Neutral Boron Radicals

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Isolation of a Neutral Boron-Containing Radical Stabilized by a Cyclic (Alkyl)(Amino)Carbene**

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Abstract: *Utilizing a cyclic (alkyl)(amino)carbene (CAAC) as a ligand, neutral CAAC-stabilized radicals containing a boryl functionality could be prepared by reduction of the corresponding haloborane adducts. The radical species with a duryl substituent was fully characterized by single-crystal X-ray structural analysis, EPR spectroscopy, and DFT calculations. Compared to known neutral boryl radicals, the isolated radical species showed larger spin density on the boron atom. Furthermore, the compound that was isolated is extraordinarily stable to high temperatures under inert conditions, both in solution and in the solid state. Electrochemical investigations of the radical suggest the possibility to generate a stable formal boryl anion species.*

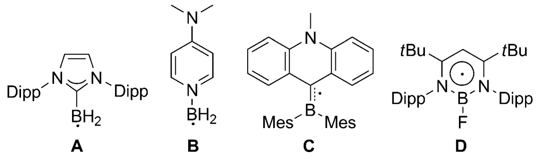

Figure 1. Examples of neutral boryl radicals.

Boryl radicals have been paid much attention as new promising candidates for radical initiators and related applications.[1] For example, Lacôte, Curran et al. recently applied their boryl radicals (described below) to various organic radical reactions, such as radical deoxygenation of xanthates, radical reductions of alkyl halides, and radical chain homolytic substitution reactions.[2] Anionic boryl radicals with seven valence electrons have been investigated for decades, including related research on one-electron-reduced diborane compounds.[3] However, isoelectronic neutral boryl radicals have emerged in recent years, and some of the Lewis base-stabilized neutral boryl radicals could be isolated and characterized (Figure 1). N-heterocyclic carbenes (NHC) have been employed as effective bases to stabilize neutral boryl radicals. Indeed, Lacôte, Curran et al. have extensively studied NHC-stabilized boryl radicals (**A**); however, these radicals have only been observed by spectroscopic methods owing to their transient nature.[4] Similarly, Lalevée et al. have developed a series of boryl radicals stabilized by pyridine derivatives (**B**), which were theoretically predicted by the Zipse group.[5] Although these two types of boryl radicals have not been structurally elucidated, spin densities at boron were calculated to be 0.3–0.5 depending on the ligands. As yet, only two examples of base-stabilized neutral boryl radicals could be characterized by X-ray structural analysis, as reported by Gabbaï et al. (**C**)[6] and Nozaki and Yamashita et al. (**D**).[7] However, these two species showed minimal spin densities at boron in the ground state, as the unpaired electrons were well delocalized throughout the acridine or β-diiminate moieties. Thus, a detailed study of a stable neutral boryl radical with large spin density on the boron atom has still not been presented.

To investigate a base-stabilized formal boryl radical with larger spin density on the boron atom, we envisioned that cyclic (alkyl)(amino)carbenes (CAACs)[8] could be used to isolate the desired radical, as CAACs have been widely utilized as ligands for stabilizing unusual reactive molecules, such as phosphorus radicals, a parent borylene, and a boryl anion.[1b,9] It is characteristic for CAACs to exert stronger σ-donating and π-accepting properties than NHCs, and moreover, the steric demand of CAACs is different from that of NHCs owing to the presence of a quaternary carbon atom next to the carbene center. Based on our recent experience in the reduction chemistry of various NHC-stabilized haloboranes,[10] we proposed that the reduction of CAAC-stabilized haloboranes would be suitable to accomplish the aforementioned goal. Herein, we report the synthesis and structure of a neutral CAAC-stabilized boron-containing radical as well as its most pertinent electronic properties.

To avoid possible intramolecular C–H activation chemistry, we chose a CAAC with two methyl groups on the quaternary carbon atom as a suitable ligand, as it is less bulky than the corresponding cyclohexyl-substituted CAAC. The ligand was prepared according to a previously described method with a slight modification (see the Supporting Information).[8b] The aforementioned NHC-stabilized boryl radicals that were derived from hydroboranes could be spectroscopically observed but not isolated, presumably due

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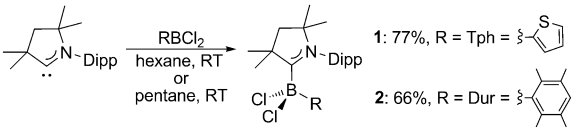
to their lack of steric protection.[4] Thus, arylhaloboranes were considered to be promising candidates for stabilizing a boryl radical and preventing its dimerization by radical homocoupling. The CAAC-stabilized thiophene (**1**) and duryl (**2**, duryl = 2,3,5,6-tetramethylphenyl) substituted boranes were isolated in 77 % and 66 % yield, respectively, as colorless solids by reaction of CAAC with the respective borane in hexane or pentane (Scheme 1). ^{11}B NMR spectroscopy of **1** (δ −0.3) and **2** (δ 3.1) in C_6D_6 corresponded well to that of typical four-coordinate boranes, and X-ray diffraction analysis also confirmed adduct formation (Figure 2).[11] Structural parameters of both adducts comply with those of corresponding NHC borane adducts.[12]



Scheme 1. Synthesis of **1** and **2**. Dipp = 2,6-diisopropylphenyl.

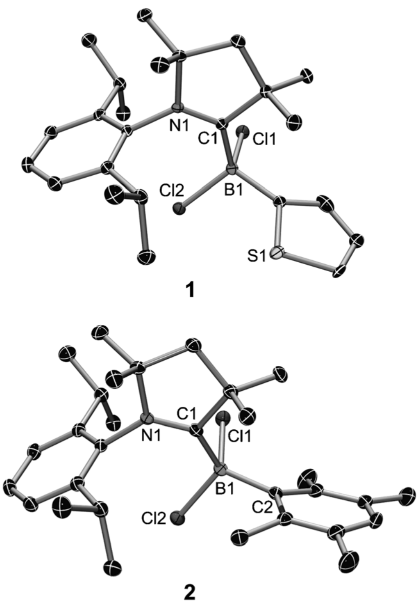
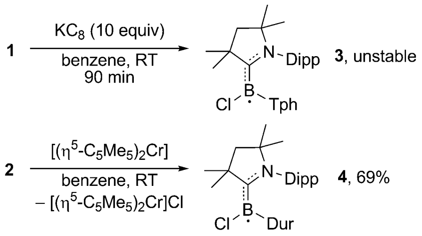


Figure 2. Molecular structures of **1** and **2** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms, solvent molecules, and disordered atoms for Tph groups in **1** are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1**: B1–C1 1.652(2), B1–Cl1 1.907(2), B1–Cl2 1.867(2), C1–N1 1.302(2); Cl1-B1-Cl2 107.18(9). **2**: B1–C1 1.658(2), B1–C2 1.624(2), B1–Cl1 1.914(2), B1–Cl2 1.879(2), C1–N1 1.315(2); Cl1-B1-Cl2 108.34(8).

With these adducts in hand, we first performed reduction of **1** with an excess of KC_8 in benzene at ambient temperature, producing an NMR-silent red crystalline solid **3** after recrystallization from hexanes at −30 °C (Scheme 2). Although attempts to determine the constitution of **3** by X-ray crystallographic analysis consistently failed owing to the instability of the crystals at room temperature, the EPR spectrum of **3** clearly confirms the presence of a radical species (see the Supporting Information). In contrast, a sterically more protected radical **4** could be isolated as an orange colored solid by applying the same method to the duryl-substituted adduct **2**. However, using KC_8 as a reductant turned out to be irreproducible. Therefore we applied decamethylchromocene as the reducing agent and developed a reliable synthetic route that allows the isolation of **4** in 69 % yield.



Scheme 2. Synthesis of radicals **3** and **4**.

In contrast to **3**, the radical **4** is very stable under an inert atmosphere. Compound **4** has a melting point at 206 °C determined by differential scanning calorimetry, followed by decomposition at even higher temperatures (ca. 245 °C).[11] Moreover, NMR spectroscopy indicated the absence of unwanted dimerization processes by homocoupling of the radical. The X-ray analysis of **4** constitutes the first structural characterization of a carbene-stabilized boryl radical (Figure 3). Most notably, the B1–C1 bond (1.508(3) Å) of **4** in the crystal is significantly shortened by about 15 pm with respect to that of the precursor **2** (B1–C1: 1.658(2) Å), and ranges between typical values known for boron–carbon single and double bonds (1.59 and 1.48 Å, respectively),[1b] whereas the C1–N1 bond (1.369(2) Å) is moderately lengthened in comparison with the corresponding bond of **2** (C1–N1: 1.3148(19) Å). In contrast, the B1–C2 bond to the duryl group (1.581(3) Å) is much less affected and contracts by only about 4 pm in comparison to that of the precursor (**2**: 1.624(2) Å). These findings indicate a significant delocalization of the unpaired electron to the CAAC ligand, reflecting

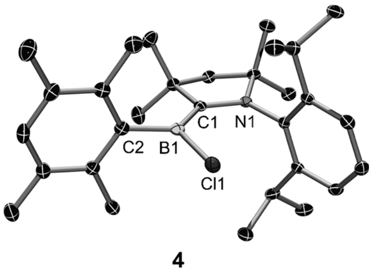


Figure 3. Molecular structure of **4** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–C1 1.508(3), B1–Cl1 1.817(2), B1–C2 1.581(3), C1–N1 1.369(2); C1-B1-Cl1 122.0(1), Cl1-B1-C2 110.1(1), C1-B1-C2 127.9(2).

its enhanced π-acceptor properties. Furthermore, the boron atom has a trigonal planar geometry with a sum of the three angles around the boron atom of 360°, also suggesting that the unpaired electron is delocalized over a p orbital, thus rendering **4** a π-type radical.[1c]

To investigate the electronic properties, the radical **4** was analyzed by EPR spectroscopy in hexane solution at room temperature (Figure 4). The EPR signal of **4** was detected as a 1:1:1 triplet (centered at $g_{iso} = 2.004$) that is due to the hyperfine interaction with the ^{14}N nucleus ($a_N = 19$ MHz). Weaker hyperfine couplings, including the coupling to boron, are not resolved. An approximation of the boron hyperfine interaction from the line width reveals a value of about 2.7 MHz, which is in good agreement with the value computed by DFT ($a(^{11}B) = 1.50$ MHz, see the Supporting Information for details). The observed nitrogen hyperfine coupling constant suggests spin delocalization onto the CAAC unit, which is slightly more pronounced when compared to the CAAC-supported (amino)(carboxy) radical reported by Bertrand ($a_N = 15.4$ MHz).[13]

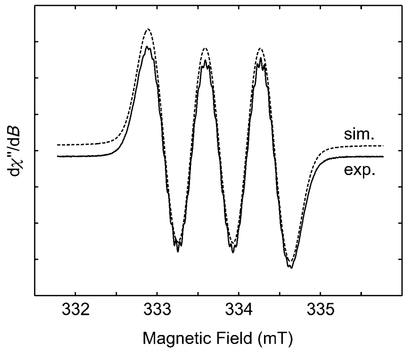


Figure 4. Experimental X-band (9.38 GHz) EPR spectrum of **4** in hexane solution at 295 K. In the simulation (-----), only the nitrogen hyperfine interaction is considered.

The spin-density distribution of **4** was further analyzed by DFT calculations (UB3LYP/6-311+G(d)). These results indicate that the unpaired spin density is mainly localized on C1 (0.496), followed by B1 (0.277) and N1 (0.241). Compared to the low spin density on the boron atom in the first isolated neutral B-heterocyclic radical (B: −0.008)[7] it is clear that **4** shows a distinct boryl radical character (Figure 5 a).

The anticipated π-bond character of the B1−C1 bond is further supported by the singly occupied molecular orbital (SOMO; Figure 5 b) in the calculated structure of **4**, showing large MO coefficients for these atoms. The UV/Vis absorption spectrum of **4** (Et_2O) was also measured, which shows broad absorptions at 285 and 297 nm, in accordance with the expected peaks predicted by TD-DFT calculation (see the Supporting Information). The calculation indicates a largest absorption at 296 nm with an oscillator strength of 0.0217, which could be mainly assigned to an excitation from the SOMO to the LUMO+4, and from the HOMO−4 to the SOMO.

To gain insight into the redox properties of **4**, cyclic voltammograms (CV) were measured in THF (Figure 6). The first reduction wave is found at $E_{1/2} = -2.03$ V (referenced against the ferrocene/ferrocenium (Fc/Fc^+) couple) and is a chemically reversible process. This result suggests a possible one-electron reduction with concomitant formation of an anionic species, that is, a formal boryl anion, examples of which are synthetically highly useful but still very rare.[9b,14] In contrast, an irreversible oxidation wave is found at $E_{1/2} =$

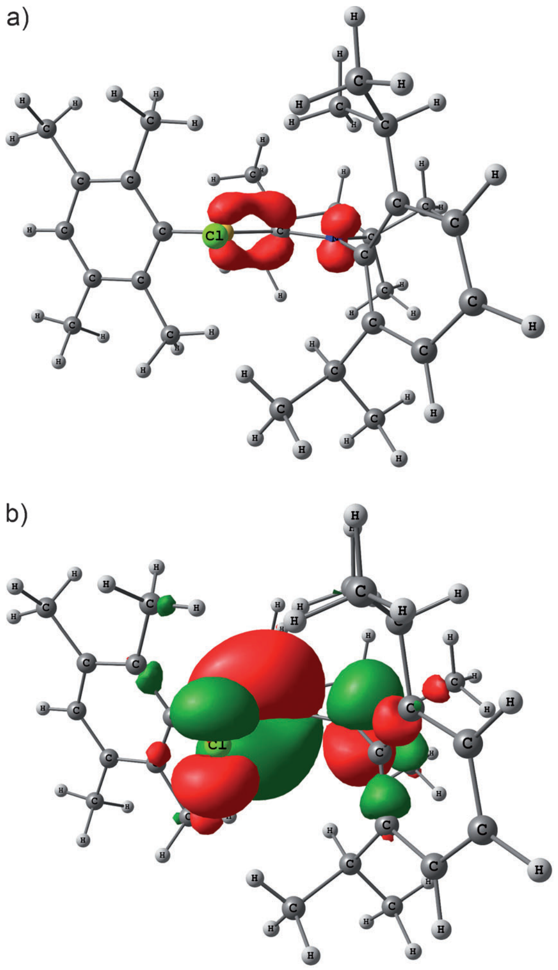


Figure 5. Plot of the a) spin density and b) SOMO of **4**.

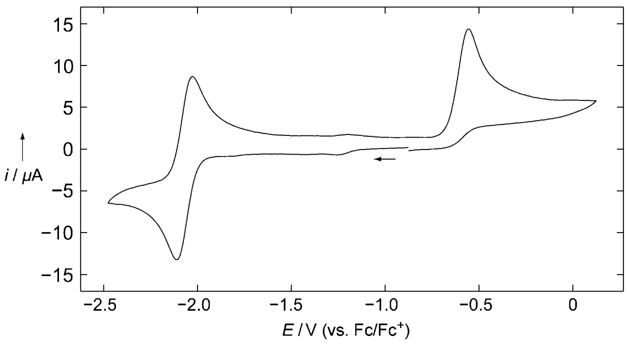


Figure 6. Cyclic voltammogram of **4** in THF/0.1 M [nBu_4N][PF_6] at room temperature. Scan rate: 250 mV s^{-1}.

−0.53 V, suggesting that a resulting cationic species would be unstable.

In conclusion, we have succeeded in the preparation and characterization of neutral CAAC-stabilized radicals containing a boryl moiety by reduction of CAAC–borane adducts with thiophene or duryl B-substituents. The identity of the duryl-substituted radical was confirmed both in solution and in the solid state. EPR data and DFT calculations indicate that the spin density is delocalized over the CAAC ligand, which is most likely a result of its strong π-accepting ability. Nevertheless, significant spin density resides on the boron atom, suggesting potential boron-centered reactivity. Furthermore, cyclic voltammetry experiments suggest that a one-electron reduction of **4** could yield a stable formal boryl anion species. Efforts to generate such an unusual boryl anion species are underway in our laboratory.

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[1] a) D. P. Curran, A. Solovyev, M. M. Brahmi, L. Fensterbank, M. Malacria, E. Lacôte, *Angew. Chem.* **2011**, *123*, 10476–10500; *Angew. Chem. Int. Ed.* **2011**, *50*, 10294–10317; b) C. D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2013**, *4*, 3020–3030; c) D. Lu, C. Wu, P. Li, *Chem. Eur. J.* **2014**, *20*, 1630–1637.

[2] a) S.-H. Ueng, L. Fensterbank, E. Lacôte, M. Malacria, D. P. Curran, *Org. Lett.* **2010**, *12*, 3002–3005; b) X. Pan, E. Lacôte, J. Lalevée, D. P. Curran, *J. Am. Chem. Soc.* **2012**, *134*, 5669–5674; c) X. Pan, A.-L. Vallet, S. Schweizer, K. Dahbi, B. Delpech, N. Blanchard, B. Graff, S. J. Geib, D. P. Curran, J. Lalevée, E. Lacôte, *J. Am. Chem. Soc.* **2013**, *135*, 10484–10491.

[3] a) J. E. Leffler, G. B. Watts, T. Tanigaki, E. Dolan, D. S. Miller, *J. Am. Chem. Soc.* **1970**, *92*, 6825–6830; b) M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1986**, *108*, 4235–4236; c) W. J. Grigsbym, P. P. Power, *Chem. Eur. J.* **1997**, *3*, 368–375; d) H. Braunschweig, V. Dyakonov, J. O. C. Jimenez-Halla, K. Kraft, I. Krummenacher, K. Radacki, A. Sperlich, J. Wahler, *Angew. Chem.* **2012**, *124*, 3031–3034; *Angew. Chem. Int. Ed.* **2012**, *51*, 2977–2980; e) J. D. Hoefelmeyer, F. P. Gabbaï, *J. Am. Chem. Soc.* **2000**, *122*, 9054–9055; f) A. Hübner, A. M. Diehl, M. Diefenbach, B. Endeward, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem.* **2014**, *126*, 4932–4935; *Angew. Chem. Int. Ed.* **2014**, *53*, 4832–4835.

[4] a) S.-H. Ueng, A. Solovyev, X. Yuan, S. J. Geib, L. Fensterbank, E. Lacôte, M. Malacria, M. Newcomb, J. C. Walton, D. P. Curran, *J. Am. Chem. Soc.* **2009**, *131*, 11256–11262; b) J. C. Walton, M. M. Brahmi, L. Fensterbank, E. Lacôte, M. Malacria, Q. Chu, S.-H. Ueng, A, Solovyev, D. P. Curran, *J. Am. Chem. Soc.* **2010**, *132*, 2350–2358; c) J. C. Walton, M. M. Brahmi, J. Monot, L. Fensterbank, M. Malacria, D. P. Curran, E. Lacôte, *J. Am. Chem. Soc.* **2011**, *133*, 10312–10321.

[5] a) J. Lalevée, N. Blanchard, A.-C. Chany, M.-A. Tehfe, X. Allonas, J.-P. Fouassier, *J. Phys. Org. Chem.* **2009**, *22*, 986–993; b) J. Lalevée, N. Blanchard, M.-A. Tehfe, A.-C. Chany, J.-P. Fouassier, *Chem. Eur. J.* **2010**, *16*, 12920–12927; c) J. Hioe, A. Karton, J. M. L. Martin, H. Zipse, *Chem. Eur. J.* **2010**, *16*, 6861–6865.

[6] C.-W. Chiu, F. P. Gabbaï, *Angew. Chem.* **2007**, *119*, 1753–1755; *Angew. Chem. Int. Ed.* **2007**, *46*, 1723–1725.

[7] Y. Aramaki, H. Omiya, M. Yamashita, K. Nakabayashi, S.-i. Ohkoshi, K. Nozaki, *J. Am. Chem. Soc.* **2012**, *134*, 19989–19992.

[8] a) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851–5855; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709; b) R. Jazzar, R. D. Dewhurst, J.-B. Bourg, B. Donnadieu, Y. Canac, G. Bertrand, *Angew. Chem.* **2007**, *119*, 2957–2960; *Angew. Chem. Int. Ed.* **2007**, *46*, 2899–2902.

[9] a) R. Kinjo, B. Donnadieu, M. A. Celik, G. Frenking, G. Bertrand, *Science* **2011**, *333*, 610–613; b) D. A. Ruiz, G. Ung, M. Melaimi, G. Bertrand, *Angew. Chem.* **2013**, *125*, 7739–7742; *Angew. Chem. Int. Ed.* **2013**, *52*, 7590–7592.

[10] a) P. Bissinger, H. Braunschweig, A. Damme, R. D. Dewhurst, T. Kupfer, K. Radacki, K. Wagner, *J. Am. Chem. Soc.* **2011**, *133*, 19044–19047; b) P. Bissinger, H. Braunschweig, T. Kupfer, K. Radacki, *Organometallics* **2010**, *29*, 3987–3990; c) P. Bissinger, H. Braunschweig, K. Kraft, T. Kupfer, *Angew. Chem.* **2011**, *123*, 4801–4804; *Angew. Chem. Int. Ed.* **2011**, *50*, 4704–4707; d) P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, A. Vargas, *Angew. Chem.* **2012**, *124*, 10069–10073; *Angew. Chem. Int. Ed.* **2012**, *51*, 9931–9934; e) H. Braunschweig, R. D. Dewhurst, C. Hörl, A. K. Phukan, F. Pinzner, S. Ullrich, *Angew. Chem.* **2014**, *126*, 3305–3308; *Angew. Chem. Int. Ed.* **2014**, *53*, 3241–3244.

[11] See the Supporting Information for full experimental, analytical, and crystallographic data as well as computational details. CCDC 992196 (**1**), 992197 (**2**), and 992198 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] a) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schäfer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412–12413; b) Y. Wang, B. Quillian, P. Wei, Y. Xie, C. S. Wannere, R. B. King, H. F. Schäfer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 3298–3299; c) Y. Wang, G. H. Robinson, *Inorg. Chem.* **2011**, *50*, 12326–12337.

[13] J. K. Mahoney, D. Martin, C. E. Moore, A. L. Rheingold, G. Bertrand, *J. Am. Chem. Soc.* **2013**, *135*, 18766–18769.

[14] a) Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113–115; b) H. Braunschweig, C.-W. Chiu, K. Radacki, T. Kupfer, *Angew. Chem.* **2010**, *122*, 2085–2088; *Angew. Chem. Int. Ed.* **2010**, *49*, 2041–2044; c) J. Monot, A. Solovyev, H. B. Dubarle, É. Derat, D. P. Curran, M. Robert, L. Fensterbank, M. Malacria, E. Lacôte, *Angew. Chem.* **2010**, *122*, 9352–9355; *Angew. Chem. Int. Ed.* **2010**, *49*, 9166–9169.