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

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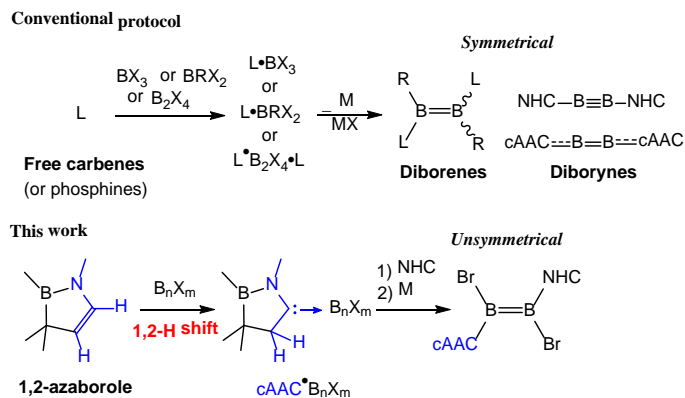
## Supporting Information Placeholder

**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 <sup>11</sup>B NMR spectrum, X-ray diffraction analysis and computational studies indicate that  $\pi$ -electrons on the central B<sub>2</sub> 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,<sup>1</sup> the chemistry of B-involving multiply bonded species has attracted considerable attention because they could be potential building blocks for the synthesis of organoboranes.<sup>2</sup> While various heteroatomic B-E multiple bonds have been realized, only a handful of isolable homoatomic B-B multiply bonded species have been reported.<sup>3</sup> In fact, diborenes RB=BR have never been isolated as stable compounds thus far.<sup>4</sup> 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.<sup>5</sup> Since then, a variety of Lewis base-stabilized low-valent main group molecules has been developed, which allowed fundamental study of otherwise elusive species.<sup>6</sup> Among them, B-B multiply bonded species supported by various Lewis bases such as cyclic (alkyl)(amino) carbenes (cAACs),<sup>7</sup> phosphines in addition to NHCs, have been described (Figure 1).<sup>8,9</sup> Interestingly, it has been revealed that the bonding nature between the two B atoms varies depending on the supporting ligands. For example, the  $\pi$ -acidic cAAC-stabilized diboron cAAC·B<sub>2</sub>·cAAC possesses the shared electrons across the four-membered CBBC core, thus exhibiting a cumulene character. Meanwhile, the diboron supported by NHC ligands NHC·B<sub>2</sub>·NHC features a genuine B≡B triple bond.<sup>9</sup> 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.<sup>8,9,10</sup> 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·BX<sub>3</sub> or L·BRX<sub>2</sub> or L·B<sub>2</sub>X<sub>4</sub>·L) that are usually formed by the direct reaction between boron halides and free carbenes (L), as shown in Figure 1.<sup>11</sup> Although there are several reports on the generation of transient carbenes from alkenes via intramolecular 1,2-hydrogen migration,<sup>12</sup> 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.

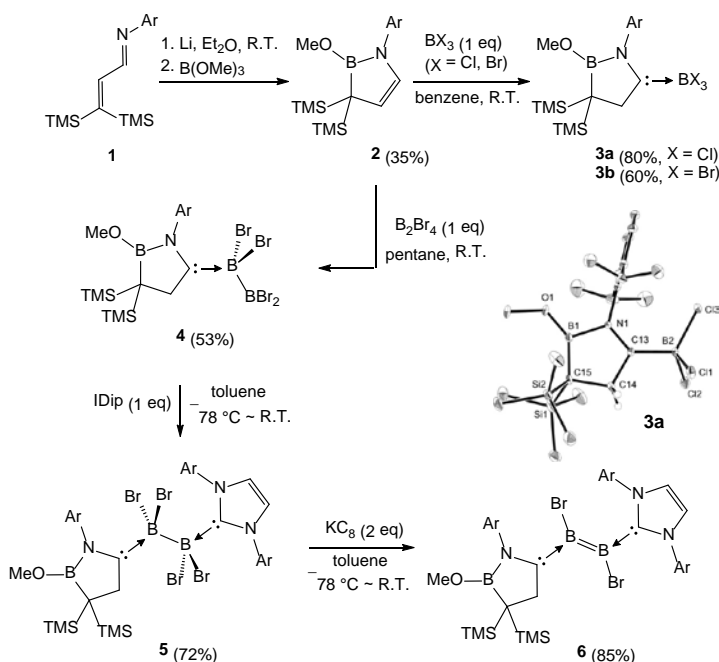


**Figure 1.** Major synthetic protocol for symmetrical low-valent diborons (top) and this work (bottom).

Reduction of the  $\alpha,\beta$ -unsaturated imine **1**<sup>13</sup> 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 <sup>11</sup>B 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.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra confirmed the presence of a methylene carbon ( $\text{CH}_2$ ) in the product whereas no peaks observed for the  $\text{sp}^2$  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**.<sup>14</sup> The five membered ring of  $\text{cAAC}$  involves a boron atom adjacent to the nitrogen atom and a secondary carbon in the position  $\alpha$  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.

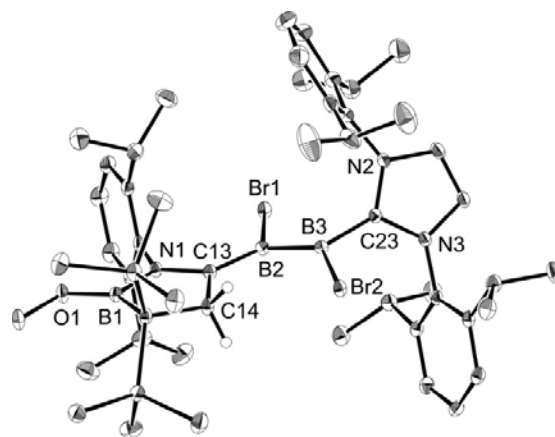
**Scheme 1.** Synthesis of compounds **2**, **3a-b**, **4**, **5** and **6** (Ar = 2,6-diisopropylphenyl. IDip = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene).



To examine the scope of this reaction, we employed other acids. The use of  $\text{BBr}_3$  led to the formation of the  $\text{cAAC}$  adduct **3b**.<sup>14</sup> Moreover, when compound **2** was treated with a stoichiometric amount of tetrabromodiborane  $\text{B}_2\text{Br}_4$  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).<sup>14</sup> In the  $^{11}\text{B}$  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  $\text{B}_2\text{Br}_4$ , 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.<sup>14</sup>

Reduction of **5** with two equivalent of  $\text{KC}_8$  in toluene underwent smoothly, and after work-up a dibromodiborene **6** was isolated as a purple solid in 85% yield. In the  $^{11}\text{B}$  NMR of **6**, two broad peaks for the central  $\text{B}_2$  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  $^{11}\text{B}$  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  $\text{cAAC}$  ligand is in the range of the related species (12–32 ppm),<sup>5,8c-d,9b,10b,15,17b,17d-e</sup> 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.

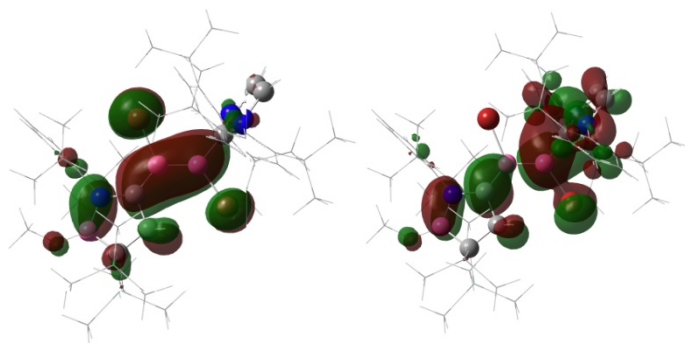
Single crystals of **6** were obtained by recrystallization from a saturated hexane solution at  $-25^\circ\text{C}$ , and the structure of **6** was confirmed by an X-ray diffraction study (Figure 2).<sup>14</sup> The  $\text{Br}_1$ ,  $\text{B}_2$ ,  $\text{B}_3$  and  $\text{Br}_2$  atoms are coplanar, and the  $\text{cAAC}$  and IDip ligands coordinate to the  $\text{B}_2\text{Br}_2$  fragment in *trans* fashion. The five-membered ring of  $\text{cAAC}$  is nearly coplanar with the  $\text{B}_2\text{Br}_2$  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  $\text{B}_2\text{Br}_2$  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  $\text{I}^i\text{Pr}\cdot(\text{I}^i\text{Pr})\text{B}=\text{B}(\text{I}^i\text{Pr})\cdot\text{I}^i\text{Pr}$  ( $\text{I}^i\text{Pr}$  = 1,3-bis(isopropyl)imidazol-2-ylidene),<sup>15</sup> 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  $\text{B}_2\text{Br}_2$  unit and  $\text{cAAC}$  ligand than that with IDip ligand. The conspicuous bonding interaction between  $\text{C}_{13}$  and  $\text{B}_2$  atoms is in line with the  $\sigma$ -donor property of  $\text{cAAC}$  superior to that of NHCs, in addition to the well-known  $\pi$ -acidic nature of the  $\text{cAAC}$  ligand.<sup>7</sup> In addition, it can be envisaged that the carbene center in  $\text{cAAC}$  is sterically less hindered than that in IDip owing to the presence of the secondary carbon  $\text{C}_{14}$  at the  $\alpha$  position of the carbene center. Note that the structure of **6** comprises the first structural authentication of the two different bases-stabilized diborene.<sup>16</sup>



**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,<sup>5,8c-d,10b,15,17d-e</sup> the HOMO of **6** is dominated by B=B  $\pi$ -bonding (Figure 3, left). Significantly, the  $\pi$ -system extends from the B<sub>2</sub> unit to the formally empty p-orbital of the carbene carbon in the cAAC ligand,<sup>10b</sup> whereas no such interaction is seen to the carbene carbon in IDip. The delocalization of the B=B  $\pi$ -electrons to cAAC ligand is in good agreement with the observed short C13-B2 bond. The LUMO is the  $\pi^*$  (B-B) orbital which mixes in a bonding fashion with p( $\pi$ ) atomic orbital of the both carbene carbon atoms (Figure 3, right). NBO analysis gave Wiberg bond index values of 1.34 for the B<sub>2</sub> unit, indicating the B-B multiple bond character. Consistent with the <sup>11</sup>B 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.

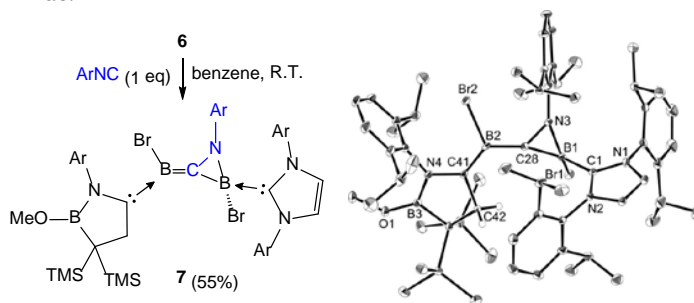


**Figure 3.** Plots of the HOMO (-4.02 eV) (left) and the LUMO (-1.54 eV) (right) of **6**.

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,<sup>10a,17</sup> 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)B<sub>2</sub> or B<sub>2</sub>Br<sub>4</sub> with <sup>t</sup>BuNC afforded the stable adducts bis(boraketeneimine) [(cAAC)·(<sup>t</sup>BuNC)·B]<sub>2</sub> and [(<sup>t</sup>BuNC)·Br<sub>2</sub>B]<sub>2</sub>, respectively.<sup>10b</sup> 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 <sup>11</sup>B 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,<sup>18</sup> 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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