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## COMMUNICATION

# Synthesis of a Diboryl-N-Heterocycle and its Conversion to a Bidentate Cationic Lewis Acid

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**Sequential reaction of 2-lithio-1-methylimidazole with 9-borabicyclo[3.3.1]nonane (9-BBN) dimer and 9-Cl-9-BBN yields diboryl-N-heterocycle  $C_4H_5N_2(H)(BC_8H_{14})_2$  (1). Reaction of 1 with  $I_2$  results in the net substitution of chelated hydride for a singly boron-bound iodide to produce  $C_4H_5N_2(I)(BC_8H_{14})_2$  (2). Conversely, reaction of 1 with  $[Ph_3C][B(C_6F_5)_4]$  results in the formation of the bidentate cationic Lewis acid  $[(C_4H_5N_2)(BC_8H_{14})_2][B(C_6F_5)_4]$  (3). Compound 3 catalyzes the hydrogenation of N-benzylidene-tert-butylamine at room-temperature.**

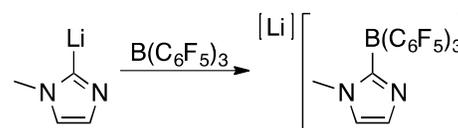
Highly electrophilic Lewis acids provide access to an ever-growing array of small molecule activations and catalytic processes. Indeed, the reactivity of bulky main-group Lewis acids and bases with small molecules in what have become known as frustrated Lewis pairs (FLPs) has allowed the emergence of metal-free avenues for hydrogenation catalysis, hydroamination and  $CO_2$  reduction.<sup>1-7</sup> Although base variation in FLPs has been extensively studied, Lewis acid variation offers a distinct opportunity to uncover new reactivity.

Though rarely encountered in synthetic chemistry, neutral<sup>8-21</sup> and cationic<sup>22-27</sup> bidentate Lewis acids often exhibit striking reactivity. In FLP chemistry,  $C_{10}H_6(B(C_6F_5)_2)_2$  has been utilized by Berke and co-workers<sup>28</sup> for hydrogen activation and hydrogenation catalysis. Furthermore, bidentate Lewis acids have been used for  $CO_2$  capture and reduction both stoichiometrically<sup>29, 30</sup> and catalytically.<sup>31</sup> Moreover, bidentate dicationic diphosphorous Lewis acids have recently been employed in FLPs capable of C-H and H-H bond activations.<sup>32, 33</sup> Certainly, the paucity of reports regarding bidentate Lewis acids can be attributed to their sensitivity and challenging syntheses. Therefore, straightforward syntheses will assure swift developments in this emerging field.

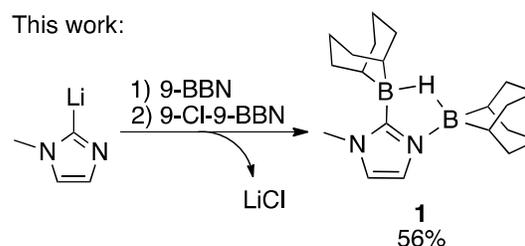
Borenium ions are three-coordinate boron cations.<sup>34-36</sup> The Lewis acidity of these compounds is enhanced, often greatly, by their cationic charge. Currently, the study of borenium ions

in catalytic roles has emerged as a burgeoning field.<sup>34, 37-50</sup> Our group reported FLP hydrogenation catalysis using an N-heterocyclic carbene (NHC) stabilized borenium ion.<sup>51</sup> Following our account, Wildgoose and Ashley and co-workers demonstrated the use of this compound for the electrocatalytic oxidation of  $H_2$ ,<sup>52</sup> while borenium mediated hydrogenations have been broadened by both Crudden and co-workers<sup>53</sup> and our group.<sup>54</sup> The latter two reports exploited the straightforward and flexible syntheses of NHC-borenium ions from readily available and robust NHC-boranes<sup>55, 56</sup> to gain access to an array of structurally and electronically diverse NHC-borenium catalysts. Synthetic ease is a key advantage of utilizing NHC-borenium ions in FLPs as an alternative to the more pervasive, yet synthetically challenging, neutral perfluoroarylboranes. Accordingly, this characteristic prompted us to investigate NHC-borenium ions as a platform for bidentate Lewis acid synthesis.

Erker, 2002:

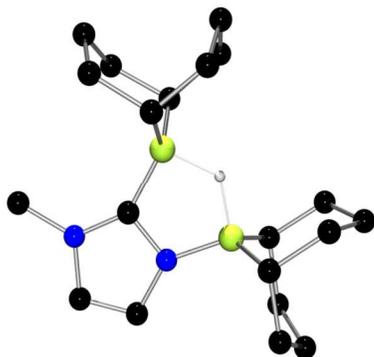


This work:



**Scheme 1** Addition of boranes to 2-lithio-1-methylimidazole.

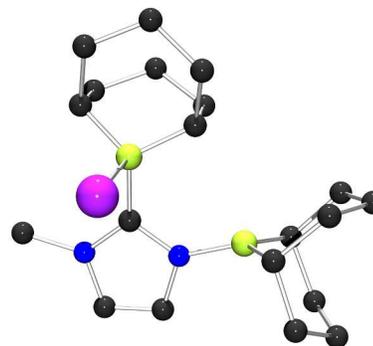
Erker and co-workers have demonstrated the synthesis of lithium borate salts through the addition of boranes to 2-lithio-1-methylimidazole (Scheme 1).<sup>57</sup> We reasoned that such a lithium borate species could be intercepted with an additional boron electrophile to synthesize a diboryl-N-heterocycle. To this end, 2-lithio-1-methylimidazole was treated with 0.5 equivalents of 9-BBN dimer followed by stoichiometric 9-Cl-9-BBN to give the hydride-bridged diboryl-N-heterocycle **1** (Scheme 1). The product was isolated via recrystallization in 56% yield and exhibits a single broad resonance by <sup>11</sup>B-NMR spectroscopy at 15.1 ppm despite two inequivalent boron centers. This chemical shift is intermediate between those generally observed for four-coordinate donor adducts of 9-BBN and three-coordinate donor-stabilized borenium ions.<sup>53, 58-60</sup> These data suggest the possibility of hydride bridging between the two boron centers of **1**. This notion was confirmed by X-ray crystallography (Figure 1). The B<sub>C<sub>NHC</sub></sub> and BN bond lengths of **1** are 1.610(5) Å and 1.562(5) Å, respectively. This B<sub>C<sub>NHC</sub></sub> bond length is intermediate to those observed for related NHC-9-BBN compounds and corresponding borenium salts [NHC-9-BBN][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].<sup>53, 54</sup> Thus, despite the presumed electronic difference between N and C donors of **1**, these data suggest no apparent preference of hydride for either boron center. This behaviour mimics the hydride chelation and corresponding NMR behaviour of closely related pyrazole 9-BBN analogues reported by Yalpani *et. al.*<sup>62</sup>



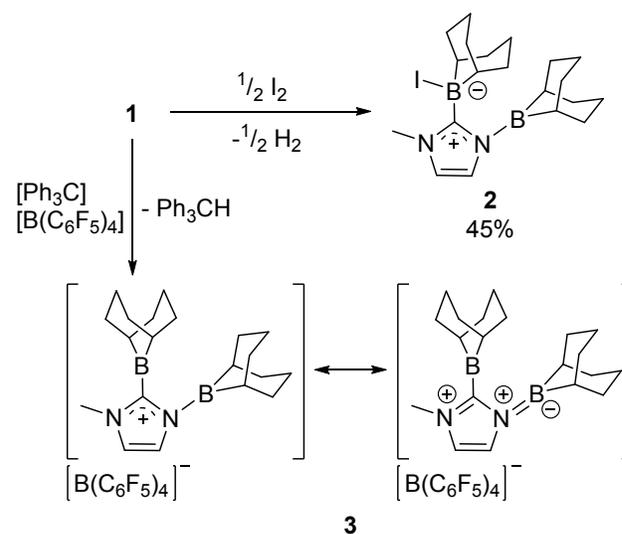
**Figure 1** POV-ray depiction of **1**. N: blue; C: black; B: yellow-green. H: gray. H-atoms except B-H are omitted for clarity.

Curran and Lacôte and co-workers have described the oxidation of NHC-BH<sub>3</sub> compounds with iodine to yield corresponding products of the form NHC-BH<sub>2</sub>I.<sup>62</sup> Using the same approach, treatment of **1** with 0.5 equivalents iodine in toluene results in the immediate evolution of gas and a loss of colour. The product **2** can be obtained as crystals from toluene solution in 45% yield (Scheme 2). The <sup>11</sup>B-NMR spectrum of **2** shows broad resonances at 67.6 and 8.50 ppm indicative of three-coordinate and four-coordinate boron environments, respectively. The structure of **2** was unambiguously confirmed by X-ray crystallography and indicates a net substitution of hydride in **1** for iodide (Figure 2). The N-bound boron center adopts near-planar geometry with a sum of bond angles of 356.1°. A B-I bond length of 2.470(2) Å is observed as well as a

B-N bond length of 1.521(2) Å and a B-C<sub>NHC</sub> bond length of 1.598(3) Å. Presumably due to its size, iodine is not "chelated" between the two boron centers as seen for hydride in **1**. Rather, iodide is preferentially bonded to the C<sub>NHC</sub>-bound boron center with the other boron center left uncoordinated in a "zwitterionic borenium" arrangement.



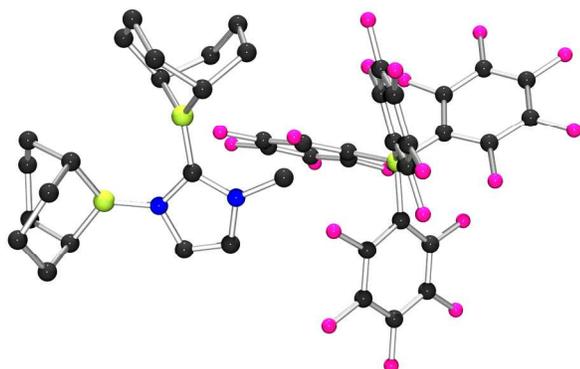
**Figure 2** POV-ray depiction of **2**. N: blue; C: black; B: yellow-green. I: purple. H-atoms are omitted for clarity.



**Scheme 2** Synthesis of compounds **2** and **3**.

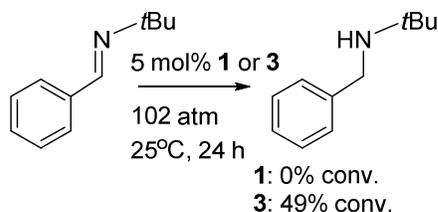
Treatment of **1** with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at room temperature in CD<sub>2</sub>Cl<sub>2</sub> results in the stoichiometric generation of triphenylmethane by <sup>1</sup>H-NMR spectroscopy. <sup>11</sup>B-NMR spectroscopy shows two broad downfield resonances indicative of two three-coordinate boron environments and a sharp upfield singlet corresponding to [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>. These data suggest quantitative hydride abstraction from **1** to give the cationic diboryl-N-heterocycle **3** (Scheme 2). Crystals suitable for X-ray analysis were obtained from the NMR-scale reaction and the X-ray structural solution supports the suggested formulation (Figure 3). Both boron centers are three-coordinate with the sums of bond angles about B<sub>N</sub> and B<sub>C</sub> found to be 358.6° and 359.3°, respectively. A B-N bond length of 1.468(5) Å and a B-C<sub>NHC</sub> bond length of 1.587(5) Å were observed. The latter bond length is similar to B-C<sub>NHC</sub> bond lengths of other [NHC-BBN]<sup>+</sup> ions.<sup>53, 54</sup> The short B-N bond

length observed for **3** together with small  $C_{\text{NHC}}\text{-N-B-C}_{\text{BBN}}$  dihedral angles (eg. a  $13.2^\circ$  dihedral angle measured in **3** greatly contrasts with a  $89.4^\circ$  dihedral angle measured in **2**) infer significant resonance contribution from a non-aromatic structure bearing a BN double bond (Scheme 2). This assessment is further supported by the significant discrepancy between the N-heterocycle N-C<sub>B</sub> bond lengths of **3**, which are 1.367(5) Å and 1.334(5) Å, respectively. These data indicate a more localized bonding character than anticipated for a pseudo-aromatic description.



**Figure 3** POV-ray depiction **3** N: blue; C: black; B: yellow-green. F: pink. H-atoms are omitted for clarity.

In order to probe the utility of **3** as a Lewis acid in FLP chemistry, we attempted the FLP catalyzed hydrogenation of an imine.<sup>63</sup> To our delight, the use of 5 mol% **3** as a catalyst effected the room-temperature hydrogenation of substrate N-benzylidene-*tert*-butylamine to N-benzyl-*tert*-butylamine. A 49% conversion to product was observed by <sup>1</sup>H-NMR spectroscopy after 24 h reaction time in CH<sub>2</sub>Cl<sub>2</sub> under 102 atm H<sub>2</sub>. Presumably the reaction proceeds in an analogous fashion to previously reported NHC-borenum catalyzed hydrogenations<sup>53, 54</sup> wherein the bulky Lewis basic imine substrate and the borenum ion comprise an FLP that heterolytically cleaves H<sub>2</sub>. The iminium ion generated is subsequently attacked by boron-bound hydride to give the reduced amine and the regenerated borenum salt. As expected based on this mechanism, a similar reaction carried out using 5 mol% of the neutral compound **1** as a catalyst in place of **3** failed to show any conversion of the substrate to hydrogenated product by <sup>1</sup>H-NMR spectroscopy after 24 h reaction time in C<sub>6</sub>D<sub>3</sub>Br under 102 atm H<sub>2</sub> at room temperature.



**Scheme 3** Hydrogenation catalysis attempts using compounds **1** and **3**.

The easily accessible compound **3** illustrates the synthetic feasibility of cationic diboryl-N-heterocycles as bidentate Lewis acids. The divergent bonding arrangements of hydride and iodide when coordinated to this Lewis acid are also striking. A consistent challenge in FLP chemistry is to overcome the poor selectivity of highly electrophilic boranes for small molecules of interest in the presence of competing donor functional groups. Therefore, the divergent bonding arrangements of anionic donors in **1** and **2** combined with the demonstration of catalytic imine hydrogenation by **3** urges future study of these compounds for selective FLP processes.

In summary, we have prepared an N-boryl substituted NHC-borane (**1**) with hydride bridging the two boron centers. This species is shown to react with I<sub>2</sub> to give the "zwitterionic borenum-borate" **2**. Treatment of **1** with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] cleanly abstracts hydride to provide facile access to the cationic bidentate Lewis acid **3**. Compound **3** readily catalyzes the room-temperature hydrogenation of N-benzylidene-*tert*-butylamine. The further use of these compounds in FLP chemistry and their structural modification through judicious choice of borane and N-heterocycle are key areas of on-going examination. The results of these studies will be reported in due course.

## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, NMR data and details of the crystal structure determinations. CCDC 1414031-1414033. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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