantities of $3\text{-}ClC_2B_5H_6$ below 100 °C. It has previously been shown that both (neat) 3- and $5\text{-}ClC_2B_5H_6$ isomers rearrange at 340 °C to give equilibrium quantities of the 5-, 3- and $1\text{-}ClC_2B_5H_6$ isomers in a ratio of nearly 2:2:1, respectively.[5] However, it is noted that no 1-Cl isomer is detected in the halogen exchange–rearrangement reactions, which result in the production of the 5-Cl- and $3\text{-}ClC_2B_5H_6$ isomers from $(CH_3)_3N{\cdot}5\text{-}IC_2B_5H_6$ and Cl^-; furthermore, the ratio of 3-Cl to 5-Cl isomer products is considerably higher in the latter reaction than that observed for the 340 °C rearrangement,[5] but not far from the ratio, ca. 3.7:1, expected by extrapolating the thermal rearrangement results to room temperature (an extrapolation that assumes entropy differences between position isomers are attributed to symmetry variations only). In order to account for the "catalytic" effect of $(CH_3)_3N$ in promoting the *B*-halocarborane rearrangement, the following argument can be advanced: it has been documented that the addition of an electron pair to a *closo*-carborane should cause the cage to open to a nido cage geometry;[22-25] the unshared pair of electrons on the nitrogen of $(CH_3)_3N$:, directly or indirectly,[26] may be serving this purpose. It is not difficult to envisage that a partially "open" structure may well be more susceptible to rearrangement at lower temperatures than is the "tighter" *closo*-carborane framework. The details of this mechanistic argument await further work.

The exchange mechanism (eq 1 and 2) proposed for the reactions starting with the trimethylamine adducts of the halogenated carboranes requires a reagent for the removal of the amine at some point during the overall reaction, for it is the amine-free halogenated carborane that is eventually produced. When

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methylene chloride is used as the solvent, it can act as such a reagent in that it is known to react with trimethylamine[11,14] to form $[(CH_3)_3N{\cdot}CH_2Cl]Cl$, which precipitates from the solution, thus effectively removing the amine from the carborane site. Substituting $CHCl_3$ for CH_2Cl_2 as the solvent in the Br/Cl exchange reaction between $(CH_3)_3N{\cdot}5BrC_2B_5H_6$ and benzyltriethylammonium chloride reduces the yield of $5\text{-}ClC_2B_5H_6$ from nearly 100% to about 50%. The ^{11}B NMR spectrum of the reaction carried out in $CHCl_3$ strongly suggests that the remaining carborane material is manifested as $2(CH_3)_3N{\cdot}XC_2B_5H_6$ (X = Br, Cl). Under the conditions of the reaction $CHCl_3$ does not remove the amine; instead it is suggested that this task is effectively carried out by another such molecule of the $(CH_3)_3N{\cdot}5\text{-}XC_2B_5H_6$, forming the diamine adduct of the latter. In control experiments it is found that $(CH_3)_3N{\cdot}5\text{-}XC_2B_5H_6$ (X = Br, Cl) compounds can react with additional $(CH_3)_3N$ to form diamine adducts of the halocarboranes.[27]

The dihalocarborane $5,6\text{-}Br_2C_2B_5H_5$ combines with trimethylamine and benzyltriethylammonium chloride in CD_2Cl_2 to give a nearly quantitative yield of $5,6\text{-}Cl_2C_2B_5H_5$. Monitoring the reaction during intermediate stages indicates the buildup of a modest amount of $5\text{-}Cl\text{-}6\text{-}BrC_2B_5H_5$ and the eventual conversion of this species to the final $5,6\text{-}Cl_2C_2B_5H_5$ product. Halogen ion exchanges of dihalogenated cage species generally occur much more rapidly than those involving monohalogenated cage species. It is not difficult to imagine that the presence of a second halogen on the polyhedral framework could significantly alter the cage boron electron density at the site of attack, resulting in a different (in this case, faster) rate of halogen exchange.

A couple of halogen ion exchange reactions, $(CH_3)_3N{\cdot}5\text{-}ClC_2B_5H_6$/tetrabutylammonium fluoride/CH_2Cl_2 and $(CH_3)_3N{\cdot}5\text{-}BrC_2B_5H_6$/tetrabutylammonium fluoride/CH_2Cl_2, produce a substantial amount of the parent $C_2B_5H_7$ along with the expected *B*-halocarborane product. A measurable quantity of $(CH_3)_3N{\cdot}BH_3$ is also formed in these reactions, suggesting that this simple amine–borane, or some other similar cage breakdown product, may well have acted as a reducing agent on one of the halocarborane reactants (or intermediates) to give the observed $C_2B_5H_7$.

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(27) Siwap, G.; Fuller, K.; Abdou, Z. J.; Onak, T., unpublished results. Generally, when a *B*-halo derivative of $C_2B_5H_7$ is treated with excess trimethylamine an upfield ^{11}B resonance is observed in the region of $\delta = -50$ and several broad low-field peaks are found in the region stretching from +30 to −10 ppm. These peaks are assigned to a species of the general formula $[(CH_3)_3N]_y{\cdot}XC_2B_5H_6$, y = 2 or 3, X = halogen.

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Substitution and Fragmentation Kinetics of $Os_3(CO)_{12}$, $Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$, and $Os_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$

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The kinetics of the stepwise reactions of $Os_3(CO)_{12}$ with P-*n*-Bu_3 in Decalin have been studied. Substitution to form $Os_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ occurs via a series of [P-*n*-Bu_3]-independent steps, but nucleophilic attack on $Os_3(CO)_{12}$ and $Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ leads to fragmentation products by a bimolecular process that can be classified as F_N2. $Os_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ is not susceptible to nucleophilic attack and does not undergo fragmentation. The relative activation energies of the various reactions are such that $Os_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ is formed quantitatively at 170 °C and fairly low [P-*n*-Bu_3] whereas under much milder conditions (70 °C, and much higher [P-*n*-Bu_3]), only mononuclear fragmentation products are found. The introduction of P-*n*-Bu_3 substituents into the $Os_3(CO)_{12}$ cluster has a pronounced effect on the activation parameters for further reaction.

Introduction

The kinetics of thermal reactions of metal carbonyl clusters have received surprisingly little study compared with the vast efforts devoted to synthesis and structural determination. Thus, although $Ru_3(CO)_{12}$,[1] $Co_4(CO)_{12}$,[2] and $Ir_4(CO)_{12}$[3] and their derivatives[2c–e,3,4] have been the subject of fairly extensive kinetic studies, virtually nothing is known about other archetypal carbonyl clusters. Apart from the ^{14}CO-exchange reaction,[1a] only two kinetic studies of a substitution reaction of $Fe_3(CO)_{12}$ have been reported,[5] and the only thermal reactions of $Os_3(CO)_{12}$ that have been studied kinetically are the exchange reaction with ^{14}CO,[1a] reactions with Cl_2 and Br_2,[6] and, quite recently, reactions with very low concentrations of some P donors.[5b] We report here a kinetic study of the reactions of $Os_3(CO)_{12}$ with P-*n*-Bu_3 and PPh_3 and of $Os_3(CO)_{11}(P\text{-}n\text{-}Bu_3)$ and $Os_3(CO)_{10}(P\text{-}n\text{-}Bu_3)_2$ with P-*n*-Bu_3.

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