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From an Electron-Rich Bis(boraketenimine) to an Electron-Poor Diborene**

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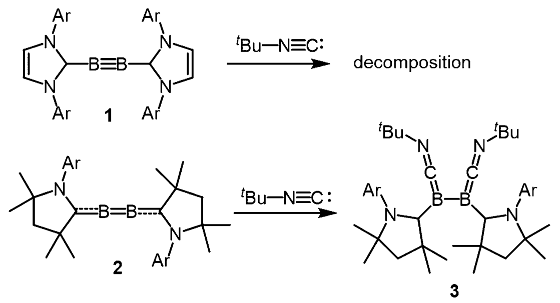
In memory of Paul von Ragué Schleyer

Abstract: *The reaction of the bisboracumulene $(CAAC)_2B_2$ (CAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene) with excess tert-butylisocyanide resulted in complexation of the isocyanide at boron. Though this compound might be formally drawn with a lone pair on boron, these electrons are highly delocalized throughout a conjugated π-network consisting of the π-acidic CAAC and isocyanide ligands. Heating this compound to 110°C liberated the organic periphery of both isocyanide ligands, yielding the first example of a dicyanodiborene. Cyclic voltammetry conducted on this diborene indicated the presence of reduction waves, making this compound unique among diborenes, which are otherwise highly reducing.*

Lewis acid/base reactions of electron-pair donors (bases) with trigonal boranes (acids) are common in general chemistry textbooks. The trigonal borane is ideally situated to accept electron density into its empty p-orbital, thereby completing its octet while assuming a tetrahedral geometry. Of course, the fact that a boron atom is tri-coordinate and planar does not guarantee electronic unsaturation, as the ever-expanding fields of main-group multiple bonding and donor-stabilized boron will attest.[1,2] The same is true of two-coordinate boron, where multiple bonding may electronically saturate the orbitals of coordinatively unsaturated boron centers.[3,4] Still, as boron is less electronegative than carbon or nitrogen, in a metal-free organic environment even electronically saturated boron usually bears a partial positive charge, and will be sought by incoming nucleophiles. In this context, what kind of interaction may be expected between a positively polarized, yet electronically saturated, boron atom and a strong two-electron donor? Herein we describe such a reactivity, in which Lewis bases add to electron-rich boron atoms, resulting in new bonding stabilized by extensive electronic delocalization.

Two related species containing two-coordinate boron (**1** and **2**) have been recently reported, described as organic/inorganic hybrid analogues of the alkyne (**1**)[4b] and cumulene (**2**)[4a] functionalities. One key difference between the two is the charge at boron, which NPA analysis computes to be −0.12 for **1**, but +0.08 for **2**. Another is the degree of electronic saturation at boron. While each compound contains two pairs of π-electrons between the two carbenes, in **1** these electrons are localized between the boron atoms, giving each boron atom a formal octet. The electron deficient nature of **2** when viewed as a diboracumulene leads to the Lewis structure shown in Scheme 1, which does not attribute a complete formal octet to each boron. These differences in charge and degree of saturation led us to believe that different behaviors might be expected for the two compounds if treated with Lewis bases small enough to fit through the bulky ligand architecture. Indeed, while treatment of **1** with excess *tert*-butylisocyanide (*t*BuNC) resulted in slow decomposition, an equivalent reaction with **2** resulted in a quick color change from the violet of **2** to a deep red solution with a new ^{11}B NMR signal at $\delta = -8.9$ ppm. Both the solvent and excess isocyanide were removed under reduced pressure, leaving a deep red powder (**3**) in good yield (69%, Scheme 1). Single crystals suitable for X-ray diffractometry were obtained by slow evaporation of its benzene solution, and crystallographic analysis determined the structure to be the bis(isocyanide) adduct **3** (Figure 1).



Scheme 1. Reactions of **1** and **2** with *t*BuNC. Ar = 2,6-diisopropylphenyl.

The solid-state structure of **3** (Figure 1) features a significantly elongated B−B single bond (1.760(4) Å), which falls in

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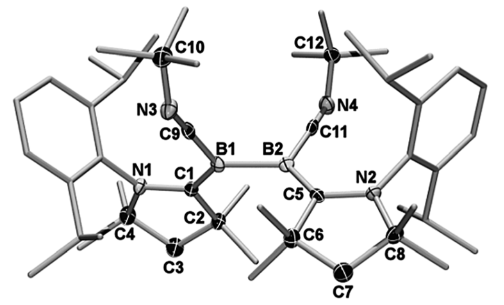


Figure 1. Crystallographically determined structure of **3**. Thermal ellipsoids set at 50% probability, and have been omitted from the phenyl portion of the CAAC ligand for clarity. All hydrogen atoms have likewise been omitted. Selected bond lengths [Å] and angles [°]: B1–B2 1.760(4), B1–C1 1.499(4), B2–C5 1.498(4), B2–C11 1.475(4), B1–C9 1.471(4), C9–N3 1.200(3), C11–N4 1.199(3); B2-B1-C9 108.0(2), B1-B2-C11 108.3(2), B1-C9-N3 165.3(3), B2-C11-N4 166.2(3), C9-N3-C10 143.6(2), C11-N4-C12 146.8(3).

the same range as the B–B single bond in 1,2-(CAAC)$_2$B$_2$Br$_4$ (1.754(5) Å)[4a] and is longer than the B–B single bond in 1,2-(*t*BuNC)$_2$B$_2$Br$_4$ (**4**, 1.716(5) Å), which was independently synthesized for structural comparison (Figure 2). The B–C

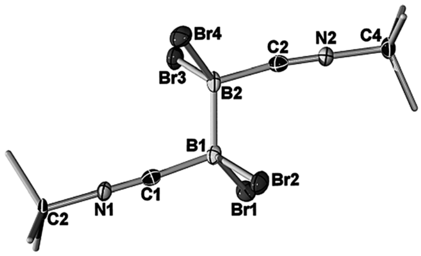


Figure 2. Crystallographically determined structure of **4**. Thermal ellipsoids set at 50% probability and have been omitted from the *tert*-butyl portion of the isocyanide for clarity. All hydrogen atoms have likewise been omitted. Selected bond lengths [Å] and angles [°]: B1–B2 1.716(5), C1–B1 1.570(5), B2–C2 1.592(5), C1–N1 1.141(4), C2–N2 1.135(4), B–Br 2.013 (avg.); C1-B1-B2 110.1(3), C2-B2-B1 106.0(3), B1-C1-N1 176.3(3), B2-C2-N2 171.5(3).

bonds linking the central B$_2$ to the carbenes (1.498(4) Å, 1.499(4) Å) are elongated with respect to their lengths in **2** (1.458(2) Å; 1.459(2) Å) to lengths similar to the σ-bonds in **1** (1.487(3) Å, 1.495(3) Å).[4b] The bonds between the boron atoms and the isocyanide carbons (1.499(4) Å, 1.498(4) Å) are longer than the typical B=C bonds in methyleneboranes (1.31–1.42 Å),[5] yet significantly shorter than the single B–C bonds in **4** (1.570(5) Å, 1.592(5) Å). Furthermore, while the B–C$_{\text{isocyanide}}$ bonds in **3** are shorter than those in tetrahedral B(CN)$_4^-$ (1.60 Å),[6] they fall in the same range as the B–C bonds in the trigonal planar B(CN)$_3^{2-}$ (1.51 Å).[2c] The overall structure of the CAAC-stabilized B=C=N-*t*Bu unit draws immediate comparison to the C=C=N-R segment of the organic ketenimine functionality, in a manner similar to the mimicry of the organic imine by a set of recently reported carbene-stabilized boraimine compounds,[7] allowing the classification of **3** as a bis(boraketenimine).

If the CAAC and isocyanide ligands are drawn as pure two-electron sigma-donors, the Lewis structure of **3** must contain a lone pair of electrons on each boron (Figure 3b, **I**). However, each boron atom is planar, with bond angles

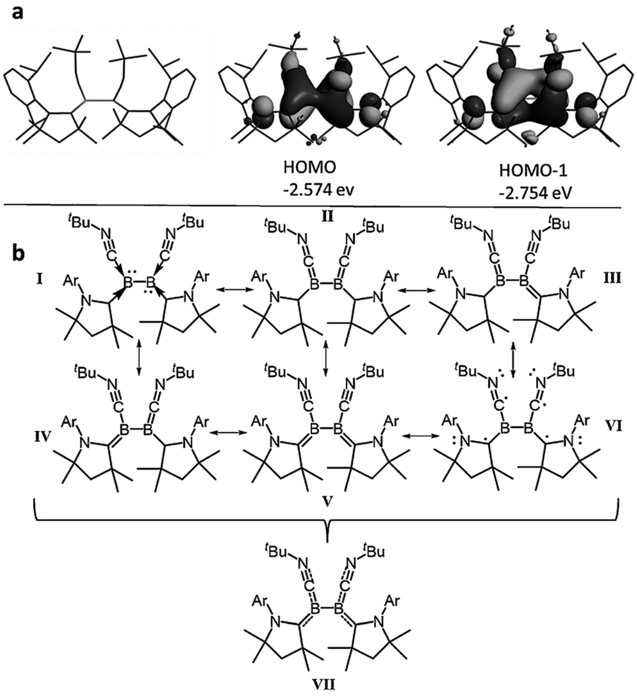


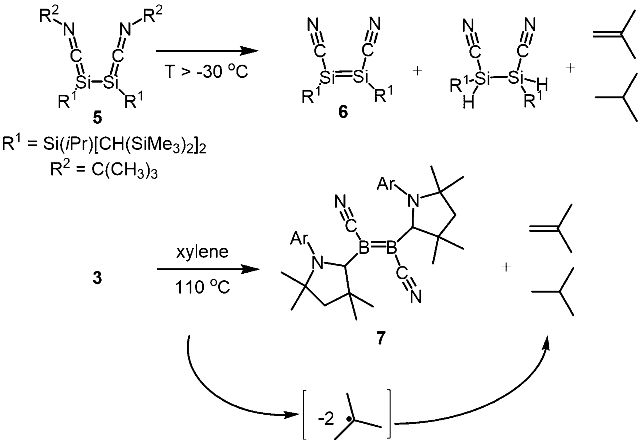
Figure 3. a) Frontier molecular orbitals of **3**, b) possible resonance structures of **3**.

summing to 360°. Examination of the structure reveals the existence of a planar, conjugated network of atoms on each side of the molecule, extending from the nitrogen on CAAC to the nitrogen of the isocyanide, on each respective side of the compound. A least squares analysis shows these atoms define two planes (N1, C1, B1, C9, N3, RMS = 0.058 Å; N2, C5, B2, C11, N4, RMS = 0.050 Å) with a 70.6° angle between them.

These π-networks are responsible for the delocalization of the excess electron density, as depicted by the frontier orbitals of **3** (Figure 3a). The spread of the HOMO and HOMO−1 across the two planes, depicting bonding with π-symmetry, clearly indicates that a single resonance structure is incapable of properly describing the actual bonding. Instead, a number of resonance structures may be imagined wherein the four π-electrons are shuffled across the two conjugated π-systems (Figure 3b, **II**–**V**). In total, the most accurate description may be represented by structure **VII**, which may be considered a superposition of **II**–**V**. As shown in structure **VI**, a neutral tetraradical resonance structure may also be drawn for **3** in which the radicals are captodatively stabilized (that is, radicals stabilized by the synergic interaction of electron-donating and electron-withdrawing groups).[8] Recent work by Hoffmann and co-workers[9] has singled out such compounds with carbon radicals stabilized between nitrogen and boron[10] as potentially useful for energy applications.

Both isonitrile $C\equiv N$ bonds in **3** (1.200(3) Å, 1.199(3) Å) are longer than the same bonds in **4** (1.135(4) Å, 1.141(4) Å), presumably as a result of population of $\pi^*_{(C\equiv N)}$ orbitals through $B\rightarrow C\equiv N$ back-donation. Consistent with this are the pronounced bends in the C-N-C units of the isocyanides (C9-N3-C10 143.6(2)°; C11-N4-C12 146.8(3)°), indicative of a decrease in bond order between C and N. The FT-IR spectrum of **3** is another clear indicator of the population of $\pi^*_{(C\equiv N)}$ orbitals. The $C\equiv N$ stretching frequency of **3** at 1932 cm^{-1} (Figure S1 in the Supporting Information) is significantly smaller than values known for free isonitriles (ca. 2130–2160 cm^{-1})[11] and for the *t*BuNC adduct of trimethylborane (2247 cm^{-1}).[12] The decrease in stretching frequency as a result of the decrease in $C\equiv N$ bond order is even more pronounced than seen in isocyanide adducts of electron-rich zero-valent late transition metals (ca. 2000–2070 cm^{-1})[11,13] for which extensive $d\rightarrow\pi^*$ back-donation is assumed.

Sekiguchi and co-workers showed that the reaction of isocyanides with disilyne ($R^1Si\equiv SiR^1$; $R^1 = Si(iPr)[CH(SiMe_3)_2]_2$) led to addition at silicon similar to the addition observed in the formation of **3**. The use of trimethylsilylisocyanide (TMS-NC) resulted in a stable (TMS-NC) adduct;[14] however, when *t*BuNC was employed, the adduct (**5**) was unstable above −30 °C, where it eliminated the *tert*-butyl segment of the isocyanide to give (among other products) a dicyanosilene ($R^1(NC)Si{=}Si(CN)R^1$ **6**, Scheme 2).[15] In contrast, **3** is stable in an inert environment up to approximately 110 °C, where differential scanning calorimetry (DSC) analysis indicated a gradual exothermic event (Figure S2). Heating a xylene solution of **3** at 110 °C for 5 min resulted in changes to the observed room temperature ^{11}B NMR spectrum, which afterward showed peaks at δ = 32 and 12 ppm. Removal of the xylene under reduced pressure and recrystallization from a concentrated benzene/hexane solution yielded crystals suitable for X-ray analysis, identifying the product as a dicyanodiborene $B_2(CAAC)_2(CN)_2$ (**7**, Figure 4). GC-MS analysis of volatiles removed from the reaction mixture indicated the presence of isobutane and isobutene, products of the homolytic elimination and subsequent disproportionation of two isobutyl radicals.[16] The greater thermal stability of **3**, as compared to **5**, is a result of the extensive conjugation and electronic delocalization in **3**. Unlike the planar boron atoms in **3**, the silicon centers in **5** are pyramidalized,[15] indicative of a comparatively lower degree of conjugative stabilization.



Scheme 2. Thermolytic syntheses of cyano-substituted disilene and diborene.

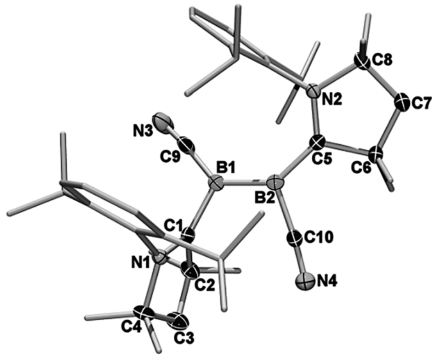


Figure 4. Crystallographically determined structure of **7**. Thermal ellipsoids set at 50% probability, and have been omitted from the phenyl portion of the CAAC ligand for clarity. All hydrogen atoms have likewise been omitted. Selected bond lengths [Å] and angles [°]: B1–B2 1.614(3), B1–C1 1.595(3), B2–C5 1.530(3), B2–C10 1.574(3), B1–C9 1.551(3), C9–N3 1.154(2), C10–N4 1.159(2), C1–N1 1.304(2), C5–N2 1.346(2); B2-B1-C1 116.4(2), B1-B2-C5 135.6(2), B1-B2-C10 110.9(2), B2-B1-C9 131.4(2), B1-C9-N3 172.4(2), B2-C10-N4 175.0(2).

The length of the B1–B2 bond in **7** (1.614(3) Å) falls at the long-end of the range for neutral $B{=}B$ double bonds (ca. 1.54–1.60 Å),[17] and is significantly shorter than the B–B bond in **3**. The near co-planarity of all the B–C bonds is in agreement with the description of the central B_2 as a double bond (C1-B1-B2-C5 179.8(2); C9-B1-B2-C5 2.7(2)°). The B–CN bond lengths (B2–C10 1.574(3) Å; B1–C9 1.551(3) Å) are longer than the same bonds in **3** (1.475(4) Å, 1.471(4) Å), as are the bonds from boron to $C_{carbene}$ (B1–C1 1.595(3); B2–C5 1.530(3)). Together, these data indicate a higher bond order between the boron atoms of **7** than in **3**, and less electronic delocalization between boron and the two peripheral ligands. The two inequivalent $C\equiv N$ bonds in **7** (N3–C9 1.154(2) Å; C10–N4 1.159(2) Å) show IR stretches at 2127 and 2149 cm^{-1} (Figure S3) that fall in the high-wavenumber range of terminal metal-cyanides,[18] but fall well below the $C\equiv N$ stretches of $B(CN_4)^-$ (2222 cm^{-1})[6] and methyl cyanide (2267 cm^{-1})[19] indicating moderate $B\rightarrow C\equiv N$ back-bonding, consistent with the frontier molecular orbitals (Figure S4).

Perhaps the most interesting facet of the solid-state structure of **7** is the alignment of the two CAAC ligands with respect to the plane of the $B{=}B$ bond. As shown in Figure 4, one of the two CAAC ligands is oriented to align the empty p-orbital on its carbene carbon with the π-system of the diborene (right-hand side of the structure), while the other CAAC ligands adopts a perpendicular orientation with respect to the plane of the $B{=}B$ bond (left-hand side of the structure). DFT calculations confirmed this orientation as a minimum, 5.0 $kcal\,mol^{-1}$ lower in energy than a local minimum where both CAAC ligands are oriented parallel to the $B{=}B$ plane. This asymmetry is the root of the seemingly odd observation of two, very different ^{11}B NMR shifts in the room temperature spectrum of **7**. DFT/GIAO analysis of the optimized structure predicted a signal at $\delta = 37$ ppm for the boron bound to the parallel CAAC ligand, while boron bound to the perpendicular CAAC ligand was predicted to resonate at $\delta = 8$ ppm. The match of the experimental signals at $\delta = 32$ and 12 ppm improved when the measurements were made at −20 °C, where signals at $\delta = 35$ and 10 ppm (Figure S5) were observed. With increasing measurement temperature, the peaks migrated towards one another, coalescing at 60 °C, at a value of $\delta = 24$ ppm. This is very close to the average of the two predicted resonances ($\delta = 23$ ppm), as expected for a rapidly interconverting (on the NMR time scale) fluxional system.[20] The observation of peak coalescence at 60 °C allowed calculation of the barrier of rotation about the B−CAAC bond to be 13.7 kcal mol^{-1}.[20]

A cyclic voltammetric comparison of **3** and **7** is given in Figure 5. While the voltammogram of **3** showed two reversible oxidation waves at −1.07 and −0.76 V (vs. Fc/Fc$^+$ Fc = $[\eta\text{-}(C_5H_5)_2Fe]$), **7** instead showed two reversible reduction waves at −2.20 and −2.25 V, and an oxidation wave at −0.36 V. The ease with which the electron-rich, highly delocalized isocyanide adduct **3** is oxidized is not surprising; however, previous work on diborenes has shown them to be highly reducing, with one-electron oxidation potentials ranging from −1.05 to −1.95 V depending on substituents.[17a,b,d] No other diborenes have shown reduction waves in their cyclic voltamograms. The strong reducing capacities of diborenes have been correlated to the energies of their respective HOMOs, where the most strongly reducing compounds were those with the highest HOMO energies. The calculated energy for the HOMO of **7** was −4.33 eV (B3LYP/6-311G(d)), significantly below the range established by previously reported diborenes (−3.53 to −2.60 eV), while the calculated LUMO (−1.68 eV) is likewise well below the range of previously reported LUMOs (−0.48 to 0.28 eV).[17a,d] These comparatively low-lying orbital energies rationalize both the unprecedented capacity for reduction (low-energy LUMO) and the relative unwillingness of **7** to be oxidized (low-energy HOMO). It is undoubtedly the combined electron-withdrawing capacity of the cyanide and CAAC substituents[21] on the diborene that delocalize the π-electrons (Figure S4), resulting in the high stability of the frontier orbitals and comparative electron deficiency between the boron atoms. Taken together, CV indicates an electron-rich compound with a B–B single bond (**3**), yet an electron-poor diborene (**7**).

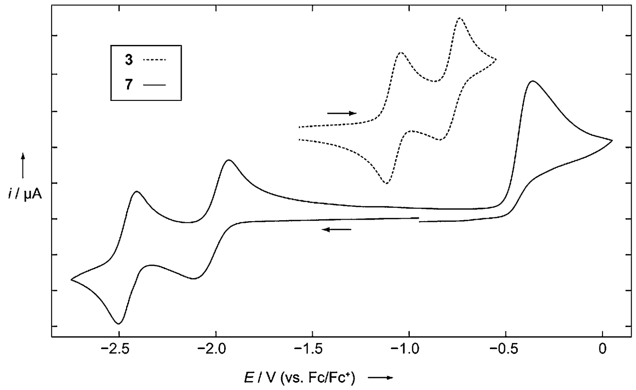


Figure 5. Cyclic voltammograms of **3** and **7**, recorded in THF (relative to the Fc/Fc$^+$ couple).

In conclusion, we have reported a reaction wherein two-coordinate, electron-rich boron atoms display Lewis acidic behavior, coordinating isocyanides to form an electron-rich, highly delocalized bis(boraketenimine). From this compound, thermolytic release of neutral fragments led to the formation of a diborene featuring the most electron poor B=B double bond yet reported.

Keywords: boron · diborenes · main-group elements · multiple bonds · thermolysis

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