This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
An efficient synthetic route to stable bis(carbene)borylenes [(L_{1})(L_{2})BH]

David A. Ruiz, Mohand Melaimi, and Guy Bertrand*

Received 00th January 2012, Accepted 00th January 2012
DOI: 10.1039/x0xx00000x

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-workers\(^{4}\) 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-BBr_{3} adduct B [CAAC = cyclic (alkyl)(amino)carbene]\(^{5,6}\) with KC_{8}. 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)-BBr_{3} 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^{+}, 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}.\(^{3,8}\) 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)BH_{3} 1\(^{12}\) with excess trifluoromethane sulfonic acid, the desired monotriflate derivative (CAAC)BH_{2}(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 {^{11}}B NMR spectrum displays a broad signal at -6.1 ppm, which is shifted downfield from 1 (-28.5 ppm), and the {^{19}}F NMR spectrum shows a singlet at -76.2 ppm, which is indicative of a trflate group covalently bound to boron. The structure of 2 was ascertained by a single crystal X-ray diffraction study (Supplementary, Fig. S31).
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 \(^{11}\text{B} \) 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 \(^{19}\text{F} \) 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.

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 \(^{19}\text{F} \) 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 \(^{11}\text{B} \) NMR signal shifts downfield compared to 3a,b and becomes broad (4a = -7.5 ppm; 4b = -5.1 ppm). The \(^1\text{H} \) 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 BPh₃ 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 \( \text{KC} \) 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 \(^1\text{H} \) NMR spectra are simplified compared to those of 4a,b as the boron center is no longer a chirality center. The \(^{11}\text{B} \) 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 5c (+12.5 ppm), a trend which is in agreement with the inferior \( \pi \)-acceptor properties of benzimidazolylidene \( L_a \) and cyclopentenylidene \( L_b \) 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.\(^{14}\) 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 \( \text{KC} \) to a DME solution of 4b. The room temperature EPR spectrum of 6b displays couplings with boron [\( a(^{11}\text{B}) = 4.994 \) G], hydrogen [\( a(^{1}\text{H}) = 10.065 \) G], and only one nitrogen nuclei [\( a(^{14}\text{N}) = 6.627 \) G] (Fig. 3). This suggests again that the unpaired electron is mainly delocalized over the CAAC and BH fragments, with very little contribution by \( L_b \). DFT calculations confirm that the spin density distribution is in line with this observation.\(^{15}\)
Notes and references

UCSD-CNRS Joint Research Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92033-0343, USA. E-mail: guybertrand@ucsd.edu; Tel: +1 858 334 5412

† Electronic Supplementary Information (ESI) available: Synthetic procedures, analytical data, and CIF files for single crystal X-ray structural analysis. CCDC 1001683-1001687. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/


6 For reviews on CAAcS, see: (a) M. Melaimi, M. Soleilhavoup and G. Bertrand, Angew. Chem., Int. Ed. 2010, 49, 8810; (b) D. Martin, M. Melaimi, M. Soleilhavoup and G. Bertrand, Organometalics 2011, 30, 5304.


---

The synthetic route described herein paves the way for the preparation of a variety of bis(carbene)borylene adducts, which are iso-electronic with amines and phosphines. Their reactivity and ligand behavior for transition metal centers are under active investigation. This work was supported by the DOE (DE-FG02-13ER16370) and the NSF (CHE-1316956). D. A. R. gratefully acknowledges the U.S. Department of Education for a GAANN fellowship. Thanks are given to L. Liu for his assistance with the computational studies.


15 For Mulliken atomic spin densities of 6b, see ESI for details.