# Bis(tertiary-amine)difluoroboron Cations

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Tertiary amines of low steric hindrance readily displace bromide ion from bromodifluoroborane adducts of tertiary amines, $D{\cdot}BF_2Br$ (D = donor), to form bis(tertiary-amine)difluoroboron cations, $D_2BF_2^+$ and $DD'BF_2^+$.

Although tetrahedral four-co-ordinate boron cations are exceptionally stable and many have been prepared,[1] few difluoroboron cations are known. Certain chelating ligands LL form $(LL)BF_2^+{\cdot}BF_4^-$ directly on reaction with $BF_3$,[2] but others do not.[3] Tetramethylurea·$BF_3$ and hexamethylphosphoramide·$BF_3$ are in equilibrium in solution with small amounts of the ionic form of the adduct, $D_2BF_2^+{\cdot}BF_4^-$,[4] (where D represents the donor ligand) but this behaviour is exceptional for $BF_3$ adducts. Hydrogen substitution in already formed $D_2BH_2^+$ cations gives a range of substituted boron cations, but elemental fluorine is required to give difluoroboron cations by this route.[5] The most widely used method for boron cation formation, halide ion displacement from $D{\cdot}BH_2X$ or $D{\cdot}BX_3$ by a neutral donor,[5,6] has not been explored as a route to difluoroboron cations because of the unsuitability of $F^-$ as a leaving group from $D{\cdot}BF_3$ and the unavailability until recently of the mixed boron trihalide adducts $D{\cdot}BF_2X$.[7] We now report that the readily available (tertiary-amine)·$BF_2Br$ adducts[7,8] give good yields of $D_2BF_2^+$ and $DD'BF_2^+$ under mild conditions, provided that the displacing amine D' is of low steric hindrance; equation (1).

$$D{\cdot}BF_2Br + D' \longrightarrow DD'BF_2^+ + Br^- \qquad (1)$$

Quinuclidine (Q; 1-azabicyclo[2.2.2]octane) is particularly favourable in this reaction. 128.4 MHz $^{11}B$ N.m.r. spectra of $CDCl_3$ solutions of $(Q)BF_nBr_{3-n}$ ($n$ = 0—3) adducts, formed by equilibrating $(Q)BF_3$ wth $BBr_3$ and quenching the resulting uncomplexed $BF_nBr_{3-n}$ with excess of quinuclidine,[8] show initially the multiplets of all four $(Q)BF_nBr_{3-n}$ adducts. On standing (25 °C, 18 h) the $(Q)BF_2Br$ 1:2:1 triplet at 3.6 p.p.m.[8] disappears and is replaced by a new triplet at 1.4 p.p.m. assigned to $(Q)_2BF_2^+$, while the multiplets of the other adducts are unaffected. In the $^{19}F$ spectrum a new 1:1:1:1 quartet at −161.5 p.p.m. replaces the $(Q)BF_2Br$ quartet at −133.0 p.p.m. The $(Q)_2BF_2^+$ species can be precipitated from $CHCl_3$ solution as the bromide and is stable in aqueous solution. Fast atom bombardment mass spectrometry[9] of the precipitate, carried out in a glycerol matrix, gives peaks at $m/z$ 271 [100%; $(Q)_2BF_2^+$], 160 [57.3; $(Q)BF_2^+$], 112 [17.1; $(Q)H^+$], and 111 [12.9; $(Q)^+$] and no other major peaks.

Table 1 gives n.m.r. parameters of the $D_2BF_2^+$ ions and indicates variations in their rates of formation. Low amine steric hindrance greatly favours the reaction. No correlation of reaction rate with base strength is evident. Mixed-donor cations $DD'BF_2^+$ have n.m.r. parameters intermediate

**Table 1.** N.m.r. parameters and formation times of bis(amine)difluoroboron cations.

| D = D' | | $\delta$ $^{19}F$ /p.p.m.[a] | $J(^{11}B-^{19}F)$ /Hz | $\delta$ $^{11}B$ /p.p.m.[b] | Formation time[c] | Amine $pK_b$ |
|---|---|---|---|---|---|---|
| Pyridine | | −155.6 | 22.9 | 1.8 | 20 min (25 °C) | 8.77 |
| Q[f] | | −161.5 | 39.5 | 1.4 | 24 h (25 °C) | 2.9 |
| $Me_3N$ | | −165.4 | 36.2 | 1.9 | 36 h (25 °C) | 4.24 |
| $Me_2NEt$ | | −158.9 | 39.3 | 2.3 | >24 h (60 °C) | 4.01 |
| $MeNEt_2$ | | | | | [d] | 3.71 |
| $Et_3N$ | | | | | [d] | 3.35 |
| D | D | | | | | |
| Pyridine | Q | −161.3 | 28.6 | 1.6 | [e] | |
| $Me_3N$ | Q | −163.7 | 38.1 | 1.5 | [e] | |
| $Me_2NEt$ | Q | −159.9 | 38.8 | 1.8 | [e] | |
| $MeNEt_2$ | Q | −155.2 | 40.5 | 1.9 | [e] | |
| $Et_3N$ | Q | −148.4 | 43.0 | 2.2 | [e] | |

[a] Relative to $CFCl_3$. [b] Relative to $Et_2O{\cdot}BF_3$. [c] Approximate time for completion of reaction (1) ($CDCl_3$ solution; 0.5 M in total adducts and in uncomplexed amine). [d] No cation detectable even after 24 h at 80 °C. [e] D' for D exchange interferes when D ≠ D'. [f] Q = quinuclidine.

between those of $D_2BF_2^+$ and $D'_2BF_2^+$, and are formed only when the attacking amine D′ has low steric hindrance ($Me_2NEt$ and above, in Table 1). Steric requirements for the already-attached amine in $D{\cdot}BF_2Br$ are much less stringent, and species such as $(Et_3N)(Q)BF_2^+$ are readily prepared. Competing reactions can, however, interfere. These include Cl, Br exchange with $CDCl_3$ solvent, donor exchange (D for D′ in the adducts and in the cation), and adduct decomposition.

Tertiary-amine adducts $D{\cdot}BFBr_2$, in striking contrast to $D{\cdot}BF_2Br$, are totally unreactive toward bromide displacement under our conditions. This is reminiscent of the mixed tetrahaloborate anions $BF_nX_{4-n}^-$ ($n$ = 0—4), in which the $BF_3X^-$ ion, with one heavy halogen, is by far the most susceptible to exchange reactions.[10]

Relative rates for $D_2BF_2^+$ formation are $D{\cdot}BF_2I \gg D{\cdot}BF_2Br \gg D{\cdot}BF_2Cl$, and otherwise-inaccessible cations such as $(PhNMe_2)_2BF_2^+$ can be formed in small amounts by iodide displacement from $D{\cdot}BF_2I$. However, halogen-redistribution equilibria are so unfavourable to $D{\cdot}BF_2I$ formation[8] that these adducts will have limited usefulness as precursors. $(Q)BF_2Cl$ reacts very slowly (only 10% reaction after 40 days at 48 °C) compared to $(Q)BF_2Br$.

The dependence of $D_2BF_2^+$ formation on amine steric hindrance is consistent with displacement reactions of $D{\cdot}BH_2X$ adducts[5] and with symmetrical *vs.* unsymmetrical cleavage of $B_2H_6$ on adduct formation, giving $D{\cdot}BH_3$ or $D_2BH_2^+{\cdot}BH_4^-$.[11] As in our work, bulky donors do not allow cation formation. Previously puzzling scattered observations of $D_2BF_2^+$ formation from $BF_2Cl$ adducts of tetramethylurea[4] and of benzoate esters[12] now fall into place: these donors have far lower steric hindrance than amines or ethers, and even $Cl^-$ can be displaced readily. In keeping with the dominant effect of donor steric hindrance, we find that $BF_2Cl$ adducts of low-steric-hindrance nitrogen donors [amidines $RC(=NR')NR''_2$, and imines $R_2C=NR'$] also lose $Cl^-$ easily to form $D_2BF_2^+$.[13]

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