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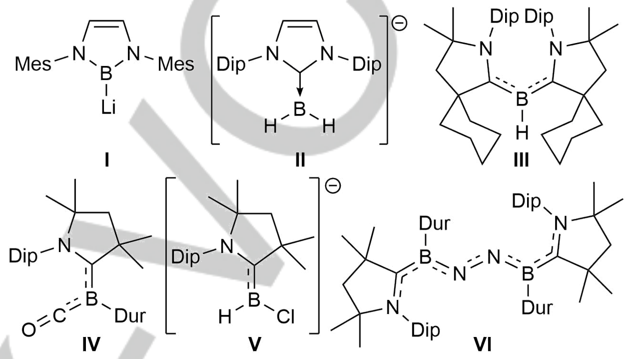
Facile Synthesis of a Stable Dihydroboryl $\{BH_2\}^-$ Anion

Merle Arrowsmith, James D. Mattock, Stephan Hagspiel, Ivo Krummenacher, Alfredo Vargas and Holger Braunschweig*

Abstract: While the one-electron reduction of (CAAC^{Me})BH$_2$Br (CAAC^{Me} = 1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene) yields a hydride-shift isomer of the corresponding tetrahydrodiborane, a further reversible reduction leads to the first stable parent boryl anion, [(CAAC^{Me})BH$_2$]$^-$, which acts as a powerful boron nucleophile.

Tricoordinate boron reagents generally behave as electrophiles due to their vacant p orbital. In 2006, however, Yamashita and Nozaki reported the first boryl anion, compound **I** (Fig. 1),[1] in which boron is in its formal +1 oxidation state and reacts as a nucleophile, thus enabling access to a wide range of novel boron-element-bonded compounds.[2] Curran and coworkers later succeeded in generating a highly reactive, fleeting N-heterocyclic carbene (NHC)-supported $\{BH_2\}^-$ parent boryl anion (**II**) at low temperature and trapping it with a variety of electrophiles,[3] while our own group isolated a nucleophilic borolyl anion that displayed not only classical salt metathesis but also single-electron transfer reactivity.[4]

A major breakthrough in low-valent boron chemistry came with the isolation by Bertrand and coworkers of the first metal-free boron(I) compound, borylene **III**,[5] which owes its remarkable stability to the excellent σ donor and π acceptor properties and the steric shielding afforded by the two supporting cyclic (alkyl)(amino)carbene (CAAC) ligands.[6] Since then, CAACs have been successfully employed to stabilize a wide range of ever more reactive borylenes[7] and boryl anions.[8] The most recent examples of these include the CAAC-CO-stabilized derivative **IV**, which under photolytic conditions liberates CO and generates a dicoordinate borylene synthon,[9] the highly reactive chloro(hydro)boryl anion **V**, which was isolated as a potassium crown ether complex,[10] and most recently, the N$_2$ activation compound **VI**, which may be viewed as a N$_2$-bridged borylene dimer.[11]

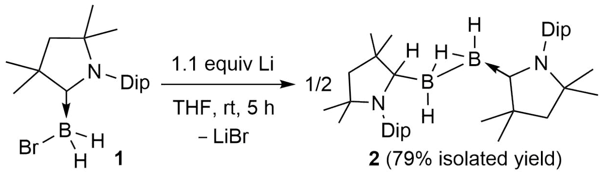


Mes = 2,4,6-Me$_3$C$_6$H$_2$; Dip = 2,6-*i*Pr$_2$C$_6$H$_3$; Dur = 2,3,5,6-Me$_4$C$_6$H

Figure 1. Selected examples of low-valent borylenes and boryl anions.

In this contribution we describe the facile stepwise reduction of a CAAC-stabilized (dihydro)haloborane to the corresponding diborane, and further to the first isolable, room-temperature-stable $\{BH_2\}^-$ parent boryl anion, which reacts as a strong boron nucleophile.

The room temperature reduction of (CAAC^{Me})BH$_2$Br (**1**, see Fig. S21 in the SI for the solid-state structure of **1**) with 1.1 equiv. lithium sand in THF (Scheme 1) yielded a pale yellow solution exhibiting a single broad ^{11}B NMR resonance at 21.2 ppm (fwmh ≈ 420 Hz). After removal of volatiles and extraction with hexanes, crystallization at –25 °C yielded a crop of gold-orange crystals of compound **2** (79% yield). The ^{1}H{^{11}B} NMR spectrum of **2** showed a single, symmetrical CAAC^{Me} ligand environment and a broad 2H B*H*$_2$ resonance at 2.66 ppm. The very broad ^{13}C NMR resonance of the carbene carbon atom was detected by an HMBC experiment at 161.5 ppm, 67 ppm upfield from that of the borane precursor **1** (δ_{13C} = 128.2 ppm).



Scheme 1. One-electron reduction and homocoupling of **1** to form diborane **2**. Dip = 2,6-diisopropylphenyl.

The symmetry implied by the NMR data contrasts with the crystallographically-derived structure of **2**, which shows an

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unsymmetrically μ^2-hydride-bridged diborane(5) (Fig. 2). B1 is supported by a neutral, purely σ-donating $\mathrm{CAAC^{Me}}$ ligand (B1-C1 1.5477(16) Å), whereas B2 is coordinated by a protonated $\mathrm{CAAC^{Me}}$ ligand ($\mathrm{CAAC^{Me}H}$), which displays an sp^3-hybridized C21 carbon atom (N2-C21-B2 114.15(9), C26-C21-B2 114.29(9)°) with B2-C21 and N2-C21 single bonds (1.6039(16) and 1.4774(14) Å, respectively). The B-B bond length of 1.6394(18) Å is significantly shorter than in related μ^2-hydride-bridged diboranes(5) obtained from the reduction of mono-NHC-stabilized 1,1-diaryl-2,2-dichlorodiboranes (ca. 1.67 – 1.68 Å),[12] presumably due to the absence of steric repulsion from the hydride ligands in **2**.

The synthesis of compound **2** is a rare example of targeted reduction of a neutral Lewis-base-stabilized sp^3-borane to a neutral diborane. All previous examples involved NHC-stabilized di- and trihaloboranes undergoing both reductive coupling and exchange of all remaining halogens with hydrides, through hydrogen abstraction from the reaction solvent by radical intermediates.[13] The formation of **2** may be facilitated by **1** undergoing a 1,2-hydride shift from boron to the $\mathrm{CAAC^{Me}}$ carbene carbon atom to form the isomeric sp^2-borane ($\mathrm{CAAC^{Me}H}$)BHBr, **1´**, the free energy of which was calculated to be only 11.9 kcal·mol^{-1} above that of **1** (see Fig. S24), thereby making it accessible under the reaction conditions employed in the reduction of **1** to **2**. Such reversible boron-to-carbon hydride shifts are well-documented in CAAC-supported hydroboron compounds[15] and are owed to the good π acceptor properties of CAACs, which result in a relatively low-lying LUMO and a small HOMO-LUMO gap.[6]

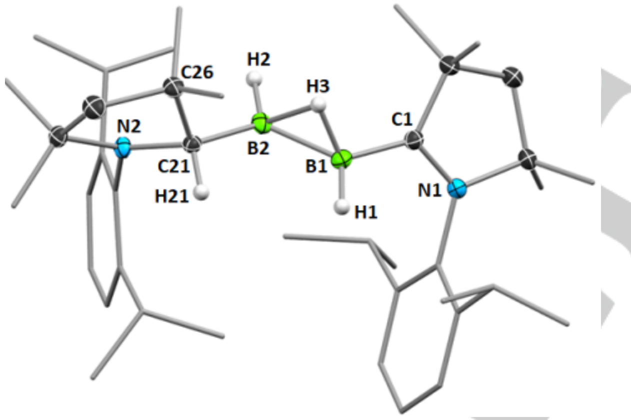
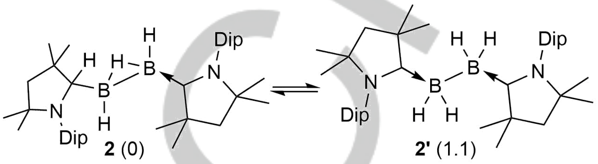


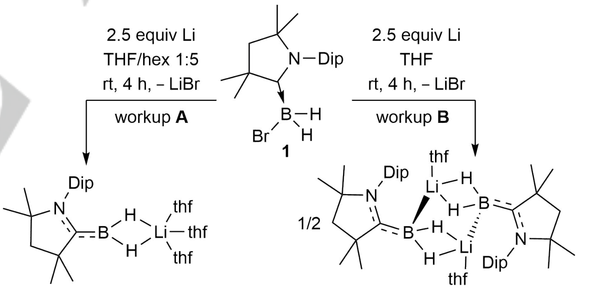
Figure 2. Crystallographically-derived molecular structure of compound **2**. Thermal ellipsoids drawn at 50% probability level. Ellipsoids on the $\mathrm{CAAC^{Me}}$ ligand periphery and most hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): B1-B2 1.6394(18), B1-C1 1.5477(16), B2-C21 1.6039(16), C1-N1 1.3169(14), C21-N2 1.4774(14), B1-H1 1.113(15), B2-H2 1.110(15), B1-H3 1.225(15), B2-H3 1.415(15), C1-B1-B2 125.07(10), C21-B2-B1 119.81(10), $\Sigma\angle_{C1}$ 359.89(10).[14]

While the solid-state structure of **2** does not reflect the solution data, such reversible hydrogen shifts are also likely to be the origin of the apparent symmetry of the compound in solution, with all four hydrogen atoms shifting back and forth between the terminal, bridging and C1-bound positions. Since cooling to –110 °C in d_8-THF did not lead to decoalescence of the ^{11}B NMR resonance, the barrier for this hydride shift is likely to be very low. Density functional theory (DFT) calculations carried out at the OLYP/TZ2P level of theory showed that the free energy of the isomeric tetrahydrodiborane(6) **2´** is only 1.1 kcal·mol^{-1} above that of **2** (Scheme 2, see Fig. S25).[16] ^{11}B NMR shift calculations at the same level of theory provided chemical shifts for **2** of –3.20 ppm for B1 and 45.4 ppm for B2, the average of which is 24.3 ppm, close to the 22 ppm observed for this resonance in solution at room temperature.



Scheme 2. Hypothesized rapid hydride-shift isomerization of **2**. Relative free energies (OLYP/TZ2P) in brackets (kcal·mol^{-1}).

The reduction of **1** with 2.5 equiv. lithium sand in a 1:5 THF/hexane mixture led to quantitative formation of the dihydroboryl anion **3** (Scheme 3, workup **A**), which displays a broad ^{11}B NMR resonance at –4.7 ppm, downfield from that of the related [($\mathrm{CAAC^{Me}}$)BH(CN)]$^-$ anion (δ_{11B} = –10.8 ppm)[8a] and a ^{7}Li NMR singlet at 0.84 ppm. After filtration and storage of the filtrate at –25 °C for three days, compound **3** was isolated as large, bright orange crystals in 81% yield. The ^{1}H{^{11}B} NMR spectrum of **3** displayed a broad B*H₂* resonance integrating for 2H with respect to the $\mathrm{CAAC^{Me}}$ resonances.



3 (81% isolated yield)
3' (66% isolated yield)

Scheme 3. Synthesis of the parent boryl anion **3** and its dimer **3´**. Workup **A**: 1) Filtration, 2) storage of filtrate at –25 °C for crystallization. Workup **B**: 1) Removal of volatiles, 2) extraction with toluene, 3) storage at –25 °C for crystallization.

X-ray structural analysis of **3** revealed a monomeric structure, comprised of a planar, anionic [(CAAC)BH$_2$]$^-$ moiety ($\Sigma\angle_{B1}$ 360.0(9)°) coordinated via the two boron-bound hydrides to a Li cation solvated by three THF residues (Fig. 3a). The B1-C1 bond length (1.440(2) Å) is similar to that in the related (cyano)hydroboryl anion dimer (1.447(3) Å),[8a] indicating strong π backdonation from the lone pair on boron to the π-acidic $\mathrm{CAAC^{Me}}$ ligand. The lithium cation is nearly aligned with the C1-B1 bond (C1-B1-Li1 165.45(15)°) and located at 2.293(3) Å from the boron(I) center. To our surprise, a change in the workup procedure involving complete removal of the reaction solvent and extraction with toluene provided the dimeric species **3´** upon crystallization (Scheme 3, workup **B**). The solid-state

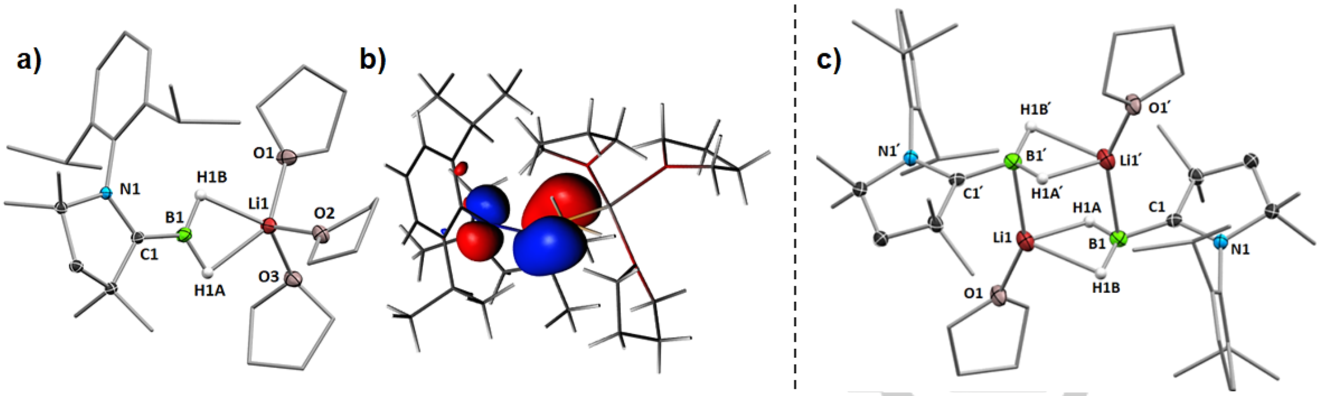
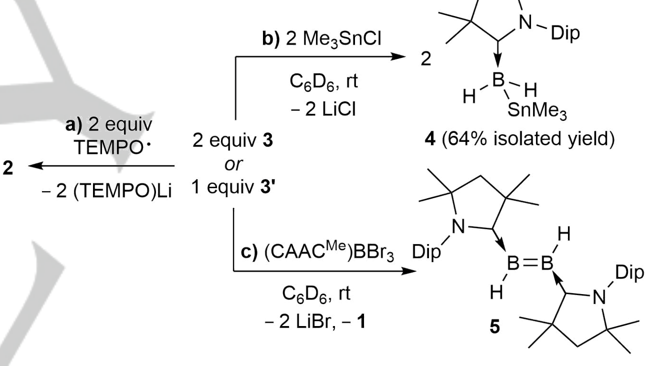


Figure 3. **a)** and **c)** Crystallographically-derived molecular structure of compounds **3** and **3´**, respectively. Thermal ellipsoids drawn at 50% probability level. Ellipsoids on the CAAC^{Me} ligand periphery and most hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): **3** B1-C1 1.440(2), C1-N1 1.4332(15), B1-H1A 1.145(17), B1-H1B 1.140(16), B1···Li1 2.293(3), Li1-H1A 2.000(17), Li1-H1B 1.917(17), C1-B1-Li1 165.45(15), $\Sigma\angle_{B1}$ 356.0(9), $\Sigma\angle_{C1}$ 359.96(11); **3´** B1-C1 1.441(6), C1-N1 1.421(4), B1-H1A 1.11(4), B1-H1B 1.19(4), B1···Li1 2.301(8), B1···Li1´ 2.407(8), Li1···Li1´ 3.041(13), H1A-Li1 1.91(4), H1B-Li1 2.07(4), Li1···C1´ 2.669(8), C1-B1-Li1´162.9(4), C1-B1-Li 83.8(3), B1-Li1-B1´ 99.6(3), $\Sigma\angle_{C1}$ 359.6(3), $\Sigma\angle_{B1}$ 360(2); **b)** Plot of the HOMO of **3** at the OLYP/TZ2P level of theory (–1.905 eV, isovalue 0.005).

structure of **3´** shows a boryl anion moiety with similar structural parameters to **3** (Fig. 3c). Its lithium cations are coordinated by a single THF residue and bridge over the boron-bound hydrides to the second boron center so as to form a distorted B_2Li_2 square (B1···Li1 2.301(8); B1···Li1´ 2.407(8) Å; B1-Li1-B1´ 99.6(3); Li1-B1-Li1´ 80.4(3)°). It is noteworthy that the coordination of each Li cation to the boron atom of the second dimer moiety occurs perpendicularly, thereby allowing the CBH_2 borylene unit to remain planar. Unlike monomeric **3**, isolated crystals of dimeric **3´** proved virtually insoluble in hydrocarbon solvents, thus precluding the acquisition of NMR data. Though indefinitely stable in THF solution up to 70 °C under inert atmosphere, both **3** and **3´** slowly decomposed in the solid state to $(CAAC)BH_3$, even when stored in the glovebox freezer at –30 °C.

Plots of the frontier molecular orbitals (MOs) of **3** show a HOMO corresponding to the B-C π-bond, with a small π antibonding contribution from the C1-N1 bonds (Fig. 3b), similar to other CAAC-supported boryl anions.[8,10] Furthermore, the B-C Mayer bond order amounts to 1.664, which is less than for the analogous $[(CAAC^{Me})BHCl]^-$ anion (1.703),[10] but still indicative of substantial π backbonding from boron to CAAC^{Me}. The calculated Hirshfeld partial charges of –0.161 for B1 and –0.077 for C1[17] confirm the negative charge accumulation on the boron atom, which is the opposite charge distribution calculated for $[(CAAC^{Me})BHCl]^-$ (–0.086 for B1 and –0.102 for C1).[10] This should make **3**/**3´** particularly nucleophilic at boron.

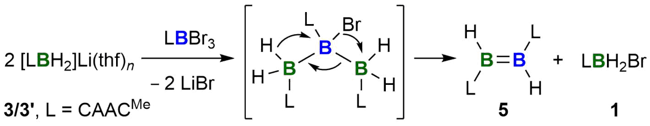
Interestingly, cyclic voltammetry performed on compounds **1**, **2** and **3** in THF showed in all three cases a reversible reduction wave at –3.2 V (referenced to the (Fc^+/Fc) couple, see Figs. S18 – S20), suggesting the possibility of a chemically reversible reduction of **2** to **3**. Indeed the reduction of isolated **2** with Li in THF led to the clean formation of **3**, a process that most likely ensues from the B-B bond cleavage of isomer **2´**. Conversely, the oxidation of **3**/**3´** with the 2,2,6,6-tetramethylpiperidyloxyl (TEMPO) radical in a 1:1 boron-to-radical ratio resulted in quantitative conversion back to diborane **2** (Scheme 4a), thus confirming the chemical reversibility of the reduction as well as of the **2**/**2´** hydride shift process.



Scheme 4. Reactivity of **3**/**3´**.

The nucleophilic character of **3**/**3´** was confirmed by salt metathesis with Me_3SnCl, which quantitatively yielded colorless $(CAAC^{Me})BH_2(SnMe_3)$ (**4**, Scheme 4b, see Fig. S23 for the solid-state structure of **4**), characterized by a ^{11}B NMR triplet at –29.7 ($^1J_{11B\text{-}1H}$ = 100 Hz) and a broad ^{119}Sn NMR quartet at –24.4 ($^1J_{11B\text{-}119Sn}$ = 314 Hz), effectively identical to that of the previously reported compound $(CAAC^{Me})BH(CN)(SnMe_3)$.[8a]

The reaction of **3** with one equiv. $(CAAC^{Me})BBr_3$ was accompanied by an instant color change to deep blue as well as the formation of a colorless precipitate, presumably LiBr. The ^{11}B NMR spectrum of the reaction mixture showed quantitative formation of **1** (broad triplet at δ_{11B} = –19.0, $^1J_{B\text{-}H}$ = 103 Hz) as well as a broad resonance at 40.0 ppm attributable to the blue-colored dihydrodiborene $(CAAC^{Me})_2B_2H_2$ (**5**, Scheme 4c),[18] which was confirmed by high-resolution mass spectrometry ($[C_{40}H_{64}B_2N_2]$: calc. 594.5250; found 594.5227). We postulate that the reaction proceeds via a double salt metathesis leading to an intermediate triborane(7), which undergoes intramolecular bromide and hydride migration, as well as B-B bond cleavage, to generate **5** and **1** (Scheme 5). While this is certainly not the most efficient way to synthesize diborene **5**, this unique reactivity has the potential to be harnessed for the synthesis of unsymmetrical B=B or new boron-element double bonds.



Scheme 5. Possible mechanism for the reaction of **3** with $(CAAC^{Me})BBr_3$.

In conclusion, we have shown that $(CAAC^{Me})BH_2Br$ (**1**) undergoes a selective, B-B bond-forming, one-electron reduction to a hydride-shift isomer of the tetrahydrodiborane $(CAAC^{Me})_2B_2H_4$, compound **2**. Subsequent two-electron reduction of **2** yields the first isolable parent boryl anion, $[(CAAC^{Me})BH_2]^-$, which may be isolated in its monomeric form **3** or dimeric form **3´**, depending on the crystallization conditions. Compound **3** owes its remarkable solution stability to the strong π acceptor properties of the CAAC ligand, their HOMO being entirely delocalized over the B-C π bond. Furthermore, $[(CAAC^{Me})BH_2]^-$ can be quantitatively oxidized back to **2**, in an unusual B-B bond-forming oxidation reaction with the TEMPO radical. While $[(CAAC^{Me})BH_2]^-$ reacts as a typical boron nucleophile towards Me_3SnCl, leading to the formation of a new B-Sn bond, it undergoes a unique B=B double-bond-forming double salt metathesis with $(CAAC^{Me})BBr_3$, generating the dihydrodiborene $(CAAC^{Me})_2B_2H_2$ and **1**. In view of these promising preliminary results, we are continuing to explore the reactivity of **3**/**3´** towards other p-block electrophiles.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boryl anion • diborane • reduction • nucleophilic boron • cyclic (alkyl)(amino)carbene

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[14] Two distinct polymorphs of **2** were obtained, one crystallizing in the triclinic space group $P\bar{1}$, presented here in Fig. 2, the other in the orthorhombic space group $P\,c\,a\,2_1$, presented in Fig. S22.
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[16] Attempts to calculate the energy barrier for this hydride shift failed as optimizations of possible transition states simply reverted to compound **2**.
[17] For the dimer **3´**, the HOMO and HOMO–1 are both symmetrically distributed over the B-C π-bonds of both moieties (see Fig. S28), the B-C Mayer bond orders amount to 1.517 and the calculated Hirshfeld partial charges are –0.167 for B1 and –0.054 for C1.
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Layout 2:

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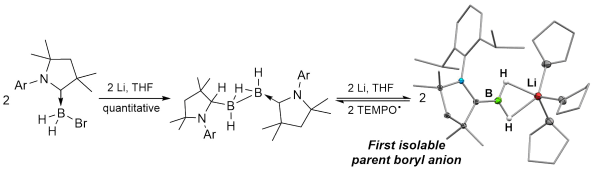

Successive reductions of a cyclic (alkyl)(amino)carbene (CAAC)-supported (bromo)dihydroborane yield a hydride-shift isomer of the corresponding tetrahydrodiborane and the first stable dihydroboryl anion, which acts as a powerful boron nucleophile.

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