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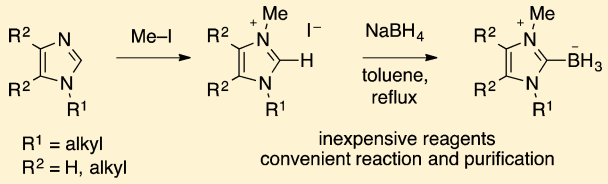
# Synthesis of 1,3-Dialkylimidazol-2-ylidene Boranes from 1,3-Dialkylimidazolium Iodides and Sodium Borohydride

Sean Gardner, Takuji Kawamoto, and Dennis P. Curran*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

Supporting Information

**ABSTRACT:** 1,3-Dialkylimidazol-2-ylidene boranes have been made in moderate yields (typically 23−53%) from the corresponding *N*-alkyl imidazole, an alkylating agent (usually MeI), and sodium borohydride ($NaBH_4$). The two-step, one-pot reaction sequence takes about 1 day to perform. The reagents are inexpensive, and the reactions are easy to conduct. The synthesis of 1,3-dimethylimidazol-2-ylidene borane has been conducted on scales up to 100 mmol and is especially convenient because the pure product can be isolated by direct recrystallization from water.




N-Heterocyclic carbene boranes (NHC-boranes) seem to strike a nice balance, often being stable and easy to isolate yet still manifesting a valuable reactivity profile. In addition to exhibiting fundamentally interesting organoboron chemistry, NHC-boranes are useful reagents in both small molecule and macromolecule synthesis.[1]

Among the various classes of NHC-boranes, the most common class is imidazol-2-ylidene boranes **3**. These are generally made by deprotonation of the corresponding imidazolium salt **1** by a strong base to make the N-heterocyclic carbene **2**, followed by addition of a reactive borane source, as shown in Figure 1a.[2] Typical strong bases are potassium *tert*-butoxide ($KO^tBu$) and sodium hexamethyldisilazide ($NaN(SiMe_3)_2$). Borane sources are complexes such as borane·tetrahydrofuran ($BH_3$·THF), borane·dimethyl sulfide ($BH_3$·$SMe_2$), and borane·triethylamine ($BH_3$·$NEt_3$). The use of such bases and boranes requires careful exclusion of air and water.

Needing increasing quantities of NHC-boranes, we began to consider procedures for synthesis that would involve less expensive reagents and more convenient reaction conditions. The preferred borane source for such reactions is sodium borohydride ($NaBH_4$) because of its low cost, stability, and ease of handling compared to ligated boranes.

As shown in Figure 1b, addition of $NaBH_4$ to imidazolium halide salt **1**/$X^-$ can result in ion exchange to give an imidazolium borohydride **1**/$BH_4^-$ and NaX. Some imidazolium borohydrides are already known to be stable at ambient temperature,[3] so onward reaction may require heating. If the borohydride reacts with the imidazolium salt by expressing its hydride basicity, then an N-heterocyclic carbene **2** and borane are formed. This Lewis acid/base pair should collapse to NHC-borane **3**. Thus, borohydride potentially fills roles as both base and borane source. The only byproducts of the proposed reaction are NaX (from the ion exchange) and dihydrogen (from the acid/base reaction). While the focus of our work is NHC-borane synthesis, such reactions may also have use in hydrogen storage/generation.[3,4]

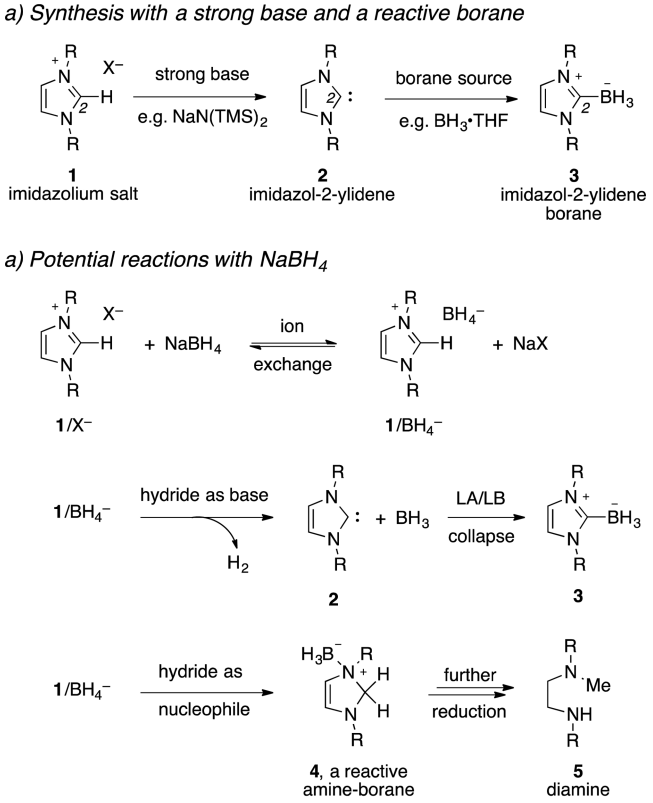



**Figure 1.** Synthetic approaches to NHC-boranes.

Sodium borohydride can also express hydride nucleophilicity of course, so reduction of the salt **1** is a competing reaction. Yamaguchi and Ito reported that lithium triethylborohydride

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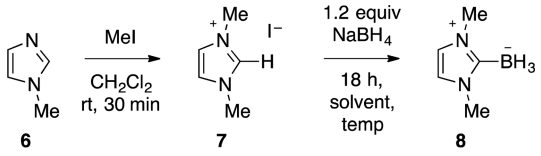
($LiBEt_3H$) reacted with two 1,3-diarylimidazolium chlorides to give NHC-triethylboranes (NHC-$BEt_3$) rather than salt reduction products.[5a] However, closer precedent is more discouraging; the reaction of 1,3-dialkylimidazolium iodides **1**/$I^-$ with excess sodium borohydride in ethanol is a good way to make *N*-methyl-*N*,*N*′-dialkyl diamines **5**.[5b] These reactions probably occur by hydride addition to C2 of the imidazolium salt to form a dihydroimidazole-borane complex such as **4**. This is in essence a reactive borane, so further reduction would follow. Amine-boranes ($R_3N{\cdot}BH_3$) have been made by reactions of ammonium salts with sodium borohydride;[6] however, in such cases there is no hydride reduction reaction to compete with the acid/base reaction.

We first targeted 1,3-dimethylimidazol-2-ylidene borane **8**[2b,7] (Scheme 1) because it is a stable white solid that has one of the lowest molecular weights of any NHC-borane (110 g $mol^{-1}$). Therefore, it is one of the most attractive reagents.[8] Compared to the known reductions to imidazolium salts to diamines,[5] the approach was to reduce the amount of borohydride and move out of protic media.

**Scheme 1. Typical Results from Three Successive Procedures to Make 8**




| expt | solvent | temp | workup | # recyrst. | yield[a] |
|---|---|---|---|---|---|
| 1 | none | 105 °C[b] | liq-liq[c] | 1 | 30% |
| 2 | dioxane | 101 °C[d] | liq-liq[e] | 3 | 27% |
| 3 | toluene | 105 °C[d] | decant | 1 | 53% |

[a]Isolated yield based on *N*-methylimidazole after water crystallization(s). [b]Bath temperature. [c]$CH_2Cl_2$/water extraction. [d]Solvent bp. [e]$CHCl_3$/water extraction.

Prior to conducting the sodium borohydride experiments, we looked at various known and new methods for purification of **8**. This can be isolated by flash chromatography, precipitated from polar solvents with hexane,[2b] sublimed (bath temp 90−100 °C, 2 Torr), or recrystallized from nonpolar solvents such as toluene. However, the preferred method was recrystallization from water. This is because the quality and appearance of the product are excellent (fine needles are obtained) and because the unreacted reagents (salts) and reaction byproducts (fully or partially reduced diamines) are all expected to be more water-soluble than **8** itself. That **8** can be recrystallized from refluxing water under standard laboratory conditions (air atmosphere) is a further testament to its stability.

Scheme 1 shows the results of three successive procedures that were used in multiple preparative runs. The salt precursor, 1,3-dimethylimidazolium iodide **7**, is hygroscopic and was best made in situ by reaction of 1-methylimidazole **6** and iodomethane (1.2 equiv) in dichloromethane.[9] After 1 h at room temperature, the volatiles were removed by rotary evaporation and the residual salt was used directly without transfer. The reactions to make **8** were all conducted with 1.2 equiv of $NaBH_4$ for 18 h at roughly the same temperature (101−105 °C).

An initial successful procedure involved simply heating the salt **7** and sodium borohydride in an oil bath at 105 °C (Scheme 1, experiment 1). Foaming began as the salt melted and continued for some hours. After 18 h, the cooled crude product (a white, glue-like substance) was partitioned in a standard liquid−liquid extraction between dichloromethane and water. The dichloromethane phase was evaporated, and the resulting solid (already mostly **8**) was recrystallized once from water to give pure **8** in 30% yield. In the first experiment, we were excited about the foaming because it meant that hydrogen gas was generated, but we quickly came to rue it. This procedure was run on scales up to about 10 mmol and then scrapped.

A second-generation procedure involved conducting the reaction in refluxing 1,4-dioxane (experiment 2). There was still some foaming, but it was much more manageable than the neat experiments. Simple use of an oversized flask prevented the bubbles from percolating into the reflux condenser. Evaporation of the dioxane, partitioning between chloroform and water, and evaporation of the chloroform gave a crude product that was again mostly **8**, but in a less pure state than from the neat reaction. Three recrystallizations from water brought the product to high purity in 27% yield.

The dioxane procedure was used on scales up to 250 mmol. This procedure addressed the foaming problem with the neat reaction, but the crude product was not as pure, necessitating three recrystallizations rather then one.

An improved result came when the reaction was conducted in refluxing toluene (experiment 3). Heating of **7** and sodium borohydride in toluene quickly formed a second ionic liquid phase as the salt melted but did not dissolve in the toluene. After heating for 18 h, the residual glue-like ionic phase had all adhered to the inside wall of the flask, making liquid−liquid extraction superfluous. The hot toluene was simply decanted, cooled, and the evaporated to give a crude product that was surprisingly good quality NHC-borane **8** in about 73% yield.[10] This sample was recrystallized once from water to give analytically pure **8** in 53% yield.

This two-step, one-pot procedure is a reliable way to make **8** in about 50% overall yield from 1-methylimidazole, iodomethane, and sodium borohydride. There is no aqueous extraction or chromatography, and the purity of the product is excellent. Reactions have been conducted on scales ranging from a few mmol up to about 100 mmol with comparable results.

We then looked briefly at the scope of the procedure under the standard conditions with in situ salt formation. Several of the other salts are not hygroscopic, but for consistency they were made prior to use with the overall yields given from the starting imidazole. The structures of the NHC-boranes made by this procedure are shown in Figure 2. Five 1,3-dialkylimidazolium salt precursors all provided NHC-borane products, though the purification methods had to be changed because none of the products **9**−**13** was very soluble in hot water. The yields are

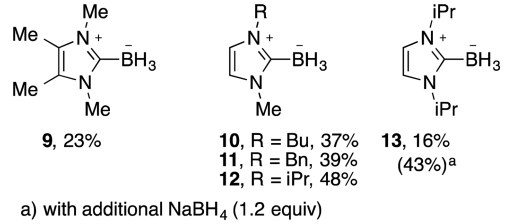



**Figure 2.** Scope: structures and yields (10 mmol scale) of di- and tetraalkylimidozol-2-ylidene boranes made in two steps from the corresponding imidazoles.



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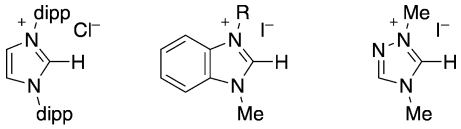
reported from 10 mmol scale reactions, and sample purities are high (see copies of spectra in Supporting Information).

1,3,4,5-Tetramethylimidazol-2-ylidene borane **9** was isolated in 23% yield after recrystallization of the crude product from 10% ethanol/water. The corresponding 1-benzyl and 1-butyl-3-methyl imidazol-2-ylidine boranes **10** and **11** were isolated by flash chromatography (40−50% EtOAc/hexane) in yields of 37% and 39%, respectively. 1-Isopropyl-3-methylimidazol-2-ylidene borane **12** was precipitated from ethanol with water in 48% yield. Finally, crude 1,3-diisopropylimidazol-2-ylidene borane **13** was purified simply by washing with water to give a good quality product according to NMR analysis. The isolated yield from the standard conditions was only 16%, but the yield was increased to 43% by addition of more sodium borohydride (1.2 equiv) throughout the reaction course (see Supporting Information).

Limitations of the procedure were also encountered (Figure 3). Perhaps not surprisingly, imidazolium salts with melting




**14** **15**, R = Bu, Me **16** (5% yield)

**Figure 3.** Limitations: structures of salts that provided little or none of the corresponding NHC-borane products.

points above the boiling point of toluene did not provide NHC-boranes. For example, 1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride **14** (mp = >250 °C) did not appear to react at all under the conditions. If the salt does not melt, then there is no ionic liquid phase and the imidazolium salt and sodium borohydride do not intermix. Reactions with several benzimidazolium salts **15** were also unsuccessful. Finally, reaction with triazolium salt **16** provided the corresponding NHC-borane, but only in 5% yield (on 1 mmol scale).

In summary, 1,3-dialkylimidazol-2-ylidene boranes can be made in moderate yields (23−53%) from the corresponding *N*-alkyl imidazole, an alkylating agent RI (often MeI), and sodium borohydride in a simple two-step, one-pot reaction sequence that takes about 1 day to perform. The yields are somewhat lower than in case of the current conventional method (strong base and reactive borane), but this detraction is more than offset by the lower cost of the sodium borohydride and by the ease of reaction (no oxygen- or water-sensitive species) and purification.

## EXPERIMENTAL SECTION

**General Procedure for Salt Synthesis.** Methyl iodide (1.2 equiv) was added in portions to a dichloromethane solution of the corresponding imidazole (5 M) over the course of 15−30 min (**Caution**: *exothermic reaction.*) The reaction mixture was allowed to stir for 1 h, after which the mixture was concentrated and dried under vacuum to give the salt sample. The salt quality was checked by a $^1$H NMR spectrum, and then the sample was used directly.

**1,3,-Dimethyl-1*H*-imidazol-3-ium Iodide 7:**[9] Prepared by the general procedure with 1-methylimidazole (4.1 g, 50 mmol) to afford **7** (11.2 g, 100%) as a slightly yellow solid; mp 66−69 °C: $^1$H NMR (500 MHz, MeOD) 8.89 (s, 1H), 7.57 (s, 2H), 3.94 (s, 6H) ppm; $^{13}$C NMR (126 MHz, MeOD) 138.7 (br), 125.0, 36.7 ppm. HRMS (ESI+): calcd for $C_5H_9N_2^+$ $[M]^+$, 97.0760; found, 97.0764.

**1,3,4,5-Tetramethyl-1*H*-imidazol-3-ium Iodide.** This was prepared according to literature procedures[11] and was the major component of a 77:23 mixture with 1,2,3,4,5-pentamethyl-1*H*-imidazol-3-ium iodide. This side product is the result of overalkylation at C2. It is water-soluble and cannot form an NHC-borane, so it was not removed prior to the $NaBH_4$ reduction: $^1$H NMR (500 MHz, $CDCl_3$) 10.19 (br s, 1H), 3.90 (s, 6H), 2.26 (s, 6H) ppm; $^{13}$C NMR (126 MHz, DMSO-$d_6$) 134.6, 126.7, 33.3, 7.8 ppm. HRMS (ESI+): calcd for $C_7H_{13}N_2^+$ [M], 125.1073; found, 125.1075.

The minor 1,2,3,4,5-pentamethyl-1*H*-imidazol-3-ium iodide[12] product exhibits the following data: $^1$H NMR (500 MHz, $CDCl_3$) 3.61 (s, 6H), 2.58 (s, 3H), 2.21 (s, 6H) ppm; $^{13}$C NMR (126 MHz, DMSO-$d_6$) 142.5, 124.9, 31.9, 10.0, 8.72 ppm. HRMS (ESI+): calcd for $C_8H_{15}N_2^+$ $[M]^+$, 139.1230; found, 139.1229.

**1-Butyl-3-methyl-1*H*-imidazol-3-ium Iodide.** This was prepared according to a literature procedure[13] with 1-methylimidazole (1.64 g, 20.0 mmol) and 1-iodobutane (3.68 g, 20.0 mmol) to afford the salt (5.32 g, 100%) as a red oil; $^1$H NMR (500 MHz, $CDCl_3$) 10.05 (s, 1H), 7.53 (t, $J$ = 2 Hz, 1H), 7.45 (t, $J$ = 2 Hz, 1H), 4.33 (t, $J$ = 7.5 Hz, 2H), 4.11 (s, 3H), 1.92 (quin, $J$ = 7.5 Hz, 2H), 1.39 (sextet, $J$ = 7.5 Hz, 2H), 0.96 (t, $J$ = 7.5 Hz, 3H) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) 137.0, 123.8, 122.3, 50.11, 37.2, 32.2, 19.6, 13.6 ppm. HRMS (ESI+): calcd for $C_8H_{15}N_2^+$ $[M]^+$, 139.1230; found, 139.1230.

**1-Benzyl-3-methyl-1*H*-imidazol-3-ium Iodide.** This was prepared by the general procedure with 1-benzylimidazole (4.00 g, 25.3 mmol) to afford the salt (7.57 g, 100%) as a slightly yellow solid; mp 88−91 °C: $^1$H NMR (500 MHz, DMSO-$d_6$) 9.23 (s, 1H), 7.80 (t, $J$ = 1.5 Hz, 1H), 7.72 (t, $J$ = 1.5 Hz, 1H), 7.43−7.37 (m, 5H), 5.43 (s, 2H), 3.86 (s, 3H) ppm; $^{13}$C NMR (126 MHz, DMSO-$d_6$) 136.6, 134.8, 128.9, 128.7, 128.2, 123.9, 122.3, 51.8, 35.9 ppm. HRMS (ESI+): calcd for $C_{11}H_{13}N_2^+$ $[M]^+$, 173.1073; found, 173.1074.

**1-Isopropyl-3-methyl-1*H*-imidazol-3-ium Iodide.** This was prepared by the general procedure with 1-isopropylimidazole (1.10 g, 10.0 mmol) to afford the salt (2.52 g, 100%) as a yellow solid; mp 54−57 °C: $^1$H NMR (500 MHz, $CDCl_3$) 10.06 (s, 1H), 7.56 (d, $J$ = 1.5 Hz, 1H), 7.52 (d, $J$ = 1.5 Hz, 1H), 4.82 (sep, $J$ = 7 Hz, 1H), 4.11 (s, 3H), 1.62 (d, $J$ = 7 Hz, 6H) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) 135.9, 123.9, 120.4, 53.6, 37.2, 23.3 ppm. HRMS (ESI+): calcd for $C_7H_{13}N_2^+$ $[M]^+$, 125.1073; found, 125.1074.

**1,3-Diisopropyl-1*H*-imidazol-3-ium Iodide.** 1-Isopropylimidazole (6.79 g, 60.6 mmol), 2-iodopropane (15.71 g, 92.5 mmol), and dichloromethane (12 mL) were combined in a round-bottom flask fitted with a water condenser and heated to 50 °C for 18 h. The mixture was concentrated to a crude oil and added to a flask containing $Et_2O$ (100 mL) while being rapidly stirred to precipitate the product from the mixture. The solid was collected by vacuum filtration to afford the salt (16.23 g, 94%) as a pale yellow solid; mp 100−103 °C: $^1$H NMR (500 MHz, $CDCl_3$) 10.40 (s, 1H), 7.44 (d, $J$ = 1.5 Hz, 2H), 4.98 (sep, $J$ = 6.5 Hz, 2H), 1.65 (d, $J$ = 6.5 Hz, 12H) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) 135.1, 120.0, 53.6, 23.4 ppm. HRMS (ESI+): calcd for $C_9H_{17}N_2^+$ $[M]^+$, 153.1386; found, 153.1386.

**Caution.** *Carbene-boranes are bases and reducing agents and should be stored, handled, and disposed as such. NHC-boranes are potentially hypergolic (can ignite spontaneously) when treated with strong oxidants such as nitric acid. An oversized flask (we used ∼5 times the solvent volume) is recommended to help prevent bubbles from reaching the reflux condenser. Proper precautions must be taken to ventilate the hydrogen gas that is released.*

**General Procedure for NHC-Borane Synthesis.** Sodium borohydride (1.2 equiv) was added to a round-bottom flask containing imidazolium salt (1 equiv) and toluene (1 mL/mmol imidazolium). The flask was fitted with a cold water condenser and placed in an oil bath at 125−130 °C for 18−24 h. The hot reaction solvent was cautiously decanted from the insoluble mixture, and the remaining residue was extracted with hot toluene (2 × 1 reaction volume). The organic extracts were combined, concentrated, and purified as described.

**(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)trihydroborate (8):**[7b] The general procedure was used with 50 mmol of salt **7** and 60 mmol $NaBH_4$. The crude product was already of good purity (4.04 g, 73%, mp 128−134 °C), and was further recrystallized from water (14 mL water per g crude product) to give the pure product as fine white crystals (2.93 g, 53%); mp 138−139 °C: $^1$H NMR (500 MHz, $CDCl_3$) 1.02 (m, 3H, $J_{11_{B-H}}$ = 86.5 Hz, $J_{10_{B-H}}$ = 29.0 Hz), 3.74 (s, 6H), 6.80 (s, 2H) ppm; $^{13}$C



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NMR (126 MHz, $CDCl_3$) 172.0 (q, $J_{B-C}$ = 50.3 Hz), 120.0, 35.9 ppm; $^{11}$B NMR (160 MHz, $CDCl_3$) − 37.5 (q, $J_{H-B}$ = 86.4 Hz) ppm; IR (NaCl, thin film) 3133, 3167, 3051, 2985, 2953, 2275, 1574, 1479, 1445, 1266, 1232, 1187, 1122, 876, 736, 702, 655 $cm^{-1}$. HRMS (ESI): *m*/*z* for $C_5H_{10}BN_2$ $[M]^+$, calcd 109.0932, found 109.0935. Anal. calcd for $C_5H_{11}BN_2$: C, 54.61; H, 10.08; N 25.47; Found: C, 54.57; H, 10.34; N, 25.75.

**(1,3,4,5-Tetramethyl-1*H*-imidazol-3-ium-2-yl)trihydroborate (9):**[14] The general procedure was followed with 10 mmol (corrected for purity) of the imidazolium salt. The crude material was recrystallized from 10% v/v EtOH/$H_2O$ (25 mL) to afford 321 mg of **9** (23%) as a white solid; mp 137−140 °C: $^1$H NMR (500 MHz, $CDCl_3$) 3.62 (s, 6H), 2.11 (s, 6H), 1.04 (q, $J_{B-H}$ = 86 Hz, 3H) ppm; $^{11}$B NMR (160 MHz, $CDCl_3$) −36.9 (q, $J_{H-B}$ = 86 Hz) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) 169.5 (q, $J_{B-C}$ = 53 Hz), 123.1, 32.5, 8.8 ppm. HRMS (ESI+): calcd for $C_7H_{14}BN_2^+$ $[M-H]^+$, 137.1245; found, 137.1241.

**(1-Butyl-3-methyl-1*H*-imidazol-3-ium-2-yl)trihydroborate (10).** The general procedure was followed with 10 mmol of the imidazolium salt prepared in situ. The crude material was purified by column chromatography (50% EtOAc/hexane) to afford **10** (596 mg, 39%) as a colorless oil: $^1$H NMR (500 MHz, $CDCl_3$) 6.81 (d, *J* = 1.5 Hz, 1H), 6.80 (d, *J* = 1.5 Hz, 1H), 4.10 (t, *J* = 7.5 Hz, 2H), 3.73 (s, 3H), 1.76 (sep, *J* = 7.5 Hz, 2H), 1.36 (sextet, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 2H), 1.02 (q, $J_{B-H}$ = 86 Hz, 3H) ppm; $^{11}$B NMR (160 Hz, $CDCl_3$) −37.4 (q, $J_{H-B}$ = 86 Hz) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) 170.8 (q, $J_{B-C}$ = 52 Hz), 119.8, 118.6, 48.1, 35.4, 31.8, 19.3, 13.3 ppm. HRMS (ESI+): calcd for $C_8H_{16}BN_2^+$ $[M-H]^+$, 151.1401; found, 151.1398.

**(1-Benzyl-3-methyl-1*H*-imidazol-3-ium-2-yl)trihydroborate (11).** The general procedure was followed with 10 mmol of the imidazolium salt prepared in situ. The crude material was purified by column chromatography (40% EtOAc/hexane) to afford **11** (691 mg, 37%) as a white solid; mp 83−84 °C: $^1$H NMR (500 MHz, $CDCl_3$) 7.38−7.29 (m, 5H), 6.79 (d, *J* = 2 Hz,1H), 6.72 (d, *J* = 2 Hz, 1H), 5.33 (s, 2H), 3.78 (s, 3H), 1.16 (q, $J_{B-H}$ = 86 Hz, 3H) ppm; $^{11}$B NMR (160 MHz, $CDCl_3$) − 37.1 (q, $J_{H-B}$ = 86 Hz) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) 172.3 (q, $J_{B-C}$ = 54 Hz), 136.1, 128.9, 128.3, 120.6, 118.7, 52.1, 36.0 ppm. HRMS (ESI+): calcd for $C_{11}H_{14}BN_2^+$ $[M-H]^+$, 185.1245; found, 185.1241.

**(1-Isopropyl-3-methyl-1*H*-imidazol-3-ium-2-yl)trihydroborate (12):**[7b] The general procedure was followed with 10 mmol of the imidazolium salt. The crude material was dissolved in EtOH (5 mL), and then water (50 mL) was added to precipitate the product. The solid was collected by vacuum filtration to afford **12** (669 mg, 48%) as a white solid; mp 54−57 °C: $^1$H NMR (500 MHz, $CDCl_3$) 6.90 (d, *J* = 2 Hz, 1H), 6.82 (d, *J* = 2 Hz, 1H), 5.08 (quin, *J* = 6.5 Hz, 1H), 3.72 (s, 3H), 1.40 (d, *J* = 6.5 Hz, 6H), 1.04 (q, $J_{B-H}$ = 86 Hz, 3H) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) 170.7 (q, $J_{B-C}$ = 53 Hz), 120.5, 114.7, 49.6, 35.7, 22.7 ppm. HRMS (ESI+): calcd for $C_7H_{14}BN_2^+$ $[M-H]^+$, 137.1245; found, 137.1241.

**(1,3-Diisopropyl-1*H*-imidazol-3-ium-2-yl)trihydroborate (13):.**[2a,14] The general procedure was followed with 10 mmol of the imidazolium salt. The crude solid was purified by washing with portions of cold water (2 × 10 mL) to afford **13** (259 mg, 16%) as a white solid; mp 121−123 °C.

In a separate experiment on a 39.5 mmol scale, additional sodium borohydride was added in two separate 0.6 equiv portions (at about 24 and 36 h) until the imidazolium peak of $H^2$ at 10.4 ppm in $^1$H NMR spectrum ($CDCl_3$) was no longer detectable. After 48 h, a 43% yield was obtained: $^1$H NMR (500 MHz, $CDCl_3$) 6.92 (s, 2H), 5.14 (sep, *J* = 7 Hz, 2H), 1.40 (d, *J* = 7 Hz, 12 H), 1.07 (q, $J_{B-H}$ = 86 Hz, 3 H) ppm; $^{11}$B NMR (160 MHz, $CDCl_3$) −37.3 (q, $J_{H-B}$ = 86 Hz) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) 169.7 (q, $J_{B-C}$ = 52 Hz), 115.1, 49.3, 22.9 ppm. HRMS (ESI+): calcd for $C_9H_{18}BN_2^+$ $[M-H]^+$, 165.1558; found, 165.1555.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01682.

Copies of NMR spectra of all products (PDF)

## ■ AUTHOR INFORMATION


### Corresponding Author

*E-mail: curran@pitt.edu.


### Notes

The authors declare no competing financial interest.

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