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Reactivity of the Diboron Tetrahalides. Diboration of Ethylene with Diboron Tetrabromide and Thermal Decomposition and Ligand Exchanges of Diboron Tetrabromide and Diboron Tetrachloride in Carbon Tetrabromide and Carbon Tetrachloride

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In contrast to previous assertions, we find that B_2Br_4 reacts readily with ethylene to generate $BBr_2CH_2CH_2BBr_2$, which can be isolated in 95% yield. While it has been reported numerous times that the disproportionation of B_2Cl_4, which eventually yields BCl_3 and the polyhedral boron halides B_nX_n ($n = 8$–12), is slowed by the addition of haloalkenes, we have found that the disproportionation rate of both B_2Cl_4 and B_2Br_4 is also significantly decreased by the addition of the haloalkanes CBr_4 and CCl_4. For example, in the presence of a 7-fold excess of CBr_4, the amount of B_2Br_4 recovered after 198 h at 96 °C corresponded to 65% of that originally present. Although less dramatic, significant retardation of the B_2Cl_4 and B_2Br_4 disproportionations has also been observed when CCl_4 was added. These results are interpreted in terms of the transient formation of (dihaloboryl)alkanes, a proposal that is buttressed by the observation of $C(BBr_2)_4$ and partially chlorinated (dihaloboryl)methanes like $C(BBrCl)_4$ which were identified by mass spectrometry. The reaction between B_2Br_4 and excess CCl_4 generates B_2Cl_4 in 84% yield, but the interaction of B_2Cl_4 with excess CBr_4 does not appear to be an effective route to B_2Br_4.

Introduction

There were several interrelated aspects of diboron tetrahalide chemistry that led to the present study. Two of these arose from a recently completed review of the diboron tetrahalide literature.[1] The first was that while B_2Cl_4 has been widely reported to add across the double bond in ethylene much more quickly (ca. 100 times faster) than B_2F_4,[2] B_2Br_4 has been stated to be inert and the lack of reaction attributed to the staggered ground state of B_2Br_4 in the liquid phase.[3] The second was that it has been frequently observed that the disproportionation of B_2Cl_4 is markedly slowed by the presence of haloalkenes[2,4,5] and these findings have been rationalized by postulating an intermolecular interaction between the unoccupied π orbital of B_2Cl_4 and the filled π orbital of the haloalkene.[4] That the apparent stabilization is not merely a dilution effect was examined by adding hexane or C_2H_5Cl to B_2Cl_4, which reportedly did not result in a dramatic reduction of the B_2Cl_4 disproportionation rate.[5]

Another consideration was derived from our previous diboron tetrahalide studies in which we found that, in the absence of added solvent, B_2Br_4 begins to darken within minutes at ambient temperature and that after ca. 5 min BBr_3 is clearly evident in the ^{11}B NMR spectrum. After only 1 h at 100 °C, samples that had originally contained neat B_2Br_4 were essentially completely decomposed to BBr_3 and the B_nBr_n ($n = 7$–10) clusters.[6] Undiluted B_2Cl_4 is more thermally stable than B_2Br_4 in that ca. 16 h at 100 °C is required for the disproportionation to proceed to completion; the products consist of BCl_3 and the polyhedral boron chlorides B_nCl_n ($n = 8$–12).[7] When B_2Cl_4 was diluted with CCl_4 (80% by weight) and the mixture heated to 100 °C, however, the polyhedral boron halides isolated consisted almost entirely of B_8Cl_8 (88%) accompanied by only a small amount of B_9Cl_9 (5%).[8] On the basis of the last observation, it seemed entirely plausible that if B_2Br_4 were to be diluted with CBr_4, the thermal reaction could well result primarily in the formation of BBr_3 and B_8Br_8.

The final consideration was based upon our recent examination of the fluorination of bromo- and chloroboranes with $Hg(CF_3)_2$, $CFBr_3$, and $CFCl_3$.[9] The reactivity of these reagents varies in the order $Hg(CF_3)_2 > CFBr_3 > CFCl_3$, and the bromoboranes are significantly more reactive than the chloroboranes. For example, the reaction between B_2Cl_4 and $CFCl_3$ required 61 h at 90 °C to generate B_2F_4 (81%), but B_2Br_4 was converted to B_2F_4 (78%) by $CFBr_3$ after only 10 h at ambient temperature. Additionally, although BF_3 (89%) was easily formed from BCl_3 and $CFCl_3$ at 130 °C, even after 336 h at 130 °C no evidence for ligand exchange between CCl_4 and BF_3 was obtained.[9] These results suggest that exchange reactions between bromoboranes and chlorocarbons might effectively generate chloroboranes but that reactions designed to provide bromoboranes from the interactions of chloroborane and bromocarbon species should be far less efficient.

The initial objectives of the current study were to reinvestigate the claim that B_2Br_4 does not add across the double bond of ethylene, to determine if the thermolysis of B_2Br_4 diluted with CBr_4 results in the generation of essentially only one polyhedral boron bromide, and to acertain whether ligand exchanges between bromoboranes and chloroalkanes (or chloroboranes and bromoalkanes) appear to be synthetically useful strategies.

Experimental Section

General Procedures. Unless otherwise stated, all manipulations were carried out in the absence of air and moisture using either standard high-vacuum lines that are equipped with Teflon valves or a Vacuum Atmospheres HE-43-2 glovebox. Halocarbon wax (Halocarbon Products) was used for all connections to the vacuum line. ^{11}B, ^{13}C, and ^{1}H NMR spectra were obtained from samples sealed into 4-mm Pyrex tubing and inserted into standard 10-mm NMR tubes into which the lock solvent, DMSO-d_6 (high-temperature spectra) or D_2O (ambient-temperature spectra), had previously been placed. They were recorded by either a Bruker AM-400 (128 MHz for ^{11}B) or an IBM 200SY (64 MHz for ^{11}B) instrument; positive chemical shifts are deshielded from the reference,[10] external $BF_3{\cdot}OEt_2$ (^{11}B) or TMS (^{13}C and ^{1}H). The mass spectra, m/e 50–500, of samples derived from the $BBr_2CH_2CH_2BBr_2$ study were obtained from an HP 5985A instrument; those from the CBr_4 or CCl_4 reactions are from an AEI MS-30 instrument operating with the source at ambient temperature. Samples were introduced into the latter through the gas-inlet system or with a solids probe that was surrounded by a nitrogen-filled glovebag.

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(10) The chemical shifts of the lock solvent and the observed nucleus are both temperature dependent. During this study, the net effect was that the apparent ^{11}B and ^{13}C chemical shifts of compounds measured from spectra acquired at high temperature are deshielded by ca. 1–2 ppm from those acquired at ambient temperature.

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Table I. Mass Spectral Data for $BCl_2CH_2CH_2BCl_2$ and $BBr_2CH_2CH_2BBr_2$[a]

ion	mass range calcd	mass range obsd	most intense ion	% abund
	$BCl_2CH_2CH_2BCl_2$[b]			
$BCl_2CH_2CH_2BCl_2$	188–198			
$BCl_2CH_2CH_2BCl$	153–161	153–161	155	100.0
BCl_2	80–85	80–85	81	14.1
BC_2H_nCl ($n = 2–4$)	71–76	71–76	73	38.1
BCH_nCl ($n = 1, 2$)	58–62	58–62	60	6.1
	$BBr_2CH_2CH_2BBr_2$[c]			
$BBr_2CH_2CH_2BBr_2$	364–374			
$BBr_2CH_2CH_2BBr$	285–293	285–293	289	100.0
$B_2C_2H_3Br_2$	205–211	205–211	209	4.5
BBr_2	168–173	168–173	171	28.4
BC_2H_nBr ($n = 2–4$)	115–120	115–120	117	72.2
BCH_2Br	103–106	103–106	104	12.7
HBBr	90–93	90–93	91	20.6
Br/HBr	79–82	79–82	81	8.3

[a] Data, m/e 50–500, were acquired by the HP 5985A (quadrupole) spectrometer with the 70-eV source at 200 °C. All of the intensities within each ion envelope were as expected. [b] All ions of greater than 0.5% intensity were reported. [c] Ions indicative of the hydrolysis of the more reactive tetrabromide within the spectrometer were observed in the spectra. These ions, e.g., $BBr_2CH_2CH_2BOH$ and $BBrCH_2CH_2B$-OH, have been omitted from the table.

Diboron tetrachloride,[7] B_2Br_4,[6,11] and 1,2-bis(dichloroboryl)ethane[12] were synthesized, separated, and characterized as previously described. Ethylene (Matheson) was fractionated at −160 °C prior to use. Carbon tetrachloride was dried over P_4O_{10}; CBr_4, mp 92 °C, was sublimed under vacuum and then finely ground.

Synthesis of 1,2-Bis(dibromoboryl)ethane by Reaction of Ethylene with Diboron Tetrabromide. Ethylene, 0.1238 g (4.41 mmol), and B_2Br_4, 0.7116 g (2.085 mmol), were sequentially condensed into a 20 × 100 mm Pyrex reactor that had been equipped with a small Teflon-covered stirring bar, and the valve was closed. The mixture was slowly warmed, and the transparent, colorless solution formed was stirred at ambient temperature for 3 days. At the conclusion of the experiment, the reactor was opened and the components of the mixture that were volatile at 0 °C were removed under vacuum. The residual was transported to the glovebox and weighed, and samples were removed for analysis.

The observed NMR chemical shifts of the product, $BBr_2CH_2CH_2BBr_2$, were $\delta(^{11}B)$ 64.2 ppm (broad), $\delta(^{13}C)$ 33.7 ppm, (broad), and $\delta(^1H)$ 1.15 ppm (broad). No other resonances were present in any of the spectra. The ion envelope of highest mass was centered at m/e 289 with sharp cutoffs at m/e 293 ($^{11}B_2{}^{81}Br_3C_2H_4{}^+$) and 285 ($^{10}B_2{}^{79}Br_3C_2H_4{}^+$). The other ions observed in the spectrum are contained in Table I. The isolated yield of $BBr_2CH_2CH_2BBr_2$ was 0.733 g (1.98 mmol), 95.2% on the basis of the diboron tetrabromide taken.

Alternative Synthesis of $BBr_2CH_2CH_2BBr_2$ by Ligand Exchange of 1,2-$(BCl_2)_2C_2H_4$ with Excess BBr_3. 1,2-Bis(dichloroboryl)ethane ($\delta(^{11}B)$ 63.3 ppm (br), $\delta(^{13}C)$ 26 ppm (br), $\delta(^1H)$ 1.62 ppm (br);[13] mass spectrum contained in Table I), 0.1919 g (1.002 mmol), and BBr_3, 1.5378 g (6.138 mmol), were sequentially condensed into the reactor described above and stirred for 72 h while being maintained at 0 °C. The volatile products resulting were slowly removed from the vessel (which was still held at 0 °C) and then fractionated. The trihaloboranes BCl_3 (46.7 ppm), $BBrCl_2$ (45.1 ppm), BBr_2Cl (42.6 ppm), and BBr_3 (39.1 ppm) all passed through a trap cooled to −45 °C whereas unreacted $BCl_2CH_2CH_2BCl_2$ was retained. The residual, that which was not volatile at 0 °C, 0.2670 g (0.723 mmol), was characterized as above and shown to be $BBr_2CH_2CH_2BBr_2$ by a combination of NMR and mass spectrometry. The properties of the $BBr_2CH_2CH_2BBr_2$ prepared by ligand exchange were identical to those of the compound synthesized by the interaction of B_2Br_4 with ethylene. The yield was 72% on the basis of the amount of $BCl_2CH_2CH_2BCl_2$ taken and 85% on the basis of that consumed.

Interaction of Diboron Tetrabromide with Carbon Tetrabromide. Carbon tetrabromide, 2.198 g (6.63 mmol), was added to a reactor 4 mm in diameter which was then evacuated, and B_2Br_4, 0.343 g (1.01 mmol), was vacuum-distilled into the vessel. The reactor was sealed. The ambient-temperature ^{11}B NMR spectrum of the clear, colorless solution contained only one resonance (69.0 ppm). The reagents were then heated in an oil bath to 96 °C for 5.75 h, after which the 96 °C ^{11}B NMR spectrum of the clear orange-green solution was characterized by a large resonance at 71.1 ppm (B_2Br_4, 87.5%), a medium-sized resonance at 40.3 ppm (BBr_3, 8.6%), and smaller resonances at 53.3 (2.6%), 43.7 (0.3%), and 38.6 (1.0%) ppm. After a further 192 h at 96 °C, in addition to the largest resonance at 70.9 ppm (B_2Br_4), the 96 °C spectrum of the then orange and black solid-containing slurry consisted of very small resonances at 66.0 ($B_{10}Br_{10}$), 61.2 (B_9Br_9), 53.2 (4%), and 43.7 (2%) ppm along with the BBr_3 resonance located at 40.2 ppm (18%). The reactor was opened, and the volatile products were separated. The amount of B_2Br_4 recovered, 0.656 mmol, corresponded to 65% of that originally taken, and when held at ambient temperature, the originally clear, colorless solution darkened within minutes.

Mass spectra of the fraction retained at −30 °C contained molecular ions arising from CBr_4, C_2Br_4, and C_3Br_6 and the fragmentation products expected from these compounds. The mass spectra from the nonvolatile portion of the reaction mixture contained the molecular ions of $B_{10}Br_{10}$ (25.8%), B_9Br_9 (57.7%), B_8Br_8 (100%), B_7Br_7 (13.8%), and B_6Br_6 (7.1%) along with M − Br, M − BBr_3, and M − $2BBr_3$ ions for each of these compounds. These spectra also contained ions not inconsistent with the presence of small amounts of carboranes among the products, e.g., m/e 1001 (3.1%), 921 (6.4%), and 681 (56.1%), ions that can most readily be assigned to $C_2B_9Br_{11}{}^+$, $C_2B_9Br_{10}{}^+$, and $C_2B_9Br_7{}^+$, respectively. They also contained ion envelopes centered at m/e 616 (13.4%), 445 (2.5%), and 365 (8.4%), ions that arise from $CB_4Br_7{}^+$, $CB_3Br_5{}^+$, and $CB_3Br_4{}^+$. The amount of the last compound present, however, was insufficient for further characterization. The ion envelopes of each of the observed cations were as expected from the isotopic abundances of bromine, boron, and carbon.

Interaction of Diboron Tetrabromide with Carbon Tetrachloride. Diboron tetrabromide, 0.319 g (0.93 mmol), and CCl_4, 1.098 g (7.14 mmol), were condensed into an evacuated 4-mm reactor which was then sealed. Initially, the ^{11}B NMR spectrum of the sample contained a single resonance at 69.9 ppm, but after the vessel had been maintained at 100 °C for 9.75 h, the spectrum consisted of four broad, overlapping resonances centered at 67.9, 66.4, 64.7, and 62.7 ppm, which contained 89% of the total intensity of the spectrum, a very broad, small resonance at 52.1 ppm, and the resonances of BCl_3, 46.8 ppm (5.5%), $BBrCl_2$, 45.2 ppm (4.5%), and BBr_2Cl, 42.6 ppm (1.3%). The reactor, which contained a clear green solution and a very small amount of black solids, was then returned to the 100 °C oil bath for an additional 12.5 h, after which the ^{11}B NMR spectrum contained only three resonances: 62.6 ppm (predominantly B_2Cl_4), 85.2%; 52.1 ppm, 1.5%; 46.8 ppm (BCl_3), 13.3% (see Figure 1). After 63 days at 0 °C, the spectrum of the sample was unchanged, save for the appearance of very small resonances (less than 0.5% each) at 92.4, 78.7, 67.5, 58.1, 53.1, and 49.9 ppm.

In a similar reaction, B_2Br_4, 1.08 mmol, and CCl_4, 10.16 mmol, were sealed together and heated to 96 °C for 20.5 h; ^{13}C NMR spectroscopy of the products indicated the presence of CBr_3Cl (5.4 ppm), CBr_2Cl_2 (37.9 ppm), and $CBrCl_3$ (68.4 ppm) as well as CCl_4 (97.0 ppm). The reactor was opened and the boron trihalide and diboron tetrahalide fraction removed and identified by ^{11}B NMR spectroscopy. Although B_2Cl_4 can be separated from CCl_4 by fractionation, to ensure an accurate value, B_2Cl_4 was hydrolyzed with water. The amount of B_2Cl_4 present corresponded to an 84.2% yield. In addition to confirming the generation of BCl_3 (m/e 115–122) and B_2Cl_4 (m/e 160–170), mass spectrometry indicated the presence of $B_8Br_nCl_{8-n}$ (n = 0–3) in the fraction that was retained in a vacuum line trap at 0 °C and the presence of $B_{12}Br_nCl_{n-12}$ (n = 7), $B_{11}Br_nCl_{11-n}$ (n = 6, 7), $B_{10}Br_nCl_{10-n}$ (n = 5, 6), and $B_8Br_nCl_{8-n}$ (n = 1–7) among the products that remained in the reactor. Molecular ions and M − X and M − BX_3 (X = Cl or Br) ions were observed for all of the cluster compounds.

Interaction of Diboron Tetrachloride with Carbon Tetrabromide. Freshly sublimed CBr_4, 1.601 g (4.83 mmol), was added to a 4-mm reactor which was evacuated, and then B_2Cl_4, 0.162 g (0.99 mmol) was added. The vessel was sealed and heated to 96 °C for 70 h. The 96 °C ^{11}B NMR spectrum, which had originally contained only a broad singlet at 63.2 ppm, now consisted of four observable overlapping resonances at 69.2, 67.6, 65.8, and 63.9 ppm (35%), resonances near 53 ppm (10%) and 51 ppm (11%), and the four resonances expected from the boron trihalides (42%) (see Figure 2). The ^{13}C NMR spectrum contained the resonances of both CBr_4 and CBr_3Cl; the relative peak height was 11.7:1.0, respectively. After a further 168 h at 96 °C, with the exception of a slight increase in the amount of the boron trihalides present (to ca. 50% of the total intensity of the spectrum) at the expense of the other compounds and the appearance of very small resonances at 70.8 and 59

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(B_9Cl_9) ppm, the ^{11}B NMR spectrum was essentially unchanged.

In a similar reaction, CBr_4 and B_2Cl_4 in a 3:1 mole ratio were sealed together and heated to 97 °C for 73 h. With the exception of very small additional resonances located at 59, 57, and 55 ppm, the ^{11}B NMR spectrum of the resulting mixture was very similar to that shown in Figure 2. This sample was opened, and all of the material that was volatile at 0 °C was removed. Mass spectra (HP5985A) of the residual contained ion envelopes centered at *m/e* 483 ($CB_4Br_4Cl_3^+$) 9.5%, 438 ($CB_4Br_3Cl_4^+$) 23.9%, 394 ($CB_4Br_2Cl_5^+$) 33.4%, 348 ($CB_4BrCl_6^+$) 21.3%, 355 ($CB_3Br_3Cl_2$) 15.6%, 311 ($CB_3Br_2Cl_3^+$) 31.2%, and 267 (CB_3BrCl_4) 29.0%. The base peak of the spectrum was located at *m/e* 127 ($BBrCl^+$); no masses higher than the envelope associated with $CB_4Br_4Cl_3^+$ were observed.

Results and Discussion

Synthesis of 1,2-Bis(dibromoboryl)ethane. As originally described by Schlesinger[12] and later by others, the reaction of B_2Cl_4 with excess ethylene proceeds smoothly to afford $BCl_2CH_2CH_2BCl_2$ in high yield. Given the alacrity with which B_2Cl_4 reacts with ethylene, we were surprised to find that B_2Br_4 has been reported to be inert.[3] While it is true that the ground state of B_2Br_4 in the liquid phase has been reported to be nonplanar,[13] the same is also true of B_2Cl_4.[14] The rotational barriers of the two molecules have been evaluated from electron diffraction results, which indicate that they differ by only ca. 1.2 kcal/mol. To us at least, this small difference appeared unlikely to preclude ethylene diboration by B_2Br_4.

Diboron tetrabromide and C_2H_4 were found to react vigorously, and the clear, colorless product resulting, $BBr_2CH_2CH_2BBr_2$, was isolated in very high yield (95%). In order to further confirm the identity of the product, the tetrabromide was also prepared by ligand exchange between the chloride and BBr_3; the properties of the material obtained from the latter synthesis were identical to those from the B_2Br_4/C_2H_4 route. Although 1,2-bis(dibromoboryl)ethane does move through a standard vacuum line very slowly, it is retained in a trap held at 0 °C; thus quantitative transfer is difficult. The compound fumes in air, especially moist air, but ^{11}B NMR spectra that were obtained from samples sealed in Pyrex tubes and maintained at ambient temperature for 8 months indicated no decomposition.

The reported ^{11}B chemical shift of $C_2H_5BCl_2$ is 63.4 ppm, while that of $C_2H_5BBr_2$ is 65.5 ppm.[15] These values are reasonably consistent with the ^{11}B shifts of $BCl_2CH_2CH_2BCl_2$[16] and $BBr_2CH_2CH_2BBr_2$ measured here, 63.3 and 64.2 ppm, respectively.

The breadth of the $BCl_2CH_2CH_2BCl_2$ ^{13}C resonance is the most probable reason that this chemical shift had not been previously reported.[17] Very broad ^{13}C resonances for other alkylboranes, e.g., $B_4(t\text{-Bu})_4$,[18] have been recently discussed.[19] The ^{13}C chemical shift of the bromide, 34 ppm, is 8 ppm deshielded from that of the chloride, which is presumably primarily the result of anisotropic effects.[20] All of the $BBr_2CH_2CH_2BBr_2$ resonances are very broad, e.g., ca. 207 Hz for the ^{11}B resonance, 4.4 Hz for the ^1H signal, and 164 Hz for the ^{13}C peak.

One of the more interesting aspects of the $BCl_2CH_2CH_2BCl_2$ data is the mass spectrum. As indicated in Table I, molecular ions are not observed (less than 0.3%) and the spectrum is dominated by the M − Cl ions. The most reasonable interpretation of these results is that, upon formation, the molecular ions cyclize with the concomitant loss of Cl; thus the majority of the M − Cl ions are sufficiently stable to survive transit through the flight tube. Similar behavior of *n*-alkyl halides, especially chlorides and bromides, has been discussed by Mc Lafferty.[21] The mass spectrum of $BBr_2CH_2CH_2BBr_2$ (Table I) is very reminiscent of that of the tetrachloride. For example, molecular ions were not observed at 70 eV and the most intense ions in the spectrum correspond to M − Br. In separate experiments that were carried out with the mass spectrometer source held at 13 eV, no evidence for the molecular ions was obtained.

The B_2Br_4/CBr_4 Interaction. By far the most dramatic effect of the CBr_4 addition to B_2Br_4 is that the disproportionation reaction is nearly quenched. Comparisons with the spectra that were published as part of the original study of the undiluted B_2Br_4 thermal reaction[6] show that, after 198 h at 96 °C in the presence of excess CBr_4, the disproportionation has proceeded to approximately the extent of the reaction of neat B_2Br_4 after 6 h at ambient temperature and not nearly as far as that of B_2Br_4 after only 1 h at 100 °C (see Figures 3 and 4 in ref 6). Even after 198 h at 96 °C, the amount of B_2Br_4 recovered corresponded to 65% of that originally taken whereas, in the absence of CBr_4, little or no B_2Br_4 remained after 1 h at 100 °C. Once the bromocarbons had been removed from B_2Br_4 by fractionation, however, the disproportionation proceeded normally.

Mass spectrometry of the cluster products obtained from the B_2Br_4/CBr_4 reaction examined here does indicate that the relative amount of B_8Br_8 is larger than that produced from B_2Br_4 in the absence of CBr_4, that small amounts of C_2Br_4 and C_3Br_6 are generated, and that perhalocarboranes like $C_2B_9Br_{11}$ (*m/e* 1001) are formed in low yield. The monocarbon ions $CB_4Br_7^+$ (*m/e* 616), $CB_3Br_5^+$ (*m/e* 444), and $CB_3Br_4^+$ (*m/e* 365) are further discussed below.

The B_2Br_4/CCl_4 Interaction. As discussed above, in the absence of added solvent, neither B_2Br_4 nor B_2Cl_4 is thermally stable; both are essentially completely decomposed after 16 h at 100 °C. When B_2Br_4 was dissolved in CCl_4, however, the ^{11}B NMR spectra demonstrate that over the course of 22 h at 100 °C, the major reaction is the conversion of B_2Br_4 into B_2Cl_4. Although the intermediate diboron tetrahalides, $B_2Br_nCl_{4-n}$, the compounds with the chemical shifts in the 62.7–67.9 ppm range, are evident after 9.75 h at 100 °C, at the conclusion of the reaction the only products observed by ^{11}B NMR spectroscopy are B_2Cl_4, BCl_3 (13%), and a small amount of the species responsible for the resonance near 52 ppm, 1.5% (see Figure 1). Both the NMR data and the confirmatory hydrolysis results indicate that B_2Cl_4 is formed in ca. 84% yield. This appears to be the first reaction in which the conversion of B_2Br_4 into B_2Cl_4 in high yield has been demonstrated.

Overall, this reaction is very similar in kind to that previously reported between B_2Cl_4 or B_2Br_4 and $CFCl_3$ or $CFBr_3$.[9] In both cases, the predominant products arise from halogen interchange between the boron and the carbon species present in the solution. As was found for the interchange of fluorine for chlorine or bromine, the equilibrium favors the formation of the products in which the smaller, more electronegative halide is bonded to boron rather than carbon.

The final ^{11}B NMR spectrum, which was obtained after a further 63 days at 0 °C, contains very small resonances that correspond in chemical shift to $B_{12}Cl_{12}$, $B_{11}Cl_{11}$, and $B_{10}Cl_{10}$. In general, this spectrum is very like that typically obtained from undiluted B_2Cl_4 after 3 or 4 days at ambient temperature; thus, like the CBr_4 addition above, the addition of CCl_4 to B_2Br_4 has strongly retarded the rate at which the disproportionation of the diboron tetrahalide occurs.

The mass spectra, which were obtained during the intermediate portions of the reaction (when the mixed $B_2Br_nCl_{4-n}$ species were present), contained molecular ions as well as M − X and M − BX_3

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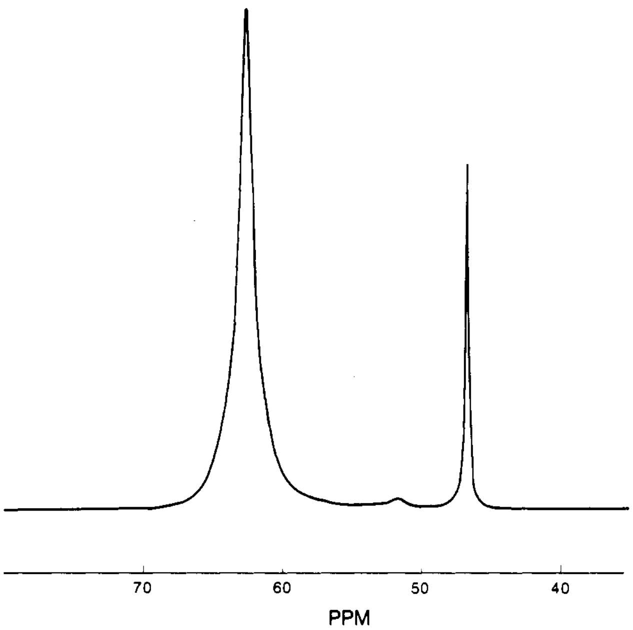

Figure 1. Ambient-temperature ^{11}B NMR spectrum of B_2Br_4 dissolved in a 7-fold excess of CCl_4 after 22 h at 100 °C. Note that the B_2Br_4 originally present and any BBr_3 formed have been completely converted to the chlorides B_2Cl_4, 62.7 ppm, and BCl_3, 46.8 ppm. The resonance at 52 ppm is ascribed to a $C(BX_2)_4$ species; see text.

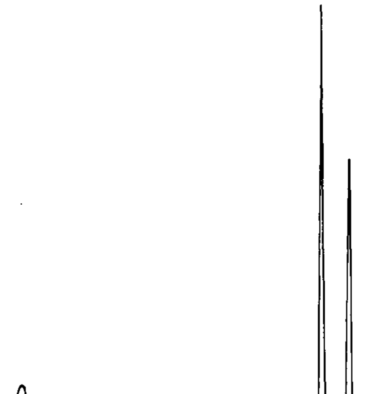

Figure 2. 96 °C ^{11}B NMR spectrum of B_2Cl_4 in a 5-fold excess of CBr_4 after 70 h at 96 °C. The spectrum of this sample after an additional 168 h at 96 °C was essentially unchanged. The most deshielded resonances, 60–70 ppm, are from the B_2X_4 mixed halides, the most shielded, 40–50 ppm, are from the boron trihalides, and the resonances of intermediate chemical shift, 50–55 ppm, are assigned to (dihaloboryl)methanes; see text.

ions that could be readily assigned to the $B_{12}X_{12}$, $B_{11}X_{11}$, $B_{10}X_{10}$, and B_8X_8 (X = Br, Cl) mixed-halide clusters, the products expected from the disproportionation of the mixed tetrahalodiboranes, but no unequivocal evidence for monocarbon ions of the type $CB_4X_7^+$, $CB_3X_5^+$, or $CB_3X_4^+$ was obtained.

The B_2Cl_4/CBr_4 Interaction. The ^{11}B and ^{13}C spectra that were obtained from the sample after 70 and 238 h at 96 °C (see Figure 2) were essentially identical, which is consistent with the interpretation that the system is at or near equilibrium with respect to halide interchange. The ^{13}C data indicate that, on the average, considerably less than one bromine ligand has been transferred to B_2Cl_4; that is, the equilibrium constant for reactions like $B_2Cl_4 + CBr_4 \rightarrow B_2BrCl_3 + CBr_3Cl$ is less than 1.

Equilibria between the monoboron trihalides BCl_3 and BBr_3 are characterized by nearly random distribution of the ligands, and the dynamics of the exchange process have been examined by ^{11}B 2-D EXSY spectroscopy.[22] Ritter and Coyle,[23] however, have shown that, in the equilibria between boron trihalides and diboron tetrahalides, reactions between species like BCl_3 and B_2F_4, the distribution of the boron–halide bonds is not random but favors the formation of the boron trihalide in which boron is bonded to the more electronegative halogen. In fact, the initial synthesis of B_2Br_4 from BBr_3 and B_2Cl_4[11] utilized just this type of halogen exchange. The combination of the B_2Br_4/CCl_4 and B_2Cl_4/CBr_4 reactions examined here in conjunction with the B_2Cl_4/CBr_3F and B_2Br_4/CBr_3F reactions reported earlier[9] clearly establishes that the equilibria favor the products in which the more electronegative halogen is bonded to boron rather than carbon.

In this experiment, the addition of the haloalkane CBr_4 to B_2Cl_4 has also significantly prolonged the apparent lifetime of the diboron tetrahalides, since the ^{11}B NMR spectra indicate that ca. one-third of the diboron tetrahalide initially present remained even after 238 h at 96 °C. The stabilization of diboron tetrahalides afforded by the interaction of B_2Cl_4 and chlorocarbons has not been explicitly addressed here, but as shown by the figure in ref 8, significant amounts of B_2Cl_4 remain in CCl_4 after 14 d at 100 °C. Additional evidence for chloroalkane stabilization of B_2Cl_4 can be found in Ritter, Coyle, and Bellama's study,[5] which indicates that at ambient temperature the initial decomposition rate of B_2Cl_4 in CH_3CH_2Cl is only about 75% of that found for B_2Cl_4 in hexane.

Proposed Mechanism for Diboron Tetrahalide Stabilization by Haloalkanes. The mechanism that has been previously proposed for the disproportionation of the diboron tetrahalides invokes equilibria in which a BX group (X = Cl, Br) is transferred from one B_2X_4 molecule to another, yielding BX_3 and B_3X_5 in the first step. Subsequent reactions of the type $B_2X_4 + B_3X_5 \leftrightarrow BX_3 + B_4X_6$ are then followed by cluster formation.[1,24] Neither B_3X_5 nor B_4X_6 is sufficiently stable for isolation, and their concentration in solution is thought to be very small.

If, however, a haloalkane is introduced into the diboron tetrahalide solution, a second type of equilibrium, one that involves BX insertions into CX bonds, becomes possible. The products anticipated from the initial BCl and BBr insertions into CCl_4 and CBr_4 are $C(BCl_2)Cl_3$ and $C(BBr_2)Br_3$, respectively.

Stone has reported the synthesis of several (dichloroboryl)chloromethanes, among them $C(BCl_2)_2Cl_2$ ($\delta(^{11}B)$ 53.1 ppm) and $C(BCl_2)_3Cl$ ($\delta(^{11}B)$ 54.1 ppm) from the reactions of BCl_3 or B_2Cl_4 with the products of a carbon arc; $C(BCl_2)Cl_3$ was not isolated. Both $C(BCl_2)_2Cl_2$ and $C(BCl_2)_3Cl$ were shown to be thermally unstable above −20 °C,[25] and presumably $C(BCl_2)Cl_3$ is also of limited thermal stability. The observation that the disproportionations of both B_2Cl_4 and B_2Br_4 are much slower in, e.g., large excesses of CBr_4 is thus ascribed to equilibria like $B_2Br_4 + CBr_4 \leftrightarrow BBr_3 + C(BBr_2)Br_3$, reactions in which the excess haloalkane acts to sequester much of the BBr generated, which dramatically reduces the rate at which the diboron tetrahalide disproportionation occurs.

Mass spectrometry of the nonvolatile products formed during the B_2Br_4/CBr_4 reaction does indicate the presence of the B_nBr_n clusters, but in addition to these expected products the mass spectra also contain M − Br, M − BBr_3, and CB_4Br_4 ions that are assigned to $C(BBr_2)_4$. Like both $BCl_2CH_2CH_2BCl_2$ and $BBr_2CH_2CH_2BBr_2$, the molecular ions of the noncluster $C(BBr_2)_4$ molecule were not observed. The resonance found at 53.2 ppm[10] in the ^{11}B NMR spectrum is also ascribed $C(BBr_2)_4$.

Similarly, the mass spectra obtained from the B_2Br_4/CCl_4 reaction contain ions arising from the bromochloroboron mono-

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[23] Ritter, J. J.; Coyle, T. D. *J. Chem. Soc. A* **1970**, 1303.

[24] Morrison, J. A. In *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH Publishers: New York, 1988; p 151.

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halide mixed-ligand clusters B_nX_n and their fragmentation products, while the mass spectra from the B_2Cl_4/CBr_4 reaction were dominated by $M - X$ and $M - BX_3$ ions from the mixed-halide $C(BX_2)_4$ species. At 97 °C. The ^{11}B NMR chemical shifts of the last compounds range from 51 to 59 ppm;[10] see, for example, Figure 2.

The tetrakis(dihaloboryl)methanes are thought to be formed from the carbon tetrahalides by means of sequential BX insertions. The separation and further study of the tetrakis(dihaloboryl)methanes like $C(BBrCl)_4$ have been hampered by the fact that while they appear to be reasonably enduring at ambient temperature in boron trihalide solvents, once the boron trihalide has been removed they begin to decompose. Stone[25] has isolated $C(BCl_2)_4$ ($\delta(^{11}B)$ 57.2 ppm) and shown that it is more stable than the less substituted (dichloroboryl)methanes in that it persists at ambient temperature for extended periods. Tetrakis(dichloroboryl)methane was retained at 0 °C on a low-temperature fractionating column, and no molecular ions were observed in the mass spectrum.[25] Aside from the base peaks, the BCl_2^+ ions, the most abundant peaks in the spectrum were derived from the $M - BCl_3$ ions.[25] These properties, of course, are all consistent with the properties of the $C(BX_2)_4$ compounds observed here.

Overall, the simplest explanation of the currently available data is that the diboron tetrahalides are "stabilized" in haloalkane solutions by equilibria that involve the formation of dihaloboryl ligands from carbon–halogen bonds.[26] The (dihaloboryl)methanes formed, however, are only of moderate stability; thus they act as chemical intermediates, usually regenerating B_2X_4 species by reaction with boron trihalide. Ultimately, however, the much more stable larger polyhedral boron halides and $C(BX_2)_4$ are slowly formed. Under the conditions employed here, the cage compounds are largely the polyhedral boron halides, although small amounts of perhalocarboranes are also generated. Whether the reported stabilization of the diboron tetrahalides by haloalkenes occurs by means of a similar series of reactions or by means of the π complexes previously postulated[4] is currently under investigation.

Acknowledgment. The financial assistance of the National Science Foundation is gratefully acknowledged.

Registry No. $H_2C{=}CH_2$, 74-85-1; B_2Br_4, 14355-29-4; $Br_2B(CH_2)_2BBr_2$, 88870-82-0; $Cl_2B(CH_2)_2BCl_2$, 20816-71-1; BBr_3, 10294-33-4; CBr_4, 558-13-4; CCl_4, 56-23-5; Cl_2BBCl_2, 13701-67-2.

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(26) A radical mechanism is thought to be much less probable than that proposed here, in part because as yet we have no mass spectral or ^{13}C NMR evidence consistent with the presence of, e.g., C_2Cl_6 ($\delta(^{13}C)$ 88 ppm), which would be expected to form in chain termination reactions like $2{\cdot}CCl_3 \rightarrow C_2Cl_6$.

Notes

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Magnetochemistry of the Tetrahaloferrate(III) Ions. 4. Heat Capacity and Magnetic Ordering in Bis[4-chloropyridinium tetrachloroferrate(III)]–4-Chloropyridinium Chloride

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Introduction

The heat capacity of bis[4-bromopyridinium tetrachloroferrate(III)]–4-bromopyridinium chloride, $[4\text{-Br(py)H}]_3Fe_2Cl_9$, was recently presented[1] as part of a comprehensive study of the magnetochemistry of the tetrahaloferrates(III). These compounds are found to be canted antiferromagnets in which the character of the long-range magnetic ordering is dependent on both the nature of the anion $[FeX_4]^-$ (X = Cl, Br, or a mixture of the two) and on chemical substitution in the cation $[4\text{-X(py)H}]^+$ (X = H, Cl, or Br).[2–6] Canted antiferromagnets of iron(III) are not very common, and the systematic rules for their preparation are not at all clear.[7]

The title compound, $[4\text{-Cl(py)H}]_3Fe_2Cl_9$, and its chemical relative $[4\text{-Br(py)H}]_3Fe_2Cl_9$ are isostructural and both undergo long-range magnetic ordering between 2 and 3 K.[2,3] The small difference in the ordering temperatures is due to the chemical substitution, for the substitution of chlorine for bromine makes the cation somewhat smaller without a change in the structure. The iron–iron distance is therefore reduced, and magnetic exchange becomes larger. The critical temperature increases from 2.29 K to 2.69 K upon replacement of the 4-bromo cation with the 4-chloro one. The large cation also enhances short-range interactions since the tetrahaloferrate(III) ions are paired and these pairs are somewhat isolated from each other. Thus, the magnetic heat capacity of $[4\text{-Br(py)H}]_3Fe_2Cl_9$ displays a λ-type phase transition at the critical temperature and an additional broad peak associated with the pairwise short-range ordering phenomenon.[1]

Experimental Section

Single crystals of $[4\text{-Cl(py)H}]_3Fe_2Cl_9$ were synthesized by a procedure that was previously described.[2,3] The single crystals were crushed and pelleted for this experiment. The sample pellet was threaded with about 0.3 g of fine copper wire in order to facilitate rapid thermal equilibrium. To establish thermal contact between the sample pellet and the calorimeter, 0.24 g of Apiezon N grease was spread on the interior of the calorimeter. The mass of the sample was 8.46767 g. Chemical analysis and structural data were previously presented.[2,3]

The heat-capacity measurements were conducted in the adiabatic calorimetric cryostat that is described elsewhere.[1] The pelleted sample was contained in a gold-plated copper calorimeter whose mass was about 6.0 g and whose heat capacity was determined in a separate experiment. Measurements were conducted using the heat-pulse technique. The precision of a single point, which is dependent on the temperature and more importantly on the temperature increments (since $C_p = (\Delta H/\Delta T)$ when C_p is the apparent heat capacity and ΔH and ΔT are the energy input and the temperature change, respectively) is less than 0.1% outside of the transition region. In the transition region where temperature increments were typically less than 0.05 K the experimental precision is somewhat reduced (for the benefit of greater resolution) and the precision of a single point is about 1%. The heat capacity of the empty calorimeter represented no more than 5% of the total heat capacity throughout the experimental region.

Results and Discussion

The molar heat capacity of bis[4-chloropyridinium tetrachloroferrate(III)]–4-chloropyridinium chloride is plotted in Figure 1a,b. A λ-type phase transition associated with the long-range ordering is found at 2.685 K, which may be identified as the critical temperature.

The heat capacity is assumed to consist of lattice and excess contributions. The lattice contribution is the heat capacity due to thermal activation of lattice vibrations when the harmonic

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