Donor–Acceptor Adducts of the Mixed Boron Trihalides

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Summary N.m.r. evidence is presented for the formation of mixed boron trihalide adducts of dimethyl ether.

THE mixed boron trihalides BX_2Y should resemble the simple trihalides in being strong Lewis acids. However, in spite of numerous recent studies of boron trihalide adducts[1] and interest in the nature of the bonding in these compounds[2] the only species reported previously which can be considered as adducts of the mixed trihalides are certain mixed tetrahalogenoborate anions.[3] The instability of the mixed boron trihalides with respect to disproportionation,[4] which prevents their isolation, has apparently deterred investigation of their adducts. We now report that methylene chloride solutions of dimethyl ether–boron trihalide adducts readily undergo halogen exchange to give adducts of the mixed boron trihalides.

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)
BF_3	3·96	158·2	11·3	*
BF_2Cl	4·04	132·6	7·2	27·0
$BFCl_2$	4·16	116·2	3·0	53·8
BCl_3	4·34		0·0	
BF_2Br	4·05	123·9	*	37·8
$BFBr_2$	4·21	103·3	*	76·1
BBr_3	4·46		14·8	
BCl_2Br	4·36		4·1	
$BClBr_2$	4·40		9·0	
$BFClBr$	4·18	109·7	*	66·5

[a] ^1H: p.p.m. to low field of tetramethylsilane; ^{19}F: p.p.m. from $CFCl_3$; ^{11}B: p.p.m. from $Me_2O{\cdot}BCl_3$. [b] from ^{19}F spectra; confirmed in some cases by ^{11}B spectra. * Inadequate resolution.

The 60 MHz ^1H n.m.r. spectrum (−90°) of a freshly prepared methylene chloride solution of dimethyl ether, boron trifluoride, and boron trichloride in the mole ratio 3 : 1 : 1 contained three peaks of similar size at δ 3·38, 3·96, and 4·34 which are assigned to Me_2O, $Me_2O{\cdot}BF_3$, and $Me_2O{\cdot}BCl_3$ respectively.[1b,c] After the sample had been allowed to stand at room temperature for several minutes the −90° spectrum contained additional peaks at δ 4·04 and 4·16 which are assigned to the adducts $Me_2O{\cdot}BF_2Cl$ and $Me_2O{\cdot}BFCl_2$, respectively. The new peaks rapidly become much larger than the peaks of the BF_3 and BCl_3 adducts. The results are in accord with a near-random distribution of fluorine and chlorine atoms among boron atoms. The intermediate complexation shifts of the mixed adducts indicate that the mixed trihalides have intermediate Lewis-acid strengths. Separate peaks for the adducts and for free ether could not be observed at room temperature because of rapid breaking and re-forming of donor–acceptor bonds.[1]

The low-temperature 56·4 MHz ^{19}F spectrum of the fresh solution consisted of a single peak arising from $Me_2O{\cdot}BF_3$.[1c] Reaction at room temperature resulted in the appearance of two 1 : 1 : 1 : 1 quartets at lower field and a decrease in the intensity of the initial peak. This is in accord with the formation of two new species containing boron–fluorine bonds. The peaks are assigned to $Me_2O{\cdot}BF_2Cl$ and $Me_2O{\cdot}BFCl_2$ as in the Table. Comparison of ^{19}F relative peak areas with ^1H relative peak areas supports our assignment. Samples containing an excess of Lewis acid gave additional low-temperature ^{19}F peaks assigned[5] to uncomplexed BF_3 and BF_2Cl.

Mixed trihalide adducts were also detected by n.m.r. in the Me_2O–BF_3–BBr_3, Me_2O–BCl_3–BBr_3, and Me_2O–BF_3–BCl_3–BBr_3 systems in methylene chloride. Chemical shifts and coupling constants are given in the Table. In the Me_2O–BCl_3–BBr_3 system ^{11}B spectra at 11·43 MHz provided the best evidence for the existence of the mixed adducts. In the presence of an excess of Lewis acid the relative intensities of the peaks show that the chlorines and bromines are very nearly randomly distributed among the boron atoms. However, in the presence of an excess of ether, the bromine-containing adducts are present in diminished amounts. The n.m.r. peaks of the tribromide and dibromide adducts vanish almost entirely after reaction for several minutes at room temperature. This is a result of the high reactivity of the boron–bromine bond with dimethyl ether.[6] The largest of the new ^1H peaks, which appears at δ 2·77 during the reaction, is assigned to methyl bromide. The presence of an excess of Lewis acid appears to increase the rate of halogen scrambling in addition to stabilizing the adducts.

Trends in ^{19}F chemical shift and in boron–fluorine coupling constant in the adducts resemble the trends previously observed[5] in the free mixed trihalides. The ^{19}F chemical shift pattern in the free trihalides can be satisfactorily explained in terms of π-bonding.[7] The similar trend in the adducts indicates that a large fraction of the π-bonding survives in the adducts. Drago and his co-workers have recently reached this conclusion in a study of the energetics of adduct formation.[2]

Preliminary studies show that the mixed adducts of a number of other weak Lewis bases form readily under similar conditions, but further rapid reactions occur in some cases. We have more recently observed halogen scrambling in the much more stable trimethylamine–boron trihalide adducts; this system will be described elsewhere.[8]

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