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Direct Access to a cAAC-Supported Dihydrodiborene and its Dianion

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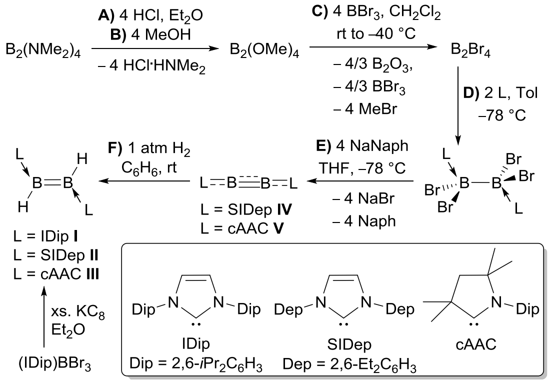
The two-fold reduction of (cAAC)BHX$_2$ (cAAC = 1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene); X = Cl, Br) provides a facile, high-yielding route to the dihydrodiborene (cAAC)$_2$B$_2$H$_2$. The (chloro)hydroboryl anion reduction intermediate was successfully isolated using a crown ether. Overreduction of the diborene to its dianion [(cAAC)$_2$B$_2$H$_2$]$^{2-}$ causes a decrease in the B-B bond order whereas the B-C bond orders increase.

Since the landmark isolation in 2007 of the first diborene, (IDip)$_2$B$_2$H$_2$ (**I**, IDip = 1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene) from the reduction of (IDip)BBr$_3$ (Scheme 1),[1,2] the targeted synthesis of doubly Lewis-base-stabilised boron-boron double bonds has greatly advanced.[3-8] It was not until 2016, however, that a rational high-yielding synthesis of two dihydrodiborenes, (SIDep)$_2$B$_2$H$_2$ (**II**, SIDep = 1,3-bis(2,6-diethylphenyl)-4,5-dihydroimidazol-2-ylidene) and (cAAC)$_2$B$_2$H$_2$ (**III**, cAAC = 1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene)[9] was achieved by selective hydrogenation of the diboryne and diboracumulene precursors, (SIDep)$_2$B$_2$ (**IV**)[9] and (cAAC)$_2$B$_2$ (**V**),[10] respectively (Scheme 1). The cyclic (alkyl)(amino)carbene-supported diborene **III** has already shown promising CO activation reactivity,[11] and unpublished work by our group is confirming the remarkable versatility of this compound in the activation of a wide range of small molecules. Until now, however, the exploration of its reactivity has been severely limited by the complex multi-step synthesis required to obtain **III** (Scheme 1): starting from the particularly challenging and unreliable three-step synthesis of highly sensitive B$_2$Br$_4$, which can only be stored at –70 °C (ca. 30 – 60% overall yield for steps **A – C**),[12] the bis(cAAC) adduct is formed by addition of 2 equiv. cAAC to B$_2$Br$_4$ (step **D**, quantitative).[10] Subsequent reduction of (cAAC)$_2$B$_2$Br$_4$ with 4 equiv. sodium naphthalenide yields the diboracumulene **V** (step **E**, 74% isolated yield),[10] which can be hydrogenated at room temperature to yield diborene **III** (step F, 74% isolated yield).[9]



Scheme 1. Current syntheses for dihydrodiborenes **I – III** (Naph = naphthalenide).

With a maximum overall yield of ca. 30% from commercial B$_2$(NMe$_2$)$_4$ over six steps, large amounts of by-products and often highly sensitive reaction conditions, the current synthesis of **III** poses serious problems of scalability. In this paper, we report an facile, high-yielding three-step synthetic route to **III** from commercially available borane precursors, and describe the isolation of a unique (halo)hydroboryl anion intermediate, as well as the doubly reduced dianion of **III**.

The cAAC-supported (dihalo)hydroboron compounds (cAAC)BHCl$_2$ (**1a**) and (cAAC)BHBr$_2$ (**1b**) were obtained in good yield from the addition of cAAC to the corresponding dimethylsulfide precursors, BHX$_2$·SMe$_2$ (X = Cl, Br; see Supporting Information for synthetic details and Fig. S16 for X-ray structure of **1b**). **1a** and **1b** each displayed a broad ^{11}B NMR *B*H doublet at –4.7 ppm ($^1J_{11B\text{-}1H}$ = 123 Hz) and at –13.1 ppm ($^1J_{11B\text{-}1H}$ = 127 Hz), respectively, as well as a corresponding ^{1}H{^{11}B} NMR B*H* hydride resonance at 3.41 and 3.39 ppm, respectively. The room temperature reduction of **1a** or

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Cif files of crystallographic structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 1825071-1825074. Electronic Supplementary Information (ESI) available: general experimental details, characterization data for all reported compounds and details of the DFT calculations. See DOI: 10.1039/x0xx00000x.

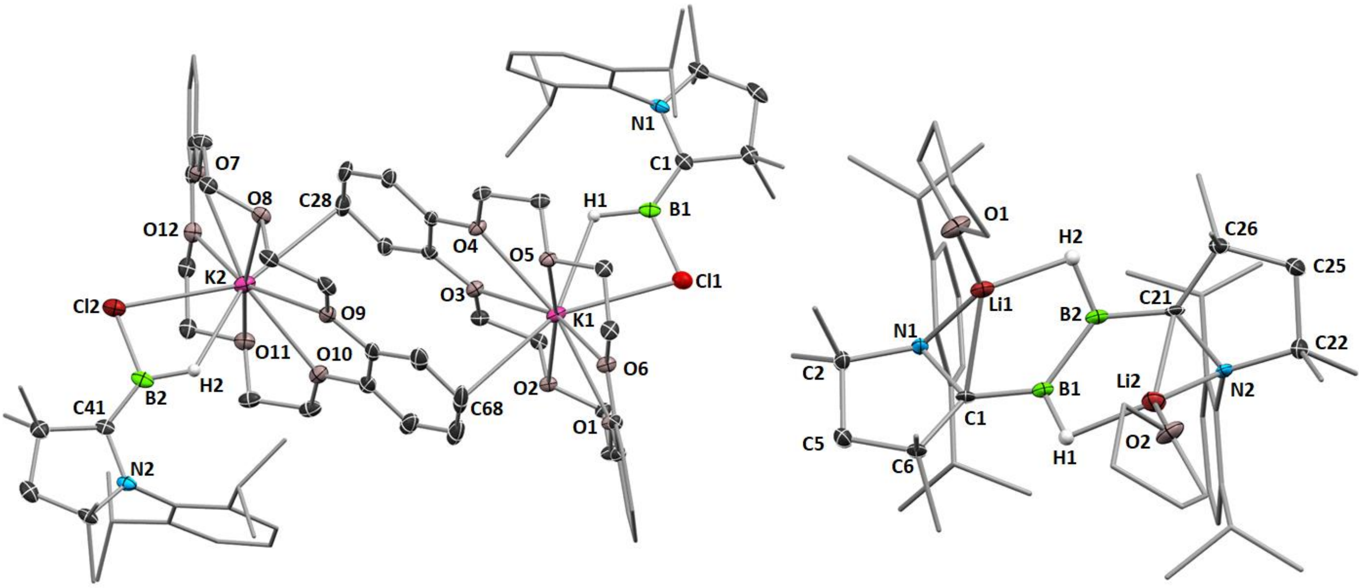
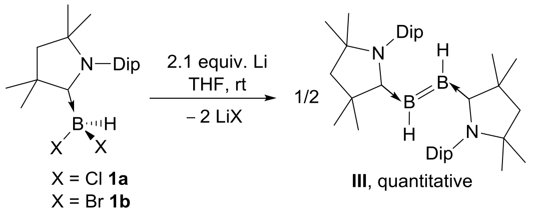


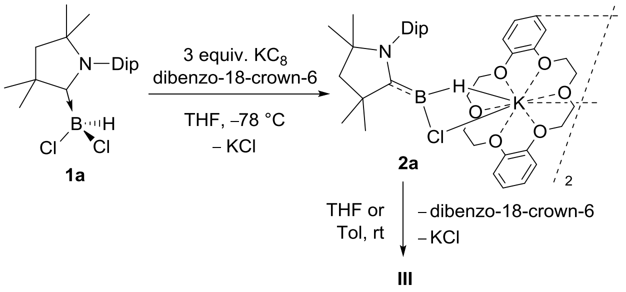
Figure 1. Crystallographically-derived molecular structures of **2a** (left) and **3** (right). Thermal ellipsoids drawn at the 50% probability level. Ellipsoids on the cAAC ligand periphery and hydrogen atoms have been omitted for clarity, except the boron-bound hydrides. Selected bond lengths (Å) and angles (°): **2a** C1-N1 1.429(5), B1-C1 1.460(6), B1-H1 1.22(4), B1-Cl1 1.864(5), H1-K1 2.64(4), Cl1-K1 3.1831(14), $\Sigma\angle_{B1}$ 359.8(14), $\Sigma\angle_{B2}$ 359.7(13); **3** C1-N1 1.492(3), B1-C1 1.458(4), B1-H1 1.12(3), B1-B2 1.712(4), Li1-H2 1.86(3), Li1-N1 2.106(6), Li1-C1 2.138(6), $\Sigma\angle_{B1}$ 358.3(12) $\Sigma\angle_{B2}$ 358.3(10).



Scheme 2. New synthetic route towards cAAC-supported dihydrodiborene **III**.

1b with 2.1 equiv. lithium sand in THF resulted in the rapid formation of a deep blue suspension. The filtrate displayed a single broad ^{11}B NMR resonance at 40.5 ppm, suggesting the formation of dihydrodiborene **III** (Scheme 2).[9] This was confirmed upon extraction and crystallisation of the product from hexanes. A scaled-up synthesis starting with 11.0 mmol of commercial $BHCl_2{\cdot}SMe_2$ provided **III** in 72% isolated yield, without need for intermediate purification. This facile, scalable three-step synthesis of dihydrodiborene **III** from commercially available $BX_3{\cdot}SMe_2$ and $BH_3{\cdot}SMe_2$, or $BHX_2{\cdot}SMe_2$, which produces SMe_2 and LiX as sole and easily removed by-products, should greatly facilitate further exploration of its reactivity towards other small molecules. Interestingly, the synthesis in Scheme 2 also represents the first example of diborene formation from the reductive coupling of a cAAC haloborane adduct, a reaction that has thus far never been shown to produce B–B-bond-containing products. Instead, studies from our group and that of Bertrand have indicated that the excellent π-acceptor properties of cAACs[13,14] favour the formation of boryl radicals,[15] boryl anions[16-18] and borylenes[19-22] through π backdonation from the electron-rich low-valent boron to the cAAC ligand.

With this in mind, we set out to isolate potential intermediates in the reduction of **1a** and **1b** to **III**. While the low-temperature reduction of **1b** in a range of solvents with varying stoichiometries of reducing agents provided no evidence of intermediates, the reduction of its dichloride analogue **1a** with 2.2 equiv. KC_8 in THF proceeded much more slowly through colour changes from green to blue, suggesting the possible formation of a boryl radical or boryl anion intermediate.



Scheme 3. Isolation of boryl anion reduction intermediate **2a**.

Indeed, the reduction of **1a** with 3 equiv. KC_8 in THF at –78 °C in the presence of dibenzo-18-crown-6 enabled the isolation of small amounts of an orange solid, determined to be the dimer of the (chloro)hydroboryl anion $[\{(\text{cAAC})\text{BHCl}\}\{\text{K}(\text{dibenzo-18-crown-6})\}]_2$ (**2a**, Scheme 3). **2a** displayed a very broad ^{11}B NMR resonance at around 18 ppm in toluene (fwmh ~ 1100 Hz) and unsymmetrical cAAC resonances, as well as very broad dibenzo-18-crown-6 resonances in the ^{1}H NMR spectrum. The ca. 30 ppm downfield shift of the ^{11}B NMR resonance compared to the related cAAC-supported (cyano)hydroboryl anion (δ_{11B} = –10.8 ppm)[17] reflects the much stronger electronwithdrawing effect of the chloride versus the cyano ligand. The X-ray crystallographic structure of **2a** shows two planar (chloro)hydroboryl anion moieties ($\Sigma\angle_B$ ca. 360°) displaying strong π backdonation into the cAAC ligands, with B-C bond lengths (1.460(6), 1.432(6) Å) comparable to that observed in the cAAC-supported (cyano)hydroboryl anions (B-C$_{cAAC}$ 1.447(3) Å).[17] The boron-bound hydride and chloride ligands bridge to the potassium cation, which is additionally complexed by the crown ether. The K1-H1 bond (2.64(4) Å) is shorter than those in the crown ether-stabilised potassium borohydride [BH$_4$][K(18-crown-6)] (2.7097(5) – 2.8417(5) Å),[23] while the K1-Cl1 interaction (3.1831(14) Å) is within the range of those observed in the doubly reduced 1-chloro-2,3,4,5-tetraphenylborole (3.1445(16) – 3.2126(16) Å).[24] The structure dimerises via cation-π interaction of each potassium centre with one of the benzo units of the opposite crown ether. Upon performing the same reaction in toluene instead of THF, crystals of a monomeric species, [(cAAC)BHCl][K(dibenzo-18-crown-6)]·tol (**2a'**) were isolated, in which the open side of the potassium countercation is capped by π interaction with a toluene molecule (see Fig. S17 for X-ray structure of **2a'**).

Calculations within the Kohn-Sham Density Functional Theory (DFT) at the OLYP/TZ2P level were conducted. Plots of the frontier molecular orbitals of one half of dimeric **2a** (see Supporting Information for details of the computations) show a HOMO largely localised on boron and extending over the B-C π-bond (Fig. S21), similar to other cAAC-supported boryl anions.[17,18] Further analysis indicated Hirshfeld partial charges of –0.086 for boron and –0.102 for the carbene carbon, while calculations give a B-C Mayer bond order of 1.703, confirming the strong π backbonding from boron to the cAAC ligand.

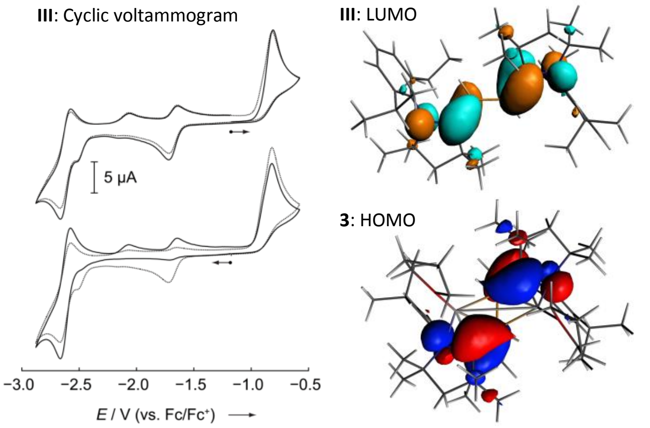
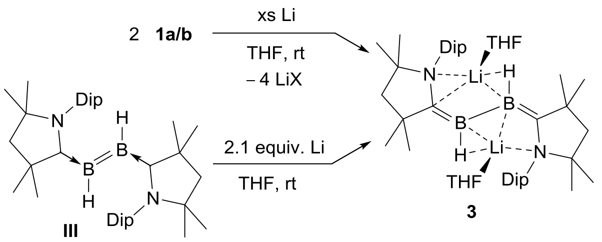


Figure 2. Left: Cyclic voltammogram of diborene **III** (in THF 0.1 M [NBu$_4$][PF$_6$]), upon scanning (0.2 V s^{-1}) in the positive (*top*) and negative (*bottom*) direction (1st scan: solid line; 2nd scan: dashed line). Right: Plot of LUMO of **III** (–2.337 eV, top) and HOMO of **3** (–2.749 eV, bottom) at the OLYP/TZ2P level of theory.

Although **2a** and **2a'** could only ever be isolated in small amounts (less than 20% yield) their formation was reproducible. At room temperature, toluene solutions of isolated crystals of **2a** or **2a'** slowly turned green then deep blue, concomitant with the slow formation of diborene **III** and free dibenzo-18-crown-6 as observed by ^{11}B and ^{1}H NMR spectroscopy, and presumably loss of KCl. These observations lead us to conclude that the reduction of **1a** or **1b** to diborene **III** most likely proceeds via a (halo)hydroboryl anion intermediate.

During the scaled-up synthesis of **III** following Scheme 2, an orange solid insoluble in aliphatic hydrocarbon solvents was isolated as a by-product in ca. 7% yield. In C$_6$D$_6$ this compound presented as single broad ^{11}B NMR resonance around 14 ppm and a ^{7}Li NMR singlet at –0.26 ppm. Cyclic voltammetry performed on diborene **III** in THF also showed a partially reversible reduction peak ($E_{1/2}$) at −2.62 V (Fig. 2). Calculations performed on **III** reveal a HOMO delocalised, as expected, over the CBBC π-bonding system (Fig. S19), whereas the LUMO is constituted of π*-bonding B-C interactions and adjacent π*-antibonding C-N interactions. Indeed the reduction of **1a** or **1b** with 4 equiv. Li or of **III** with 2.1 equiv. Li provided clean access to the doubly reduced dianion **3** (Scheme 4), which was isolated from a 2:1 THF/hexanes mixture stored at –30 °C as a bright yellow crystalline solid. X-ray crystallographic data show a near-planar C=B(H)-B(H)=C core (torsion angle (C1,B1,B2,C21) 171.3(3)°) displaying discrete B-B single (1.712(4) Å) and B=C double bonds (B-C 1.464(4), 1.458(4) Å), making this compound indeed a 1,2-dialkylidene-1,2-dihydrodiborane dianion. The C-N bonds of the cAAC ligands now display clear single bond character (1.492(3), 1.488(3) Å). Both lithium cations are positioned on the same side above the planar (CBBC) core, and coordinate to one cAAC nitrogen atom, one boron-bound hydride and one THF molecule, with an additional weak interaction with the alkylidene carbon atom (Li-C$_{cAAC}$ 2.138(6), 2.139(6) Å). Further calculations show that the HOMO of dianion **3** maps with the LUMO of diborene **III**, showing π-bonding B-C and π-antibonding C-N character (Fig. 2). Calculations indicate a B-B Mayer bond order of 1.018 and B-C Mayer bond orders of 1.344 and 1.345, which are inverted from those in diborene **III** (Mayer bond orders: B-C 1.084; B-B 1.282).



Scheme 4. Overreduction of precursors **1a** and **1b** or diborene **III** to dianion **3**.

Solutions of dianion **3** left to stand open in the glovebox underwent a slow colour change from orange via green to blue, concomitant with the reformation of diborene **III**, presumably through hydrolysis with trace water in the glovebox atmosphere.

In this work we have presented the first example of diborene formation by the reductive coupling of two cAAC-supported dihaloboranes. Furthermore we succeeded in isolating a unique and extremely sensitive (halo)hydroboryl anion intermediate, as well as the doubly reduced dianion of (cAAC)$_2$B$_2$H$_2$, which displays formal B=C double and B-B single bonds. With this facile, high-yielding synthesis in hand we will report on the reactivity of diborene **III** and its dianion **3** in due course.

Acknowledgements

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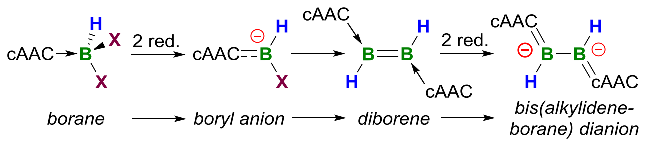

The stepwise reduction of cyclic (alkyl)(amino)carbene-supported (dihalo)hydroboranes provides access to a highly sensitive (halo)hydroboryl anion, followed by a dihydrodiborene and, finally, a bis(alkylidene-borane) dianion.