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THE SUBHALIDES OF BORON

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I. Introduction

The last major review of the boron subhalides was published in Volume 10 of *Advances* in 1967 (*84*), although several brief discussions (*42, 85, 133*) have appeared in the intervening years. The present article attempts to cover comprehensively the work that has been

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published since 1967. Undoubtedly, the most outstanding advance has been Timms' synthesis of BF, from which he has been able to make a variety of new boron fluorides.

A curious facet of boron subhalide chemistry is that fluorine does not appear to support a series of monohalides as do chlorine, bromine, and, probably, iodine. It has been suggested several times that a monofluoride such as B_4F_4 may be less stable than the corresponding chloride because of relatively weak back-bonding from the fluorine p orbitals into cage bonding orbitals. That this is not the whole answer is shown by the preparation of alkyl-substituted cages such as $B_4(t\mathrm{Bu})_4$ and $B_9Br_{9-n}Me_n$, where n can range from 1 to at least 6. Calculations show that B_4F_4 should be at least as stable as B_4Cl_4 relative to four BX units, which suggests that the present nonexistence of B_4F_4, and possibly other B_nF_n derivatives, is due only to a lack of suitable synthetic routes to them. Starting from the monochlorides, what is required is a mild, volatile fluorinating agent that produces a volatile chloride byproduct; diboron tetrafluoride (*56*) and allyl fluoride (*15*) would appear to fulfil these criteria. As a possible incentive to the preparative chemist, intense peaks due to $B_nF_n^+$ fragment ions have been noted in the mass spectra of several boron subfluorides. However, the very low thermal stability of B_3F_5 and B_8F_{12} lends little hope of even their chlorine analogs ever being synthesized when it is remembered that B_2F_4 is so much more stable then either B_2Cl_4 or B_2Br_4.

Two interesting phenomena arising from the interaction of diboron tetrachloride with unsaturated hydrocarbons are worthy of further study. It has been noted a number of times that the thermal decomposition of B_2Cl_4 is arrested in the presence of haloolefins (*15, 110, 112*); NMR (*20*), and infrared (*104*) studies have failed to detect any evidence of interaction between the components of such mixtures but some must surely take place. Striking visual evidence of quite strong interaction between acetylene and B_2Cl_4 can be obtained by mixing them at −78°C; a solid mass is formed from which the acetylene can be pumped off intact when the B_2Cl_4 reverts to its normal liquid form (*133*). A further study of both these systems should reveal considerable information about the mechanism involved in the addition of diboron tetrachloride to alkenes and alkynes (see Section V,B).

Table I shows the subhalides that are known to date, including a number that have not been fully characterized. The diboron tetrahalides possess rather daunting properties in that they are pyrophoric in air and water sensitive, they attack both hydrocarbon and silicone greases, and, furthermore, they decompose spontaneously at room temperature. The tetrafluoride, tetrachloride, and tetrabromide (together

TABLE I

THE KNOWN BORON SUBHALIDES[a]

B_2F_4	B_2Cl_4	B_2Br_4	B_2I_4 (pale yellow)
B_3F_5	—	—	—
—	B_4Cl_4 (pale yellow)	—	—
—	—	B_7Br_7 (black?)	—
—	B_8Cl_8 (very dark purple)	B_8Br_8 (dark red-brown)	(B_8I_8)[b]
B_8F_{12} (yellow)	—	—	—
—	B_9Cl_9 (yellow-orange)	B_9Br_9 (red)	B_9I_9 (dark brown)
—	$B_{10}Cl_{10}$ (orange-brown)	$(B_{10}Br_{10})$[b]	—
—	$B_{11}Cl_{11}$ (orange-red)	—	—
—	$(B_{12}Cl_{12})$[b]	—	—
$B_{14}F_{18}$	—	—	—

[a] Colorless unless indicated otherwise. The colors of these compounds are worthy of note because the vast majority of boron compounds are colorless. Had the monohalides not been colored they would have been virtually impossible to separate because it is only by observing color changes that one can assess how a separation is progressing. The observed colors are somewhat dependent on the physical state of the halides. For example, B_8Cl_8 forms greenish, thin films, black crystals, and a purple vapor, whereas B_9Br_9 forms dark red crystals but has a bright yellow vapor.

[b] Detected but not isolated.

with B_4Cl_4, B_3F_5, and B_8F_{12}) are sufficiently volatile to be handled in conventional vacuum lines equipped with greaseless taps and may be stored in traps at low temperatures until required.

Mercury manometers and mercury float valves are not recommended for use with the bromides or iodides because of the possibility of hydrogen halides, which attack mercury, being produced by adventitious hydrolysis. New glassware must be thoroughly baked out, first under vacuum and then under a slight pressure of boron trihalide, to drive off adsorbed water and so prevent such hydrolyses.

Ground glass joints that are exposed to the halides for relatively brief periods may be lubricated with halocarbon greases, although even Kel-F grease turns brown after 4 days contact with BCl_3–B_2Cl_4 mixtures (*7*). Diboron tetrabromide rapidly attacked Apiezon W wax used as a window seal for an infrared cell; a mixture of powdered PTFE and fluorocarbon oil was found to make a better sealant, but even this showed signs of attack after several days (*99*).

II. Identification

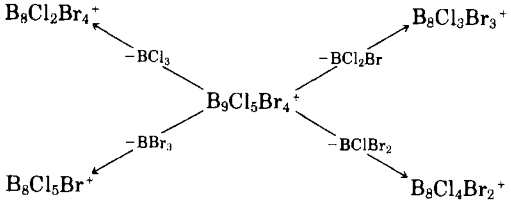
Conventional analytical techniques are difficult to carry out on all but the diboron tetrahalides. High-temperature decomposition to boron and boron trifluoride has been used as a means of obtaining the B : F ratio in the lower boron fluorides (*69, 70, 126*).

The high thermal stability and volatility of the monohalides make them suitable subjects for mass-spectral analysis. That boron, chlorine, and bromine all possess two stable isotopes rather complicates the appearance of the mass spectra but at the same time provides a powerful means of "fingerprinting" the various ions present. Even for a simple ion like $B_2Cl_2^+$ there are nine possible isotopic species—isotopomers—although under normal resolution only seven separate peaks are observed due to overlap at $m/e = 92$ and again at $m/e = 94$ (see Table II). By using the known relative abundances of the ^{10}B, ^{11}B, ^{35}Cl, and ^{37}Cl isotopes, it is possible to compute (*79*) the expected intensities of the various peaks making up the $B_2Cl_2^+$ ion cluster—such an intensity pattern is highly characteristic of the ion under study and can be used in conjunction with the *m/e* values estimated from the spectrum to identify positively an unknown ion species. This is demonstrated for the parent ion of $B_{12}Cl_{12}$ in Fig. 1.

A prominent group of peaks found in the mass spectra of all the monohalides represents the loss of BX_3 from the parent ion and is accompanied by the corresponding metastable peak, showing that the process occurs in a single step. Sometimes, a second metastable peak can also be observed for the loss of another BX_3 molecule from the $(P—BX_3)^+$ ion.

$$B_9Cl_9^+ \xrightarrow{-BCl_3} B_8Cl_6^+ \xrightarrow{-BCl_3} B_7Cl_3^+$$

In the case of a mixed halide $B_nCl_{n-x}Br_x$, the boron trihalide molecule lost from the parent ion can be BCl_3, BCl_2Br, $BClBr_2$, or BBr_3.



Due to the number of isotopomeric ions involved in these processes, the metastable peaks are very broad indeed and in some cases can span 8–10 mass units. The stability toward loss of BX_3 from $B_9X_9^+$ increases as the halogen is changed from chlorine to iodine, the relative intensity ratios $B_9X_9^+ : B_8X_6^+$ being 0.4(Cl), 1.3(Br), and 8(I); the spectrum of B_9I_9 even shows a group of peaks due to the doubly charged parent ion.

TABLE II

THEORETICAL PEAK INTENSITIES FOR THE ION $B_2Cl_2^+$ (*79*)

$B_2Cl_2^+$ (mass no.)	Probability (%)	
90	2.22	**
91	18.04	******************
92	38.04	**************************************
93	11.77	***********
94	24.11	**********************
95	1.92	**
96	3.89	****
	100.00	

Isotope	Mass	Abundance (%)
^{10}B	10.01294	19.78
^{11}B	11.00931	80.22
^{35}Cl	34.96885	75.53
^{37}Cl	36.96590	24.47

Species produced by $B_2Cl_2^+$ in the mass spectrum	*m/e*		
$^{10}B^{10}B^{35}Cl^{35}Cl$	90		
$^{10}B^{10}B^{35}Cl^{37}Cl$	92	91.96063	
$^{10}B^{10}B^{37}Cl^{37}Cl$	94		93.95768
$^{11}B^{10}B^{35}Cl^{35}Cl$	91		
$^{11}B^{10}B^{35}Cl^{37}Cl$	93		
$^{11}B^{10}B^{37}Cl^{37}Cl$	95		
$^{11}B^{11}B^{35}Cl^{35}Cl$	92	91.95632	
$^{11}B^{11}B^{35}Cl^{37}Cl$	94		93.95337
$^{11}B^{11}B^{37}Cl^{37}Cl$	96		

So facile is the loss of boron trifluoride from the parent ions of the lower boron fluorides that the P^+ ion is often unobservable, as happens in the case of B_8F_{12} (*69*). A major difference between the subfluorides and the other subhalides is that the latter have a B : X ratio of 1 whereas the B : F ratio is apparently variable. It is interesting to note, therefore, that prominent ions noted in the mass spectra of boron subfluorides include $B_9F_9^+$, $B_{11}F_{11}^+$, and $B_{12}F_{12}^+$ (*69*), showing that such clusters are stable under certain conditions, a point that should stimulate attempts to synthesize the parent B_nF_n compounds.

Infrared spectra of the volatile subhalides may be obtained using conventional gas cells to which the windows may be attached with

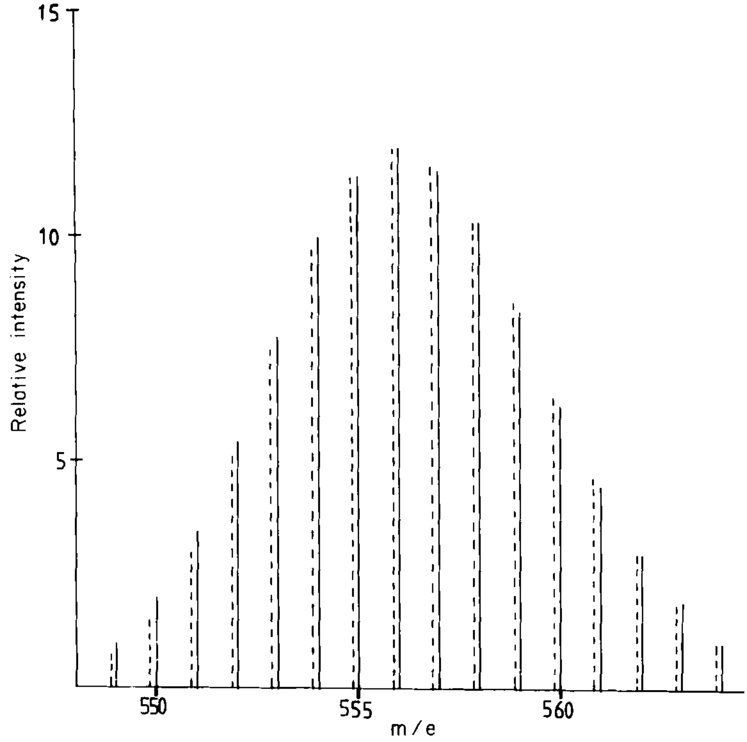


FIG. 1. Comparison of the observed (——) and theoretical (- - -) intensities for the molecular ion of $B_{12}Cl_{12}$.

halocarbon grease or cyanoacrylate resin; an all-metal seal consisting of an amalgamated lead gasket set between a silvered glass cell and rock-salt window has also been found useful in boron halide studies (46). The spectrum of the highly unstable B_8F_{12} has been laboriously recorded in 200-cm^{-1} stages at room temperature, a fresh sample being used for each stage (*70*). Such thermally fragile compounds are better studied using a low-temperature "spray-on" infrared cell (*14, 69, 99, 126*). The greater all-around stability of B_9Cl_9, B_9Br_9, and B_9I_9 allows their infrared spectra to be obtained from either nujol mulls or disks of the respective potassium halide. The spectrum of the very water-sensitive B_8Cl_8 has been obtained from a cyclopentane solution using matched cells (*76*).

Raman and NMR spectra can be recorded either on neat liquids or on solutions in a variety of solvents: B_8F_{12} (B_3F_5; *126*); CCl_4 (B_4Cl_4; *14, 25*); BCl_3 (B_4Cl_4; *25*); BBr_3 (B_9Br_9; *75*); pentane (B_9Br_9, $B_{10}Br_{10}$; *75*).

Visible–ultraviolet spectra have been obtained using gaseous samples or solutions in the solvents BCl_3 (B_8Cl_8; *76*; B_9Cl_9; *77*) and BBr_3 (B_9Br_9; *108*).

III. Preparation

A. FLUORIDES (BF, B_2F_4, B_3F_5, B_8F_{12})

The original method, involving treatment of B_2Cl_4 with antimony trifluoride (*36, 111*), is still frequently used for small-scale (up to 22 g; *32*) preparations of diboron tetrafluoride, including $^{10}B_2F_4$ (*95*). Titanium tetrafluoride can also be used as the fluorinating agent (*82*).

A more recent synthesis (*126*) involves cocondensation of boron monofluoride and boron trifluoride in an approximate 1 : 1 ratio, when up to 25% of the BF is recovered as diboron tetrafluoride. The monofluoride is produced by passing boron trifluoride over boron heated to 1950–2000°C in the apparatus shown in Fig. 2; the yield of diboron tetrafluoride is very dependent on the amount of BF_3 condensed with the BF.

Cocondensation of B_2F_4 with boron monofluoride results in the formation of the very unstable B_3F_5 (*126*). Boron monofluoride is thus capable of insertion into the B—F bonds of both BF_3 and B_2F_4. When no BF_3 or B_2F_4 is cocondensed with boron monofluoride, then a mixture of B_2F_4, B_3F_5, and higher boron fluorides is obtained, the first two presumably arising from one, and two, BF insertions into boron trifluoride molecules that passed unchanged over the heated boron (under these conditions there would be a high BF : BF_3 ratio). No free $B(BF_2)_3$, which would require three BF insertions into an original boron trifluoride molecule, was obtained, but small amounts of its carbon monoxide adduct $OCB(BF_2)_3$ were isolated. The source of the CO was thought to be oxygen-containing impurities in the boron trifluoride starting material that had reacted with the graphite apparatus. Deliberate addition of carbon monoxide to the BF_3 stream increased the relative yield of $OCB(BF_2)_3$ but at the same time reduced the efficienty of BF condensation (CO is noncondensable at −196°C).

Disproportionation of liquid B_3F_5 at −30°C occurs slowly according to the equation

$$4B_3F_5 \rightarrow 2B_2F_4 + B_8F_{12}$$

The yellow compound B_8F_{12} may be separated from the other fluorides by low-temperature fractional distillation. Although the dispropor-

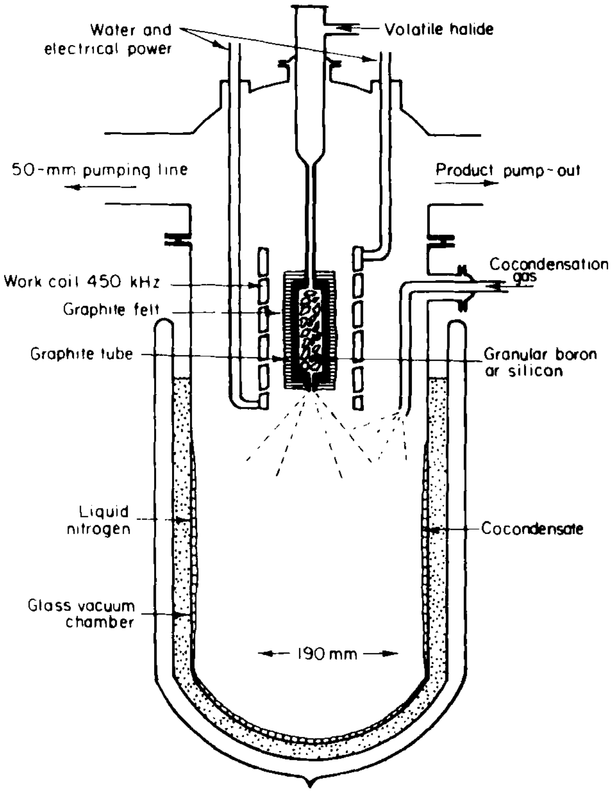


FIG. 2. Apparatus for production of BF and its subsequent reaction with other gases. Reprinted from Timms (*139*, p. 139).

tionation becomes more rapid at high temperatures, it may become violent, resulting in lower yields of B_8F_{12} due to the production of boron trifluoride and yellow, nonvolatile polymers (*126*).

B. CHLORIDES (BCl, B_2Cl_4, B_4Cl_4, B_8Cl_8, B_9Cl_9, $B_{10}Cl_{10}$, $B_{11}Cl_{11}$)

Preparative amounts of boron monochloride may be made by passing B_2Cl_4 vapor rapidly through a narrow-bore quartz tube maintained at 1000°C. Under the optimum conditions an approximately 50% yield of BCl may be obtained to give between 10 and 20 mmol in an hour (*131*, *132*). A competing reaction produces a deposit of elemental boron, which tends to block the quartz tube. Alternatively, the BCl molecules can be made by passing diboron tetrachloride through an ac discharge in the apparatus shown in Fig. 3 (*132*). The direct reduction of boron

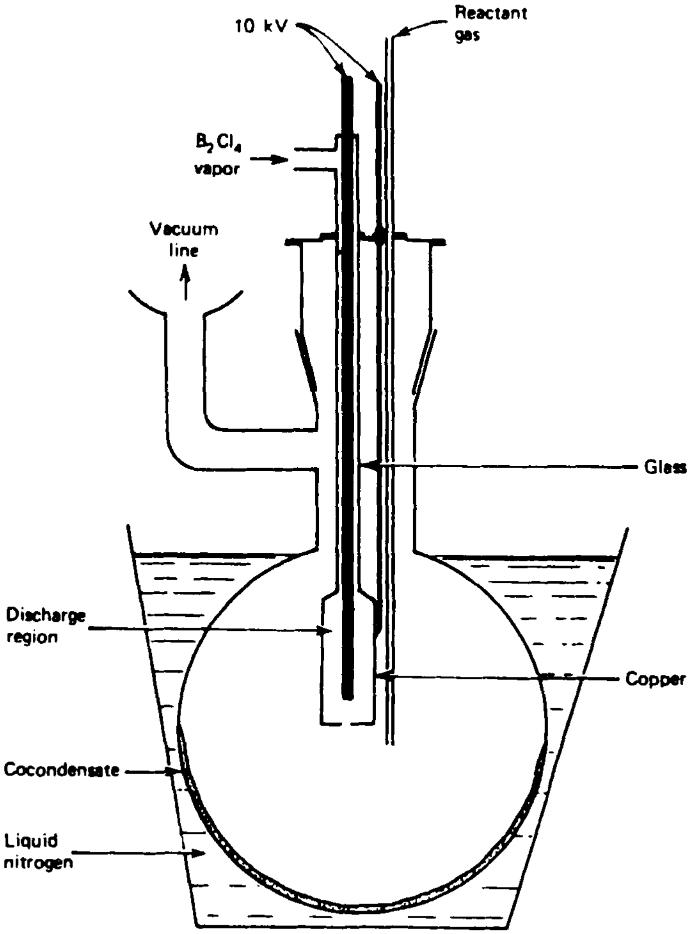


FIG. 3. Apparatus for the formation of BCl and its subsequent reaction with other gaseous species. Reprinted from Timms (*132*, p. 111).

trichloride vapor by heated boron (*74*) is not considered a practical route to BCl (*131*).

The mercury-discharge synthesis of diboron tetrachloride (*11, 90*) is still used for small-scale preparations, including that of $^{10}B_2Cl_4$ (*8*). However, for multigram quantities the copper-atom method of Timms is recommended (*128, 129*). In a typical experiment 10 g of copper are slowly evaporated over about 1 h from an electrically heated crucible contained in the apparatus shown in Fig. 4. The copper vapor and boron trichloride, passed in at the rate of about 2.5 g min^{-1}, are

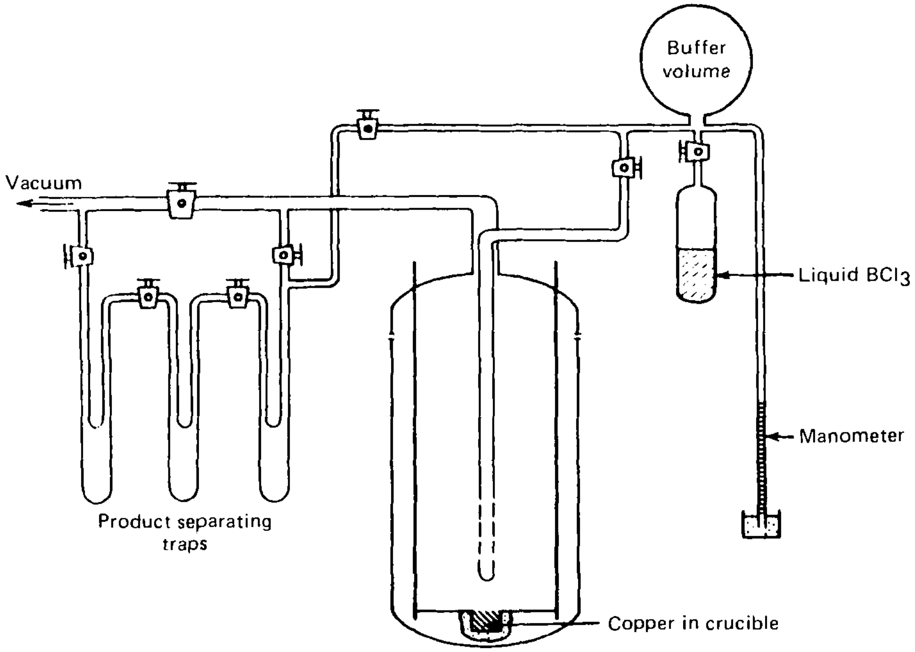


FIG. 4. Apparatus for treating boron trichloride with copper atoms. Reprinted from Timms (*129*, p. 76), *Inorganic Syntheses*, Vol. 19. Copyright 1979 Inorganic Syntheses, Inc. With permission of John Wiley & Sons, Inc.

condensed together at −196°C in the bottom of the reactor. After an hour the BCl_3 flow is stopped, the crucible allowed to cool, and the liquid-nitrogen bath removed from around the reactor, thus allowing it to warm up slowly to room temperature. Fractionation of the issuing vapors yields up to 4 g of diboron tetrachloride, representing a 30% yield based on evaporated copper. The method can be scaled up to produce 10 g of B_2Cl_4 in a 1-h run, starting from 20–30 g of copper. Silver may be used in place of copper, but the yields of diboron tetrachloride obtained are lower; no B_2Cl_4 is formed using nickel (*130*). Separate experiments show that no detectable reaction occurs when copper and B_2Cl_4 are condensed together.

Cocondensation of gaseous B_2O_2 with boron trichloride at −196°C gives a 60% yield of diboron tetrachloride based on the reaction

$$3B_2O_2(g) + 4BCl_3 \rightarrow 2B_2O_3 + 3B_2Cl_4$$

but full details of the system are lacking (*130*). Low yields of B_2X_4 are also formed when either boron trifluoride or boron trichloride is cocondensed with boron atoms *(130)*. Irradiation of boron trichloride–hydrogen mixtures with the 10.55-μm radiation from a high-power TEA CO_2 pulse laser in the presence of a lead catalyst produced $^{10}B^{11}BCl_4$, $^{11}B^{11}BCl_4$, and HCl, but no $^{10}B^{10}BCl_4$. It was assumed that selective excitation of $^{11}BCl_3$ molecules occurred, and the following mechanism was proposed to account for the observed products *(80)*.

$$^{11}BCl_3 + h\nu\ (10.55\ \mu m) \rightarrow {}^{11}BCl_2 + Cl$$

$$^{11}BCl_2 + H_2{-}{-}{-}Pb \rightarrow {}^{11}BCl_2{-}{-}{-}Pb + H_2$$

$$^{11}BCl_2{-}{-}{-}Pb + {}^{10,11}BCl_3 \rightarrow {}^{10,11}B^{11}BCl_4 + Cl$$

$$2Cl + H_2 \rightarrow 2HCl$$

A small amount of diboron tetrachloride is formed when boron trichloride is cocondensed with carbon vapor, the mechanism suggested being that of chlorine abstraction followed by $\cdot BCl_2$ radical coupling *(32)*.

Tetraboron tetrachloride, which occurs in tiny amounts as a by-product from the discharge synthesis of B_2Cl_4, can now be made at the rate of about 10 mg h^{-1} by passing diboron tetrachloride vapor through a mercury discharge *(65, 92)*. A more convenient synthesis, giving 3–5 mg h^{-1} of product, consists of setting up a radiofrequency discharge in a low-pressure stream of boron trichloride vapor and using mercury as a chlorine "getter" *(25)*. Contrary to earlier reports *(121)*, B_4Cl_4 is not produced by decomposing diboron tetrachloride *(65)*.

Condensation of BCl in the presence of BCl_3 at −196°C gives good yields of tetraboron tetrachloride *(131)*, but formidable problems associated with the preparation of BCl would not appear to make this an attractive synthesis.

Diboron tetrachloride decomposes thermally to give a number of boron monochlorides, B_nCl_n. Urry *(135)* described a dark purple, volatile decomposition product melting at 185°C but was unable to identify it fully. It has since been shown to be B_8Cl_8 *(76)*, and, along with B_9Cl_9, it may be volatilized from the other decomposition products on gentle warming (it is very slightly volatile under a good vacuum at room temperature); vacuum sublimation up a long tube affords about 95% pure B_8Cl_8, which may be further purified by fractional crystallization from dichloromethane.

Schram and Urry described *(121)* a "non-crystalline yellow solid slightly volatile *in vacuo* at room temperature"; from its description this compound would appear to be B_9Cl_9 (although the latter can be readily induced to crystallize). When isolated from the B_2Cl_4 decomposition products, B_9Cl_9 is contaminated with B_8Cl_8, which may be removed by heating the mixture under vacuum (*77*). A high yield of pure B_9Cl_9 is obtained by heating $B_{10}Cl_{10}$–$B_{11}Cl_{11}$ mixtures with chlorine (*6*).

A breakthrough in the preparative chemistry of the boron monohalides has been achieved by Wong and co-workers. They have shown that it is possible to oxidize $B_9X_9^{2-}$ ions (X = H, Cl, Br, I) to the respective neutral halide B_9X_9. In particular, B_9Cl_9 may be obtained in over 30% yield by treating $(n\text{Bu}_4\text{N})_2B_9H_9$ in CH_2Cl_2 with a large excess of sulfuryl chloride, removing the volatiles and extracting the residue with *n*-hexane (*63*). If $B_9Cl_9^{2-}$ or $B_9Cl_9^{\cdot-}$ is used as starting material, the oxidation can be carried out with thallium(III) trifluoroacetate (*143*).

Removal of B_8Cl_8 and B_9Cl_9 from the decomposition products of diboron tetrachloride leaves a reddish solid, which may be resolved, by warming, into a volatile, red $B_{10}Cl_{10}$–$B_{11}Cl_{11}$ mixture and a white, nonvolatile residue. The volatile, red mixture was originally considered to be a free radical $B_{12}Cl_{11}$ (*121, 135*), on the basis of its elemental analysis and its ESR spectrum; however, after the red solid is sublimed repeatedly it exhibits no ESR spectrum, showing that the paramagnetic properties are due to impurities. The $B_{11}Cl_{11}$ component of the mixture can be removed by heating to 350°C (*109*).

Dilute solutions of diboron tetrachloride in BCl_3 form mainly $B_{11}Cl_{11}$ when allowed to decompose at room temperature for many weeks. After removal of the boron trichloride, $B_{11}Cl_{11}$ may be sublimed carefully from the reaction tube, using a free flame. The product is only about 95–97% pure and is contaminated with $B_{12}Cl_{12}$ (*6*).

C. BROMIDES (B_2Br_4, B_7Br_7, B_8Br_8, B_9Br_9, $B_{10}Br_{10}$)

When boron tribromide vapor at low pressure is passed through a radiofrequency discharge in the presence of mercury, diboron tetrabromide is produced in yields of 200–300 mg hr^{-1} (*75*). This represents a convenient and relatively simple synthesis, giving about a 70% yield based on BBr_3 consumed. Nöth has described a nondischarge preparation in which tetramethoxydiboron in CH_2Cl_2 is treated with an excess of boron tribromide at room temperature; the yield was 49% after 30 min reaction. The corresponding reaction between $B_2(OMe)_4$ and BCl_3 gave no diboron tetrachloride (*96*). The reaction of copper atoms with boron tribromide has been reported to yield B_2Br_4, but no details were given (*75*).

Diboron tetrabromide decomposes rapidly at room temperature, visibly darkening after 5 min and depositing dark-brown solids after 20 min (*66, 75*). Removal of the product boron tribromide allows separation of highly colored, slightly volatile bromides from the nonvolatile residue; fractional sublimation resolves the mixture of bromides into black B_7Br_7 and dark red B_9Br_9 (*66*). Although B_8Br_8 can be detected among the decomposition products (*66*), it has yet to be isolated from this source and is better made by treating B_8Cl_8 with aluminum bromide at 100°C in BBr_3 solvent (*83*). In the original study of the decomposition of diboron tetrabromide no $B_{10}Br_{10}$ was observed (*66*), but it has since been confirmed as a product (*108*) and has been separated from contaminating B_9Br_9 by precipitating the latter from a strongly cooled pentane solution (*75*).

Pure B_9Br_9 can be prepared from diboron tetrabromide more conveniently than by the fractional sublimation mentioned previously. Passage of diboron tetrabromide through a silent electric discharge produces B_9Br_9 and BBr_3; the latter can be used as a solvent to manipulate the relatively nonvolatile B_9Br_9 into strategically placed sidearms, which are sealed with a torch. It is then a simple matter to remove the BBr_3 and purify the B_9Br_9 by sublimation (*108*). Because diboron tetrabromide is formed by passing BBr_3 through a silent electric discharge the same apparatus may be used both to prepare and decompose the B_2Br_4. However, the rate of production of the tetrabromide is very low, and it is more convenient to prepare B_2Br_4 by other processes before decomposing it in the discharge (*108*). For small-scale syntheses diboron tetrabromide is decomposed at 200°C and the solid residues treated with bromine to give B_9Br_9 in 46% yield, based on the equation (*75*)

$$9B_2Br_4 \rightarrow 9BBr_3 + B_9Br_9$$

D. IODIDES (B_2I_4, B_9I_9)

Although B_2I_4 has been mentioned as one of the products when zirconium tetrahydroborate, $Zr(BH_4)_4$, is treated with iodine (*150*), the radiofrequency-discharge synthesis reported many years ago by Schumb, Gamble, and Banus remains the only practical method for the preparation of the tetraiodide (*122*). This yellow solid is relatively stable at room temperature but decomposes very rapidly on melting at 94–95°C. Only two volatile monoiodides appear to be formed during the decomposition at temperatures between 100 and 400°C; these are B_8I_8 and B_9I_9. Heating the discharge apparatus strongly after a synthesis of B_2I_4 has been carried out allows isolation of the same two monoiodides, which presumably arise from B_2I_4 decomposed in the hot discharge zone, not as primary discharge products (*87*).

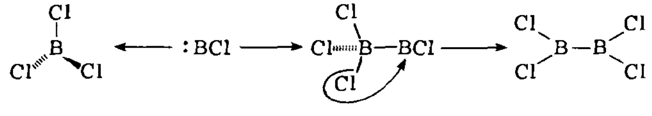
B_9I_9 can be made without recourse to discharge procedures. Addition of thallium(III) trifluoroacetate to either $(n\text{Bu}_4\text{N})_2\text{B}_9\text{I}_9$ or $(n\text{Bu}_4\text{N})\text{B}_9\text{I}_9$ in CH_2Cl_2 gives a red-purple solution; after solvent removal and extraction with carbon tetrachloride, B_9I_9 is obtained in 30% yield as dark brown crystals (*142*).

E. Possible Intermediates in the Discharge Synthesis of Diboron Tetrahalides

When Schlesinger first prepared B_2Cl_4 by passing BCl_3 vapor through a mercury discharge, he assumed the product arose by simple dimerization of BCl_2 radicals formed by stripping of a chlorine atom from boron trichloride molecules by excited mercury atoms (*136*). It was shown many years later (*13*) that the spectrum of such mercury discharges contains no lines attributable to BCl_2 radicals, whereas strong emission due to the diatomic molecule BCl is present. Similarly, the spectrum of BCl was observed during the microwave excitation of BCl_3 vapor, a system that also produces diboron tetrachloride (and chlorine) (*59*). These results suggest that BCl is a precursor in the formation of diboron tetrachloride. Thermodynamically, the reaction

$$\begin{array}{lccc} & \mathrm{BCl_3} + & \mathrm{BCl} & \rightarrow \ \mathrm{B_2Cl_4} \\ \Delta G_f^{\ominus} & -92.9 & +28.9 & -110.11\ \text{kcal mol}^{-1}\ (\textit{138}) \end{array}$$

is favored ($\Delta G_f^{\ominus} = -46.1\ \text{kcal mol}^{-1}$) and, presumably, proceeds via the donation of a lone pair of electrons on BCl into the empty 2p orbital of boron trichloride.



Urry (*133*) has objected to such a mechanism for the mercury-discharge system, mainly on the grounds that mercury(I) chloride is a by-product of reaction [Urry presumably thought mercury(II) chloride would be a more obvious product of stripping two chlorines from a boron trichloride molecule] and because no mixed boron–silicon chlorides were observed when BCl_3 and $SiCl_4$ were passed through the discharge (BCl might be expected to be inserted into silicon tetrachloride: $BCl + SiCl_4 \rightarrow Cl_2BSiCl_3$).

It is well known (*123*) that mercury(II) chloride will react with mercury to form Hg_2Cl_2. Also, the molecule Cl_2BSiCl_3 has been isolated as a by-product in the discharge preparation of diboron tetrachloride (*88*), presumably arising from $SiCl_4$, an impurity in the boron trichloride passing through the discharge (see also *147*). Thus two of Urry's objections can be disregarded. The other objection was that no Cl_2BPCl_2 could be detected (*40*) when a mixture of boron and phosphorus trichlorides was passed through the mercury discharge; perhaps this experiment ought to be repeated.

Whether or not BCl reacts with boron trichloride must depend to some extent on the prevailing conditions, because Timms and Maddren have shown (*132*) that BCl and BCl_3 do not form diboron tetrachloride when these compounds are condensed together at −196°C [under similar conditions BF is inserted into BF_3 to give diboron tetrafluoride (*126*)].

Boron trichloride, when passed at low pressure through a radiofrequency discharge in the presence of mercury, produces diboron tetrachloride and B_4Cl_4 (*25*). The emission spectrum of the discharge contains lines that are due to atomic mercury as well as bands in the region 2660–2880 Å, which are due to the (0,0), (1,0), (0,1), (1,1), (2,0), (2,1), (2,2), (0,3), (4,4), and (5,5) transitions of the BCl molecule (*12*). Thus once again we are led to the conclusion that the production of the two subchlorides B_2Cl_4 and B_4Cl_4 occurs via the BCl intermediate.

For the reaction

$$\begin{array}{lcccl} & BBr_3\ + & BBr \rightarrow & B_2Br_4 & \\ \Delta G_f^\ominus & -\ 57.0 & +46.7 & — & \text{kcal mol}^{-1} \end{array}$$

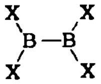
the free energy of formation of diboron tetrabromide, $\Delta G_f^\ominus$ (B_2Br_4), is unknown, but the positive value of $\Delta G_f^\ominus$ (BBr) ensures that $\Delta G^\ominus$ (reaction) = $\Delta G_f^\ominus$ (B_2Br_4) − (−57.0 + 46.7) will be highly negative for any plausible value assigned to $\Delta G_f^\ominus$ (B_2Br_4). It would, therefore, appear reasonable to suggest BBr as a possible intermediate in the formation of diboron tetrabromide from BBr_3. Diener and Pflugmacher (*31*) prepared diboron tetrabromide by passing boron tribromide through an electrical discharge maintained between nickel electrodes; previously, an almost identical system had been used to study the emission spectrum of BBr in the discharge zone (*114*). When boron tribromide is passed at low pressure through a radiofrequency glow discharge, diboron tetrabromide is formed (*75*). Strong bands of the BBr molecule can be observed in the emission spectrum of the discharge; when mercury is added to the system to act as a bromine getter, the only observable change in the spectrum is that additional lines appear due to atomic mercury (*12*).

Iodine dominates the spectrum of the radiofrequency discharge in boron triiodide vapor, and because of this it was impossible to observe any bands due to BI or any other boron system. Lebreton (*78*) used argon to suppress the iodine spectrum in studies on BI made in a Schuler-type discharge. Even when argon was bled into the radiofrequency discharge at such a pressure just to sustain the glow, iodine still emitted too strongly to allow detection of BI (*12*).

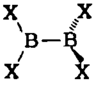
IV. Structure and Bonding

A. DIBORON TETRAHALIDES

Diboron tetrahalides have been fairly extensively studied in recent years as models to test the spectroscopist's art, because their adopted structure depends on the prevailing conditions. X-Ray crystallography has been used to show that diboron tetrafluoride and tetrachloride are planar (**I**) in the crystalline state at low temperatures (*84*). The planar form of B_2Cl_4 is a result of crystal packing forces and not an inherent thermodynamic stability of the D_{2h} rotamer at low temperatures (*33*). However, the anisotropic forces in an argon matrix at 20 K, unlike those in the crystal, must be less than the barrier to rotation because both tetrahalides assume the staggered conformation (**II**) under these conditions (*95*).



D_{2d} (**I**)



D_{2h} (**II**)

The gas-phase electron-diffraction pattern of diboron tetrafluoride has been interpreted in terms of the planar, D_{2h}, structure (*24*). In particular, the two peaks corresponding to cis and trans F---F distances (3.1 and 3.8 Å) would be a single peak at about 3.4 Å in the pattern given by the staggered, D_{2d}, molecule. The very marked temperature dependence of the shape of these two peaks, which represent rotation-sensitive distances, was thought compatible only with a low rotational barrier in the B_2F_4 molecule; the average value estimated for this barrier was 0.42 ($\pm$0.16) kcal mol^{-1}.

Because five infrared-active fundamentals are expected for both the D_{2h} and D_{2d} forms of diboron tetrafluoride, the infrared technique alone is incapable of differentiating between them. However, from a combination of infrared and Raman spectroscopy it was concluded that B_2F_4 is planar in all states (*34*), a fact that is at variance with earlier studies (*84, 95*). Ab initio (*37, 43, 60*) and MNDO (*28*) calculations on the diboron tetrafluoride molecule suggest that the D_{2d} model is the more stable, with a barrier to rotation of 0.3–1.1 kcal mol^{-1}. Extended Hückel-theory calculations suggest either that the two ends of the B_2F_4 molecule rotate virtually freely about the B—B axis [although slightly stable in the D_{2d} form; (*93*)] or that the D_{2h} rotamer is lower in energy (*18*).

In contrast to diboron tetrafluoride, B_2Cl_4 appears to adopt the staggered conformation in both the liquid and the gaseous states, as judged by electron diffraction (*54, 116*), vibrational spectroscopy (*8, 84, 95*), and most calculations (*1, 43, 93*); Hückel-type calculations lead to the suggestions that either the planar molecule is the more stable (*18*) or "the rotation about the B—B bond is very easy and that the conversion between the two forms may be carried out without a great hindrance" (*67*). The barrier to rotation determined from the electron-diffraction data (*116*) is 1.85 ± 0.03 kcal mol^{-1}, in good agreement with the value 1.8 ± 0.1 kcal estimated from the torsional mode in the Raman spectrum (*62*); calculations give the slightly lower values of 1.48 (*43*) and 1.67 (*93*) kcal mol^{-1}. The mean amplitudes of vibration and force constants have also been calculated for both B_2F_4 and B_2Cl_4 (*21, 22, 101, 105*).

For the larger halogen bromine there will be increased steric interaction in the planar B_2Br_4 molecule relative to B_2F_4 and B_2Cl_4. It is not too surprising, therefore, to find that vibrational spectra show that the staggered, D_{2d}, conformation is adopted in all three states (*99*).

Table III summarizes the structural data for diboron tetrafluoride and tetrachloride. The boron–fluorine bonds in B_2F_4 are about 0.05 Å

TABLE III

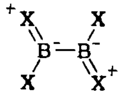
MOLECULAR PARAMETERS FOR DIBORON TETRAFLUORIDE AND TETRACHLORIDE

	B_2F_4		B_2Cl_4	
Species	Gas[a] (*24*)	Crystal (*84*)	Gas (*116*)	Crystal (*84*)
B—X (Å)	1.317 (2)	1.32 (4)	1.750 (10)	1.73 (2)
B—B (Å)	1.720 (4)	1.67 (5)	1.702 (69)	1.75 (5)
< XBX	117.2(2)°	120(2.5)°	118.65(66)°	120.5(1.3)°

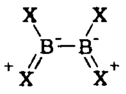
[a] MNDO calculations for the D_{2d} form give B—B and B—F distances of 1.747 and 1.316 Å, respectively (*28*).

shorter than the sum of the single bond radii, corrected for electronegativity differences, which suggests a π-type interaction between the two atoms (*24*), a point apparently verified by calculation (*37, 43*). Less B—X π bonding is thought to occur in diboron tetrachloride (*43, 116*), which is consistent with the assignments made in the photoelectron spectra of the two molecules (*82*).

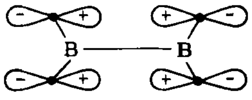
Electron delocalization in the conjugated π system of bonds in structures **IIIa** and **IIIb** is thought to occur, which would tend to stabilize the planar form of a B_2X_4 molecule. The contrasting gaseous structures of B_2F_4 and B_2Cl_4 thus result from a delicate balance between this conjugation and opposing steric effects (*24*). The B—B π-bond order in diboron tetrachloride is calculated to be 0.08 (*1*). It has also been argued that a σ-type 1,4 interaction (**IV**) may be an important factor in the stabilization of a planar B_2X_4, the stabilization being least in B_2F_4, when the small fluorine orbitals are involved (*60*). The B—B bond dissociation energy of B_2F_4 [103 kcal mol^{-1} (*29*)] is larger than that of B_2Cl_4 [87.6 kcal mol^{-1}, (*30*)]. This may be due, at least in part, to the greater electronegativity difference between B and F than between B and Cl (*41*).



(IIIa)



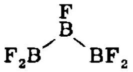
(IIIb)



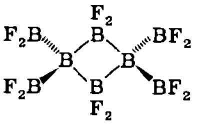
(IV)

B. B_3F_5 AND B_8F_{12}

Although no diffraction studies have been reported for B_3F_5 and B_8F_{12}, their spectroscopic properties are consistent with structures **V** (*26*) and **VI** (*70*).



(V)



(VI)

C. $B_{14}F_{18}$

The compound $B_5(BF_2)_9$ may be a formal analog of B_5H_9 in which BF_2 groups have replaced both bridging and terminal hydrogen atoms (cf. the analogy between B_2H_6 and B_8F_{12}) (*131*).

D. TETRABORON TETRAHALIDES

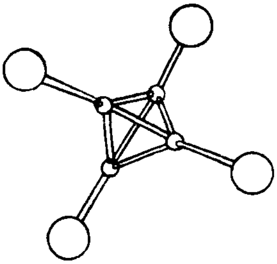
Only tetraboron tetrachloride has so far been isolated. In the solid state, tetraboron tetrachloride has the structure shown in Fig. 5, the molecule deviating only very slightly from T_d symmetry, possibly due to molecular packing in the crystal (*84*). The infrared and Raman spectra of the solid and gaseous phases have been interpreted fully on the basis of T_d symmetry, the slight distortions in the solid producing some splittings in the Raman spectrum (*14*); boron isotopic splitting into three (or four?) of the expected five peaks is clearly visible on the Raman bands at 1302 and 685 cm^{-1}, but the effect of the ^{35}Cl and ^{37}Cl isotopes is smaller and not seen. Although the B—Cl stretching force constant of 4.076 mdyne $Å^{-1}$ is in the middle of the range of values quoted for boron trichloride, the B—B constant (2.3 mdyne $Å^{-1}$) is rather low and suggests that the B—B bonds in B_4Cl_4 are abnormally weak (*14*). There are no features in the spectra that suggested the presence of the planar isomer of B_4Cl_4, which was suggested as a possibility by Lipscomb (*72*).

The bonding in B_4F_4 and B_4Cl_4 has been discussed by numerous authors (*1, 43–45, 68, 89, 125, 137*). Qualitative Hückel-type calculations (*89*), semiempirical CNDO calculations (*1*), and more sophisticated ab initio SCF calculations (*43, 45*) all suggest that B_4Cl_4 is stabilized by a π-type back donation of charge from the chlorine atoms to the B_4 cage orbitals; this appears to be verified by a study of the photoelectron spectrum (*81*). However, there is some dispute as to whether more (*45*) stabilization occurs in B_4F_4 than in B_4Cl_4, or less (*43, 89*). The lower stabilization suggested for B_4F_4 seems to be in agreement with the repeated failures to fluorinate B_4Cl_4 with typical reagents such as PbF_2, SbF_3, and TiF_4 (*86, 92*) and the lack of B_4F_4 when BF is condensed at low temperatures [BCl under similar conditions gives good yields of B_4Cl_4 (*131*)].

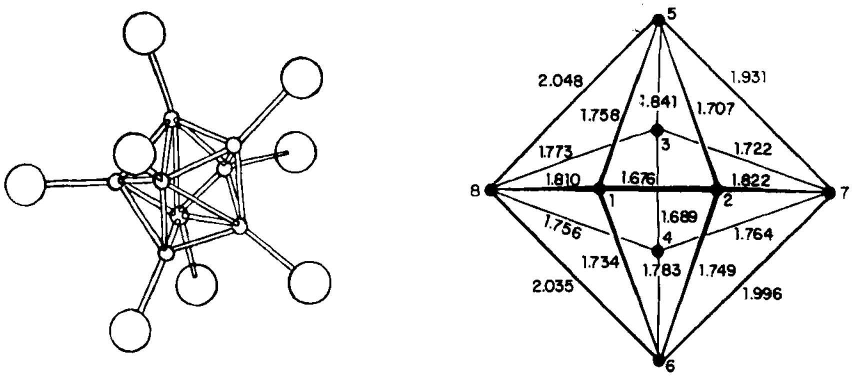
Substantial energy barriers exist for the transformations

$$B_4F_4\ (T_d) \rightarrow B_4F_4\ (D_{4h}) \rightarrow B_4F_4\ (T_d)$$

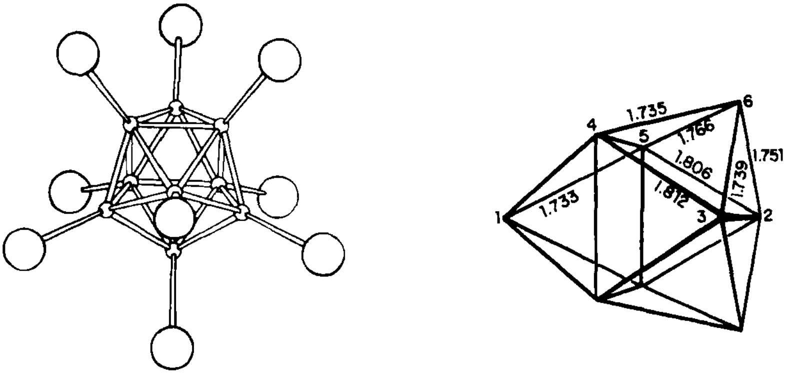
apparently due to a HOMO–LUMO crossing. From this, and the similar energies calculated for the two forms of B_4F_4, it has been suggested



B_4Cl_4



B_8Cl_8



B_9Cl_9

FIG. 5. The structure of, and bond lengths (Å) in B_4Cl_4 (B—B, 1.70 ± 0.04; B—Cl, 1.70 ± 0.04) *(4)*, B_8Cl_8 [B(*n*)—Cl: *n* = 1, 1.739; 2, 1.722; 3, 1.720; 4, 1.721; 5, 1.772; 6, 1.748; 7, 1.746; 8, 1.721] *(5)*, and B_9Cl_9 [B(*n*)—Cl: *n* = 1, 1.729; 2, 1.748; 3, 1.738; 4, 1.741; 5, 1.746; 6, 1.721] *(61)*. ○, B; ◯, Cl.

that B_4F_4 (once formed) and B_4Cl_4 could exist under some conditions as either the tetrahedral or the planar isomer, or perhaps a mixture of both (*72*). Under all the conditions so far studied, B_4Cl_4 has been found to adopt the tetrahedral structure (*14*).

E. B_8Cl_8

The B_8Cl_8 molecule has the dodecahedral structure shown in Fig. 5 (*5*). The source of the crystal used in the structure determination was a sample of red solid product arising from the decomposition of diboron tetrachloride and was at that time known only by the formula $(BCl_{0.9})_x$. Later work by Urry (*121*) showed that such red solids contain about 5% of a dark purple subchloride impurity; it is this dark purple subchloride that is B_8Cl_8 (*76*) and not the bulk of the red material (which is mainly a mixture of $B_{10}Cl_{10}$ and $B_{11}Cl_{11}$).

B_8Cl_8 is diamagnetic (*76*), hence the ESR spectrum observed by Urry (*135*) must have been due to the presence of impurities in his "dark purple crystalline solid"; traces of water in systems used to handle B_8Cl_8 produce paramagnetic hydrolysis products (*76*). Theoretical discussions of B_8Cl_8 have been only briefly summarized in the literature (*68, 100, 137*).

F. B_9X_9 (X = Cl, Br, I)

B_9Cl_9 has the tricapped trigonal-prismatic structure shown in Fig. 5 (*61*). The very similar infrared spectra of B_9Cl_9, B_9Br_9, and B_9I_9 (*142*) suggest that all three halides are isostructural. If this is so, it is interesting to note that the ^{11}B-NMR spectrum of B_9Br_9 consists of a single peak, even down to −60°C, suggesting that the molecule is fluxional (*75*).

V. Chemical and Physical Properties

A. BF AND BCl

The short-lived species BF and BCl have been studied by cocondensation reactions at low temperatures. As described in Section III,A, the condensation of BF with BF_3 at −196°C yields B_2F_4, B_3F_5, and small amounts of more complex fluorides containing between 10 and 16 boron atoms (*69, 126, 131*). The presence of CO or PF_3 in the system results in the formation of the adducts $OCB(BF_2)_3$ and $F_3PB(BF_2)_3$ (*126*). Although BF is readily inserted into BF_3 and B_2F_4, only traces of

F_3SiBF_2 were obtained when insertion into SiF_4 was attempted (*126*). When silicon tetrafluoride is passed over heated boron, the exit gases contain BF, BF_3, and SiF_2, and when condensed at −196°C these give rise to $F_2Si(BF_2)_2$, possibly via the reaction sequence (*71*)

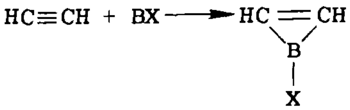
$$SiF_2 + BF \rightarrow [\cdot SiF_2BF \cdot] \xrightarrow{BF_3} F_2Si(BF_2)_2$$

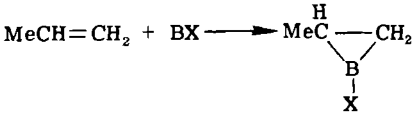
Other products include the known species BF_3, B_2F_4, SiF_4, Si_2F_6, Si_3F_8, and $Si_2F_5BF_2$; an electron-diffraction study has confirmed that the latter compound has the structure $F_3SiSiF_2BF_2$ (*17*).

Condensation of BCl with boron trichloride produces good yields of B_4Cl_4, but no diboron tetrachloride (*132*); similarly, BF is not inserted into $MeBF_2$ to give B_2F_3Me (*69*).

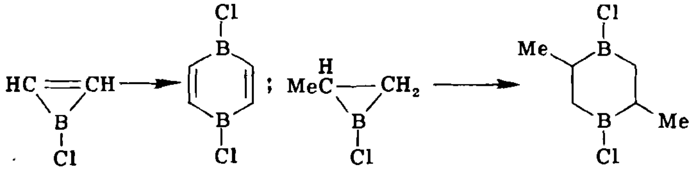
Attempts have been made to use BF as a ligand to transition metals because it is formally isoelectronic with carbon monoxide. Condensation of iron atoms with a mixture of B_2F_4 (as BF precursor) and PF_3 gave two products, one of which was the known $Fe(PF_3)_5$ and the other a very unstable compound of probable formula $Fe(PF_3)_4BF$ (*131*). Similar products were obtained using other transition metals, but attempts to characterize them fully have been frustrated by their extreme thermal instability.

BF and BCl readily add to alkenes and alkynes; propene has been used as the model alkene because C_2H_4 is slightly volatile at −196°C and interferes with the production of BX, by destroying the required high-vacuum conditions. Both types of hydrocarbon are thought to form unstable, three-membered heterocycles as the initial products.



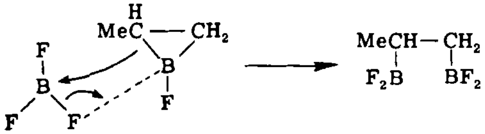


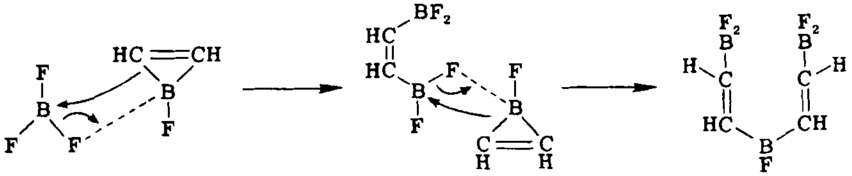
The fate of these heterocycles depends on the halogen X. With the chloride simple dimerization would give the observed products,



(VII)

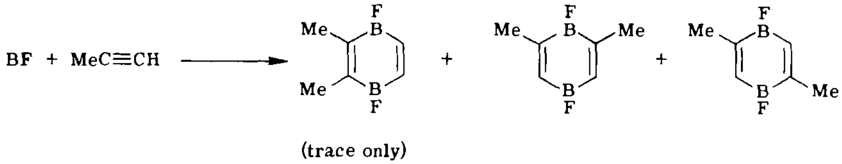
whereas interaction with boron trifluoride (always present in the BF system) appears to occur when X = fluorine. When heated to 70°C,

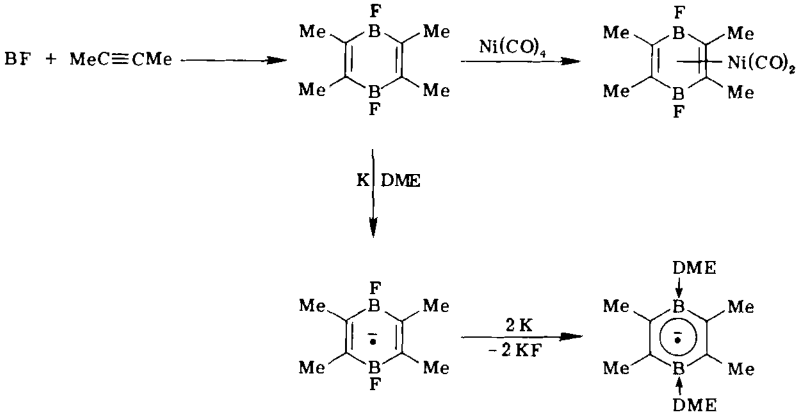




(VIII)

VIII loses boron trifluoride to form the fluorine analog of the boracyclohexadiene **VII** (*131*). Intermediates similar to **VIII** are not formed when BF reacts with methylacetylene or dimethylacetylene (*127*).





(*82a*)

(*64*)

B. DIBORON TETRAHALIDES

The physical properties of the diboron tetrahalides are shown in Table IV. They all spontaneously ignite in air when in the vapor state and are thermally unstable. The fluoride is the most stable, decomposing to the extent of about 40% when held at 200°C for several hours; the products are boron trifluoride and a yellow solid that does not sublime, even at 375°C (*7*). Diboron tetrachloride decomposes to the extent of 13% in 29 h at 25°C, and 32% after 4 h at 155°C; between 138 and 155°C the decomposition data support a second-order heterogeneous reaction that is strongly retarded by products and promoted by systems with a high surface-to-volume ratio (*7*). Colored decomposition products can be detected when diboron tetrabromide is held at room temperature for only 5 min (*75*). Although the tetraiodide appears to be reasonably stable in the solid state at room temperature, dark-colored decomposition products begin to form immediately on melting (*87*).

After liquid B_2Cl_4 and B_2Br_4 have been held at room temperature for several hours, it is possible to detect the presence of long-lived paramagnetic species that give rise to a broad, featureless peak in the ESR spectra (*75, 86*).

The decomposition of diboron tetrachloride has been the most fully studied. Adiabatic flash photolysis shows the initial reaction to be the extrusion of a BCl molecule (*91*)

$$B_2Cl_4 \rightarrow BCl_3 + BCl \tag{1}$$

which is in agreement with McHale's observation that when diboron tetrachloride decomposes, a 1:1 $B_2Cl_4:BCl_3$ ratio is always obtained (*92*). By passing diboron tetrachloride through a narrow silica tube held at 1100°C, Timms has used the decomposition [Eq. (1)] to form preparative amounts of boron monochloride (*131, 132*); a side reaction, not noted under any other conditions, gives solid boron (which tends to block the silica tube).

$$3B_2Cl_4 \rightarrow 2B + 4BCl_3$$

Under some conditions (Section III,E) BCl will add to BCl_3 to give diboron tetrachloride so that Eq. (1) may well be reversible in the liquid state. The other option open to the BCl molecules is polymerization, forming the observed products B_nCl_n. Contrary to earlier reports, no B_4Cl_4 can be detected among the decomposition products of B_2Cl_4, and, furthermore, deliberately added B_4Cl_4 may be isolated unchanged

TABLE IV

PHYSICAL PROPERTIES OF THE DIBORON TETRAHALIDES[a,b]

Property	B_2F_4	B_2Cl_4	B_2Br_4	B_2I_4
Melting point (°C)	−56.0; −55 (*126*)	−92.6; −92.95	0.5–1.5	94–95 (*87*)
Boiling point (°C)	−34	65.5	—	—
Vapor pressure relation for solid: $\log p_{\text{mm}} = A - B/T$ (T in K)	$A = 10.82$ $B = 1856$	—	—	Vapor pressure at 60–70°C is 10^{-3} Torr
Vapor pressure relation for liquid: $\log p_{\text{mm}} = A - B/T$ (T in K)	$A = 9.009$ $B = 1446$	$A = 8.057$ $B = 1753$	Vapor pressure at 22.5°C is 5 Torr	—
Trouton constant	28	23.7	—	—
Heat of evaporation (cal mol^{-1})	6700	8029	—	—
Heat capacity	—	Normal from 20 to 220 K	—	—
Heat of fusion (cal mol^{-1})	—	2579 ± 4	—	—
$\Delta H_f^\ominus$ (298 K (kcal mol^{-1}) (l)	—	−125.0 (*138*)	—	—
$\Delta H_f^\ominus$ (298 K) (kcal mol^{-1}) (g)	−344.2 (*138*)	−117.2 (*138*)	—	—
$\Delta G_f^\ominus$ (kcal mol^{-1}) (l)	—	−111.1 (*138*)	—	—
$\Delta G_f^\ominus$ (kcal mol^{-1}) (g)	−337.1 (*138*)	−110.1 (*138*)	—	—
$S^\ominus$ (cal deg^{-1} mol^{-1}) (l)	—	62.7 (*138*)	—	—
$S^\ominus$ (cal deg^{-1} mol^{-1}) (g)	75.8 (*138*)	85.4 (*138*)	—	—
D_0 (X_2B—BX_2) (kcal mol^{-1})	103.1 (*29*)	87.6 (*30*)	—	—
$\Delta H_{f0}^\ominus(B_2X_4^+)$ (kcal mol^{-1})	−65.2 (*29*)	120.8 (*30*)	—	—

[a] Calculated enthalpies of formation of B_2F_3Cl, B_2FCl_3, F_3BBCl_3, and FClBBFCl are (kcal mol^{-1}): −287.1, −173.5, −230.8, and −229.7, respectively (*35*).

[b] Reference (*84*) unless stated otherwise.

at the end of the experiment, showing that it is not an intermediate necessary for the formation of the other monochlorides (*106*). [On the other hand, very high local concentrations of BCl, which are formed when BCl vapor is condensed at −196°C, produce B_4Cl_4 in good yield (*132*).] If polymerization of the BCl molecules produces the observed B_nCl_n products (n = 8 to 12), there must be open-cage species, which are possibly stabilized by interaction with BCl_3 or B_2Cl_4 molecules, acting as intermediates.

It is possible to exercise some slight control as to which decomposition products are formed. By holding the liquid diboron tetrachloride at about 70°C instead of room temperature, a higher proportion of B_8Cl_8 is obtained (*106, 121*). If dilute solutions of B_2Cl_4 in BCl_3 are allowed to decompose over a period of weeks at room temperature, the product is $B_{11}Cl_{11}$, contaminated with small amounts of $B_{12}Cl_{12}$ (*6*).

When diboron tetrabromide decomposes, the products are BBr_3, involatile solid debris, and a series of monobromides, B_nBr_n (n = 7 to 10) (*66, 75*). The latter have been separated by fractional sublimation (*66*) or fractional precipitation from pentane at low temperatures (*75*). Diboron tetraiodide decomposes to give mainly BI_3, B_8I_8, and B_9I_9 (*87*).

Stabilization of the diboron tetrahalides may be accomplished by complexing them with a suitable donor molecule such as trimethylamine. Cryoscopic measurements on the molecular weight of the adduct $B_2Cl_4 \cdot 2NMe_3$ originally suggested that the compound was tetrameric (*136*), but more recent work shows it to be monomeric in the solid and gaseous phases (*119*). The B—B and B—N bond lengths are 1.72 and 1.75 Å, respectively (*119*). For the solid bisphosphine adducts $B_2Cl_4 \cdot 2PH_3$ and $B_2Cl_4 \cdot 2PD_3$, the vibrational spectra have been interpreted on the basis of a trans (C_{2h}) molecular conformation with a rotation barrier about the B—P bonds of 2.92 ± 0.18 kcal mol^{-1} (*98*).

The diboron tetrahalides are capable of acting as either mono- or dibasic Lewis acids. For example, Schlesinger originally showed that, on pumping, the bis(diethyl ether) adduct $B_2Cl_4 \cdot 2OEt_2$ loses a mole of diethyl ether to give $B_2Cl_4 \cdot OEt_2$ (*136*). When a tensiometric titration is carried out between diboron tetrafluoride and trimethylamine, two breaks are observed in the pressure: mole-ratio curve (Fig. 6), the first representing the formation of $B_2F_4 \cdot NMe_3$ and the second, $B_2F_4 \cdot 2NMe_3$ (*3*). By using this technique to form $B_2F_4 \cdot NMe_3$ and then adding a second mole of triethylamine, it is possible to make the mixed adduct $B_2F_4 \cdot NMe_3NEt_3$ (*3*). Only a single broad peak at +11.7 ppm (relative to $BF_3 \cdot OEt_2$) is observed in the ^{11}B-NMR spectrum of $B_2F_4 \cdot NMe_3$, which implies rapid exchange of trimethylamine between the two boron sites (*3*).

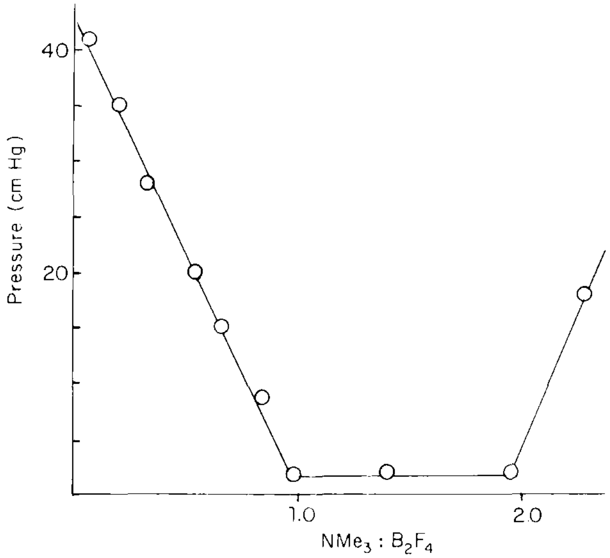


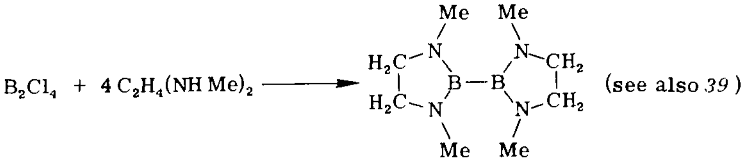
FIG. 6. Tensiometric titration of trimethylamine against diboron tetrafluoride.

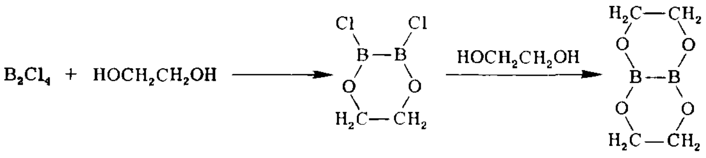
Diboron tetrafluoride is liberated by BF_3 from several of its adducts, including $B_2F_4 \cdot 2NMe_3$, showing that the trifluoride is the stronger Lewis acid (*46*).

Bases that contain reactive hydrogens on the donor atom readily evolve hydrogen chloride when treated with diboron tetrachloride

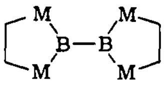
$$4ROH + B_2Cl_4 \rightarrow B_2(OR)_4 + 4HCl \qquad (84)$$

Advantage has been taken of this to form heterocyclic species, starting with difunctional bases such as ethylene glycol, ethanedithiol, 1,3-propanediol, catechol, *sym*-dimethylethylenediamine, and *o*-phenylenediamine (*141*).

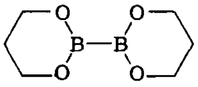


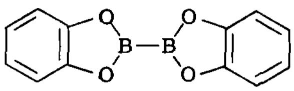


Only polymeric products were obtained with 1,3-propanedithiol, 2-aminophenol, 2-mercaptoethanol, and styrene glycol. It has since been suggested that the NMR data of the oxygen and sulfur heterocycles are more consistent with structures similar to the nitrogen complex (*97*).



(M = O, S)





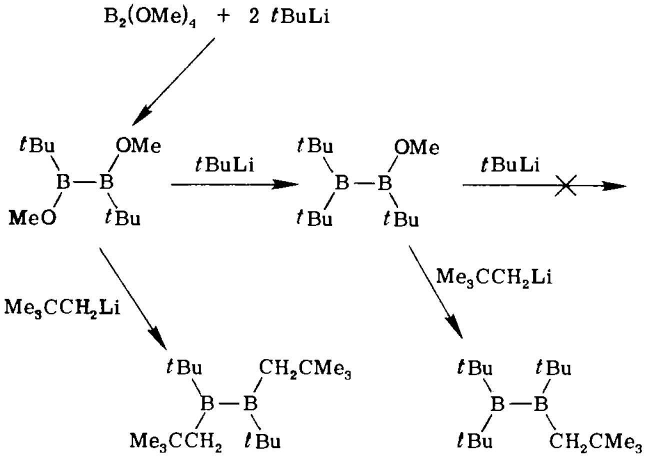
Conductimetric titrations of diboron tetrachloride in liquid hydrogen chloride with either Me_4NCl or PCl_5 indicate the formation of the hexachlorodiborate anion, which may be isolated as the tetramethylammonium or tetrachlorophosphonium salts. The titration curves showed no breaks at mole ratios of 1 : 1, corresponding to the $B_2Cl_5^-$ ion; attempts to prepare tetramethylammonium pentachlorodiborate by mixing stoichiometric amounts of reagents have resulted only in the formation of the hexachlorodiborate. The reactions of diboron tetrafluoride in liquid hydrogen chloride are complicated by the occurrence of partial solvolysis (*103*).

Early attempts to methylate diboron tetrachloride with dimethylcadmium (*136*) or tetramethyllead (*55*) gave BMe_3 as the only volatile, boron-containing product; treatment with dimethylmercury resulted in explosions (*139*). Later work, however, shows that MeB_2Cl_3 is formed, along with methylchloroboranes, when B_2Cl_4 is treated with Me_4Ge, Me_4Sn, or Me_4Pb; unfortunately, it has proven impossible to separate the MeB_2Cl_3 from unchanged diboron tetrachloride (*110*). The thermally unstable 1,2-dimethyldichlorodiboron can be made by treating $MeBCl_2$ with copper atoms (*128*)

$$2MeBCl_2 + 2Cu \xrightarrow{-196^\circ C} Me(Cl)B{-}BMe(Cl)$$

Very slow, partial methylation of $B_2Cl_4 \cdot 2NMe_3$ appears to occur at room temperature with tetramethyllead; presumably, the methylated products are stabilized by coordination to trimethylamine (*55*). No alkylated products containing B—B bonds could be detected when the tetramethylethylenediamine and glyme adducts of B_2F_4 were treated with diethylzinc (*46*).

Although B_2R_4 derivatives have not been prepared from the diboron tetrahalides, thermally stable tetraalkyldiborons containing bulky R groups have been described (*10, 120*). The products do not react at room temperature with methanol, ammonia, hydrazine, or pyridine; **IX** is even stable toward oxygen.



(IX)

Simple cleavage of the B—B bonds in diboron tetrachloride occurs with chlorine and bromine (*84*); however, the slow reaction with iodine at room temperature produces a black, solid monoiodide (*92*).

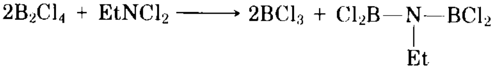
$$3B_2Cl_4 + 2I_2 \rightarrow 4BCl_3 + BI_3 + (BI)_x$$

Small quantities of mixed chloroiodoboranes were also present, which, presumably, were formed by interaction between the two trihalides.

Chloramines readily cleave the B—B bonds of diboron tetrachloride, the products depending on the temperature and reaction stoichiometry (*53*).

$$\begin{tikzcd}B_2Cl_4 + Me_2NCl \arrow[r, "20^\circ C"] & BCl_3 + Me_2NH \cdot BCl_3 + \text{nonvolatile residue} \arrow[d, "80^\circ C"] \\ & Me_2NBCl_2\end{tikzcd}$$

$$B_2Cl_4 + EtNCl_2 \longrightarrow BCl_3 + EtNCl{-}BCl_2$$

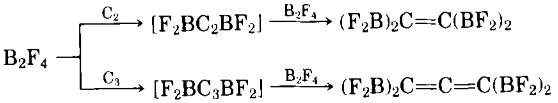


$$2B_2Cl_4 + EtNCl_2 \longrightarrow 2BCl_3 + Cl_2B{-}\underset{\displaystyle Et}{\underset{|}{N}}{-}BCl_2$$

Diboron tetrachloride, when cocondensed with carbon vapor generated in a carbon arc, gives a mixture of $C(BCl_2)_4$, $ClC(BCl_2)_3$, $Cl_2C(BCl_2)_2$, and $(Cl_2B)_2C{=}C(BCl_2)_2$. For example, the process leading to tetrakis(dichloroboryl)methane probably involves a double-insertion reaction (*32, 130*).

$$:C: + Cl_2BBCl_2 \rightarrow Cl_2B\ddot{C}BCl_2 \xrightarrow{B_2Cl_4} C(BCl_2)_4$$

When B_2F_4 is used, rather unstable compounds are isolated that originate from only C_2 and C_3 species (*32*).



$$B_2F_4 \begin{cases} \xrightarrow{C_2} [F_2BC_2BF_2] \xrightarrow{B_2F_4} (F_2B)_2C{=}C(BF_2)_2 \\ \xrightarrow{C_3} [F_2BC_3BF_2] \xrightarrow{B_2F_4} (F_2B)_2C{=}C{=}C(BF_2)_2 \end{cases}$$

Any fluoro derivatives containing single carbon atoms were probably too unstable to be isolated; the chloro analog of tetrakis(difluoroboryl)allene may have been formed, but it was thought too nonvolatile to be removed from the reaction vessel.

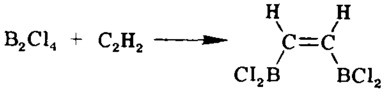
The reaction of silicon atoms with diboron tetrafluoride at −196°C is complex, but it has proved possible to isolate the pyrophoric $FSi(BF_2)_3$ in about 2% yield (based on silicon); a trace of $F_2Si(BF_2)_2$ is also formed (*71, 131*). Silicon difluoride and B_2F_4 give a blue solid at −196°C, which on warming evolves BF_3, SiF_4, B_2F_4, Si_2F_6, and a very unstable volatile compound that may be $(F_5Si_2)BFBF_2$; in the presence of phosphorus trifluoride, $(F_5Si_2)_2(BF_2)B \cdot PF_3$ is formed (*131*). In the hope of making $Cl_3SiBClBCl_2$, silicon dichloride and diboron tetrachloride were condensed together at −196°C and then allowed to warm up to room temperature; only nonvolatile solids, $SiCl_4$, and Cl_3SiBCl_2 were obtained (*131*). [The latter compound has also been made at the rate of 12 mg h^{-1} by passing a $SiCl_4$–BCl_3 mixture through a pulsed discharge (*147*).] When carbon monoxide is added to the $SiCl_2$–B_2Cl_4 matrix during warmup to room temperature, a very stable carbonyl adduct $(Cl_3Si)_2(BCl_2)B \cdot CO$ results. Partial halogen exchange occurs when CO is replaced by phosphorus trifluoride, and the product is then $(Cl_3Si)_2(BF_2)B \cdot PF_3$ (*131*).

It appears (*131*) from these silicon dihalide experiments and from a study of B_3F_5 (Section V,D) that compounds of the formula $XBY{-}BY_2$ ($X = BF_2$, $SiCl_3$, or Si_2F_5) are highly unstable toward disproportionation into B_2Y_4 and $[X_2(BY_2)B]_2$. The CO and PF_3 adducts mentioned previously probably arise via cleavage of the latter dimer (compare B_8F_{12}, Section V,E).

$$[X_2(BY_2)B]_2 + 2CO \rightarrow 2X_2(BY_2)BCO$$

$$\begin{array}{ll} X = BF_2, & Y = F \\ X = SiCl_3, & Y = Cl \\ X = Si_2F_5, & Y = F \end{array}$$

There has been considerable interest shown in the stereochemistry of products formed by addition of B_2F_4 and B_2Cl_4 to alkenes and alkynes. With acetylene (*52, 115*), 2-butyne (*145*), *trans*-2-butene (*115, 145*), *cis*-2-butene (*115, 145*), *trans*-2,2,5,5-tetramethyl-3-hexene (*149*), norbornylene (*144*), cyclohexane (*9, 145*), 1,3-cyclohexadiene (*148*), cyclopropene (*113*), cyclobutene (*113*), cyclopentene (*113*), and naphthalene (*144*) cis addition occurs



(**X**)

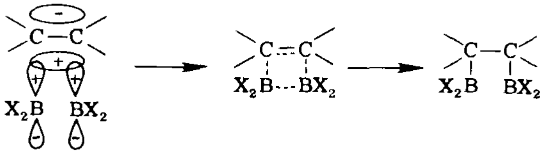
On standing (*52*) or under the influence of ultraviolet radiation (*19*), **X** changes to the trans isomer. Addition of another mole of diboron tetrachloride to both **X** and its trans isomer can occur.

$$Cl_2BCH = CHBCl_2 + B_2Cl_4 \rightarrow (Cl_2B)_2CHCH(BCl_2)_2 \qquad (20, 84)$$

When **X** is used, some *trans*-1,2-bis(dichloroboryl)ethylene is also formed, presumably by isomerization of **X** under the reaction conditions (*19*). Treatment of **X** with CH_3COOD at 80°C gives both *cis*- and *trans*-$C_2H_2D_2$, showing that this cleavage is not entirely sterospecific; alkaline hydrolyses or reductions by ammoniacal silver oxide are recommended as better cleavage systems (*19*). In contrast to C_2H_2, the substituted alkynes propyne, 2-butyne, and di-*t*-butylacetylene only add 1 mol of B_2Cl_4 (*144*).

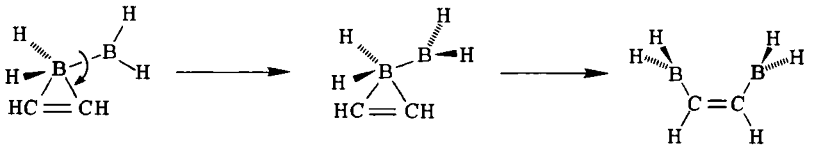
In apparent contrast to these reactions, addition of B_2Cl_4 to cyclopentene has been claimed to give 1,2-bis(dichloroboryl)cyclopentane, which on cleavage with alkaline peroxide yielded only *trans*-1,2-cyclopentanediol (*117*). However, this work has been repeated under a wide variety of conditions and the reaction shown to give only the expected cis product (*113*).

The formation of only cis products from these addition reactions has been interpreted by most workers in terms of a mechanism involving a four-centered intermediate, which is assumed to arise by interaction of the hydrocarbon's π system with the vacant boron 2p orbitals.



A planar B_2X_4 would clearly be preferred for such an interaction. That $B_2(NMe_2)_4$ and B_2Br_4 (both of which adopt the nonplanar conformation in all phases) do not react with ethylene appears to be in keeping with this mechanism.

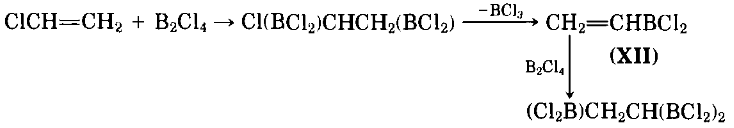
However, a theoretical study of the B_2H_4–C_2H_2 reaction suggests that it proceeds in two steps. The first, which is rate determining with an activation energy of 12.8 kcal mol^{-1}, results in the formation of the three-center π complex **XI**; the second step is the attachment of the other BH_2 to the second carbon and involves rotation of the BH_2 group until it comes out of the B_2C_2 plane.



(XI)

Like the previous one, this new mechanism predicts the formation of cis products (*16*). Naturally enough, after their formation by cis addition, saturated products adopt a structure appropriate to the prevailing conditions. Thus the planar "trans" conformation of 1,2-bis(dichloroboryl)ethane is found in the crystal (*94*) and is the main constituent of the liquid and gaseous phases (*124*).

Contrary to earlier reports (*84, 144*), haloolefins slowly add diboron tetrahalides. For example, 2 mol of B_2Cl_4 react with vinyl chloride, yielding 1,1,2-tris(dichloroboryl)ethane and boron trichloride; the reaction sequence is considered to be (*112*)



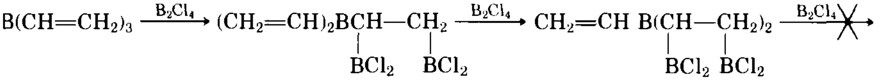
$$\begin{tikzcd} \mathrm{ClCH{=}CH_2 + B_2Cl_4} \arrow[r] & \mathrm{Cl(BCl_2)CHCH_2(BCl_2)} \arrow[r, "-\mathrm{BCl_3}"] & \mathrm{CH_2{=}CHBCl_2}\ \mathbf{(XII)} \arrow[d, "\mathrm{B_2Cl_4}"'] \\ & & \mathrm{(Cl_2B)CH_2CH(BCl_2)_2} \end{tikzcd}$$

The rapid addition of B_2Cl_4 to vinyldichloroborane (**XII**) had been demonstrated previously (*20*). Similar reactions occur with *trans*-2-chlorovinyldichloroborane, fluoroethylene, vinyl bromide, and 1-bromopropene, or when B_2F_4 is substituted for diboron tetrachloride (*110, 112*). This work also confirmed earlier observations (*15*) that diboron tetrachloride is stabilized toward decomposition by haloolefins; it is not a simple dilution effect because B_2Cl_4 decomposes normally in either *n*-hexane or ethyl chloride (*112*).

Addition of diboron tetrahalides occurs even when the double bonds are attached, as vinyl groups, to a variety of elements such as boron, silicon, germanium, and tin.

$$Me_3MCH{=}CH_2 + B_2X_4 \rightarrow Me_3MCH(BX_2)CH_2BX_2 \qquad (20)$$
$$M = C, Si$$

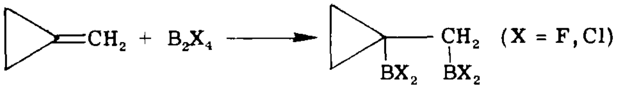
$$Cl_3MCH{=}CH_2 + B_2X_4 \rightarrow Cl_3MCH(BX_2)CH_2BX_2 \qquad (20)$$
$$M = Si, Ge, Sn$$

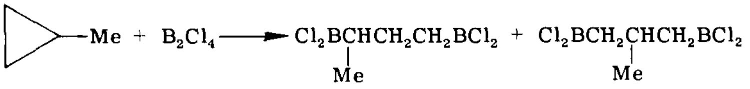


$$B(CH{=}CH_2)_3 \xrightarrow{B_2Cl_4} (CH_2{=}CH)_2B\underset{BCl_2}{\underset{|}{CH}}-\underset{BCl_2}{\underset{|}{CH_2}} \xrightarrow{B_2Cl_4} CH_2{=}CH\;B(\underset{BCl_2}{\underset{|}{CH}}-\underset{BCl_2}{\underset{|}{CH_2}})_2 \cancel{\xrightarrow{B_2Cl_4}} \qquad (57)$$

As an exception, tetravinyltin does not yield simple addition products with B_2F_4; instead, ethylene, vinyldifluoroborane, and nonvolatile residues are obtained (*58*).

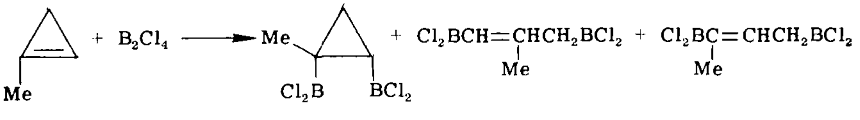
Diboron tetrachloride reacts with cyclopropane and methylcyclopropanes to give ring-cleavage addition products. Deboronation of **XIII** and **XIV** with propionic acid produces *n*-butane and methylpropane, respectively. The ring cleavage has been shown to occur stereospecifically for *cis*- and *trans*-1,2-dimethylcyclopropane (*146*). When the cyclopropane ring is substituted with either a methylene or a vinyl group, addition of diboron tetrahalide takes place only on the exocyclic double bond, even when an excess of halide is used (*50*).





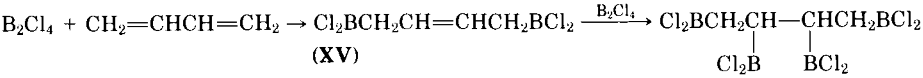
(XIII) (XIV)

Addition to the double bond and not ring cleavage also occurs when diboron tetrachloride reacts with cyclopropene; however, when methylcyclopropene is used both types of addition product are formed in competing reactions (*113*).



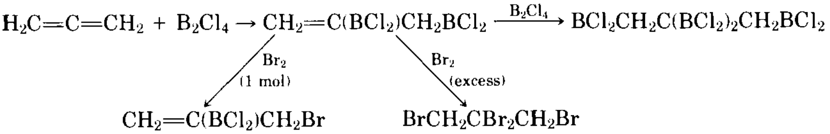
Cyclobutane does not react with diboron tetrachloride (*146*).

One mole of either B_2F_4 or B_2Cl_4 will add to 1,3-butadiene to yield 1,4-bis(dihaloboryl)-2-butene, and, in the case of the tetrachloride, further addition occurs to the butene double bond



$$B_2Cl_4 + CH_2{=}CHCH{=}CH_2 \rightarrow \underset{(XV)}{Cl_2BCH_2CH{=}CHCH_2BCl_2} \xrightarrow{B_2Cl_4} Cl_2BCH_2\underset{\displaystyle Cl_2B}{\underset{|}{C}}H{-}\underset{\displaystyle BCl_2}{\underset{|}{C}}HCH_2BCl_2$$

Cautious hydrolysis of **XV** followed by oxidation with H_2O_2 gives wholly *cis*-1,4-dihydroxy-2-butene. Methyl-substituted conjugated or cumulated dienes rapidly polymerize in the presence of diboron tetrahalides (*51*). Allene itself will undergo both 1 : 1 and 2 : 1 addition with diboron tetrachloride (*47*).



$$\begin{tikzcd} H_2C{=}C{=}CH_2 + B_2Cl_4 \arrow[r] & CH_2{=}C(BCl_2)CH_2BCl_2 \arrow[r, "B_2Cl_4"] \arrow[dl, "Br_2\ (1\ mol)"'] \arrow[d, "Br_2\ (excess)"] & BCl_2CH_2C(BCl_2)_2CH_2BCl_2 \\ CH_2{=}C(BCl_2)CH_2Br & BrCH_2CBr_2CH_2Br & \end{tikzcd}$$

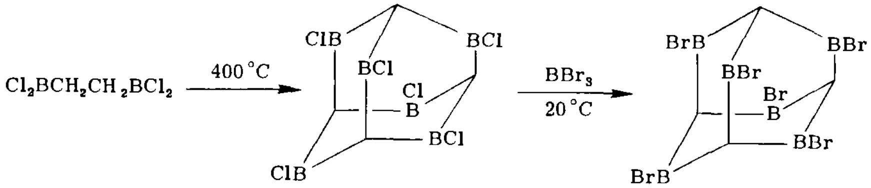
With ferrocene, diboron tetrachloride undergoes substitution rather than addition to form ferrocenyldichloroborane, $C_5H_5FeC_5H_4BCl_2$ (**XVI**). The other product, $HBCl_2$, also reacts with ferrocene to give **XVI** and hydrogen; this latter process is cyclic because H_2 gives more dichloroborane with unchanged diboron tetrachloride. A simpler process by which to make **XVI** is to treat boron trichloride with ferrocenyl mercurichloride in hexane (*73*). Diboron tetrafluoride fails to react with ferrocene (*104*).

C. Properties of B_2X_4–Hydrocarbon Addition Products

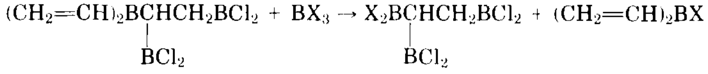
In the main, B_2X_4–hydrocarbon addition products are thermally stable but water-sensitive, colorless solids or liquids; among the least stable are the products derived from methylenecyclopropane and vinylcyclopropane; they decompose at or around room temperature (*50*). On heating, loss of boron trihalide occurs with, usually, the formation of complex mixtures of products (e.g., *20, 84*); atypically, 1,2-bis(dichloroboryl)-1-trichlorostannylethane decomposes almost quantitatively to three well-defined products at 100°C (*20*).

$$Cl_2BCH_2CH(BCl_2)SnCl_3 \rightarrow CH_2{=}CHBCl_2 + BCl_3 + SnCl_2$$

At 400°C, 1,2-bis(dichloroboryl)ethane undergoes rapid charring, and from among the many products it is possible to isolate low yields of the crystalline hexachlorohexaboroadamantane (*107*).



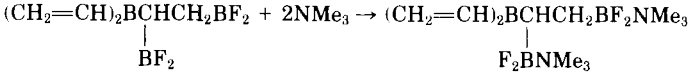
The overall stability of 1,2-bis(dichloroboryl)-1-divinylborylethane allows both vinylic double bonds to be hydrogenated, using a Raney nickel catalyst, and the vinyl groups to be exchanged for chloride or dimethylamino (*57*).



$$(CH_2{=}CH)_2B\underset{\substack{|\\ BCl_2}}{C}HCH_2BCl_2 + BX_3 \rightarrow X_2B\underset{\substack{|\\ BCl_2}}{C}HCH_2BCl_2 + (CH_2{=}CH)_2BX$$

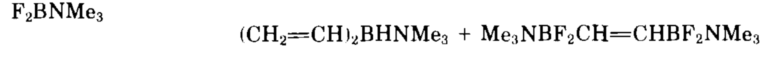
$X = Cl, NMe_2$

The addition products contain trigonal boron atoms and thus can be expected to react with Lewis bases such as trimethylamine (*9, 84, 117*) and dimethyl ether (*9*). In some cases, however, simple adducts are not obtained. The decomposition of 1,1,2,2-tetrakis(difluoroboryl)ethane is promoted by trimethylamine, and Me_3NBF_3 is the only identifiable product (*56*). At room temperature 2 mol of trimethylamine are taken up by 1,2-bis(difluoroboryl)-1-divinylborylethane in a typical acid–base reaction



$$(CH_2{=}CH)_2B\underset{\substack{|\\ BF_2}}{C}HCH_2BF_2 + 2NMe_3 \rightarrow (CH_2{=}CH)_2B\underset{\substack{|\\ F_2BNMe_3}}{C}HCH_2BF_2NMe_3$$

But at 80°C in the presence of another mole of base, dehydroboration occurs (*57*).

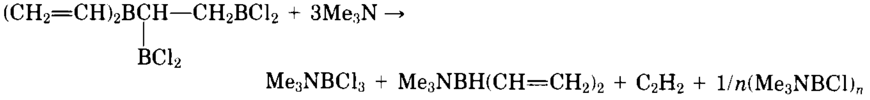


$$(CH_2{=}CH)_2B\underset{\substack{|\\ F_2BNMe_3}}{C}HCH_2BF_2NMe_3 + NMe_3 \rightarrow (CH_2{=}CH)_2BHNMe_3 + Me_3NBF_2CH{=}CHBF_2NMe_3$$

The decomposition is even more complex when 1,2-bis(dichloroboryl)-1-divinylborylethane is used, because the intermediate compound $Cl_2BCH{=}CHBCl_2$, unlike the corresponding fluoride, releases acetylene in the presence of trimethylamine

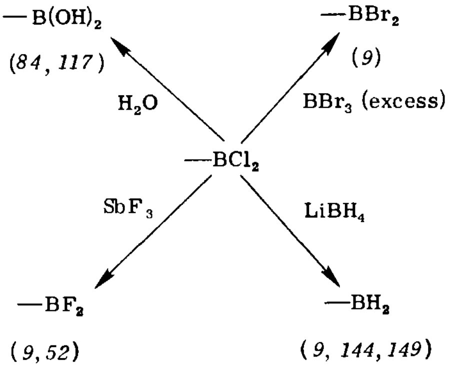
$$Cl_2BCH{=}CHBCl_2 + 2NMe_3 \xrightarrow{120°C} C_2H_2 + Me_3NBCl_3 + 1/n(Me_3NBCl)_n$$

so that the overall reaction then becomes (*57*)



$$(CH_2{=}CH)_2B\underset{\displaystyle BCl_2}{\underset{|}{C}}H{-}CH_2BCl_2 + 3Me_3N \rightarrow Me_3NBCl_3 + Me_3NBH(CH{=}CH_2)_2 + C_2H_2 + 1/n(Me_3NBCl)_n$$

The BCl_2 groups of the B_2Cl_4 addition compounds behave normally and undergo typical substitution reactions.



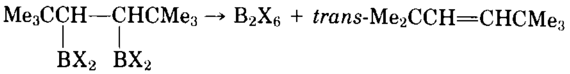
Sometimes when there are several BCl_2 groups to substitute, as in 1,1,2,2-tetrakis(dichloroboryl)ethane, the antimony trifluoride reaction fails and a better fluorinating agent in this case was found to be diboron tetrafluoride (*56*). Attempted methylation of 1,2-bis(dichloroboryl)ethylene with tetramethyllead at room temperature gave trimethylborane as the only identifiable boron compound (*55*).

$$C_2H_2(BCl_2)_4 + 2B_2F_4 \rightarrow C_2H_2(BF_2)_4 + 2B_2Cl_4$$

A typical reaction of dihydroxyborylethanes, formed by hydrolysis of the corresponding chlorides, is that on heating they lose the carbon backbone to form saturated alkanes, sometimes quantitatively. Similarly, some dihydridoboryl derivatives are pyrolyzed with (apparently stereospecific) release of hydrocarbon.

$$2[(HO)_2B]_2CHCH_2B(OH)_2 \xrightarrow{200°C} 3B_2O_3 + 3H_2O + C_2H_6 \qquad (57)$$

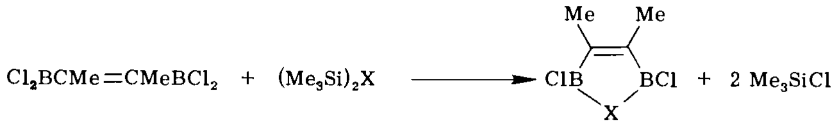
$$[(HO)_2B]_2CHCH[B(OH)_2]_2 \longrightarrow 2B_2O_3 + 2H_2O + C_2H_6 \qquad (56)$$



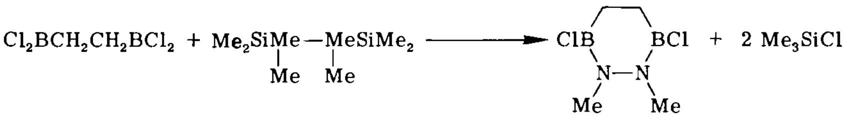
$$Me_3C\underset{\displaystyle BX_2}{\underset{|}{C}}H{-}\underset{\displaystyle BX_2}{\underset{|}{C}}HCMe_3 \rightarrow B_2X_6 + trans\text{-}Me_2CCH{=}CHCMe_3$$

X = H, D (50–70% yield) (*144, 149*)

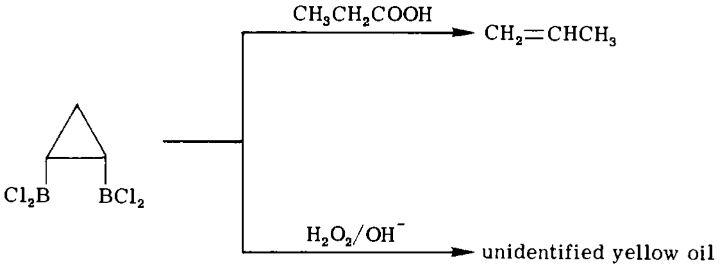
Starting with bifunctional trimethylsilyl derivatives, $(Me_3Si)_2X$, and bis(dichloroboryl) compounds, Haubold has succeeded in making a variety of heterocycles by a Me_3SiCl extrusion reaction (*49*).



X = S, NMe, MeNNMe

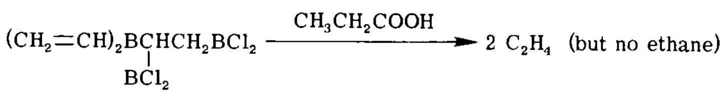


Cleavage of the B—C bonds in dihaloboryl derivatives by either propionic acid or alkaline peroxide is widely used as a diagnostic aid to structure determination. However, the products in a few cases are not always those anticipated.



(*113*)

(*113*)

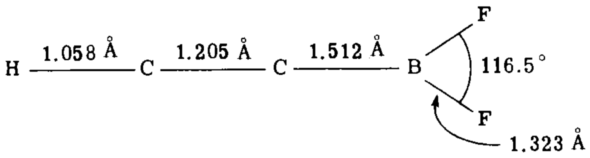


$$(CH_2{=}CH)_2B\underset{BCl_2}{CH}CH_2BCl_2 \xrightarrow{CH_3CH_2COOH} 2\ C_2H_4 \text{ (but no ethane)}$$

(*57*)

The nonstereospecific nature of the propionic acid reaction, when applied to the cleavage of $Cl_2BCH{=}CHBCl_2$ (*19*), was referred to in Section V,B.

The transformation of *cis*-bis(dichloroboryl)ethylene into the trans isomer on irradiation (*19*) is accompanied by a side reaction that produces about a 15% yield of $HC{\equiv}CBCl_2$; treatment of this chloride with antimony trifluoride gives $HC{\equiv}CBF_2$, which releases acetylene when heated with propionic acid. A microwave-spectral study of ethynyldifluoroborane gave the following parameters (*110*).



Assignments have been made of the bands in the vibrational spectra of $F_2BCH{=}CHBF_2$ (*52*), $F_2BCH_2CH_2BF_2$ (*124*), $Cl_2BCH{=}CHBCl_2$ (*52, 115*), and $Cl_2BCH_2CH_2BCl_2$ (*124*).

D. TRIBORON PENTAFLUORIDE (B_3F_5)

The air- and water-sensitive compound triboron pentafluoride, the first reported (*126*) to have a simple chain of three boron atoms, melts between −55 and −50°C. Decomposition is very rapid above −30°C and produces mainly B_2F_4 and B_8F_{12}. Carbon monoxide apparently catalyzes this decomposition, because reaction occurs even at temperatures as low as −70°C to form $OCB(BF_2)_3$ and B_2F_4, the carbonyl arising from interaction of CO with B_8F_{12} (see following discussion).

Hydrogen reacts rapidly with B_3F_5 at temperatures from −70°C upward to give a mixture of HBF_2, B_2F_4, and B_2H_6, together with a nonvolatile BF polymer.

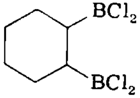
A smooth reaction occurs at −100°C with liquid tetrafluoroethylene to produce fair yields of *cis*-1,2-bis(difluoroboryl)difluoroethylene, $CF(BF_2){=}CF(BF_2)$; above −100°C the C_2F_4 is explosively polymerized by triboron pentafluoride. No reaction occurs with hexafluorobenzene.

E. DODECAFLUOROOCTABORANE(12) (B_8F_{12})

As found with most boron–fluorine derivatives containing B—B bonds, B_8F_{12} reacts explosively with air and water; the only inert solvents appear to be liquid B_2F_4 or B_3F_5. No crystalline state of B_8F_{12} has yet been obtained; below −90°C the glassy solid is faintly yellow. On warming, a bright yellow liquid is formed, the viscosity of which decreases with increasing temperature until at about −20°C it is fairly mobile; the vapor is intensely yellow-brown. The visible spectrum of the gas shows a broad peak at 345 nm, and then an intense maximum starts at 320 nm and extends well into the ultraviolet region (*70*).

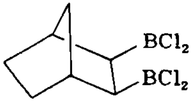
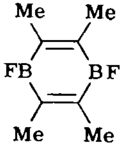
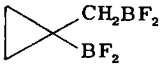
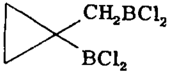
TABLE V

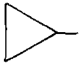
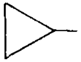
^{11}B-NMR Chemical Shifts of Boron Subhalides and Their Derivatives[a]

Compound	^{11}B-NMR shift (relative to BF_3OEt_2)	Reference	Comments
B_2F_4	−23.0	(*52, 70*)	
B_2Cl_4	−62.4 ± 0.1	(*25, 52*)	
B_2Br_4	−70.0	(*75*)	
MeClBBClMe	−91.0	(*128*)	
B_3F_5	−25	(*70*)	
B_8F_{12}	−25	(*70*)	Peak width, 800 Hz
B_4Cl_4	−85.0 ± 0.3	(*25*)	Temperature range −78 to +118°C; peak width, Hz (°C): 35 (−78°); 16–18 (25°C); 8 (118°C)
$B_4(t\text{-Bu})_4$	−135.1	(*26*)	
B_7Br_7	−69.5	(*75*)	
B_8Br_8	−67.3	(*75*)	
B_9Br_9	−60.4	(*75*)	Peak width ~30 Hz at −60°C
$B_{10}Br_{10}$	−65.2	(*75*)	
$B_9Br_9^{2-}$	−0.77; −8.15	(*143*)	
MeB_9Br_8	−62.2	(*118*)	τ, ^{1}H = 10.06
$MeEtB_9Br_7$	−62.4	(*118*)	Shoulder slightly to lower field; τ, ^{1}H = 10.06(Me); 10.10(CH_3, Et); 10.16(CH_2, Et)
$Cl_2BCH{=}CHBCl_2$	−54.0	(*52*)	
$Cl_2BCH_2CH_2BCl_2$	−63.0	(*52*)	
$Cl_2BCMe_3CHCHCMe_3BCl_2$	−64.0	(*144*)	
$Cl_2BCMe_3CHCHMeBCl_2$	−64.9	(*144*)	
	−65.0	(*144*)	

(*continued*)

TABLE V (*continued*)

Compound	^{11}B-NMR shift (relative to BF_3OEt_2)	Reference	Comments
	−59.7	(*144*)	
$F_2BCH=CHBF_2$	−23.0	(*32*, *52*)	J_{BF} = 64 (*52*); 58 Hz (*32*)
$F_2BCH_2CH_2BF_2$	−29.5	(*52*)	J_{BF} = 76 Hz
$Me_3CC(H)(BH_2)C(H)(BH_2)CMe_3$	−25	(*149*)	
$(Cl_2B)_2CCl_2$	−53.1	(*32*)	
$(Cl_2B)_3CCl$	−54.1	(*32*)	
$(Cl_2B)_4C$	−57.2	(*32*)	
$(BF_2)_2C=C=C(BF_2)_2$	−23.5	(*32*)	
$FB(CH=CHBF_2)_2$	−23.0	(*127*)	Single broad peak
$(BF_2)_2C=C(BF_2)_2$	−23.0	(*32*)	
	−40.2	(*82a*)	
	−27.3	(*50*)	1:2:1 triplet, J_{BF} = 68 Hz
	−59.5	(*50*)	

 $-CH(BF_2)CH_2BF_2$	−27.1; −30.5	(*50*)	Relative intensity 1 : 1; broad
 $-CH(BCl_2)CH_2BCl_2$	−58.5	(*50*)	Broad
$Cl_2BCH_2CH{=}CHCH_2BCl_2$	−58	(*51*)	
$Cl_2BCH_2CH(BCl_2)CH(BCl_2)CH_2BCl_2$	−59.0	(*51*)	Single broad peak
$B_2(O_2C_2H_4)_2$	−31.5	(*97, 141*)	
$B_2(S_2C_2H_4)_2$	−68.3	(*97, 141*)	
$B_2(O_2C_3H_6)_2$	−28.6	(*97, 141*)	
$B_2(O_2C_6H_4)_2$	−30.7	(*97, 141*)	
$B_2Cl_2(O_2C_2H_4)$	−30.8	(*97, 141*)	
$B_2Cl_2(S_2C_2H_4)$	−67.8	(*97, 141*)	
$B_2[(NMe)_2C_2H_4]_2$	−33.7	(*97, 141*)	
$B_2[(NH)_2C_6H_4]_2$	−27.9	(*97, 141*)	
Cl_3SiBCl_2	−63.0	(*70*)	
F_3SiBF_2	−28.0	(*70*)	
Cl_3SiBCl_2	−63	(*70*)	

	3-Coordinate B	4-Coordinate B	Reference	
$(Cl_3Si)_2(BCl_2)BCO$	−70	+20	(*70*)	
$(Si_2F_5)(SiF_2)(BF_2)BPF_3$	−30	+52	(*70*)	
$(Cl_3Si)_2(BF_2)BPF_3$	−30	+36	(*70*)	
$(BF_2)_3BPF_3$	−32	+49	(*70*)	
$B_2F_4 \cdot 2NMe_3$	—	+ 6.7	(*3*)	
$B_2F_4 \cdot 2NEt_3$	—	+ 8.3	(*3*)	
$B_2F_4 \cdot NMe_3NEt_3$	—	+ 8.4	(3)	Single very broad peak
$B_2F_4 \cdot NMe_3$	+11.7		(*3*)	Single broad peak

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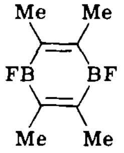
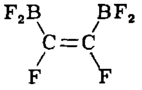
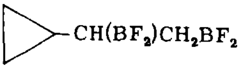
[a] For the shifts of other diboron compounds not synthesized from the subhalides, see Table L in Nöth and Wrackmeyer (*97*).

TABLE VI

^{19}F-NMR CHEMICAL SHIFTS OF BORON SUBFLUORIDES AND THEIR DERIVATIVES

Compound	^{19}F-NMR shift (relative to $CFCl_3$ unless specified)	Reference
B_2F_4	+55.7	(*70*)
B_3F_5	−26.2 (BF); +61.0 (BF_2)	(*126*)
B_8F_{12}	+44.1	(*70*)
F_3SiBF_2	+40.9 (BF_2)	(*70*)
$(Si_2F_5)(SiF_3)(BF_2)BPF_3$	+33.5 (BF_2)	(*70*)
$(Cl_3Si)_2(BF_2)BPF_3$	+35.2 (BF_2)	(*70*)
$(BF_2)_3BPF_3$	+37.4 (BF_2)	(*70*)
$(BF_2)_3BCO$	+38.4	(*70*)
$(BF_2)_3BPCl_3$	+40.3	(*70*)
$(BF_2)_3BPH_3$	+43.5	(*70*)
$(BF_2)_3BSMe_2$	+46.8	(*70*)
$(BF_2)_3BNMe_3$	+44.0	(*48*)
$F_3PB(BF_2)_{3-n}(BF_2 \cdot NMe_3)_n$	*n* = 1: +132.8 (complexed BF_2); +43.5 (free BF_2)	(*48*)
	n = 2: +133.1 (complexed BF_2); +41.9 (free BF_2)	(*48*)
	n = 3: +126.8; 130.7 (complexed BF_2)	(*48*)
	+67.8	(*82a*)
	+80.6 (BF_2); +158 (CF)	(*126*)
	+2.7; −12 (relative to CF_3COOH)	(*50*)
	+9.6; −0.5 (relative to CF_3COOH)	(*50*)

The vapor pressure is about 23 Torr at 0°C, but decomposition is quite rapid at this temperature. Although pure B_8F_{12} shows no ESR spectrum at −50°C, partially decomposed samples contain unidentified paramagnetic species that produce a complex spectrum. There appears to be no dissociation of the vapor to free $B(BF_2)_3$ (*70*).

The single broad peak observed in the ^{19}F-NMR spectrum between

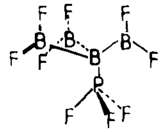
-80 and 0°C suggests that an exchange process is occurring to make all the BF_2 groups in structure **VI** equivalent on the NMR time scale. The single ^{11}B-NMR peak (800 Hz wide) may result from coincidence between the chemical shifts of the three types of boron atom (*70*).

Only BF_3 adducts are formed when B_8F_{12} is treated with an excess of strong Lewis bases such as diethyl ether, trimethylamine, and acetonitrile (*70*). However, there is some NMR evidence for the formation of the unstable Me_3N—$B(BF_2)_3$ when B_8F_{12} is treated with a deficiency of trimethylamine at low temperatures. A little boron trifluoride is released during the reaction, and this remains uncomplexed, showing that $B(BF_2)_3$ is a stronger Lewis acid than BF_3 toward trimethylamine, a point apparently confirmed by the values of the complexation shifts of the protons in $Me_3N \cdot B(BF_2)_3$ and $Me_3N \cdot BF_3$ relative to those in free NMe_3 [0.81 and 0.45 ppm, respectively (*48*)].

In contrast, "soft" bases such as carbon monoxide symmetrically cleave B_8F_{12} and form thermally stable complexes. Other bases that

$$B_8F_{12} + 2CO \rightarrow 2OCB(BF_2)_3 \qquad (69, 70, 126)$$

react similarly are PF_3 (*126*), PCl_3, PH_3, AsH_3, and SMe_2 (*70*). The complex $F_3PB(BF_2)_3$ has the structure shown in **XVII** (27) (Table VII).



(XVII)

Approximately C_{3v} symmetry; Bond lengths (Å; ± 0.015):
B—B = 1.68; B—F = 1.305; B—P = 1.825; P—F = 1.51

Attempts to investigate the relative base strengths of the ligands toward $B(BF_2)_3$ have failed because replacement reactions between an adduct and a different base do not occur; in all cases the original

TABLE VII

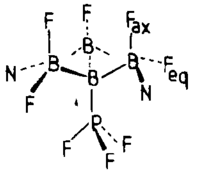
PHYSICAL DATA FOR $B(BF_2)_3$ ADDUCTS

Adduct	Vapor pressure[a]	Melting point (°C)	Reference
$(BF_2)_3BCO$	$A = -2078$; $B = 8.742$	40	(*70, 126*)
$(BF_2)_3BPF_3$	$A = -2008$; $B = 8.665$	55	(*70, 126*)
$(BF_2)_3BPCl_3$	10 Torr at 59°C	134	(*70*)
$(BF_2)_3BPH_3$	10 Torr at 53°C	112	(*70*)
$(BF_2)_3BSMe_2$	10 Torr at 43°C	107	(*70*)

[a] $\log p$ (Torr) $= A/T + B$.

adduct was the only one to be recovered (*70*). However, competition reactions between B_8F_{12} and equimolar amounts of CO and PF_3 give the respective adducts in approximately equal amounts (*69*). The range of bases complexing with $B(BF_2)_3$ shows it to be an even stronger acid than BH_3, prompting Timms to call it a *super acid*. The rather large 5.9-ppm shift to high field in the ^{19}F resonance of B_8F_{12} dissolved in CH_2Cl_2, relative to its position in the free liquid or $CFCl_3$ solution, suggests that B_8F_{12} may even interact weakly with the chlorine atoms of dichloromethane (*48*).

The other three boron atoms in $B(BF_2)_3$ can be made to complex with trimethylamine once the acid has been stabilized by coordination of PF_3 to the unique boron. Thus low-temperature NMR studies on the reaction of **XVII** with trimethylamine indicate the formation of all three adducts in the series $F_3PB(BF_2NMe_3)_n(BF_2)_{3-n}$ (n = 1, 2, or 3). The $n = 1$ adduct is stable, whereas the $n = 2$ and 3 complexes dissociate on warming; a high NMe_3 : **XVII** ratio is required to shift the equilibrium in favor of the $n = 3$ complex, even at −90°C. Two ^{19}F-NMR peaks are observed when the $n = 3$ complex is held at −90°C, but these are found to coalesce at about −85°C. This behavior may be due to the adoption of the preferred conformation **XVIII**, in which the bulky NMe_3 groups coordinate in the "equatorial" positions, giving rise to



N = NMe_3

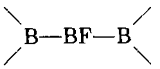
(XVIII)

two types of fluorine, F_{ax} and F_{eq}; hindered rotation about the B—B bonds is then assumed to be slow on the ^{19}F-NMR time scale at −90°C. The phenomenon was not observed with either the $n = 1$ and 2 complexes or free B_8F_{12} (*48*).

Tetrafluorohydrazine and B_8F_{12} explode when mixed together at −70°C, giving boron trifluoride and nitrogen; the latter does not react with B_8F_{12} (*69*). Sulfur tetrafluoride forms an explosive, slightly volatile solid of unknown composition when treated with B_8F_{12} (*69, 70*). Nonvolatile solids and small quantities of $PF_3B(BF_2)_3$ are the only products from the reaction between B_8F_{12} and $P(PF_2)_3$ (*70*). Hydrogen and B_8F_{12} give nonvolatile solids, BF_3 and HBF_2 (*70*).

F. OTHER BORON FLUORIDES

At least five boron fluorides having molecular weights greater than that of B_8F_{12} have been detected. They are formed in very small amounts as by-products in B_2F_4 and B_3F_5 production or arise from the decomposition of simpler boron fluorides. Their volatilities are similar, all of them condensing in a −40°C trap (*69*). From their ^{19}F-NMR spectra it would appear that none of them possesses any



groups, because the only resonances occur between +30 and +45 ppm (relative to $CFCl_3$), the region typical of BF_2 groups (*131*).

1. *Compound A*

The best characterized (*69*) of the five is a clear, colorless liquid arising from the decomposition of B_8F_{12}. Broad, strong peaks occur in the infrared spectrum at 1160, 1210, 1230, and 1390 cm^{-1}; the highest, but very weak, mass-spectral peak is due to $B_{12}F_{16}^+$, with the base peak corresponding to $B_{10}F_8^+$. At 15 eV, two series of peaks are observed due to the ions $B_8F_6^+$, $B_9F_9^+$, $B_{10}F_{12}^+$, and $B_9F_5^+$, $B_{10}F_8^+$, $B_{11}F_{11}^+$, $B_{12}F_{14}^+$.

The B : F ratio, determined by thermal decomposition into elemental boron and boron trifluoride, is 0.85 ± 0.05. Three broad singlets occur in the ^{19}F-NMR spectrum at +31.9, +37.1, and +45.8 ppm (relative to $CFCl_3$ contained in an internal capillary).

It has been suggested (*131*) that this compound may be $B_{14}F_{18}$, a formal analog of B_5H_9 in which both terminal and bridging hydrogen atoms are replaced by BF_2 groups. (As described in Section II, the boron subfluorides tend not to exhibit a molecular ion in their mass spectra.)

2. *Compound B*

Compound B (*69*), a liquid, was isolated from the products of cocondensation of BF and B_2F_4 in an all-glass system (only minute amounts were observed when a stainless steel apparatus was used). Relatively sharp peaks occur at 1160, 1230, 1245, 1385, and 1435 cm^{-1} in its infrared spectrum.

The mass spectrum is particularly complex, with 17 ions having a relative intensity above 20% at 30 eV. The 15-eV spectrum shows the same two series of peaks as compound A plus a third series starting at $B_8F_5^+$ and including $B_9F_8^+$, $B_{10}F_{11}^+$, and $B_{11}F_{14}^+$; the highest mass ion observed is $B_{12}F_{14}^+$, and the B : F ratio is 0.89 ± 0.05.

3. *Compound C*

The use of a stainless steel apparatus for B_8F_{12} production leads to the formation of compound C (*69*), a yellow solid, as a by-product. Its infrared spectrum is similar to that of A, with broad absorptions centered at 760, 812, and 843 cm^{-1} as weak secondary features. Only very small peaks are observed in the mass spectrum for ions heavier than $B_{10}F_{12}^+$, with $B_{12}F_{17}^+$ being the maximum; the 15-eV spectrum consists of only six peaks, four of them, corresponding to $B_7F_3^+$, $B_8F_6^+$, $B_9F_9^+$, and $B_{10}F_{12}^+$, related by loss of BF_3. This series of ions does not occur in the other fluorides.

4. *Compounds D and E*

Compounds D and E (*69*) are formed in the glass BF-production apparatus and have not been completely separated. The most volatile fraction shows a set of BF_3-related ions $B_6F_4^+$, $B_7F_7^+$, and $B_8F_{10}^+$, whereas the least volatile component is similar but has an additional series of peaks due to $B_{10}F_6^+$, $B_{11}F_9^+$, and $B_{12}F_{12}^+$. This latter fraction has an intense $B_{12}F_{12}^+$ peak at 15 eV, but the presence of $B_{13}F_{12}^+$ shows that at least 13 boron atoms are present.

The reason why fluorine behaves so differently from the other halogens regarding the formation of these curious subfluorides is not known.

G. TETRABORON TETRACHLORIDE (B_4Cl_4)

Tetraboron tetrachloride melts sharply under vacuum at 95°C (*25*, *65*). A redetermination of the vapor pressure between 26.3 and 63.5°C shows that the pressure may be reproduced accurately by the equation

$$\log p\ (\text{Torr}) = -3455/T + 11.5398,$$

the values being consistently lower than those previously published. From these data the heat of sublimation has been calculated as 15.81 kcal mol^{-1} (*92*). The vapor pressure of about 1 Torr at room temperature allows B_4Cl_4 to be handled in a conventional vacuum line, provided that greaseless valves are used.

The compound is also much more thermally stable than has previously been supposed. It can be recovered unchanged after many days at 60–65°C (*92*) or 3 days at 154°C (*7*); even at 240–275°C in the gas phase less than 10% decomposition occurs during 10 min (*92*). In the liquid state 10% decomposition occurs after 6 h at 125°C, and 80% after 28 h at 152°C (*25*). After 6 h at 320°C, complete decomposition occurs to give boron trichloride, involatile debris, and a slightly volatile, yellow solid (*7*) (probably B_9Cl_9, judging from its description).

There is no evidence of any fluxionality as measured on the ^{11}B-NMR time scale over a 200°C temperature range (*25*).

Tetraboron tetrachloride is pyrophoric at room temperature. A close study of the oxidation reaction under more controlled conditions in a solvent has shown that the products are boron trichloride, boric oxide, and an unidentified, red boron monochloride; when a deficiency of oxygen is used some diboron tetrachloride also appears to be formed (*92*).

Although hydrogen sulfide does not react with tetraboron tetrachloride between −112°C and room temperature, water rapidly produces hydrogen, hydrogen chloride, boric acid and subboric acid (*92*). Acid hydrolysis gives 3 mol of hydrogen, and alkaline hydrolysis 4 mol (*133*).

A variety of substitution reactions have been attempted on B_4Cl_4, but most have been without much success. Lithium tetrahydroborate gave only about a 3% yield of diborane after 40 h at room temperature (*92*). Trimethylborane does not react below 65°C; trimethylborane was the only identified boron-containing product when trimethylaluminum (*92*), tetramethyllead (*55*), and dimethylzinc (*92*) were used as methylating agents; the latter reagent had previously been claimed to give B_4Cl_3Me (*134*). Substitution of alkyl groups onto the B_4 cage is more readily accomplished using organolithium reagents. Thus ethyllithium gives B_4Cl_3Et and $B_4Cl_2Et_2$, whereas $B_4(CMe_3)_4$ can be achieved using *t*-butyllithium (*26*). No B_4F_4 is formed when tetraboron tetrachloride is treated with BF_3, SbF_3, PbF_2, or TiF_4 (*86, 92*); the latter three reagents produce only boron trifluoride. Boron tribromide gives chlorobromoboranes and much solid debris (*66, 92*) together with tiny amounts of B_4Cl_3Br and $B_4Cl_2Br_2$ (*66*); further substitution by bromine does not appear to be possible.

Cleavage of the B_4 tetrahedron occurs when B_4Cl_4 is treated with the halogens. Controlled reactions with chlorine and bromine give some of the corresponding diboron tetrahalides in addition to the trihalides (*92, 140*). Any diboron tetraiodide formed on iodination apparently decomposes during the 3 weeks of reaction time to give an unidentified black solid thought to be $(BI)_y$ (*92*).

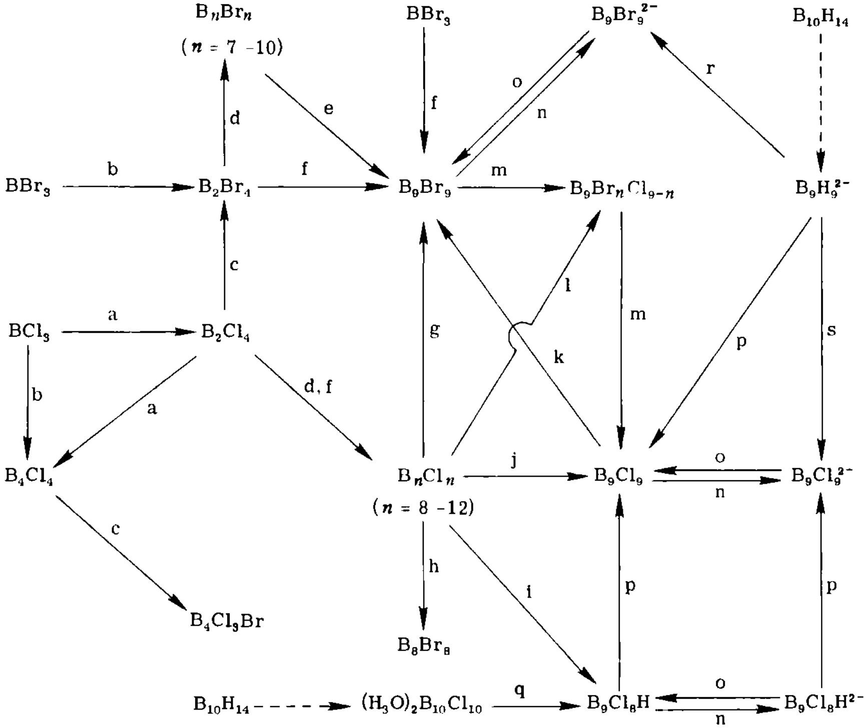
Trimethylamine, triethylamine, pyridine, and tetramethylethylenediamine react with B_4Cl_4 to give solid products, but no meaningful stoichiometries could be established. Although qualitative tests showed that the solids possessed boron–boron bonds, their structures remain in doubt (*92*). No evidence for simple adducts was obtained when B_4Cl_4 was treated with dimethyl or diethyl ethers; methyl or ethyl chloride and glassy, unidentified solids were the major products (*92*).

H. B_8Cl_8, B_9X_9, $B_{10}Cl_{10}$, AND $B_{11}Cl_{11}$

Little is known about the chemistry of B_8Cl_8, B_9X_9, $B_{10}Cl_{10}$, or $B_{11}Cl_{11}$. Complete exchange of chlorine for bromine occurs in B_8Cl_8 and B_9Cl_9 when they are heated with aluminum tribromide at 100 and 265°C, respectively (*83*). A range of mixed chlorobromides, $B_9Br_{9-n}Cl_n$, can be made by heating B_9Br_9 with tin or titanium tetrachlorides, but no halogen exchange occurs with BCl_3, BF_3, SbF_3, or TiF_4 (*108*). About 90% of the boron is recovered as trimethylborane when B_9Br_9 is added to trimethylaluminum at room temperature (*75*); partial methylation of the B_9 cage is possible using $SnMe_4$ or $PbMe_4$ (*75, 83, 108*).

The heated vapor of B_8Cl_8 ignites in air with a mild explosion (*83*). The air sensitivity of the B_9X_9 series decreases markedly from Cl to I, the iodide being stable for months in air (*142*); B_9Br_9 will withstand limited contact with degassed water under vacuum conditions (*108*). Chlorinated hydrocarbons, boron trichloride, and boron tribromide are among the best solvents for all the B_9X_9 derivatives; donor organic solvents produce a characteristic dark blue coloration with B_9I_9, due to the formation of $B_9I_9^-$ (*142*).

Mixtures of $B_{10}Cl_{10}$ and $B_{11}Cl_{11}$ give a variety of B_{10} and B_{11} chlorobromides when treated with aluminum tribromide in BBr_3 at 20°C (*109*). B_8Cl_8 and B_9Cl_9 show no reaction with chlorine at 70 and 250°C, respectively (*6*). When the $B_{10}Cl_{10}$–$B_{11}Cl_{11}$ mixtures are heated with dry chlorine, a contraction in cluster size occurs and high yields of B_9Cl_9 are produced (*6*); bromine and iodine give a number of mixed halides $B_9Cl_{9-n}X_n$ ($X = Br, I$) (*6*). $B_{10}Cl_{10}$ and $B_{11}Cl_{11}$ undergo a similar reaction with hydrogen to produce B_9Cl_8H and $B_9Cl_7H_2$, respectively (*6, 83*). Pyrolysis of $(H_3O)_2B_{10}Cl_{10}$ is known to give low yields of B_9Cl_8H (*38*); it is possible that this product arises via the initial formation of $B_{10}Cl_{10}$, which then undergoes reduction to B_9Cl_8H with hydrogen present in the system from hydrolysis of some of the boron cages. The mechanism by which B_9Cl_8Me and B_9Br_8Me arise from pyrolysis of either $(Me_4N)_2B_{10}Cl_{10}$ (*83*) or $(Me_4N)_2B_{10}Br_{10}$ (*118*) is less clear.



SCHEME 1. Interconversion reactions among the boron subchlorides and subbromides. a, Mercury discharge (*65, 90*); b, radiofrequency discharge (*25, 75*); c, BBr_3 at room temperature (*66, 136*); d, thermal decomposition (*66, 75, 84, 84*); e, pyrolysis at 200°C (*75, 108*); f, silent electric discharge (*108*); g, BBr_3 at 250°C (*108*); h, $AlBr_3$ at 100°C (n = 8) (*83*); i, H_2 at 150°C (n = 10) (*6, 83*); j, Cl_2 at 140°C (n = 10, 11) (*6*); k, $AlBr_3$ at 260°C (*83*); l, Br_2 at 115°C (n = 10, 11) (*6*); m, $TiCl_4$ or $SnCl_4$ at 250°C (*108*); n, $(Bu_4N)I$ (*143*); o, $Tl(OOCCF_3)_3$ (*143*); p, SO_2Cl_2 (*63, 143*); q, pyrolysis at 260°C (*38*); r, *N*-bromosuccinimide (*143*); s, *N*-chlorosuccinimide (*143*).

Reduction of the B_9 halides occurs smoothly with tetrabutylammonium iodide in dichloromethane, giving first $B_9X_9^{\cdot-}$ and then $B_9X_9^{2-}$. Competition reactions of the type

$$B_9X_9 + B_9Y_9^{\cdot-} \rightarrow B_9X_9^{\cdot-} + B_9X_9$$

$$B_9X_9^{\cdot-} + B_9Y_9^{2-} \rightarrow B_9X_9^{2-} + B_9X_9^{\cdot-}$$

reveal that the oxidative power follows the order $B_9I_9 > B_9Br_9 > B_9Cl_9$ and $B_9I_9^{\cdot-} > B_9Br_9^{\cdot-} > B_9Cl_9^{\cdot-}$. Oxidation of the ions with thallium(III) trifluoroacetate releases the neutral boron cluster, thus establishing the redox sequence (*142, 143*)

$$B_9X_9^{2-} \rightleftharpoons B_9X_9^{\cdot -} \rightleftharpoons B_9X_9$$

The hydrogen-substituted derivative B_9Cl_8H undergoes a similar series of reactions (*143*). The paramagnetic $B_9X_9^{\cdot -}$ ions show featureless, broad ESR peaks at g values of 2.018, 2.080, and 2.191 (X = Cl, Br, and I, respectively), the breadth increasing from the chloride to the iodide (*143*).

It appears likely that all the B_9X_9 species have a very similar cage structure, that of a tri-capped trigonal prism (*61, 108, 142, 143*). The HOMO in a B_9^{2-} cage has a_2' symmetry so that the B_9X_9, $B_9X_9^{\cdot -}$, and $B_9X_9^{2-}$ sequence will have outer electron configurations $(a_2')^0$, $(a_2')^1$, and $(a_2')^2$, respectively. Although B_9Cl_9, for example, has a closed-shell configuration, it has been pointed out by Wade (*100*) that the skeletal bonding will be greatest when the a_2' orbital is occupied, that is, when there are nine bonding pairs of electrons. In apparent agreement with this, the average B—B bond length in $B_9H_9^{2-}$ is 1.76 Å, compared with 1.81 Å in B_9Cl_9 (*100*). Similarly, the HOMO of dodecahedral B_8^{2-} has b_2 symmetry, so B_8Cl_8 has a closed-shell configuration, $(b_2)^0$; the various B—B bond lengths in $B_8H_8^{2-}$ are consistently shorter than those of B_8Cl_8, in keeping with the extra pair of cage-bonding electrons in the ion (*100*).

The HOMOs of a D_{4d} B_{10}^{2-} cage and an I_h B_{12}^{2-} cage are degenerate (e_1 and g_u, respectively). The neutral clusters $B_{10}X_{10}$ and $B_{12}X_{12}$ would thus be expected either to be paramagnetic or to undergo distortion to achieve spin-paired closed-shell electron configurations. The ^{11}B-NMR spectrum of $B_{10}Br_{10}$ consists of a single peak for sample temperatures down to −60°C; the obvious implication is that the molecule is fluxional, but there is nothing about the spectrum that suggests that the molecule is paramagnetic (*75*). All the cage MOs of B_{11}^{2-} (C_{2v} symmetry) are nondegenerate, hence a neutral $B_{11}X_{11}$ species should be diamagnetic and undistorted (*100*).

The list of possible binary halides is obviously not yet complete because there is mass-spectral evidence (*106*) that $B_{13}Cl_{13}$ and $B_{14}Cl_{14}$ exist among the decomposition products of diboron tetrachloride. Furthermore, there are indications that a dark red chloride of very low volatility (*6*) and a bromide (*75*) may possess structures in which two B_9 cages are linked together as $(B_9X_8)_2$. If such linked cages are generally possible then the theoretical number of halides yet to be found, because of isomers, is large indeed.

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