Trimethylamine and 4-Methylpyridine Adducts of the Mixed Trihalides of Boron: Exchange Reactions and Nuclear Magnetic Resonance Spectra

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Trimethylamine and 4-picoline adducts of the mixed boron trihalides have been identified in solution by ^{1}H and ^{19}F n.m.r. spectroscopy. All 20 of the possible boron trihalide adducts of trimethylamine have been detected. Halogen exchange to give the mixed boron trihalide adducts occurs only when an excess of boron trihalide is present. In contrast to the free boron trihalides and oxygen-donor adducts of the boron trihalides, the slow halogen redistribution in the nitrogen-donor adducts allows isolation of individual mixed-halogen species.

ALTHOUGH the mixed boron trihalides, like the unmixed, are strong Lewis acids, adducts of the mixed boron trihalides have been reported only recently.[1-5] Already a number of methods of forming the mixed adducts have been reported, which include: (i) displacement of halogen from an adduct by reaction with a second boron trihalide;[1] (ii) halogen redistribution among adducts;[2] (iii) formation of adducts from already-equilibrated mixtures of free boron trihalides, known[6-8] to contain large amounts of the mixed boron trihalides;[1,2] (iv) reaction of mono- and di-halogenoborane adducts with a halogenating agent;[3,4] and (v) reaction of a diboron tetrafluoride adduct with hydrogen chloride.[5]

Early in our studies[1,2a] it became evident that halogen redistribution occurs much more readily in dimethyl

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

[2] (*a*) D. E. Hamilton, J. S. Hartman, and J. M. Miller, *Chem. Comm.*, 1969, 1417; (*b*) M. J. Bula, D. E. Hamilton, and J. S. Hartman, *J.C.S. Dalton*, 1972, 1405.

[3] G. E. Ryschkewitsch and W. J. Rademaker, *J. Magnetic Resonance*, 1969, **1**, 584.

[4] G. Jugie, J-P. Laussac, and J-P. Laurent, *Bull. Soc. chim. France*, 1970, 2542, 4283.

[5] B. W. Ashcroft and A. K. Holliday, *J. Chem. Soc.* (*A*), 1971, 2581.

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

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

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

ether adducts than in trimethylamine adducts. Differences in redistribution behaviour were found to be so great that adducts of nitrogen and oxygen donors have been studied separately. The absence of halogen exchange among trimethylamine adducts when no excess of Lewis acid was present suggested that, once formed, the individual mixed-halogen adducts would be isolable.[1] In this paper the isolation of the mixed boron trihalide adducts Me_3N,BF_2Br and $Me_3N,BFBr_2$ is described. The halogen exchange behaviour of the trimethylamine adducts is compared with that of a second series of nitrogen-donor adducts, those of 4-methylpyridine.

EXPERIMENTAL

Instrumentation.—^1H N.m.r. spectra were obtained on a modified Varian A-60 n.m.r. spectrometer used with a model V 6058 A homonuclear decoupler in phase-lock mode for added stability. An NMR Specialties HD-60 heteronuclear decoupler was used for ^{11}B decoupling. Pseudo-'noise' decoupling was achieved with an HP 4204 A decade oscillator (also used for calibration in conjunction with an Eldorado 224 frequency counter), to drive at 30 Hz the input to a Waveteck 141 Voltage Controlled Generator which, in turn, supplied the audio-sideband to the HD-60 decoupler. In this way, all ^{11}B nuclei were effectively decoupled over *ca.* 3 kHz of the nominal 19·2 MHz ^{11}B frequency. Triple irradiation was carried out by using the homonuclear and heteronuclear decouplers simultaneously.

^{19}F N.m.r. spectra were run on a Varian DP-60 spectrometer at 56·4 MHz.

Formation of the Me_3N,BX_2Y *Adducts.*—Separate methylene dichloride solutions of BI_3, BBr_3, BCl_3, Me_3N,BBr_3, Me_3N,BCl_3, and Me_3N,BF_3 were prepared with concentrations ranging from 1 to 10 mol %. Measured quantities of a BX_3 solution and an adduct solution were mixed in an n.m.r. tube. Vigorous BF_3 evolution occurred immediately in the case of the BF_3 adducts. The composition of the resulting mixtures could be studied at ambient temperature by ^1H and ^{19}F n.m.r. spectroscopy. Proportions of the various adducts could be altered by changing the ratio of adduct to acid, or by measuring out known quantities of the base and each acid, and then preparing the samples on a vacuum line and sealing the tubes at low temperature before allowing the components to react. ^{11}B Decoupling and variation of concentrations were used to identify the overlapping ^{11}B quartets in the ^1H spectra.

Isolation of Me_3N,BF_2Br *and* $Me_3N,BFBr_2$.—$Me_3N,BFBr_2$ was isolated from a mixture obtained by the reaction of Me_3N,BF_3 (1 g) in CH_2Cl_2 (10 ml) with neat BBr_3 (0·25 ml). The solvent and unchanged Lewis acid were pumped off after *ca.* 10 min. The crude product was shown by ^1H n.m.r. to contain 40% of $Me_3N,BFBr_2$, 50% of Me_3N,BF_2Br, and 10% of Me_3N,BF_3. Vacuum sublimation for several hours at 60 °C removed most of the more volatile BF_3 and BF_2Br adducts. The residue was then recrystallized from CH_2Cl_2, the volatile materials were again sublimed out at 60 °C, followed by a final recrystallization and heating under vacuum. The residue, obtained in low yield, was shown by ^1H and ^{19}F n.m.r. spectroscopy and by mass spectroscopy[9] to be $Me_3N,BFBr_2$. The pure material was stable for several weeks when stored under vacuum in the dark.

Me_3N,BF_2Br was isolated by the reverse of the above procedure, additional BBr_3 being added so that minimal BF_3 adduct remained. Me_3N,BF_3 (2·3 g) in CH_2Cl_2 (20 ml) was treated with neat BBr_3 (1·4 ml) for 10 min and the volatile materials were pumped away. The resulting solid was sublimed at 35 °C on to a cold finger at −78 °C in small portions, the initial portions containing BF_3 adduct being discarded. The later fractions were combined and resublimed to remove any $BFBr_2$ adduct. The resulting product showed only a trace of $Me_3N,BFBr_2$ impurity in the ^{11}B decoupled ^1H n.m.r. spectrum.

G.l.c. and t.l.c. on silica and alumina plates proved unsuccessful as a means of separating the adducts.

I.r. spectra of purified Me_3N,BF_2Br and $Me_3N,BFBr_2$ were too complex, owing to lack of symmetry, to assign by analogy with the spectra of the trimethylamine adducts of BF_3, BCl_3, and BBr_3.[10,11]

Preparation of the 4-Methylpyridine Adducts in Solution.—The reaction of a boron trihalide with CH_2Cl_2 solutions of the 4-Mepy,BX_3 adducts gave mixed adducts as was observed with trimethylamine as the base. Since the ^1H chemical shifts were slightly dependent (*ca.* 1—2 Hz for the 2- and 6-protons) upon the Lewis acid concentrations all samples were prepared and sealed off on the vacuum line, usually by using an acid : base ratio of 1·008 (±0·003) : 1·000, followed by adding a known excess of acid. ^{11}B Decoupling was required to observe the chemical shifts of the 2- and 6-protons of the mixed adducts.

RESULTS AND DISCUSSION

N.m.r. Spectra.—The n.m.r. data for the trimethylamine and 4-methylpyridine adducts is summarized in Tables 1 and 2. The ^1H spectra of each Me_3N,BX_3–BY_3

TABLE 1

N.m.r. data for trimethylamine adducts

Me_3N complexed with	δ ^1H p.p.m.[a]	$J(^1H-^{11}B)$ Hz	δ ^{19}F p.p.m.[b]	$J(^{11}B-^{19}F)$ Hz	$J(^1H-^{19}F)$ Hz
—[c]	2·20	—	—	—	—
BF_3	2·60	*	164·1	15·1	0·6
BF_2Cl	2·71	1·8	143·4	44·8	0·7
$BFCl_2$	2·83	2·1	132·6	69·5	0·7
BCl_3	2·98	2·8	—	—	—
BCl_2Br	3·05	2·9	—	—	—
$BClBr_2$	3·09	2·9	—	—	—
BBr_3	3·15	3·0	—	—	—
BF_2Br	2·75	2·1	134·0	54·2	0·8
$BFBr_2$	2·93	2·6	120·8	89·3	0·8
BF_2I	2·77	*	119·6	65·8	0·9
BFI_2	3·02	3·4	†	†	0·8
BI_3	3·35	3·5	—	—	—
BCl_2I	3·08	3·0	—	—	—
$BClI_2$	3·20	3·2	—	—	—
BBr_2I	3·21	3·2	—	—	—
$BBrI_2$	3·28	3·5	—	—	—
BFClBr	2·89	‡	126·0	78·0	0·7
BFClI	2·92	‡	—	—	0·8
BFBrI	2·97	‡	—	—	0·8
BClBrI	3·14	‡	—	—	—

[a] P.p.m. downfield of Me_4Si. [b] P.p.m. upfield of CCl_3F. [c] Free Me_3N in CH_2Cl_2.

* Not resolved. † Too dilute to observe. ‡ Decoupling required to observe.

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[9] G. F. Lanthier and J. M. Miller, *J. Chem. Soc.* (*A*), 1971, 346.

[10] R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, 1964, **20**, 1486.

[11] A. Derek, H. Claque, and A. Danti, *Spectrochim. Acta*, 1967, **23**, *A*, 2359.

system consisted of four superimposed 1 : 1 : 1 : 1 quartets due to coupling with boron-11.[1] ^{11}B Decoupling collapsed these quartets and removed ambiguities due to overlap of peaks. In adduct systems containing three boron trihalides this simplification made it possible to detect ^{1}H resonances of all four of the possible ternary-halogen adducts $Me_3N,BXYZ$. Thus for the first time all 20 of the possible boron trihalides have been detected in solution, in the form of their Me_3N adducts. When one of the halogens was fluorine the ^{11}B-decoupled ^{1}H spectra showed the additional fine splittings (0·6—0·9 Hz) expected for coupling to fluorine. These splittings, to give 1 : 1 doublets when one fluorine was present and 1 : 2 : 1 triplets when two fluorines were present, confirmed our assignment of peaks to the mixed adducts.

TABLE 2

^{1}H and ^{19}F N.m.r. parameters of the 4-methylpyridine adducts

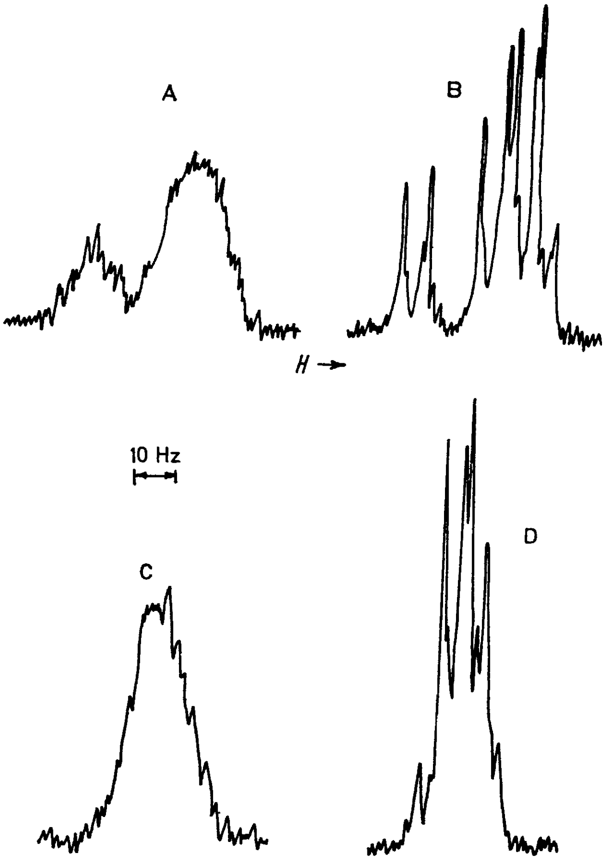
4-Mepy complexed with	^{1}H Chemical shift [a] $H_{2,6}$	$H_{3,5}$	H_{Me}	$J_{2,3}$ Hz	δ ^{19}F p.p.m.[b]	$J(^{11}B-^{19}F)$ Hz
— [c]	8·36	7·04	2·48	5·9	—	—
BF_3	8·44	7·50	2·56	6·6	142·4	11·8
BF_2Cl	8·53	—	—	6·6	125·4	38·3
$BFCl_2$	8·68	—	—	6·6	118·8	62·8
BCl_3	9·02	7·58	2·61	6·8	—	—
BCl_2Br	9·11	—	—	6·8	—	—
$BClBr_2$	9·18	—	—	6·8	—	—
BBr_3	9·28	7·60	2·62	6·9	—	—
BF_2Br	8·56	7·57	—	6·7	117·3	49·2
$BFBr_2$	8·77	7·56	—	6·7	110·5	82·2
BF_2I	8·62	—	—	6·7	†	†
BFI_2	8·93 *	—	—	6·7	†	†
BI_3	9·60	7·53	2·58	6·8	—	—
BCl_2I	9·12 *	—	—	6·8	—	—
$BClI_2$	9·32 *	—	—	6·9	—	—

[a] P.p.m. downfield of Me_4Si. [b] P.p.m. upfield of CCl_3F. [c] Free 4-methylpyridine in CH_2Cl_2.

* Poor resolution. † Too dilute.

Most of the possible boron trihalides have been detected in their uncomplexed form [6-8] but in spite of a number of attempts [8,12,13] uncomplexed BF_2I and BFI_2 have not been detected in solution although their positive ions have been observed by mass spectrometry.[14] The Me_3N adducts of these species are present, but only in small amounts. Since the small amounts were detected in initial spectra and additional reaction time did not increase them, an unfavourable equilibrium rather than a slow exchange reaction is responsible. This BF_nI_{3-n} adduct system was the only one in which the mixed adducts were not stable in solution for a period of at least several days. It is apparent that fluorine and iodine do not readily coexist on the same boron atom. The effectiveness of iodide as a leaving group may be enhanced by the presence of fluorine. Anomalous effects have also been observed in Me_2O adducts of the BF_nI_{3-n} system.[2b]

In the ^{1}H spectra of the 4-methylpyridine adducts the ring 2- and 6-protons are most sensitive to changes in the Lewis acid. This is consistent with the findings of Fratiello *et al.*[15,16] who studied the BF_3 and BCl_3 adducts. The 2,6-proton resonances appear as broad poorly resolved multiplets owing to coupling with boron and overlap of mixed-adduct peaks. On ^{11}B decoupling the individual 2,6-proton resonances are reduced to broadened doublets (Figure) similar in appearance to those of the uncomplexed base but somewhat broadened by unresolved coupling to ^{10}B. Single-peak adduct resonances were obtained by triple irradiation, *i.e.*, while observing the 2,6-proton signal the ^{11}B nuclei and the 3,5-proton signal were simultaneously irradiated.



^{1}H N.m.r. spectra of the 2,6-protons of 4-methylpyridine adducts: A, 4-Mepy–BF_3–BCl_3 system; B, 4-Mepy–BF_3–BCl_3 system, ^{11}B decoupled; C, 4-Mepy–BCl_3–BBr_3 system; and D, 4-Mepy–BCl_3–BBr_3 system, ^{11}B decoupled

Only the 2,6-proton resonances show increases in complexation shift in the order $BF_3 < BCl_3 < BBr_3 < BI_3$. The methyl and 3,5-proton complexation shifts were largest for the BBr_3 adduct rather than for the BI_3

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[12] R. E. Williams, K. E. Harmon, and J. R. Spielman; U.S. ONR Res. Report (1964), 39 (19), 22.AD603782.

[13] Unpublished work from this laboratory.

[14] M. F. Lappert, M. R. Litzow, J. B. Pedley, P. N. K. Riley, and A. Tweedale, *J. Chem. Soc.* (*A*), 1968, 3105.

[15] A. Fratiello and R. E. Schuster, *Inorg. Chem.*, 1968, **7**, 1581.

[16] A. Fratiello, R. E. Schuster, and M. Giesel, *Inorg. Chem.*, 1972, **11**, 11.

adduct. The mixed-adduct ^1H resonances of the methyl and 3,5-protons were not readily observable even with the aid of ^{11}B decoupling, because of very similar chemical shifts throughout the series. The 3,5-protons appeared as distorted doublets, and the methyl resonances as broadened singlets.

In Me_3N,BX_3 adducts the ^1H complexation shifts, which increase in the order $BF_3 < BCl_3 < BBr_3 < BI_3$, are approximately proportional to the heats of complexation.[17] A similar near-linear relationship being assumed between ^1H complexation shift and heat of complexation in the mixed adducts, the nearly-linear variation of ^1H complexation shift across each series Me_3N,BX_nY_{3-n} indicates intermediate acceptor strengths for the mixed-halogen Lewis acids, and hence that the Lewis acidity of a boron trihalide is related to a simple additivity of the halogen substituents. From the same assumption, we can now estimate the following order of acceptor power of the boron trihalides toward Me_3N: $BI_3 > BBrI_2 > BBr_2I > BClI_2 > BBr_3 > BClBrI > BClBr_2 > BCl_2I > BCl_2Br > BFI_2 > BCl_3 > BFBrI > BFBr_2 > BFClI > BFClBr > BFCl_2 > BF_2I > BF_2Br > BF_2Cl > BF_3$. The 2,6-proton complexation shifts for the incomplete series of 4-methyl pyridine adducts give an identical ordering.

The above order of acceptor power of the boron trihalides can be explained in terms of π-bonding from halogen to boron in the free boron trihalides and the survival of some residual π-bonding in the tetrahedral adducts,[18] this π-back-donation being greatest for fluorine and least for iodine in both the free boron trihalides and the tetrahedral adducts. Reorganization energy [19,20] alone cannot account for the observed order of acceptor power [17] in spite of earlier theories to the contrary.[19,20] Although some recent papers [14,21] suggest that back-donation from halogen to boron is in the order $BI_3 > BBr_3 > BCl_3 > BF_3$, Bassett and Lloyd [22] have pointed out that the stabilization energy due to this back-donation is in the opposite order, and thus is consistent with the greatest π-bonding energy being in boron–fluorine bonds.

A regular increase in the ^1H–^{11}B coupling constant as lighter halogens are replaced stepwise by heavier halogens parallels the above estimate of relative acceptor power of the boron trihalides, as for the unmixed-halogen adducts.[17] The increase in the ^1H–^{11}B coupling constant may be rationalized as the effect of differing electron density in the $N \rightarrow B$ bond on the Fermi contact term. Directly-bonded ^{11}B–^{31}P coupling constants across the donor–acceptor bond in phosphine–boranes have been correlated with donor–acceptor bond strength.[23,24] It is of interest that the small longer-range ^1H–^{19}F coupling in the fluorine-containing Me_3N adducts, which is also transmitted across the donor–acceptor bond, shows somewhat less dependence on the Lewis acid than does the ^1H–^{11}B coupling.

The ^1H 1 : 1 : 1 : 1 quartets observed for the BF_3, BF_2Cl, and BF_2Br adducts of Me_3N are partially collapsed. This is apparently a result of partial quadrupole relaxation of boron in these adducts [25] and indicates a lower symmetry about boron than in the other adducts where the quartet peaks are sharper.

^{19}F Spectra of the fluorine-containing mixed adducts of Me_3N and 4-methylpyridine were similar to those reported for the corresponding Me_2O adducts [2] and resemble those of the mixed boron trihalides [26] and the mixed tetrahalogenoborate ions.[27] Each fluorine-containing adduct gives rise to a 1 : 1 : 1 : 1 quartet owing to coupling with boron. It was not possible to resolve the small splittings due to ^1H–^{19}F coupling. The relative intensities of the ^{19}F quartets were consistent with the peak intensities observed in the ^1H spectra. In the Me_3N,BF_nI_{3-n} system where mixed-adduct concentrations are low, only one of the mixed-adduct ^{19}F quartets could be detected. When fluorine, chlorine, and bromine were present together in the system, it was possible to observe a ^{19}F quartet which was not present in any of the binary-halogen systems, and this was assigned to $Me_3N,BFClBr$. However, the BFClI adduct was present in too low concentration to be detected by ^{19}F n.m.r.

As in other mixed boron trihalide adduct series [2,27] and in the free boron trihalides,[26,28] substitution of heavier halogens for fluorine causes the remaining fluorines to shift to lower field in the ^{19}F spectrum, and the boron–fluorine coupling constant to increase in magnitude. In the adducts these changes in n.m.r. parameters are smaller than in the free trihalides, perhaps indicative of reduced π-bonding in the adducts compared with the free boron trihalides.[2]

Exchange Reactions.—Nitrogen as opposed to oxygen, sulphur, and phosphorus donors. Halogen exchange does not occur when two adducts Me_3N,BX_3 and Me_3N,BY_3 are heated together in solution. Even heating of Me_3N,BF_3 and Me_3N,BCl_3 in trichlorobenzene at 180 °C, at which temperature some decomposition occurred, did not give the mixed adducts. No exchange could be observed in the presence of an excess of Me_3N. Only when a free boron trihalide was added to a solution of an adduct was there exchange of halogen between the adducted and free trihalides to give the mixed adducts.

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[17] J. M. Miller and M. Onyszchuk, *Canad. J. Chem.*, 1964, **42**, 1518; 1966, **44**, 899, and references therein.

[18] D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, 1968, **90**, 2182.

[19] H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.*, 1956, **78**, 2173.

[20] F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, 1959, **30**, 993.

[21] J. A. S. Smith and D. A. Tong, *J. Chem. Soc.* (*A*), 1971, 173.

[22] P. J. Bassett and D. R. Lloyd, *J. Chem. Soc.* (*A*), 1971, 1551.

[23] A. H. Cowley and M. C. Damasco, *J. Amer. Chem. Soc.*, 1971, **93**, 6815.

[24] R. W. Rudolph and C. W. Schultz, *J. Amer. Chem. Soc.*, 1971, **93**, 6821.

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

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

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

[28] S. A. Fieldhouse and I. R. Peat, *J. Phys. Chem.*, 1969, **73**, 275.

The reaction occurred most readily when a heavier-halogen boron trihalide was added to a lighter-halogen adduct. Similarly, mixed adducts of 4-methylpyridine did not form on heating together the BX_3 and BY_3 (X and Y = F, Cl, and Br) adducts in solution in the absence of free boron trihalide, but the addition of a free boron trihalide to an adduct solution resulted in rapid halogen exchange to give the mixed adducts.

The unique feature of the nitrogen-donor adducts is the absence of halogen exchange under ordinary conditions, which makes possible the isolation of individual mixed-halogen adducts. Rapid halogen exchange in the free boron trihalide systems has prevented the isolation of the parent mixed boron trihalides,[6,7] and a similar rapid exchange occurs in boron trihalide adducts of a number of oxygen,[2] sulphur,[29] and phosphorus [13,30] donors. In the Me_2O adducts, exchange is especially rapid when an excess of boron trihalide is present, but also occurs when only the pure adducts are present in solution, or with an excess of Lewis base present.[2] The presence of traces of free boron trihalide is probably the critical factor in causing halogen exchange in both ether and amine adduct systems. The low heats of complexation of ethers [31] should result in sufficient dissociation of the adducts in solution that the required trace of free boron trihalide is present to initiate exchange. Amine adducts, with their much higher heats of complexation,[31] do not dissociate appreciably in solution and halogen exchange is not initiated unless an excess of boron trihalide is added to the solution. Isotope-labelling studies confirm that the donor–acceptor bond remains intact in the Me_3N adducts under conditions of rapid halogen exchange in solution,[32] and only in the case of the BI_3 adducts is there any indication of a dissociative mechanism.[32] Further studies are being carried out to elucidate the halogen exchange mechanism.

The increase in the number of potentially isolable boron trihalide adducts of a single donor from four to 20 should be of value in studies of these adducts as model compounds for Lewis acid–base interaction.

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[29] M. J. Bula and J. S. Hartman, Abstracts of the 55th Canadian Chemical Conference, Quebec City, June 5—7, 1972, p. 77.

[30] J. E. Drake, personal communication.

[31] C. T. Mortimer, 'Reaction Heats and Bond Strengths,' Pergamon Press, Oxford, 1962, ch. 6.

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