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An efficient synthetic route to stable bis(carbene)borylenes $[(L_1)(L_2)BH]$

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Two-electron reduction of bis(carbene) boronium salts allows for the preparation of unsymmetrically substituted nucleophilic boron derivatives of type $(L_1)(L_2)BH$, which are characterized by X-ray crystallography. A single electron reduction of the same starting materials leads to the corresponding boron-centered radical cations $(L_1)(L_2)BH^{*+}$, X⁻.

Since the isolation of the heterocyclic boryl anion A by Yamashita, Nozaki and co-workers¹ in 2006 (Chart 1), the number of boron centered nucleophiles has grown gradually.^{2,3} However, up to now, compound C is the only example of a stable neutral, nucleophilic, tricoordinate boron derivative.4 This compound, which is isoelectronic with amines and phosphines, was prepared by reduction of the CAAC-BBr₃ adduct **B** [CAAC = cyclic (alkyl)(amino)carbene]^{5,6} with KC₈. This synthetic route, which leads to C in only 33% yield, is far from being understood, and certainly does not have a broad scope. For example, Robinson and co-workers have reported that the reduction of the analogous (NHC)-BBr3 adduct D $(NHC = N-heterocyclic carbene)^7$ with KC_8 affords dimers of type E.⁸ Moreover, the preparation of derivatives, featuring two different carbene ligands, which would allow for a fine tuning of the electronic properties of the boron center, could not be achieved. Herein, we report a stepwise and more versatile synthesis that allows for the isolation of different unsymmetrically substituted derivatives of type $(L_1)(L_2)BH$, as well as for the EPR characterization of one of the corresponding radical cations $(L_1)(L_2)BH^{\bullet+}$, X⁻.

We first envisaged a synthetic route, in which a second carbene would be introduced by simple displacement of a triflate group from the known (CAAC)BH(OTf)₂.^{3g} However, no reaction was observed with the benzimidazolylidene L_a^9 and cyclopropenylidene $L_b^{,10}$ probably due the excessive steric hindrance around boron.



Therefore, we turned our attention to the less bulky but unknown CAAC monotriflate borane 2. As already observed with NHC adducts,¹¹ we found that although (CAAC)BH(OTf)₂ is readily available by treatment of (CAAC)BH₃ 1^{12} with excess trifluoromethane sulfonic acid, the desired monotriflate derivative (CAAC)BH₂(OTf) could not be selectively prepared. In contrast, when the CAAC borane complex 1 is instead reacted with methyl trifluoromethanesulfonate, the desired CAAC monotriflate borane 2 is formed, and can be isolated in 95% yield as a white powder (Scheme 1). The ¹¹B NMR spectrum displays a broad signal at -6.1 ppm, which is shifted downfield from 1 (-28.5 ppm), and the ¹⁹F NMR spectrum shows a singlet at -76.2 ppm, which is indicative of a triflate group covalently bound to boron. The structure of 2 was ascertained by a single crystal X-ray diffraction study (Fig. S31, ESI⁺).

We were pleased to observe that 2 readily reacts with carbenes L_a and L_b , affording the desired bis(carbene) boronium salts **3a,b**, which were isolated as white solids in 95 and 80% yields, respectively. The ¹¹B NMR spectrum of these derivatives shows an upfield well-defined triplet (**3a** = -28.6 ppm, J_{BH} = 82.9 Hz; **3b** = -27.7 ppm, J_{BH} = 87.9 Hz), whereas the ¹⁹F NMR spectrum indicates that the triflate group is no longer covalently bound (**3a** = -78.0 ppm; **3b** = -79.3 ppm). Interestingly, these species are not sensitive to air and moisture, but all attempts to obtain the desired neutral tricoordinate boron derivatives **5a,b** by deprotonation or reduction of **3a,b** failed.

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In order to further increase the acidity of the proton bonded to boron, we chose to replace one of the hydrogen atoms by a triflate group. This is readily achieved by simple treatment of **3a,b** with triflic acid. Compounds **4a,b** were isolated as white solids in 70 and 67% yield, respectively. The ¹⁹F NMR spectrum displays two peaks indicative of both a bound and a free triflate group (**4a** = -75.4, -78.1 ppm; **4b** = -76.2, -78.0 ppm), and the ¹¹B NMR signal shifts downfield compared to **3a,b** and becomes broad (**4a** = -7.5 ppm; **4b** = -5.1 ppm). The ¹H NMR spectra are quite convoluted, probably because of the steric hindrance, which prevents rotation around the boron–carbon bonds. This is confirmed by the solid-state structure of the corresponding BPh₄ salts, obtained by anion exchange. These compounds are extremely robust, as during work-up a water wash is performed.

Attempted deprotonation of 4a,b failed again. However, mixing 4a and 4b with two equivalents of KC8 in THF leads to an immediate and intense blue and red colored solutions, respectively. After workup, the reduced products 5a,b were isolated in 87 and 82% yield, respectively. Although extremely sensitive to air and moisture, derivatives 5a,b can be stored for months, under an inert atmosphere, with no signs of decomposition. The ¹H NMR spectra are simplified compared to those of **4a**,**b** as the boron center is no longer a chirality center. The ¹¹B NMR spectrum appears as a doublet at -1.3 ($J_{BH} = 82.4$ Hz) and 0.8 ppm (J_{BH} = 89.7 Hz) for 5a and 5b, respectively. It is interesting to note that these signals are high-field shifted compared to that observed for C (+12.5 ppm), a trend which is in agreement with the inferior π -acceptor properties of benzimidazolylidene L_a and cyclopropenylidene L_b compared to CAACs.¹³

Single crystals of **5a** and **5b**, suitable for X-ray diffraction studies, were obtained from a concentrated pentane solution (Fig. 1). The B1–C2 bond lengths [**5a**: 1.572(2); **5b**: 1.5521(17) Å] are typical for B–C single bonds. In contrast, for both compounds, the B1–C1 bond [**5a**: 1.462(3); **5b**: 1.4692(16) Å] is short, and falls into the range of known boron–carbon double bonds.¹⁴



Fig. 1 Molecular structure of **5a** (left) and **5b** (right) in the solid state. Hydrogen atoms, except the B–H, and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: **5a** B1–C1 1.462(3), B1–C2 1.572(2), B1–H1 0.930, C1–N1 1.418(2), C2–N2 1.371(2), C2–N3 1.366(2); C1–B1–C2 127.84(15), C1–B1–H1 116.07, C2–B1–H1 116.08. **5b** B1–C1 1.4692(16), B1–C2 1.5521(17), B1–H1 1.107, C1–N1 1.4262(15); C1–B1–C2 128.50(10), C1–B1–H1 121.58, C2–B1–H1 111.86.

Concomitantly there is an elongation of the C1–N1 bond [5a: 1.418(2); 5b: 1.4262(15) Å] compared to that of the salt precursors [4a: 1.307(2); 4b: 1.297(5) Å]. These geometric parameters clearly indicate that the formal boron lone pair is mainly delocalized on the CAAC ligand. This is confirmed by DFT calculations, as can be seen from the HOMO diagrams (Fig. 2).

Despite the delocalization of the lone pair, the boron center of **5a,b** is electron rich. Indeed, both compounds react with trifluoromethanesulfonic acid, leading to the conjugate acids **3a,b**. Moreover, we found that the radical cation **6b** is persistent for several hours at room temperature. It can be prepared by adding one equivalent of KC₈ to a DME solution of **4b**. The room temperature EPR spectrum of **6b** displays couplings with boron $[a(^{11}B) = 4.994 \text{ G}]$, hydrogen $[a(^{1}H) = 10.065 \text{ G}]$, and only one nitrogen nuclei $[a(^{14}N) = 6.627 \text{ G}]$ (Fig. 3). This suggests again that the unpaired electron is mainly delocalized over the CAAC and BH fragments, with very little contribution by L_b.



Fig. 2 HOMO diagrams for **5a** (left) and **5b** (right) [BVP86/6-311+g(2d,p) level of theory].



Fig. 3 Simulated (top) and experimental (bottom) EPR spectra, and spin density representation (right) of **6b**. [(U)BVP86/6-311+g(2d,p) level of theory].

DFT calculations confirm that the spin density distribution is in line with this observation.¹⁵

The synthetic route described herein paves the way for the preparation of a variety of bis(carbene)borylene adducts, which are isoelectronic with amines and phosphines. Their reactivity and ligand behavior for transition metal centers are under active investigation.

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