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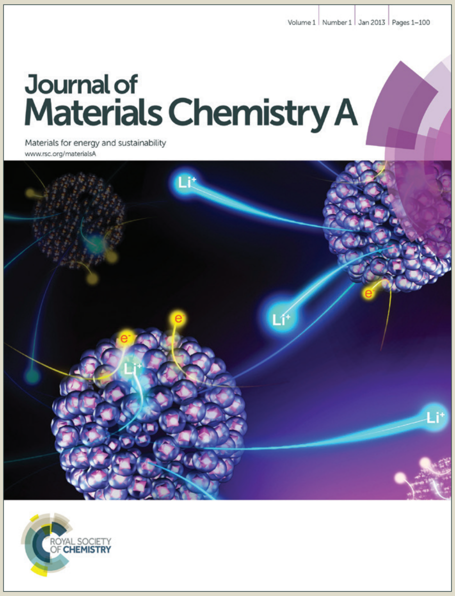

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N-substituted Amine-Borane Ionic Liquids as Fluid Phase, Hydrogen Storage Materials

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A selection of task specific N-substituted amine-borane ionic liquids (N-ABILs) were synthesized in good yield using silyl protecting groups with the aim of developing hydrogen (H_2) storing fuels for automotive applications. A new anhydrous anion exchange method, based on trimethylsilyl reagents, was employed so sensitive pendant functionalities like borane could be incorporated. Controlled thermoylsis of N-ABILs indicate members of this class may be liquids pre- and post-dehydrogenation, jointing a relatively small population of putative H_2 storing fuels that can be readily loaded/unloaded from a vehicle. N-ABILs were also blended with ammonia-borane to improve overall H_2 capacity, in one case by ~2.5x. The products of thermolysis consist of co-oligomerized BN species and highly pure (< 1% impurity) H_2 gas.

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Introduction

The development of compact hydrogen (H_2) storage technologies is a promising alternative to petroleum for meeting our everyday energy needs. New H_2 storage methods will provide a medium for a range of renewable, domestic energy sources to be deployed and become one of the cornerstones of post-petroleum energy storage. In recent years, a very promising liquid material reported by Sneddon et al, consisting of ammonia-borane (AB) and ionic liquids (IL), emerged as a strong candidate for automotive applications.[1, 2] The AB/IL material was found to meet many of the targets established by the U.S. Department of Energy (DOE),[3] including H_2 release free from an induction period, and total hydrogen release (11.4 wt%); however, several obstacles persisted. Of particular concern was the solidification of the AB/IL material post-H_2 release. This impediment prohibits automotive applications, which are dependent upon rapid refuelling. Recent work from Liu has shown that amine-boranes heterocycles remain liquid after H_2 release at *ca.* room temperature,[4] although one example recently had its physical characteristics revised.[5] Furthermore, our group has demonstrated that N-substituted amine-boranes (RNH_2BH_3; R = *n*-hexyl, methoxypropyl) could also overcome the phase problem and were capable of having their total usable H_2 wt% increased by blending the amine-borane with AB to reach 6.0 wt %.[6, 7] In a model reactor system, however, N-substituted amine-boranes show sufficient volatility that reduces conversion. In light of this, we aimed to develop a new task-specific[8] class of ionic liquids which contain an amine-borane moiety, the N-substituted amine-borane ionic liquids (N-ABILs). A survey approach, using three different cations (imidazolium, pyrrolidinium, pyrazolium) and 3 different anions (Cl, OTf, NTf_2), is used to determine if this methodology might be successful at meeting the DOE targets (Figure 1). Furthermore, we demonstrate that an N-ABIL can be blended with at least 2 equivalents of AB to give a liquid material before and after dehydrogenation, providing a proof-of-concept that fuel blends may ultimately achieve DOE targets for H_2 storage and rapid de/refueling.

Experimental

All reactions were carried out under a nitrogen or argon atmosphere. Unless otherwise noted, chemicals were used as received. Anhydrous grade solvents were further dried using molecular sieves (3Å). $ClCH_2CH_2N(SiMe_3)_2$ was prepared according to literature procedure. The ^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were run on either a Bruker Avance 300 MHz or Bruker Avance 400 MHz NMR spectrometer. Samples were made in either d_3-MeCN or d_6-DMSO. Dehydrogenation reactions were carried out in a C80 cell placed in a 132 °C oven. Low resolution mass-spec was evaluated with a Varian 500-MS Ion Trap. An Agilent 1100 LC was equipped with two PLgel 5µm (50Å 300 x 7.5mm) columns kept at constant temperature (30 °C) and an RID kept at 40 °C. Distilled or anhydrous grade THF (Mettler-Toledo Coulumbic Karl Fisher titrator measurements are below detection limit [1 ppm] with 4-5 g samples, using Aldrich's Coulomat AD anolyte and a diaphragmless generator electrode), kept under a constant UHP Ar purge, was used as the mobile phase. Calibration was performed with Agilent polystyrene standards prepared with dry THF at ~2 mg/mL. A flow rate of 0.5 mL/min was used for known/unknown sample evaluation. All samples were prepared in a dry (below detection limit of Karl Fisher) 1:1 (by volume) DMSO:THF solution and filtered through a 0.2 µm filter prior to data collection. IR spectra were collected on a Nicolet Diamond ATR-IR [iS10]. Single crystal X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer, with a KRYO-FLEX liquid nitrogen vapour cooling device. The instrument was equipped with a graphite monochromated MoKα X-ray source (λ = 0.71073 A), with MonoCap X-ray source optics. Viscosity measurements were evaluated with a Cambridge Viscosity Viscolab 3000 viscometer operating at 32 °C, checked against known standards prior to use. Elemental analysis was performed by Midwest Microlab (Indianapolis, IN).

Gas quantification of compound **6c** and a blend combining **6c** and 2 equivalents of AB was determined using a 10 mL Schlenk flask (containing the sample) connected to a Schlenk manifold and a ChemGlass Gas Evolution Apparatus via a T-connector with a 2-way control dial. Samples were heated to 130 °C. **6c** and a blend of **6c** with 2 molar equivalents of AB were loaded into 100 mL Parr reaction vessels, respectively, and pressurized to *ca.* 9 bar UHP N_2 gas. The samples were heated to 130 °C for 8 h using a Parr MRS system. The head space gas of the samples was then passed into a Nicolet Avatar 370 IR spectrometer equipped with a 2M cell at 40 sccm. A Pfeiffer Thermo-Star mass-spectrometer sampled the gas via a stainless steel heated (150 °C) capillary at a rate of 1 sccm.

For DSC experiments, the samples were loaded into either a Swissi high pressure, gold-plated stainless steel crucible sealed using a Schmidt press, or, an incoloy high pressure cell. The samples were run on a Setaram [Sensys Evo] with Calisto software. Samples were ramped to 30 °C and equilibrated for 30 min. Afterwards, the samples were ramped at a rate of 1 °C/min up to 250 °C. Baseline corrections were achieved by subtracting the trace of a blank run.

1. $ClCH_2CH_2CH_2N(SiMe_3)_2$. A 500 mL flask was charged with 13.002 g (100 mmol) of $[ClCH_2CH_2CH_2NH_3]Cl$ that was dissolved in 300 mL of CH_2Cl_2 and 46.4 mL (300 mmol) of triethylamine. After *ca.* 10 min, a precipitate began to evolve. The flask was cooled to 0 °C and a solution containing 28.2 mL (222 mmol) of TMSCl and 50 mL of CH_2Cl_2 was added slowly over 2 h. The solution was stirred for an additional 2 h and then allowed to return to ambient temperature where it was stirred for 3 days. The supernatant liquid was decanted and then all volatile components were removed in vacuo to produce both a solid residue and a liquid. The liquid was extracted using *ca.* 200 mL of hexanes and subsequently the volatile components were removed under reduced pressure to yield 18.3898 g (77.3 mmol, 77.3%) of **1** as a colorless liquid. ^1H NMR (300 MHz, CD_3CN) δ = 0.11 (s, $-Si(CH_3)_3$, 18H), 1.83 (m, CH_2N, 2H, J_{HH}= 5.29 Hz), 3.52 (t, $ClCH_2$, 2H, J_{HH}= 6.3 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN) 2.30, 38.50, 43.74, 43.93.

2a. $[MImEtN(SiMe_3)_2]Cl$. A 100 mL flask was charged with 7.109 g (29.9 mmol) of $ClCH_2CH_2N(SiMe_3)_2$ and 3.004 g (36.6 mmol) of methylimidazole which formed two layers. The flask was heated to *ca.* 115 °C with vigorous stirring. During the initial heating, the two layers coalesced at *ca.* 75 °C. After *ca.* 5 min of stirring, a new layer appeared in the flask that progressively increased over 8 h at which it became a singular phase again. Additionally, after 10 min of stirring, colorless crystals sublimed at the near the top of the flask. The flask was stirred overnight to give an orange-yellow liquid. The flask was then allowed to cool for 10 min after which *ca.* 30 mL of diethyl ether was added and stirred with the liquid until it formed a white solid. The flask was allowed to cool to ambient temperature and the ether was filtered. The white solid was washed with 25 mL of diethyl ether (x3) and then dried under vacuum to yield 8.736 g (28.5 mmol, 95.5%) of **2a** as a colorless powder. M.p. = 105-110 °C; ^1H NMR (300 MHz, d_6-DMSO) δ = 0.10 (s, $-Si(CH_3)_3$, 18H), 3.15 (t, 2H, J_{HH}= 7.4 Hz), 3.88 (s, 3H, CH_3), 4.04 (t, $MImCH_2$, 2H, J_{HH}= 7.4 Hz), 7.81 (s, 1H), 7.82 (s, 1H), 9.50 (s, 1H, NC*H*N); $^{13}C\{^1H\}$ NMR (75 MHz, d_6-DMSO) 1.84, 35.62, 44.67, 51.40, 122.67, 123.38, 136.88; FT-IR (cm^{-1}): 3034 (C-H), 2951 (C-H), 1574 (C-C).

3a. $[MImEtNH_3]Cl_2$. 18.63 mL of 1.25 M HCl in EtOH was slowly added over 15 min to a 100 mL flask containing 6.362 g (20.8 mmol) of **2a** dissolved in *ca.* 60 mL EtOH. After adding 25% of the HCl solution, a white precipitate emerged. The solution was stirred for 3 h after which all of the volatile components were removed under reduced pressure and gentle heating to *ca.* 45 °C to give a pale yellow residue. The solid was washed with 30 mL of MeCN (x3) and 30 mL of diethyl ether (x2) and dried under vacuum to yield 4.047 g (20.4 mmol, 98.2 %) of **3a** as a colourless powder. M.p. = 189.1 °C; ^1H NMR (300 MHz, d_6-DMSO) δ = 3.31 (m, 2H, CH_2NH_3), 3.85 (s, 3H, CH_3), 4.56 (t, $MImCH_2$, 2H, J_{HH}= 5.8 Hz), 7.74 (s, 1H), 7.86 (s, 1H), 8.72 (s *broad*, 3H,$-NH_3$), 9.30 (s, 1H, NC*H*N); $^{13}C\{^1H\}$ NMR (75 MHz, d_6-DMSO) δ = 35.76, 38.41, 46.15, 122.46, 123.70, 137.46; FT-IR (cm^{-1}): 3143 (N-H), 3084 (N-H), 3035 (N-H), 2932 (C-H), 2717, 2633, 2573, 2498, 2421, 2086, 1610, 1570, 1526, 1449.

4a. $[MImEtNH_2BH_3]Cl$. To a 100 mL flask containing 4.039 g (20.4 mmol) of **3a** dissolved in *ca.* 80 mL of DMSO, 0.810 g (21.4 mmol) of $NaBH_4$ was added in 4 portions over 15 min. Upon each addition, large amounts of gas evolved and a white precipitate emerged. The solution was stirred for 12 h and the precipitate was filtered-off to give a clear, pale yellow solution. The DMSO was distilled at *ca.* 60 °C to give an off-white solid. The product was washed with *ca.* 30 mL (x2) of MeCN and 30 mL (x2) of diethyl ether and dried under vacuum to give 3.8473 g (21.9 mmol, 107.5 % (sodium chloride impurity remains) **4a** as a colourless powder. M.p. = 142.4 °C (dec); ^1H NMR (400 MHz, d_6-DMSO) δ = 1.25 (s br, 3H, BH_3), 2.89 (pent *broad*, 2H, CH_2NH_2), 3.85 (s, 3H, CH_3), 4.43 (t, 2H, $MImCH_2$, J_{HH}= 4.0 Hz), 5.64 (s *broad*, 2H,$-NH_2$), 7.77 (s, 1H), 7.85 (s, 1H), 9.33 (s, 1H, NC*H*N); $^{13}C\{^1H\}$ NMR (100.6 MHz, d_6-DMSO) δ = 35.64, 46.94, 47.12, 122.29, 123.58, 137.28; ^{11}B NMR (128.3 MHz, 400.2 K, d_6-DMSO) δ = -19.47 (q, $^1J_{BH}$= 97.5 Hz); FT-IR (cm^{-1}):3231 (N-H), 3131 (N-H), 3109 (C-H), 3054 (C-H), 2965 (C-H), 2342 (B-H), 2311 (B-H), 2273 (B-H), 1612 (C-C), 1561 (C-C).

5a. $[MImEtNH_2BH_3]OTf$. 2.06 mL (11.4 mmol) of TMSOTf was dissolved in *ca.* 50 mL of MeCN and then added dropwise to a slurry consisting of 2.000 g (11.4 mmol) of **4a** in *ca.* 20 mL of MeCN, cooled to *ca.* 0 °C. Upon complete addition, most of the precipitate had dissolved. The reaction was stirred for 3 h and then allowed to warm to ambient temperature where it was stirred for 2 h. Subsequent filtration gave a clear, colorless solution. All of the volatile components were removed under reduced pressure and gentle heating to *ca.* 34 °C. The resulting solid was washed with *ca.* 25 mL (x3) of diethyl ether to give 3.007 g (10.4 mmol, 91.2 %) of **5a** as a white powder. M.p. = 81.3 °C; ^1H NMR (400 MHz, d_3-MeCN) δ = 1.31 (s br, 3H, BH_3), 3.05 (pent, 2H, CH_2NH_2, J_{HH}= 6.0 Hz), 3.83 (s, 3H, CH_3), 4.40 (t, 2H, $MImCH_2$, J_{HH}= 6.0 Hz), 5.43 (s *broad*, 2H,$-NH_2$), 7.39 (s, 1H), 7.44 (s, 1H), 8.59 (s, 1H, NC*H*N); $^{13}C\{^1H\}$ NMR (100.6 MHz, d_3-MeCN) δ = 36.95, 47.94, 48.24, 121.85 (quart, 1C, $-CF_3$, J= 320.4 Hz), 123.54, 125.09, 137.75; ^{11}B NMR (128.3 MHz, 400.2 K, d_6-DMSO) δ = -19.51 (q, $^1J_{BH}$= 95.1 Hz); FT-IR (cm^{-1}): 3265 (N-H), 3244 (N-H), 3165 (C-H), 3153 (C-H), 3113 (C-H), 3098 (C-H), 2375 (B-H), 2326 (B-H), 2290 (B-H), 1605, 1577, 1560, 1455, 1428.

2b. $[EImEtN(SiMe_3)_2]Cl$. Compound **2b** was prepared by a similar method as **2a**. Yield: 9.873 g (30.85 mmol, 67.7%); M.p =

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104-108 °C; ^{1}H NMR (300 MHz, d$_6$-DMSO) δ = 0.09 (s, 18H, $\mathrm{Si(C}H_3)_3$), 1.42 (t, 3H, $\mathrm{CH_2C}H_3$, *J*= 7.0 Hz), 3.17 (t, 2H, *J*= 7.0 Hz), 4.04 (t, 2H, *J*= 7.0 Hz), 4.23 (quart, 2H, $\mathrm{ImC}H_2\mathrm{CH_3}$, J_{HH}= 7.0 Hz), 7.81 (s, 1H), 7.90 (s, 1H), 9.50 (s, 1H, NC*H*N); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 1.83, 15.16, 44.11, 44.62, 51.60, 121.95, 122.88, 136.05; FT-IR (cm^{-1}): 3229 (N-H impurity), 3070 (C-H), 2993 (C-H), 2953 (C-H), 2855 (C-H), 1560, 1472, 1447, 1424, 1402.

3b. [EImEtNH$_3$]Cl$_2$. Compound **3b** was prepared by a similar method as **3a**. Yield: 3.382 g (15.94 mmol, 91.3%); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.44 (t, 3H, $\mathrm{CH_2C}H_3$, *J*= 7.0 Hz), 3.33 (t, 2H, *J*= 7.0 Hz), 4.19 (quart, 2H, $\mathrm{ImC}H_2\mathrm{CH_3}$, *J*= 7.0 Hz), 4.56 (t, 2H, J_{HH}= 7.0 Hz), 7.85 (s, 1H), 7.89 (s, 1H), 8.80 (s *broad*, 3H,-N*H*$_3$), 9.44 (s, 1H, NC*H*N); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 14.79, 38.32, 44.22, 46.18, 122.20, 122.62, 136.62; FT-IR (cm^{-1}): 3144 (N-H), 3085 (N-H), 3047 (N-H), 2933 (C-H), 2882 (C-H), 2824 (C-H), 2772, 2718, 2628, 2575, 2496, 2419, 2090, 1660, 1610, 1570, 1450, 1411.

4b. [EImEtNH$_2$BH$_3$]Cl. Compound **4b** was prepared by a similar method as **4a**. Yield: 2.061 g (10.57 mmol, 115.2 %); M.p= 122.1 (dec); ^{1}H NMR (400 MHz, *d*$_6$-DMSO) δ = 1.27 (s *broad*, 3H, B*H*$_3$), 1.42 (t, 3H, $\mathrm{CH_2C}H_3$, *J*= 7.0 Hz), 2.90 (pent *broad*, 2H,$\mathrm{C}H_2\mathrm{NH_2}$), 4.18 (quart, 2H, $\mathrm{ImC}H_2\mathrm{CH_3}$, J_{HH}= 7.0 Hz), 4.41 (t, 2H, *J*= 5.0 Hz), 5.63 (s *broad*, 2H,-N*H*$_2$), 7.84 (s, 1H), 7.86 (s, 1H), 9.39 (s, 1H, NC*H*N); ^{13}C{^{1}H} NMR (100.6 MHz, *d*$_6$-DMSO) δ = 14.82, 40.43, 46.76, 47.15, 122.05, 122.42, 136.38; ^{11}B NMR (128.3 MHz, 383.2 K, *d*$_6$-DMSO) δ = -19.42 (quart, $^1J_{\mathrm{BH}}$= 94.9 Hz); FT-IR (cm^{-1}): 3216 (N-H), 3152 (N-H), 3102 (C-H), 3057 (C-H), 2984 (C-H), 2861, 2350 (B-H), 2307 (B-H), 2260 (B-H), 1623, 1560, 1466, 1450.

5b. [EImEtNH$_2$BH$_3$]OTf. Compound **5b** was prepared by a similar method as **5a**. Yield: 1.061 g (3.50 mmol, 63.9%); M.p= 88.0 (dec); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.26 (s *broad*, 3H, B*H*$_3$), 1.42 (t, 3H, $\mathrm{CH_2C}H_3$, *J*= 7.0 Hz), 2.92 (pent *broad*, 2H,$\mathrm{C}H_2\mathrm{NH_2}$), 4.17 (quart, 2H, $\mathrm{ImC}H_2\mathrm{CH_3}$, J_{HH}= 7.0 Hz), 4.29 (t, 2H, *J*= 5.0 Hz), 5.44 (s *broad*, 2H,-N*H*$_2$), 7.73 (s, 1H), 7.78 (s, 1H), 9.08 (s, 1H, NC*H*N); ^{13}C{^{1}H} NMR (100.6 MHz, *d*$_6$-DMSO) δ = 40.42, 44.14, 46.50, 47.39, 120.66 (quart, 1C, -*C*F$_3$, *J*= 323.5 Hz), 122.18, 122.46, 136.29; ^{11}B NMR (128.3 MHz, 383.2 K, *d*$_6$-DMSO) δ = -19.41 (quart, $^1J_{\mathrm{BH}}$= 92.2 Hz).

7b. [EImEtNH$_2$]Cl. 1.547 g (4.83 mmol) of **2b** was dissolved in *ca.* 20 mL MeOH and was stirred for 6 days. All volatile components were removed under reduced pressure to give a solid residue. The solid was washed with a 50/50 toluene/diethyl ether mixure (20 mL x 2) and diethyl ether (20 mL x 3). The product was dried under vacuum to give **7b** as a colourless solid. Yield: 0.803 g (4.57 mmol, 94.6 %); M.p. = 66-68 °C (dec. >165 °C); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.42 (t, 3H, $\mathrm{CH_2C}H_3$, *J*= 7.3 Hz), 1.68 (s broad, 2H, -N*H*$_2$), 2.90 (t, 2H, *J*= 5.7 Hz), 4.14 (t, 2H, J_{HH}= 5.8 Hz), 4.22 (quart, 2H, $\mathrm{ImC}H_2\mathrm{CH_3}$, *J*= 7.3 Hz), 7.82 (s, 1H), 7.86 (s, 1H), 9.46 (s, 1H, NC*H*N); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 15.02, 41.26, 44.00, 51.83, 121.72, 122.60, 136.05; FT-IR (cm^{-1}): 3302 (N-H), 3255 (N-H), 3173, 3134, 3074, 3052, 2975, 2869, 1785, 1709, 1614, 1565, 1455, 1421. EA ($\mathrm{C_7H_{14}ClN_3}$): Calculated C: 47.86, H 8.03, N 23.92. Found C: 47.45, H 7.87, N 23.62.

2c. [EImPrN(SiMe$_3$)$_2$]Cl. Compound **2c** was prepared by a similar method as **2a**. Yield: 19.322 g (58.02 mmol, 81.43%); M.p.= 100-105 °C; ^{1}H NMR (300 MHz, *d*$_3$-MeCN) δ = 0.08 (s, 18H, $\mathrm{Si(C}H_3)_3$), 1.49 (t, 3H, *J*= 7.0 Hz), 1.90 (multi, 2H), 2.82 (multi, 2H), 4.21 (t, 2H, *J*= 7.0 Hz), 4.27 (quart, 2H, $\mathrm{ImC}H_2\mathrm{CH_3}$, J_{HH}= 5.0 Hz), 7.56 (s, 1H), 7.61 (s, 1H), 9.97 (s, 1H, NC*H*N); ^{13}C{^{1}H} NMR (75 MHz, *d*$_3$-MeCN) δ = 2.12, 15.69, 36.13, 42.89, 45.63, 48.21, 122.97, 123.22, 137.56.

3c. [EImPrNH$_3$]Cl$_2$. Compound **3c** was prepared by a similar method as **3a**. Yield: 11.860 g (52.45 mmol, 96.8%); M.p.= 124.8; ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.43 (t, 3H, $\mathrm{CH_2C}H_3$, *J*= 7.0 Hz), 2.18 (pent, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$, *J*= 7.0 Hz), 2.77 (s *broad*, 2H), 4.21 (quart, 2H, *J*= 7.0 Hz), 4.38 (t, 2H, J_{HH}= 7.0 Hz), 7.87 (s, 1H), 7.92 (s, 1H), 8.56 (s *broad*, 3H,-N*H*$_3$), 9.51 (s, 1H, NC*H*N); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 14.95, 27.43, 35.31, 44.26, 45.87, 122.23, 122.38, 136.09; FT-IR (cm^{-1}): 3142 (N-H), 3092 (N-H), 3062 (N-H), 2988 (C-H), 2942 (C-H), 2854 (C-H), 2818 (C-H), 2744, 2726, 2675, 2647, 2565, 2495, 2034, 1653, 1604, 1578, 1559, 1533, 1461, 1424. EA ($\mathrm{C_8H_{17}Cl_2N_3}$): Calculated C: 42.49, H 7.58, N 18.58. Found C: 42.32, H 7.31, N 18.35.

4c. [EImPrNH$_2$BH$_3$]Cl. Compound **4c** was prepared by a similar method as **4a**. Yield: 9.2312 g (45.36 mmol, 101.7%); M.p. = 129.5 (dec); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.30 (s *broad*, 3H, B*H*$_3$), 1.41 (t, 3H, $\mathrm{CH_2C}H_3$, *J*= 7.0 Hz), 2.07 (t, 2H, *J*= 7.0 Hz), 2.39 (pent *broad*, 2H,$\mathrm{C}H_2\mathrm{NH_2}$), 4.23 (quart, 2H, $\mathrm{ImC}H_2\mathrm{CH_3}$, J_{HH}= 7.0 Hz), 4.30 (t, 2H, *J*= 7.0 Hz), 4.58 (s *broad*, 2H,-N*H*$_2$),7.89 (s, 1H), 7.92 (s, 1H), 9.60 (s, 1H, NC*H*N); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 15.05, 28.33, 40.43, 44.00, 44.18, 46.37, 122.22, 122.35, 135.97; ^{11}B NMR (96.2 MHz, 373.2 K, *d*$_6$-DMSO) δ = -19.53 (quart, $^1J_{\mathrm{BH}}$= 100.05 Hz); FT-IR (cm^{-1}): 3231 (N-H), 3131 (N-H), 3109 (C-H), 3055 (C-H), 2988 (C-H), 2964 (C-H), 2893 (C-H), 2348 (B-H), 2310 (B-H), 2272 (B-H), 1612, 1561, 1465, 1561, 1465, 1442.

5c. [EImPrNH$_2$BH$_3$]OTf. Compound **5c** was prepared by a similar method as **5a**. Yield: 2.721 (8.58 mmol, 83.5%); M.p = 85.7 (dec); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.33 (s *broad*, 3H, B*H*$_3$), 1.42 (t, 3H, $\mathrm{CH_2C}H_3$, *J*= 7.0 Hz), 2.02 (pent, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$, *J*= 7.0 Hz), 2.42 (pent *broad*, 2H, $\mathrm{C}H_2\mathrm{NH_2}$), 4.19 (s *broad*, 2H), 4.21 (s *broad*, 2H), 4.30 (s *broad*, 2H,-N*H*$_2$),7.75 (s, 1H), 7.81 (s, 1H), 9.14 (s, 1H, NC*H*N); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 14.97, 28.43, 44.07,44.26, 46.51, 122.30, 122.34, 135.75; ^{11}B NMR (96.2 MHz, 400.15 K, *d*$_6$-DMSO) δ = -19.39 (quart, $^1J_{\mathrm{BH}}$= 95.24 Hz); FT-IR (cm^{-1}): 3344 (N-H), 3147 (N-H), 3114 (C-H), 2982 (C-H), 2966 (C-H), 2897 (C-H), 2369 (B-H), 2321 (B-H), 2282 (B-H), 1607, 1566, 1464, 1452.

6c. [EImPrNH$_2$BH$_3$]NTf$_2$. 0.954 g (2.70 mmol) of TMSNTf$_2$ was dissolved in *ca.* 20 mL of MeCN and then added dropwise to a slurry consisting of 0.549 g (2.70 mmol) of **4c** in *ca.* 20 mL of MeCN, cooled to *ca.* 0 °C. Upon complete addition, most of the precipitate dissolved. The reaction was stirred for 3 h and then allowed to warm to ambient temperature where it was stirred for 2 h. Subsequent filtration gave a clear, colorless solution. All of the volatile components were removed under reduced pressure and gentle heating to *ca.* 34 °C to give 0.960 g (2.14 mmol, 79.4 %) of **6c** as a pale yellow liquid. M.p. < -30 C; ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.21 (s *broad*, 3H, B*H*$_3$), 1.42 (t, 3H, $\mathrm{CH_2C}H_3$, *J*= 7.0 Hz), 2.01 (pent *broad*, 2H,$\mathrm{C}H_2\mathrm{NH_2}$), 2.42 (pent *broad*, 2H), 4.20 (quart, 2H, $\mathrm{CH_2C}H_3$, *J*= 7.0 Hz), 4.20 (t, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$, *J*= 7.0 Hz), 5.31 (s *broad*, 2H,-N*H*$_2$), 7.75 (s, 1H), 7.81 (s, 1H), 9.16 (s, 1H, NC*H*N); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 14.96, 28.47, 44.08, 44.28, 46.53, 119.50 (quart, *C*F$_3$, $^1J_{\mathrm{CF}}$ = 320.3 Hz), 121.31, 122.36, 135.79; ^{11}B NMR (96.2 MHz, 400.15 K, *d*$_6$-DMSO) δ = -19.43 (quart, $^1J_{\mathrm{BH}}$ = 95.24 Hz); FT-IR (cm^{-1}): 3261 (N-H), 3152 (N-H), 3117 (C-H), 2985 (C-H), 2967 (C-H), 2901 (C-H), 2375 (B-H), 2323 (B-H), 2384 (B-H), 1600, 1566, 1463, 1452.

2d. [MPyrroPrN(SiMe$_3$)$_2$]Cl. Compound **2d** was prepared by a similar method as **2a**. Yield: 10.180 g (31.5 mmol, 79.9 %); M.p = 130.1 °C; ^{1}H NMR (300 MHz, *d*$_3$-MeCN) δ = 0.11 (s, 18H, $\mathrm{Si(C}H_3)_3$), 1.73 (m, 2H), 2.13 (broad singlet, 4H), 2.81 (t, 2H, *J*= 7.8 Hz), 3.03 (s, 3H, $\mathrm{N(C}H_3)$), 3.38 (t, 2H, *J*= 6.0 Hz), 3.50 (m, 2H), 3.55 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, *d*$_3$-MeCN) δ = 2.06 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 22.09, 30.01, 40.82, 48.66, 61.95, 64.89; FT-IR (cm^{-1}): 2951 (C-H), 2893 (C-H), 1568, 1477, 1460, 1411.

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3d. [MPyrroPrNH$_3$]Cl$_2$. Compound **3d** was prepared by a similar method as **3a**. Yield: 5.517 g (25.6 mmol, 94.5 %); ^{1}H NMR (300 MHz, d$_6$-DMSO) δ = 2.09 (m, 4H,), 2.14 (m, 2H), 2.84 (m, 2H), 3.04 (s, 3H, NC*H*$_3$), 3.52 (m, 2H), 3.57 (m, 2H), 8.70 (s *broad*, 3H,-N*H*$_3$); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 21.11, 21.34, 35.95, 47.60, 59.86, 63.61; FT-IR (cm^{-1}): 3198 (N-H), 3113 (N-H), 3002 (N-H), 2927 (C-H), 2846 (C-H), 2783, 2750, 2651, 2587, 2499, 2015, 1604, 1507, 1471, 1420.

4d. [MPyrroPrNH$_2$BH$_3$]Cl. Compound **4d** was prepared by a similar method as **4a**. Yield: 4.500 g (23.4 mmol, 103.2 %); M.p= 126.5 (dec); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.24 (s *broad*, 3H, B*H*$_3$), 1.96 (pent, 2H, *J*= 7 Hz), 2.07 (*broad*, 6H), 2.99 (s, 3H, N(C*H*$_3$)), 2.45 (m, 6H) 5.45 (s *broad*, 2H,-N*H*$_2$); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 21.09, 22.13, 44.46, 47.52, 60.43, 63.46; ^{11}B NMR (96.2 MHz, 383.2 K, *d*$_6$-DMSO) δ = -19.55 (quart, $^1J_{\mathrm{BH}}$= 94.15 Hz); FT-IR (cm^{-1}): 3229 (N-H), 3130 (N-H), 3058 (C-H), 2968 (C-H), 2895 (C-H), 2353 (B-H), 2306 (B-H), 2265 (B-H), 1607, 1463, 1410.

5d. [MPyrroPrNH$_2$BH$_3$]OTf. Compound **5d** was prepared by a similar method as **5a**. Yield: 4.524 g (14.8 mmol, 85.9 %); M.p= 80.1 (dec); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.31 (s *broad*, 3H, B*H*$_3$), 1.93 (pent, 2H, *J*= 7 Hz), 2.09 (*broad*, 6H), 2.97 (s, 3H, N(C*H*$_3$)), 3.41 (m, 6H) 5.29 (s *broad*, 2H,-N*H*$_2$); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 21.09, 22.18, 44.32, 47.59, 60.62, 63.64, 120.64 (quart, *C*F$_3$, $^1J_{\mathrm{CF}}$ = 322.3 Hz); ^{11}B NMR (96.2 MHz, 383.2 K, *d*$_6$-DMSO) δ = -19.51 (quart, $^1J_{\mathrm{BH}}$= 93.95 Hz); FT-IR (cm^{-1}): 3245 (N-H), 3175 (N-H), 2972 (C-H), 2900 (C-H), 2367 (B-H), 2320 (B-H), 2278 (B-H), 1609, 1467, 1434.

7d. [MPyrroPrNH$_2$]Cl. Compound **7d** was prepared by a similar method as **7b**. Yield: 0.733 g (4.10 mmol, 95.7%); M.p= 88.1 °; ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.72 (s *broad*, 2H, -N*H*$_2$), 2.07 (s *broad*, 4H,), 2.58 (t, 2H, *J*= 7.0 Hz), 3.02 (s, 3H, NC*H*$_3$), 3.52 (m, 2H), 3.46 (m, 6H); ^{13}C{^{1}H} NMR (100.6 MHz, *d*$_6$-DMSO) δ = 21.01, 26.81, 38.63, 47.41, 61.31, 63.23.

2e. [MPyraPrN(SiMe$_3$)$_2$]Cl. A 100 mL flask was charged with 4.847g (20.4 mmol) of **1**, 11.362 g NaI (75.8 mmol), and 13.096 g (159.5 mmol) of N-methylpyrazole. The flasked was heated to *ca.* 105 °C with vigorous stirring. The flask was stirred 2 days to give an orange-yellow microcrystalline solid. The flask was allowed to cool to ambient temperature. 80 mL of dichloromethane was added to the flask, vigorously stirred, and filtered. The supernatant liquid was removed under reduced pressure to give an orange-yellow solid residue. The residue was washed with a solution consisting of *ca.* 30 mL of diethyl ether and 3 mL of MeCN (x3), followed by 30 mL of diethyl ether (x3). The product was dried under vacuum, to give **2e** as a pale orange solid. Yield: 11.560 g (36.1 mmol, 177 % (NaI mixed in is removed in later steps); M.p. = 131.7 °C; ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 0.06 (s, 18H, -Si(C*H*$_3$)$_3$), 1.82 (pent, 2H, $^3J_{HH}$= 7.8 Hz), 2.78 (t, 2H, $^3J_{HH}$= 7.8 Hz), 4.14 (s, 3H, N-C*H*$_3$), 4.44 (t, 2H, $^3J_{HH}$= 7.3 Hz), 6.88 (t, 1H, $^3J_{HH}$= 3.0 Hz), 8.53 (d, 1H, $^3J_{HH}$= 3.0 Hz), 8.60 (d, 1H, $^3J_{HH}$= 3.0 Hz); ^{13}C{^{1}H} NMR (75 MHz, *d*$_6$-DMSO) δ = 1.92, 33.48, 36.80, 41.43, 47.12, 107.10, 137.01, 138.04; FT-IR (cm^{-1}): 3079 (C-H), 3038 (C-H), 3000 (C-H), 2951 (C-H), 2872 (C-H), 1683, 1585, 1536, 1442, 1419.

3e. [MPyraPrNH$_3$]Cl$_2$. Compound **3e** was prepared by a similar method as **3b**. Yield: 2.093 g (9.87 mmol, 49.1 %); ^{1}H NMR (500 MHz, *d*$_6$-DMSO) δ = 2.19 (pent, 2H, $^3J_{HH}$= 7.0 Hz), 2.85 (m, 2H), 4.17 (s, 3H, N-C*H*$_3$), 4.66 (t, 2H, $^3J_{HH}$= 7.1 Hz), 6.90 (t, 1H, $^3J_{HH}$= 2.8 Hz), 8.18 (s *broad*, 3H, N*H*$_3$), 8.56 (d, 1H, $^3J_{HH}$= 1.8 Hz), 8.68 (d, 1H, $^3J_{HH}$= 2.1 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, *d*$_6$-DMSO) δ = 25.89, 35.45, 36.95, 46.94, 107.22, 136.96, 138.31. FT-IR (cm^{-1}): 3194 (N-H), 3081 (N-H), 3046 (N-H), 2949 (C-H), 2877 (C-H), 2810, 2741, 2635, 2510, 2009, 1683, 1595, 1534, 1440, 1418.

4e. [MPyraPrNH$_3$BH$_3$]Cl. Compound **4e** was prepared by two methods starting from either ammonium or amine ionic solids. Using the ammonium salt, **3e**, **4e** was prepared by a similar method as **4b**. Yield: 1.090 g (5.75 mmol, 100.5%); (Alternative method): To a 20 mL scintillation vile, 1.013 g (5.77 mmol) **7e** (*infra vide*) was slurrified in *ca.* 10 mL of MeCN. A *ca.* 1.01 mL (11.5 mmol) of BH$_3$(SMe$_2$) was added via syringe. The mixture was stirred for 6 day to give 1.082 (5.71 mmol, 99.0 %) of **4e** as a white powder. M.p= 111.9 (dec); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.35 (s *broad*, 3H, B*H*$_3$), 2.07 (pent, 2H, $^3J_{HH}$= 7.8 Hz), 2.48 (pent, 2H), 4.13 (s, 3H, N-C*H*$_3$), 4.52 (t, 2H, $^3J_{HH}$= 7.3 Hz), 5.34 (s *broad*, -N*H*$_2$), 6.91 (t, 1H, $^3J_{HH}$ = 3.0 Hz), 8.52 (d, 1H, $^3J_{HH}$= 3.0 Hz), 8.53 (d, 1H, $^3J_{HH}$= 3.0 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, *d*$_6$-DMSO) δ = 26.85, 36.77, 43.83, 47.00, 107.21, 136.79, 138.24; ^{11}B NMR (128.3 MHz, 383.2 K, *d*$_6$-DMSO) δ = -19.46 (quart, $^1J_{\mathrm{BH}}$= 95.3 Hz); FT-IR (cm^{-1}): 3173 (N-H), 3136 (N-H), 3099 (C-H), 2971 (C-H), 2948 (C-H), 2877 (C-H), 2372 (B-H), 2319 (B-H), 2279 (B-H), 1576, 1535, 1443, 1418.

7e. [MPyraPrNH$_2$]Cl. Compound **7e** was prepared by a similar method as **7b**. Yield: 1.282 g (7.30 mmol, 56.1%); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ = 1.93 (pent, 2H, $^3J_{HH}$= 7.8 Hz), 2.62 (t, 2H, $^3J_{HH}$= 7.8 Hz), 3.90 (s *broad*, -N*H*$_2$), 4.16 (s, 3H, N-C*H*$_3$), 4.53 (t, 2H, $^3J_{HH}$= 7.3 Hz), 6.88 (t, 1H, $^3J_{HH}$= 3.0 Hz), 8.51 (d, 1H, $^3J_{HH}$= 3.0 Hz), 8.54 (d, 1H, $^3J_{HH}$= 3.0 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, *d*$_6$-DMSO) δ = 30.35, 36.78, 37.38, 47.11, 107.06, 136.83, 137.93; FT-IR (cm^{-1}): 3329 (N-H), 3249 (N-H), 3081 (C-H), 3034 (C-H), 2997 (C-H), 2946 (C-H), 2867 (C-H), 2360, 2323, 1682, 1635, 1615, 1589, 1534, 1440.

Results and Discussion

The synthesis of the N-ABILs (Scheme 1) proceeds through the addition of a trivalent amine (imidazole, pyrrolidine, pyrazole) with a silylamine alkyl halide. There have been previous reports of ionic liquids functionalized with primary amines,[9-11] however the products are typically impure, containing oligomeric amines.[12] In order to avoid oligomer formation, amines protected with silyl groups[13, 14] were investigated. The ethyl and *n*-propyl bistrimethylsilylamines were prepared by adding the commercially available chloroalkylammonium chloride with trimethylsilylchloride and triethylamine in DCM and stirring for 1 week (Scheme 1, i). Insufficient stirring duration leads to an impurity of the monosilylated amine; however, separation is not required as both species lead to the same deprotected product in subsequent steps. The chloroalkylsilylamine was then heated (110-120 °C, 3 days) to give the silylamine IL in *ca.* 81% yield (Scheme 1, ii). The silylamine IL can then be deprotected and borylated via two methods. Reaction of the silyamine in EtOH with 1.05 equivalents of HCl quickly produced the dicationic ammonium dichloride within *ca.* 10 min, giving 95 % yields (Scheme 1, iii). Slow addition of NaBH$_4$ to the ammonium imidazolium dichloride in DMSO gave the amine-borane IL chloride as indicated by the spontaneous gas evolution, presumably H$_2$. The byproduct NaCl and DMSO were removed by filtration and by distillation (*ca.* 65 °C, 0.1 mmHg), respectively. The solid residue was washed repeatedly with THF to remove NaCl to give the N-ABIL in a small excess of 100% yield (excess due to incomplete removal of NaCl) (Scheme 1, iv). In order to simplify purification, an alternative route to the N-ABIL from the silylamine IL was developed. Deprotection of the silylamine to the primary amine using MeOH at ambient temperature occurs over a period ranging from 1-6 days, depending on the cation (Scheme 1, v). Attempts to heat the reaction mixture in MeOH or EtOH resulted in a mixture of products, whereas, moderate conditions provided the pure amine in *ca.* 95 % yield. The N-ABIL was then synthesized by

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addition of $BH_3(SMe_2)$ dissolved in MeCN and stirring for 6 days, giving *ca.* 99 % yields (Scheme 1, vi). Due to the moisture-sensitivity of the amine-borane moiety and the desire to have a particulate free material, standard anion metathesis methods were not available (which require an H_2O washing step(s)), while quantitative precipitation of silver salts can be very slow—often leaving small particles behind that are difficult to filter,[15] an anhydrous anion substitution method was developed that readily converts the halide salts to the trifluoromethanesulfonate (OTf) or bis(trifluorosulfonyl)amide (NTf_2) derivatives. Addition of either TMSOTf or $TMSNTf_2$ to the N-ABIL chloride in MeCN at 0 °C, gave the corresponding OTf and NTf_2 analogues (*ca.* 80% yield) as well as trimethylsilyl chloride which is easily removed under reduced pressure and is available to be recycled in the preparation of the chloroalkylsilylamine (Scheme 1, vii).

Structural confirmation of the N-ABILs was principally achieved using ^{11}B NMR (*vide infra*), ESI-MS (*vide infra*), with further evidence provided by single crystal X-ray structures of N-ABIL 2 (**5a, Figure 2**), the precursor ammonium dichloride (**3b, ESI**), and the silylamine (**2a, ESI**). The B(1)-N(1) distance of 1.6038 (18) Å is characteristic of amine-borane moieties (1.587-1.610, non-aniline)[16] and AB (1.565(7) Å).[17, 18] Although the imidazolium ring formally balances the charge of the triflate anion, the closest interaction is observed between O(3) of the triflate and H(1G) of the amino functionality (2.016 A, **Figure 2**), likely a consequence of the proximal Lewis acidic BH_3 moiety. It is difficult to gauge the magnitude of this interaction since the CSD only (version 5.35, thru Feb 2014 updates) contains two structures of similar ionic liquids (different anions), an amino-containing imidazolium triflimide with N-H••••O distances of ~2.3 Å and a protonated tertiary amine variant with a N-H••••O distance of 2.038 Å, both produced by Bentivolgio et al.[19]

Thermogravimetric evaluation of N-ABILs' dehydrogenation temperature is shown in **Table 1**, along with the initial and final state of the material at room temperature. Trends in the data reveal that the dehydrogenation temperature of the N-ABILs to be largely influenced by the anion. This is likely due to both the degree of interaction the anion has with amine-borane moiety versus the formal cation, as shown in the X-ray crystal structure of **5a**, and that the anion readily alters the melting point,[20] where a liquid would more readily allow for intermolecular interactions and dehydrogenation mechanisms.[13] The data also show substituting chloride for either the OTf or NTf_2 anion lowers the dehydrogenation temperature by *ca.* 50 °C. In contrast, altering between the three cations only has a *ca.* 10 °C variance. In addition, the dehydrogenation of the triflate and bistriflimide N-ABILs occurs more gradually, allowing for easier engineering control of the dehydrogenation rate as these species zero-induction period prior to dehydrogenation akin to the AB/IL blends reported by Sneddon.[1] Compounds **5a-c** and **6a-c** display the expected exothermic dehydrogenation ranging between 348-409 K, similar to other amine-boranes,[21] and AB (onset at 360 K).[22] Mixtures of the N-ABILs with AB were dehydrogenated to assess whether readily flow-able products are formed (**Table 2**). A 1:2 mixture of compound **6c** with AB gave a liquid product at STP after heating for 18+ hours at 130 °C, producing a H_2 storing fuel blend of 2.6 wt. %. This fuel blend remains liquid below -20 °C for months (glovebox freezer), which closely approaches the DOE target of -40 °C,[23] although the material does not readily flow (we did not attempt flashing freezing of the sample followed by slow warming in DSC, although this is good idea). That said, a mixture of **6c** and AB represent an improvement over other H_2 storing material/AB blends whose freezing points are close to room temperature.[5]

The ^{11}B NMR spectra of the materials (example in **Figure 3**) reveal a characteristic quartet for the amine-borane moieties at *ca.* -19.5 ppm for all derivatives with $^{1}J_{BH}$ coupling constants of *ca.* 95.4±2.1 Hz. This is comparable to both the recently reported 3-methoxypropylamine-borane (-21 ppm),[7] and ammonia-borane (-21.6 ppm)[24] that also feature $^{1}J_{BH}$ coupling around 96 Hz. The samples were sealed in a C80 DSC cell and rapidly heated and held for *ca.* 18 h at 130 °C in an oven to release H_2. The ^{11}B NMR spectra of the dehydrogenated species revealed large, broad signals at ~34 ppm as well as a small broad hump observed at 24.5 ppm. These signals are believed to correspond to a BH signal (*ca.* 34 ppm) in a six-membered, borazine-type ring structure and a coordinatively saturated B signal (24.5 ppm) of potential $B(NR)_3$ moieties, where NR is a mixture of RNH_n (n = 0-2) reminiscent of a polyborazylene substructure.[24] In some instances, a small triplet at *ca.* -20 ppm is present indicating the formation of the diammoniate of diborane NABIL analogue, the characteristic intermediate of amine-borane dehydrogenation.[25]

Blending the N-ABILs with AB also produces broad signals at 34 and 24.5 ppm, respectively, in the ^{11}B NMR spectra of the spent products (**Figure 4**). The signal at 24 ppm becomes more prominent due to an increasing amount of strictly N-substituted boron sites. Whereas the 1:2 **6c** /AB blend is a liquid, increasing the ratio to 1:5 yields an intractable product likely due to extensive polymerization, which does not dissolve in DMSO at 110 °C. This represents the upper limit of AB blends with **6c**, the best performing N-ABIL, equating to 2.6 wt. % of usable stored H_2.

The ESI-MS data of the dehydrogenated N-ABILs reveals that primarily a cyclic product is formed, similar to species prepared by Framery.[26] Although we can not fully account for everything observed, when the anion is NTf_2, the substituted borazine structure remains intact while one of the NTf_2 anions is lost to give a positively charged species at m/z =1052 (**Figure 5**). For the N-ABIL/AB blends, the ESI-MS signals correspond to co-oligomerized N-ABIL:AB blends (**Figure 5**) such species are corroborated by the ^{11}B NMR data (**Figure 4**). These range from a single substitution of the borazine ring to species with polyborazylene sheets. Due to the positive charge of the products becoming progressively more diffuse as the oligomer becomes larger, the anion is more readily lost resulting in smaller m/z values for the oligomeric species. Also, since a charge is an inherent component of the BN species, the mildest ionization settings can be used on the already "soft" ESI-MS technique—thereby providing strong evidence that the signals are derived from the oligomers rather than sample fragmentation. This is supported by a report from Goldberg and Heinekey who reached the same conclusion while investigating the dehydrogenation products of AB:MeAB blends using an iridium catalyst.[27] Attempts to confirm the oligomers size using size-exclusion chromatography proved ultimately unsuccessful.

The quantity and purity of H_2 released from NABIL's was measured to gauge fuel capacity and compatibility with fuel cells. Previous evaluations of AB have observed borazine, diborane, and ammonia, all of which require scrubbing in order to avoid poisoning the fuel cell.[28] Gas evolution measurement of **6c** shows it to release *ca.* 0.009 grams of H_2 per gram of material, corresponding to 2.0 equivalents of H_2 evolved from the system. This was corroborated by mass-balance measurement post-dehydrogenation. When the N-ABILs are blended with AB, an increase in the usable H_2 (corresponding to 2.3 equivalents of H_2 per AB) is produced. The maximum available wt% of H_2, for a continuously fluid system, is 2.6%.

Elimination of the borazine, diborane, and ammonia side-products is crucial for engineering any H_2 based fuel cells as these contaminants will poison the catalysts or gum up the

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MEA in the case of diborane and borazine.[8, 26] In addition, previous work by the Hydrogen Storage Engineering Center of Excellence has shown increased complexity and overall system weight due to the filtration apparatus—potentially disallowing a system design from meeting the DOE targets. Evolved gas analysis (EGA) measurements reveal that **6c** releases predominantly H_2 (<1 % impurities) while the blended N-ABIL/AB materials include a small quantity of borazine at *ca.* 500 ppm with only trace quantities of diborane (*ca.* 12 ppm) and ammonia (*ca.* 3 ppm) while still maintaining the high purity profile. This demonstrates a significant improvement over pure AB which produces 20 ppm ammonia, >2200 ppm borazine, and 540 ppm diborane per mmol AB.[7] Furthermore, the neutral amine-boranes, hexylamine-borane and 3-methoxypropylamine-borane blended with AB in a 1:1/3 ratio produce comparable quantities of diborane (2, 30 ppm) and borazine (900, 120 ppm) but at only 1/6th the AB ratio to **6c**.[6] Mass-spec data (**Fig. S24, ESI**) corroborates the IR observations, showing very low quantities of NH_3 – even from AB blends.

Conclusions

In conclusion, the novel syntheses of N-ABILs present a new class of hydrogen storage materials. In some cases, the material remains in the liquid phase in both the charged and spent states, even at temperatures less than -20 °C. During this work, an anhydrous anion exchange method was developed—giving the ionic liquid community an avenue for incorporating more sensitive pendant functionalities. In addition, **6c** can be blended with 2 equivalents of AB to increase the available hydrogen storage capacity while maintaining a fluid phase by forming oligomeric products. Dehydrogenation of both the pure and blended N-ABILs readily produces H_2 with less than 1% impurities, easing the engineering requirements for automotive applications.[7] This provides a proof-of-concept that such systems may ultimately be capable of storing sufficiently dense H_2 that can be utilized in fuel cells in a new age of automotive systems.

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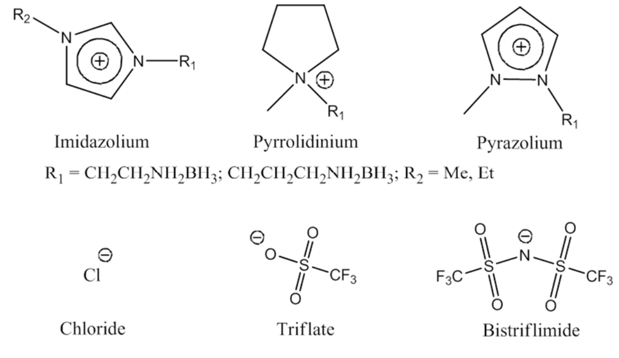
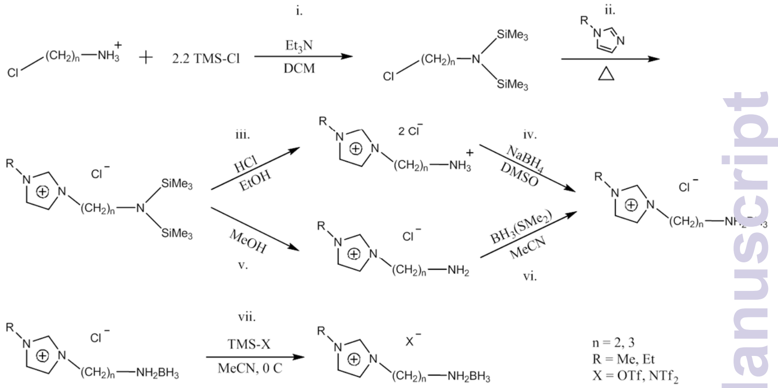


Figure 1. Cations and anions discussed in this article.



Scheme 1. Synthetic pathways to N-substituted amine-borane ionic liquids represented using imidazolium cation.

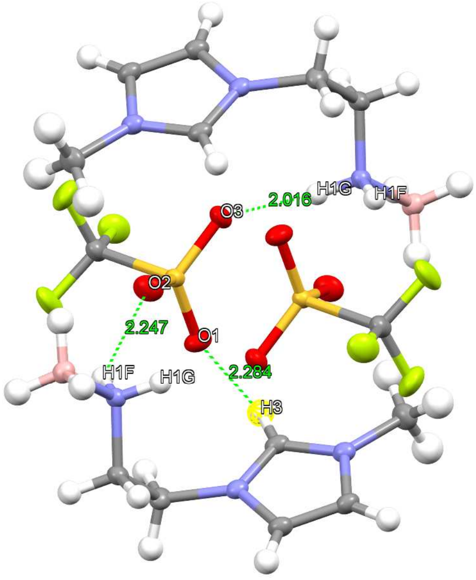


Figure 2. Unit cell N-ABIL 2 (**5a**) showing the relatively close interactions of the amine N-H bonds with the oxygens of triflate

Compound	Peak Onset Temp	Peak Max Temp	Initial State	Spent State	H_2 wt.%	^{11}B NMR [δ (Hz)]
(**4a**) MeImEtAB Cl	142.4	148.8	Solid	Solid	2.3	-19.47 (97.5)
(**5a**) MeImEtAB OTf	81.3	90.1	Solid	Thick Taffy	1.4	-19.51 (95.1)
(**4b**) EtImEtAB Cl	122.1	136.1	Solid	Solid	2.1	-19.42 (94.9)
(**5b**) EtImEtAB OTf	88.0	122.4	Oily Wax	Taffy	1.3	-19.39 (92.2)
(**4c**) EtImPrAB Cl	129.5	136.5	Solid	Solid	2.0	-19.53 (100.05)
(**5c**) EtImPrAB OTf	85.7	103.2	Liquid	Viscous Liquid	1.3	-19.39 (95.24)
(**6c**) EtImPrAB NTf_2	82.6	101.9	Liquid	Liquid	0.9	-19.43 (95.24)

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(**4d**) MePyroPrAB Cl	126.5	134.9	Solid	Solid	2.1	-19.55 (94.15)
(**5d**) MePyroPrAB OTf	80.1	109.4	Liquid	Thick Taffy	1.3	-19.51 (93.95)
(**4e**) MePyraPrAB Cl	111.9	126.3	Solid	Solid	2.1	-19.46 (95.3)

Table 1. Properties of Ionic Liquid Amine-boranes. DSC peak onset and peak max temperatures[23] (°C); initial and final phase (*ca.* 21 °C); c) wt. % of usable H_2 d) initial shift (ppm) and coupling constant.

Compound	Eq. AB	Initial State	Spent State	H_2 wt.%
(**4a**) MeImEtAB OTf	0.5	Slurry	Solid	2.1
(**5c**) EtImPrAB OTf	0.5	Slurry	Solid	1.9
(**5c**) EtImPrAB OTf	1	Slurry	Solid	2.5
(**6c**) EtImPrAB NTf_2	0.5	Liquid	Liquid	1.4
(**6c**) EtImPrAB NTf_2	1	Liquid	Liquid	1.9
(**6c**) EtImPrAB NTf_2	2	Liquid	Liquid	2.6
(**6c**) EtImPrAB NTf_2	3	Slurry	Thick Taffy	3.5
(**6c**) EtImPrAB NTf_2	5	Slurry	Solid	4.9

Table 2. Mixtures of Amine_borane Ionic Liquids and AB. Gas analysis (*vide infra*) shows that greater than 99% mass loss during dehydrogenation is due to H_2 evolution. As such, mass loss is assumed to be all H_2.

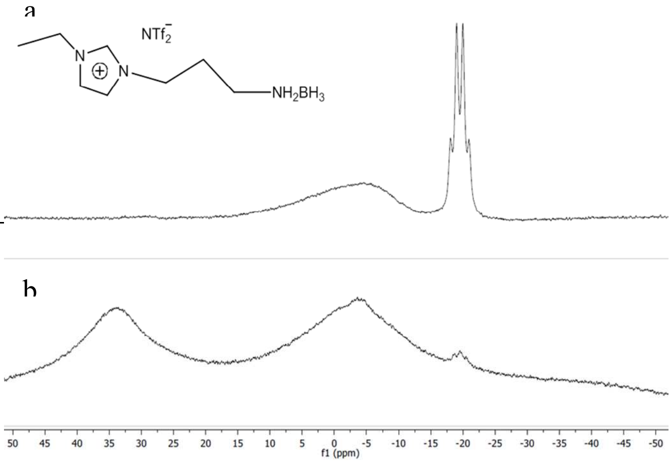

Figure 3. ^{11}B NMR in d_6-DMSO at 110 °C of (a) initial NABIL 7 (b) dehydrogenated product featuring a sp^2 BN network at *ca.* 34 ppm and a small side product of DABH at (20.5 ppm). The large broad signal from *ca.* 5 to -15 ppm is due to borosilicate glass NMR tube and instrument components.

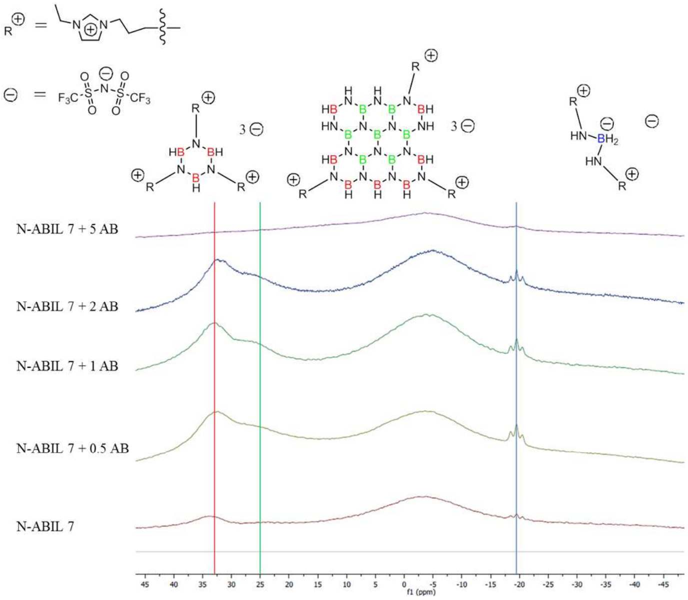

Figure 4. ^{11}B NMR spectra showing the change is signals of dehydrogenated **6c** from the unblended material up to 5 equivalents. Excessive mixing with AB produces non-fluid, intractable oligomers/polymers. The large broad signal from *ca.* 5 to -15 ppm is due to borosilicate glass NMR tube and instrument components.

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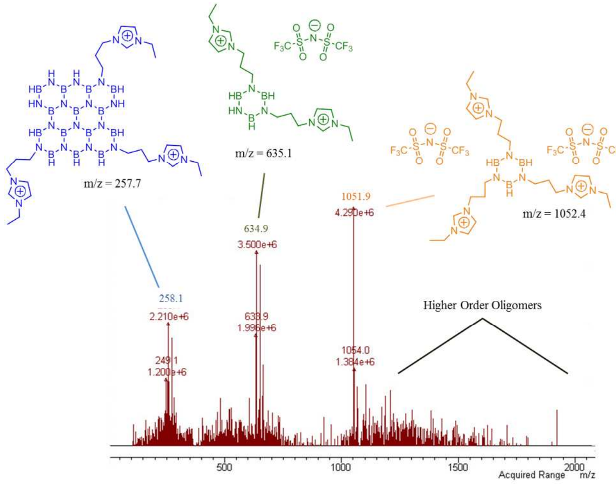

Figure 5. ESI-Mass Spectrum of **6c** mixed with 1 equivalent of AB. Signals are representative of various orders of co-oligomerization.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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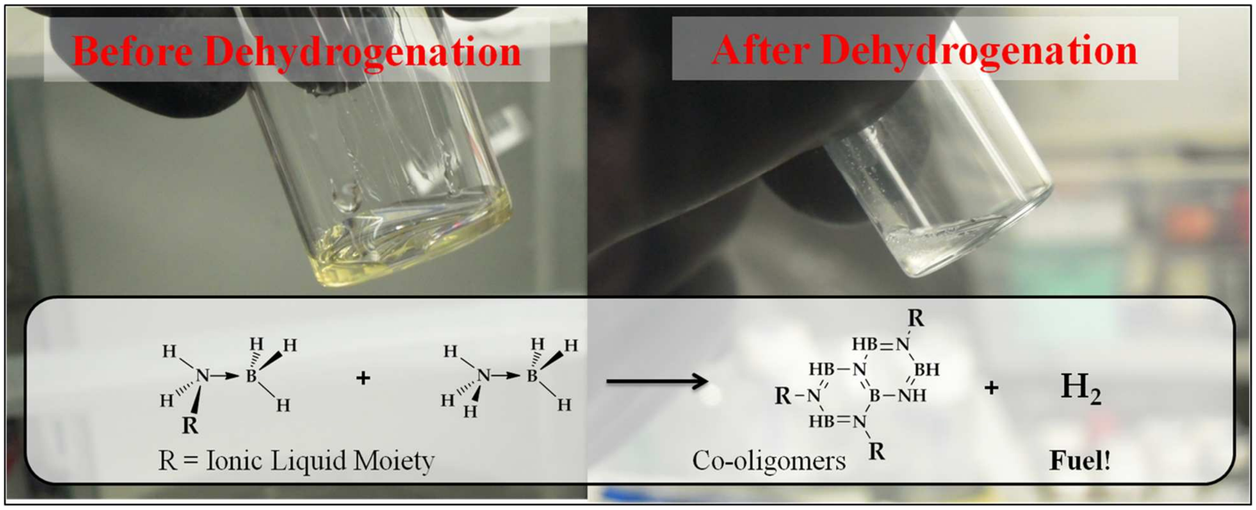

Ionic liquids incorporating an amine-borane functionality can remain liquid below -20 °C and remain liquid after H_2 release..

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