Chemistry of the Polyhedral Boron Halides and the Diboron Tetrahalides

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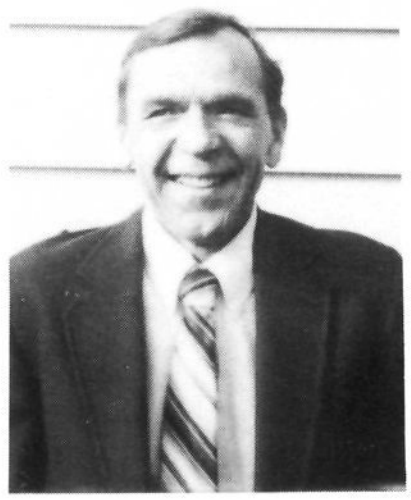

John Morrison was born in Sacramento, CA. His undergraduate degree is from the University of California at Berkeley and his Ph.D. degree was obtained from the University of Maryland at College Park. After his postdoctoral study at the Massachusetts Institute of Technology, he moved to the University of Illinois at Chicago in 1976. His research interests are centered on the chemistry of the boron halides and the preparation of perfluoroalkyl-substituted inorganic and organometallic compounds.

I. Introduction

Legend has it that Alfred Stock initiated his examination of boron hydride chemistry from a deep and abiding conviction that boron, the element adjacent to carbon in the periodic table, must partake in more interesting bonding combinations than those that had been found in boric acid and the boron oxides that were then known.[1] Subsequent findings, of course, have more than amply borne out Stock's predictions. Perhaps even more important than the then undreamed of structural complexities of the boron hydrides and their derivatives, however, is the way in which the structural and bonding considerations that were first uncovered in borane chemistry have later, sometimes much later, been encountered in areas that are entirely unrelated to boron chemistry. One trivial example is the M–H–C "agostic" interaction which is nothing more (or less) than the well-studied B–H–B and B–H–M bridge bonding translated into an organometallic setting.

Another example is the framework electron counting methods that have been derived for transition-metal clusters.[2,3] Many of the precepts of these very powerful tools that relate electron counts to the anticipated cluster structures are readily derivable from those originally deduced from boron hydride structures by Lipscomb, Williams, Wade, Rudolph, and others.

Simply stated, the geometries of borane cluster compounds containing n vertex atoms (n = 5–12) are expected to be based upon the n vertex deltahedra shown in Figure 1 if there are $2n + 2$ framework electrons. Usually, but not always, there are exopolyhedral ligands bonded to the framework atoms (which are situated at the corners of the deltahedra depicted in Figure 1). When the $n + 1$ bonding molecular orbitals that are generated if each framework atom donates three valence atomic orbitals to the cluster bonding are filled, the cluster is often very thermally stable, sometimes to 600 °C, or more. Generally, the cluster framework is very chemically inert as well.

The results sketched above have been so commonly observed that the $2n + 2$ framework electron count has been referred to as a "magic" number of electrons and the correlation itself has occasionally been dubbed the "inorganic Huckel rule". For the more open, but less stable, nido, arachno, and hypho structural classes, the appropriate framework electron counts for n framework atom clusters are $2n + 4$, $2n + 6$, and $2n + 8$, respectively.[4,5]

Among the deltahedra shown in Figure 1, the tetrahedron (n = 4) is unique in that symmetry-imposed considerations dictate that the framework electron count for a diamagnetic cluster can only be eight or 12

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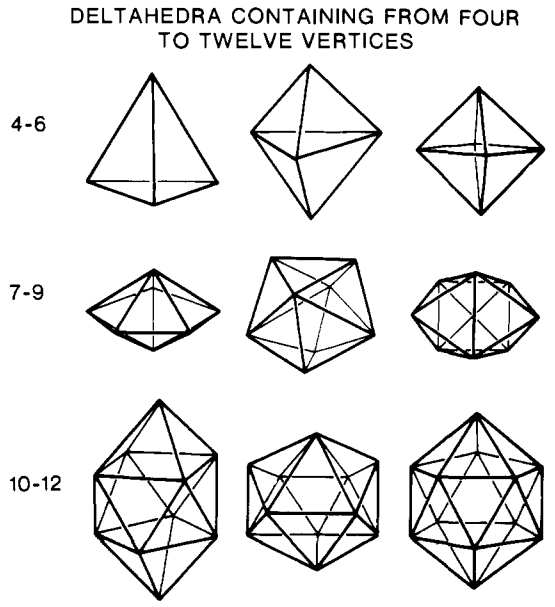

Figure 1. Triangulated deltahedra of n vertices from $n = 4$–12. These three-dimensional geometries can be derived from the appropriate placement of $2(n - 2)$ equilateral or near-equilateral triangles. The observed structures of $2n + 2$ framework electron clusters like the borane dianions, $B_nH_n^{2-}$ (n = 6–12), and the carboranes, $C_2B_{n-2}H_n$ (n = 5–12), are all based upon these structures. In each case the boron or carbon atoms are located at the corners (vertices) of the figure. The ligands are exopolyhedral, that is, BH or CH bond vectors all point away from the center of the polyhedron. For the tetrahedron ($n = 4$) the expected framework electron count is either 8 ($2n$) as in B_4Cl_4 or, much more commonly, 12 ($3n$) as in P_4 or $C_4(t\text{-Bu})_4$. One of the interesting aspects of the polyhedral boron halides is that the structures of B_8Cl_8 and B_9Cl_8 are also reported to be based upon these same deltahedra, even though they do not contain $2n + 2$ framework electrons. The structures of the larger polyhedral boron chlorides, $B_{10}Cl_{10}$, $B_{11}Cl_{11}$, and $B_{12}Cl_{12}$ are currently unknown.

and not the 10 that would have been expected from the $2n + 2$ formula that is applied to the other-sized clusters. Almost always the framework electron count in tetrahedral clusters is 12 as is encountered in $Ir_4(CO)_{12}$, P_4, or $C_4(t\text{-Bu})_4$, for example. In the 12 framework electron tetrahedra the framework bonding is typically described as localized, with the six electron pairs forming six two-center–two-electron bonds. Of the structures found in Figure 1, only in the 12 framework electron tetrahedron can the lines that are shown in the figure be reasonably identified with bonds. In the other cases, the lines are best considered as connectivity guides.

While there are a few isolated examples of cluster structures that cannot be easily correlated with their framework electron counts, as far as we are aware, there is only one fairly complete series of compounds, the polyhedral boron halides, B_nX_n, that as a group seem to have been able to evade the strictures of the commonly encountered framework electron count–structural correlations. These compounds and their chemical precursors, the diboron tetrahalides, are the focus of this review.[6] In the polyhedral boron halides, for example, B_7Br_7, B_8Cl_8, and $B_{11}Cl_{11}$, there are only $2n$ framework electrons, thus they are electron deficient with respect to most clusters of the same nuclearity.

In many ways, tetraboron tetrachloride is a typical example of the polyhedral boron halides in that there are only $2n$ framework electrons (eight in this case), thus B_4Cl_4 is electron deficient, at least in comparison to other tetrahedral clusters. Clearly, with only eight framework electrons, the bonding in the B_4 cage cannot be localized between the vertex atoms. It must be multicentered. Within the styx (valence bond) formalism, the accepted value for B_4Cl_4 is 0400, which implies that the framework bonding can be visualized as four three-centered bonds, one in each triangular face of the tetrahedron.

This multicentered-bonding picture is one of the reasons that we consider B_4Cl_4 to be the smallest true cluster compound, one in which the framework bonding is representative of that found in the larger species. Further, we believe that the reactions of B_4Cl_4 may well be prototypical of those that are encountered in larger, more difficult to study species.

The results presented below describe the current state of the art (1990) for the polyhedral boron halides and the diboron tetrahalides. Although historically the rate of development in this area of chemistry has been fairly moderate, due in large part to the inherent difficulties of studying these compounds, a number of recent developments have yielded some fascinating insights into the consequences of electron deficiency in cluster compounds in general and into the guiding principles of the chemistry of the boron subhalides in particular.

II. Chemistry of the Polyhedral Boron Halides and the Diboron Tetrahalides

Traditionally, the chemistry of the boron halides has been divided into two categories, that of the boron trihalides and their derivatives and that of compounds in which the formal valence of the boron atoms is less than three. The latter have been referred to as the boron subhalides and been further differentiated into the diboron tetrahalides and their derivatives—compounds in which the ratio between the boron atoms and their ligands is two—and the polyhedral boron halides and their derivatives—species in which this ratio is one. All of the latter appear to have polyhedral (cluster) structures.

In practice the chemistries of the two types of boron subhalide are intimately related since, although there are a few exceptions, the only known source for the vast majority of the polyhedral boron halides, B_nX_n, is the disproportionation of a diboron tetrahalide. As described below, this reaction yields the appropriate boron trihalide and, usually, several boron monohalides. A vastly simplified version of the B_2Cl_4 disproportionation is $nB_2Cl_4 \rightarrow nBCl_3 + B_nCl_n$ (n = 8–12).

Historically, the sole polyhedral boron halide that was not obtained from a diboron tetrahalide is B_4Cl_4, which is only available from discharge reactions. In the sections that follow, the chemistry of the boron subhalides has been separated into the chemistry of the larger polyhedral boron halides, B_nX_n (n = 7–12) (section A), the chemistry of B_4Cl_4 (section B), and the chemistry of the diboron tetrahalides (section C).

A. Syntheses, Structures, and Reactivities of the Polyhedral Boron Halides, B_nX_n (n = 7–12)

With the exception of the nine boron atom clusters[7–9] and B_4Cl_4, the only source of the polyhedral boron halides is the disproportionation of the appropriate

TABLE I. Properties of the Polyhedral Perhaloboranes

compd	dec, °C[a]	volatile	sublimes	δ, ^{11}B NMR[c]	mass spec (rel intensity)
B_4Cl_4	125 (21 h)	yes	yes	85.5	B_4Cl_4 (100) B_4Cl_3 (90)
B_8Cl_8	200 (18 h)	yes	yes	65.2	B_8Cl_8 (26) B_7Cl_5 (100)
B_9Cl_9	400 (85 h)	yes[b]	yes	58.4	B_9Cl_9 (30) B_8Cl_6 (100)
$B_{10}Cl_{10}$	300 (ca. 100 h)	no	yes	63.5	$B_{10}Cl_{10}$ (20) B_9Cl_7 (100)
$B_{11}Cl_{11}$	300 (3 h)	no	yes	69.5	$B_{11}Cl_{11}$ (15) $B_{10}Cl_8$ (100)
$B_{12}Cl_{12}$	200 (5 h)	no	yes	77.7	$B_{12}Cl_{12}$ (8) $B_{11}Cl_9$ (100)
B_7Br_7	200 (18 h)	no	yes	69.5	B_7Br_7 (14) B_6Br_4 (100)
B_8Br_8	200 (18 h)	no		67.3	B_8Br_8 (98) B_7Br_5 (100)
B_9Br_9	300 (7 days)	no	yes	60.4	B_9Br_9 (100) Br_8Br_6 (89)
$B_{10}Br_{10}$	200 (24 h)	no	yes	65.2	$B_{10}Br_{10}$ (100) B_9Br_7 (100)

[a] The times are *very approximate* half-lives when samples are maintained in sealed tubes. [b] In a standard vacuum line at ambient temperature. B_9Cl_9 moves *very* slowly under dynamic vacuum. [c] ppm deshielded from external $BF_3{\cdot}OEt_2$.

diboron tetrahalide. The early work in this area was quite controversial and, in fact, the findings of each of the initial reports[10-12] have been questioned by later studies. More recent examinations, however, have shown that the thermal reaction of B_2Br_4 yields BBr_3, B_7Br_7, B_8Br_8, B_9Br_9, $B_{10}Br_{10}$, a radical species of undetermined composition, and a number of coupled nine-atom cages, including $B_9Br_8B_9Br_8$ and $B_9Br_8B_9Br_7B_9Br_8$.[13] The combined yield of the bromoborane cluster compounds from B_2Br_4 is ca. 50% and the relative thermal stabilities of these compounds is $B_9Br_9 > B_{10}Br_{10} > B_8Br_8 \approx B_7Br_7$.[13] Some of the properties of these cluster compounds have been collected in Table I.

The chloride B_2Cl_4 generates BCl_3, B_8Cl_8, B_9Cl_9, $B_{10}Cl_{10}$, $B_{11}Cl_{11}$, $B_{12}Cl_{12}$, a radical, coupled nine-atom cages, and a yellow solid, the last of which is the primary source of B_9Cl_9. The combined yields of the diamagnetic B_nCl_n species frequently approach 90%, although, as described below, the identities of the products can vary dramatically with the conditions under which the reaction has been carried out. The relative thermal stabilities of the chloroboranes are in the order $B_9Cl_9 > B_{10}Cl_{10} > B_{11}Cl_{11} > B_{12}Cl_{12} \approx B_4Cl_4 \approx B_8Cl_8$;[14] see Table I.

At 100–400 °C the thermal reaction of diboron tetraiodide has been reported to yield BI_3, B_8I_8, and B_9I_9, only. The yields of this reaction were not stated.[15]

All of these polyhedral products are sufficiently stable to survive sublimation under vacuum and some, e.g., B_9Cl_9, $B_{10}Cl_{10}$, and B_9Br_9, are stable to temperatures well over 300 °C, which is much higher than one might have anticipated for compounds that lack the "magic" numbers of electrons that are required for the cluster to obey the "inorganic Huckel rule". The halides are all intensely colored with B_4Cl_4 and the larger boron chlorides B_9Cl_9 through $B_{12}Cl_{12}$ being yellow to orange whereas B_8Cl_8 is purple-black. The bromides and iodides are all darker in hue, ranging from coal black (B_7Br_7) to ruby red (B_9Br_9). The very deshielded resonances found in the ^{11}B NMR spectra of many of these compounds have been discussed previously.[16] Representative properties of the polyhedral boron chlorides and bromides are presented in Table I.

One of the most curious aspects of the polyhedral boron halides is that despite the theoretical findings discussed below, experimentally, the fluorides are unknown. In no case has the separation of any polyhedral boron halide that contained even one fluorine atom ever been claimed.

1. Seven Vertex Cage

No reaction of B_7Br_7 has been reported. Aside from ^{11}B NMR data, no spectroscopic information is currently available. The structure of B_7Br_7 is unknown; neither B_7Cl_7 nor B_7I_7 have ever been observed.

2. Eight Vertex Cage

Octaboron octachloride is most easily prepared by the disproportionation of a B_2Cl_4 solution that is 20% by weight in CCl_4.[17] After 14 days at 100 °C, the purple-black, very air-sensitive B_8Cl_8 is readily separated (88%) by fractionation.[17] Although B_8Br_8 and B_8I_8 are also available from the appropriate diboron tetrahalides, an alternative synthesis of the former involves the interaction of B_8Cl_8 with a combination of BBr_3 and $AlBr_3$ at 100 °C.[18]

In the absence of solvents both B_8Cl_8 and B_8Br_8 are thermally stable to ca. 200 °C;[13,14] however, in solution B_8Cl_8 has been shown to be slightly less stable than B_4Cl_4.[19] The structure of B_8Cl_8 has been examined by X-ray crystallography and the molecular architecture of the cluster framework was shown to be based upon the eight vertex deltahedron depicted in Figure 1.[10,20,21] In fact, the reported framework atom geometry of B_8Cl_8 is exceptionally similar to that of $B_8H_8^{2-}$.[22] PES and molecular orbital calculations[23] have shown that, overall, the bonding pattern in B_8Cl_8 is very like that of B_4Cl_4, discussed below.

Most B_8Cl_8 reactions are characterized by products in which the conversion of the eight framework atom reagent into a nine framework atom product has occurred;[17,19] thus the reaction of either H_2 or B_2H_6 with B_8Cl_8 at ambient temperature results in HB_9Cl_8, $H_2B_9Cl_7$, and B_9Cl_9, while that with $AlMe_3$ generates $B_9Me_nCl_{9-n}$ (n = 0–4) and BMe_3. Similarly, the reaction of B_8Cl_8 with excess Li(t-Bu) yields both the neutral ($B_9(t\text{-Bu})_9$) and the reduced ($B_9(t\text{-Bu})_9^{2-}$), peralkylated nonaborane clusters.[17]

One of the more surprising aspects of B_8Cl_8 chemistry is the avidity with which B_8Cl_8 accepts hydrogen. For example, at 100 °C, B_8Cl_8 readily reacts with excess pentane to form pentene and, among other boron-containing products, $H_nB_9Cl_{9-n}$ (n = 0–5). Approximately 4 mol of pentene are separated/mol of B_8Cl_8 initially employed.[17] Octaboron octachloride and CH_2Cl_2 interact in similar fashion to generate the nine-atom cluster compounds B_9Cl_9, HB_9Cl_8, and $H_2B_9Cl_7$ along with C_2HCl_3.[19] The reactions described above are summarized in Figure 2.

3. Nine Vertex Cage

Nonaboron nonachloride is most easily prepared by the thermal decomposition of B_2Cl_4. After 5 min at 450 °C, removal of the volatile materials, BCl_3 and B_9Cl_9, followed by gentle heating of the remaining yellow solid results in B_9Cl_9 (75%).[14] Once separated, B_9Cl_9 survives

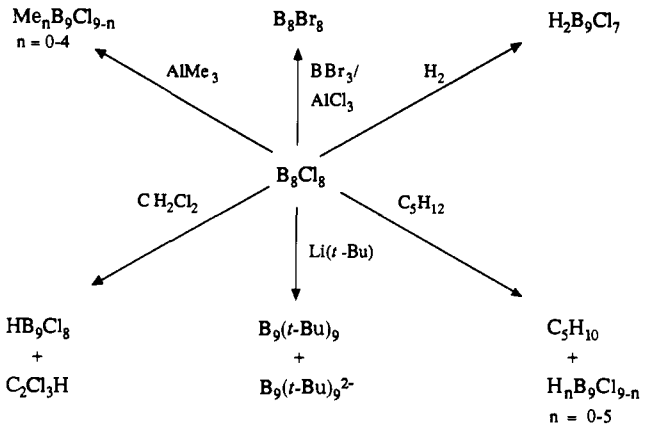

Figure 2. Major products derived from the reactions of B_8Cl_8. Note that with the exception of the $AlBr_3/BBr_3$ reaction,[18] the boron cluster products isolated from these reactions are all derivatives of the nine-atom cage. In the latter reactions the combined yields of all of the nonaboranes is ca. 50%, which suggests that a cage expansion reaction of the type $2B_8X_8 \rightarrow B_9X_9 + B_7X_7$ occurs during the course of the ligand exchange. The less stable seven-atom borane is thought to decompose leaving only the nine-atom cage in solution.

at least 85 h at 400 °C. The bromide[13] B_9Br_9 (50%), and iodide B_9I_9 (unknown yield)[15] can be generated by a similar procedure. Alternative syntheses of the nine framework atom clusters involve either thermolyses[7,8] of alkyl ammonium or hydronium salts of $B_{10}Cl_{10}^{2-}$ or $B_{10}Br_{10}^{2-}$ or two-electron oxidations of nonahalononaborates.[9]

An incomplete X-ray structural examination of B_9Cl_9 is not inconsistant with a framework geometry that is based upon the nine vertex deltahedron shown in Figure 1[24] and B_9Br_9 has been stated to be isostructural.[25] He(I) photoelectron spectra and molecular orbital calculations have demonstrated the correspondence between the bonding in B_9Cl_9 with that found in B_8Cl_8 and B_4Cl_4;[23] see below.

In addition to being by far the most thermally stable of the polyhedral boron halides, B_9Cl_9 is also the least reactive of these species. For example, B_9Cl_9 has been reported to be unreactive toward either H_2 or Cl_2 at 300 °C.[26] The interaction of B_9Cl_9 with molten $AlBr_3$ at 260 °C, however, does result in B_9Br_9.[18]

The bromide B_9Br_9 appears to be somewhat less inert. For example, at 150 °C, $SnMe_4$ exchanges ligands with B_9Br_9 to yield the alkylated nonaboranes $B_9Me_nBr_{9-n}$ (n = 1–9), whereas at ambient temperature, the reaction of $PbMe_4$ in BBr_3 predominantly yields B_9MeBr_8. In pentane, however, $PbMe_4$ concurrently alkylates and reduces B_9Br_9.[13] Ligand exchanges between B_9Br_9 and $TiCl_4$ or $SnCl_4$ are observed at 250 °C.[25] The only reported reaction of B_9I_9 is the reduction of the neutral compound to the dianion with iodide ion.[9]

4. Ten Vertex Cage

Currently $B_{10}Cl_{10}$ and $B_{10}Br_{10}$ are best synthesized from B_2Cl_4 or B_2Br_4 samples that have been held at slightly elevated temperatures.[13,14] Although the structures of neither $B_{10}Cl_{10}$ nor $B_{10}Br_{10}$ have been experimentally examined, symmetry arguments indicate that the framework atom geometries of these compounds cannot be based upon the fully triangulated 10 vertex deltahedron shown in Figure 1.[16] One alternative possibility is a C_{3v} structure with the boron atoms in a 1:3:3:3 stack, a structure somewhat akin to that postulated for (η^6-Mes)FeB_9H_9.[27] Thermal decomposition of $B_{10}Cl_{10}$ and $B_{10}Br_{10}$ is observed after long periods at 300 (100 h) and 200 °C (24 h), respectively.[13,14]

To date the only reactions of $B_{10}Cl_{10}$ that have been reported are those of H_2 at 150 °C, which yields HB_9Cl_8,[18] of Cl_2, Br_2, or I_2 at 135 °C, which results in nine cage atom derivatives, e.g., B_9Cl_9,[26] and of BBr_3 at 200 °C, which forms B_9Br_9.[28]

5. Eleven Vertex Cage

The compound $B_{11}Cl_{11}$ is most conveniently prepared by diluting B_2Cl_4 with a large excess of BCl_3, then allowing the disproportionation of B_2Cl_4 to proceed at ambient temperature. The reported yield is 97%.[26] In this compound, there are no orbital symmetry constraints to prevent $B_{11}Cl_{11}$ from adopting a structure that is based upon that of the 11 vertex deltahedron found in Figure 1. Structural examinations, however, are yet to be carried out.

The interaction of $B_{11}Cl_{11}$ with H_2 at 150 °C yields $H_2B_9Cl_7$,[18] that with Cl_2, Br_2, or I_2 at 135 °C forms, e.g., B_9Cl_9,[26] and that with BBr_3 at 200 °C generates B_9Br_9.[28]

6. Twelve Vertex Cage

The 12 framework atom compound $B_{12}Cl_{12}$ is best prepared from the ambient-temperature reaction of B_2Cl_4.[14] The structure of $B_{12}Cl_{12}$ is currently undetermined, but due to the framework electron count of $B_{12}Cl_{12}$ (24) and the degeneracies of the highest occupied molecular orbitals of both the icosahedron and cuboctahedron, the structure of $B_{12}Cl_{12}$ cannot be based upon these polyhedra without Jahn–Teller distortions of the structures occurring.[16] Aside from thermal decompositions (200 °C),[14] no reactions of $B_{12}Cl_{12}$ have ever been reported.

B. Synthesis, Structure, and Reactivity of Tetraboron Tetrachloride

1. Preparation of B_4Cl_4

Tetraboron tetrachloride, first reported by Schlesinger in 1952, is a bright yellow sublimable solid that was initially separated in very small yields, ca. 0.5 mg/*day*, from electrical discharges of BCl_3 that were carried out in the presence of Hg.[29,30] With two exceptions,[31,32] subsequent studies[12,33,34] confirmed that the amounts of this compound that could be isolated from ozonizer and dc discharges were indeed "minute".[35]

More recently, however, we have examined the formation of B_4Cl_4 from BCl_3 in the presence of elemental mercury using radio-frequency discharges and found that much higher yields, 3–5 mg/h, are afforded by this technique[36] and that within a wide pressure range the B_4Cl_4 yields are not appreciably dependent upon the BCl_3 flow rate.[19] While this is certainly not a generous amount of the compound, it is 2 orders of magnitude higher than that previously available and it has proven sufficient to begin to lay out the chemical behavior of this smallest cluster compound.

2. Structure and Bonding of B_4Cl_4

The strikingly different types of reactions that were initially observed for B_2Cl_4 and B_4Cl_4 clearly indicated

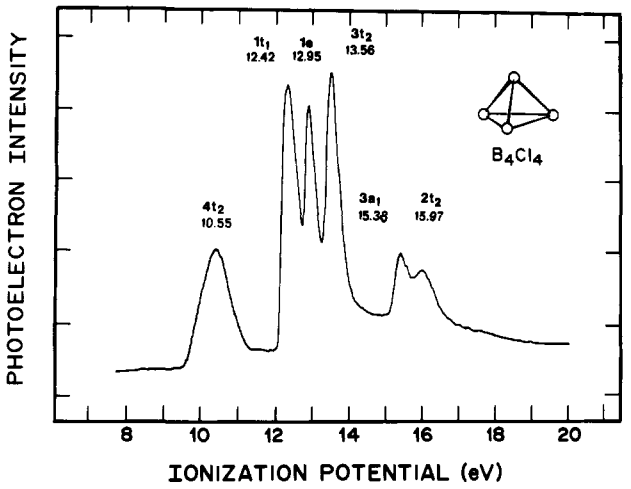

Figure 3. He(I) photoelectron spectrum of B_4Cl_4. The geometry of the B_4 cage is indicated in the inset. The bands at the right of the spectrum arise from the $2t_2$ and the $3a_1$ molecular orbitals, the orbitals that are most closely identified with B–Cl σ bonds. The central bands, 12.4–13.6 eV, chiefly result from the lone pairs of the chlorine atoms. A small amount of bonding overlap with the B_4 cage orbitals is present in the 1e and the $3t_2$ orbitals, but not in the $1t_1$ orbitals. The band furthest to the left, 10.6 eV, is also predominantly Cl 3p in character, but the overlap between the B_4 cage orbitals and the ligand orbitals in the $4t_2$ orbitals, while of π character, is antibonding in nature.

that the bonding within the latter molecule was much different than that in B_2Cl_4.[29,30] These chemical observations were confirmed within the year by Lipscomb[37] who determined that the solid-state configuration of the atoms was near tetrahedral with four exopolyhedral chlorine atoms, $\bar{r}$(B–Cl) = 1.70 Å, surrounding a central core of boron atoms that was only very slightly distorted from tetrahedral, $\bar{r}$(B–B) = 1.70 Å. The essentials of the geometry have since been amply confirmed in the vapor phase by UV,[38] vibrational,[35,39] and photoelectron[23,40] (Figure 3) spectroscopic examinations.

Due to the highly symmetric nature of the B_4Cl_4 structure and the unprecedented framework electron count of this unusual cluster compound, it quickly attracted the attention of a variety of theoreticians who examined the bonding at numerous levels of sophistication.[23,41-44] In fact, until very recently this rare molecule had been subjected to many more theoretical than chemical studies.

Certainly one of the most interesting conclusions was that due to an orbital crossing of the HOMO and LUMO orbitals, the diamond–square–diamond rearrangement ($T_d \rightarrow D_{4h} \rightarrow T_d$) should have an appreciable energy barrier, and it was thus considered likely that under the proper conditions B_4Cl_4, and/or its derivatives, might be separated in both the cluster (T_d) and planar (D_{4h}) geometries.[45] In the latter geometry, the B–B bonds would be two-center–two-electron in nature, rather than the three-center bonds found in the tetrahedral geometry.

To date, however, aside from one early (erroneous) result which is discussed below, there have been no chemical or spectroscopic reports in which a planar polytope of B_4Cl_4 or any of its derivatives has been implicated. This, of course, may merely be a reflection of the fact that at the present time there is only one source of B_4Cl_4, the discharge reactions described above; therefore, if the rearrangement barrier were quite high, the alternative B_4Cl_4 geometry might well be chemically inaccessible from the tetrahedral geometry.

The He(I) photoelectron spectrum of B_4Cl_4 (Figure 3) is typical of the vapor-phase spectroscopic examinations of B_4Cl_4 in that all of the spectral features are readily interpretable from the assumption that the molecule is only present in the tetrahedral geometry. All electron ab initio molecular orbital calculations with a variety of basis sets are all in agreement that the most strongly bonded of the 20 valence pairs of electrons in B_4Cl_4 are the four pairs of Cl 3s electrons and that the next higher orbital in energy, the $2a_1$ orbital, is largely the B_4 cage bonding orbital into which some B–Cl σ bonding character has been mixed. These five orbitals are all too deep in energy to be observed by He(I) spectroscopy.

The $2t_2$ and $3a_1$ orbitals (near 15.5 eV) are the molecular orbitals that can most closely be identified with B–Cl σ bonds. The next three sets of orbitals, 12.4–13.6 eV, are the $3t_2$, the 1e, and the $1t_1$ orbitals. They predominantly arise from the "lone pairs" of the chlorine atoms, the tangential Cl 3p electron pairs. The electrons in the $3t_2$ (13.6 eV) and the 1e (13.0 eV) orbitals are slightly more difficult to remove from the molecule than those in the $1t_1$ orbitals due to a small, but significant, bonding overlap of the chlorine ligand group orbitals with the B_4 framework orbitals. In the $1t_1$ orbitals no such overlap is present.

The most interesting orbitals in B_4Cl_4, however, are the $4t_2$ orbitals. The electrons in these orbitals are substantially less tightly bound (10.6 eV) than the $1t_1$ electrons because of an antibonding interaction (largely of π character) between the Cl ligand group orbitals and the B_4 cage orbitals of the same symmetry. A similar decrease in the binding energy of the HOMO orbitals, relative to the energies of the "pure" Cl 3p lone pairs, arises from antibonding overlaps between the cage and the ligands in B_8Cl_8 and B_9Cl_9.[23] It is this feature of the bonding that results in the stability of the neutral boron chlorides whereas the analogous hydrides, e.g., B_8H_8 and B_9H_9, have never been observed. Restated in the language of Wade's rules, due to the unfavorable cage to ligand overlap in the chlorides the $(n + 1)$th framework orbitals of $B_8Cl_8^{2-}$ and $B_9Cl_9^{2-}$ are more nearly nonbonding in character than are the $(n + 1)$th framework orbitals of $B_8H_8^{2-}$ and $B_9H_9^{2-}$.

3. *Chemistry of Tetraboron Tetrachloride*

Schlesinger's preliminary examination of B_4Cl_4 chemistry established that this compound was unreactive with H_2, C_2H_4, and PCl_3 at temperatures less than 70 °C, the point at which thermal decomposition was observed,[35] and that it reacted with 6 mol of H_2O (or MeOH) to generate 4 mol of HCl (or MeCl) along with 3 mol of H_2 if neutral pH conditions had been employed for the solvolysis or 4 mol of H_2 if the reaction had been carried out under alkaline conditions. The interactions with $ZnMe_2$ (which had been reported to form B_4Cl_3Me[35]), B_2H_6, and $HNMe_2$ are further described below.

Later Wartik reported upon the reactions of B_4Cl_4 with a deficit of the halogens.[47] He found that with Cl_2, for example, B_2Cl_4 and BCl_3 were formed, but no other boron-containing products could be isolated. The reaction pathway was assumed to consist of two stages:

TABLE II. Chemical Shifts of Alkylated Tetraboron Tetrachloride Derivatives[19,52]

compd	δ ^{11}B(B–Cl)[a]	int[b]	δ ^{11}B(B–R)[a]	int[b]
B_4Cl_4	85			
$CH_3B_4Cl_3$	90	3	117	1
$C_2H_5B_4Cl_3$	90	3	120	1
$(C_2H_5)_2B_4Cl_2$	95	2	125	2
$(t\text{-Bu})_4B_4$			135	

[a] Versus external $BF_3{\cdot}OEt_2$. Positive shifts deshielded. [b] Relative intensities of the resonances.

(1) the formation of B_2Cl_4 by the symmetric cleavage of B_4Cl_4 and (2) the attack of Cl_2 upon B_2Cl_4, the last forming the BCl_3 that was isolated.

$$B_4Cl_4 + 2Cl_2 \rightarrow 2B_2Cl_4$$

$$B_2Cl_4 + Cl_2 \rightarrow 2BCl_3$$

Based upon this presumed reaction sequence, the yield of B_2Cl_4 was 18% and the yield of B_2Br_4 from the reaction between B_4Cl_4 and Br_2 in BBr_3 was 14%.

Holliday[48] investigated the products arising from the exposure of B_4Cl_4 to $PbMe_4$, a reaction that eventually resulted in BMe_3 and $(BMe)_n$. Finally, Massey[49] indicated that at 20–100 °C, B_4Cl_4 reacted with BBr_3 to form tiny amounts of B_4BrCl_3 and traces of $B_4Br_2Cl_2$ (both identified by mass spectrometry only) and observed that further substitution by bromine did not seem to be possible.[50]

Because of the conflicting claims about the physical properties of B_4Cl_4 in the literature, once we had developed a reasonably secure source of supply for the compound,[36] our first examinations centered upon the thermal stability (Table I) and the then unknown boron NMR spectral properties of the molecule (Table II). In bulk, B_4Cl_4 is yellow; it melts sharply at 95 °C. Over the temperature range −78 to 118 °C there is no evidence for fluxionality in the boron NMR spectra. In the absence of air, this smallest boron cluster, one which contains only eight framework electrons, is quite stable thermally. In BCl_3 at 125 °C, the half-life is ca. 48 h and if a neat sample of B_4Cl_4 is maintained at 125 °C for 18 h and then the temperature is raised to 150 °C for a further 21 h, 46% of the compound can be recovered unchanged.[36] Somewhat surprisingly, this thermal stability is greater than that of $C_2B_3H_5$,[51] the $2n + 2$ framework electron carborane most nearly comparable in size to B_4Cl_4, and much greater than that of the only known four-atom borane, B_4H_{10}.

The first reactions that we carried out with B_4Cl_4 had originally been designed to generate hydride, fluoride, or alkyl derivatives and, as might be imagined, there was considerable consternation when the putative reagents Si_2H_6, $LiAlH_4$, $ZnMe_2$ (in the gas phase), BMe_3, BBr_3 (at 80 °C), and $(CF_3)_2Hg$ (at 100 °C) all failed to react with B_4Cl_4. Clearly, tetraboron tetrachloride was not only much more thermally stable but it was also much less chemically reactive than had been previously supposed. The only "successful" reaction of this series was that with liquid $CdMe_2$, an interaction that appeared to come to equilibrium after ca. 2% of the B_4Cl_4 had been converted to $CH_3B_4Cl_3$ (see Table II).

Later studies were more productive and one of the central themes that has developed from the study of B_4Cl_4 chemistry is that the reaction channels of this molecule appear to be well-developed in the sense that

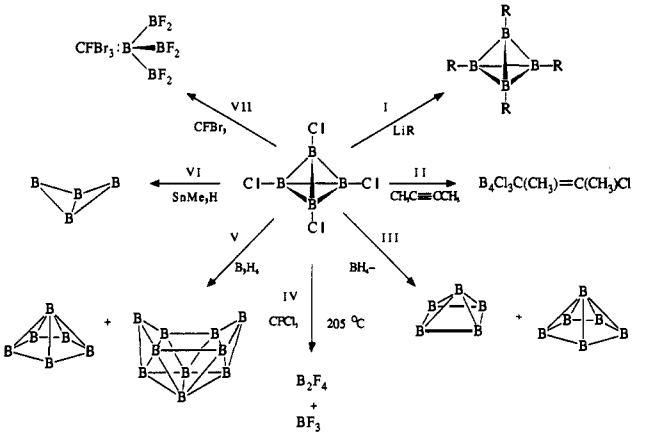

Figure 4. Cluster reaction modes of tetraboron tetrachloride: (I) ligand exchange, (II) alkyne chloroboration, (III) framework expansion (ligands omitted), (IV) cluster fragmentation, (V) cluster fusion (ligands omitted), (VI) cluster core reduction (ligands omitted), (VII) conversion from cluster to electron precise bonding.

TABLE III. Chemical Shifts of Brominated Tetraboron Tetrachloride Derivatives[53]

compd	δ ^{11}B(B–Cl)[a]	int[b]	δ ^{11}B(B–Br)[a]	int[b]
B_4Cl_4	85			
B_4BrCl_3	88	3	84	1
$B_4Br_2Cl_2$	91	2	87	2
B_4Br_3Cl	94	1	90	3
B_4Br_4			93	

[a] Versus external $BF_3{\cdot}OEt_2$. Positive shifts deshielded. [b] Relative intensities of the resonances.

the products formed are commonly generated in relatively high yield and they seem to have resulted from only one type of reaction for each reagent. Currently, we catalog the known reactions of B_4Cl_4 by the type of product that is predominantly obtained and refer to the different types of transformation as modes of reaction in order to differentiate them from the mechanism by which the reaction occurs. At the present time seven different reaction modes have been demonstrated. An eighth is suspected, but not yet proven (see Figure 4).

a. Ligand Exchange. This reaction mode (Figure 4) is found with lithium alkyls at ambient temperature (see Table II) and also with BBr_3 (Table III). The reactions of LiEt or Li(*t*-Bu) appear to be nearly quantitative.[52] The ligand exchanges with BBr_3 are illustrative of the reasonably tight thermal control that is required for some of the B_4Cl_4 reactions. Below 97 °C, exchange does not proceed; above 103 °C cluster fragmentation (see below) is favored. Typical times for the BBr_3 reactions with B_4Cl_4 are 1000–2000 h.[53] The final product of this reaction is B_4Br_4, which is only the third molecule of its type (homoleptic B_4X_4) to have been observed.

For the alkylated and brominated derivatives $CH_3B_4Cl_3$, $C_2H_5B_4Cl_3$, B_4BrCl_3, and B_4Br_3Cl, only two resonances are observed in the boron-11 NMR, which is an indication that tetrahedrally based structures must predominate in solution since three resonances would be anticipated for the alternative planar polytope. The boron atom connectivity of the mixed halide clusters has been proven by standard ^{11}B–^{11}B 2D NMR.

The ^{11}B NMR resonances of alkyl-substituted boron atoms are typically well deshielded relative to those of comparable boron atoms that are chlorine substituted. The chemical shifts of BMe_3 and BCl_3, for example, are

about 86 and 46 ppm, respectively. The values of the ^{11}B chemical shifts contained in Table II illustrate that the same trend is also evident for the alkylated derivatives of B_4Cl_4 with the boron atoms bearing alkyl substituents found in the 117–135 ppm chemical shift region while the chlorine-substituted boron atoms are located between 85 and 95 ppm. The substitution of an alkyl group onto the cage deshields the resonances of the remaining boron atoms by ca. 5 ppm.

Table I demonstrates that the chemical shifts of the larger polyhedral boron bromides are slightly greater than those of the analogous chlorides. An examination of the entries in Table III indicates that while the relationship between the chemical shifts of the two types of boron atom in the mixed-ligand species is somewhat more complex, the chemical shift of B_4Br_4 (93 ppm) is substantially larger than that of B_4Cl_4 (85 ppm). For comparison, the chemical shift of B_2Br_4 is ca. 70 ppm while that of B_2Cl_4 is ca. 64 ppm. The data in Table III also reveal that in this series of compounds bromine for chlorine substitution deshields the resonances of the remaining boron atoms by 3 ppm.

b. Alkyne Chloroboration. This reaction mode (Figure 4) occurs with alkynes like CH_3CCCH_3 at ca. 150 °C. Both cis and trans addition products are observed. The chloroboration reaction appears to be similar in nature to other B–Cl and B–H alkyne additions, for example, the metal-catalyzed alkyne hydroborations that have been recently reported by Sneddon.[54]

c. Framework Expansion. Within minutes B_4Cl_4 and $LiBH_4$ react in Bu_2O to form B_5H_9 (63%) and B_6H_{10} (19%). The reaction pathway appears to involve the sequential insertion of boron atoms into the chloroborane B_4Cl_4, thereby first generating pentaboron and then hexaboron frameworks. The framework expansion reaction (Figure 4) is accompanied by hydride for halide exchanges with the excess BH_4^- in solution. Ultimately the *nido*-boranes B_5H_9 and B_6H_{10} are produced in excellent yields.[55]

d. Cluster Core Reduction. Trimethylstannane and B_4Cl_4 react within seconds to give a dark red solution from which B_4H_{10} can be separated in 95% yield. In this reaction a six-electron reduction of the eight framework electron core of B_4Cl_4 occurs to yield the fully reduced 14 framework electron butterfly-shaped B_4H_{10}.[55]

e. Cluster Fusion. The reaction of B_4Cl_4 with diborane, which was originally reported to give an uncharacterized adduct $B_4Cl_4 \cdot B_2H_6$,[35] in fact occurs in two stages. The first stage is the formation of $B_6Cl_4H_6$, a B_6H_{10} derivative, by the addition of B_2H_6 to B_4Cl_4. The second stage is the fusion of the chlorinated B_6H_{10} derivative with another molecule of B_4Cl_4 to yield a decaborane-14 derivative (see Figure 4). Ligand exchanges of both the chlorinated hexaborane and decaborane clusters with B_2H_6 occur contemporaneously. In this reaction two four-atom eight framework electron B_4Cl_4 clusters and one two-atom six framework electron B_2H_6 molecule are all fused together to form chlorinated derivatives of the 10-atom 22 framework electron $B_{10}H_{14}$.[55]

f. Conversion of Cluster Bonding to Electron Precise Bonding. In this mode of reactivity, which is exemplified by the reaction between $CFBr_3$ and B_4Cl_4 at 100 °C, conversion of the boron–boron bonding from delocalized to electron precise occurs. In the product $CFBr_3 \cdot B(BF_2)_3$, the chloride that was originally attached to B_4Cl_4 has been exchanged for fluoride, and then two more fluorine atoms were abstracted from the solvent to generate $B(BF_2)_3$, which both boron and fluorine NMR indicate is present as the $CFBr_3$ adduct.[56] Although halomethanes are not strong Lewis bases in general, both Timms and Brown have previously reported evidence for adduct formation between chloromethanes and group 3A halides.[57,58]

g. Cluster Fragmentation. In this reaction mode, the tetraboron core of the B_4Cl_4 molecule is dismembered by the reagent to generate diboron tetrachloride and boron trichloride, or their derivatives. For example, the reaction of $HNMe_2$ with B_4Cl_4 results in $BCl(NMe_2)_2$, $B_2Cl_4 \cdot 2HNMe_2$, and $B_2Cl_2(NMe_2)_2$.[19] The reaction of B_4Cl_4 with $HNMe_2$ has been previously reported to result in a stable product, $B_4(NMe_2)_4$, that, because of the absence of an infrared absorption at 1010 cm^{-1}, was thought to contain the boron atoms in a square array.[35] However, in our studies even when a large excess of B_4Cl_4 had been employed, no evidence for a tetraboron compound like the previously postulated $B_4(NMe_2)_4$ was obtained by either mass spectrometry or boron NMR.[19] The interaction of $CFCl_3$ with B_4Cl_4 at 205 °C is similar in that the predominant products are BF_3 and B_2F_4.[59]

One interesting question about the cluster fragmentation reaction is the, as yet, unknown mechanism by which it occurs. At the present time there is no direct experimental evidence to indicate whether the B_2Cl_4 or $B_2Cl_2(NMe_2)_2$ that arose from the reactions of, e.g., Cl_2 or $HNMe_2$ with B_4Cl_4, was produced by the simple cleavage of the tetraboron cage into two B_2X_4 molecules or is the end result of the reaction mode in which conversion to electron precise bonding occurs (see pathway VII in Figure 4). Clearly, mechanistic investigation of the reactions of B_4Cl_4, although exceptionally difficult experimentally, is an area that merits further study.

Some aspects of tetraboron tetrachloride chemistry are touched upon below, but it should be observed here that B_4Cl_4 is actually far less reactive than either BCl_3 or B_2Cl_4. For example, B_2Cl_4 and BCl_3 both react with $CFCl_3$ at temperatures well below 200 °C, but B_4Cl_4 does not. Similarly, BCl_3 and B_2Cl_4 both undergo ligand exchange with BBr_3 at temperatures below ambient, but as discussed above, temperatures of 100 °C are required for the reaction of B_4Cl_4 with BBr_3 to proceed.

The different reaction modes shown in Figure 4 have all been demonstrated in other cluster systems, but it is very rare for them all to have been observed in the reactions of a single compound.

C. Syntheses, Reactivity, and Disproportionation of the Diboron Tetrahalides

Stock first synthesized colorless B_2Cl_4 in 1925 by passing an electric discharge through liquid BCl_3, but the amounts that he obtained were so small that they were only sufficient to establish the identity of the product and to observe that it slowly decomposed into BCl_3 and yellow or brown boron chlorides which may have been accompanied by elemental boron.[60] Later Schlesinger vastly improved the synthesis by carrying it out in the gas phase and by employing a series of eight discharge units simultaneously. The amount of

B_2Cl_4 that was afforded by each unit was ca. 1 g/week.[30,61]

Schlesinger also prepared the first derivatives of B_2Cl_4 by reacting it with BBr_3 to form B_2Br_4, with alcohols and dialkyl amines to generate $B_2(OR)_4$ and $B_2(NR_2)_4$, with $LiBH_4$ or $Al(BH_4)_3$ to yield boranes, including B_2H_6 and B_4H_{10}, and with Lewis bases to synthesize $B_2Cl_4 \cdot 2Et_2O$ and $B_2Cl_4 \cdot 2NMe_3$. Diboron tetrachloride was found to be unreactive with BF_3, $Ca(AlH_4)_2$, and $LiAlH_4$.[30,61]

The reactions of B_2Cl_4 with H_2 in the gas phase yielded B_2H_6 essentially quantitatively, but in the liquid phase, the interaction is much more complex and mixtures of uncharacterized solids and viscous liquids were formed in addition to diborane. Similarly, the nature of the "adduct", $B_2Cl_4BH_3 \cdot 2Et_2O$, generated from B_2Cl_4, B_2H_6, and Et_2O, was (and is) unknown. The reaction of B_2Cl_4 and $ZnMe_2$ resulted in BMe_3 and black solids, no B_2Me_4 was (or ever has been) separated. Finally, the disproportionation of B_2Cl_4 was reported to generate BCl_3, B_4Cl_4, and uncharacterized red and white solids.[30]

In 1949 Schumb prepared B_2I_4 by the radio-frequency discharge of BI_3.[62] The final diboron tetrahalide, B_2F_4, was synthesized from B_2Cl_4 and SbF_3 in 1958.[63] Diboron tetrafluoride was reported to be far more thermally stable than B_2Cl_4, but at temperatures near 200 °C it decomposed into BF_3 and other uncharacterized products.[63]

More recently, a variety of alternative B_2F_4 syntheses have been put forth, including the reactions of $CFCl_3$ or $(CF_3)_2Hg$ with B_2Cl_4.[32,59,64,65] Improved preparations of B_2Cl_4 and B_2Br_4, using radio-frequency discharges of gaseous BCl_3 and BBr_3 in the presence of elemental mercury, have been shown to generate these diboron tetrahalides at rates of ca. 250–350 mg/h,[13,14] but in contrast to the B_4Cl_4 synthesis discussed above, the rates of formation of both B_2Cl_4 and B_2Br_4 are linearly dependent upon the flow rate of BCl_3 through the plasma zone of the radio-frequency reactor. As far as we are aware the radio-frequency syntheses of B_2Cl_4, $BrBr_4$, and B_4Cl_4 are the most efficient that are currently available.[16]

Since B_2Cl_4 was the first compound containing a localized two-center–two-electron (2c/2e) boron–boron bond that had been isolated, there was, and still is, a considerable interest in the chemistry of this molecule. The reactions of B_2Cl_4 with a number of inorganic substrates like NO, which forms $B_2(NO)_3 \cdot BCl_3$,[66] with PCl_3 and P_2Me_4,[67] and with nonmetallic elements[68] should be mentioned, but the vast majority of the reported diboron tetrachloride reactions involved unsaturated organic reagents.

1. Reactions of Diboron Tetrachloride with Unsaturated Organic Substances

The initial chemical investigations in this area were carried out by Schlesinger, who found that at −80 °C, B_2Cl_4 cleanly and rapidly reacts with ethylene to generate $CH_2(BCl_2)CH_2(BCl_2)$, a product in which the boron–boron bond of B_2Cl_4 has been cleaved and the boron atoms of the resulting BCl_2 groups are bonded to the carbon atoms of the substrate (see Figure 5). The product, bis(dichloroboryl)ethane, is thermally stable to ca. 150 °C, but it reacts with MeOH or $ZnMe_2$ to give the expected $CH_2[B(OMe)_2]CH_2[B(OMe)_2]$ or $CH_2(BMe_2)CH_2(BMe_2)$. The methylated derivative is thermally unstable, however, and it loses BMe_3 if gently heated.[69]

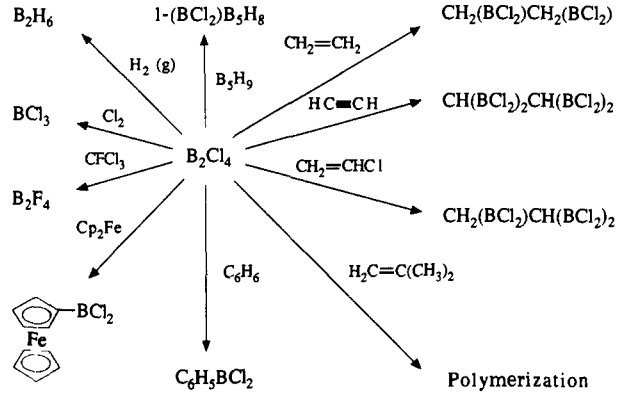

Figure 5. Major products of representative reactions of diboron tetrachloride with organic and inorganic substrates.

The above reaction was the first report of a diboration, one of the four currently known types of reaction that B_2Cl_4 undergoes with organic compounds. Subsequently, Schlesinger demonstrated that B_2Cl_4 also adds to the double bonds in propene, 2-butene, butadiene, and allyl halides, but more slowly, and that B_2F_4 reacts, very slowly, in a similar fashion.[70] The B_2F_4 addition compounds, e.g., $CH_2(BF_2)CH_2(BF_2)$, were found to be much more stable than the analogous chlorides.

Other reports have shown that B_2Cl_4 adds twice to acetylene, giving $CH(BCl_2)_2CH(BCl_2)_2$,[71] and that diboration reactions occurs with numerous cyclic alkenes and dienes, as well as with a variety of vinyl-containing organometallic compounds.[72–75]

The generally accepted mechanism for this reaction invokes the formation of a B_2Cl_4–alkene adduct which is stabilized by the interaction of the electron pair contained in the alkene π bonds with the empty p orbitals of the boron atoms in B_2Cl_4. This adduct then decomposes to form the observed products.[76] With only one exception (the diboration of cyclopentene[72]) all of the stereochemistries of the (dihaloboryl)alkane products indicate that cis addition to the alkene occurred, in accord with the mechanism outlined above.

A reexamination of the B_2Cl_4 haloalkene interactions has demonstrated that typically vinyl halides also react with B_2Cl_4, albeit very slowly.[77] The ultimate product from C_2H_3Cl, for example, is $CH_2(BCl_2)CH(BCl_2)_2$. The evidence was interpreted in terms of a reaction sequence that involved the diboration of the olefin (eq 1), fol-

$$B_2Cl_4 + CH_2{=}CHCl \rightarrow CH_2(BCl_2)CH(BCl_2)Cl \quad (1)$$

$$CH_2(BCl_2)CH(BCl_2)Cl \rightarrow CH_2{=}CH(BCl_2) + BCl_3 \quad (2)$$

$$CH_2{=}CH(BCl_2) + B_2Cl_4 \rightarrow CH_2(BCl_2)CH(BCl_2)_2 \quad (3)$$

lowed by the loss of BCl_3 (eq 2), and then the addition of a second molecule of B_2Cl_4 to yield the observed products (eq 3), rather than the alternative: BCl insertion into the CCl bond followed by diboration.

Very early on, Schlesinger showed that a second type of B_2Cl_4 reaction, ring opening, occurs with cyclopropane. Here the product is $CH_2(BCl_2)CH_2CH_2(BCl_2)$.[70] Diboron tetrachloride also cleaves alkylated

cyclopropanes, but not halocyclopropanes or cyclobutane.[78]

A third type of diboron tetrachloride reaction, polymerization of the organic species, has been reported for isobutylene.[79]

The final type of reaction, BCl_2 for hydrogen substitution on an aromatic ring, was discovered by Wartik,[74] who separated $C_6H_5BCl_2$ from the reaction of benzene with B_2Cl_4. Similarly, ferrocene has been shown to react with B_2Cl_4 to initially generate $FcBCl_2$ and $HBCl_2$[80] (see Figure 5).

2. Reactions of Diboron Tetrachloride with Typical Boron Hydrides[56]

There were several considerations that led us to this study. First, although the reactions of B_2Cl_4 with relatively electron-rich substances, with the halogens,[68] and with the boron trihalides had all been well-investigated, very little was known about the reactions of B_2Cl_4 with electron-deficient substrates. The boron hydrides, of course, are prototypical electron-deficient compounds. Second, relatively little is known about the structures and the bonding of species containing 2c/2e boron–boron linkages, especially when compared to the tremendous amount of information that is available for carbon–carbon single bonds. Third, as described below, we currently believe that the pathway for the disproportionation of B_2Cl_4 and indeed all of the diboron tetrahalides proceeds via chloroborane intermediates that are structurally analogous to the normal boron hydrides. The consequences of our postulated mechanism (below) are inevitable: It may well be possible to synthesize and separate BCl_2 (or BBr_2) substituted boron hydrides, species like $(BCl_2)_nB_5H_{9-n}$ where n is small, but the compounds where n is large must be of limited thermal stability. Further, they must decompose into BCl_3 and chlorinated derivatives of $B_{10}H_{14}$.

a. B_4H_{10}. The *arachno*-borane B_4H_{10} began to react with B_2Cl_4 instantaneously. The 29 resonances of nearly equal intensity in the ^{11}B NMR spectrum indicated the complexity of this reaction. Here no single type of product was favored.

b. B_5H_9 and $B_{10}H_{14}$. When 3-fold excesses of the *nido*-boranes B_5H_9 or $B_{10}H_{14}$ were employed, they smoothly reacted with B_2Cl_4 or B_2Br_4 to form the (dihaloboryl)boranes shown in eqs 4–7.

$$B_5H_9 + B_2Cl_4 \rightarrow 1\text{-}(BCl_2)B_5H_8 + HBCl_2 \quad (4)$$

$$B_5H_9 + B_2Br_4 \rightarrow 1\text{-}(BBr_2)B_5H_8 + HBBr_2 \quad (5)$$

$$B_{10}H_{14} + B_2Cl_4 \rightarrow 2\text{-}(BCl_2)B_{10}H_{13} + HBCl_2 \quad (6)$$

$$B_{10}H_{14} + B_2Br_4 \rightarrow 2\text{-}(BBr_2)B_{10}H_{13} + HBBr_2 \quad (7)$$

The yields of these compounds were very good. For example, $1\text{-}(BCl_2)B_5H_8$ was separated in 73% yield, $1\text{-}(BBr_2)B_5H_8$ in 80% yield.[56] The ^{11}B NMR spectrum of $1\text{-}(BBr_2)B_5H_8$ is presented as Figure 6. All of the properties of $1\text{-}(BCl_2)B_5H_8$, as generated above, are fully in accord with those reported by Gaines,[81] who originally formed the compound from B_5H_9 and BCl_3 in a reaction that was catalyzed by a combination of PCl_3 and $AlCl_3$. His yield was 9%.[81] The other (dihaloboryl)boranes are new compounds.

In these reactions the BCl_2 or BBr_2 substituent has replaced a hydrogen atom that was originally bonded

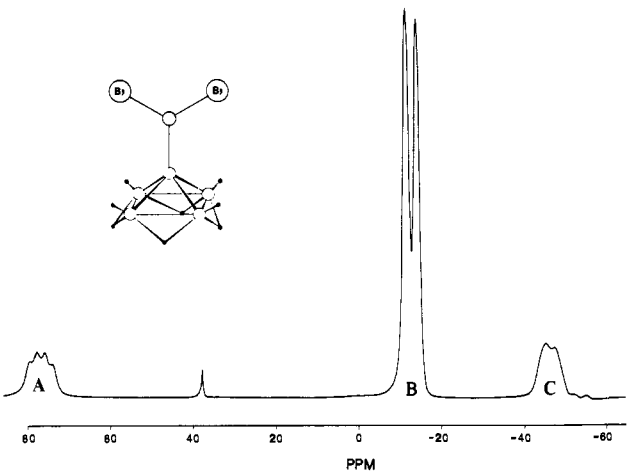

Figure 6. The ^{11}B NMR spectrum of $1\text{-}(BBr_2)B_5H_8$. The resonance labeled A (78 ppm) arises from the dibromoboryl boron atom, that labeled B (−12 ppm) from the basal boron atoms of the cage, and that labeled C (−46 ppm) from the apical boron atom. The small singlet at 39 ppm and the doublet evident at −54 ppm are due to the small amounts of BBr_3 and B_5H_9 that are generated by decomposition. In general appearance these spectra are very representative of the ^{11}B NMR spectra of all of the $1\text{-}(BX_2)B_5H_8$ derivatives discussed in the text.

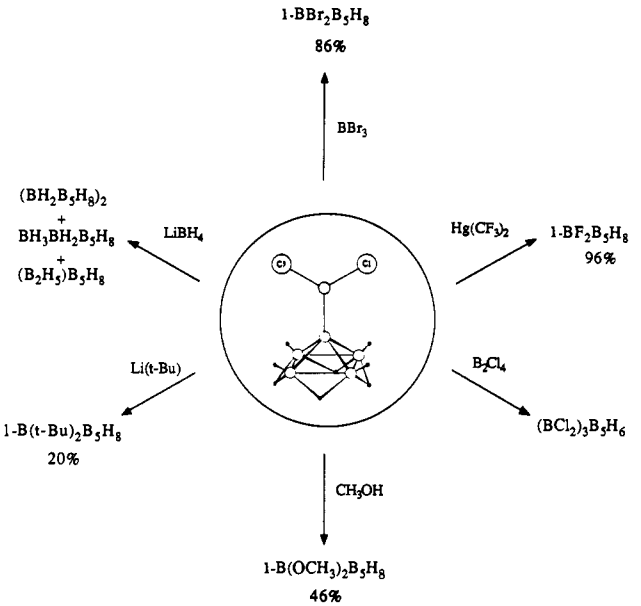

Figure 7. Reactions of $1\text{-}(BCl_2)B_5H_8$.

to one of the most electron-rich boron atoms of the molecule, thus they can be characterized as electrophilic in nature. In addition, these diboron tetrahalide interactions are all formally related to category four above—dihaloboryl substitution for "aromatic" protons. One significant difference between the two types of substrate is that in the boron hydrides resonance stabilization is by delocalization of electron pairs in three dimensions whereas in the carbon hydrides (arenes) the delocalization is two dimensional. Nevertheless, the types of products formed are analogous.

c. Derivative Chemistry of $1\text{-}(BCl_2)B_5H_8$.[56] A variety of 1-(dichloroboryl)pentaborane reactions were examined to determine if ligand exchanges appeared to yield products that were analogous to the B_2Cl_4 derivatives described above, or if the substitution of a B_5H_8 cage for one of the BCl_2 groups in B_2Cl_4 markedly altered the reactivity of the B–Cl bonds remaining. The results

TABLE IV. ^{11}B NMR Chemical Shifts for 1-(Dihaloboryl)pentaborane Derivatives; Comparisons with Diboron Tetrahalide Derivatives[a]

compd	δ B boryl	δ B basal	δ B apical	compd	δ B
$B(t\text{-Bu})_2B_5H_8$	116.6	-10.7	-47.9	$B_2(t\text{-Bu})_3R$	104,[b] 103[c]
$B(t\text{-Bu})ClB_5H_8$	94.3	-10.6	-50.7	$1,2\text{-}B_2Cl_2(t\text{-Bu})_2$	84.3[b]
$BBr_2B_5H_8$	77.9	-12.0	-45.8	B_2Br_4	69.5
$BCl_2B_5H_8$[d]	75.5	-12.4	-51.3	B_2Cl_4	63.0
$BCl(OMe)B_5H_8$	50.0	-12.6	-56.0		
$B(OMe)_2B_5H_8$	37.7	-12.7	-59.4	$B_2(OMe)_4$	30.5
$BF_2B_5H_8$	35.5[e]	-12.5	-57.7	B_2F_4	23.8
$(BH_3)BH_2B_5H_8$	30.7	-12.7	-54.5	B_2H_6	18.1
$(B_2H_5)B_5H_8$	-3.1	-11.2	-58		
B_5H_9	-	-13.5	-53.5		

[a] All values in ppm, positive values deshielded from $BF_3{\cdot}OEt_2$. [b] R = $CH_2C(CH_3)_3$, ref 87. [c] R = Me, ref 87. [d] Reference 81: 75.7, -13.1, and -51.8 ppm, respectively. [e] This resonance is a 1:3:4:4:3:1 sextet.

of this study are summarized in eqs 8–14 below and illustrated in Figure 7.

$$1\text{-}(BCl_2)B_5H_8 + BBr_3 \rightarrow 1\text{-}(BBr_2)B_5H_8 \quad 86\% \quad (8)$$

$$1\text{-}(BCl_2)B_5H_8 + Hg(CF_3)_2 \rightarrow 1\text{-}(BF_2)B_5H_8 \quad 96\% \quad (9)$$

$$1\text{-}(BCl_2)B_5H_8 + MeOH \rightarrow 1\text{-}[B(OMe)_2]B_5H_8 \quad 46\% \quad (10)$$

$$1\text{-}(BCl_2)B_5H_8 + MeLi \rightarrow BCl_2Me + BMe_4^- \quad (11)$$

$$1\text{-}(BCl_2)B_5H_8 + t\text{-BuLi} \rightarrow 1\text{-}[B(t\text{-Bu})_2]B_5H_8 \quad 20\% \quad (12)$$

$$1\text{-}(BCl_2)B_5H_8 + HSnMe_3 \rightarrow BCl_2SnMe_3 \quad (13)$$

$$1\text{-}(BCl_2)B_5H_8 + LiBH_4 \rightarrow 1\text{-}(\eta^2\text{-}B_2H_5)B_5H_8 \quad (14)$$

In general, all of the new pentaborane derivatives are very similar to the corresponding diboron tetrahalide derivatives. For example, at ambient temperature the half-lives for thermal decomposition range from well over 1 year for $BF_2B_5H_8$ to only a few minutes for $B(t\text{-Bu})_2B_5H_8$. Collectively, the thermal stabilities are similar to, but usually slightly less than, those of their diboron tetrahalide analogues. The ^{11}B NMR chemical shifts and the trends in the chemical shifts of the (dihaloboryl)pentaboranes and their derivatives (Table IV) are also clearly related to those of the "parent" diboron tetrahalides. In each case the resonance of the boryl boron atom of the pentaborane derivative is ca. 10 ppm deshielded from that of the corresponding diboron tetrahalide derivative.

Reaction 11 is only one example of many different reagents and conditions that were employed in attempts to isolated $1\text{-}(BMe_2)B_5H_8$. All were unsuccessful, as have been all attempts to isolated B_2Me_4. Reactions that involved the more bulky *t*-Bu groups, however, were more productive. They yielded $1\text{-}[B(t\text{-Bu})_2]B_5H_8$, which could be isolated in 20% yield.[56]

Reactions 13 and 14 are only two of the many syntheses that were designed to form $1\text{-}(BH_2)B_5H_8$. The initial objectives had been to examine $1\text{-}(BH_2)B_5H_8$ in light of its isomer, *nido*-B_6H_{10}, and then to determine if $1\text{-}(BH_2)B_5H_8$ dimerizes by means of the kind of hydrogen bridging found in B_2H_6.

This reaction was much more complex, however. The ^{11}B NMR spectra of the products indicated that 1:1′,2′-$[B_5H_8][B_2H_5]$, which might alternatively be described as $1\text{-}(\eta^2\text{-}B_2H_5)B_5H_8$, was ultimately generated, rather than the anticipated species. This product is one of the very few known examples of an exceptionally rare class of compound—boron hydrides that contain seven boron atoms. The only other reported example is the isomeric 2:1′,2′-$[B_5H_8][B_2H_5]$, i.e., $2\text{-}(\eta^2\text{-}B_2H_5)B_5H_8$, which has been separated by Sneddon.[82] The proposed structure of our heptaborane is most easily envisioned by "replacing" one of the bridge hydrogen atoms of B_2H_6 with the apical boron atom of a B_5H_8 cage; the B_2H_5 ligand thus serves as a one-electron donor toward the *nido*-B_5 cluster.

Taken together, the results of this study demonstrated that common boranes like B_4H_{10}, B_5H_9, and $B_{10}H_{14}$ readily react with B_2Cl_4 or B_2Br_2 and that the *nido*-boranes B_5H_9 and $B_{10}H_{14}$ react in a regiospecific manner. Ligand substitutions of the chloride in $1\text{-}(BCl_2)B_5H_8$ proceed easily and the nature of the products obtained and their relative stabilities parallel that found for the analogous diboron tetrahalide derivatives. The results of our studies have been summarized in Figure 7. In the only other study of $1\text{-}(BCl_2)B_5H_8$ chemistry, Gaines[81] has demonstrated that the diboration of ethylene proceeds very slowly to give $CH_2(BCl_2)CH_2(B_5H_8)$ in 80% yield.

3. Disproportionation of Diboron Tetrachloride

The thermal reaction of B_2Cl_4 has been referred to by a variety of different names, only a few of which can be printed. We prefer the term disproportionation rather than the more common "thermal decomposition" since, as described below, it is now becoming apparent that the pathway from B_2Cl_4 to, e.g., $B_{12}Cl_{12}$ or $B_{10}Cl_{10}$, while fairly lengthy, can also be very straightforward under the appropriate conditions.

At first glance the early reports of the various examinations of the B_2Cl_4 thermal reaction appear to be mutually contradictory. For example, Stock observed yellow and brown deposits as the reaction progressed, whereas Schlesinger, and then Schram and Urry,[83] reported that the solids were red. Whether or not B_8Cl_8 was formed has been disputed several times in the literature, as has the existence or nonexistence of large amounts of radical species among the products.

Our own investigation of this reaction[14] indicated that there are at least three distinct pathways that result in the formation of the various boron monohalides, B_nCl_n (n = 8–12). Although the three pathways usually occur contemporaneously, they can be segregated by varying the conditions.

a. Pathway to B_9Cl_9. The first pathway results in the production of B_9Cl_9 from a yellow solid that may be deposited during the thermolysis of B_2Cl_4. This reaction can be observed by heating B_2Cl_4 to 450 °C for a few minutes, removing all of the volatile components, and then gently heating the remaining yellow material. No cluster compounds other than those containing nine atom cages are formed and, aside from traces of BCl_3, the only other product is a tan extremely unreactive solid. The yield of B_9Cl_9 under these conditions is 50–75%.[14]

b. Pathway to B_8Cl_8 and the Radical Species. The second reaction pathway results in the formation of B_8Cl_8 and the radical species observed by Schram and Urry. When B_2Cl_4 is dissolved in CCl_4 and heated to 100 °C for 336 h, B_8Cl_8 is isolated from the purple-black

solution in 88% yield. Small amounts of B_9Cl_9 (5%) are formed, but $B_{12}Cl_{12}$, $B_{11}Cl_{11}$ and $B_{10}Cl_{10}$ are not.[17]

c. Pathway to $B_{12}Cl_{12}$, $B_{11}Cl_{11}$, and $B_{10}Cl_{10}$. If B_2Cl_4 is maintained at ambient temperature or only very gently heated ($T < 60$ °C), the first polyhedral boron chlorides observed are $B_{12}Cl_{12}$ and $B_{11}Cl_{11}$, with the former present in greater amounts. As time progresses, the amount of $B_{11}Cl_{11}$, relative to $B_{12}Cl_{12}$, increases dramatically; $B_{10}Cl_{10}$ is observed later.[14] Under these conditions, if the B_2Cl_4 has been greatly diluted with BCl_3, neither B_9Cl_9 nor B_8Cl_8 are formed.[26]

One of the more interesting aspects of the B_2Cl_4 reaction, when carried out under very mild thermal conditions, is that although BCl_3 is liberated and yellow and brown solids begin to precipitate from the red solution within hours, the presence of $B_{12}Cl_{12}$ and $B_{11}Cl_{11}$ is not indicated by boron NMR during the first three days. Clearly, $B_{12}Cl_{12}$ and $B_{11}Cl_{11}$ must arise from a precursor of moderate thermal stability, one that is only sparingly soluble in BCl_3.

d. Postulated Reaction Mechanism. The first three steps that we have proposed[14] for the disproportionation of B_2Cl_4 are shown in eqs 15–17 below. The third step

$$2B_2Cl_4 \rightarrow B_3Cl_5 + BCl_3 \quad (15)$$

$$B_3Cl_5 + B_2Cl_4 \rightarrow B_4Cl_6 + BCl_3 \quad (16)$$

$$2B_4Cl_6 \rightarrow B_8Cl_{12} \quad (17)$$

(eq 17) is thought to be the dimerization of $B(BCl_2)_3$ to B_8Cl_{12}, a diborane derivative in which all of the H atoms have been replaced by BCl_2 groups. It is at this third step that the initial formation of compounds containing boron atoms bonded together by means of multicentered orbitals is thought to occur.

The fourth step of the B_2Cl_4 reaction is the fusion of two B_8Cl_{12} molecules to form $B_{14}Cl_{18}$ (eq 18); the liberation of 2 mol of BCl_3 accompanies the accretion reaction. It is this compound, $B_{14}Cl_{18}$, that we propose as the direct precursor of the polyhedral boron monochlorides $B_{10}Cl_{10}$, $B_{11}Cl_{11}$, and $B_{12}Cl_{12}$. The overall stoichiometry for the formation of $B_{14}Cl_{18}$ from B_2Cl_4 can be written as shown in eq 19.

$$2B_8Cl_{12} \rightarrow B_{14}Cl_{18} + 2BCl_3 \quad (18)$$

$$12B_2Cl_4 \rightarrow B_{14}Cl_{18} + 10BCl_3 \quad (19)$$

Timms has reported that the fluorine analogue of $B_{14}Cl_{18}$ was formed during the thermal disproportionation of B_3F_5.[32] He suggested that the structure of $B_{14}F_{18}$ is based upon the B_5 cage in B_5H_9, but that all of the H atoms had been replaced by BF_2 groups. However, because of the evidence discussed below, we believe that the structure of the $B_{14}Cl_{18}$ that is the precursor of the boron monohalides is more likely to be based upon a B_{10} cage of the type found in $B_{10}H_{14}$, with four μ_2-BCl_2 groups.

The ultimate steps of the B_2Cl_4 reaction generate the polyhedral boron chlorides, B_8Cl_8, $B_{10}Cl_{10}$, $B_{11}Cl_{11}$, and $B_{12}Cl_{12}$. These compounds are envisioned as arising from $B_{14}Cl_{18}$ by means of two different pathways. In reactions carried out at low temperature, little or no carbene-like or carbenoid-like BCl is thought to be formed and any BCl that is present immediately inserts into BCl_3, reforming B_2Cl_4. Thus at low temperatures, if excess BCl_3 is present, the only reaction channel that leads to the boron monochlorides involves the evolution of BCl_3 from $B_{14}Cl_{18}$ (eq 20).

$$B_{14}Cl_{18} \rightarrow B_{12}Cl_{12} + 2BCl_3 \quad (20)$$

This product, $B_{12}Cl_{12}$, is the least thermally stable of the larger polyhedral boron chlorides, B_nCl_n, and it decomposes to the more stable $B_{11}Cl_{11}$ by the elimination of a BCl group which, under these conditions, reacts with the BCl_3 present to regenerate B_2Cl_4 (eq 21). Reaction 21 is thought to be one of the sources of the B_2Cl_4 that is observed in solutions of B_2Cl_4 that have been maintained at ambient temperature for 5 years or more.[14] Eventually, $B_{11}Cl_{11}$ decomposes to $B_{10}Cl_{10}$ by a similar process (eq 22).

$$B_{12}Cl_{12} + BCl_3 \rightarrow B_{11}Cl_{11} + B_2Cl_4 \quad (21)$$

$$B_{11}Cl_{11} + BCl_3 \rightarrow B_{10}Cl_{10} + B_2Cl_4 \quad (22)$$

The overall stoichiometry for the formation of $B_{12}Cl_{12}$ is shown in eq 23; that for $B_{10}Cl_{10}$ is shown in eq 24.

$$12B_2Cl_4 \rightarrow B_{12}Cl_{12} + 12BCl_3 \quad (23)$$

$$10B_2Cl_4 \rightarrow B_{10}Cl_{10} + 10BCl_3 \quad (24)$$

Experimentally, however, if the disproportionation of B_2Cl_4 has been carried out at higher temperatures in the presence of a solvent like CCl_4, the formation of the larger clusters $B_{10}Cl_{10}$ through $B_{12}Cl_{12}$ is quenched and the generation of B_8Cl_8 occurs nearly quantitatively (88%). We have proposed that B_8Cl_8 arises as shown in eqs 25 and 26 below.[14]

$$B_2Cl_4 \rightarrow BCl_3 + \text{"BCl"} \quad (25)$$

$$B_{14}Cl_{18} + 2\text{"BCl"} \rightarrow B_8Cl_8 + B_8Cl_{12} \quad (26)$$

Reaction 25 is meant to imply that in reactions at higher temperatures and/or lower BCl_3 concentrations, the amount of (presumably singlet) BCl that is present becomes chemically significant. Our current speculation is that the first addition of BCl to $B_{14}Cl_{18}$ gives rise to the radical species, and the second addition generates B_8Cl_8. The overall stoichiometry for the formation of B_8Cl_8 then becomes as shown in eq 27.

$$8B_2Cl_4 \rightarrow B_8Cl_8 + 8BCl_3 \quad (27)$$

In a typical B_2Cl_4 thermal reaction, one in which undiluted B_2Cl_4 has been gently heated, B_8Cl_8, $B_{10}Cl_{10}$, $B_{11}Cl_{11}$, and $B_{12}Cl_{12}$ are all formed, which indicates that under these conditions the reactions shown in eqs 20–22 and 26 are all operating simultaneously. At temperatures below 60 °C, the most thermally stable polyhedral boron chloride of them all, B_9Cl_9, is neither observed nor, upon the basis of the reaction sequences postulated above, expected.

Although there is obviously still much to be learned in this area, clearly the proposed steps of the thermal disproportionation of B_2Cl_4 are an indication of our personal conviction that the chemistry of the polyhedral boron chlorides is probably rather closely related to that of the boron subfluorides, rather than the two being distinctly different as has been previously suggested.[32,50] Even more interestingly, with crucial mechanistic divergences due to the differences in the stabilities of the substances involved, it is entirely possible that both could be intimately related to the framework transformations found in boron hydride chemistry. The thermal reactions of B_2H_6, the dimer of BH_3, eventually

result in the production of $B_{10}H_{14}$; the thermal reactions of B_2Cl_4, we believe, proceed through the diborane-like dimer $[B(BCl_2)_3]_2$, then, in the presence of excess BCl_3, progress on to a decaborane-like perchloroborane.

4. Attempted Syntheses of $(BCl_2)_nB_5H_{9-n}$ ($n \geq 3$) Compounds

In these experiments the focus was upon attempting to determine whether pentaborane or decaborane derivatives containing large numbers of BCl_2 groups were thermally stable or if they decomposed to yield products that could be related to the diboron tetrachloride disproportionation scheme discussed above.

a. Evidence for the Preparation of $(BCl_2)_3B_5H_6$. When 1-$(BCl_2)B_5H_8$ was reacted with a 2-fold excess of B_2Cl_4 and then the volatile components were removed, the ^{11}B NMR spectrum of the nonvolatile portion contained resonances in three discrete chemical shift regions: ca. 70 ppm, −5 to −14 ppm, and ca. −46 ppm.[56] Sequentially, these resonances are attributable to dihaloboryl boron atoms substituted on the apical and basal positions of the B_5 cage, the four basal atoms of the cage, and the apical cage atom (see Figure 6). The integrated intensities of the resonances were in the relative ratios of 3.0:4.0:0.92. The mass spectrum of these products contained strong ion envelopes centered at *m/e* 305, 269, and 223, which are assigned to $(BCl_2)_3B_5H_6$, $(BCl_2)_2(BCl)B_5H_6$, and $(BCl_2)_2B_5H_6$, respectively. The ^{11}B NMR data were most easily interpreted in terms of the formation of both the 1,2,3- and the 1,2,4-$(BCl_2)_3B_5H_6$ isomers during the reaction, but further characterization of the products was precluded by their thermal instability.[56]

b. Attempted Preparations of More Completely Substituted Pentaborane Derivatives. Many attempts to synthesize and isolate compounds of the type $(BCl_2)_nB_5H_{9-n}$ or $(BBr_2)_nB_5H_{9-n}$, where *n* was greater than 3, were carried out. In these reactions the excess B_2Cl_4 reacted with B_5H_9 or 1-(dichloroboryl)pentaborane within a few minutes, but the products were insufficiently stable for isolation. Mass spectrometry indicated that a variety of dichloroboryl substituted pentaboranes, including $(BCl_2)_2B_5H_7$, $(BCl_2)_2B_5H_6Cl$, and $(BCl_2)B_5H_5Cl_3$, were present. Much more interestingly, however, the mass spectra also contained ions that clearly originated from decaborane-14 derivatives, compounds like $B_{10}H_{13}Cl$, $B_{10}H_{12}Cl_2$, and $B_{10}H_{11}Cl_3$; the highest mass ion of this type that was observed corresponded to $B_{10}H_8Cl_6$. Similar results were obtained from reactions carried out between B_2Br_4 and B_5H_9.[56]

c. Attempted Preparations of More Completely Substituted Decaborane Derivatives. During the course of numerous experiments, B_2Cl_4 was found to react more slowly with $B_{10}H_{14}$ than with B_5H_9, but it was usually consumed within 1 h. The boron NMR data from these reactions indicated that BCl_2 for H substitutions preferentially occur at the 2,4-positions of $B_{10}H_{14}$, followed by the 1,3- and 6,9-positions. Neither the hydrogen atoms at the symmetry-equivalent 5,7,8,10-positions nor the bridging hydrogen atoms appeared to react with B_2Cl_4. The mass spectra were confirmitory in that ion envelopes corresponding to $(BCl_2)_nB_{10}H_m^+$ (where n = 2, 3, 4, 5, and 6, but not 7) were present along with the fragments expected from those ions. The poly(dichloroboryl)decaboranes decomposed with the liberation of BCl_3 and chlorodecaborane derivatives at ambient temperature, but there was no evidence for structural alteration of the B_{10} cage during these reactions.[56]

The implication of this last study is that while polysubstituted (dichloroboryl)pentaborane and decaborane species can be synthesized easily, they are of little thermal stability. This, of course, is exactly as required by the B_2Cl_4 disproportionation mechanism described above.

III. Prospects

Until recently, progress in delineating the chemistry of the boron subhalides, especially the polyhedral boron halides, has proceeded at a relatively moderate rate due in large part to two separate factors. The first is the inherent difficulties that are associated with the transformation of boron into the di- or monovalent state. Numerous attempts to chemically reduce a variety of boron compounds have been reported, but as yet, none have been able to supplant the discharge or metal atom reactions that have been previously developed. The more modern radio-frequency discharge methods have resulted in much higher sustained rates of formation for B_2Cl_4, B_2Br_4, and B_4Cl_4, rates that are sufficiently high to provide enough of these substrates for a reasonably detailed examination of their chemistry. For many laboratories, however, the lack of a method that employs more readily available technology still provides a significant barrier to the examination of the chemistry of these very unusual species.

The laboratories of Walter Siebert are clearly one example of those that have surmounted the barrier. They have reported a long series of extremely interesting studies that have been centered upon the formation and the derivative chemistry of a variety of diboracycloalkenes. One common type of synthesis from this laboratory might involve the diboration of an alkyne with B_2Cl_4 or its derivatives,[84] followed by thermally or chemically induced ring closure which typically gives cyclo-$B_2C_nR_{n+2}$ products or their dimers. The carboranes thus synthesized have then often been employed as planar multihaptoligands for the construction of very large transition-metal-containing multidecker sandwich compounds.[85]

Historically, the second major stumbling block in the area of boron monohalide chemistry has been an almost complete lack of knowledge about which of the larger boron monohalides might be generated in what amounts during the disproportionation reactions. Here the classic example is B_8Cl_8, a compound whose structure was reported in 1959, but which could not be resynthesized for another 20 years. Within the past few years, however, it has become possible to prepare any of the monohalides in reasonable yields by means of a set of well-defined reaction conditions. Because of these developments, it is fair to assert that the chemistry of the polyhedral boron subhalides has entered a second phase, one in which the reactivities, the structures, and the bonding of these compounds can be addressed in a cohesive, systematic fashion.

From the viewpoint of structure and bonding, the most interesting of the polyhedral boron monohalides are the B_7, B_{10}, and B_{12} cages since molecular orbital theory indicates that because of the degeneracies of the

framework orbitals none of these species can have structures that are based upon the deltahedra depicted in Figure 1.[16] Another intriguing aspect of the $2n$ framework electron cage compounds is that at present there are no known examples of hydrides, fluorides, alkoxides, or dialkylamides of the general formulation B_nX_n (X = H, F, OR, or NR_2). Given the great thermal stabilities of, e.g., B_9Cl_9, B_9Br_9, and B_9I_9, the nonexistence of, e.g., $B_9(NR_2)_9$ and B_9F_9, almost surely arises from the lack of a proven synthetic route to these species, rather than from any thermodynamic instability of the compounds. Our molecular orbital calculations on B_8H_8 and B_9H_9[23] indicate that while these compounds are anticipated to be very electrophilic, they should be sufficiently stable to isolate.

We are aware of two pieces of evidence which indicate that fluoroboranes of the B_nF_n type might be separable. The first comes from the theoretical studies of Lipscomb's group,[45] who examined the stability of the hypothetical molecule B_4F_4 and demonstrated that in principle it should be stable. The second piece of evidence is experimental in nature. It is contained in the Ph.D. thesis of Ralph Kirk, one of Peter Timms' students. Kirk observed that at least four high molecular weight boron fluorides, two liquid and two solid, are generated from the thermal reactions of B_3F_5 and/or B_8F_{12}. Among the peaks in the mass spectra of one of his fractions were those attributed to $B_{11}F_{11}^+$ and $B_{10}F_8^+$ ions which were present in a 59:100 ratio. In the spectrum of a second fraction, $B_9F_9^+$ and $B_8F_8^+$ ions were found in a 113:100 ratio.[86] Examination of the mass spectral results in Table I demonstrates that these ion ratios are those that might be expected for polyhedral boron fluorides, upon the basis of the spectra of the corresponding chlorides and bromides.

Although the rate of formation of B_4Cl_4 is by far the lowest of any of the boron subhalides, the reactivity of this smallest cluster is by far the best understood. There are, however, several aspects of tetraboron tetrachloride chemistry that remain unsettled. One major area of interest is to determine the detailed mechanism by which the various transformations depicted in Figure 4 occur. Another area of interest is to identify the number of different cluster modes of reactivity that can be rigorously defined. Currently, we are examining an eighth mode—the generation of coupled clusters.

Finally, even though B_2Cl_4 was initially isolated some 65 years ago, the chemistry of this small molecule is still far from completely understood. Salient examples of possible studies include determining the nature of the products that arise from the interaction of B_2Cl_4 with readily oxidized transition-metal compounds, species akin to Vaska's complex, and finding whether or not B_2Cl_4 adds across other multiple bonds such as those in transition-metal alkylidenes.

Other unanswered questions are related to the extent to which the thermal disproportionation pathway of B_2Cl_4 proposed above is applicable to the disproportionation of other diboron tetrahalide derivatives or even the lower valent derivatives of other elements. Almost certainly computational chemistry will prove to be a crucial tool for any detailed understanding of these reactions.

Ultimately, however, much of the lasting impact of polyhedral boron monohalide chemistry may well result from the extent to which the properties of these compounds can be utilized to rationalize the results obtained from other systems. Very recently a growing number of $2n$ framework electron cluster compounds ranging from $(CpIn)_6$ to small clusters of elemental silicon have been reported, and we anticipate that just as the $2n + 2$ framework electron carboranes and borane dianions have served as role models for other isoelectronic but non-boron-containing clusters, eventually the $2n$ framework electron polyhedral boron halides will shed light upon the structural and chemical consequences of electron deficiency in isoelectronic but non-boron-containing clusters.

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