VIP Nucleophilic Boron

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Deprotonation of a Borohydride: Synthesis of a Carbene-Stabilized Boryl Anion**

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Owing to their electron deficiency, trivalent boron compounds are usually electrophilic. As a result, boranes and borohydrides are regarded as the archetypical Lewis acids and hydride donors, respectively. On the other hand, the synthesis of trivalent nucleophilic boron derivatives has eluded chemists for decades, and only recently has their isolation been achieved.[1] In 2006, Yamashita, Nozaki, and co-workers reported the preparation and full characterization of the boryl anion **A**,[2,3] and since then a few boron centered nucleophiles have been described (Figure 1). Braunschweig et al. have isolated the NHC-stabilized borole **B**[4] (NHC = N-heterocyclic carbene), as well as metalloborylene **C**,[5] which feature π-nucleophilic and sp-hybridized boron atoms, respectively. Curran et al. have generated the NHC-stabilized parent boryl anion **D**; although it could not be isolated, they did trap it with a variety of electrophiles.[6] Also noteworthy is the synthesis by Bernhardt et al. of the dianion $[B(CN)_3]^{2-}$ (**E**), generated by reduction of $K[B(CN)_4]$ with potassium.[7] Lastly, in 2011 our group isolated the neutral tricoordinate nucleophilic boron **F**, which is isoelectronic with amines and phosphines.[8] Unfortunately, the steric environment around the boron center of **F** hampered its reactivity from any electrophile larger than a proton.

The synthesis of all of these nucleophilic boron compounds, **A**–**F**, has been achieved through the reduction of the boron halide or pseudo-halide precursors. Thus far, all attempts to deprotonate a borohydride to generate a boryl species have failed. Nozaki and Yamashita reported that the boryl anion **A** cannot be prepared by deprotonation, instead a Lewis acid–base adduct is formed.[3] Curran also mentioned that strong bases did not lead to the desired boryl anion **D**.[6] Indeed, owing to the higher electronegativity of hydrogen (2.20) compared to boron (2.04), hydrogen atoms bonded to boron are regarded as hydrides, and thus deprotonation does not seem feasible.

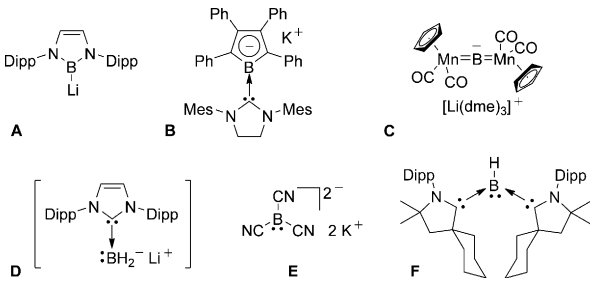
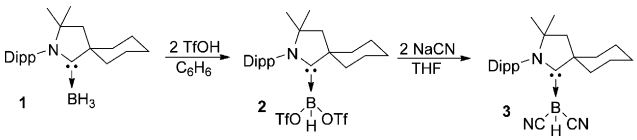


Figure 1. Known nucleophilic boron compounds. Dipp = 2,6-diisopropylphenyl, dme = 1,2-dimethoxyethane, Mes = 2,4,6-trimethylphenyl.

Herein, we report the first deprotonation reaction of a neutral borohydride, the isolation of the corresponding carbene-stabilized boryl anion, and the reactivity of the latter as a boron-centered nucleophile.

Inspired by the work of Braunschweig et al.[4] and Curran et al.,[6,9] we targeted a carbene-stabilized boryl anion. To favor the deprotonation of a borohydride, the obvious option is to place electron-withdrawing groups at boron. We chose a cyclic alkyl amino carbene (CAAC)[10] as the Lewis base, as they are slightly more nucleophilic, but much more electrophilic than NHCs.[11] The recently prepared $CAAC(BH_3)$ adduct **1**[12] provided a suitable and simple starting point for our study (Scheme 1). However, all attempts to deprotonate **1** failed, indicating that additional electron-withdrawing groups at boron were necessary. Reacting **1** with two equivalents of trifluoromethane sulfonic acid (TfOH) led to rapid evolution of hydrogen,[9b] and after workup, the bis-(triflate) derivative **2** was isolated in 80% yield. The ^{11}B NMR spectrum displays a broad signal at −2.2 ppm, which is significantly upfield from **1** (−30.6 ppm), and a single crystal X-ray diffraction study[13] reveals that both of the triflate groups are covalently bound to boron. Disappointingly, all attempts to deprotonate **2** again failed. Thus, the more electron-withdrawing cyano groups were installed by simple displacement of the triflate substituents with sodium cyanide. Compound **3**, which was isolated in 87% yield, gives a ^{11}B NMR signal at −34.6 ppm (d, $J_{BH} = 94$ Hz), and was fully characterized, including an X-ray diffraction study (Figure 2, upper).

Reacting dicyanide **3** with KHMDS leads to a yellow solution, which displays a broad singlet at −17.9 ppm in the ^{11}B NMR spectrum. After workup, a yellow solid was obtained (95% yield) and single crystals were grown by slow evaporation of a THF solution. An X-ray diffraction



Scheme 1. Synthesis of borohydride precursor **3**. Tf = trifluoromethylsulfonyl.

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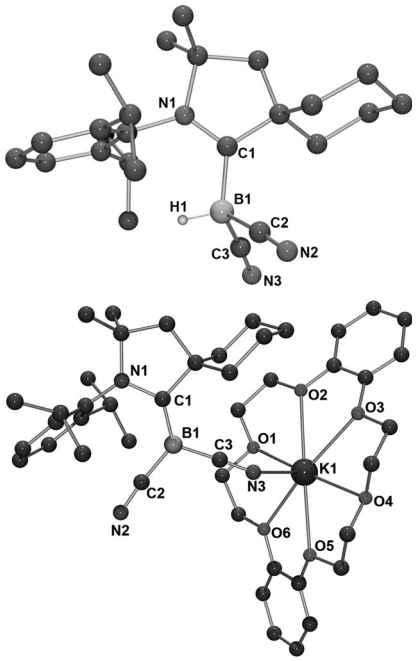
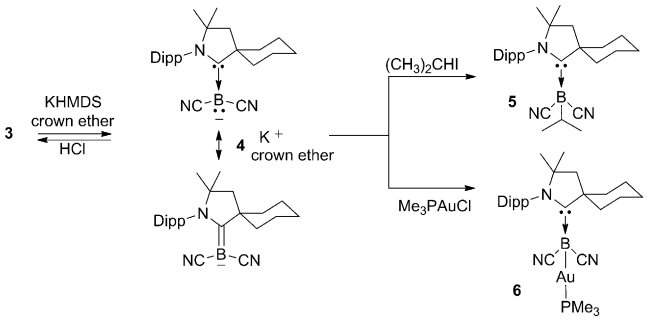


Figure 2. Structures of **3** and **4** in the solid state. All hydrogen atoms, except H1, omitted for clarity.

study revealed the polymeric nature of the boryl anion **4′**.[13] Subsequent treatment with dibenzo-18-crown-6 allowed for the isolation of the monomeric boryl anion **4**, with the potassium cation trapped within the sphere of the crown ether (Figure 2, lower). As observed by Bernhardt et al., in the case of dianion **E**,[7] the potassium cation is bound to a nitrile nitrogen (2.7884(15) Å). The B–$C_{nitrile}$ bond lengths in **4** (B1–C2: 1.553(2), B1–C3: 1.552(2) Å) are slightly shorter than in **3** (B1–C2: 1.605(6), B1–C3: 1.595(6) Å), but longer than in **E** (1.513 Å), which indicates a weaker delocalization of the negative charge on the nitrile groups. Concomitantly, the B1–C1 bond distance in **4** (1.473(2) Å) is considerably shortened compared to **3** (1.617(6) Å), which indicates a strong delocalization of the electron density onto the carbene moiety. This is confirmed by the significant lengthening of the C1–N1 bond (**3**: 1.294(4), **4**: 1.396(2) Å), and the trigonal planar geometry of boron, which is characteristic of an sp^2 hybridization (sum of angles = 359.96°). Clearly, the π-accepting properties of CAACs play an important role in the stabilization of **4**, as shown by the borataalkene resonance form.[14]

Boryl anion **4** is stable in the solid state and in solution for weeks under an inert atmosphere with no signs of decomposition, although it is extremely air and moisture sensitive. It readily reacts with HCl, giving back borohydride **3** (Scheme 2). Despite the presence of the potassium cation at nitrogen, the addition of isopropyl iodide gave the isopropylborane **5**, as shown by the high field ^{11}B NMR signal (−21.9 ppm) and by an X-ray diffraction study (Figure 3, upper).[13] The boryl behavior of **4** was confirmed by reaction with (trimethylphosphine)gold chloride, which afforded the rare boryl–gold complex **6**.[15,16] The ^{11}B NMR of this compound displayed a doublet at −26.2 ppm, which is due to boron–phosphorus coupling (J_{BP} = 30 Hz). An X-ray diffraction study of **6** (Figure 3, lower) revealed a B1–Au1 bond



Scheme 2. Synthesis and reactivity of boryl anion **4**. KHMDS = potassium bis(trimethylsilyl)amide.

length of 2.210(5) Å, whereas the B1–C1 bond is elongated to 1.544 Å compared to **4**, although being shorter than in **3**.

In summary, this work demonstrates that the use of both an electrophilic carbene and electron-withdrawing substituents makes a neutral carbene–borohydride adduct acidic enough to be deprotonated by a strong base. The resulting boryl anion is perfectly stable in the absence of air and moisture. Work is in progress to further examine the reactivity and ligand properties of **4**. Thus far, we have found that electrophiles react at boron. However, we wish to investigate the potential ambiphilic nature of the BCN fragments in the hope of preparing neutral and even cationic tricoordinated boron nucleophiles by mono- and di-*N*-alkylation, respectively.

Experimental Section

Synthesis of **3**: Derivative **2** (5.0 g, 7.8 mmol) was dissolved in THF (80 mL) and NaCN (0.81 g, 16.5 mmol) was added under a flow of argon. The mixture was stirred for three days, while monitoring the reaction by ^{19}F and ^{11}B NMR. The solvent was removed under vacuum, and the residue extracted with dichloromethane (80 mL). After evaporation under vacuum, the resulting solid was washed with

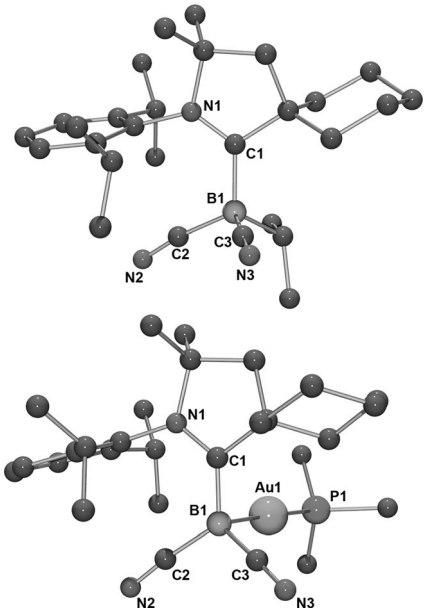


Figure 3. Structures of **5** and **6** in the solid state. Hydrogen atoms and co-crystallized solvent molecules omitted for clarity.

hexanes (3 × 20 mL) and dried to afford **3** (2.6 g, 87% yield). Colorless single crystals were obtained by vapor diffusion of hexanes in a chloroform solution. Mp: 282 °C; ^{11}B NMR (160 MHz, $CDCl_3$): $\delta = -34.6$ (d, $J_{BH} = 94$ Hz). HRMS: *m/z* calculated for $C_{25}H_{37}BN_3$ $[M+H]^+$ 390.3080, found 390.3064.

Synthesis of carbene–boryl **4** and **4′**: Derivative **3** (366 mg, 0.94 mmol) and potassium bis(trimethylsilyl)amide (200 mg, 1.00 mmol) were loaded in a Schlenk tube under argon. THF (15 mL) was added to the solids and the mixture stirred for 45 min. The volatiles were evaporated under vacuum and the residue was washed with ether (15 mL), then dried, affording **4′** as a yellow solid (382 mg, 95% yield). Single yellow crystals were obtained by slow evaporation of a THF solution of **4′**. Mp: 345 °C; ^{11}B NMR (160 MHz, $[D_8]$THF): $\delta = -17.9$ ppm. HRMS: *m/z* calculated for $C_{25}H_{35}BN_3$ $[M]^-$ 388.2930, found 388.2992. An excess of dibenzo-18-crown-6 was added to the THF solution of **4′**. Single crystals of **4** were obtained by slow evaporation. The ^{11}B NMR spectrum is identical to that of **4′**.

Synthesis of **5**: **4′** (100 mg, 0.23 mmol) was loaded in a Schlenk tube under argon and dissolved in THF (5 mL). Isopropyl iodide (80 mg, 0.46 mmol) was added and the mixture stirred overnight. Potassium iodide precipitated out of the reaction. The solvent was evaporated and the residue was extracted with dichloromethane (10 mL). The solvent was partly evaporated to obtain a saturated solution. Hexanes were added, and the suspension was stored overnight at −20 °C. After filtration, **5** (76 mg, 75% yield) was obtained as a solid. Single colorless crystals were obtained by vapor diffusion of hexanes in a chloroform solution. Mp: 294 °C; ^{11}B NMR (160 MHz, $CDCl_3$): $\delta = -21.9$ ppm. HRMS: *m/z* calculated for $C_{28}H_{42}BN_3Na$ $[M+Na]^+$ 453.3400, found 453.3401.

Synthesis of **6**: **4′** (100 mg, 0.23 mmol) and (trimethylphosphine)gold chloride (73 mg, 0.24 mmol) were loaded in a Schlenk tube and THF (10 mL) was added. The mixture was stirred for 2 h and a precipitate appeared. The solvent was removed under vacuum and the residue was extracted with dichloromethane (10 mL). The solvent was removed and the solid was washed with ether (15 mL) to afford **6** (107 mg, 69% yield) as an off-white solid. Single crystals were grown from a saturated chloroform/ether solution. Mp: 160 °C; ^{11}B NMR (160 MHz, $CDCl_3$): $\delta = -26.2$ ppm (d, $J_{BP} = 30$ Hz); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): $\delta = 10.1$ ppm (br m). HRMS: *m/z* calculated for $C_{28}H_{45}AuBN_3P$ $[M+H]^+$ 662.3109, found 662.3110.

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[13] CCDC 931828 (**2**) 931829 (**3**), 931831 (**4**), 931830 (**4′**) 931832 (**5**) and 931833 (**6**) 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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