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**Super Bases**

# Assessing the Brønsted Basicity of Diaminoboryl Anions: Reactivity toward Methylated Benzenes and Dihydrogen[**]

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***Abstract:*** *Treatment of toluene or p-xylene with diaminoboryllithium results in consecutive reactions, involving boryl-anion-mediated deprotonation at the benzylic position followed by nucleophilic substitution at the boron center, producing benzylborane species and LiH. Diaminoboryllithium also cleaves $H_2$ heterolytically affording diaminohydroborane and LiH, while the reaction of lithium diaminoboryl(bromo)cuprate with $H_2$ takes place accompanied by reduction of $Cu^I$ to give diaminohydroborane, LiH, and $Cu^0$.*

Since the isolation of boryllithium $(THF)_2Li[B(NDipCH)_2]$ (**1a**, Dip = 2,6-$i$Pr$_2$C$_6$H$_3$),[1] the nucleophilicity of the boryl anion has been thoroughly studied by employing various organic and inorganic electrophiles.[1,2] Although carbanions have been extensively utilized as Brønsted bases, little attention has been paid to the basicity of boryl anions.[3] One of the few examples shows that treatment of $Br[B(N\mathit{t}BuCH)_2]$ with Na/K alloy and 15-crown-5 in toluene generates $PhCH_2[B(N\mathit{t}BuCH)_2]$ and $H[B(N\mathit{t}BuCH)_2]$.[4] The boron-bonded hydrogen atom in product $H[B(N\mathit{t}BuCH)_2]$ was proven to originate from toluene by use of [D$_8$]toluene. Two possible mechanisms were proposed for the formation of the B−H bond, namely either proton abstraction by a boryl anion or hydrogen radical abstraction by a boryl radical. Radical coupling would also induce the formation of the benzyl−B bond in $PhCH_2[B(N\mathit{t}BuCH)_2]$. Later on, targeting putative $Li[B(NMesCH_2)_2]$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$) as a structural modification of seminal boryllithium **1a**[1] led to the intramolecular cyclization product **e** (Scheme 1).[2h] Of the two possible reaction mechanisms, radical versus ionic, the anionic pathway shown in Scheme 1 seemed more likely based on the clean conversion of boryllithium **b** into cyclic hydridoborate **d**. More recently, Bertrand et al. reported that the B–H moiety in CAAC (cyclic (alkyl)(amino)carbene) coordinated dicyanoborane could be deprotonated by treatment with $KN(SiMe_3)_2$ in the presence of dibenzo-18-crown-6 to form the corresponding boryl anion $[(CAAC)B(CN)_2]^-$.[2d] This finding indicated that the basicity of the donor-stabilized boryl anion $[(CAAC)B(CN)_2]^-$ is lower than that of $KN(SiMe_3)_2$ [p$K_a$ of $HN(SiMe_3)_2$: 25.8].[5] Herein, we provide clear evidence for the deprotonation of benzylic methyl groups by **1a**, implying that the basicity of $^-[B(NDipCH)_2]$ is higher than that of $^-H_2CPh$ (p$K_a$ of toluene: 40–43),[6] which means that the p$K_b$ of $^-[B(NDipCH)_2]$ must be lower than −26. Deprotonation of the dihydrogen molecule (p$K_a \approx 35$)[6] was also examined to clarify the nature of the boryl anion as a Brønsted base.

The reaction of isolated boryllithium **1a** with toluene afforded the benzylborane species $PhCH_2[B(NDipCH)_2]$ (**2**, Scheme 2).[7] When **1a** was treated with 1.6 equiv of toluene at ambient temperature in a [D$_{12}$]cyclohexane solution, an almost complete conversion of **1a** into **2** was observed after four days. In addition to **2**, the formation of a small amount of a white precipitate was detected. In contrast, the reaction of $p$-xylene with 2 equiv of **1a** in [D$_{12}$]cyclohexane afforded mono- (**4**) and disubstituted products (**5**), accompanied by the formation of $H[B(NDipCH)_2]$ (**3a**) and again a white precipitate. Analysis of the resulting white solid by diffuse reflectance FTIR spectroscopy indicated the presence of LiH. Formation of **4** could not be suppressed by either applying 3 equiv of **1a** or by changing the solvent to [D$_8$]THF. Products **4** and **5** could be isolated from a reaction in $n$-hexane as crystalline solids in yields of 19 and 15 %, respectively, suitable for X-ray crystallographic analyses (Figure 1 and Figure S37; Supporting Information).[8]

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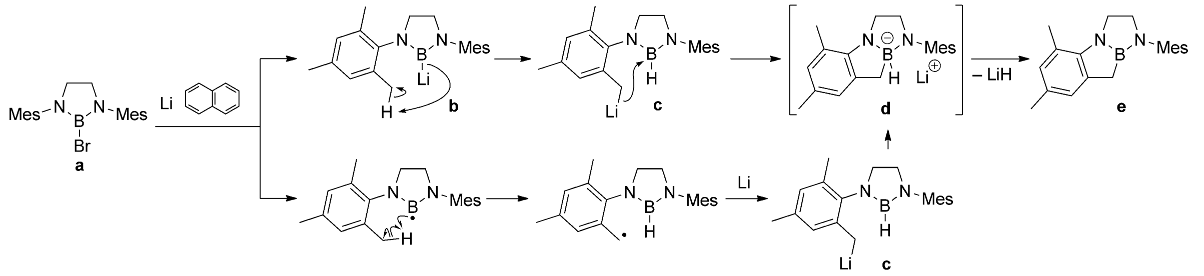
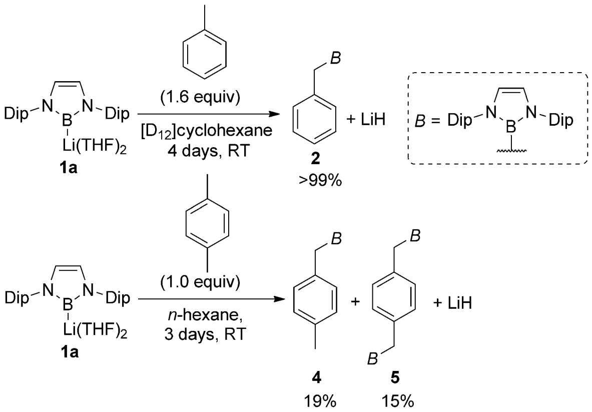


*Scheme 1.* Two previously proposed reaction mechanisms for the formation of cyclic diaminoalkylborane **e** by the reduction of bromoborane **a**.



*Scheme 2.* The reaction of boryllithium **1a** with toluene and *p*-xylene.

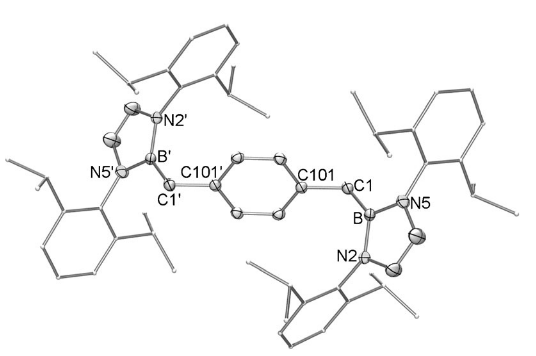
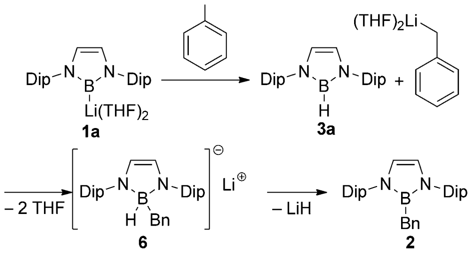


*Figure 1.* ORTEP view of compound **5**. The atomic displacement parameters are set at the 50% probability level, hydrogen atoms are omitted for clarity, and the carbon atoms of the aromatic parts are shown with reduced radii. Selected bond lengths [Å] and angles [°]: B1–C1 1.578(2), C1–C101 1.516(2); B1-C1-C101 115.97(9).

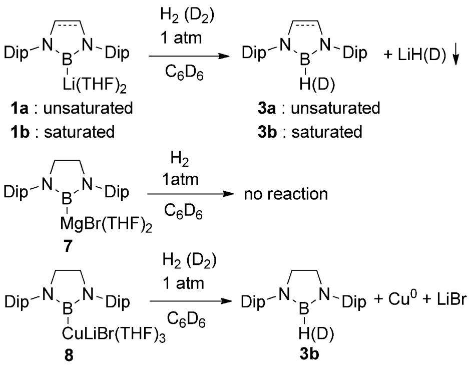
Moreover, we examined the reaction of mesitylene with 3 equiv of **1a** in an NMR-scale experiment (Figure S9, Supporting Information). Heating to 45 °C for 20 h gave a reaction mixture showing two peaks for the benzylic protons in a 1:3 ratio. We tentatively assigned the major product as the mono-activated product, $(3,5\text{-}Me_2C_6H_3)CH_2[B(NDipCH)_2]$. The fact that mesitylene is activated at only one of the three methyl groups can be explained by the increased steric demand resulting from boryl units at *meta*-methyl groups.



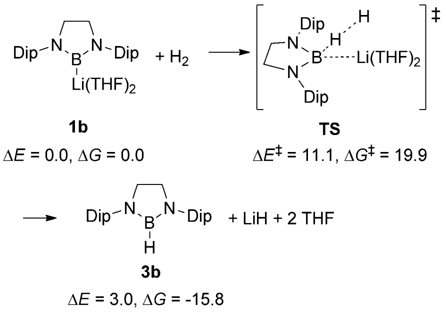
*Scheme 3.* Proposed mechanism for the formation of benzylborane **2** and LiH from **1a** and toluene. Bn = benzyl.

With the products in hand, we propose the reaction mechanism summarized in Scheme 3, which bears resemblance to the anionic pathway (top path) hypothesized in Scheme 1.[2h] Since the incorporation of deuterium into the products was not observed in $[D_8]$THF, this solvent can be excluded as a proton source. Hence, boryllithium initially deprotonates the methyl group of toluene to give **3a** and benzyllithium. Next, a nucleophilic attack of the anionic benzyl carbon at the boron center leads to the formation of hydridoborate intermediate **6**. Subsequent elimination of hydride affords benzylborane **2** and LiH precipitation. Since the reaction started from isolated boryllithium, and not by reduction of borylbromide, a radical pathway is unlikely due to the polarity of the B–Li bond. The ionic reaction mechanism, involving boryllithium as a strong base, was corroborated by the formation of **2** (via **6**) from the reaction of hydroborane **3a** with benzyllithium as monitored by $^{1}$H NMR spectroscopy.[9]

The deprotonation capability of boryllithium could be further proven by the heterolytic cleavage of dihydrogen. Exposure of a $[D_6]$benzene solution of $(THF)_2Li[B(NDipCH_2)_2]$ (**1b**) to $H_2$ for 10 min produced a fine-grained white precipitate (LiH), while the $^{1}$H NMR spectrum indicated complete conversion of **1b** into hydroborane **3b** (Scheme 4, top). This result clearly indicated that boryllithium **1b** splits the H–H bond heterolytically. The reaction of **1b** with $D_2$ gave a broad signal at 4.3 ppm in the $^{2}$H NMR spectrum; this chemical shift corresponds to that of the B–H unit of **1b** in its $^{1}$H NMR spectrum. Addition of $B(C_6F_5)_3$ to the reaction mixture led to the appearance of a small singlet at −25.1 ppm in the $^{11}$B NMR spectrum, suggesting the presence of $Li[DB(C_6F_5)_3]$. An analogous $H_2$-splitting reaction was also confirmed to take place with boryllithium **1a**,[1,2h] featuring an unsaturated backbone. Similarly, when 3 equivalents of $B(C_6F_5)_3$ were added to the reaction mixture, new resonances appeared in the $^{11}$B and $^{19}$F NMR spectra, indicating the generation of $Li[HB(C_6F_5)_3]$ and $(THF)B(C_6F_5)_3$. As $Li[HB(C_6F_5)_3]$ is not completely



***Scheme 4.*** The reaction of boryllithium **1a**,**b**, borylmagnesium bromide **7**, and lithium borylbromocuprate **8** with $H_2$ or $D_2$.



***Scheme 5.*** DFT-calculated relative energies for the reaction of **1b** with $H_2$ [*E*: thermal energy; *G*: Gibbs free energy (kcal mol$^{-1}$)]. TS: transition state.

soluble in [D$_6$]benzene, only about 25 % of it was observed by $^1$H NMR spectroscopy.

In sharp contrast to the case of boryllithium **1**, other borylmetal species exhibited different reactivities with $H_2$ (Scheme 4, middle and bottom). For example, borylmagnesium bromide **7**[2f] did not react with dihydrogen at ambient temperature over a period of two days, according to $^1$H NMR spectroscopy. On the other hand, lithium borylbromocuprate **8**[2g] gradually reacted with $H_2$ to give hydroborane **3b** over a period of six days at ambient temperature. During the reaction, no other signals of significant intensity besides those of **3b** and **8** were detected in the $^1$H NMR spectrum. As the reaction proceeded, the formation of a bronze metallic luster was observed on the inner surface of the NMR tube. This metallic substance was confirmed as Cu$^0$ by XPS, most likely originating from the decomposition of CuH at ambient temperature.[10] Lithium borylbromocuprate **8** also reacted with $D_2$ and the generation of deuterated **3b** was confirmed by $^1$H and $^2$H NMR spectroscopy.

The driving force for the reaction of boryllithium compounds **1a** and **1b** and lithium borylbromocuprate **8** with $H_2$ could be the lattice energy (LiH: 219 kcal mol$^{-1}$;[11] CuH: 288.6 kcal mol$^{-1}$).[12] However, in spite of the much higher lattice energy of $MgH_2$ (650 kcal mol$^{-1}$),[10] borylmagnesium bromide **7** did not react with $H_2$. Therefore, the lattice energy is not the only crucial factor governing this reaction. The higher reactivity of boryllithium **1** relative to that of borylmagnesium bromide **7** can be rationalized on the basis of the enhanced reactivity of organolithium compared to that of the respective Grignard reagents. In the case of borylcuprate, dihydrogen would undergo oxidative addition to form labile (boryl)Cu$^{III}$H$_2$ species, which undergo reductive elimination to hydroborane and CuH.

In order to elucidate the mechanism of the reaction of **1b** with dihydrogen, DFT calculations were performed using the B3LYP[13] method and 6-311G(d,p) as a basis set and the polarizable continuum model (PCM)[14] (solvent: benzene). The Gibbs free energy of activation was calculated as $\Delta G^{\ddagger} =$ 19.9 kcal mol$^{-1}$ (Scheme 5), which is consistent with the experimental observation that the reaction of **1b** with $H_2$ proceeded at ambient temperature. It is noteworthy that the value $\Delta G^{\ddagger} = 19.9$ kcal mol$^{-1}$ is lower than that of cyclic alkyl(amino)carbene (CAAC) with $H_2$ (23.6 kcal mol$^{-1}$).[15] This is also consistent with the fact that the reaction of **1b** with $H_2$ is much faster than that of CAAC with $H_2$.

Additionally, natural bond orbital (NBO) analysis was performed to elucidate the interactions among the molecular orbitals. The optimized transition state with NBO 143 and NBO 102 is shown in Figure 2. In the transition state, boron, lithium, and two hydrogen atoms form a planar, four-membered ring with a nearly linear bond angle of B-H-H (177.6°). NBO analysis revealed that the stabilization energy ($E_2$) between the lone pair of the central boron atom in boryllithium and a σ*-orbital of H−H bond was 178.64 kcal mol$^{-1}$, reflecting the shape of the NBO 143. On the other hand, $E_2$ for the interaction between the bonding electrons in

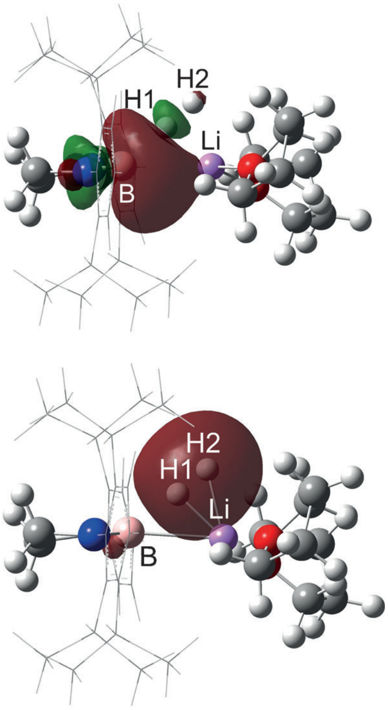


***Figure 2.*** Optimized transition state for the reaction of **1b** with $H_2$ determined by using NBO analysis (isovalue = 0.02); the NBO 143 (top) and NBO 102 molecular orbitals (bottom) describe the donor–acceptor interactions. (Dip groups are shown as wire-frame models for clarity).

H–H bond and the Li cation was estimated as 21.11 kcal mol$^{-1}$ and this interaction appeared as the shape of the NBO 102 molecular orbital.[16]

An additional weak interaction of a σ-orbital of $H_2$ with a vacant p-orbital on the boron atom was also suggested by an $E_2$ value of 10.69 kcal mol$^{-1}$. Overall, the contribution of electron donation from a lone pair on the boron atom to a σ*-orbital of the H–H bond seems to be dominant, with minor contributions of electron donation from a σ-orbital of the H–H bond to vacant orbitals on the Li cation.

In conclusion, the reactivity of boryllithium as a Brønsted base has been demonstrated. The deprotonation of benzylic methyl groups by Li[B(NDipCH)$_2$] has been clearly proven, suggesting that the p$K_\mathrm{b}$ of $^{-}$[B(NDipCH)$_2$] must be lower than −26. A more accurate p$K_\mathrm{b}$ value estimation according to the NMR method by Fraser et al.[5,17] is hampered by the occurrence of a consecutive reaction involving nucleophilic substitution on the boron center. The deprotonation or heterolytic cleavage of $H_2$ by boryllithium and lithium borylbromocupurate also proceeded. The present study not only gives further evidence for the carbanionic behavior of boryllithium, but also establishes features that are distinct from those of true carbanions.[9,18] The comparatively slower deprotonation of benzylic methyl groups (by boryllithium) should be attributed to enhanced steric hindrance imparted by the two bulky diisopropyl (Dip) groups. On the other hand, the faster reaction with $H_2$ should be due to the stronger basicity of the boryl anion that originates from the lower electronegativity of boron relative to carbon.

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**Keywords:** boryllithium · basicity · diaminoboryl anions · hydrogen · methylated benzenes

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[7] Compound **2** was previously isolated from the reaction of **1a** with PhCH$_2$Cl, see Ref. [2h].

[8] Compound **4** ($C_{34}H_{45}BN_2$, $M_r = 492.53$): $R\bar{3}$, $a = 41.0460(6)$, $b = 41.0460(6)$, $c = 9.3554(1)$ Å, $V = 13650.1(3)$ Å$^3$, $d_\mathrm{calcd} = 1.078$ g cm$^{-3}$, $Z = 18$, $wR2 = 0.1182$, $R1 = 0.0453$. Compound **5** ($C_{60}H_{80}B_2N_4$, Mr = 878.90): *Pbca*, $a = 9.9970(4)$, $b = 20.1712(8)$, $c = 27.029(2)$ Å, $V = 5450.4(4)$ Å$^3$, $d_\mathrm{calcd} = 1.071$ g cm$^{-3}$, $Z = 4$, $wR2 = 0.1045$, $R1 = 0.0410$. CCDC 982036 (**4**) and 982037 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[16] Addition of 18-crown-6 to boryllithium **1a** induced a simple deprotonation to form hydroborane **3a**. Therefore, enhancement of the basicity of boryllithium by this method may be difficult.

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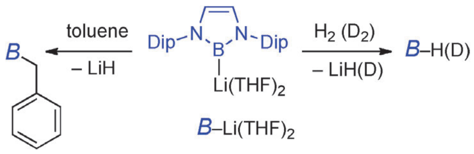

**Back to basics**: The deprotonation reactions of methylated benzenes and $H_2$ by superbasic boryl anions were studied. In the reaction of methylated benzenes, subsequent nucleophilic substitution on the boron center of intermediate *B*–H produces benzylborane species (structure of the *B* unit shown in the scheme; Dip = 2,6-$i$Pr$_2$C$_6$H$_3$). A general mechanism for these reactions is elaborated and the reactivity of *B*-Li(THF)$_2$ toward $H_2$ investigated by DFT calculations.