Reduction of a dihydroboryl cation to a boryl anion and its air-stable, neutral hydroboryl radical through hydrogen shuttling†

Stephan Hagspiel,ab Merle Arrowsmith,ab Felipe Fantuzzi,abc Alexander Hermann,ab Valerie Paprocki,ab Regina Drescher,ab Ivo Krummenacherabc and Holger Braunschweig†abc

The addition of Lewis bases to a cyclic (alkyl)(amino)carbene (CAAC)-supported dihydroboron trflate yields the mixed doubly base-stabilised dihydroboryl cations [(CAAC)BH₂L]+. Of these, [(CAAC)₂BH₂]OTf (OTf = trflate) underwent facile two-electron reduction with KC₈ owing to a 1,2-hydride migration from boron to the carbene carbon to yield a stable hydroboryl anion. One-electron oxidation of the latter yielded the first neutral hydroboryl radical, which is bench-stable in the solid state.

Introduction

Cyclic (alkyl)(amino)carbenes (CAACs) have become the ligands of choice for the stabilisation of many main group compounds in low oxidation states owing to their excellent σ-donor and π-acceptor properties derived from a relatively high-lying HOMO and low-lying LUMO.1–4 In the field of low-valent mononuclear boron chemistry, they have been successfully employed to synthesise unusual boron(n) species such as boryl radicals [(CAAC)BXY]^·; X, Y = anionic ligands, e.g. I, Fig. 1a),5–10 boryl radical cations [(CAAC)LBXY]^+ (CAAC, L = Lewis donor)11–13 and boryl anions [(CAAC)BX]–, e.g. II),14–17 as well as boron(n) species such as borylenes (CAAC)LBX, e.g. III, and (CAAC)BNR).5,6,11–15,16,18–20 In all these compounds, the accumulation of negative charge on the low-valent boron centre is stabilised through π back-bonding to the CAAC ligand(s) (Fig. 1a), making many of them surprisingly stable under inert conditions.1–4 Recently, transient dicoordinate (CAAC)-stabilised borylenes have drawn particular attention as compounds capable of activating and catenating N₂,21–25 the latter reaction being unprecedented even in transition metal chemistry.

Furthermore, CAACs have been shown to act as element-hydrogen σ bonds, including H–H, N–H, P–H, Si–H and B–H by addition to their nucleophilic carbene carbon.1,4 In CAAC-supported hydroboron compounds, the B–H bond activation process can be reversible (Fig. 1b)14,16,21 and is favoured by electron-donating ligands at boron,22–28 thereby affording additional stabilisation for electron-rich lower oxidation state species through facile hydrogen shuttling. In this contribution we combine the excellent σ-donating/π-accepting and B–H bond activating properties of CAACs to synthesise and isolate a solvent-free alkyl(hydro)boryl anion, and selectively oxidise it to the corresponding radical, which is surprisingly air-stable in the solid state.

Results and discussion

Following a procedure by Bertrand and co-workers,12 methyl trifluoromethanesulfonate (MeOTf) was employed to abstract a hydride from (CAACMe)BH₃ ([CAACMe]BH₃ = 1-(2,6-dimethylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene). The resulting trflate derivative 1 was treated in a 1 : 1 ratio with a series of Lewis bases in benzene to generate the bis(base)-stabilised boronium cations [(CAACMe)₂BH₂L]OTf (L = CAACMe, ImMe = 1,3-dimethylimidazol-2-ylidene, PMe₃, Scheme 1a), all presenting a characteristic upfield 11B NMR BH₃ triplet in the −22 to −30 ppm region.§ In the case of the 4-dimethylaminopyridine (DMAP) derivative, 2-DMAP (δBH₃ = −10.6 ppm, broad), the synthesis had to be carried out in THF as treatment of 1 with one equivalent of DMAP in benzene resulted in the formation of the bis(DMAP) adduct 3-DMAP (δBH₃ = 4.2 ppm, Scheme 1b), in which the second DMAP equivalent has promoted a typical 1,2-migration of one hydrogen atom from boron to the CAACMe ligand.29 The solid-state structure of 3-DMAP (Fig. 2) evidences the binding of the DMAP residues and the migration of H₁ to C₁, which is now sp³-hybridised (B₁–C₁ 1.619(4), C₁–N₁ 1.490(3) Å). In contrast, the binding of a second equivalent of pyridine to 2-Pyr (δBH₃ = −9.3 ppm,
(broad) was found to be reversible: even in neat pyridine only ca. 75% conversion to 3-Pyr (δ_{11B} = 6.9 ppm) was observed. The use of 4,4'-bipyridine as a base led to the formation of the 4,4'-bipyridine-bridged bis(boron) species 4-Bipy (δ_{11B} = −8.6 ppm, broad, Scheme 1c). Attempts to synthesise the derivative 2-thf in THF resulted in ring-opening polymerisation of the solvent within two days at room temperature.

Attempts to reduce 2-CAACMe, 3-L, and 4-L under various conditions all resulted in unselective reactions, except for 2-CAACMe, which was readily reduced with excess KC₈ to the red-coloured (alkyl) hydroboryl anion 5 by 1,2-migration of one hydrogen atom from boron to CAAC-Me (Scheme 2a). The ¹¹B NMR spectrum of 5

![Scheme 1](image1.png)

**Scheme 1** Syntheses of bis- and tris(base)-stabilised boronium cations (a) 2-L, (b) 3-L and (c) 4-L. Isolated yields in brackets. IMeMe = 1,3,4,5-tetramethylimidazol-2-ylidene, Pyr = pyridine, DMAP = 4-dimethylaminopyridine.

![Scheme 2](image2.png)

**Scheme 2** Reduction of 2-CAACMe to boryl anions (a) 5 and (b)–(c) 5-thf, and subsequent comproportionation to (d) boryl radical 6.
shows a single broad resonance at 16.7 ppm, significantly downfield-shifted from that of other CAAC-stabilised boryl anions, which range from $\delta_{B^1} = -4.7$ ppm for $[(CAACMe)BH_3]$ to $\delta_{B^1} = -17.9$ ppm for $[(CAAC^C)B(CN)_2]$; likely because of the electron-withdrawing nature of the aminoalkyl substituent CAACMeH. The $^1H^{^{11B}}$ NMR spectrum shows a $B$/$D$ doublet at 1.90 ppm ($J = 6.6$ Hz), coupling to the BCH resonance of the CAACMeH ligand at 4.38 ppm, as well as two sets of unsymmetrical CAACMe ligand resonances. An X-ray crystallographic analysis revealed a monomeric structure with a trigonal-planar boron atom ($\Sigma \angle B_1 359(1) \degree$), in which the potassium cation bound to the BH hydride ($K1 \cdots H2 2.53(3)$ Å) is encapsulated by the ligand sphere through $\eta^6\pi$ interactions with the Dip (=2,6-diisopropylphenyl) substituents of the CAACMe and CAACMeH ligands (Fig. 3). The $B1$–$C1A$ bond length of 1.439(11) Å is significantly shorter than in the 2-CAACMe precursor ($B$–$C_{avg}$ 1.69 Å, Fig. 2) and typical of a $B$=C double bond. This is indicative of strong $\pi$ backdonation from the lone pair of the boryl anion to the $\pi$-accepting CAACMe ligand, as found in all CAAC-stabilised boryl anions.\textsuperscript{6,14-17} According to DFT calculations carried out at the $\omega$B97XD/6-31+G$^*$ level of theory, the HOMO of 5 possesses $\pi$-bonding character between $B1$ and $C1A$, with a nodal plane located at the $C1A$-$N1'$ bond region (Fig. 4). As in 3-DMAP, a 1,2-hydrde shift has occurred and $C1B$ is now sp$^3$-hybridised ($B1$–$C1B$ 1.633(9), $N1$–$C1B$ 1.520(8) Å). The presence of the hydrogen atom at boron was further confirmed by a solid-state infrared absorption at 2329 cm$^{-1}$, corresponding to the B–H stretching mode. The computed B–H stretching mode of 2352 cm$^{-1}$ at $\omega$B97XD/6-31+G$^*$ agrees well with the experimental value.

The reduction of 2-CAACMe in THF or the dissolution of 5 in THF both yielded the analogue 5-thf (Scheme 2b, c and Fig. 3), in which the hydride-bound potassium cation is $\eta^6\pi$-stabilised now only by the Dip substituent of the neutral CAACMe ligand, its coordination sphere being completed by three THF molecules and an agostic interaction with one of the vicinal methyl groups (C25) of the CAACMeH ligand. The bond lengths and angles of the boryl anion core change little compared to those of solvent-free 5, the major difference being the conformation of the pyrrolidine rings of CAACMeH and CAACMe, which flip so that the Dip substituents now point in opposite directions.

Cyclic voltammograms of 2-CAACMe and 5-thf in THF (0.1 M [nBu$_4$N][PF$_6$]) were essentially identical, showing a reversible redox event at $E_{1/2} = -2.31$ V and an irreversible oxidation around $-0.90$ V (relative to $Fe/Fe^+$), suggesting that chemical oxidation of 5 to 6 should be possible. Indeed, the reaction of 5-thf with 2-CAACMe led to quantitative comproportionation to the boryl radical 6 (Scheme 2d). Attempts to generate 6 by the direct one-electron reduction of 2-CAACMe failed, resulting instead in incomplete consumption of 2-CAACMe and generating a mixture of 5 and 6. Radical 6 is deep purple in solution ($\lambda_{max} = 523$ nm in the UV-vis spectrum) and $^{11B}$ NMR-silent. In the solid state, however, isolated crystals of 6 are deep orange. X-ray diffraction analysis showed a structure very similar to 5 bar the potassium cation, with a trigonal planar B1 centre ($\Sigma \angle B_1 359.5(6) \degree$) and the Dip groups of the CAACMeH and CAACMe ligands both pointing in the same direction (Fig. 3).
Unlike in 5 and 5-thf, the B1–C1 and C1–N1 bonds at the neutral CAACMe ligand (1.5174(18) and 1.4601(18) Å, respectively) are within the range typical of partial double bonds, as is typical for CAAC-stabilised boryl radicals due to the delocalisation of the unpaired electron over the N1–C1–B1 π framework.5,9,21,32,31,33

The IR spectrum of 6 shows a B–H stretching band at 2533 cm⁻¹ (calc.: 2558 cm⁻¹ at ωB97XD/6-31+G*), ca. 200 wavenumbers higher than that in 5, and 100 higher than in Bertrand’s hydroborylene III (Fig. 1a, ω(B–H) = 2455 cm⁻¹), suggesting a significant strengthening of the B–H bond in radical 6. The EPR spectrum of 6 displays a broad triplet from the hyperfine coupling to the ¹⁴N nucleus (aH = 18.5 MHz, Fig. 5a). The simulated spectrum further provides hyperfine coupling parameters to the quadrupolar ¹¹B nucleus (aq = 9.7 MHz), which is responsible for the line-broadening, and the BH and CAACMeH¹H nuclei (aq = 13.6 and 4.8 MHz, respectively). The presence of two distinct couplings to these ¹H nuclei suggests that the compound displays no fluxional B-to-CAAC hydrogen migration in solution.

Calculations show that the SOMO consists mainly of the B1–C1 π bond with some p antibonding character on the C1–N1 bond (Fig. 5c). The calculated Mulliken atomic spin densities are 53% on C1, 21% on N1 and only 15% on B1, showing that the unpaired electron is mainly delocalised on the CAAC ligand (Fig. 5d), as already suggested by the much stronger EPR hyperfine coupling to N1 than B1 (vide supra). To our knowledge, 6 is the first example of a neutral, structurally characterised hydroboryl radical. Moreover, to our surprise, isolated crystals of 6 proved air-stable at room temperature over a period of one week, making this compound a rare example of an air-stable boron-centred radical. This is presumably owed to a combination of the high degree of spin delocalisation, the low spin density at boron and the very effective encapsulation of the B–H unit by the CAACMe and CAACMeH ligands as seen in the electrostatic potential map in Fig. 5b. The only other air-stable boron-based radical reported is a permethylated icosahedral borane (closo-B12(CH3)12)⁻ radical anion, in which the unpaired electron is trapped and delocalised within the B12 cage.34

Reactions of the boryl anion 5 with a wide range of electrophiles including haloboranes, organohalides, heavier group 14 chlorides, as well as Zn(II), Cu(I) and Au(I) halides all resulted in quantitative oxidation of 5 to radical 6, and reduction of the corresponding electrophile. This contrasts with the boron nucleophile behaviour observed for CAAC-stabilised cyanoboronyl anions.16,17 With elemental sulfur, double oxidation back to the 2-CAACMe cation was observed by NMR spectroscopic analysis (δH = –22.4 ppm, τ, JH–H⁻ = 84.7 Hz), the counteranion presumably being a S²⁻ polysulfide (7, Scheme 3a). The only nucleophilic reactivity observed was with methyl triflate, which yielded clean salt metathesis to the methylated trialkylborane through migration of the second hydride to the remaining CAACMe ligand (δH = 93.9 ppm, Scheme 3b).

Conclusions

We have shown herein that the ability of CAACs to stabilise electron-rich boron centres and reversibly activate B–H bonds can be harnessed together to reduce a [L₂BH₄]⁻ anion without the usual need for halide abstraction, thanks to B-to-CAAC hydrogen shuttling. This boryl anion reacts principally as a one-electron reducing agent to yield the neutral hydroboryl radical [LRBH]⁺, the surprising stability of which is ensured by the unique stereoelectronic properties of the two encapsulating CAACMe ligands.

Conflicts of interest

The authors declare no conflict of interest.

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Notes and references

† The boron-bound hydrides of each structure were detected as residual electron density in the difference Fourier map and freely refined.
§ The X-ray crystallographically-determined structures of 1,2-Pyr and 2-DMAP can be found in the ESI, Fig. S55–S57.