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Chemistry of Tetraboron Tetrachloride. Synthesis and Characterization of Tetraboron Tetrabromide (B_4Br_4) and Observation of B_4BrCl_3, $B_4Br_2Cl_2$, and B_4Br_3Cl

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In the absence of added solvent, B_4Cl_4 and BBr_3, present in a 1:5 mole ratio, generated B_4BrCl_3 in approximately 13% yield after 800 h at 95 °C. Repeated exposure of B_4Cl_4 to fresh aliquots of BBr_3 and pentane at 95 °C did ultimately (2200 h) form B_4Br_4 and the mixed ligand species B_4Br_3Cl, $B_4Br_2Cl_2$, and B_4BrCl_3, but the quantities provided were small. The boron-11 NMR data for the bromochlorotetraboranes are consistent with a tetrahedral configuration of the boron atoms rather than a square-planar-based array. In the presence of $AlBr_3$, B_4Br_4 was generated from the interaction of B_4Cl_4 with BBr_3 at 95 °C and isolated in 80% yield. After 144 h at 110 °C, the reaction of B_4Br_4 with excess BCl_3 regenerated B_4Cl_4 in ca. 90% yield.

Introduction

The chemistry of tetraboron tetrachloride has been of considerable interest for many years due in large part to the fact that if the usual electron counting rules[1] are applied to this smallest closo cluster, only eight framework electrons are utilized to bond the boron framework atoms together rather than the twelve that are found in almost all other tetrahedral clusters. The chemistry of B_4Cl_4 has been recently reviewed, and the different types of reactions that have been observed for this smallest cluster compound mapped into seven distinct types.[2] The subject of the present article is a further examination of the first type of reaction reported, ligand exchanges in which the tetrahedral core of the molecule is preserved.

The synthesis of the parent compound, B_4Cl_4, was first disclosed in 1952,[3] and in the normal sequence of events one would have anticipated that other tetrahalides like B_4F_4 and B_4Br_4 might have been prepared shortly thereafter. However, although several ab initio molecular orbital studies[4-6] have indicated that, if prepared, B_4F_4 could well be sufficiently stable to isolate, a variety of experimental investigations designed to fluorinate B_4Cl_4 have all failed to provide any experimental evidence for the monofluoride, B_4Cl_3F, let alone B_4F_4.[7-9]

The reactions of B_4Cl_4 with the potential ligand-exchange reagent BBr_3 have also been examined several times. McHale and Wartik[7] observed the formation of BCl_3 along with the deposition of a red-orange solid but concluded that the solid was most probably a boron chloride and that B_4Br_4 was not present as an isolatable product. Kane and Massey[10] reported that at 20-100 °C, BBr_3 and B_4Cl_4 reacted to form tiny quantities of the volatile B_4BrCl_3 along with traces of $B_4Br_2Cl_2$ in addition to the major product of the reaction, a rustlike involatile solid. The amounts of the bromochlorotetraboranes formed were too small to characterize by means other than mass spectrometry, however, and Kane and Massey concluded that the B_4 cage was not stable when more than two atoms of bromine had been substituted for the chlorine originally present.[10]

Aside from B_4Cl_4, the only reasonably well-characterized compounds reported in which the tetraboron core is thought to have remained in a tetrahedral configuration are the alkyls B_4Cl_3Et, $B_4Cl_2Et_2$, and $B_4(t\text{-}Bu)_4$ which were synthesized by reaction of the appropriate lithium reagent with B_4Cl_4.[11] The objective of the present study was to attempt to determine whether B_4Br_4 was generated from the interaction of B_4Cl_4 with BBr_3 and whether tetraboron tetrabromide could be isolated or if it decomposed upon formation as has been previously suggested.

Table I. ^{11}B NMR Chemical Shifts and Relative Areas of Tetraboron Tetrahalide Resonances[a]

compd	δ(B–Cl)[b]	δ(B–Br)[b]	B–Cl/B–Br rel area[b]
B_4Cl_4	85.2		
B_4BrCl_3[c]	88.0	84.1	3/1
$B_4Br_2Cl_2$[d]	90.8	87.1	2/2
B_4Br_3Cl[e]	93.6	89.8	1/3
B_4Br_4		92.5	

[a] Chemical shifts in ppm; positive shifts deshielded from external $BF_3\cdot OEt_2$. [b] B–Cl refers to chlorine-substituted boron atoms; B–Br refers to bromine-substituted boron atoms. [c] The B–Cl resonance appeared as a quartet broadened by relaxation effects, $J_{^{11}B-^{11}B}$ = ca. 15 Hz. The expected splitting of the B–Br resonance into 10 lines was not resolved. [d] Resonances appeared as greatly broadened singlets; splitting into the expected seven-line pattern was not resolved. [e] The B–Br resonance appeared as a quartet broadened by relaxation effects, $J_{^{11}B-^{11}B}$ = ca. 15 Hz. The expected splitting of the B–Cl resonance into 10 lines was not resolved.

Experimental Section

General Considerations. All manipulations of boron-containing compounds were carried out in a standard vacuum line that is equipped with Teflon valves. Halocarbon wax (Halocarbon Products) was used in all connections to the vacuum line. Boron-11 NMR spectra were recorded on either an IBM 200-SY or a Bruker AM-400 instrument; positive chemical shifts are deshielded from the reference, external BF_3OEt_2. The $^{11}B-^{11}B$ COSY spectra were obtained from the AM-400 instrument utilizing the DISR 87 system software. Commonly, the sweepwidth (SW2) was ca. 10 000 Hz, the relaxation delay was 0.5 s, and 64 transients were collected for each FID. The F_1-F_2 matrices were symmetrized prior to plotting the absolute value spectrum. The mass spectra were obtained from an AEI MS-30 spectrometer that is equipped with a gas inlet system, and the high-resolution mass spectral data were acquired by means of standard peak-matching techniques. Unless otherwise indicated all of the reactions were carried out in sealed 4-mm (o.d.) Pyrex vessels that were approximately 200 mm in length.

Tetraboron tetrachloride was prepared and purified as previously described.[12] BBr_3 (Aldrich) was placed over elemental mercury, the mixture was vigorously shaken, and then it was fractionated. Aluminum tribromide (Aldrich) was sublimed at least three times, the last immediately prior to use. After degassing, pentane was stored over P_4O_{10}.

Reactions of B_4Cl_4 with BBr_3. Mole Ratio 1.0:5.3. Tetraboron tetrachloride, 10.0 mg (0.054 mmol), and BBr_3, 72.0 mg (0.287 mmol), were sealed together and heated to 95 ± 2 °C in an oil bath, and the interaction was then periodically monitored by ^{11}B NMR spectroscopy. After 288 h, a new resonance at 88 ppm (B_4BrCl_3; see Table I) was first observed. During the next 550 h at 95 °C the amount of B_4BrCl_3, relative to the amount of B_4Cl_4 then present slowly increased from 1 to 16%, but simultaneously, the total intensity of the tetraborane resonances decreased by ca. 20% relative to the intensity of the BBr_3 resonance.

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After a total of 837 h at 95 °C, the solution began to darken from the original lime coloration to brown. After 853 h, ^{11}B NMR spectroscopy indicated that the amount of B_4BrCl_3 present was 40% of that of B_4Cl_4, but the total amount of the two compounds corresponded to only ca. 15% of that of the B_4Cl_4 originally taken. After 1000 h at 95 °C, both B_4Cl_4 and B_4BrCl_3 were present in only very small amounts and cage decomposition was clearly indicated by resonances in the 60–70 ppm region of the ^{11}B NMR spectrum. No evidence for the formation of bromotetraboranes more highly substituted than B_4BrCl_3 was obtained during the course of this reaction.

Mole Ratio 1.0:1.1 in the Presence of Pentane. Boron tribromide, 12.0 mg (0.048 mmol), and B_4Cl_4, 7.8 mg (0.042 mmol), were separately condensed into a reactor along with 100 mg of pentane. The vessel was sealed, and the contents were heated to 95 ± 2 °C. After 253 h, the more intense B_4BrCl_3 resonance, 88 ppm, $J_{^{11}B-^{11}B} \sim 15$ Hz, ca. 5% as intense as the B_4Cl_4 resonance, was initially observed. After 1018 h at 95 °C, three broad new resonances, at 91.1 and 87.3 ppm ($B_4Br_2Cl_2$) and at 84.1 ppm (the less intense B_4BrCl_3 resonance), were apparent. The approximate B_4Cl_4:B_4BrCl_3 mole ratio was 1:1, but only a small amount of $B_4Br_2Cl_2$ had formed. During the next 250 h at 95 °C, the resonances at 88 and 84 ppm, which were in the intensity ratio 3.00:0.94, and those at 91 and 87 ppm, present in a 1.03:1.00 intensity ratio, slowly increased in size, relative to the B_4Cl_4 resonance. After 1258 h at 95 °C, the more intense B_4Br_3Cl resonance (89.8 ppm) was first observed. At this point the boron atom connectivity of B_4BrCl_3 and $B_4Br_2Cl_2$ was confirmed by means of standard ^{11}B–^{11}B COSY 2D NMR spectra.

During the next 500 h at 95 °C, except for a decrease (ca. 20%) in the collective intensity of the tetraborane cage resonances relative to the intensity of the BBr_3 resonance, the spectrum was essentially unchanged. As indicated by ^{11}B NMR analysis, after a total of 1760 h, the approximate mole ratios of the tetraboron tetrahalides were B_4Cl_4 (1.00), B_4BrCl_3 (0.99):$B_4Br_2Cl_2$ (0.55):B_4Br_3Cl (0.14). The vessel was then heated to 140 °C for 17 h, but the predominant reaction was cage decomposition.

The reactor was opened, and the tetraboron cage compound fraction was separated. The presence of B_4Cl_4, B_4BrCl_3, and $B_4Br_2Cl_2$ was then demonstrated by the appropriate ions, including the molecular ions, in the mass spectrum, but the identity of B_4Br_3Cl could not be so confirmed. During this reaction, no evidence for the formation of B_4Br_4 was obtained.

Mole Ratio 1.0:1.4 in the Presence of Pentane. Tetraboron tetrachloride, 30.0 mg (0.162 mmol), BBr_3, 57.3 mg (0.229 mmol), and pentane, 94.6 mg (1.31 mmol), were condensed into a reactor which was then sealed, and the vessel contents were heated to 95 ± 2 °C in an oil bath. The appearance of B_4BrCl_3 was first observed by ^{11}B NMR spectroscopy after 213 h, $B_4Br_2Cl_2$ after 1100 h, and B_4Br_3Cl after 1750 h. After 2200 h at 95 °C, a new resonance at 93 ppm, B_4Br_4, 0.3% as intense as that of the B_4Cl_4 then remaining, was located. The reactor was opened, and the boron trihalides and solvent were replaced by fresh BBr_3, 0.288 mmol, and pentane, 1.19 mmol. The reactor was resealed and heated to 95 ± 2 °C for 214 h at which time solids had just begun to precipitate. At this point ^{11}B NMR analysis indicated that the relative amounts of B_4Cl_4 and B_4Br_4 were ca. 3:2, respectively. The BBr_3 and solvent were again replaced, and the mixture was reheated until solids began to form (168 h). Standard ^{11}B–^{11}B COSY experiments were utilized to demonstrate the connectivity of the two B_4Br_3Cl resonances and to confirm the absence of a cross peak associated with the 93 ppm (B_4Br_4) resonance. Peak integration indicated that the approximate relative mole ratios of the tetraboranes were B_4Br_4 (2.5):B_4Br_3Cl (11.6):$B_4Br_2Cl_2$ (14.9):B_4BrCl_3 (8.2):B_4Cl_4 (1.0).

After separation of the tetraboron tetrahalides, 13.0 mg in total, fractional sublimations resulted in enrichment of the less volatile, more highly brominated cage compounds, but complete separation into the components of the mixture was not achieved. Low-resolution mass spectrometry demonstrated the presence of the tetraboranes containing at least one chlorine atom, but the molecular ion of B_4Br_4 was not observed.

Synthesis, Separation, and Properties of Tetraboron Tetrabromide. After a preliminary reaction had been carried out in a sealed tube (see Figure 1), B_4Cl_4 0.019 90 g (0.1075 mmol), $AlBr_3$, 0.195 35 g (0.7324 mmol), and BBr_3, 1.151 00 g (4.594 mmol), were sealed together in an 8 × 100-mm Pyrex reactor that was equipped with a Teflon valve and heated to 95 °C for 13.5 h. Subsequently, the reactor was attached to a vacuum line, opened while the contents were at −196 °C, and then warmed to −41 °C at which time all of the materials that were volatile at that temperature were removed into the line. A further 1.711 85 g (6.8327 mmol) of BBr_3 was added to the residual, and then the reactor was resealed and heated to 95 °C for another 12.5 h. After the vessel had been reopened, it was again maintained at −41 °C until all of the volatile components had been removed. The tetraboron tetrabromide remaining was recovered by allowing the reactor to warm to ambient temperature and fractionating the resulting material at −5 °C. The weight of B_4Br_4 isolated, 0.031 30 g (0.0863 mmol), corresponded to an 80.3% yield.

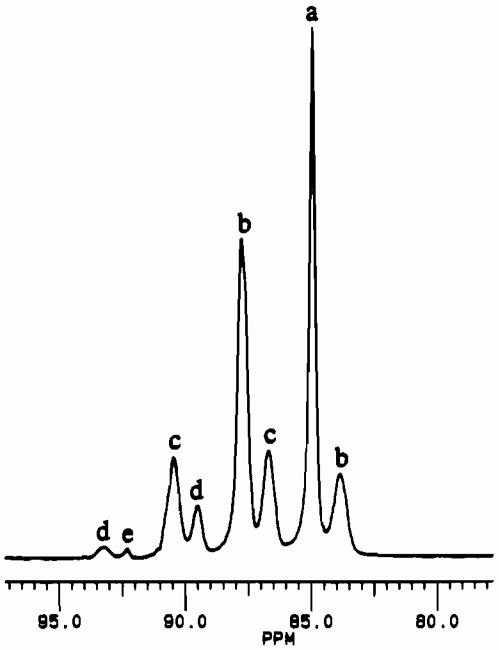

Figure 1. 77–98 ppm region of the ^{11}B NMR spectrum obtained after a sealed sample of B_4Cl_4 (0.05 mmol), BBr_3 (2 mmol), and $AlBr_3$ (0.7 mmol) had been heated to 85 °C for 5.5 h. In this spectrum the resonances of B_4Cl_4 (a), B_4BrCl_3 (b), $B_4Br_2Cl_2$ (c), B_4Br_3Cl (d), and B_4Br_4 (e) are all evident, but the boron–boron coupling of B_4BrCl_3 and B_4Br_3Cl described in the text is not observed. The chemical shift data are located in Table I. As described in the Experimental Section, continued heating of similar samples resulted in the formation of B_4Br_4 which was ultimately isolated in 80% yield.

Table II. Mass Spectral Data for B_4Br_4[a]

m/e[b]	ion	% abundance[b]	m/e[b]	ion	% abundance[b]
364	B_4Br_4	78.6	182	B_2Br_2	32.1
283	B_4Br_3	100.0	171	BBr_2	28.6
272	B_3Br_3	17.9	112	B_3Br	12.5
204	B_4Br_2	7.1	101	B_2Br	14.3
193	B_3Br_2	37.5	90	BBr	14.3

[a] Mass spectrum obtained from MS 30 dual-beam double-focusing instrument, with the 70-eV source operated at ambient temperature. [b] Most intense peak in the ion envelope. In each case the appropriate isotopic abundances were observed.

Tetraboron tetrabromide is a deep yellow solid that very slowly sublimes in a standard vacuum line at ambient temperature. It passes through a trap that has been cooled to −5 °C, but it is insufficiently volatile to move from a vessel held at −41 °C. The apparent melting point of a B_4Br_4 sample that had been sealed in Pyrex tubing was 108 °C dec. In BCl_3 (46.8 ppm) the ^{11}B NMR chemical shift of the compound is 92.5 ppm and the width of the resonance at half-height is 10.5 Hz. The measured exact mass of the m/e 361 peak ($^{10}B^{11}B_3{}^{79}Br_3{}^{81}Br$) was 360.7126; calculated, 360.7121; $\Delta m/m$ = 1.4 ppm. The measured mass of the m/e 365 peak ($^{10}B^{11}B_3{}^{79}Br^{81}Br_3$) was 364.7080; calculated, 364.7081, $\Delta m/m$ = 0.3 ppm. The low-resolution mass spectrum is characterized by M^+, $M - Br^+$, and $M - 2Br^+$ envelopes, among others (see Table II).

Regeneration of B_4Cl_4 from the Reaction of B_4Br_4 with BCl_3. After B_4Br_4, 5 mg (0.01 mmol), and BCl_3, 1.5 g (13 mmol), had been sealed together, maintained at ambient temperature for 48 h, and then exposed to 98 °C for 2 h without a change in the ^{11}B NMR spectrum, they were heated to 110 °C for 24 h at which time the resonances of B_4Br_3Cl (ca. 25% of the total of the B_4 cage compounds present) were evident along with a much smaller resonance near 62 ppm. After a further 24 h at 110 °C, the formation of B_4Cl_4 (17%), B_4BrCl_3 (33%), and $B_4Br_2Cl_2$ (33%) was indicated by the appearance of resonances with the appropriate chemical shifts in the ^{11}B spectrum (see Table I). At that time, however, only relatively small amounts of B_4Br_3Cl (17%) remained and B_4Br_4 was not observed. After 72 h at 110 °C B_4Cl_4 and B_4BrCl_3 were present in a 2:1 mole ratio and after a total of 144 h at 110 °C, although small

Table III. Mass Spectral Data for B_4Cl_4[a]

m/e[b]	ion	% abundance[b]	m/e[b]	ion	% abundance[b]
184	B_4Cl_4	100.0	92	B_2Cl_2	51.9
149	B_4Cl_3	77.8	81	BCl_2	33.3
138	B_3Cl_3	70.4	68	B_3Cl	6.9
113	B_4Cl_2	2.1	57	B_2Cl	12.1
103	B_3Cl_2	40.1	46	BCl	8.3

[a] Mass spectrum obtained from MS 30 dual-beam double-focusing instrument, with the 70-eV source operated at ambient temperature. [b] Most intense peak in the ion envelope. In each case the appropriate isotopic abundances were observed.

resonances near 62 ppm were present along with those of the tricoordinate boron halides (39–46 ppm), the only resonance found in the 80–90 ppm chemical shift range of the boron NMR spectrum was that of B_4Cl_4. Peak integrations of the spectrum indicated that B_4Cl_4 had been generated in 90% yield. After separation, the identity of the tetraboron tetrachloride formed was confirmed by mass spectrometry (see Table III).

Results and Discussion

B_4Cl_4/BBr_3 Interaction. When BBr_3 was employed as both solvent and reagent, the ^{11}B data indicated that after prolonged reaction (ca. 800 h) at 95 °C the monosubstituted B_4BrCl_3 had been generated from B_4Cl_4 in about 13% yield, but further exposure of B_4Cl_4 to neat BBr_3 under the conditions employed during this study led to extensive cage decomposition rather than the formation of, e.g., B_4Br_4. The decomposition products derived from the tetraboron tetrahalides have not been conclusively identified, but the boron NMR data suggest the presence of the diboron tetrahalides, B_2X_4, and the polyhedral boranes, B_nX_n, where the latter are thought to have been formed from B_2X_4 disproportionation.[13]

The B_4Cl_4/BBr_3 reactions that were diluted with pentane demonstrated that the previously uncharacterized B_4Br_4 and the mixed halides B_4BrCl_3, $B_4Br_2Cl_2$, and B_4Br_3Cl can be prepared by this route and that they are sufficiently stable for isolation. This synthesis, however, is inefficient, extraordinarily tedious, and results in intractable product mixtures. The most productive of these reactions involved the repeated reintroduction of small amounts of BBr_3 and solvent, followed by the removal of pentane and the partially chlorinated trihaloboranes that were formed; however, the ^{11}B NMR data indicated that even if the separations of the resulting tetraboranes had been straightforward, the yield of the desired B_4Br_4 was low.

The B_4Cl_4/BBr_3 reactions that were carried out in the presence of $AlBr_3$ easily formed B_4Br_4 in high yield, 80%. This product, B_4Br_4, is only the third compound of its type, homoleptic B_4X_4, to have been synthesized and characterized. All of the properties of the molecule including the volatility, the ^{11}B NMR data (see Figure 1 and Table I), and the high- and low-resolution mass spectral data (Tables II and III), especially the intensities within the ion envelopes that are the result of the natural abundances of the B and Br isotopes as well as the sharp high-mass cutoff at *m/e* 368, are entirely as expected in light of the analogous properties of B_4Cl_4.

^{11}B NMR Spectra. The ^{11}B NMR chemical shift of B_4Br_4 (93 ppm) is about as deshielded from that of B_4Cl_4 (85 ppm) as is that of B_2Br_4 (70 ppm) from that of B_2Cl_4 (63 ppm). The chemical shifts of the intermediate halides, B_4BrCl_3, $B_4Br_2Cl_2$, and B_4Br_3Cl, can be easily related to the B_4Cl_4 and B_4Br_4 shifts in that in each case the substitution of a chlorine atom by a bromine atom results in the deshielding of the resonances of the remaining boron atoms by ca. 3 ppm (see Table I). This same type of chemical shift pattern has been previously reported for the partially alkylated tetraboranes, $B_4Cl_nR_{4-n}$, R = CH_3, $C(CH_3)_3$, but in the chloroalkyltetraboranes the effect is slightly greater, approximately 5 ppm/substitution of Cl by R.[2,11]

The observation of two resonances each for B_4BrCl_3, $B_4Br_2Cl_2$, and B_4Br_3Cl (see Figure 1) is clearly in accord with the supposition that the solution-state structures of these compounds are based upon tetrahedral geometries rather than square-planar arrays of boron atoms, since for the latter case three resonances each would be expected for B_4BrCl_3 and B_4Br_3Cl and as many as four additional resonances could be anticipated if both isomers of $B_4Br_2Cl_2$ were present. The currently available data do not exclude the possibility of fluctionality, but the experimental data derived from the parent (tetrahedral) B_4Cl_4 indicate that the activation energies for fluctional processes are quite high.[12]

The apparent ^{11}B–^{11}B coupling constants found for B_4BrCl_3 and B_4Br_3Cl in the absence of $AlBr_3$, ca. 15 Hz, are much smaller in magnitude than the 110–130 Hz typically found for boron atoms that are held together by means of two-center–two-electron bonds, for example, in compounds like the dihaloborylpentaboranes, $BX_2B_5H_8$.[14] The $B_4XX'_3$ splittings, however, are similar in size to the ca. 19-Hz couplings typically measured between the apical and basal boron atoms of pentaborane (9) derivatives.[14] The cage atoms in pentaborane, of course, are also held together by means of multicentered B–B bonding.

B_4Br_4/BCl_3 Interaction. The B_4Br_4/BCl_3 ligand interchange is much more facile than that between B_4Cl_4 and BBr_3, as it leads to the formation of regenerated B_4Cl_4 in high yields (ca. 90%) within 144 h at 110 °C. These results indicate that the products preferentially formed are those in which the smaller, more electronegative halide is bonded to the polynuclear borane rather than the trihaloborane. This finding is consistent with the previously reported results from diboron tetrahalide/boron trihalide[15] and diboron tetrahalide/carbon tetrahalide[16] ligand interchanges whereas ligand interchanges between the mononuclear boron trihalides BCl_3 and BBr_3 result in mixtures that arise from near-random ligand substitution.[17]

Finally, at the present time, none of the available results indicate any inherent reason that B_4I_4 or B_4F_4 could not be synthesized and characterized, provided that an appropriate preparative pathway could be devised.

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