Boron Trihalide Adducts of Dimethyl Sulphide. A Nuclear Magnetic Resonance Study of Exchange Reactions and Mixed Boron Trihalide Adducts †

By **Michael J. Bula** and **J. Stephen Hartman,*** Department of Chemistry, Brock University, St. Catharines, Ontario, Canada

Rapid donor–acceptor bond-breaking and halogen-redistribution reactions occur in solutions of dimethyl sulphide–boron trihalide adducts. Relative rates of donor–acceptor bond breaking are in the order $BF_3 > BF_2Cl > BFCl_2 > BCl_3 > BBr_3 > BI_3$ for these adducts. Halogen redistribution gives large amounts of the non-fluorine-containing mixed boron trihalide adducts, including the ternary-halogen adduct $Me_2S,BClBrI$. However fluorine is incompatible with the heavier halogens in these adducts. Only small amounts of Me_2S,BF_2Cl and $Me_2S,BFCl_2$ are present at equilibrium, and mixed F,Br- and F,I-containing adducts could not be detected. This behaviour contrasts with that of the analogous Me_2O adducts. Possible explanations are discussed.

OUR studies of halogen-redistribution reactions in boron trihalide adducts [1,2] and in tetrahalogenoborate anions [3] have shown that rates and equilibria in these reactions are highly dependent on the Lewis base involved. Thus halogen redistribution occurs under a wider range of conditions in Me_2O adducts than in Me_3N adducts.[1,2] In the tetrahalogenoborate anions rates of halogen redistribution show a complex dependence on the halogens present,[3] and in the Me_3N adducts the mechanism of halogen exchange may vary with the halogens present.[4] Our studies of the mixed boron trihalide adducts of the hard bases Me_2O and Me_3N are now complemented by a study of adducts of Me_2S which is a soft base according to Pearson's classification of 'hard and soft acids and bases'.[5] We have again chosen a simple base in which there is only one proton environment and in which Brønsted acidity of the adduct [6] is not a complicating factor. As in the Me_2O adducts [1] a very rapid donor–acceptor bond-breaking reaction complicates the study.

Some n.m.r. data are available for the unmixed boron

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† Presented in part at the 55th Canadian Chemical Conference, Quebec City, June 1972.

[1] M. J. Bula, D. E. Hamilton, and J. S. Hartman, *J.C.S. Dalton*, 1972, 1405.

[2] (*a*) J. S. Hartman and J. M. Miller, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 831; (*b*) B. Benton-Jones, M. E. A. Davidson, J. S. Hartman, J. J. Klassen, and J. M. Miller, *J.C.S. Dalton*, 1972, 2603.

[3] J. S. Hartman and G. J. Schrobilgen, *Inorg. Chem.*, 1972, **11**, 940.

[4] B. Benton-Jones and J. M. Miller, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 485.

[5] R. G. Pearson, *J. Chem. Educ.*, 1968, **45**, 581, 643; *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

[6] R. J. Gillespie and J. S. Hartman, *Canad. J. Chem.*, 1967, **45**, 2243.

trihalide adducts of Me_2S [7-9] but extensive n.m.r. studies have not been reported. The order of Lewis acidity toward Me_2S has been shown to be $BF_3 \ll BCl_3 < BBr_3 < BI_3$.[8,10] The BF_3 adduct, unlike the BCl_3 adduct, is extensively dissociated in the gas phase at room temperature.[10] Although Me_2O is a stronger base than Me_2S toward BF_3, Me_2S is a stronger base than Me_2O toward BCl_3.[7] This and related cases of base-strength reversal have been discussed by Young, McAchran, and Shore [7] but as yet there is no complete explanation. A similar reversal of base strength toward BF_3 and BCl_3 seems to occur with 1,4-thioxan, with oxygen and sulphur the donors in the BF_3 and BCl_3 adducts respectively.[11] The availability of adducts of the intermediate Lewis acids BF_2Cl and $BFCl_2$ should throw further light on the phenomenon of base-strength reversal.

EXPERIMENTAL

Dimethyl sulphide (J. T. Baker) was dried over molecular sieves, then trap-to-trap distilled on a high-vacuum system, the initial and final cuts being rejected. Methylene dichloride was dried over phosphoric oxide before use. The boron trihalides and n.m.r. reference compounds were purified as described.[1]

Sealed n.m.r. samples were prepared on a high-vacuum system [1] with methylene dichloride as solvent. Dilute samples (0·1—0·3M in adduct) were used because of solubility limitations, but nevertheless some mixed-adduct samples containing bromine and iodine were only partially soluble. Solubilities of the adducts in methylene dichloride and in numerous other solvents diminish markedly in the order $BF_3 > BCl_3 > BBr_3 > BI_3$. Negligible decomposition of the adducts occurs on prolonged standing in methylene dichloride solution at room temperature. Uncomplexed BI_3, but not Me_2S,BI_3, will react with tetramethylsilane to give Me_3SiI as one of the products.

^{11}B Decoupling of ^1H spectra was carried out on the Varian Associates A-60 n.m.r. spectrometer described previously [1] equipped with an NMR Specialties HD-60 heteronuclear decoupler. An HP 4204A decade oscillator was used to drive at 30 Hz a Waveteck 141 Voltage Controlled Generator used to tune the HD-60 side bands, thus providing pseudo 'noise' decoupling over a 3 kHz bandwidth. The ^{19}F instrumentation has been described.[1] The 25·1 MHz ^{11}B spectra were obtained on a Varian Associates HA-100 spectrometer.

RESULTS AND DISCUSSION

N.m.r. Spectra.—N.m.r. parameters for the dimethyl sulphide–boron trihalide adducts are in Table 1. As usual the ^1H resonance of the base shifts to low field on complexation, but the shifts do not parallel the order of donor–acceptor bond strengths, $BF_3 < BCl_3 < BBr_3 < BI_3$.[8,10] Instead the BCl_3, BBr_3, and BI_3 adducts have very similar shifts. Although ^1H complexation shifts may correlate with the strength of the donor–acceptor interaction in series of closely related adducts,[1,2,12,13] such relationships are not of general applicability.[14,15] Over a range of temperatures the ^1H spectra of the BCl_3, BBr_3, and BI_3 adducts consist of 1 : 1 : 1 : 1 quartets owing to coupling with boron-11, but broadening and collapse occurs at both higher and lower temperatures (Figure 1). Similar effects have not been observed in the ^1H spectra of fluorine-containing adducts, but were observed in the ^{19}F spectra. Quadrupole relaxation of boron [16] collapses the quartets at low temperatures while chemical exchange collapses them at higher temperatures.

TABLE 1

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

Me_2S adduct of:	Chemical shifts [a] ^1H	^{19}F	^{11}B	Coupling constants $J(^1H–^{11}B)$ [b]	$J(^{11}B–^{19}F)$ [c]
— [d]	2·14				
BF_3	2·42	139·3	15·2 [e]	*	24 ± 2
BCl_3	2·58 [f]		11·2 [e]	2·9	
BBr_3	2·64 [f]		29·5	3·7	
BI_3	2·65 [f]		87·0	3·8	
BF_2Cl	2·47	125·0	*	*	59·8
$BFCl_2$	2·53	123·8	*	*	85·8
BCl_2Br	*		16·4	*	
$BClBr_2$	*		22·6	*	
BCl_2I	*		29·6	*	
$BClI_2$	*		54·9	*	
BBr_2I	*		46·1	*	
$BBrI_2$	*		65·3	*	
BClBrI	*		37·6	*	

[a] In methylene dichloride solution; ^1H, −93 °C, p.p.m. to low field of tetramethylsilane; ^{19}F, −50 °C, p.p.m. to high field of $CFCl_3$; ^{11}B, 30 °C, p.p.m. to high field of external trimethoxyboron. [b] From ^1H spectra. [c] From ^{19}F spectra. [d] Uncomplexed Me_2S. [e] Literature ^{11}B chemical shifts:[6] Me_2S,BF_3, 15·5 p.p.m.; Me_2S,BCl_3, 10·8 p.p.m. [f] Literature ^1H chemical shifts:[7] Me_2S,BCl_3, 2·60; Me_2S,BBr_3, 2·70; Me_2S,BI_3, 2·76; $J(^1H—^{11}B)$ 3·7 Hz for Me_2S,BI_3.

* Inadequate resolution.

Halogen redistribution gives rise to a number of signals assigned to mixed boron trihalide adducts. The ^1H and ^{11}B chemical shifts of the mixed-halogen adducts are intermediate between those of the corresponding unmixed-halogen adducts, as in the Me_2O [1] and Me_3N [2,17] systems. The trend in ^{19}F chemical shifts and ^{11}B–^{19}F coupling constants across the series Me_2S,BF_nCl_{3-n} (n = 1—3) resembles that in other mixed boron trihalide adduct systems,[1-3] but the near-linear relationship between chemical shift and coupling constant observed in the Me_2O adducts [1] no longer holds. The coupling constant increases in the usual fashion between Me_2S,-

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

[8] M. Schmidt and H. D. Block, *Chem. Ber.*, 1970, **103**, 3705.

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BF_2Cl and $Me_2S,BFCl_2$ but there is only a small change in the chemical shift. In numerous other series of compounds the ^{19}F resonance of the remaining fluorines about a central atom shifts to lower field as fluorines are replaced by chlorine or bromine[18] but the magnitudes of the shifts are irregular. It should be possible to systematize these ^{19}F parameters in terms of pairwise interaction parameters,[19] as we have done for the mixed tetrahalogenoborate anions,[3] and studies along these lines are being carried out.

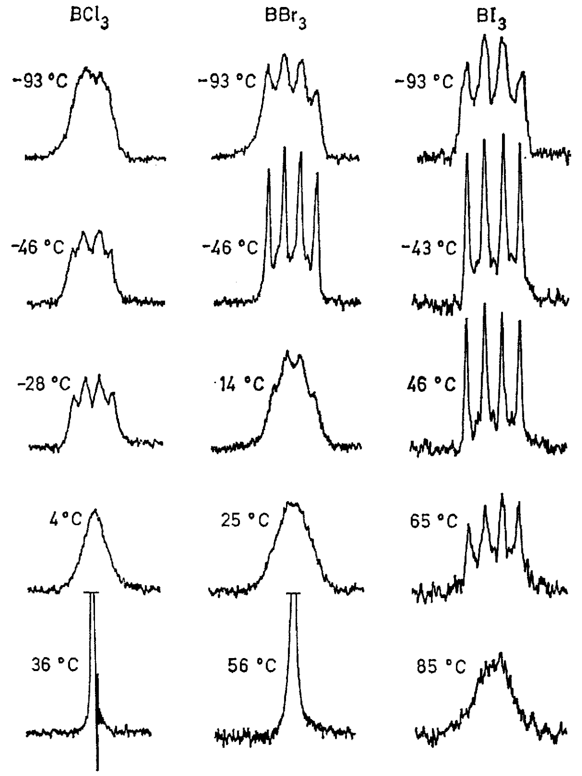

FIGURE 1 Temperature-dependence of the ^1H n.m.r. spectra of Me_2S,BCl_3, Me_2S,BBr_3, and Me_2S,BI_3

^{11}B Resonances of the Me_2S adducts occur somewhat to higher field of those of the corresponding Me_2O[1] and Me_3N[20] adducts, probably because of the greater polarizability of sulphur than of oxygen and nitrogen. The exception is the BF_3 adduct. Changes in adduct chemical shift when the donor is changed are very much less than the change between a free boron trihalide and its adducts (Figure 2). Thus ^{11}B complexation shifts are not related in any simple fashion to the strength of the donor–acceptor bond, but instead the change in environment between trigonal planar and tetrahedral boron is responsible for most of the complexation shift.

The anomalous ^{11}B absorption of Me_2S,BF_3 to low field of the BF_3 adducts of Me_3N (Figure 2) and Me_2O is probably a result of the extremely weak[10] donor–acceptor bond in this adduct. According to Brown, Drago, and Bolles[21] a weak donor–acceptor interaction should only partially change the boron trihalide fragment from trigonal planar to the pyramidal geometry required to give a tetrahedral adduct. If this change in chemical environment is responsible for most of the complexation shift, an incomplete change would give the observed shift.

Broadening and collapse of 1 : 1 : 1 : 1 quartets at lower temperatures is characteristic of a spin-$\frac{1}{2}$ nucleus coupled to boron-11 ($I = \frac{3}{2}$) and is due to more effective quadrupole relaxation of boron-11 at lower temperatures.[16] Quadrupole relaxation is made more effective by (i) a greater electric-field gradient at boron-11; (ii) an increased correlation time for molecular reorientation; and (iii) a smaller coupling constant. The increased correlation times at lower temperatures account for the temperature dependence of the spectra. Neither changes in coupling constants nor changes in correlation times for molecular reorientation in the different adducts can account for (i) the much more collapsed −93 °C ^1H spectrum of the BCl_3 adduct compared with the successively less broadened BBr_3 and BI_3 quartets at the same temperature, or (ii) the similar degree of collapse in the −93 °C ^1H spectrum of the BCl_3 adduct and the −90 °C ^{19}F spectrum of the BF_3 adduct in spite of the much greater coupling constant in the BF_3 case. Differences in electric-field gradient about boron-11 must be responsible. To account for the results the asymmetry of charge about boron must be in the order $Me_2S,BF_3 > Me_2S,BCl_3 > Me_2S,BBr_3 > Me_2S,BI_3$. The asymmetry apparently arises from one weak boron–sulphur bond and three stronger boron–halogen bonds. As fluorines are replaced by heavier halogens the boron–halogen bonds become weaker and the donor–acceptor bond becomes

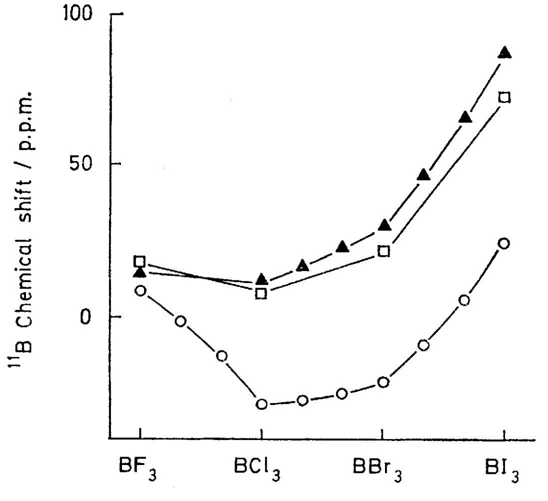

FIGURE 2 Changes in ^{11}B chemical shifts across the series BF_nCl_{3-n}, BCl_nBr_{3-n}, and BBr_nI_{3-n}, for ▲, Me_2S adducts, □, Me_3N adducts, and ○, free boron trihalides. ^{11}B Chemical shifts of Me_2O adducts[1] are very similar to those of the corresponding Me_3N adducts

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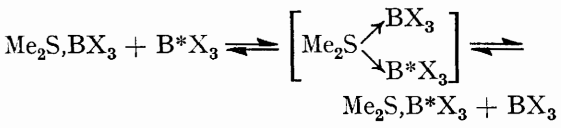
stronger, giving a greater symmetry of charge distribution.

Donor–Acceptor Bond Breaking.—Collapse of the quartet splittings in the ^1H spectra of the BCl_3, BBr_3, and BI_3 adducts (Figure 1) as the temperature is raised must result from rapid breaking and re-forming of donor–acceptor bonds. The survival of the quartet to successively higher temperatures in the BCl_3, BBr_3, and BI_3 adducts shows that the donor–acceptor bond becomes longer-lived across this series. The single sharp Me_2S,BF_3 ^1H peak observed at all temperatures down to −95 °C indicates an especially short-lived donor–acceptor bond. This is confirmed by the observation of a single averaged peak for Me_2S,BF_3 and Me_2S at the lowest temperatures in samples containing an excess of base, in contrast to the other adducts which give separate low-temperature peaks for free and complexed base. Thus relative rates of donor–acceptor bond breaking are $Me_2S,BF_3 > Me_2S,BCl_3 > Me_2S,BBr_3 > Me_2S,BI_3$, which is the reverse of the order of donor–acceptor bond strengths. A similar inverse relationship between exchange rates and donor–acceptor bond strengths has been noted in related systems.[22]

Coalescence temperatures observed for Me_2S–boron trihalide ratios of 1 : 2 and 2 : 1 as well as 1 : 1 are given in Table 2. At each of the acid–base ratios, donor–acceptor bond breaking is faster in the lighter-halogen adducts. An excess of boron trihalide causes the ^1H quartet splittings to coalesce at much lower temperatures, showing that the rate of donor–acceptor bond breaking is greatly increased. If a second sulphur lone pair is available to allow transitory formation of a 1 : 2 complex, a likely exchange mechanism would be (A).



$$Me_2S,BX_3 + B^*X_3 \rightleftharpoons \left[Me_2S\begin{matrix} \nearrow BX_3 \\ \searrow B^*X_3 \end{matrix} \right] \rightleftharpoons Me_2S,B^*X_3 + BX_3 \quad \text{(A)}$$

An excess of Me_2S gives a different ^1H coalescence pattern for the BCl_3, BBr_3, and BI_3 adducts since there is coalescence of free and complexed Me_2S signals as well as of the adduct quartets. As the temperature is raised the quartets collapse first, but before the adduct peak sharpens coalescence with the free-base peak sets in. This indicates that free and complexed base molecules are interchanged in the breaking of donor–acceptor bonds. The quartet coalescence temperatures are not greatly different from those in the 1 : 1 samples and the differences observed may be due to variations in adduct concentrations. The results are consistent with a dissociative mechanism but kinetic studies[22,23] would be required to confirm this.

The ^1H chemical shifts of the BCl_3, BBr_3, and BI_3 adducts show the same temperature dependence as the chemical shift of free Me_2S. The more pronounced temperature dependence of the BF_3 adduct peak (Table 3) apparently results from increasing dissociation of the adduct as the temperature is raised. The room-temperature peak arises from an average of adduct and free Me_2S absorptions, rather than from the adduct alone as has been assumed.[9] Partial dissociation of Me_2S,BF_3 is confirmed by the temperature-dependent chemical shift of the ^{19}F resonance. Dissociation is negligible at −80 °C, and remains negligible up to room temperature in the presence of an equivalent amount of free Me_2S. ^1H and ^{19}F spectra both indicated that the 1 : 1 adduct alone (0·3M in CH_2Cl_2) is 15 ± 5% dissociated at 25 °C, in contrast to the much greater dissociation (over 95%) in the gas phase.[10]

TABLE 2

^1H Coalescence temperatures in solutions of Me_2S,BX_3 adducts [a]

Halogen (X)	Quartet coalescence temp./°C for the following $Me_2S : BX_3$ mole ratios :			Coalescence temp./°C of Me_2S,BX_3 and free Me_2S signals (2 : 1 mole ratio of Me_2S to BX_3)
	2 : 1	1 : 1	1 : 2	
F	<-93	<-93	<-93	<-93
Cl	-10	-1	$\lesssim-93$	$+7$
Br	$+52$	$+22$	-48	$+64$
I	$+66$	$+80$	$+43$	$>+78$

[a] Adduct concns.: 0·2—0·3M for BF_3, BCl_3, and BBr_3 adducts; 0·10—0·15M for BI_3 adducts.

TABLE 3

Temperature dependence of ^1H chemical shifts in 1 : 1 solutions of Me_2S and boron trihalide [a]

Sample composition	Chemical shift at 35 °C	Chemical shift at −93 °C	Shift to low field on cooling
Me_2S	2·08	2·14	0·06
1 : 1 Me_2S–BF_3	2·26	2·40	0·14
1 : 1 Me_2S–BCl_3	2·50	2·58	0·08
1 : 1 Me_2S–BBr_3	2·56	2·64	0·08
1 : 1 Me_2S–BI_3	2·58	2·65	0·07

[a] 0·3M Solutions in methylene dichloride.

Halogen Redistribution.—Halogen redistribution is detectable by n.m.r. only in Me_2S,BF_3 among the unmixed-halogen systems. The appearance of mixed boron trihalide adducts from the corresponding unmixed adducts showed that it occurs in many of the mixed-halogen systems. Mixed adducts were detected in small amounts in the Me_2S–BF_3–BCl_3 system and in large amounts in all mixed-halogen systems not containing fluorine, but could not be detected in the Me_2S–BF_3–BBr_3 and Me_2S–BF_3–BI_3 systems.

(a) *The* Me_2S–BF_3 *system.* A 2 : 1 solution of Me_2S and BF_3 gave a broadened ^{19}F 1 : 1 : 1 : 1 quartet between −55 and −15 °C but the splittings collapsed at both higher and lower temperatures. The collapse as the temperature is raised shows that rapid breaking and re-forming of boron–fluorine bonds occurs.[24] Donor–acceptor bond breaking alone would not collapse these splittings. A 1 : 1 solution did not give ^{19}F quartet

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[22] J. Fogelman and J. M. Miller, *Canad. J. Chem.*, 1972, **50**, 1262.

[23] A. H. Cowley and J. L. Mills, *J. Amer. Chem. Soc.*, 1969, **91**, 2911.

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

splittings; instead a broad resonance sharpened as the temperature was raised. Thus fluorine scrambling is faster in the 1 : 1 solution. The inhibition of exchange by an excess of Me_2S is in accord with a requirement for uncomplexed BF_3 in the reaction, since an excess of Me_2S decreases the concentration of free BF_3.

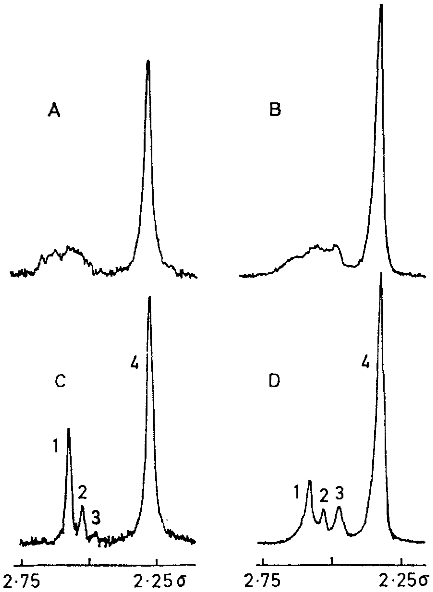

FIGURE 3 −93 °C ^1H Spectra of Me_2S–BF_3–BCl_3 solutions of mole ratios A, 3 : 1 : 1 and B, 4 : 2 : 1. Double irradiation at the ^{11}B resonance frequency gave the lower traces C and D respectively. Peak assignments: 1, Me_2S,BCl_3; 2, $Me_2S,BFCl_2$; 3, Me_2S,BF_2Cl; 4, averaged peak of Me_2S and Me_2S,BF_3

(b) *The* Me_2S–BF_3–BCl_3 *system.* Low-temperature ^1H spectra of samples containing an excess of Me_2S contained a sharp peak due to chemical-exchange averaging of the Me_2S,BF_3 and Me_2S signals and a broad, unsymmetrical absorption band to lower field (Figure 3, A and B). Double irradiation at the ^{11}B resonance frequency (19·2 MHz) gave spectra in which the broad band was resolved into a series of singlets (Figure 3, C and D) which are assigned to Me_2S,BF_2Cl, $Me_2S,BFCl_2$, and Me_2S,BCl_3 as in Table 1. Only small amounts of the mixed-halogen adducts were present. The same small proportions were present regardless of whether the samples were prepared by separate additions of BF_3 and BCl_3 or by addition of a pre-equilibrated mixture of BF_3 and BCl_3 known [25] to contain large amounts of BF_2Cl and $BFCl_2$. Thus the small amounts of the mixed adducts are a result of an unfavourable equilibrium rather than slow halogen redistribution. Unlike the corresponding Me_2O adduct system,[1] halogen redistribution is too rapid to allow n.m.r. observation of the approach to equilibrium. Even in samples which had not been warmed above −78 °C equilibration was complete. The especially rapid halogen redistribution involving the especially easily dissociated Me_2S,BF_3 adduct supports our postulate [1-3] that halogen redistribution about tetrahedral boron occurs *via* a step involving free boron trihalide.

Equilibrium constants for the halogen-redistribution reactions (1) and (2) were estimated from relative ^1H peak areas. K_1 and K_2 were determined to be: $K_1 = 6{\cdot}3 \pm 3{\cdot}0$; $K_2 = 2{\cdot}3 \pm 0{\cdot}7$.

$$2Me_2S,BFCl_2 \rightleftharpoons Me_2S,BF_2Cl + Me_2S,BCl_3 \qquad (1)$$

$$2Me_2S,BF_2Cl \rightleftharpoons Me_2S,BF_3 + Me_2S,BFCl_2 \qquad (2)$$

$$K_1 = \frac{[Me_2S,BF_2Cl][Me_2S,BCl_3]}{[Me_2S,BFCl_2]^2} \qquad (3)$$

$$K_2 = \frac{[Me_2S,BF_3][Me_2S,BFCl_2]}{[Me_2S,BF_2Cl]^2} \qquad (4)$$

These non-statistical equilibria give such small concentrations of the mixed species that their integrated intensities could not be obtained accurately. However K_1 and K_2 remained roughly constant, within the large experimental error, when the ratio of fluorine to chlorine was changed. These K_1 and K_2 values contrast with values of 0·80 and 0·23 in the corresponding Me_2O adducts,[1] 2·4 and 1·4 in the free trihalides in 1,1-dichloroethane solvent,[25] and 0·33 for both K_1 and K_2 in the ideal random case.[26] It is of interest that complexation of the BF_nCl_{3-n} mixture to Me_2S causes the halogens to ' unscramble ' to some extent, whereas complexation to Me_2O causes a more random scrambling. Formation of the mixed-halogen species from the unmixed is very nearly thermoneutral in the Me_2O adducts, but endothermic by several kcal mol^{-1} in the Me_2S adduct. Larger enthalpy changes on redistribution of substituents are well known, but these usually occur when the exchanging species are very different in kind and tend to favour the mixed species.[25,27]

The temperature dependence of the ^1H spectrum of an excess-of-base sample under ^{11}B decoupling is shown in Figure 4. The adduct peaks coalesce one by one with the free-base peak as the temperature is raised, showing that free base is involved in the exchange process, and thus that donor–acceptor bond breaking collapses the peaks. Approximate coalescence temperatures are: BF_3 adduct, < -93 °C; BF_2Cl adduct, −65 °C; $BFCl_2$ adduct, −37 °C; BCl_3 adduct, +5 °C. A similar trend was found in a sample containing a slight excess of Lewis acid. The BF_3 and BF_2Cl peaks were coalesced below −93 °C; the $BFCl_2$ and BCl_3 peaks coalesced with this averaged peak at −40 and +5 °C respectively. Since only the BCl_3 adduct is formed when a sufficiently large excess of the boron trihalides are present, BCl_3 is a stronger Lewis acid than any of the fluorine-containing species. Thus, as in the series of unmixed-halogen adducts, the strongest donor–acceptor bond is the least susceptible to exchange of Me_2S.

−40 °C ^{19}F Spectra of samples containing an excess of Me_2S showed a large Me_2S,BF_3 1 : 1 : 1 : 1 quartet and

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

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

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

two small overlapping mixed-adduct quartets at −50 °C (Figure 5). Near room temperature rapid halogen redistribution collapsed the quartets, and at higher temperatures coalescence of the mixed-adduct and BF_3 adduct peaks set in. When a small excess of Lewis acid was present all three fluorine-containing adducts could be detected at low temperatures, but when sufficient BCl_3 was present to complex with all the Me_2S no fluorine-containing adducts could be detected.

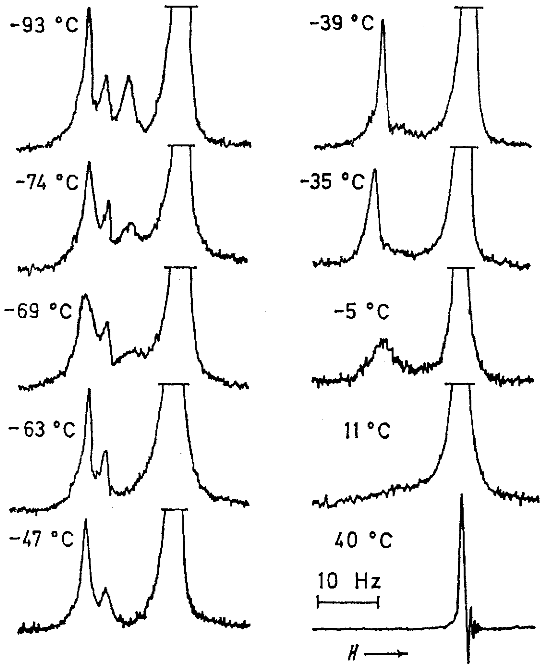

FIGURE 4 Temperature dependence of the ^{11}B-decoupled ^1H spectrum of a Me_2S–BF_3–BCl_3 solution of mole ratio 4 : 2 : 1

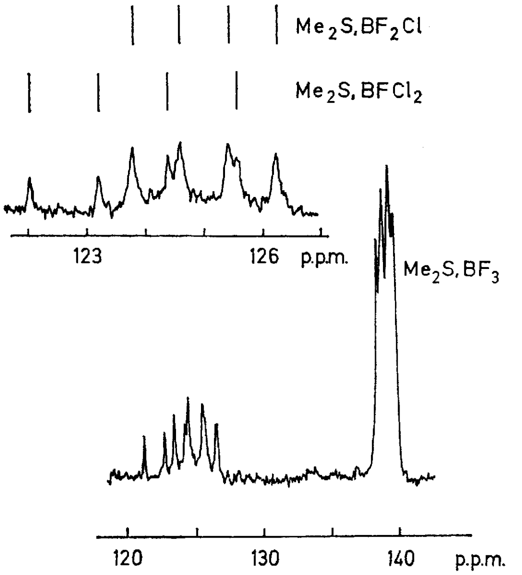

FIGURE 5 −40 °C ^{19}F Spectrum of a Me_2S–BF_3–BCl_3 solution of mole ratio 3 : 1 : 1. The two overlapping mixed-adduct quartets are clearly visible in the expanded upper trace

^{11}B Resonances of Me_2S,BF_2Cl and $Me_2S,BFCl_2$ were not detected at room temperature. This is not surprising because of the small amounts present, the complexity due to boron–fluorine coupling, and the likelihood of averaging of signals due to chemical exchange.

(c) *The* Me_2S–BF_3–BBr_3 *and* Me_2S–BF_3–BI_3 *systems.* No ^1H or ^{19}F n.m.r. evidence was obtained for mixed-halogen adducts of Me_2S in either of these systems. With an excess of Me_2S present the ^1H n.m.r. spectrum consisted of a sharp peak due to averaging of the Me_2S and Me_2S,BF_3 signals, and a 1 : 1 : 1 : 1 quartet due to Me_2S,BBr_3 or Me_2S,BI_3. Irradiation of the Me_2S,BBr_3 quartet at the ^{11}B resonance frequency collapsed it to a singlet, but no mixed-adduct singlets could be detected. In both the bromine- and iodine-containing systems, the ^{19}F spectrum consisted of only the Me_2S,BF_3 resonance unless an excess of boron trihalide was present. Since no mixed adduct could be detected when Me_2S reacted with an equilibrated mixture of BF_3 and BBr_3 known[25] to contain BF_2Br and $BFBr_2$, complexation to Me_2S ' unscrambles ' these halogens. Mixed-adduct concentrations of less than 2% of the total adduct have not been excluded by our work and might be detected by time-averaging of the ^1H or ^{19}F spectra. However K_1 and K_2 for these systems [equations (1)—(4) but with Cl replaced by Br or I] are almost certainly greater than 20.

(d) Me_2S *mixed-adduct systems not containing fluorine.* The very similar ^1H chemical shifts of the BCl_3, BBr_3, and BI_3 adducts and of their mixed adducts prevented resolution of the mixed-adduct ^1H peaks in these systems. In contrast the ^{11}B chemical shifts of the BCl_3, BBr_3, and BI_3 adducts are very different, and in each of the binary-halogen systems Me_2S–BX_3–BY_3 (X, Y = Cl, Br, or I) two additional resonances assigned to the BX_2Y and BXY_2 adducts were observed between the BX_3 and BY_3 adduct resonances. In the ternary-halogen system Me_2S–BCl_3–BBr_3–BI_3 an ^{11}B signal was detected which appeared in none of the binary-halogen systems; this is assigned to $Me_2S,BClBrI$. All the resonances were rather broad and splittings due to ^1H–^{11}B coupling were not resolved. Large amounts of the mixed-halogen adducts were present. This behaviour is similar to that observed in the tetrahalogenoborate anions[3] and in a number of different metal tetrahalide systems, in which redistribution of chlorine and bromine is near-statistical.[28]

Me_2S vs. Me_2O: *Competitive Donor Strengths.*—Differences in halogen redistribution equilibria between the Me_2S,BF_nCl_{3-n} and Me_2O,BF_nCl_{3-n} series of adducts prompted a comparison of donor strengths of Me_2S and Me_2O toward BF_2Cl and $BFCl_2$. A study of relative donor strengths utilizing relative ^1H peak areas is summarized in Table 4. BF_3 and BCl_3 are present as well since halogen redistribution cannot be avoided, so that eight different adducts are possible. However, none of the solutions studied contained significant amounts of all eight adducts. In samples A—C of Table 4, in which

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[28] D. E. H. Jones, *J.C.S. Dalton*, 1972, 567, and references therein.

there is competition for halogen between the two bases, the predominant adducts are Me_2O,BF_3 and Me_2S,BCl_3. This is consistent with previous work.[7] Me_2S Competes successfully for BCl_3 but cannot compete for $BFCl_2$, BF_2Cl, or BF_3. In contrast, Me_2O complexes to all four of the Lewis acids. There are appreciable amounts of its mixed adducts even when there is competition for halogen from Me_2S. When there is no competition between bases for halogen (sample D) the preference of Me_2O shifts to BF_2Cl because of a slight extra stability of Me_2O,BF_2Cl.[1]

Reversal of the relative base strengths of Me_2S and Me_2O occurs between the $BFCl_2$ and BCl_3 adducts. Me_2S,BCl_3 Has sufficient additional stability that the mixed adducts of Me_2S tend to ' unscramble ' to give more of this adduct. A similar but more pronounced effect in Me_2S,BBr_3 and Me_2S,BI_3 apparently accounts for the absence of mixed F,Br and F,I adducts of Me_2S. The fluorine-containing mixed adducts of Me_2S seem to Have stabilities similar to Me_2S,BF_3, whereas in the Me_2O adducts [1] the stabilities seem to increase in a regular fashion across the series BF_3, BF_2X, BFX_2, and BX_3.

TABLE 4

Competitive donor strengths of Me_2O and Me_2S toward BF_3, BF_2Cl, $BFCl_2$, and BCl_3

	Sample composition [a] (mole ratio)					Percentage of species present at equilibrium [b]				
Sample	Me_2O	Me_2S	BF_3	BCl_3		Un-complexed D	D,BF_3	D,BF_2Cl	D,BF_2Cl	D,BCl_3
A	1·0	2·2	0·4	0·4	D = Me_2O	18	10	3	1	—
					D = Me_2S	57	—	—	—	11
B	1·0	1·4	0·5	0·5	D = Me_2O	17	19	4·2	1·4	0·4
					D = Me_2S	38	—	—	—	20
C	1·0	0·9	1·0	1·0	D = Me_2O	—	54	—	—	—
					D = Me_2S	—	—	—	—	46
D	1·0	0·9	2·2	2·2	D = Me_2O	—	—	43	7	3
					D = Me_2S	—	—	—	—	47

[a] Me_2O Concentration *ca.* 0·3M in methylene dichloride solution. [b] By −90 °C ^1H n.m.r. under ^{11}B decoupling.

The Donor–Acceptor Interaction in Me_2S *Adducts: Fluorine* vs. *the Heavier Halogens*.—Halogen atoms about boron act as internal bases, donating to boron *via* a p_π–p_π mechanism. If this internal interaction is strong the planar-to-pyramidal reorganization of the molecule, which must occur on adduct formation, becomes difficult, so that the donor–acceptor interaction is weaker. Thus BF_3 is a weaker Lewis acid than BCl_3 because of the stronger boron–fluorine π bonding, some of which survives in the adduct.[21] If the donor–acceptor bond involves σ interaction only, the relative acid strengths of BF_3 and BCl_3 should remain roughly constant regardless of the donor. The relative acid strengths vary widely, however, especially with bases such as Me_2S which can be classified as soft bases; [5] BF_3 adducts of certain soft bases (*e.g.*, phosphine [29]) cannot be detected at all whereas the BCl_3 adducts are fairly stable. Interactions in addition to the conventional co-ordinate σ bond are most likely to occur in adducts of soft bases.

Young, McAchran, and Shore [7] have tentatively rejected the concept of multiple bonding in BCl_3 adducts. Instead they have suggested that the apparent order of base strength of Me_2O and Me_2S depends on the ability of the Lewis acid to form a σ bond between boron and the donor atom, and that as the Lewis acid becomes stronger the tendency to reverse the ' normal ' order of base strength increases. However they appear to give no adequate explanation of *why* this reversal takes place. Graham and Stone's discussion of experimental evidence in favour of multiple bonding in BH_3 adducts,[30] which has since been supported by calculations,[31] is more convincing. Similar reasoning can be applied to the more recent BCl_3 adduct data.

The weakness of the donor–acceptor bond in Me_2S,BF_3 indicates that Me_2S is a very weak σ donor. The increase in donor–acceptor bond strength by a factor of 3·5 in the BCl_3 adduct [10] strongly suggests a ' soft–soft ' interaction involving π as well as σ overlap. Without carrying out detailed calculations it is difficult to account for the apparent ability of BCl_3 to act as a soft acid. Overlap of heavier-halogen orbitals and donor orbitals, either directly or *via* an orbital of boron, seems plausible. The weakening of the donor–acceptor bond in Me_2S,BF_2Cl and $Me_2S,BFCl_2$ might be due to fluorine–boron back bonding interfering with the interaction between donor and heavier halogen.

Conversion of hard behaviour of a fluorine-substituted Lewis acid into soft behaviour when the substituents are heavier halogens is not limited to the boron trihalides. A similar effect has been observed in the silicon tetrahalides [32] and in the niobium and tantalum pentahalides.[33] Studies of other Lewis acid halides would be of interest

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[29] J. E. Drake and B. Rapp, *J.C.S. Dalton*, 1972, 2341.

[30] W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, 1956, **3**, 164.

[31] J.-F. Labarre and C. Leibovici, *J. Chim. phys.*, 1972, **69**, 404.

[32] G. A. Ozin, *Chem. Comm.*, 1969, 104.

[33] D. B. Copley, F. Fairbrother, and A. Thompson, *J. Chem. Soc.*, 1964, 315; F. Fairbrother, K. H. Grundy, and A. Thompson, *J. Chem. Soc.*, 1965, 765.

to determine whether similar reversals of base strength occur in a wide range of systems.

We thank the National Research Council of Canada for financial support, Dr. J. M. Miller for discussions and assistance with the instrumentation, and the Department of Chemistry, McMaster University, for the use of ^{19}F and ^{11}B n.m.r. facilities.

[2/2119 *Received, 11th September,* 1972]