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2*n* Framework Electron Clusters: Diamagnetic Polyhedral Boron Chlorides, B_nCl_n (n = 8–12), from the Thermal Disproportionation of Diboron Tetrachloride

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In the presence of elemental mercury, diboron tetrachloride, B_2Cl_4, is generated from the radio frequency discharge of BCl_3 at the rate of 250–350 mg/h. The disproportionation of undiluted B_2Cl_4 has been examined at a variety of temperatures and found to occur in five stages. The amounts of the polyhedral diamagnetic products, B_8Cl_8, B_9Cl_9, $B_{10}Cl_{10}$, $B_{11}Cl_{11}$, $B_{12}Cl_{12}$, and $(B_9Cl_8)_2$, formed during the reaction are highly dependent upon the thermal history of the sample. In undiluted B_2Cl_4 the maximum yield of B_9Cl_9 (29%) occurs at elevated temperatures, 400–450 °C, whereas the most B_8Cl_8 (38%) is produced at 100 °C. At temperatures below 100 °C, more $B_{12}Cl_{12}$ than $B_{10}Cl_{10}$ is observed whereas the reverse is true above 100 °C. At ambient temperature the ^{11}B NMR resonances of the polyhedral boron chlorides B_nCl_n (n = 8–12) are all deshielded singlets, 58–78 ppm from $BF_3{\cdot}OEt_2$. The relative thermal stabilities of these compounds, $B_9Cl_9 > B_{10}Cl_{10} > B_{11}Cl_{11} > B_{12}Cl_{12} > B_8Cl_8$, do not correspond to the relative thermal stabilities of $2n + 2$ framework electron clusters, such as the borane dianions.

Introduction

Diboron tetrachloride was first synthesized by Alfred Stock and his students in 1925.[1] This group was also the first to report that B_2Cl_4 is thermally unstable, slowly decomposing at ambient temperature to give a substance more volatile than B_2Cl_4 while a brown material is precipitated from solution. After 12 h at 200 °C, tetrachlorodiborane was stated to yield boron trichloride along with a yellowish deposit of "chlorine-poor boron chloride". The precipitate was found to be less reactive than either BCl_3 or B_2Cl_4.[1]

During the 60 years since the initial study, the thermal decomposition of neat B_2Cl_4 has been reexamined several times with conflicting results. The first product that was reportedly isolated from the disproportionation of B_2Cl_4 was tetrachlorotetraborane, B_4Cl_4,[2] although this finding was later disputed.[3] The second product suggested, primarily on the basis of isopiestic molecular weight determinations and elemental analyses, was formulated as $B_{12}C_{11}$, a paramagnetic species.[4] However, after $B_{12}Cl_{11}$ had been recrystallized from (or had reacted with) BCl_3, X-ray diffraction data indicated that two distinct forms of B_8Cl_8, a diamagnetic compound, were then present.[5] The products arising from the decomposition of neat B_2Cl_4 were again restudied; no B_8Cl_8 was observed.[6] The presence of a paramagnetic species in the earlier study has been attributed to an inadvertent hydrolysis.[7,8]

More contemporary studies of the thermal reaction of unidiluted B_2Cl_4 have been confined to mass spectrometric investigations. These studies indicate that the polyhedral boron chlorides, neutral cluster compounds of the formula B_nCl_n, where n = 8–11 and possibly 12, are formed during the course of the disproportionation of B_2Cl_4.[8] However, many questions remain unanswered. For example, the yields of the diamagnetic products arising from the thermal decomposition of B_2Cl_4 have not been revealed; the only indication now available is that the amounts formed are very low.[6,9] The ^{11}B NMR spectrum of B_9Cl_9 has been reported to contain two resonances in an intensity ratio of 8:1; chemical shift data were not supplied.[7] However, in the ^{11}B NMR spectra of B_9Cl_9 synthesized by an alternative route (the thermal decomposition of $B_{10}Cl_{10}^{2-}$ salts), the resonances were singlets as is the resonance of B_9Br_9.[10-12] Whether $B_{12}Cl_{12}$, which might be one of the most interesting of the neutral halides, was formed in reasonable amounts during the thermal disproportionation of B_2Cl_4 was unclear.

The polynuclear boron chlorides B_nCl_n are currently of interest because the framework electron count for each of these cluster compounds is only 2*n*, two fewer than the $2n + 2$ count that is most frequently observed in deltahedral main-group clusters and their transition-metal-containing analogues.[13] Two specific interests result from the low electron density within the framework. First, it seems eminently reasonable that these compounds will prove to have a rich and diverse chemistry of their own, one which is very different in nature than that of the reduced $B_nCl_n^{2-}$ cages. For example, the molecular clusters might be expected to be much more electrophilic than the anionic species. Second, again because of the 2*n* framework electron count, some of the neutral clusters, e.g. $B_{10}Cl_{10}$ and $B_{12}Cl_{12}$, should have structures of unusual interest because in these diamagnetic compounds the 2*n* framework electron count cannot be accommodated by the $n + 1$ bonding framework molecular orbitals that are formed in the usual closo geometries.[13] If one presumes the absence of ligand effects, $B_{10}Cl_{10}$ and $B_{12}Cl_{12}$ must adopt alternative structures, structures related to the so called iso–closo or hyper–closo geometries.[14]

Clearly any systematic attempt to study the structures or the reactivity of the perhaloboranes is contingent upon an adequate supply of the reagents. As noted above, however, there is very little concrete information available about the yields, or even the identities, of some of the products formed during the thermal decomposition of diboron tetrachloride.

The major objectives of the present study were threefold: first, to examine the thermal decomposition of undiluted B_2Cl_4 in order to determine the identities and approximate yields of the diamagnetic clusters that result; second, to obtain the ^{11}B NMR chemical shifts and multiplicities of these compounds for comparison with the more electron-rich dianions; third, to determine the relative thermal stabilities of the polyhedral boron chlorides for the purpose of comparing the order of stability with that previously obtained for species that do have $2n + 2$ framework electrons, clusters like the borane dianions and the carboranes.

Experimental Section

General Considerations. Diboron tetrachloride was synthesized, purified, characterized, and thermally decomposed under anerobic condi-

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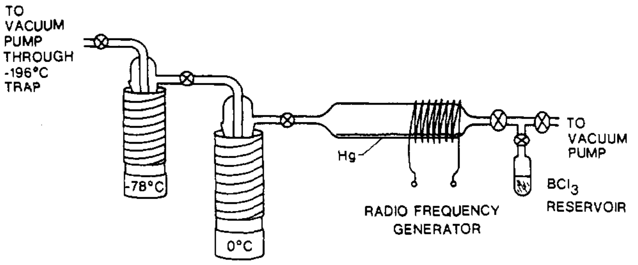

Figure 1. Schematic diagram of the radio frequency discharge apparatus. In operation BCl_3, 40 g/h, flows from the reservoir at the right into the discharge chamber. B_2Cl_4 and B_4Cl_4 are recovered from the traps at the left. B_9Cl_9 is found in a yellow deposit formed throughout the apparatus.

Table I. Approximate Thermal Stability, Chemical Shift, and 70-eV Mass Spectrometry Data for the Boron Halides

compd	dec temp, °C	δ^a	mass spectrum, m/e (ion, intensity)
B_8Cl_8	200	65.1	370 ($B_8Cl_8^+$, 26%); 253 ($B_7Cl_5^+$, 100%)
B_9Cl_9	450	58.4	416 ($B_9Cl_9^+$, 30%); 299 ($B_8Cl_6^+$, 100%)
$B_{10}Cl_{10}$	~350	63.5^b	463 ($B_{10}Cl_{10}^+$, 20%); 345 ($B_9Cl_7^+$, 100%)
$B_{11}Cl_{11}$	300	69.5	509 ($B_{11}Cl_{11}^+$, 15%); 392 ($B_{10}Cl_8^+$, 100%)
$B_{12}Cl_{12}$	200	77.7	555 ($B_{12}Cl_{12}^+$, 8%); 438 ($B_{11}Cl_9^+$, 100%)
$(B_9Cl_8)_2$		63.3^b	381 ($B_9Cl_8^+$, 50%); 264 ($B_8Cl_5^+$, 100%)
BCl_3		46.7	
B_2Cl_4	100	62.4	

^{a}Positive values deshielded vs. external $BF_3 \cdot OEt_2$. All resonances singlets at ambient temperature. ^{b}Resonances of $B_{10}Cl_{10}$ and $(B_9Cl_8)_2$ coincident at the available field strength[17].

tions by using standard vacuum line techniques. Samples of the less volatile polyhedral boron chlorides that arise from the disproportionation of B_2Cl_4 were prepared for analysis by means of the usual glovebox technology. Radio frequency discharges were maintained by a modified Lepel 2.5-kW generator, which operates at a frequency of ca. 8.6 MHz.[11,15] The X-band ESR spectra were obtained with a reflection-type instrument whose properties have been previously described.[16] Gas-phase infrared spectra are from a PE-521 spectrophotometer. Boron-11 NMR data were obtained at 28.9 MHz (Bruker HFX-90) while 70-eV mass spectra (AEI MS-30) were recorded with the source at ambient temperature. All solvents were dried over P_2O_5 and then vacuum distilled.

Preparation of B_2Cl_4. The synthesis of diboron tetrachloride occurred in the radio frequency discharge apparatus depicted schematically in Figure 1. The boron trichloride flow through the load coils of the generator was controlled by the stopcocks and/or by surrounding the BCl_3 reservoir with low-temperature (−64 °C) baths.

Immediately after the initiation of the discharge, yellow deposits began to form on the walls of the reactor and on the surface of the mercury pool. During the course of the experiment, typically 2–3 days, the amount of solid material steadily increased and the color of the deposit darkened until yellow and brown solids were found throughout the vacuum line. Extraction of the solids with methylene chloride yielded yellow B_9Cl_9, which was identified by ^{11}B NMR ($\delta = 58.4$) and mass spectrometry; see below and Table I.

After the termination of the discharge, the volatile material in the traps downstream from the reactor (see Figure 1) was found to be a mixture most easily separated by a combination of fractionation and distillation. First the majority, ca. 90%, of the unreacted BCl_3 was recovered by fractionation through a trap held at −78 °C. (B_2Cl_4 does pass through a trap maintained at −78 °C but only very slowly.) After the bulk of the BCl_3 had been removed, the material retained in the −78 °C trap was carefully fractionated at −96 °C, to separate any residual BCl_3, and then at −64 °C, to isolate the B_4Cl_4, which was also formed in the discharge. Finally, with the head temperature of the column at −80 °C, $SiCl_4$, bp 58 °C, was removed from B_2Cl_4, bp 65 °C, by low-temperature vacuum distillation.

The amount of B_2Cl_4 recovered is dependent upon the flow rate of the BCl_3 through the reaction zone. When the BCl_3 flow is sufficiently high, 40–50 g/h, diboron tetrachloride is formed at a rate of 250–350 mg/h. Prior to use, the purity of the B_2Cl_4 was routinely assessed by infrared, mass, and NMR spectra ($\delta = 62.4$). No contaminants were observed.

Thermal Decompositions of B_2Cl_4. Typically, ca. 0.25 g (1.53 mmol) of B_2Cl_4 was encapsulated in a 5-mm Pyrex tube, which was then placed into a tube furnace that had been preheated to the temperature indicated below. The thermal decomposition of the sample was periodically monitored by ^{11}B NMR and by ESR. Because typical isolation techniques such as sublimations may result in isolated yields that are not reflective of the amounts of the various products originally present (see B_9Cl_9 below), unless otherwise stated, the reported yields of the products rely upon NMR integrations of intact samples and are based upon the amounts of BCl_3 simultaneously formed. At the conclusion of the experiments the ampules were opened, and the identity of the components was confirmed by mass spectrometry.

Decomposition at 450 °C. After 3 min at 450 °C, B_2Cl_4, 0.3685 g (2.255 mmol), yielded an orange solution containing yellow solids. ^{11}B NMR spectra of this mixture contained two resonances located at 46.7 and 58.4 ppm. Removal and analysis of the material volatile at ambient temperature indicated the presence of BCl_3, 0.2887 g (2.464 mmol), only. Sublimation of the residual solid at 60 °C yielded the second molecular component of the solution, B_9Cl_9 ($\delta = 58.4$, singlet). Mass spectrum of B_9Cl_9, m/e, ion (intensity): 416, $B_9Cl_9^+$ (30%); 381, $B_9Cl_8^+$ (1%); 299, $B_8Cl_6^+$ (100%); 264, $B_8Cl_5^+$ (2%). Integration of the NMR spectrum obtained immediately subsequent to the thermal decomposition indicated a 29% yield of B_9Cl_9 in the reaction, based upon the amount of B_2Cl_4 originally taken. As in all cases presented below, small amounts of a tan, insoluble, and nonvolatile material remained after the sublimation.

Decomposition at 400 °C. Diboron tetrachloride decomposes within minutes at 400 °C, yielding a mixture in which yellow solids are suspended in an orange solution. ^{11}B NMR spectra of these samples contain three resonances, one at 63.3 ppm, one at 58.4 ppm, and one at 46.7 ppm. After 45 min at 400 °C, the three are present in the relative intensities 3:10:100. While ESR spectra did indicate the presence of a very small amount of a paramagnetic material, the concentration was too low to determine the g value. The most volatile component of the mixture, $\delta = 46.7$, was removed and identified as BCl_3 by infrared spectrophotometry.

Mass spectra of the material less volatile than BCl_3 contained ions at m/e 416 ($B_9Cl_9^+$, 30%), 381 ($B_9Cl_8^+$, 9.8%), 299 ($B_8Cl_6^+$, 100%), and 264 ($B_8Cl_5^+$, 18.3%). The solid was placed into a sublimation apparatus, which was evacuated and then heated to 60 °C. ^{11}B NMR spectra of the yellow-orange sublimate, in pentane, contained only one resonance, at 58.4 ppm. Mass spectrometry confirmed that the sublimate was B_9Cl_9 (see Table I). ^{11}B NMR spectra of the residual material, in pentane, were characterized by two resonances centered at 58.4 and 63.3 ppm. After removal of the solvent, mass spectra contained B_9Cl_9 and B_9Cl_8 ions in the intensity ratio 67:100. No ions of higher mass were observed.

Decomposition at 350 °C. After a sample of B_2Cl_4 was held at 350 °C for 60 min, ^{11}B NMR and mass spectrometry again indicated the presence of BCl_3, B_9Cl_9, and the substance for which the chemical shift is 63.3 ppm, $(B_9Cl_8)_2$. After the removal of the BCl_3, the ratio of the ions $B_9Cl_9^+$ (m/e 416) to $B_9Cl_8^+$ (m/e 381) was 50:100 in the mass spectrum. Thus after 1 h at 350 °C or higher, five diamagnetic products were observed in the thermal decomposition of B_2Cl_4: BCl_3, B_9Cl_9, "$(B_9Cl_8)_2$", the yellow solid, and the tan, intractable polymeric material. Repeated efforts to sublime $(B_9Cl_8)_2$ were unsuccessful as the substance decomposes to yield, in part, B_9Cl_9.

Decomposition at 300 °C. After 30 min at 300 °C, B_2Cl_4 yields a red solution containing brown solids. ^{11}B NMR absorptions at 46.7, 58.4, 63.5,[17] and 69.5 ppm were present in the intensity ratio 100:7:5:1. After the vessel was opened and the BCl_3 removed, the molecular ion region of the mass spectrum contained contributions from $B_9Cl_9^+$, m/e 416 (100%), $B_{10}Cl_{10}^+$, m/e 463 (45%), $B_9Cl_8^+$, m/e 381 (45%), and $B_{11}Cl_{11}^+$, m/e 509 (16%); see Tables I and II.

Decomposition at 200 °C. After a period of 30 min at 200 °C samples of B_2Cl_4 contain brown solids suspended in a reddish solution. ^{11}B NMR spectra (Figure 2) indicated and mass spectra confirmed the presence of the compounds observed above: BCl_3, B_9Cl_9, $(B_9Cl_8)_2$, $B_{10}Cl_{10}$ and $B_{11}Cl_{11}$. Additionally, two new resonances, at 65.2 and 77.7 ppm, were present. Mass spectrometry demonstrated that the two previously unobserved species were $B_8Cl_8^+$, m/e 370, and $B_{12}Cl_{12}^+$, m/e 555; see Table I.

Because of the breadth of the individual resonances and their overlap (at 28.9 MHz) it was not possible to reliably integrate the resonances due

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(17) At the available field strength, the difference between the chemical shifts of the $B_{10}Cl_{10}$ and $(B_9Cl_8)_2$ resonances is very small, ca. 0.2 ppm. Mass spectrometry, however, clearly indicates the presence of the two different species. For example, $B_{10}Cl_{10}$ is unobserved in the reactions in which the temperatures were in excess of 300 °C whereas $(B_9Cl_8)_2$ is unobserved in the products of reactions carried out near ambient temperature; cf. $B_{12}Cl_{11}$ resynthesis.

Table II. Diamagnetic Cage Compounds from the B_2Cl_4 Thermal Reaction

		obsd products,[a] %						
temp, °C	time	total B_nCl_n	$B_{12}Cl_{12}$	$B_{11}Cl_{11}$	$B_{10}Cl_{10}$ + $(B_9Cl_8)_2$[b]		B_9Cl_9	B_8Cl_8
450	0.05 h	29	0	0	0	0	29	0
400	0.75 h	13	0	0	0	3	10	0
300	0.50 h	13	0	1	2.5	2.5	7	0
200	0.50 h	53	6	14	10	4	6	13
100	16 h	81	5.5	12.5	20		5	38
80	72 h	75	11	24	10		2	28
80	336 h	58	8	21	6		1	22
25	5 y	30[c]	4.5	11	1	1	1	12
25	48 h		0.4	0.4			0.0	

[a] Approximate yields obtained by integrations of ^{11}B NMR spectra. [b] Chemical shifts of $B_{10}Cl_{10}$ and $(B_9Cl_8)_2$ coincident at 28.9 MHz; yields apportioned by mass spectrometry. [c] Reaction still in progress.

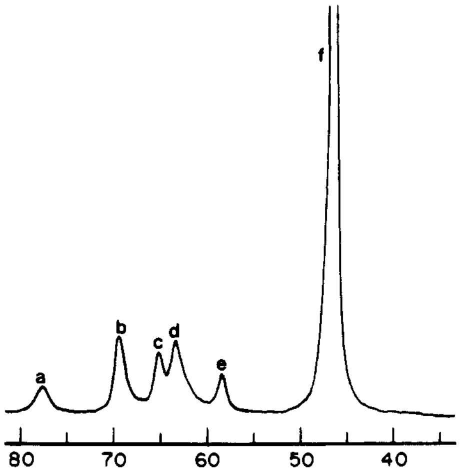

Figure 2. ^{11}B NMR spectrum of the products arising from the thermal reaction of B_2Cl_4 after 30 min at 200 °C. The chemical shifts from left to right are δ (a) 77.7 ($B_{12}Cl_{12}$), (b) 69.5 ($B_{11}Cl_{11}$), (c) 65.2 (B_8Cl_8), (d) 63.5 ($B_{10}Cl_{10}$ + $(B_9Cl_8)_2$), (e) 58.4 (B_9Cl_9), and (f) 46.7 (BCl_3). Note that the resonances due to $B_{10}Cl_{10}$ and $(B_9Cl_8)_2$ are unresolved at 28.9 MHz. The combined yield of the cluster compounds in this reaction is 53% of the amount of BCl_3 formed simultaneously.

to all of the cage compounds individually; see Figure 2. The ratio of the intensity of the BCl_3 absorption to the sum of the intensities of the cluster compounds, however, is 1.0:0.53. The approximate yields, based upon BCl_3, are contained in Table II.

Decompositions at 25–120 °C. Numerous samples of B_2Cl_4 were exposed to temperatures in the 25–120 °C range. At ambient temperatures B_2Cl_4 turns yellow within a few minutes, becoming red after 36 h. Over the course of 2 weeks, the solutions became very dark brown, with brown solids suspended in the liquid. ^{11}B NMR spectra obtained during the first 24 h contain only the resonances due to BCl_3 and B_2Cl_4. ESR experiments indicate that the sample is diamagnetic during this period. After 48 h the sample becomes paramagnetic (see below), and the resonances due to $B_{11}Cl_{11}$ and $B_{12}Cl_{12}$ are first observed. After 48 h the relative amounts of B_2Cl_4, BCl_3, $B_{11}Cl_{11}$, and $B_{12}Cl_{12}$ are approximately 100:18:0.08:0.07.

In one experiment B_2Cl_4 was maintained at ambient temperature for 5 years. ^{11}B NMR of the solution, which contained brown solids, indicated the presence of the polyhedral boron chlorides in the following relative molar amounts: B_8Cl_8, 100% $B_{11}Cl_{11}$, 92; $B_{12}Cl_{12}$, 37; $B_{10}Cl_{10}$ [+$(B_9Cl_8)_2$)],[17] 19; B_9Cl_9, 9. The combined intensities of the cage compound resonances totaled 30% of that due to the BCl_3 formed. Diboron tetrachloride was still present in the mixture.

If B_2Cl_4 is held at slightly elevated temperatures, at 100 °C for 16 h, for example, the sample becomes dark brown in color. On the basis of the integration of the NMR spectrum, the combined yield of the polynuclear boron chlorides in this reaction was 81% of the BCl_3 simultaneously formed; see Table II. Diboron tetrachloride was not observed.

At moderate temperatures (~100 °C) and reaction times of a few days, both ^{11}B NMR and mass spectrometry indicate that B_8Cl_8 is formed in the largest yields followed closely by $B_{11}Cl_{11}$ and that the yields of $B_{10}Cl_{10}$ are greater than those of $B_{12}Cl_{12}$. At ambient, or nearly ambient temperatures, however, typically more $B_{11}Cl_{11}$ than B_8Cl_8 and more $B_{12}Cl_{12}$ than $B_{10}Cl_{10}$ are formed; see Figures 2–4.

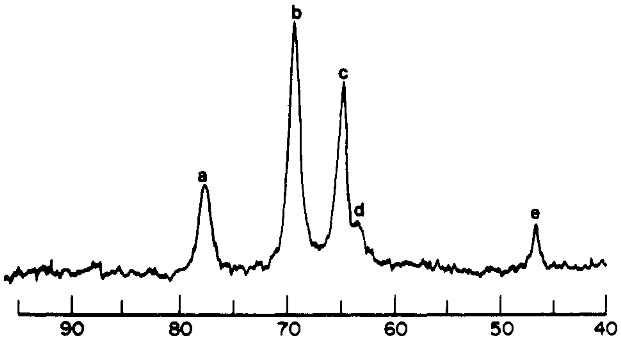

Figure 3. ^{11}B NMR spectrum resulting from the attempted resynthesis of $B_{12}Cl_{11}$. The diamagnetic products are (a) $B_{12}Cl_{12}$ (δ = 77.7), (b) $B_{11}Cl_{11}$ (δ = 69.5), (c) B_8Cl_8 (δ = 65.1), and (d) $B_{10}Cl_{10}$ (δ = 63.5) along with a small amount of (e) BCl_3 (δ = 46.7). Note that B_9Cl_9 (δ = 58.4) is unobserved.

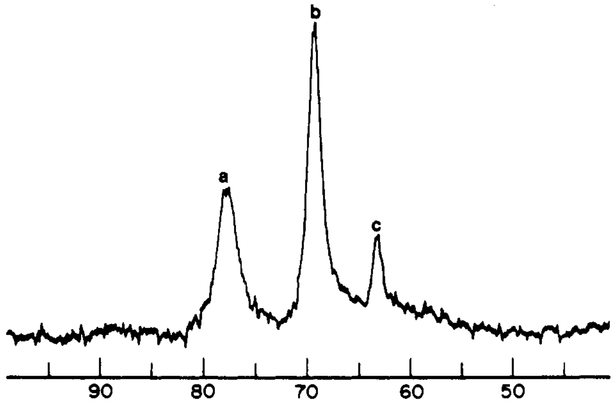

Figure 4. ^{11}B NMR spectrum of sublimed sample from 24-h thermal decomposition of B_2Cl_4 at 60 °C (see text). Approximate molar ratios: (a) $B_{12}Cl_{12}$, 0.58; (b) $B_{11}Cl_{11}$, 1.00; (c) $B_{10}Cl_{10}$, 0.16.

During the initial stages of the thermal decomposition of B_2Cl_4, neither B_9Cl_9 nor $(B_9Cl_8)_2$ are observed. Unless the reaction times are exceedingly long, trace amounts, at most, of B_9Cl_9 are formed when the decomposition temperature is below 80 °C; see below. Thus near 100 °C the relative amounts of the cage compounds generated are typically in the following order: $B_8Cl_8 > B_{11}Cl_{11} > B_{10}Cl_{10} \geqslant B_{12}Cl_{12} > B_9Cl_9$. At ambient temperature $B_{11}Cl_{11} > B_8Cl_8 > B_{12}Cl_{12} > B_{10}Cl_{10}$. In this temperature regime, in the absence of added solvent, yields of B_8Cl_8 and $B_{11}Cl_{11}$ are ca. 20–40% each, while the yields of $B_{10}Cl_{10}$ and $B_{12}Cl_{12}$ are usually ca. 5–20% each.

While the nature of the paramagnetic species formed during this reaction is the subject of a separate study, each sample of B_2Cl_4 is diamagnetic when prepared. Strong paramagnetism is always observed after thermal decompositions in the temperature range 25–120 °C are initiated. In each instance the measured *g* value is 2.01. For example, the aliquot maintained at ambient temperature for 5 years was very strongly paramagnetic; the *g* value was 2.01, and the breadth of the resonance was 25 G. Macroscopic amounts of B_4Cl_4, δ = 85, have not been observed to form in any of the reactions reported above.

Attempted Resynthesis of "$B_{12}Cl_{11}$". Diboron tetrachloride, 1.19 g (7.28 mmol), was vacuum distilled into a vessel, which was then sealed. The contents of the vessel were maintained at 60 °C for 24 h, following which the material that was volatile at ambient temperature was removed, separated, and identified. Boron trichloride, 0.22 g (1.88 mmol), diboron tetrachloride, 0.88 g (5.02 mmol), and a very small amount of a dark green solid that mass spectrometry indicated was B_8Cl_8 were recovered.

Under vacuum, cyclohexane, ca. 2 mL, was condensed into the reaction vessel and the resulting slurry was filtered through a fritted glass disk. The cyclohexane was removed and then the filtrate was held at 45 °C for 24 h. Although a small amount of BCl_3 was formed, no volatile paramagnetic species was observed.

Spectroscopic examination of the reddish material resulting from this reaction clearly established that it is a mixture. The ^{11}B NMR of the residue (in CCl_4) (see Figure 3) indicates the presence of $B_{12}Cl_{12}$, $\delta = 77.7$, $B_{11}Cl_{11}$, $\delta = 69.5$, and B_8Cl_8, $\delta = 65.1$, along with small amounts of $B_{10}Cl_{10}$, $\delta = 63.4$, and BCl_3, $\delta = 46.7$. The approximately relative concentrations are as follows: $B_{12}Cl_{12}$, 0.38; $B_{11}Cl_{11}$, 1.00; B_8Cl_8, 0.73; $B_{10}Cl_{10}$, 0.11. The mass spectra contain large molecular ion envelopes corresponding to $B_{12}Cl_{12}$, $B_{11}Cl_{11}$, and B_8Cl_8 along with a much smaller envelope corresponding to $B_{10}Cl_{10}$. Nonachlorononaborane is not observed.

The ESR spectra obtained from a sample of this material contain a single, very strong, and almost featureless resonance, which is 25 G from peak to trough; the g value is 2.0172. The resonance is exceptionally intense with a density of spins that corresponds to an effective concentration of several tenths of a mole per liter. This resonance could not be saturated at the highest available signal strength.

Relative Thermal Stabilities of the Polynuclear Boron Chlorides. In order to ascertain the relative thermal stabilities of the three largest clusters, $B_{10}Cl_{10}$, $B_{11}Cl_{11}$, and $B_{12}Cl_{12}$, 2 g of B_2Cl_4 was held at 60 °C for 48 h. The vessel was opened, and the material that was volatile at ambient temperature was removed. The solid residue was placed into a vacuum sublimator, and green-black B_8Cl_8 was removed at 40 °C. Increasing the temperature to 80 °C resulted in the sublimation of a mixture that consisted of $B_{12}Cl_{12}$, $B_{11}Cl_{11}$, and $B_{10}Cl_{10}$; see Figure 4.

One sample of this mixture, in pentane, was sealed under vacuum and heated to 200 °C. After 2 h at 200 °C, the resonance due to $B_{12}Cl_{12}$ (77.7 ppm) was absent while those due to $B_{11}Cl_{11}$ and $B_{10}Cl_{10}$ remained. New absorptions at 46.7 ppm (BCl_3) and 58.4 ppm (B_9Cl_9) were evident along with a yellow solid. Mass spectrometry (see Table I) demonstrated the presence of $B_{11}Cl_{11}$, $B_{10}Cl_{10}$, and B_9Cl_9 and the absence of $B_{12}Cl_{12}$.

The temperature of a second sample of the mixture, also in pentane, was elevated to 200 °C for 70 min and then to 300 °C for 30 min. NMR spectra of this sample then contained BCl_3, B_9Cl_9, and $B_{10}Cl_{10}$ resonances but not those expected for $B_{11}Cl_{11}$ or $B_{12}Cl_{12}$. After removal of the pentane and BCl_3, mass spectra confirmed the presence of B_9Cl_9 and $B_{10}Cl_{10}$; $B_{11}Cl_{11}$ and $B_{12}Cl_{12}$ were unobserved.

When B_9Cl_9 is dissolved in BCl_3 and then exposed to 400 °C for 85 h, the resonance due to B_9Cl_9 does diminish but it is still clearly evident at the end of that time. The relative thermal stability of B_8Cl_8 in BCl_3 was assessed by following one of the thermal decompositions of B_2Cl_4 at 200 °C. After 30 min the intensities of the B_8Cl_8, $B_{11}Cl_{11}$, and $B_{12}Cl_{12}$ resonances were in the ratio 71:100:46. After 2.5 h the relative intensities were found to be 0:100:38. In CCl_4, however, B_8Cl_8 persists for at least 18 h at 200 °C.

Results and Discussion

Formation of B_2Cl_4. Diboron tetrachloride is readily generated by the radio frequency discharge of BCl_3 in the presence of elemental mercury. The amount of B_2Cl_4 obtained is linearly dependent upon the BCl_3 flow rate[15], a dependence which is analogous to that previously observed in the preparation of B_2Br_4 from BBr_3 in a similar system.[11] When the BCl_3 flux is sufficiently high, ca. 40 g/h, the rate of formation of B_2Cl_4 is 300 mg/h. Under these conditions the conversion of BCl_3 to B_2Cl_4 is 1.1%, based upon the reaction $2BCl_3 + 2Hg \rightarrow B_2Cl_4 + Hg_2Cl_2$.

Overall, especially in terms of operator time, the rf discharge method is the most effective B_2Cl_4 synthesis of which we are aware since the amounts formed are greater than those that are typically obtained from electrical (ozonizer) or dc discharges[7,18] or the amounts (1 g/4 h run)[19] that we have been able to isolate when a conventional (Klabunde type) metal atom reactor has been employed for the reaction between copper atoms and BCl_3.[20]

The most difficult step in the purification procedure is the separation of B_2Cl_4 from the $SiCl_4$ that is generated simultaneously. The latter presumably arises from the interaction of the chlorine formed in the discharge with the Pyrex walls of the reactor.[15] Although very careful fractionation can be employed to separate B_2Cl_4 from $SiCl_4$, the most effective separations occur when low-temperature distillation techniques are utilized.

Thermal Disproportionation of B_2Cl_4. In principle, the thermal reaction of B_2Cl_4 is a simple disproportionation in which the formally divalent boron atoms of B_2Cl_4 form equivalent amounts of monovalent (B_nCl_n) and trivalent (BCl_3) products. The overall reaction can be most generally expressed as

$$nB_2Cl_4 \rightarrow nBCl_3 + B_nCl_n \qquad (1)$$

The objective of this first portion of the study was to identify the diamagnetic products arising from the thermal reaction of undiluted B_2Cl_4 and to determine the approximate yields of these species as a function of the temperatures utilized, thereby evaluating the type of thermal conditions that might be required to maximize the yield of the various compounds. The approximate yields of the polyhedral boron halides obtained directly from the thermal decompositon of B_2Cl_4 are contained in Table II. For B_8Cl_8 ($n = 8$), for example, the maximum yield clearly occurs near 100 °C. Once this thermal parameter had been obtained, the yield of B_8Cl_8 at 100 °C could be readily increased from 38% to 88% by the introduction of an alternative solvent, CCl_4.[21]

At elevated temperatures (450 °C) the only molecular cluster compound present in macroscopic amounts is the nine-atom cage compound B_9Cl_9, which is directly obtained in 29% yield, again based upon the foregoing reaction, with $n = 9$. At slightly lower temperatures, the nonvolatile species with the chemical shift of 63.3 ppm and the mass spectrum containing the $B_9Cl_8^+$ ions, which we believe is due to the linked cluster $(B_9Cl_8)_2$, is also observed. The amount of B_9Cl_9 initially present at the lower temperature is reduced, only 10% at 400 °C. At the present time the preparative procedure of choice for B_9Cl_9 involves the thermal decomposition of B_2Cl_4 in the 300–450 °C temperature range, followed by the removal of the BCl_3 generated and then gentle heating at 70–100 °C under vacuum. In a standard vacuum sublimation apparatus the yellow solid described above slowly decomposes to generate substantial amounts of B_9Cl_9. Although variable, typical overall yields of B_9Cl_9 are 50–75%, based upon eq 1.[19]

At intermediate temperatures, 16 h at 100 °C, for example, all of the polynuclear boron monochlorides B_nCl_n ($n = 8$–12) are formed and the combined yields of these species are quite high, 81%, again based upon eq 1 above. The available data, Table II, indicate that improved yields of $B_{10}Cl_{10}$ and $B_{11}Cl_{11}$ are most likely be encountered at temperatures between 80 and 200 °C whereas the most effective syntheses of $B_{12}Cl_{12}$ may well involve slightly subambient temperatures.

Three of the most surprising findings of this part of the study came from the reactions that were carried out near ambient temperature. The first was that while the evolution of BCl_3 and the coloration of the solution are apparent almost immediately, neither the radical species nor the polyhedral boron clusters are evident for at least 24 h. The second interesting feature is that B_2Cl_4 is still found in solution 5 years after the initiation of the thermal decomposition. Since the initial rate of the reaction is approximately 7% per day, it seems most probable that B_2Cl_4 is regenerated during the course of the reaction.[22] The third curious fact is that at or near ambient temperature B_9Cl_9, by far the most

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(20) Using similar apparatus, Timms reports yields of 10 g/h from this reaction: Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1972**, 830. In our hands the two methods generate comparable amounts of B_2Cl_4 per hour of reaction, but the separation procedures are much less time consuming with the discharge apparatus.

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(22) The longest B_2Cl_4 decomposition of which we are aware has been in progress at Penn State for over 10 years: Wartik, T., personal communication, 1985.

stable of all of the cage compounds examined here, is not obtained during the same time frame in which $B_{12}Cl_{12}$, $B_{11}Cl_{11}$, and B_8Cl_8, the radical species, and very small amounts of $B_{10}Cl_{10}$ are observed; see Figure 3. Alternatively stated, the thermal dependence of the B_9Cl_9 yield is much different than that of e.g., $B_{12}Cl_{12}$; this is most clearly evident from Table II. The implications of these results are further discussed below.

Thermal Stability of the Polyhedral Boron Chlorides. The most thermally stable of the boron monochlorides is B_9Cl_9, which is observed for at least 85 h at 400 °C. The relative thermal stabilities of the three largest cluster compounds in pentane were established by means of competative experiments, which demonstrate that in this medium the order of stability is $B_{10}Cl_{10} > B_{11}Cl_{11} > B_{12}Cl_{12}$, which is the same order as indicated in BCl_3. Thus the stability of the four largest cages studied here decreases as the cage size increases. The smallest of these compounds, B_8Cl_8, however, is also the least stable in both pentane and BCl_3.

The overall stability order found for the polyhedral boron chlorides, $B_9Cl_9 > B_{10}Cl_{10} > B_{11}Cl_{11} > B_{12}Cl_{12} > B_8Cl_8$, may well be typical of $2n$ framework electron clusters since the same order has been previously observed for the boron monobromides, B_nBr_n ($n = 7$–10).[11] The thermal stabilities of the polyhedral boron chlorides is dependent upon the medium employed; B_8Cl_8, for example, survives more than 18 h at 200 °C in CCl_4 but is completely decomposed after 2.5 h at that temperature in BCl_3.

The relative stability order for more reduced deltahedral clusters, those containing $2n + 2$ framework electrons, is much different. Previous experimental results have clearly established that the most stable of the borane dianions is the 12-atom cluster, $B_{12}H_{12}^{2-}$, which is followed by the 10-atom cage. The $B_6H_6^{2-}$, $B_8H_8^{2-}$, and $B_9H_9^{2-}$ ions appear to be comparable to the $B_{10}H_{10}^{2-}$ ion in terms of thermal stability, while the $B_{11}H_{11}^{2-}$ and $B_7H_7^{2-}$ ions are the least stable.[23] Lipscomb's calculations, which result in an average energy/BH unit, are generally reflective of this stability order: $B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} > B_{11}H_{11}^{2-} > B_9H_9^{2-} > B_8H_8^{2-} > B_7H_7^{2-}$.[24]

^{11}B Nuclear Magnetic Resonance Spectra. In $2n + 2$ framework electron clusters like the borane dianions, $B_nH_n^{2-}$, fluxionality is generally observed in the 8- and 11-atom systems but not in the 12, 10, or 9 framework atom species.[25] The ^{11}B NMR data for $B_9Cl_9^{2-}$ and $B_{10}Cl_{10}^{2-}$, for example, are indicative of static structures for both of these anions in solution.[26,27] In contrast, at ambient temperature the ^{11}B NMR resonances of all of the polyhedral boron chlorides B_nCl_n ($n = 8$–12) are singlets in the solvents employed. Thus one general difference between the $2n$ framework electron cages and the $2n + 2$ electron species is that collectively the former appear to be more plastic in solution than the latter.

The structures of $B_{12}Cl_{12}$, $B_{11}Cl_{11}$, and $B_{10}Cl_{10}$ are currently unknown, but the crystallographic data for B_8Cl_8 and B_9Cl_9 indicate that each of these compounds has two structurally distinct boron sites.[5,28] Thus the observed magnetic equivalence of the atoms in these compounds most probably arises from fluxionality (accidental overlap of their resonances at the available field strength appears less likely).[29]

Muetterties "points on a sphere" calculations have shown that for the nine-atom system the lowest energy rearrangment pathway correponds to the $D_{3h} \leftrightarrow C_{4v}$ (diamond–square–diamond) transit and that the barrier for this transformation should be relatively low.[30] King's topological approach indicates that the tricapped trigonal prism should be inherently fluxional, and he concludes that the structural rigidity of, e.g., $B_9Cl_9^{2-}$ is most difficult to explain.[31] Similarly, Kepert's analysis of the structure and bonding in the borane dianions (where the strength of the bond between any two boron atoms is expressed as a bireciprocal function of the distance between the two atoms) suggests that there are no barriers in the potential surface between the two lowest energy topomers, the tricapped trigonal prism and the monocapped square antiprism.[32]

Table III. Chemical Shift Data for Polyhedral Boranes and Dianions[a]

	δ				
compd (fec)	$n = 12$	$n = 11$	$n = 10$	$n = 9$	$n = 8$
B_nCl_n ($2n$)	77.7	69.5	63.5	58.4	65.2
$B_nCl_n^{2-}$ ($2n + 2$)	−12.9[b]		−9.5[b]	−4.1[c]	
$B_nH_n^{2-}$ ($2n + 2$)	−16.9[d]	−17.0[d]	−23.2[d]	−15.8[d]	−6.0[d]
$\Delta(B_nCl_n - B_nH_n^{2-})$	94.6	86.5	86.7	74.2	71.2
$\Delta(B_nCl_n - B_nCl_n^{2-})$	90.6		73.0	62.5	

[a] *All chemical shifts vs.* $BF_3{\cdot}OEt_2$; *Weighted chemical shifts employed for static species.* [b] Reference 26. [c] Reference 27. [d] Reference 34.

The explanation for the difference in solution state behavior of the nine-atom compounds B_9Cl_9 and $B_9Cl_9^{2-}$, both of which have tricapped-trigonal-prismatic ground-state structures, can be traced to the degeneracies of the highest occupied molecular orbitals. Extended-Hückel calculations have shown that for the $B_9H_9^{2-}$ ion, which is diamagnetic in the D_{3h} ground state, the rearrangement to the C_{4v} intermediate would result in a species in which the highest occupied molecular orbitals, the 5e orbitals, would be doubly degenerate, but only half-filled, resulting in a triplet ground state for the $B_9H_9^{2-}$ ion in the C_{4v} geometry.[32] Thus what should be the lowest energy rearrangement pathway in this ion is accompanied by a spin-crossing process. To the extent that the calculations on $B_9H_9^{2-}$ are reflective of the molecular orbitals of $B_9Cl_9^{2-}$, a relatively high barrier to rearrangement would also be expected in $B_9Cl_9^{2-}$. For neutral B_9Cl_9, however, the HOMO orbitals in both the D_{3h} and C_{4v} structures are filled, doubly degenerate orbitals; the diamond–square–diamond rearrangement process proceeds readily.[33,34]

The second major difference between the ^{11}B NMR spectra of the B_nCl_n and $B_nCl_n^{2-}$ species is also a result of the decrease in the electron density found in the neutral compounds. Relative to the dianions, the chemical shifts of the neutral species are extensively deshielded as shown in Table III, which presents the boron chemical shifts of the boron halides along with the chemical shifts of related polyhedral species as a function of cage size and electron count. These data indicate that the resonances of all of the $2n$ framework electron clusters are deshielded by 70–95 ppm relative to the analogous borane dianions and by 63–91 ppm relative to the perchlorinated dianions.

The effect of chloride for hydride substitution in the largest of the borane dianions, $B_{12}H_{12}^{2-}$, is a 4 ppm deshielding of the resonance from −17 to −13 ppm. The net effect of removing two electrons from $B_{12}Cl_{12}^{2-}$ to generate the uncharged $B_{12}Cl_{12}$ cluster is much larger, 91 ppm. This difference in chemical shifts arises

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from at least three separate sources. The first is the effect of decreasing the electron density near the boron nuclei upon "oxidation" of the cluster, the second is any effect upon the chemical shift that might accompany a change in the ground-state structure of the cluster upon the loss of the two electrons, and the third is the net result of any differences between the solvation of the neutral and anionic species. The directions and the magnitude of the individual contributions to the differences in chemical shift between the B_nCl_n and $B_nCl_n^{2-}$ species are unknown at present; however, for B_9Cl_9, a cluster in which only the first and the third components operate, the difference in chemical shift between B_9Cl_9 and the $B_9Cl_9^{2-}$ dianion is 63 ppm.

Stages of the Diboron Tetrachloride Thermal Reaction. The mechanistic details of the B_2Cl_4 reaction are under further study; however, the currently available evidence clearly demonstrates that this reaction occurs via five discrete stages. Each stage results in different products.

Stage One. The first stage is characterized by the first appearance of BCl_3 in the ^{11}B NMR and by the yellow color, which is apparent within minutes at ambient temperature. The boron monochlorides and the radical species, however, are not yet observed; at ambient temperatures they are not present in concentrations sufficiently high for detection until the second day. The polyhedral boron halides and the radical must arise from a metastable precursor or series of precursors.

Conceptually at least, the most plausible first step of the reaction is the formation of B_3Cl_5, the chlorinated analogue of the well-known B_3F_5, by the reaction $2B_2Cl_4 = B_3Cl_5 + BCl_3$. Subsequent chain-growth reactions would result in unstable compounds such as B_4Cl_6, species with the general formulation B_nCl_{n+2}. Dimerization or even incorporation of a tricoordinate boron compound would form compounds of the type B_nCl_{n+4}, compounds that in stoichiometry correspond to the well-known nido boron hydrides.

Several lines of evidence are in accord with a reaction sequence of the general type postulated above. First, in both the B_2Cl_4 and B_2Br_4[11] thermal reactions, the time delay between the appearance of the colored substance(s) and the appearance of the NMR and ESR signals arising from the monohalides and the paramagnetic species mandates that some form of metastable species is formed. Second, the above sequence demands that the chlorine to boron molar ratio of the solid material obtained very early in the reaction be greater than unity, rather than less as has been previously reported.[1,4] During the attempted synthesis of $B_{12}C_{11}$ described above, after 24 h at 60 °C, 31% of the B_2Cl_4 (2.26 mmol), which had been originally taken, decomposed with the liberation of 1.88 mmol of BCl_3 (83% based upon the unrecovered B_2Cl_4). Elementary mass balance considerations indicate that the overall B:Cl ratio in the solid is 1.00:1.29, which corresponds to an average emperical formula of B_7Cl_9. After the first stage of the reaction, the solid material thus contains more chlorine than boron. If these results are reflective of only one intermediate, B_7Cl_9, $B_{14}Cl_{18}$, or $B_{21}Cl_{27}$ is implicated; the first and last of these seem unlikely. Perchlorinated *nido*-boranes like $B_{14}Cl_{18}$ are currently unknown; however, compounds of the type $B_{10}Cl_nH_{14-n}$ ($n = 2$–8) have been prepared. They are bright yellow, a color very much like that initially observed in the B_2Cl_4 reaction.[36]

Several reviews have emphasized the differences between the polynuclear boron fluorides and the analogous chlorides. Typically, theoretical justifications based upon supposed differences in the back-bonding effects of the halides have been cited to rationalize the current lack of any compound of the type B_nF_n.[8,37,38] An alternative view is that these reported differences may well arise primarily from kinetic factors and not from any inherent differences in the course of the thermal reaction caused by the substitution of fluorine for chlorine or bromine. The polynuclear boron fluorides (like B_2F_4) are well-known to be more stable than the analogous chlorides (such as B_2Cl_4), which in turn are more stable than the corresponding bromides (e.g, B_2Br_4). The course of the B_2Br_4 thermal reaction has previously been shown to be very similar to that of B_2Cl_4,[11] and as a whole, the boron–fluoride chemistry reported by Timms is surprisingly supportive of the type of intermediate postulated above. Timms, who generated BF from the reaction of BF_3 with boron, has shown (1) that BF readily inserts into B_2F_4 forming B_3F_5, (2) that B_3F_5 decomposes at ca. −50 °C according to the equation $4B_3F_5 \rightarrow 2B_2F_4 + B_8F_{12}$, (3) that at about −20 °C B_8F_{12} in turn decomposes to yield BF_3 and a product thought to be $B_{14}F_{18}$, and (4) that isolation of $B_{14}F_{18}$ is difficult because it decomposes to other products with the further evolution of BF_3. The intermediate B_8F_{12} is the dimer of $B(BF_2)_3$ which, like its hydrogen-containing analogoue BH_3, can be trapped with Lewis bases such as CO or PF_3. The structure of $B_{14}F_{18}$ is undetermined.[38-41]

The overall stoichiometry for the analogous reaction of B_2Cl_4 is shown in eq 2. The experimental results are presented in eq 3.

$$12B_2Cl_4 \rightarrow B_{14}Cl_{18} + 10BCl_3 \tag{2}$$

$$12B_2Cl_4 \rightarrow (1/n)(B_{14.00}Cl_{18.04})_n + 9.98BCl_3 \tag{3}$$

Stage Two. In the second stage of the B_2Cl_4 thermal reaction the loss of BCl_3 from the precursor(s) occurs, resulting in the formation of polyhedral boron halides and the radical species. In the thermal reaction of undiluted B_2Cl_4, the diamagnetic clusters formed in the largest amount during the very early parts of this stage are $B_{12}Cl_{12}$, $B_{11}Cl_{11}$, and B_8Cl_8; see Figure 3. The experimental evidence for this part of the sequence is again most easily seen from the results of the $B_{12}Cl_{11}$ resynthesis when BCl_3 was evolved from the red solids maintained in cycylohexane for 24 h. A resonance due to small amounts of BCl_3, which have been liberated from the red solid, can be seen in Figure 3. Schram and Urry have also reported the loss of small amounts of BCl_3 from their red solid at 115 °C.[4]

Disregarding for the moment the effects of the radical species upon the yields, if the reaction could be stopped at the end of the second stage, the amount of boron contained in BCl_3 and that contained in all of the polyhedral boron halides should be equal, as shown in eq 1. Experimentally, the amount of boron contained in the diamagnetic B_nCl_n species present after 16 h at 100 °C is at least 81% of that in the BCl_3 present; see Table II.

There are clearly two distinct reaction channels available during this second stage of the reaction. The first pathway is favored by slightly elevated temperatures, ca. 100 °C, and inert solvents like CCl_4. Under these conditions B_8Cl_8 is isolated in 88% yield, the radical species is clearly observed, and the only other diamagnetic compound present is B_9Cl_9 in small amounts, ca. 5%.[21] At ambient temperature, however, the formation of $B_{12}Cl_{12}$ and $B_{11}Cl_{11}$ predominates; see Table II. Additionally, Massey has reported that at ambient temperature, in the presence of excess BCl_3, the only cluster compound that could be identified was $B_{11}Cl_{11}$; B_8Cl_8 and B_9Cl_9 were unobserved.[7]

The formation of B_8Cl_8 is thus favored by experimental conditions that are conducive to the formation of the carbene analogue BCl. In the absence of a BCl trap and in the presence of slightly elevated temperatures, a reaction sequence that is consistent with the currently available evidence for the second stage of the reaction is

$$4B_2Cl_4 \rightarrow 4BCl_3 + 4BCl \tag{4a}$$

$$2B_{14}Cl_{18} + 4BCl \rightarrow 2B_8Cl_8 + 2B_8Cl_{12} \tag{4b}$$

$$2B_8Cl_{12} \rightarrow 2BCl_3 + B_{14}Cl_{18} \tag{4c}$$

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(42) The seven-atom compound, B_7Cl_7, which might be expected to arise from the reaction $B_{14}Cl_{18} + BCl \rightarrow B_7Cl_7 + B_8Cl_{12}$, is yet to be observed; however, the corresponding bromide, B_7Br_7, is well-known.[11]

Combined with the first stage, the overall stoichiometry of this reaction can be expressed as

$$12B_2Cl_4 \rightarrow 10BCl_3 + B_{14}Cl_{18} \tag{2}$$

$$4B_2Cl_4 \rightarrow 4BCl_3 + 4BCl \tag{4a}$$

$$4BCl + 2B_{14}Cl_{18} \rightarrow 2B_8Cl_8 + B_{14}Cl_{18} + 2BCl_3 \tag{4b + 4c}$$

$$\text{net:}\quad 16B_2Cl_4 \rightarrow 16BCl_3 + 2B_8Cl_8 \tag{5}$$

$$\text{or}\quad nB_2Cl_4 \rightarrow nBCl_3 + B_nCl_n \quad n = 8 \tag{1}$$

At lower temperatures and especially in the presence of excess BCl_3, the reaction channel to B_8Cl_8 is quenched[7] and $B_{12}Cl_{12}$ and $B_{11}Cl_{11}$ are initially observed in equivalent amounts; see Table II. Reactions consistent with the high dilution data are

$$B_{14}Cl_{18} \rightarrow B_{12}Cl_{12} + 2BCl_3 \tag{6a}$$

$$B_{12}Cl_{12} + BCl_3 \rightarrow B_{11}Cl_{11} + B_2Cl_4 \tag{6b}$$

Thus $B_{12}Cl_{12}$, which is one of the least stable of the boron monochlorides, decomposes with the extrusion of BCl, the latter reacting with BCl_3 to regenerate B_2Cl_4. This is one source of the B_2Cl_4 that is observed at least 5 years after the initiation of the ambient-temperature decomposition of B_2Cl_4. This mode of decomposition, the ejection of a BX unit, has been previously reported for both the borane dianions and the carboranes.[43] In the presence of a BCl trap and in the absence of elevated temperatures, the overall reaction stoichiometry through the second stage can be expressed as follows:

$$24B_2Cl_4 \rightarrow 20BCl_3 + 2B_{14}Cl_{18} \tag{2}$$

$$2B_{14}Cl_{18} \rightarrow 2B_{12}Cl_{12} + 4BCl_3 \tag{6a}$$

$$B_{12}Cl_{12} + BCl_3 \rightarrow B_{11}Cl_{11} + B_2Cl_4 \tag{6b}$$

$$\text{net:}\quad 23B_2Cl_4 \rightarrow 23BCl_3 + B_{12}Cl_{12} + B_{11}Cl_{11} \tag{7}$$

$$\text{or}\quad nB_2Cl_4 \rightarrow nBCl_3 + B_nCl_n \quad n = 11, 12 \tag{1}$$

Again the chemistry of the polynuclear boron fluorides is reminiscent in that while B_8F_{12} is diamagnetic, samples of B_8F_{12} become paramagnetically upon standing.[40] Additionally, $B_{14}F_{18}$ is reported to decompose with the liberation of BF_3 and a series of other products one of which has a strong $B_{12}F_{12}^+$ ion in its mass spectrum.[3,40,41]

Stage Three. The third observed stage of the reaction is the stepwise decomposition of the cage compounds $B_{12}Cl_{12}$, $B_{11}Cl_{11}$, and B_8Cl_8 and the radical species, as well as $B_{10}Cl_{10}$, the last presumably arising from loss of BCl from $B_{11}Cl_{11}$, to generate BCl_3 and the yellow solid, which appears to be a cross-linked polymeric material; it is not soluble in the solvent, BCl_3. This phase of the reaction is responsible for the overall decline in the combined yields of the polyhedral boron halides, which is observed as the thermal conditions become more rigorous. Although B_9Cl_9 is formed during this stage, this is not the major source of B_9Cl_9, as shown by the reactions at 80 °C in Table II. It is during this stage that the solid(s) become boron rich.[1,4] For example, after B_2Cl_4 had been held at 450 °C for 3 min, the amount of BCl_3 recovered corresponded to 109% of that expected from reaction 1.

Stage Four. The fourth stage of the reaction is the formation of B_9Cl_9 from the yellow polymeric substance. This reaction, which in solution may also involve BCl_3, presumably yields first $(B_9Cl_8)_2$ and then B_9Cl_9. Both the decomposition of the clusters B_nCl_n ($n = 8$, 10–12) to yield yellow insoluble solids (along with B_9Cl_9) and the formation of B_9Cl_9 from the yellow solid during the attempted sublimation of $(B_9Cl_8)_2$ have been independently observed; see above. The yield of B_9Cl_9 at elevated temperatures only is at least as high as 50%, based upon the same equation, which gave an 81% yield of largely different products after 16 h at 100 °C.

Stage Five. The final stage of the reaction is the decomposition of B_9Cl_9 to yield the white to tan involatile material, which is insoluble in all common solvents. This stage requires 4–6 days at 450 °C.[44]

Summary. Although the thermal decomposition of B_2Cl_4 in the absence of solvent is in principle a very simple reaction, in practice the answers to even the most basic questions such as whether radical species are formed or whether B_8Cl_8 or $B_{12}Cl_{12}$ are observed depend upon the thermal history of the sample. It should be emphasized that although the various stages discussed above have been conceptually separated, typically several or indeed all may occur contemporaneously. Unless special precautions have been taken, such as not utilizing temperatures above 80 °C, all of the products derived from all of the stages may be found together. The thermal reaction of B_2Br_4 is completely analogous to that of B_2Cl_4. At ambient temperature BBr_3 is observed within 5 min; however, the radical species is not detected for 8 h, again an indication that metastable species are also present in that reaction.[11]

The results obtained above do answer several of the questions that were of interest at the outset of the investigation. The yields of the individual clusters obtainable range from reasonable to good (10–50%). The red material, previously described as $B_{12}Cl_{11}$, both looks and acts like a single compound, yet this substance is in fact a mixture that contains, among others, B_8Cl_8. The intensity of the ESR signal obtained from the samples is astonishing, indicating an effective spin density that corresponds to at least several tenths of a mole/liter. The signal breadth and the fact that this signal could not be saturated is indicative of an electron that is located such that relaxation processes are exceptionally efficient, e.g. an electron located in a cavity comprised of nuclei with large quadrupole moments. The paramagnetic species does not arise from hydrolysis. It has been observed in each and every sample that we have studied provided that the appropriate thermal history has been maintained.

The results obtained above also raise several questions that are currently under study. Some are related to the postulated chlorine-rich precursor $(B_{14}Cl_{18})$. Direct spectroscopic observation of this species by the available instrumentation has been precluded by the low concentration in solution. The synthesis of this compound by an alternative route is in progress. Another question is related to the compound previously described as B_8Cl_8, which was stated to be red in color and stable to moist air.[5] The B_8Cl_8 that we (and others[7]) have obtained is a very dark green-purple, almost black substance. It is exceptionally reactive with air resulting in a violet product. Finally, the composition of the radical species is still under investigation.

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Registry No. BCl_3, 10294-34-5; Hg, 7439-97-6; B_2Cl_4, 13701-67-2; B_9Cl_9, 12008-47-8; B_8Cl_8, 32915-80-3; $B_{11}Cl_{11}$, 12230-26-1; $B_{12}Cl_{12}$, 84879-96-9; $B_{10}Cl_{10}$, 61674-49-5.

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(43) See, for example: Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1966**, *5*, 1955.

(44) Saulys, D. A., unpublished observation.