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ADDUCTS OF THE MIXED TRIHALIDES OF BORON

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I. Introduction

The chemistry of the boron trihalides has been extensively studied. These compounds are strong Lewis acids and form a wide range of simple 1:1 adducts that have served as model compounds for the study of Lewis acid–base interactions. Many reviews of their coordination chemistry have appeared (*41*, *60*, *66*, *120*, *174*, *178*) and these are summarized in the more recent reviews appearing in the mid-1960s (*41*, *120*).

In boron trifluoride adducts, fluorine displacement is relatively difficult and, thus, the widest range of adducts has been prepared for the trifluoride (*66*, *120*). As fluorine is replaced by successively heavier halogens the displacement of halogen occurs more readily and secondary reactions of the initially formed donor–acceptor adducts

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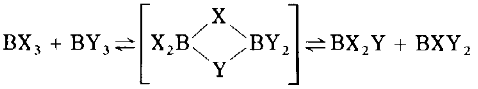
become more important. Whereas the initial formation of a donor–acceptor bond is a simple process, the secondary reactions of the adducts need not be simple. Many such reactions, and related catalytic activity of donor–acceptor adducts of the boron trihalides, have been reported (*41*, *60*, *66*, *120*, *174*, *178*).

Uncomplexed boron trihalides undergo halogen-exchange reactions that are too rapid to allow isolation of the individual mixed halogen species formed (*113*, *114*, *120*). This rapid redistribution of halogens apparently deterred early investigation of adducts of the mixed boron trihalides, and these obvious but elusive compounds remained unknown until the late 1960s. The application of nuclear magnetic resonance spectroscopy during the 1960s greatly simplified the study of even very rapid redistribution reactions (*127*, *128*). It became obvious that redistribution reactions are widespread and tend to occur more rapidly when the species involved are not coordinatively saturated (*31*). The nature of the substituents is also important in determining rates of redistribution, with alkyl groups tending to redistribute much more slowly than halogens (*113*, *114*). Redistribution reactions in many three-coordinate boron compounds have been studied (*68*, *136*, *147*, *168*). These can be either fast or slow depending on substituents. A dimethylamino group slows halogen redistribution, and the mixed-halogen compound $Me_2NBClBr$ can be isolated (*68*).

Redistribution of substituents tends to be especially facile for halides, hydrides, and alkyls of Groups I–III nontransition elements because these compounds are electron-deficient. Bridging groups are present in many of these compounds. Even in the boron trihalides that are not bridged, a bridged transition state making use of the empty valence shell orbitals is possible, so that redistribution can occur with a relatively low activation energy (*113*):



$$BX_3 + BY_3 \rightleftharpoons \left[X_2B \overset{X}{\underset{Y}{\langle\rangle}} BY_2 \right] \rightleftharpoons BX_2Y + BXY_2 \qquad (1)$$

Such a low-energy reaction pathway is not available for four-coordinate boron compounds that are coordinatively saturated.

The donor–acceptor bond in many boron trihalide adducts is fairly weak (*132*, *170*) and for such adducts a characteristic reaction is the rapid breaking and re-forming of this bond (*39*, *62*). Nuclear magnetic resonance studies of the exchange of BX_3 among an excess of Lewis base molecules show that the dissociative mechanism of exchange predominates in a number of cases (*14*, *16*, *39*, *55*, *115*, *151*). Breaking and re-forming of boron–halogen bonds is a less obvious process, although it was known to occur in the heavier tetrahaloborate anions (*172*) and in BF_4^- (*63*).

In 1968 reports of halogen redistribution in neutral boron halide adducts appeared. Chlorine–bromine exchange was detected in the formation and disproportionation of a mixed dihaloborane adduct, $PH_3 \cdot BHClBr$ (*50*), by observation of separate ^1H NMR peaks due to the $BHCl_2$, BHClBr, and $BHBr_2$ adducts at low temperatures. Fluorine exchange between boron atoms was detected in ketone–BF_3 adducts (*62*) as well as in the tetrafluoroborate anion (*63*) by ^{19}F NMR. This reaction did not give mixed-halogen species but was detectable through the collapse of the ^{10}B—^{11}B isotope shift (*7*, *25*) in the ^{19}F spectra at higher temperatures, due to rapid and random fluorine exchange between ^{10}B and ^{11}B. In the ketone–BF_3 systems, the fluorine exchange reaction is much slower than the breaking and re-forming of the weak donor–acceptor bond (*62*).

This work indicated a widespread halogen-exchange process in boron trihalide adducts and the likelihood of easy formation of many adducts of the mixed trihalides of boron. Extensive work being done at the time on nucleophilic displacement of halogen in monohaloborane adducts, $D \cdot BH_2X$ (X = Cl, Br, I) (*152*), also suggested the susceptibility to displacement of halogens by other halogens in boron trihalide adducts. Since then, application of NMR techniques to the study of halogen redistribution in boron trihalide adducts has provided most of the available information on the mixed boron trihalide adducts, in spite of complication of the studies by other rapid exchange reactions in many of the systems.

II. Preparation, Detection, and Properties of Mixed Boron Trihalide Adducts

A. METHODS OF FORMATION

Rapid halogen redistribution at ambient temperature precludes isolation of many mixed-halogen boron trihalide adducts, and most such adducts have been observed only in solution in inert solvents such as methylene chloride. Amine adducts of the mixed boron trihalides are stable to halogen disproportionation and a few of these have been isolated (*3*, *10*, *155*) as have compounds containing mixed tetrahaloborate anions (*120*, *183*). Other nitrogen-donor mixed boron trihalide adducts could no doubt be isolated, by analogy with nitrogen-donor adducts of BH_2X and BHX_2 (Section II,D).

The following methods have been used to prepare the mixed boron trihalide adducts $D \cdot BX_nY_{3-n}$ for *in situ* study by spectroscopic methods.

1. $D{\cdot}BX_3 + D{\cdot}BY_3$

If the donor–acceptor bond is weak, two different boron trihalide adducts of the same donor will exchange halogen to form the mixed-halogen adducts. The weaker the donor–acceptor bond, the more rapidly the mixed adducts form, indicating that free boron trihalide formed by dissociation is an active species in halogen exchange.

2. $D{\cdot}BX_3 + BY_3$

This method is a general route to mixed boron trihalide adducts. Reaction occurs readily in solution at ambient temperature even with amine adducts that do not exchange halogen in the absence of free boron trihalide (*10*). Adducts that do exchange halogen slowly in the absence of uncomplexed trihalide react much faster when uncomplexed trihalide is added (*27*). This method gives mixed $Me_3N{\cdot}BF_nI_{3-n}$ adducts (*10*), whereas free BF_2I and BFI_2 have never been detected except as positive ions in the mass spectrometer (*110*, *111*).

3. $D + BX_nY_{3-n}$ $(n = 0\text{–}3)$

Reaction of a donor molecule with a previously equilibrated mixture of free boron trihalides gives an initial adduct mixture corresponding to the equilibrium mixture of the free boron trihalides. This method should be suitable for all mixtures except BF_3/BI_3 (as noted previously). However, equilibria in the adducts can be quite different from the corresponding equilibria in the free boron trihalides. If halogen redistribution is fast and if the mixed adducts are discriminated against, then this method does not succeed (*28*).

4. $D{\cdot}BX_3 + Y^-$

Halide ion Y^- in the form of soluble tetraalkylammonium salts can in some cases displace halide ion X^- forming a mixed-halogen adduct. However, the method has met with variable success. It is successful with tetrahaloborate ions (*80*) and with $Me_3N{\cdot}BI_3$ (*9*). A similar reaction with insoluble silver halides or pseudohalides has also given mixed adducts (*43*).

5. $BX_3 + Y^-$

Uncomplexed BX_3 interacts with triphenylmethyl halides, $(C_6H_5)_3CY$, to give the BX_3Y^- salt (*120*, *183*). Halide ion Y^- can also be extracted from metal complexes by BX_3 to give species that are probably BX_3Y^- salts (*51*).

6. *Reactions of Diboron Tetrafluoride Adducts*

The reaction of HCl with the bis(trimethylamine) adduct of B_2F_4 gives $Me_3N{\cdot}BF_2Cl$ (*3*).

7. *Other Halogen Sources*

Trimethylsilyl halides will exchange halogen with $Me_3N{\cdot}BX_3$ adducts (*9*) and BF_4^- (*80*). Phosphorus pentahalides (*9*, *13*), Al_2Cl_6 (*9*), and $AsCl_3$ (*9*) act similarly on amine adducts.

Tetrahaloborate ions undergo halogen exchange with methylene halides to give mixed tetrahaloborate anions (*80*). Because these ions are appreciably dissociated in solution (*172*), the reaction appears to involve halide ion attack on CH_2X_2. The complexed boron trihalide might also exchange halogen with halocarbons (*64*, *74*).

B. DETECTION

Of the *in situ* detection methods, infrared spectroscopy was very useful in studying halogen redistribution in the uncomplexed boron trihalides (*69*, *92*, *137*). However, the mixed-halogen adducts have very low symmetry and give very complex spectra, complicated further by overlapping ligand absorptions. Thus, $Me_3N{\cdot}BF_2Br$ and $Me_3N{\cdot}BFBr_2$ gave infrared spectra that were too complex to assign by analogy with unmixed-halogen Me_3N adducts (*10*). An investigation of the carbonyl stretching frequency of carbonyl donor–mixed boron trihalide adducts has been carried out (*87*), but even here where a single strong infrared absorption can be assigned to each mixed-halogen adduct, peak overlap was serious; NMR gave more information. Raman spectroscopy has not yet been applied to the mixed adducts. Due to their higher symmetry, the mixed tetrahaloborate anions are more amenable to study by infrared and Raman spectroscopy. Such studies have been carried out on other mixed-halogen tetrahedral species, such as $AlCl_nBr_{4-n}^-$ (*18*) and $TiCl_nBr_{4-n}$ (*35*) where all members of the series ($n = 0$–4) are present together in solution, and equilibrium constants for the rapid redistribution reactions have been obtained.

Mass spectroscopy can be applied to study of the adducts only when the donor–acceptor bond is strong enough to remain intact in the gas phase under the vigorous conditions of electron impact. Thus only when the donor–acceptor bond is strong enough to allow isolation of individual mixed-halogen species does it also remain intact to a useful extent in the mass spectrometer (*108*); even then, halogen scrambling in the ion source is a complication (*126*). It has not proved possible to apply conventional mass spectroscopy to the study of the weak adducts that undergo halogen redistribution rapidly. Field desorption or field ionization mass spectroscopy might, however, be applicable.

Nuclear magnetic resonance spectroscopy has the advantage that spectra of several different nuclei may be observed in the same adduct system, providing independent verification of the species present. For adducts of organic donors, at least ^{1}H, ^{13}C, and ^{11}B nuclei are suitable for NMR studies, and ^{19}F is especially suitable for the study of fluorine-containing adducts. Resolution is generally good. Moreover, heteronuclear coupling patterns (^{1}H—^{11}B and ^{11}B—^{19}F coupling in particular) provide further confirmation of peak assignments in many cases. The importance of NMR in studying rates and kinetics of rapid reactions is well known (*94*). The principal experimental method in these studies has been NMR, as in extensive recent work on other rapid redistribution reactions (*114*, *127*, *128*).

C. Properties of Specific Systems

Boron trihalide adducts of different classes of donor molecule show striking differences in both rates and equilibria of halogen redistribution. Only with phosphine adducts has this reaction been studied for a significant number of different donors of the same class, and significant variations in behavior are found even within this class. Halogen redistribution can be a complex reaction and can be strongly affected by the presence of other species in solution. As expected, the mixed boron trihalide adducts are intermediate between the corresponding unmixed adducts in properties such as NMR chemical shifts, carbonyl stretching frequencies of carbonyl-donor adducts, and donor–acceptor bond strength (where this is indicated by mass spectrometry or by equilibration studies with a limited quantity of Lewis base).

1. Ether Adducts

The first neutral mixed boron trihalide adducts were detected by NMR with dimethyl ether as donor (*27*, *73*). Near-statistical amounts of mixed- and unmixed-halogen species are formed in the $Me_2O \cdot BF_nCl_{3-n}$ system. Equilibration is almost complete in an hour at 0°C when uncomplexed dimethyl ether is present, and is extremely rapid when excess boron trihalide is present.

Dialkyl ether adducts are typical of many boron trihalide adduct systems in that the BF_3 adducts tend to be stable, whereas the BCl_3, BBr_3, and BI_3 adducts become successively more reactive, decomposing to alkyl halide and alkoxyboron dihalide (*60*, *120*). This in-stability of the boron–halogen bonds persists in the mixed-halogen adducts, limiting the study of bromine-containing mixed species and preventing study of iodine-containing mixed species. Although decomposition prevents attainment of equilibrium in bromine-containing adducts, all of the non-iodine-containing adduct species, including the ternary halogen species $Me_2O \cdot BFClBr$, have been detected.

Preliminary studies of mixed boron trihalide adducts of other ethers have been carried out (*78*), but many of these adducts are highly susceptible to decomposition.

2. *Amine Adducts*

Mixed boron trihalide adducts of trimethylamine have been extensively studied (*9–11, 13, 75, 105, 108, 155*). Halogen exchange among adducts does not occur spontaneously. The mixed boron trihalide adducts form readily near ambient temperature by reaction of the unmixed-halogen adducts with suitable halogenating agents such as the free boron trihalides (*9–11, 75, 105*), PCl_5 (*9, 13*) and arsenic, aluminum, and silicon chlorides (*9*). Lighter-halogen adducts have their halogens readily replaced by heavier halogens, but the reverse reactions are slower (*9*). Complexes $Me_3N \cdot BF_2Br$ and $Me_3N \cdot BFBr_2$ have been isolated from the series $Me_3N \cdot BF_nBr_{3-n}$ by vacuum sublimation and recrystallization (*10*) and are stable to disproportionation. The complex $Me_3N \cdot BF_2Cl$ has been obtained pure from the reaction of HCl on $Me_3N \cdot F_2BBF_2 \cdot NMe_3$ (*3*). All of the possible mixed boron trihalide adducts of Me_3N, including the four ternary halogen species $Me_3N \cdot BFClBr$, $Me_3N \cdot BFClI$, $Me_3N \cdot BFBrI$, and $Me_3N \cdot BClBrI$, have been detected in solution by NMR (*10*).

Mixed boron trihalide adducts of amines must have been present as intermediates in earlier halogen displacement studies (*40, 124*), but the experimental methods used led to detection of only the final unmixed-halogen product.

Boron trihalide adducts of 4-methylpyridine show halogen exchange behavior similar to that of the adducts of trimethylamine (*10*), and isolation of individual mixed-halogen species is feasible here too. The stability of nitrogen-donor adducts of the mixed boron trihalides parallels the stability of nitrogen-donor adducts of BH_2X and BHX_2 which have been more extensively studied (*19, 153, 156*).

The Me_3N adducts of mixed halogen–pseudohalogen boron compounds have a similar stability. Although three-coordinate mixed halogen–pseudohalogen boron species BX_nY_{3-n} have been known for a long time (*120*), adducts of these have been reported only recently, e.g., $Me_3N \cdot BBr_2CN$ (*143*), $Me_3N \cdot BCl_2[N(SCF_3)_2]$ (*72*), $R_3N \cdot BX_n(NCS)_{3-n}$

(R = Me, Et; X = Cl, Br, I; $n = 1, 2$) (*129*), and $Et_3N{\cdot}BCl_2X$ where X is $(CO)_9Co_3CO$, with the oxygen of the triply bridged carbonyl coordinated to boron (*8*). However, amine·BF_2OR adducts disproportionate above −30°C in solution to give trialkoxyboron and the trialkylamine–BF_3 adduct (*176*).

Exchange of alkyl groups (R = propyl, butyl) with halogen (X = F, Cl) in $Me_3N{\cdot}BR_nX_{3-n}$ is slow and, like halogen exchange in $Me_3N{\cdot}BX_3$ adducts, requires the presence of three-coordinate boron (*37*).

3. *Tetrahaloborate Anions*

The tetrahaloborate anions BX_4^- constitute a special high-symmetry case of boron trihalide adducts having a halide ion as donor but with all halogens bonded in an equivalent fashion to the central boron. Synthesis and isolation of salts of a number of mixed-halogen species BX_3Y^- were reported many years ago (*120*, pp. 100–101) by methods involving hydrogen halide solvents. However, the best-characterized species, BF_3Cl^-, gave a low analysis for chlorine (*183*), suggesting that halogen redistribution may have occurred and that the salt may have contained some BF_4^- (*80*). These BX_3Y^- salts seemed in general to be difficult to handle and remained poorly characterized (*120*). More recent studies of BF_3Cl^- have indicated that disproportionation readily occurs (*26*, *80*, *186*). The most convincing evidence for halogen redistribution in the $BF_nCl_{4-n}^-$ ($n = 0$–4) system was provided by ^{19}F and ^{11}B NMR; methylene chloride solutions of BF_4^- and BCl_4^-, after standing at 60°C, gave the resonances and spin-spin splitting patterns expected for all of the $BF_nCl_{4-n}^-$ ($n = 0$–4) species (*80*). The redistribution process is complex and rates of redistribution are strongly affected by the presence of other species in solution (*80*, *82*). Thus, impurities may account for an early solution NMR study that indicated a very rapid fluorine–chlorine exchange (*102*). Tetrahaloborate halogen redistribution is, in fact, slowest in the $BF_nCl_{4-n}^-$ system (*80*) and is sufficiently slow to be consistent with Waddington's reported isolation of individual mixed tetrahaloborate species (*120*, *183*). However, temperatures well below room temperature may be required to "freeze out" all halogen exchange.

Detection of $BF_nCl_{4-n}^-$ species by NMR has been used as evidence for the formation of ionic boron trihalide adducts $D_2BF_2^+{\cdot}BF_nCl_{4-n}^-$ from simple covalent adducts (*82*, *83*) and as evidence for the abstraction of chloride ion from $(C_6H_5)_3PCl_2$ by BF_3 (*32*). Boron trihalides are often used as halide abstraction reagents, and when two different halogens are involved the mixed-halogen species should be formed, but often only indirect evidence has been obtained (*51*).

Further mixed tetrahaloborates detected by NMR include the $BF_nBr_{4-n}^-$, $BCl_nBr_{4-n}^-$, $BCl_nI_{4-n}^-$, and $BBr_nI_{4-n}^-$ ($n = 0$–4) series, and a number of ternary halogen species such as BF_2ClBr^- (*80*).

Boron trichloride has been reported to react with pseudohalide ions to give the mixed halogen–pseudohalogen ions $BCl_nZ_{4-n}^-$ ($Z = CN^-$, NCO^-, NCS^-, N_3^-), none of which were isolated (*107*). However, only for the $BCl_n(CN)_{4-n}^-$ series were any individual mixed-ion ^{11}B resonances reported. The BX_3OMe^- ions [X = F (*117*), Cl (*54*), Br (*54*)] apparently disproportionate rapidly to give the BX_4^- ions. Early reports of fluorine-containing $BF_nX_{4-n}^-$ species (X = halide, hydroxyl, etc.) have been summarized (*162*).

4. Dimethylsulfide Adducts

All possible non-fluorine-containing boron trihalide adducts of Me_2S, including the ternary halogen adduct $Me_2S{\cdot}BClBrI$, have been detected by ^1H and ^{11}B NMR (*28*). However, only small amounts of the mixed-halogen $Me_2S{\cdot}BF_nCl_{3-n}$ adducts could be detected at equilibrium and neither the BF_nBr_{3-n} nor the BF_nI_{3-n} mixed adducts could be detected. These adducts undergo especially rapid breaking and re-forming of donor–acceptor bonds and especially rapid halogen redistribution.

Contrasting behavior of dialkyl ethers and dialkyl sulfides as donors to BF_3 and BCl_3 has been discussed (*28*, *189*) and is related to an earlier discussed discrepancy between BF_3 and BH_3 adducts (*65*). Sulfur-donor BF_3 bonds are anomalously weak compared to corresponding donor–acceptor bonds to BH_3 or BCl_3. There is no such anomaly in oxygen-donor bonding to BF_3 where the donor–acceptor bond strength is similar to that of the corresponding BH_3 adduct and not much less than that of the BCl_3 adduct. The peculiar halogen redistribution equilibria in Me_2S adducts appear to be related to these anomalies.

5. Phosphine Adducts

Complexes $Et_3P{\cdot}BCl_2Br$ and $Et_3P{\cdot}BClBr_2$ were the first mixed boron trihalide adducts of phosphines to be detected (*100*). Halogen redistribution is near-random in the BCl_nBr_{3-n} adducts of Et_3P (*100*) and Me_3P (*112*). The same is true for Cl—Br, Cl—I, and Br—I redistribution in $MePH_2$ and PH_3 adducts (*49*). However, phosphorus, like sulfur, is a "soft donor" (*140*) and anomalies similar to those in Me_2S adducts appear when fluorine is involved. Compound CD_3PH_2, like Me_2S, forms an anomalously weak BF_3 adduct, while PH_3 does not form a BF_3 adduct (*21*, *48*, *49*). As with Me_2S, an anomalously weak or nonexistent BF_3 adduct corresponds to anomalously small amounts of BF_nCl_{3-n} and BF_nBr_{3-n} mixed adducts (*48*, *49*). Successive methylation of PH_3 gives successively more stable BF_3 adducts (*21*) and as the number of methyls is increased there is a corresponding tendency toward larger amounts of the BF_nX_{3-n} mixed adducts at equilibrium; these are no longer markedly discriminated against when Me_3P is the donor (*30*).

Certain methyldichlorophosphine–boron tribromide adducts undergo chlorine–bromine redistribution between the phosphorus and boron atoms, apparently leading to mixed boron trihalide adducts, although attempts at isolation of these species failed (*104*). However, spontaneous chlorine–bromine redistribution between P—Cl species and BBr_3 does not seem to occur in $aryl_nPCl_{3-n}{\cdot}BBr_3$ adducts (*133*, *135*); the mixed adducts were formed by equilibrating BCl_3 and BBr_3 prior to adduct formation (*134*).

6. *Esters and Thioesters*

Mixed boron trihalide adducts of esters (*29*, *78*, *87*) follow the pattern of oxygen donation as already described for Me_2O adducts. The carbonyl oxygen is the donor (*109*); halogen redistribution occurs readily to give mixed F, Cl and F, Br species. The heavier halogen adducts are prone to decomposition (*60*, *61*). Mixed boron trihalide adducts of isomeric monothioesters have been studied (*29*). Replacement of the ether oxygen of methyl acetate by sulfur causes little change in adduct properties or equilibria. However, replacement of the carbonyl oxygen by sulfur causes a shift to the characteristic Me_2S adduct properties; none of the BF_nCl_{3-n} or BF_nBr_{3-n} mixed adducts can be detected. The dithioester shows similar behavior.

7. *Tetramethylurea and Tetramethylthiourea*

Ureas are oxygen donors in their 1:1 adducts with the boron trihalides (*79*, *81*, *88*). Mixed boron trihalide adducts have been observed in the tetramethylurea—BF_3—BCl_3 system and follow the oxygen-donor pattern of Me_2O and ester adducts (*82*). Thus, the mixed-halogen adducts form spontaneously from the unmixed-halogen adducts. The tetramethylurea$\cdot BF_3$ adduct is among the few where spontaneous donor-for-fluorine exchange about boron has been observed, giving the ionic 1:1 adduct $(tetramethylurea)_2BF_2{}^+{\cdot}BF_4{}^-$ (Section V) (*82*). Although in the fluorine-only system the equilibrium is strongly on the side of the simple covalent adduct, the mixed boron trihalide adduct tetramethylurea$\cdot BF_2Cl$ is susceptible to attack by excess tetramethylurea giving $(tetramethylurea)_2BF_2{}^+{\cdot}BF_nCl_{4-n}^-$ ($n = 0$–4) (*82*).

Tetramethylthiourea·BF_3 has some typical sulfur-donor BF_3 adduct characteristics, e.g., very fast exchange between free and complexed donor, and also exchanges donor for halogen to give the ionic species (tetramethylthiourea)$_2BF_2{}^+ \cdot BF_4{}^-$ (*83*). A brief study of the tetramethylthiourea—BF_3—BCl_3 adduct system showed the presence of BF_2Cl and $BFCl_2$ adducts as well as ionic species (tetramethylthiourea)$_2BF_2{}^+ \cdot BF_nCl_{4-n}^-$ (*83*).

8. *Ketones*

Fluorine exchange in BF_3 adducts of simple methyl ketones was reported in 1968 (*62*). However the heavier halogen, boron trihalide adducts of simple ketones decompose readily (*60*), and only a preliminary NMR study of fluorine–chlorine exchange in the acetone—BF_3—BCl_3 system has been carried out; this shows that fluorine and chlorine do exchange to give BF_2Cl and $BFCl_2$ adducts of acetone (*78*). Ketones without α-hydrogens form much more stable adducts with the heavier boron trihalides (*60*), and IR and NMR studies of benzophenone and xanthone adducts show the presence of mixed BF_nCl_{3-n} and BF_nBr_{3-n} adducts (*87*).

9. *Other Donors*

Trimethylphosphine oxide and trimethylphosphine sulfide show a pattern of mixed-halogen adduct formation that is consistent with the oxygen-donor and sulfur-donor patterns described in the foregoing for the Me_2O and Me_2S adducts (*30*). Thus Me_3PS, unlike Me_3PO, gives only small amounts of mixed F, Cl and F, Br adducts. Binder and Fluck have reported BF_nCl_{3-n} mixed adducts of $MeN{=}PCl_3$ (*13*). The ^{11}B NMR peaks, which apparently arise from mixed BCl_nBr_{3-n} adducts of perchlorate ion, formed by halogen exchange with the chloroform solvent, were not recognized as such by Titova *et al.* (*173*). Compound $(Me_2N)_2C{=}CH_2$, which forms carbon-donor boron trihalide adducts (*88*), also forms mixed-halogen adducts (*89*). Rapid fluorine–chlorine redistribution occurs in the $CH_3CN \cdot BF_3/CH_3CN \cdot BCl_3$ system (*77*).

D. COMPARISON WITH BH_2X AND BHX_2 ADDUCT SYSTEMS

Many BH_2X and BHX_2 (X = F, Cl, Br, I) adducts have been prepared from the corresponding BH_3 adducts by various halogenation procedures (*19, 44, 50, 99, 101, 153, 180, 181*) and are isolable without complications due to halogen–hydrogen redistribution. Amine-cyanoboranes have also been prepared (*185*). Many of these systems are stabilized by nitrogen donors and, thus, are analogous to the stable mixed boron trihalide adducts of Me_3N and 4-methylpyridine.

Weak donor–BH_nX_{3-n} adducts appear to have properties similar to those of corresponding weak donor–mixed boron trihalide adducts. Species $Et_2O{\cdot}BH_2Cl$ and tetrahydrofuran$\cdot BH_2Cl$, which have been used as sources of BH_2Cl for hydroboration of olefins (*23*), are typical weak-donor adducts. The weaker and more readily broken donor–acceptor bond in the Et_2O adduct is the cause of this adduct's greater utility over the tetrahydrofuran adduct in hydroboration. Halogen–hydrogen exchange does not seem to occur readily to give other BH_nCl_{3-n} adducts (*23*, *24*).

Although most known BH_nX_{3-n} adducts are stable and most known BX_nY_{3-n} adducts are unstable to redistribution of substituents about boron, this need not reflect a major difference in behavior of the two types of adduct but may, instead, reflect the interests of the investigators. The BH_nX_{3-n} adduct studies have emphasized synthesis and, hence, systems that are stable to redistribution, whereas mixed boron trihalide adduct studies have emphasized redistribution reactions, which are easier to observe when the donor is weak and redistribution is rapid.

III. Mechanisms of Halogen Redistribution

Halogen exchange in the coordinatively saturated boron trihalide adducts requires either a preliminary dissociative step or an associative interaction different from the doubly halogen-bridged transition state available to three-coordinate boron compounds [Eq. (1)] (*113*, *114*). The reactions can be classified as follows.

A. DISSOCIATION OF THE DONOR–ACCEPTOR BOND

Apparently, equation

$$D{\cdot}BX_3 \rightleftharpoons D + BX_3 \tag{2}$$

is the rate-determining step for halogen exchange in many adducts of weak donors such as ethers (*27*), esters (*29*), ketones (*62*), ureas (*82*), phosphines (*30*, *142*), and sulfides (*28*) when adduct is the only halogen source. Rates of fluorine–chlorine redistribution show an approximate inverse relationship with the donor–acceptor bond strength of the weakest adduct, i.e., the BF_3 adduct, consistent with an initial dissociation step. Thus, for $Me_2S{\cdot}BF_nCl_{3-n}$ [ΔH_{dissoc} of $Me_2S{\cdot}BF_3$ = 3.5 kcal/mole (*131*)], redistribution is very rapid at −78° (*28*), whereas, for $Me_2O{\cdot}BF_nCl_{3-n}$ [ΔH_{dissoc} of $Me_2O{\cdot}BF_3$ = 13.1 kcal/mole (*132*)], equilibration takes an hour at 0°C (*27*), and, for $Me_3N{\cdot}BF_nCl_{3-n}$ (ΔH_{dissoc} of $Me_3N{\cdot}BF_3$ = 30.9 kcal/mole (*132*)], halogen exchange does not occur at room temperature in solution (*10*).

Adduct dissociation would normally be followed by recombination of BX_3 with a donor molecule, and only a small fraction of the BX_3 generated would exchange halogen first. Breaking and re-forming of donor–acceptor bonds is, indeed, a much faster process than halogen redistribution (*27*, *84*). The small proportion of free boron trihalide that does not recombine unchanged with donor would probably exchange halogen by the associative bridging mechanism described in Section III,C), although the direct $BX_3 + BY_3$ reaction [Eq. (1)] would be important at high concentrations of uncomplexed BX_3. Addition of excess boron trihalide greatly increases the rate of halogen redistribution in such systems (*27*).

B. Dissociation of Halide Ion

Halide ion dissociation

$$D{\cdot}BX_3 \rightleftharpoons D{\cdot}BX_2^+ + X^- \qquad (3)$$

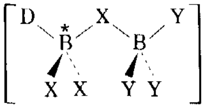
occurs in the tetrahaloborates (*172*) but has not been unambiguously established in neutral adducts. Its probability is greatest with the heaviest halogens because boron–halogen bond strengths decrease in the order F > Cl > Br > I. Krishnamurthy and Lappert (*105*) proposed adduct halogen dissociation as the mechanism of exchange of all of the $Me_3N{\cdot}BX_3$ adducts with BY_3, but Benton and Miller could not duplicate their results (*9*, *11*). The latter workers found that the reaction of $Me_3N{\cdot}BI_3$ with tetraalkylammonium halides did give $Me_3N{\cdot}BXI_2$ (*9*) but that the lighter-halogen $Me_3N{\cdot}BX_3$ adducts did not react. Even with $Me_3N{\cdot}BI_3$, a concerted reaction has not been excluded. Blackborow (*15*) proposed dissociations involving chloride ion in his studies of exchange reactions of *N*,*N*-dimethylaniline—BCl_3 systems, but direct evidence was lacking, and his proposal does not seem consistent with the results of Benton and Miller (*9*) since halide dissociation should give spontaneous halogen redistribution in amine adducts. Benton and Miller found that traces of water increased the rate of bromine–iodine exchange between $Me_3N{\cdot}BI_3$ and HBr (*9*), and previous inconsistent results (*15*, *105*) may arise from the presence of small amounts of HX and/or H_2O.

Kelly and co-workers have proposed that a rate-determining boron–halogen bond cleavage occurs in the hydrolysis of trimethylamine-monohaloborane adducts (*116*, *184*), but they have not excluded a concerted reaction involving H_2O attack (*116*), such as seems to occur in the hydrolysis of $Me_3N\cdot BCl_3$ (*90*, *158*). The existence of a trigonal boron cation $D\cdot BH_2{}^+$ has been established (*157*), and trigonal dihaloborane cations are equally plausible.

C. Associated Bridging Mechanism

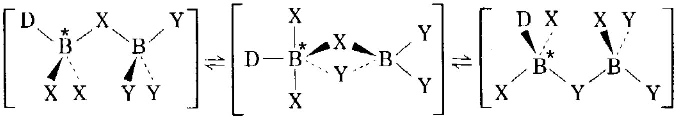
Addition of free boron trihalide to an adduct gives halogen exchange in all cases studied. The initial associated species probably resembles the known (*26a*, *85*) $B_2F_7{}^-$ ion in having a single halogen bridge:

$D\cdot B^*X_3 + BY_3 \rightleftharpoons$



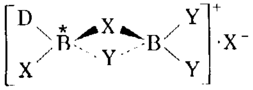
(4)

Exchange of halogen could then proceed either through a four-center transition state (which, however, requires one boron atom to be five-coordinate):

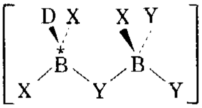


(5)

or through an ion pair such as $D\cdot \overset{*}{B}X_2{}^+\cdot BXY_3{}^-$ or



In the final dissociation to give the mixed-halogen species both boron atoms retain their initial coordination number:



$\rightleftharpoons D\cdot \overset{*}{B}X_2Y + BXY_2$ (6)

Boron-10 isotope substitution studies on $Me_3N\cdot BX_3 + BY_3$ systems, with all possible combinations of X and Y, confirm that the four-coordinate and three-coordinate borons retain their identities (*9*). Only above 180°C in the gas phase, where dissociation does occur (*40*), is there loss of isotopic purity (*9*).

Heavy-halogen boron trihalides rapidly replace light halogens in adducts, whereas light-halogen boron trihalides replace heavy halogens in adducts only slowly (*9*). This finding could be interpreted in various ways, but a clear choice cannot be made at present among the possible transition states. Boron trihalides also exchange halogen with CF_3 groups under mild conditions, and an ionic ($BFCl_3^-$) intermediate was suggested (*33*). However, exchange of halogen between alkyl halides and boron trihalides seems more likely to involve a four-center transition state because an ionic intermediate would involve a carbonium ion, and the isomerization of alkyl groups expected in carbonium ions was not observed (*64*).

Taken as a whole the evidence seems to support a doubly bridged transition state. Intermediates or transitions states of this type have been suggested in many redistribution reactions (*64*).

Halogen–alkyl group exchange in $Me_3N{\cdot}BR_nY_{3-n}$ (R = propyl, butyl; X = F,Cl) also requires the presence of three-coordinate boron and a similar mechanism is probable (*37*).

D. Exchange Mechanisms in Tetrahaloborates

The dissociation mechanisms [Eqs. (2) and (3)] are equivalent in tetrahaloborate anions. Spontaneous halide ion dissociation occurs in solution in the heavier halogen species, the degree of dissociation being I > Br > Cl (*172*):

$$BX_4^- \rightleftharpoons BX_3 + X^- \qquad (7)$$

This reaction is confirmed by attack of the halide ion X^- so generated on methylene halide solvents CH_2Y_2 to give CH_2XY (*80*). Possible mechanisms of formation of the mixed tetrahaloborate anions following this initial dissociation have been discussed by Hartman and Schrobilgen (*80*) and include (*a*) recombination of BX_3 with a different halide ion Y^-, (*b*) exchange via a singly halogen-bridged intermediate analogous to $B_2F_7^-$; (*c*) halide ion attack on a tetrahaloborate anion, and (*d*) halogen exchange between two three-coordinate boron species. Of these, mechanisms *a* and *b* are probably the most important.

The requirement for an initial dissociation step implies that halogen redistribution rates should parallel the ease of dissociation of one of the halogens, and this expectation is confirmed in fluorine–heavier halogen redistributions where the rates change from slow to very fast over the series Cl, Br, I as the B—X bond becomes weaker. Rates should also be related to stabilization of the residual boron trihalide formed on dissociation. The boron trihalide with the greatest number of fluorine atoms is the most stable, i.e., $BF_3 > BF_2X > BFX_2 > BX_3$. (The most stabilized species, BF_3, is of course the weakest Lewis acid.) It follows that mixed-halogen species $BF_nX_{4-n}^-$, and especially BF_3X^-, should be more prone to dissociation than either BF_4^- or BX_4^- because both factors favoring dissociation can be optimized. This is indeed observed (*80*). Fluorine redistribution in BF_4^- alone is fairly slow, the rate being quite solvent-dependent (*63*). Exchange of Cl—Br, Cl—I, and Br—I is slow on the NMR time scale in the tetrahaloborates except in the presence of fluorine when it becomes much faster, and this can be attributed to the especially easy dissociation of the mixed fluorine–heavier halogen tetrahaloborates that are formed (*80*). In such systems, BF_3X^- species exchange halogen rapidly, $BF_2X_2^-$ species at intermediate rates, and BFX_3^- species slowly. Also BF_4^- exchanges halogen rapidly under these conditions; fluoride ion dissociation is not required here as exchange can take place via fluorine-bridged $B_2F_7^-$, utilizing BF_3 from the easy dissociation of BF_3X^-.

A rate-determining initial dissociation step does account for most of the observed features of halogen exchange in the tetrahaloborates (*80*). An anomaly in the BF_4^-/BCl_4^- system is the late appearance of $BFCl_3^-$, which is expected to appear initially along with BF_3Cl^-. A similar anomaly was observed in an ion cyclotron resonance study of fluoride ion affinities (*71*) in which BF_3Cl^- and BF_4^- were observed instead of the expected $BFCl_3^-$. This is at present unexplained. There is considerable scope for more accurate kinetic analyses of halogen exchange reactions of tetrahaloborates (*115*). However, because carbenes can be generated from BF_4^- or F^- and a methylene halide or haloform (*34*), carbene reactions could further complicate such systems.

IV. Equilibria in Halogen Redistribution

Random or statistical redistribution of substituents X and Y, present in equal amounts about a central atom E in a system $E(X, Y)_n$, gives the following amounts of species (*127*):

$$EX_3 : EX_2Y : EXY_2 : EY_3 = 1:3:3:1 \qquad (\text{for } n = 3)$$

$$EX_4 : EX_3Y : EX_2Y_2 : EXY_3 : EY_4 = 1:4:6:4:1 \qquad (\text{for } n = 4)$$

In boron trihalide adducts and tetrahaloborate ions, halogen redistribution equilibria are reasonably close to this ideal random case when chlorine, bromine, and iodine are involved (*27*, *28*, *80*, *100*, *112*), as are equilibria in the uncomplexed heavier boron trihalides (*111*).

Redistribution of these halogens is near-random about a number of other central atoms as well (*97*, *119*).

However, equilibria may be far from random when fluorine is involved. Table I shows the effects of the donor on disproportionation constants K_1 and K_2 (*127*) for redistribution of fluorine and chlorine:

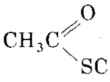
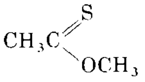
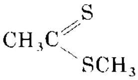
$$K_1 = \frac{[D{\cdot}BF_2Cl]\,[D{\cdot}BCl_3]}{[D{\cdot}BFCl_2]^2} \tag{8}$$

$$K_2 = \frac{[D{\cdot}BF_3]\,[D{\cdot}BFCl_2]}{[D{\cdot}BF_2Cl]^2} \tag{9}$$

Practically all deviations from random redistribution are in the direction of less than the statistical amounts of mixed-halogen species. Deviations are especially pronounced with the sulfur-donor adducts, with uncomplexed BF_nCl_{3-n} being intermediate between the oxygen-donor and sulfur-donor systems. Constant K_1 is consistently larger

TABLE I

HALOGEN REDISTRIBUTION EQUILIBRIUM CONSTANTS FOR $D{\cdot}BF_nCl_{3-n}$ [a]

Donor	K_1	K_2	Ref.
Ideal random case	0.33	0.33	*127*
Oxygen donors:			
Dimethyl ether	0.80	0.23	*27*
Methyl acetate	0.92	0.51	*29*
 $CH_3C(=O)SCH_3$	1.27	0.53	*29*
Uncomplexed BF_nCl_{3-n}	2.4	1.4	*111*
Sulfur donors:			
Dimethylsulfide	6.3	2.3	*28*
 $CH_3C(=S)OCH_3$	Large[b]	Large[b]	*29*
 $CH_3C(=S)SCH_3$	Large[b]	Large[b]	*29*

[a] Dichloromethane solvent was used except for the uncomplexed boron trihalides where 1,1-dichloroethane was the solvent.

[b] No mixed-halogen adducts detected.

than K_2, i.e., the $BFCl_2$ species is somewhat less favored than the BF_2Cl species.

Deviations from statistical redistribution equilibria have been studied in a variety of systems (*119*, *127*, *128*), and various explanations have been put forward. It should be kept in mind that stability differences of only a few kilocalories per mole between mixed- and unmixed-ligand complexes are sufficient to cause very large deviations from random redistribution (*97*). Mixed-ligand species are frequently favored over unmixed (*128*), and this can be explained in terms of stronger bonding in the mixed species due to decreased competition for orbitals. Thus, in $(RO)_3B$ compounds, there is strong π-bonding from oxygen to boron (*170*). When alkoxy ligands are mixed with non-π-bonding ligands, there are fewer RO groups to compete for boron's p_z orbital and, hence, each O—B bond can be stronger, and the mixed-ligand species are strongly favored (*113*, *165*). Thus, dimethylamine diphenylboron (*93*) and aryl esters of dialkylborinic acids (*22*) can be synthesized by simply mixing the unmixed-ligand species in the correct ratio. By contrast, less than the statistical amounts of fluorine-containing mixed boron trihalides are present at equilibrium (*111*).

Deviations favoring the unmixed-ligand species are not as rare as is sometimes assumed (*128*). Such deviations can be rationalized using Pearson's concept of hard and soft acids and bases (*140*). It was pointed out some time ago that soft bases tend to cluster together on a central metal atom and, similarly, that hard bases tend to cluster together (*98*). Although this was originally discussed in terms of d-orbital filling in transition metal complexes (*98*), Pearson and Songstad extended this "symbiotic principle" to give qualitative explanations of equilibria and kinetics in a wide range of systems (*141*). The principle predicts that there should be extra stabilization if either several soft bases or several hard bases cluster about a single central atom. Thus, Pearson and Songstad classified BH_3 as a soft acid because H^- is soft, and BF_3 as a hard acid because F^- is hard; the symbiotic effect is maximized if a further soft base coordinates to BH_3, and if a further hard base coordinates to BF_3. Similarly, an increasing degree of soft acid character can be attributed to the other boron trihalides in the order $BCl_3 < BBr_3 < BI_3$.

In the uncomplexed boron trihalides, mixtures of fluorine with chlorine, bromine, and iodine are successively less favored (*111*), in accord with the symbiotic principle. This principle can rationalize halogen redistribution equilibria in adducts of the mixed boron trihalides as well. Incompatibility of fluorine with the heavier halogens is greatest with the softest donors. In the extreme case of PH_3 as donor, BF_3 is unable to form an adduct at all (*21*), and this can be attributed to the very unfavorable combination of a soft PH_3 and 3 hard fluorines about boron. The combination of Me_2S or CH_3PH_2 with 3 fluorines about boron is not prevented, but the BF_3 adducts of these donors are anomalously weak (*21*, *131*). All three of these donors discriminate against mixed fluorine–heavier halogen adducts: the adducts are either not observed at all or are present in abnormally small amounts (*28*, *48*). Some irregularities exist, however. The symbiotic principle predicts that F,Br mixing should be less favorable than F,Cl mixing in the adducts, and this is borne out in the Me_2S adduct system (*28*), but not in the PH_3 adduct system where the mixed F,Br adducts, but not the mixed F,Cl adducts, have been detected (*48*). [Both F,Cl and F,Br mixed adducts of CD_3PH_2 have been detected (*48*).] The symbiotic principle does help to rationalize results but is clearly not quantitative in its predictions.

The near-random redistribution of fluorine and chlorine in oxygen-donor boron trihalide adducts (*27*, *29*) might be rationalized using this principle since oxygen is between fluorine and chlorine on the hard–soft scale (*140*), and there is less discontinuity of ligands in terms of hard–soft properties. However, amine adducts of BHF_2 do tend to disproportionate to give the BF_3 and BH_3 adducts (*130*).

A similar tendency for fluorine to segregate itself from the heavier halogens has been noted in redistribution reactions about many other central atoms, including phosphorus (*47*, *144*, *145*), silicon (*139*, *146*, *163*), germanium (*139*), arsenic (*139*), tungsten (*56*), niobium (*36*), and tantalum (*36*). However, relative stabilities of mixed and unmixed species involving fluorine vary greatly in systems with other central atoms, as they do in boron systems. The mixed fluorine-containing tetrahaloborate ions are formed in large amounts (*80*), as are mixed-halogen adducts in the TiF_nCl_{4-n} system (*17*).

Because hardness and softness are qualitative concepts that no doubt originate from a variety of factors (*140*), ambiguities in interpretation may arise (*96*). Recently, more quantitative treatments of the bonding in series of mixed-ligand trigonal and tetrahedral boron compounds have been reported. Application of the virial partitioning method by Runtz and Bader (*150*) indicates that Lewis acidity of BH_3 and BF_3 is determined more by the properties of the H and F fragments than by the net charge and energy of the boron fragment. However, these calculations do not show an incompatibility of H and F ligands in $BH_nF_{4-n}^-$. These authors discuss destabilizing repulsions between fluorine and neighboring atoms that may account for anomalies in the chemistry of fluorine but show that in specific cases other factors may compensate. An *ab initio* molecular orbital study of the $BF_n(OH)_{3-n}$ ($n = 0$–3) species indicates that replacement of a fluorine of BF_3 by a hydroxyl group is energetically unfavored, and the authors relate this to known stability of BF_4^- with respect to BF_3OH^- (*1*). Unfortunately, discussions become more qualitative when the heavier halogens are involved. Comparisons of BF_3 and BCl_3 adducts have concentrated on the donor–acceptor rather than on the boron–halogen bonds (*148*, *171*). The uncomplexed heavier boron trihalides have been investigated in much more detail than their adducts (*5*, *6*, *12*, *103*).

V. Donor-for-Halogen Exchange: Difluoroboron Cations

Because both donor–acceptor and boron–halogen bonds are labile in many adducts, donor-for-halogen exchange is possible giving ionic adducts of 1:1 stoichiometry:

$$2D\cdot BX_3 \rightleftharpoons D_2BX_2^+ + BX_4^- \qquad (10)$$

Some BCl_3 and BBr_3 adducts have been reported to rearrange spontaneously in solution according to Eq. (10) to give varying amounts of the ionic adducts (*120*, *160*, *161*). Reaction of either excess base or excess acid with an initially formed covalent adduct of a secondary amine can also give ionic adducts $(R_2NH)_2BX_2^+\cdot BX_4^-$ ($X = Cl, Br$) (*154*). The heavier the halogen, the more easily it is displaced from boron. Thus one, two, or three bromines of $Me_3N\cdot BBr_3$ can be displaced by pyridines to give boron cations of charge $+1$, $+2$, and $+3$, respectively, and the formation of the $+3$ ions occurs even more readily with the BI_3 adduct (*152*). Highly charged ions have been postulated to form spontaneously in amine·BCl_3 systems as well, but direct evidence is lacking (*15*).

Fluorine is the least readily displaced halogen, and few BF_3 adducts have been reported to rearrange to the ionic form. Ionic species do form when chelating donors favor $D_2BF_2^+$ over $D\cdot BF_3$ (*4*, *187*), although these chelates form less readily than other boron chelates due to the difficulty of displacing fluorine (*177*). Other chelating ligands with BF_3 form neutral BF_2 species by loss of HF (*25*, *122*, *175*). With similar but nonchelating ligands, i.e., mono- rather than diketones, fluorine redistribution does occur but ionic species have not been detected (*62*), indicating that the equilibrium of Eq. (10) is far to the left. A slow rearrangement of vinyl BF_3^- to $(vinyl)_2BF_2^-$ and BF_4^- has been reported to occur in aqueous solution (*167*).

The tetramethylurea–BF_3 adduct in methylene chloride is in equilibrium with a very small amount of the corresponding ionic adduct, (tetramethylurea)$_2$BF$_2$$^+$·BF$_4$$^-$ (*82*), and similar ionic-covalent equilibria occur in tetramethylthiourea–BF$_3$ and tetramethylselenourea–BF$_3$ adducts (*83*). Ionic species can be favored by excess BF$_3$ which gives D$_2$BF$_2$$^+$·B$_2F_7$$^-$ (*83*). Mixed boron trihalide adducts can also favor the formation of fluoroboron cations. Excess tetramethylurea displaces Cl$^-$ from the tetramethylurea·BF$_2$Cl adduct to form large amounts of (tetramethylurea)$_2$BF$_2$$^+$ and mixed chlorofluoroborate anions; mixed donor cations, DD′·BF$_2$$^+$, can also be formed in this way (*82*). It should be possible to prepare many fluoroboron cations by preferential displacement of heavier halogens from mixed fluorine—heavier halogen boron trihalide adducts. The reaction is analogous to the formation of dihydroboron cations DD′·BH$_2$$^+$ (*138, 152, 164*) through halide ion displacement from D·BH$_2$Cl and D·BH$_2$Br by D′ (*152*).

Johnson and Shore have discussed factors favoring symmetrical vs. unsymmetrical cleavage of B$_2$H$_6$, giving D·BH$_3$ or D$_2$BH$_2$$^+$·BH$_4$$^-$, respectively (*95*). Similar stability factors may be applicable to reaction (10), i.e., bulky donors may be prevented from forming D$_2$BX$_2$$^+$. However, the type of initial adduct that forms from B$_2$H$_6$ is related to the preferred course of bridge cleavage reactions (*95*), whereas the monomeric boron trihalides should form an initial D·BX$_3$ adduct and any ionic species should form by subsequent rearrangement. Thus ionic boron trihalide adducts have not been observed as frequently as ionic borane adducts. The presence of fluorine and a heavier halogen does favor the formation of ionic boron trihalide adducts by displacement of the heavier halogen.

VI. NMR Applied to Adducts: Advantages and Pitfalls

A. RELIABILITY OF MIXED-ADDUCT NMR DATA

Identification of most mixed boron trihalide adducts, and all information on rates and equilibria of halogen redistribution in these systems, depends on correct NMR peak assignments. The reliability of these is assured by a combination of two or more of the following: distinctive heteronuclear NMR coupling patterns; systematic variation of peak areas as the ratio of two halogens is changed; identification and consistent behavior of peaks due to the same species in spectra of two or more of ^{1}H, ^{19}F, ^{11}B, and ^{13}C nuclei; agreement of observed parameters with values calculated from "pairwise interaction" parameters (*76, 123*). Fine points of structure can also be determined by

NMR; thus, ^{19}F splittings due to $^{11}B—^{19}F$ coupling, and their disappearance at lower temperatures due to quadrupole relaxation of ^{11}B, give a measure of the electric field gradient about boron and, hence, of the adduct structure (*27*, *28*).

B. COMPLEXATION SHIFTS AND DONOR–ACCEPTOR BOND STRENGTH

Conclusions about Lewis acidity should not be based solely on shifts of donor ^1H resonances to low field on adduct formation (*45*, *159*). The assumption that this shift is a measure of Lewis acid strength neglects other factors, such as bond reorganization of the Lewis acid prior to adduct formation, that can affect the heat of formation of the adduct (*106*, *125*). Thus Kristoff and Shriver have pointed out that spectroscopic probes in general measure the relative strength of the donor–acceptor bond but not the Lewis acidity (*106*). Lewis acid strengths usually parallel acidities because the donor–acceptor bond strength usually dominates the heat of formation of the adduct. Even the use of complexation shifts as a measure of donor–acceptor bond strengths neglects factors such as changes in long-range shielding and hybridization that can occur on adduct formation. A major change in donor hybridization on adduct formation does cause quite different donor ^1H chemical shifts in the adduct (*88*). In a few cases, donor ^1H resonances can even shift to high field on adduct formation (*67*, *88*). An anisotropic solvent, such as benzene, can change the direction of a normally "well-behaved" complexation shift (*30*, Table I).

When the base is changed, ^1H complexation shifts bear little relationship to the heat of dissociation of the donor–acceptor bond, as illustrated in Table II. The same is true even when the donor atom stays the same, as in a series of amine–BF_3 complexes (*179*). A number of factors affect NMR parameters in adducts, and trends in chemical shifts in closely related series of adducts (*70*).

However, when boron trihalide adducts of the same base are studied and only the halogens are changed, and there is negligible hybridization change in the donor on complexation, the ^1H complexation shifts do correlate with the heats of formation of the complexes, as in $Me_3N{\cdot}BX_3$ and pyridine$\cdot BX_3$ ($X = F, Cl, Br, I$) (*125*). In such cases, ^1H complexation shifts should give a measure of donor–acceptor bond strength for the mixed-halogen adducts as well (*10*). For trimethylamine adducts, this order is also consistent with mass spectrometric data for the mixed boron trihalide adducts (*108*). In $Me_2O{\cdot}BF_nCl_{3-n}$ ($n = 1$–3) adducts, ^1H complexation shifts do correlate with Lewis

TABLE II

ADDUCT COMPLEXATION SHIFTS AND HEATS OF DISSOCIATION OF THE DONOR–ACCEPTOR BOND

Adduct	ΔH_{dissoc} (kcal/mole)	Ref.	Complexation shifts (ppm)[a] ^1H	^{19}F	^{11}B	Ref.
$Me_2S{\cdot}BF_3$	3.5	*131*	0.31	15.3	8.6	*28*
$Me_2S{\cdot}BCl_3$	12.1	*131*	0.45	—	40.5	*28*
$Me_2O{\cdot}BF_3$	13.1	*132*	0.62	34.2	11.5	*27*
$Me_3P{\cdot}BF_3$	18.9	*2, 21*	0.45	13.4	10.7	*30,189*
$Me_3N{\cdot}BF_3$	30.9	*65*	0.40	40.1	11.1	*10,189*
	26.6	*121*				
$Me_3N{\cdot}BCl_3$	30.5	*121*	0.78	—	37.8	*10,189*

[a] ^1H, to low field; ^{19}F, to high field; free BF_3 absorbs at 124.0 ppm to high field of $CFCl_3$; ^{11}B, to high field of free BF_3 and free BCl_3 [6.6 ppm to high field, and 29.3 ppm to low field, respectively, from external $(MeO)_3B$.]

acidity as determined by relative proportions of the different BF_nCl_{3-n} species complexed with a limited quantity of Me_2O (*27*).

When a donor such as methyl acetate, with more than one proton absorption, is complexed to a series of mixed and unmixed boron trihalides, the different proton environments give similar but not identical orderings of complexation shift for the series of Lewis acids (*29*). This confirms that the relationship between proton complexation shift and acceptor strength can be only approximate and that the complexation shift cannot arise solely from an inductive shift of electron density toward the donor site. Changes in long-range shielding are likely to be important in causing irregularities in series of complexation shifts, especially when heavy halogens can be in close proximity to some of the protons being observed.

Use of the complexation shift as a measure of donor–acceptor interaction is especially treacherous with nuclei other than protons, because chemical shifts of these nuclei are more dependent on the paramagnetic than on the diamagnetic term of the screening tensor (*52*, *53*). Both ^{19}F and ^{11}B resonances of the boron trihalides do shift to high field on complexation, as expected if the complexation shift were due to the increase in electron density on the boron trihalide, and early work indicated that ^{19}F complexation shifts of BF_3 could be correlated with enthalpies of formation of the complexes. Although this is true for BF_3 adducts of some series of closely related donors (*42*, *91*, *151*), such correlations do not occur in other series (*169*). Table II illustrates that, although there is a tendency for the strongest

BF_3 adducts to have ^{19}F resonances at the highest field, there are inversions in this order.

Much of the ^{19}F complexation shift appears to be related to the change of coordination geometry about boron from trigonal planar to tetrahedral; this component is related to donor strength only to the extent that weak donors may be unable to cause this change to be carried through to fully tetrahedral boron (*20*). The buildup of negative charge on BF_3 is only one of the factors determining ^{19}F complexation shifts in BF_3 adducts. Similar considerations apply to mixed fluorine–heavier halogen adducts, and it would be unwise to attempt to deduce relative donor–acceptor bond strengths of BF_3, BF_2X, and BFX_2 adducts from ^{19}F complexation shifts.

Mooney and co-workers considered ^{11}B complexation shifts of boron Lewis acids to be a measure of the acceptor strengths of the Lewis acids and of the donor abilities of various ligands (*59*). However, conclusions based on these assumptions are not valid. Tetrahedral boron shifts do not follow the same pattern as trigonal boron shifts, and boron trihalide complexes with quite different heats of formation can have very similar ^{11}B complexation shifts, e.g., the BF_3 adducts of Table II. Also $Me_2S{\cdot}BCl_3$ and $Me_2O{\cdot}BF_3$, with similar heats of formation, have very different complexation shifts (Table II). The ^{11}B chemical shifts and complexation shifts are determined by the halogens present as well as by the donor (*76*), as discussed in the following. In spite of this, some workers continue to use ^{11}B complexation shifts as a measure of donor–acceptor bond strength (*134*).

Also, ^{13}C complexation shifts cannot be directly related to donor–acceptor bond strength. In ether and ketone complexes with BF_3, different carbons shift to high and to low field in the same donor molecule (*57*, *58*, *86*). Similar irregularities occur in the only series of mixed boron trihalide adducts for which ^{13}C NMR data are available. The ^{13}C complexation shift of $Me_3N{\cdot}BF_3$ is to high field, but, in all other mixed- and unmixed-halogen adducts of Me_3N, the shift is to low field (*123*). Trends in chemical shift are regular in all series of adducts $Me_3N{\cdot}BX_nY_{3-n}$, from $n = 0$ to $n = 3$, and are consistent with the ordering of ^1H shifts, i.e., the lowest-field resonance appears to correspond to the strongest donor–acceptor bond, but the complexation shifts are not related quantitatively to donor–acceptor bond strength in any of these systems.

Correlations of NMR parameters to electronic structure have been carried out for a wide range of three-coordinate boron compounds (*12*, *188*). However, the extensive NMR data that exist for boron trihalide adducts (*70*) are less easily interpreted. Among the factors leading to difficulties in correlating NMR parameters with structure is the lack of a σ-π separation of orbitals in tetrahedral molecules, such as occurs in trigonal planar molecules. Interpretations of NMR parameters of the mixed tetrahaloborate anions by various methods, including CNDO calculation of chemical shifts, allows a "fluorine anomaly" in ^{11}B chemical shifts to be interpreted in various ways (*80*). Correlations of ^{11}B and ^{19}F chemical shifts in fluorine-containing adducts can be made in terms of survival of varying amounts of fluorine-to-boron multiple bonding in the adducts (*20*). However, interpretation has lagged behind the accumulation of NMR data.

Similar difficulties have occurred in attempts to find a general correlation between coupling constants across the donor–acceptor bond in borane adducts and the strength and nature of the donor–acceptor bond (*38*, *149*).

Mixed boron trihalide adducts should facilitate interpretation of NMR parameters because properties can be changed gradually by changing a single halogen rather than all three. Studies of mixed boron trihalide adducts have already led to application of pairwise interaction NMR parameters, which are discussed next. Although these are not appreciably closer to an explanation of NMR parameters in terms of electronic structure and bonding, they do have the virtue of greater simplicity.

C. "PAIRWISE INTERACTION" NMR PARAMETERS

Nuclear spin-spin coupling constants and chemical shifts of various nuclei can be pairwise additive with respect to the substituent groups (*182*), i.e., the chemical shift (or spin- spin coupling) can be expressed as

$$\delta = \sum \eta_{i,j} \tag{11}$$

where $\eta_{i,j}$ is a parameter associated with substituents i and j and independent of all other substituents. The sum is taken over all substituents about a central atom, excluding the nucleus observed in the NMR experiment. In the case of $BF_2Cl_2^-$

$$\begin{aligned} \delta_{^{11}B} &= \eta_{F,F} + 4\eta_{F,Cl} + \eta_{Cl,Cl} \\ \delta_{^{19}F} &= 2\eta'_{F,Cl} + \eta'_{Cl,Cl} \end{aligned} \tag{12}$$

where $\eta_{i,j}$ is different for each nucleus observed.

Theoretical justification of the pairwise additivity rule for chemical shifts and nuclear spin-spin couplings can be found in the work of Vladimiroff and Malinowski (*182*). Chemical shifts of ^{27}Al (*118*), ^{13}C

(*123, 166*), ^{11}B (*76, 80, 166*), and ^{19}F (*76, 80*) as well as of a number of other nuclei are pairwise additive, as are many coupling constants. Application of the pairwise approach to the mixed boron trihalide adducts eliminates some apparent anomalies in chemical shifts and shows that ^{11}B complexation shifts cannot correlate to donor–acceptor bond strengths in the general case (*76*). The halogen–halogen pairwise interaction terms, rather than the donor–halogen terms, frequently dominate in determining complexation shifts.

Pairwise interaction parameters can perhaps be interpreted in chemical bonding terms (*76, 80, 123, 182*). Pairwise terms involving fluorine are often anomalous and this may be related to some surviving multiple bonding in the boron–fluorine bonds in the adducts (*20*). Pairwise interaction parameters of the Me_3N mixed trihalide adduct system are reported to correlate consistently for ^{1}H, ^{13}C, ^{19}F, and ^{11}B chemical shifts and for ^{11}B—^{19}F coupling constants (*123*). It is perhaps surprising that even the proton shifts can be correlated in this way.

VII. Conclusion

The mixed boron trihalide adducts hold few surprises in terms of their donor–acceptor bond behavior, but provide striking examples of dependence of halogen redistribution behavior on the nonhalogen substituent. The simplicity and accessibility of these systems suggests their use as model compounds in the study of ligand redistribution reactions. Many of the features complicating ligand redistribution in, for example, metal carbonyl systems (*46*) are simplified or absent here.

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