Representative synthesis and synthetic notes

Preparation of [(1-methylimidazole)(trimethylamine)BH_2]$^+$ I^-

A 500 mL flask was charged with a magnetic stirbar purged with dry nitrogen.[1] While maintaining the nitrogen atmosphere, 250 mL of anhydrous benzene was added. To the benzene was added 14.60 g (0.20 mol) of trimethylamine-borane complex (purchased from Aldrich Chemical Co.). Once the complex had completely dissolved, 23.11 g (0.18 gram atom; 0.091 mol elemental iodine) of I_2 was added in small portions over a ten-minute period of time, all the while maintaining a slow purge of nitrogen gas through the system. After stirring for an additional 30 min, the solution remained slightly red-brown.[2] To the stirred solution of Me_3N-BH_2I thus prepared was then added in one portion 17.47 g (0.21 mol) 1-methylimidazole.[3,4] The solution immediate became colorless, and within a few minutes a white solid had begun to precipitate.[5,6] The precipitation was accompanied by a moderate exotherm, which was controlled by cooling in an icebath.[7] After cooling for 30 min, the solid was separated by suction filtration in air.[8] The solid was washed with small portions of benzene and ether then dried in vacuo. Yield: 43.3g (unoptimized; 85% based upon I).

Notes

1. Repeat preparations were run variously in air or under nitrogen, with yields in the nitrogen reactions usually being slightly higher.
2. In repeat reactions the solution was at this stage colored at times and colorless on other occasions. No consistent variation in yield or product purity appears to be manifest as function of this phenomenon.
3. Extensive subsequent experimentation determined that the use of an excess of alkyl imidazole (heterocycle) was unnecessary and in some cases undesirable, leading to difficulties in isolating pure products. This is especially the case where the imidazole is relatively lipophilic (e.g., 1-butylimidazole or 1-decyl-2-methylimidazole, where the boronium salts formed remain partially soluble in the benzene phase rather than fully precipitating as in the case of the present example. In these cases, removal of excess imidazole from the product boronium salts may be accomplished but only after exhaustive extraction or tedious chromatographic processes. It should also be noted that symmetrical bis(tertiary amine)BH_2^+ and bis(heterocycle)BH_2^+ compounds may be prepared using similar approaches.
4. Other heterocycles or substituted imidazoles successfully used to date include (but are not limited to) 3- and 4-methyl thiazole, 3-butyl pyridine, 3-picoline, 4-picoline, butyl nicotinate, 1,2-dimethyl imidazole, and miconazole. Other amine-boranes successfully used include (but are not limited to) tributylamine-borane, dimethyldodecylamine-borane and tropane-borane.
5. Repeat syntheses of this material, as well as syntheses of other boronium ions were sometimes characterized by a completely colorless solution at this stage.
6. The iodide salts do not appear to be hygroscopic or air sensitive.

7. In syntheses where only one equivalent of heterocycle was used (see note 3), the exotherm was generally less marked to non-existant. In these cases, stirring was continued for longer periods of time (1-12 h) prior to work-up.
8. In procedures involving more lipophilic heterocycles (e.g., 1-butylimidazole) the iodide salt usually separates as a colorless (dense) liquid phase which is separated from the organic phase by decantation. This phase is subsequently washed with additional portions of benzene then ether before all volatiles are removed using rotary evaporation then a mechanical vacuum pump. A number of the iodide salts remain as supercooled liquids for prolonged periods, though we have yet to find one which does not eventually crystallize.

Preparation of [(1-methylimidazole)(trimethylamine)BH_2]$^+$ Tf_2N^-

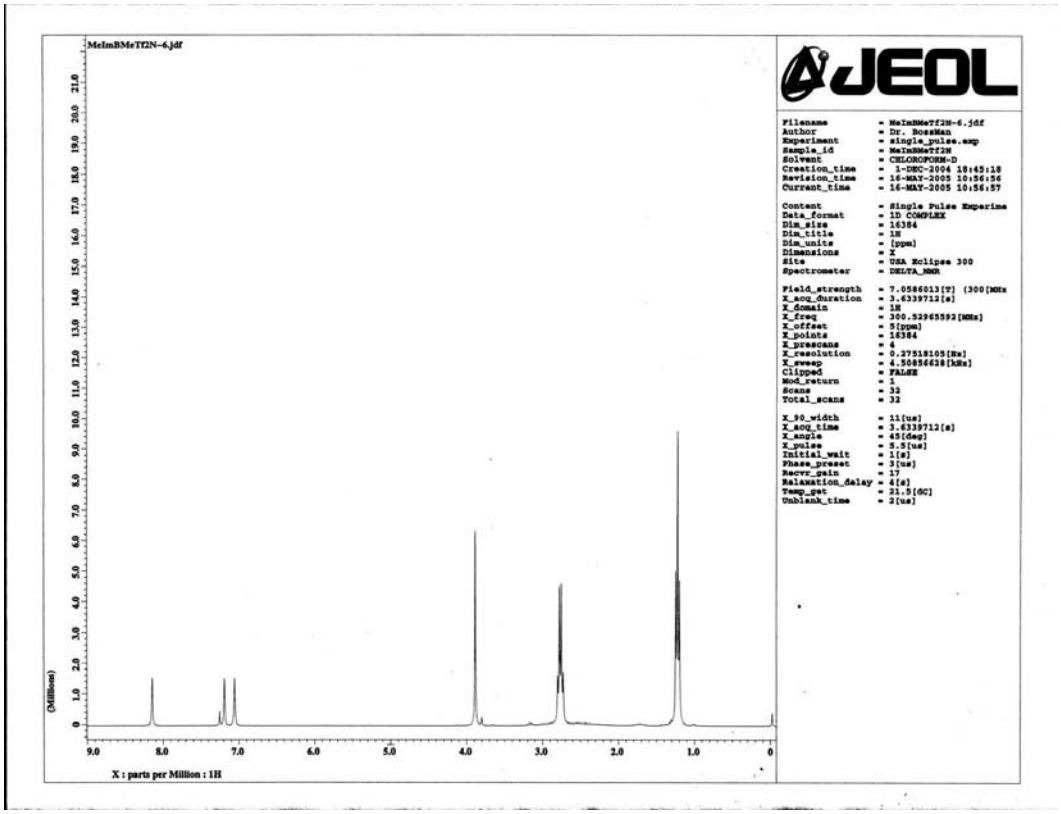
In a 100 mL Erlenmeyer flask charged with a magnetic stirbar, 2.54 g of [(1-methylimidazole)(trimethylamine)BH_2]$^+$ I^- was dissolved in 25 mL of deionized water. To the stirred solution was added in one portion 3.43 g of lithium bis(trifluoromethanesulfonyl)amide, the dissolution of which into the water was accompanied by a near-simultaneous separation from the water of a dense, colorless, second liquid phase. To this two-phase system was added 20 mL of chloroform, which admixed with the denser (boronium salt) phase. The water and organic phases were separated and the chloroform phase dried with a small quantity of anhydrous magnesium sulfate. The latter was then removed by filtration and the chloroform evaporated under reduced pressure. It remained as a stable supercooled phase for several days before slowly crystallizing into a colorless mass (mp = 60.2^{o}C by DSC, scan rate 10^{o}C/min). Bis(trifyl)amide salts of other boronium cations are prepared similarly, and all to date have proven to be persistent room-temperature ionic liquids. The corresponding PF_6^- and BF_4^- salts of a number of these cations have also been prepared, several of them also being RTIL, although all are visibly more viscous than same-cation salts of the Tf_2N^- anion.

<u>Colorless and hydrophobic nature of the boronium RTILs</u>

The two-phase system in the photo below contains the boronium RTIL **2** from the present paper, [(1-methylimidazole)(triethylamine)BH_2]$^+$ Tf_2N^-. The IL is the lower layer, water is the upper phase. Note both the hydrophobic character and the completely colorless nature of the RTIL.

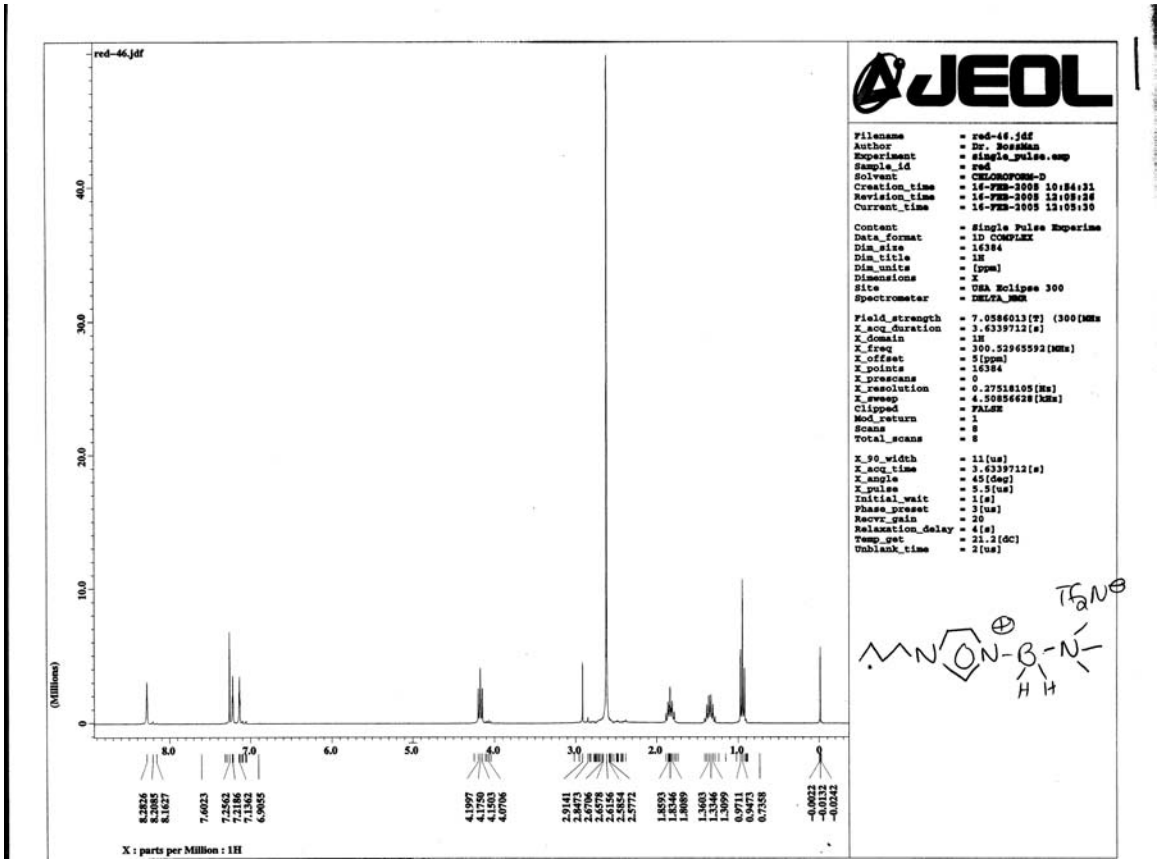
Representative NMR Spectrum of an as-isolated boronium IL

The ^{1}H-NMR spectrum shown is of an as-isolated (non-chromatographed/non-high vacuum treated) sample of boronium IL **2** - [(1-methylimidazole) (triethylamine)BH_2]$^{+}$ Tf_2N^{-}. Peak assignments (left to right) are: imidazole C^2-H; imidazole C^4-H or C^5-H; imidazole C^5-H or C^4-H; imidazole N-methyl; triethylamine CH_2 groups; triethylamine CH_3 groups. Though not shown in this spectrum, integrated intensities are 1:1:1:3:6:9. The small peak at 7.26 is residual $CHCl_3$ in the NMR solvent; Trace impurities of 1-methyl imidazole and diethyl ether are also present, these materials being subsequently removed under high vacuum. Note the quite high level of purity achieved in the crude reaction product. The barely perceptible, broad rise in the baseline from around 2 ppm to just past 3 ppm is from the BH_2 group. Also note the unusually high-field chemical shifts for the imidazolium ring protons; Tf_2N^{-} salts of "conventional" imidazolium ions would have these resonances offset to lower field by 0.5 – 1.0 ppm.

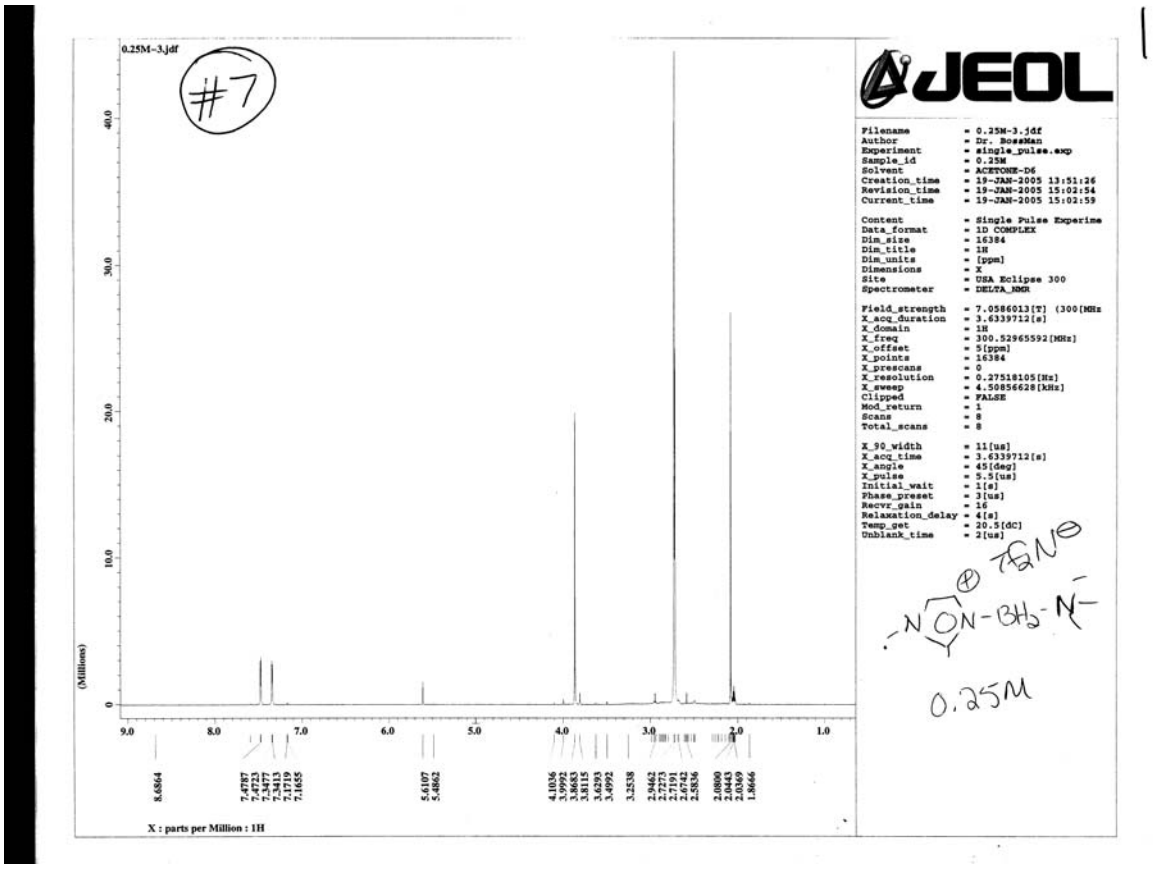


Other representative spectra:

Boronium RTIL **4**



Boronium RTIL **7**



^{1}H-NMR spectra (below) of the imidazole-ring region of **3** before (lower) and after (upper) thermolysis resulting in the clean transformation of the minor cation form into the major form.

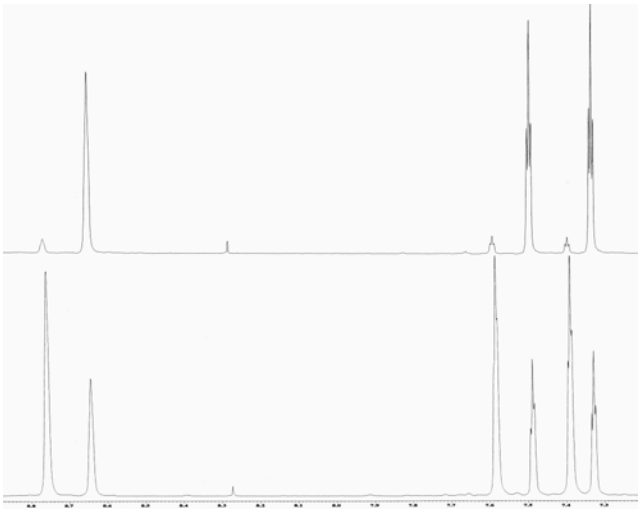


Table 1. Crystal data and structure refinement for $[(\text{N-alkylimidazole})(\text{amine})BH_2]^+Tf_2N^-$

Empirical formula	$C_9\ H_{17}\ B\ F_6\ N_4\ O_4\ S_2$
Formula weight	434.20
Crystal system	Triclinic
Space group	P-1 (no. 2)
a/Å	9.1544(14)
b/Å	10.1383(16)
c/Å	10.7424(17)
α/°	77.628(3)
β/°	72.260(3)
γ/°	80.393(3)
V/Å^3	922.0(2)
Z	2
D_c/g cm^3	1.564
Crystal size/mm	0.56 x 0.24 x 0.22
μ(MoKα)/mm^{-1}	0.369
F(000)	444
T/K	173(2)
$\theta_{min,\ max}$/°	2.02 / 23.29
Reflections collected	4238
Independent reflections, R_{int}	2628, 0.0129
Goodness-of-fit on $F^{2(a)}$	1.039
Final R indices [I>2σ(I)], R_1[b], wR_2[c]	0.0348, 0.0869
R indices (all data)	0.0416, 0.0916

[a] GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of data and p is the number of parameters refined. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(w(F_o^2)^2]\}^{1/2}$.

MoKα radiation (λ = 0.71073 Å).

For crystallographic note/footnote:

Data were collected on a Siemens CCD area detector-equipped diffractometer with MoKα (λ= 0.71073 Å) radiation and solved using the SHELXTL software package. The crystallographically unique anions were resolved into disordered positions. All non-hydrogen atoms were anisotropically refined and all hydrogen atoms were isotropically refined. Crystal data for $[(\text{N-alkylimidazole})(\text{amine})BH_2]^+Tf_2N^-$: formula $C_9H_{17}BF_6N_4O_4S_2$, M = 434.20, Triclinic, a = 9.1544(14), b = 10.1383(16), c = 10.7424(17) Å, α = 77.628(3), β = 72.260(3), γ = 80.393(3) ^{o}, V = 922.0(2) Å^3 , T = 173(2) K, space group *P-1*, Z = 2, μ(MoKα) = 0.369 mm^{-1}, independent reflections = 2628, R_{int} = 0.0129, R_1 = 0.0348, wR_2 = 0.0869 [$I > 2\sigma(I)$]. CCDC 268268. See http://www.rsc.org/suppdata/cc/b0/b000000a for crystallographic data in CIF or other electronic format.