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Boron–Carbene Adducts

Synthesis and Reactivity of a CAAC–Aminoborylene Adduct: A Hetero-Allene or an Organoboron Isoelectronic with Singlet Carbenes**

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***Abstract:** A one-electron reduction of a cyclic (alkyl)-(amino)carbene (CAAC)–bis(trimethylsilyl)aminodichloroborane adduct leads to a stable aminoboryl radical. A second one-electron reduction gives rise to a CAAC–aminoborylene adduct, which features an allenic structure. However, in manner similar to that of stable electrophilic singlet carbenes, this compound activates small molecules, such as CO and H_2.*

Compounds of low-valent main-group elements have been a subject of considerable interest. Among them, singlet carbenes (**A**) have arguably been the most widely studied (Figure 1). These species feature a carbon center with a lone pair of electrons and a vacant orbital, and they are therefore both Lewis acids and Lewis bases. Despite their expected high reactivity, many types of carbenes,[1] as well as their heavier group 14 congeners,[2] are stable at room temperature. By contrast, there is only one nitrene (**B**)[3] that has been isolated, and no metal-free borylenes (**C**).[4] Although the latter are often considered to be the group 13 element analogues of carbenes, they are not isoelectronic with carbenes since they possess one lone pair of electrons but two vacant orbitals. To fulfil the isoelectronic criteria, a Lewis base, such as a singlet carbene, should be appended to borylenes (**C**), as shown by **D**. As a matter of fact, such compounds can also be described as alkylideneboranes (**D′**), but all known derivatives have a formal triplet carbene fragment[5] and therefore feature a conventional double bond. Recently, in efforts to favor carbene-to-boron σ donation and boron-to-carbene π back-donation, several groups have attempted to prepare compounds of type **D** with a stable singlet carbene unit through the reduction of carbene–borane adducts **E**,[6] **G**,[7] and **I**.[8] From **E** and **I**, the diborene **F** and the bis(carbene) adduct **J**, respectively, were isolated, whereas from **G**, the transient existence of the desired carbene–borylene adduct was based on characterization of the trapping product **H**.

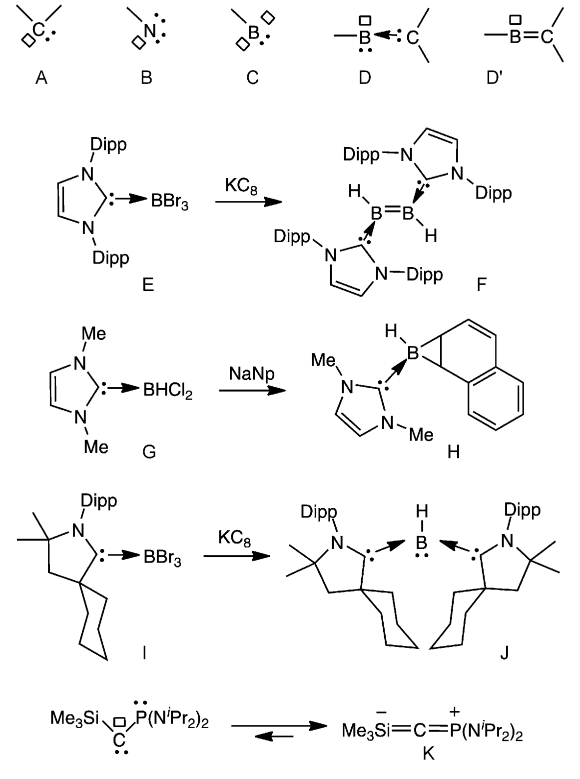

Figure 1. Representations of singlet carbenes **A**, nitrenes **B**, borylenes **C**, singlet carbene–borylene adducts **D**, and alkylideneboranes **D′**. Previous attempts at preparing compounds of type **D** through the reduction of carbene–borane adducts **E**, **G**, and **I**. The first isolated carbene **K**, which was stabilized by push-pull substituents.

The first successful isolation of a carbene (**K**)[9] followed the prediction in 1980 by Pauling[10] that substituents of opposing electronic properties (push–pull effect) should stabilize singlet carbenes by preserving the electroneutrality of the carbon center. As a consequence of this mode of stabilization, carbene **K** features an allene-like structure, albeit a highly flexible one.[11] We chose to apply the same strategy for the preparation of a stable singlet carbene–borylene adduct. We show that similar to carbene **K**, this adduct has a carbene-like reactivity despite its allenic structure. Of particular interest, it mimics the reactivity of stable electrophilic singlet carbenes[12] by activating small molecules, such as CO and H_2.

As the push substituent, we chose an amino group, arguably a better π donor than a phosphino moiety.[13] Addi-

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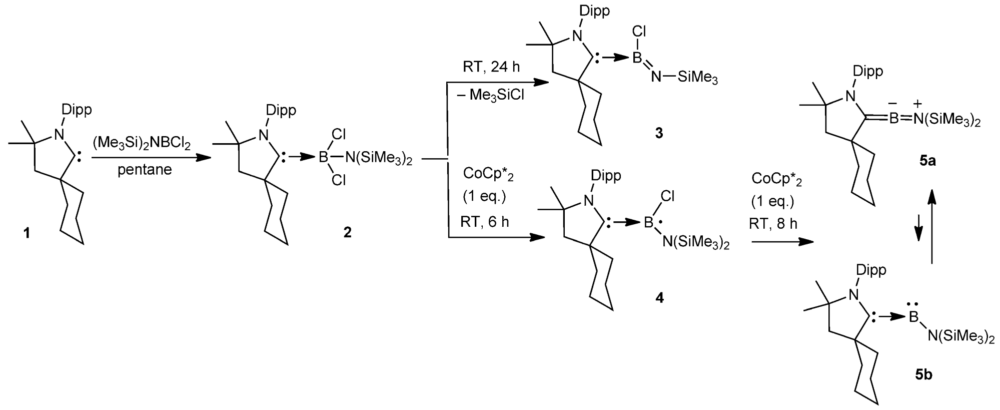
tionally, we selected silyl groups at the nitrogen atom to further stabilize the electron deficiency at the boron center through the well-known β effect. As a Lewis base and the pull-substituent, our choice was a cyclic (alkyl)(amino)carbene (CAAC), which is strongly π accepting[14] and can withdraw excessive electron density from boron.



Scheme 1. Synthesis of compounds **2**–**5**, with schematic representations of the observed allenic structure (**5a**) and the putative reactive bent form (**5b**). Dipp = 2,6-diisopropylphenyl.

By analogy with recent results in carbene chemistry,[15] we selected a reduction route with the aminodichloroborane–CAAC adduct **2** as a precursor (Scheme 1). This compound was readily prepared through the addition of CAAC **1**[16] to the bis(trimethylsilyl)aminodichloroborane in pentane, and it was isolated in 65% yield.[17] It should be noted that in solution, **2** loses trimethylsilyl chloride over 24 h at room temperature to give rise to the CAAC-stabilized iminoborane **3**. We found that the addition of one equivalent of Co(Cp*)$_2$ at 25 °C to a freshly prepared C_6H_6 suspension of **2** quickly afforded the aminoboryl radical **4**, which has been fully characterized (see the Supporting Information) and is reminiscent of the arylboryl radical recently prepared by Braunschweig et al.[18] Thanks to the thermal stability of **4**, it was possible to perform a second reduction with one equivalent of Co(Cp*)$_2$ in benzene at 25 °C for 8 h. After workup, the desired compound **5** was isolated as a red solid in 86% yield.

The ^{11}B{^{1}H} NMR spectrum of **5** shows a broad singlet at +83.7 ppm, which is shifted downfield compared to aminoboraalkenes ($R_2C{=}BNR'_2$; +59–+71 ppm)[14] and is in the range observed for transition-metal-stabilized terminal aminoborylenes ($L_nM{=}BNR_2$; +67 to +92 ppm).[4] In the solid state, the boron is in an almost linear environment (C-B-N angle of 174.8(3)°; Figure 2a). The B–C distance [1.401(5) Å] is significantly shorter than in **3** [1.612(3) Å] and **4** [1.527(3) Å], as expected from the pull effect of the CAAC substituent. The B–N distance [1.382(5) Å] is longer than in **3** [1.300(3) Å], in agreement with an increase in electron density at the boron center, but shorter than in **4** [1.460(3) Å]. From these data, and by analogy to aminoboraalkenes,[5] it can be concluded that **5** features an allenic structure as depicted by **5a**.

DFT calculations at the 6-311g(d,p) level of theory well reproduce the solid-state geometry of **5** [B–N: 1.383 Å; B–C: 1.412 Å; C-B-N angle 175.4°]. The highest occupied molecular orbital (HOMO) results from a bonding interaction between the vacant π* molecular orbital of the CAAC fragment and the occupied p orbital of the boron atom, as expected for the stabilization of the formal lone pair at the boron center by the π-accepting CAAC ligand (Figure 2b). Similarly, the interaction of the lone pair at nitrogen with the formal empty p orbital at boron results in a high-energy π* molecular orbital (+0.16 eV). This is not even the lowest unoccupied molecular orbital (LUMO), but the LUMO+2. However, a vibrational analysis indicates that the C-B-N bending mode corresponds to an abnormally low energy frequency (389 cm^{-1}), thus suggesting a significant flexibility of the molecule along this coordinate. Indeed, bending the C-B-N angle up to 155° has negligible energetic cost (5.7 kcal mol^{-1}). In marked contrast with the linear form **5a**, the resulting bent structure **5b** has pronounced electrophilicity, since the formal empty p orbital at boron becomes sp^2 hybridized and is lower in energy. As a consequence, the π* orbital of the B–N moieties now becomes the LUMO, its energy dramatically decreasing by more than 0.6 eV (see the Supporting Information). Although the minimum on the energy hypersurface of **5** corresponds to an apparently non-electrophilic molecule with a nearly linear C-B-N alignment (**5a**), its flexibility provides access to a highly electrophilic boron center (**5b**).

To demonstrate the carbene-like and electrophilic properties of **5**, we performed preliminary reactivity studies. In contrast to NHCs,[19] more electrophilic stable singlet carbenes, such as CAACs and diamidocarbenes,[20] readily react with CO to give the corresponding adducts.[12] Similarly, exposing a solution of **5** in pentane to 1 atmosphere of ^{13}CO resulted in the formation of **6** as a pink solid in 80% yield (Scheme 2). The ^{11}B{^{1}H} NMR spectrum showed a doublet ($^{1}J_{BC} = 87$ Hz) at high field (−3.4 ppm), a result indicative of an increase coordination number at the boron center. The ^{13}CO carbon was observed as a broad multiplet at 236.3 ppm in the ^{13}C{^{1}H} NMR spectrum. A single-crystal X-ray diffraction study confirmed that **6** is a rare example[21] of an isolable organoboron–CO adduct (Figure 3). Moreover, in contrast with previous examples that involved trivalent boron derivatives, the addition of CO appeared to be irreversible.

The formation of **6** is in line with DFT calculations, which predict the reaction of carbon monoxide with **5** to be exothermic ($\Delta H^{298\,K} = -17.5$ kcal mol^{-1}). The bonding situation is clearly reminiscent of the bis(carbene)borylene adduct

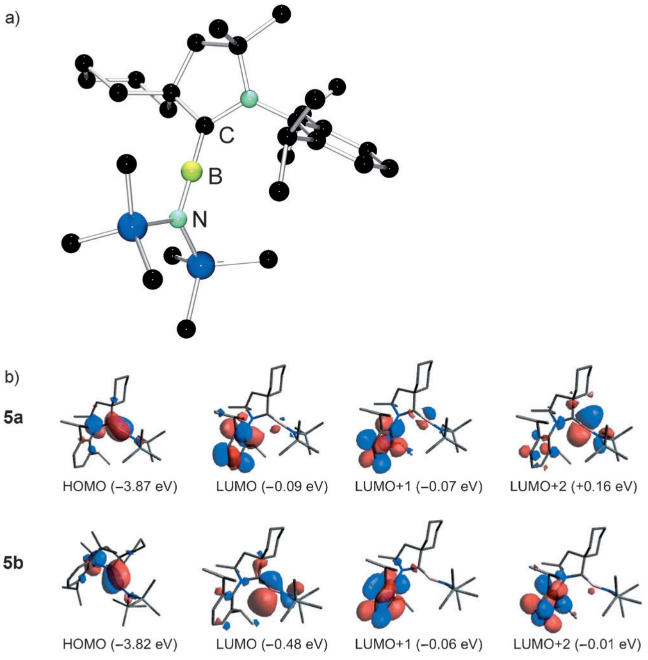
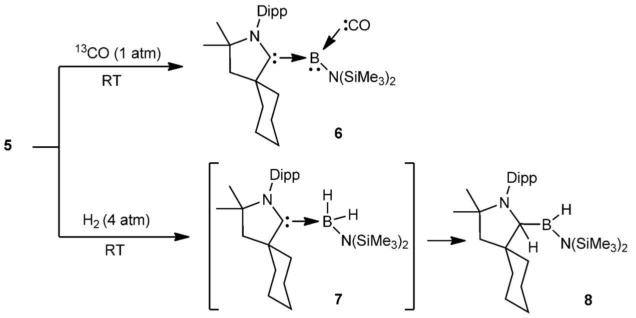


Figure 2. a) POV-Ray depiction of the molecular structure of organoboron **5** in the solid state (C black, N aquamarine, Si blue, B yellow–green; H atoms omitted for clarity). b) Selected MOs of linear **5a** and bent **5b** with a frozen C-B-N angle at 155°.



Scheme 2. Compound **5** reacts with carbon monoxide to give the (CAAC)–(CO)–aminoborylene adduct **6**, and with hydrogen to afford the borane **8** via the carbene–borane adduct **7**.

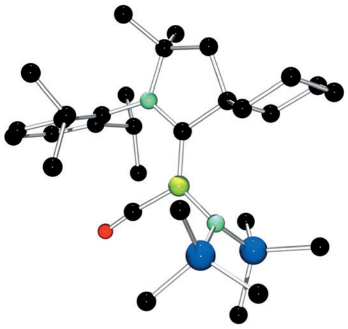


Figure 3. POV-Ray depiction of the molecular structure of organoboron **6** in the solid state (C black, N aquamarine, Si blue, B yellow–green, O red; H atoms omitted for clarity).

J,[8,22] in which a boron atom is surrounded by one X and two L ligands. The interaction of the lone pair of CO with the LUMO of the bent form of **5** leads to the formation of a low-lying σ orbital. The HOMO of **6** is a bonding combination of a p orbital of boron with π* molecular orbitals of the CAAC and CO moieties, thus suggesting some π back-donation from the boron to both L ligands.

Some carbenes able to add CO are also capable of splitting hydrogen;[11] similarly a toluene solution of **5** reacted with H_2 (4 atm). The ^{11}B{^{1}H} NMR spectrum showed a broad singlet at +51.2 ppm, which is indicative of a three- and not a four-coordinate boron as expected for the boron dihydride **7**. A single-crystal X-ray diffraction study demonstrated that the isolated compound was the monohydride **8**, which results from a formal 1,2-addition through the B−C bond of **5**. However, it has already been reported[23] that CAAC–borohydride adducts, such as **7**, can rearrange through 1,2-hydride migration. Therefore, it is quite likely that the first step of the reaction of **5** with H_2 is an oxidative addition of hydrogen at the boron center. Such a two-step process leading to **8** is supported by DFT calculations, with both steps being strongly exergonic ($\Delta G = -18$ and $-12\,\mathrm{kcal\,mol^{-1}}$, respectively). Not surprisingly, the rate-limiting step is the oxidative addition ($\Delta G^{\ddagger} = +25\,\mathrm{kcal\,mol^{-1}}$); the hydride migration has a very low activation barrier ($\Delta G^{\ddagger} = +4.6\,\mathrm{kcal\,mol^{-1}}$). The approach of dihydrogen results in the primary interaction of the low-lying LUMO of the bent form of **5** with the bonding σ orbital of H_2 (Figure 4b). Note that although this first step corresponds to an early transition state, **5** is already bent by 153° (Figure 4a). The concomitant secondary back-donation from the HOMO of the bent **5** to the antibonding σ* orbital of H_2 finally triggers the cleavage of the activated H−H bond (Figure 4c). Altogether, this process is reminiscent of the homolytic bond cleavage of H_2 by electrophilic metals.[24] Importantly, despite multiple attempts, we were unable to find a transition state for the formation of **8** by direct addition of hydrogen to the B−C bond of **5**.

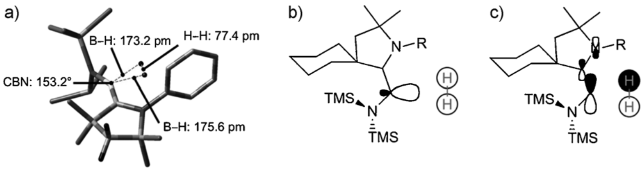


Figure 4. a) Calculated transition state for the activation of H_2 by **5**; isopropyl substituents were omitted for clarity. b) Primary interaction between the LUMO of the bent form of **5** and the σ orbital of H_2. c) Secondary interaction between the HOMO of the bent form of **5** and the σ* orbital of H_2.

More than two decades after the discovery of a stable carbene with allenic character,[9] this work demonstrates that isoelectronic group 13 derivatives can be isolated as well. Moreover, although other main-group-element species have been shown to mimic to some extent the behavior of transition metals,[12c,25] the electrophilicity of the boron center of **5** makes it the closest analogue of a metal center. Cyclic versions of **5** featuring enhanced electrophilicity should be available in the near future.

Experimental Section

Preparation of **5**: 15 mL of C_6H_6 was added to a mixture of **4** (0.200 g, 0.376 mmol) and $Co(Cp^*)_2$ (0.124 g, 0.376 mmol). The reaction mixture was stirred at 25 °C for 8 h and was then filtered over celite. The filtrate was concentrated to 1 mL and 15 mL of pentane was added dropwise to precipitate residual $[Co(Cp^*)_2][Cl]$. The mixture was then filtered over a pad of celite and the solvent was removed in vacuo to yield a dark orange/red solid (0.186 g, 86 %). X-ray quality crystals were grown by slow evaporation of a benzene solution at 25 °C. $^{11}B\{^1H\}$ NMR (96 MHz, C_6D_6): $\delta = 83.7$ ppm (br s). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): $\delta = 151.8$ (C_6H_3), 142.3 (C_6H_3), 128.6 (C_6H_3), 126.7 (C_6H_3), 124.1 (C_6H_3), 64.0 (Dipp-N$\mathit{C}(CH_3)_2$), 53.9 (C_6H_{10}), 47.0 (C_6H_{10}), 43.7 (C_6H_{10} + Dipp–NC$\mathit{C}H_2$), 28.0 ($\mathit{C}H(CH_3)_2$), 27.6 (Dipp-NC($\mathit{C}H_3)_2$), 26.8 ($CH(\mathit{C}H_3)_2$), 26.5 ($CH(\mathit{C}H_3)_2$), 25.5 (C_6H_{10}), 25.4 (C_6H_{10}), 2.7 ppm (s, $(\mathit{C}H_3)_3Si$). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): $\delta = 7.2$ ppm (s, $(CH_3)_3\mathit{Si}$).

Preparation of **6**: A solution of **5** (0.100 g, 0.201 mmol) was dissolved in 2 mL pentane and transferred to a Schlenk tube and sealed. The solution was degassed over three freeze-pump-thaw cycles before being warmed to 25 °C and charged with 1 atm. ^{13}CO. The mixture was stirred at 25 °C for 18 h to yield a pale red solution and pink solid. The volatile components were removed in vacuo and a pink solid was obtained (0.085 g, 80 %). X-ray quality crystals were grown from pentane at −35 °C. $^{11}B\{^1H\}$ NMR (96 MHz, C_6D_6): $\delta = -3.4$ ppm (d, $^1J_{BC} = 87$ Hz). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): $\delta = 236.3$ (br m, B–CO), 148.9 (C_6H_3), 133.6 (C_6H_3), 129.8 (C_6H_3), 127.9 (C_6H_3), 125.6 (C_6H_3), 68.1 (Dipp–N$\mathit{C}(CH_3)_2$), 48.4 (C_6H_{10}), 37.4 (C_6H_{10} + Dipp-NC$\mathit{C}H_2$), 30.2 ($\mathit{C}H(CH_3)_2$), 27.9 (Dipp–NC($\mathit{C}H_3)_2$), 27.2 (CH-($\mathit{C}H_3)_2$), 25.4 ($CH(\mathit{C}H_3)_2$), 25.0 (C_6H_{10}), 22.9 (C_6H_{10}), 4.2 ppm (s, $(\mathit{C}H_3)_3Si$). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): $\delta = 3.01$ ppm (s, $(CH_3)_3\mathit{Si}$). IR (solid) 1956 cm^{-1} (^{12}CO); 1904 cm^{-1} (^{13}CO).

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