THE HALIDES OF BORON

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I. Introduction

It is now almost 150 years since Gay-Lussac and Thenard first isolated ammonia-boron trifluoride, H_3NBF_3, and so initiated a study of the boron halides. Since that time, notably during the past 30 or so years, a tremendous volume of research has been carried out on the halides, ranging from their use in syntheses of hydrides and borohydrides required for rocketry and wartime atomic energy projects (*279*, *534*) to the very extensive use of boron trifluoride as a catalyst in the petroleum industry, polymer production, and organic chemistry generally (*817*). This review will be concerned only with the chemistry of the boron halides, and will neglect studies of their catalytic activity and of their more physical properties except where the latter (e.g., structural studies) have a direct bearing on the chemistry.

Nomenclature is always a headache and never more so than in boron chemistry; thus B_2Cl_4 might be more correctly called tetrachlorodiborane-4, but few chemists would immediately recognize this as diboron tetrachloride. For this reason I have elected to call compounds by what appears to be their most frequently used literature-name and so, while BCl_3 is boron trichloride, BMe_3 is written as trimethylborane; similarly diboron tetrachloride is used for B_2Cl_4, whereas $B_2(OMe)_4$ is called tetramethoxydiboron (*97*).

The review deals first with the preparation and molecular structures of the boron halides, and then an account is given of their main chemical properties; by far the most research has been carried out on the trihalides and, while attempting to cover the maximum number of references in the minimum of space, some have obviously had to be left out or given under a collective review reference. Table I lists by formulas the boron halides known to date (1966). As these compounds are all water-sensitive and one or two ignite spontaneously in air, they are best handled in a glass high-vacuum apparatus, preferably out of contact with hydrocarbon- or silicone-based stopcock lubricants. Most constructional metals appear to be unaffected by the halides at reasonable temperatures; although data are mainly lacking for the action of the halides on polymeric materials, a careful study on boron trifluoride (*421*) shows it

TABLE I

THE HALIDES OF BORON[a]

B_nX_m	X = F	X = Cl	X = Br	X = I
BX_3	BF_3	BCl_3	BBr_3	BI_3
B_2X_4	B_2F_4	B_2Cl_4	B_2Br_4	B_2I_4
B_4X_4	—	B_4Cl_4	—	—
B_8X_8	—	B_8Cl_8	—	—
B_9X_9	—	B_9Cl_9	—	—
$B_{11}X_{11}$	—	$B_{11}Cl_{11}$	—	—
$B_{12}X_{11}$	—	$B_{12}Cl_{11}$	—	—
B_nX_n	$*(BF)_x$	$(BCl)_x$	$(BBr)_x$	$(BI)_x$
B_nX_m	B_3F_5 B_8F_{12}	$*BCl_{0.6}$	$*BBr_{0.2}$ $*BBr_{0.4}$	$*B_xI_y$
BX	BF	BCl	BBr	BI

[a] x, y = unknown. Compounds marked with asterisk are known to be involatile in high vacuum. "$B_{11}Cl_{11}$" and "$B_{12}Cl_{11}$" appear, from their physical properties, to be the same compound, but it is not perfectly clear which formula is the correct one (see text).

to be without action on Teflon, polystyrene, Araldite, and pure polyvinylchloride up to at least 80°, whereas rubber tubing, phenol-formaldehyde resins, Nylon, cellulose, and commercial polyvinylchloride are readily attacked.

The literature has been covered up to June 1966. [The reader is referred to Martin *et al.* (*82*, *330*, *528*, *817*) for earlier accounts of the chemistry of boron trifluoride, Lappert *et al.* (*288*, *476*, *528*) for chemistry involving the other boron trihalides, and Holliday and Massey (*410*) for a discussion of the diboron tetrahalides. General articles in which the boron halides are frequently mentioned are to be found in references (*187*, *280*, *378*, *621*, *793*).]

II. Preparation of the Boron Halides

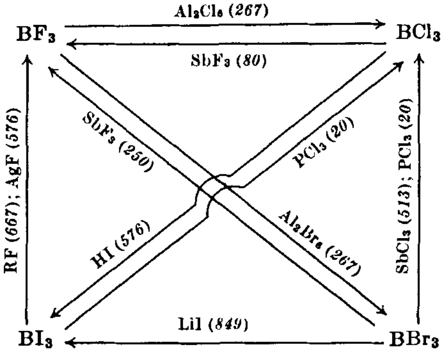
A. BORON TRIHALIDES

The trifluoride (*430*, *868*), trichloride (*250*, *265*), tribromide (*849*), and triiodide (*549*) can be prepared by treating elemental boron with the appropriate halogen. A better method for the trifluoride is to heat a mixture of fluospar, concentrated sulfuric acid, and boric oxide (*86*),

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \rightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$

while the triiodide is formed in good yield by refluxing sodium borohydride and iodine in either hexane or benzene (*452*, *757*).

Having obtained one boron trihalide it is possible to make the others from it by various halogen-exchange processes, of which the following are typical:



While these reactions are normally of little value to the preparative chemist (all four halides are now available commercially), they can be employed in making an isotopically labeled trihalide, e.g., $^{10}BCl_3$ from an available sample of $^{10}BF_3$ (*439, 499, 506*). Also, since some of the halogen-interchange reactions appear to be quite general in scope they can be of help in synthesizing new boron compounds, as in the fluorinations carried out with antimony trifluoride[1]:

$$B_2Cl_4 \xrightarrow{SbF_3} B_2F_4 \qquad (246)$$
$$CF_2{=}CFBCl_2 \longrightarrow CF_2{=}CFBF_2 \qquad (789)$$
$$(CH_2{=}CH)_2BCl \longrightarrow (CH_2{=}CH)_2BF \qquad (92)$$
$$Cl_2BC_2H_4BCl_2 \longrightarrow F_2BC_2H_4BF_2 \qquad (149)$$
$$C_6H_5BCl_2 \longrightarrow C_6H_5BF_2 \qquad (557)$$

Sometimes it is necessary to prepare a boron trihalide labeled with radioactive halogen atoms for use in tracer experiments. Special synthetic methods can be devised, such as heating silver chloride with boron (*504*)

$$AgCl^* + B \xrightarrow[\text{vacuum}]{600^\circ} BCl_3^* \qquad (70\%\ \text{yield})$$

but exchange of halogen atoms between a suitable reagent and a boron trihalide is more convenient. Tetramethylammonium chloride, containing radioactive chlorine, exchanges rapidly with boron trichloride and this has been used to prepare specimens of the labeled trichloride (*392–394*); the method should be applicable to other trihalides:

$$X^{*-} + BX_3 \rightleftharpoons BX_4^{*-} \rightleftharpoons X^- + BX_3^* \qquad \text{eq. } X = F\ (33a)$$

The rapid exchange between free bromine and boron tribromide (*238*) could also make a useful route to the labeled tribromide.

B. Diboron Tetrahalides

Stock made the first compound of this series, diboron tetrachloride, in low yield (ca. 1%) by striking an arc between zinc electrodes immersed in liquid boron trichloride; the product contained about 12% of silicon tetrachloride impurity (*800*). Subsequently it was found better to carry out the reduction of the trichloride in the gaseous phase using an electrical discharge between either mercury (*406, 545, 718, 751, 826, 843*) or copper (*845*) electrodes, and about 1 mmole/hr can now be obtained relatively easily. Exact details of the synthesis can be found in references (*545, 845*); care has to be taken in the construction of the cell so that the hot discharge does not touch the glass walls at any point, otherwise silicon is etched away and contaminates the diboron tetrachloride with $SiCl_4$, Si_2Cl_6, Si_3Cl_8, and $Cl_3SiOSiCl_3$ (*535, 542*).

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[1] The stepwise fluorination of alkoxyboron compounds by sulfur tetrafluoride should also prove to be an extremely useful synthetic technique, e.g. (*210*):

$$B(OR)_3 \xrightarrow{SF_4} \text{successive replacement of OR by F} \rightarrow BF_3$$

When boron trichloride vapor at 1–2 mm pressure is passed through a resonance cavity operating in the microwave region of the spectrum, a glow discharge is set up in the vapor and diboron tetrachloride is formed (*256*):

$$2BCl_3 \rightarrow B_2Cl_4 + Cl_2$$

Since chlorine reacts with diboron tetrachloride (*18*), it must be removed rapidly by fractionation; the method is useful when small intermittent supplies of diboron tetrachloride are required, and can be made more efficient by passing the effluent gases from the cavity through a plug of copper wool that reacts with and removes the chlorine (*88*). The spectra of discharges through boron trichloride vapor have been shown to contain lines due only to BCl (*419*, *691*), and it is thought that BCl, not BCl_2, may actually be an intermediate in the preparation of diboron tetrachloride (*419*, *546*).

It is possible to make diboron tetrachloride without resorting to the use of electrical discharges. The simplest method in theory is to pass boron trichloride over boron at 1000°C but, in practice, attack of the reaction vessel at these temperatures makes the method very difficult to operate (*633*). When boron trichloride is passed over heated boron monoxide a 13% yield of diboron tetrachloride is obtained (*552*, *553*):

$$B_2O_2 + BCl_3 \xrightarrow[450\text{ mm}]{200°\text{-}236°} B_2Cl_4$$

The boron monoxide (which has a structure involving boron-to-boron bonds, eq. 626) can be made either by heating boric oxide with boron (*425*, *436*, *744*) or by first hydrolyzing tetrakis(dimethylamino)diboron carefully at low temperature (*647*) and then dehydrating the sub-boric acid so formed (*841*, *842*):

$$B_2(NMe_2)_4 + 4H_2O \longrightarrow 4HNMe_2 + B_2(OH)_4$$
$$B_2(OH)_4 \xrightarrow{\text{heat}} B_2O_2 + 2H_2O$$

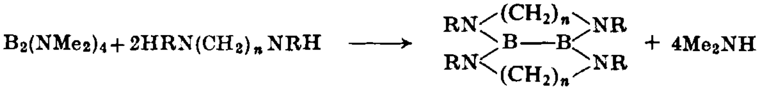
Tetrakis(dimethylamino)diboron is the only diboron compound commercially available, being prepared on a large scale by treating bis(dimethylamino)boron chloride or bromide with highly dispersed sodium (*96*, *647*):

$$2(Me_2N)_2BCl + 2Na \rightarrow 2NaCl + B_2(NMe_2)_4$$

Much effort has been expended in trying to convert the rather unreactive tetrakis(dimethylamino)diboron to more useful diboron reagents. Transamination, which may involve some rupture of the boron-

boron bond (*650*), takes place with primary and secondary amines (*15*, *96*, *121*, *638*, *650*),

$$B_2(NMe_2)_4 + 4RR'NH \rightarrow B_2(NRR')_4 + 4Me_2NH$$
$$(R = \text{alkyl};\ R' = \text{alkyl or H})$$



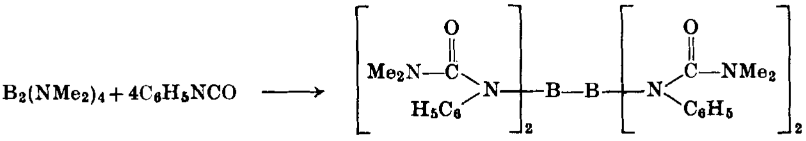
while alcohols, at low temperatures and in the presence of hydrogen chloride, produce the tetraalkoxydiborons in good yield (*97*, *615*):

$$B_2(NMe_2)_4 + 4ROH + 4HCl \xrightarrow{-80^\circ} B_2(OR)_4 + 4Me_2NH_2Cl$$

Although one, two, or four dimethylamino groups in tetrakis(dimethylamino)diboron can be replaced with halogen atoms on treatment with HCl, HBr, or HF (*120*, *524*, *632*, *648*), BX_3 (X = F, Cl, or Br) (*651*), or $BCl_3 \cdot NMe_3$ (*120*), no free diboron tetrahalides can be isolated from the reaction mixtures; e.g.:

$$\begin{tikzcd}
B_2(NMe_2)_4 + 4HCl \arrow[r] & (Me_2N)_2B_2Cl_2 + 2Me_2NH_2Cl \\
B_2(NMe_2)_4 + BCl_3 \arrow[r] & NMe_2(Cl)B_2(Cl)NMe_2 + (Me_2N)_2BCl \arrow[d, "B_2(NMe_2)_4"] \\
 & (NMe_2)_2B_2(Cl)NMe_2 \\
B_2(NMe_2)_4 + 6HX \arrow[r] & B_2X_4 \cdot 2HNMe_2 + 2Me_2NH_2X
\end{tikzcd}$$

Addition of the B—NMe_2 groups in tetrakis(dimethylamino)diboron across the N=C bond of phenyl isocyanate occurs when the two are mixed in hexane solution at room temperature (*74*):



The corresponding symmetrical bis(dimethylamino)dialkyldiborons can be made by a Würtz-type coupling reaction, using sodium-potassium alloy (*95*, *638*):

$$Me_2N(R)BCl + Na/K \rightarrow Me_2N(R)B_2(R)NMe_2$$

Diboron tetrafluoride is formed during the fluorination of boron monoxide, sub-boric acid, or tetraalkoxydiborons using sulfur tetrafluoride (*98*, *266*), so that the production of the tetrafluoride is not now dependent on diboron tetrachloride from which it had been previously synthesized using antimony trifluoride (*246*) or allyl fluoride (*149*).

Attempts to fluorinate tetrakis(dimethylamino)diboron directly to diboron tetrafluoride with BF_3 (*98*, *651*), SF_4 (*98*, *540*), IF_5 (*540*), and SF_5Cl (*540*) were unsuccessful. Although boron trifluoride is not reduced by a mercury discharge (*246*), the absorption spectrum of BF can be detected when the trifluoride either flows through a silica tube connected to an oscillator operating at 2340 Mc/sec (*722*), or is subjected to an electrical discharge in helium gas (*673*); furthermore, when it is mixed with hydrogen and passed through a tungsten arc, a small amount of crystalline boron is formed (*194*).

Diboron tetrabromide has been synthesized by passing boron tribromide through a glow discharge maintained between nickel electrodes (*208*), or by treating the tetrachloride with boron tribromide at room temperature (*826*):

$$3B_2Cl_4 + 4BBr_3 \rightarrow 3B_2Br_4 + 4BCl_3$$

Neither the tetrabromide nor the tetraiodide (formed in about 30% yield when boron triiodide passes at low pressure through a radiofrequency discharge) (*757*) has been studied in detail and little is known of their properties.

C. TETRABORON TETRAHALIDES

The only known member of this group, the chloride, is one of the products when boron trichloride is reduced in a mercury arc (*545*, *827*); the yield is very low and amounts to only 1 or 2 mg per day of discharge operation. Tetraboron tetrachloride is also probably formed in the thermal decomposition of diboron tetrachloride (*545*, *823*), but it is difficult to judge if the very small amounts obtained from this source do not arise, at least in part, from imperfect separation of B_4Cl_4 from the original diboron tetrachloride.

One might predict that the other tetraboron tetrahalides would be formed by treating the tetrachloride with SbF_3, BBr_3, or BI_3, although it has been suggested that tetraboron tetrafluoride might be thermally unstable (*544*). The stability of the partially methylated chloride, B_4Cl_3Me (*823*), however, leaves little doubt that mixed halides (at least) should be capable of existence, even if only as participants in an equilibrium.

D. OTHER BORON HALIDES

During the thermal decomposition of the diboron tetrahalides, compounds of formulas $(BX_n)_x$ are formed. When $X =$ fluorine, the value of n is unity and the product is a yellow, involatile polymer (*414*). When the halogen is chlorine there are several polymers having the composition $(BCl)_x$ [where x is equal to 8 (*426*), 9 (*253, 541, 543*), 10 (*541*), 11 (*543*), 12 (*543*), but see also (*753, 825*)], which can be separated by vacuum sublimation (*545, 753*). During the mercury discharge preparation of diboron tetrachloride a yellow polymeric film of $(BCl)_x$ is formed on the apparatus walls, but it has yet to be studied; it may be similar to the yellow monochloride produced when diboron tetrachloride is subjected to a silent electric discharge (*724*). A colored boron monobromide, $(BBr)_x$, is formed when diboron tetrabromide decomposes thermally or when boron tribromide is passed through a glow discharge or a silent electric discharge (*208*); at least two other products of empirical formulas $BBr_{0.2}$ and $BBr_{0.4}$ are also produced in the discharges. The position regarding the boron sub-iodides is obscure, but it appears that many dark-colored compounds having formulas B_xI_y arise during the preparation (and from the decomposition) of diboron tetraiodide (*757*); nothing is known about their chemistry or structures.

$B_{10}X_{10}^{2-}$ and $B_{12}X_{12}^{2-}$ Ions. The borohydride ions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ (*375, 376*) have been shown to react with the halogens (and with HCl or HF) to give many substituted ions, such as $B_{10}Br_{10}^{2-}$, $B_{12}I_{12}^{2-}$, $B_{12}F_4H_8^{2-}$, $B_{12}H_3Br_6Cl_3^{2-}$ to mention but a few (*454, 455*).

E. MIXED BORON HALIDES

Although the existence of stable mixed halides, MX_nY_{4-n}, of several Group IV elements has prompted a search for similar compounds of boron, the only successful isolation of mixed boron halides is that of the bromo-iodides, BBr_2I and $BBrI_2$, described by Besson 75 years ago (*73*). A study of the chlorination of boron tribromide using a variety of inorganic chlorides (*250, 513*) gave no isolable boron chlorobromides, although Raman and infrared spectra of the reaction mixture (and of mixtures of pure boron trichloride and tribromide) showed that the chlorobromides were present (*148, 321, 438, 439, 506, 513*). Although the distribution of the halogens was almost random, the equilibrium is so mobile, even at −50°, that separation of the various species is impossible and the only end products of repeated distillation or low temperature fractionation are the pure trichloride and the pure tribromide (*513*).

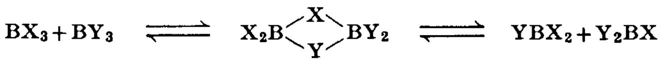
The interchange of halogen atoms in binary mixtures of boron trifluoride and trichloride has been the subject of both kinetic and equilibrium studies; the components of the equilibrium,

$$BF_3 + BCl_3 \xrightleftharpoons{T_{1/2} \sim 10\ \text{min}} BFCl_2 + BF_2Cl$$

while not being separable by distillation, were estimated by quantitative infrared and mass spectral measurements (*125*, *359*, *396*, *625*). Two slightly differing values for the equilibrium constant, K, were obtained: $K = 1.6$ (*711a*) and $K = 0.53$ (*359*, *396*) at 27°–29°, the heat of reaction being about 1 kcal/mole (*359*).

In a ternary mixture the halide BClBrF has been detected by ^{19}F nuclear magnetic resonance (n.m.r.), its identity being verified by the chemical shift of the fluorine atom relative to those in $BFCl_2$ and $BFBr_2$ prepared from the respective binary mixtures (*184*). This technique suffers from the disadvantage that fluorine must be present in the species being studied; however, boron possesses a nuclear spin in both its natural isotopes: ^{11}B, 80% abundance, spin 1; and ^{10}B, 20% abundance, spin 3. Hence the ^{11}B isotope makes an ideal probe for investigating the the mixed boron halides (*471*), and all ten components in a $BCl_3/BBr_3/BI_3$ mixture have been identified in this manner (*271*). Molecular orbital calculations on the system $BCl_3/BBr_3/BF_3$ have resulted in the evaluation of the ^{11}B n.m.r. shifts of the various mixed fluoroboron halides, the local paramagnetic effect being assumed the chief contributor to the shifts (*22*). The agreement with the experimental shifts is shown in Table II.

It is usually assumed that the mechanism for the halogen redistribution reaction involves boron-halogen bridges, either like those found in the aluminum chloride dimer or a close approximation to them found in favorably oriented collisions; cleavage of such bridges can then take place via two paths, one of which results in halogen exchange:



$$BX_3 + BY_3 \rightleftharpoons X_2B\overset{X}{\underset{Y}{\diamond}}BY_2 \rightleftharpoons YBX_2 + Y_2BX$$

However, such dimers have not been detected in pure liquid boron trifluoride at low temperatures[2] (*506*, *795*) (considering the combined effects of electronegativity and π-bonding on dimer formation, one might expect boron trifluoride to be the least favorable case for such a study) or in mixtures of the trichloride and tribromide (*439*).

Ogg (*660*) has shown that the ^{11}B n.m.r. spectrum of boron trifluoride exhibits no boron-fluorine coupling, which might suggest that the fluorine atoms are exchanging rapidly as expected if a monomer-dimer equilibrium exists similar to that given above. As the converse boron splitting of the fluorine resonance spectra in boron trifluoride and mixed chloro-bromo-fluorides is readily observed (see Table III),

[2] Infrared studies on crystalline boron trifluoride suggest that some intermolecular association occurs in the solid, perhaps via weak B—F—B bridges (*214*).

TABLE II

^{11}B n.m.r. CHEMICAL SHIFTS OF MIXED BORON HALIDES (IN P.P.M.)[a]

Halide	Observed (*370*)	Observed (*271*)	Calculated (*22*)
BF_3	36.2	—	36.2
BF_2Cl	25.6	—	27.5
$BFCl_2$	14.4	—	18.0
BCl_3	0.0	0.0	—
BCl_2Br	1.4	1.2	—
$BClBr_2$	3.7	3.9	—
BBr_3	7.1	7.4	—
BF_2Br	26.1 $J_{B-F} = 56$ c/s	—	26.0
$BFBr_2$	16.0 $J_{B-F} = 107.5$ c/s	—	13.2
BCl_2I	10.2	10.3	—
$BClI_2$	27.8	28.3	—
BI_3	53.6	53.5	—
$BFClBr$	14.5 $J_{B-F} = 89$ c/s	—	15.7
$BFBrI$	18.9 $J_{B-F} = 178$ c/s	—	—
$BClBrI$	14.3	14.5	—
BBr_2I	19.1	19.6	—
$BBrI_2$	35.2	34.8	—

[a] Boron trifluoride and triiodide do not exchange in heptane after 24 hours at room temperature, and because of this it is thought (*370*) that BFI_2 and BF_2I may be nonlabile and therefore isolable.

TABLE III

^{19}F CHEMICAL SHIFTS AND ^{11}B–^{19}F COUPLING CONSTANTS FOR MIXED BORON TRIHALIDES (*184*)

Halide	Chemical shift (p.p.m.)	$J_{^{11}B-^{19}F}$ (c.p.s.)
BF_3	0	15 ± 2
BF_2Cl	− 51.5 ± 0.2	34 ± 1
BF_2Br	− 68.4 ± 0.3	56 ± 1
$BFCl_2$	− 99.0 ± 0.6	74 ± 1
$BFClBr$	− 114.8 ± 0.6	92 ± 2
$BFBr_2$	− 130.4 ± 0.7	108 ± 3

the failure to detect the boron-fluorine coupling of 15 c.p.s. in the ^{11}B resonance may be due to other factors, including line width (*471*). In some cases, however, e.g. (*245, 285, 509*),

$$C_6H_5BBrCl \rightleftharpoons C_6H_5BCl_2 + C_6H_5BBr_2$$

the exchange between the halides may be so rapid that the ^{11}B n.m.r. resonance lines due to the various species cannot be observed separately and only a single line intermediate between the pure halides results (*245*); equilibria involving B—F compounds are apparently slower, and in systems containing $C_6H_5BF_2$ the discrete resonance line of the mixed halide, C_6H_5BFX, can be observed. No substantial proportion of a dimer species could be detected.

It has been pointed out (*513*) that halogen exchange, instead of involving dimers, might occur via a slight ionization process such as:

$$BBr_3 + BCl_3 \rightleftharpoons BBr_2^+ + BCl_3Br^-$$

The rapid exchange (*392*) between labeled tetramethylammonium chloride and liquid boron trichloride is compatible with such an ionization:

$$2BCl_3 \rightleftharpoons BCl_2^+ + BCl_4^-$$

However, in view of the very low conductivity of boron trichloride, a simple exchange involving the tetrachloroborate anion is more likely,

$$Me_4NCl + BCl_3 \rightleftharpoons Me_4N^+BCl_4^-$$

especially as several tetrachloroborates can be made directly in this manner (see page 98).

If the temperature is held low enough to stop their disproportionation, the alkylboron halides will also undergo ready exchange of halogen with the boron trihalides (*91, 93*):

$$3EtBF_2 + 2BCl_3 \rightarrow 3EtBCl_2 + 2BF_3$$
$$3Me_2BCl + BF_3 \rightarrow 3Me_2BF + BCl_3$$

These systems are not too labile and all compounds shown in the equations can be separated by fractional distillation. A mass spectral study of these exchanges using $^{10}BF_3$ showed that reactions such as:

$$3RBCl_2 + 2BF_3 \rightarrow 3RBF_2 + 2BCl_3$$

occur only via exchange of halogen, which supports a mechanism involving halogen-bridged dimers. The same work indicated the existence of the labile mixed halides RBFCl and RBFBr in these mixtures (*93*).

A particularly novel chemical method has been devised for detecting the presence of C_4H_7BFCl in mixtures of butylboron dichloride and butylboron difluoride (*126*). $BuBF_2$ does not react with alcohols to give alkoxyboron derivatives whereas butylboron dichloride readily forms $BuB(OR)_2$. Hence, although no mixed-halogen product could be distilled from a $BuBF_2/BuBCl_2$ mixture, treatment with an alcohol, ROH (R = cyclohexyl or isopropyl), gave good yields of BuB(OR)F:

$$\begin{tikzcd}
\mathrm{BuBF_2}\ + \arrow[d, "\mathrm{ROH}"'] & \mathrm{BuBCl_2} \arrow[d, "\mathrm{ROH}"] \arrow[r, shift left] & \mathrm{BuBFCl} \arrow[d, "\mathrm{ROH}"] \arrow[l, shift left] \\
\text{no action} & \mathrm{BuB(OR)_2}\ (50\%) & \mathrm{BuB(OR)F}\ (20\text{–}40\%)
\end{tikzcd}$$

The first report of halogen interchange involving the diboron tetrahalides did not record the formation of mixed diboron halides (*826*):

$$3B_2Cl_4 + 4BBr_3 \xrightarrow[30\ \mathrm{min}]{20^\circ} 3B_2Br_4 + 4BCl_3$$

Later work using ^{19}F n.m.r. and infrared spectroscopy (*89*, *90*) has shown that small amounts of mixed halides are slowly formed when diboron tetrafluoride and tetrachloride are held together at 0° or during the controlled fluorination of the tetrachloride using antimony trifluoride. Whereas boron trichloride and diboron tetrafluoride over a period of 16 hours give the trifluoride and tetrachloride, a similar reaction using dimethylboron fluoride and the tetrachloride shows that the fluorine ends up almost wholly in the diboron compound (i.e., as B_2F_4); boron trifluoride and the tetrachloride do not react. All the scrambling reactions studied using the diboron tetrahalides were very much slower than the corresponding ones involving the trihalides alone.

In the case of the ions $B_{10}X_{10}^{2-}$ and $B_{12}X_{12}^{2-}$, any halogen can apparently be substituted at will during the preparation; this makes the number of theoretically possible mixed halides enormous. The mixed-halogen ions are very stable toward disproportionation, while their exchange with other boron halides has not yet been reported (*454*, *455*). An exchange of halogen can be accomplished by irradiating these ions, in aqueous solution, in the presence of halide (*821*):

$$\begin{aligned}
&B_{12}X_{12}^{2-} + nY^- \xrightarrow{h\nu} B_{12}X_{12-n}Y_n^{2-} + nX^- \\
&B_{10}X_{10}^{2-} + nY^- \xrightarrow{h\nu} B_{10}X_{10-n}Y_n^{2-} + nX^-
\end{aligned}
\qquad Y = F, Cl;\ X = Br$$

III. Structures of the Boron Halides

A. Boron Trihalides

The boron trihalides are symmetrical planar molecules (*26*, *495*, *503*, *720*, *848*, *849*) in which the angle XBX is 120° and the boron atom is assumed to be sp^2 hybridized. In such a configuration the boron atom has only a sextet of electrons, the vacant $2p_z$ orbital being at 90° to the plane of the molecule. Therefore, as would be expected, the trihalides are electrophilic and behave as strong Lewis acids.

TABLE IV

THE B—X BOND LENGTHS IN THE TRIHALIDES AND THEIR ADDUCTS[a]

Trihalide, BX_3	B—X distance in BX_3 (in Å)	B—X distance in BX_3D (in Å)
BF_3	1.295[b] (*624, 848*)	1.43[c] BF_4^- (*705*)
	1.30[d] (*503*)	1.38 BF_3NH_3 (*399*)
		1.39 BF_3NH_2Me (*400*)
		1.39 BF_3NMe_3 (*277*)
		1.33 BF_3NCMe (*400*)
		1.41 $BF_3NC_5H_5$ (*879*)
		1.43[d] BF_3OMe_2 (*49*)
BCl_3; boron covalent radius 0.82 Å (*720*)	1.75 (*26, 848*)	
	1.72[d] (*503*)	
BBr_3; boron covalent radius 0.83 Å (*720*)	1.87[d] (*503, 848*)	
BI_3; boron covalent radius 0.84 Å (*720*)	2.10[e] (*720*)	

[a] Unless noted otherwise, the structures were determined by X-ray diffraction studies on single crystals. The early literature on B—X bond lengths in general is summarized in Bauer and Beach (*48*).

[b] Infrared study of gas phase.

[c] N.m.r. study of single crystal.

[d] Electron diffraction.

[e] Powder X-ray determination.

Table IV compares the boron-halogen bond lengths in the trihalides with those found in the halide adducts, BX_3D, where the boron atom is tetracoordinate and approximately sp^3 hybridized. The short B—X distance in the case of the trihalides has been taken as partial proof of p_π—p_π bonding (back-bonding) caused by overlap of filled halogen p orbitals with the boron $2p_z$ orbital, although other factors no doubt operate simultaneously. For example, the electronegativity difference between X and B causes an electrostatic contribution $B^{\delta+}$—$X^{\delta-}$ to the bonding, which will be greater for the trihalides than for their adducts. There has been considerable effort recently to obtain other physical evidence for this π-bonding, since it has important consequences when one attempts to correlate the relative Lewis acid strengths of the trihalides (417).

TABLE V

Some References[a] to Physical Data for the Boron Trihalides

Data	BF_3	BCl_3	BBr_3	BI_3	Mixed trihalides
Melting point (°C)	– 127.6 (*310a*)	– 107 (*310a*)	– 45.8 (*39*)	49.9 (*757*)	—
Boiling point (°C)	– 100.0 (*310a*)	12.1/752 mm (*310a*)	89.9 (*39*)	212	—
Vapor pressure	(*85, 443*)	—	19 mm at 0° (*39*)	1 mm at 90°	—
Infrared and Raman spectra	(*215, 310a*) (*216*)	(*216, 310a*)	(*242, 310a*) (*216*)	(*242, 310a*) (*216*)	(*148*); also see text
Mass spectrum	(*443, 526*)	(*457*)	(*457*)	(*457*)	—
nmr spectra	(*657*)	(*657*)	(*657*)	(*657*)	(*184, 271, 370*); also see text
Calculation of thermodynamic functions from infrared data	(*605*)	(*605*)	—	—	(*604*)
Force field calculations from infrared data	(*500a*)	(*500a*)	(*500a*)	(*500a*)	—
Heat of formation	(*355, 868*)	(*355, 356*)	(*783*)	(*239*)	(*531*)
Heat of hydrolysis	(*355*)	(*782*)	(*783*)	(*239*)	—
Nuclear quadrupole resonance	—	(*495, 508*)	(*495*)	(*495*)	—
Force constants	(*468, 565, 777*)	(*468, 777*)	(*468, 777*)	(*468, 777*)	—

[a] Nöth and Vahrenkamp (*657*) have given a catalog of both old and new ^{11}B n.m.r. data for boron compounds in general and boron halide derivatives and adducts in particular. The thesis of Laurent (*494*) contains, in addition to the details of preparation, a useful collection of melting points, boiling points, and refractive indices of many adducts of boron trifluoride and trichloride with amines, ethers, ketones, esters, carboxylic acids, alcohols, and dialkyl sulfides; ditto refs. *330* and *528*.

Using molecular orbital theory, the amount of π-bonding in the trihalides has been calculated to be in the order $BF_3 > BCl_3 > BBr_3$ (*177*, *706*), which is the exact order of the constant K_D/l^2 ($l =$ B—X bond length, and K_D is the restoring force of the vibration) for the out-of-plane bending mode in BX_3. The restoring force of such a vibration will be strongly influenced by B—X π-bonding, since this will be greatest when the molecules are planar.

If a halogen is replaced by a group R that is incapable of π-bonding to the boron atom (e.g., R = alkyl), then in the series BX_3, RBX_2, R_2BX there should be an increase in the amount of π-bonding in the remaining B—X bonds, which should be manifested by an increase in the force constant of the B—X stretching frequency. This was apparently verified for the case R = methyl and X = chlorine (*59*), but the method has since been criticized (*506*) on the grounds that calculation of the correct force constant can be difficult.

The presence of π-bonding between the boron atom and the C═C bond in tricoordinate vinyl- and perfluorovinylboron derivatives has been demonstrated by infrared and ultraviolet spectroscopy (*182*, *311*). However, in $CH_2{=}CHBF_2$ and $CF_2{=}CFBF_2$ the C═C stretching frequency attains its maximum value for such compounds (showing a marked increase, for example, compared to the corresponding dichloro derivatives), the carbon-carbon double bond interacting only weakly with the boron $2p_z$ orbital. Although strong B—F π-bonding has made the $2p_z$ orbital less available for bonding with the C═C bond than when the other halogens are linked to the boron (*182*, *183*, *790*), electron impact studies show that the B—C bond in vinylboron difluoride is still significantly stronger than that found in the alkylboron difluorides (*791*).

^{19}F and ^{11}B n.m.r. chemical shifts have been considered to reflect the electron densities (shielding) at these atoms (e.g., *671*, *672*, *709*, *737*), and using this concept it is possible to follow, qualitatively or semiquantitatively, changes in the electron distribution that take place on substitution. For example, as fluorine is progressively replaced by chlorine or by bromine in the mixed trihalides, the ^{19}F n.m.r. resonance moves downfield due to deshielding of (removal of electrons from) the remaining atoms by increased π-bonding to the boron (*185*); see Table III. Similar deshielding of the fluorine atoms occurs on substitution of alkyl, aryl, vinyl, and perfluorovinyl for fluorine in the tricoordinate compounds RBF_2 and R_2BF. In the tetracoordinate trimethylamine adducts of BF_3, $EtBF_2$, and $CH_2{=}CHBF_2$, however, the ^{19}F chemical shift stays relatively constant since little or no B—F π-bonding can occur to alter the shielding of the fluorine atoms (*182*).

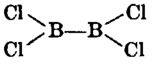
It is of interest to note that an almost linear relationship exists between the ^{19}F chemical shift and the boron-fluorine coupling constant, J_{B-F}, in the mixed trihalides (see Table III), the coupling constant being largest for $FBBr_2$ where most B—F π-bonding is expected to occur. This suggests that, for the mixed halides, J_{B-F} may also be some measure of the boron-fluorine interaction; outside this series, however, the value of J_{B-F} varies widely, being well over 50 c.p.s. even in the tetracoordinate RBF_3^- ions (*788*) where one might have been tempted to predict a value close to zero.

The chemical shifts of the ^{11}B n.m.r. spectra of the trihalides (Table II) are in agreement with the assumption that the shielding of the boron atom is in the order $F > Cl > Br > I$ (*271, 311, 671, 709*). However, in the tetrahalogenoborates the shifts are 1.8, − 6.6, 23.9, and 128 p.p.m. for BF_4^-, BCl_4^-, BBr_4^-, and BI_4^-, respectively, as measured relative to boron trifluoride etherate (*813*). Thus, although the opportunity for π-bonding between the halogen and boron atoms has been removed by making the boron atom tetracoordinate, the resonance due to BF_4^- (and BF_3 adducts) (*709*) occupies an anomalous position, the boron atom still being "too shielded" if judged purely on electronegativity (*671, 709*) grounds.

B. Diboron Tetrahalides

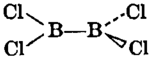
The first compound of this series to be made was the tetrachloride isolated by Stock in 1925 (*800*). Vapor density measurements and a study of the hydrolysis of diboron tetrachloride (*800, 826, 843*) suggested that the molecule probably contained a boron-to-boron bond; this was verified by Lipscomb (*27, 28*), who worked out the structure using X-ray diffraction on a single crystal held at − 165°. In the crystal at this temperature the diboron tetrachloride molecule is planar (I). The B—Cl distance is shorter than that found in the tetracoordinate boron trichloride adducts, and probably manifests B—Cl π-bonding of the type found in the boron trihalides. The boron-boron bond is rather longer than one would expect for a single bond[3] (ca. 1.60 Å) (*122, 384*) and may be

(D_{2h})



(I)

(D_{2d})



(II)

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[3] The boron–boron bond length in the B_2 molecule is 1.59 Å (*211*).

almost 0.1 Å longer than the same bond in diboron tetrafluoride. The two ^{35}Cl resonances at 38 65 and 40.38 Mc/sec noted in the nuclear quadrupole resonance spectrum of solid diboron tetrachloride are thought to arise from the nonequivalence of the halogen lattice positions (*774*).

In the liquid and gaseous states, diboron tetrachloride has Raman and infrared spectra that suggest that the molecule is in a staggered configuration with the two BCl_2 units mutually at right angles (*525*); this symmetry is supported by electron diffraction data on the vapor (*383*, *385*), which show that, although free rotation about the boron-boron bond does not take place, there is a large torsional vibration of the two BCl_2 groups. The barrier to rotation is approximately 2 kcal/mole (*385*, *525*).

TABLE VI

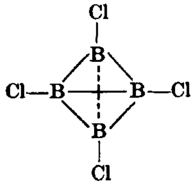
DISTANCES (IN Å) AND ANGLES BETWEEN THE ATOMS IN B_2X_4 MOLECULES

	B_2Cl_4		B_2F_4
	D_{2h} (*27, 28*)	D_{2d} (*385*)	D_{2h} (*820*)
B—B	1.75 ● 0.05	1.74 ± 0.05	1.67
B—X	1.73 ± 0.02	1.74 ± 0.05	1.32
X---X in BX_2	—	3.02 ± 0.06	—
B---X in BX_2—B	—	3.02 ± 0.06	—
X---X in different BX_2	—	4.06 ± 0.2	—
Angle XBX	—	120°	—

Diboron tetrafluoride has also been found to be planar in the solid state at $-120°$ (*820*), and to be either staggered (*266*) or undergoing essentially free rotation (*243*) in the gaseous state; see Table VI. The two remaining tetrahalides have yet to be studied structurally. Tetramethoxydiboron is thought to be planar in the liquid state, but to satisfy steric requirements the NC_2 and BN_2 groups in liquid tetrakis (dimethylamino)diboron are twisted against the molecular plane (*65*).

C. TETRABORON TETRACHLORIDE

Tetraboron tetrachloride was the first electron-deficient boron halide to be discovered. (The term electron-deficient is used here to describe a molecule with insufficient bonding electrons to form 2-electron, 2-center bonds throughout the molecule.) The structure in the solid state is that of an almost regular tetrahedron of boron atoms (III), to each of which is bonded a single terminal chlorine in such a manner that the four chlorine



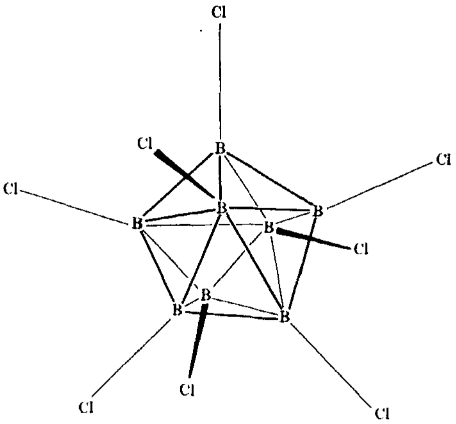
(III)

B–B = 1.70 ± 0.04 Å
B–Cl = 1.70 ± 0.03 Å

atoms also form a tetrahedron (*25*). The electronic structure of tetraboron tetrachloride has been discussed (*544*) in terms of multicentered bonds involving all four boron atoms, the boron framework being strengthened by π-donation from p-orbitals of suitable symmetry on the chlorine atoms. No other tetraboron tetrahalides are known to date (1966) and, indeed, it has been suggested (*544*) that the fluoride might be unstable.

D. OCTABORON OCTACHLORIDE, B_8Cl_8

This red compound was isolated from among the decomposition products of diboron tetrachloride and crystals grown from boron trichloride for the X-ray diffraction measurements (*426*). Recent attempts to isolate the molecule from the same source but under very stringent conditions of moisture and air exclusion have failed (*543*, *753*). The molecule has a boron-cage structure, IV, containing the eight boron atoms in the shape of a dodecahedron (*426*).

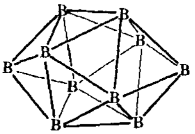


(IV)

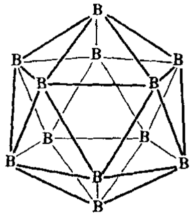
Several other boron chlorides have been isolated that probably have boron-cage structures [e.g., B_9Cl_8H (*253*); B_9Cl_9 (*541*); $B_{12}Cl_{11}$ (*753*, *825*); $B_{11}Cl_{11}$ (*543*)] but none has yet been studied structurally.

E. $B_{10}X_{10}^{2-}$ AND $B_{12}X_{12}^{2-}$ IONS

The borohydride ions $B_{10}H_{10}^{2-}$ (*375*) and $B_{12}H_{12}^{2-}$ (*376*) have been shown to have the boron-cage structures V and VI; the hydrogen atoms, attached one to each boron, can be substituted either partially or wholly by the respective halogen or halogens (*454*, *455*).



(V)



(VI)

IV. Chemistry of the Boron Halides

A. BORON TRIHALIDES

As we have seen, in the trihalides the boron atom is hybridized to the sp^2 planar configuration and shares only six valency electrons. The trihalides are therefore coordinatively unsaturated, and their chemistry in the main is the satisfying of this unsaturation by the formation of adducts with suitable Lewis bases; many hundreds of boron halide adducts are now known and vary greatly in thermal stability. However, it is possible to make two general rules that are followed by the majority of adducts, and therefore help to predict the chemistry of new compounds.

(1) In the main, the donor atom of the Lewis base is a member of Group V (N, P, As) or Group VI (O, S) of the Periodic Table. If the base contains a hydrogen atom directly bonded to the donor atom, the adduct with a boron trihalide is susceptible to an intramolecular decomposition in which HX is eliminated:

$$BCl_3 + HSMe \xrightarrow[\text{temperature}]{\text{low}} (Me)HSBCl_3 \xrightarrow{-20^\circ} HCl + MeSBCl_2 \qquad (\mathit{323})$$

$$S_7NH + BBr_3 \rightarrow HBr + S_7NBBr_2 \qquad (\mathit{379})$$

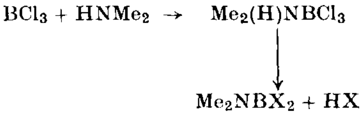
The adducts of boron trifluoride with this type of donor molecule are much more stable toward intramolecular decomposition than are those of the other trihalides due to the very much greater strength (*738*) of the B—F bond; see Table VII. This is exemplified by the adduct dimethylamine-boron trifluoride, which is stable at room temperature in the presence of excess dimethylamine, while the other boron trihalides react vigorously at low temperatures to release HX (which combines with excess of amine to give $H_2NMe_2^+X^-$), e.g.:

TABLE VII

BOND ENERGIES OF THE BORON TRIHALIDES (*239*)

BX_3	$E(B—X)^a$ in kcal
BF_3	154 ± 2
BCl_3	106 ± 1.5
BBr_3	88 ± 1.5
BI_3	68 ± 2

$^a E(B—X) = \frac{1}{3}[\Delta H_f^\circ B(g) + 3\Delta H_f^\circ X(g) - \Delta H_f^\circ BX_3(ss) - \Delta H(BX_3;\ ss \rightarrow g)]$ (where g = gaseous state, ss = standard state)



$$\begin{tikzcd} BCl_3 + HNMe_2 \arrow[r] & Me_2(H)NBCl_3 \arrow[d] \\ & Me_2NBX_2 + HX \end{tikzcd}$$

However, the loss of hydrogen fluoride from dimethylamino-boron trifluoride can be accelerated by treatment of the adduct with a reactive metal such as aluminum when a good yield of dimethylamino-boron difluoride is obtained (*773*):

$$3Me_2(H)NBF_3 + Al \rightarrow 3Me_2NBF_2 + AlF_3 + 1\tfrac{1}{2}H_2$$

The reaction of lithium with various amine complexes of boron trifluoride is similar (*459*). Substitution of a boron halide by an amine can sometimes take place via an S_N2 process (e.g., phenylboron dichloride and 2,4-dinitronaphthylamine, *510*) instead of via the more usual Lewis adduct formation (*509*).

(2) If the donor atom is attached only to alkyl or aryl groups (e.g., R_3N, R_2S, or R_2O), the adducts formed with the trihalides are comparatively stable to intramolecular decomposition (e.g., *582, 684, 688*), although in certain cases thermal instability of the adduct is due to dissociation:

$$BX_3 + D \rightleftharpoons DBX_3$$

$$\text{e.g. } BF_3 + Me_2O \rightleftharpoons Me_2OBF_3 \qquad (\textit{104, 105})$$

The adducts with ethers decompose (often only slowly at room temperature) with the evolution of RX. Again the strength of the B—F bond influences the stability of the trifluoride etherates and, for example, boron trifluoride diethyletherate is a well-known laboratory reagent whereas boron trichloride etherate readily evolves ethyl chloride:

$$Et_2OBCl_3 \xrightarrow{56^\circ} EtCl + EtOBCl_2 \qquad (\textit{715})$$

However, it may be significant that diborane prepared by the reaction of Et_2OBF_3 with lithium borohydride or lithium aluminum borohydride has been shown to contain small quantities of ethyl fluoride (*197*).

For many years it was considered that the acceptor power of the boron trihalides would be governed by electronegativity and steric effects, so that the acceptor strength series would be $BF_3 > BCl_3 > BBr_3 > BI_3$. However, evidence slowly accumulated that did not agree with this order. Thus the heat of formation of BCl_3MeCN was found to be greater than that of BF_3MeCN (*491*); also boron trichloride (*792*) and tribromide (*798*) complex with arsine, whereas boron trifluoride does not form an adduct even at low temperatures (*529*). The diphenyl ether adduct of boron trifluoride is unknown (*330*) while the trichloride, contrary to earlier reports, forms a rather unstable complex (m.p. ca. 4°), which loses boron trichloride quantitatively on heating (*380*). Phosphoryl chloride forms a reasonably stable adduct with boron trichloride (*138*) but only a very unstable one (*83*, *138*) with the trifluoride. Phosphorus trichloride and tribromide do not interact with boron trifluoride but both give adducts with boron tribromide (*416*). The now classic work of H. C. Brown on the calorimetric determination of the heats of reaction between BF_3, BCl_3, and BBr_3 with nitrobenzene and pyridine finally showed in a quantitative manner that the acceptor strength of the three halides was in the reverse order of the electronegativities of the halogens, namely, $BBr_3 > BCl_3 > BF_3$ (*108*).

It was suggested (*108*) that this new order of acceptor strengths was due to the internal π-bonding between the boron and halogen atoms previously proposed by Pauling (*699*) to account for the rather short

B—X bond lengths found in the boron trihalides. When a boron halide and a donor molecule like trimethylamine enter into 1 : 1 adduct formation, several factors must be taken into account when attempting to compute the stability of the resulting complex:

$$\underset{\substack{sp^2\text{ hybridized}\\ \text{(planar; B—X }\pi\text{-bonding)}}}{BX_3} \longrightarrow \underset{\substack{sp^3\text{ hybridized}\\ \text{(tetrahedral; no B—X }\pi\text{-bonding)}}}{BX_3} \qquad (1)$$

Step (1) involves a radical change in shape of the BX_3 entity, and energy will be required for (a) the orbital rehybridization to the reaction state, (b) overcoming any π-bonding in the original BX_3 molecule, (c) overcoming increased electron pair repulsions as the B—X bond angle decreases from 120° to about 109°, and (d) overcoming possible steric overcrowding due to the decreasing X—B—X angle (this will be partially offset by an increase in the B—X distance as the π-bonding is removed).

$$\underset{(sp^3)}{BX_3} + \underset{\text{(roughly }sp^3\text{ hybridized)}}{NMe_3} \longrightarrow Me_3N\text{—}BX_3 \qquad (2)$$

In step (2), little steric *change* will be experienced by the $BX_3(sp^3)$ or the donor molecule, since the initial and final state of rehybridization is close to the sp^3 tetrahedral configuration (in some cases, if the donor molecule has very bulky groups, steric *hindrance* may cause a lowering of the stability of the adduct). This means that the donor molecule will suffer roughly the same readjustment whichever boron trihalide is used for adduct formation; an inductive effect due to the halogen atoms in $BX_3(sp^3)$ will also presumably influence the strength of the donor-acceptor bond at this point, the effect paralleling the electronegativities of the halogen atoms, $F > Cl > Br > I$. [It is assumed that the 1 : 1 adducts are monomeric; trimethylamine-boron trifluoride, once thought to be associated in the vapor state (*133*), is now known to be monomeric (*137*).] Hence any large variations in heats of reaction of the boron trihalides with a particular base will be due almost entirely to the acceptor molecules, and not the donor. Theoretical calculations (*177*, *706*) show that the main contribution to the total reorganization energies of the boron trihalides is caused by loss of the boron-halogen π-bonding; these π-bond energies are approximately 48 (BF_3), 30 (BCl_3), and 26 (BBr_3) kcal/mole, while the $sp^2 \rightarrow sp^3$ reorganization energy makes a much smaller contribution (*177*). Hence if the reorganized boron trifluoride molecule forms a donor-acceptor bond with a particular Lewis base without releasing 18 kcal/mole more energy than when boron trichloride makes a bond with the same donor, it will be the weaker

Lewis acid. The relative acceptor strengths of the trihalides are therefore expected to be in the order $BBr_3 > BCl_3 > BF_3$.

We have supposed above that the donor undergoes little steric or electronic change on coordination to the boron trihalide molecule. It is interesting therefore to compare the reactions of trimethylamine and trisilylamine, $(H_3Si)_3N$, with the boron halides. Since trimethylamine readily forms stable adducts with many tricoordinate boron compounds, it might be expected on electronegativity grounds ($N > C > Si$) that trisilylamine would be an even stronger donor molecule; however, it has been demonstrated that trisilylamine does not form adducts with either borane (BH_3) or trimethylborane (*134*) while boron trifluoride reacts only at low temperatures (*134*, *805*). Unfortunately the reactions between trisilylamine and the boron halides are complicated by a ready cleavage of silyl groups from the nitrogen atom,

$$(H_3Si)_3N + BCl_3 \xrightarrow[\text{temperature}]{\text{low}} SiH_3Cl + (H_3Si)_2NBCl_2 \qquad (134)$$

but the indications are that trisilylamine is a much weaker base than is trimethylamine. This is probably due in the main to the substantial d_π-p_π bonding between Si and N that holds the molecule in a planar configuration (*220*). On reaction with an acceptor molecule, therefore, the trisilylamine has to undergo considerable steric and electronic change and its adducts correspondingly suffer in stability. Similar results were obtained using the two series of amines $Me_n(SiH_3)_{3-n}N$ (*804*, *805*) and $Me_n(MeSiH_2)_{3-n}N$ (*221*). The π-bonding that is thought to occur in silyl (and in alkylsilyl) analogs of ethers and sulfides may help to account for the inertness of disilyl sulfide toward boron trifluoride (*674*), but attempts to measure the stability of adducts formed with the silyl ethers and boron halides have been largely unsuccessful owing to cleavage of silyl groups from the oxygen atom (*2*, *219*, *229*, *674*, *797*).

As the strength of a donor-acceptor bond depends, in part, on the availability of electrons at the donor atom (cf. the work on the silyl compounds described above), the presence of electronegative substituents on the donor atom should reduce the stability of the adduct. Thus phosphine complexes with boron trifluoride (*107*) but the phosphorus trihalides PF_3 and PCl_3 do not (*416*). A similar trend of decreasing stability is noted when hydrogen is progressively replaced by chlorine in the acetic acid complex of boron trifluoride (*572*). The bis(1-chloroalkyl) ethers are so reduced in basic strength that no adduct formation was observed with boron trichloride (*258*, *288*) while the bis(2-chloroethyl) ether complex $(ClCH_2CH_2)_2OBCl_3$ undergoes dissociation as well as irreversible decomposition (*258*).

The substitution of phenyl groups for alkyl bound to oxygen markedly affects the stability of boron trifluoride etherates; the diethyletherate is a general laboratory reagent and can be distilled unchanged, but phenylmethyl ether–boron trifluoride readily loses BF_3 on warming (*86*, *571*) and diphenyl ether forms no compound with boron trifluoride at all (*86*, *380*, *571*). Such considerations are of help when searching for a suitable system to use in the separation of the boron isotopes; an equilibrium such as

$$\mathrm{D\overset{*}{B}X_3(liq) + BX_3(g) \rightleftharpoons DBX_3(liq) + \overset{*}{B}X_3(g)}$$

must be rapid, and also the isotopically enriched boron trihalide should be capable of 100% recovery from its adduct, DBX_3, on heating. These requirements are met when D is not too powerful a donor molecule (as are pyridine and trimethylamine), and a typical system studied is that of phenylmethylether–boron trifluoride (*380*, *685*, *689*, *690*), the donor properties of the ether having been depressed to a suitable extent by introduction of the phenyl group. Boron trifluoride is used mainly in such equilibrium studies because it undergoes only slight irreversible decomposition with donor molecules; the other trihalides are much more reactive and, for example, readily cleave many ethers. Phenyl groups also decrease the Lewis basicity of a nitrogen donor, as shown by the fact that triphenylamine does not react with boron trifluoride (*770*).

The effect of steric strain on boron complexes in general has been studied calorimetrically by H. C. Brown (*103*), but only the adducts of the trifluoride were so studied. Pyridine is a weaker base (proton acceptor) in aqueous solution than is 2,6-dimethylpyridine, but pyridine-boron trifluoride is a more stable adduct than 2,6-dimethylpyridine–boron trifluoride owing to the steric effect of the two methyl groups (*114*); as expected, there is virtually no difference in the stability of adducts formed by 4-substituted pyridines and boron trifluoride (*109*) or diborane (*106*). The relative order of strain introduced by alkyl groups on the base appears to be in the order *tert*-Bu > iso-Pr > Et > Me. For example, in a series of boron trifluoride etherates the order of stabilities is $Me_2O > Et_2O > (iso\text{-}Pr)_2O$; if the ether is cyclic (e.g., tetrahydrofuran) the alkyl groups are effectively "tied back" so that steric interference is greatly reduced, and the tetrahydrofuran-boron trifluoride adduct is found to be more stable than the other three etherates (*104*). This relative order of base strengths for the ethers has been supported by gas phase dissociation studies (*566*), proton n.m.r. equilibrium measurements (*190*), and infrared distribution studies (*867*) using boron trifluoride as the reference acid; similarly it is found that $NMe_3 > NEt_3$ (*388*). Recently

Gore and Danyluk have shown by calculating the equilibrium constants for the reaction

$$R_2O + BX_3 \rightleftharpoons R_2OBX_3 \qquad (R = Me, Et, iso\text{-}Pr \quad X = Cl, F)$$

using proton n.m.r. chemical shift-concentration data, that the order of basicity is $Et_2O > (iso\text{-}Pr)_2O > Me_2O$ when the reaction is carried out in dichloromethane solvent (*312*); they also cite electrical conductivity and vapor pressure measurements as evidence for their order.

Owing to the linear structure of nitrile compounds, $R—C{\equiv}N$, steric changes in R do not affect the stability of adducts with boron trifluoride to a significant degree (*110*), and this can be exploited when studying other effects connected with the donor-acceptor bond (*808*).

In the boron trihalide series there is an increase in steric requirements from F to I, which will tend to mask some of the effects discussed above and make boron triiodide, for example, a somewhat weaker Lewis acid than might be anticipated; Harmon (*366*) has calculated the I—I distance in boron triiodide to be 3.64 Å, which is considerably less than the value of twice the van der Waals radius of iodine, 4.30 Å. This steric overcrowding, being the greatest for the triiodide, may account for the comparatively low stability of BI_3 (*757*).

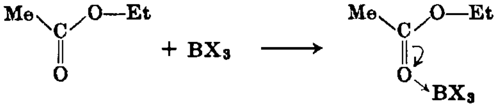
It will now be appreciated that the acceptor strength series of the boron halides depends on many factors (which can act in different directions). The considerable effort recently expended on this problem has shown that the series is the same as that found by Brown (*108*) and predicted by Cotton and Leto (*177*), namely, $BI_3 > BBr_3 > BCl_3 > BF_3$.

Displacement studies involving reactions such as

$$DBX_3 + BY_3 \rightarrow DBY_3 + BX_3$$
$$DBY_3 + BX_3 \rightarrow DBX_3 + BY_3$$

can show, clearly and in a dramatic way, the relative acceptor strengths of BX_3 and BY_3 *toward the donor molecule D.* An underlying assumption in such experiments is that the compounds being investigated should be closely related and have similar entropies and lattice energies (*217*, *582*, *801*). The technique has also been used to compare the acceptor strengths of other tricoordinate boron compounds with those of the trihalides (*324*, *325*, *582*). An interesting study of the above reactions, when $D = NEt_3$, $X = F$, and $Y = Cl$, showed that below 60° the "displacement" took place without rupture of the B—N bond; above 60°, B—N bond cleavage could be detected (*179a*).

Bases in which the donor atom is connected to the rest of the molecule by a bond having a characteristic vibrational frequency in the infrared (e.g., ketones, aldehydes, carboxylic acids, esters, and nitriles) can be used in infrared spectral studies for comparing Lewis acidities (*171*, *481*). For example, in complexes of esters with the boron halides (*480*, *481*) the decrease in stretching frequency of the C=O bond is considered to be a measure of the O—B bond strength:



In a study of the infrared spectra of acetonitrile adducts, however, it was shown that the C—N stretching frequency was very insensitive to changes in the B—N bond, making this system unfavorable for a study of acceptor strengths (*57*).

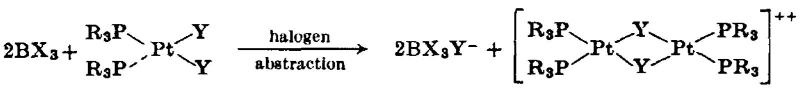
Nuclear magnetic resonance chemical shifts of the protons in trimethylamine adducts of the boron trihalides have been correlated (*581*) with the heats of formation of the corresponding pyridine complexes (*108*, *340*). It was therefore suggested that the shifts were a measure of the acceptor strengths of the trihalides, the loss of electron density at the nitrogen atom being compensated by electron release from the methyl groups, resulting in a deshielding of the protons; the stronger the acceptor, the greater will be the deshielding of the protons and will result in a larger chemical shift (*539*, *581*). Similar work has been carried out using methyl cyanide (*583*) and polycyclic phosphites (*829*) as the ligands. The internal chemical shifts (i.e., $\Delta = |\delta CH_2 - \delta CH_3|$) for triethylamine adducts have also been taken as a measure of the acceptor strength of the boron halides (*270*, *539*), but the chemical shifts of the ring protons in pyridine adducts could not be measured with sufficient accuracy (*270*). The *para* fluorine atom in 4-fluorobenzonitrile is sensitive to changes in electronic structure of the molecule on coordination to a boron halide, and the chemical shift of it has been used to give a quantitative scale of acceptor strengths (*808*); the shape of the nitrile donor virtually rules out any steric interference in these adducts.

The ^{11}B chemical shifts show marked changes in shielding when the boron halides are complexed with various Lewis bases (*672*) and the value $\Delta\delta$ = (^{11}B shift of complex − ^{11}B shift of the free halide) gives information about both the relative acceptor strengths of the halides and the donor abilities of various ligands (*270*). The almost constant variation in $\Delta\delta$ noted for the tetrahaloborate ions BX_4^- (*366*) must have been due to fortuitously chosen solute concentrations, because the ^{11}B chemical shifts of these ions are very concentration-dependent (*813*).

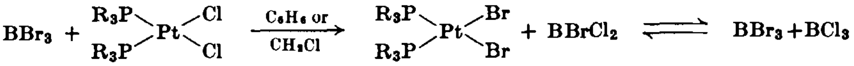
A more direct approach to the problem would be to calculate the moment of the $B^{-}—N^{+}$ bond in a series of adducts from observations of the dipole moments of the adducts; this is difficult to do in practice since it is not possible to measure the contribution of the tetrahedral BX_3 group. However, by assuming that the dipole moment of HCX_3 is a suitable approximation for BX_3 (tetrahedral) a rough measure of the B—N moment can be obtained and, using trimethylamine or pyridine as the donor molecules, the relative acceptor strengths of the boron halides have been obtained (*56*).

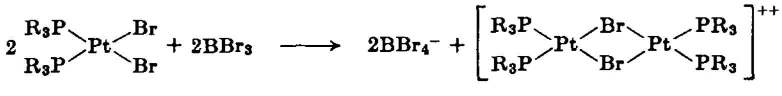
1. *Reactions with the Transition Elements and Their Compounds*

Comparatively little has been reported concerning reactions of the transition elements and their compounds with the boron trihalides, although many transition metals form ionic tetrafluoroborates in which the metal ion is often aquated or ammoniated, e.g., $Mn(H_2O)_6(BF_4)_2$, $Cu(H_2O)_6(BF_4)_2$, $Ag(NH_3)_4BF_4$, and $Co(NH_3)_6(BF_4)_3$ (*769, 817*). The readiness of the trihalides to accept a halide ion and form the tetrahaloborates has been exploited in the synthesis of binuclear halogen-bridged platinum(II) cations, starting from the *cis*-diphosphine platinum halides (*487*):

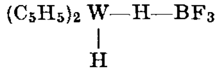


Halogen exchange may also take place before the halogen abstraction reaction if X and Y are different halogens:





Several organometallic derivatives of the transition elements have a lone pair of electrons in a low energy orbital, which make them potential donor molecules. Dicyclopentadienyltungsten dihydride, $(C_5H_5)_2WH_2$, is such a molecule and readily adds on 1 mole of boron trifluoride (*431, 780*); the W—H stretching frequency in the infrared spectrum of the adduct is found to be virtually unchanged compared to that in the parent hydride, thus ruling out a singly hydrogen-bridged species



$$(C_5H_5)_2\underset{\displaystyle H}{\underset{|}{W}}\text{—}H\text{—}BF_3$$

Furthermore, since C_5H_5Tl (*178*) and $[C_5H_5M(CO)_3]_2$ (M = Mo or W) (*431*) do not react with boron trifluoride or trichloride, it is unlikely that the cyclopentadienyl rings in $(C_5H_5)_2WH_2$ are directly involved in bonding with the boron trifluoride, and so a tungsten-to-boron bond was considered to be the most likely possibility; other hydrides that form adducts with boron trifluoride and trichloride are $(C_5H_5)_2MoH_2$ and $(C_5H_5)_2ReH$ (*431*).

Although the pentacarbonylmanganate(− 1) and similar anions show basic properties toward borane (*692*), no addition occurs when the ions $C_5H_5W(CO)_3^-$ and $C_5H_5Mo(CO)_3^-$ are treated with boron trifluoride (*431*); in certain cases, however, coupling products have been obtained when sodium carbonylmetallates are added to boron trichloride or substituted boron chlorides (*652*):

$$BCl_3 + NaFe(C_5H_5)(CO)_2 \rightarrow Cl_2BFe(C_5H_5)(CO)_2$$
$$(Me_2N)_2BCl + NaMn(CO)_5 \rightarrow (Me_2N)_2BMn(CO)_5$$

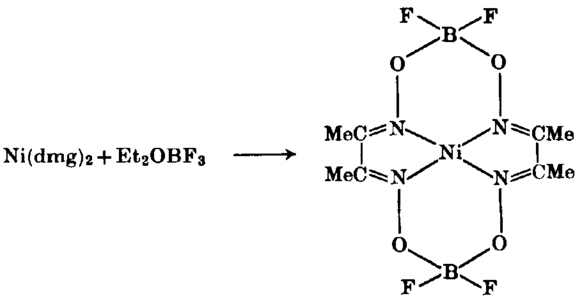
The reaction of boron trifluoride with a diarylchromium is considered to give diboron tetrafluoride (*386*),

$$2Ar_2Cr + 4BF_3 \rightarrow 2Ar_2Cr^+BF_4^- + B_2F_4$$

whereas dicyclopentadienyltitanium(III) borohydride reduces the boron trihalides to diborane (*643*):

$$3(C_5H_5)_2TiBH_4 + 4BF_3OEt_2 \rightarrow 3(C_5H_5)_2TiBF_4 + 2B_2H_6 + 4Et_2O$$
$$3(C_5H_5)_2TiBH_4 + BX_3 \rightarrow 3(C_5H_5)_2TiX + 2B_2H_6$$
$$(X = Cl, Br)$$

When boron trifluoride etherate is heated with nickel dimethylglyoxime or diphenylglyoxime, hydrogen fluoride is eliminated and the boron is incorporated into the metal chelate system:



These new chelate compounds will add on 2 moles of Lewis base (e.g., pyridine, phosphines, ammonia, piperidine), the acceptor site being the nickel atom (*754*).

The free transition elements are mostly inactive toward the boron trihalides and, for example, tungsten and tantalum surfaces can be used in the high temperature pyrolysis of the tribromide and triiodide to crystalline boron (*16*, *66*, *201*, *550*). Under the conditions of an electrical discharge other metals, such as copper (*845*), nickel (*208*), and mercury (*826*), can be made to reduce the trihalides to subhalides but, in the case of the more unstable boron triiodide, heating with silver at 185° is sufficient to produce boron monoiodide, $(BI)_x$ (*757*). Mercury is not attacked by any of the trihalides at room temperature and can therefore be used in vacuum lines for manometers and float-valves; traces of water must be removed completely by baking out any vacuum apparatus used for handling boron tribromide or triiodide, otherwise hydrolysis will produce hydrogen bromide or hydrogen iodide, both of which readily attack mercury.

Several refractory oxides used in apparatus construction (e.g., TiO_2, Fe_2O_3, ZrO_2, SiO_2, Al_2O_3) are attacked at high temperatures (*29*, *50*, *51*), producing the metal halide and boric oxide. It has been suggested that, using boron trichloride, this may be a convenient way of preparing anhydrous metal chlorides on a small scale (*29*).

2. *Reactions with Noble Gas Compounds*

The noble gases contain several lone pairs of electrons that might conceivably be used in bonding to strong acceptor molecules like the boron halides. However, a careful search using argon and xenon (*855*) has shown that no adducts are formed, disproving the earlier claim (*84*) that argon and boron trifluoride give rise to several unstable compounds.

Xenon tetrafluoride does not combine with boron trifluoride up to 200° (*42*, *222*), although at low temperatures (ca. − 100°) a blue-violet solid of unknown structure may be formed (*756*). Attempts to use a stronger acceptor than the trifluoride results only in complete fluorination of the boron halide (*43*):

$$3XeF_4 + 4BCl_3 \rightarrow 4BF_3 + 6Cl_2 + 3Xe$$

On the other hand, xenon hexafluoride and boron trifluoride react in a 1 : 1 ratio to give a white solid that melts at 90° to a pale yellow viscous liquid (*766*). The infrared spectrum of the vapor shows extensive dissociation while that of the solid indicates the presence of the BF_4^- ion; the Raman spectrum of the solid is similar to that obtained from xenon hexafluoride dissolved in anhydrous hydrogen fluoride and could be due to XeF_5^+ ions:

$$XeF_6 + BF_3 \rightarrow XeF_5^+ + BF_4^-$$
$$XeF_6 + HF \rightleftharpoons XeF_5^+ + HF_2^-$$

If the solid, which reacts with sodium fluoride at 100° to give sodium tetrafluoroborate

$$XeF_6BF_3 + NaF \xrightarrow{100^\circ} NaBF_4 + \text{“ill-defined complex”}$$

does contain XeF_5^+ ions, it might be considered as the acid analog of a nonaqueous solvent system based on liquid xenon hexafluoride (*704*):

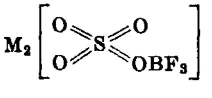
$$2XeF_6 \rightleftharpoons XeF_5^+ + XeF_7^-$$

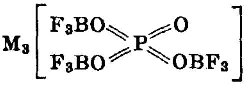
3. *Reactions with Compounds of Group I and II Elements*

The boron trihalides react on heating with the alkali and alkaline earth metals, boron and the metal halides being the principal products (e.g., *200, 202, 213, 273, 445, 614, 711, 716, 751, 785*); in the presence of hydrogen the reduction produces diborane (*398, 422*) and HBX_2 (*520*). Becher has also shown that the boron halides can be reduced by some metallic borides to give elemental boron of high purity (*64*). The only boron trihalide not ammonolyzed in liquid ammonia is the fluoride, which dissolves as the adduct ammonia-boron trifluoride. Attempted reduction of this adduct with solutions of the alkali metals in ammonia leads to ammonolysis and the production of boron amides and imides (*428, 563*), e.g.:

$$H_3NBF_3 + K \rightarrow H_2NBF_2 + KF + \tfrac{1}{2}H_2$$
$$2H_3NBF_3 + 6Na + 2NH_3 \rightarrow (H_2N)_2BNHBNH + 6NaF + 3H_2$$

Alkali metal sulfates and phosphates form coordination compounds with boron trifluoride having compositions such as M_2SO_4,BF_3; $M_2SO_4,2BF_3$; $M_3PO_4,3BF_3$; and $M_3P_2O_7,4BF_3$ (*53, 54, 168*); they are considered to be adducts in which the oxygen atoms of the anions are acting as donors:





On heating to 300° or higher the complexes decompose with the evolution of boron trifluoride. The oxide and hydroxide ions can also be donors, as shown by the formation of $BaOBF_3$ (*150*) and $NaHOBF_3$ (*453, 593, 732, 838*). Other oxysalts and oxides, however, give no adducts but produce the metal fluoride (or fluoroborate) and boron oxyfluoride $(BOF)_3$, on heating with boron trifluoride (*50*, *51*):

$$\begin{aligned}
KNO_3 + BF_3 &\rightarrow (BOF)_3 + KBF_4 + NO_2 + O_2\\
MgO + BF_3 &\rightarrow MgF_2 + (BOF)_3\\
Li_2CO_3 + BF_3 &\rightarrow 2LiBF_4 + (BOF)_3 + CO_2\\
MSiO_3 + BF_3 &\rightarrow MF_2 + (BOF)_3 + SiF_4
\end{aligned}$$

The complex cyanometallates of the alkali metals react in a similar way to sulfates and phosphates in that they slowly absorb 1 mole of boron trifluoride for each cyanide group in the complex, the bonding taking place between the nitrogen atom and boron to give a cyano bridge, M—C—N—B (*778*, *779*, *781*). Thus, where *RT* = room temperature,

$$\begin{aligned}
Na_2Fe(CN)_5NO + 5BF_3 &\xrightarrow{\qquad} Na_2Fe(CN)_5NO, 5BF_3\\
K_2Ni(CN)_4 + 4BF_3 &\xrightarrow[\text{7 weeks}]{\text{RT}} K_2Ni(CN)_4, 4BF_3\\
K_4Mo(CN)_8 + 8BF_3 &\xrightarrow[\text{3 weeks}]{\text{RT}} K_4Mo(CN)_8, 8BF_3\\
Fe(phen)_2(CN)_2 + 2BX_3 &\xrightarrow[\text{1 day}]{\text{RT}} Fe(phen)_2(CN)_2, 2BX_3\\
&\qquad\qquad (X = F, Cl, Br)\\
Fe(phen)_2(CN)_2, 2BF_3 + 2BCl_3 &\xrightarrow{\qquad} Fe(phen)_2(CN)_2, 2BCl_3 + 2BF_3
\end{aligned}$$

The cyanometallates have to be dehydrated before use, and it is thought that this may leave the crystals in an activated form because those cyanides that do not form hydrates ($K_3Fe(CN)_6$, $K_3Cr(CN)_6$) react much more sluggishly with boron trifluoride.

Alkali and alkaline earth metal hydrides react with a deficiency of boron halide or boron halide adduct in several solvents (usually ethers) to produce good yields of diborane (*11*, *116*, *236*, *315*, *347*, *387*, *501*, *579*, *747–749*), but if a reaction ratio ($MH:BF_3$) of 1 : 1 is used the hydridotrifluoroborate anion, HBF_3^-, can be isolated as its sodium salt (*315*). If the NaH/BCl_3 reaction is carried out in benzene, addition of aluminum chloride to the solvent facilitates removal of sodium chloride from the surface of the sodium hydride as the soluble $NaAlCl_4$, and almost theoretical yields of diborane result (*47*). However, at 300° in the absence of a solvent, calcium hydride reduces boron trifluoride directly to boron (*363*). Complex hydrides of the alkali metals ($MAlH_4$, MBH_4, $MHB(OMe)_3$) also reduce the boron halides to diborane (*11*, *113*, *116*, *247*, *631*, *747–749*, *876*) but an excess of boron trichloride must be avoided, otherwise diborane is lost due to side reactions:

$$\begin{aligned}
B_2H_6 + 4BCl_3 &\xrightarrow{R_2O} 6HBCl_2\cdot R_2O\\
B_2H_6 + BCl_3 &\xrightarrow{R_2O} 3H_2BCl\cdot R_2O
\end{aligned}$$

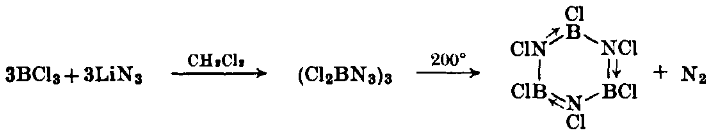
An excess of trifluoride, on the other hand, is beneficial to diborane production because it decomposes any $B_2H_7^-$ ions formed in a side reaction between diborane and the metal borohydride (*116*):

$$2NaBH_4 + B_2H_6 \rightarrow 2NaB_2H_7$$
$$NaB_2H_7 + BF_3 \rightarrow NaBF_4 + B_2H_6$$

The commercial preparation of diborane in ether solvents using lithium hydride (*227*, *395*) or sodium borohydride and boron trifluoride (*41*) has been described.

Tetrafluoroborates or tetrachloroborates result when alkali metal fluorides and chlorides are stirred, heated under pressure, or cold-milled with the corresponding boron trihalide (*595*, *599*, *748*, *813*), while substituted boron fluorides, RBF_2 (R = vinyl, methyl, or pentafluorophenyl), react with potassium fluoride to give $K[RBF_3]$ (*154*, *788*). Potassium fluoride will even extract boron trifluoride from the compound $SF_3^+BF_4^-$ to produce the tetrafluoroborate anion and pure sulfur tetrafluoride (*762*); boron trifluoride used in the formation of tetrafluoroborates may be prepared *in situ* by heating a stoichiometric mixture of, for example, boric oxide and potassium fluoride, with sulfur tetrafluoride (*442*). Halogen exchange occurs on heating calcium fluoride with boron trichloride (*80*).

Exchange of halogen for a pseudohalogen group is possible by treating a boron trihalide with the corresponding metal (often alkali metal) pseudohalide. Boron trichloride (or a substituted boron chloride) reacts with sodium and lithium azides in dichloromethane or benzene to give boron azide derivatives (*678–681*, *683*):



$$RBCl_2 + 2LiN_3 \longrightarrow RB(N_3)_2$$
$$R_2BCl + LiN_3 \longrightarrow R_2BN_3$$
$$(R = Me_2N,\ Et_2N,\ C_6H_5,\ C_3H_7)$$

By carrying out the reaction in pyridine, all three chlorine atoms can be replaced by azide to give pyridine-boron triazide (*681*):

$$BCl_3 + 3LiN_3 \xrightarrow{\text{pyridine}} C_5H_5N\text{—}B(N_3)_3$$

Boron triazide had previously been described by Wiberg (*859*), who prepared it by reacting hydrazoic acid with alkali metal borohydrides.

Boron trichloride reacts only very slowly with sulfur dioxide (*381*) [although the reaction is catalyzed by chloride ion (*132*)], making this a useful solvent for these exchanges:

$$BCl_3 + 3MSCN \xrightarrow{\text{liq. } SO_2} B(NCS)_3 + 3MCl \quad (786)$$

Boron triisothiocyanate (IR evidence)

$$\downarrow D$$

$$D{-}B(NCS)_3$$

($M = K$, Na; $D = NEt_3$, pyridine, acetonitrile, phenylacetonitrile)

Nitrile adducts of boron trichloride also react with potassium thiocyanate in liquid sulfur dioxide (*786*):

$$RCN{-}BCl_3 + 3KSCN \rightarrow RCN{-}B(NCS)_3 + 3KCl$$

$$(R = Me, C_6H_5CH_2, C_6H_5)$$

The analogous treatment of boron tribromide with silver thiocyanate in benzene was reported (*165*) to give boron trithiocyanate, but later work apparently failed to confirm the reaction (*710*); silver isocyanate, on the other hand, reacts readily (*250*):

$$3AgNCO + BBr_3 \rightarrow B(OCN)_3$$

However, the work of Lappert (*485*, *486*) shows that the products claimed previously to be boron cyanates and thiocyanates are probably the isomeric iso compounds (see also *316*, *451*):

$$R_2BX + MSCN \text{ (or } M'(SCN)_2) \rightarrow R_2BNCS$$

$$(M = Na, K, Ag;\ M' = Pb;\ X = Cl \text{ or } Br)$$

With boron tribromide the remarkable mixed halide-pseudohalide $BBr(NCS)_2$ was isolated and proved to be stable to distillation at low pressure (*486*) (cf. the mixed halides, page 8). Similar reactions between silver cyanide (*151*, *482*) or perchlorate (*592*) and the boron halides give boron cyanides and boron perchlorates (although the reaction between silver cyanide and boron trichloride is rather slow!):

$$R_2BX + AgCN \rightarrow R_2BCN$$

$$BCl_3 + nAgClO_4 \rightarrow BCl_{3-n}(ClO_4)_n \qquad (n = 1, 2, 3)$$

Alkali metal alkoxides or their complexes with trialkoxyboranes react with boron trifluoride, trichloride, and tribromide to give the trialkoxyborane (*427*, *572*, *793*):

$$BX_3 + MOR \rightarrow M[X_3BOR] \xrightarrow{2MOR} B(OR)_3 + 3MX$$

$$(X = Cl, Br)$$

$$BX_3 + 3MB(OR)_4 \rightarrow 3MX + 4B(OR)_3$$

The corresponding thioboranes may be prepared either by reacting the sodium mercaptide with boron tribromide in the absence of solvent (*140*) or by carrying out the reaction in benzene or pentane using silver or lead mercaptide (*323*, *478*). Mercuric sulfide and boron tribromide, however, give the borthiin (thioboroxine) and not boron sulfide (*188*):

$$3BBr_3 + 3HgS \rightarrow (BrBS)_3 + 3HgBr_2$$

The substitution of alkyl or aryl groups for halide by the use of Grignard or lithio reagents has been practised for many years in the preparation of BR_3 or $LiBR_4$ derivatives (*82*, *280*, *288*, *476*, *817*), but sometimes isomerization can take place during reaction as in the formation of triisobutylborane from *tert*-butylmagnesium chloride and a boron trihalide (*390*). More recently the method has been used to prepare tris(pentafluorophenyl)boron and several of its derivatives (*538*, *539*):

$$\begin{aligned} 3LiC_6F_5 \text{ (or } C_6F_5MgBr) + BX_3 &\rightarrow B(C_6F_5)_3 \\ LiC_6F_5 + B(C_6F_3)_3 &\rightarrow LiB(C_6F_5)_4 \end{aligned} \qquad (X = F, Cl)$$

The high thermal stability of tris(pentafluorophenyl)boron is in direct contrast to the perfluoroalkyl derivatives of tricoordinate boron, which readily decompose by forming B—F bonds (*45*, *693*, *802*). The only reported instance of a fluorine shift to boron in the pentafluorophenylboron series is the thermal decomposition of $KC_6F_5BF_3$ (*154*):

$$KC_6F_5BF_3 \xrightarrow{200^\circ} KBF_4 + \text{perfluoropolyphenylenes}$$

It may well be that the present nonexistence of tris(perfluoroalkyl)boron compounds ($R_{F3}B$ or $R_{F3}B$—ligand) is more closely related to difficulties of preparing suitable Grignard or lithio reagents than to their thermal instability.

Sodium acetylide and phenylacetylide react with boron trihalides to give the rather unstable compounds, triethynylborane and triphenylethynylborane (*24*):

$$3NaC{\equiv}CR + BX_3 \rightarrow 3NaX + B(C{\equiv}CR)_3$$
$$(X = F, Cl;\ R = H, C_6H_5)$$

Similar reactions have been described for substituted boron halides, RBX_2 and R_2BX [see Lappert and Prokai (*484*) and references therein].

If an excess of sodium phenylacetylide is added to boron tribromide, the more stable tetraphenylethynylborate anion results (*461*),

$$4NaC{\equiv}CC_6H_5 + BBr_3 \xrightarrow[-60^\circ]{C_6H_6} NaB(C{\equiv}CC_6H_5)_4 + 3NaBr$$

which has also been prepared by heating potassium tetrafluoroborate with phenylethynylmagnesium bromide (*740*):

$$\begin{tikzcd}[column sep=small] C_6H_5C{\equiv}CMgBr + KBF_4 \arrow[r] & KB(C{\equiv}CC_6H_5)_4 \arrow[d, "\text{add } NH_4Cl"] \\ & NH_4B(C{\equiv}CC_6H_5)_4 \end{tikzcd}$$

The triethynylboranes can be stabilized by forming tetracoordinate complexes using pyridine and amines, which is best accomplished by treating the corresponding boron trihalide adducts with $NaC{\equiv}CR$ (*24*):

$$NaC{\equiv}CR + DBX_3 \xrightarrow{THF} DB(C{\equiv}CC_6H_5)_3$$
$$(X = F, Cl;\ R = H, C_6H_5;\ D = \text{pyridine}, Et_2NH, \text{or } Me_3N)$$

A paramagnetic species, possibly $B(C_{10}H_8N_2)_2$, is formed when a mixture of the mono- and dilithium salts of 2,2′-dipyridyl reacts with boron trichloride in cyclopentane solvent (*463*).

Other organometallic compounds of Group II elements used to form partially substituted boron halides include the alkyls and aryls of mercury and zinc (*615a*), but the sample of phenylboron difluoride, thought to be obtained from boron trifluoride using diphenylzinc (*819*), may be only a decomposition product of boron trifluoride etherate (*557*):

$$\begin{array}{rcll}
HgAr_2 + BCl_3 & \rightarrow & ArHgCl + ArBCl_2 & (476) \\
ArHgX + BX_3 & \rightarrow & HgX_2 + ArBX_2 & (118, 285) \\
HgAr_2 + BBr_3 & \rightarrow & HgBr_2 + Ar_2BBr & (476) \\
HgR_{F2}\ (\text{or } R_FHgI) + BX_3 & \rightarrow & \text{no } R_F{-}B \text{ compounds isolated} & (469, 765) \\
 & & (R_F = CF_3, C_2F_5) & \\
(CH_2{=}CH)_2Hg\ (\text{or Zn}) + BF_3 & \rightarrow & CH_2{=}CHBF_2 & (44, 46, 92) \\
ZnR_2 + BX_3 & \rightarrow & ZnX_2 + R_nBX_{3-n} & (46, 60, 476, 860) \\
 & & (n = 1, 2) &
\end{array}$$

Although the hydrolysis of products obtained by treatment of boron trihalides with a deficiency of Grignard reagent yields alkyl/arylboric acids, the method is normally not well suited to preparation of the alkyl/arylboron halides (*554*, *557*, *562*); in some cases (e.g., $RBCl_2$) the difficulties may arise from complex formation between the solvent ether and the alkyl/arylboron halide (*562*).

4. *Reaction with Compounds of Group III Elements*

Reduction of boron trichloride with either aluminum or gallium produces elemental boron (*272*):

$$Ga + BCl_3 \rightarrow B + GaCl_2$$

In the presence of hydrogen, reduction of boron trifluoride, trichloride, or tribromide gives good yields of diborane (*252*, *398*, *422*, *578*); aluminum can also be used to initiate the decomposition of dimethylamine-boron trifluoride (*773*):

$$\mathrm{Al + 3HNMe_2BF_3 \rightarrow 3Me_2NBF_2 + AlF_3 + 1\tfrac{1}{2}H_2}$$

When the reduction of a trihalide is carried out using elemental boron at high temperature the boron monohalide, BX, is formed (*78*, *249*, *350*, *351*). It is also possible to isolate small quantities of diboron tetrachloride when boron trichloride vapor is passed over heated boron (*633*).

The many facile exchange reactions that take place between boron compounds have proved very useful in synthetic boron chemistry. One of the first to be studied, that between diborane and boron trichloride (*128*, *750*, *799*), was thought to be a simple equilibrium:

$$\mathrm{2BCl_3 + 5B_2H_6 \rightleftharpoons 6B_2H_5Cl}$$

More recent evidence from spectroscopic studies shows the reaction (which does not take place at room temperature or below in a clean apparatus free of boric oxide) to be more complex,

$$\mathrm{BCl_3 + B_2H_6 \rightleftharpoons BHCl_2 + B_2H_5Cl}$$

with the added possibility of intermediates such as monochloroborane, BH_2Cl, and asymmetrical dichlorodiborane, $B_2H_4Cl_2$, also being present (*444*, *518*, *603*, *719*); the main products, $BHCl_2$ and B_2H_5Cl, can be isolated by low temperature vacuum fractionation (*719*, *750*) or by vapor phase chromatography (*601*, *602*). A similar exchange between diborane and boron tribromide has been reported on briefly (*719*) and used to prepare pure bromodiborane; a structure determination on bromodiborane has shown the bromine atom to be in a terminal position (*175*). In the presence of ethers or amines, the equilibria in the B_2H_6/BCl_3 exchange are disturbed due to removal of one or more species by complex formation (*115*, *117*, *635*), e.g.:

$$\begin{aligned}
\mathrm{BCl_3 + B_2H_6 + 3R_2O} &\rightarrow \mathrm{3R_2OBH_2Cl}\\
\mathrm{4BCl_3 + B_2H_6 + 6R_2O} &\rightarrow \mathrm{6R_2OBHCl_2}\\
\mathrm{3R_3NBH_3 + BBr_3} &\rightarrow \mathrm{3R_3NBH_2Br + \tfrac{1}{2}B_2H_6}\\
\mathrm{3R_2NBH_3 + 2BBr_3} &\rightarrow \mathrm{3R_3NBHBr_2 + B_2H_6}
\end{aligned}$$

Diborane and boron trifluoride apparently do not undergo an exchange reaction at room temperature, but the pyrolysis of diborane at 100° in the presence of boron trifluoride (*181*) or subjecting a mixture of the two to an electrical discharge (*517*) results in the formation of small amounts of difluoroborane, F_2BH; dialkoxyboranes, e.g. $(MeO)_2BH$, may be used in place of the diborane (*181*). The addition of an excess of boron trihalide to trimethylamine-borane results in the displacement of borane (*458*, *582*, *635*):

$$\mathrm{Me_3NBH_3 + BX_3 \rightarrow Me_3NBX_3 + \tfrac{1}{2}B_2H_6}$$

Similarly, gallane is displaced from trimethylamine gallane, Me_3NGaH_3, by the stronger Lewis acid, boron trifluoride (*345*).

A more general method for preparation of the dihaloboranes is the reaction between boroxine and a boron trihalide:

$$(HBO)_3 + BX_3 \rightarrow HBX_2 \qquad [X = F \ (714); \qquad Br \ (846)]$$

The dihaloboranes (and the deuterated species) have been studied spectroscopically by ^1H, ^{19}F, and ^{11}B n.m.r. (*181*, *235*, *851*) and infrared (*517*, *519*, *521*, *714*, *846*) techniques. In analogous reactions, alkyl- and aryl-boroxines or -boric acids can be used to prepare the dihaloboron alkyls and aryls (*6*, *8*, *129*, *226a*, *293*, *554*, *557*, *561*, *562*, *623*),

$$\left.\begin{array}{l} (RBO)_3 + BX_3 \rightarrow RBX_2 \\ RB(OH)_2 + BX_3 \rightarrow RBX_2 \end{array}\right. \qquad (X = F, Cl)$$

while the dialkyl- or diaryl-boric anhydrides react readily with boron trihalides, giving R_2BX (*6*, *7*, *129*, *680*):

$$R_2B{-}O{-}BR_2 + BX_3 \rightarrow R_2BX + [BOX]$$

Aluminum trichloride may also be used to provide the chlorine atoms for these reactions (*554*).

At room temperature and low pressure (ca. 10^{-6} mm), boron trifluoride and boric acid have been observed, mass spectrometrically, to give hydroxyboron difluoride, $(HO)BF_2$; at higher temperatures a further fluorine is substituted to give $(HO)_2BF$ (*711a*). When boron trifluoride and boric oxide are heated together at 130°–800°, trifluoroboroxine is the major product (*77*, *234*, *248*, *318*, *397*, *711a*) unless hydrogen is added to the system when $B_3O_3HF_2$, $B_3O_3H_2F$, and $B_3O_3H_3$ are also formed (*713*). All the haloboroxines may be made in this way, but are unstable toward disproportionation back to BX_3 and B_2O_3 below about 250° and 1 atmosphere pressure (*317–319*). It has proved possible to trap trifluoroboroxine trimer at very low temperatures and to study its infrared spectrum (*248*) because the disproportionation becomes rapid only above $-135°$; it is only at low pressures and about 1000° that the equilibrium $3BOX \rightleftharpoons (BOX)_3$ lies well to the left-hand side[4] [*77*, *233*, *234*, *397*; see also Hofmeister and van Wazer (*402*)]. Tracer experiments using ^{10}B showed that boron trifluoride reacts more quickly with silica than with boric oxide and, apparently, trifluoroboroxine is best prepared by passing boron trifluoride over silica at 500° (*248*). Although aluminum oxide is said to be impervious to boron

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[4] A tetramer $B_4O_4Cl_4$ of unknown structure has also been observed mass spectrometrically (*712*).

trifluoride up to about 1200° [(*78*); see, however, Baumgarten and Bruns (50)], boron trichloride (*29*) and boron triiodide (*549*) attack it on heating to between 500° and 1000°; conversely, a mixture of aluminum trichloride and boric oxide gives some boron trichloride on heating (*423*).

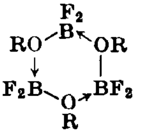
Mutual replacement of alkoxyl and halide groups between trialkoxy- or triaryloxyboranes and boron trihalides leads usually to the alkoxyboron halide (*169*, *260*, *280*, *288*, *314*, *403*, *477*, *793*), unless the latter happens to be unstable (*288*, *314*),

$$\left.\begin{array}{rcl} BX_3 + 2B(OR)_3 & \rightarrow & XB(OR)_2 \\ 2BX_3 + B(OR)_3 & \rightarrow & X_2BOR \end{array}\right\} \text{also for } B(SR)_3$$

$$BBr_2OMe \rightarrow B_3O_3Br_3 + MeBr \qquad (314)$$

$$BBr(OMe)_2 \rightarrow B_3O_3(OMe)_3 + MeBr \qquad (314)$$

but in the case of the trifluoride a compound of empirical formula $B(OR)_3 \cdot 2BF_3$ (R = alkyl) is produced. The structure of this compound has received much discussion in the literature but the dispute appears to have been settled by a careful n.m.r. investigation of the system, which showed that all three boron atoms were equivalent (*471*). The proposed cyclic structure,



is in accord with the earlier chemical evidence summarized in (*556*). *n*-Butoxyboron difluoride and dichloride may also be prepared by treating *n*-butoxyboroxine with either boron trifluoride or trichloride (*479*).

Aluminum alkoxides react with boron trifluoride to give trialkoxyboranes and aluminum trifluoride (*793*).

Tris(primary-amino)boranes, $(RNH)_3B$, can sometimes undergo group exchange when treated with the boron trihalides (*328*):

$$(RNH)_3B + 2BX_3 \rightarrow 3RNHBX_2$$
$$(X = F, Cl, Br;\ R = i\text{-Pr}, t\text{-Bu})$$

However, in the case of the trifluoride, mixtures of B-alkylamino- and B-fluoroborazines are the more usual products (*328*):

$$(RNH)_3B + BF_3 \rightarrow RNH_2BF_3 + (\text{borazines})$$
$$(R = Me, Et, n\text{-Pr}, i\text{-Bu})$$

The low stability of sterically hindered aminoborazines may account for the formation of $RNHBF_2$ only in those cases where branching of the alkyl group, R, occurs at the carbon atom joined to nitrogen. A quantitative yield of ethylamine-boron trichloride is formed when boron trichloride and tris(ethylamino)borane are mixed (*328*):

$$2(\mathrm{EtNH})_3\mathrm{B} + 4\mathrm{BCl}_3 \rightarrow 3\mathrm{EtNH}_2\mathrm{BCl}_3 + (\mathrm{EtNBCl})_3$$

Tris(dialkylamino)boranes give dialkylaminoboron dihalides or bis(dialkylamino)boron halides when treated with the stoichiometric amount of the boron trihalide (*38*, *96*, *290*, *320*, *642*, *645*, *650*):

$$\mathrm{B(NR_2)_3} + 2\mathrm{BX_3} \rightarrow \mathrm{R_2NBX_2} \xrightarrow{\text{slow}} [\mathrm{R_2NBX_2}]_2$$
$$2\mathrm{B(NR_2)_3} + \mathrm{BX_3} \rightarrow \mathrm{(R_2N)_2BX}$$
$$\mathrm{B(NH{-}NMe_2)_3} + 2\mathrm{BX_3} \rightarrow 3\mathrm{X_2BNH{-}NMe_2}$$

The dialkylaminoboron dihalides, which slowly dimerize when allowed to stand, have been studied by infrared spectroscopy in the gas phase and by X-ray diffraction in the solid (*38*). Dimethylaminoboron difluoride is also one of the products when boron trifluoride reacts with tetramethylaminoborane at low temperature (*130*):

$$\begin{tikzcd}
\mathrm{BF_3} + \mathrm{Me_2NBMe_2} \arrow[r] & 1:1 \text{ adduct} \arrow[d, "\text{above } -78^\circ"] \\
& \mathrm{Me_2BF} + \mathrm{Me_2NBF_2}
\end{tikzcd}$$

The same compound is obtained on mixing boron trifluoride and bis-(dimethylamino)boron fluoride (*130*):

$$\mathrm{BF_3} + \mathrm{(NMe_2)_2BF} \rightarrow 2\mathrm{Me_2NBF_2}$$

Borazine and boron trichloride react to give B-monochloro- and B-dichloroborazines (*742*); similarly, trichloroborazine exchanges halogen with boron trifluoride but the method is not suitable for large-scale preparation of trifluoroborazine (*492*).

The exchange of alkyl (or aryl) groups for halide has proved useful for preparation of alkyl/arylboron halides (*8*, *59*, *125*, *280*, *288*, *515*, *555*, *613*, *615a*, *616*, *623*, *741*):

$$\mathrm{BX_3} + 2\mathrm{BR_3} \rightarrow 3\mathrm{R_2BX}$$
$$2\mathrm{BX_3} + \mathrm{BR_3} \rightarrow 3\mathrm{RBX_2}$$
$$\mathrm{BX_3} + \mathrm{R_2BX} \rightarrow 2\mathrm{RBX_2}$$

The alkylboron halides can often be distilled unchanged in a vacuum below 100°, but at higher temperatures disproportionation may take place, e.g.:

$$2\mathrm{R_2BCl} \rightarrow \mathrm{RBCl_2} + \mathrm{BR_3} \qquad (\mathit{555})$$

Alkylaluminum halides and aluminum trialkyls give trialkylboranes or alkylboron halides on reaction with the boron trihalides (*40*, *500*, *852*), but, when lithium borohydride is added to the mixture, alkylated diboranes result (*514*). A mixture of hydrogen chloride, aluminum carbide Al_4C_3, and boron trichloride gave the two methylboron chlorides when heated at 400° for 3 hours (*40*).

A remarkable boron alkyl $[B_2(C_2H_4)_3]_x$ results when an excess of acetylene reacts with diborane in dimethoxyethane solvent; this alkyl generates the 1,2-bis(dihaloboryl)ethanes on treatment with boron trihalides (*162*):

$$[B_2(C_2H_4)_3]_x + 4xBX_3 \rightarrow 3xX_2BC_2H_4BX_2 \qquad (X = F, Cl)$$

These compounds had previously been accessible only by using diboron tetrahalides. The reaction of boron trihalides with boron monoxide and tetrakis(dimethylamino)diboron have been discussed previously (pp. 5–6).

More complicated reactions involving the redistribution of three different groups have been attempted; thus Gerrard (*94*) prepared RBX_2 compounds by the route,

$$(R'O)_2BR + BX_3 \rightarrow RBX_2$$
$$(X = F, Cl;\ R = n\text{-Bu}, C_6H_5)$$

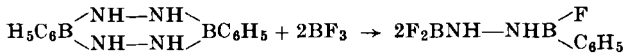
while Becher (*61*) and Niedenzu (*616*, *623*) studied the interaction of the trihalides with aminoborane derivatives:

$$R_2'NBR_2 + BX_3 \rightarrow R_2BX + R_2'NBX_2$$
$$(R_2'N)_2BR + BX_3 \rightarrow RBX_2 + (R_2'N)_2BX$$
$$(X = F, Cl;\ R = Me, C_6H_5;\ R' = H, Me, Et, n\text{-amyl})$$

Substituted hydrazinoboranes react in the same manner (*650*):

$$(C_6H_5)_2BNH{-}NHC_6H_5 + BF_3 \rightarrow (C_6H_5)_2BF + C_6H_5NH{-}NHBF_2$$
$$Bu_2BNH{-}NHBBu_2 + 2BF_3 \rightarrow 2Bu_2BF + F_2BNH{-}NHBF_2$$
$$Pr_2BNH{-}NMe_2 + BCl_3 \rightarrow Pr_2BCl + Cl_2BNH{-}NMe_2$$

The hydrazinoboron halides formed as products in these reactions have yet to be made by treating the corresponding hydrazine with a boron halide, thus, this exchange constitutes a useful synthetic method. The heterocyclic compound, $(C_6H_5BNH{-}NH)_2$, adds on 2 moles of boron trifluoride to form what is possibly $C_6H_5FBNH{-}NHBF_2$ (650):



$$H_5C_6B\begin{smallmatrix}\diagup NH{-}NH \diagdown\\ \diagdown NH{-}NH \diagup\end{smallmatrix}BC_6H_5 + 2BF_3 \rightarrow 2F_2BNH{-}NHB\begin{smallmatrix}\diagup F\\ \diagdown C_6H_5\end{smallmatrix}$$

Mixed phosphine-aminoboranes are cleaved by boron trichloride (*653*),

$$2(Me_2N)_2BPEt_2 + 2BCl_3 \rightarrow 2(Me_2N)_2BCl + [Cl_2B{-}PEt_2]_2$$

as are the aminoborazines (*622*):

$$[R_2NB{-}NH]_3 + BCl_3 \rightarrow R_2NBCl_2 + [ClB{-}NH]_3$$

It has also been demonstrated that, for some asymmetrically substituted alkyl or aryl boranes $R'BR_2$, treatment with a boron halide results in cleavage of one alkyl (or aryl) group from the original borane:

$$(C_6H_5)_2BC{\equiv}CC_6H_5 + BBr_3 \rightarrow (C_6H_5)_2BBr \qquad (484)$$

$$CF_3B(n\text{-}C_4H_7)_2 + BF_3 \rightarrow CF_3BF_2 + (n\text{-}C_4H_7)_2BF \qquad (693)$$

$$CF_3B(n\text{-}C_4H_7)_2 + 2BF_3 \rightarrow CF_3BF_2 + 2n\text{-}C_4H_7BF_2 \qquad (694)$$

5. *Reactions with Compounds of Group IV Elements*

Little has been reported on the reaction of the free Group IV elements with the boron trihalides; silicon reduces the halides to boron (*614*) (or gives low yields of boron-silicon fluorides) (*816*), but graphite can be used to make the filaments used in the high-temperature hydrogen reduction of the trichloride to boron (*796*) and is apparently not attacked up to about 1000°.

The saturated hydrocarbons show little affinity for the boron halides, although boron trifluoride has been used in the catalytic isomerization of certain paraffins [see Chapter Nine of Topchiev *et al.* (*817*)].

Monosilane has been stated (*226*) to react with boron trichloride to give silicon tetrachloride and dichloroborane, Cl_2BH (which disproportionated to diborane), but later work (*218*) has shown that reduction of the trichloride to diborane is possible with disilane but not monosilane. However, diborane is formed when methyl radicals are generated (from azomethane) in a mixture of monosilane and boron trichloride (*743*).

Tetraorgano-substituted stannanes have proved valuable synthetic reagents in the preparation of alkyl/arylboron halides; since many such stannanes are now commercially available, this method of preparing alkyl/arylboron halides is more useful than one employing poisonous mercury reagents or spontaneously inflammable zinc alkyls. Boron trichloride reacts smoothly with R_4Sn at room temperature or on slight heating, the products depending on the reaction ratios:

$$R_4Sn + 2BCl_3 \rightarrow RBCl_2$$

$$R_4Sn + BCl_3 \rightarrow R_2BCl$$

[R = Me, alkyl (*91, 92, 303, 639*), $CH_2{=}CH$ (*91, 92*), C_6H_5 (*127, 620*), $CF_2{=}CF$ (*435, 789*)]

The method is suitable both for small-scale vacuum line procedure and for large-scale bench use. The tetraalkyl and tetravinyl stannanes lose only half the possible number of R groups during reaction, the tin ending up as R_2SnCl_2. As this is rather wasteful if R_4Sn is expensive or difficult to make, then, by making use of the known series for cleavage of groups from tin by boron trichloride, it is possible to use mixed stannanes, $R_2'SnR_2$, in the synthesis:

$$R_2'SnR_2 + 2BCl_3 \rightarrow R_2'SnCl_2 + 2RBCl_2$$
$$R_2'SnR_2 + BCl_3 \rightarrow R_2'SnCl_2 + R_2BCl$$

R′, n-C_4H_9;	R, $CH_2{=}CH$	(*92*)
R′, Me;	R, $CF_2{=}CF$	(*789*)
R′, Me;	R, C_6F_5	(*155*)

In the latter case, an added advantage of using $Me_2Sn(C_6F_5)_2$ is that tetrakis(pentafluorophenyl)tin has proved very unreactive and difficult to cleave. When mixed alkylalkoxystannanes are treated with boron trichloride, it is found that the alkyl groups remain attached to tin (*305*):

$$(RO)_2SnR_2' + 2BCl_3 \rightarrow 2ROBCl_2 + R_2'SnCl_2$$
$$(R = R' = n\text{-Bu};\ R = Me,\ R' = n\text{-octyl})$$

However, sometimes the alkoxyboron dichloride proves to be unstable and in such a case the alkyl halide corresponding to the alkoxy group is formed (*305*):

$$(RO)_2SnR_2' + BCl_3 \rightarrow R_2'SnCl_2 + RCl + B_2O_3$$
$$(R = s\text{-Bu},\ R' = n\text{-Bu})$$

Similar reactions occur (*92*, *264*, *639*) when boron tribromide reacts with alkylstannanes, except that RBR_2, R_2BBr, and R_3B tend to be produced simultaneously, making purification difficult. Mercury has been found to be a catalyst when tetravinyltin is treated with boron tribromide, since it ensures that all the vinyl groups are cleaved from the tin and that vinylboron dibromide is the only product (*264*):

$$(CH_2{=}CH)_4Sn + 4BBr_3 \xrightarrow{Hg} 4CH_2{=}CHBBr_2 + SnBr_4$$

Apparently mercury is a specific catalyst for the tetravinyltin reaction because cleavage of tetraalkyltin compounds stops at the stage R_2SnX_2 even in the presence of mercury.

Boron trifluoride produces only RBF_2 even when an excess of tin reagent is employed:

$$SnR_4 + BF_3 \rightarrow RBF_2$$

[R = Me (*139a*), C_3H_7 (*92*), $CH_2{=}CH$ (*92*), C_6H_5 (*92*, *771*), $CH_2{=}CH{-}CH_2$ (*92*), $CF_2{=}CF$ (*789*)]

When mixed tin derivatives such as $R_3'SnR$ are treated with boron trifluoride, exchange of R and F does take place but sometimes a side reaction can take place between $R_3'SnF$ and either RBF_2 or BF_3 (depending on which is the stronger Lewis acid):

$$\begin{tikzcd}
\mathrm{Me_3SnCF_3 + BF_3} \arrow[r] & \mathrm{Me_3SnBCF_3F_3} \arrow[d, "\mathrm{KF\ in\ H_2O}"] & (157) \\
 & \mathrm{Me_3SnF + K[CF_3BF_3]} &
\end{tikzcd}$$

$$\mathrm{Me_4Sn + 2BF_3 \rightarrow MeBF_2 + Me_3SnBF_4} \qquad (139a)$$

Tetraorganolead compounds, e.g., $(C_6H_5)_4Pb$ (*620*), react similarly with the boron halides but RBX_2 and R_2BX are produced in somewhat lower yields.

Hexamethylditin is catalytically decomposed by boron trifluoride (*139a*):

$$\mathrm{Me_6Sn_2 \xrightarrow{BF_3} Me_4Sn + (SnMe_2)_{\mathit{x}}}$$
$$\mathrm{(SnMe_2)_{\mathit{x}} \xrightarrow{BF_3} (SnMe_{2-\mathit{n}})_{\mathit{y}}}$$

The tetramethyltin produced in the first stages of the reaction leads to the formation of methylboron difluoride and Me_3SnBF_4 (see above).

An attempt to couple tin and boron using trimethylstannylsodium and boron trifluoride resulted only in the catalytic decomposition of the sodium compound to hexamethylditin, which then reacted with the boron trifluoride in the usual manner (*139a*). However, it has proved possible to couple metals and nonmetals to the substituted boron halides using similar metal–salt reactions (e.g., *632*, *644*, *652*, *653*).

Only benzene of the unsaturated hydrocarbons has been shown to form (weak) adducts with the trihalides at room temperature (*241*). Although phase diagrams of benzene-BBr_3 and benzene-BI_3 mixtures showed no definite compound formation, intensity measurements on the symmetrical boron-halogen stretching frequency and a study of the ^{11}B n.m.r. spectra of solutions of the two trihalides in benzene indicated the formation of 1 : 1 complexes.

Much effort has been expended in efforts to synthesize arylboron compounds directly and thus, under forcing conditions, benzene and substituted benzenes have been shown to react with the boron halides in the presence of suitable catalysts (aluminum halides or palladium):

$$\mathrm{C_6H_6 + BX_3 \rightarrow C_6H_5BX_2} \qquad (125, 597, 677, 726)$$
$$\mathrm{(X = Cl, Br, I)}$$
$$\mathrm{C_6H_5OC_6H_5 + BBr_3 \xrightarrow{reflux} C_6H_5OC_6H_4BBr_2} \qquad (125)$$

There is also some evidence that, during preparation of phenylboron dichloride from tetraphenyltin in benzene solution, some attack of the solvent occurs to give higher than theoretical yields of $C_6H_5BCl_2$ (*616*).

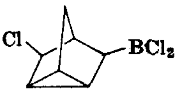
The boron halides (especially the trifluoride in the presence of a promoter) are effective catalysts in the polymerization of olefins [see Chapter Six of Topchiev *et al.* (*817*)]. Only recently has it proved possible to detect the presence of unstable complexes between polar olefins and boron halides at very low temperatures; by measurements on the isotopic exchange reaction,

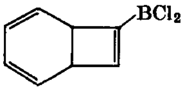
$$^{10}BF_3(g) + {}^{11}BF_3ol(liq) \overset{-112°}{\rightleftharpoons} {}^{11}BF_3(g) + {}^{10}BF_3ol(liq)$$

$$(ol = olefin)$$

it was concluded that propylene, 1-butene, and *cis*-2-butene (but not ethylene) complexed with boron trifluoride (*609–611*). The absorption spectra of olefin solutions of boron trifluoride also indicated complex formation at −112°.

Brief mention (*433*, *434*) has been made of the chloroboration of norbornadiene and bicyclo[4,2,0]octatriene using boron trichloride, the products being given the following structures:





In the presence of suitable catalysts such as active carbon (*310*) or mixtures of mercuric chloride and active carbon (*23*), acetylene and alkyl-substituted acetylenes also undergo haloboration to give halovinylboron halides in good yields:

$$BX_3 + C_2H_2 \rightarrow XCH{=}CHBX_2$$

$$BX_3 + C_2R_2 \rightarrow (XCR{=}CR)_nBX_{3-n}$$

$$(X = Cl, Br;\ R = H \text{ or alkyl, but at least one } R = H)$$

Diphenylacetylene reacts exothermally with boron tribromide to give 2-bromo-1,2-diphenylvinylboron dibromide (*484*):

$$\underset{(1 \text{ mole})}{(C_6H_5)_2C_2} + \underset{(1 \text{ mole})}{BBr_3} \rightarrow \underset{(75\% \text{ yield})}{Br(C_6H_5)C{=}C(C_6H_5)BBr_2}$$

The somewhat similar reaction of diazomethane with boron trifluoride gives fluoromethylboron difluoride (*322*):

$$BF_3 + CH_2N_2 \xrightarrow[\text{as diluent}]{N_2 \text{ gas}} FCH_2BF_2$$

In ether solution, polymethylene is produced, but no proof could be obtained that the insertion of CH_2 proceeded further than FCH_2BF_2 (although it could be achieved with other groups in place of fluorine on the boron) (*198*). Boron trichloride catalyzes the polymerization of diazomethane to polymethylene (*874*).

Cycloheptatriene readily undergoes hydride abstraction in the presence of the boron halides and produces tropenium (i.e., cycloheptatrienylium) tetrahaloborates, the yields of which are very low in the case of the fluoride (*365–369*). Similar reactions occur when trianisylmethane, $(p\text{-MeOC}_6\text{H}_4)_3\text{CH}$, and triphenylmethane are treated with the boron halides, the trianisylmethyl or triphenylmethyl tetrahaloborates being formed (*367–369*). Under the conditions of reflux of the neat liquids, cycloheptatriene and boron trichloride apparently undergo a different reaction and give benzylboron dichloride (*433*).

Several alkyl halides form 1:1 complexes with boron trifluoride at low temperatures. The composition of the complexes was deduced by measuring the isotopic exchange between ^{10}B and ^{11}B at various concentrations for the system (*606–608*),

$$^{11}\text{BF}_3(\text{gas}) + {}^{10}\text{BF}_3\text{RX}(\text{liq}) \rightleftharpoons {}^{10}\text{BF}_3(\text{gas}) + {}^{11}\text{BF}_3\text{RX}(\text{liq})$$
$$(\text{RX} = t\text{-BuCl, iso-PrF, iso-PrCl, EtF, MeF})$$

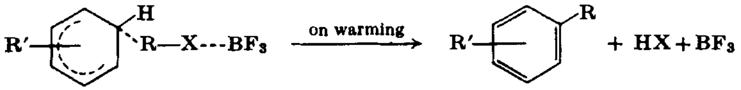
or by studying the electrical conductivity of RF/BF_3 mixtures (*670*):

$$\text{RF} + \text{BF}_3 \rightarrow \text{RFBF}_3$$
$$(\text{R} = \text{Me, Et}, n\text{-Pr}, t\text{-Bu, cyclohexyl})$$

The complexes are thought to have the structure $\text{RX}^{\delta+}\text{---BF}_3^{\delta-}$, although the electrical conductivities of the complexes with certain alkyl fluorides (R = Pr, Bu, cyclohexyl) were rather high (ca. $10^{-3}\ \text{ohm}^{-1}\ \text{cm}^{-1}$) and this may be due to the formation of some carbonium ions, R^+BF_4^- (*670*). Prolonged contact of ethyl fluoride with boron trifluoride at room temperature produces a brown polymer (*606*) while methyl and ethyl chloride, when passed over heated aluminum or zinc in the presence of the boron halides, form boron trialkyls (*424*):

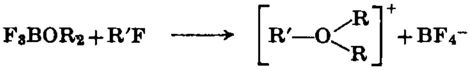
$$\text{RCl} + \text{BX}_3 \xrightarrow{350^\circ} \text{BR}_3 \qquad (\text{X} = \text{F, Cl, Br})$$

The adducts of boron trifluoride and alkyl halides mentioned above form brightly colored, isolable complexes (1:1:1) with aromatic hydrocarbons at low temperatures (*1*, *606*, *607*, *666*), which are intermediates in Friedel-Crafts alkylation reactions. Since the infrared spectra of these complexes do not show absorption bands that can be assigned to free BF_4^- (or BF_3X^-) ions, they have been assumed to have structures such as:



When a fluoroalkane is used for the alkylation reaction, the ease of catalytic activity of the boron trihalides is $BI_3 > BBr_3 > BCl_3 > BF_3$ (*667*). A halide RX that contains a phenyl group has been shown to eliminate HX on being heated with a boron trihalide [e.g., BCl_3 (*288*)], due possibly to a Friedel-Crafts reaction. Somewhat related to these studies are the reports that 1 : 1 : 1 complexes can be obtained with alkylbenzenes, anhydrous hydrogen fluoride, and boron trifluoride (*330*, *551*, *661*), in which the aromatic ring is protonated to give the tetrafluoroborate, $RH^+BF_4^-$. This might, at first sight, have been considered as a protonation by tetrafluoroboric acid, but it has been shown (*551*, *769*) that boron trifluoride obeys Henry's law on dissolution in liquid hydrogen fluoride and hence cannot form a strong complex with the solvent.

If boron trifluoride etherate is treated with an alkyl fluoride, oxonium tetrafluoroborates are formed (*570*, *817*):



$$F_3BOR_2 + R'F \longrightarrow \left[R'\text{—}O\begin{smallmatrix}R\\R\end{smallmatrix}\right]^+ + BF_4^-$$

Similar ionic complexes are formed with certain sulfur (e.g., Et_2S) or nitrogen (e.g., pyridine) systems (*330*, *817*).

The triphenylmethyl halides react readily with the corresponding boron halides to give 1 : 1 adducts now known to be tetrahaloborates (although the earlier workers did not recognize them as such):

$$(C_6H_5)_3CX + BX_3 \rightarrow (C_6H_5)_3C^+BX_4^-$$

[X = F (*760*), Cl (*368*, *369*, *854*), Br (*232*, *367*), I (*366*)]

Triphenylmethyl fluoride and boron trichloride also form a 1 : 1 complex (*440*, *832*, *854*) that may be a mixed-halogen tetrahaloborate, $(C_6H_5)_3C^+BFCl_3^-$, but the fluoroalkanes undergo halogen exchange with the boron trihalides, e.g.:

$$F(CH_2)_nCl + BX_3 \rightarrow X(CH_2)_nCl + BF_3$$

[X = Cl, Br, I (*667*)]

Trimethylsilyl fluoride forms only a weak complex with boron trifluoride, for which no structure was proposed (*231*); trimethyltin fluoride, on the other hand, forms trimethyltin tetrafluoroborate (*139a*), which in the solid state is thought to contain bidentate tetrafluoroborate groups (*373*).

Carbon tetrachloride undergoes a complete halogen interchange when heated with boron tribromide (*360*) or boron triiodide (*587*), but

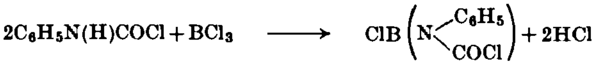
$CClF_3$, CCl_2F_2, and CF_4 are without action on boron trifluoride (*83*). Silicon difluoride, SiF_2 (made by heating silicon with silicon tetrafluoride at 1150°), interacts with boron trifluoride at low temperatures to give compounds of formulas $F_3Si(SiF_2)_nBF_2$ where $n = 1, 2, 3,$ or 4 (*816*); no trifluorosilylboron difluoride, F_3SiBF_2, could be detected (mass spectrometrically) in the reaction products. This was thought to be due to the initial step in the reaction being the production of a Si_2F_4 biradical to which the boron trifluoride or silicon difluoride may add:

$$\begin{tikzcd}
SiF_2 \arrow[r, "SiF_2"] & Si_2F_4 \arrow[r, "SiF_2"] \arrow[d, "BF_3"] & Si_3F_6 \arrow[r, "SiF_2"] \arrow[d, "BF_3"] & \text{etc.} \\
 & Si_2F_5BF_2 & Si_3F_7BF_2 &
\end{tikzcd}$$

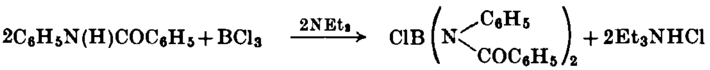
Less clearly defined products were obtained when boron trichloride was used in place of the trifluoride (*816*), although mixed fluoride-chloride was probably present. Trichlorosilylboron dichloride results when boron trichloride and silicon tetrachloride are passed through a mercury discharge (*542*), but no chemical reaction takes place in the SiX_4/BX_3 systems under normal conditions of temperature and pressure (*21*, *392*, *584*, *627*). Germanium tetrachloride and tetrabromide (*584*) and tin tetrabromide and tetraiodide (*12*) have been shown to form no compounds with boron tribromide, whereas tin tetrachloride (and titanium tetrachloride) undergoes a quantitative halogen exchange (*250*).

Formyl fluoride and acetyl fluoride both form 1 : 1 compounds with boron trifluoride, the infrared spectra and electrical conductivity of which suggests that they contain the tetrafluoroborate anion (*665*, *666*, *763*, *807*, *872*). Acetyl chloride forms rather low-melting, unstable complexes with boron trifluoride (*112*, *571*, *763*) and trichloride (*339*, *344*, *702*), but it is not clear whether these are tetrahaloborates; no complex results when benzoyl chloride is treated with boron trichloride (*344*).

Phase diagrams indicate that carbonyl chloride gives two unstable complexes with boron trifluoride, $COCl_2BF_3$ and $(COCl_2)_2BF_3$ (*530*); on heating in a sealed tube, carbonyl chloride and boron tribromide exchange halogen (*576*). Carbon monoxide under normal conditions shows no affinity for the boron trihalides but, when mixtures of carbon monoxide and either boron trifluoride or boron trichloride are subjected to a silent electric discharge, a slow reaction takes place to give polymers of unknown structure having the approximate composition BX_32CO (*844*); although some carbonyl chloride is produced when the trichloride is used, diboron tetrachloride (which might have been expected as the other product) could not be detected. Carbamoyl chloride and benzanilide both lose hydrogen chloride to give bis(amido)chloroboranes when treated with boron trichloride (*483*):

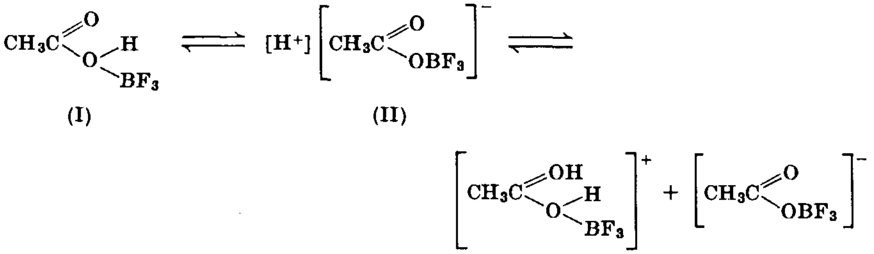


$$2C_6H_5N(H)COCl + BCl_3 \longrightarrow ClB\left(N{<}^{C_6H_5}_{COCl}\right) + 2HCl$$



$$2C_6H_5N(H)COC_6H_5 + BCl_3 \xrightarrow{2NEt_3} ClB\left(N{<}^{C_6H_5}_{COC_6H_5}\right)_2 + 2Et_3NHCl$$

Carboxylic acids form two series of compounds with boron trifluoride: $RCOOH \cdot BF_3$ and $(RCOOH)_2BF_3$ (*330*, *572*, *817*). The acetic acid complex $CH_3COOH \cdot BF_3$, a typical member of the series, has a fairly high electrical conductivity at its melting point (ca. 2.2×10^{-3} ohm^{-1} cm^{-1} at 37.5°), which suggests that it may ionize as acetoxytrifluoroboric acid (*71*, *331*, *338*):



(I) (II)

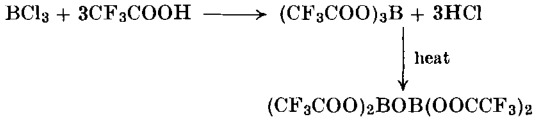
(i.e., solvated proton)

The second mole of acetic acid in the 2:1 acetic acid–boron trifluoride complex may then be attached to (I) by hydrogen bonding [as in $(H_2O)_2BF_3$, page 79], or may solvate the proton in (II). The 1:1 acetic acid complex is rather unstable and begins to lose boron trifluoride a few degrees above its melting point. Electrolysis of the pure liquid produces 1 mole of hydrogen at the cathode per Faraday, together with variable amounts of boron trifluoride, while the anode gas consists of a mixture of oxygen, carbon dioxide, ethane, and boron trifluoride. A rather unusual method of preparing $(CH_3COOH)_2BF_3$ in good yield is to treat a mixture of boric oxide and acetic anhydride with hydrogen fluoride (*596*).

The other boron halides react differently with carboxylic acids and evolve hydrogen halide in a complex sequence of reactions. With excess of acid, the tetraacyldiborates are usually formed (*280*, *288*, *307*, *377*, *476*, *793*),

$$2BX_3 + 6RCOOH \rightarrow 6HX + (RCOO)_2BOB(OOCR)_2$$

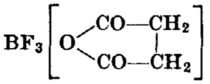
although trifluoroacetic acid produces the expected tris(trifluoroacetyl)-borate on treatment with boron trichloride (*294*):



$$\begin{array}{l} BCl_3 + 3CF_3COOH \longrightarrow (CF_3COO)_3B + 3HCl \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{heat} \\ \qquad\qquad\qquad\qquad\qquad (CF_3COO)_2BOB(OOCCF_3)_2 \end{array}$$

A deficiency of carboxylic acid leads to the formation of haloacyl-diborates [e.g., Cl(RCOO)BOB(OOCR)ClCl] together with the acyl halide and carboxylic anhydride, both of which react further with boron trihalides. Attempts to make triacetylborate, using the reaction of silver acetate with boron trichloride in dioxan solution, gave only acetic anhydride, silver chloride, and small amounts of tetraacetyldiborate; sodium acetate did not react (*159*). Thus, the apparently low thermal stability of triacylborates would suggest that the triacylborates, reputedly formed in the reaction of boron tribromide with acetic, propionic, and butyric acids (*793*), were incorrectly analyzed.

Boron trifluoride normally does not give simple addition compounds with carboxylic acid anhydrides, although succinic anhydride, as an exception, gives a 1 : 1 complex (*571*):

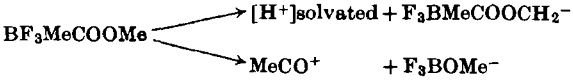


With acetic acid anhydride, the product of the reaction, which takes place readily in the cold, is an adduct of diacetic anhydride $(BF_3)_3[(MeCO)_2CHCO]_2O$ (*569*, *573*). The other boron halides cleave anhydrides to give the acyl halide, as for example in the case of acetic anhydride and boron trichloride (*288*):

$$2BCl_3 + 3(RCO)_2O \rightarrow (RCOOBCl)_2O + 4ROCl$$

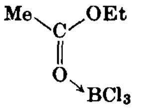
$$2BCl_3 + 5(RCO)_2O \rightarrow [(RCOO)_2B]_2O + 6ROCl$$

Boron trifluoride and trichloride react with carboxylic esters to form rather unstable 1 : 1 complexes. The trifluoride complexes tend to dissociate on slight warming and, when left in the liquid state, slowly form brown-colored decomposition products (*335*); the conductivities of the pure liquids (*333–355*) are very much higher than those of the parent esters or boron trifluoride, which may be due to possible self-ionization reactions such as (*330*):



$$\mathrm{BF_3MeCOOMe} \rightarrow [\mathrm{H^+}]\mathrm{solvated} + \mathrm{F_3BMeCOOCH_2^-}$$
$$\mathrm{BF_3MeCOOMe} \rightarrow \mathrm{MeCO^+} + \mathrm{F_3BOMe^-}$$

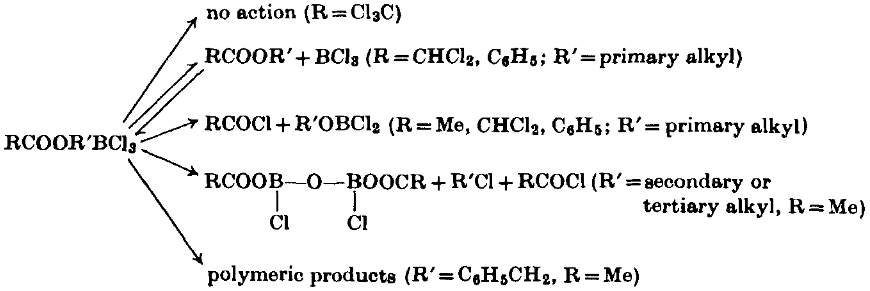
The ethyl acetate-boron trichloride compound is only a simple adduct at, or below, room temperature since treatment of it with *n*-octyl alcohol produces high yields of *n*-octyl borate, a result expected if the adduct has not undergone any internal rearrangement (*257*). With this established it was then proved, spectroscopically, that the donor site was the acyl oxygen atom (*480*):



(also for BF_3 and BBr_3)

By assuming that the magnitude of the shift, Δ, of the carbonyl stretching frequency in a complex, $EtOOCCH_3MX_3$ ($\Delta = \nu_{\text{ligand}} - \nu_{\text{complex}}$), was a measure of the acceptor strength of the trihalide MX_3, Lappert showed that the acceptor strength series for the boron halides was in the order $BBr_3 > BCl_3 > BF_3$. Similarly, the acceptor series for the Group III halides (toward ethyl acetate) is apparently $BCl_3 > GaCl_3 > AlCl_3 > InCl_3$ and $BBr_3 > AlBr_3 > InBr_3$ ($GaBr_3EtOOCCH_3$ was not studied), which is in accord with the Pauling electronegativity values for these elements (*481*).

The boron trichloride-ester complexes can decompose in several ways on warming, and all the following possibilities have been realized by changing the group R′ in a series of esters, RCOOR′ (*257, 308*):



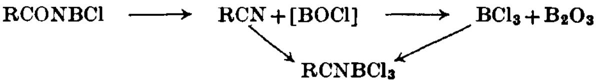
$$\mathrm{RCOOR'BCl_3} \rightarrow \text{no action } (\mathrm{R = Cl_3C})$$
$$\mathrm{RCOOR'BCl_3} \rightarrow \mathrm{RCOOR' + BCl_3}\ (\mathrm{R = CHCl_2,\ C_6H_5;\ R' = \text{primary alkyl}})$$
$$\mathrm{RCOOR'BCl_3} \rightarrow \mathrm{RCOCl + R'OBCl_2}\ (\mathrm{R = Me,\ CHCl_2,\ C_6H_5;\ R' = \text{primary alkyl}})$$
$$\mathrm{RCOOR'BCl_3} \rightarrow \mathrm{RCOOB(Cl){-}O{-}B(Cl)OOCR + R'Cl + RCOCl}\ (\mathrm{R' = \text{secondary or tertiary alkyl},\ R = Me})$$
$$\mathrm{RCOOR'BCl_3} \rightarrow \text{polymeric products } (\mathrm{R' = C_6H_5CH_2,\ R = Me})$$

Hydroxy esters (e.g., ethyl glycolate, β-hydroxypropionate, malate, or lactate) act purely as expected of an alcohol and form borates, $(RO)_3B$ (*257*).

Carboxylic acid amides form 1 : 1 complexes with the boron halides, in which the nitrogen atom provides the donor site [(*291, 297, 599a, 702, 817*; see, however, Gore *et al.* (*312a*)]. Boron trichloride-acetamide, a fairly typical member of the series, slowly loses hydrogen chloride on heating,

$$CH_3CONH_2BCl_3 \xrightarrow{\text{ca. } 100°} CH_3CONHBCl_2 \xrightarrow{\text{ca. } 200°} CH_3CONBCl$$

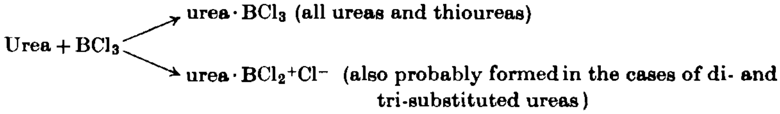
but the structures of the various products are unknown; in certain cases, further heating produces nitrile complexes of boron trichloride:



$$\begin{tikzcd}
RCONBCl \arrow[r] & RCN + [BOCl] \arrow[r] \arrow[dr] & BCl_3 + B_2O_3 \arrow[d] \\
 & & RCNBCl_3
\end{tikzcd}$$

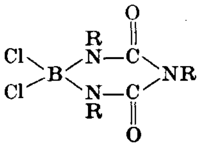
Triamidoboranes can be isolated from the reaction of amides with boron trichloride in the presence of triethylamine, the latter removing hydrogen chloride from the reaction zone as triethylamine hydrochloride (*483*).

Ureas and thioureas also form 1 : 1 complexes with the boron trihalides (*62, 721*) and, although strong intermolecular association in solution made spectral interpretation difficult for the urea $\cdot BF_3$ complexes, it was possible to show that a nitrogen atom was the donor in the thiourea $\cdot BF_3$ adducts; the n.m.r. spectra were consistent with a rapid exchange of boron trifluoride among the thiourea ligand molecules (*721*). Chemical evidence suggests that, in the urea adduct, the boron trifluoride is also attached to a nitrogen atom (*62*); this contradicts earlier work summarized, for example, in reference (*187*). The position regarding the other boron trihalide-urea complexes is more complicated, since the type of adduct formed depends upon the substituents on the nitrogen atoms (*721*):



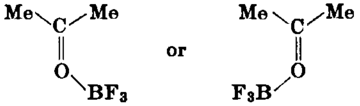
$$\begin{tikzcd}
 & \text{urea} \cdot BCl_3 \text{ (all ureas and thioureas)} \\
\text{Urea} + BCl_3 \arrow[ur] \arrow[dr] & \\
 & \text{urea} \cdot BCl_2^+Cl^- \text{ (also probably formed in the cases of di- and tri-substituted ureas)}
\end{tikzcd}$$

On standing in certain solvents the nonionic complexes give compounds of probable structure:



Boron tribromide-urea complexes are very unstable and have only a transitory existence, decomposing to insoluble solids of empirical composition urea $\cdot BBr_{2.5}$ (*721*).

Both aldehydes and ketones form fairly stable 1:1 complexes with boron trifluoride (*112*, *511*, *817*); the infrared spectra of the latter indicate that their structure is $R_2C{=}O \rightarrow BF_3$ (R = alkyl, aryl) (*152*, *153*). The proton n.m.r. spectrum of $(CH_3)_2COBF_3$ exhibits only a single sharp line even at − 70° (*480*) although two possible donor sites are available on the oxygen atom,

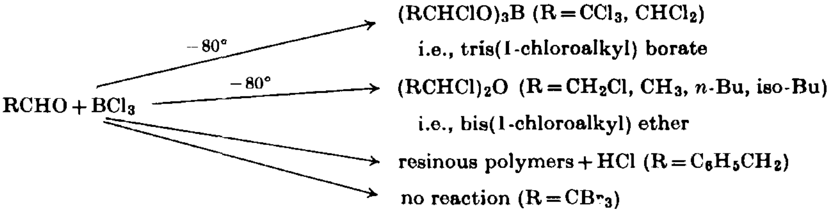


which should make the methyl groups inequivalent in the complexes. This suggests that the boron trifluoride is undergoing a rapid exchange between the two donor sites and/or between acetone molecules. By carrying out a spectroscopic study of equilibria, such as:

$$BF_3Et_2O + L_1 \rightleftharpoons BF_3L_1 + Et_2O$$

for ligands L_1, L_2, L_3, it was deduced that the donor strength of a series of ketones was in the order *p*-methoxyacetophenone > *p*-methylacetophenone > acetophenone (*588*), in agreement with the expected order of electron release by the phenyl rings in these ketones.

The reactions of boron trichloride (and no doubt the tribromide and triiodide also) with aldehydes and ketones are more complex. Only in a few cases (e.g., crotonaldehyde) does an aldehyde give a 1:1 complex with boron trichloride (*258*). Gerrard has treated a series of aldehydes with the trichloride and a summary of his findings is (*258*):



Aliphatic ketones are similarly very reactive toward boron trichloride and evolve hydrogen chloride while forming polymers[5] (*339*,

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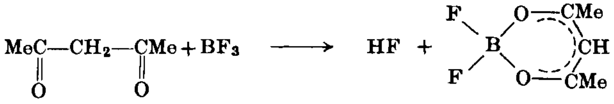
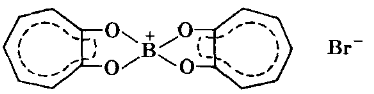
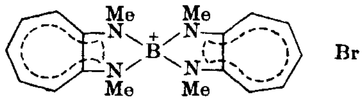
[5] Hexafluorocyclobutanone reacts differently and adds to boron trichloride, giving esters of 1-chlorohexafluorocyclobutanol (*692a*).

533, *702*). The aromatic ketones on the other hand, give stable adducts, xanthone and benzophenone having been used in n.m.r. and infrared spectral studies to deduce the relative acceptor strengths of the boron trihalides (*171*, *270*) (the latter workers also demonstrated that the ^{11}B chemical shifts of adducts can be used to compare the strengths of chemically unrelated bases). Certain diketones and epoxyketones form chelates with boron trifluoride (*35*, *374*, *420*, *590*, *818*),

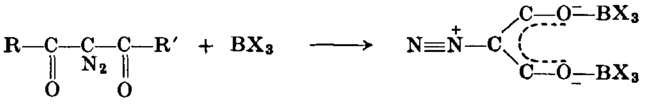


which are rather similar to the ionic species formed between either tropolone or aminotroponimine and boron tribromide (*600*):

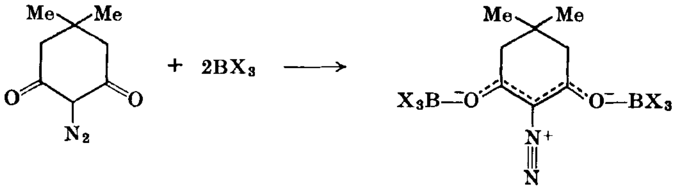




Boron trifluoride and trichloride react in benzene solution with α-carbonyldiazo compounds and with diazodimedone to form complexes containing 2 moles of trihalide, the donor sites being the carbonyl oxygen atoms (*231a*):



[$R = C_6H_5$; $R' = OMe$ $R = Et, Me$; $R' = OEt$
$R = C_6H_5$; $R' = Me$; $R = R' = C_6H_5$]



The 1 : 1 compounds formed between boron trifluoride and nitrosamines release the unchanged nitrosamine on treatment with alkali, demonstrating that no rearrangement takes place during preparation, while spectroscopic studies show that the boron trifluoride is bonded to the oxygen atom (*450*):

$$RR'NNO + BF_3 \longrightarrow RR'N\overset{+}{N}O{-}\overset{-}{B}F_3$$

(R = alkyl, aryl; R′ = alkyl; R,R′ = cyclic residue)

Nitrobenzene forms 1 : 1 complexes with the trihalides (boron triiodide has yet to be studied), the structure of which are unknown (*108*, *446*, *686*); the boron tribromide adduct is rather unstable and just above its melting point (63°–64°C) rapidly decomposes (*108*). Neither 4-methylnitrobenzene nor 4-methoxynitrobenzene forms complexes with boron trifluoride but both give rather unstable adducts, which slowly lose hydrogen chloride at room temperature when treated with boron trichloride at − 30° (*364*).

6. *Reactions with Compounds of Group V Elements*

The free elements of Group V are inactive toward the trihalides under normal conditions, but active nitrogen is thought to give diboron tetrachloride on reaction with the trichloride (*803*), while trace amounts of boron trichloride and nitrogen in a helium electrical discharge produce the spectrum of BN (*212*). A mixture of hydrogen with either boron trichloride (*863*) or tribromide (*568*) gives boron phosphide when passed over heated phosphorus; aluminum phosphide gives the same product (*863*):

$$AlP + BCl_3 \xrightarrow{1000^\circ} BP + AlCl_3$$

In the absence of hydrogen, phosphorus and boron trichloride apparently give elemental boron (*614*) but it should be noted that boron and phosphorus can react together to give boron phosphide (*863*). White phosphorus reacts with boron tribromide or triiodide (but not BCl_3) in chloroform solution to give polymers, P_2BX_3, of unknown structure (*275*).

The Group V halides have received considerable attention regarding their possible Lewis basicity; some of the earlier work with phosphorus trichloride has been found misleading since the adducts described are not those of phosphorus trichloride but are formed from an impurity, phosphoryl chloride. The trifluorides of nitrogen (*189*) and phosphorus (*83*, *147*) do not form isolable adducts with boron trifluoride or trichloride even at low temperatures; tetrafluorohydrazine and chloro- and trifluoromethyl-difluoramine similarly show only a weak association below about $-80°$ (*189*). The substitution of a fluorine atom by a less electronegative group allows solid adducts to be isolated:

$$RNF_2 + BX_3 \rightarrow RNF_2BX_3 \qquad (189, 707)$$
$$(X = F, Cl; R = H, Me, Et, CD_3)$$
$$Me_2NPF_2 + BF_3 \rightarrow Me_2NPF_2BF_3 \qquad (147)$$

The difluoramine adducts, which have infrared spectra consistent with their being covalently bonded, are thermally unstable (*189*):

$$MeNF_2BX_3 \rightarrow HCN + HF + BX_3 + BF_3 \qquad (X = F, Cl)$$
$$C_2H_5NF_2BX_3 \rightarrow CH_3CNBX_3 + HF \qquad (X = F, Cl)$$

A study of the reactions of several chloroamines with boron trifluoride revealed that the basic properties decreased as $NMe_2Cl > NMeCl_2 > NCl_3$, no adduct being formed at all with nitrogen trichloride (*14*).

The other phosphorus halides form complexes with boron trichloride, tribromide, and triiodide but not with the trifluoride, this presumably being a manifestation of the relative Lewis acidities of the boron halides:

$$PY_3 + BX_3 \rightarrow Y_3PBX_3$$

$Y = Cl; X = Cl$ (*831, 833*)
$Y = Cl; X = I$ (*20, 471*)
$Y = Cl, Br; X = Br$ (*20, 416, 505, 861*)
$Y = I; X = Br$ (*20, 586*)
$Y = I; X = I$ (*20, 586*)

Exchange of halogen also occurs in these systems, when phosphorus trichloride is used as the donor molecule:

$$Cl_3PBBr_3 \xrightarrow{0°} PBr_3 + BCl_3 \qquad (20, 416, 861)$$
$$Cl_3PBI_3 \xrightarrow{35°} PI_3 + BCl_3 \qquad (20)$$

The trichlorides or tribromides of arsenic and antimony do not react with the boron trihalides to give adducts (*12*, *416*, *528*, *811*) but, as indicated (page 4), the halides of antimony are valuable synthetic reagents in that they readily undergo halogen exchange with the boron trihalides (or substituted boron halides) (e.g., *512*), the lighter halogen being transferred from antimony to boron. Halogen exchange also occurs when diphosphorus tetrachloride (which does not react with either BF_3 or BCl_3) is treated with boron tribromide; the reaction is complicated due to the quantitative disproportionation of diphosphorus tetrachloride to phosphorus trichloride and $(PCl)_x$ that occurs initially (*505*),

$$P_2Cl_4 \rightarrow PCl_3 + (PCl)_x$$

to be followed by halogen exchange:

$$\mathrm{BBr_3 + PCl_3 + (PCl)_{\mathit{x}} \xrightarrow[\text{excess}]{\text{BBr}_3\text{ in}} PBr_3 + (PBr)_{\mathit{x}} + BBr_2Cl}$$

$$\mathrm{BBr_3 + PCl_3 + (PCl)_{\mathit{x}} \xrightarrow[\text{excess}]{\text{P}_2\text{Cl}_4\text{ in}} BCl_3 + PCl_2Br + (PCl)_{\mathit{x}}}$$

However, an adduct $P_2I_4 \cdot 2BBr_3$ is formed when boron tribromide and diphosphorus tetraiodide react together (*586*). Phosphorus-boron coupling does not occur when a mixture of boron trichloride and phosphorus trichloride is passed through a mercury discharge (*268*).

Phosphorus pentachloride and pentabromide form 1:1 compounds with the boron trihalides, which probably contain the tetrahaloborate anions $PCl_4^+BCl_4^-$ (*349*, *833*), $PBr_4^+BBr_4^-$ (*809*, *837*), and $PCl_4^+BF_3Cl^-$ (*833*, *834*). Phosphorus pentachloride is also capable of adding on a second mole of boron trichloride (*833*) or of boron tribromide (*810*) to give $PCl_5 \cdot 2BX_3$. Although the mode of bonding in these comparatively weak complexes is not understood, it is possible that monohalogen bridges are formed either between two boron atoms $[X_3BX{-}]{}^{-}BX_3$ or between boron and phosphorus $[X_3PX{-}]{}^{+}BX_3$, as in known adducts $L \cdot 2BX_3$ discussed later (page 68).

Phosphoryl chloride and bromide[6] react readily in 1:1 ratios with boron trifluoride, trichloride, and tribromide to give white solids that sublime at room temperature (*138*, *361*, *362*, *576*, *628*, *833*, *834*, *840*). Two possible structures have been proposed for the solid $POCl_3BCl_3$; the ionic form $POCl_2^+BCl_4^-$ was suggested on the basis of the infrared spectrum (*304*), but other workers argued that the spectrum supported a covalent structure $Cl_3PO \rightarrow BCl_3$ (*393*, *834*, *840*). A halogen exchange study of the $BCl_3/POCl_3$ system was also interpreted in terms of the covalent structure (*393*). By using substituted phosphorus oxychlorides such as $R_2P(Cl)O$ or $C_6H_5P(X_2)O$, it was shown (*362*, *703*) that the complex $R_2P(Cl)OBCl_3$ still exhibited a P—Cl stretching frequency in the infrared spectrum so that the ionic structure, involving chlorine transfer, can probably be ruled out in these complexes, and hence the bonding is most likely via the oxygen atom (in keeping with all other known phosphoryl chloride complexes that have been studied structurally). Furthermore, conductivity measurements on $POCl_3BCl_3$ dissolved in liquid phosphoryl chloride show that the dissociation constant for the equilibrium,

$$\mathrm{POCl_3BCl_3 \rightleftharpoons POCl_2^+ + BCl_4^+}$$

is only about 3×10^{-7} (*34*). Phosphoryl fluoride (*703*) and thiophosphoryl chloride (*840*) do not react with boron trichloride.

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[6] Thermal analysis suggests that phosphoryl fluoride and boron trifluoride may also form a 1:1 adduct (*83*).

Nitrosyl fluoride and chloride react with the boron halides to form the nitrosyl cation, NO^+:

$$NOF + BF_3 \rightarrow NO^+BF_4^- \qquad (230, 761)$$
$$NOCl + BX_3 \rightarrow NO^+ClBX_3^-$$
$$[X = F, Cl \quad (831, 834);\ X = Cl \quad (663);\ X = Br,\ \text{no salt formed} \quad (663)]$$

If the nitrosyl halide reaction is carried out in liquid sulfur dioxide, nitrosyl fluorosulfinate is formed initially:

$$NOF + SO_2 \rightarrow NOSO_2F$$
$$NOSO_2F + BF_3 \rightarrow NOBF_4 + SO_2 \qquad (763)$$

Boron trichloride is converted to the trifluoride under these conditions, and so the product is again nitrosyl tetrafluoroborate (*763*):

$$NOSO_2F + BCl_3 \rightarrow BF_3 \rightarrow NO^+BF_4^-$$

The same cation is formed when nitrogen trioxide is treated with boron trifluoride in liquid sulfur dioxide (*230*):

$$3N_2O_3 + 8BF_3 \rightarrow 6NO^+BF_4^- + B_2O_3$$

Sublimation of nitrosyl tetrafluoroborate in an atmosphere of ozone gives nitryl tetrafluoroborate (*787*), which can also be made by treating boron trifluoride with either nitryl fluoride (*172*, *464*, *669*) or nitrogen pentoxide (*230*, *872*),

$$3N_2O_5 + 8BF_3 \longrightarrow 6NO_2^+BF_4^- + B_2O_3 \qquad (230)$$
$$BF_3 + HF + N_2O_5 \xrightarrow[\text{solvent}]{CH_3NO_2} NO_2^+BF_4^- \qquad (464, 669, 872)$$

while dinitrogen tetroxide gives a mixture of both these cations (*230*):

$$3N_2O_4 + 8BF_3 \rightarrow 3NO^+BF_4^- + 3NO_2^+BF_4^- + B_2O_3$$

This work, involving a study of the reaction products by Raman and infrared spectroscopy and X-ray powder diffraction, apparently disproves earlier reports (e.g., *787*), which suggested that the complexes formed between the nitrogen oxides and boron trifluoride involved the bonding of the trifluoride to nitrite and nitrate ions; however, boron trifluoride reacts with both sodium nitrate and nitrite to give mainly nitrosyl and sodium tetrafluoroborates [(*759*); see Evans *et al.* (*230*) for a discussion of the subject]. Boron tribromide reacts with dinitrogen tetroxide to give nitryl and nitrosyl bromides and not the tetrabromoborates[7] (*464*):

$$3N_2O_4 + 2BBr_3 \rightarrow B_2O_3 + 3NO_2Br + 3NOBr$$

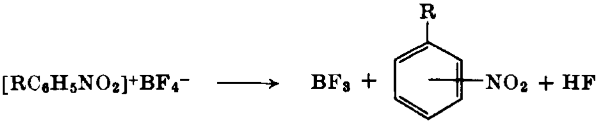
[7] The tetranitratoborate anion is formed when tetramethylammonium tetrachloroborate is dissolved in an excess of liquid dinitrogen tetroxide (*354*):

$$Me_4NBCl_4 + N_2O_4(\text{liq.}) \rightarrow Me_4N^+B(NO_3)_4^-$$

When nitryl fluoride and boron trifluoride are mixed in the presence of a substituted benzene, a colored 1:1:1 complex is formed (*662*, *668*),

$$BF_3 + NO_2F + RC_6H_5 \rightarrow 1:1:1 \text{ complex}$$
$$(\text{i.e., } [RC_6H_5NO_2]^+BF_4^-)$$

which on decomposing at low temperature gives good yields of the aromatic nitro compound:



Trimethylamine oxide, trimethylphosphine oxide, triphenylphosphine oxide, and pyridine oxide all form 1:1 complexes on direct reaction with the boron trihalides in a suitable solvent, such as chloroform (*131*, *136*, *262*, *465*, *703*, *735*, *817*, *839*), e.g.:

$$BCl_3 + Me_3NO \rightarrow Me_3\overset{+}{N}O—\overset{-}{B}Cl_3$$

The latter complex also results when hydrogen chloride is displaced from trimethylamine oxide hydrochloride by boron trichloride (*262*, *703*),

$$Me_3NOHCl + BCl_3 \rightarrow Me_3NOBCl_3 + HCl$$

while the trifluoride adduct results from the treatment of hydroxylamine-boron trifluoride with diazomethane (*839*):

$$NH_3OBF_3 + 3CH_2N_2 \rightarrow 3N_2 + Me_3NOBF_3$$

The hydroxylamine-boron trifluoride can be made by suspending the amine in ether cooled to − 10° and then adding boron trifluoride (*313*, *839*) or by displacing hydrogen chloride from hydroxylamine hydrochloride using boron trifluoride etherate (*594*, *734*); the donor site was originally considered to be the nitrogen atom, but it is now thought (*734*) that the boron atom is bonded to oxygen. Hydroxylamine hydrochloride reacts further on heating with boron trichloride until *N*-hydroxy-*B*-trichloroborazine is produced (*622*). This is an extension of the well-known method of borazine synthesis in which an ammonium (or mono-substituted ammonium) halide is heated with a boron trihalide (usually the trichloride is used but never the trifluoride) (*100*, *128*, *228*, *574*, *618*, *775*).

However, by suitably altering such reaction conditions as the temperature and the solvent, substituted ammonium halides (and also phosphonium halides) (*831*, *833*) can be made to form tetrahaloborates:

$$R_4NX + BX_3 \rightarrow R_4N^+BX_4^-$$

X = F; in methyl ether (*850*); many other solvents can be used, see (*769*)
X = Cl; in liquid HCl (*833*); in boiling $CHCl_3$ (*466*, *467*); in liquid BCl_3 at − 78° (*813*)
X = Br; in liquid HBr (*835*, *837*)
X = I; in liquid HI (*836*, *837*)

$$Me_4NCl + BF_3 \xrightarrow{\text{liq. HCl}} Me_4N^+BF_3Cl^- \qquad (833)$$

The pyridinium halides react in a similar manner (*475*). A useful collection of preparative methods covering all the tetrahaloborates, together with a discussion of their n.m.r. spectra, may be found in reference (*813*).

The reaction of ammonia and free amines with the boron halides has become one of the most extensively studied branches of boron chemistry since ammonia-boron trifluoride was first reported in 1808 by Gay-Lussac. The latter adduct can be sublimed in a vacuum but decomposes above 125° to give ammonium tetrafluoroborate and boron nitride (*490*); it also dissolves in liquid ammonia without change, unless an alkali metal is present (*428*, *563*), e.g.:

$$H_3NBF_3 + K \rightarrow \tfrac{1}{2}H_2 + KF + H_2NBF_2$$

The kinetics of the ammonia/boron trifluoride reaction have been studied by a modification of Polanyi's spherical diffusion flame (*447*). The equilibrium constant for the formation of ammonia-boron trifluoride is greater than 5×10^9 cm^3/mole, while the unusually large ratio between the rates for NH_3 and ND_3 was explained by assigning to the transition state a large degree of charge transfer stabilization and a negligible activation energy.

The other boron trihalides react vigorously with ammonia and lose hydrogen halide in a condensation process until boron imide remains:

$$\begin{tikzcd} BCl_3 + NH_3 \arrow[r, "\text{in excess}", "\text{of } BCl_3"'] & Cl_2BNH_2 + NH_4Cl \arrow[d] & \\ & ClB(NH_2)_2 + NH_4Cl & (814) \end{tikzcd}$$

$$\begin{tikzcd} 2BX_3 + 9NH_3 \arrow[r, "NH_3\text{ in}", "\text{excess}"'] & B_2(NH)_3 + 6NH_4X \\ & \text{(polymeric)} \arrow[d, "\text{heat}"] \\ & (BN)_x + NH_3 \end{tikzcd}$$

X = Cl (*429*, *717*, *814*), X = Br (*429*), X = I (*564*)

The weaker base, phosphine, forms a complex with boron trifluoride only at low temperatures (*529*, *801*) whereas arsine does not complex even below – 100°C (*529*). With the other trihalides, which are stronger Lewis acids than boron trifluoride, both phosphine and arsine form 1 : 1 complexes (*792*, *798*) but on strong heating phosphine and boron trichloride react further to give boron phosphide (*863*).

With the bidentate ligand, hydrazine, boron trifluoride forms both a 1:1 and a 1:2 adduct, depending on the conditions employed (*79*, *695a*, *696*):

$$BF_3 + N_2H_4 \xrightarrow[\text{vacuum}]{25° \text{ in a}} N_2H_4BF_3$$

$$2BF_3 + N_2H_4 \xrightarrow[\text{solvent}]{\text{THF as}} N_2H_42BF_3$$

The thermal decomposition of the 1:1 adduct above 190° is complex; nitrogen, ammonia, ammonium tetrafluoroborate, and boron nitride are formed. The hydrazine is not replaced by ammonia at –80°, but a diammoniate $N_2H_4BF_32NH_3$ is formed in which the ammonia is thought to be held by dipole-dipole forces; on warming to room temperature the ammonia is lost (*695a*). Boron trifluoride displaces silicon tetrafluoride from the adduct $SiF_4 \cdot 2N_2H_4$ (*13*).

When either boron trichloride or tribromide is treated with hydrazine, hydrogen halide is eliminated that reacts with excess of hydrazine to give N_2H_4HX; thus with boron trichloride in tetrahydrofuran the combining ratio was 1:6 (BCl_3:N_2H_4), suggesting the reaction (*697*):

$$BCl_3 + 6N_2H_4 \xrightarrow{\text{THF}} B(NHNH_2)_3 + 3N_2H_4HCl$$

Diphosphine gives a 1:2 adduct with boron trifluoride at very low temperatures but above – 118° this slowly decomposes to give phosphine; at –78° the evolution of phosphine and boron trifluoride becomes rapid (*70*).

Primary and secondary aliphatic amines complex readily with boron trifluoride to form 1:1 compounds (*330*, *817*). However, Russian work apparently casts doubt on some of the earlier reports of simple adducts by showing that a white solid, thought for many years to be Et_2NHBF_3, is in fact $Et_2NH_2^+BF_4^-$; the true 1:1 adduct is a viscous, colorless liquid that rapidly decomposes at room temperature (*732*). Dimethylamine forms a more stable adduct, which begins to decompose only above 240° (*119*):

$$Me_2NHBF_3 \rightarrow HF + Me_2NBF_2$$

$$Me_2NHBF_3 + HF \rightarrow Me_2NH_2^+BF_4^-$$

Owing to the strong B—F bonds, loss of hydrogen fluoride from amine-boron trifluoride adducts can usually be accomplished only at elevated temperatures, which may cause pyrolysis of the desired end products; the hydrogen fluoride can be removed at much lower temperatures by employing a "getter," such as a reactive metal (*459*, *773*) or a Grignard reagent (*209*):

$$R_2NHBF_3 + 2R_2NH + 3RMgX \rightarrow 3MgXF + RH + (R_2N)_3B$$

Heating an amine-boron trifluoride adduct with a tertiary amine does not remove hydrogen fluoride (*119*), although this technique has been found useful in the cases of the other trihalides (see below).

From kinetic measurements on the reactions of boron trifluoride with a series of amines in the gas phase, it has been deduced that about one collision in thirty is fruitful and, surprisingly in view of the steric changes and strains that occur on complex formation, the activation energies for the reactions are very small (*269*, *449*); the reaction rates are $Me_3N > Me_2NH > MeNH_2$ (*196*).

Primary aromatic amine complexes with boron trifluoride have been reported to have infrared spectra and chemical properties that are in agreement with their formulation as hydrohalides of the arylaminoboron halides, $[C_6H_5NHBX_2]HX$ (*301*). This formulation has been questioned (*739*) since, on reexamination, the spectra were shown to support simple adduct formation of the type $R(H)_2N \rightarrow BF_3$; the rapid decomposition of solutions of these adducts during spectral studies may account for the different conclusions reached by the previous workers.

A ready loss of hydrogen halide is observed when the other boron trihalides are treated with an excess of a primary or secondary amine (*288*, *476*). By careful use of stoichiometric amounts (1:1) of amine, however, it is possible to isolate the addition compounds in many cases (*143*, *144*, *286*, *618*, *621*, *656*); a quantitative yield of ethylamine-boron trichloride is obtained by mixing boron trichloride and tris(ethylamino) borane (*328*). On being refluxed with a tertiary amine in a suitable solvent or on heating alone, these complexes readily lose hydrogen halide as $R_3NH^+X^-$, leaving either an N-substituted borazine (*119*, *143*, *144*, *195*, *618*, *621*, *775*, *822*),

$$3RNH_2BCl_3 + 6NR_3' \rightarrow R_3N_3B_3Cl_3 + 6NR_3'HCl$$

$$CF_3CH_2NH_2\cdot HCl + BCl_3 \rightarrow HCl + CF_3CH_2NH_2BCl_3 \rightarrow (CF_3CH_2NBCl)_3 \qquad (575)$$

or an aminoboron dichloride (*63*, *119*, *617–619*, *656*), e.g.:

$$R_2NHBCl_3 + NR_3' \rightarrow R_2NBCl_2 + NR_3'HCl$$

$$(CF_3)_2NH + BCl_3 \text{ or } BBr_3 \rightarrow (CF_3)_2NBCl_2 \text{ or } (CF_3)_2NBBr_2 \qquad (329)$$

Pyridine cannot be used in these latter HX-abstraction reactions since Nöth has shown that a salt, $[R_2NHB(Cl)_2Py]^+Cl^-$, is formed (*636*, *656*).

When using secondary amines it is sometimes possible, by a suitable alteration of reaction ratios, to obtain several aminoborane derivatives (*32*, *288*, *476*, *621*).

$$BX_3 \xrightarrow{R_2NH} R_2NBX_2 \xrightarrow{R_2NH} (R_2N)_2BX \xrightarrow{R_2NH} (R_2N)_3B$$

the amine often removing hydrogen halide from the reaction zone as $R_2NH^+X^-$, although when R = ethyl the quaternary ammonium salt reacts further with boron trihalide to give diethylammonium tetrahaloborate (*286*). If the alkyl group of the secondary amine is branched in the α-position (*30*) or if diphenylamine is used (*32*), the above reaction sequence proceeds only as far as $(R_2N)_2BCl$ due to steric interactions. Branching in the β-position allows the formation of $(R_2N)_3B$, but substitution of the last chlorine atom is slow (*30*). Analogous reactions are observed when primary amines are used (*621*):

$$RNH_2 + BCl_3 \longrightarrow RNHBCl_2 + RNH_3Cl \text{ (or } RNH_3{}^+BCl_4{}^-) \qquad (300)$$

$$RNH_2 + BCl_3 \xrightarrow[-78^\circ\text{, excess amine}]{\text{inert solvent}} B(NHR)_3 \qquad (31)$$

It has been demonstrated that the reaction

$$R_2NHBCl_3 \rightarrow HCl + R_2NBCl_2$$

is reversible, since the treatment of aminoboron dichlorides with hydrogen chloride results in the reformation of 1:1 adducts (*288*, *476*, *621*, *637*, *645*). Tris(dialkylamino)boranes also react with hydrogen chloride (*645*), the products depending on the reaction ratios:

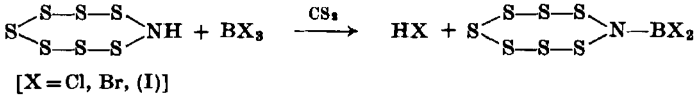
$$B(NMe_2)_3 + 2HCl \rightarrow (Me_2N)_2BCl + Me_2NH_2Cl$$

$$B(NMe_2)_3 + 4HCl \rightarrow [(Me_2NH)_2BCl_2]^+Cl^- + Me_2NH_2Cl$$

$$B(NMe_2)_3 + 5HCl \rightarrow Me_2NH{-}BCl_3 + 2Me_2NH_2Cl$$

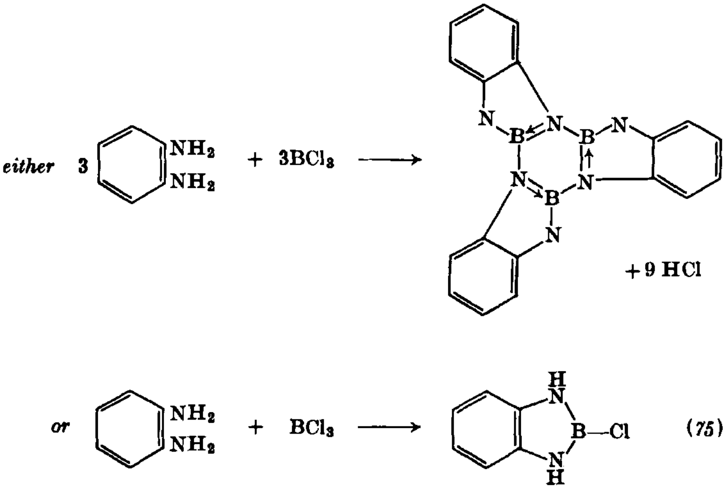
but substituted dialkylamino boranes give ionic complexes, containing the boron in the cation, when treated with hydrogen chloride (*646*).

Cyclic secondary amines, such as piperidine, react as typical members of the amine series. A 1:1 complex is formed with boron trifluoride (*86*, *671*, *817*), whereas the other trihalide complexes (*340*, *344*) undergo a ready loss of hydrogen halide (especially in the presence of triethylamine) to give aminoboron dihalides (e.g., *288*). Heptasulfurimide is rather similar, except that no adduct is formed with boron trifluoride between 80° and −78° (*379*); evolution of hydrogen halide occurs when the trichloride and tribromide are treated with heptasulfurimide in carbon disulfide solution, but the products of the boron triiodide reaction were too unstable to isolate (*379*):

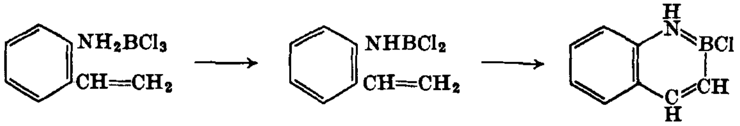


Sulphur tetranitride gives 1:1 complexes, only, when treated with boron trifluoride or trichloride, the bonding site being one of the nitrogen atoms (*873a*).

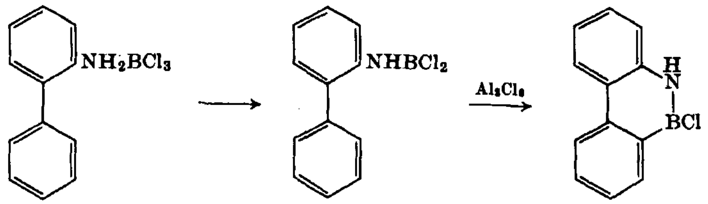
Typical aromatic amines such as aniline, pentafluoroaniline, *p*-toluidine, and *p*-anisidine form 1:1 complexes with boron trichloride and tribromide when the two are mixed in a suitable solvent; on heating the solutions, hydrogen halide is evolved until finally the *N*-triaryl-*B*-trihaloborazines are formed (*288*, *302*, *575*, *612*, *621*, *725*, *775*). The three phenylenediamines also give 1:1 complexes with boron trichloride, which lose hydrogen chloride on heating (*758*) as in the case of *o*-phenylenediamine (*99*, *725*, *758*):



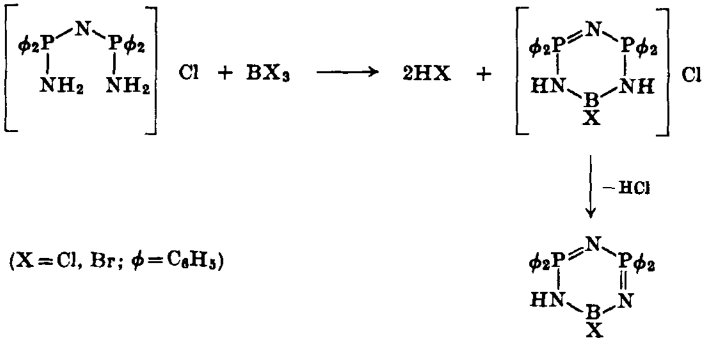
The ready loss of hydrogen chloride from aromatic amine-boron trichloride complexes has been used to advantage in the synthesis of heterocyclic molecules containing boron-nitrogen bonds (which are isoelectronic to C—C bonds). Ring closure is effected, after loss of hydrogen chloride, either by placing reactive groups in suitable positions (*203*, *523*),



or by a Friedel-Crafts addition of the boron to the aromatic nucleus (*205*, *523*):

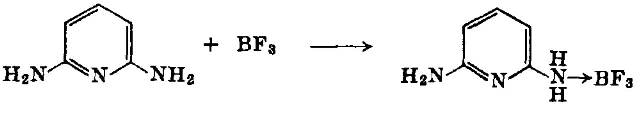


Boraphosphazenes, which are heterocycles containing boron, phosphorus, and nitrogen in the same ring, have been synthesized by a somewhat similar series of reactions (*776*):

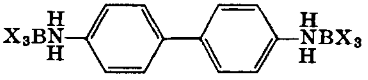


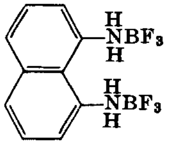
(X = Cl, Br; $\phi = C_6H_5$)

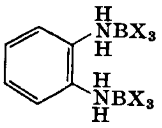
Heterocyclic polyamines usually give only a 1 : 1 adduct when treated with boron trifluoride, the donor site being provided by an exocyclic nitrogen atom; the addition of one boron trifluoride molecule appears to decrease the electron availability on the other possible donor atoms (*460*),



but polyamines in benzenoid systems are able to act as multicenter donor molecules toward all the boron trihalides, as shown by the following examples (*281, 460*):







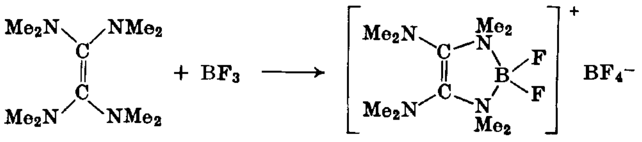
The boron trihalides will also displace hydrogen halide from the phenylenediamine hydrohalides to give the 2:1 adducts of the corresponding diamines (*281*). Hexamethylenetetramine (*135*) and the polymethylenediamines (*101, 281*) react readily with boron trifluoride, trichloride, or tribromide to form adducts:

$$\begin{tikzcd} (CH_2)_6(NH_2)_4 + 4BF_3 \arrow[r] & (CH_2)_6(NH_2)_4\cdot 4BF_3 \arrow[d, "\text{heat}"] \\ & (CH_2)_6(NH_2)_4\cdot BF_3 \end{tikzcd}$$

$$H_2N(CH_2)_nNH_2 + 2BX_3 \rightarrow X_3BH_2N(CH_2)_nNH_2BX_3$$

$$(n = 2;\ X = F;\ n = 6;\ X = F, Cl, Br)$$

An ionic complex is formed, however, in similar reactions involving tetrakis(dimethylamino)ethylene (*853*):



Tertiary amines as a general rule form stable 1:1 complexes with the boron trihalides, an exception being that tertiary aromatic amines are usually too feebly basic (or too sterically hindered) to react. Thus triphenylamine does not form an adduct with boron trifluoride (*770*), although *N*,*N*-dimethylaniline and diphenylmethylamine react quite readily (*87, 686*). Boron triiodide, the least studied halide, reacts as a typical Lewis acid toward trialkylamines and *N*,*N*-dimethylformamide in giving 1:1 adducts (*471, 598*), but in the reaction with pyridine its behavior is anomalous and further work with other amines seems warranted. Two moles of pyridine react with each mole of triiodide to give what is considered to be a boronium salt (*598*):

$$2C_5H_5N + BI_3 \rightarrow [(C_5H_5N)_2BI_2]^+I^-$$
$$\text{cf. } 4C_5H_5N + SiI_4 \rightarrow [(C_5H_5N)_4SiI_2]^{++}2I^- \qquad (58, 598)$$

Although addition of iodine to a solution of this solid gave rise to the triiodide ion, I_3^- (identified by its spectrum), no tetraiodoborate anion was produced in the presence of excess boron triiodide. The trichloride and tribromide react normally in a 1 : 1 ratio with pyridine forming simple adducts (*56*, *598*), the solutions of which do not conduct electricity and show only a single ^{11}B n.m.r. peak in the region expected for BX_3 adducts. In the molten state, pyridine-boron trichloride behaves as if there is some dissociation into kinetically free ions, thought to be $(C_5H_5N)_2BCl_2^+BCl_4^-$ (*344*), but certainly, in benzene solution, molecular weight determinations show the compound to be monomeric (*56*) —if it was present as the above salt, ion-pair formation under these conditions would result in a molecular weight closely corresponding to a dimer.

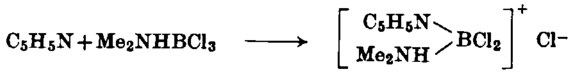
TABLE VIII

BOND DISTANCES (IN Å) AND ANGLES (IN DEGREES) IN BORON TRIFLUORIDE ADDUCTS

Compound	B—N	B—F	N—C_{CH_3}	F-B-F	F-B-N	B-N-C	Reference
H_3NBF_3	1.60	1.38	—	111	107	—	(*399, 400*)
$MeNH_2BF_3$	1.57	1.39	1.50	110.5	108.5	114	(*277, 400*)
Me_3NBF_3	1.585	1.39	1.50	107	112	105	(*277, 400*)
$MeCNBF_3$	1.635	1.33	—	114	103	—	(*400, 401*)
$C_5H_5NBF_3$	1.53	1.41	1.36	109.5	108.5	—	(*879*)

Very few amine adducts of boron trifluoride have been studied structurally by X-ray diffraction on single crystals, the results being summarized in Table VIII. In those adducts with strong donor molecules (ammonia and the amines), it can be seen that the disposition of groups around the boron atom is reasonably close to the tetrahedral, as expected if the boron were to use pure sp^3 orbitals for bond formation. Probably because of the inductive effect of the methyl group, the strengths of amine-boron trifluoride adducts are in the order $NMe_3 > NHMe_2 > NH_3Me > NH_3$, as deduced from the ^{19}F n.m.r. chemical shifts (*388*); this would be expected to cause a slight elongation of the B—N bond length along the series $NMe_3 \rightarrow NH_3$, but unfortunately the errors in the X-ray measurements (between ±0.015 and ±0.03 Å) tend to conceal subtle changes of this nature. The B—F bond distance is virtually constant in the amine adducts; however, if a weak donor molecule such as methyl cyanide is used, marked changes occur in the geometry of the boron trifluoride adduct. The angle F—B—F increases to 114° and so makes the boron lie closer to the plane of the three fluorine atoms (indicating a smaller deformation of the original boron trifluoride molecule); the decreased B—F distance no doubt signifies a certain amount of π-bonding between boron and fluorine, while another significant factor is the increased B—N bond length. In keeping with these structural properties, which suggest a weak complex, methyl cyanide-boron trifluoride is partially dissociated in nitrobenzene solution at room temperature (*583*) and completely dissociated in the vapor state at 50°; the methyl cyanide is also readily displaced by several amines. The short B—N bond length (1.53 Å) in pyridine-boron trifluoride is apparently at variance with n.m.r. data (*123*), which suggests that trialkylamines form stronger complexes with boron trifluoride than does pyridine.

A boronium salt is thought to be formed when pyridine is added to a solution of dimethylamine-boron trichloride (*636, 656*),



$$C_5H_5N + Me_2NHBCl_3 \longrightarrow \left[\begin{matrix}C_5H_5N\\ Me_2NH\end{matrix} > BCl_2\right]^+ Cl^-$$

but the evidence (*102*) put forward to suggest, although the authors agreed it did not prove, that dimethylamine-boron trichloride is ionic (either as $Me_2NHBCl_2^+Cl^-$ or $(Me_2NH)_2BCl_2^+BCl_4^-$) would seem to be less convincing now that the compound Et_2NHBCl_3 has been shown (*290*) to closely resemble the simple adduct triethylamine-boron trichloride in its chemical properties and, like Me_2NHBCl_3 (*320*), to have a very low electrical conductivity in solution.

The substitution of silyl, disilanyl, or methylsilyl groups (i.e., SiH_3, SiH_2SiH_3, $MeSiH_2$ or Me_3Si) onto nitrogen in place of alkyl drastically alters the chemistry of the ensuing reactions from that expected by a study of the organoamines. Unlike the organoamines, which do not undergo N—C bond cleavage on reaction with the boron halides, the silylamines undergo a very facile N—Si cleavage often with such rapidity that the initial complexes (should they be formed) cannot be isolated except in a few cases (*2, 67, 134, 167, 221, 630, 676, 805*). An excellent example is the reaction of bis(trimethylsilyl)amine, $(Me_3Si)_2NH$, with boron trichloride, which can give a 30% yield of *B*-trichloroborazine (*630*),

$$3BCl_3 + 3(Me_3Si)_2NH \rightarrow (BClNH)_3 + 6Me_3SiCl$$
$$\text{(also for } BBr_3 \text{ and } BI_3)$$

while under other conditions only one trimethylsilyl group is cleaved from the nitrogen (*67*),

$$(Me_3Si)_2NH + BCl_3 \rightarrow Me_3SiCl + Me_3SiN(H)BCl_2$$

neither case resembling the analogous dialkylamine/boron trichloride reaction:

$$R_2NH + BCl_3 \rightarrow R_2NHBCl_3 \rightarrow HCl + R_2NBCl_2$$

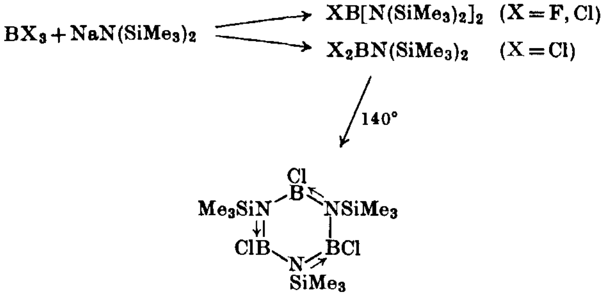
Trimethylsilyldialkylamines, Me_3SiNR_2, also undergo N—Si cleavage when treated with boron trichloride, tribromide, or triiodide, a 1:1 adduct being formed at − 78° when the trichloride is used (*5*, *630*), e.g.:

$$Me_3SiNMe_2 + BCl_3 \xrightarrow{-78^\circ} Me_3Si(Me)_2NBCl_3 \rightarrow Me_2NBCl_2 + Me_3SiCl$$

Similar reactions occur when trichlorosilyldimethylamine (*352*, *353*) and trimethylsilyldiethylphosphine (*655*) are employed:

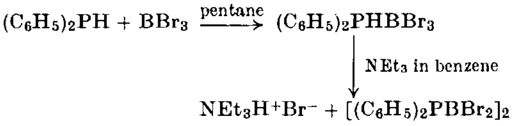
$$Cl_3SiNMe_2 + BF_3 \rightarrow Cl_3SiNMe_2BF_3 \longrightarrow Cl_3SiF + Me_2NBF_2$$
$$Me_3SiPEt_2 + BX_3 \rightarrow Me_3Si(Et)_2PBX_3 \xrightarrow{\text{heat}} Me_3SiX + [Et_2PBX_2]_n$$
$$(X = F, Cl, Br;\ n = 2 \text{ when } X = Cl, Br)$$

It is possible to make several of the silylaminoboron halides by employing a sodium salt coupling reaction in diethyl ether (*309*):



Some tertiary amine ligands, notably pyridine and triethylamine, will add 2 moles of a boron trihalide at low temperatures to form unstable solids, base • $2BX_3$ (*115*), which are considered to contain a single halogen bridge between the boron atoms: base • $X_2B—X—BX_3$. Indirect evidence from n.m.r. studies on boron trifluoride/pyridine mixtures in toluene also indicates the formation of these 1:2 adducts (*123*). An alternative explanation of the bonding in the case of similar ether • $2BX_3$ adducts is that the two trihalide molecules *may* be accommodated by the two lone pairs on the oxygen atom; however, this fails to account for $Et_2O \cdot 3BF_3$ in which at least one of the second and third boron trifluoride molecules must be assumed to bond in the same way as the above amine $\cdot 2BX_3$ adducts (*865*). Several examples are known in which an adduct contains more than 1 mole of base per mole of boron trihalide; thus ammonia and boron trifluoride have been shown to form BF_3NH_3, $BF_3(NH_3)_2$, $BF_3(NH_3)_3$, and $BF_3(NH_3)_4$ at low temperatures (*111*). In almost every case it is possible to assume that the excess of ligand is held to the 1:1 adduct via hydrogen-bond formation. Such behavior has been shown to occur, for example, in the alcoholates, hydrates, and carboxylic acid derivatives of boron trifluoride [(*330, 817*); see also page 79 and Bang and Carpenter (*37*)].

The alkyl-substituted phosphines react with boron trifluoride in a similar fashion to the corresponding amines, except that the complexes formed are less stable (*103*) and tend to dissociate readily; the base strength of a series of phosphines toward boron trifluoride has been shown to be $Me_3P > Me_2PH > MePH_2$ (*103*). A gas phase kinetic study of the reaction between boron trifluoride and trimethylphosphine indicated that about one collision in fifteen is fruitful in giving the adduct Me_3PBF_3 (*448*). Diphenylphosphine forms 1:1 complexes with boron tribromide and triiodide, which readily lose hydrogen halide when refluxed with a tertiary amine (*274, 276*),



$$\begin{tikzcd}(C_6H_5)_2PH + BBr_3 \arrow[r, "\text{pentane}"] & (C_6H_5)_2PHBBr_3 \arrow[d, "NEt_3\text{ in benzene}"] \\ & NEt_3H^+Br^- + [(C_6H_5)_2PBBr_2]_2\end{tikzcd}$$

while triphenylphosphine gives a stable 1:1 adduct with boron trifluoride (*671*), trichloride (*708*), tribromide (*274, 276*), and triiodide (*274, 598*). Nitrogen compounds form more stable adducts with the boron trihalides than the corresponding phosphorus derivatives because of the decreasing electronegativity of the elements down Group V. Hence, the nonexistence of triphenylamine-boron trifluoride (*770*) must be due to steric interaction involving the phenyl groups; a similar effect is found in Group VI where the diphenylsulfide complex of boron trichloride is found to be more stable than the diphenyletherate (*686*). As expected, the base strength of the trimethyl derivatives of Group V decreases down the group, so that trimethylarsine forms a comparatively weak complex with boron trifluoride whereas trimethylstibine does not give a complex even at −78° (*187*). With the stronger Lewis acid boron trichloride, trimethylphosphine forms a very stable adduct (*708*).

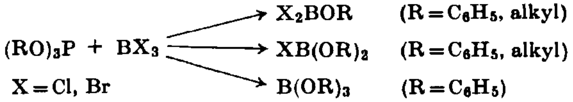
Dimethylaminophosphines, $(Me_2N)_nPMe_{3-n}$, undergo a slow reaction with boron trifluoride and trichloride in which the dimethylamino groups are cleaved from the phosphorus:

$$(NMe_2)_nPMe_{3-n} + nBX_3 \rightarrow nMe_2NBX_2 + Me_{3-n}PX_n$$
$$(n = 3, 2, 1)$$

When the chloride is used, side reactions also occur due to the formation of rather unstable 1:1 complexes between methylchlorophosphines and boron trichloride (*418*):

$$Me_2PCl + BCl_3 \rightarrow Me_2PClBCl_3$$
$$MePCl_2 + BCl_3 \rightarrow MePCl_2BCl_3$$

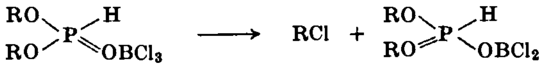
Alkoxy and aryloxy groups bound to phosphorus in the alkyl/aryl phosphites are similarly transferred to boron when the phosphite and boron trihalide are mixed (*259*, *260*, *299*):



$$\text{cf. } (CF_3)_2AsOR + BF_3 \longrightarrow 1:1 \text{ adduct} \longrightarrow (CF_3)_2AsF + ROBF_2 \quad (139)$$

Cleavage reactions apparently also occur when boron trifluoride and phosphites are mixed together, but the products were not studied (*829*).

The dialkylhydrogen phosphites (*68*) form 1:1 complexes when treated with boron trichloride, the donor site being the oxygen atom; decomposition of these complexes occurs by loss of alkyl chloride:



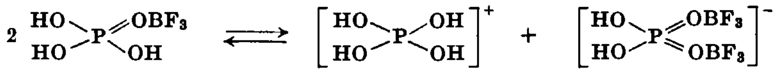
When diphenylhydrogen phosphite is used, hydrogen chloride is evolved from the complex instead of chlorobenzene (*68*):

$$(C_6H_5O)_2P(H)OBCl_3 \rightarrow HCl + (C_6H_5O)_2P\text{—}O\text{—}BCl_2$$

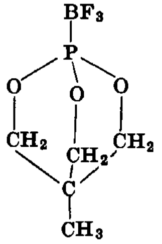
Trialkyl phosphates, after first forming 1:1 adducts at low temperatures, readily eliminate alkyl chloride, hydrogen chloride, and olefin when treated with boron trichloride; strong heating toward the end of the reaction gives a product resembling boron phosphate (*261*, *282–284*):

$$OP(OR)_3 + BCl_3 \xrightarrow{-70°} (RO)_3POBCl_3 \xrightarrow{-RCl} BPO_4$$
$$(R = Me, Et, n\text{-}Pr, iso\text{-}Pr, n\text{-}Bu, s\text{-}Bu, iso\text{-}Bu)$$

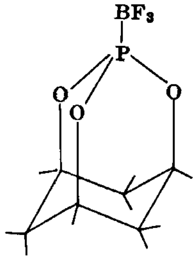
Free phosphoric acid reacts in a 1 : 1 ratio with boron trifluoride to form a complex that conductance measurements have shown to be highly ionized in the liquid state (*342*):



Triaryl phosphates form 1 : 1 complexes, $(RO)_3PO—BX_3$, when treated with boron trifluoride, trichloride, and tribromide. The substitution of one, or two, chlorine atoms in group R (e.g., R = $4\text{-}ClC_6H_4$ or $2,4\text{-}Cl_2C_6H_3$) is sufficient to depress the basicity of the phosphate below that required for complex formation with the trifluoride, although adducts are formed with the two stronger acceptors (*261*). Boron trifluoride forms 1 : 1 complexes with the two polycyclic phosphites $C_5H_9O_3P$ and $C_6H_9O_3O$ (*389*, *828*, *829*):

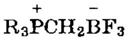


$C_5H_9O_3PBF_3$

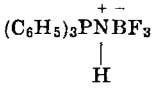


$C_6H_9O_3PBF_3$

The acid strength for several Lewis acids toward these cyclic phosphites was deduced to be $BH_3 > BMe_3 \cong BF_3$ from proton n.m.r. chemical shift measurements on the corresponding adducts (*829*). Methylenephosphoranes, R_3PCH_2 (*348*), and triphenylphosphinimine, $(C_6H_5)_3PNH$ (*17*), also give 1 : 1 adducts when reacted with boron trifluoride or boron trifluoride etherate:



$$R_3\overset{+}{P}CH_2\overset{-}{B}F_3$$



$$(C_6H_5)_3\overset{+}{P}\underset{\substack{|\\H}}{N}\overset{-}{B}F_3$$

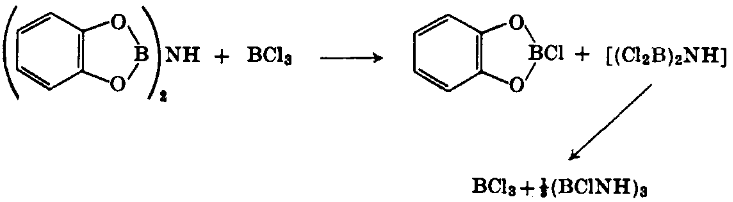
An adduct is first formed when bis(dimethylamino)diethylphosphinoborane, $(Me_2N)_2BPEt_3$, is treated with boron trichloride (*653*), but this readily decomposes at room temperature:

$$2(Me_2N)_2BPEt_2BCl_3 \rightarrow 2(Me_2N)_2BCl + [Cl_2BPEt_2]_2$$

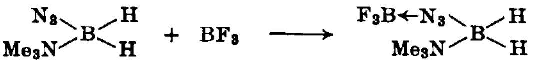
The reaction is reminiscent both of Burg's work on the dimethylamino-dimethylborane/boron trifluoride system (*130*),

$$Me_2NBMe_2 + BF_3 \xrightarrow{-78^\circ} Me_2NBMe_2BF_3 \xrightarrow{\text{warm}} Me_2BF + Me_2NBF_2$$

and of Lappert's on the reaction of boron trichloride with a borylamine (*489*):



Another boron compound able to complex with a boron trihalide is trimethylamine-azidodihydridoborane, which adds on 1 mole of boron trifluoride, the azide group providing the donor site (*585*):



Similar adducts are formed between certain Group IV azides and boron tribromide (*812*):

The nitrogen atom of the cyanide group is an effective donor site; the addition of boron trifluoride to complex metal cyanides (*330*) (page 31) has already been discussed. Hydrogen cyanide and silver cyanide (*710*) may also be used as donor molecules for example toward boron tribromide, while the organonitriles form many complexes with the boron trihalides (see Table X). The complexes formed are rather weak, as shown by the fact that pyridine, tetrahydrofuran, and di-*n*-butyl sulfide will displace boron trichloride from its methyl cyanide adduct (*298*); however, methyl cyanide is a stronger base than 2-chloroethyl ether:

$$MeCN + (ClCH_2CH_2)_2OBCl_3 \rightarrow MeCNBCl_3 + (ClCH_2CH_2)_2O$$

The complexes formed by pentafluorophenyl cyanide are much weaker than the corresponding phenyl derivatives, the boron trifluoride complex being highly dissociated at room temperature while the trichloride complex exhibits a dissociation pressure of a few mm at 18° (*496*).

Silyl cyanide and trimethylsilyl cyanide give very unstable complexes with the boron trihalides, which readily eliminate the silyl halide (*231*)

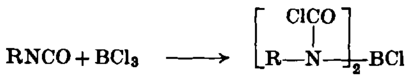
$$\mathrm{Me_3SiCN + BX_3 \rightarrow Me_3SiX + (CNBX_2)_{\mathit{x}}}$$
$$\mathrm{(X = F, Cl, Br)}$$

Due to a spontaneous decomposition, only in the case of X=F was it possible to isolate a specimen of pure $(\mathrm{CNBX_2})_x$:

$$\mathrm{(CNBF_2)_{\mathit{x}} \xrightarrow{heat} BF_3 + BC_3N_3\ (approx.)}$$

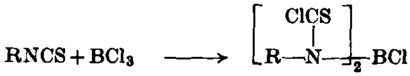
These solid chlorocyanides may well be related to the polymeric product $(\mathrm{CN})_3\mathrm{BCl}$ formed during the reaction between cyanogen and diboron tetrachloride (*19*).

Methyl isocyanide reacts with boron trifluoride to form a black tar with complete disruption of the organic molecule (*686*). Although phenyl isocyanate forms a weak complex with boron trifluoride (*483*), aryl isocyanates, and isothiocyanates generally undergo chloroboration when treated with boron trichloride (*483*):



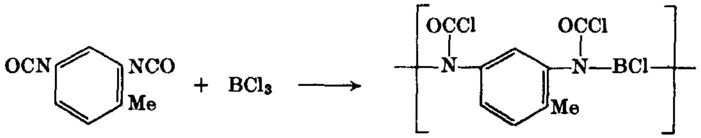
$$\mathrm{RNCO + BCl_3 \longrightarrow \left[R{-}\overset{ClCO}{\overset{|}{N}}{-}\right]_2BCl}$$

$(\mathrm{R = C_6H_5,\ \alpha\text{-}C_{10}H_7})$ (a diamidochloroborane)



$$\mathrm{RNCS + BCl_3 \longrightarrow \left[R{-}\overset{ClCS}{\overset{|}{N}}{-}\right]_2BCl}$$

When a diisocyanate is used, a polymeric product is formed (*483*):



7. *Reactions with Compounds of Group VI Elements*

At normal temperatures the free Group VI elements are inactive toward the boron trihalides, but oxygen and boron trifluoride in a discharge give the spectrum of the planar molecule $\mathrm{OBF_2}$ (*548*) and, when mixtures of oxygen and boron trichloride are irradiated with ultraviolet light (*456*) or sparked (*576*), boric oxide and chlorine are produced. Trichloroboroxine was an intermediate in the irradiation experiments and found to be fairly stable in the gas phase at room

TABLE IX

Tertiary Amine Adducts of the Boron Trihalides[a]

Amine	Reference to BF_3	Reference to BCl_3	Reference to BBr_3	Reference to BI_3	Reference when all trihalides studied
NMe_3	IR (*437*); NMR (*388*); NMR (*581*); Gen (*582*); Dip (*56*); Kin (*269*); Kin (*196*); X (*277, 400*); Gen (*133*)	NMR (*581*); IR (*437*); Dip (*56*); Gen (*582*)	IR (*437*); NMR (*581*); Dip (*56*); Gen (*582*)	—	NMR (*539*)
NEt_3	NMR (*388*); NMR (*123*); Gen (*731*); Gen (*688, 689*)	Gen (*290*)	Gen (*528*)	—	NMR (*270*)
NR_3 (R = aryl)	Gen (*441*)	Gen (*441*)	Gen (*441*)	—	—
$MeNR_2$ (R = aryl)	Gen (*686*)	—	—	—	—
(R = alkyl)	NMR (*186*)	—	—	—	—
Me_2NR (R = aryl)	Gen (*686*); Gen (*87*)	Gen (*87*)	Gen (*528*)	—	—
Pyridine	IR (*437*); IR, RAM (*516*); NMR (*123*); NMR (*270*); Dip (*56*); X (*879*); Cal (*114*); Cal (*108*); Kin (*449*)	IR (*437*); Dip (*56*); IR (*341*); NMR (*270*); NMR (*598*); Cal (*108*); Cal (*340*)	Cal (*340*); NMR (*270*); NMR (*598*); IR (*437*); Dip (*56*); Cal (*108*); Gen (*391*)	Gen (*598*)	—
4-R-pyridine	Cal (*109*)	IR (*437*); Dip (*56*) Dip (*55*)	IR (*437*); Gen (*170*)	—	—
2,6-R_2-pyridine	Cal (*114*); Cal (*107*)	—	—	—	—
2-R-pyridine	Cal (*107*)	—	—	—	—
3-R-pyridine	—	IR (*437*)	Gen (*391*)	—	—

[a] Cal = calorimetric study
IR = infrared spectral study
Ram = Raman spectral study
Kin = gas phase kinetics study
NMR = n.m.r. study
Dip = dipole moment study
X = X-ray crystal structure determination
Gen = general study

TABLE X

NITRILE ADDUCTS OF THE BORON TRIHALIDES[a]

R in RCN	Reference to BF_3	Reference to BCl_3	Reference to BBr_3	Reference to BI_3
Me	IR (*166*); IR (*57*); Cal, Dip (*491*); NMR (*583*); Gen (*702*)	IR (*166*); IR (*57*); IR (*292*); NMR (*583*); Cal, Dip (*491*); Gen (*298, 702*)	IR (*57*); NMR (*583*); Cal (*583*); Gen (*528*)	Gen (*598*)
Et	IR (*166*)	IR (*166*)	—	—
C_6H_5	IR (*166*); Cal (*110*); Gen (*364*)	Gen (*702*)	—	—
4-FC_6H_4	NMR (*808*)	NMR (*808*)	NMR (*808*)	—
MeC_6H_4 (2-, 3-, or 4-substituted)	Cal (*110*)	—	—	—
2,4,6-$Me_3C_6H_2$	Cal (*110*)	—	—	—
4-ClC_6H_4	Gen (*364*)	Gen (*364*)	—	—

[a] IR = infrared spectral study
NMR = proton or ^{19}F n.m.r. study
Cal = calorimetric or gas phase dissociation study
Dip = dipole moment study
Gen = general study

TABLE XI

PHYSICAL PROPERTIES OF THE DIBORON TETRAHALIDES

	B_2F_4	B_2Cl_4	B_2Br_4	B_2I_4
Melting point (°C)	-56.0 (*246*)	-92.6 (*826*) -92.95 (*507*)	0.5–1.5 (*208*)	—
Boiling point (°C)	-34 (*246*)	65.5 (*826*)	—	—
Vapor pressure relation for solid: $\log p_{\text{mm}} = A - \frac{B}{T}$ (T in °Abs)	$\left.\begin{matrix} A = 10.82 \\ B = 1856 \end{matrix}\right\}$(*246*)	—	—	Vapor pressure at 60°–70° is 10^{-3} mm (*757*)
Vapor pressure relation for liquid: $\log p_{\text{mm}} = A - \frac{B}{T}$ (T in °Abs)	$\left.\begin{matrix} A = 9.009 \\ B = 1446 \end{matrix}\right\}$(*246*)	$\left.\begin{matrix} A = 8.057 \\ B = 1753 \end{matrix}\right\}$(*826*)	Vapor pressure at 22.5° is 5.5 mm (*826*)	—
Trouton constant	28 (*246*)	23.7 (*826*)	—	—
Heat of evaporation (cal mole^{-1})	6700 (*246*)	8029 (*826*)	—	—
Infrared spectrum	(*243, 266*)	(*525*)	—	—
Raman spectrum	—	(*525*)	—	—
Heat capacity	—	Normal from 20° to 220°Abs (*507*)	—	—
Heat of fusion (cal mole^{-1})	—	2579 ± 4 (*507*)	—	—

TABLE XII

Olefin and Acetylene Addition Compounds of Diboron Tetrafluoride and Tetrachloride[a]

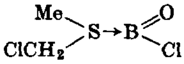
Olefin or acetylene used	Compound formed	M.P. (°C)	B.P. (°C)	A	B	H	Trouton constant	Ref.
C_2H_4	$B_2F_4C_2H_4$	−31.5	35	8.259	1656	7,550	24.4	(*149*)
C_2H_4	$B_2Cl_4C_2H_4$	−28.5	142	8.230	2220	10,140	24.4	(*149*, *824*)
$CH_3CH{=}CHCH_3$	$B_2F_4(CH_3CH)_2$	—	68	7.770	1667	7,600	22.3	(*149*)
$CH_3CH{=}CHCH_3$	$B_2Cl_4(CH_3CH)_2$	(variable)	171	8.147	2339	10,700	24.1	(*149*, *237*)
$CH_3CH{=}CH_2$	$B_2Cl_4CH_3CHCH_2$	−130	165	7.701	2105	9,600	22.1	(*149*)
1,3-Cyclohexadiene	—	—	—	—	—	—	—	(*878*)
trans-Di(*tert*-butyl)-ethylene	1:1 with B_2Cl_4	(liquid at room temp.)	—	—	—	—	—	(*878*)
Norbornalene	—	1–1.5	—	—	—	—	—	(*878*)
$HC{\equiv}CH$	$B_2F_4C_2H_2$	−81.7 to −82.6	15	8.565	1635	7,450	25	(*149*)
$HC{\equiv}CH$	$B_2Cl_4C_2H_2$	−129 to −130	144	7.666	1995	9,100	21.8	(*158*, *184*)
$HC{\equiv}CH$	$(B_2Cl_4)_2C_2H_2$	29–30	—	—	—	—	—	(*158*)
$C_{10}H_8$	—	46.5–47.5	—	—	—	—	—	(*255*, *877*, *878*)

[a] Vapor pressure equation: $\log_{10} p(\text{mm}) = A - \frac{B}{T}$; H = heat of vaporization in cal mole^{-1}.

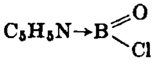
temperature but, on contact with glass, it decayed rapidly giving boric oxide, chlorine, and possibly boron trichloride. This mode of decomposition is in direct contrast to that described (page 37) for trichloroboroxine made from boric oxide and boron trichloride:

$$3BOCl \xrightarrow{\text{high temp.}} (BOCl)_3 \underset{\text{heat}}{\overset{\text{room temp.}}{\rightleftharpoons}} BCl_3 + B_2O_3$$

Several other papers are to be found in the literature that describe boron oxyhalides having considerable thermal stability. Thus boron trifluoride, when passed over heated boric oxide or silica, gave a solid product that was stable for days at room temperature but melted at about 80° with decomposition to boric oxide and boron trifluoride; the solid did not analyze accurately to $(BOF)_x$ and always contained more boric oxide than required (*522*). A similar stable boron oxyfluoride, approximating to B_2O_3F, has been obtained from the reaction of oxygen with diboron tetrafluoride (*414*), and a compound given the formula B_3O_4Br has been mentioned as appearing among the decomposition products of methoxyboron dibromide (*314*). The true position is far from clear; BOX and $(BOX)_3$ are definite, unstable entities that can be studied only by mass spectrometry or by infrared spectroscopy at low temperature, but apparently there are other B—O—X species (containing less halogen than oxygen) that have radically different properties and appear to be fairly stable at room temperature. Obviously further work is required on the problem to determine if these latter substances are more than solutions of boron trihalide in boric oxide [see Hofmeister and van Wazer (*402*)]. It has been shown to be possible to stabilize the BOCl monomer by complex formation:



(*488*)



(*473*)

Boron triiodide burns on heating in air or oxygen, forming copious clouds of iodine, and with sulfur, either molten or in solution, boron sulfide is produced (*576*).

Dioxygen difluoride, O_2F_2, reacts with boron trifluoride to give dioxygenyl tetrafluoroborate, $O_2^+BF_4^-$ (*784*), while sulfur tetrafluoride forms a 1 : 1 compound recently shown, by an X-ray structure determination, to be a salt $SF_3^+BF_4^-$ (*145*); neither the corresponding chloro compound SCl_4BCl_3 nor SCl_2BCl_3 can be isolated (*649*). Disulfur decafluoride fluorinates boron trichloride (*167*):

$$S_2F_{10} + BCl_3 \rightarrow SF_5Cl + BF_3 + Cl_2 + SF_6$$

but sulfur chloride-pentafluoride at room temperature (*536*) and the hexafluoride at 200° (*146*) are without reaction. Halogen interchange also occurs on heating sulfur monochloride and boron tribromide together (*250*).

When disulfur monoxide and boron trifluoride are mixed below −160°, a wine-colored complex is formed having the composition $S_2O \cdot nBF_3$ where $n = 2$ or 3, but on raising the temperature to −140°, to release any trapped boron trifluoride, the complex decomposes (*745*). By thermal analysis a 1 : 1 compound (m.p. −96°) has been shown to be formed when sulfur dioxide is mixed with boron trifluoride (*81*), but there is no evidence for the analogous SO_2BCl_3 (*527*) (contrary to earlier reports). This is one of the rare examples of a complex being known for boron trifluoride but not for the stronger Lewis acid boron trichloride (neglecting those cases where the latter undergoes cleavage reactions with the ligand without a complex being isolated), and it is noteworthy that these complexes [e.g., $NOBF_3$ (*409*) and SO_2BF_3] are extremely unstable and may not, therefore, contain "normal" donor-acceptor bonds; liquid sulfur trioxide and boron trifluoride give the compound $S_3O_8F_2$ (*498*). Sulfuryl fluoride (*83*) and thionyl tetrafluoride, SOF_4 (*762*), give unstable 1 : 1 compounds with boron trifluoride, but sulfuryl chloride and thionyl chloride gave no isolable adducts with either boron trifluoride or trichloride (*138*, *833*).

Boron trifluoride undergoes a certain amount of hydrolysis when dissolved in water (*378*) and an ^{19}F n.m.r. study of the solution showed that the following ions were probably present: BF_4^-, BF_3OH^-, $BF_2(OH)_2^-$, and $BF(OH)_3^-$ (*206*). With controlled amounts of water it is possible to isolate two hydrates, H_2OBF_3 and $(H_2O)_2BF_3$ (*332*, *700*) or D_2OBF_3 and $(D_2O)_2BF_3$ (*327*); conductance measurements on and electrolysis of the liquid hydrates suggest that some ionization occurs (*332*),

$$H_2OBF_3 \rightleftharpoons H^+_{\text{solvated}} + BF_3OH^-$$

$$(H_2O)_2BF_3 \rightleftharpoons H_3O^+ + BF_3OH^-$$

but an X-ray crystal structure determination (*37*) and an n.m.r. study (*251*) on the slowly crystallized solid dihydrate both support the presence of a molecular complex H_2OBF_3, the second water molecule being held by hydrogen bonds. It is only the 1 : 1 adducts of boron trifluoride that can add a second molecule of ligand by hydrogen bonding (e.g., ligand = MeCOOH, ROH, H_2O), since the other boron trihalides readily undergo a loss of hydrogen halide with ligand hydrogen atoms polar enough to form hydrogen bonds. Thus, water causes the rapid hydrolysis of the other trihalides,

$$BX_3 + H_2O \rightarrow B(OH)_3 + 3HX$$

and an excess of water added rapidly to, say, boron trichloride held at room temperature in a confined apparatus can cause an explosion due to the violence of the hydrolysis.[8]

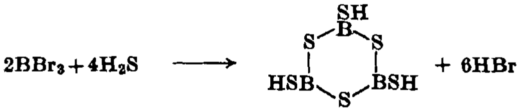
Hydrogen sulfide forms a 1 : 1 adduct with boron trifluoride that is considerably dissociated at its melting point, −137° (*81, 278*), this being a reflection of the greatly decreased Lewis basicity of hydrogen sulfide compared to water. The less reactive nature of the hydrogen atoms in hydrogen sulfide allows the formation at low temperature of a 1 : 1 complex (m.p. −35.3°) with boron trichloride (*527*), but at higher temperatures hydrogen chloride is evolved; boron tribromide reacts in a similar way (*862*):

$$3BX_3 + 3H_2S \rightarrow 6HX + (BXS)_3$$

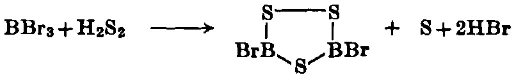
As with the oxygen analogs (page 37), the thioboroxines can be made by mixing trisulfide with a boron trihalide (*528, 842*):

$$BX_3 + B_2S_3 \rightarrow (BXS)_3$$

If an excess of hydrogen sulfide is used, all the halogen is removed from boron (*862*):



Hydrogen disulfide reacts with boron tribromide in carbon disulfide to form a five-membered sulfur-boron ring system (*752*):



(a 1,2,4-trithia-3,5-diborolane)

Alcohols form 1 : 1 and 2 : 1 (ROH:BF$_3$) adducts with boron trifluoride (*817*), which conductivity and electrolytic studies suggest are ionized (at least partially) in the liquid state (*330, 336*),

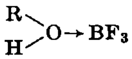
$$ROHBF_3 \rightleftharpoons H^{+}_{\text{solvated}} + ROBF_3^{-}$$

$$(ROH)_2BF_3 \rightleftharpoons ROH_2^{+} + ROBF_3^{-}$$

---

[8] An account has recently been given in the daily newspapers (see, for example, *The Guardian*, June 2, 1966) of a physicist being killed in a severe explosion resulting from the hydrolysis of boron tribromide.

although n.m.r. studies suggest that a molecular complex,



$$\mathrm{R(H)O \rightarrow BF_3}$$

is formed to which the second alcohol molecule is bound via hydrogen bonds (*206*, *207*). In a mixture of two alcohols at low temperature, two sharp ^{19}F n.m.r. signals can be observed due to $ROHBF_3$ and $R'OHBF_3$, and measurements of the respective peak areas allow a calculation of the equilibrium constant. As the temperature is raised, the signals broaden and begin to merge into one peak due to exchange of the boron trifluoride between the alcohol molecules. From a series of equilibrium studies using pairs of alcohols, it is possible to establish the donor strength series $H_2O > MeOH > EtOH > n\text{-}PrOH > n\text{-}BuOH$ toward boron trifluoride (*207*), which is the order of steric requirements of the various alcohols.

Two methyl proton resonances occur in the n.m.r. spectrum of sulfur dioxide solutions of boron trifluoride containing an excess of methyl alcohol, due to exchange processes between $MeOHBF_3$ and MeOH and between $(MeOH)_2BF_3$ and MeOH. Using the stoichiometry of the reaction mixtures and the relative areas under these two peaks, it proved possible to calculate an equilibrium constant of roughly 3 for the reaction:

$$\mathrm{MeOHBF_3 + MeOH \rightleftharpoons (MeOH)_2BF_3}$$

When an excess of boron trifluoride was used, all the methyl alcohol was shown to be present as the 1 : 1 complex (*695*).

The other trihalides react readily with alcohols and evolve hydrogen halide at low temperature (*223*, *280*, *288*, *295*, *476*, *477*, *793*):

$$\begin{aligned}\mathrm{BX_3 + ROH} &\rightarrow \mathrm{ROBX_2 + HX}\\ \mathrm{BX_3 + 2ROH} &\rightarrow \mathrm{(RO)_2BX + 2HX}\\ \mathrm{BX_3 + 3ROH} &\rightarrow \mathrm{(RO)_3B + 3HX}\end{aligned}$$

(R = primary or secondary alkyl; allyl; methallyl; ω-chloroalkyl)

The alkoxyboron halides are sometimes unstable (e.g., $ROBX_2$ where R = secondary or tertiary alkyl, X = Cl; and $(RO)_2BX$ where R = electron-releasing group, X = Cl) and in such cases the products are the alkyl halides and a boroxine:

$$\begin{aligned}\mathrm{ROBX_2} &\rightarrow \mathrm{RX + [BOX] \rightarrow BX_3 + B_2O_3} && (288)\\ \mathrm{(RO)_2BCl} &\rightarrow \mathrm{RCl + (ROBO)_3 \rightarrow B(OR)_3 + B_2O_3} && (288)\\ \mathrm{(MeO)_2BBr} &\rightarrow \mathrm{(MeO)_3B_3O_3 + MeBr} && (314)\end{aligned}$$

Tertiary alcohols (and $C_6H_5CH_2OH$ or $C_6H_5(CH_3)CHOH$) give the alkyl chloride and boric acid when treated with boron trichloride (*288*),

$$\mathrm{BCl_3 + 3ROH \rightarrow 3RCl + B(OH)_3}$$

but in the presence of pyridine it is possible to form the borates of these and other alcohols (*288*, *473*):

$$BCl_3 + 3ROH + 3C_5H_5N \xrightarrow[\text{solvent}]{\text{inert}} 3C_5H_5NHCl + B(OR)_3$$

Group exchange reactions may be used to obtain alkoxyboron dihalides and dialkoxyboron halides (*288*):

$$B(OR)_3 + 2BX_3 \rightarrow 3ROBX_2$$
$$2B(OR)_3 + BX_3 \rightarrow 3(RO)_2BX$$

Under forcing conditions, using heat and pyridine to remove the hydrogen halide formed, it is possible to obtain alkyl borates from boron trihalide adducts:

$$C_5H_5NBCl_3 + 2C_5H_5N + 3ROH \xrightarrow[\text{solvent}]{CHCl_3\text{ as}} B(OR)_3 + 3C_5H_5NHCl \qquad (288)$$
$$4BF_32ROH + 3C_5H_5N \rightarrow B(OR)_3 + 5ROH + 3C_5H_5NHBF_4 \qquad (793)$$

Polyfluoroalkyl-substituted methyl alcohols have also been used to prepare borates (*9*, *470*, *755*),

$$3R_FCH_2OH + BCl_3 \rightarrow (R_FCH_2O)_3B$$
$$[R_F = \text{perfluoroalkyl; } H(CF_2CF_2)_n]$$

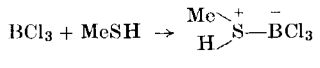
but the fully fluorinated borates cannot be made in this manner because the corresponding alcohols, R_FOH, are unknown. The recently obtained sodium perfluoromethoxide may prove to be of value in the preparation of perfluoromethoxyboron compounds using reactions such as:

$$BX_3 + 3NaOCF_3 \rightarrow 3NaX + B(OCF_3)_3$$

or

$$\text{ligand-}BX_3 + 3NaOCF_3 \rightarrow \text{ligand-}B(OCF_3)_3 + 3NaX$$

The decreased reactivity of the proton in the alkyl mercaptans, RSH, allows the formation of a boron trichloride adduct at low temperature,



$$BCl_3 + MeSH \rightarrow {}^{Me}_{H}\!\!>\overset{+}{S}-\overset{-}{B}Cl_3 \qquad (323)$$

but above about −20° hydrogen chloride is eliminated:

$$2MeSHBCl_3 \rightarrow 2HCl + (MeSBCl_2)_2$$

Even in the presence of excess methylmercaptan the remaining B—Cl bonds are not substituted (*323*). The reaction proceeds further, however, if the tribromide is used (*323*):

$$\begin{tikzcd} BBr_3 + MeSH \arrow[r] & MeSBBr_2 \arrow[r] & (MeS)_2BBr \arrow[d] \\ & & (MeS)_3B + MeSBBr_2 \end{tikzcd}$$

Better yields of the alkylthioborates are obtained if an amine is used to remove the hydrogen halide (*698*),

$$BX_3 + 3RSH + 3A \rightarrow (RS)_3B + 3A{\cdot}HX$$
$$(X = Cl, Br;\ R = Me,\ n\text{-amyl};\ A = \text{amine})$$

or if the corresponding lead mercaptide is added to a boron trihalide:

$$3Pb(SR)_2 + 2BX_3 \rightarrow 3PbX_2 + 2B(SR)_3$$
$$(X = Cl,\ R = n\text{-Bu};\ X = Br,\ R = Me)$$

Again, group exchange reactions have been used to form mercaptoboron chlorides (*288*):

$$B(SR)_3 + 2BCl_3 \rightarrow 3RSBCl_2$$
$$2B(SR)_3 + BCl_3 \rightarrow 3(RS)_2BCl$$

Hydroperoxides react with boron trichloride in a similar manner to alcohols, eliminating hydrogen chloride to give peroxyborates (*199*):

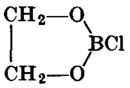
$$BCl_3 + 3ROOH \rightarrow 3HCl + (ROO)_3B$$
$$(R = n\text{-Bu},\ t\text{-Bu})$$

However, peroxy acids do not form peracylboron compounds and peroxycaprylic acid, for example, gives caprylic acid, boric oxide and chlorine (*199*). Dialkyl peroxides, in contrast to ethers, undergo a vigorous and complex reaction when added to boron trichloride, producing hydrogen chloride, boric acid, and olefin (*199*).

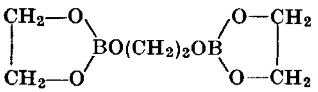
Polyhydroxy alcohols form stable complexes with boron trifluoride (*817*) but evolve hydrogen chloride on reaction with boron trichloride (*288*). Thus the reaction of ethylene glycol with the trichloride can be made to produce all the expected borates and alkoxyboron chloride by a suitable manipulation of the reaction ratios (glycol:BCl_3):

$Cl_2BO(CH_2)_2OBCl_2$

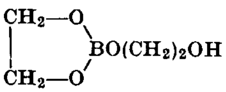
(1:2)



(1:1)



(2:3)

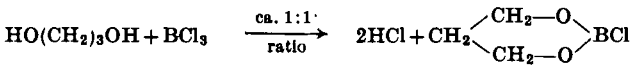


(2:1)

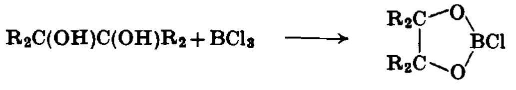
$B(OCH_2CH_2OH)_3$

(3:1)

Similar boron heterocycles are formed when trimethylene glycol and the pinacols are mixed with boron trichloride:

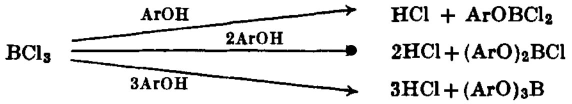


(244)



(240)

Both a 1:1 and a 2:1 complex (phenol:BF_3) are formed when boron trifluoride and phenol interact (*687*, *817*), but boron trichloride readily loses hydrogen chloride when treated with most phenols (*169*, *288*, *793*):

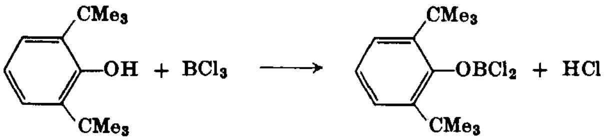


$$BCl_3 \xrightarrow{ArOH} HCl + ArOBCl_2$$
$$BCl_3 \xrightarrow{2ArOH} 2HCl + (ArO)_2BCl$$
$$BCl_3 \xrightarrow{3ArOH} 3HCl + (ArO)_3B$$

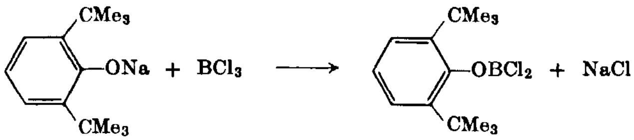
The usual group exchange reactions are also applicable to the formation of aryloxyboron halides (*169*, *288*, *403*):

$$2BX_3 + (ArO)_3B \rightarrow 3ArOBX_2$$
$$BX_3 + 2(ArO)_3B \rightarrow 3(ArO)_2BX$$

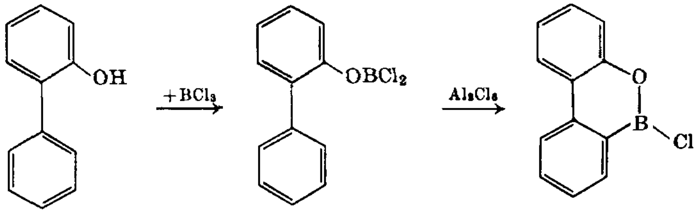
The use of metallic alkoxides or phenoxides in the production of borates has been referred to previously (page 33). In certain cases this has proved a superior method to the straight reaction of alcohols or phenols with boron trichloride. Thus the reaction



does not take place, probably due to steric interaction, but the sodium salt reacts smoothly in toluene at −60° (*794*):

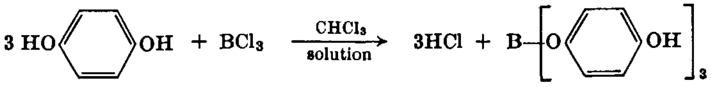


Formation of an aryloxyboron dichloride followed by a Friedel-Crafts reaction has resulted in the successful isolation of several boron heterocycles, e.g. (*204*, *523*):

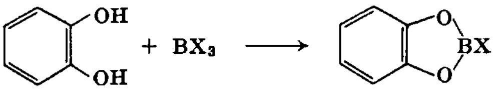


9-Chloro-9,10-boroxarophenanthrene

Polyhydroxyphenols can react to give monomeric aryl borates or aryloxyboron halides when treated with boron trichloride or tribromine,

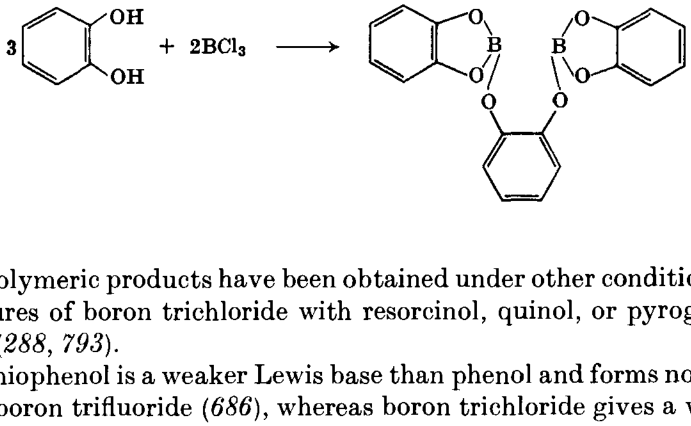


(*634*)



(*289*)

(X = Cl, Br)



(*289*)

but polymeric products have been obtained under other conditions when mixtures of boron trichloride with resorcinol, quinol, or pyrogallol are used (*288*, *793*).

Thiophenol is a weaker Lewis base than phenol and forms no adducts with boron trifluoride (*686*), whereas boron trichloride gives a weak 1 : 1 complex that is fully dissociated at 25° (*509*, *686*). On refluxing a mixture of this phenol and boron trichloride in benzene, a smooth evolution of hydrogen chloride occurs and the thioborate is produced (*509*, *875*):

$$3C_6H_5SH + BCl_3 \rightarrow (C_6H_5S)B + 3HCl$$

Boron tribromide may also be used in this reaction (*793*). The use of an amine to remove hydrogen halide has been suggested when making the thioborate from boron triiodide (*698*),

$$BI_3 + C_6H_5SH + n\text{-}PrNH_2 \rightarrow B(SC_6H_5)_3 + n\text{-}PrNH_3Cl$$

or triethylsilyl borates from boron trichloride (*10*):

$$3Et_3SiOH + BCl_3 + 3C_5H_5N \rightarrow (Et_3SiO)_3B + 3C_5H_5NHCl$$

Better yields of the silyl borate are obtained if the sodium salt of triethylsilanol is used,

$$3Et_3SiONa + BX_3 \rightarrow 3NaX + (Et_3SiO)_3B$$

$$[X = Cl\ (\mathit{10}),\ Br(\mathit{857})]$$

but only boric acid is produced when triethylsilanol reacts with boron tribromide in the absence of an amine (*857*):

$$BBr_3 + 3Et_3SiOH \rightarrow B(OH)_3 + 3Et_3SiBr$$

Many ethers complex readily with boron trifluoride to give 1:1 adducts (*330*, *817*), but the substitution of fluorine in the alkyl chain, as in perfluoroethyl ether and cyclo-C_4F_8O (*866*), or the substitution of two aryl groups for alkyl, as in diphenyl ether (*380*), so reduces the base strength of the ether that no complexes can be formed. Normally the 1:1 adducts are stable toward an ether-cleavage reaction to give the alkoxyboron difluoride, but isopropyl ether–boron trifluoride has been shown to decompose in this manner above 50° (*104*),

$$(iso\text{-}Pr)_2OBF_3 \rightarrow iso\text{-}PrF + iso\text{-}PrOBF_2$$

and diborane made from diethyl ether–boron trifluoride contains small amounts of ethyl fluoride (although it was suggested that the ethyl fluoride arose from attack of active fluorine or fluorine atoms on the ether solvent) (*197*); irreversible decompositions of the adducts Me_2OBF_3 and Et_2OBF_3 have also been mentioned (*380*, *689*) but no details were given. Conductivity measurements and electrolytic studies on liquid diethyl ether–boron trifluoride indicate that the complex may partially ionize either as ethyl ethoxytrifluoroborate, $Et^+EtOBF_3^-$ (*337*), or as $[BX_2OEt_2]^+$ with BF_4^- and F^- as the anions (*772*).

Cyclic ethers also form 1:1 complexes with boron trifluoride (*69*, *123*, *567*, *865*), but with the small-ring ethers (ethylene oxide, trimethylene oxide, furan, and tetrahydrofuran) there is also a tendency toward polymerization in the presence of boron fluoride; for example, a mixture of 0.5 mole of boron trifluoride and 1.0 mole of tetrahydrofuran has been found to gel within a few minutes at room temperature (*686*). The glymes (dimethyl ethers of polyethylene glycols) form stable adducts with boron trifluoride that show no signs of cleavage even after 6 months at room temperature (*115*).

At low temperatures the 1 : 1 etherates will absorb a further one (or, in the case of $Et_2O \cdot BF_3$, two) mole of boron trifluoride (*865*) to form complexes that probably contain single fluorine bridges: $R_2OBF_2—F—BF_3$ (see page 68); the excess boron trifluoride is readily lost at temperatures well below 0° to leave the original 1 : 1 adducts.

It has been shown by ^{19}F and ^{1}H n.m.r. studies that, when boron trifluoride is dissolved in a mixture of two ethers (*190*, *728–730*) or is dissolved in an inert solvent containing a single ether (*123*, *312*), a rapid exchange of the trifluoride between the ether molecules occurs, the mean lifetime of an ether complex at room temperature being of the order of 10^{-4} second. When the temperature in the mixed-ether system is lowered the exchange rate slows down, and the ^{19}F n.m.r. peak (which was originally sharp) begins to broaden and then to separate into two peaks due to R_2OBF_3 and $R_2'OBF_3$ (*728*, *729*). The equilibrium constant of the reaction

$$R_2OBF_3 + R_2'O \rightleftharpoons R_2'OBF_3 + R_2O$$

can then be calculated from the areas under the two n.m.r. peaks (the area under a peak being proportional to the amount of the species in the mixture that is responsible for that particular absorption peak) and a knowledge of the original mixture composition. In this way it was shown that dimethyl ether forms a more stable etherate with boron trifluoride than does diethyl ether (*729*).

At room temperature, measurements on the chemical shifts of either the single ^{19}F resonance or the protons in the ether molecules can also be used to calculate the equilibrium constant of the above reaction (the chemical shift of a nucleus in molecules involved in a rapid exchange reaction occurs at a position that is the weighted mean of the shifts in the two free molecules). From studies on several pairs of ethers, the following base strength series can be drawn up (*190*, *729*, *730*): $Me_2O > MeOE > Et_2O > C_6H_5OMe$. Typical values for some equilibrium constants are (at 26°):

$$Et_2OBF_3 + Me_2O \rightleftharpoons Et_2O + Me_2OBF_3 \qquad K = 3.3\ (\mathit{190})\ K = 2.5\ (\mathit{729})$$

$$EtMeOBF_3 + Me_2O \rightleftharpoons EtOMe + Me_2OBF_3 \qquad K = 1.5\quad (\mathit{190})$$

The mechanism of these exchange reactions is believed not to involve an initial dissociation of the complex, since the energy of activation is less than the heat of formation of either of the complexes (*729*, *730*); the analogous boron trifluoride exchange taking place in solution of a single ether (*69*),

$$\overset{\bullet}{B}F_3 + R_2OBF_3 \xrightarrow[\text{solvent}]{\text{inert}} BF_3 + R_2O\overset{*}{B}F_3$$

is also considered to be a displacement reaction (*123*). The values of the equilibrium constant for the Et_2OBF_3/Me_2O exchange quoted above are close to that of 4.2, which can be calculated (*190*) from the *gas phase* dissociation data given by McLaughlin and Tamres for Me_2OBF_3 and Et_2OBF_3 (*566*).

The order of base strengths of ethers can also be deduced from pressure measurements on the reversible gas phase dissociation of the complexes, R_2OBF_3 (since the measurements allow the calculation of the heats of formation of the complexes). Thus tetrahydrofuran forms stronger complexes with boron trifluoride than tetrahydropyran (*567*), and an increase in alkyl chain length in acyclic ethers decreases the base strength probably due to steric influence, i.e., $Me_2O > Et_2O > (\text{iso-Pr})_2O$ (*104*, *566*).

Calculation of the equilibrium constants for the reaction

$$L_1 + L_2BF_3 \rightleftharpoons L_1BF_3 + L_2$$

$$(L_1, L_2 = \text{ether, alcohol, or dialkyl sulphide})$$

has been carried out, using known initial concentrations of reactants and obtaining a measure of the equilibrium concentration of both adducts from infrared spectral studies using Beer's law; the series obtained by this method is (*867*) THF > EtOH > tetrahydrofuran > MeOH > Me_2O EtOMe > propylene oxide > Et_2O > $(n\text{-Pr})_2O$ > $(\text{iso-Pr})_2O$ > tetrahydrothiophene > Et_2S. This is in agreement with the n.m.r. studies as far as the ethers are concerned, but the position EtOH > MeOH is in direct contrast to Diehl's n.m.r. work (*206*, *207*) on boron trifluoride dissolved in EtOH/MeOH mixtures; sulfur donors are weaker than the oxygen analogs, as expected from the electronegativity values O > S.

When the reaction

$$BF_3 + R_2O \rightleftharpoons R_2OBF_3$$

was studied in methylene dichloride solution by n.m.r., the ether basicities were found to be in the order $Et_2O > (\text{iso-Pr})_2O > Me_2O$ (*312*). As it is known that chloroform interacts strongly with boron trifluoride (*123*), the methylene dichloride may not have been as inert a solvent toward the trifluoride as was assumed by Gore and Danyluk, although Henry's law appears to be obeyed when the two compounds are mixed (*124*); however, this should not give rise to a different base strength series. These workers suggested that weak hydrogen bonding of the solvent to the alcohols may explain why their series was different from those obtained in other systems. (Solute–solvent interaction may account for the anomalous position of methyl and ethyl alcohols when the series given above was obtained from infrared measurements taken in benzene solution, as this might be expected to affect methyl alcohol to the greater extent.)

On coordination of an ether with boron trifluoride to form R_2OBF_3, simple n.m.r. theory suggests that the ^{19}F resonance of the adduct should move to higher field compared to boron trifluoride, since there is additional shielding due to the increased electron density on the boron atom; the stronger the donor molecule the greater will be the observed shift. This has been confirmed for the acyclic ethers and the dialkyl sulfides where the shifts are in agreement with the base strength series (*190*, *728*). Similarly, the hydrogen atoms attached to the α-carbon atom should experience a decreased shielding, and their resonance will move to lower field compared to the same protons in the free ether; the more basic the ether molecule, the more deshielded will be these protons and the greater should be the observed shift. In practice it is found that the shifts are in the order $Me_2O > MeOEt > Et_2O$ as predicted (*190*).

The 1 : 1 adducts formed by many ethers with boron trichloride and tribromide are unstable with respect to an ether-cleavage reaction:

$$ROR'BX_3 \rightarrow ROBX_2 + R'X$$

For example, boron trichloride readily forms a solid 1 : 1 adduct with diethyl ether at – 80° that regenerates ether on hydrolysis, indicating that the structure is $Et_2O \rightarrow BCl_3$ (*280*, *715*). The rather large n.m.r. chemical shift noted for the protons in diethyl ether–boron trichloride dissolved in methylene dichloride has been interpreted as evidence for an ionic formulation $Et^+[EtOBCl_3]^-$ (*312*), which receives some support from the high value of the equivalent conductance measured in the same solvent (being higher than that observed for liquid Et_2OBF_3) (*337*). However, the hydrolysis experiment appears to rule out the possibility of the ion $EtOBCl_3^-$ being present in large amounts, since this would be expected to produce ethyl alcohol on contact with water. Russian work (*772*) involving cryoscopy and conductivity measurements suggests that the species present in solutions of ether and boron trichloride (also BF_3 and BBr_3) are BCl_3OEt_2, $BCl_2OEt_2^+BCl_4^-$, and $BCl_2OEt_2^+Cl^-$, which could explain the large n.m.r. chemical shift and still be consistent with the hydrolysis experiments. The ionic forms of the adduct $Et^+EtOBCl_3^-$ may possibly be an intermediate (*288*) in the ether-cleavage reaction that takes place when the solid etherate melts at 56°:

$$Et_2OBCl_3 \rightarrow EtCl + EtOBCl_2 \qquad (715)$$

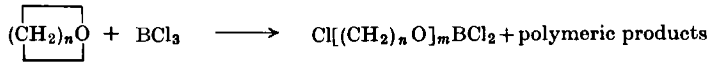
If the decomposition is carried out in the presence of an excess of ether, the ethoxyboron dichloride forms an unstable 2:1 etherate and then disproportionates (*715*):

$$2EtOBCl_2 + Et_2O \rightarrow Et_2O[B(OEt)Cl_2]_2 \rightarrow Et_2OBCl_3 + (EtO)_2BCl$$

In ether (*671*) or methylene dichloride (*312*) solution, the slow ether cleavage can be followed at room temperature by observing the build-up and decay of the various species by proton n.m.r.; the rapid disproportionation of ethoxyboron dichloride in the presence of ether was also confirmed by this method (*671*).

The presence of electron-attracting groups in an ether molecule reduces its basicity so that diphenyl ether gives only a very unstable etherate with boron trichloride (*380*) (contrary to earlier reports), and bis(chloromethyl) ether gives no adduct at all (*225*). However, chloromethylmethyl ether forms a 1:1 adduct, from which the ether can be displaced by pyridine and which gives butyl borate on treatment with *n*-butyl alcohol (*225*). When a mixed ether is cleaved on heating with boron trichloride (*225, 287, 295, 296*) or tribromide (*72*), the more electron-releasing group is found in the alkyl halide; similarly, boron trichloride dissolved in monoglyme (*364, 536*) or diglyme (*116*) causes a slow ether cleavage at room temperature, giving methyl chloride.

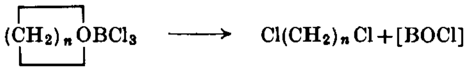
Boron trichloride reacts rapidly with cyclic ethers,[9] the products depending on the ring size. With tetrahydrofuran and tetrahydropyran, 1:1 adducts can be isolated (*223, 288*) but, with ethers having smaller rings, ring fission occurs even at −80° to form chloroalkoxyboron dichlorides when 1:1 ratios are used (*224, 288*),



$$(CH_2)_nO + BCl_3 \longrightarrow Cl[(CH_2)_nO]_mBCl_2 + \text{polymeric products}$$

$(n = 2, 3;\ m = 1, 2\ \ldots)$

Ring fission in the cases of the 1:1 adducts of tetrahydrofuran and tetrahydropyran with boron trichloride produces the α,ω-dichloroalkane (*288*), presumably due to the instability of the chloroalkoxyboron dichloride:

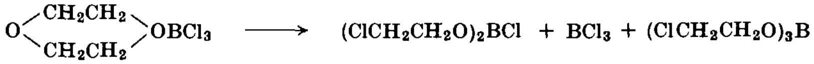


$$(CH_2)_nOBCl_3 \longrightarrow Cl(CH_2)_nCl + [BOCl]$$

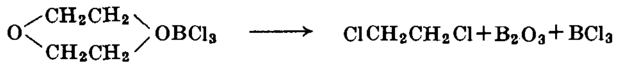
[9] However, the basicity of some ethers is so reduced by substituents that no reaction occurs with boron trichloride even on heating, e.g., perfluoro-1-butyltetrahydrofuran, $C_8F_{16}O$ (*815*).

With an excess of cyclic ether, the chloroalkyl borates are formed (*288*), e.g., with ethylene oxide:

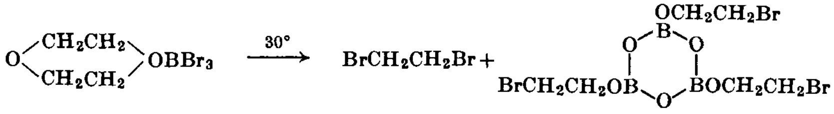
Cyclic diethers react in a similar manner with boron trichloride and tribromide. Dioxan forms a 1:1 complex with the trichloride, which undergoes ring fission when heated just above its melting point (*174*, *472*),



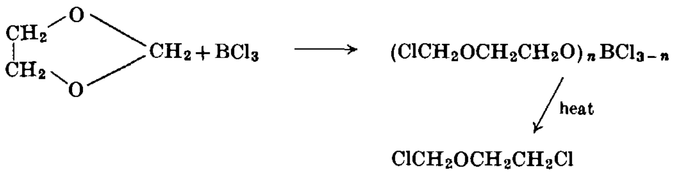
but, at higher temperatures (180°), 1,2-dichloroethane is produced (*174*):



The boron tribromide complex decomposes in a different manner, giving an alkoxyboroxine (*174*):



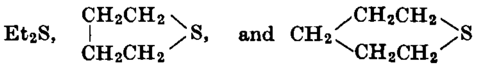
Ring fission and chlorine migration also occur when 1,3-dioxolan is treated with boron trichloride (*174*):



The expected 2:1 adducts of these two diethers with the boron trihalides could not be obtained, although at low temperature dioxan and boron trichloride formed a complex, $(C_4H_8O_2)_2 3BCl_3$, of unknown structure (*288*).

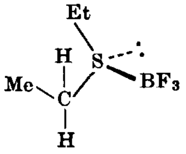
The dialkyls of the other members of Group VI are much less basic than the ethers, as shown by the fact that Me_2OBF_3 is 20% dissociated into its components at room temperature and 65 mm pressure while Me_2SBF_3 is more than 95% dissociated under the same conditions;

dimethyl selenide–boron trifluoride, although formed as a solid at −78°, is completely dissociated in the vapor at room temperature (*324*). This gives the base strength series as $Me_2O > Me_2S > Me_2Se$ toward boron trifluoride. Similarly, the adducts of boron trifluoride with



have been shown to be extensively dissociated at room temperature (*180*, *591*, *689*); $\overline{(CH_2)_2}S$ is polymerized in the presence of either boron trifluoride or trichloride (*591*). Diphenyl sulfide, like diphenyl ether, is too weak a base to react with boron trifluoride (*686*).

The distribution of groups around the sulfur atom in diethylsulfide–boron trifluoride can be assumed to be close to tetrahedral,



which will make the two protons in the methylene groups inequivalent; a similar inequivalence can be detected, for example, in the proton n.m.r. spectrum of the related complex Et_2SBH_3 (*186*). However, the proton n.m.r. of Et_2SBF_3 shows only a single quartet in the methylene region of the spectrum (*186*), which shows that the boron trifluoride, unlike the borane group, is rapidly exchanging between the two donor sites on the sulfur atom (*186*, *190*) or between different diethyl sulfide molecules; the lack of ^{19}F-^{11}B coupling also supports this conclusion.

The dialkyl sulfides and the two cyclic sulfides,

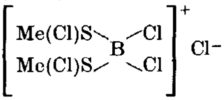
$$\overline{\underline{(CH_2)_4S}} \quad \text{and} \quad \overline{\underline{(CH_2)_5S}},$$

complex readily with boron trichloride to form 1 : 1 adducts that are stable toward irreversible decomposition (*288*, *474*, *591*, *708*); the trichloride and tribromide also give 1 : 1 adducts with dimethyl selenide (*873*). Diphenyl sulfide gives a more stable 1 : 1 complex than diphenyl ether when treated with boron trichloride (ΔH_f, $(C_6H_5)_2SBCl_3 = -8.7$ kcal/mole; ΔH_f, $(C_6H_5)_2OBCl_3 = -5.3$ kcal/mole) (*380*, *686*). Although this is the reverse of the stabilities predicted from electronegativity values, O > S, it can be explained by assuming a higher steric interaction in the case of the diphenyl ether complex. The presence of an α-chlorine atom in the alkyl chain of a sulfide decreases the stability of the boron trichloride adduct; thus chloromethylmethyl sulfide–boron trichloride has a dissociation pressure of 10 mm at 20° (*488*).

Ionic complexes are thought to be formed when tributylsulfonium chloride (*288*, *474*), methylsulfur chloride (*649*), and dimethylselenium dihalides (*873*) react with boron trichloride or tribromide:

$$(n\text{-Bu})_3SCl + BCl_3 \rightarrow (n\text{-Bu})_3S^+BCl_4^-$$

$$2MeSCl + BCl_3 \rightarrow$$



$$Me_2SeX_2 + BX_3 \rightarrow Me_2SeX^+BX_4^-$$

$$(X = Cl, Br)$$

The reaction of silylmethyl ether with the boron trihalides at low temperature gives the silyl halide and methoxyboron dihalide (*797*):

$$H_3SiOMe + BF_3 \xrightarrow{-96^\circ} H_3SiF + MeOBF_2$$

Disiloxane (disilyl ether) undergoes a typical ether-splitting reaction at low temperature when treated with boron trifluoride or trichloride (*674*) without an addition compound being isolated:

$$\begin{tikzcd}
H_3SiOSiH_3 + BX_3 \arrow[r] & H_3SiX + H_3SiOBX_2 \arrow[d] \\
 & H_3SiX + [BOX]
\end{tikzcd}$$

Similar reactions occur when $(SiH_3SiH_2)_2O$ (*219*), $(MeH_2Si)_2O$ (*229*), $(Me_3Si)_2O$ (*352*, *858*), and $(Me_3Ge)_2O$ (*346*) are used:

$$3(SiH_3SiH_2)_2O + 2BCl_3 \rightarrow B_2O_3 + 6SiH_3SiH_2Cl$$

$$3Me_3SiOSiMe_3 + 2BBr_3 \rightarrow B_2O_3 + 6Me_3SiBr$$

$$3Me_3GeOGeMe_3 + 2BF_3 \rightarrow B_2O_3 + 6Me_3GeF$$

Trimethylsilylalkyl ethers (i.e., alkoxytrimethylsilanes) react with boron trichloride and tribromide, giving the trimethylsilyl halide,

$$EtOSiMe_3 + BX_3 \rightarrow EtOBX_2 + Me_3SiX \qquad (856)$$

$$s\text{-BuOSiMe}_3 + BCl_3 \rightarrow s\text{-BuOBCl}_2 + Me_3SiCl \qquad (263)$$

but a halogen on the silicon atom (e.g., Cl_3SiOR or $ClSi(Me)_2OR$) causes the reaction to proceed via C—O fission (*263*):

$$Cl_3SiOR + BCl_3 \rightarrow (Cl_3SiO)_3B + RCl$$

$$(R = s\text{-Bu, iso-Pr})$$

Trimethylsilyl (*4*) and trimethylstannyl (*3*) thioethers (R_3MSR') cleave readily at the M—S bond, giving thioborate derivatives when treated with boron trichloride.

Trimethylgermylmethyl ether (methoxytrimethylgermane) forms a 1:1 adduct with boron trifluoride, which sublimes at 25° without irreversible decomposition (*346*). The products (93% SiH_3Cl and 7% Me_3SiCl) formed when trimethylsilylsilyl ether is treated with boron trichloride indicated that the main cleavage reaction was (*219*):

$$Me_3SiOSiH_3 + BCl_3 \rightarrow H_3SiCl + Me_3SiOBCl_2$$

Disilanylsilyl ether, $SiH_3SiH_2OSiH_3$, was cleaved by boron trichloride to give mainly SiH_3SiH_2Cl,

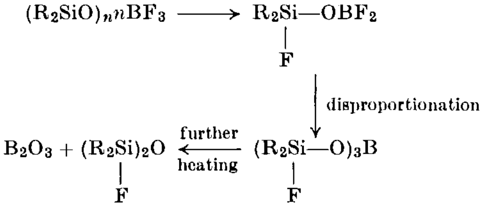
$$6SiH_3SiH_2OSiH_3 + 2BCl_3 \rightarrow 6SiH_3SiH_2Cl + 3(SiH_3)_2O + B_2O_3$$

although the isolation of small quantities of silyl chloride showed that the opposite cleavage probably occurred to some extent (*219*).

The cyclic dialkylpolysiloxanes react to form adducts with boron trifluoride (*560*),

$$(R_2SiO)_n + nBF_3 \rightarrow (R_2SiO)_n nBF_3$$
$$(n = 3, 4;\ R = Me, Et)$$

which decompose on heating to give dialkylfluorosiloxyboron derivatives (*560*):



$$\begin{tikzcd} (R_2SiO)_n nBF_3 \arrow[r] & R_2\underset{\displaystyle F}{\underset{|}{Si}}\text{—}OBF_2 \arrow[d, "\text{disproportionation}"] \\ B_2O_3 + (R_2\underset{\displaystyle F}{\underset{|}{Si}})_2O & (R_2\underset{\displaystyle F}{\underset{|}{Si}}\text{—}O)_3B \arrow[l, "\text{further}", "\text{heating}"'] \end{tikzcd}$$

Similar dialkylhalosiloxyboron compounds are obtained when either boron trichloride (*559*) or tribromide (*558*) is substituted for the trifluoride. Boron trifluoride will also attack some silicone vacuum greases to form dimethylsilicon difluoride.

Tetraalkoxysilanes undergo a group exchange when treated with a boron trihalide, there being a noticeable fall in rate as each alkoxy group is removed from the silicon atom:

$$\begin{tikzcd} (RO)_4Si + BCl_3 \arrow[r, "\text{room temp.}"] & (RO)_3SiCl + ROBCl_2 \arrow[d] \\ & \text{etc.} \end{tikzcd}$$ (*263, 306*)

$$ROSiCl_3 + BCl_3 \xrightarrow[3\text{ hr}]{50°} 80\%\ \text{recovery of}\ ROSiCl_3\ \text{but some}\ SiCl_4\ \text{detected}$$ (*263, 306*)

$$(RO)_4Si + BBr_3 \longrightarrow ROSiBr_3 + B(OR)_3$$ (*856*)

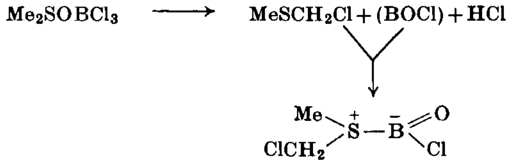
$$(MeO)_4Si + BF_3 \longrightarrow (MeO)_2BF + SiF_n(OMe)_{4-n}$$ (*856*)

A steady replacement of alkoxy groups for chlorine also occurs, below 0°, when titanium alkoxides are treated with boron trichloride (*173*).

Bis(dimethylamino) sulfide, $(Me_2N)_2S$, forms a very stable 2:1 (sulfide:BF_3) adduct when treated with an excess of boron trifluoride at 100°; heating to 169° in a vacuum fails to dislodge the boron trifluoride, both molecules of which are considered to be bound to the nitrogen atoms (*141*). Attachment of oxygen atoms to the sulfur results in a lower stability of the trifluoride adducts, and it is found impossible to complex 2 moles of boron trifluoride to either $(Me_2N)_2SO$ or $(Me_2N)_2SO_2$, although 1:1 adducts can be isolated (*141*). Thionylmethylamine, MeSNO, forms a 1:1 adduct with boron trifluoride, which is highly dissociated at 50° (*141*). When boron trichloride is treated with amino-sulfur compounds, a group exchange occurs (*649*):

$$R_2NSMe + BCl_3 \rightarrow R_2NBCl_2 + RSCl$$
$$(R = Me, Et)$$
$$2(Me_2N)_2S + 4BCl_3 \rightarrow (Me_2NBCl_2)_2 + 2Me_2NSClBCl_3$$

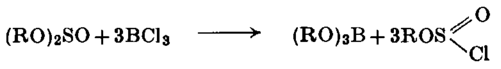
The dialkyl sulfoxides, R_2SO, form 1:1 adducts when treated with boron trifluoride (*176*, *488*, *493*) or trichloride (*488*, *703*): infrared spectra of the trifluoride adducts suggest that the boron is bonded to the oxygen atom (*176*), which is in keeping with the order of stability of the trifluoride complexes, $R_2SO > R_2S, R_2SO_2$ (*493*). The adduct, dimethyl sulfoxide–boron trichloride, is unstable (*703*) and rapidly decomposes to give chloromethylmethyl sulfide (*488*):



Diphenyl sulfoxide forms a stable 1:1 adduct with boron trichloride (*488*, *703*), but the dialkyl and diaryl sulfone complexes were unstable (*703*); the decomposition products were not, however, identified.

Borates and alkoxyboron chlorides result when alkyl or aryl sulfites are added to boron trichloride (*160*):

$$(RO)_2SO + BCl_3 \longrightarrow ROBCl_2 + ROS\begin{matrix}{}^{\nearrow O}\\{}_{\searrow Cl}\end{matrix} \text{ (chlorosulfinate)}$$



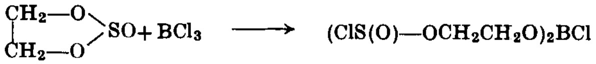
$$(RO)_2SO + 3BCl_3 \longrightarrow (RO)_3B + 3ROS\begin{matrix}{}^{\nearrow O}\\{}_{\searrow Cl}\end{matrix}$$

$$(R = n\text{-}Bu, C_6H_5)$$

The alkyl chlorosulfinates do not react with boron trichloride but phenyl chlorosulfinate forms thionyl chloride (*160*):

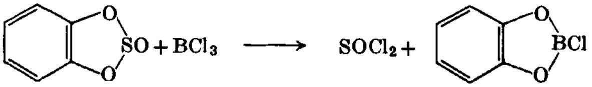
$$C_6H_5OS\overset{O}{\underset{Cl}{\lessgtr}} + BCl_3 \longrightarrow SOCl_2 + C_6H_5OBCl_2$$

Ethylene sulfite undergoes ring fission with boron trichloride (*160*),



$$(ClS(O){-}OCH_2CH_2O)_2BCl$$

while *o*-phenylenesulfite gives thionyl chloride (*160*):



Dialkyl sulfates react with boron trichloride in an inert solvent to give alkyl chloride and a yellow solid approximating to a mixed anhydride ($B_2S_3O_{12}$); (*160*); in the absence of a solvent the reaction is vigorous at 20°, hydrogen chloride and sulfur dioxide being evolved with the formation of ill-defined solid products (*160*). Esters of sulfonic acid give sulfonylboron dichloride (*161*).

Boron trifluoride (*382*) and trichloride (*337*) are solvolyzed in pure sulfuric acid, giving the tetra(hydrogen sulfato)borate ion, $B(HSO_4)_4^-$; the reactions are rather complex for boron trifluoride:

$$BF_3 + 7H_2SO_4 \rightarrow B(HSO_4)_4^- + 3H_3O^+ + HSO_3F + 2SO_3F^-$$

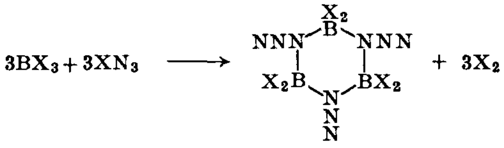
This reaction probably does not go to completion, since boron trifluoride can be manufactured commercially by heating boric acid with fluorosulfonic acid (*382*),

$$B(OH)_3 + 3HSO_3F \rightarrow BF_3 + 3H_2SO_4$$

while a further complicating factor is that intermediate species $BF(HSO_4)_3^-$, $BF_2(HSO_4)_2^-$, and $BF_3(HSO_4)^-$ may be present in solution. It is possible to isolate the intermediate white solid, boron tri(hydrogen sulfate), when boron trichloride is treated with sulfuric acid (*343*).

8. *Reactions with Compounds of Group VII Elements*

Displacement of halogen from a boron trihalide by a halogen of lower atomic weight is to be expected and, for example, chlorine ousts bromine from boron tribromide (*250*). The free halogens do not behave as strong Lewis bases toward the boron trihalides, as shown by the fact that iodine does not react with boron trifluoride (*52*, *817*), nor bromine with the tribromide (*193*), and iodine dissolves in boron triiodide to give only a purple-colored solution. Radioactive bromine, on the other hand, undergoes a rapid exchange when mixed with boron tribromide (*238*), indicative of at least a slight mutual interaction. Chlorine and bromine azides react with boron trichloride or tribromide to form the respective trimeric boron dihaloazide (*682*):



Cyanogen gives colored adducts with boron trichloride and tribromide (*19*) but hydrogen cyanide reacts only with the tribromide (*710*).

Although Henry's law is obeyed when boron trifluoride dissolves in anhydrous liquid hydrogen fluoride (*551*, *769*) (strongly suggesting that no reaction occurs between the two), the ^{11}B n.m.r. chemical shift of the solution is exceedingly close to the value observed for the tetrafluoroborate ion (*813*), i.e.:

$$HF + BF_4 \xrightarrow{\text{liq. HF}} H^+_{\text{solvated}} + BF_4^-$$

In aqueous solution, however, hydrogen fluoride and boron trifluoride definitely react to give fluoroboric acid (*700*) and the heat of the reaction

$$BF_3(g) + 15.67HF\cdot 58.72H_2O \rightarrow HBF_414.67HF\cdot 58.72H_2O$$

has been measured as -28.29 ± 0.07 kcal/mole (*355*). With the more dilute aqueous solutions of hydrogen fluoride formed during its partial hydrolysis, boron trifluoride forms the hydroxyfluoroborate anions $HOBF_3^-$, $(HO)_2BF_2^-$, and $(HO)_3BF^-$, which can be detected by ^{19}F n.m.r. techniques (*206*, *547*, *769*), but a partial hydrolysis in the presence of an amine [e.g., triphenylamine (*770*), aniline (*733*), or pyridine (*659*)] yields the quaternary tetrafluoroborate:

$$C_6H_5NH_2BF_3 + H_2O \rightarrow C_6H_5NH_3^+BF_4^- + C_6H_5NH_3^+BF_3OH^-$$

$$C_5H_5NBF_3 \xrightarrow[\text{ethanol}]{5\%\ H_2O\ \text{in}} C_5H_5NH^+BF_4^-$$

Thermal analysis shows that hydrogen chloride forms no compounds with boron trifluoride (*81*), but the molar conductivities of boron trifluoride and trichloride dissolved in liquid hydrogen chloride are reasonably high (ca. 10^{-4}) (*832*), indicative of a slight ionization, e.g.:

$$2HCl + BCl_3 \xrightarrow{\text{ca. } -90^\circ} H_2Cl^+ + BCl_4^-$$

The exchange of radioactive chlorine noted between hydrogen chloride and boron trichloride in the gas phase at 24° is thought to be an atom-transfer process (*392*), which may involve the formation of an intermediate "$HClBCl_3$" species. The relatively weak interaction of the hydrogen halides (HCl, HBr, and HI) with their respective boron trihalides makes them useful solvents in which to study reactions of the trihalides (*830*), but halogen exchange occurs in the mixed systems HCl/BBr_3 (*250*), HF/BCl_3 (*310a*), HBr/BCl_3 (*830*).

Iodine pentoxide and boron trifluoride do not react together (*52*), but chloryl fluoride, ClO_2F, and chlorine trifluoride give 1 : 1 solid complexes regarded as $ClO_2^+BF_4^-$ (*870*) and $ClF_2^+BF_4^-$ (*767*). Similarly, solutions of boron trifluoride in bromine trifluoride may contain bromonium tetrafluoroborate, $BrF_2^+BF_4^-$, which would be an "acid" in the liquid bromine trifluoride system (*411*, *830*):

$$\underset{\text{(base)}}{KF} + \underset{\text{(acid)}}{BrF_2^+BF_4^-} \rightarrow \underset{\text{(salt)}}{KBF_4} + \underset{\text{(solvent)}}{BrF_3}$$

Other nonaqueous solvents used for the preparation of tetrafluoroborates include liquid hydrogen fluoride (*869*), liquid arsenic trifluoride (*871*), liquid sulfur dioxide (*727*, *764*), and liquid iodine pentafluoride (*869*).

The simplest method by which to prepare the tetrahaloborates is to add a suitable halide (preferably containing a large cation when the chloride, bromide, or iodide is used) to the corresponding boron trihalides, with or without an inert solvent:

$$MX + BX_3 \rightarrow MBX_4$$

M = alkali metal, NR_4^+, H_3NR^+, Ar_2MeC^+, Ar_3C^+, diazonium (ArN_2^+)

X = F (*769*)

X = Cl (***144, 368, 466, 467, 475, 595, 599, 663, 702, 813, 833***)

X = Br (***367, 471, 475, 663, 813, 835, 837***)

X = I (***144, 366, 813, 836***)

$$N_2H_6^{2+} + 2F^- + 2BF_3 \rightarrow N_2H_6^{2+}(BF_4)_2^- \qquad (79)$$

For the tetrafluoroborates, the boron trifluoride can be prepared *in situ* by using the reaction between sulfur tetrafluoride and boric oxide:

$$NH_4F + B_2O_3 \xrightarrow{SF_4} NH_4BF_4 \qquad (442)$$

$$B_2O_3 + SF_4 \rightarrow SF_3BF_4 \qquad (675)$$

Another useful tetrahaloborate synthesis involves the addition of cycloheptatriene (either neat or in an organic solvent) to a boron trihalide, and gives good yields of the tropenium tetrahaloborates, $C_7H_7^+BX_4^-$ (X = Cl, Br, I) (*365–369*). The solubilities of sodium and potassium chlorides in liquid sulfur dioxide are low, but have been found to increase greatly on addition of boron trichloride; conductance measurements on

MCl/BCl_3 mixtures indicate a sharp break at ratios of 1 : 1, as expected if the tetrachloroborate ion was produced. However, on evaporation of the solvent and boron trichloride, only the metal chloride remains behind (*142*), which may indicate that an unstable ion such as $Cl_3BSO_2Cl^-$, and not BCl_4^-, is synthesized under these conditions [(*132*), see, however, Creighton (*191*)]. There are one or two discrepancies concerning the stability of tetrachloroborates, and the above experiment may be another; Herber has shown (*392*) that exchange of radioactive chlorine between tetramethylammonium chloride and pure boron trichloride occurs at 0° and, although he argued that this was evidence for the BCl_4^- ion, he did not isolate Me_4NBCl_4 on evaporation of the boron trichloride; yet later workers (*813*) obtained a 100% yield of tetramethylammonium tetrachloroborate by using almost the same procedure.

The ^{11}B n.m.r. chemical shifts of BX_4^- anions (except BF_4^-) show a marked dependence upon halide ion concentration when they are measured in organic solvents (*471*, *813*); this is probably due to an exchange equilibrium such as

$$BX_4^- + \text{solvent} \rightleftharpoons BX_3\cdot\text{solvent} + X^-$$

occurring in these solvents. There is no dependence on halide concentration when the ^{11}B chemical shifts are measured for solutions in the corresponding hydrogen halides (*813*), lending further support to the idea that slight ionization takes place when the boron trihalides dissolve in a liquid hydrogen halide:

$$BX_4^- + \text{solvent (i.e., HX)} \rightleftharpoons BX_3\cdot\text{solvent (i.e., } H^+_{\text{solv.}}BX_4^-) + X^-$$

As no fluoride ion concentration dependence is observed for the ^{11}B chemical shift of tetrafluoroborates dissolved in organic solvents and no exchange occurs between F^- and BF_4^- in water (*442*), the BF_4^- ion must be virtually undissociated in solution; in other words, the stability series for tetrahaloborates is $BF_4^- > BCl_4^-$ [$> BBr_4^- > BI_4^-$], assuming that the magnitude of the chemical shift dependence on the concentration of X^- is inversely proportional to the stability of BX_4^-. This stability relationship is probably a manifestation of several factors, including the strong Lewis basicity of F^- and adverse steric conditions operating for BCl_4^-, BBr_4^-, and BI_4^-. The hydrolytic instability (and other chemical properties) of tetrachloro-, tetrabromo-, and tetraiodoborates can be explained in terms of the above dissociation equilibrium, but the solubility of tetramethylammonium tetrachloroborate in dimethyl sulfoxide is rather remarkable considering the vigor with which boron trichloride and the sulfoxide react together; however, such solutions become gelatinous during several hours at room temperature (*813*). The thermal decomposition of many alkylammonium tetrachloroborates has been closely studied and shown to proceed via the 1 : 1 amine-boron trichloride adducts to the *N*-trialkyl-*B*-trichloroborazines (*143*, *144*, *195*):

$$RNH_3^+BCl_4^- \rightarrow RNH_2BCl_3 \rightarrow \tfrac{1}{3}(RNBCl)_3$$

Mixed tetrahaloborates, MBX_nY_{4-n}, may be formed when boron trifluoride reacts with triphenylmethyl chloride (*442*, *701*), phosphonium chloride (*833*), tetraalkylammonium chlorides (*833*), phosphorus pentachloride (*834*), nitrosyl chloride (*834*), and when boron trichloride reacts with triphenylmethyl fluoride (*442*, *701*, *854*). The infrared spectrum of $(C_6H_5)_3CClBCl_3$ in the solid state shows that the ions $(C_6H_5)_3C^+$ and BCl_4^- are present, but owing to an overlap of absorption bands it is impossible to judge from infrared spectra whether BF_3Cl^- and $BFCl_3^-$ are present in $(C_6H_5)_3CClBF_3$ and $(C_6H_5)_3CFBCl_3$ or whether disproportionation to BF_4^- and BCl_4^- took place on crystallization (*442*); however, the spectra of several other solid salts, thought definitely to contain the chlorotrifluoroborate ion, have been described (*834*).

The mixing together of methylene dichloride solutions of triphenylmethyl tetrafluoroborate and tetrachloroborate produces an evolution of heat, and both the ^{19}F and ^{11}B n.m.r. spectra of the resulting solutions shows a single resonance line, the chemical shift of which varies systematically with the concentration of either BF_4^- or BCl_4^-. This is the expected behavior if a series of mixed tetrahaloborates were formed in the solution; the n.m.r. spectra of $(C_6H_5)_3CFBCl_3$ and $(C_6H_5)_3CClBF_3$ show single peaks having shifts corresponding to the relative amounts of fluorine and chlorine, and cannot be used to deduce whether discrete $BFCl_3^-$ or BF_3Cl^- ions are present. Mixed tetrahaloborates are formed when boron tribromide is mixed with chloride ions in nitrobenzene or when either the trichloride or tribromide reacts with a tetrafluoroborate (*442*); however, fluorine-bridged complex ions such as $B_2F_7^-$ and $B_3F_{10}^-$ may be formed when boron trifluoride reacts with various tetrafluoroborates in methylene dichloride solution (*124*). An attempt to isolate tetramethylammonium trifluorochloroborate using the reaction

$$Me_4NCl + BF_3OMe_2 \rightarrow Me_4NBF_3Cl + Me_2O$$

failed (*850*). The observed products

$$3Me_4NCl + 4BF_3OMe_2 \rightarrow 3Me_4NBF_4 + MeCl + B(OMe)_3 + Me_2O$$

can be explained if it is assumed that the ion BF_3Cl^- was formed initially and that under the experimental conditions it disproportionated to give the series of mixed tetrahaloborates, the tetrafluoroborate, and the tetrachloroborate; the latter, in the presence of dimethyl ether, will dissociate slightly (see above) giving the unstable dimethylether–boron trichloride:

$$\begin{tikzcd}
BCl_4^- + Me_2O \arrow[r, phantom, "\rightleftharpoons"] & Cl^- + Me_2OBCl_3 \arrow[d] \\
& MeCl + (MeO)_3B
\end{tikzcd}$$

Tetraalkylammonium halides (*593*, *850*) and diazonium chlorides (*658*, *723*, *806*) produce the corresponding tetrafluoroborates when added to aqueous tetrafluoroboric or trifluorohydroxyboric acid. A useful property of the tetrafluoroborates of silver and copper(II) is that they are soluble in organic solvents such as diethyl ether, benzene, and nitromethane (*36*), while the diazonium tetrafluoroborates are used in the Balz-Shiemann reaction, e.g.,

$$ArN_2BF_4 \xrightarrow{\text{heat}} ArF + N_2 + BF_3 \qquad (806)$$

and in the presence of nickel carbonyl form ArH, Ar_2CO, or $ArCO_2R$ when the reaction conditions are suitably manipulated (*163*).

Somewhat surprisingly, the ^{11}B n.m.r. chemical shifts of the tetrahaloborates, as measured in the corresponding liquid hydrogen halides, do not show a linear dependence on the electronegativity of the halogen, the boron atom in the BF_4^- ion being more highly shielded than expected (*813*). A similar trend is found in the boron trihalides, where ^{11}B chemical shifts of BCl_3, BBr_3, and BI_3 show a direct correlation with the electronegativity of the halogen, but in the trifluoride the boron atom is "too shielded" (*311*); this was explained by assuming that the chemical shift, δ, was composed of two components, one arising from the electronegativity of the halogen, the other being proportional to the π-electron density on the boron atom due to "back donation," i.e., $\delta = \delta_E + \delta_\pi$. In the case of the tetrahaloborates, however, π-bonding cannot reasonably be assumed, and some interaction between the halogen and low lying antibonding orbitals on the boron may be involved to affect the tetrafluoroborate ^{11}B shift to the greatest extent.

In contrast to the rather poorly characterized, mixed tetrahaloborates, several substituted trihaloborates have been isolated:

$$\begin{aligned}
KF + CH_2{=}CHBF_2 &\xrightarrow[\text{solution}]{\text{aqueous}} KCH_2{=}CHBF_3 && (788)\\
KF + MeBF_2 &\longrightarrow KMeBF_3 && (788)\\
KF + C_6F_5BF_2 &\longrightarrow KC_6F_5BF_3 && (154)\\
R_4NHS + BX_3 &\xrightarrow[\text{as solvent}]{\text{liq. }H_2S} R_4NX_3BSH \quad (X = F, Cl, Br) && (179)
\end{aligned}$$

The trifluoromethyltrifluoroborate anion, the first boron compound to be isolated that contained a perfluoroalkyl group, results when trimethyltrifluoromethyltin is mixed with boron trifluoride (*156*, *157*):

$$Me_3SnCF_3 + BF_3 \rightarrow Me_3SnCF_3BF_3 \xrightarrow{KF} KCF_3BF_3$$

This is somewhat reminiscent of the preparation of the triphenylfluoroborate ion, $(C_6H_5)_3BF^-$, by addition of boron triphenyl to a fluoride in a suitable solvent (*254*), whereas an ionic pseudohalide (cyanide, cyanate, thiocyanate, or azide) when added to boron trichloride in nitrobenzene gives mixed ions such as BCl_3CN^-, $BCl_2(CN)_2^-$, $BCl(CN)_3^-$, and $B(CN)_5^-$ (*471*). More recently this type of reaction has led to some interesting substituted tetrahaloborates containing tin-boron and germanium-boron bonds being isolated from addition of boron trichloride or trifluoride to the tetraphenylarsonium and tetramethylammonium salts of the trichlorostannate(II) and trichlorogermanate(II) ions (*432*), e.g.:

$$(C_6H_5)_4AsMCl_3 + BX_3 \rightarrow (C_6H_5)_4As^+[Cl_3M—BX_3]^-$$
$$(X = F, Cl;\ M = Sn, Ge)$$

B. DIBORON TETRAHALIDES

Although Stock first made minute quantities of the tetrachloride in 1925 (*800*), the chemistry of the diboron tetrahalides did not begin to unfold until the late 1940's when Schlesinger considerably modified the tetrachloride synthesis (*843*) and was able to obtain about 10 gm per week by his new procedure. Even at the present time only a few laboratories are actively engaged in the study of the diboron halides, since it is commonly assumed that they are very difficult to prepare; it is hoped that the recent publication of the exact details involved in the synthesis of diboron tetrachloride (*545*, *845*) will encourage more workers to enter the field.

The diboron tetrahalides (see Table XI) are of interest to the chemist mainly because they are the simplest boron derivatives that contain a boron-to-boron bond (see page 16); similar bonds of course occur in certain of the boranes and carboranes, but a chemical study of them in such an environment is greatly complicated by the simultaneous presence of relatively large numbers of reactive boron-hydrogen bonds. In the tetrahalides the only complicating factor is the presence of the halogens; however, as was seen from the first part of this review, the chemistry of boron-halogen bonds has been extensively worked out, and it is thus possible to predict fairly accurately that part of a reaction that involves attack on the boron-halogen bonds. The chemistry of the diboron tetrahalides will therefore be governed by two factors: the reactivity of the boron-halogen bonds on the one hand, and the boron-boron bonds on the other.

The thermal stability of the tetrahalides is very much less than the corresponding trihalides, and diboron tetrafluoride, the most stable member of the series, decomposes to the extent of about 8% in 1 day at room temperature (*414*). It was originally thought that decomposition involved disproportionation to elemental boron (*800*), e.g.,

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

but subsequent studies on many diboron compounds, including the halides, show that no boron is formed; instead polymers of empirical formula BX are often produced (*641*):

$$nB_2X_4 \rightarrow nBX_3 + (BX)_n$$

[X = F (*246, 414*), Cl (*545, 546, 753, 825, 826*), Br (*208*), I (*757*), OMe (*97*), OEt (*97*), $ClCH_2CH_2O$ (*537*), $B_2R_2(NMe_2)_2$ (*640*)]

The decomposition of the tetrachloride has been intensively studied and is in fact more complicated than is shown by the general equation above. The polymeric $(BCl)_n$, e.g., is not a single compound and, by fractional sublimation under vacuum conditions, it is possible to resolve the solid mixture into its several (often highly colored) components, all of which have empirical formulas either equal or at least close to BCl. The major volatile polymeric product is a dark red solid of melting point 115° [incorrectly stated by Massey (*410*) to be octaboron octachloride], which classical analyses and molecular weight determinations indicate to be $B_{12}Cl_{11}$ (*753, 825*) whereas the mass spectrum gives a molecular weight corresponding to $B_{11}Cl_{11}$ (*543, 545*); at the present time it is not possible to choose between these two formulations but, should $B_{12}Cl_{11}$ be later proved the correct one, the mass spectrum shows, by the lack of a parent ion, the presence of a remarkably labile boron atom. Another red solid isolated from the decomposition products of diboron tetrachloride was shown by X-ray diffraction to be octaboron octachloride (*426*), but other workers (*545, 753*) have been unable to isolate this chloride when very stringent precautions were taken to prevent access of air and moisture to the apparatus. Mass spectral evidence has also been obtained for B_9Cl_9 (*541, 545*), while the same work suggests that minute quantities of $B_{10}Cl_{10}$ and $B_{12}Cl_{12}$ may also occur in the decomposition mixture. As well as the volatile polymers a white involatile solid is also formed (*826*), which analyzes as $BCl_{0.6}$, but nothing further is known of its properties or indeed if it is a single compound. Small amounts of tetraboron tetrachloride may also occur among the decomposition products of diboron tetrachloride, but the quantities obtained make this a very unattractive source of B_4Cl_4.

The structures of these curious polyboron halides [except B_4Cl_4 (*25*) and B_8Cl_8 (*426*)] are not yet known, but probably involve cages of boron atoms; liquid diboron tetrachloride, which has been held at room temperature for some time, exhibits an electron-spin resonance spectrum. Urry (*753*, *825*) has traced this paramagnetism to the red $B_{12}Cl_{11}$ and to a purple polyboron chloride of unknown formulation, which suggests that intriguing molecular structures and bonding are involved in these halides; structure determinations are therefore awaited with great interest.

Although diboron tetrachloride is at present the only source of many of these polyboron chlorides (and for this reason alone B_2Cl_4 will no doubt be actively studied in the future), a new approach to the synthesis of boron-cage halides involves the thermal decomposition of the acid $H_2B_{10}Cl_{10} \cdot xH_2O$ (*253*) since at about 260° a 5% yield of the red volatile solid octachlorononaborane B_9Cl_8H can be isolated. It is interesting to note that this compound apparently exhibits an electron-spin resonance spectrum, but after several vacuum sublimations the paramagnetism decreases markedly without change in the analysis of the borane and may therefore be associated with an impurity. This suggests caution in the interpretation of the e.s.r. spectrum of $B_{12}Cl_{11}$, especially as liquid diboron tetrachloride does not develop an e.s.r. spectrum until it has remained at room temperature for many hours, even though the liquid chloride is previously colored deep red presumably due to dissolved $B_{12}Cl_{11}$ or $B_{11}Cl_{11}$ (*536*).

Since several BCl polymers are formed during the thermal decomposition of diboron tetrachloride, the first step may well involve the production of a BCl species,

$$B_2Cl_4 \rightarrow BCl_3 + BCl \rightarrow BCl \text{ polymers}$$

and strong evidence in support of this comes from flash photolysis experiments on diboron tetrachloride carried out under essentially adiabatic conditions (*546*). The action of a silent electric discharge accelerates the decomposition of the tetrachloride (*724*) and a new boron polymer, a yellow solid of formula $(BCl)_x$ but unknown structure, is formed along with boron trichloride. During the microwave synthesis of diboron tetrachloride the spectrum of the ensuing discharge shows only those lines attributable to BCl (*419*), which, coupled to the fact that B_4Cl_4 and a yellow boron monochloride polymer are produced simultaneously with the B_2Cl_4 when boron trichloride is passed through a mercury discharge, suggests that BCl is a precursor in the formation of diboron tetrachloride,

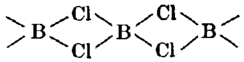
$$BCl_3 + BCl \rightarrow B_2Cl_4$$

and not BCl_2 radicals as might have been expected; under some conditions the spectrum of the B_2 molecule is also observed (*212*). Since this equation is the exact opposite to that postulated for the thermal decomposition of the tetrachloride, it would appear that the reaction is reversible under certain conditions,

$$B_2Cl_4 \rightleftharpoons BCl + BCl_3$$

and that during decomposition the equilibrium is shifted to the right by the formation of BCl polymers. Diboron tetrafluoride is not formed when boron trifluoride is passed through an electric discharge (*246*), and this may be due to the fact that boron trifluoride will not react with BF since this species is readily detected spectroscopically in discharges passed through boron trifluoride vapor (*673*, *722*); the other tetrahalides are formed when the respective trihalides are subjected to an electric discharge (*208*, *757*). Again, unlike the other halogens, fluorine apparently forms only a single, involatile, lower fluoride with boron (*246*, *414*), whereas several bromides (*208*) and iodides (*757*) have been isolated although not identified.

A study of the fragmentation pattern obtained in the mass spectra of the above volatile polyboron chlorides suggests that the chlorine atoms are terminally bonded one to each boron; however, tentative evidence (*502*) has been advanced for the formation of a white $(BCl_2)_x$ polymer when mixtures of boron trichloride and hydrogen are subjected to γ-radiation, in which the possibility of boron-chlorine bridges was recognized:



If this compound does indeed possess such bridging chlorine atoms, it will represent the first example in boron chemistry, although such halogen bridges are of course well known among the halides of other members of the Group III elements.

Not only do difficulties arise in handling the diboron tetrahalides owing to their thermal instability (which requires that most reactions be studied below room temperature), but the halides attack stopcock grease, hydrolyze readily with even traces of water, and are extremely oxygen-sensitive—the tetrafluoride in fact explodes on contact with dry oxygen (*414*, *820*). Since the tetrafluoride, tetrachloride, and their hydrolysis products do not attack metallic mercury, they may conveniently be handled in vacuum lines equipped with mercury float-valves and mercury manometers; in recent years, however, increasing use has been made of greaseless stopcocks manufactured from polytetrafluoroethylene.

1. *Reduction Reactions*

Schlesinger, having managed to prepare reasonable quantities of diboron tetrachloride, was interested in its possible reduction to give the unknown hydride diborane-4, B_2H_4. He found that lithium aluminum hydride would not react either in the presence or in the absence of an ether solvent; calcium aluminum hydride also failed to react in tetrahydrofuran solution (*826*). However, both lithium and aluminum borohydrides react rapidly, even in the absence of solvents and at temperatures as low as −45°, to produce mixtures of diborane-6, tetraborane-10, pentaborane-9, and traces of decaborane-14. The ratios of the hydrides formed varied somewhat with temperature, but the initial reaction appeared to be, e.g.:

$$4LiBH_4 + B_2Cl_4 \rightarrow 4LiCl + B_4H_{10} + B_2H_6$$

The other boranes arose in the products due to the thermal decomposition of the unstable tetraborane. This suggests that diborane-4 may indeed have been formed in the reduction but that it quickly reacted with diborane-6 to form tetraborane-10 (*826*):

$$B_2H_4 + B_2H_6 \rightarrow B_4H_{10}$$

There have been two recent claims to have isolated stabilized adducts of diborane-4, both of which involve what amounts to the reverse of the above equation. Tetraborane-10 on treatment with 2 moles of trimethylamine produces trimethylamine-borane and trimethylamine-triborane-7:

$$B_4H_{10} + 2NMe_3 \rightarrow Me_3NBH_3 + Me_3NB_3H_7$$

Triphenylphosphine is then used to displace trimethylamine-borane from the triborane-7 adduct to give what was considered to be bis(triphenylphosphine)-diborane-4 (*326*):

$$Me_3NB_3H_7 + 2P(C_6H_5)_3 \rightarrow Me_3NBH_3 + [(C_6H_5)_3P]_2B_2H_4$$

By using pyridine at 0° it is possible to remove the elements of diborane, as pyridine-borane, from tetraborane in a single step to form the monopyridine adduct of diborane-4 (*580*):

$$B_4H_{10} + C_5H_5N \rightarrow 2C_5H_5NBH_3 + C_5H_5NB_2H_4$$

The reduction of diboron tetrachloride using hydrogen yields diborane and boron trichloride, the reaction being assumed to proceed via the initial addition of hydrogen across the boron-boron bond to give tetrachlorodiborane-6 [the monomer, BCl_2H, has actually been detected among the products (*719*)], which would be expected to disproportionate readily to diborane and boron trichloride (*826*):

$$3B_2Cl_4 + 3H_2 \rightarrow 3B_2Cl_4H_2 \rightarrow 4BCl_3 + B_2H_6$$

However, the position is considerably more complex than this, since side reactions occur between the diborane and both boron trichloride (see page 36) and diboron tetrachloride (*719, 826*):

$$B_2Cl_4 + B_2H_6 \xrightarrow{0^\circ} \text{unknown solid} + BCl_3, BCl_2H, B_2H_5Cl, H_2, BClH_2, \text{asym. } B_2H_4Cl_2$$

A different reaction occurs in the presence of diethyl ether when, at –23°, 1 mole of diboron tetrachloride absorbs 1 mole of diborane; removal of the excess of ether at room temperature was accompanied by loss of some diborane and the formation of a crystalline compound (melting point just above –80°), which analyzed to $(B_2Cl_4BH_3)2Et_2O$ (*826*). Although nothing is known about this intriguing compound except that treatment with methanol liberates *four* moles of hydrogen suggesting that the boron-boron bond is still intact), it is possibly a tetrachloro derivative of the borane fragment, triborane-7, stabilized in some manner by the presence of the ether. The reaction obviously warrants further study.

2. *Reactions Involving Compounds Containing Nitrogen or Phosphorus*

Gaseous nitrogen and white phosphorus are inactive toward diboron tetrachloride at room temperature (*18*).

The diboron tetrahalides contain two tricoordinate boron atoms (see page 16), and typically the tetrafluoride and tetrachloride both add 2 moles of donor molecules like trimethylamine and triethylamine:

$$B_2X_4 + 2NR_3 \rightarrow B_2X_42NR_3$$

[X = F (*246, 364*); X = Cl (*826*)]

As often happens in boron chemistry, the addition of a donor molecule greatly increases the thermal stability of the tetrahalides and, for example, $B_2Cl_42NMe_3$ may be sublimed in a vacuum and melts at 228° without appreciable decomposition (*826*). Therefore a possibility was that on reduction of $B_2Cl_4 \cdot 2NMe_3$ by lithium borohydride the resulting diborane-4 would be stabilized by the 2 moles of trimethylamine: however, the only major product isolated from this reaction was diborane-6 (*746*); neither hydrogen nor diborane reacts with $B_2Cl_42NMe_3$ (*826*). The trimethylamine adducts of both diboron tetrafluoride and tetrachloride have been shown to be tetrameric in benzene solution and may not be simple adducts (*246, 826*); since both sublime on heating, it would be interesting to determine (e.g., mass spectrometrically) their degree of polymerization in the vapor phase.

Probably one of the easiest derivatives of diboron tetrachloride to obtain is the monomeric $B_2Cl_4 2NHMe_2$, which can be prepared by treating the commercially available tetrakis(dimethylamino)diboron with an excess of hydrogen chloride (*120*, *524*, *632*, *648*):

$$B_2(NMe_2)_4 \xrightarrow{HCl} B_2(NMe_2)_3Cl \xrightarrow{HCl} Cl(NMe_2)B{-}B(NMe_2)Cl \xrightarrow{HCl} B_2Cl_4 2NHMe_2$$

The formation of the dimethylamine adducts of diboron tetrafluoride and tetrabromide in a similar manner (*524*) could possibly open up another method for synthesis of free diboron tetrafluoride:

$$\begin{tikzcd} B_2(NMe_2)_4 + 10HF \arrow[r] & 2Me_2NH\cdot 3HF + B_2F_4 2NMe_2H \arrow[d, "BF_3\ \text{(see below)}"] \\ & B_2F_4 + 2BF_3NHMe_2 \end{tikzcd}$$

The dimethylamine adduct of diboron tetrachloride is reasonably reactive: thus acid hydrolysis gives sub-boric acid, while the halogen atoms are capable of substitution, for example, by silver cyanide (*524*):

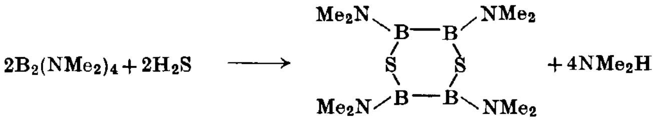
$$B_2Cl_4 2NHMe_2 + 4AgCN \rightarrow B_2(CN)_4 2NHMe_2 + 4AgCl$$

The tetracyanodiboron derivative is identical to that formed when hydrogen cyanide reacts with tetrakis(dimethylamino)diboron (*524*):

$$4HCN + B_2(NMe_2)_4 \rightarrow B_2(CN)_4 2NHMe_2 + 2Me_2NH$$

The removal of dimethylamino groups from tetrakis(dimethylamino)-diboron by protonation has also been used in preparation of sulfur derivatives containing boron-boron bonds, e.g.:

$$B_2(NMe_2)_4 + 2BuSH \rightarrow B_2(NMe_2)_2(SBu)_2 + 2Me_2NH \qquad (641)$$



(*524*)

The free amine formed in the latter reaction is removed by the slow addition of hydrogen chloride dissolved in ether. With diboron tetrachloride, tetramethylaminoborane, Me_2NBMe_2, reacts in ratios that suggest the initial addition of 2 moles of borane via the nitrogen atoms to the diboron tetrachloride, but the adduct breaks up rapidly to evolve dimethylaminoboron dichloride (*412*).

A question of theoretical importance is how the Lewis acidity of a diboron tetrahalide compares with that of the corresponding trihalide. Obviously in the tetrahalides less overall π-bonding can occur than in the trihalides, since there is one less halogen atom to form a π-bond to the boron (unless there is considerable π-bonding in the boron-boron bond, and this is unlikely considering both the B—B distance in these compounds and the fact that almost free rotation has been shown to occur in B_2F_4 and B_2Cl_4); as a result, less energy will be required to reorganize the boron atoms in B_2X_4 molecules to the tetrahedral state, and simple theory predicts that the diboron compounds would form stronger adducts than the corresponding trihalides.

In a study on diboron tetrafluoride (*364*) the reverse was found to be true, and boron trifluoride displaced diboron tetrafluoride from its adducts with trimethylamine, triethylamine, and dimethoxyethane; furthermore, boron trifluoride forms a weak compound with *p*-chlorobenzonitrile whereas the tetrafluoride does not react at all. The difference between the observed and expected behavior of diboron tetrafluoride was assumed to be due to adverse steric interactions. When diboron tetrafluoride is bonded to a chelating ligand, such as *N*,*N*,*N'*,*N'*-tetramethylethylenediamine, boron trifluoride or trichloride cannot displace the diboron tetrafluoride, and it appears that ring formation gives the adduct an increased stability (*364*).

Boron trifluoride and trichloride, on the other hand, are without action on the trimethylamine adduct of diboron tetrachloride (*826*), which appears to support the expected order of Lewis acidities although the n.m.r. chemical shift of the protons in this adduct indicates little difference between the acceptor strengths of the tetrachloride and trichloride (*539*). However, a complicating issue in all these studies is the apparently tetrameric nature of the $B_2X_42NMe_3$ adducts, which may invalidate some of the conclusions drawn from the experimental results.

Bidentate donor molecules are to be expected to form 1:1 adducts with diboron tetrahalides, and a typical complex of this type is formed when tetramethyldiphosphine reacts with diboron tetrachloride (*268*):

$$P_2Me_4 + B_2Cl_4 \xrightarrow{-80^\circ} B_2Cl_4P_2Me_4 \qquad \text{(undissociated below } 150^\circ\text{)}$$

Addition of trimethylamine to this adduct results in the production of $B_2Cl_4P_2Me_4NMe_3$; the isolation of this compound, coupled with the fact that only traces of $B_2Cl_42NMe_3$ could be detected in the products, shows that trimethylamine is a stronger base than the diphosphine when the latter is acting as a bidentate donor, whereas the position is reversed when the diphosphine interacts with only one boron atom. The

1 : 1 diphosphine adduct undergoes a transformation reaction when heated in a sealed tube at 250° to give a crystalline solid, which, from infrared evidence, was given the ionic structure $[(\mathrm{B}\underset{\leftarrow}{-}\mathrm{PMe_2})_2]^+\mathrm{BCl_4}^-$ (*268*).

Substitution of the methyl groups in the diphosphine for chlorine, as in P_2Cl_4, reduces the basicity of the phosphorus atoms and no compound is formed with diboron tetrachloride, although phosphorus trichloride gives a weak adduct, $B_2Cl_42PCl_3$ (*268*); nor does tetrafluorohydrazine form an adduct with diboron tetrachloride, but in this case a slow reaction occurs as fluorine is transferred to boron (*268*):

$$6\mathrm{B_2Cl_4} + 3\mathrm{N_2F_4} \rightarrow 3\mathrm{N_2} + 4\mathrm{BF_3} + 8\mathrm{BCl_3}$$

No reaction occurs between diboron tetrachloride and bis(trifluoromethyl)diazine, $(CF_3)_2N_2$ (*545*). Bidentate ligands such as ethylenediamine, hydrazine, and 1,2-dimethylhydrazine, which contain reactive hydrogen atoms, evolve hydrogen chloride on treatment with diboron tetrachloride and form the amine hydrochlorides as by-products (*405*).

Similar loss of hydrogen chloride occurs when an excess of either ammonia or dimethylamine reacts with diboron tetrachloride (*826*):

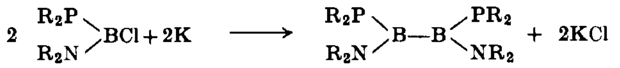
$$6x\mathrm{NH_3} + x\mathrm{B_2Cl_4} \rightarrow 4x\mathrm{NH_4Cl} + 2(\mathrm{BNH})_x$$

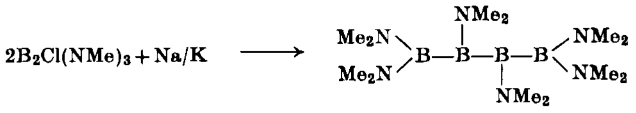
$$8\mathrm{Me_2NH} + \mathrm{B_2Cl_4} \rightarrow 4\mathrm{Me_2NH_2Cl} + \mathrm{B_2(NMe_2)_4}$$

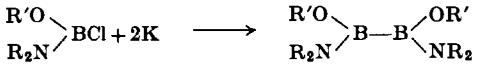
The product of this last reaction, tetrakis(dimethylamino)diboron, is identical to that formed in the Würtz-type synthesis (*96*, *647*):

$$2(\mathrm{Me_2N})_2\mathrm{BX} + 2\mathrm{Na} \rightarrow 2\mathrm{NaX} + \mathrm{B_2(NMe_2)_4}$$
$$(\mathrm{X} = \mathrm{Cl}, \mathrm{Br})$$

Nöth and others have shown that this type of coupling reaction can be extremely useful for the general synthesis of diboron derivatives, e.g.:

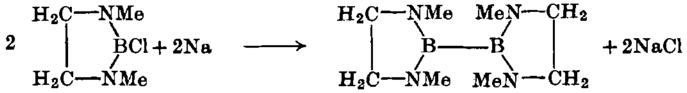

(*654*)


(*640*)

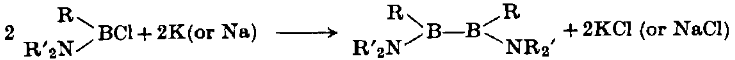

(*641*)

$$2(\mathrm{RO})_2\mathrm{BCl} + 2\mathrm{K} \longrightarrow (\mathrm{RO})_4\mathrm{B_2} + 2\mathrm{KCl} \qquad (647)$$

(In the latter reaction there is also a considerable amount of the normal borate, $B(OR)_3$, formed.)



(*121*)



$$2\,\frac{R}{R'_2N}{>}BCl + 2K(\text{or Na}) \longrightarrow \frac{R}{R'_2N}{>}B{-}B{<}\frac{R}{NR_2'} + 2KCl\ (\text{or NaCl})$$

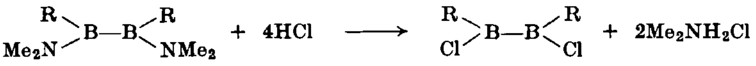
(*95, 638*)

The formation of this latter series of diboron compounds is interesting since they are the only definitely known derivatives that contain boron-carbon bonds.[10] Any attempt to alkylate diboron tetrachloride using, for example, zinc dimethyl (*826*) results in the rupture of the boron-boron bond and the formation of the corresponding boron trialkyl; the same product is obtained if dialkyl boron halides are treated with alkali metals (*860*). However, if the reduction of dibutylboron chloride (*33*) is carried out in ether, a solution is obtained that may contain tetrabutyldiboron stabilized by ether-coordination:

$$Bu_2BCl + K \rightarrow KBBu_2$$
$$KBBu_2 + Bu_2BCl \rightarrow B_2Bu_4$$

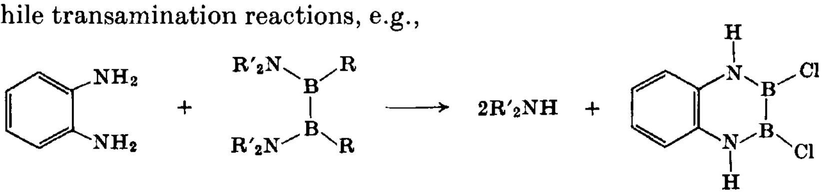
An electron-spin resonance study (*497*) of the reaction between dimesitylboron fluoride and sodium-potassium alloy shows (*847*) that the main radical produced is not the $Ar_2B{-}BAr_2^-$ ion as might be expected, but is the trimesitylborane negative ion, Ar_3B^-, presumably formed from trimesitylborane derived from the disproportionation of B_2Ar_4.

Although the bis(dialkylamino)dialkyldiborons react in a complex manner with hydrogen chloride, under the correct conditions dialkyldichlorodiborons can be isolated (*638*),



$$\frac{R}{Me_2N}{>}B{-}B{<}\frac{R}{NMe_2} + 4HCl \longrightarrow \frac{R}{Cl}{>}B{-}B{<}\frac{R}{Cl} + 2Me_2NH_2Cl$$

while transamination reactions, e.g.,



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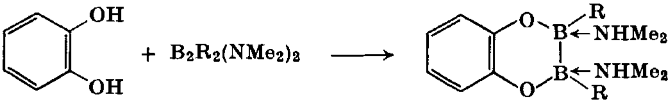
[10] The thermal decomposition of triallylborane yields diallyl and a compound that analyzes as tetraallyldiboron:

$$2B(C_3H_5)_3 \rightarrow (C_3H_5)_2 + B_2(C_3H_5)_4 \qquad (864)$$

and treatment with hydroxy derivatives, e.g.,

$$B_2R_2(NMe_2)_2 + 2R'OH \longrightarrow B_2R_2(OR')_2 + 2HNMe_2$$
$$(R' = H,\ \text{alkyl})$$



can be used for the production of many other diboron compounds (*638*).

When dissolved in anhydrous liquid hydrogen chloride at low temperature,[11] diboron tetrachloride reacts with both tetramethylammonium chloride and phosphorus pentachloride to give the hexachlorodiborate anion, $B_2Cl_6^{2-}$; no evidence was obtained for the corresponding pentachlorodiborate ion (*413*). Attempts to remove trimethylamine from the adduct $B_2Cl_4 2NMe_3$ by treatment with dry hydrogen chloride failed, but 2 moles of hydrogen chloride were taken up by the adduct (*405*); similarly, $B_2Cl_4 2NMe_3$ will absorb about 2 moles of hydrogen cyanide (*405*), methyl cyanide (*405*), and diethyl ether (*826*). It is possible, although evidence is lacking, that these products may be ionic and contain derivatives of the hexachlorodiborate anion:

$$B_2Cl_4 2NMe_3 + 2RX \rightarrow [NMe_3R^+]_2B_2Cl_4X_2^{2-}$$
$$(RX = HCl,\ HCN,\ MeCN,\ EtOEt)$$

The salts $Na_2B_2(C_6H_5)_6$ and $Na_2B_2Me_5H$ (*410*) may contain fully substituted derivatives of the same ion.

Phosphine (unlike ammonia) when treated with diboron tetrachloride gives a 2:1 adduct (PH_3:B_2Cl_4), which is stable at room temperature in a vacuum; at about 65°, cleavage of boron-chlorine bonds becomes apparent as phosphonium chloride begins to be evolved (*842*). Stable, white 2:1 adducts are also formed when hydrogen cyanide and methyl cyanide react with diboron tetrachloride (*405*).

3. *Reactions Involving Compounds Containing Oxygen or Sulfur*

Although being inactive toward sulfur (*18*) or sulfur dioxide (*415*) at room temperature, diboron tetrachloride ignites when exposed to oxygen or air, producing boric oxide and boron trichloride (*18*); the amount of oxygen consumed suggests that the following reaction occurs:

$$6B_2Cl_4 + 3O_2 \rightarrow 8BCl_3 + 2B_2O_3$$

For this the postulated mechanism (*409*) involves, initially, the addition of 1 mole of diboron tetrachloride to an oxygen molecule followed by

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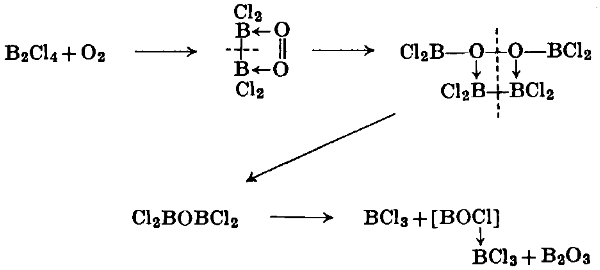
[11] Hydrogen chloride and hydrogen iodide have no action on diboron tetrachloride even at 0° (*842*).

rupture of the B—B bond to give $Cl_2B—O—O—BCl_2$; this peroxy compound is then considered able to add on a further molecule of diboron tetrachloride:



When diboron tetrafluoride reacts with oxygen the position is complicated by the formation of a solid residue containing boron, oxygen, and varying amounts of fluorine (*414*). Other diboron compounds are also sensitive to dry oxygen, but only at temperatures much higher than −78°. At 25° tetraethoxydiboron and oxygen give triethyl borate and a compound thought to be triethoxyboroxine (*97*):

$$6B_2(OEt)_4 + 3O_2 \rightarrow 6(EtO)_3B + 2(EtOBO)_3$$

Tetrakis(dimethylamino)diboron does not react with oxygen at 100° (*97*), but at 200° tris(dimethylamino)borane and tris(dimethylamino)-boroxine are formed (*540*),

$$6B_2(NMe_2)_4 + 3O_2 \rightarrow 6(Me_2N)_3B + 2(Me_2NBO)_3$$

although the reaction is complicated by the concurrent oxidation of the methyl groups.

The careful treatment of diboron tetrachloride with an excess of distilled water at, or below, room temperature produces sub-boric acid (*841, 842*):

$$B_2Cl_4 + 4H_2O \rightarrow B_2(OH)_4 + 4HCl$$

At higher temperatures some cleavage of the boron-boron bond in the sub-boric acid occurs simultaneously, and hydrogen is evolved; at 160° the cleavage is complete within a few hours (*841, 842*):

$$B_2Cl_4 + 4H_2O \xrightarrow{160^\circ} B_2(OH)_4 \xrightarrow[2H_2O]{160^\circ} 2B(OH)_3 + H_2$$

The presence of alkali catalyzes this cleavage, and in ca. 10% sodium hydroxide the evolution of 1 mole of hydrogen is essentially complete after 3 hours at 70° (*826*); this alkaline hydrolysis has since been used extensively as a convenient method for the quantitative analysis of boron-boron bonds in general. A more useful source of sub-boric acid is the readily hydrolyzable tetrakis(dimethylamino)diboron (*553*, *647*):

$$B_2(NMe_2)_4 + 4H_2O \rightarrow B_2(OH)_4 + 4NHMe_2$$

Sub-boric acid is stable for weeks at room temperature if stored in a vacuum, but begins to lose water on heating to 90°–100° (*647*, *841*, *842*); the loss of water is quantitative after 4 hours at 250°, the white solid, boron monoxide, being formed (*841*, *842*):

$$B_2(OH)_4 \rightarrow B_2O_2 + 2H_2O$$

This monoxide is of some interest since it is possible to synthesize diboron tetrafluoride and tetrachloride directly from it either by heating with boron trichloride (*552*) or by the action of sulfur tetrafluoride at $-78°$ (*98*). Other methods of preparing boron monoxide involve strong heating of boric oxide/boron mixtures at low pressure (*436*, *744*) or by reducing a metal oxide, such as zirconium dioxide, with elemental boron (*410*); under the low pressure involved in these processes the boron monoxide can be made to sublime away from the other reaction products. The major component of "boron monoxide" in the vapor phase at 1500°K is actually the dimer, B_2O_2 (*744*).

Although the reaction of water with diboron tetrafluoride has yet to be studied, it has been stated that small amounts of silicon tetrafluoride are formed when diboron tetrafluoride is allowed to stand for some time in a Pyrex apparatus (*414*); this suggests that hydrolysis to hydrogen fluoride (which would then attack the glassware) occurs readily even with water adsorbed on the vessel walls. Hydrogen is quantitatively evolved when diboron tetrafluoride and tetrabromide are heated with sodium hydroxide solution (*246*, *826*). Diboron tetraiodide reacts vigorously with pure water, and in alkaline solution hydrogen is produced (*757*).

Hydrogen sulfide forms two adducts, $B_2Cl_4H_2S$ and $B_2Cl_42H_2S$, when allowed to react with diboron tetrachloride at $-78°$; however, above $-78°$ cleavage of the boron-boron bond occurs (*842*),

$$3B_2Cl_4 + 3H_2S \rightarrow 3H_2 + B_2S_3 + 4BCl_3$$

together with several concurrent side reactions:

$$BCl_3 + B_2S_3 \rightleftharpoons B_3S_3Cl_3$$
$$B_2S_3 + 3H_2S \rightarrow 2B(SH)_3$$
$$2B(SH)_3 + 4BCl_3 \rightarrow 6BCl_2SH$$

The boron-chlorine bonds in diboron tetrachloride are susceptible to attack by alcohols, giving hydrogen chloride and the corresponding tetraalkoxydiboron (*826*):

$$B_2Cl_4 + 4ROH \rightarrow B_2(OR)_4 + 4HCl$$
$$(R = Me, Et)$$

Again, tetrakis(dimethylamino)diboron is a more convenient source of the tetraalkoxydiborons (*647*):

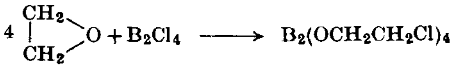
$$B_2(NMe_2)_4 + 4ROH \rightarrow B_2(OR)_4 + 4Me_2NH$$
$$(R = Me, Et, Pr, Bu)$$

Hydrogen chloride has been used in large-scale preparations to remove the dimethylamine as it is formed (*97*):

$$B_2(NMe_2)_4 + 4ROH + 4HCl \xrightarrow[Et_2O]{-78^\circ} B_2(OR)_4 + 4Me_2NH_2Cl$$
$$(R = Me, Et, CHMe_2, C_6H_5)$$

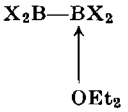
The tetraalkoxydiborons, unlike the tetraaminodiborons, will react with sulfur tetrafluoride to give diboron tetrafluoride (*98*). Some loss of diboron tetrafluoride occurs in this synthesis owing to the formation of a 1:1 adduct, $B_2F_4SF_4$, which slowly decomposes via the elimination of boron trifluoride.

Tetrakis(2-chloroethoxy)diboron is formed as the major product when ethylene oxide reacts with diboron tetrachloride (*537*):

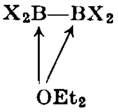


Like the other tetraalkoxydiborons, this compound is more thermally stable than the tetrahalides, hydrolyzes readily to lose the alkyl group as $HOCH_2CH_2Cl$, and does not react with dry oxygen at room temperature.

Diethyl ether forms a solid 2:1 etherate, $B_2X_42Et_2O$, with both diboron tetrafluoride (*246*) and tetrachloride (*826*). On pumping at room temperature the 2:1 adducts lose ether, finally giving 1:1 adducts (*246*, *826*). The structures of the 1:1 etherates is not known but at least two modes of bonding are possible for the ether:



(oxygen using a single lone pair)



(oxygen using both available lone pairs)

On standing at room temperature the monoetherates lose ethyl halide as the B—X bonds are attacked[12]:

$$B_2X_4OEt_2 \rightarrow B_2X_3OEt + EtX$$
$$[X = F\ (\mathit{246}),\ Cl\ (\mathit{826})]$$

Dimethyl ether (*826*) and dimethyl sulfide (*842*) both form a 2:1 and a 1:1 complex with diboron tetrachloride; in the case of dimethyl sulfide, adduct formation is accompanied by the loss of some methyl chloride. 1,2-Dimethoxyethane gives a stable 1:1 complex on treatment with diboron tetrafluoride (*364*).

Acetone, like diethyl ether, yields a 2:1 adduct with diboron tetrachloride, which loses acetone in a vacuum at room temperature; however, decomposition via hydrogen chloride evolution takes place before the 1:1 adducts can be isolated (*533*). No adduct formation occurs when diboron tetrafluoride and propionic acid are mixed at 20°, instead an almost quantitative cleavage of the boron-boron bond occurs, resulting in the isolation of propionyloxyboron difluoride (*404*):

$$B_2F_4 + 2EtCOOH \rightarrow H_2 + 2EtCOOBF_2$$

Mixtures of oxygen difluoride and diboron tetrafluoride ignite at temperatures as low as −78°, forming boron trifluoride and boric oxide (*415*):

$$6B_2F_4 + 3F_2O \rightarrow 10BF_3 + B_2O_3$$

Similar vigorous reactions, giving the same products, occur when certain metal oxides are in contact with diboron tetrafluoride, the vigor of reaction being in the same order as the ease of oxygen evolution on heating the oxides alone, e.g., $HgO > MnO_2 > CuO$ (*415*). As the metal oxide/B_2F_4 mixtures often ignited, reaction would obviously be accompanied by some thermal decomposition of the diboron tetrafluoride to give $(BF)_n$ and, in separate experiments, it was shown that the above metal oxides react with boron monofluoride to give oxygen (*415*).

4. *Other Reactions Involving Rupture of the Boron–Boron Bond*

Chlorine reacts readily with diboron tetrafluoride to form a mixture of boron trifluoride, trichloride, and the two chlorofluorides (*357*):

$$B_2F_4 + Cl_2 \rightarrow 0.92BF_3 + 0.30BCl_3 + 0.46BF_2Cl + 0.32BFCl_2$$
$$\Delta H = -82 \pm \text{kcal mole}^{-1}$$
$$\Delta H_f^\circ(B_2F_4g) = -342 \text{ kcal mole}^{-1}$$

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[12] It is not yet established whether the adduct F_3BOEt_2 loses ethyl fluoride under the same conditions (see page 86).

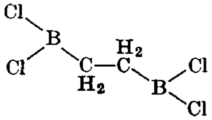
A more simple reaction occurs at –45° when diboron tetrachloride is used (*18, 358*):

$$B_2Cl_4(l) + Cl_2(g) \rightarrow 2BCl_3(g)$$
$$\Delta H = 68 \pm 2 \text{ kcal mole}^{-1}$$
$$\Delta H_f{}^\circ(B_2Cl_4l) = -126.2 \text{ kcal mole}^{-1}$$
$$\Delta H_f{}^\circ(B_2Cl_4g) = -118.2 \text{ kcal mole}^{-1}$$

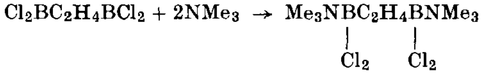
The thermochemical data from these two reactions allow the derivation of the bond energy for the B—B bond in B_2F_4 as 72.4 kcal (*357*) and in B_2Cl_4 as 79 kcal (*358*); these values are close to the B—B bond energy obtained from calorimetric data for sub-boric acid of 84 ± 5 kcal (*239*). By assuming the B—B bond energy in all the diboron compounds to be constant within about ±5 kcal of 78 kcal,[13] Finch has been able to estimate the heats of formation in the gas phase of diboron tetrabromide to be ca. –50 kcal and of the tetraiodide to be ca. +20 kcal mole^{-1} (*239*).

Bromine reacts smoothly with diboron tetrachloride at – 23° to give a mixture of boron trichloride, tribromide, and the two chloro-bromides (*18*); iodine has no action on diboron tetrachloride even at room temperature (*18*).

One of the most interesting reactions involving the cleavage of the boron-boron bond in the diboron tetrahalides is the reaction that occurs between the tetrafluoride or tetrachloride and C—C multiple bonds. Thus, ethylene reacts with diboron tetrachloride even at –78° to form a virtually quantitative yield of the adduct $B_2Cl_4C_2H_4$ (*824*). Schlesinger found that this adduct, a volatile liquid having a vapor pressure of a few mm at room temperature, did not yield hydrogen on alkaline hydrolysis, and therefore suggested that it was 1,2-bis(dichloroboryl)ethane. This has been verified by X-ray diffraction studies on single crystals, which also show that the molecule has a planar *trans* configuration in the solid state (*589*):



This molecule, being essentially an alkylboron dichloride, has properties intermediate between triethylborane and boron trichloride (see Fig. 1). Trimethylamine will add quantitatively to the boron atoms (*407*),



$$Cl_2BC_2H_4BCl_2 + 2NMe_3 \rightarrow \underset{Cl_2}{Me_3NB}C_2H_4\underset{Cl_2}{B}NMe_3$$

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[13] This value is considerably higher than the dissociation of the B_2 molecule, which has been calculated to be ca. 69 kcal mole^{-1} (*358*).

while ammonia (*407*) attacks the boron-chlorine bonds, forming hydrogen chloride; alcohols give the corresponding 1,2-bis(dialkoxyboryl)ethanes (*824*), and zinc dimethyl substitutes methyl groups for the chlorine atoms (*824*). Ignition occurs in dry oxygen (cf. the lower members of the trialkylborane series), one of the products being free ethylene (*407*). Although boron-carbon bonds are normally stable to the action of water even at 100°, carboxylic acids cleave the alkyl groups from boron and give the corresponding alkane; the case of 1,2-bis(dichloroboryl)ethane is no exception, since ethane (together with a trace of ethylene) is produced when the compound is heated for some hours in a sealed tube with propionic acid (*192*, *532*). Antimony trifluoride undergoes fluorine exchange with 1,2-bis(dichloroboryl)ethane (*149*) to give 1,2-bis(difluoroboryl)ethane, which can also be made by allowing ethylene to react with diboron tetrafluoride, although this reaction is slower than the addition to B_2Cl_4 (*149*):

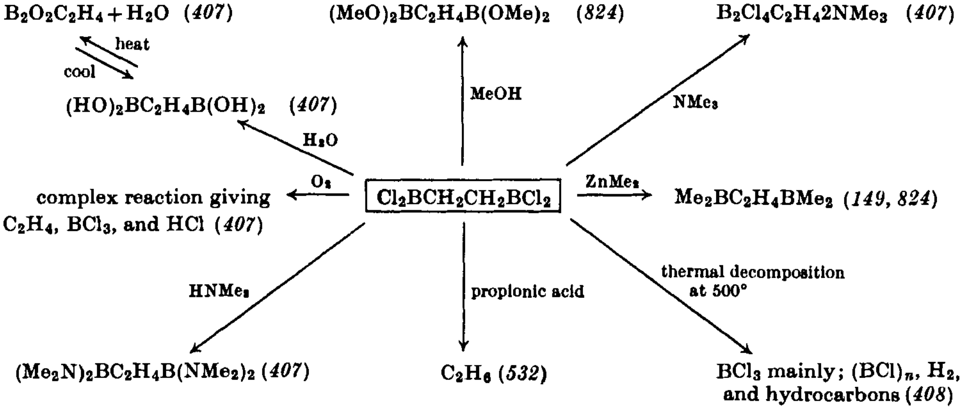
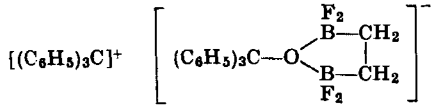


FIG. 1. Some reactions of 1,2-bis(dichloroboryl)ethane.

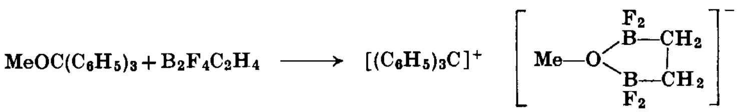
$$B_2F_4 + C_2H_4 \rightarrow F_2BC_2H_4BF_2$$

1,2-Bis(difluoroboryl)ethane forms the normal 1:2 adducts when treated with either dimethyl ether or tetrahydrofuran (*76*), but when bis(triphenylmethyl) ether is used only a 1:1 compound can be obtained, which has the structure (*76*):



In the corresponding case of methyl(triphenylmethyl) ether, it is possible to prepare the expected 1:2 adduct, but when an excess of

1,2-bis(difluoroboryl)ethane is used a similar chelated product is formed (76):



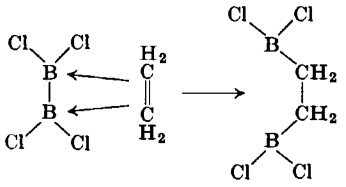
$MeOC(C_6H_5)_3 + B_2F_4C_2H_4 \longrightarrow [(C_6H_5)_3C]^+$

The olefin addition reaction seems to be fairly general; thus the use of butadiene gives either 1:1 addition (diene:B_2Cl_4) or 1:2 addition, depending on the reaction ratios, on treatment with diboron tetrachloride (*149*). However, allyl fluoride exchanges fluorine for chlorine when allowed to react with diboron tetrachloride:

$$4C_3H_5F + B_2Cl_4 \rightarrow B_2F_4 + 4C_3H_5Cl \qquad (\mathit{149})$$

More usually the presence of halogen in the olefin greatly interferes with the addition of diboron tetrachloride. One chlorine on a carbon atom forming the double bond is sufficient to stop the addition of diboron tetrachloride even at room temperature; if the halogen is on a carbon not involved in the olefinic double bond, then the addition of diboron tetrachloride can take place (e.g., in the cases of allyl chloride or 4-chlorobutene-1) (*149*) but even so it is found that the allyl chloride adduct is very thermally unstable.

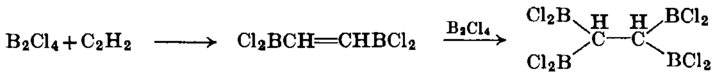
The mechanism suggested (*409*) for this olefin addition reaction involves the initial formation of an adduct by overlap of the vacant boron orbitals with the olefinic π-bond, the diboron tetrachloride taking up the planar configuration followed by rupture of the boron-boron bond and



the simultaneous formation of two normal boron-carbon bonds. Deactivation of the olefinic π-bond by electron withdrawal in the case of halo-olefins would explain why such olefins do not undergo the addition reaction. However, it is interesting to point out that, whereas diboron tetrachloride will decompose rapidly above 0°, in the presence of the unreactive olefins the decomposition of the tetrachloride is inhibited even at temperatures well above 25° (*149*); this phenomenon has since been confirmed in several laboratories. It is natural to assume that some weak interaction does occur between the halo-olefins and diboron tetrachloride, but all efforts so far to detect changes in the proton n.m.r. spectra of the olefins due to such an interaction have failed (*90*). The availability of the vacant orbitals on the boron atoms for attack by the olefin will also be an important factor in governing the kinetics of the addition reaction; and possibly the much slower reactions of diboron tetrafluoride with the olefins, compared to the tetrachloride, are a reflection of the stronger π-bonding that occurs between boron and fluorine than between boron and chlorine. The unreactivity of tetrakis(dimethylamino)-diboron toward ethylene can probably be explained by considerable B—N π-bonding (*540*), but there is also a complicating steric factor operating in this case when the diboron molecule attempts to adopt the planar configuration required for the initial stage of the reaction [see Becher *et al.* (*65*) for a discussion on the structures of tetramethoxydiboron and tetrakis(dimethylamino)diboron].

Cyclopropane will also add across the boron-boron bond of diboron tetrachloride at about 0° and, in this case, a three-membered carbon chain separates the boron atoms in the product, 1,3-bis(dichloroboryl)-propane (*149*). It might be an interesting experiment to attempt the synthesis of the yet unknown bis(dichloroboryl)methane by treating diazomethane with diboron tetrachloride.

When acetylene reacts with diboron tetrachloride, the 1 : 1 addition compound 1,2-bis(dichloroboryl)ethylene is initially formed (*149*, *158*). The presence of the carbon-carbon double bond is shown by the fact that bromine will add quantitatively, while treatment of 1,2-bis(dichloroboryl)ethylene with propionic acid releases 1 mole of ethylene (*158*). Thus, as might be expected, it is possible to add a further mole of diboron tetrachloride to the double bond, giving 1,1,2,2-tetrakis(dichloroboryl)-ethane (*158*):



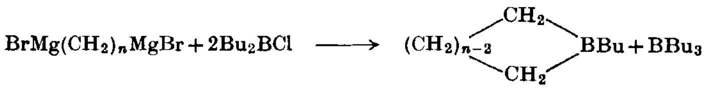
Although the 1,2-bis(dihaloboryl)alkanes are readily prepared from the diboron tetrahalides, syntheses not involving the use of the rather inaccessible tetrahalides would obviously be welcome to the preparative chemist. The first attempt at such a synthesis involved the treatment of the di-Grignard reagent $BrMgC\equiv CMgBr$ with dialkylboron iodides (*372*):

$$2R_2BI + BrMgC\equiv CMgBr \rightarrow R_2BC\equiv CBR_2$$

The products are 1,2-bis(dialkylboryl)acetylene derivatives; the action of oxygen will convert these compounds to the corresponding alkoxides:

$$R_2BC\equiv CBR_2 + O_2 \rightarrow (RO)_2BC\equiv CB(OR)_2$$

However, this method of synthesis, when applied to the bis(dialkylboryl)-alkanes, results only in the formation of boron heterocycles (*164*):



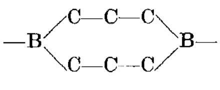
The addition of diborane to an excess of acetylene in 1,2-dimethoxyethane resulted in the formation of a white solid of approximate composition $(C_2H_2)_3B_2H_6$, which gave no hydrogen on hydrolysis but yielded ethane quantitatively on treatment with propionic acid; these properties suggest a polymeric structure made up of $>BC_2H_4B<$ links, and in accord with this it was found that the solid reacted with either boron trifluoride or trichloride to give good yields of the corresponding 1,2-bis(dihaloboryl)ethane (*162*):

$$[B_2(C_2H_4)_3]_x + 4xBX_3 \rightarrow 3xX_2BC_2H_4BX_2$$

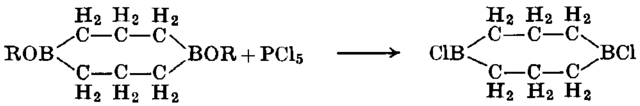
Similarly, dimethylenetetraborane, formed from ethylene and tetraborane-10 (*768*) produces 1,2-bis(dimethoxyboryl)ethane on methanolysis (*371*):

$$C_2H_4B_4H_8 + 10MeOH \rightarrow (MeO)_2BC_2H_4B(OMe)_2 + 9H_2$$

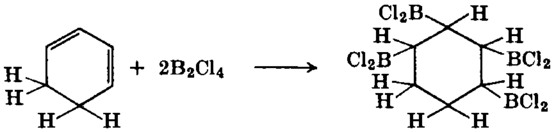
A somewhat related series of heterocycles involving



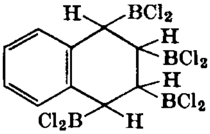
bridges have been made by heating triallylborane with triisobutylborane at 130–140° (*410*); butene is evolved and the resulting polymer, on boiling with an alcohol, gives the dialkoxy-1,5-diborocanes, which can be treated with phosphorus pentachloride to give the dichloro derivatives:



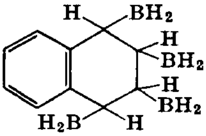
Cyclo-olefins will add on diboron tetrachloride quite readily; thus 1,3-cyclohexadiene reacts to give a 2:1 adduct when the temperature is allowed to rise from −78° to 20° over a period of 10 days (*878*).



Benzene and diboron tetrachloride appear to react at room temperature but an olefin-type addition product is not isolated, instead a high yield of phenylboron dichloride is obtained (*255*). However, if naphthalene is used, 2 moles of diboron tetrachloride are taken up at room temperature over about 2 weeks to give the yellow liquid, $C_{10}H_8 2B_2Cl_4$, for which chemical and ^1H n.m.r. evidence suggest the structure:



By treatment of this chloride with lithium borohydride it is possible to reduce it to the corresponding borane (*877*, *878*):



A similar reduction of 1,2-bis(dichloroboryl)ethane, however, gives only an unstable colorless oil, which on decomposition at about −20° produces diborane (*878*).

Although the boron-boron bond is broken when diboron tetrafluoride is treated with diphenylmercury, a different reaction takes place, in which phenylboron difluoride is the principal product (*415*):

$$B_2F_4 + (C_6H_5)_2Hg \rightarrow Hg + 2C_6H_5BF_2$$

Diethylmercury reacts similarly, ethylboron difluoride being formed; the presence of ethane among the by-products might suggest that some ethyl radicals were liberated:

$$2C_2H_5 \rightarrow C_2H_6 + C_2H_4$$

However, only traces of ethylene were isolated while no 1,2-bis(difluoroboryl)ethane could be detected (*415*).

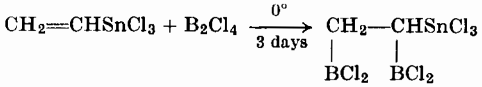
Tetravinylstannane produces a red viscous oil, tin, ethylene, and vinylboron difluoride when allowed to stand in contact with diboron tetrafluoride at −80°; again, although ethylene was among the products, no 1,2-bis(difluoroboryl)ethane was detected (*415*). This is somewhat similar to the reactions that take place between either tetramethylstannane and diboron tetrafluoride (*90*),

$$Me_4Sn + B_2F_4 \xrightarrow{20^\circ} Me_2BF + MeBF_2 + (SnMe_2)_x + Sn$$

or between tetramethylstannane and diboron tetrachloride (*90*):

$$Me_4Sn + B_2Cl_4 \xrightarrow[10\ \text{months}]{-80^\circ} MeBCl_2 + BCl_3 + \text{products}$$

If vinyltrichlorostannane is treated with diboron tetrachloride, it is found that slow addition of the diboron compound to the olefinic double bond occurs (*89, 90*):



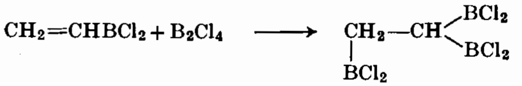
$$CH_2{=}CHSnCl_3 + B_2Cl_4 \xrightarrow[3\ \text{days}]{0^\circ} \underset{\displaystyle BCl_2}{CH_2}-\underset{\displaystyle BCl_2}{CHSnCl_3}$$

A similar addition occurs over a period of days when diboron tetrachloride and vinyltrichlorosilane are mixed together, the reaction being conveniently monitored by proton n.m.r. spectroscopy (*90*); rotational isomers complicate the n.m.r. spectrum of the products, as was found to be the case in the adduct formed by either *cis-* or *trans-*butene and diboron tetrachloride (*237*). However, no addition occurred between either vinyltrifluorosilane or vinylsilane and diboron tetrachloride (*90*):

$$CH_2{=}CHSiF_3 + B_2Cl_4 \rightarrow BF_3 + BF_2Cl + SiF_4 + \text{products}$$

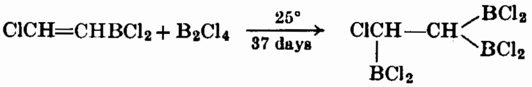
$$CH_2{=}CHSiH_3 + B_2Cl_4 \rightarrow \text{stabilization of } B_2Cl_4 \text{ against thermal decomposition}$$

Vinylboron dichloride and chlorovinylboron dichloride both undergo a smooth, although slow, addition of diboron tetrachloride, the latter being presumably stabilized for many days before the reaction is complete:



$$CH_2{=}CHBCl_2 + B_2Cl_4 \longrightarrow \underset{\displaystyle BCl_2}{CH_2}-CH{<}^{BCl_2}_{BCl_2} \qquad (90)$$

(*90*)

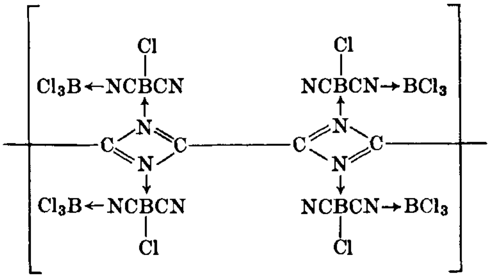


$$ClCH{=}CHBCl_2 + B_2Cl_4 \xrightarrow[37\ \text{days}]{25^\circ} \underset{\displaystyle BCl_2}{ClCH}-CH{<}^{BCl_2}_{BCl_2}$$

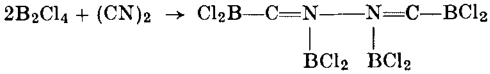
(*90*)

However, no adduct is formed when diboron tetrafluoride and vinylboron dichloride are heated to 100° (*90*).

Diboron tetrachloride readily absorbs 1.5 moles of cyanogen to form a dark brown solid, which evolves no hydrogen on alkaline hydrolysis (showing the absence of B—B bonds), and adds 2 moles of trimethylamine without loss of cyanogen; strong heating to 400° causes the solid to lose 1 mole of boron trichloride, leaving a residue of composition $BCl(CN)_3$ (*19*). On the basis of these properties the following polymeric structure was proposed for the solid:



However, since cyanogen contains a triple carbon-nitrogen bond, it appears more attractive to assume that the molecule adds across the boron-boron bond in the same way as acetylene,



$$2B_2Cl_4 + (CN)_2 \rightarrow Cl_2B{-}C{=}\underset{BCl_2}{\underset{|}{N}}{-}\underset{BCl_2}{\underset{|}{N}}{=}C{-}BCl_2$$

while a further mole of cyanogen might be used for forming donor-acceptor bonds with the tricovalent boron atoms [cyanogen has been shown to react quite readily with boron trichloride to form $(CN)_2 2BCl_3$ (*19*)], and in this way a polymeric structure would be built up.

Nitric oxide, while interacting only weakly with the boron trihalides, readily reacts in a 1 : 1 ratio with diboron tetrachloride even at temperatures below −78°, giving a green solid; unfortunately this solid is unstable thermally and at −40° decomposes with the evolution of about 1 mole of boron trichloride, so that it was impossible to discern the presence or absence of a boron-boron bond by alkaline hydrolysis. Neither ethylene nor oxygen reacted with the adduct at −78°, although both readily attack diboron tetrachloride at that temperature. Attempts to stabilize the solid by treatment with trimethylamine resulted only in the loss of the boron trichloride (recovered as Me_3NBCl_3) at −78°. On this rather meager evidence it was suggested that addition of the nitric oxide across the boron-boron bond had occurred (*409*):

$$B_2Cl_4 + NO \xrightarrow{-78^\circ} Cl_2B{-}NO{-}BCl_2 \xrightarrow{-40^\circ} BCl_3 + [B_3N_3O_3]$$

Ignition occurs if diboron tetrachloride and nitric oxide are mixed rapidly at room temperature. When the tetrafluoride is used, ignition sometimes occurs even at –78°, the products including boron trifluoride, nitrous oxide, and nitrogen (*414*); again a green colored unstable solid is formed at low temperatures. Neither carbon monoxide nor carbon dioxide reacts with diboron tetrachloride at room temperature (*409*).

C. OTHER BORON HALIDES

1. *Tetraboron Tetrachloride*, B_4Cl_4

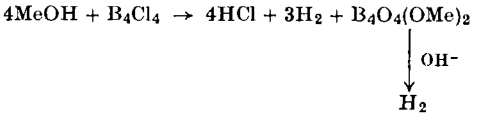
Probably little more than 1 or 2 grams of this rare, slightly yellow, solid chloride has ever been obtained, and in consequence comparatively little is known concerning its properties. The vapor pressure of the solid is suitably summarized by the equation:

$$\log p\,(\text{mm}) = -\frac{2719}{T} + 9.464$$

At room temperature, p is about 2 mm (*823*, *827*). The vapor density is normal at 70° (*823*, *827*) and the mass spectrum of the vapor shows a strong group of peaks around mass 184 due to the parent ion $B_4Cl_4^+$ (*543*, *545*).

Tetraboron tetrachloride is spontaneously inflammable in dry air (*823*), producing boron trichloride as was found in the combustion of diboron tetrachloride. However, in general, the chemistry of the two tetrachlorides is quite widely dissimilar. Hydrogen apparently produces traces of hydrogen chloride when heated with tetraboron tetrachloride to 70° (the decomposition point of the tetrachloride), but even after 18 hours at this temperature 95% of the starting material was recovered unchanged (*823*). A complex reaction occurs between diborane and tetraboron tetrachloride at 55° giving boron trichloride, $(BH)_x$, and possibly a compound of formula $B_4Cl_4B_2H_6$ (*823*); the reaction is being studied further in the hope of ascertaining if this latter compound is a tetrachloro derivative of the little known hexaborane-10.

At room temperature the boron-boron bonds in tetraboron tetrachloride are cleaved by water to product 3 moles of hydrogen in 12 hours; a further mole of hydrogen is generated in the presence of alkali (*823*). A similar reaction occurs during the methanolysis of tetraboron tetrachloride:



$$4MeOH + B_4Cl_4 \rightarrow 4HCl + 3H_2 + \underset{\substack{\downarrow\, OH^- \\ H_2}}{B_4O_4(OMe)_2}$$

The compound $B_4O_4(OMe)_2$ was not suitably identified and may well be a mixture (*823*). Ethylene did not cleave the boron-boron bonds even at 70° (*823*).

Attempts to form adducts of tetraboron tetrachloride with either phosphorus trichloride or diethyl ether failed; in diethyl ether solution at room temperature, the tetrachloride slowly evolves ethyl chloride in an ether-splitting reaction (*823*).

Substitution of the chlorine atoms is apparently possible in certain cases; dimethylzinc gives the monomethyl derivative B_4Cl_3Me at room temperature, which has a normal vapor density at 63° (*823*). Dimethylamine, on the other hand, removes all four of the chlorine atoms from tetraboron tetrachloride as hydrogen chloride (which then reacts with excess of the amine to give dimethylamine hydrochloride):

$$B_4Cl_4 + 8Me_2NH \rightarrow B_4(NMe_2)_4 + 4Me_2NH_2Cl$$

It was thought (*823*) that the nonexistence of a strong infrared band close to 1010 cm^{-1} in the spectrum of $B_4(NMe_2)_4$ indicated the loss of the boron-cage structure in this dimethylamino compound; however, the intense band at 1010 cm^{-1} in tetraboron tetrachloride is more likely to be associated with the B—Cl vibrations (in line with several other boron chlorides) than solely with a boron-cage absorption, and thus there is no evidence to suggest that the tetrahedral B_4 cage of tetraboron tetrachloride did not survive reaction with dimethylamine and so still exist in $B_4(NMe_2)_4$.

2. *Dodecaboron Undecachloride, $B_{12}Cl_{11}$*

This dark red solid is, next to boron trichloride, the major product formed during thermal decomposition of diboron tetrachloride; it melts at 115 ± 1° (*753*, *825*) and sublimes in a vacuum above room temperature. There is some dispute as to the correct formulation since mass spectral studies suggest a molecular formula of $B_{11}Cl_{11}$ (*543*, *545*), but, for a discussion of the few exploratory experiments carried out on the compound, it will be assumed to be $B_{12}Cl_{11}$. The most interesting physical property of the solid is its apparent paramagnetism, which gives rise to a broad, featureless peak in the electron-spin resonance spectrum of g value 2.011 and peak width 25 gauss (*753*, *825*).

In contrast to diboron tetrachloride and tetraboron tetrachloride, $B_{12}Cl_{11}$ hydrolyzed more rapidly in acid solution than in alkali, but in neither case was the amount of hydrogen evolved equal to that required for the complete decomposition of the solid to boric acid:

$$2B_{12}Cl_{11} + 72H_2O \rightarrow 22HCl + 24B(OH)_3 + 25H_2$$

The optimum amount of hydrogen was about 80% over a period of 27 days in acid solution (*753*). In the alkaline solution the extreme slowness of hydrolysis was assumed to be due to the formation of very stable derivatives of the $B_{10}X_{10}^{2-}$ ions, e.g.:

$$2B_{12}Cl_{11} + 14OH^- \rightarrow 2B_{10}Cl_8(OH)_2^{2-} + 4BO_2^- + 3H_2 + 6Cl^- + 2H_2O$$

Trimethylamine discharged the red color of $B_{12}Cl_{11}$ when the two were mixed at −78° and a light tan-colored solid of composition $B_{12}Cl_{11}2NMe_3$ was formed, which decomposed at 75° by evolving trimethylamine-boron trichloride; it was suggested that the loss of color may have been due to the loss of paramagnetism via dimerization (*753*).

$B_{12}Cl_{11}$ on ethanolysis gave a mixture of triethyl borate, hydrogen chloride, ethyl chloride, diethyl ether, and an uncharacterized brown solid (*753*). The complex reaction with trimethylaluminum gave methane, boron trimethyl, and a series of volatile, highly colored, interesting, but uncharacterized solids (*753*), which obviously warrant further study. Nitric oxide did not react with $B_{12}Cl_{11}$, even though both molecules have an unpaired electron and nitric oxide attacked the boron-boron bond in diboron tetrachloride (*753*).

3. (BX)$_x$

Comparatively little is known about the chemistry of the other boron monohalides; the involatile yellow solid, $(BF)_x$, releases oxygen when treated with manganese dioxide, cupric oxide, or mercuric oxide (*415*), while $(BBr)_x$ (*208*) and $(BI)_x$ (*757*) evolve a little hydrogen during hydrolysis, giving rise to solutions with strong reducing properties. Ammonolysis of $(BBr)_x$ gives a white compound of composition $(B_2NH)_x$ (*208*). Both boron monobromide (*208*) and monoiodide (*757*) appear to sublime above room temperature in a good vacuum (a mass spectrometric study of the vapor may give useful information concerning the identity of these halides) but, on strong heating, decomposition occurs (*757*), e.g.:

$$(BI)_x \xrightarrow{125^\circ} I_2 + \text{black residue} \xrightarrow[\text{heating}]{\text{strong}} B + I_2$$

Although not prepared from the monohalides, some substituted derivatives are known such as $(BH)_x$ (*410*), $(BC_4H_9)_x$ (*33*), $(BC_6H_{13})_x$ (*864*), and $(BC_6H_5)_x$ (*462*); the latter phenyl compound, the most studied of these, has a value of x lying between 9 and 12. It is an amorphous powder, readily oxidized by air and soluble in benzene, dioxan, and toluene to give a yellowish brown solution; hydrolysis gives some phenylboric acid, but only about 10% of the hydrogen required by the equation:

$$(C_6H_5B)_x + 2xH_2O \rightarrow xC_6H_5B(OH)_2 + xH_2$$

Ammonia, when passed into a benzene solution of $(C_6H_5B)_x$, gives a colorless compound, $[(C_6H_5B)NH_3]$.

V. Conclusion

There is little on which to comment concerning the boron trihalides, as their chemistry is comparatively well worked out, and advances in the main appear to center around new potential Lewis bases (e.g., *329*) or the use of different reactive organic compounds (e.g., *433*, *434*). As in most other branches of chemistry, X-ray structural determinations on boron halide derivatives lag far behind preparative investigations, and one hopes that some of the many structural queries raised in this review will shortly be settled. This is especially so in the case of the many intriguing compounds arising from the study of the diboron tetrahalides.

Although it is now possible to obtain reasonable quantities of diboron tetrachloride, the search for good nondischarge routes to its synthesis should continue, as success in this direction would open up the chemistry not only of diboron tetrachloride itself but also of the polyboron chlorides that arise from it by thermal degradation. An exploration of halogen exchange reactions using these polyboron chlorides should prove rewarding and, for example, extend the number of known boron monofluorides from the single $(BF)_x$ to B_4F_4 (although it has been suggested that this compound may be unstable thermally) (*544*), B_9F_9, and $B_{11}F_{11}$.

Many of the reactions described in this review, especially those involving the diboron tetrahalides, were carried out in the absence of a solvent, whereas in many cases it may well prove better to use a solvent provided that no reaction occurs between solvent and solute either by formation of stable adducts or by loss of hydrogen halide; for example, little advantage has yet been taken of the fact that halo-olefin solutions of diboron tetrachloride are quite stable thermally even at temperatures well above 20°. Such solvents should prove ideal media for studying the chemistry of diboron tetrachloride above 0°, while a study of such a system by several physical methods may reveal the nature of the solute-solvent interaction.

The difficulties experienced in the analysis and molecular weight determinations of several B—X polymers and of certain amine adducts of the diboron tetrahalides (often due to their air and moisture sensitivity) may well be overcome by the use of mass spectrometry, since these compounds are often quite volatile in high vacuum. Mass spectrometry should also be of great help in mapping out certain areas of the chemistry of tetraboron tetrachloride and $B_{12}Cl_{11}$, where the air sensitivity of the compounds augments the practical difficulties experienced when working with the extremely small quantities of starting materials available; a particular area for such a study might be the reaction of $B_{12}Cl_{11}$ with aluminum trimethyl, where several highly colored, volatile species were detected, but in amounts too small to permit conventional analyses (*753*).

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NOTE ADDED IN PROOF

B_3F_5 AND B_8F_{12}

When boron trifluoride is passed over boron at 2000°C and 0.1 to 1.0 mm Hg, a high yield of BF is obtained which can be condensed onto a surface, cooled to liquid temperatures. The resulting greenish-white polymeric deposit, on warming to room temperature, gives off three major fractions besides boron trifluoride: B_2F_4, B_3F_5 and colorless, slightly-volatile boron fluorides containing up to 14 boron atoms. At least some of the diboron tetrafluoride is thought to be formed from the direct combination of BF and BF_3.

The colorless triboron pentafluoride is probably the first compound to be isolated which has a simple B_3 chain structure; it melts at $-50°$ to $-55°C$ and above $-30°$ rapidly decomposes to BF_3, B_2F_4 and B_8F_{12}. The latter compound is a yellow oil with a vapor pressure at 0° of 2.3 cm. Hg. and is unstable above $-10°$.

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