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# Boryltrihydroborate: Synthesis, Structure, and Reactivity as a Reductant in Ionic, Organometallic, and Radical Reactions

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***Abstract:*** Reaction of lithium 1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-1,3,2-diazaborol-2-ide with borane·THF provides the first boryl-substituted borohydride: lithium [1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-1,3,2-diazaborol-2-yl]trihydroborate. The compound is fully characterized by $^{11}$B, $^{1}$H, and $^{7}$Li NMR spectra and other means, and these data are compared to neutral and anionic benchmark compounds. The compound crystallizes as a dimer complexed to four THF molecules. The dimer lacks the bridging B−H bonds seen in neutral boranes and is instead held together by ionic Li---HB interactions. A preliminary scan of reactions with several iodides shows that the compound participates in an ionic reduction (with a primary-alkyl iodide), an organometallic reduction (Pd-catalyzed with an aryl iodide), and a radical reduction (AIBN-initiated with a sugar-derived iodide). Accordingly the new borylborohydride class may share properties of both traditional borohydrides and isoelectronic N-heterocyclic carbene boranes.

Tetrahydroborates ($BH_4^-$) are parents of an exceptionally important class of reagents in both organic and inorganic chemistry.[1] Often called borohydrides, these reagents are used as reductants, as precursors for all kinds of interesting main group and organometallic compounds, and as hydrogen storage reagents, among other applications. Countless substituted borohydrides are known, with one or more hydrogen atoms replaced by carbon, oxygen, nitrogen, or other atoms.[1] However, simple boron-substituted borohydrides appear to be unknown. Their absence might be due to a gap in methodology—the boron Lewis bases (boryl anions) needed to make borylborohydrides have been unknown until recently.[2]

We set out to explore the prospect of using new methods to make boryl anions a stepping stone to make borylborohydrides. In particular, boryl anions **3** are isoelectronic with well-known N-heterocyclic carbenes **1** (Figure 1).[3] Addition of a boryl anion **3** to borane might give borylborohydride **4**, which is isoelectronic with the N-heterocyclic carbene borane (NHC-borane) **2**. NHC-boranes **2** are an emerging class of reagents with applications in ionic, organometallic, and radical reactions.[4] Thus, we felt that compounds like **4** were doubly interesting as boryl-substituted borohydrides and as anionic analogs of neutral NHC-boranes.[5] According to the latter analogy, anions like **4** can also be viewed as unusual examples of complexes between a boron-derived Lewis acid ($BH_3$) and a boron-derived Lewis base (**3**).

Reaction of boryllithium **5**[6] with $BH_3$·THF gave a colorless, crystalline lithium boryltrihydroborate **6**, which was isolated in 19% yield after two recrystallizations (Scheme 1). Unlike NHC-boranes but like many borohydrides, **6** is sensitive to ambient laboratory conditions, and it was synthesized and stored in a glovebox for this preliminary study.

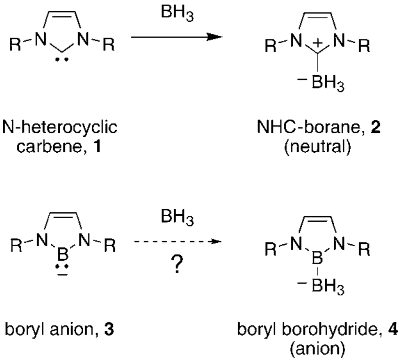

***Figure 1.*** Neutral N-heterocyclic carbenes **1** and NHC-boranes **2** are isoelectronic with boryl **3** and borylborohydride **4** anions, respectively.

***Scheme 1.*** Synthesis of Boryltrihydroborate **6**

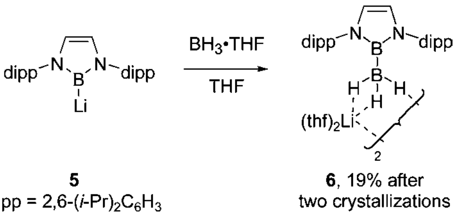

***Table 1.*** Comparison of Selected NMR Spectroscopic Values of **6** with Benchmarks[a]

| Compd | $^{1}$H NMR | $^{11}$B NMR | $^{1}J(^{11}B^{1}H)$ | $^{7}$Li NMR | $^{7}$Li $\nu_{1/2}$ |
|---|---|---|---|---|---|
| **6** | −0.98, br | 37.1, −44.7 | broad | −0.73 | 11 |
| $LiBH_4$ | −0.52, quadruplet | −42.0, quintet | 81 | −0.53 | 18 |
| dipp-Imd-$BH_3$[b] | 0.52, br | −36.2 | 89 | — | — |

[a] Solvent is THF-$d_8$, chemical shifts are in ppm, $J$ and $\nu_{1/2}$ are in Hz. [b] Compound **2** with R = 2,6-diisopropylphenyl.

Comparisons of representative spectroscopic data of **6** with data of benchmarks lithium borohydride ($LiBH_4$) and 2,6-diisopropylphenylimidazol-2-ylidene borane (dipp-Imd-$BH_3$, **2**: R = 2,6-diisopropylphenyl)[7] are summarized in Table 1. The $^{1}$H NMR spectrum of **6** in THF-$d_8$ shows a broad signal assignable to three hydrogen atoms on the borate at a relatively high field of $\delta_H$ −0.98. The signal was sharper in the $^{1}H\{^{11}B\}$ decoupled NMR spectrum.

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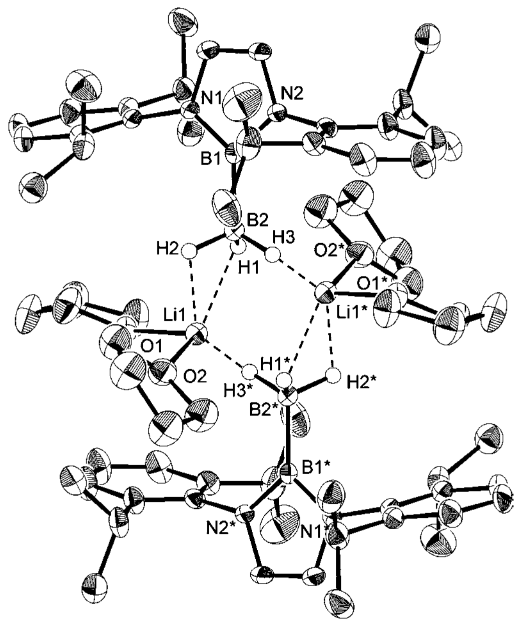


***Figure 2.*** ORTEP drawing of **6**. (50% thermal ellipsoids. One half of the whole structure is the asymmetric unit. Asterisks on atomic labels show the other half. Disordered THF molecules and all hydrogen atoms except the hydroborate hydrogens are omitted for clarity.)

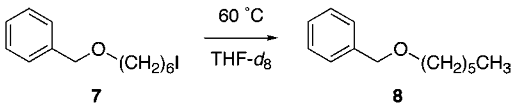
A similar broadened signal was also observed in the spectrum of dipp-Imd-$BH_3$ ($\delta_H$ 0.52). In contrast, $LiBH_4$ showed a sharp quadruplet due to coupling with $^{11}B$ ($I = 3/2$, $J = 81$ Hz) paired with a satellite septuplet due to coupling with $^{10}B$ ($I = 3$, $J = 27$ Hz) at $\delta_H$ −0.52. The difference in sharpness between the signals of **6** and $LiBH_4$ probably comes from the difference in the strength of the quadrupolar interaction because of the symmetry of the molecules.[8] Compared to dipp-Imd-$BH_3$, the upfield-shifted $BH_3$ signal of **6** may reflect more partial negative charge on the borate center.

The $^{11}B$ NMR spectrum of **6** in THF-$d_8$ showed resonances at $\delta_B$ 37.1 and −44.7. The downfield resonance is assigned to the boryl substituent and the upfield one to borate anion (compare $\delta_B$ −42.0 for $LiBH_4$ and −36.2 for dipp-Imd-$BH_3$).[9] The shape of the $BH_3$ signal seemed to be a broad quartet due to a coupling with three equivalent protons with a very small shoulder. In comparison, $LiBH_4$ and dipp-Imd-$BH_3$ exhibit sharp quintet [$^1J(^{11}B^1H) = 81$ Hz] and quartet [$^1J(^{11}B^1H) = 89$ Hz] signals, respectively. The significant broadening of the $BH_3$ signal in **6** may come from the direct connection to the quadrupolar boron nucleus in the boryl substituent. A sharp ($\nu_{1/2} = 11$ Hz) $^7Li$ NMR signal of **6** appeared at $\delta_{Li}$ −0.73. Quadrupolar coupling between boron and lithium atoms was observed in boryllithium **5** to afford a broadened signal ($\nu_{1/2} = 36$ Hz) but not in **6**. The aforementioned $^7Li$ NMR chemical shift is close to that of $LiBH_4$ ($\delta_{Li}$ −0.53), indicating a similar situation in anion−cation interactions.

Colorless single crystals of **6** suitable for X-ray analysis were obtained from ether solution with a slow vapor diffusion of pentane. Compound **6** crystallized as a contact ion pair with two THF molecules coordinating to the lithium atom (Figure 2). The boryltrihydroborate moiety simultaneously coordinated to two lithium atoms to assemble a dimeric structure with no other interaction between the two units. The Fourier map showed the existence of three hydrogen atoms on B2. Unlike $B_2H_6$, there is no bridging hydrogen atom between the two boron atoms of **6**. The B1−B2 length of 1.699(4) Å is comparable to previously reported B($sp^2$)−B($sp^3$) bonds.[10] Interatomic distances, B2−Li1 of 2.441(5) Å and B2−Li1* of 2.542(5) Å, are in the range of $\mu_1$ and $\mu_2$ coordination modes. The N1−B1−N2 bond angle of 101.52° is close to those of other boryllithium species [98.7(2)°−101.89(16)°]. The two different B1−B2−Li angles [129.3(2)°, 158.6(2)°] support an unsymmetrical coordination of the boryltrihydroborate moiety to the two lithium atoms.

***Table 2.*** Preliminary Ionic, Organometallic and Radical Reactions of **6**, and Benchmarks $LiBH_4$ and dipp-Imd-$BH_3$

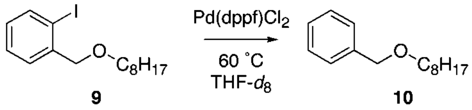
***Ionic Reactions***



| entry | reagent | rxn time | conv **7** | yield **8** |
|---|---|---|---|---|
| 1 | **6** | 28 h | >95% | 75% |
| 2 | $LiBH_4$ | 5 h | >95% | 72% |
| 3 | dipp-Imd-$BH_3$ | 28 h | 29% | 92%[a] |

a) combined yield of **7** and **8**

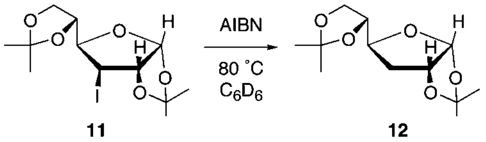
***Organometallic Reactions***



| entry | reagent | rxn time | conv **9** | yield **10** |
|---|---|---|---|---|
| 4 | **6** | 3 h | >95% | 65% |
| 5 | $LiBH_4$ | 15 min | >95% | 66% |
| 6[a] | $LiBH_4$ | 3 h | ~0% | – |
| 7 | dipp-Imd-$BH_3$ | 50 h | ~0% | – |

a) catalyst omitted

***Radical Reactions***



| entry | reagent | rxn time | conv **11** | yield[a] |
|---|---|---|---|---|
| 8 | **6** | 2 h | 78% | 73% |
| 9 | $LiBH_4$ | 2 h | ~0% | – |
| 10 | dipp-Imd-$BH_3$ | 2 h | 37% | 65% |

a) isolated yield of **11** and **12** (inseparable)

With this understanding of the structural features, we scaled up the reaction in Scheme 1 to produce about 1 g of **6** for a preliminary study of its reactivity. Typical substrates for ionic, organometallic, and radical reactions were reacted under identical conditions with boryltrihydroborate **6**, $LiBH_4$, and dipp-Imd-$BH_3$. The results of this study are summarized in Table 2 with a focus on products and yields. Many of the reactions were followed by $^{11}B$ NMR spectroscopy. This and other additional information such as stability tests are found in the Supporting Information.

To compare the hydridic character, we examined three reactions with reactive primary iodide **7**, all at 60 °C in THF-$d_8$. The reaction with $LiBH_4$ (entry 2) was completed in 5 h and gave **8** in 72% isolated yield, while the reaction with **6** (entry 1) took 28 h to complete, giving **8** in comparable yield. The reaction of **7** with dipp-Imd-$BH_3$ (entry 3) was stopped after 28 h, at which point the

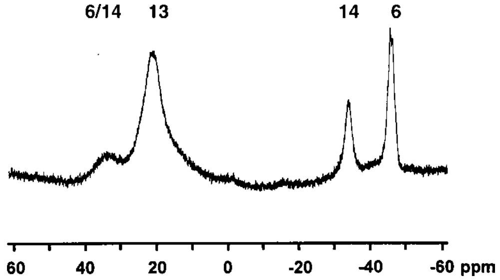


***Figure 3.*** $^{11}$B NMR spectrum of the reaction of **6** with **7** at the 5 h time point showing the presense of **6** (decreasing), **14** (increasing, then decreasing), and **13** (final boron product).

**13**, secondary product isolated

**14**, primary product detected in situ

***Figure 4.*** Structures of boron-containing reaction products **13** and **14**.

conversion was 29%. The reduction of **7** by dipp-Imd-$BH_3$ is a high yielding reaction but needs much higher temperatures for speedy conversion.[4d] These results suggest that **6** is less reactive than $LiBH_4$ but more reactive than dipp-Imd-$BH_3$ in ionic reductions.

We selected aryl iodide **9** as the substrate for preliminary organometallic reductions because it has been used previously in analogous NHC-borane reactions.[4d] Again reactions were conducted at 60 °C in THF-$d_8$, now with Pd(dppf)$Cl_2$ (12%) as the catalyst. Boryltrihydroborate **6** and $LiBH_4$ reactions were completed quickly (3 h and 15 min) and gave product **10** in comparable isolated yields (65% and 66%, entries 4,5). Dipp-Imd-$BH_3$ did not react under these conditions (entry 7).

For the radical reduction, we selected hindered, electronically deactivated iodide **11**, which we assume will resist $S_N2$ substitution. These reactions were conducted in $C_6D_6$ with AIBN for a fixed time of 2 h. The precursor **11** and the product **12** were inseparable, but their combined isolated yields were good in each case. In this sequence of reactions, **6** provided the best result, giving 78% conversion to **12** (entry 8). In contrast dipp-Imd-$BH_3$ gave 37% conversion (entry 10) and $LiBH_4$ gave no conversion, possibly due to its low solubility (entry 9).

We also obtained significant information about the boron-containing products in both the ionic and organometallic reactions of **6**. The time course $^{11}$B NMR spectra for both reactions showed the growth of a new broad signal at $\delta_B$ −35.5. This later declined, being replaced by a signal at $\delta_B$ 20. Parallel changes were seen in the series of $^1$H NMR spectra. The complete set of spectra showing reaction progress are provided in the Supporting Information. Figure 3 shows a typical $^{11}$B NMR spectrum at the 5 h point during the reduction of **7** (Table 2, entry 1) by **6**. At this point, resonances for the starting borate **6** ($\delta_B$ 37.1 and −44.7) still accompany those of the two new products.

The known borane **13**[6a] (Figure 4) is responsible for the signal at $\delta_B$ 20, and indeed this product was isolated in excellent yield from both the ionic (97%) and organometallic (81%) reductions (entries 1 and 4). We attribute the intermediate signal at $\delta_B$ −35.5 to the sp$^3$ boron atom in boryldihydroiodoborate **14**,[11] whose other boron signal presumably overlaps with that of the starting material **6**. The instability of **14** resembles the analogous carbene borane (dipp-Imd-$BH_2I$), which can also be readily made and characterized in situ[4d] but reverts to the corresponding imidazolium salt on workup and chromatography.

In summary, we have prepared and characterized the first borylborohydride: lithium [1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-1,3,2-diazaborol-2-yl]trihydroborate **6**. A preliminary scan of ionic, organometallic, and radical reactions suggests that **6** and presumably other members of this new class of compounds will have interesting properties. For example, **6** exhibits ionic reactivity similar to that of $LiBH_4$ and very different from that of NHC-benchmark dipp-Imd-$BH_3$, but it exhibits radical reactivity similar to that of dipp-Imd-$BH_3$ and very different from that of $LiBH_4$. With the advent of methods to make boryl anions, it should now be possible to make and study a range of borylborohydrides.

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**Supporting Information Available:** Contains details of synthesis and characterization of **6**, details of experiments in Table 2, copies of spectra, and a cif file of the crystal structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Likewise, in the reduction of **7** with $LiBH_4$ (Table 2, entry 2), we observed the formation of $LiBH_3I$. See the Supporting Information.

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