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Difluoroboron Cations from Benzoate Ester–mixed Boron Trihalide Adducts

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As part of our current study of mixed boron trihalide adducts [1] we have studied the adducts of a number of carboxylic esters [2]. We now report that mixed boron trihalide adducts of benzoate esters undergo a reaction to give $(ester)_2BF_2^+$ ions.

Benzoate ester/BF_3/BCl_3 solutions in $CDCl_3$ or in CH_2Cl_2 give low temperature ^{19}F spectra as shown in Fig. 1A. The major peaks are assigned to (ester)·BF_nCl_{3-n} (n = 1–3) adducts as in Table I, consistent with chemical shifts of mixed boron trihalide adducts of other oxygen donors [2–4], and confirmed by the application of 'pairwise interaction' NMR parameters [5]. Electron-donating and withdrawing *para*-substituents have only small effects (~1.5 ppm) on the ^{19}F chemical shifts of specific adducts, much less than the effects of changing the halogens. This is in keeping with the general observation that local diamagnetic effects are less important than other effects in determining ^{19}F chemical shifts [6].

These systems give an additional ^{19}F resonance in the −135 to −139 ppm region that has no analogue in acetate ester–mixed boron trihalide adduct systems [2]. The chemical shifts are consistent with the few known oxygen-donor $D_2BF_2^+$ ions [4, 7] and chemical shift variations with the donor molecule's *para*-substituent are roughly twice as great as for the $D{\cdot}BF_nCl_{3-n}$ resonances (3.1 ppm *vs.* approximately 1.5 ppm), suggesting a species involving two donor molecules. Especially suggestive is the observation of a resonance of identical chemical shift in the corresponding ester/BF_3/BBr_3 system, indicating that the heavy halogen is not incorporated.

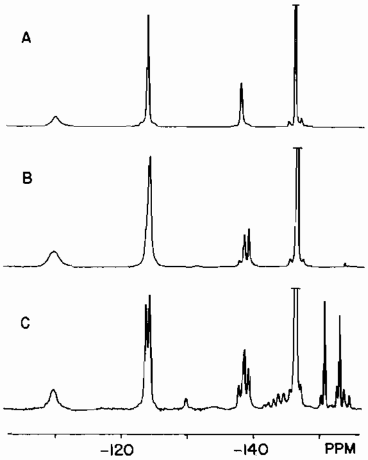

Fig. 1. −48 °C ^{19}F NMR spectra of benzoate ester/BF_3/BCl_3 systems in $CDCl_3$; 3:1:1 mol ratio. A, ester is methyl benzoate alone; B and C, esters are methyl benzoate and methyl *para*-methoxybenzoate in a 1:1 molar ratio (B) and a 1.53:1 molar ratio (C). C also shows peaks due to decomposition products which have not yet been investigated.

Confirmation that $D_2BF_2^+$ cations are present comes from samples containing more than one benzoate ester. These give low-temperature ^{19}F spectra consisting of a superposition of the separate adduct spectra, but with an additional peak between the $D_2BF_2^+$ peaks of the two esters (Fig. 1B, C), assigned to the mixed-donor cation $DD'{\cdot}BF_2^+$. This peak can be detected in all cases in which the chemical shift separation of the $D_2BF_2^+$ resonances is sufficient (Table II). Incorporation of methyl *para*-methoxybenzoate in the cation is favoured due to its enhanced electron-donating ability (Fig. 1B and 1C). Chemical exchange is sufficiently rapid that only a single $D_2BF_2^+$ resonance can be observed at ambient temperature. Chemical exchange also affects the other adduct resonances; the $D{\cdot}BF_2Cl$ and $D'{\cdot}BF_2Cl$ resonances are

TABLE I. ^{19}F Chemical Shifts of Methyl Benzoate Adducts.[a]

Benzoate *para* Substituent X	CH_3O	H	F	NO_2
Hammett σ_p of X[b]	−0.27	0.00	+0.06	+0.78
$D{\cdot}BF_3$	−146.4	−145.7	−145.7	−144.5
$D{\cdot}BF_2Cl$	−122.7	−122.1	−122.2	−121.3
$D{\cdot}BFCl_2$	−107.4	−107.4	−105.3	−106.9
$D_2BF_2^+$	−138.6	−137.1	−137.0	−135.4

[a] Ppm from internal $CFCl_3$, $CDCl_3$ solution, −48 °C. [b] Reference 9.

TABLE II. ^{19}F Chemical Shifts of $DD'BF_2^+$ Cations.[a]

Methylbenzoate *para*-substituents		Chemical Shift
D	D'	
H	CH_3O	−137.8
H	NO_2	−136.4
CH_3O	F	−137.8
CH_3O	NO_2	−137.0
F	NO_2	−136.1

[a] Ppm from internal $CFCl_3$, $CDCl_3$ solution, −48 °C.

sometimes resolved at −48° (Fig. 1C) but usually only an averaged resonance is observed (Fig. 1B).

The ionic species are not observed in the ester/BF_3 systems in the absence of a heavier-halogen boron trihalide. This is consistent with the reaction

$$\text{ester} + \text{ester}\cdot BF_2X \rightleftharpoons (\text{ester})_2BF_2^+ + X^- \qquad (1)$$

i.e., a mixed boron trihalide adduct must be present initially. Furthermore, the $D_2BF_2^+$ peak is small when X = Cl but may be large when X = Br, consistent with Br^- being a better leaving group.

Displacement of a heavy halide ion from $D\cdot BH_2X$ adducts by neutral donors is an effective method for preparing $D_2BH_2^+$ cations [8]. We are investigating the scope of the analogous reaction (eqn. 1) for the preparation of $D_2BF_2^+$ cations.

Experimental

Solutions and reagents were handled in a nitrogen-filled dry box. NMR samples were made up on a high-vacuum system by condensing known amounts of the purified boron trihalides onto 0.5 *M* solutions of the esters in $CDCl_3$. The samples were sealed under high vacuum, warmed slowly to −50 °C, and mixed by repeated inversion at this temperature.

^{19}F NMR spectra were obtained on a Bruker WP-60 Fourier Transform NMR spectrometer operating at 56.4 MHz. Varying numbers of 30° pulses up to 2,000 were accumulated. The transformed spectra contained 4K data points. Chemical shifts were determined from an internal hexafluorobenzene secondary standard (−161.4 ppm from $CFCl_3$ at −48 °C in $CDCl_3$, temperature-dependent) and converted to ppm to low field of $CFCl_3$.

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