Table VIII. Comparison of Bond Lengths[a] in $C_2B_5H_6F$ and $C_2B_5H_7$

	bond length, Å		
bond	$C_2B_5H_6F$	$C_2B_5H_7$	Δ
B_1–B_7	2.343 (02) (2.410)	2.329 (05) (2.412)	0.014
B_1–B_3	1.825 (03) (1.894)	1.818 (05) (1.908)	0.007
B_1–B_5	1.813 (05) (1.882)	1.815 (05) (1.812)	−0.002
B_1–B_6	1.844 (05) (1.826)	1.815 (05) (1.812)	0.029
B_3–B_5	2.667 (12) (2.742)	2.648 (05) (2.675)	0.019
B_3–B_6	2.700 (13) (2.716)	2.648 (05) (2.675)	0.052
B_5–B_6	1.559 (31) (1.659)	1.651 (05) (1.672)	−0.092

[a] MNDO-calculated values are shown in parentheses below the experimental values.

its value was insensitive to any adjusted boron, carbon, or hydrogen coordinate, and no consistent fittings resulted for positive values. Furthermore, varying the assumed B–H bond lengths from 1.15 to 1.20 Å had negligible effects on the final fit.

Discussion

The planarity condition calculations shown in Table VII were used in calculating molecular structure parameters of $C_2B_5H_6F$, which are compared with those of the parent $C_2B_5H_7$ structure in Table VIII. It is seen that slight increases in bond lengths occur upon fluorination at the B_5 site. The B_1–B_7 distance is 0.013 Å larger in the fluoro derivative. Due to the larger than usual uncertainties in the locations of the B_5 and B_6 atoms, some structural comparisons are not as definitive as desired. Upon fluorination, the B_3–B_6 distance increases by 0.052 Å, while B_3–B_5 increases by 0.019 Å.

The estimated B–F bond length of 1.33 ± 0.03 Å is consistent with partial double-bond character. This can be compared with B–F bond lengths in several other molecules. Boron monofluoride, BF, is isoelectronic with CO and N_2 and with a short bond length of 1.26 Å is consistent with having a triple bond.[1,2] BF_3, with a 1.30-Å B–F bond length, has been described as having three sets of equivalent double bonds.[1,2] The B–F bond in $NH_4^+BF_4^-$ is a pure single bond, as expected by assuming four equivalent sp^3-hybridized orbitals on the boron, which agrees with the observed long 1.43-Å bond length.[13] By analogy, the B–F bond in $C_2B_5H_6F$ is thus viewed as having partial double-bond character.

Despite the problems associated with two boron atoms lying close to a principal axis, this molecule is slightly enlarged compared to the parent compound. This tends to support the hypothesis that back-donation by the fluorine atom causes the cage to expand. The only exception to this is the B_5–B_6 bond length, which appears contracted by 0.09 Å. This may be due to problems in locating the B_5 atom or may reflect an actual structural difference.

Interesting work remaining includes a comparison of structures of B_1- or B_3-substituted monofluoro compounds, along with successively further fluorinated species.

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Fluorination of Boron Chlorides and Boron Bromides by Reaction with Bis(trifluoromethyl)mercury, Trichlorofluoromethane, or Tribromofluoromethane: Synthesis of $BF_2B_5H_8$

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The interaction of BCl_3 with excess $CFCl_3$ has been examined by ^{11}B and ^{19}F NMR. Although small amounts of $BFCl_2$ and BF_2Cl, 9% each, are observed after 283 h at 65 °C, BF_3 is not a major product. At 130 °C, however, BF_3 is formed in 89% yield after 33 h. Boron trifluoride is isolated in 98 and 97% yields from the reactions of BCl_3 and BBr_3, respectively, with $CFBr_3$ at 130 °C. At ambient temperature, $Hg(CF_3)_2$ reacts with BCl_3 and BBr_3, generating BF_3 in 99 and 98% yields, respectively. The reaction of B_2Cl_4 with excess $CFCl_3$ was followed spectroscopically at 65, 90, and 130 °C, and the ^{19}F chemical shifts of the partially fluorinated diboron tetrahalides have been assigned. Diboron tetrafluoride was isolated from the reaction between B_2Cl_4 and $CFBr_3$ in 89% yield, from B_2Br_4 and $CFBr_3$ in 78% yield, and from B_2Cl_4 and $Hg(CF_3)_2$ in 89% yield. Within 45 min the reaction between 1-$BCl_2B_5H_8$ and $Hg(CF_3)_2$ produces the new compound 1-$BF_2B_5H_8$ in 96% yield. Tetraboron tetrachloride is by far the least reactive of the boron chlorides examined.

Introduction

Recently we have become interested in the preparation of the polynuclear boron fluorides, and as one early phase of this investigation we have elected to examine the possibility of developing fluorinating procedures that are viable alternatives to those currently employed. The classic reagent, of course, is antimony trifluoride, which was originally reported to transform B_2Cl_4 into B_2F_4 in 78% yield.[1] The disadvantage of the antimony fluoride reactions is that generally the reagent must be twice sublimed and then two separate applications of SbF_3 are required.[1]

Diboron tetrafluoride, the simplest of the polynuclear boron fluorides, has also been prepared by the action of SF_4 on B_2O_2, $B_2(OEt)_4$, and $B_2(OH)_4$, but in lesser yields, 50, 30, and 34%, respectively.[2] An alternative synthesis of B_2F_4 involves the interaction of TiF_4 with B_2Cl_4, a reaction that is stated to proceed readily.[3] Another preparative route to B_2F_4 is that developed by Timms, the high-temperature reduction of BF_3 with elemental boron.[4]

For the purposes at hand, however, the most interesting report in the literature is the one in which Schlesinger describes the reaction between allyl fluoride and B_2Cl_4, an apparently complex

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interaction from which B_2F_4 is eventually separated in 40% yield.[5] This publication demonstrated that ligand interchange between carbon–fluorine and boron–chlorine bonds can occur readily, and despite the relatively low yield encountered, the results suggest that haloborane fluorinations might well proceed easily in high yields if a more appropriate fluorocarbon were utilized.

For our initial examination of the reactivities of boron halides with fluorinated species two different types of fluorine-containing reagents immediately suggested themselves. The first category was composed of fluoromethanes that were drawn from one of the most readily available types of organofluorine compounds, the Freons; thus, all of the original experiments were carried out with $CFCl_3$ (Freon-11). The second category that it seemed appropriate to examine involved a slightly different type of compound, trifluoromethyl organometallic species of the type $M(CF_3)_n$.[6] Here, the most conveniently available member is $Hg(CF_3)_2$, a compound that has the added interest that, in principle at least, it can deliver either a fluoride or a trifluoromethyl group to another center.

The haloboranes studied were chosen to reflect several different types of bonding situations that are commonly found in boron chemistry. Thus, the boron halide substrates ranged from the boron trihalides, the simplest possible haloboranes, to the diboron tetrahalides, more complex species containing localized boron–boron single bonds, to tetrachlorotetraborane, a compound in which multicentered, delocalized bonding is featured.

The final boranes examined, 1-$BCl_2B_5H_8$ and 1-$BBr_2B_5H_8$, were selected for two reasons. First, the bonding both in the substrates and in the anticipated product is a composite of all of the motifs that are commonly encountered in boron chemistry. In these compounds boron–halogen bonds, localized boron–boron bonds, delocalized bonding within the pentaborane cage, and both terminal and bridging boron–hydrogen bonds are all present in the same molecule. Second, since the desired product, 1-$BF_2B_5H_8$, was unknown, the successful preparation of this compound seemed to be one reasonably appropriate test of the efficiency of organofluorine compounds as fluorinating agents for haloboranes.

Experimental Section

General Considerations. To ensure the absence of air and moisture, all manipulations of the boron-containing compounds were carried out by using a standard vacuum line that was equipped with Teflon valves. Fourier transform NMR spectra at 64.2 MHz (^{11}B), 188.3 MHz (^{19}F), and 50.3 MHz (^{13}C) were obtained on an IBM 200SY instrument. Positive shifts are deshielded from the standard, external $BF_3{\cdot}OEt_2$, CF_3CO_2H, or $Si(CH_3)_4$. Mass spectra were obtained from samples admitted into an AEI MS-30 spectrometer through a gas inlet system. The 70-eV source was at ambient temperature.

Boron tribromide (Aldrich) was decolorized by treatment with mercury and then fractionated prior to use. Boron trichloride (Matheson) was freed from HCl by fractionation. Diboron tetrachloride,[7] B_2Br_4,[8] and B_4Cl_4[9] were synthesized and separated as previously described. 1-(Dichloroboryl)pentaborane and 1-$BBr_2B_5H_8$ were prepared by the reaction of B_2Cl_4 and B_2Br_4, respectively, with pentaborane-9 (Callery).[10]

Trichlorofluoromethane (Aldrich) was passed through a trap maintained at −95 °C; $CFBr_3$ (Aldrich) was passed through a trap held at −22 °C and then retained within a −64 °C trap. Carbon tetrachloride was vacuum-distilled from P_2O_5. Bis(trifluoromethyl)mercury was generated by the thermal decarboxylation of $Hg(CF_3CO_2)_2$[11] and resublimed immediately prior to use.

The spectroscopic reactions were carried out by condensing the reagents into evacuated vessels that had been constructed from 4-mm Pyrex tubing. The lengths of these reactors were adjusted such that the final pressures, as estimated from the ideal-gas law, would not exceed 20 atm. The reactors were sealed with a torch and then placed into oil baths that were maintained at the indicated temperatures by conventional hot plates.

Table I. Observed Chemical Shifts and Coupling Constants for the Mononuclear Boron Halides[a]

compd	$\delta(^{19}F)$, ppm[b]	$\delta(^{11}B)$, ppm[c]	$^1J_{BF}$, Hz
BCl_3		47.1 (s)	
BCl_2F	49 (q)	32.7 (d)	74
$BClF_2$	2 (q)	20.7 (t)	33
BF_3	−51 (q)	10.8 (q)	15

[a] In $CFCl_3$, δ = 76.4 ppm.[12] [b] vs exernal CF_3CO_2H. [c] vs external $BF_3{\cdot}OEt_2$.

Table II. Reaction of BCl_3 with Excess $CFCl_3$: Relative Amounts of Boron Trihalides[a]

		amt, %			
temp, °C	time, h	BCl_3	BCl_2F	$BClF_2$	BF_3
65	0	100	0	0	0
65	105	86	14	0	0
65	151	85	8	7	0
65	283	81	9	9	1
130	4[b]	61	13	12	14
130	21[b]	0	0	18	82
130	33[b]	0	0	11	89

[a] Relative amounts of chlorofluoroboranes obtained from integration of boron NMR resonances. [b] Reaction maintained at 65 °C for 283 h and then raised to 130 °C for time indicated.

Unless otherwise stated, the reactions in which the products were separated were contained in vessels that were 70–100 mm in length made from Pyrex tubing 15–20 mm in diameter. These reactors, which were equipped with small magnetic stirring bars, could be attached to vacuum lines by 18/9 ball joints and then evacuated through 4-mm vacuum valves. The maximum pressure was ca. 5 atm.

Fluorination of Trihaloboranes. Spectroscopic Examination of the Reaction between BCl_3 and $CFCl_3$. The interaction of BCl_3 (0.048 41 g, 0.4132 mmol) with $CFCl_3$ (0.8862 g, 6.452 mmol) was monitored by boron-11 and fluorine-19 NMR.[12] During the first 283 h the temperature was held at 65 °C and thereafter at 130 °C. The data obtained from this reaction are summarized in Tables I and II.

Synthesis of BF_3 by Reaction between BCl_3 and $CFBr_3$. When they were heated to 130 °C for 30 h, BCl_3 (84.4 mg, 0.720 mmol) and $CFBr_3$ (719.9 mg, 2.66 mmol) generated BF_3 (48.0 mg 0.708 mmol) in 98% yield based upon BCl_3. After fractionation, the product was identified by ^{19}F and ^{11}B NMR and by mass spectrometry.

Synthesis of BF_3 by Reaction of BBr_3 with $CFBr_3$. Boron tribromide (0.2594 g, 1.035 mmol) and $CFBr_3$ (2.569 g, 9.489 mmol) were sealed together and heated to 130 °C for 30 h. Separation at −160 °C yielded 68.3 mg (1.007 mmol) of BF_3, which had been formed in 97% yield.

Synthesis of BF_3 by Reaction of BCl_3 with $Hg(CF_3)_2$. After $Hg(CF_3)_2$ (0.278 g, 0.821 mmol) was placed into a reactor under N_2, the vessel was evacuated and then BCl_3 (0.112 g, 0.956 mmol) was condensed above the mercurial. With vigorous stirring, the reactor contents were allowed to warm to ambient temperature. After 35 min the reactor was cooled to 0 °C and all material volatile at that temperature was removed to the vacuum line and separated.

Fractionation of the products at −160 °C yielded 64.1 mg (0.95 mmol) of BF_3, which was thus obtained in 99% yield. The identity of the fluoride was confirmed by ^{11}B and ^{19}F NMR spectra and then by mass spectrometry. One other volatile species was present, but under these conditions it was formed in amounts much too small to isolate and identify.

Synthesis of BF_3 by Reaction between BBr_3 and $Hg(CF_3)_2$. Under nitrogen $Hg(CF_3)_2$ (0.3756 g, 1.109 mmol) was added to a reactor of the type described above and, after evacuation, BBr_3 (0.1427 g, 0.569 mmol) was vacuum-distilled onto the mercurial. After it was warmed to ambient temperature, the mixture was stirred for 60 min and then separated. Boron trifluoride (0.038 g, 0.56 mmol) was recovered in 98% yield and identified by boron and fluorine NMR.

Spectroscopic Examination of the Interaction between BF_3 and CCl_4. Carbon tetrachloride (0.3795 g, 2.467 mmol) and BF_3 (19.4 mg, 0.286

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Table III. Observed Chemical Shifts and Approximate Coupling Constants for the Diboron Tetrahalides[a]

compd	δ(F), ppm[b]	δ(B), ppm[b]	*J*, Hz
BF_2BF_2	26.6	23.8	...
BF_2BClF	21.7	~24	~120
BF_2BCl_2	17.8	~24.5	~135
$BClFBF_2$	73.4	~41.7	~120
$BClFBClF$	68.0	~42.6	...
$BClFBCl_2$	64.6	~43.5	~140
BCl_2BF_2	...	~62.5	
BCl_2BClF	...	~62.8	
BCl_2BCl_2	...	63.0	...

[a] Fluorocarbon ^{13}C data: CCl_4, 97.5 ppm; CBr_4, −28.1 ppm; CBr_3Cl, 6.1 ppm; $CFBr_3$, 47.2 ppm, J_{CF} = 374 Hz. Fluorocarbon ^{19}F data: $CFBr_3$, 84 ppm; $CFCl_3$, 76.6 ppm.[12] [b] Positive chemical shifts deshielded from the external references CF_3CO_2H and $BF_3{\cdot}OEt_2$. Chemical shift values ($CFCl_3$) refer to the boron or fluorine nucleus listed *first* in the formulas.

Table IV. Products of the Reactions between Excess $CFCl_3$ and B_2Cl_4 at 65, 90, and 130 °C: Relative Amounts of Diboron Tetrahalides[a]

	amt, %					
time, h	Cl_2BBX_2[b]	$ClFBBX_2$[c]	F_2BBX_2[d]	BCl_3	BF_3	B_nCl_n
			Reaction at 65 °C			
0	98[e]	0	0	2	0	0
15	82	3	9	1	5	*f*
105	61	9	24	0	6	*f*
151	44	7	42	0	7	*f*
283	25	10	51	0	9	ca. 5[f]
597	0	0	81[g]	0	10	9[h]
			Reaction at 90 °C			
0	99[e]	0	0	1	0	0
2	85	4	9	1	1	*f*
5.5	81	5	9	1	1	ca. 3[f]
61	0	0	81[g]	0	11	8[i]
			Reaction at 130 °C			
0	99[e]	0	0	1	0	0
4	35	11	42	0	12	*f*
21	0	0	80[g]	0	10	10[j]

[a] Table values correspond to the integrated areas of the ^{11}B resonances expressed as a percentage of the whole. [b] Because of overlap, areas from the italic boron atoms integrated together: *B*Cl$_2$*B*Cl$_2$, BClF*B*Cl$_2$, BF$_2$*B*Cl$_2$ (see Results and Discussion). [c] Because of overlap, areas from the underlined boron atoms integrated together: BCl$_2$*B*ClF, *B*ClF*B*ClF, BF$_2$*B*ClF (see Results and Discussion). [d] Because of overlap, areas from the underlined boron atoms integrated together: BCl$_2$*B*F$_2$, BClF*B*F$_2$, *B*F$_2$*B*F$_2$ (see Results and Discussion). [e] B_2Cl_4 only. [f] Resonance intensities obscured by the resonance of B_2Cl_4. [g] B_2F_4 only. [h] B_8Cl_8 (65.6 ppm), 6%; $B_{10}Cl_{10}$ (64.1 ppm), 2%; B_9Cl_9 (58.9 ppm), 1%. [i] B_8Cl_8, 6%; $B_{10}Cl_{10}$, 1%; B_9Cl_9, 1%. [j] B_8Cl_8, 5%; $B_{10}Cl_{10}$, 4%; B_9Cl_9, 2%.

mmol) were sealed into a Pyrex tube that, except for periodic spectroscopic examination, was held at 130 °C for a total of 360 h. The course of this interaction was followed by both ^{11}B and ^{19}F NMR. The resonances of BF_2Cl, $BFCl_2$, and BCl_3 were never observed.

Fluorination of Diboron Tetrahalides. Spectroscopic Examinations of the Reaction between B_2Cl_4 and $CFCl_3$. At 65 °C. Diboron tetrachloride (0.101 61 g, 0.6217 mmol) and an 11-fold excess of $CFCl_3$ (0.948 15 g, 6.9031 mmol) were condensed into a 4-mm tube, which was then sealed. The initial boron spectrum indicated the presence of B_2Cl_4 (98%) and BCl_3 (2%) only. The vessel was then heated to 65 °C and the progress of the reaction monitored by ^{11}B NMR after 15, 105, 151, 283, and 597 h. The results obtained from these spectra are collected in Tables III and IV. During the course of the reaction, the initially clear colorless solution first became a dark green liquid containing black solids (14 h) and then, after 105 h, became opaque and even darker in color.

After 105 h ^{19}F NMR indicated the following relative molar concentrations for the diboron tetrahalides: B_2F_4 (100), BF_2BClF (50), BF_2BCl_2 (245), $BClFBClF$ (5), and $BClFBCl_2$ (108). After 151 h the indicated relative concentrations for the diboron tetrahalides were as follows: B_2F_4 (100), BF_2BClF (33), BF_2BCl_2 (152), $BClFBClF$ (8), and $BClFBCl_2$ (58). After 597 h, the only fluoroboranes observed in the ^{19}F spectrum were B_2F_4 and BF_3, then present in the molar ratio 78:22. Fluorine NMR chemical shift data for the diboron tetrahalides are collected in Table III. All of the ^{19}F resonances of the fluorinated diboron tetrahalides are very broad, and BF coupling is not resolvable under the spectroscopic conditions employed.

At 90 °C. Diboron tetrachloride (ca. 0.5 mmol) and a 10-fold excess of $CFCl_3$ were sealed together. The initial boron NMR spectra demonstrated that only B_2Cl_4 (99%) and BCl_3 (1%) were present. The vessel was heated to 90 °C, and ^{11}B spectra were obtained after 2, 5.5, and 61 h. The results from these spectra are displayed in Tables III and IV. After 2 h the initially clear, colorless solution had become green with a small band of purple sublimate above the liquid. After the completion of the reaction (61 h) the solution was very dark green with black solids dispersed throughout.

The reactor was opened, and the more volatile components were partially separated by fractionation. The presence of CCl_4, which is retained at −95 °C was confirmed by ^{13}C spectra (δ = 97.5 ppm). The boron NMR spectrum of the fraction that passed through a trap held at −95 °C but was retained at −160 °C contained only one resonance, that at 23.9 ppm (B_2F_4), but there were two resonances in the fluorine NMR spectrum, at 76.2 ppm ($CFCl_3$) and 26.2 ppm (B_2F_4). Only one resonance, that due to BF_3, was observed in the ^{11}B and ^{19}F NMR spectra that were obtained from the fraction that passed through a −160 °C bath.

A large excess of fresh $CFCl_3$ was added to the less volatile components, and the reactor was resealed and then heated to 190 °C. The cluster compounds B_8Cl_8 and $B_{10}Cl_{10}$ (see Table IV) decomposed, but B_9Cl_9 did not. The only new resonance detected by boron NMR was that of BF_3.

At 130 °C. Boron NMR spectra of a solution composed of B_2Cl_4 (0.094 09 g, 0.5757 mmol) and $CFCl_3$ (1.080 68 g, 7.857 mmol) indicated that the ratio of B_2Cl_4 to BCl_3 was 99:1. The reagents were heated to 130 °C and the contents of the reactor examined by boron NMR after 4 and 21 h (see Tables III and IV).

At the conclusion of this reaction, the vessel was opened and the CCl_4 that had formed (0.331 69 g, 2.1563 mmol) was identified by ^{13}C NMR (97.6 ppm).

Synthesis of B_2F_4 from the Reaction of B_2Cl_4 with $CFBr_3$. After 2.5 h at 130 °C, a boron NMR spectrum of the solution obtained from mixing B_2Cl_4 (0.082 53 g, 0.5050 mmol) with $CFBr_3$ (2 g) contained only the resonances of B_2F_4 and BF_3. Diboron tetrafluoride (0.043 77 g, 0.4484 mmol) was isolated by fractionations at −160 and −95 °C. On the basis of the amount of B_2Cl_4 taken, B_2F_4 was formed in 89% yield in this reaction. The CBr_3Cl recovered was identified by ^{13}C NMR (see Table III).

Synthesis of B_2F_4 by Reaction of B_2Br_4 with $CFBr_3$. The ambient-temperature reaction between B_2Br_4 (0.3857 g, 1.130 mmol) and $CFBr_3$ (2.8637 g, 10.577 mmol) was carried out in an NMR tube, and the progress was monitored by ^{11}B and ^{19}F NMR. After 45 min, the ^{11}B spectrum obtained from the then orange solution indicated the presence of B_2Br_4 (69.5 ppm, 77%), BBr_3 (38.7 ppm, 1%), BF_3 (10.2 ppm, 3%), and a broad resonance in the B_2F_4 chemical shift region (23.2 ppm, 19%). After 3.75 h, in addition to the small absorptions arising from BF_3 (7%) and BBr_3 (2%), the ^{11}B spectrum contained a very small resonance at 59.4 ppm, assigned to B_9Br_9 (2%), as well as very broad resonances in the B_2F_4 (39%) and the B_2Br_4 (50%) regions of the spectrum. The ^{19}F spectrum contained only two resonances, one at 27 ppm (25%) and a broad singlet at 17 ppm (12%) in addition to the resonances of $CFBr_3$ (48%) and BF_3 (15%). After 9.75 h at ambient temperature, in addition to those of B_2F_4 (81%) and BF_3 (13.5%), the boron-11 NMR spectrum contained four deshielded resonances, at 66.2 ppm (2%), 64.2 ppm (1%), 58.3 ppm (1.5%), and 53.6 ppm (1%). The presence of CBr_4 (−28 ppm) was demonstrated by ^{13}C NMR.

The reactor was attached to the vacuum line and the contents removed, fractionated, and identified. Diboron tetrafluoride (0.086 25 g, 0.8836 mmol) was isolated in 78% yield.

Synthesis of B_2F_4 by Reaction between B_2Cl_4 and $Hg(CF_3)_2$. Under N_2 $Hg(CF_3)_2$ (0.4657 g, 1.375 mmol) was added to a reactor; then, at −196 °C, B_2Cl_4 (0.1037 g, 0.635 mmol) was frozen above the fluorinating agent. With constant, vigorous stirring the vessel was allowed to slowly warm to ambient temperature. After 60 min at room temperature, the mixture was separated by fractionation. Diboron tetrafluoride (0.0553 g, 0.567 mmol) was isolated in 89% yield.

Reactions with Larger Boranes. Spectroscopic Examination of the Interaction between B_4Cl_4 and $(CF_3)_2Hg$. Equimolar amounts of B_4Cl_4 and $(CF_3)_2Hg$ were dissolved in CCl_4; then the vessel was maintained at ambient temperature for 30 days. No evidence for reaction was obtained.

Spectroscopic Examination of the Reaction of B_4Cl_4 with $CFCl_3$. Upon mixing, all of the B_4Cl_4 (0.026 11 g, 0.1411 mmol) dissolved completely in $CFCl_3$ (0.6799 g, 4.949 mmol), resulting in a clear, very light green solution. The sample was heated to 65 °C for a total of 283 h, to 130 °C for 33 h, to 160 °C for 19 h, and finally, to 190 °C for 4 h. At the

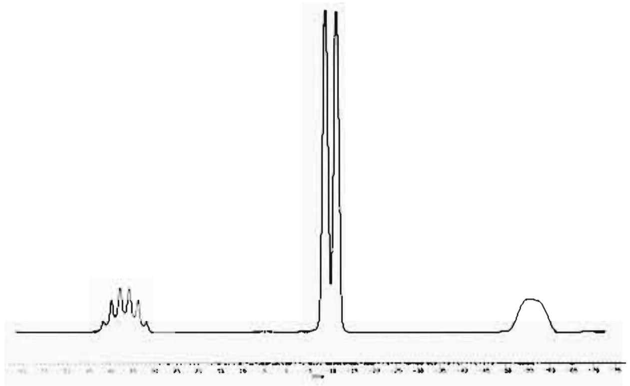

Figure 1. Boron-11 NMR spectrum of $BF_2B_5H_8$ in CH_2Cl_2.

end of this period the physical appearance of the sample was unaltered, although boron and fluorine spectra, which had been taken periodically throughout the reaction, did indicate the presence of a small amount of BF_3 (<10%) in addition to the B_4Cl_4.

After 46 h at 205 °C, however, the sample was drastically altered. An opaque black solid covered the lower walls of the sample tube, and the liquid portion of the sample was dark orange, with flecks of black solid dispersed throughout. Additionally, a small band of yellow material was present immediately above the liquid. Boron NMR contained the resonances of BF_3 (10.7 ppm, 48%), a broad singlet (58.8 ppm, 27%), and B_2F_4 (23.8 ppm, 12%) as well as a triplet (26.6 ppm, $J_{BF} \approx 61$ Hz, 11%) and a very small singlet (54.4 ppm, 2%). The fluorine NMR spectrum was dominated by the resonance of $CFCl_3$ (85%), but BF_3 (−53.4 ppm, 8%), B_2F_4 (26.7 ppm, 2%), CF_2Cl_2 (69.6 ppm, 1%), and CF_3Cl (48 ppm, 0.3%) were also present. Several other small resonances (<1%), one of which was a 1:1:1:1 quartet ($J_{BF} = 61$ Hz) located at 11.7 ppm, were also observed.

Spectroscopic Examination of the Reaction of 1-$BBr_2B_5H_8$ and $CFCl_3$. Trichlorofluoromethane, ca. 3 mmol, and 1-$BBr_2B_5H_8$, ca. 2 mmol, were heated to 65 °C for 4 h. Approximately 25% of the dibromide decomposed with the formation of B_5H_9, BBr_3, BF_3, and a yellow precipitate, but there was no ^{11}B evidence for the formation of $BF_2B_5H_8$.

Synthesis of 1-$BF_2B_5H_8$ by Reaction of $BCl_2B_5H_8$ with $Hg(CF_3)_2$. Bis(trifluoromethyl)mercury (0.4287 g, 1.266 mmol) was placed into a reactor, which was then evacuated. After the addition of 1-$BCl_2B_5H_8$ (0.1709 g, 1.189 mmol), the reactor contents were allowed to warm with vigorous stirring. Forty-five minutes later, the volatile components of the vessel were removed and separated. The major boron-containing product was 1-$BF_2B_5H_8$, a clear colorless liquid that passes through traps held at −45 °C but is retained at −78 °C.

This new compound was identified by mass spectrometry and ^{11}B, ^{19}F, and ^1H NMR. Low-resolution mass spectrum, based upon ^{11}B, (mass (m/e), ion, abundance): 112, $F_2{}^{11}B_6H_8$, 14%; 93, $F^{11}B_6H_8$, 4.5%; 62, $^{11}B_5H_7$, 100%; 49, $F_2{}^{11}B$, 59%. All of these ions exhibited the mass envelopes anticipated from the natural abundances of ^{10}B and ^{11}B. In particular there was a sharp cutoff at m/e 112, which corresponds to the highest mass of the $BF_2B_5H_8$ molecular ion. Ions corresponding to $B_5H_8^+$ were unobserved. Exact mass determination: calcd for $F_2{}^{10}B^{11}B_5H_8$, 111.1188; measd, 111.1181; $\Delta m/m$, 6.3 ppm.

Boron-11 spectra of the new compound $BF_2B_5H_8$ in methylene chloride (see Figure 1) contain three resonances, an apparent sextet at 35.2 ppm (apparent $J \approx 129$ Hz) from the BF_2 boron, which is coupled to both the fluorine atoms and the apical boron of the cage, a large doublet at −10.1 ppm ($J_{BH} = 167$ Hz) from the basal borons of the cage, and a very broad resonance at −57.1 ppm from the apex boron. The fluorine spectrum contains only one broad resonance, centered at 37.2 ppm; coupling is evident but is unresolved. The ^1H spectra contain two resonances, the first a quartet at 2.49 ppm ($J_{BH} = 167$ Hz) and the second a broad featureless resonance at −2.23 ppm. On the basis of the chloride taken, the amount of $BF_2B_5H_8$ isolated (0.1269 g, 1.144 mmol) corresponds to a 96% yield.

Mass spectrometric examination of the material that remained in the reactor after the removal of the volatile components and residual $Hg(CF_3)_2$ indicated, among others, molecular ions corresponding to $Hg(CCl_3)_2$ and $HgC_2Cl_3F_3$. Neither C_2F_4 nor c-C_3F_6 were observed to have been products of this reaction.

Results and Discussion

Reactions of the Boron Trihalides. As shown in Table II, the initial spectroscopic examination of the interaction between $CFCl_3$ and BCl_3 demonstrated that this reaction does indeed generate chlorofluoroboranes even at temperatures as low as 65 °C. However, the data contained in Table II also clearly indicate that at 65 °C this reaction is far too slow to serve as a viable preparative route to BF_3 since, even after 283 h at that temperature, the formation of boron trifluoride occurs to only a very modest extent, ca. 1%. When the temperature of the mixture was raised to 130 °C, however, BF_3 was produced readily, and after 33 h, boron NMR indicated that approximately 90% of the boron atoms in the mixture were present as BF_3.

Table V. Isolated Yields of Fluorinated Boranes

reagents	conditions	product	yield, %
$CFBr_3 + BCl_3$	30 h, 130 °C	BF_3	98
$CFBr_3 + BBr_3$	30 h, 130 °C	BF_3	97
$CFBr_3 + B_2Cl_4$	2.5 h, 130 °C	B_2F_4	89
$CFBr_3 + B_2Br_4$	9.8 h, 23 °C	B_2F_4	78
$CFCl_3 + BBr_2B_5H_8$	4 h, 65 °C		
$Hg(CF_3)_2 + BCl_3$	0.6 h, 23 °C	BF_3	99
$Hg(CF_3)_2 + BBr_3$	1 h, 23 °C	BF_3	98
$Hg(CF_3)_2 + B_2Cl_4$	1 h, 23 °C	B_2F_4	89
$Hg(CF_3)_2 + B_4Cl_4$	30 days, 23 °C		
$Hg(CF_3)_2 + BCl_2B_5H_8$	0.8 h, 23 °C	$BF_2B_5H_8$	96

Additionally, the results from the 65 °C reaction (Table II) suggest that the second ligand-exchange reaction, the one that results in $BClF_2$, may proceed more readily than the first interchange, that which forms BCl_2F. Both appear to have smaller activation energies than the reaction that generates BF_3. From the data presented here, it is, of course, not possible to evaluate the extent to which disproportionation reactions between the haloboranes contribute to the formation of BF_3.

In order to examine the possibility that the equilibrium constants for the reactions between the carbon-bonded halides and the boron-bonded halides could be evaluated by NMR techniques, the mixture formed when BF_3 had been dissolved in CCl_4 was studied at 130 °C. Under these conditions, however, no evidence for the transformation of BF_3 into, e.g., BF_2Cl was obtained.

As shown in Table V, in which the results obtained during this study are assembled, the reactions of either BBr_3 or BCl_3 at 130 °C with the alternative fluoromethane, $CFBr_3$, resulted in BF_3, which was isolated in excellent yields, 97–98%. In that a higher yield of BF_3 was obtained during a shorter period, the brominated Freon $CFBr_3$ appears to fluorinate BCl_3 more effectively than $CFCl_3$.

The third reagent examined here, $Hg(CF_3)_2$, has previously been shown to act as a trifluoromethylating agent toward some substrates but as a fluorinating agent toward others. For example, $Hg(CF_3)_2$ and AsI_3 form $As(CF_3)_3$ in 75% yield,[13] but the reaction between $Hg(CF_3)_2$ and $SiBr_4$ results in the fluoride SiF_4 instead.[14]

Only one product, BF_3, was generated in amounts sufficient for characterization during the ambient-temperature reactions of the boron trihalides and $Hg(CF_3)_2$ examined here. Given the diagonal relationship between boron and silicon in the periodic table, it is perhaps not surprising that $Hg(CF_3)_2$ reacts with both of their halides (both hard acids) to give the same type of product. Overall, the mercurial is clearly a much more reactive reagent toward the boron trihalides BCl_3 and BBr_3 than either $CFCl_3$ or $CFBr_3$.

Reactions of the Diboron Tetrahalides. There are two competitive reactions that occur during the exposure of B_2Cl_4 and B_2Br_4 to either $CFCl_3$ or $CFBr_3$. The first of these is the thermal decomposition of the diboron tetrahalide to generate polynuclear boron monohalides, cluster compounds of the generic formulation B_nX_n (X = Br, Cl; n = 8–10), along with the appropriate boron trihalide. The last is eventually fluorinated to form BF_3. In each of the reactions with $CFCl_3$ or $CFBr_3$ examined here, 10–20% of the tetrahalodiborane was consumed by this disproportionation, which can be loosely represented as shown in eq 1.[7]

$$nB_2X_4 \rightarrow nBX_3 + B_nX_n \qquad X = \text{Br, Cl};\ n = 8\text{–}10 \qquad (1)$$

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Although $B_{11}Cl_{11}$ and $B_{12}Cl_{12}$ were occasionally observed during the very early stages of the B_2Cl_4 reactions that were carried out at lower temperatures, they were not present in significant amounts at the conclusion of any of the experiments. The chemical shifts and the relative amounts of the boron monohalides formed are all in accord with the results from previous examinations of the thermal reactions of B_2Cl_4 and B_2Br_4.[7,8,15,16]

Fluorinated clusters of the type B_nF_n have yet to be described. Only one boron resonance in the spectral region of interest, that found at 54 ppm in the reaction of B_2Br_4 with $CFBr_3$, could not be assigned. The identity of this compound is currently under investigation.

The remaining 80–90% of the diboron tetrahalide taken initially appears to have been fluorinated quantitatively, as shown in eq 2. No evidence for boron–boron bond cleavages by reactions of

$$B_2X_4 + 4CFX_3 \rightarrow B_2F_4 + 4CX_4 \qquad (2)$$

$$B_2X_4 + CFX_3 \rightarrow BFX_2 + BX_2CX_3 \qquad (3)$$

the type portrayed in eq 3 was obtained.

In the experiment between B_2Cl_4 and $CFCl_3$ that was carried out at 130 °C, the amount of CCl_4 that was recovered corresponded to 99% of that required by the stoichiometries of the fluorination reactions that had occurred.

Overall, as shown in Tables IV and V, B_2F_4 is formed in very good yields (80–90%) from the reactions of either $CFCl_3$ or $CFBr_3$ with B_2Cl_4 and in 78% yield from the interaction of B_2Br_4 with $CFBr_3$. Because the reactions of $CFBr_3$ are faster than those of $CFCl_3$, 2.5 h at 130 °C vs 21 h at 130 °C for the fluorination of B_2Cl_4, for example, and because the product separation is much more easily accomplished, $CFBr_3$ is currently the reagent of choice for the preparation of B_2F_4. An alternative is the reaction of $Hg(CF_3)_2$ with B_2Cl_4, which within 1 h generates B_2F_4 in 89% yield.

By way of comparison, the original preparation of B_2F_4 from B_2Cl_4 called for two separate exposures of the diboron tetrahalide(s) to freshly sublimed portions of SbF_3, the mixture to be held at −80 °C overnight in each case.[1] A second synthesis of B_2F_4, obtained in 90% yield, calls for the interaction of B_2Cl_4 with a 25-fold molar excess of SbF_3, the mixture to be held at −80 °C for 1 week with occasional shaking of the reactor to break up the surface of the solid reagent by means of the small glass beads that had previously been introduced for that purpose.[17]

Nuclear Magnetic Resonance. Two effects of the substitution of fluorine for chlorine in the boron trihalides are apparent in the fluorine NMR data contained in Table I. The first is that the fluorine resonance is more shielded. For example, the ^{19}F chemical shift of $BClF_2$ is 47 ppm less than that of BCl_2F. The second effect is that the magnitude of J_{BF} decreases by ca. 20–40 Hz.

The first of these effects is also apparent in the fluorine NMR spectra obtained from the diboron tetrachloride reactions (Table III). There are five fluorine-containing diboron tetrachloride derivatives possible: B_2Cl_3F, 1,2-$B_2Cl_2F_2$, 1,1-$B_2Cl_2F_2$, B_2ClF_3, and B_2F_4. All five are observed to form during the course of the reaction. The first, second, and fourth of these derivatives contain BClF subunits and the last three BF_2 subunits. There are three resonances each in the 65–73 and the 18–27 ppm chemical shift ranges of the experimental spectra. The first of these chemical shift regions contains the resonances of the fluorine atoms that are found in the BClF groups, the second, which contains the resonances of the fluorine atoms in BF_2 groups, is more shielded by ca. 50 ppm, a difference in chemical shift that is very similar to that found in the chlorofluoroboranes (Table I).

Within the broader chemical shift regions, the chemical shifts of the individual compounds were most easily assigned by observing the relative peak intensities as a function of reaction time. Overall, the substitution of chlorine by fluorine on the adjacent boron atom deshields the resonance of a fluorine atom attached to the first boron atom by 4–5 ppm (see Table III).

Although B–F coupling is anticipated for the mixed diboron tetrahalides, all of the resonances of the boron-bonded fluorine atoms were very broad and boron–fluorine coupling was obscured, presumably by relaxation effects. Collectively, the fluorine NMR data indicate that the first substitution of a fluorine atom into a BCl_2 group activates that portion of the molecule toward further substitution. Thus, the ratio of the BCl_2BF_2 to BClFBClF concentrations is on the order of 20:1 during the reaction and not the 1:1 relationship that would be expected from random substitution of B_2Cl_3F. This is also the reason that the amount of BF_2BCl_2 exceeds the amount of $BClFBCl_2$ present even relatively early in the reaction. This conclusion is amply confirmed from the ^{11}B spectra by comparing the values of the entries in the third column of Table IV with the much larger values found in both columns 2 and 4. In all three columns X is either Cl or F.

The fluorine NMR data from the ambient-temperature reaction between B_2Br_4 and $CFBr_3$ indicate that mixed-ligand species of the type $BrFBBX_2$ (X = Br, F) are present in even lesser relative concentrations in this system. Only two fluorine-containing diboron compounds, B_2F_4 (δ = 27 ppm) and BF_2BBr_2 (δ = 17 ppm), were observed by fluorine NMR, and no concrete evidence for intermediates containing BBrF groups was obtained by either fluorine or boron NMR. As in the reactions of the boron trihalides, the extent to which ligand redistribution reactions among the boranes contribute to the amount of the various products that are observed cannot be reliably separated from the contributions of the fluoroalkane reagents.

Like the ^{19}F chemical shifts, the ^{11}B chemical shifts of the chloro fluoro diboron tetrahalides fall into distinct chemical shift regions (see Table III). Here there are three regions, one near 63 ppm (that arises from the boron atoms with two chlorine atoms attached), the second near 42.5 ppm (from those with one Cl and one F), and the third near 23 ppm (contributed by the boron atoms that are directly bonded to two fluorine atoms).

In contrast to the fluorine spectra, however, the resonances within each chemical shift region are not discrete in the ^{11}B NMR spectra since (at 64 MHz) the differences in chemical shift are not larger than the coupling constants. For example, in the boron NMR spectra, the resonances of the BClF groups of $BClFBCl_2$ and $BClFBF_2$, $\delta \approx 43$ ppm, often overlapped to form an apparent asymmetric quintet, $J \approx 140$ Hz. One practical result of this overlap is that the intensities of the resonances from the different diboranes in the mixture cannot be integrated separately; thus, it is the combined intensities of the resonances from all of the boron atoms containing the same two halogen ligands that has been entered in Table IV.

The chemical shifts in Table III were assigned by examining the spectra as a function of reaction time. As was the case with the boron trihalides, increasing the number of fluorine atoms on the boron atom observed decreases the chemical shift. Similarly, increasing the number of fluorine atoms on the adjacent boron atom appears to decrease the chemical shift, but only by a very small amount.

Reactions of the Larger Boranes. Tetraboron Tetrachloride. Even though the framework of B_4Cl_4 is bonded by only 8 framework electrons rather than the 12 that are usually associated with tetrahedral cluster geometry,[18] tetrachlorotetraborane is by far the least reactive of the perhaloboranes examined here. The exceptional inertness of the B–Cl bonds in B_4Cl_4 is clearly demonstrated by the facts that B_4Cl_4 alone does not react with $Hg(CF_3)_2$ at ambient temperature and that only B_4Cl_4 must be heated to over 200 °C before significant reaction with $CFCl_3$ occurs.

Five products containing boron are formed in the latter reaction. The chemical shifts of three of the five products correspond to those of BF_3, B_2F_4, and B_9Cl_9. The identities of the remaining two are under investigation, but the spectral properties of the species that is produced in larger amount (11%) are consistent with those expected from BF_2CCl_3 (cf. Table I). The chemical

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shift (54 ppm) of the compound that is formed in smallest amount (2%) is very similar to that of one of the products of the reaction between B_2Br_4 and $CFBr_3$ that is discussed above.

There are a few ligand-exchange reactions of B_4Cl_4, such as those of the lithium alkyls, in which the tetraboron framework does stay intact,[19] but more commonly the reactions of B_4Cl_4 results in cage fragmentation, often generating mono- and diboranes that are related to those found in the $CFCl_3$ reaction. In the reaction of B_4Cl_4 with $HNMe_2$, for instance, $B(NMe_2)_3$ (50%), $B_2Cl_4{\cdot}2HNMe_2$ (25%), and $B_2Cl_2(NMe_2)_2$ (25%) are the major products observed.[20] Similarly, the reactions of B_4Cl_4 with the halogens Cl_2 and Br_2 result in the formation of B_2Cl_4 (18%) and B_2Br_4 (14%) along with the boron trihalides.[21]

The most satisfying single explanation for the similarity of the product distributions from these reactions is that all of these reagents initially attack one of the faces of the tetraboron tetrahedron, rather than one of the relatively inert B–Cl bonds; thus, the product similarities in these reactions primarily reflect the manner by which B_4Cl_4 fragments. Given the results from the halogenation reactions above, at 200 °C $CFCl_3$ might well be expected to react with B_4Cl_4, resulting in fluoroboranes, BF_2CCl_3, and B_9Cl_9, the last presumably resulting from the partial thermal decomposition of the diboron tetrahalide formed as one of the initial products of the cage fragmentation.

(Dihaloboryl)pentaboranes. As discussed in the Introduction, the bonding in 1-$BCl_2B_5H_8$ and 1-$BBr_2B_5H_8$ is a composite of almost all of the different types that are commonly found in boron hydride chemistry. Fluorination with $Hg(CF_3)_2$ proceeded smoothly to generate the previously unknown $BF_2B_5H_8$ in excellent yields, 96%, an indication that B–H bonds, the pentaborane cage, and B–B single bonds are all essentially unaffected by $Hg(CF_3)_2$ under these conditions.

Both the absence of C_2F_4 and c-C_3F_6 and the mass spectrometric results from the mercurials formed during the reaction are supportive of direct fluorination of the boron–chlorine bonds as the primary means by which the boron–fluorine bonds are formed. The properties of the product $BF_2B_5H_8$ will be commented upon separately,[10] but to the extent that this reaction of $BCl_2B_5H_8$ with $Hg(CF_3)_2$ can be taken as a test of the effectiveness of these new flourinating agents, it appears that on the scale employed here $Hg(CF_3)_2$ has performed quite well.

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Synthesis and Coordination Properties of Bis(bis(pentafluoroethyl)phosphino)ethane

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The efficient synthesis of $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe) by direct alkylation of $Cl_2PCH_2CH_2PCl_2$ with C_2F_5Li at −95 °C is described. Thermal substitution reactions of dfepe and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) with $M(CO)_6$ (M = Cr, Mo, W) gave high yields of the corresponding tetracarbonyls $(\overset{\frown}{PP})M(CO)_4$ ($\overset{\frown}{PP}$ = dfppe, M = Cr, Mo, W; $\overset{\frown}{PP}$ = dfepe, M = Cr, Mo). The reaction of dfepe with *fac*-$Mo(EtCN)_3(CO)_3$ afforded *fac*-Mo(dfepe)(EtCN)$(CO)_3$. From a literature comparison of (dfepe)$Mo(CO)_4$ IR ν(CO) data with those of a range of analogous phosphine derivatives, it is concluded that dfepe rivals fluorophosphines in π-acceptor strength. Cone angle estimates for dfepe give a value of 123°, comparable to that of $Ph_2PCH_2CH_2PPh_2$ and significantly greater than typical cone angle values for fluorophosphines.

Introduction

The development of new π-acceptor ligands and their associated coordination chemistry remain a conspicuous challenge to inorganic and organometallic chemists. In contrast to donor ligand classes such as PR_3, OR, and NR_2 (R = alkyl, aryl, amide, alkoxide, etc.), which have a wide range of accessible steric and electronic properties,[1] prototypical π-acceptor ligands (CO, NO, PF_3) lack suitable "handles" for modification. King[2] and Nixon[3] have noted in particular the absence of potentially chelating acceptor ligands and have examined the chemistry of heteroatom-bridged fluorophosphines, $RN(PF_2)_2$, with a variety of metal systems. Although these chelates efficiently displace carbon monoxide in many cases, the susceptibility of P–F and P–N bonds toward cleavage side reactions limits their general application as innocent spectator ligands. Other examples of substituted fluorophosphine ligands that have been reported include $F_2P(C_6H_{10})PF_2$, $F_2PCX_2CX_2PF_2$ (X = H, F),[4] and $(Y)_xPF_{3-x}$ (x = 1, 2; Y = Me, Pr, CF_3, Me_2N, $NC(CF_3)_2CO$).[5] It is noteworthy that the coordination chemistry of these ligands remains essentially undeveloped.

A potentially useful class of π-acceptor ligands that has received little attention is that of fluoroalkyl-substituted phosphines, $(R_f)_xPR_{3-x}$. Replacement of fluorine with inductively similar fluoroalkyl groups maintains the acceptor character of the phosphorus center while providing a means for steric control. Additionally, P–R_f bonds are considerably more inert than P–F bonds and should support applications where reactive, electron-deficient metal centers are generated.[6] Some time ago, Burg reported the synthesis of the fluoroalkyl-substituted phosphine chelates $(CF_3)_2PCX_2CX_2P(CF_3)_2$ (X = H, F).[7] Although these ligands were demonstrated to be strong π-acceptors, practical

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