Direct Access to a cAAC-Supported Dihydrodiborene and its Dianion

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The two-fold reduction of (cAAC)BHCl (cAAC = 1-(2,6-dimisopropylphenyl)-3,5,5-tetramethylpyrrolidin-2-ylidene; X = Cl, Br) provides a facile, high-yielding route to the dihydrodiborene (cAAC)BHBrH. The (chloro)hydroboryl anion reduction intermediate was successfully isolated using a crown ether. Overreduction of the diborene to its dianion ([cAAC]BHBrH)\(^2^-\) 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)BH\(_2\)H (IDip = 1,3-bis(2,6-dimisopropylphenyl)imidazol-2-ylidene) from the reduction of (IDip)BB\(_4\) (Scheme 1),\(^1\)\(^\text{a,b}\) the targeted synthesis of doubly Lewis-base-stabilised boron-boron double bonds has greatly advanced.\(^1\)\(^\text{a,b}\) It was not until 2016, however, that a rational high-yielding synthesis of two dihydrodiborenes, (SIDep)BH\(_2\)H (SIDep = 1,3-bis(2,6-diethynylphenyl)-4,5-dihydroimidazol-2-ylidene) and (cAAC)BH\(_2\)H (cAAC = 1-(2,6-dimisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene)\(^7\) was achieved by selective hydrogenation of the diboronyl and diboracumulene precursors, (SIDep)BH\(_2\) (\(\text{SIDep} = \text{IV}^7\)) and (cAAC)BH\(_2\) (V),\(^7\) 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cyclic (alkyl)(amino)carbene-supported diborene III has already shown promising CO activation reactivity,\(^11\) and unpublished work by our group is confirming the remarkable versatility of this compound in the activation of a wide range of small molecules.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 \(-70^\circ\text{C}\) (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)BHBr\(_2\) 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).\(^9\)

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 diion 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 dimethylsulphide precursors, BH\(_2\)SMES (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 \(^1\)B NMR BH doublet at \(-4.7\) ppm (J\(_{1\text{B},1\text{H}}\) = 123 Hz) and at \(-13.1\) ppm (J\(_{1\text{B},1\text{H}}\) = 127 Hz), respectively, as well as a corresponding \(^3\)H(J\(_{1\text{B},1\text{H}}\)) NMR BH hydride resonance at 3.41 and 3.39 ppm, respectively. The room temperature reduction of 1a or

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\(^{\text{e}}\) 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/s000000x.

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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. KC₈ 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.

Indeed, the reduction of 1a with 3 equiv. KC₈ 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 [(cAAC)BHCl][K(dibenzo-18-crown-6)]₂ (2a, Scheme 3). 2a displayed a very broad ²⁷B NMR resonance at around 18 ppm in toluene (fwhm ~ 1100 Hz) and unsymmetrical cAAC resonances, as well as very broad dibenzo-18-crown-6 resonances in the H NMR spectrum. The ca. 30 ppm downfield shift of the ²⁷B NMR resonance compared to the related cAAC-supported (cyano)hydroboryl anion (δ₁₁₈ = −10.8 ppm)¹⁷ reflects the much stronger electron-
withdrawing effect of the chloride versus the cyano ligand. The X-ray crystallographic structure of 2a shows two planar (chloro)hydroboryl anion moieties (ΣC=8 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 [KH][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)B(H)][K(dibenzo-18-crown-6)]·tol (2a’), were isolated, in which the open side of the potassium counterion 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 diborene 1a (Fig. S18) in the positive (top) and negative (bottom) partial charges demonstrated that the HOMO largely localises on one cAAC atom, one boron-bound hydride and one THF molecule, with 2 equiv. Li or of 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)–(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).

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 11B and 1H 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 C6D6 this compound presented as single broad 11B NMR resonance around 14 ppm and a 2Li NMR singlet at –0.26 ppm. Cyclic voltammetry performed on diborene III in THF also showed a partially reversible reduction peak (Ec1/2) 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)–(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).

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![Figure 2](image-url)  
**Figure 2.** Left: Cyclic voltammogram of diborene III (in THF 0.1 M [NBu4][PF6]), 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.  

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)2B2H2, 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 \( \text{III} \) and its dianion \( \text{3} \) in due course.

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**Notes and references**

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.