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## The Synthesis of B<sub>2</sub>(SIDip)<sub>2</sub> and its Reactivity Between the Diboracumulenic and Diborynic Extremes

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Dedicated to Professor Todd B. Marder on the occasion of his 60th birthday

Abstract: A new compound with the formula L- $B_2$ -L wherein the stabilizing ligand (L) is 1,3-bis[diisopropylphenyl]-4,5dihydroimidazol-2-ylidene (SIDip) has been synthesized, isolated, and characterized. The  $\pi$ -acidity of the SIDip ligand, intermediate between the relatively non-acidic IDip (1,3bis[diisopropylphenyl]imidazol-2-ylidene) ligand and the much more highly acidic CAAC (1-[2,6-diisopropylphenyl]-3,3,5,5-tetramethylpyrrolidin-2-ylidene) ligand, gives rise to a compound with spectroscopic, electrochemical, and structural properties between those of L- $B_2$ -L compounds stabilized by CAAC and IDip. Reactions of all three L-B<sub>2</sub>-L compounds with CO demonstrate the differences caused by their respective ligands, as the  $\pi$ -acidities of the CAAC and SIDip carbones enabled the isolation of bis(boraketene) compounds (L(OC)B-B(CO)L), which could not be isolated from reactions with  $B_2(IDip)_2$ . However, only  $B_2(IDip)_2$  and  $B_2(SIDip)_2$ could be converted into bicyclic bis(boralactone) compounds.

Since Arduengo's initial isolation of a stable N-heterocyclic carbene (NHC),<sup>[1]</sup> these extraordinarily useful ligands have become widely available and have truly transformed many aspects of organometallic and main-group chemistry. Work since Arduengo, particularly by Bertrand and co-workers, has shown the diamino-NHC, where the carbon is part of a ring and flanked by two nitrogen atoms, is just one example of a broad array of stable, singlet carbenes.<sup>[2]</sup> Alterations in the identity of the elements adjacent to the carbon atom, as well as in the size, degree of unsaturation, and substitution pattern on the backbone of the carbene, lead to significant electronic differences in both the  $\sigma$ -donating capacity of the lone-pair of electrons on the carbon atom and in the  $\pi$ -acidity of the formally vacant p orbital on the carbon atom. On top of the numerous computational studies seeking to theoretically evaluate and compare

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the electronic properties of stable carbenes,<sup>[3]</sup> a number of different experimental methods have been employed in hopes of quantifying their respective donor/acceptor capabilities.<sup>[4]</sup> Strategies involving NMR spectroscopy, notably comparing the <sup>31</sup>P, <sup>77</sup>Se, and <sup>13</sup>C NMR signals of carbene phosphinidine,<sup>[5]</sup> carbene selenide,<sup>[6]</sup> and carbene platinum<sup>[7]</sup> complexes have shown the method to be a sensitive tool for the evaluation of carbene character. Measurements of the structural, vibrational, and redox characteristics of organometallic complexes bearing a wide range of carbenes have likewise provided a wealth of information.<sup>[4,8]</sup>

In recent years, our group has reported the syntheses of two similar compounds utilizing carbenes with distinct and divergent electronic characters. One of these was the first example of a diboryne (B<sub>2</sub>(IDip)<sub>2</sub>, **1**, IDip = 1,3-bis[diisopropylphenyl]imidazol-2-ylidene),<sup>[9]</sup> a compound containing a triple bond between two boron atoms. The second was a molecule best described as a diboracumulene (B<sub>2</sub>(CAAC)<sub>2</sub>, **2**, CAAC = cyclic (alkyl)(amino) carbene, in this case 1-[2,6diisopropylphenyl]-3,3,5,5-tetramethylpyrrolidin-2-yli-

dene),<sup>[10]</sup> an analogue of dicationic butatriene. The differences in the B–B and C–B bond lengths in these compounds are the direct result of differences in the  $\pi$ -acidities of the IDip and CAAC ligands. The formally empty p orbital on the carbene carbon atom of the CAAC ligand, stabilized by only one nitrogen lone-pair, is the recipient of a larger degree of  $\pi$ backdonation from the electron rich B<sub>2</sub> unit than the comparatively electronically saturated p orbital on the carbene carbon atom of IDip. This results in more extensive spread of  $\pi$ -electron density across the B–C bonds of **2** than in **1**, in turn resulting in a longer B–B bond and shorter B–C bonds in **2**.

In hopes of further probing the sensitivity of the B<sub>2</sub> unit to changes in carbene electronic character, we turned to a carbene with  $\pi$ -acidity between those of CAAC and IDip, synthesizing B<sub>2</sub>(SIDip)<sub>2</sub> (**3**, SIDip=1,3-bis[diisopropylphenyl]-4,5-dihydroimidazol-2-ylidene) in a method similar to the syntheses of **1** and **2**. The aforementioned comparative studies of carbenes have indicated that SIDip, identical to IDip with the exception that the C<sub>2</sub> backbone of the five-membered ring is saturated, is more  $\pi$ -acidic than IDip, but much less acidic than CAAC (Scheme 1).<sup>[5-7]</sup>

The sodium napthalenide reduction of  $1,2-(\text{SIDip})_2-\text{B}_2\text{Br}_4$ furnished **3** in moderate yields. In agreement with previous NMR studies,<sup>[5-7]</sup> the <sup>11</sup>B NMR shift in **3** ( $\delta$  = 58 ppm) falls between that of **1** ( $\delta$  = 39 ppm) and **2** ( $\delta$  = 80 ppm). Single





Scheme 1. The syntheses of compounds 1–3.

crystals suitable for X-ray diffractometry were grown by slowly evaporating a benzene solution of 3 (Figure 1 a).

As in both 1 and 2, the central C-B-B-C unit of 3 is linear, with B-B-C angles measuring 179.6(2)° and 178.6(2)°. The length of the B–B bond in 3 lies between those of the B–B bonds in 1 and 2, as do the B–C bonds in 3 that are, on average, shorter than in 1 and longer than in 2 (Figure 1b). The N1-C1-C2-N3 and N2-C1-C2-N4 dihedral angles, roughly describing the angle formed by the planes of the fivemembered NHC rings, measure approximately 73° and 72°, respectively. This can be compared to the angle between the NHC planes in 1 (ca. 56°) and 2 (ca. 80°), which speak to the comparative importance of overlap of the  $\pi$  orbitals of the B<sub>2</sub>



*Figure 1.* a) Crystallographically determined solid-state structure of **3**. Thermal ellipsoids are set at 50% probability and have been omitted for atoms on the organic periphery. Hydrogen atoms have likewise been omitted, save those on the backbone of the NHCs. Selected bond lengths [Å] and angles [°]: B1–B2 1.465(2), C1–B1 1.480(2), C2–B2 1.482(2); C<sub>carbene</sub>-N 1.383 avg., B1-B2-C2 178.6(2), C1-B1-B2 179.6-(2), N1-C1-N2 106.4(1), N4-C2-N3 106.4(1). b) The B–C and B–B bond lengths [Å] in **1–3**.

unit and the empty p orbital on the carbon ecarbon atom. In 2, where the conjugation between B and C is large, the nearly orthogonal orientation of these ligands allows the alignment of the carbene p orbitals with the two  $\pi_{BB}$  orbitals. In 1, where the double-bond character of the B-C bond is substantially lower, this angle is less important. Computational analysis has hinted that rotation about the B-C bond in 1 is not substantially hindered by  $\pi$ -overlap, and that the 56° angle between the planes of the NHCs is a result of optimal packing of the bulky ligand architecture.<sup>[11]</sup> The intermediate angle in 3 is a compromise between these two factors, as the double bond character of the B-C bond is slightly greater, while the bulk of the ligands is the same as in 1. Interestingly, there is a slight but noticeable degree of pyramidalization at each of the nitrogen atoms of the NHCs in **3** ( $\Sigma_{angles} = 352.9^{\circ}$  avg.). This pyramidalization, owing to the presence of  $\pi_{BB} \rightarrow$  carbene backdonation, is notably absent from the nitrogen atoms of 1<sup>[9]</sup> and un-complexed SIDip.<sup>[12]</sup> All of these factors, in conjunction with cyclic voltammetry data (Figure S1 in the Supporting Information) indicating two one-electron oxidation peaks at -1.05 V and +0.44 V (vs. Fc/Fc<sup>+</sup>; Fc =  $[(C_5H_5)_2Fe])$ , falling between those of 1 (-1.28 V and  $+0.11 \text{ V})^{[9]}$  and 2 (-0.55 V, no second oxidation was observed),<sup>[10]</sup> agree with the electronic description of **3** as intermediate between diborynic 1 and diboracumulenic 2 as a result of the intermediate  $\pi$ -acidity of the SIDip ligand.

Beyond the structural and spectroscopic comparisons of 1-3, the existence of a reactive B-B multiple bond in each compound presents a unique opportunity to compare the influence of the carbene through reactivity studies. The reaction of 1 with CO has been previously shown to result in the reductive insertion of four CO molecules in the formation of a bicyclic bis(boralactone) (4, Scheme 2).<sup>[13]</sup> Bertrand and Stephan also reported an example of CO complexed to a CAAC-stabilized boron atom.<sup>[14]</sup> When 2 was treated with an excess of CO at room temperature, the solution turned from deep purple to orange, concomitant with the emergence of a new peak in the <sup>11</sup>B NMR spectrum at  $\delta = -22$  ppm. Slow evaporation of the reaction mixture yielded crystals suitable for X-ray study, which proved to be the bis(boraketene) 5 (Figure 2a). When 3 was stirred under an atmosphere of CO, the immediate emergence of a new <sup>11</sup>B NMR resonance at  $\delta =$ -29 ppm was observed and identified as the bis(boraketene) 6 on account of its highfield <sup>11</sup>B NMR shift, in reasonable agreement with the DFT predicted chemical shift ( $\delta =$ -33 ppm), and the observation of a new lowfield <sup>13</sup>C NMR resonance. A second very small <sup>11</sup>B NMR resonance was observed at  $\delta = -2$  ppm that grew over the course of three days as the signal at  $\delta = -29$  ppm gradually disappeared. Isolation and crystallization of this new product indicated the formation of the SIDip-stabilized bis(boralactone) (7, Figure 2b). Stopping the reaction after 15 min allowed the isolation of 6, and conversion into 7 could be halted by holding the reaction at -30°C. In the absence of a CO atmosphere 6 slowly decomposed, even at low temperatures. The conversion of 6 into 7 led us to believe that 5 might likewise be pushed into forming a bis(boralactone) if heated under a CO atmosphere; however, even at 150°C and under 50 bar of CO, no formation of the hypothetical compound II

## 13802 www.angewandte.org



**Scheme 2.** Syntheses of **4–7** and thermochemistry of the reaction sequences. The  $\Delta G$  values (kcal mol<sup>-1</sup>) have been calculated at 298.15 K at the M05-2x/6-311G(d) level of theory for the reaction of the substrate with two molecules of CO to the subsequent products.

was observed. The unexpected stability of **5** is highlighted by the fact that **5** was air and moisture stable, showing no change when stored open on the benchtop for more than one day.

The solid-state structure of 5 (Figure 2a) is reminiscent of the previously reported bis(isocyanide) adducts of 2,<sup>[15]</sup> while the B=C=O unit is similar to those found in Stephan and Bertrand's CAAC-B(CO) compound<sup>[14]</sup> and a recently reported bis(carbonyl) arylborylene.<sup>[16]</sup> Each of these compounds, with neutral boron bound to two Lewis bases, may be drawn with formal lone pairs of electrons on boron, but their planarity indicates delocalization of these electrons into extended  $\pi$  systems. The B-C<sub>CAAC</sub> bonds in 5 (1.514(2) Å, 1.512(2) Å) are short relative to CAAC bound to tetrahedral  $(1,2-(CAAC)_2-B_2Br_4, 1.754(5) \text{ Å}),^{[10]}$  indicating boron a degree of multiple bond character, but less than in 2 where these bonds measure 1.459(2) and 1.458(2) Å.<sup>[10]</sup> Multiple bond character is also observed in the B-C<sub>CO</sub> bonds, which at 1.477(2) Å are shorter that the bonds between CO and tetrahedral boron (e.g.,  $(C_3F_7)_3B(CO)$  1.660(3) Å,  $(C_2F_5)_3B(CO)$  1.618(2) Å, 1.623(2) Å).<sup>[17,18]</sup> The slightly greater length of the C  $\equiv$  O bond (1.173(2) Å, 1.173(2) Å) in comparison to CO bound to tetrahedrally coordinated boron (1.105–1.124 Å)<sup>[17,18]</sup> is likewise indicative of  $p_B \rightarrow \pi^*_{C=0}$  backdonation. This idea is borne out in the C=O stretching frequency ( $\tilde{\nu} = 1928 \text{ cm}^{-1}$ ), which is significantly decreased from that of free CO ( $\tilde{\nu} = 2143 \text{ cm}^{-1}$ ), and is in line with the stretching frequencies of CO ligands on electron-rich, late transition metals, where  $M \rightarrow CO_{\pi^*}$  backbonding is substantial.<sup>[19]</sup> The CO stretching frequency in 6 ( $\tilde{\nu} = 1929 \text{ cm}^{-1}$ ) is in the same range, indicating an equivalent amount of back-



*Figure 2.* Crystallographically determined solid-state structures of a) **5** and b) **7**. Thermal ellipsoids are set at 50% probability and have been omitted for the ligand periphery. For **5**: B1–B2 1.744(2), C3–B1 1.514(2), C2–B7 1.512(2), B1–C1 1.477(2), B2–C2 1.477(2), C1–O1 1.173(2), C2–O2 1.173(2); B1-C1-O1 170.0(2), B2-C2-O2 170.6(2), Ci-B1-B2-C2 93.3(1). For **7**: C3–B1 1.548(2), B1–C1 1.450(2), C1–O1 1.394(2), O1–C2 1.432(2), C2–O2 1.213(2); N1-C3-N2 109.1(1).

bonding into the CO fragment as found in **5**, as observed in HOMO and HOMO-1 of both compounds (Figure S14a). The  $\pi$ -systems depicted in these orbitals show delocalization across both the CO and carbene moieties, but the degree to which the orbital encompasses the carbene is greater in **5** than in **6** (Figure S14a).

The thermochemistry of the reaction sequence from compounds 1-3 to their bis(boraketene) compounds and on to their respective bis(boralactone) forms is indicative of the electronic properties of the stabilizing carbenes. The initial bis(boraketene) formation is the most favorable for 2  $(-34.1 \text{ kcalmol}^{-1})$ , which is able to stabilize the extra pair of electrons (formally residing at boron) through backdonation into both CO and CAAC. NPA analysis of the three bis(boraketene) complexes (I, 5, and 6) shows 5 to have the least negative charge on boron (5 -0.27, 6 -0.31, I -0.33, Figure S15). The formation of 6 from 3 is slightly less favorable  $(-29.6 \text{ kcal mol}^{-1})$  as the lone pair of electrons cannot be distributed as freely into the carbene ligand, and formation of the hypothetical I is the least favorable, since IDip is the least acidic of the carbenes studied. The relative stabilities of the bis(boraketene) compounds are further reflected in the conversion into their respective bis(boralactone) forms, where the opposite trend is observed. In this case, the formation of 4 from I is highly exergonic (-30.5 kcal)



mol<sup>-1</sup>), while the formation of **7** from **6** is slightly less favorable  $(-26.1 \text{ kcal mol}^{-1})$ , and the conversion of **5** to the undetected compound **II** is essentially thermoneutral.

Simply based on these numbers, it is perhaps surprising that no formation of **II** is observed, as the energetic equivalence of the two forms suggests an equilibrium between the two and the possibility of pushing the reaction to **II** forward under high CO pressures. The fact that **II** was not observed led us to examine potential energetic barriers blocking the formation of **II** from **5** by computationally determining the mechanistic pathways from  $B_2L_2$  to bis(boralactone) (Figure S16–S18).<sup>[20]</sup> According to these pathways the intermediate immediately following the bis(boraketene) complex is a bis( $\mu$ -carbonyl) arrangement wherein each CO ligand bridges the two boron atoms (Scheme 3). Calculations



**Scheme 3.** The conversion of bis (boraketene) to bis ( $\mu$ -carbonyl) and the related energetics of reaction. The  $\Delta E$  values (kcal mol<sup>-1</sup>) have been calculated as single-point energies at the M05-2x/6-311G(d) level of theory on geometries from the mechanisms given in Figures S16–S18, and are not ZPE corrected.

indicated that this conversion is highly unfavorable for 5  $(+23.8 \text{ kcal mol}^{-1})$ , though energetically favorable for 6  $(-14.7 \text{ kcal mol}^{-1})$  and I  $(-17.3 \text{ kcal mol}^{-1})$ . The trend in calculated activation energies, with the conversion of 5 representing the most unfavorable by far, best explains why the reaction halts at this point, even under large overpressures of CO. The large differences in these energies are a direct result of the stabilization of 5 through delocalization of electrons into both the CO and CAAC ligand.

In conclusion, we have used a carbene with intermediate acidity in the construction of a complex with properties between those of compounds stabilized by highly acidic carbenes and relatively non-acidic carbenes. Beyond the conventional spectroscopic comparisons of these three related species, we have herein demonstrated how the choice of carbene can effectively modulate reactivity along a given reaction pathway.

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