Donor–acceptor Adducts of the Mixed Boron Trihalides: Adducts of Dimethyl Ether

By **M. J. Bula, D. E. Hamilton,** and **J. S. Hartman,*** Department of Chemistry, Brock University, St. Catharines, Ontario, Canada

N.m.r. studies of halogen redistribution in dimethyl ether–boron trihalide adducts in solution show that equilibrium between mixed and unmixed-halogen adducts is attained rapidly. Near-statistical amounts of the mixed and unmixed-halogen species are present at equilibrium in the Me_2O,BF_nCl_{3-n} (n = 0—3) system. Decomposition is a serious competing reaction in adducts containing boron–bromine and especially boron–iodine bonds. Exchange reactions and trends in the n.m.r. parameters are discussed.

THE mixed boron trihalides BX_2Y are unstable to disproportionation and have not been isolated. They are, however, well known in mixtures of the corresponding simple halides BX_3 and BY_3.[1-3] Although numerous

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[1] A. G. Massey, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 1.

[2] J. C. Lockhart, *Chem. Rev.*, 1965, **65**, 131.

[3] M. F. Lappert, M. R. Litzow, J. B. Pedley, T. R. Spalding, and H. Nöth, *J. Chem. Soc. (A)*, 1971, 383.

studies of boron trihalide adducts have been carried out, adducts of the mixed boron trihalides have been reported only recently.[4-6] Previous work has shown that boron trifluoride adducts of ketones undergo two distinct exchange reactions in solution in methylene chloride.[7] As well as a rapid breaking and re-forming of donor–acceptor bonds, a much slower process occurs which exchanges fluorine among boron atoms. Dimethyl ether–boron trihalide adducts are found to undergo analogous reactions which exchange not only fluorine but also chlorine and bromine among boron atoms, so that adducts of the mixed boron trihalides are formed readily in solution.[4] These reactions are typical halogen redistribution reactions.[2] A similar formation of a mixed dihaloborane adduct, $PH_3,BHClBr$, by halogen scrambling has been reported.[8]

A number of n.m.r. studies of BF_3 and BCl_3 adducts of simple aliphatic ethers have shown that there is rapid breaking and re-forming of the relatively weak donor–acceptor bond in solution.[1,9] Whereas the BF_3 adducts are fairly stable to decomposition, the BCl_3 adducts are reported to react to give alkyl chloride and alkoxyboron dichloride as the initial products.[1,10] Ether adducts of BBr_3 and BI_3 are very reactive and few of these have been studied.[1,9,11] We now report detailed n.m.r. studies of dimethyl ether adducts of the mixed and unmixed boron trihalides, with emphasis on the halogen redistribution and the novel mixed-halogen species.

EXPERIMENTAL

Materials.—Boron trifluoride (Matheson) was triply distilled on a high-vacuum system from a trap at −78° to a trap at liquid-nitrogen temperature, the initial and final cuts being rejected each time. Boron trichloride (Matheson) was distilled under vacuum through a −78° trap and a liquid-nitrogen trap connected in series. The boron trichloride collected in the −78° trap. Boron tribromide (Alfa Inorganics) was treated with mercury to remove bromine and then purified by the technique used for boron trichloride. Boron tri-iodide (Alfa Inorganics) was used without further purification. Dimethyl ether (Matheson), tetramethylsilane (Alfa Inorganics), and trichlorofluoromethane (K & K Chemicals) were allowed to stand over molecular sieves, and were then trap-to-trap distilled on the high-vacuum system before use. Methylene chloride (Fisher) was dried over molecular sieves and fractionated before use.

Preparation of Samples.—Methylene chloride was the solvent in all the samples studied. Variations in concentration of Me_2O and the boron trihalides from 0·1 to 1 molar had little effect on the chemical shifts, but had some effect on the coalescence temperatures in temperature-dependent spectra. Boron tri-iodide was added to the n.m.r. sample tubes under anhydrous conditions in a glove bag. All the other materials were added by standard high-vacuum techniques. Me_2O, BF_3, and BCl_3 were condensed from calibrated volumes directly into the sample tubes. Quantities of BBr_3 added were determined using a weight burette. The samples were sealed off under vacuum with the contents still at liquid-nitrogen temperature and allowed to warm slowly to −78°.

N.m.r. Spectra.—60 MHz Proton n.m.r. spectra were obtained on a Varian Associates A-60 spectrometer equipped with a variable-temperature probe modified for operation down to −150°. Proton chemical shifts (δ) are given in p.p.m. to low field of tetramethylsilane.

^{19}F and ^{11}B N.m.r. spectra were obtained on a Varian Associates DA-60-IL n.m.r. spectrometer operating in HR sideband mode at 56·4 MHz for ^{19}F and 11·43 MHz for ^{11}B. The spectra were calibrated by the audio sideband method, using a Muirhead–Wigan D-890-A decade oscillator, or by using 2500 Hz sidebands, 180° out of phase with the normal signals, arising from a Hewlett–Packard 200 CDR audio oscillator. Sideband frequencies were checked with a General Radio type 1191 frequency counter. Varian V-6040 and V-4340 variable-temperature probes were used in obtaining the ^{19}F and ^{11}B spectra, respectively. ^{19}F and ^{11}B Chemical shifts are given in p.p.m. to high field of internal $CFCl_3$ and external $(MeO)_3B$, respectively. The 25·1 MHz ^{11}B spectrum of a Me_2O–BF_3–BCl_3 solution was obtained using a Varian Associates HA-100 spectrometer.

RESULTS

N.m.r. data for the dimethyl ether–boron trihalide adducts are given in the Table. Boron–fluorine coupling was observed but boron–proton and proton–fluorine coupling could not be detected. Halogen redistribution and adduct decomposition reactions are strongly dependent on whether acid or base is present in excess. When an excess of boron trihalide is present halogen exchange becomes much more rapid whereas adduct decomposition becomes much slower. No evidence was obtained for adducts of other than 1 : 1 stoicheiometry.

The behaviour and n.m.r. spectra of the BF_3 and BCl_3 adducts are in accord with previous reports[1,9,12,13] except that in the BF_3 adduct: (i) the ^{19}F peak is split by a ^{10}B–^{11}B isotope shift[7,14] of 0·059 ± 0·010 p.p.m. at temperatures below −40° when an excess of Me_2O is present; (ii) the previously reported[15] extensive dissociation of the adduct in solution is not apparent; and (iii) there is a discrepancy of 3 p.p.m. in the ^{11}B chemical-shift value.[13] Although there was negligible decomposition of the BF_3 adduct, or of the BCl_3 adduct when an excess of BCl_3 was present, a slow decomposition of the BCl_3 adduct in solution when an excess of Me_2O was present gave additional −90° ^1H peaks at δ 3·14 (methyl chloride) and δ 3·76.

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[4] Preliminary communication, D. E. Hamilton, J. S. Hartman, and J. M. Miller, *Chem. Comm.*, 1969, 1417.

[5] J. S. Hartman and J. M. Miller, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 831.

[6] G. Jugie, J.-P. Laussac, and J.-P. Laurent, *Bull. Soc. chim. France*, 1970, 2542, 4238; G. E. Ryschkewitsch and W. J. Rademaker, *J. Magnetic. Res.*, 1969, **1**, 584.

[7] R. J. Gillespie and J. S. Hartman, *Canad. J. Chem.*, 1968, **46**, 2147.

[8] J. E. Drake and J. Simpson, *J. Chem. Soc.* (*A*), 1968, 974.

[9] A. Fratiello, T. P. Onak, and R. E. Schuster, *J. Amer. Chem. Soc.*, 1968, **90**, 1194.

[10] W. Gerrard and M. F. Lappert, *Chem. Rev.*, 1958, **58**, 1081.

[11] D. R. Martin and J. M. Cannon, in 'Friedel–Crafts and Related Reactions,' G. A. Olah, ed., Interscience, New York, vol. 1, 1963, pp. 509—510.

[12] R. A. Craig and R. E. Richards, *Trans. Faraday Soc.*, 1963, **59**, 1962.

[13] D. E. Young, G. E. McAchran, and S. G. Shore, *J. Amer. Chem. Soc.*, 1966, **88**, 4390.

[14] R. J. Gillespie, J. S. Hartman, and M. Parekh, *Canad. J. Chem.*, 1968, **46**, 1601.

[15] E. Gore and S. S. Danyluk, *J. Phys. Chem.*, 1965, **69**, 89.

Decomposition of Me_2O,BBr_3 was rapid in the presence of an excess of Me_2O,[9] but much slower in the presence of an excess of BBr_3, the times for half reaction at 30° being 5 min and 2 h, respectively. With an excess of Me_2O equimolar quantities of adduct and Me_2O were consumed and two new peaks appeared at δ 2·80 (methyl bromide) and δ 3·84 in the ^1H spectrum. With an excess of BBr_3 a number of peaks including the methyl bromide peak appeared; a small peak at δ 0·63, assigned to Me_3SiBr,[16] indicated the occurrence of halogen-methyl exchange with tetramethylsilane.[17]

N.m.r. parameters of dimethyl ether–boron trihalide adducts

Me_2O Adduct of:	Chemical shifts [a] ^1H	^{19}F	^{11}B	^{11}B–^{19}F Coupling constant [b] (Hz)
[c]	3·34			
BF_3	3·96	158·2	18·1	*
BCl_3	4·34		6·8	
BBr_3	4·46		21·6	
BI_3	4·61			
BF_2Cl	4·04	132·6	13·0	27·0
$BFCl_2$	4·16	116·2	9·8	53·8
BF_2Br	4·05	123·9	*	37·8
$BFBr_2$	4·21	103·3	*	76·1
BCl_2Br	4·36		10·9	
$BClBr_2$	4·40		15·8	
BFClBr	4·18	109·7	*	66·5

[a] In methylene chloride solution, ^1H: p.p.m. to low field of tetramethylsilane; ^{19}F: p.p.m. from $CFCl_3$; ^{11}B: p.p.m. from external trimethoxyboron. [b] From ^{19}F spectra; confirmed in some cases by ^{11}B spectra. [c] Uncomplexed Me_2O.

* Inadequate resolution.

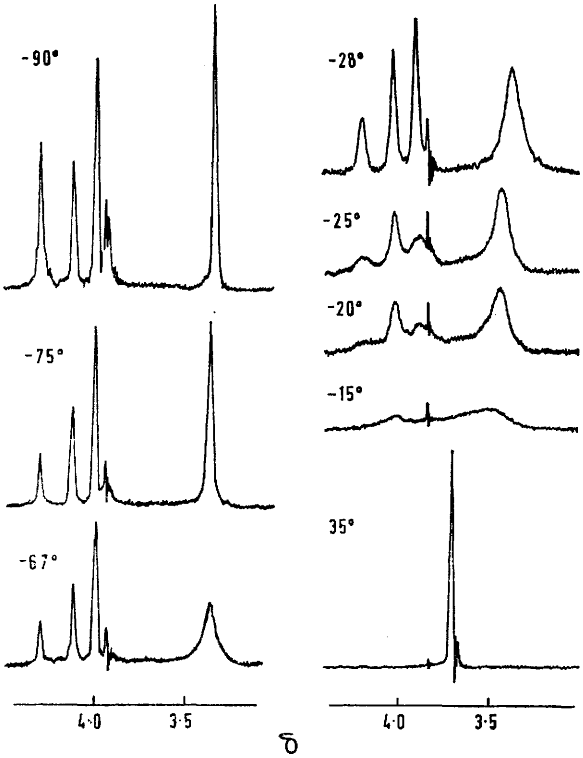

FIGURE 1 ^1H Spectra of a methylene chloride solution of Me_2O, BF_3, and BCl_3 in a 3 : 1 : 1 molar ratio, after the attainment of equilibrium in the halogen redistribution reaction. The small sharp peak near δ = 4 p.p.m. which does not coalesce at higher temperatures arises from a ^{13}C satellite of CH_2Cl_2

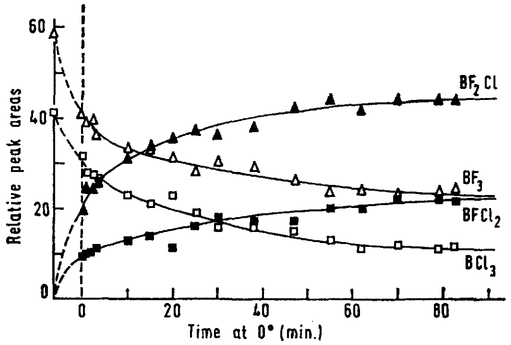

FIGURE 2 Plot of the changes in relative peak areas of the −90° ^1H adduct peaks with reaction time at 0°, for a sample in which 59% of the halogen was fluorine and 41% was chlorine. △, Me_2O,BF_3; ▲, Me_2O,BF_2Cl; ■, $Me_2O,BFCl_2$; □, Me_2O,BCl_3

With an excess of BI_3 present, fresh solutions of Me_2O and BI_3 gave −90° ^1H peaks at δ 2·29 (methyl iodide) and δ 4·61 (probably Me_2O,BI_3). Very brief warming to 0° led to the disappearance of the δ 4·61 peak and a corresponding increase in the intensity of the methyl iodide peak.

The Me_2O–BF_3–BCl_3 *System*.—Solutions of dimethyl ether, BF_3, and BCl_3 which contained an excess of Me_2O gave initial −90° ^1H spectra containing three major peaks due to Me_2O, Me_2O,BF_3, and Me_2O,BCl_3. Warming of the solutions to room temperature caused the appearance of two new −90° peaks at δ 4·04 and 4·16, which are assigned to Me_2O,BF_2Cl and $Me_2O,BFCl_2$ respectively. These peaks increased rapidly in size at the expense of the Me_2O,BF_3 and Me_2O,BCl_3 peaks on further warming to room temperature, while the size of the free Me_2O peak remained constant. The ^1H spectra were temperature-dependent (Figure 1). Monitoring of the reaction at 0° shows the approach to equilibrium in the halogen redistribution (Figure 2). The small ^1H impurity peaks characteristic of decomposition in the Me_2O–BCl_3 system appeared, but only after the attainment of equilibrium in the halogen redistribution.

Equilibrium constants for the following reactions were determined from relative ^1H peak areas:

$$2\,Me_2O,BFCl_2 \rightleftharpoons Me_2O,BF_2Cl + Me_2O,BCl_3 \qquad (1)$$

$$2\,Me_2O,BF_2Cl \rightleftharpoons Me_2O,BF_3 + Me_2O,BFCl_2 \qquad (2)$$

$$K_1 = \frac{[Me_2O,BF_2Cl][Me_2O,BCl_3]}{[Me_2O,BFCl_2]^2} \qquad (3)$$

$$K_2 = \frac{[Me_2O,BF_3][Me_2O,BFCl_2]}{[Me_2O,BF_2Cl]^2} \qquad (4)$$

K_1 and K_2, which completely define the halogen redistribution equilibria in the system,[18] were found to be: $K_1 = 0{\cdot}80 \pm 0{\cdot}10$; $K_2 = 0{\cdot}23 \pm 0{\cdot}10$. Since the values for K_1 and K_2 remained constant when the ratio of fluorine to chlorine was changed, our assignment of peaks to the mixed adducts is confirmed.

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[16] H. Schmidbaur, *J. Amer. Chem. Soc.*, 1963, **85**, 2336.

[17] R. J. Gillespie and J. S. Hartman, *Canad. J. Chem.*, 1968, **46**, 3799.

[18] K. Moedritzer, *Adv. Organometallic Chem.*, 1968, **6**, 171; *Organometallic Reactions*, 1971, **2**, 1.

When boron trihalide rather than Me_2O was present in excess, initial spectra contained large mixed-adduct peaks, and warming did not further increase their size. Since even samples which had not been warmed above −78° had reached equilibrium in the halogen redistribution, the formation of the mixed adducts is several orders of magnitude faster under these conditions than when an excess of Me_2O is present.

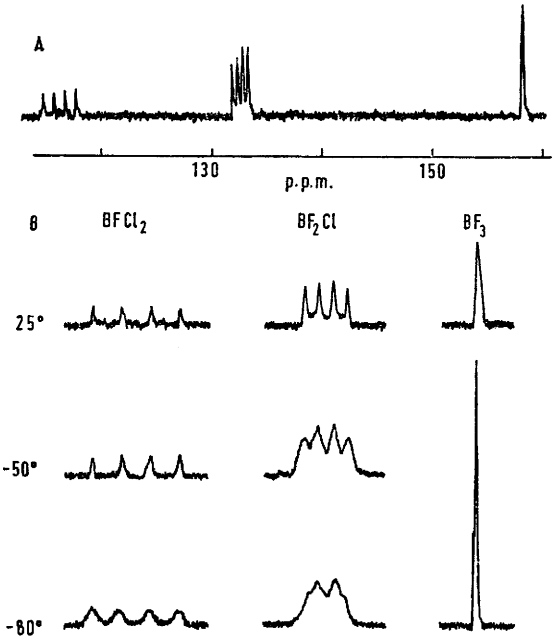

FIGURE 3 ^{19}F Spectra of a methylene chloride solution of Me_2O, BF_3, and BCl_3 in a 3 : 1 : 1 mole ratio, after the attainment of equilibrium in the halogen redistribution reaction. A, the room temperature (+25°) spectrum; B, expansion of the resonances obtained at +25, −50, and −80°, showing the broadening of the mixed-adduct quartets at low temperatures and the broadening of the Me_2O,BF_3 resonance at room temperature

^{19}F Spectra confirm the formation of Me_2O,BF_2Cl and $Me_2O,BFCl_2$. Initial low-temperature ^{19}F spectra of samples containing an excess of Me_2O showed only the Me_2O,BF_3 peak. Reaction at room temperature gave a spectrum (Figure 3A) containing two new 1 : 1 : 1 : 1 quartets at lower field, with a corresponding decrease in the intensity of the Me_2O,BF_3 peak. The 1 : 1 : 1 : 1 quartets arise from coupling with boron-11 ($I = 3/2$) and confirm that boron–fluorine bonds are present in the new species. Figure 3B shows the individual adduct resonances in more detail at 25, −50, and −80°. The broadening of the Me_2O,BF_3 peak at room temperature suggests that a chemical exchange process is beginning to affect the spectrum in this temperature range. The broadening of the mixed-adduct quartets as the temperature is *lowered*, and the collapse of the Me_2O,BF_2Cl quartet to a broad doublet-like structure at −80°, is characteristic of the coupling of a spin-1/2 nucleus to a spin-3/2 nucleus which is undergoing intermediate rates of quadrupole relaxation.[19] Changes in the relative areas of the mixed-adduct peaks at equilibrium when the ratio of fluorine to chlorine is changed confirm the ^{19}F peak assignments given in the Table.

When an excess of boron trihalide was present, the ^{19}F spectra contained additional peaks and were temperature-dependent (Figure 4). −90° Peaks at 73·5 and 124·2 p.p.m. are assigned to uncomplexed BF_2Cl and BF_3.[20] No uncomplexed $BFCl_2$ was detected. The coalescence of the BF_3 and Me_2O,BF_3 peaks near −75°, and of the BF_2Cl and Me_2O,BF_2Cl peaks near −45°, indicates rapid breaking and re-forming of donor–acceptor bonds. The survival of three peaks in the spectrum up to 5° shows that halogen exchange remains slower than donor–acceptor bond breaking. However the loss of the quartet splittings in the $Me_2O,BFCl_2$ resonance above −10° and lack of sharpening of the other peaks at the higher temperatures suggests that an additional chemical exchange process such as halogen redistribution may be affecting the line shapes in this temperature range.

^{11}B Spectra confirm the existence of the mixed boron trihalide adducts. Spectra at 11·43 MHz were weak and complex due to overlapping of multiplets due to boron–fluorine coupling. Spectra at 25·1 MHz showed simple non-overlapping multiplets. From low to high field the spectrum consisted of: a singlet (Me_2O,BCl_3), a 1 : 1 doublet ($Me_2O,BFCl_2$), a 1 : 2 : 1 triplet (Me_2O,BF_2Cl), and a singlet (Me_2O,BF_3). At both frequencies the splittings agreed with those determined from the ^{19}F spectra.

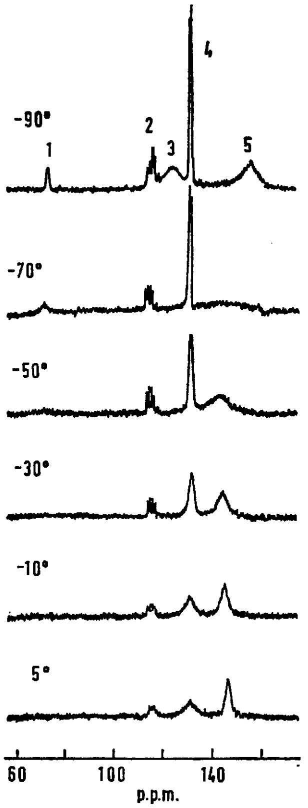

FIGURE 4 ^{19}F Spectra of a methylene chloride solution of Me_2O, BF_3, and BCl_3 in a 1 : 1 : 1 molar ratio. The −90° peak assignments are: 1, BF_2Cl; 2, $Me_2O,BFCl_2$; 3, BF_3; 4, Me_2O,BF_2Cl; 5, Me_2O,BF_3

The Me_2O–BF_3–BBr_3 *System*.—This system resembles the Me_2O–BF_3–BCl_3 system, the chief difference being that when

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[19] J. Bacon, R. J. Gillespie, and J. W. Quail, *Canad. J. Chem.*, 1963, **41**, 3063.

[20] T. D. Coyle and F. G. A. Stone, *J. Chem. Phys.*, 1960, **32**, 1892.

an excess of Me_2O is present the decomposition and halogen scrambling reactions occur at comparable rates. Thus the ^1H singlets and the ^{19}F quartets of the mixed adducts reached their maximum size after a few minutes of reaction at room temperature and then diminished. When an excess of Lewis acid was present, equilibrium in the halogen redistribution was attained before initial n.m.r. spectra could be obtained, and decomposition was quite slow. ^{19}F Spectra showed that chemical exchange between BF_2Br and its adduct is slower than that between BF_2Cl and its adduct. 11·43 MHz ^{11}B spectra of this system were poorly resolved, presumably because of the small ^{11}B chemical shift range between Me_2O,BF_3 and Me_2O,BBr_3 (Table).

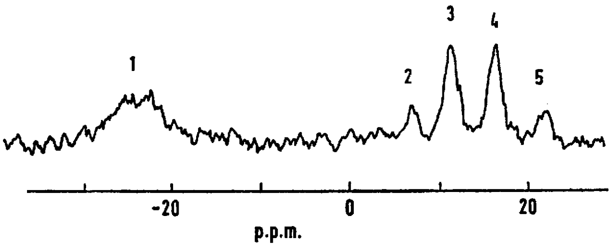

FIGURE 5 The −90° 11·43 MHz ^{11}B spectrum of a methylene chloride solution of Me_2O, BCl_3, and BBr_3 in the mole ratio 1 : 1 : 1. The peak assignments are: 1, unresolved band of the free boron trihalides; 2, Me_2O,BCl_3; 3, Me_2O,BCl_2Br; 4, $Me_2O,BClBr_2$; 5, Me_2O,BBr_3

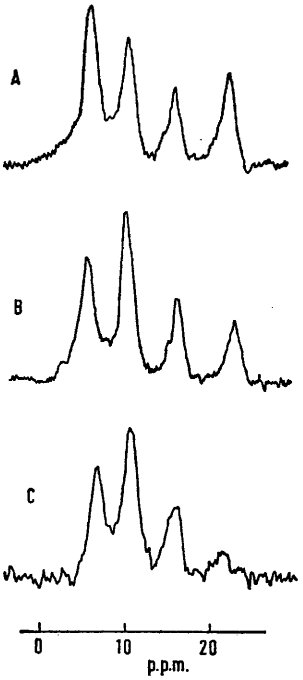

FIGURE 6 −80° 11·43 MHz ^{11}B spectra of a methylene chloride solution of Me_2O, BCl_3, and BBr_3 in the mole ratio 3 : 1 : 1. A, initial spectrum; B, after 1 min of reaction at 25°; C, after 2 min of reaction at 25°

The Me_2O–BCl_3–BBr_3 *System*.—The ^1H peaks assigned to mixed-halogen species in this system were poorly resolved because of very small chemical-shift differences. The best evidence for the mixed-halogen species was provided by ^{11}B spectra (Figures 5 and 6). Initial spectra showed the presence of near-statistical amounts of the mixed- and unmixed-halogen adducts when an excess of Lewis acid was present (Figure 5). No changes were observed in the spectrum after the sample had been allowed to stand at room temperature for several minutes. Competition between halogen scrambling and adduct decomposition in the presence of an excess of Me_2O was shown by changes in the ^{11}B spectra after brief periods at room temperature (Figure 6). Species such as $(MeO)_2BBr$ which are formed in these reactions are reported [21] to absorb to much lower field in the ^{11}B spectrum.

The Me_2O–BF_3–BCl_3–BBr_3 *System*.—Similar halogen scrambling and decomposition reactions occur in this system. In the presence of an excess of Lewis acid it was possible to identify a ^1H singlet and a ^{19}F 1 : 1 : 1 : 1 quartet which could not be assigned to any of the binary–halogen systems. These are assigned to $Me_2O,BFClBr$ as in the Table.

The Me_2O–BF_3–BI_3 *System*.—Only when Lewis acid was present in excess was this system stable enough for n.m.r. studies. A solid, probably BI_3, was present in all samples. Initial −90° ^1H spectra contained a large peak at δ 3·99 (Me_2O,BF_3) and small peaks at δ 2·77 (methyl iodide), 4·30, and 4·44 but no Me_2O,BI_3 peak could be detected at δ 4·61. Brief warming to 0° caused the disappearance of the δ 4·30 and 4·44 peaks and a corresponding growth of the methyl iodide peak. Initial ^{19}F spectra contained large broad peaks at 122·3 p.p.m. (BF_3) and 158·2 p.p.m. (Me_2O,BF_3), sharp peaks of intermediate size at 152·1 and 157·0 p.p.m., and a number of minor peaks. Brief warming caused changes in some of the minor peaks and the appearance of a new peak at 153·0 p.p.m. Since there are no low-field ^{19}F peaks with the expected splittings or broadening due to boron–fluorine coupling, it seems unlikely that the simple mixed adducts are present.

The Me_2O–BCl_3–BI_3 *and* Me_2O–BBr_3–BI_3 *Systems*.—Each of these systems gave a single ^1H adduct peak, the chemical shift corresponding to either Me_2O,BCl_3 or Me_2O,BBr_3. A solid was present in all samples at the low temperatures used. No evidence was obtained for the mixed adducts.

DISCUSSION

The ^1H, ^{19}F, and ^{11}B n.m.r. evidence is conclusive in establishing the existence of Me_2O,BF_2Cl and $Me_2O,BFCl_2$. N.m.r. evidence from two nuclei establishes the existence of the mixed adducts Me_2O,BF_2Br, $Me_2O,BFBr_2$, Me_2O,BCl_2Br, $Me_2O,BClBr_2$, and $Me_2O,BFClBr$. These species form by typical redistribution reactions.[2,18] As in many such reactions the halogen exchange is slow on the n.m.r. time scale but too fast to allow the isolation of the individual mixed-halogen species. The equilibrium constants K_1 and K_2 in the Me_2O,BF_nCl_{3-n} system are quite close to the value of 0·33 which is obtained in the ideal random case, and thus the reactions are very nearly thermoneutral.[18] The K_1 and K_2 values for the corresponding free trihalides can be calculated from the data of Lappert and his co-workers,[3] and are 2·40 and 1·39 in 1,1-dichloroethane. The formation of BF_2Cl and $BFCl_2$ from BF_3 and BCl_3 is endothermic and the heat of reaction is of the order of 1 kcal mol^{-1}.[3] The distribution of halogen is much closer to the ideal random case in the

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[21] H. Nöth and H. Vahrenkamp, *Chem. Ber.*, 1966, **99**, 1049.

Me_2O adducts than in the free trihalides. This is to be expected if the deviations from randomness in the free boron trihalides are related in some way to boron–fluorine π bonding.[1] The distribution of halogens should become more random on adduct formation since much of the π bonding is destroyed.[22]

Halogen redistribution in trigonal boron compounds probably occurs *via* a doubly-bridged transition state.[1,2] When only the four-co-ordinate Me_2O adducts are present, a preliminary dissociation of the weak boron–oxygen bond is probably required, after which halogen redistribution might proceed by various routes.[2] The fact that halogen redistribution is much more rapid when an excess of boron trihalide is present supports a mechanism involving three-co-ordinate boron. Because the donor–acceptor bonds are weak (13·1 kcal mol^{-1} in Me_2O,BF_3 [23]) a slight dissociation of the adduct is to be expected even in the presence of an excess of Me_2O, so that there is sufficient free boron trihalide present to allow the halogen redistribution to proceed slowly. Support for the involvement of free boron trihalide in halogen redistribution in adducts comes from studies of trimethylamine–boron trihalide systems.[5,24] The stronger donor–acceptor bonds (30·9 kcal mol^{-1} in Me_3N,BF_3 [23]) do not break,[24] and halogen redistribution occurs in solution *only* when excess boron trihalide is present; the mechanisms involved may be complex.[24,25]

The relative stabilities of the boron–halogen bonds, with respect to decomposition to give methyl halide, are in the order F > Cl > Br > I expected from previous studies.[1,11] The same order is observed in the mixed and the unmixed boron trihalide adducts. Decomposition varies from being unobservable with the BF_3 adduct to being so fast with the BI_3 adduct that our evidence for its existence is not conclusive. However, our assignment of the new ^1H peak in the Me_2O–BI_3 system to the 1 : 1 adduct is supported by: (i) the regularity of the ^1H chemical shifts in the series of BF_3, BCl_3, BBr_3, and BI_3 adducts, which is similar to the trend in complexation shifts of the trimethylamine–boron trihalide adducts [26] and is in accord with the expected [1,26] order of Lewis acid strengths, $BF_3 < BCl_3 < BBr_3 < BI_3$; (ii) the rapid and complete disappearance of this peak on even very brief warming to 0 °C, together with growth of the methyl iodide peak; and (iii) the fact that this peak is detectable only when BI_3 is present in excess, as predicted by extrapolation from the behaviour of the BBr_3 adduct.

In the mixed boron trihalide systems which do not contain iodine, each boron–halogen bond appears to react independently of the other halogens present. However, the Me_2O–BF_3–BI_3 system shows an even greater reactivity than the Me_2O–BI_3 system. The mixed boron trihalide adducts have not been detected in this system, but there are a number of products which do not form when only one of the halogens is present. The contrast of the ^{19}F spectra of the Me_2O–BF_3–BBr_3 and the Me_2O–BF_3–BI_3 systems is striking. The bromine-containing system gave only adduct and free boron trihalide peaks when an excess of boron trihalide was present, but the iodine-containing systems gave a number of different peaks, none of them corresponding to the absorptions expected for the iodine-containing mixed adducts. Thus, BI_3 is much more reactive than BBr_3 in causing the incorporation of fluorine into new species, but much less effective in forming the mixed adducts. The unique behaviour of the Me_2O–BF_3–BI_3 system is of special interest since fluorine and iodine are the only pair of halogens that are 'incompatible' in the free boron trihalides, so that the mixed species BF_2I and BFI_2 cannot be detected.[3] The unique behaviour of the Me_2O–BF_3–BI_3 system may be due to the boron–iodine bonds being even more reactive in Me_2O,BF_2I and Me_2O,BFI_2 than in Me_2O,BI_3.* If the mixed adducts form initially, rapid reaction with an excess of BF_3 might occur to give species such as $Me_2O,BI_2{}^+BF_4{}^-$. The cation, similar to one proposed by Ryschkewitsch and Wiggins,[27] would readily decompose to give methyl iodide but $BF_4{}^-$ is stable. Such reactions could account for the observed ^1H and ^{19}F spectra.

N.m.r. Parameters.—The ^1H and ^{11}B chemical shifts of the mixed-halogen species are intermediate between those of the corresponding unmixed-halogen species. Thus the ^1H complexation shifts of Me_2O follow the expected order of Lewis acidity of the boron trihalides, as in unmixed boron trihalide adducts.[26] Trends in ^{19}F chemical shift and in boron–fluorine coupling constant in the Me_2O,BF_nX_{3-n} (n = 1—3) species resemble the trends previously observed [20] in the uncomplexed mixed boron trihalides, as is evident from a plot of chemical shifts *vs.* coupling constant (Figure 7). This plot for the free trihalides has been presented as evidence that the sign of the coupling constant in BF_3 is opposite to the sign in the mixed boron trihalides.[28] Also, the ^{11}B chemical shifts of the adducts resemble those of the corresponding free boron trihalides in that the lowest-field ^{11}B resonance is found for BCl_3 and for its adduct, in the free trihalide series [1,29] and the Me_2O adduct series respectively (Figure 8). A similar trend in ^{11}B chemical shifts is

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* The BF_2I and BFI_2 adducts of trimethylamine show normal behaviour.[5] However, trimethylamine adducts of the boron trihalides are so much more stable than the corresponding dimethyl ether adducts that similar reactions are not expected.

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found for the unmixed boron trihalide adducts of trimethylamine.[21] The shift of the ^{11}B resonance to lower field as bromine is successively replaced by the more electronegative chlorine is in accord with the expected decrease in electron density about boron, but when the even more electronegative fluorine replaces chlorine the shift is to higher field. This cannot be explained by electronegativity considerations alone.

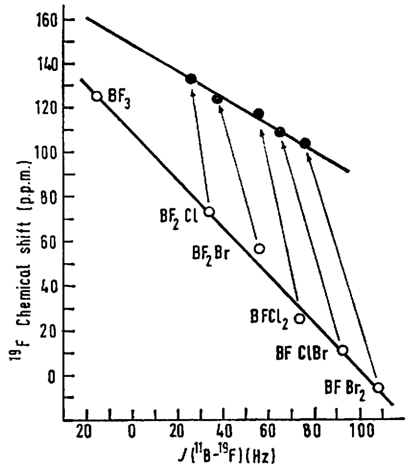

FIGURE 7 Changes in ^{19}F chemical shifts and in ^{11}B–^{19}F coupling constants in mixed boron trihalides on complexation with Me$_2$O: ○, free trihalides; ●, Me$_2$O adducts

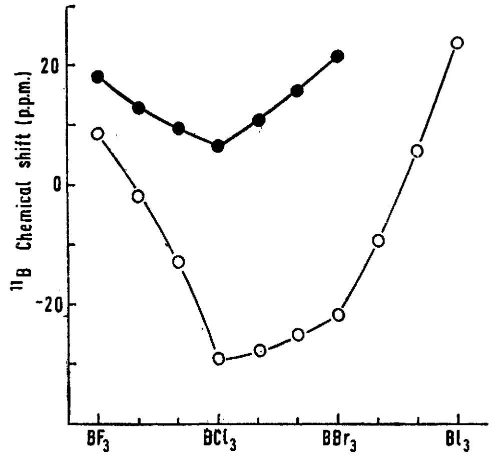

FIGURE 8 Changes in ^{11}B chemical shifts of boron trihalides [29] and of their Me$_2$O adducts across the series BF$_n$Cl$_{3-n}$, BCl$_n$Br$_{3-n}$, and BBr$_n$I$_{3-n}$ ($n = 0$—3). ○, free trihalides; ● Me$_2$O adducts

In the free boron trihalides the ^{19}F chemical shift trend has been explained in terms of boron–fluorine π bonding.[1,20] The reversal in the ^{11}B chemical shift trend when fluorine is involved might be explained in a similar fashion. If such explanations are valid, the survival of these trends in an attenuated form on adduct formation indicates that π bonding is still important in the adducts but is less effective than in the free boron trihalides. In a detailed study of the energetics of boron trihalide adduct formation, Drago and his co-workers have proposed that some of the boron–fluorine π bonding survives on adduct formation.[22] Armstrong and Perkins have reached the same conclusion on different grounds.[30] Our n.m.r. data support this. However, as discussed in a related paper,[31] other factors may be involved in the trends in chemical shifts.

Donor–acceptor Bond Breaking.—Although some dissociation of Me$_2$O,BF$_3$ to give Me$_2$O and BF$_3$ is expected, our results indicate that only a very small proportion of the adduct is dissociated in solution. This contrasts with Gore and Danyluk's calculation of an equilibrium constant for the dissociation.[15] The limits of error inherent in their method, which involved chemical-shift variations in room temperature spectra, seem to be too large for their results to be meaningful. The conflict of their order of relative base strengths of ethers toward BF$_3$ with the order determined by other workers[1] supports our conclusion that the degree of dissociation is much less than that reported by Gore and Danyluk.

Even in the absence of a second halogen, exchange reactions of ether–boron trihalide adducts can be complex. Thus a competition between dissociative and concerted mechanisms is reported in the exchange of BF$_3$ among ether molecules in the presence of an excess of ether, and an additional mechanism appears to be important in the presence of excess BF$_3$.[32] Although the presence of a second halogen further complicates the system, the breaking and re-forming of donor–acceptor bonds remains faster than halogen redistribution in the Me$_2$O–BF$_3$–BCl$_3$ system and can be studied with little interference from the slower reaction. This remains true even when an excess of boron trihalide is present and greatly increases the rate of halogen redistribution. Thus the ^{19}F peaks due to (i) free and complexed BF$_3$, and (ii) free and complexed BF$_2$Cl, collapse at low temperatures, whereas three ^{19}F peaks, each corresponding to an average of free and complexed forms of a boron trihalide, remain separate to much higher temperatures (Figure 4). In accord with the expected order of Lewis acid strengths, $BF_3 < BF_2Cl < BFCl_2 < BCl_3$, much of the BF$_3$ is displaced from its adduct while successively smaller proportions of BF$_2$Cl and BFCl$_2$ are uncomplexed. The weakest Lewis acid, BF$_3$, apparently exchanges the most rapidly between free and complexed forms.

When dimethyl ether is present in excess in the Me$_2$O–BF$_3$–BCl$_3$ system, breaking and re-forming of donor–acceptor bonds is several orders of magnitude faster than halogen redistribution. The coalescence of ^{1}H peaks in the equilibrated Me$_2$O–BF$_3$–BCl$_3$ system (Figure 1) must be attributed to the breaking and re-forming of donor–acceptor bonds. A detailed kinetic

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interpretation of the coalescence pattern would involve calculation of signal shapes for chemical exchange among five sites and has not yet been attempted. However, the coalescence pattern shows collapse of the Me_2O and Me_2O,BF_3 peaks at quite low temperatures (−70°) and a further collapse at higher temperatures (−30 to 0°) of all the remaining adduct peaks. We can conclude that: (i) free and complexed base molecules are interchanged in the chemical exchange process; (ii) the BF_3 adduct is the most susceptible to chemical exchange; and (iii) the donor–acceptor bond lifetimes are similar in the BF_2Cl, $BFCl_2$, and BCl_3 adducts. No obvious explanation suggests itself for the difference between the reactivity of the BF_3 adduct and of all the other adducts. This point is being further investigated in studies of the mixed boron trihalide adducts of other Lewis bases.

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