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### 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  $\sigma$ -donor and  $\pi$ acceptor properties derived from a relatively high-lying HOMO and low-lying LUMO.<sup>1-4</sup> In the field of low-valent mononuclear boron chemistry, they have been successfully employed to synthesise unusual boron(II) species such as boryl radicals ([(CAAC) BXY]; X, Y = anionic ligands, e.g. I, Fig. 1a),<sup>5-10</sup> boryl radical cations ([(CAAC)LBY]<sup> $\cdot$ +</sup>, L = Lewis donor)<sup>10–13</sup> and boryl anions ([(CAAC)BXY]<sup>-</sup>, e.g. II),<sup>14-17</sup> as well as boron(1) species such as borylenes ((CAAC)LBX, e.g. III, and (CAAC)BNR<sub>2</sub>).<sup>6-8,11-13,16,18-20</sup> In all these compounds, the accumulation of negative charge on the low-valent boron centre is stabilised through  $\pi$  backbonding to the CAAC ligand(s) (Fig. 1a), making many of them surprisingly stable under inert conditions.<sup>1-4</sup> Recently, transient dicoordinate (CAAC)-stabilised borylenes have drawn particular attention as compounds capable of activating and catenating  $N_2$ ,<sup>21-25</sup> the latter reaction being unprecedented even in transition metal chemistry.

Furthermore, CAACs have been shown to activate elementhydrogen  $\sigma$  bonds, including H–H, N–H, P–H, Si–H and B–H by addition to their nucleophilic carbene carbon.<sup>3,4</sup> In CAAC-

## Reduction of a dihydroboryl cation to a boryl anion and its air-stable, neutral hydroboryl radical through hydrogen shuttling<sup>+</sup>

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The addition of Lewis bases to a cyclic (alkyl)(amino)carbene (CAAC)-supported dihydroboron triflate yields the mixed doubly base-stabilised dihydroboryl cations [(CAAC)BH<sub>2</sub>L]<sup>+</sup>. Of these, [(CAAC)<sub>2</sub>BH<sub>2</sub>]OTf (OTf = triflate) underwent facile two-electron reduction with KC<sub>8</sub> 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.

supported hydroboron compounds, the B–H bond activation process can be reversible (Fig. 1b)<sup>14,26,27</sup> and is favoured by electron-donating ligands at boron,<sup>8,26–30</sup> thereby affording additional stabilisation for electron-rich lower oxidation state species through facile hydrogen shuttling. In this contribution we combine the excellent  $\sigma$ -donating/ $\pi$ -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,<sup>12</sup> methyl trifluoromethanesulfonate (MeOTf) was employed to abstract from (CAAC<sup>Me</sup>)BH<sub>3</sub> (CAAC<sup>Me</sup> hydride = 1-(2,6а diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene). The resulting triflate 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  $[(CAAC^{Me})BH_2L]OTf$  (2-L,L =  $CAAC^{Me}$ ,  $IMe^{Me} = 1,3$ -dimethylimidazol-2-ylidene,  $PMe_3$ , Scheme 1a), all presenting a characteristic upfield <sup>11</sup>B NMR BH<sub>2</sub> triplet in the -22 to -30 ppm region.§ In the case of the 4dimethylaminopyridine (DMAP) derivative, 2-DMAP ( $\delta_{^{11}B}$  = -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 ( $\delta^{11}B$ = 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 CAAC<sup>Me</sup> ligand.<sup>26</sup> 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 sp<sup>3</sup>-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 ( $\delta_{11B} = -9.3$  ppm,

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<sup>†</sup> Electronic supplementary information (ESI) available: Synthetic procedures, NMR, EPR, UV-vis, IR, CV, X-ray crystallographic data and details of the computational analyses. CCDC 1956847–1956854. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc05026d



Fig. 1 (a) Selected examples of CAAC-stabilised B(II) and B(I) species; (b) example of reversible Lewis-base-induced B-to-CAAC hydrogen shuttling.

broad) was found to be reversible: even in neat pyridine only ca. 75% conversion to **3-Pyr** ( $\delta_{^{11}B} = 6.9$  ppm) was observed. The use of 4,4'-bipyridine as a base led to the formation of the 4,4'bipyridine-bridged bis(boronium) species **4-Bipy** ( $\delta_{11}_{B}$  = -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.



Fig. 2 Crystallographically derived molecular structures of the 2-CAAC<sup>Me</sup> (one of the two crystallographically distinct cations present in the asymmetric unit) and 3-DMAP cations. Atomic displacement ellipsoids are set at 50% probability. Ellipsoids of CH<sub>3</sub> and iPr groups, triflate counteranion and hydrogen atoms omitted for clarity except for boron-bound hydrides.<sup>‡</sup> Selected bond lengths (Å) for 2-CAAC<sup>Me</sup>: B1-C1 1.597(7), B1-C21 1.607(7), B1-H1 1.11(6), B1-H2 1.16(6), C1-N1 1.316(6), C21-N2 1.310(6); for 3-DMAP B1-C1 1.619(4), B1-N2 1.585(3), B1-N4 1.597(3), B1-H2 1.10(2), C1-N1 1.490(3),

Attempts to reduce 2-L, 3-L and 4-L under various conditions all resulted in unselective reactions, except for 2-CAAC<sup>Me</sup>, which was readily reduced with excess KC<sub>8</sub> to the red-coloured (alkyl) hydroboryl anion 5 by 1,2-migration of one hydrogen atom from boron to CAAC<sup>Me</sup> (Scheme 2a). The <sup>11</sup>B NMR spectrum of 5



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.  $IMe^{Me} =$ 1,3,4,5-tetramethylimidazol-2-ylidene, Pyr = pyridine, DMAP = 4dimethylaminopyridine.



Scheme 2 Reduction of 2-CAAC<sup>Me</sup> to boryl anions (a) 5 and (b)–(c) 5thf, and subsequent comproportionation to (d) boryl radical 6.



Fig. 3 Crystallographically derived molecular structures of 5, 5-thf and 6. Atomic displacement ellipsoids are set at 50% probability. Ellipsoids of CH<sub>2</sub>, CH<sub>3</sub> and iPr groups and hydrogen atoms omitted for clarity except for boron-bound hydrides.<sup>‡</sup> Selected bond lengths (Å) and angles (°) for 5: B1–C1A 1.439(11), B1–C1B 1.633(9), B1–H2 1.14(3), C1A-N1' 1.450(7), C1B–N1 1.520(8), K1…H1 2.53(3), K1…B1 3.141(4), K1…centroid 2.91,  $\Sigma \angle$  B1 359.4(12),  $\Sigma \angle$  C1A 359.7(5), B1–H2–K1 111.8(12); for 5-thf: B1–C1 1.452(2), B1–C21 1.620(2), B1–H1 1.159(17), C1–N1 1.4601(18), C21–N2 1.5076(19), K1…H1 2.653(16), K1…B1 3.599(2), K1…centroid 2.95, K1…C25 3.2933(17),  $\Sigma \angle$  B1 359.9(1),  $\Sigma \angle$  C1 359.9(1), B1–H1–K1 138(1); for 6: B1–C1 1.5174(18), B1–C21 1.5817(18), B1–H1 1.142(18), C1–N1 1.3777(15), C21–N2 1.4616(15),  $\Sigma \angle$  B1 359.5(6),  $\Sigma \angle$  C1 359.6(1).

shows a single broad resonance at 16.7 ppm, significantly downfield-shifted from that of other CAAC-stabilised boryl anions, which range from  $\delta_{11B} = -4.7$  ppm for [(CAAC<sup>Me</sup>)BH<sub>2</sub>]<sup>-</sup> to  $\delta_{11B} = -17.9$  ppm for [(CAAC<sup>Cy</sup>)B(CN)<sub>2</sub>]<sup>-</sup>, <sup>14-17</sup> likely because of the electron-withdrawing nature of the aminoalkyl substituent CAAC<sup>Me</sup>H. The  ${}^{1}H{}^{11}B$  NMR spectrum shows a BH doublet at 1.90 ppm ( ${}^{3}I = 6.6$  Hz), coupling to the BCH resonance of the CAAC<sup>Me</sup>H ligand at 4.38 ppm, as well as two sets of unsymmetrical CAAC<sup>Me</sup> ligand resonances. An X-ray crystallographic analysis revealed a monomeric structure with a trigonal-planar boron atom ( $\Sigma \angle B1$  359(1)°), in which the potassium cation bound to the BH hydride (K1···H2 2.53(3) Å) is encapsulated by the ligand sphere through  $\eta^6$ - $\pi$  interactions with the Dip (=2,6diisopropylphenyl) substituents of the CAAC<sup>Me</sup> and CAAC<sup>Me</sup>H ligands (Fig. 3). The B1-C1A bond length of 1.439(11) Å is significantly shorter than in the 2-CAAC<sup>Me</sup> precursor (B-C<sub>avg.</sub> 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 CAAC<sup>Me</sup> ligand, as found in all CAAC-stabilised boryl anions.<sup>6,14-17</sup> 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-hydride shift has occurred and C1B is now sp<sup>3</sup>-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  $\rm cm^{-1}$ , corresponding to the B-H stretching mode. The computed B-H stretching mode of 2352 cm<sup>-1</sup> at ωB97XD/6-31+G\* agrees well with the experimental value.

The reduction of **2-CAAC<sup>Me</sup>** 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 CAAC<sup>Me</sup> ligand, its coordination sphere being completed by three THF molecules and an agostic interaction with one of the vicinal methyl groups (C25) of the CAAC<sup>Me</sup>H ligand. The bond lengths and



Fig. 4 (a) Calculated structure of 5 at the  $\omega$ B97XD/6-31+G\* level of theory. (b) Plot of the HOMO of 5 ( $\omega$ B97XD/6-311++G\*\*).

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 CAAC<sup>Me</sup>H and CAAC<sup>Me</sup>, which flip so that the Dip substituents now point in opposite directions.

Cyclic voltammograms of 2-CAAC<sup>Me</sup> and 5-thf in THF (0.1 M [*n*Bu<sub>4</sub>N][PF<sub>6</sub>]) 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 Fc/Fc<sup>+</sup>), suggesting that chemical oxidation of 5 to 6 should be possible. Indeed, the reaction of 5thf with 2-CAAC<sup>Me</sup> led to quantitative comproportionation to the boryl radical 6 (Scheme 2d). Attempts to generate 6 by the direct one-electron reduction of 2-CAAC<sup>Me</sup> failed, resulting instead in incomplete consumption of 2-CAAC<sup>Me</sup> and generating a mixture of 5 and 6. Radical 6 is deep purple in solution  $(\lambda_{\text{max}} = 523 \text{ nm in the UV-vis spectrum})$  and <sup>11</sup>B 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  $(\Sigma \angle B1 359.5(6)^{\circ})$  and the Dip groups of the CAAC<sup>Me</sup>H and CAAC<sup>Me</sup> 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 CAAC<sup>Me</sup> 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  $\pi$  framework.<sup>5–9,21,22,31–33</sup>

The IR spectrum of **6** shows a B–H stretching band at 2533 cm<sup>-1</sup> (calc.: 2558 cm<sup>-1</sup> at  $\omega$ B97XD/6-31+G\*), *ca.* 200 wavenumbers higher than that in **5**, and 100 higher than in Bertrand's hydroborylene **III** (Fig. 1a,  $\nu$ (B–H) = 2455 cm<sup>-1</sup>), 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 <sup>14</sup>N nucleus ( $a_{^{14}N} = 18.5$  MHz, Fig. 5a). The simulated spectrum further provides hyperfine coupling parameters to the quadrupolar <sup>11</sup>B nucleus ( $a_{^{11}B} = 9.7$  MHz), which is responsible for the line-broadening, and the BH and CAAC<sup>Me</sup>H <sup>1</sup>H nuclei ( $a_{^{14}H} = 13.6$  and 4.8 MHz, respectively). The presence of two distinct couplings to these <sup>1</sup>H 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  $\pi$  bond with some  $\pi$ -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



Fig. 5 (a) Experimental (black solid line) and simulated (red line) continuous-wave X-band EPR spectra of **6** in hexane solution at rt. *Simulation parameters*:  $g_{iso} = 2.0027$ ,  $a^{(11}B) = 9.7$  MHz,  $a^{(14}N) = 18.5$  MHz,  $a^{(1}H_{(H1)}) = 13.6$  MHz and  $a^{(1}H_{(H21)}) = 4.8$  MHz; (b) electrostatic potential (ESP) map of **6** at the  $\omega$ B97XD/6-31+G\* level of theory. ESP charges following the notation of Fig. 3: N2: -0.46, C21: -0.01, B1: +0.19, H1: -0.17, C1: -0.27, N1: -0.14. (c) Plot of the SOMO of **6** (surface isovalue:  $\pm 0.03$  [e  $a_0^{-3}$ ]<sup>1/2</sup>). (d) Left: plot of the calculated spin density of **6** (surface isovalue: 0.005 [e  $a_0^{-3}$ ]). Right: Mulliken atomic spin densities.



Scheme 3 (a) Reducing and (b) nucleophilic reactivity of boryl anion 5.

crystals of **6** proved air-stable at room temperature over a period of one week, making this compound a rare example of an airstable 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 CAAC<sup>Me</sup> and CAAC<sup>Me</sup>H 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*-B<sub>12</sub>(CH<sub>3</sub>)<sub>12</sub>]<sup>•–</sup> radical anion, in which the unpaired electron is trapped and delocalised within the B<sub>12</sub> cage.<sup>34</sup>

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 cyanoboryl anions.<sup>16,17</sup> With elemental sulfur, double oxidation back to the **2-CAAC<sup>Me</sup>** cation was observed by NMR spectroscopic analysis ( $\delta^{11}_{B} = -22.4 \text{ ppm}, t, {}^{1}J_{11}_{B^{-1}H} = 84.7 \text{ Hz}$ ), the counteranion presumably being a  $S_n^{2-}$  polysulfide (7, Scheme 3a). The only nucleophilic reactivity observed was with methyl triflate, which yielded clean salt metathesis to the methylated trialkylborane **8** through migration of the second hydride to the remaining CAAC<sup>Me</sup> ligand ( $\delta^{11}_{B} = 93.9 \text{ ppm}$ , 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  $[L_2BH_2]^+$  cation to a  $[LRBH]^-$  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 CAAC<sup>Me</sup> 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.†

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