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Relative Reactivities of the Small Closo Carboranes 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ and of *closo*-1,10-$C_2B_8H_{10}$ toward "Electrophilic" Reagents

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The relative reactivities of the closo carboranes $C_2B_nH_{n+2}$ (n = 4, 5, 8), and some of their derivatives, toward electrophilic reagents of the type $RX/AlCl_3$ (RX = CH_3Cl, C_2H_5Cl, Cl_2, Br_2) are reported from competition studies. Among the three parent carborane compounds, *closo*-2,4-$C_2B_5H_7$ is the most reactive toward an electrophilic type of substitution. Alkyl substituents on *closo*-2,4-$C_2B_5H_7$ enhance the reactivity of the compound toward an electrophilic substitution, whereas halogen substituents decrease the reactivity. However, in the *closo*-1,6-$C_2B_4H_6$ system, the reactivity of the chloro-substituted compound, 2-Cl-1,6-$C_2B_4H_5$, toward an electrophilic substitution is greater, at the 4-position, than that of the parent carborane. The nature (halogen or alkyl) and cage position of a substituent on *closo*-2,4-$C_2B_5H_7$ appear to have little or no influence on the site of "electrophilic" substitution.

Introduction

Substituent effects on the reactivity of benzene, and many of its derivatives, toward "electrophilic" substitution are well-established. And although "Friedel–Crafts type" alkylation[1-3] and halogenation[4-10] of small closo carboranes such as *closo*-2,4-$C_2B_5H_7$ have previously been studied, a study of relative reactivities of various carboranes under presumed "electrophilic" attack has not yet been reported. In the present work, the relative reactivities of a few carboranes, *closo*-1,6-$C_2B_4H_6$, *closo*-2,4-$C_2B_5H_7$, and, in one instance, *closo*-1,10-$C_2B_8H_{10}$, toward $RCl/AlCl_3$ (R = alkyl, halogen) are assessed. The effect of a halogen and/or an alkyl substituent on some related carborane chemistry is also reported.

Experimental Section

Materials and Handling of Chemicals. The parent closo carboranes 2,4-$C_2B_5H_7$, 1,6-$C_2B_4H_6$, and 1,10-$C_2B_8H_{10}$ were obtained from R. E. Williams. *closo*-2,4-$C_2B_5H_7$ and *closo*-1,10-$C_2B_8H_{10}$ were used without further purification. *closo*-1,6-$C_2B_4H_6$ was purified by complexing the impurity 2-CH_3-1,5-$C_2B_3H_4$ (present to the extent of ca. 5%) with tetramethylethylenediamine at ambient temperature over a period of several minutes. 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. Many of the carborane derivatives used in this study were prepared by using known literature procedures: 1-Cl-2,4-$C_2B_5H_6$, 3-Cl-2,4-$C_2B_5H_6$, 5-Cl-2,4-$C_2B_5H_6$;[5,7,10] 1-CH_3-2,4-$C_2B_5H_6$, 3-CH_3-2,4-$C_2B_5H_6$;[2,11] 5-CH_3-2,4-$C_2B_5H_6$;[1,2,11] 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$;[1,11] 5-I-$C_2B_5H_6$;[9] 2-Cl-1,6-$C_2B_4H_5$.[7,8] Aluminum trichloride (Aldrich) was sublimed directly into the reaction vessel prior to use. Chlorine gas (Matheson) was passed through −78, −140, and −190 °C traps to remove H_2O and HCl. Liquid bromine was placed in a storage tube over molecular sieves several weeks before use. Chloromethane (J. T. Baker), chloroethane (Matheson), trimethylchloromethane (J. T. Baker), CCl_4 (MCB), C_6D_6 (Norrell Chemical Co.), C_6H_6 (Eastman Kodak), and ClC_6H_5 (Aldrich) were used without further purification.

Standard high-vacuum techniques were used in the handling of all chemicals. Purification of volatile compounds was accomplished either by cold-column separation[12] or by trap-to-trap fractionation in a high-vacuum apparatus.[13]

Instrumentation. 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 19.255 25 MHz for both HB(3,5,6) and HC(2,4) proton regions and 19.254 85 MHz for the HB(1,7) apex region; the ^{10}B decoupler frequencies were 6.447 85 MHz for the HB(3,5,6) and HC(2,4) regions and 6.447 69 MHz for the HB(1,7) apex region. Application of a modified NMRENIT iterative computer program[14] to some of the more complex proton 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 the California Institute of Technology, Pasadena, CA. 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: $\delta(1,7)$ = −21.73, $\delta(3)$ = +7.02, $\delta(5,6)$ = +3.83.

General Procedures. All reactions were carried out in a 16-cm length 3-mm NMR tube equipped, at the "top" end, with a 1.5-mL glass expansion bulb. A small amount of $AlCl_3$ catalyst was sublimed onto the interior surface of the bulb from a side-arm container (which has a 19/38 ground glass cap) connected to the middle of an 8-cm length of NMR tubing above the expansion bulb. Then, the side-arm container was removed by sealing the connecting tube. Volatile reagents were condensed at −190 °C into the NMR tube. Subsequently, the NMR tube was sealed at a point 2 cm above the bulb. Proton and boron-11 NMR spectra were recorded routinely. The percentages of reactants and products at various reaction times were assessed by standard peak area measurement techniques.

Competitive Methylation (Employing $CH_3Cl/AlCl_3$) of a *closo*-2,4-$C_2B_5H_7$/5-Cl-*closo*-2,4-$C_2B_5H_6$ Mixture. $AlCl_3$ (ca. 0.2 mmol) was sublimed into a 3-mm NMR tube equipped with a 1.5-mL bulb; *closo*-2,4-$C_2B_5H_7$ (53 mol %) and 5-Cl-*closo*-2,4-$C_2B_5H_6$[10] (47 mol %) were then added (ca. 1.0 mmol total of the carborane mixture), followed by the addition of 0.4 mmol of CH_3Cl. The NMR tube was sealed and warmed from −190 °C to room temperature. ^1H NMR indicated that some methylation of 2,4-$C_2B_5H_7$ ensued at room temperature. After the sample was heated at 83 °C for 8 h, it was determined by ^1H NMR that all the CH_3Cl had disappeared. From both ^{11}B and ^1H NMR spectra the following products were identified (yield data, in parentheses, are based on total starting carborane boron content): 2,4-$C_2B_5H_7$[15] (19.5 mol %), 5-Cl-2,4-$C_2B_5H_6$ (42.0%) [^{11}B NMR: −20.04 (d, 2 B, B(1,7), J(BH) = 183.9 Hz), +5.15 (d, 1 B, B(3), J(BH) = 188.7 Hz), +13.81 (s, 1 B, B(5)), +1.05 ppm (d, 1 B, B(6), J(BH) = 176.4 Hz)] [^1H NMR: 0.550 ppm (H(1,7))],[10] 5-CH_3-2,4-$C_2B_5H_6$ (12.0%) [^{11}B NMR: −21.03 (d, 2 B, B(1,7), J(BH) = 177.5 Hz), +6.52 (d, 1 B, B(3), J(BH) = 183.3 Hz), +11.36 (s, 1 B, B(5)), +2.25 ppm (d, 1 B, B(6), J(BH) = 169 Hz)] [^1H NMR: 0.158 (H(1,7)), 0.699 ppm (CH_3)],[1,2,11] 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ (7.5%) [^{11}B NMR: −20.46 (d, 2 B, B(1,7), J(BH) = 175.5 Hz), +5.34 (d, 1 B, B(3), J(BH) = 182.8 Hz)), +9.50 ppm (s, 2 B, B(5,6))] [^1H NMR: 0.221 (H(1,7)), 0.620 ppm (CH_3)],[1,11] 5-Cl-6-CH_3-2,4-$C_2B_5H_5$ (3.0%) [^{11}B NMR: −19.49 (d, 2 B, B(1,7)), +3.82 (d, 1 B, B(3)), +12.22 (s, 1 B, B(5)), +8.64 ppm (s, 1 B, B(6))] [^1H NMR: 0.599 (H(1,7)), 0.652 ppm (CH_3)],[3,16] CH_3BCl_2 (7.4%) [^{11}B NMR: 62.3 ppm],[17]

(1) Ditter, J. F.; Klusmann, E. B.; Williams, R. E.; Onak, T. *Inorg. Chem.* **1976**, *15*, 1063–1065.
(2) Oh, B.; Onak, T. *Inorg. Chem.* **1982**, *21*, 3150–3154.
(3) Siwapinyoyos, G.; Onak, T. *Inorg. Chem.* **1982**, *21*, 156–163.
(4) Olsen, R. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 5072–5075.
(5) Warren, R.; Paquin, D.; Onak, T.; Dunks, G.; Spielman, J. R. *Inorg. Chem.* **1970**, *9*, 2285–2287.
(6) Spielman, J. R.; Warren, R. G.; Bergquist, D. A.; Allen, J. K.; Marynick, D.; Onak, T. *Synth. React. Inorg. Met.-Org. Chem.* **1975**, 347–356.
(7) Takimoto, C.; Siwapinyoyos, G.; Fuller, K.; Fung, A. P.; Liauw, L.; Jarvis, W.; Millhauser, G.; Onak, T. *Inorg. Chem.* **1980**, *19*, 107–110.
(8) Beltram, G.; Fehlner, T. *J. Am. Chem. Soc.* **1979**, *101*, 6237.
(9) Ng, B.; Onak, T.; Banuelos, T.; Gomez, F.; DiStefano, E. W. *Inorg. Chem.* **1985**, *24*, 4091–4096.
(10) Abdou, Z. J.; Soltis, M.; Oh, B.; Siwap, G.; Banuelos, T.; Nam, W.; Onak, T. *Inorg. Chem.* **1985**, *24*, 2363–2367.
(11) Onak, T.; Fung, A. P.,; Siwapinyoyos, G.; Leach, J. B. *Inorg. Chem.* **1979**, *18*, 2878–2882.
(12) Dobson, J.; Schaefer, R. *Inorg. Chem.* **1970**, *9*, 2183–2184.
(13) Jolly, W. L. *Synthetic Inorganic Chemistry*; Prentice-Hall: Englewood, NJ, 1960.
(14) Bowers, M. T.; Chapman, T. I.; Manatt, S. L. *J. Chem. Phys.* **1969**, *50*, 5412–5417.
(15) Eaton, G. R.; Lipscomb, W. N. *NMR Studies of Boron Hydrides and Related Compounds*; W. A. Benjamin: New York, 1969.

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$CH_2(BCl_2)_2$ (4.2%) [^{11}B NMR: 59.1 ppm], BCl_3 (2.4%) [^{11}B NMR: 46.6 ppm].[17]

Competitive Methylation (Employing $CH_3Cl/AlCl_3$) of a 5-Cl-2,4-$C_2B_5H_6$/5-CH_3-2,4-$C_2B_5H_6$ Mixture. Into a 3-mm NMR tube containing freshly sublimed $AlCl_3$ were added 5-Cl-2,4-$C_2B_5H_6$ (1.24 mmol, 69% of total carborane reactants), 5-CH_3-2,4-$C_2B_5H_6$ (0.46 mmol, 27%), and CH_3Cl (0.31 mmol). The NMR tube was sealed and allowed to warm from −190 °C to room temperature. Methylation of 5-CH_3-2,4-$C_2B_5H_6$ ensued at room temperature as determined by monitoring the contents of the NMR tube by ^1H NMR. When the mixture was heated at 81 °C for 9 h, all of the CH_3Cl disappeared and methylated products were formed. The contents of the NMR tube were analyzed by using ^1H and ^{11}B NMR, and the relative amounts of the products as well as unreacted starting materials were determined to be as follows: 5-Cl-2,4-$C_2B_5H_6$[7,10] (69%), 5-CH_3-2,4-$C_2B_5H_6$[1,2,11] (10.5%), 5-CH_3-6-Cl-2,4-$C_2B_5H_5$[3] (3.5%), 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$[1,11] (13.0%), CH_3BCl_2[17] (3%), $CH_2(BCl_2)_2$[17] (1%).

Competitive Methylation (Employing $CH_3Cl/AlCl_3$) of a 5-Cl-2,4-$C_2B_5H_6$/5-I-2,4-$C_2B_5H_6$ Mixture. A prepared mixture (0.4 mmol) of 5-Cl-2,4-$C_2B_5H_6$ (48 mol %) and 5-I-2,4-$C_2B_5H_6$ (52 mol %) was added to a 3-mm NMR tube containing freshly sublimed $AlCl_3$. After CH_3Cl was added (0.3 mmol), the tube was sealed, warmed from −190 °C to room temperature, and subsequently heated at 80 °C for 21.5 h. A ^1H NMR spectrum of the sample indicated that all of the CH_3Cl had disappeared and methylated 5-Cl-2,4-$C_2B_5H_6$ and methylated 5-I-2,4-$C_2B_5H_6$ were formed. Also, some peaks were assigned to cleavage products (CH_3BCl_2, $CH_2(BCl_2)_2$, and BCl_3);[7,17] however, one sharp peak at 2.07 ppm in the ^1H NMR spectra could not be assigned. The mole percentages as determined by ^{11}B and ^1H NMR were as follows: 5-Cl-2,4-$C_2B_5H_6$[7,10] (25%), 5-I-2,4-$C_2B_5H_6$[9] (22%), 5-Cl-6-CH_3-2,4-$C_2B_5H_5$[3] (25%), 5-I-6-CH_3-2,4-$C_2B_5H_5$ (23%) [^1H NMR: 0.714 (CH_3), 0.459 ppm H(1,7)] [^{11}B NMR: −19.9 (calcd −19.6,[3,9] B(1,7)), +5.9 (calcd = +6.1, B(3)), −8 (calcd −8.9, B(5)), +11 ppm (calcd +11.4, B(6))], cleavage products (CH_3BCl_2:$CH_2(BCl_2)_2$:BCl_3[17] = 5:4:1, 4%).

Competitive Methylation (Employing $CH_3Cl/AlCl_3$) among 1-CH_3-2,4-$C_2B_5H_6$, 3-CH_3-2,4-$C_2B_5H_6$, and 5-CH_3-2,4-$C_2B_5H_6$. A mixture (0.15 mmol) of three *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ isomers, 1-CH_3-2,4-$C_2B_5H_6$ (31 mol %), 3-CH_3-2,4-$C_2B_5H_6$ (28 mol %), and 5-CH_3-2,4-$C_2B_5H_6$ (41 mol %), was added to a 3-mm NMR tube (equipped with a 1.5-mL bulb) containing CH_3Cl (0.05 mmol) and freshly sublimed $AlCl_3$. The NMR tube was sealed and allowed to remain at room temperature for 63 days; ^1H NMR indicated that all of the CH_3Cl had disappeared, whereas only 25% of the starting materials had reacted with the chloromethane. Therefore, all condensable materials in the NMR tube were transferred into a new NMR tube containing freshly sublimed $AlCl_3$. Subsequently, additional CH_3Cl (0.15 mmol) was added to the new NMR tube. The NMR tube was sealed and allowed to stand at room temperature for 126 days. The amounts of products and unreacted starting materials, expressed as mole percentages, were determined by using ^1H and ^{11}B NMR: 1-CH_3-2,4-$C_2B_5H_6$[2,11] (11%), 3-CH_3-2,4-$C_2B_5H_6$[2,11] (12%), 5-CH_3-2,4-$C_2B_5H_6$[1,2,11] (27%), 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$ (10%) [^{11}B NMR: −11.23 (s, 1 B, B(1)), +7.76 (d, 1 B, B(3)), +11.44 (s, 1 B, B(5)), +2.34 (d, 1 B, B(6)), −26.69 ppm (d, 1 B, B(7))] [^1H NMR: −0.017 (H(1,7)), −0.477 (1-CH_3), 0.684 ppm (5-CH_3)],[11] 1,5,6-$(CH_3)_3$-2,4-$C_2B_5H_4$ (8%) [^{11}B NMR: −11.0 (s, 1 B, B(1)), +6.52 (d, 1 B, B(3)), +9.50 (d, 2 B, B(5,6)), −25.9 ppm (d, 1 B, B(7))] [^1H NMR: 0.056 (H(1,7)), −0.477 (1-CH_3), 0.581 ppm (5,6-CH_3)], 3,5-$(CH_3)_2$-2,4-$C_2B_5H_5$ (15%) [^{11}B NMR: −19.64 (d, 2 B, B(1,7)), +13.68 (s, 1 B, B(3)), +11.44 (s, 1 B, B(5)), +2.34 ppm (d, 1 B, B(6))] [^1H NMR: 0.221 (H(1,7)), 0.943 (3-CH_3), 0.654 ppm (5-CH_3)],[11] 3,5,6-$(CH_3)_3$-2,4-$C_2B_5H_4$ (5%) [^{11}B NMR: −18.8 (d, 2 B, B(1,7)), +12.6 (s, 1 B, B(3)), +9.50 ppm (s, 2 B, B(5,6))] [^1H NMR: 0.301 (H(1,7)), 0.919 (3-CH_3), 0.581 ppm (5,6-$(CH_3)_2$)], 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$[1,11] (12%).

Competitive Ethylation (Using $C_2H_5Cl/AlCl_3$) of 2,4-$C_2B_5H_7$ and 5-CH_3-2,4-$C_2B_5H_6$. Both *closo*-2,4-$C_2B_5H_7$ (0.15 mmol, 60% of total carborane reactants) and 5-CH_3-*closo*-2,4-$C_2B_5H_6$ (0.10 mmol, 40%) were added into a 3-mm NMR tube containing freshly sublimed $AlCl_3$. Subsequently, chloroethane (0.15 mmol) was added and the tube sealed and warmed from −190 °C to room temperature. By monitoring of the ^1H NMR of the mixture, it was noted that all of the C_2H_5Cl disappeared within 6 days at room temperature. The relative amounts, expressed as mole percentages, of the products as well as unreacted starting materials were determined from the ^1H and ^{11}B NMR spectra of the sample: 2,4-$C_2B_5H_7$[15] (35.6 mol %), 5-CH_3-2,4-$C_2B_5H_6$[1,2,11] (26.9%), 5-C_2H_5-2,4-$C_2B_5H_6$ (19.1%) [^{11}B NMR: −21.29 (d, 2 B, B(1,7), J(BH) = 177.5 Hz), +6.40 (d, 1 B, B(3), J(BH) = 183.5 Hz), +13.45 (s, 1 B, B(5)), +1.93 ppm (d, 1 B, B(6), J(BH) = 168.7 Hz)] [^1H NMR: 0.171 ppm (H(1,7))],[18] 5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ (4.2%) [^{11}B NMR: −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 ppm (s, 2 B, B(5,6))] [^1H NMR: 0.264 ppm (H(1,7))],[18] 5-CH_3-6-C_2H_5-2,4-$C_2B_5H_5$ (12.3%) [^{11}B NMR: −20.64 (d, 2 B, B(1,7)), +5.28 (d, 1 B, B(3)), +9.33 (s, 1 B, B(5)), +11.16 ppm (s, 1 B, B(6))] [^1H NMR: 0.249 (H(1,7)), 0.631 ppm (CH_3)], cage-cleavage products (CH_3BCl_2 and $C_2H_5BCl_2$, 2%) [^{11}B NMR: 63.5 ppm].[17]

Competitive Ethylation (Employing $C_2H_5Cl/AlCl_3$) of a 1-CH_3-2,4-$C_2B_5H_6$/5-CH_3-2,4-$C_2B_5H_6$ Mixture. A mixture (0.3 mmol) of 1-CH_3-2,4-$C_2B_5H_6$ (34.4 mol %) and 5-CH_3-2,4-$C_2B_5H_6$ (65.6 mol %) was added to a 3-mm NMR tube into which $AlCl_3$ had been previously sublimed. Chloroethane (0.17 mmol) was subsequently added to the same NMR tube. The NMR tube was sealed off and warmed from −190 °C to room temperature. By use of ^1H NMR to monitor the contents of the tube, it was detected that all of the C_2H_5Cl disappeared within 10 days. The contents of the NMR tube were analyzed by ^1H and ^{11}B NMR, and the relative amounts, expressed as mole percentages, of the products as well as unreacted starting materials were determined: 1-CH_3-2,4-$C_2B_5H_6$ (13.3%) [^{11}B NMR: −11.86 (s, 1 B, B(1)), +8.13 (d, 1 B, B(3), J(BH) = 182.1 Hz), +4.09 (d, 2 B, B(5,6), J(BH) = 167.5 Hz), −27.63 ppm (d, 1 B, B(7), J(BH) = 179.9 Hz)],[2,11] 5-CH_3-2,4-$C_2B_5H_6$[1,2,11] (44.9%), 1-CH_3-5-C_2H_5-2,4-$C_2B_5H_5$ (13.5%) [^{11}B NMR: −11.44 (s, 1 B, B(1)), +7.63 (d, 1 B, B(3)), +13.36 (s, 1 B, B(5)), +2.25 (d, 1 B, B(6)) −26.90 ppm (d, 1 B, B(7))] [^1H NMR: −0.025 (H(1,7)), −0.465 ppm (CH_3)], 1-CH_3-5,6-$(C_2H_5)_2$-$C_2B_5H_4$ (6.6%) [^{11}B NMR: −11.13 (s, 1 B, B(1)), +8.15 (d, 1 B, B(3)), 10.92 (s, 2 B, B(5,6)), −26.30 ppm (d, 1 B, B(7))] [^1H NMR: 0.070 (H(1,7)), −0.437 ppm (CH_3)], 5-CH_3-6-C_2H_5-2,4-$C_2B_5H_5$ (18.5%), CH_3BCl_2 (1.4%), $C_2H_5BCl_2$ (0.8%), $CH_2(BCl_2)_2$ (0.9%).[17]

Competitive Chlorination (Using $Cl_2/AlCl_3$) among 1-CH_3-2,4-$C_2B_5H_6$, 3-CH_3-2,4-$C_2B_5H_6$, and 5-CH_3-2,4-$C_2B_5H_6$. Aluminum chloride (ca. 0.2 mmol) was sublimed into the interior surface of a 3-mm NMR tube equipped with a 1.5-mL bulb. A mixture (0.15 mmol) of the three different methyl-substituted isomers 1-CH_3-$C_2B_5H_6$ (30 mol %), 3-CH_3-$C_2B_5H_6$ (32 mol %), and 5-CH_3-2,4-$C_2B_5H_6$ (29 mol %) was subsequently added to the same NMR tube, followed by the addition of Cl_2 gas (0.05 mmol). Upon warming of the mixture from −190 °C to room temperature, the color of Cl_2 disappeared within 30 min. By monitoring of the ^1H and ^{11}B NMR of the mixture, it was noted that only 20% of the starting materials had reacted with the chlorine in 8 days; therefore, the NMR tube was opened to the vacuum line and all condensable materials in the NMR tube were transferred and condensed into a new NMR tube containing freshly sublimed $AlCl_3$, followed by the addition of more Cl_2 (0.15 mmol). After the sample was allowed to stand at room temperature for 10 days, ^{11}B and ^1H NMR spectra indicated the following materials were present: 1-CH_3-2,4-$C_2B_5H_6$[2,11] (12%), 3-CH_3-2,4-$C_2B_5H_6$ (16%) [^{11}B NMR: −20.38 (d, 2 B, B(1,7), J(BH) = 177 Hz), +14.08 (s, 1 B, B(3)), +3.46 ppm (d, 2 B, B(5,6), J(BH) = 167 Hz)] [^1H NMR: 0.118 (H(1,7)), 0.997 ppm (CH_3)],[2,11] 5-CH_3-2,4-$C_2B_5H_6$[1,2,11] (15%), 1-CH_3-5-Cl-2,4-$C_2B_5H_5$ (10%) [^{11}B NMR: −10.03 (s, 1 B, B(1)), +6.37 (d, 1 B, B(3)), +13.97 (s, 1 B, B(5)), ca. +1.5 (d, 1 B, B(6)), −25.6 ppm (d, 1 B, B(7))] [^1H NMR: 0.358 (H(1,7)), −0.293 ppm (CH_3)],[16] 1-CH_3-5,6-Cl_2-2,4-$C_2B_5H_4$ (8%) [^{11}B NMR: −8.76 (s, 1 B, B(1), calcd[16] −8.51), −24.02 ppm (d, 1 B, B(7), calcd 24.28)] [^1H NMR: −0.122 ppm (CH_3)], 3-CH_3-5-Cl-2,4-$C_2B_5H_5$ (9%) [^{11}B NMR: −18.68 (d, 2 B, B(1,7)), +12.64 (s, 1 B, B(3)), +13.25 (s, 1 B, B(5)), +0.44 ppm (d, 1 B, B(6))] [^1H NMR: 0.603 (H(1,7)), 0.950 ppm (CH_3)],[16] 3-CH_3-5,6-Cl_2-2,4-$C_2B_5H_4$ (8%) [^{11}B NMR: −17.39 ppm (d, 2 B, B(1,7), calcd[16] 17.06] [^1H NMR: 0.950 ppm (CH_3)], 5-CH_3-6-Cl-2,4-$C_2B_5H_5$[3,16] (14%), CH_3BCl_2[17] (3%), $CH_2(BCl_2)_2$[17] (6%).

Competitive Chlorination (Using $Cl_2/AlCl_3$) of a 1-Cl-2,4-$C_2B_5H_6$/3-Cl-2,4-$C_2B_5H_6$ Mixture. After a catalytic amount (approximately 0.2 mmol) of $AlCl_3$ was sublimed into a 3-mm NMR tube equipped with a 1.5-mL bulb, a mixture (0.40 mmol) of 1-Cl-$C_2B_5H_6$ (0.20 mmol) and 3-Cl-$C_2B_5H_6$ (0.20 mmol) was added to the same NMR tube, followed by the addition of Cl_2 (0.25 mmol). The NMR tube was sealed and allowed to warm from −190 °C to room temperature. The chlorine color disappeared within 1 h. After 1 day at room temperature, the ^1H NMR indicated the appearance of the H(1,7)B peaks for 1,5-Cl_2-$C_2B_5H_5$ (0.450 ppm) and 3,5-Cl_2-$C_2B_5H_5$ (0.979 ppm).[7,10] After 8 days at room temperature a ^{11}B NMR spectrum of the mixture indicated the following products, as well as reactants, present: 1-Cl-2,4-$C_2B_5H_6$ (20%) [^{11}B NMR: −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 ppm (d, 1 B, B(7), J(BH) = 186.4 Hz)] [^1H NMR: −0.064 ppm (H(1,7))],[7,10] 3-Cl-2,4-

(16) Abdou, Z. J.; Abdou, G.; Onak, T.; Lee, S. *Inorg. Chem.* **1986**, *25*, 2678–2683.
(17) Noth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: Berlin, 1978.
(18) Nam, W.; Onak, T., unpublished studies.

$C_2B_5H_6$ (17%) [^{11}B NMR: −18.35 (d, 2 B, B(1,7), J(BH) = 182.5 Hz), +14.97 (s, 1 B, B(3)), +3.25 ppm (d, 2 B, B(5,6), J(BH) = 172.3 Hz)] [^{1}H NMR: 0.548 ppm (H(1,7))],[10] 1,5-Cl_2-2,4-$C_2B_5H_5$ (32%) [^{11}B NMR: −14.69 (s, 1 B, B(1)), +6.46 (d, 1 B, B(3), J(BH) = 191.6 Hz), +12.89 (s, 1 B, B(5)), +0.64 (d, 1 B, B(6)), −31.22 ppm (d, 1 B, B(7), J(BH) = 186.4 Hz)] [^{1}H NMR: 0.450 ppm (H(1,7))],[10] 3,5-Cl_2-2,4-$C_2B_5H_5$ (31%) [^{11}B NMR: −17.05 (d, 2 B, B(1,7)), +12.58 (s, 1 B, B(3)), +12.31 (s, 1 B, B(5)), −0.07 ppm (d, 1 B, B(6))] [^{1}H NMR: 0.979 ppm (H(1,7))],[10] cleavage products (BCl_3:$CH_2(BCl_2)_2$:CH_3BCl_2[17] = 3:2:1, 0.5%).

Competitive Chlorination (Using Cl_2/$AlCl_3$) of a *closo*-2,4-$C_2B_5H_7$/*closo*-1,6-$C_2B_4H_6$ Mixture. A mixture (0.3 mmol) composed of 2,4-$C_2B_5H_7$ (57.5 mol %) and 1,6-$C_2B_4H_6$ (42.5 mol %) was added to a 3-mm NMR tube containing freshly sublimed $AlCl_3$. Subsequently, Cl_2 (0.3 mmol) was added; the NMR tube was sealed off and warmed from −190 °C to room temperature. The color of Cl_2 disappeared within 1 h. ^{11}B NMR and ^{1}H spectra of the sample, taken after 7 days at room temperature, indicated the following materials were present (given as relative amounts, expressed in mole percentages): 2,4-$C_2B_5H_7$ (37.5%), 5-Cl-2,4-$C_2B_5H_6$ (19.6%),[7,10] 5,6-Cl_2-2,4-$C_2B_5H_5$ (0.7%) [^{11}B NMR: −18.71 (d, 2 B, B(1,7)), +1.83 (d, 1 B, B(3)), +10.16 ppm (s, 2 B, B(5,6))] [^{1}H NMR: 0.972 ppm (H(1,7))],[7,10] 1,6-$C_2B_4H_6$ (30.8%) [^{11}B NMR: −17.60 ppm (d, B(2−5), J(BH) = 198.9 Hz)] [^{1}H NMR: 2.98 (H(1,6)), 1.91 ppm (H(3−5))],[15] 2-Cl-1,6-$C_2B_4H_5$ (1.5%) [^{11}B NMR: −8.92 (s, 1 B, B(2)), −16.63 (d, 2 B, B(3,5), J(BH) = 194 Hz)), −28.64 ppm (d, 1 B, B(4), J(BH) = 197.9 Hz)] [^{1}H NMR: 3.27 (H(1,6)), 2.10 (H(3,5)), 1.79 ppm (H(4))],[7] 2,4-Cl_2-1,6-$C_2B_4H_4$ (1.3%) [^{11}B NMR: −16.33 (s, 2 B, B(2,4)), −15.70 ppm (d, 2 B, B(3,5))] [^{1}H NMR: 3.61 (H(1,6)), 2.28 ppm (H(3,5))],[7] CH_3BCl_2 (3.6%), $CH_2(BCl_2)_2$ (3.9%), BCl_3 (1.1%).[17] A consideration of the quantities of each of the carboranes leads to the conclusion that most of the cage-cleavage products formed in the reaction came from the 1,6-$C_2B_4H_6$ type species.

Competitive Ethylation (Employing C_2H_5Cl/$AlCl_3$) of a *closo*-2,4-$C_2B_5H_7$/*closo*-1,6-$C_2B_4H_6$ Mixture. A prepared mixture (0.6 mmol) composed of 2,4-$C_2B_5H_7$ (49 mol %) and 1,6-$C_2B_4H_6$ (51 mol %) was added into a 3-mm NMR tube into which $AlCl_3$ had been previously sublimed; this step was followed by the addition of C_2H_5Cl (0.3 mmol). The NMR tube was sealed off and allowed to warm from −190 °C to room temperature; after 8 days ^{1}H and ^{11}B NMR spectra indicated the following materials were present: 2,4-$C_2B_5H_7$ (22%), 1,6-$C_2B_4H_6$ (47%), 5-C_2H_5-2,4-$C_2B_5H_6$ (20%),[18] 5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ (7%),[18] $C_2H_5BCl_2$ (2%), CH_3BCl_2 (1%), $CH_2(BCl_2)_2$[17] (1%). No ethylated 1,6-$C_2B_4H_6$ compounds were observed, and a consideration of the carborane product quantities leads to the conclusion that most of the cage-cleavage products formed in the reaction came from the 1,6-$C_2B_4H_6$ type species.

Competitive Bromination (Utilizing Br_2/$AlCl_3$) of a *closo*-1,6-$C_2B_4H_6$/*closo*-2-Cl-1,6-$C_2B_4H_5$ Mixture. Into a 3-mm NMR tube containing freshly sublimed $AlCl_3$ was added a prepared mixture (0.4 mmol) of 1,6-$C_2B_4H_6$ (50 mol %) and 2-Cl-1,6-$C_2B_4H_5$ (50 mol %). Subsequently, Br_2 (0.2 mmol) was added and the tube was sealed and warmed from −190 °C to room temperature. The color of Br_2 disappeared within 30 min. When the contents of the tube after 1 day at room temperature were monitored by ^{11}B NMR, the relative amounts, expressed as mole percentages, of the unreacted starting materials and products were determined to be as follows: 1,6-$C_2B_4H_6$ (36%), 2-Cl-1,6-$C_2B_4H_5$[7] (16%) [^{1}H NMR: 3.27 (H(1,6)), 2.30 ppm (H(3,5), J(1,3/1,4/1,5/3,6/4,6/5,6) = 0.59 Hz, J(3,4/4,5) = 3.23 Hz], 2-Br-1,6-$C_2B_4H_5$ (8%) [^{11}B NMR: −15.73 (s, 1 B, B(2)), −16.30 (d, 2 B, B(3,5), J(BH) = 205.4 Hz), −24.93 ppm (d, 1 B, B(4), J(BH) = 197.6 Hz)][8] [^{1}H NMR: 3.29 (H(1,6)), 2.09 ppm (H(3-5))], 2,4-Br_2-1,6-$C_2B_4H_4$ (4%) [^{11}B NMR: −20.36 (s, 2 B, B(2,4)), −14.98 ppm (d, 2 B, B(3,5), J(BH) = 199.7 Hz)][8] [^{1}H NMR: 3.29 (H(1,6)), 2.29 ppm (H(3,5))], 2-Cl-4-Br-1,6-$C_2B_4H_4$ (28%) [^{11}B NMR: −13.81 (s, 1 B, B(2)), −15.54 (d, 2 B, B(3,5)), −23.22 ppm (s, 1 B, B(4))] [^{1}H NMR: 3.63 (H(1,6)), 2.30 ppm (H-(3,5))], cleavage products (CH_3BCl_2, $CH_2(BCl_2)_2$, and/or $CH_2(BBr_2)_2$),[17] 8%).

Competitive Chlorination (Employing Cl_2/$AlCl_3$) of a *closo*-2,4-$C_2B_5H_7$/*closo*-1,10-$C_2B_8H_{10}$ Mixture. $AlCl_3$ (0.1 mmol) was sublimed into a 3-mm NMR tube equipped with a 1.5-mL bulb. A mixture (0.8 mmol) of 2,4-$C_2B_5H_7$ (43 mol %) and 1,10-$C_2B_8H_{10}$ (57 mol %) was added to the same tube, followed by the addition of Cl_2 (0.35 mmol). The NMR tube was sealed and warmed from −190 °C to room temperature for 3 h. Subsequently a ^{1}H NMR spectrum indicated that the H(1,7)B peak of 5-Cl-2,4-$C_2B_5H_6$ (0.550 ppm),[7] as well as several other new peaks, was present. After the mixture was allowed to stand at room temperature for 6 days, ^{11}B NMR spectra showed the following product distribution: 5-Cl-2,4-$C_2B_5H_6$ (10%), 2-Cl-1,10-$C_2B_8H_9$ (10%). A "new" NMR tube containing freshly sublimed $AlCl_3$ was prepared, and all volatile materials in the "old" NMR tube were transferred to the "new" tube, followed by the addition of Cl_2 gas (0.4 mmol) and CCl_4 (as solvent). When the mixture was warmed from −190 °C to room temperature, the color of the mixture immediately turned to reddish yellow and returned to colorless in 5 min. After 5 days at room temperature, peaks assigned to $CHCl_3$ and CH_2Cl_2 now appeared in the ^{1}H NMR spectrum. From ^{11}B NMR, the relative amounts of carborane produts and unreacted starting materials were determined to be as follows: 2,4-$C_2B_5H_7$ (3%), 1,10-$C_2B_8H_{10}$ (25%) [^{11}B NMR: −12.79 ppm (d, B(2−9), J(BH) = 165.6 Hz)],[15] 5-Cl-2,4-$C_2B_5H_6$[7,10] (36%), 2-Cl-1,10-$C_2B_8H_9$ (32%) [^{11}B NMR: −1.87 (s, 1 B, B(2)), −9.69 (d, 4 B), −12.79 (d, 2 B), −17.72 ppm (d, 1 B, B(4), J(BH) = 161.8 Hz)],[19] cleavage products (CH_3BCl_2, $CH_2(BCl_2)_2$, and BCl_3,[17] 4%).

Competitive Chlorination (Employing Cl_2/$AlCl_3$) of *closo*-2,4-$C_2B_5H_7$ and Benzene. A mixture (0.3 mmol) of *closo*-2,4-$C_2B_5H_7$ and benzene was added to a 3-mm NMR tube containing freshly sublimed $AlCl_3$, followed by the addition of Cl_2 (0.15 mmol). The NMR tube was sealed off and warmed from −190 °C to room temperature. The yellow color of Cl_2 disappeared within 0.5 h. A ^{1}H NMR spectrum taken after 17 h at room temperature indicated that no chlorinated carborane compounds had formed but that some new peaks appeared near the benzene resonance. These peaks were assigned to chlorobenzene (ca. 25% yield).[20] A second ^{1}H NMR spectrum taken after a total of 8 days showed no change. After a total of 19 days at room temperature, a ^{11}B NMR spectrum showed that some carborane cage-cleavage products had formed but no chlorinated $C_2B_5H_7$ was present.

Competitive Methylation (Utilizing CH_3Cl/$AlCl_3$) of *closo*-2,4-$C_2B_5H_7$ and Benzene. Aluminum chloride (approximately 0.2 mmol) was sublimed into a 3-mm NMR tube equipped with a 1.5-mL bulb; *closo*-2,4-$C_2B_5H_7$ (0.3 mmol), benzene (0.2 mmol), and CH_3Cl (0.2 mmol) were subsequently added to the same NMR tube. The tube was sealed and warmed from −190 °C to room temperature for 5 h. A ^{1}H NMR spectrum showed that methylation of C_6H_6 ensued. All of the CH_3Cl disappeared after 150 days at room temperature, and methyl ^{1}H NMR peaks of toluene (ca. 13%), and a xylene isomer mixture (ca. 9%),[20] appeared in the region of 2.1−2.3 ppm; no methylated $C_2B_5H_7$[1,11] was observed in the ^{1}H NMR spectrum. Two unidentified broad peaks appeared at 0.8 ppm in the ^{1}H NMR spectrum, and there was evidence in the ^{11}B NMR of a small amount of cage-cleavage products of the type CH_3BCl_2 and $CH_2(BCl_2)_2$.

Competitive Methylation (Employing CH_3Cl/$AlCl_3$) of a *closo*-2,4-$C_2B_5H_7$/Chlorobenzene Mixture. *closo*-2,4-$C_2B_5H_7$ (0.45 mmol), C_6H_5Cl (0.35 mmol), and CH_3Cl (0.35 mmol) were added to a 3-mm NMR tube containing freshly sublimed $AlCl_3$. The NMR tube was sealed and warmed from −190 °C to room temperature. After 2 days a ^{1}H NMR spectrum indicated that methylation of C_6H_5Cl occurred faster than that of $C_2B_5H_7$ by a factor of ca. 2. A second ^{1}H NMR spectrum, which was taken after 6 days, showed that all of the CH_3Cl had disappeared. Also, it was observed that the contents in the NMR tube formed two layers; the upper layer was a mobile liquid and the lower was a viscous layer. The ^{1}H NMR spectra of the two layers showed different peak patterns at 0.8 and 2.2 ppm; the upper layer had a large broad peak at 0.8 ppm and three sharp peaks centered at 2.2 ppm, whereas the lower layer had a small broad peak at 0.8 ppm and one broad peak and two small sharp peaks centered at 2.2 ppm. The ^{11}B NMR spectrum did not show any difference between the two layers. The relative amounts of 2,4-$C_2B_5H_7$, 5-CH_3-2,4-$C_2B_5H_6$,[1,2,11] and cleavage products, as determined by ^{11}B NMR, were the same for both upper and lower layers: $C_2B_5H_7$ (88%), 5-CH_3-$C_2B_5H_6$ (5%), and cleavage products (BCl_3:$CH_2(BCl_2)_2$:CH_3BCl_2[17] = 1:1:2, 7%).

Methylation of 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ with CH_3Cl/$AlCl_3$. Aluminum chloride (approximately 0.2 mmol) was sublimed into a 3-mm NMR tube equipped with a 1.5-mL bulb. After 5,6-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$ (1.0 mmol) and CH_3Cl (1.3 mmol) were added, the tube was sealed off and warmed from −190 °C to room temperature. The ^{1}H NMR of the sample was monitored at 2, 10, 19, 54, 65, 88, and 147 days, at room temperature; the ^{11}B NMR was monitored at 4, 32, 61, and 116 days, at room temperature. It was noted that a small amount of oily liquid formed at the bottom of the sample tube by the end of 147 days at room temperature. The sample was subsequently heated at 58 °C for 118 h. The amount of the oily liquid increased to 10% of the sample. The ^{1}H NMR spectra of the upper and lower layers exhibited different peak patterns. The peaks of the lower layer were sharper than those of the upper layer. All ^{1}H and ^{11}B NMR chemical shifts of the reactants and products were determined, and the relative amounts of the products, expressed as mole percentages, were determined by ^{11}B and ^{1}H NMR[1,2,11] analyses. A very small unidentified peak appeared at −3.2 ppm. Some monoboron cleavage products appeared in the downfield region of 55−80

(19) Fuller, K.; Onak, T., unpublished studies.
(20) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic: New York, 1969.

Table I. Percent Composition of the Various Products Obtained from the Methylation of 5,6-$(CH_3)_2$-$C_2B_5H_5$

compds	mol % of starting reactant and products: 4 days, room temp	116 days, room temp	147 days, room temp; 118 h, 58 °C
5,6-$(CH_3)_2$-$C_2B_5H_5$	85	45	18
1,5,6-$(CH_3)_3$-$C_2B_5H_4$	9	20	16
3,5,6-$(CH_3)_3$-$C_2B_5H_4$	0	2	2
1,3,5,6-$(CH_3)_4$-$C_2B_5H_3$	0	2	4
1,5,6,7-$(CH_3)_4$-$C_2B_5H_3$	0	10	11
1,3,5,6,7-$(CH_3)_5$-$C_2B_5H_2$	0	6	24
cleavage products (CH_3BCl_2, BCl_3, $CH_2(BCl_2)_2$)	6	15	25

ppm. Summary analyses of the reaction progress at various monitoring stages are given in Table I.

Results and Discussion

The relative reactivities of the three closo carborane compounds 2,4-$C_2B_5H_7$, 1,6-$C_2B_4H_6$, and 1,10-$C_2B_8H_{10}$ toward $Cl_2/AlCl_3$ at ambient temperature (to give *B*-chlorocarborane derivatives) are found to be 2,4-$C_2B_5H_7$ > 1,10-$C_2B_8H_{10}$ and 2,4-$C_2B_5H_7$ > 1,6-$C_2B_4H_6$. In the case of 2,4-$C_2B_5H_7$, only the 5- and/or 6-positions are initially susceptible to substitution under the conditions of the reaction, whereas all four equivalent borons in 1,6-$C_2B_4H_6$ and all eight borons in 1,10-$C_2B_8H_{10}$ can provide a site for chlorination. With this in mind during a statistical treatment of the experimental data, it is possible to derive a rough quantitative reactivity scale (at a reactive boron site) for these three carboranes toward $Cl_2/AlCl_3$ under ambient conditions: 1:0.3:0.3 for 2,4-$C_2B_5H_7$, 1,6-$C_2B_4H_6$, and 1,10-$C_2B_8H_{10}$, respectively. Competing with the chlorination reaction is cage carborane cleavage, presumably caused by reaction of the carborane with the side product, HCl, in the presence of $AlCl_3$,[7] to yield products such as CH_3BCl_2, $Cl_2BCH_2BCl_2$, and BCl_3. The extent of cage cleavage appears less serious with the larger carborane cages, 2,4-$C_2B_5H_7$ and 1,10-$C_2B_8H_{10}$, at ambient conditions, than with 1,6-$C_2B_4H_6$. The reactivity scale mentioned above for the carborane chlorination is derived with the assumption that the cage-cleavage products from the 1,6-$C_2B_4H_6$/2,4-$C_2B_5H_7$ competition reaction come entirely from chlorinated 1,6-$C_2B_4H_6$ species and is subject to minor revision should the cage-cleavage products have come from the parent 1,6-$C_2B_4H_6$ instead. An earlier study, however, supports the assumption that the chlorinated carborane(s) is less stable toward $HCl/AlCl_3$ cleavage than the parent system(s).[7]

The $Cl_2/AlCl_3$ reagent combination is traditionally associated with electrophilic attack at a substrate site. Thus, it is not surprising to find that the above reactivity order 2,4-$C_2B_5H_7$ > 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ > 1,10-$C_2B_8H_{10}$ is in qualitative agreement with MO calculated framework charges.[21] The greater reactivity of 2,4-$C_2B_5H_7$ over that of 1,6-$C_2B_4H_6$ toward electrophilic reagents is also manifested in a competition study that utilizes the reagent combination $C_2H_5Cl/AlCl_3$; none of the 1,6-$C_2B_4H_6$ is ethylated at ambient temperature during an initial time period in which both 5-C_2H_5-2,4-$C_2B_5H_6$ and 5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ are formed in ample quantities.

The reactivity of 2,4-$C_2B_5H_7$ toward $Cl_2/AlCl_3$, and toward $CH_3Cl/AlCl_3$, is found to be considerably less than that of C_6H_6 toward the same reagents; with the latter reagent combination, $CH_3Cl/AlCl_3$, the reactivity of 2,4-$C_2B_5H_7$ is also found to be a factor of about half that for C_6H_5Cl. The relative unavailability, and/or inaccessability, of an electron-rich π cloud in the carborane (in contrast to the situation in benzene ring systems) may account, in part, for this. Also, the high coordination number of the cage atoms in the carborane (5 or 6), as compared to that of each skeletal atom of benzene (3), may well make it more difficult for the carborane to undergo electrophilic attack in a fashion analogous to that of the well-established aromatic electrophilic reaction mechanism (i.e., involving a phenonium ion in which the coordination of the ring carbon is increased by one). It is also to be noticed that carborane substitution of the type in the present study always takes place at a boron site rather than at a cage-carbon site, but the borons are believed to be the sites of greater negative (less positive) charge.[21]

Halogenation of the *B*-halo derivative of 1,6-$C_2B_4H_6$, 2-X-1,6-$C_2B_4H_5$ (X = Cl, Br, I), takes place at the antipodal 4-position.[7,8] In the present study, the relative reactivity of 2-Cl-1,6-$C_2B_4H_5$ is found to be ca. 10 times greater than that of the parent 1,6-$C_2B_4H_6$ toward bromination with $Br_2/AlCl_3$. This is in contrast to the results found in the 2,4-$C_2B_5H_7$ system (vide infra) in which a deactivating effect of chlorine is observed. Chlorine on a boron atom of 1,6-$C_2B_4H_6$ obviously enhances the reactivity of this octahedral carborane toward (presumed) electrophilic attack; and the chlorine of 2-Cl-1,6-$C_2B_4H_5$ may well serve as an electron-donating group through "back bonding" (or "π donation"). It can be suggested that the electron density of

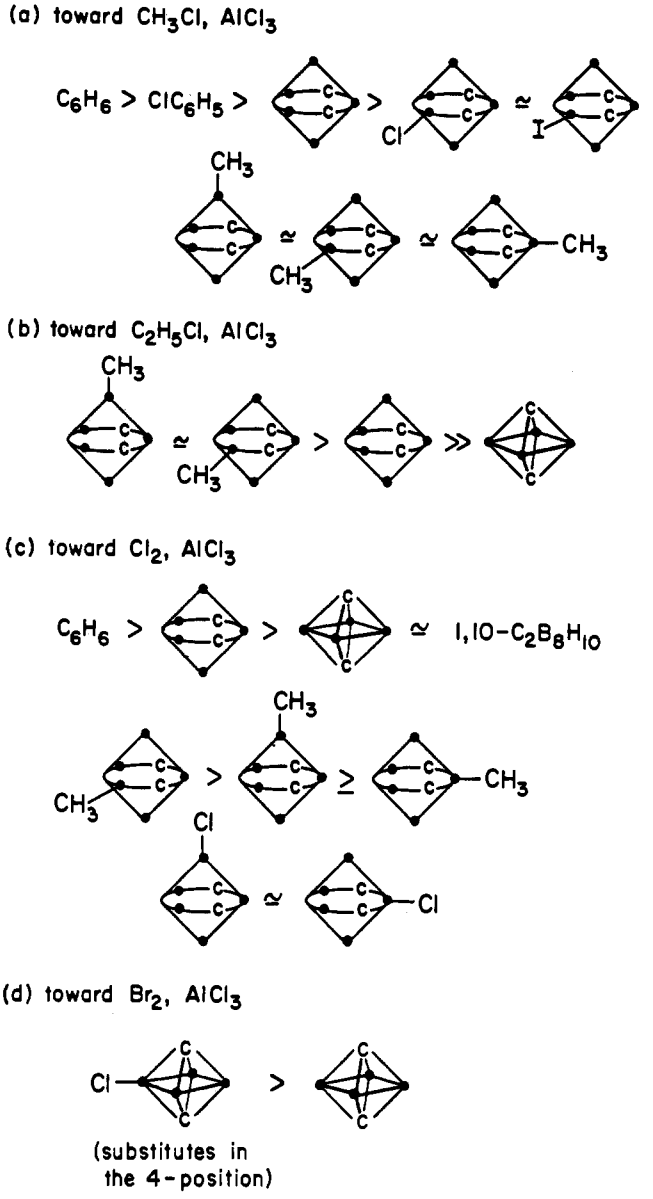

Figure 1. Summary of compound (relative) reactivities toward "electrophilic" reagents. Note that *closo*-C_2B_5 species prefer substitution at the "5" or "6" BH cage position.

(21) Dixon, D. A.; Kleier, D. A.; Halgren, T. A.; Hall, J. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226–6237. A value for the group charge of B(3)H of 2,4-$C_2B_5H_7$ in this reference has been corrected to read +0.06: Koetzle, T. F.; Lipscomb, W. N. *Inorg. Chem.* **1970**, *9*, 2743.

2-Cl-1,6-$C_2B_4H_5$ at the "para" (antipodal) position, B(4), may well be enhanced by the chloro substituent at the 2-position; in this regard, it should be noted that a substantial upfield antipodal ^{11}B NMR shift is noted for B(4) of 2-Cl-1,6-$C_2B_4H_5$.[7,8]

The relative reactivities of the substituted carborane system 5-X-2,4-$C_2B_5H_6$ (X = CH_3, Cl, I) toward $CH_3Cl/AlCl_3$, to give 5-X-6-CH_3-2,4-$C_2B_5H_5$, are X = CH_3 > Cl ≅ I. The last two (X = Cl, I) show about one-fifth the reactivity of the compound in which X = CH_3. In order to obtain some idea of the relative reactivity of 5-CH_3-2,4-$C_2B_5H_6$ (as compared to that of the parent 2,4-$C_2B_5H_7$) toward $RCl/AlCl_3$, it was obviously desirable to use an alkyl group other than methyl for R. The results obtained by using $C_2H_5Cl/AlCl_3$ show that the 6-position of 5-CH_3-2,4-$C_2B_5H_6$ is about 50% more reactive than the 5- and 6-positions of the parent carborane toward this reagent combination. This is compatible with the observation that attempts to monomethylate the parent 2,4-$C_2B_5H_7$ by using $CH_3Cl/AlCl_3$ are complicated by the simultaneous formation of a considerable quantity of 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$.[11] The relative reactivities of 5-CH_3-, 5-Cl-, and 5-I-2,4-$C_2B_5H_6$, as compared to that of the parent compound, toward $RCl/AlCl_3$ are ca. 1.5, 0.3, and 0.3, respectively. From a qualitative standpoint the reactivities of 2,4-$C_2B_5H_7$ and its derivatives toward electrophiles parallel those of benzene and analogous derivatives in that a methyl substituent is an activating group and chlorine and iodine are deactivating substituents. But, as mentioned above, the reactivities of 5-I-$C_2B_5H_6$ and 5-Cl-$C_2B_5H_6$ toward B(6) methylation are nearly the same; by comparison, it is interesting to note that for the X-C_6H_5 system (X = Cl, I) the reactivity of iodobenzene is about 5 times greater than that of chlorobenzene.[22] The traditional explanation for the reactivity observations in the benzene system, of course, involves the argument that chlorine is a more electron-withdrawing atom than iodine, thus making the π cloud of the benzene ring of chlorobenzene less available than that of iodobenzene for electrophilic attack. A plausible explanation for the more equivalent reactivity of 5-Cl-2,4-$C_2B_5H_6$ and 5-I-2,4-$C_2B_5H_6$ involves the chlorine atom of the chlorocarborane in a "back donation" of "unshared" electrons to the cage. This type of donation has been proposed in many other boron systems and would help to "neutralize" the Cl electron-withdrawing effect. Another explanation involves the size of iodo substituent. When the methyl group attacks the B(6) position adjacent to the iodine of the 5-iodocarborane, slightly greater steric hindrance may be encountered than when 5-Cl-2,4-$C_2B_5H_6$ is methylated at the B(6) position.

The three mono-*B*-methyl isomers, 1-CH_3-, 3-CH_3-, and 5-CH_3-2,4-$C_2B_5H_6$, display nearly equal reactivities toward chlorination ($Cl_2/AlCl_3$); similarly, there appears to be no significant difference in these *B*-methylcarborane reactivities toward alkylation ($RCl/AlCl_3$, R = CH_3, C_2H_5). In all of these reactions it is the 6-position (for 5-CH_3-2,4-$C_2B_5H_6$) and the 5,6-positions (for the 1- and the 3-CH_3-2,4-$C_2B_5H_6$) that are primarily involved in further substitution (note that only these 5(6)-equatorial positions are used, after statistical correction, for the reactivity comparisons). Also, the results of a competition reaction that entails the use of $Cl_2/AlCl_3$ as the reagent on a mixture of 1-Cl-$C_2B_5H_6$ and 3-Cl-$C_2B_5H_6$ indicate that the 5(6)-positions of the chlorocarborane isomers are about equally reactive toward further chlorination. In summary, the reactivity of *B*-methyl or *B*-chloro isomers of 2,4-$C_2B_5H_7$ do not appear to be much affected by the position of the substituent. This is in contrast to the case for the *closo*-1,6-$C_2B_4H_6$ carborane, in which the reactivity of a boron site toward electrophilic attack is greatly enhanced by a chlorine situated in an antipodal position (vide supra).

tert-Butylation of C_6H_6 using $(CH_3)_3CCl/AlCl_3$ is known to be a facile reaction; however, the *tert*-butylation of *closo*-2,4-$C_2B_5H_7$ with the same reagent combination has not been successful. Instead of obtaining *B*-$(CH_3)_3$C-*closo*-2,4-$C_2B_5H_6$, all of the *tert*-butyl chloride is converted to presumed polymer, possibly because the reactivity of 2,4-$C_2B_5H_7$ toward the reactive intermediate carbocation, $[(CH_3)_3C]^+$, is not as great as C_6H_6 toward the same carbocation.

Nuclear Magnetic Resonance. An interesting feature associated with the electrophilic reactivity of 2,4-$C_2B_5H_7$ and its derivatives is that generally greater reactivity appears to be associated with those cage boron sites having smaller $J(^{11}B-H)$ values. The magnitude of $J(^{11}B-H)$ for B(5,6)–H in the parent compound is the smallest among the three chemically different boron–hydrogen bonds; i.e., the $J(^{11}B-H)$ values of B(5)–H (symmetry related to B(6)–H), B(1)–H (symmetry related to B(7)–H), and B(3)–H are 169.5, 179.5, and 184.2 Hz, respectively. And it is the 5-(6)-position that is the most reactive toward Friedel–Crafts type reagents. When the three *B*-Cl-2,4-$C_2B_5H_6$ isomers 1-Cl-2,4-$C_2B_5H_6$, 3-Cl-2,4-$C_2B_5H_6$, and 5-Cl-2,4-$C_2B_5H_6$ are considered, it is noted that the magnitudes of all $J(^{11}B-H)$ values increase by 2–7 Hz compared to the analogous positions of $C_2B_5H_7$;[10] nevertheless, the $J(^{11}B-H)$ value of the B(5)–H and/or B(6)–H bond is the smallest among B(1)–H (and/or B(7)–H), B(3)–H, and B(5)–H (and/or B(6)–H) bonds and it is the 5- and/or 6-position that is most prone to initial electrophilic substitution. However, the rates of *B*-Cl-2,4-$C_2B_5H_6$ electrophilic substitution, for all three *B*-Cl isomers, are slower than that of the comparison parent compound. Within the three B-methylated 2,4-$C_2B_5H_7$ compounds 1-CH_3-, 3-CH_3-, and 5-CH_3-2,4-$C_2B_5H_6$, the magnitudes of $J(^{11}B-H)$ values for the various chemically different boron–hydrogen bonds decrease by 0.5–2 Hz (compared to the analogous positions in the parent compound), but the magnitude of the $J(^{11}B-H)$ value is again smallest for B(5 and/or 6)–H among the chemically different boron–hydrogen bonds; again, it is the 5- and/or 6-position that is subject to initial electrophilic substitution. In this case, the rates of *B*-CH_3-2,4-$C_2B_5H_6$ electrophilic substitution, for all three *B*-CH_3- isomers, are faster than for the comparison parent compound. To sum up, Friedel–Crafts type methylation or chlorination of the *B*-methyl or *B*-chloro derivatives of 2,4-$C_2B_5H_7$ always takes place initially at the boron position of the (substituted) carborane substrate that has the smallest $J(^{11}B-H)$ value (i.e., B(5) and/or B(6) position). Furthermore, the reactivities of 5-X-2,4-$C_2B_5H_6$ (as noted earlier) are X = CH_3 > H > Cl ≅ I, which are inversely related to the magnitude of the $J(^{11}B-H)$ value of the borons under attack ($J(^{11}B(6)-H)$ = 167 Hz for X = CH_3,[2] 170 Hz for X = H, 176 Hz for X = Cl,[10] and 176 Hz for X = I).[9] Additionally, the methylation ($CH_3Cl/AlCl_3$) of 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ takes place at the B(1) or B(7) apical position, where the magnitude of $J(^{11}B-H)$ is smaller (175.5 Hz) than that of B(3) (182.8 Hz). For 1,5,6-$(CH_3)_3$-2,4-$C_2B_5H_4$ the magnitude of the $J(^{11}B-H)$ value at B(7) is 4 Hz less than that at B(3)–H, and when the compound is methylated with $CH_3Cl/AlCl_3$, the entering substituent attaches to B(7). The relationship between $J(^{11}B-H)$ and electrophilic reactivity may be fortuitous, but should it prove otherwise, some justification may be provided by the following consideration: reduced s-orbital character and thus weaker bond strength are generally associated with bonds with smaller *J* values;[20,23] if this also reflects the B–H bond character of a transition state (in which the attacking electrophilic species has partially attached to the boron), then loss of the hydrogen (as hydrogen ion) may well be facilitated. Obviously other factors can come into play but the *J*(BH)/reactivity correlation may well be more visible among closely related systems where these "other factors" may cancel out.

The observed $J(^{11}B-H)$ values for B(5) of 2,4-$C_2B_5H_7$ and B(2–5) of 1,6-$C_2B_4H_6$ are 169.5 and 198.9 Hz, respectively; we have found that electrophilic substitution of 1,6-$C_2B_4H_6$ occurs with great difficulty as compared to that of 2,4-$C_2B_5H_7$. On the other hand, the 1,10-$C_2B_8H_{10}$ carborane is less reactive toward an electrophilic substitution than is 2,4-$C_2B_5H_7$ although the $J(^{11}B-H)$ value of 1,10-$C_2B_8H_{10}$ is smaller than that of the reactive B(5,6)–H site of 2,4-$C_2B_5H_7$. This may be explained in part by

(22) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper & Row: New York, 1981; Chapter 7.

(23) Onak, T.; Leach, J. B.; Anderson, S.; Frisch, M. J. *J. Magn. Reson.* **1976**, *23*, 237–248.

a consideration of boron coordination number. The B(5) of $2,4\text{-}C_2B_5H_7$ has a coordination number of 5, whereas B(2) of $1,10\text{-}C_2B_8H_{10}$ has a coordination number of 6. A substitution reaction at a boron atom that has a higher coordination number might be less susceptible toward attack by an external reagent than a boron atom that has a lower coordination number.[1]

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Sulfur–Nitrogen-Bonded Metal Chelates. 16. Reactivities of Coordinated Nitriles in the Nickel(II) Complexes [Ni(S⌒N⌒N)(NCR)](ClO$_4$) with Alcohols, Amines, and Different Nucleophiles. Synthesis, Characterization, and Stereochemistry of Imino–Ether, Amide, and Amidine Complexes

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The reactions of the nitrile complexes [NiL(NCR)]ClO$_4$ (HL^1 = methyl 2-((2-aminoethyl)amino)cyclopent-1-enedithiocarboxylate, HL^2 = methyl 2-((2-(dimethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate, HL^3 = methyl 2-((2-(diethylamino)ethyl)-amino)cyclopent-1-enedithiocarboxylate; R = Me, Et, Ph) with dry alcohols, wet alcohols, water, alkali, secondary aliphatic and heterocyclic amines, aliphatic primary amines, pyridine, PPh_3, $Ph_2P(CH_2)_2PPh_2$, and some anions (N_3^-, CN^-, NCO^-) have been investigated. Dry alcohols (R'OH) add on to the coordinated nitrile in the presence of excess of free nitrile to form imino–ether complexes, [NiL(NH=C(OR')R)](ClO$_4$). The reaction becomes much faster when sodium alkoxide is used as a catalyst. If the alcohol used is wet, the product is an amido complex, [NiL(NH$_2$COR)](ClO$_4$). Secondary amines (HNR'$_2$) react with the nitrile to form the amidine complexes [NiL(NH=C(NR'$_2$)R)](ClO$_4$). With primary amines both addition to and substitution of the nitrile take place. With the remaining other nucleophiles displacement of the nitrile takes place. All of the reaction products have been isolated and characterized. The ^1H NMR spectra of the imino–ether and amidine complexes have revealed the presence of two (*E* and *Z*) isomeric species, whose distribution at ambient temperature has been determined.

Introduction

Augmented reactivities of coordinated molecules in metal complexes have wide implications in chemistry. Metal ions in complexes can have the effect of a "superacid" to polarize ligands and thus to render them susceptible to nucleophilic attack.[1] Such reactions are usually facilitated by the charge on cationic complexes, especially by the charge density of the metal ion. Aside from thermodynamic and kinetic factors, the stereochemical role of the metal ion and stabilization of the product molecule through complex formation often become important in deciding the course of a reaction.

Over the past 20 years considerable attention has been focused on the reactions based upon nucleophilic attack on coordinated nitriles[2] in metal complexes. These include reactions with alcohols to form imino–ethers[3–7] and with amines to form amidines[8–13] and base-catalyzed hydrolysis to imidates.[14–16] The nucleophilic attack of [CH(PPh$_2$)X]$^-$ (X = CO$_2$Et, CN)[17] and [CH(COMe)(COR)]$^-$ (R = Me, Ph)[18] anions on the nitrile carbon atom of [Pt(NCPh)$_2$Cl$_2$] has also been reported. In all these reactions the product molecule remains bound to the metal center. However, in a few cases metal ion catalyzed hydrolysis of uncomplexed nitrile

(1) (a) Busch, D. H., Ed. *Reactions of Coordinated Ligands and Homogeneous Catalysis*; Advances in Chemistry 37; American Chemical Society: Washington, DC, 1963. (b) Collman, J. P. *Transition Met. Chem. (N.Y.)* **1966**, *2*, 1–114.
(2) For review, see: (a) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1–29. (b) Granik, N. G. *Russ. Chem. Rev. (Engl. Transl.)* **1983**, *52*, 377–394.
(3) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 489–496.
(4) Barnard, P. F. B. *J. Chem. Soc. A* **1969**, 2140–2144.
(5) (a) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1971**, *10*, 2699–2704. (b) Appleton, T. G.; Chisholm, M. H.; Clark, H. C.; Manzer, L. E. *Ibid.* **1972**, *11*, 1786–1794. (c) Clark, H. C.; Manzer, L. E. *Ibid.* **1972**, *11*, 2749–2755. (d) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *47*, C17–C20. (e) Manzer, L. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1535–1540.
(6) (a) Ros, R.; Renaud, J.; Roulet, R. *J. Organomet. Chem.* **1975**, *87*, 379–387. (b) Ros, R.; Renaud, J.; Roulet, R. *Ibid.* **1976**, *104*, 271–279. (c) Ros, R.; Michelin, R. A.; Boschi, T.; Roulet, R. *Inorg. Chim. Acta* **1979**, *35*, 43–48.
(7) Wada, M.; Shimohigashi, T. *Inorg. Chem.* **1976**, *15*, 954–958.
(8) (a) Tschugaev, L.; Lebedinski, W. *C. R. Hebd. Seances Acad. Sci.* **1915**, *161*, 563. (b) Stephenson, N. C. *J. Inorg. Nucl. Chem.* **1962**, *24*, 801–808.
(9) (a) Buckingham, D. A.; Foxman, B. M.; Sargeson, A. M.; Zanella, A. *J. Am. Chem. Soc.* **1972**, *94*, 1007–1009. (b) Nolan, K. B.; Hay, R. W. *J. Chem. Soc., Dalton Trans.* **1974**, 914–920.
(10) Ros, R.; Renaud, J.; Roulet, R. *J. Organomet. Chem.* **1976**, *104*, 393–400.
(11) (a) Calligaro, L.; Michelin, R. A.; Uguagliati, P. *Inorg. Chim. Acta* **1983**, *76*, L82–L87. (b) Calligaro, L. *Polyhedron* **1984**, *3*, 117–120.
(12) Pinnell, D.; Wright, G. B.; Jordan, R. B. *J. Am. Chem. Soc.* **1972**, *94*, 6104–6106.
(13) Maresca, L.; Natile, G.; Intini, F. P.; Gasparrini, F.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Am. Chem. Soc.* **1986**, *108*, 1180–1185.
(14) (a) Buckingham, D. A.; Keene, F. R.; Sargeson, A. M. *J. Am. Chem. Soc.* **1973**, *95*, 5649–5652. (b) Creaser, I. I.; Harrowfield, J. M.; Keene, F. R.; Sargeson, A. M. *Ibid.* **1981**, *103*, 3559–3564. (c) Curtis, N. J.; Sargeson, A. M. *Ibid.* **1984**, *106*, 625–630.
(15) (a) Balahura, R. J. *Can. J. Chem.* **1974**, *52*, 1762–1773. (b) Balahura, R. J.; Cock, P.; Purcell, W. L. *J. Am. Chem. Soc.* **1974**, *96*, 2739–2742. (c) Balahura, R. J.; Purcell, W. L. *Inorg. Chem.* **1979**, *18*, 937–941. (d) Balahura, R. J.; Purcell, W. L. *Ibid.* **1981**, *20*, 4159–4163. (e) De La Vega, R. L.; Ellis, W. R., Jr.; Purcell, W. L. *Inorg. Chim. Acta* **1983**, *68*, 97–101.
(16) Zanella, A. W.; Ford, P. C. *Inorg. Chem.* **1975**, *14*, 42–47, 700–701.
(17) (a) Braunstein, P.; Matt, D.; Dusausoy, Y.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1979**, 763–764. (b) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J. *Organometallics* **1983**, *2*, 1410–1417.
(18) Uchiyama, T.; Takagi, K.; Matsumoto, K.; Ooi, S.; Nakamura, Y.; Kawaguchi, S. *Chem. Lett.* **1979**, 197–198; *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1077–1084.

0020-1669/87/1326-1586$01.50/0