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Alkene-Carbene Isomerisation induced by Borane: Access to an Asymmetrical Diborene

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Supporting Information Placeholder

ABSTRACT: A 2,3-dihydro-1*H*-1,2-azaborole derivative **2** was converted to a cyclic (alkyl)(amino)carbene (cAAC) via 1,2-hydrogen migration triggered by boranes to afford cAAC-borane adducts. This procedure allowed to develop an asymmetrical diborene cAAC·(Br)B=B(Br)·IDip **6**, which was isolated and fully characterized. The ¹¹B NMR spectrum, X-ray diffraction analysis and computational studies indicate that π -electrons on the central B₂ moiety in **6** are unequivalently distributed, and thus polarized. A complete scission of the B=B double bond in **6** was achieved by the treatment with an isonitrile, which led to the formation of a base-stabilized B,N-containing methylenecyclopropane **7**.

Since the pioneering works by the groups of Berndt, Power and Nöth employing a reduction protocol for the synthesis of anionic diboron species featuring the B-B multiple bond character,¹ the chemistry of B-involving multiply bonded species has attracted considerable attention because they could be potential building blocks for the synthesis of organoboranes.² While various heteroatomic B-E multiple bonds have been realized, only a handful of isolable homoatomic B-B multiply bonded species have been reported.³ In fact, diborenes RB=BR have never been isolated as stable compounds thus far.⁴ In 2007, the landmark study by the group of Robinson demonstrated that N-heterocyclic carbenes (NHCs) serve as supporting ligands for a neutral diborene featuring a B-B double bond.⁵ Since then, a variety of Lewis base-stabilized low-valent main group molecules has been developed, which allowed fundamental study of otherwise elusive species.⁶ Among them, B-B multiply bonded species supported by various Lewis bases such as cyclic (alkyl)(amino) carbenes (cAACs),⁷ phosphines in addition to NHCs, have been described (Figure 1).^{8,9} Interestingly, it has been revealed that the bonding nature between the two B atoms varies depending on the supporting ligands. For example, the π -acidic cAAC-stabilized diboron cAAC·B₂·cAAC possesses the shared electrons across the four-membered CBBC core, thus exhibiting a cumulene character. Meanwhile, the diboron supported by NHC ligands NHC·B₂·NHC features a genuine B≡B triple bond.⁹ Accordingly, not only the electronic structures of the B-B bonds but also the reactivity can be modulated by the property of the supporting lig-

ands.^{8,9,10} With this regard, extant diborenes and diborynes are limited to the derivatives involving the same Lewis base on each B atom, and no asymmetrically supported derivatives, despite its significance for elucidation of the essential bonding nature of B-B multiple bonds, have been reported.

From a synthetic point of view, those base-stabilized low valent species of boron have been most likely prepared under the reduction condition from the corresponding haloborane-carbene adducts (L·BX₃ or L·BRX₂ or L·B₂X₄·L) that are usually formed by the direct reaction between boron halides and free carbenes (L), as shown in Figure 1.¹¹ Although there are several reports on the generation of transient carbenes from alkenes via intramolecular 1,2-hydrogen migration,¹² such pathway has synthetically never been applied for carbene-coordinated main-group element complexes. Herein we report the synthesis of carbene-borane adducts via a borane-induced H-shift of a 1,2-azaborole derivative. We also show that this elementary step can be applied to access to an asymmetrical diborene.

Figure 1. Major synthetic protocol for symmetrical low-valent diborons (top) and this work (bottom).

Reduction of the α,β -unsaturated imine **1**¹³ with Li followed by treatment with trimethylborate afforded 1,2-azaborole derivative **2** in 35 % yield (Scheme 1). Next, a stoichiometric amount of boron trichloride was added to a benzene solution of **2**, and the reaction mixture was stirred at ambient condition overnight. After work-up, the ¹¹B NMR

spectrum exhibited a characteristic sharp signal at 2.7 ppm indicating the presence of a tetracoordinate boron, in addition to a broad singlet at 41.7 ppm for the skeletal B atom in the five-membered ring. ^1H and ^{13}C NMR spectra confirmed the presence of a methylene carbon (CH_2) in the product whereas no peaks observed for the sp^2 carbon atoms in the azaborole ring in **2** were detected. Colorless single crystals were obtained by recrystallization from a saturated benzene solution at room temperature, and the X-ray diffraction study revealed the formation of $\text{cAAC}\cdot\text{BCl}_3$ complex **3a**.¹⁴ The five membered ring of cAAC involves a boron atom adjacent to the nitrogen atom and a secondary carbon in the position α to the carbene center. To the best of our knowledge, this is the first example of 1,2-H shift from a cyclic enamine to a carbene induced by a borane.

Scheme 1. Synthesis of compounds **2**, **3a-b**, **4**, **5** and **6** (Ar = 2,6-diisopropylphenyl. IDip = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene).

To examine the scope of this reaction, we employed other acids. The use of BBr_3 led to the formation of the cAAC adduct **3b**.¹⁴ Moreover, when compound **2** was treated with a stoichiometric amount of tetrabromodiborane B_2Br_4 in pentane, a white precipitate appeared immediately, and after work-up the $\text{CAAC}\cdot\text{B}_2\text{Br}_4$ adduct **4** was obtained in a moderate yield (53%) (Scheme 1).¹⁴ In the ^{11}B NMR spectrum, two characteristic resonances appear at 67.3 ppm and -6.3 ppm indicating the presence of a tetracoordinate boron, in addition to a singlet at 41.8 ppm for the B atom in the ring. We also attempted a 2:1 reaction between **2** and B_2Br_4 , which gave **4** again instead of the 2:1 adduct. On the other hand, the addition of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IDip) to a toluene solution of **4** afforded $\text{cAAC}\cdot\text{B}_2\text{Br}_4\cdot\text{IDip}$ adduct **5** as a white solid, which was fully characterized by standard spectroscopic methods and a single-crystal X-ray diffraction study.¹⁴

Reduction of **5** with two equivalent of KC_8 in toluene underwent smoothly, and after work-up a bibromodiborene **6** was isolated as a purple solid in 85% yield. In the ^{11}B NMR of **6**, two broad peaks for the central B_2 unit were observed at 51.7 ppm and 27.8 ppm, that significantly shifted down-field compared with those of **5** (around -3.8 ppm: two peaks are overlapped). The calculated ^{11}B NMR chemical shifts with the computationally optimized molecule **opt-6** ($\text{cAAC}\cdot\text{B}(\text{Br})$: 28.5 ppm, $\text{IDip}\cdot\text{B}(\text{Br})$: 53.8 ppm) are nearly identical to those observed experimentally. The chemical shift (27.8 ppm) of the B atom bound to the cAAC ligand is in the range of the related species (12–32 ppm),^{5,8c-d,9b,10b,15,17b,17d-e} whereas the boron (51.7 ppm) bound to IDip ligand is significantly shifted downfield, suggesting that the central $\text{B}=\text{B}$ double bond is highly polarized.

Single crystals of **6** were obtained by recrystallization from a saturated hexane solution at -25°C , and the structure of **6** was confirmed by an X-ray diffraction study (Figure 2).¹⁴ The Br_1 , B_2 , B_3 and Br_2 atoms are coplanar, and the cAAC and IDip ligands coordinate to the B_2Br_2 fragment in *trans* fashion. The five-membered ring of cAAC is nearly coplanar with the B_2Br_2 moiety ($\text{C}_{14}\text{--C}_{13}\text{--B}_2\text{--B}_3$ torsion angle, $8.3(4)^\circ$), while the NHC ring is significantly twisted with respect to the B_2Br_2 cores ($\text{N}_2\text{--C}_{23}\text{--B}_3\text{--B}_2$ torsion angle, $62.5(6)^\circ$). The central $\text{B}_2\text{--B}_3$ bond distance ($1.602(4)$ Å) is significantly shorter than that ($1.733(6)$ Å) in **5**, and comparable to that ($1.578(3)$ Å) reported for $\text{I}^i\text{Pr}\cdot(\text{I}^i\text{Pr})\text{B}=\text{B}(\text{I}^i\text{Pr})\cdot\text{I}^i\text{Pr}$ (I^iPr = 1,3-bis(isopropyl)imidazol-2-ylidene),¹⁵ confirming its double bond character. The $\text{B}_3\text{--C}_{23}$ bond distance ($1.586(4)$ Å) is slightly shorter than the corresponding bond distance ($1.5963(18)$ Å) in $\text{I}^i\text{Pr}\cdot(\text{I}^i\text{Pr})\text{B}=\text{B}(\text{I}^i\text{Pr})\cdot\text{I}^i\text{Pr}$. On the contrary, the $\text{B}_2\text{--C}_{13}$ bond distance ($1.492(4)$ Å) is relatively short, indicating the stronger interaction between the B_2Br_2 unit and cAAC ligand than that with IDip ligand. The conspicuous bonding interaction between C_{13} and B_2 atoms is in line with the σ -donor property of cAAC superior to that of NHCs, in addition to the well-known π -acidic nature of the cAAC ligand.⁷ In addition, it can be envisaged that the carbene center in cAAC is sterically less hindered than that in IDip owing to the presence of the secondary carbon C_{14} at the α position of the carbene center. Note that the structure of **6** comprises the first structural authentication of the two different bases-stabilized diborene.¹⁶

Figure 2. Solid-state structure of **6** (hydrogen atoms ex-

cept for those on C14 and solvent molecules are omitted for clarity). Thermal ellipsoids are set at the 30% probability level.

To gain further insight into the electronic features of **6**, we performed a molecular orbital (MO) analysis and natural bond orbital (NBO) analysis. Similar to the reported NHCs-stabilized neutral diborenes,^{5,8c-d,10b,15,17d-e} the HOMO of **6** is dominated by B=B π -bonding (Figure 3, left). Significantly, the π -system extends from the B₂ unit to the formally empty p-orbital of the carbene carbon in the cAAC ligand,^{10b} whereas no such interaction is seen to the carbene carbon in IDip. The delocalization of the B=B π -electrons to cAAC ligand is in good agreement with the observed short C13-B2 bond. The LUMO is the π^* (B-B) orbital which mixes in a bonding fashion with p(π) atomic orbital of the both carbene carbon atoms (Figure 3, right). NBO analysis gave Wiberg bond index values of 1.34 for the B₂ unit, indicating the B-B multiple bond character. Consistent with the ¹¹B NMR chemical shifts, Natural population analysis indicates that the charges at the B-B moiety are -0.089 for cAAC-B(Br) and +0.125 for IDip-B(Br), respectively, supporting the polarized B-B unit.

Figure 3. Plots of the HOMO (-4.02 eV) (left) and the LUMO (-1.54 eV) (right) of **6**.

Study of the reactivity of Lewis base-stabilized diborenes and diborynes is limited to its redox reaction, hydroboration reaction, coordination to metal and cycloaddition with alkyne,^{10a,17} and to the best of our knowledge, the reactions between diborenes and isonitriles have never been reported. Meanwhile, Braunschweig and coworkers reported that treatments of a symmetrical diboracumulene (cAAC)B₂ or B₂Br₄ with ^tBuNC afforded the stable adducts bis(boraketeneimine) [(cAAC)·(^tBuNC)·B]₂ and [(^tBuNC)·Br₂B]₂, respectively.^{10b} These results prompted us to assess the reactivity of **6** toward isonitriles. When a stoichiometric amount of 2,6-diisopropylphenyl isonitrile (DippNC) was reacted with **6** in benzene, the reaction proceeded quickly as indicated by the fast decoloration of the reaction mixture (Scheme 2). After work-up, compound **7** was isolated as a yellow solid in 55% yield, which displays three broad peaks at 36.2 ppm, 9.9 ppm and -16.2 ppm in the ¹¹B NMR spectrum. The X-ray diffraction study of **7** revealed the methylenecyclopropane-like structure, in which the exocyclic terminal B atom is supported by a cAAC ligand whereas the B atom in the BCN three-membered ring is coordinated by a IDip lig-

and. Thus, the B=B double bond in **6** was completely cleaved by the isonitrile,¹⁸ concomitant with the formation of two B-C bonds and a B-N bond.

Scheme 2. Reaction of **6** with 2,6-diisopropylphenyl isocyanide.

ASSOCIATED CONTENT

Supporting Information

Synthesis, NMR spectra, and crystallographic data (CIF) and computational details including Cartesian coordinates for stationary points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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