Generation of reactive borenium ions in the 2,3-benzazaborolidine series

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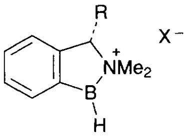
Borenium ions 1, generated by hydride abstraction from 3 using trityl salts, are exceptionally potent electrophiles, as evidenced by fluoride abstraction from tetrafluoroborate and even from tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate.

Cationic, trivalent boron complexes (borenium ions) have been characterized in the solid state by Narula and Nöth using X-ray crystallography.[1a] Certain borenium ions also exist in solution, but few have been directly observed because of their exceptional Lewis acidity and the resulting counterion limitations.[1–3] Recently, Hayashi *et al.* reported that related chiral, cationic oxazaborinanes generated from the neutral (tetravalent boron) bromide adducts are exceptionally reactive catalysts for enantioselective Diels–Alder reactions.[3a] Our own study of chiral borenium ions was stimulated by the Nöth[1b] and Ryschkewitsch[2] precedents, and began with efforts designed to probe stability and counterion issues for highly electrophilic species such as **1a** and **b**.

The arylboronic anhydrides **2a**,**b**[4] were reduced with LiAlH$_4$[5] to give 2,3-benzazaborolidines **3a**[†] (71%) and **3b**[†] (81%). Treatment of **3b** with triphenylmethyl (trityl) tetrafluoroborate[6] in a solution containing pyridine (1.15 equiv.) in acetonitrile at *ca.* −40 °C followed by warming to room temperature afforded a mixture of diastereomeric adducts **4** and **5** (*ca.* 2 : 1 ratio **4** : **5**, 66% isolated of a diethyl ether-insoluble solid) and crystallization from water afforded the pure major diastereomer **4**[‡] (Fig. 1). The diethyl ether extract from the above experiment contained triphenylmethane, the expected byproduct of hydride abstraction that must accompany the generation of **1b**.[6] In addition, soluble B–F species were present according to ^{19}F NMR spectral assay. The presence of **6b**[§] (^{19}F NMR: δ −158 and −160 *vs.* CFCl$_3$) was confirmed by comparison with authentic material prepared from **3b** and methanolic KHF$_2$[7] (66% of **6b** isolated). Additional ^{19}F NMR signals at δ −189 and −197 were tentatively assigned to the monofluoro adduct diastereomer **7b**. This evidence indicates that **1b** is trapped by fluoride transfer from BF$_4^-$ within the ion pair in competition with trapping by pyridine.



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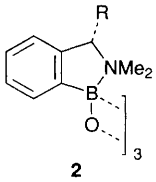

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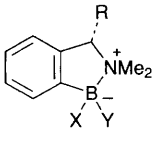
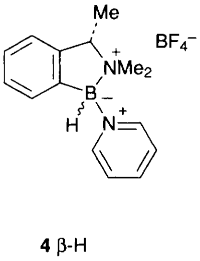
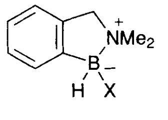
a R = H
b R = Me



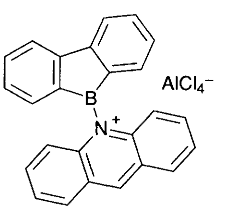
3 X = Y = H
6 X = Y = F
7 X = H, Y = F



4 β-H
5 α-H



8 X = 
9 X = Cl



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We hoped that a non-nucleophilic tetraarylborate counterion might allow direct observation of **1b**. The hydride abstraction was therefore performed using trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[8] in CD$_2$Cl$_2$ at −78 °C. Incredibly, this produced the characteristic ^{1}H and ^{19}F NMR signature of **6b** as the only identifiable product at −78 °C. The CF$_3$ groups of the tetraarylborate anion are the only possible sources of fluoride in this experiment. We could find no precedent for fluoride abstraction from an aryl-CF$_3$ group in borenium ion chemistry,[1b] but there is a silicon cation analogy.[8] This result confirms that **1b** is a highly potent Lewis acid, perhaps approaching the notoriously electrophilic silylium (silicenium) cations in reactivity.[8,9] The low temperature ^{11}B NMR spectrum contained no evidence that **1b** had survived, and extensive decomposition was indicated by complex ^{1}H as well as ^{11}B NMR signals.

To facilitate interpretation of ^{1}H NMR spectra, further attempts to detect borenium ion intermediates were made starting from **3a** (achiral series). Treatment of **3a** with trityl tetrakis(pentafluorophenyl)borate[10] in CH$_2$Cl$_2$ at −78 °C was monitored by ^{11}B NMR. The resulting spectrum contained a singlet for the (C$_6$F$_5$)$_4$B$^-$ anion (δ −17.22) and unidentified broad signals from δ *ca.* 5–15 (tetravalent boron). In addition, a new absorption in the trivalent boron region at δ 38.7 (broad singlet, width at half-height 460 Hz) appeared and increased with time and careful warming. The intensity of two singlets in the ^{1}H NMR spectrum [δ 4.67 (benzylic CH$_2$) and 3.24 (*N*-methyl)] also increased in proportion to the δ 38.7 boron signal, but both sets of signals disappeared when the sample was warmed to room temperature.

Assignment of the δ 38.7 boron signal to **1a** is supported by low temperature quenching experiments. When the −50 °C solution was treated with pyridine, a doublet appeared in the tetravalent boron region [δ 7.92 (*J* 119 Hz)] corresponding to the formation of the pyridinium adduct **8**. Curiously, the

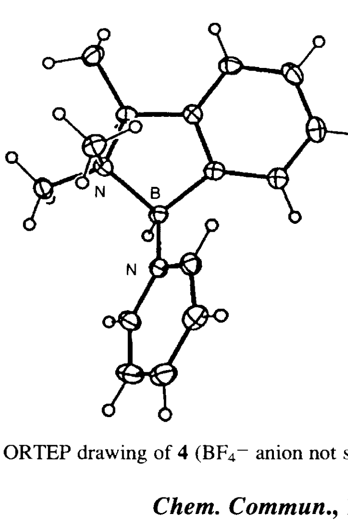

Fig. 1 ORTEP drawing of **4** (BF$_4^-$ anion not shown)

experiment also produced a small triplet at δ − 1.64 ($J_{\mathrm{B-H}}$ 103 Hz), identical in chemical shift with **3a**. This signal had not been present before the pyridine was added. The asignment was confirmed by chromatographic isolation of **3a** and by ^{11}B and ^{1}H NMR chemical shift comparisons. Furthermore, assay of the recovered **3a** by mass spectroscopy revealed the presence of *ca.* 15% deuterium label that could only have originated from the CD$_2$Cl$_2$ solvent. We cannot explain this finding, except to note that it suggests unusual avenues for destruction of **1a** and reflects the extraordinary reactivity of the borenium ion. The result also requires partial decomposition of the solvent, CD$_2$Cl$_2$.

As already mentioned, warming the solution of **1a** eventually resulted in the disappearance of the δ 38.7 boron signal. However, complex tetravalent boron absorptions were still present at room temperature. To eliminate the possibility that these signals are related to **9** (conceivably formed from **1a** by incorporation of chloride from CD$_2$Cl$_2$), authentic **9** was generated *in situ* using trityl chloride as the reagent for hydride abstraction from **3a** (−50 °C to room temp.). In this case, a doublet ($J_{\mathrm{B-H}}$ 127 Hz) appeared in the ^{11}B NMR spectrum at δ 5.27, consistent with **9**, and the ^{1}H NMR spectrum contained a characteristic AB quartet for the diastereotopic benzylic CH$_2$ protons at δ 4.13 (J_{AB} 13.5 Hz). These signals were not detected in the experiment that produced the borenium ion **1a**.

Based on the above evidence, **1b** and **1a** are formed as reactive intermediates in the hydride abstractions as expected. However, other reaction pathways compete despite the precautions taken to minimize the nucleophilicity of the counterions. It is clear that **1a** and **1b** are exceptionally reactive electrophiles.

Among the several borenium ion structures characterized by X-ray crystallography, **10**[1a] is the closest analogue to **1**. This substance was not fully characterized in solution because it equilibrates with other boron species. The solution evidence is stronger in the case of borenium ions containing one or two trivalent nitrogen substituents at boron.[1b] Nitrogen electron pairs help compensate for the electron deficiency of sextet boron, but even then, the borenium ions tend to be stable only if additional sources of electron density are present. Hindered pyridine derivatives bound to boron *via* the sp^2 nitrogen electron pair provide the necessary stabilization (apparently by a π-delocalization effect) in nearly all previous examples where borenium ion ^{11}B NMR shifts have been reported.[1b] The absence of analogous stabilization in **1a,b** may be one reason why these cations are so reactive. Further studies of borenium ions are under way to define suitable moderating substituents that will allow the decisive characterization of cationic, trivalent boron in a chiral environment.

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Footnotes

† *Selected data* for **3a**: mp 110 °C (hexane–benzene); ^{1}H NMR (300 MHz;): δ 7.32 (1 H, d, *J* 7.2 Hz), 7.16–7.03 (3 H, m), 4.03 (2 H, s), 2.73 (6 H, s); ^{11}B NMR (160 MHz; CDCl$_3$; BF$_3$·OEt$_2$): δ −1.67 (t, *J* 101 Hz). For **3b**: mp 83–4 °C (sublimed); ^{1}H NMR (300 MHz; CDCl$_3$): δ 7.42 (1 H, d, *J* 7.0 Hz), 7.20 (1 H, dd, *J* 7.4, 7.0 Hz), 7.12 (1 H, dd, *J* 7.4, 7.0 Hz), 7.05 (1 H, d, *J* 7.0 Hz), 4.16 (1 H, q, *J* 7.0 Hz), 3.35–2.10 (2 H, brs), 2.79 (3 H, s), 2.39 (3 H, s), 1.48 (3 H, d, *J* 7.0 Hz); ^{11}B NMR (160 MHz; CDCl$_3$; BF$_3$·OEt$_2$): δ −2.09 (dd, *J* 102, 102 Hz).

‡ *Selected data* for **4**: mp 187–8 °C (Calc: C, 55.26; H, 6.20. Found: C, 54.97; H, 6.07%); ν_{max}(KBr)/cm^{-1} 2448 (B–H), 1630 (C=C), 1057 (B–F); ^{1}H NMR (300 MHz; CD$_3$CN): δ 8.72 (2 H, dd, *J* 6.8, 1.5 Hz), 8.52 (1 H, tt, *J* 7.9, 1.5 Hz), 7.98 (2 H, dd, *J* 7.9, 6.8 Hz), 7.43–7.33 (2 H, m), 7.31–7.24 (2 H, m), 4.51 (1 H, q, *J* 6.9 Hz), 2.90 (3 H, s), 2.14 (3 H, s), 1.59 (3 H, d, *J* 6.9 Hz). The B–H signal was not observed due to quadrupolar line broadening.

Crystal data: Space group $P2_12_12_1$, T = 113(2) K, a = 9.1349(14), b = 11.0876(10), c = 15.511(2) Å, α = β = λ = 90°. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/297.

§ *Selected data* for **6b**: mp 68–69 °C (sublimed); ^{1}H NMR (300 MHz; CDCl$_3$): δ 7.59–7.56 (1 H, m), 7.31–7.28 (2 H, m), 7.11–7.07 (1 H, m), 4.25 (1 H, q, *J* 7.0 Hz), 2.67 (3 H, d, $^{4}J_{\mathrm{HF}}$ 1.9 Hz) 2.34 (3 H, d, $^{4}J_{\mathrm{HF}}$ 1.8 Hz), 1.51 (3 H, d, *J* 7.0 Hz); ^{11}B NMR (160 MHz; CD$_2$Cl$_2$; BF$_3$·OEt$_2$): δ 7.7 (dd, *J* 59, 59 Hz); ^{19}F NMR (282 MHz; CDCl$_3$; CFCl$_3$): δ −158 (m), −160 (m).

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