Cumulenes Hot Paper

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Diborabutatriene: An Electron-Deficient Cumulene**

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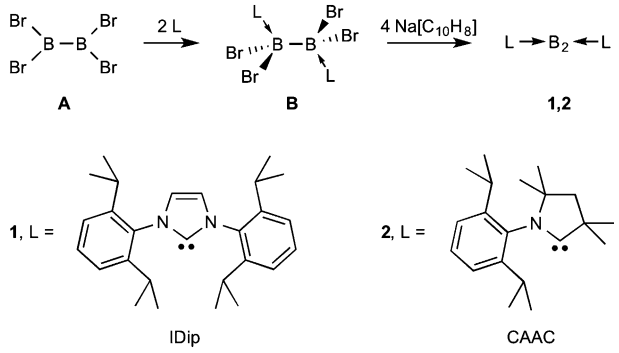
Abstract: *The complexation of two equivalents of a cyclic (alkyl)(amino)carbene (CAAC) to tetrabromodiborane, followed by reduction with four equivalents of sodium naphthalide, led to the formation of the CAAC-stabilized linear diboracumulene $(CAAC)_2B_2$. The capacity of the CAAC ligand to facilitate $B_2 \rightarrow CAAC$ donation of π-electron density resulted in important differences between this species and a previously reported complex featuring a B≡B triple bond stabilized by cyclic di(amino)carbenes, including a longer B–B bond and shorter B–C bonds. Frontier orbital analysis indicated sharing of valence electrons across the entire linear C-B-B-C unit in $(CAAC)_2B_2$, which is supported by natural population analysis and cyclic voltammetry.*

Stable carbenes have an established and impressive track record in enabling new reactivity, with important discoveries now reported weekly. We employed one such carbene (1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene, IDip) in the synthesis and isolation of the first room-temperature-stable example of a compound with a triple bond between two boron atoms (Scheme 1).[1] The importance of the carbene ligand was evidenced by the fact that previous attempts at the isolation of complexes with B≡B triple bonds using CO and BO^- as stabilizing ligands gave spectroscopically observed products that were unstable outside frozen matrices.[2] In contrast to these compounds, $IDip_2B_2$ (**1**) showed exceptional thermal stability, along with an extremely short B–B bond and linearity across the central B_2 unit. The importance of IDip in the formation and stability of **1** suggested that the central B_2 unit might show sensitivity to the electronic structure of the stabilizing ligand, and thereby function as a useful probe of carbene character. Therefore, we began exploring the use of other carbenes in the formation of diborynes, starting with, as suggested by Frenking and Holzmann,[3] cyclic (alkyl)(amino)carbene. The result was a previously unknown example of an organic/inorganic analogue of butatriene.



Scheme 1. Synthesis of **1** and **2**.

Since their first synthesis in 2005,[4] cyclic (alkyl)-(amino)carbene have been extensively utilized to affect a range of new and interesting reactions.[5–7] The combination of strong σ-donating ability, coupled with a greater capacity for accepting π-back-donation than cyclic di(amino)carbenes, has been shown to promote reactivities not observed in systems employing other N-heterocyclic carbenes (NHC).[8] When two equivalents of 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene (CAAC) were reacted with B_2Br_4 at −78 °C, the bis(CAAC) adduct (Scheme 1, **B**) precipitated from the pentane solvent. This white solid was separated by filtration and washed several times with pentane. The residual solid was identified by its broad peak at 2 ppm in the ^{11}B NMR spectrum, in the same range as the peak found in the spectrum of 1,2-$(IDip)_2$-B_2Br_4 (−5 ppm).[1] The ^1H NMR of the bis-CAAC adduct (Supporting Information, Figure S1) was likewise in good agreement with the formulation of the species as 1,2-$(CAAC)_2$-B_2Br_4, which was unequivocally confirmed by single-crystal X-ray diffractometry (Supporting Information, Figure S2).

Treatment of this adduct with four equivalents of sodium naphthalenide at −78 °C gave the solution a deep red color, which remained as it was brought to room temperature and stirred for one hour. The solvent was evaporated in vacuo, and the residual material was redissolved in pentane and filtered. Evaporation of the pentane, followed by sublimation of the residual naphthalene at 60 °C under reduced pressure (1×10^{-3} mbar) left a purple solid (**2**). The ^{11}B NMR resonance for **2** was observed at 80 ppm, which is significantly downfield of the resonance observed for **1** (39 ppm), though in good agreement with the DFT-predicted resonance based on an optimized structure of **2** as linear $(CAAC)_2B_2$ (Supporting Information, Figure S3). The ^1H NMR spectrum of **2** (Supporting Information, Figure S4) was consistent with the solution-state D_2 symmetry suggested by the DFT-optimized geometry. Analysis by DSC indicated that **2** decomposed

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prior to melting at 229 °C, which is only slightly below the observed decomposition temperature of **1** (234 °C).[1]

Crystals of **2** suitable for study by single-crystal X-ray diffractometry were grown from a saturated pentane solution at −35 °C (Figure 1). As was observed for **1**, the central C1-B1-B2-C5 unit in **2** is essentially linear, with B-B-C angles of

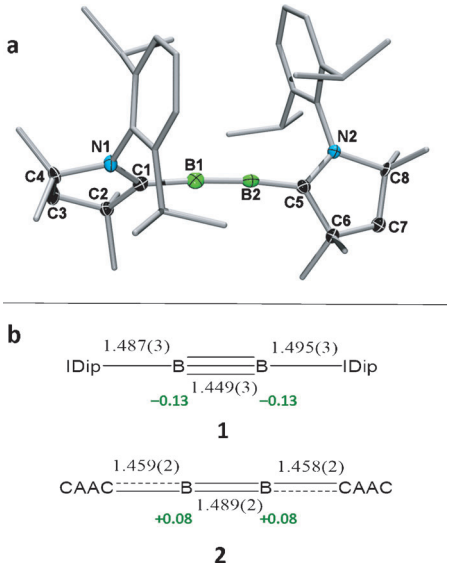

Figure 1. a) Crystallographically determined structure of **2**. Ellipsoids are set at 50% probability, and have been omitted from the exocyclic CAAC substituents for clarity. All hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: B1–B2 1.489(2), C1–B1 1.459(2), C5–B2 1.458(2), C1–N1 1.366(2), C5–N2 1.365(2); C1-B1-B2 174.6(1), B1-B2-C5 174.3(1), N1-C1-B1 127.4(1), B2-C5-N2 127.4(1), C2-C1-N1 108.4 (av.), C6-C5-N2 108.4(1). b) Comparison of the experimental bond lengths (black, [Å]) and computed NPA charges (green, B3LYP/6-311G(d)) in the central B_2 units of **1** and **2**.

174.6(1)° and 174.3(1)°. The very slight deviation from linearity is a result of steric repulsion between the diisopropylphenyl segments of the CAAC ligand. The central B–B bond (1.489(2) Å) shows a significant reduction from the value of 1.754(5) Å measured in 1,2-$(CAAC)_2B_2Br_4$ (Supporting Information, Figure S2). It is noticeably longer than the same bond in **1** (1.449(3) Å),[1] falling between this value and the values observed for B=B double bonds (1.56–1.71 Å).[9] Furthermore, the C–B bonds between the central B_2 and the stabilizing ligands are substantially shorter in **2** (1.459(2) Å, 1.458(2) Å) than in **1** (1.487(3) Å, 1.495(3) Å).[1] Taken together, these structural data indicate sizeable electronic differences induced by the respective stabilizing ligands, best visualized by the two Lewis structures in Figure 1b. While the extremely short B–B bond and longer B–C bonds in **1** are best described as a triple bond between the boron atoms flanked by single bonds from ligand to boron, the longer B–B bond and shorter B–C bonds in **2** suggest more equal sharing of electron density across all three bonds of the C-B-B-C core, resulting in a cumulene structure.

The CAAC ligand has been demonstrated to function as a superior acceptor of electron density as compared to diaminocarbene ligands such as IDip, a fact which is often manifested in reactivity differences between the two types of ligands.[10] The frontier orbitals of **1** and **2** are depicted in Figure 2. As was described for **1**, the HOMO and HOMO−1 of **2** are strongly π-bonding across the central B_2 unit.[1] However, unlike **1**, in which the π-electron density is localized between the two central boron atoms, in **2** the π-system

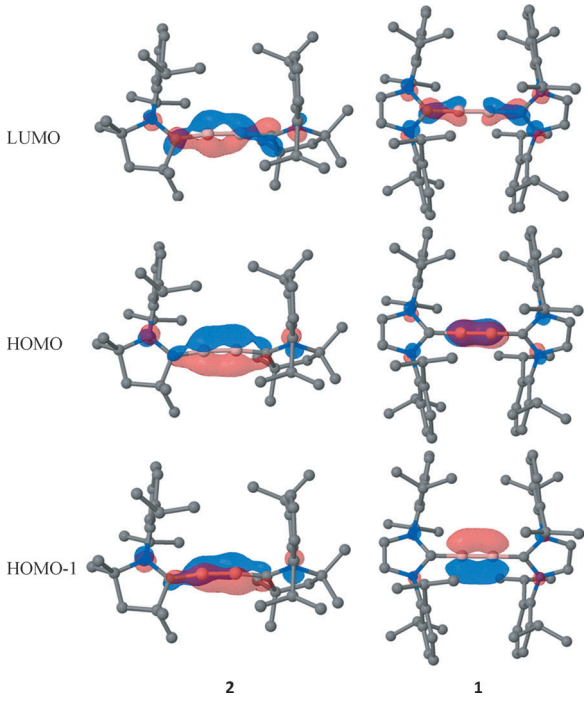

Figure 2. Comparison of the frontier orbitals of **1** and **2**. Theory = B3LYP/6-311G(d), isovalue = 0.07.

extends from carbene to carbene, twisting slightly to accommodate the orthogonal alignment of the CAAC ligands. The spatial extent of these orbitals demonstrates the ability of the CAAC ligand to accept π-electron density and delocalize bonding electrons across the entire C-B-B-C unit. Both the HOMO and HOMO−1 of **2** display lobes at the nitrogen of the CAAC ligand that are out of phase with the central portion of the orbital, giving the orbital antibonding character across the C1–N1 and C5–N2 bonds. This π*-character is manifest in the longer C–N bond lengths observed in **2** (1.366(2) Å), 1.365(2) Å) than found in a recently characterized CAAC-$GaCl_3$ adduct for which π-back-donation from the tetrahedral Lewis acid fragment is presumably negligible (1.303(3) Å),[11] as well as the C–N bond length in 1,2-$(CAAC)_2$-B_2Br_4 (1.323(4) Å, 1.320(4) Å; Supporting Information, Figure S2).

The central B_2 unit in **1** is exceptionally electron-rich. The negative NPA charges (−0.13, Figure 1b) assigned to the boron atoms in **1** are unusual for boron bound to more electronegative elements, such as carbon. An NPA study of **2** assigned a charge of +0.08 for each boron atom, indicating less electron density in the central B_2 unit, in support of the Lewis structure proposed in Figure 1b and in line with the orbital analyses in Figure 2. The reductive power of **1** was shown by cyclic voltammetric measurements indicating

a reversible one-electron oxidation at −1.28 V measured against the ferrocene/ferrocenium couple, followed by a second, irreversible oxidation at +0.11 V.[12] Indeed, when **1** was reacted with an excess of CO, the central B_2 core underwent a six-electron oxidation, coupling four CO molecules in the formation of a bis-boralactone.[12] The cyclic voltammogram of **2**, with its relatively less electron-dense B_2 unit, showed an oxidation wave at −0.55 V against the ferrocene/ferrocenium couple (Supporting Information, Figure S5), demonstrating **2** to be a less powerful reducing agent than **1**, again in agreement with a more even distribution of valence electrons in **2**.

An irreversible reduction wave observed at −3.15 V in the CV profile of **2** presents the intriguing possibility of further populating the B_2 unit. Though the bond lengths and electronic distribution of **2** elicit comparisons to the cumulene butatriene ($R_2C{=}(C_2){=}CR_2$), the nearly orthogonal alignment of the planes formed by the five-membered rings of the CAAC ligands of **2** (80.4(4)°, determined by least squares) stands in contrast to the typical structure of neutral butatrienes, in which the planes formed by the sp^2-hybridized terminal carbon atoms are parallel (eclipsed).[13] This difference may be explained by the substitution of two carbon atoms by two boron atoms, causing the cumulene to be electron-deficient by one electron pair. Computational work has shown that while neutral butatrienes have eclipsed geometries, their terminal $=CR_2$ units are orthogonal (staggered) in the ground state structures of their dications,[14] which are isoelectronic with **2**. Unsurprisingly, optimization of the dianionic $\mathbf{2}^{2-}$ by DFT (Supporting Information, Figure S6) identified two minima (*cis* and *trans*) wherein the CAAC ligands aligned in an eclipsed, parallel conformation. Therefore, chemical reduction of **2** has the potential to yield the dianionic CB_2C analogue of a neutral butatriene.

Very recently, a C_4-cumulene containing two CAAC ligands ((CAAC)=C_2=(CAAC)) (**3**) has been reported.[15] While the CAAC ligands in this neutral compound are expectedly co-planar, when twice-oxidized to a dication ($\mathbf{3}^{2+}$), which is isoelectronic with **2**, the ligands remain essentially eclipsed rather than adopting a staggered conformation. As the eclipsed conformation allows the bulky diisopropylphenyl moieties of the CAAC ligand to relieve steric stress by adopting a *trans*-orientation, the crowded steric environment is likely the cause of the anomalous rigidity. The steric stress is less cumbersome in **2** on account of the larger radius of B, and the greater distance between the carbenes (**2** C-B-B-C, ca. 4.41 Å; $\mathbf{3}^{2+}$ C-C-C-C, ca. 4.07 Å).[15]

The UV/Vis spectrum of **2** consists of one intense feature at 382 nm (Figure 3). Analysis by TD-DFT predicted such a spectrum, showing three overlapping transitions at $\lambda = 353$, 366, and 380 nm. Each of these absorbances arises from promotion of electrons from the HOMO and HOMO−1 orbitals, centered at the C-B-B-C unit, into orbitals on the phenyl portion of the CAAC ligand. When these three transitions are summed, the overall predicted spectrum (solid blue line, Figure 3) shows a maximum at 364 nm, in excellent agreement with the observed spectrum. The strongest feature in the UV/Vis spectrum of **1** is an excitation from the HOMO and HOMO−1 (B≡B π-bonding) to a combination of orbitals,

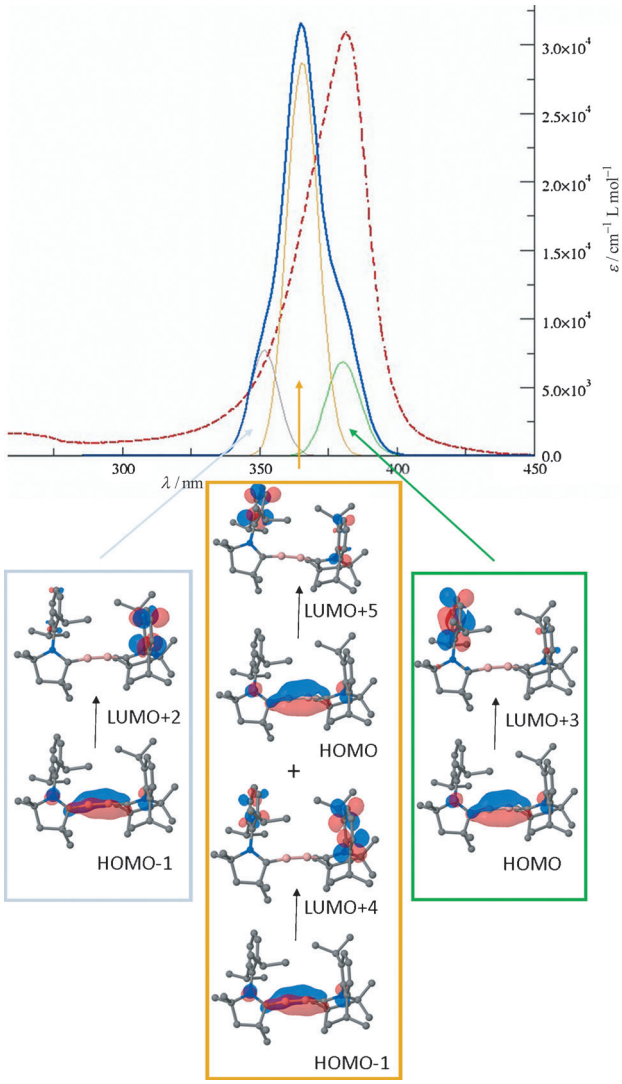

Figure 3. UV/Vis spectrum of **2** (red dashed line) compared to a theoretical spectrum calculated by TD-DFT (B3LYP/6-311G(d)). The solid blue line represents the overall theoretical spectrum as the sum of the three calculated transitions.

dominated by the LUMO, with antibonding character between the boron atoms.[1] This absorption is notably absent in **2**, which shows no lower-energy features than the peak at 382 nm, and a lack of π*-character between the boron atoms in the LUMO (Figure 2).

In summary, the employment of the π-acidic CAAC ligand has enabled the synthesis of a new kind of cumulene that demonstrates the generality with which the elements of the first row of the p-block behave when provided with equivalent electron counts. Likewise, the distinct differences observed between **1** and **2** confirm the utility of the B_2 unit in the comparison of the electronics of stabilizing ligands. Reactivity studies that are currently underway will undoubtedly further elucidate these differences, and the use of new stabilizing ligands will enable the establishment of useful trends.

Experimental Section

$B_2(CAAC)_2$ (**2**): A 19.7 mL (6.8 mmol) portion of a freshly prepared 0.34 M sodium naphthalenide solution in THF was added dropwise to a suspension of 1,2-$(CAAC)_2B_2Br_4$ (1.50 g, 1.6 mmol) in 10 mL of THF at −78 °C and stirred for 1 h. The deep red solution was stirred for 1 h at room temperature, and the solvent was then evaporated under reduced pressure. The remaining residue was taken up in pentane and filtered. The pentane was evaporated under reduced pressure, and the remaining naphthalene was subsequently removed by sublimation under reduced pressure at 60 °C. For **2**: Purple solid, yield: 718 mg (1.2 mmol, 74 %), decomp.: 229 °C. Full characterization is provided in the Supporting Information.

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