Table I. Quantum Yield for Cr(III) Complexes

complex	ϕ_R (λ^a)	medium	ref
$Cr(ox)_3{}^{3-}$	0.045 (570)^b	aqueous	11
$Cr(phen)_3{}^{3+}$	0.018 (458)^c	aqueous	12
$Cr(aa)_3{}^d$	0.005 (546)	chlorobenzene	27
$Cr(en)_3{}^{3+}$	0.015 (br)^e	aqueous	this work

[a] Wavelength in nm. [b] This is the value consistent with the definition of ϕ_R in Scheme I. [c] ϕ_R is somewhat sensitive to vibronic level populated. [d] aa^- is 2,4-pentanedionato anion. [e] Broad band.

There are no definitive experimental data to discriminate between the two mechanisms noted above. There are, however, data that suggest that the twist mechanism might be preferable at this time. In Table I[27] are listed the quantum yields for isomerization of various Cr(III) complexes of octahedral microsymmetry. Note that the values are very similar; this is especially true if only the three systems studied in water are considered. If the bond-rupture mechanism were to hold, k_I would be expected to be an important parameter in determining ϕ_R. For the widely differing ligands listed in Table I, differing in rigidity, conjugation, and chain length, it would be expected that k_I would differ greatly from one to another. This change is not reflected insofar as ϕ_R depends on k_I. On the other hand, the constancy of ϕ_R can at least be rationalized by the "twist" mechanism if it is assumed that fractionation toward the S_6 pathway is determined at the vibronic level populated by absorption and that this fractionation is relatively independent of the nature of the coordination shell.

Registry No. Λ-$Cr(en)_3{}^{3+}$, 41509-53-9; Δ-$Cr(en)_3{}^{3+}$, 51002-41-6; $Cr(en)_3{}^{3+}$, 15276-13-8.

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2*n* Framework Electron Clusters: Preparation and Relative Thermal Stabilities of the Polyhedral Boron Subbromides

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Discharge of BBr_3 in the presence of mercury yields B_2Br_4 at rates of 200–300 mg/h. The decomposition of B_2Br_4 results in the formation of BBr_3 and a number of boron subbromides, B_nBr_n (n = 7–10), which are formed in combined yields of about 50% at ambient temperature. Under different conditions B_9Br_9 is isolated in 48% yield from the decomposition of B_2Br_4. The formation and subsequent decomposition of a paramagnetic species is observed by ESR. The boron NMR resonances of B_9Br_9 and $B_{10}Br_{10}$ in pentane solution are shown to be singlets at −60 °C, and the chemical shifts of the subhalides are found to be about 60–80 ppm deshielded relative to their electron-rich analogues which contain $2n + 2$ framework electrons. The nine-membered cage, B_9Br_9, is more stable both thermally and to air than the ten-membered cage, $B_{10}Br_{10}$. Preliminary investigations indicate that ligand substitutions proceed at ambient temperatures in the reaction of B_9Br_9 with $Pb(CH_3)_4$ although cage reduction also appears to occur.

Introduction

In many cluster compounds the geometric shape of the framework atoms is dictated by the number of electrons delocalized within the framework orbitals.[1] Polyhedral species with $2n + 2$ framework electrons frequently have deltahedral (closo) geometries while frameworks with only $2n$ electrons, e.g., $Os_7(CO)_{21}$ and $(C_5H_5)_3Co_3B_4H_4$, are often found as capped deltahedra.[2,3] There are a few exceptions, most notably $Bi_9{}^{5+}$ and a growing number of metal-rich metalloboranes, like $(C_5H_5)_4Co_4B_4H_4$ and $(C_5H_5)_4Ni_4B_4H_4$[4,5] but typically main-group-containing clusters are found to have the structures expected on the basis of Wade's rules.

The polyhedral boron subhalides, which are compounds of the general formula B_nX_n (X = Cl, Br), however, appear to be an entire class of molecules that do not adopt the structures predicted by the framework count method. Each of these halides has only $2n$ framework electrons, yet the structures observed for, e.g., B_8Cl_8 (dodecahedral)[6] or B_9Cl_9 (tricapped trigonal prism),[7] are the structures usually associated with frameworks containing two additional electrons. Whether this apparent violation of the framework electron count–structural correlation by the boron subhalides results from ligand–framework interactions, which are ignored in the FEC method, or arises from other sources is, as yet, unknown.

The boron subhalides are also of interest because so little is known about them. The thermal decomposition of B_2Cl_4 has been variously reported to yield $B_{12}C_{11}$, $B_{11}Cl_{11}$, or, after recrystallization from (or possibly reaction with) BCl_3, B_8Cl_8 as the major polyhedral product.[6,8,9] The first named compound, $B_{12}Cl_{11}$, was reported to be paramagnetic although the adventitious addition of water to the sample was later held to be responsible for the formation of the free-radical species observed.[9] Irrespective of the source of the radical, however, it was reported to be extremely stable, persisting for years at ambient temperatures.[8,9] The decomposition of B_2Br_4 has been less studied although a mass spectral examination did indicate that, in addition to BBr_3, the compounds B_nBr_n (n = 7–10) were formed, but no indication of the amounts of these clusters produced in the reaction is available.[10]

In order to learn more of the boron subhalides and of the consequences of "electron hyperdeficiency", we have begun to study the formation, stability, and reactivity of these compounds. With the expectation that they might prove to be

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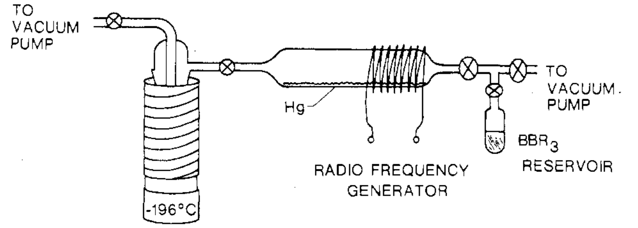

Figure 1. Diagram of plasma apparatus.

more tractable than the chlorides, we elected to investigate the boron subbromides during the early stages of this study.

Previous syntheses of small amounts of the subhalide precursor, B_2Br_4, used electrical discharges of BBr_3 in the presence of mercury or the reaction of B_2Cl_4 with BBr_3 at −78 °C.[10] However, radio frequency discharges have recently been shown to be fairly efficient for the preparation of relatively large amounts of products in a number of different chemical systems.[11,12] The synthesis of B_2Br_4 was therefore attempted by using mercury-scavenged discharges which were maintained by inductively coupled radio frequency generators.

The major goals of the present preliminary study were to determine whether the boron subbromides could be produced from B_2Br_4 in sufficient quantity to allow their possible use as synthetic reagents, further, to find which, if any, of these compounds are stable enough to allow their isolation and characterization, and, finally, to ascertain whether any derivatives of these compounds appeared sufficiently stable to allow their ready isolation, once formed. Thus one aspect of the study was centered about the utility of the rf discharge as a preparative tool, including the determination of the yields of B_2Br_4 formed from BBr_3. Another was to follow the thermal decomposition of B_2Br_4 under various conditions, in part to find whether one or more paramagnetic species analogous to those indicated in the B_2Cl_4 decomposition would be observed, and in part to determine the approximate amounts of the various subbromides formed. Third, since very little information is currently available about any of these clusters, even the ^{11}B NMR spectra of the products needed to be determined. Finally, the interaction of one subhalide, B_9Br_9, with a number of common chemical solvents and reagents was observed in order to begin to assess the chemical properties of these compounds.

Experimental Section

General. All manipulations were carried out by using either a standard vacuum line equipped with Teflon valves or a Vacuum Atmospheres Model HE-43-2 glovebox. Fourier transform ^{11}B NMR spectra at 28.9 MHz were acquired with a Bruker HFX-90 spectrometer. Chemical shifts are referenced to external $BF_3 \cdot OEt_2$ at 26 °C; positive values denote resonances shielded relative to the standard. A PE 521 spectrophotometer was used to obtain the gas-phase infrared spectra. Mass spectra are from an AEI MS30 double-focusing spectrometer operating at 70 eV. The X-band ESR spectra were determined with a reflection-type instrument constructed on site.[13] Radio frequency discharges were maintained by a Lepel 2.5-kW generator which had been modified to operate at approximately 7.1 MHz.

Boron tribromide (ROC/RIC) was treated with mercury to remove bromine; any traces of HBr were separated by low-temperature distillation. The purity of the BBr_3 was assessed by IR, mass, and NMR (δ −39.5) spectra. No impurities were observed. Carbon tetrachloride and pentane were dried with calcium hydride; diethyl ether was dried with sodium benzophenone ketyl. Mercury and $Al(CH_3)_3$ were used as received. Tetramethyltin and $Pb(CH_3)_4$ were formed from the interaction of CH_3MgI with $SnBr_4$ and $PbBr_2$, respectively.

Table I. Variation in B_2Br_4 Formed with BBr_3 Flow Rate[a]

flow rate (BBr_3), mg/min	B_2Br_4 formed, mg/h	conversion, %	reservoir temp, °C
248[b]	196	1.93	0
174	131	1.87	−23
132	98.6	1.58	−30
37.2	23.5	1.54	−45

[a] The maximum rate at which B_2Br_4 is formed can easily be increased to 350 mg/h by increasing the power supplied to the discharge. [b] In the present configuration, at the stated power levels (see text), higher flow rates than 250 mg/min result in unstable discharges.

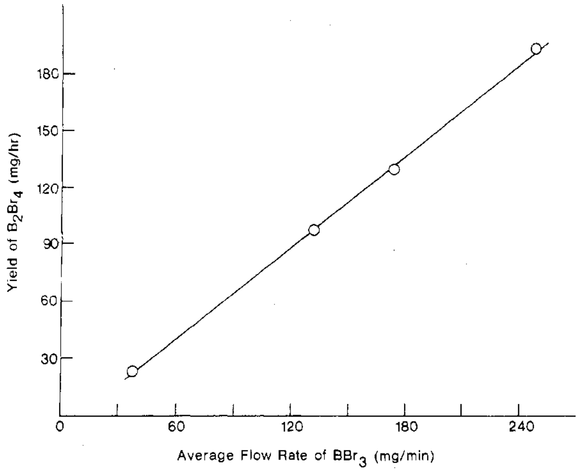

Figure 2. Rate of formation of B_2Br_4 as a function of average BBr_3 flow rate.

Preparation of B_2Br_4. The synthesis of B_2Br_4 was accomplished in the discharge apparatus depicted in Figure 1. Approximately 100 cm^3 of mercury was placed in the horizontally maintained 70 × 290 mm cylindrical Pyrex reaction chamber which had been surrounded by a seven-turn helix constructed of $^1/_4$-in. copper tubing. After the vessel was evacuated BBr_3 was allowed to flow through the reactor, and the discharge was initiated by passing current (16.9 A) through the load coil; the power required was typically 59 W. Volatile materials issuing from the discharge region were condensed in a trap maintained at −196 °C to be separated and identified later. Although several methods of controlling flow rates were assessed, eventually the BBr_3 reservoir was immersed in slush baths which solidified at the various temperatures reported in Table I. During the first few minutes of the discharge, small amounts of elemental bromine were often recovered, especially at the larger flow rates. If, however, the mercury pool was preheated to 50 °C prior to the initiation of the discharge, bromine was not observed.

In one typical experiment the BBr_3 reservoir was surrounded by an ice bath, the reservoir stopcock was opened, and the discharge was maintained for 4 h and 35 min. During this time 68.26 g (272 mmol) of BBr_3 passed through the reactor. The volatile material collected was then separated by fractionation and distillation and found to consist of BBr_3, 66.45 g (265 mmol), and B_2Br_4, 0.899 g (2.63 mmol). Diboron tetrabromide, identified by mass and IR spectra,[14] was thus recovered in 72% yield, on the basis of the amount of BBr_3 consumed; the conversion of BBr_3 to B_2Br_4 was 1.93%. The previously unreported chemical shift of neat B_2Br_4 is −70.0 ppm. Other boron-containing products include orange to yellow sublimable solids that accumulate on the walls of the discharge apparatus during the reaction.

The rate of formation of B_2Br_4 as a function of BBr_3 flow rate was determined by varying that parameter but keeping all others, e.g.,

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Table II. Relative Intensities of ESR Resonances of B_2Br_4 Decomposition Products[a]

23 °C	time, h	0	2.00	29	72	720	2160
	intens	0	0	6	26	69	27
100 °C	time, h	0	0.53	1.37	12	24	192
	intens	0	100	70	6	3	0
200 °C	time, h	0	1.35	12			
	intens	0	8	0			
300 °C	time, h	0	1.33	12			
	intens	0	0	0			

[a] Reported intensities are measured peak heights relative to the sample maintained at 100 °C for 0.53 h.

Table III. Mass Spectra of B_2Br_4 Thermal Decompositions

	% intens[a]			
conditions	$B_{10}Br_{10}$	B_9Br_9	B_9Br_8	B_9Br_7[c]
200 °C, 64 h	37	100	15	36
200 °C, 1.3 h	17	100	42	14
200 °C, 0.25 h	18	100	84	47
100 °C, 6 h/200 °C, 0.5 h[b]	12	100	434	136

[a] All mass spectral intensities normalized to that of the molecular ion of B_9Br_9. [b] Integration of the NMR spectrum of this sample indicated that the ratio of the peaks observed at chemical shifts of −64.9 and −60.4 ppm was 5:1. [c] In all cases yet observed, the presence of substantial amounts of the ion B_9Br_7 in the mass spectrum have been accompanied by a small absorption at −70.2 ppm in the NMR.

the plate current supplied to the oscillator tube (0.22 A), constant. The rate of formation of B_2Br_4 at various BBr_3 net flow rates is found in Table I and Figure 2.

Thermal Decomposition of B_2Br_4. Samples of B_2Br_4 (0.2–0.4 g) were sealed into 4-mm Pyrex tubes under vacuum, maintained at 23, 100, 200, or 300 °C, and periodically monitored by visual, ESR, NMR, and mass spectral means.

At ambient temperature (23 °C) the originally clear, colorless samples begin to darken within 5 min, eventually becoming a brown rusty color. Within 20 min a dark brown solid begins to deposit upon the walls of the tube. After three months at 23 °C the solution is opaque, and the sample is dark brown throughout. When heated, for example, to 300 °C for 72 h, the brown color of the solid and liquid is slowly discharged, and the contents of the tube, both solid and liquid, become deep red. When the tube is then opened and the volatile materials are removed by, e.g., gentle heating under vacuum, a small amount of a tan nonvolatile residue remains.

ESR spectra of freshly isolated samples of B_2Br_4 contain no observable resonances. As indicated in Table II, however, after 29 h at 23 °C a weak resonance which grows in intensity during the next week is present, and the absorption remains fairly strong even after 90 days (2160 h) at 23 °C. After 32 min at 100 °C (Table II) a second sample was found to be strongly paramagnetic, but the intensity of the signal decreases during the following 24 h and is unobservable after 8 days. After 12 h at 200 °C the absorption which is observed after 81 min at 200 °C is absent.

In each case the ESR spectrum consists of a single, fairly broad resonance with a *g* value of 2.0860. The peak to trough line width of the first derivative signal is 51.3 G. The resonance is very intense, so intense that the observed number of spins/cm^3 implies an effective radical concentration of the order of several tenths molar in the more strongly absorbing samples. The approximate relative signal intensities are presented in Table II.

^{11}B NMR spectra initially contain only the absorption due to B_2Br_4 (δ −70.0), but at room temperature BBr_3 (δ −39.5) is evident within 5 min. Six hours later new resonances at −60.4 and −65.2 ppm (identified in Table IV) are present as shown in Figure 3a. After 121 h at 23 °C (Figure 3b) a fourth absorption at −67.3 ppm is well resolved. Finally, as shown in Figure 3c, taken after 70 days at ambient temperature, a small absorption is found as a shoulder at −69.5 ppm. Integration of the last spectrum yields a BBr_3:boron subhalide (δ −60 to −70) ratio near 2:1.

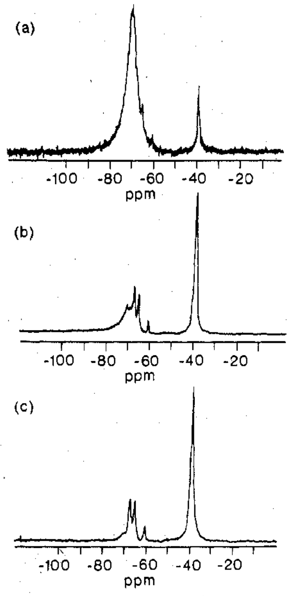

Figure 3. Thermal decomposition of B_2Br_4 at ambient temperature: boron NMR Spectra after (a) 6 h, (b) 121 h, and (c) 70 days.

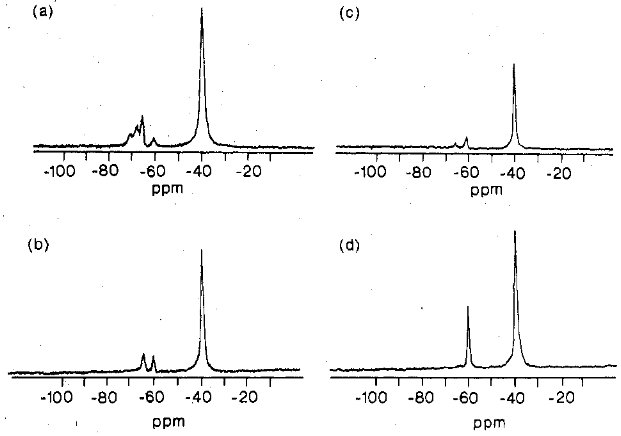

Figure 4. Thermal decomposition of B_2Br_4 at elevated temperatures: boron NMR after (a) 1 h at 100 °C, (b) 18 h at 200 °C, (c) 0.25 h at 300 °C, and (d) 18 h at 300 °C.

Table IV. Boron NMR and Mass Spectra of Boron Subhalides

compd	δ[a]	prominent ions:[b] *m/e*, ion (intens, %)
B_2Br_4	−70.0	341, B_2Br_4 (22); 262, B_2Br_3 (18); 250, BBr_3 (14); 171, BBr_2 (100)
B_7Br_7	−69.5	636, B_7Br_7 (14); 385, B_6Br_4 (100); 134, B_5Br (8)
B_8Br_8	−67.3	726, B_8Br_8 (98); 475, B_7Br_5 (100); 225, B_6Br_2 (11)
B_9Br_9	−60.4	817, B_9Br_9 (100; 737, B_9Br_8 (7.3); 657, B_9Br_7 (1); 646, B_8Br_7 (8.9); 567, B_8Br_6 (89); 486, B_8Br_5 (13.2); 396, B_7Br_4 (15.7); 315, B_7Br_3 (27.3)
$B_{10}Br_{10}$	−65.2	908, $B_{10}Br_{10}$ (100); 828, $B_{10}Br_9$ (10); 737, B_9Br_8 (21); 657, B_9Br_7 (100); 406, B_8Br_4 (40)

[a] Vs. external $BF_3{\cdot}OEt_2$. [b] Most intense ion in envelope.

At 100 °C the decomposition is much faster, requiring only 60 min to proceed to the extent shown in Figure 4a. Note, however, the differences in the relative intensities between Figure 4a and Figure 3b or c. At 200 °C the decomposition requires ca. 10 min to proceed as far as that shown in Figure 3c, but after 18 h at 200 °C the resonances at −67.3 and −69.5 ppm are absent (Figure 4b). After an additional 63 days at 200 °C the resonance at −65.2 ppm, though still present, is substantially reduced in intensity. As shown in Figure 4c, after 15 min at 300 °C, the resonances at −39.5, −60.4, and −65.2 ppm only are observed. After 17.5 h at 300 °C, however, only B_9Br_9 (identified below, δ −60.4) and BBr_3 (δ −39.5) are found, the former in amounts corresponding to about a 25% yield as indicated by integration of the NMR spectrum (Figure 4d). After a total of 240 h at 300 °C the resonance due to B_9Br_9, though reduced in intensity, is still clearly evident.

Mass spectrometry served to conclusively identify the fully ligated boron subhalides formed during the various decompositions. The reaction vessels were opened under vacuum, and the volatile contents, BBr_3 and B_2Br_4, were removed and identified. The remaining material was analyzed by using the solids probe of the spectrometer which was maintained at ambient temperature. Although exposure to air was routinely minimized, the boron subhalides appear to be unaffected by short exposures to the atmosphere. Each subhalide could be easily identified since for each compound the spectrum contains very strong ions $B_nBr_n^+$, the molecular ions, each with the calculated isotopic abundance, as well as strong ions corresponding to the loss of BBr_3 from that ion; see Table IV.

The mass spectrum of the sample in Figure 4d, after removal of BBr_3, contained only ions arising from B_9Br_9; see Table IV. The mass spectrum of samples that were held at 200 °C for 64 h contained ions due to both B_9Br_9 and $B_{10}Br_{10}$ (Table III); however, samples exposed to other, less harsh conditions contained $B_9Br_8^+$ ions far in excess of that expected from any possible combination of only B_9Br_9 and $B_{10}Br_{10}$.

To examine one further aspect of the decomposition, to determine if all of the boron halides are formed from B_2Br_4 approximately simultaneously, mass spectra were obtained after 32 min at 100 °C. They contain the following ions (intensity): $B_{10}Br_{10}$ (5), B_9Br_9 (100), B_9Br_8 (33), B_8Br_8 (63), B_9Br_7 (17), B_8Br_7 (12), B_7Br_7 (535), and B_6Br_6 (35), where again the intensities have been normalized to that of $B_9Br_9.^+$ Another sample, 0.3 g of B_2Br_4, was opened after 10% of the sample had decomposed, which required 1.5 h at room temperature, and the remaining B_2Br_4 and any BBr_3 which had formed were removed under vacuum. The mass spectrum of the material which was nonvolatile in the vacuum system contained the following ions (intensities): $B_{10}Br_{10}$ (74), B_9Br_9 (100), B_9Br_8 (126), B_8Br_8 (55), B_9Br_7 (68), B_8Br_7 (22), and B_7Br_7 (17). Upon addition of pentane, boron NMR spectra indicated the presence of each of the subhalides in approximately the concentrations found in Figure 4a. This sample was then heated to 100 °C for 14 h at which time BBr_3, B_9Br_9, and $B_{10}Br_{10}$ only were found in the relative concentrations of 10:1:1.

Properties of the Subhalides. In the absence of solvent all of the boron subhalides, B_nBr_n, appear to be fairly stable to the atmosphere, surviving from several minutes to 1 h. They are all soluble in nonpolar solvents like CH_2Cl_2, BBr_3, BCl_3, CCl_4, or hydrocarbons like pentane and soluble in, but slowly reactive toward, more polar solvents, like ethers. Nonabromononaborane, for example, is completely consumed by dry, degassed diethyl ether in 4–8 h. Toward more polar, stronger Lewis bases, like H_2O, Et_3N, diglyme, THF, or CH_3CN, the subhalides are much more reactive; decomposition, as measured by NMR methods, occurs within 10 min. The color of these compounds varies from a deep ruby red for B_9Br_9 to a coal black for the seven-membered cluster, B_7Br_7.

Since B_9Br_9 is presumably a tricapped trigonal prism[10] in solution, yet the NMR signal in pentane is a singlet, low-temperature NMR spectra were obtained. At −45 °C in BBr_3 and at −60 °C in pentane, essentially no change in the resonance was observed, although between −30 and −60 °C the peak width did increase from 15 to 30 Hz at half-height. Between −30 and −60 °C the $B_{10}Br_{10}$ resonance similarly broadened from 20 to 26 Hz. Below −60 °C B_9Br_9 slowly precipitates from pentane solution. In pentane solutions held at low temperatures, e.g., −78 °C, 1:2 molar ratios of B_9Br_9 and $B_{10}Br_{10}$ precipitate the nine-membered cluster from solution, leaving behind $B_{10}Br_{10}$, which forms the basis of one subhalide separation scheme. NMR and mass spectral data are collected in Table IV.

Reactivity of B_9Br_9: Preliminary Studies. Air. To examine the relative stabilities of the nine- and ten-membered clusters toward the atmosphere, B_9Br_9 and $B_{10}Br_{10}$ in a 1:2 molar ratio were dissolved in ether and exposed to air. Three minutes later the NMR resonance of $B_{10}Br_{10}$ was absent, but a resonance at −60.4 ppm, though reduced in intensity, indicated that B_9Br_9 was still present. After 1 h the B_9Br_9 had also reacted, and only resonances near −20 ppm (B–O linkages) were observed.

Bromine. Diboron tetrabromide, 0.41 g (1.2 mmol), was heated to 200 °C for 0.25 h, and excess bromine, 1 g (6.2 mmol), was added to the solid material formed (see Table III). Fourteen hours later, B_9Br_9, 0.05 g (0.06 mmol), was removed from the residual bromine and recovered in 46% yield, on the assumption that the original decomposition, i.e., $9B_2Br_4 \rightarrow 9BBr_3 + B_9Br_9$, had been quantitative.

Alkylating Agents. The interaction of B_9Br_9 with several common methylating agents was followed by ^{11}B NMR to determine whether alkylation or fragmentation of the cage, the latter accompanied by the formation of $B(CH_3)_3$ (δ −86), might be indicated. After 20 h at ambient temperature, the reaction of B_9Br_9 with excess $Al(CH_3)_3$ resulted primarily in the formation of $B(CH_3)_3$ in 90% yield, although a number of minor absorptions deshielded from B_9Br_9 were also present.

In excess $Sn(CH_3)_4$ reaction was not observed at temperatures lower than ca. 150 °C, but over an 80-h period at that temperature, exclusive of B_9Br_9, $B(CH_3)_3$, and the mixed $B(CH_3)_nBr_{3-n}$ species present, eight resonances at chemical shifts ranging from −63 to −104 ppm were observed to increase in intensity. Proton NMR data indicated the presence of $Sn(CH_3)_3Br$ and $Sn(CH_3)_2Br_2$, each resonance accompanied by the appropriate tin-119 and -117 satellites.

To moderate the reaction, excess $Pb(CH_3)_4$ was added to B_9Br_9, 2% solution in BBr_3. At ambient temperature the slow appearance of absorptions at −63, −67, and −80 ppm was observed. After 26 h the absorption at −63 ppm dominated the spectrum, and mass spectral analysis of the materials of low volatility indicated the presence of the substituted cluster compound $CH_3B_9Br_8$ [*m/e*, ion (intensity)]: 752, $CH_3B_9Br_8$ (96); 567, B_8Br_6 (100); 501, $CH_3B_8Br_5$ (51)], as well as $Pb(CH_3)_3Br$.

In pentane solution, however, the reaction between $Pb(CH_3)_4$ and B_9Br_9 (4:1 mole ratio) was quite different. Immediately upon warming the solution from −196 °C, a copious brown precipitate formed, and no resonance could be detected in the boron NMR spectra. The pentane was removed under vacuum, and CH_3CN, which has been found to react with B_9Br_9, was added. The ^{11}B NMR spectrum of this solution was found to contain strong absorptions at δ +9.0 and +12.7 in the intensity ratio of 3:6, respectively, which indicates alkylation and cage reduction to the dianion. The chemical shifts of the related compound $B_9Br_9^{2-}$ have been recently reported to be +0.8 and +8.2 ppm, again in a 3:6 ratio of intensities.[15] The details of these reactions and the full characterization of the products will be published separately.

Results and Discussion

Formation of B_2Br_4. The radio frequency discharge of BBr_3 is a very convenient preparation from which B_2Br_4 can be isolated in good yield (72% based upon BBr_3 consumed). Under conditions selected to enhance the formation of B_2Br_4 the product is easily formed at rates of 200–300 mg/h of machine time. In general the synthesis and product separation are straightforward, much less involved than the reaction of BBr_3 with B_2Cl_4, since the latter reaction requires the preparation of B_2Cl_4 which is also typically accomplished by discharge methods. Another alternative preparation of B_2Br_4 is the metal atom reaction of copper with BBr_3 which, if the equipment is readily available, we have found to be about as convenient as the discharge method reported.[16]

The rate at which B_2Br_4 forms is dependent upon many factors including the voltage across and the current through the load coil. If, however, the current and the voltage supplied to the coil are constant, the amount of B_2Br_4 formed has been shown (Figure 2) to vary in a linear manner with the amount of BBr_3 that passes through the discharge when the BBr_3 flow rate is between 37 and 250 mg/min. The isolation of elemental bromine during the initial phases of the reaction, but not later, is an indication that, until the mercury is inductively heated to the operating temperature of the reactor (50 °C) by the load coil, its vapor pressure is insufficient to scavenge all of the bromine produced at high BBr_3 throughput. This point was confirmed by preheating the mercury pool prior to the reaction, whence bromine was no longer observed.

Thermal Decomposition of B_2Br_4. The thermal decomposition of B_2Br_4 is clearly very complex, but it eventually results in the formation of BBr_3, a series of compounds of the formula B_nBr_n, a radical species, the species with a chemical shift near −65.2 ppm and mass spectrum containing an intense $B_9Br_8^+$

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(15) E. H. Wong and R. M. Kabbani, *Inorg. Chem.*, **19**, 451 (1980).
(16) P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, **14**, 121 (1972).

Table V. Boron Chemical Shift Data, Deltahedral Boranes[a, b]

	δ				
	$n = 7$	$n = 8$	$n = 9$	$n = 10$	$n = 12$
$B_nH_n^{2-}$	+6.4	+5.8	+15.3	+23.5	+16.7
$B_nBr_n^{2-}$			+5.4	+13.7	+12.4
B_nBr_n	−69.5	−67.3	−60.4	−65.2	
B_nBr_n–$B_nH_n^{2-}$	−75.9	−73.1	−75.7	−88.7	

[a] Weighted average chemical shifts vs. $BF_3 \cdot OEt_2$. [b] Literature chemical shifts from ref 15 and 18.

ion, and a tan solid. Overall, the reaction is formally a disproportionation in which B_2Br_4, valence of 2 for boron, is transformed into BBr_3 and a variety of other products in which boron is in lower formal valence states. Virtually nothing is known about the mechanism of the reaction, although in the decomposition of B_2Cl_4 the intermediacy of an unspecified nido borane has been postulated.[10]

The *g* value of the radical ($g = 2.0860$) is near the value ($g = 2.011$) reported by Urry for $B_{12}Cl_{11}\cdot$[8] and closely corresponds to that of $B_9Br_9^{-}\cdot$ ($g = 2.080$) reported by Wong.[15] The paramagnetic species is under further investigation as is the species with the intense $B_9Br_8^+$ ion in the mass spectrum. The latter is currently thought to be a dimer, possibly two nine-membered cages bonded by a boron–boron bond similar to that found in coupled borane anion polyhedra.[17]

Irrespective of the mechanism of their formation, the polyhedral boron subhalides, B_nBr_m are all formed in moderate to good yields from B_2Br_4. At 300 °C B_9Br_9, for example, can be isolated in ca. 50% of the amount that would be expected from the hypothetical reaction $9B_9Br_9 \rightarrow B_9Br_9 + 9BBr_3$. At lower temperatures, e.g., 200 °C, after long reaction times $B_{10}Br_{10}$ and B_9Br_9 are the only polyhedral subhalides found, the former in larger amount, ca. 25%. The seven- and eight-membered clusters are stable for long periods only at temperatures less than 200 °C, where they are formed in amounts comparable to B_9Br_9 and $B_{10}Br_{10}$. Separation procedures by, e.g., low-temperature filtrations will be discussed in a subsequent publication. At present the only alternative preparation of any of these clusters is the bromination of $B_9H_9^{2-}$ by *N*-bromosuccinimide, followed by the oxidation of the perbromo salt with thallium trifluoroacetate, which yields B_9Br_9 in 48% yield.[15]

Nuclear Magnetic Resonance. The NMR absorptions of the subbromides all appear to be singlets, indicative of either magnetic equivalence at the resolution of the instrument or, possibly, fluctionality. This result is unusual since, with the nine-membered cages as examples, all other nine-membered D_{3h} boron clusters are reported to have spectra which contain multiple resonances indicative of static structures. At −60 °C however, the spectra of both B_9Br_9 and $B_{10}Br_{10}$ are still singlets.

The effect of two fewer framework electrons upon the chemical shift of a boron cluster can be assessed by means of Table V, which presents the weighted average chemical shifts of a number of borane dianions, the reported perbrominated borane dianions, and the bromoboranes prepared here.

Typically, for the 10- or 12-membered cage, for example, complete substitution of hydrogen by bromine with no change in the number of framework electrons results in an average deshielding of the resonance by 4–10 ppm, comparable to the 3–5 ppm found upon bromination of carboranes.[19] From Table V however, it is evident that the boron subhalides are deshielded by 70–90 ppm relative to the borane dianions with the same number of boron atoms. Ligand exchange, bromine for hydrogen, is seen to account for only as much as 10 ppm, and a large portion of the remainder can most likely be ascribed to the absence of the two "extra" electrons found in the dianions. Although at this point it is possible that two of the subhalides, B_7Br_7 and $B_{10}Br_{10}$, for which structures are not available, may not be polyhedral, the observed NMR data and the very strong molecular ions in the mass spectra argue strongly against this interpretation. The structures of these two subhalides are under further investigation.

Stability of Polyhedral Boron Subhalides. Especially for compounds that lack the number ($2n + 2$) of framework electrons that are usually associated with "superaromatic" bonding, e.g., in borane anions and carboranes, the boron subbromides are surprisingly thermally stable. In BBr_3 the most stable of the compounds, B_9Br_9, survives temperatures of 300 °C for days and 200 °C for weeks. The slightly less stable $B_{10}Br_{10}$ is stable for days to 200 °C and appears to be indefinitely stable at lower temperatures. One of the more interesting results of this preliminary study is that the nine-atom polyhedron appears to be more stable than the ten-atom cluster, which is the opposite of the results which have been reported for carboranes or borane anions. The results here indicate that the relative stability of polyhedra may depend, in part, upon the number of electrons delocalized within the cluster. The effect on cage stabilities of the back-bonding which has been postulated to occur between the boron cage and the halogen ligands may also be important, but the details of this interaction, if any, are as yet unknown. In the series of boron subbromides the relative thermal stabilities vary in the order $B_9Br_9 > B_{10}Br_{10} > B_8Br_8 \simeq B_7Br_7$.

Chemically, the subhalides also appear to be fairly stable to reagents other than Lewis bases, with which they react almost immediately. In view of the electron "hyperdeficient" nature of these clusters such reactivity is not unexpected. The nine-atom cluster easily survives exposure to liquid bromine, but the compound is reactive toward alkylating agents, and three types of interactions have been found: cluster fragmentation to yield $B(CH_3)_3$, substitution to yield alkylnonaboranes like $CH_3B_9Br_8$, and cage reductions to yield the dianion.

Conclusion

The purposes of the experiments reported here were to determine whether the polyhedral boron subbromides, about which very little is known, could be formed in amounts suitable for chemical studies of their reactivity, if they appeared to be sufficiently stable to allow their isolation, and if they appeared to be reactive in, e.g., ligand-exchange reactions. Diboron tetrabromide, the precursor, is easily formed at rates of 200–300 mg/h from the discharge of BBr_3 in the presence of mercury. The decomposition of B_2Br_4 proceeds smoothly to yield the desired subhalides in yields that can approach 50%. The relative amounts of the subhalides formed vary with the thermal history of the sample. During the decomposition of B_2Br_4 a paramagnetic species is observed to form and then decay. The subbromides are stable in the absence of air and very stable thermally, the stability varying in the order $B_9Br_9 > B_{10}Br_{10} > B_8Br_8 \simeq B_7Br_7$. An initial, preliminary study of the reactivity of these compounds indicates that ligand-exchange reactions occur with alkylating agents like $Pb(CH_3)_4$ although in some situations cage reduction appears to occur.

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Registry No. B_2Br_4, 14355-29-4; BBr_3, 10294-33-4; B_7Br_7, 12589-29-6; B_8Br_8, 12589-30-9; B_9Br_9, 12589-31-0; $B_{10}Br_{10}$, 74562-12-2; $CH_3B_9Br_3$, 74542-90-8; $Pb(CH_3)_4$, 75-74-1.

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(19) T. Onak in ref 18, p 359.