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Registry No. *fac*-[Co(*ms*-bn)$_3$]Br$_3$, 71883-55-1; *mer*-[Co(*ms*-bn)$_3$]Br$_3$, 71883-56-2; *fac*-[Co(*ms*-bn)$_3$][Co(CN)$_6$], 71884-47-4; *mer*-[Co(*ms*-bn)$_3$][Co(CN)$_6$], 71883-58-4; *fac*-[Co(*ms*-bn)$_3$]Cl$_3$, 71883-59-5; *mer*-[Co(*ms*-bn)$_3$]Cl$_3$, 71883-608; [Co(*R*,*R*(*S*,*S*)-bn)$_3$]Cl$_3$, 14266-71-8; [Co(*R*,*R*(*S*,*S*)-bn)$_2$(*S*,*S*(*R*,*R*)-bn)]Cl$_3$, 14266-71-8; *ms*-bn·2HCl, 55536-62-4; (±)-bn·2HCl, 66427-25-6; Na$_3$[Co(CO$_3$)$_3$], 23311-39-9.

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A Study on the Preparation and Rearrangement of the Halogenated *closo*-Carboranes $Cl_nC_2B_4H_{6-n}$ ($n = 1, 2$) and $Cl_nC_2B_5H_{7-n}$ ($n = 1, 2$)

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Dichloro as well as monochloro derivatives of 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ are prepared, and the effect of the first chlorine substituent on the position of the entering second chlorine substituent is discussed. Both mono- and dichloro derivatives of $C_2B_5H_7$ rearrange at approximately 300 °C to a mixture of isomers.

Introduction

Some monochlorinated derivatives of the small *closo*-carboranes 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$, Figure 1, have been previously prepared by reactions of the parent cage compound with molecular chlorine.[1,2] The present study was undertaken to determine the influence of the first halogen substituent on the direction of further substitution. Additionally, it was of interest to see if the product(s) from the aluminum chloride catalyzed chlorination reaction are kinetically or thermodynamically controlled. It is now known that the methylation of 2,4-$C_2B_5H_7$ using Friedel–Crafts conditions produces kinetically controlled methyl derivatives[3] which, in turn, can be thermally rearranged to more thermodynamically stable isomers.[4,5]

Experimental Section

Materials and Handling of Chemicals. Both 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ were available from R. E. Williams and J. F. Ditter, Chemical Systems, Calif. To remove a small amount (ca. 5%) of 2-CH_3-1,5-$C_2B_3H_4$ impurity from 1,6-$C_2B_4H_6$, we treated the mixture with tetramethylethylenediamine which quantitatively complexes the former but not the latter carborane over a period of several minutes at room temperature. Pure 1,6-$C_2B_4H_6$ was then obtained by passing the volatile material through a trap at −78 °C and collecting the carborane at −190 °C. Purification of Cl_2 (Matheson) was effected by fractionation through −78, −140, and −190 °C traps to remove H_2O and HCl; chlorine condensed in the −140 °C trap.

All materials were handled in conventional high-vacuum equipment or in a drybox under an atmosphere of dry nitrogen. Cold-column fractionation was carried out by using the apparatus similar to that described in the literature.[6]

Nuclear Magnetic Resonance. Proton spectra were recorded on Varian A-60 and HA-100 spectrometers. The boron-11 spectra were obtained at 32.1 MHz with the Varian HA-100 instrument. Boron-11 decoupled proton spectra at 100 MHz were observed while irradiation was done at 32.1 MHz with a General Radio Model 1061 frequency synthesizer with a power booster provided by an Electronic Navigation Industries Model 320L RD power amplifier. Proton-decoupled ^{11}B spectra at 32.1 MHz were observed while irradiation was done at 100 MHz with the above-mentioned system. Boron-11 decoupled ^1H NMR were also obtained by using a FT-Bruker WP-60 instrument equipped with a Fluke 6160 frequency synthesizer and the ENI-320L amplifier.

The boron-11 chemical shift data (Table I) are reported relative to boron trifluoride–ethyl etherate and were obtained by using boron trichloride, δ −46.8, downfield from $(C_2H_5)_2O{\cdot}BF_3$, as a secondary external standard. The proton chemical shifts are reported relative to internal tetramethylsilane, $\tau = 10.00$.

Mass Spectra. Mass spectra were recorded on a Varian CH-5 high-resolution mass spectrometer and GLC–MS data were gathered by using a Varian Mat 111 equipped with 10% Kel-F grease on a 60/80 mesh Chrom W 20 ft × $^1/_8$ in. column.

Synthesis of 5-Cl-2,4-$C_2B_5H_6$ and 5,6-Cl_2-2,4-$C_2B_5H_5$. After a catalytic amount of $AlCl_3$ was sublimed into a 25-mL glass flask, $C_2B_5H_7$ (3.5 mmol) was added, followed by the same quantity of Cl_2. The flask was sealed and the reaction mixture warmed from −190 °C to room temperature. The color of Cl_2 disappeared within 30 min. The product mixture was fractionated through −140 and −190 °C traps, and a small amount of noncondensable gas was observed. The material in the −140 °C trap was further purified by cold-column[6] fractionation, whereby 5-Cl-$C_2B_5H_6$ (2.2 mmol, 77% yield based upon 2.85 mmol of $C_2B_5H_7$ consumed) distilled between −73 and −47 °C. The remaining volatile material, removed from the column while warming to room temperature, was 5,6-Cl_2-$C_2B_5H_5$ (0.15 mmol, 5% yield).

Into the same 25 mL flask with the $AlCl_3$ catalyst were added 5-Cl-$C_2B_5H_6$ (1.5 mmol) and Cl_2 (1.5 mmol). The flask was sealed and warmed to room temperature. By monitoring the ^{11}B NMR of the mixture, we noted that approximately 50% of the $ClC_2B_5H_6$ had reacted in 0.5 h at room temperature and the reaction was nearly complete in a 2-h period. The product mixture was fractionated through −140 and −190 °C traps to remove HCl. The material in the −140 °C trap was further fractionated by cold-column distillation with the removal of 5,6-Cl_2-$C_2B_5H_5$ (1.08 mmol, 72% yield based on starting 5-Cl-$C_2B_5H_6$) between −17.5 and 0 °C (5,6-Cl_2-$C_2B_5H_5$ is a liquid at room temperature). There was no $Cl_3C_2B_5H_4$ observed, but an isomeric dichloro derivative, 1,5-Cl_2-2,4-$C_2B_5H_5$, having a ^{11}B NMR singlet at δ ca. +14.5 and a 1:1 doublet at +31.8, $J(BH) = 192.6$ Hz, mixed with unreacted 5-Cl-$C_2B_5H_6$, was formed in less than 5% yield.

Synthesis of 2-Cl-1,6-$C_2B_4H_5$ and 2,4-Cl_2-1,6-$C_2B_4H_4$. Friedel–Crafts Route. In a typical reaction, measured amounts of 1,6-$C_2B_4H_6$ and Cl_2 were condensed into a glass reactor with a small quantity

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Table I. Nuclear Magnetic Resonance Data

	^{11}B			^{1}H		
compd	nucleus	δ^a	$J(^{11}B-H)$/Hz	nucleus	τ^b	J/Hz
5-Cl-2,4-$C_2B_5H_6$	B(1,7)	+19.8	183	HC	4.571 m	
	B(3)	−4.9	183	HB(1,7)	9.450 s	
	B(6)	−0.8	168	HB(3)	5.258 *m*	~9 HB(6)C(2)*H*
	B(5)	−12.8		HB(6)	6.124 m	
3-Cl-2,4-$C_2B_5H_6$	B(1,7)	+18.4	184	HC	4.637 m	~9 *H*C(2)B(6)*H*
	B(3)	−14.8		HB(1,7)	9.450 s	
	B(5,6)	−2.9	169	HB(5,6)	6.046 d	~9 *H*B(6)C(2)*H*
1-Cl-2,4-$C_2B_5H_6$	B(7)	+33.0	189	HC	4.070 q	~9 *H*C(2)B(6)*H*
						~7 *H*C(2)B(3)*H*
	B(1)	+15.8		HB(1,7)	10.060 s	
	B(3)	−8.2	178	HB(3)	4.893 t	~7 *H*B(3)C(2)*H*
	B(5,6)	−2.9	169	HB(5,6)	5.750 d	~9 *H*B(6)C(2)*H*
2-Cl-1,6-$C_2B_4H_5$	B(2)	+8.3		HC	6.68	
	B(3,5)	+16.2	189	HB(3,5)	7.86	
	B(4)	+28.2	200	HB(4)	8.16	
2,4-Cl_2-1,6-$C_2B_4H_4$	B(2,4)	+15.3		HC	6.32	
	B(3,5)	+14.5	189	HB	7.65	
5,6-Cl_2-$C_2B_5H_5$	B(5,6)	−10.6		HC	4.655 d	7.1 *H*CB(3)*H*
	B(3)	−2.2	193	HB(3)	5.430 t	7.1 *H*B(3)C*H*
	B(1,7)	+18.6	193	HB(1,7)	9.030	

[a] δ relative to $(C_2H_5)_2O·BF_3$. [b] τ relative to $(CH_3)_4Si$; spectra taken both with and without ^{11}B decoupling. Splitting patterns are reported for ^{11}B decoupled resonances only.

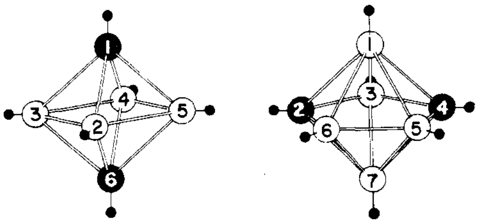

Figure 1. Structures of 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$.

of $AlCl_3$ sublimed onto the inside surface. The reactor was then allowed to warm to room temperature, and the disappearance of the Cl_2 yellow-green color, usually within an hour, signified completion of the reaction. In three separate experiments the full quantity of Cl_2 was added to the $C_2B_4H_6$ in one step (in an approximate ratio of 1:1 Cl_2:$C_2B_4H_6$), and at completion of the reaction, all volatile products were separated by fractionation through −78, −130, and −190 °C traps. The material in the −190 °C trap is largely HCl, in the −130 °C trap unreacted 1,6-$C_2B_4H_6$ and side products CH_3BCl_2[7] and BCl_3, and in the −78 °C trap the chlorinated carborane products $ClC_2B_4H_5$ and $Cl_2C_2B_4H_4$ as well as $Cl_2BCH_2BCl_2$.[8] Over the three separate experiments the total yield of chlorinated $C_2B_4H_6$ products (based upon $C_2B_4H_6$ consumed) varies from 10 to 35% with $ClC_2B_4H_5$:$Cl_2C_2B_4H_4$ ratios averaging approximately 3:1.

In a separate reaction half the total amount of Cl_2 (2.5 mmol) was added to $C_2B_4H_6$ (5.0 mmol), the mixture was subsequently allowed to react to completion in the presence of $AlCl_3$, and then all volatiles were fractionated. Unreacted $C_2B_4H_6$ was then recondensed into the reactor, and the other half (an additional 2.5 mmol) of Cl_2 was added and allowed to react, after which volatiles were again removed and separated. This procedure gave the highest yields, 45 mol % of $C_2B_4H_6$, of combined mono- and dichlorinated carborane products with an observed ratio of 3.5:1 for $ClC_2B_4H_5$/$Cl_2C_2B_4H_4$. Some of the consumed $C_2B_4H_6$ was accountable in terms of volatile cage cleavage products, BCl_3 (0.05 mmol), CH_3BCl_2[7] (0.34 mmol), and $Cl_2BCH_2BCl_2$[8] (0.11 mmol).

Cold-column fractionation[6] was utilized to obtain pure 2-Cl-1,6-$C_2B_4H_5$ (−82 to −60 °C) and 2,4-Cl_2-1,6-$C_2B_4H_4$ (~−35 to −10 °C) as well as to separate out the side products BCl_3 (~−100 °C), CH_3BCl_2[7] (~−100 °C), and $Cl_2BCH_2BCl_2$[8] (~−55 °C). Pure 2,4-Cl_2-1,6-$C_2B_4H_4$ is a white crystalline solid (mp 51–52 °C) and 2-Cl-1,6-$C_2B_4H_5$ is a clear colorless liquid at room temperature.

The mass spectrum of 2-Cl-1,6-$C_2B_4H_5$ exhibits the following peaks: *m/e* 110, 15% of base peak; *m/e* 109, 30.0%; *m/e* 108 (parent, $^{35}Cl^{12}C_2{}^{11}B_4{}^{1}H_5$), 66.0%; *m/e* 107 (base peak); *m/e* 106, 81.0%; *m/e* 105, 52.0%; *m/e* 104, 22.4%; *m/e* 103, 10.4%; *m/e* 102, 9.0%; *m/e* 101, 4.5%. Calculated monoisotopic spectrum: P, 100.0%; P − 1, 37.5%; P − 2, 25.3%; P − 3, 1.0%; P − 4, 8.0%; P − 5, 10.8%.

The mass spectrum of 2,4-Cl_2-1,6-$C_2B_4H_4$ exhibits the following peaks: *m/e* 146, 6.0% of base peak; *m/e* 145, 17.0%; *m/e* 144, 31.0%; *m/e* 143, 56.0%; *m/e* 142 (parent $^{35}Cl_2{}^{12}C_2{}^{11}B_4{}^{1}H_4$), 65.3%; *m/e* 141, 100.0% (base peak); *m/e* 140, 76.0%; *m/e* 139, 38.7%; *m/e* 138, 12.0%; *m/e* 137, 13.3%; *m/e* 136, 9.0%. Calculated monoisotopic mass spectrum: P, 30.7%; P − 1, 100.0%; P − 2, 6.0%; P − 3, 4.2%.

Photolysis Route. A quantity of 1,6-$C_2B_4H_6$ (2.5 mmol) was condensed over frozen BCl_3 (2.5 mmol) and followed by Cl_2 (2.5 mmol) in a 25-mL flask equipped with an NMR side arm. The tube was sealed at −190 °C and allowed to warm slowly to room temperature in the dark. There was no reaction in an overnight period, indicating that BCl_3 is not a sufficiently strong catalyst to effect a "Friedel-Crafts" chlorination of the carborane. Subsequently, the flask was exposed to sunlight and almost immediately a vigorous fuming of gas inside the vessel was observed. The reaction terminated when the color of Cl_2 disappeared within 1 h. The volatile material was fractionated through a cold column; $C_2B_4H_6$ was recovered (1.55 mmol) and 2-Cl-1,6-$C_2B_4H_5$ (0.34 mmol, 37.7% yield based on $C_2B_4H_6$ consumed) was isolated. No 2,4-Cl_2-1,6-$C_2B_4H_4$ was found.

5-Cl-$C_2B_5H_6$ and 5,6-Cl_2-$C_2B_5H_5$ Rearrangements. A 0.5-mmol liquid sample of 5-Cl-$C_2B_5H_6$, sealed in a 4-mm evacuated NMR tube, was heated at 300–310 °C for 5 h (temperatures significantly lower than 300 °C did not result in a reasonable rate of reaction or rearrangement). A small amount of a colorless glossy translucent solid appeared at the bottom of the tube and the ^{11}B NMR spectrum of the remaining liquid indicated that a moderate quantity of 1-Cl-$C_2B_5H_6$ had formed. The contents of the NMR tube were subsequently heated at 300–310 °C for an additional 16 h. Additional solid was formed representing about one-third the original liquid volume. The tube was frozen to −190 °C and was opened into a high vacuum system, and approximately 0.4 mmol of noncondensable gas was measured. The contents of the tube were slowly warmed to room temperature and fractionated through traps at 0, −78, and −190 °C. A trace amount of $C_2B_5H_7$ was found in the −190 °C trap, and a mixture of $ClC_2B_5H_6$ isomers was present in the −78 °C trap. The ^{11}B NMR (both undecoupled and ^{1}H decoupled) of the liquid above the solid exhibited resonances at δ = −15.9, −14.1, −8.2, −5.6, −3.8, −2.4, −0.1, +15.9, +18.3, +19.7, and +32.7, the intensity and pattern of which matched composite spectra for a nearly equal molar mixture of 1-, 3-, and 5-Cl-$C_2B_5H_6$ isomers. The ^{1}H spectrum (both undecoupled and ^{11}B decoupled) of the mixture was compatible with this assignment. Repeating the 300 °C thermal rearrangement by starting with a

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(7) H. Nöth and H. Vahrenkamp, *J. Organomet. Chem.*, **12**, 23 (1968); H. Nöth and H. Vahrenkamp, *Chem. Ber.*, **99**, 1049 (1966); J. E. DeMoor and G. P. Van der Kelen, *J. Organomet. Chem.*, **6**, 235 (1966).

(8) D. S. Matteson and P. K. Mattschei, *Inorg. Chem.*, **12**, 2472 (1973); also identified by comparison to an authentic sample provided by D. Matteson.

mixture of 0.40 mmol of 1-Cl-$C_2B_5H_6$ and 0.07 mmol of 3-Cl-$C_2B_5H_6$ in a 4-mm NMR tube produced nearly the same ^{11}B and ^1H NMR spectra pattern for the rearranged products as observed for the 5-Cl-$C_2B_5H_6$ rearrangement products but with slightly more 3-Cl-$C_2B_5H_6$ present.

The rearrangement of 5-Cl-2,4-$C_2B_5H_6$ (4.50 mmol) was also carried out in a flask sufficiently large, 250 mL, to ensure that the entire quantity of the reactant (and rearranged isomeric products) was committed to the gas phase during a 300 °C, 41-h rearrangement. No buildup of solid nor noncondensable side products was found (vide supra). Cold-column chromatography[6] of the rearrangement mixture gave 2.35 mmol (52.3%) of 5-Cl-2,4-$C_2B_5H_6$ (coming off the column at −55 to −45 °C), 1.28 mmol (28.3%) of 3-Cl-2,4-$C_2B_5H_6$, and 0.87 mmol (19.4%) of 1-Cl-2,4-$C_2B_5H_6$. The 3-Cl and 1-Cl isomers were difficult to obtain pure from each other (in several fractions taken between −85 and −59 °C the more volatile fractions were enriched with 3-Cl-2,4-$C_2B_5H_6$ and the less volatile with 1-Cl-2,4-$C_2B_5H_6$) but ^{11}B and ^1H NMR analyses allowed for unambiguous NMR assignments and calculation of yields.

Thermal treatment of 5,6-Cl_2-$C_2B_5H_5$ (0.5 mmol) in an NMR tube at 310 °C for 21 h produces some nonvolatile brown solids and a liquid having the ^{11}B NMR pattern expected for a rearranged $Cl_xC_2B_5H_{7-x}$ ($x = 1, 2$) isomer mixture. The liquid portion of the sample was vacuum fractionated through traps at −40 and −190 °C. The ^{11}B NMR of the contents of the −190 °C trap (~0.05 mmol) indicated the presence of BCl_3 and a mixture of $ClC_2B_5H_6$ isomers. The ^{11}B and ^1H NMR of the −40 °C fraction (0.1 mmol) was complex but clearly a composite of *B,B'*-Cl_2-$C_2B_5H_5$ isomers in which the ratio of isomers 1,5- + 1,3-Cl_2-$C_2B_5H_5$/3,5- + 5,6- + 1,7-Cl_2-$C_2B_5H_5$ = 2/1.5 as derived from the pattern of the ^{11}B high-field, $\delta = +5$ to $+40$ NMR resonance region.

Reaction of HCl with $C_2B_5H_7$ with and without Aluminum Chloride. A mixture of 2,4-$C_2B_5H_7$ (0.52 mmol) with HCl (2.5 mmol) was sealed in a 25-mL flask equipped with a 5-mm NMR tube. By use of ^{11}B NMR to monitor the contents of the tube, no reaction between the reagents was observed both after 43 h at room temperature and after heating to 200 °C for 2 h, and then at 245 °C for 2.5 h. The contents were then transferred to a similar glass container containing a catalytic amount of freshly sublimed aluminum chloride. After the container was sealed, the contents were allowed to stand at room temperature for 5 months. In addition to a small quantity of unreacted $C_2B_5H_7$ the ^{11}B NMR of the reaction mixture exhibited three singlets at $\delta = -62.3, -59.2$, and -46.8, area ratio 1.4:1:1.8, assigned to CH_3BCl_2,[7] $Cl_2BCH_2BCl_2$,[8] and BCl_3, respectively. The ^1H NMR indicated an area ratio of 4.5:1 for two singlets, $\tau = 9.0$ (CH_3BCl_2) and $\tau = 7.8$ ($Cl_2BCH_2BCl_2$), respectively. Combining the ^{11}B and ^1H NMR information gives a ratio of ca. 2.9:1:3.6 for CH_3BCl_2:$Cl_2BCH_2BCl_2$:BCl_3.

Reaction of HCl/$AlCl_3$ with 1,6-$C_2B_4H_6$. Into a 23-mL container with an NMR side arm was sublimed a catalytic quantity of $AlCl_3$, after which were condensed 0.50 mmol of 1,6-$C_2B_4H_6$ and 5.0 mmol of anhydrous HCl. After 4 weeks at room temperature the ^{11}B and ^1H NMR spectrum of the sample indicated that more than 75% of the carborane had decomposed to a mixture of CH_3BCl_2[7] (^{11}B, $\delta = -62.3$; ^1H, $\tau = 9.0$, external Me_4Si), $Cl_2BCH_2BCl_2$[8] (^{11}B, $\delta = -59.2$; ^1H, $\tau = 7.8$ external Me_4Si), and BCl_3 (^{11}B, $\delta = -46.8$) in a ratio of 1.5:1:1.1.

Discussion

The dichlorination of 2,4-$C_2B_5H_7$ with Cl_2/$AlCl_3$ proceeds to give almost exclusively the 5,6-Cl_2-2,4-$C_2B_5H_5$ isomer with chlorine atoms on *adjacent* low coordination cage borons. This is reminiscent of the dimethylation of this same parent carborane when subjected to a methyl chloride/aluminum chloride mixture. In contrast, the dichlorination of 1,6-$C_2B_4H_6$ with Cl_2/$AlCl_3$ appears to produce the 2,4-Cl_2-1,6-$C_2B_4H_4$ isomer in which chlorine atoms are attached to boron atoms at *opposite* vertices on the octahedral cage framework. Some cage decomposition accompanies the chlorination reactions with the more serious occurring with the smaller carborane. In all likelihood a byproduct, HCl, is partly responsible for the cage cleavage to give methyldichloroborane and bis(dichloroboryl)methane. For, in control experiments both $C_2B_4H_6$ and $C_2B_5H_7$ are found to react with an HCl/$AlCl_3$ mixture to form CH_3BCl_2, $Cl_2BCH_2BCl_2$, and BCl_3, and possibly other cleavage products, and there is evidence to indicate that the chlorinated carboranes may even be less stable toward this same reagent mixture. To minimize the cage cleavage problem during the chlorination of $C_2B_4H_6$, it is advantageous to carry out the reaction by adding the Cl_2 in portions, removing the formed HCl before each new Cl_2 addition.

Rearrangements of both 5-Cl-2,4-$C_2B_5H_6$ and 5,6-Cl_2-2,4-$C_2B_5H_5$ to isomeric products proceed at reasonable rates in the vicinity of 300 °C. In both instances substantial decomposition to a glossy, almost translucent, intractable solid accompanies the rearrangement when carried out in small containers where it is certain that $Cl_xC_2B_5H_{7-x}$ ($x = 1, 2$) is present as a liquid and/or as a gas at high pressures at 300 °C. But when 5-Cl-2,4-$C_2B_5H_6$ is rearranged to a mixture of 1- and 3- (and 5-) Cl-2,4-$C_2B_5H_l$ isomers under conditions in which reactant and products are present only in the gas phase, at reduced pressures, no visible decomposition occurs.

The relative volatility of the $ClC_2B_5H_6$ isomers, experienced from the cold-column fractionation of the rearrangement mixture, is found to be 3-Cl > 1-Cl > 5-Cl. This may be a reflection of the relative polarity of these molecules in which the dipole moments are expected to follow the order 5-Cl > 1-Cl > 3-Cl. This prediction is based upon drawing an analogy to the halogenated derivatives of 1,2- and 1,7-$C_2B_{10}H_{12}$. In the case of the icosahedral carboranes the carbon atoms are at the positive end of the cage dipole, and halogen atoms situated on the cage adjacent, or near, to the carbon atoms result in a lowering of the molecular dipole moment.[9,10]

The ^{11}B NMR of the 2,4-Cl_2-1,6-$C_2B_4H_4$ supports the assignment of the two halogens on antipodal situated borons, assuming the validity of chemical shift additivity relationships as found in other cage systems.[3,5,11] A relationship $\delta(^{11}B) = +17.6 + \sigma_c + \sigma_n + \sigma_a$ is derived by comparing the chemical shifts of 2-Cl-1,6-$C_2B_4H_6$ with the parent molecule, where σ_c is the chlorine substituent effect on a contiguous boron, σ_n is the effect of the chlorine substituent on the nearest neighbor boron [e.g., effect of ClB(2) on B(3)], and σ_a is the effect of the chlorine atom on an antipodal situated boron. From the data for 2-Cl-1,6-$C_2B_4H_5$ (Table I) and the parent 1,6-$C_2B_4H_6$,[12] $\sigma_c = -9.3$, $\sigma_n = -1.4$, and $\sigma_a = +10.6$ ppm. This predicts shifts of $\delta = +14.8$ for B(2,4) and $\delta = +18.9$ for B(3,5) of the 2,4-Cl_2-$C_2B_4H_4$ isomer and $\delta = +6.9$ for B(2,3) and $\delta = +26.8$ for B(4,5) of the 2,3-Cl_2-1,6-$C_2B_4H_4$ isomer. Clearly, the observed chemical shifts, Table I, for the obtained *B,B'*-Cl_2-1,6-$C_2B_4H_4$ are more in agreement with 2,4-dichloro substitution than with 2,3-dichloro substitution.[13]

In the case of 5,6-Cl_2-2,4-$C_2B_5H_5$ the positions of the two chlorine atoms are assigned from both the ^{11}B and ^1H NMR data, and the chemical shift trends and coupling patterns are obvious extensions of further (6-) substitution onto the 5-monochloro compound.

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(12) A ^{11}B chemical shift of +17.6 ppm for the parent 1,6-$C_2B_4H_6$ was determined consecutively with the NMR measurements on the chlorinated derivatives (Table I).

(13) The synthesis of 2,4-Cl_2-1,6-$C_2B_4H_4$ has also been accomplished by G. A. Beltram and T. P. Fehlner, *J. Am. Chem. Soc.*, **101**, 6237 (1979); T. P. Fehlner, private communication.

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Registry No. 5-Cl-2,4-$C_2B_5H_6$, 28347-92-4; 5,6-Cl_2-2,4-$C_2B_5H_5$, 71849-86-0; 2-Cl-1,6-$C_2B_4H_5$, 33616-59-0; 2,4-Cl_2-1,6-$C_2B_4H_4$, 71849-87-1; 3-Cl-2,4-$C_2B_5H_6$, 28347-93-5; 1-Cl-2,4-$C_2B_5H_6$, 28347-69-5; 1,5-Cl_2-$C_2B_5H_5$, 71849-88-2; 1,3-Cl_2-$C_2B_5H_5$, 71849-89-3; 3,5-Cl_2-$C_2B_5H_5$, 71849-90-6; 1,7-Cl_2-$C_2B_5H_5$, 71849-91-7; 2,4-$C_2B_5H_7$, 20693-69-0; 1,6-$C_2B_4H_6$, 20693-67-8; CH_3BCl_2, 7318-78-7; $Cl_2BCH_2BCl_2$, 40710-68-7; BCl_3, 10294-34-5.

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Donor and Acceptor Behavior of Divalent Tin Compounds

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Reactions of some tin(II) halide–donor adducts with trifluoroborane produce complexes which contain BF_3, a tin(II) halide, and a donor in a 1:1:1 formulation. Mössbauer and multinuclear (^1H, ^{11}B, ^{19}F, and ^{119}Sn) NMR spectra support a diadduct structure for the products wherein the trifluoroborane moiety is coordinated directly to the tin atom to which the donor molecule also remains coordinated. The proposed structure in the trimethylamine diadduct, $BF_3{\cdot}SnCl_2{\cdot}N(CH_3)_3$, is indicated by a large increase in the isomer shift and decrease in the quadrupole splitting as compared to those of $SnX_2{\cdot}N(CH_3)_3$ and by an unusual low-field shift of the ^{11}B NMR signal. Alternative product formulations arising from a Lewis acid displacement reaction or insertion of the tin(II) moiety into a B–F bond were rejected on the basis of the products' spectral characteristics. Other diadducts prepared were $BF_3{\cdot}SnX_2{\cdot}OS(CH_3)_2$, $BF_3{\cdot}SnX_2{\cdot}TMED$ (TMED = *N,N,N′,N′*-tetramethylethylenediamine), and $BF_3{\cdot}SnX_2{\cdot}DP$ (DP = dipyridyl) (X = Cl, Br, I). The TMED and DP species appeared to adopt chelating structures in the diadducts. Isomeric diadducts $BF_3{\cdot}TMED{\cdot}SnX_2$ and $BF_3{\cdot}DP{\cdot}SnX_2$, structures in which the acceptor and donor coordinate to separate nitrogens of the ligands, were prepared and proved to be different compounds than those where the divalent tin halide exhibits simultaneous acceptor and donor behavior.

Introduction

Previous work in this laboratory[1-3] has considered the acceptor and donor functions of divalent tin[4] in terms of both SnX_2·donor and SnR_2·acceptor complexes. The spectroscopic properties and thermodynamic stabilities of several such adducts have been determined. Through these investigations and those of other workers (vide infra), it has been shown that the divalent tin compounds with electron-withdrawing substituents act as Lewis acids forming adducts such as $SnCl_2{\cdot}N(CH_3)_3$ while those with less electron-withdrawing substituents act as Lewis bases forming adducts such as $BF_3{\cdot}Sn[N(CH_3)_2]_2$. The purpose of the present work was to determine whether stable diadducts, wherein tin exercises its donor and acceptor functionalities simultaneously, could be prepared. In principle, species such as $PtCl_2(SnCl_3)_2^{2-}$[5] and $(t\text{-}C_4H_9)_2SnCr(CO)_5{\cdot}NC_5H_5$[6-8] fulfill this requirement; however, we felt it was important to investigate complexes between tin(II) halide–amine adducts and trifluoroborane in search of structurally analogous diadducts in which the bonding to tin might be more clearly defined.

Table I. ^1H NMR Parameters of Trimethylamine Adducts[a]

compd	$\delta(CH_3)$[b]	compd	$\delta(CH_3)$[b]
$BF_3{\cdot}SnCl_2{\cdot}N(CH_3)_3$	1.77	$SnBr_2{\cdot}N(CH_3)_3$	1.75[c]
$BF_3{\cdot}SnBr_2{\cdot}N(CH_3)_3$	1.73	$SnI_2{\cdot}N(CH_3)_3$	1.70[c]
$BF_3{\cdot}SnI_2{\cdot}N(CH_3)_3$	1.67	$F_3B{\cdot}N(CH_3)_3$	1.97[d]
$SnCl_2{\cdot}N(CH_3)_3$	1.81[c]	$(CH_3)_3N$	1.91

[a] Solvent, aniline. [b] ±0.02 ppm. [c] Reference 2. [d] Broad multiplet.

Table II. ^{119}Sn NMR Parameters of Adducts of Divalent Tin Halides[a]

compd	δ[b]	fwhh, Hz
$SnCl_2{\cdot}N(CH_3)_3$	111.8	27.5
$SnCl_2{\cdot}Me_2SO$	369.5	59.8
$SnBr_2{\cdot}Me_2SO$	833.2	479.0
$SnI_2{\cdot}Me_2SO$	684.2	439.0
$SnF_2{\cdot}Me_2SO$	−56.9	78.7
$SnCl_2{\cdot}Py$	294.0	35.9
$BF_3{\cdot}SnCl_2{\cdot}N(CH_3)_3$	332.8	24.9
$BF_3{\cdot}SnCl_2{\cdot}Me_2SO$	416.1	99.8
$BF_3{\cdot}SnBr_2{\cdot}Me_2SO$	881.0	279.0
$BF_3{\cdot}SnI_2{\cdot}Me_2SO$	625.1	431.0
$BF_3{\cdot}SnF_2{\cdot}Me_2SO$	not found	
$BF_3{\cdot}SnCl_2{\cdot}Py$	303.7	32.5

[a] Saturated solutions in dimethyl sulfoxide; all spectra are broad, unresolved multiplets. [b] ±0.2 ppm; referred to external $Sn(CH_3)_4$.

Experimental Section

A. Equipment and Materials. All reactions were carried out either under flowing dry nitrogen or by using vacuum techniques; a LabConCo glovebox was used for transfer of nonvolatile air-sensitive materials. Tin(II) halide adducts were found to be very air sensitive. ^1H NMR spectra were obtained on a Varian T-60 instrument at 60 MHz (accuracy ±0.02 ppm). A Varian Model XL-100-15 with Nicolet 1080 data system and NT-440 Mona multinuclear accessory was employed in the pulse Fourier transform mode to obtain ^{11}B spectra at 32.1 MHz and ^{119}Sn spectra at 37.28 MHz (accuracy ±0.2 ppm) while a Varian 4412 probe was used for ^{19}F spectra at 94.1 MHz.

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