

Activation of a Zerovalent Diboron Compound by Desymmetrization

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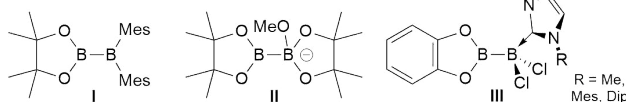
ABSTRACT: The desymmetrization of the cyclic (alkyl)(amino)carbene-supported diboracumulene, $B_2(cAAC^{Me})_2$ ($cAAC^{Me} = 1-(2,6\text{-diisopropylphenyl})-3,3,5,5\text{-tetramethylpyrrolidin-2-ylidene}$) by mono-adduct formation with IMe^{Me} (1,3-dimethylimidazol-2-ylidene) yields the zerovalent $sp\text{-}sp^2$ diboron compound $B_2(cAAC^{Me})_2(IMe^{Me})$, which provides a versatile platform for the synthesis of novel symmetrical and unsymmetrical zerovalent $sp^2\text{-}sp^2$ diboron compounds by adduct formation with IMe^{Me} and CO, respectively. Furthermore, $B_2(cAAC^{Me})_2(IMe^{Me})$ displays enhanced reactivity compared to its symmetrical precursor, undergoing spontaneous intramolecular C-H activation and facile twofold hydrogenation, the latter resulting in B-B bond cleavage and the formation of the mixed-base parent borylene, $(cAAC^{Me})(IMe^{Me})BH$.

Diboron compounds play an essential role in organic chemistry, mainly in the form of commercially available, symmetrical diborane(4) reagents for catalytic diboration and borylation reactions.¹ Recently the focus has been shifting towards generating more reactive desymmetrized diboranes through either i) different substitution at each sp^2 boron atom,² such as in Mes_2BBPin (**I**,^{2e} Fig. 1, Pin = pinacolato, Mes = 2,4,6- $Me_3C_6H_2$), ii) addition of a Lewis or Brønsted base to a symmetrical diborane(4) to generate an $sp^2\text{-}sp^3$ diborane(5),^{3,4} as for example in $[(MeO)_2B_2Pin_2]^-$ (**II**),⁵ or iii) a combination of the two,^{4c,6} as in the N-heterocyclic carbene (NHC) adducts of Cl_2B_2Cat (**III**,^{6a} Cat = catecholato). All these strategies create a polarized B-B single bond, in which one moiety is intrinsically nucleophilic, which often leads to unprecedented reactivity. Thus **I** adds across alkynes without the need for a catalyst or additives,⁷ and spontaneously activates small molecules like CO, isocyanides and pyridine,^{2e,8} while **II** engages in transition metal-free diboration and borylation reactions.⁹

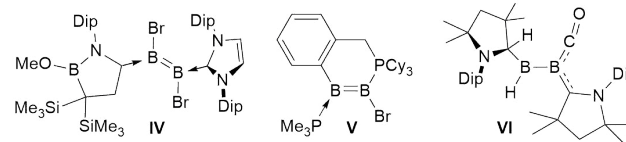
In the field of low-valent diboron chemistry, the last two years have also been marked by the quest for unsymmetrical congeners in the hope of enhancing their reactivity, which still remains limited.¹⁰ In 2017, ten years after the isolation of the first neutral NHC-supported 1,2-dihydrodiborene(4) with boron in the formal B^I oxidation state,¹¹ Kinjo reported the first unsymmetrical 1,2-dibromodiborene(4), compound **IV**, supported by a cyclic (alkyl) (amino)carbene (cAAC) on one side and a bulky NHC on the other.¹² Our own efforts in this area recently yielded the first fully unsymmetrical diborene(4), compound **V**, which upon heating rearranges to a highly polar *gem*-diborene.¹³ An attempt to desymmetrize our *trans*-dihydrodiborene ($cAAC^{Me}$) $_2B_2H_2$ ($cAAC^{Me} = 1-(2,6\text{-diisopropylphenyl})-3,3,5,5\text{-tetramethylpyrrolidin-2-ylidene}$)¹⁴ by adduct formation with CO led to hydride migration from boron to the cAAC carbene carbon atom, generating the unsymmetrical $B^{II}\text{-}B^0$ borylborylene **VI**, which upon heating underwent B-B bond cleavage, cAAC ring expansion and spontaneous $C\equiv C$ bond formation.¹⁵ Furthermore, we showed

that the first stable zerovalent diboron compound, $B_2(IDip)_2$ ($IDip = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$),¹⁶ could be desymmetrized by mono-adduct formation with CO at $-78^\circ C$, yielding the unsymmetrically bridged compound **VII**, which upon warming under a CO atmosphere underwent fourfold CO coupling.¹⁷ More recently, the group of Kinjo isolated the allenic *gem*-bis(phosphine)-supported $sp\text{-}sp^2$ diborene **VIII**, in which both boron atoms are also formally zerovalent,¹⁸ and which rearranges in the presence of a heavier tetrylene dichloride catalyst to an unsymmetrical *gem*-diborene(4).¹⁹

Unsymmetrical $sp^2\text{-}sp^2$ and $sp^2\text{-}sp^3$ diboranes ($B^I\text{-}B^I$)



Unsymmetrical $sp^2\text{-}sp^2$ diborenes ($B^I\text{-}B^I$) and borylborylene ($B^{II}\text{-}B^0$)



Unsymmetrical $sp\text{-}sp^2$ diboryne and allenic diborene ($B^0\text{-}B^0$)

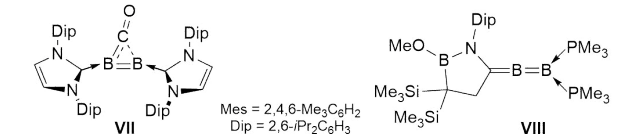


Figure 1. Selection of unsymmetrical diboron compounds.

While the body of work on unsymmetrical low-valent diboron compounds is thus growing, there has been no clear demonstration yet of their enhanced reactivity compared to analogous symmetrical compounds. In this work we show that the unsymmetrical mono-NHC adduct of a zerovalent diboracumulene enables facile access to novel symmetrical and

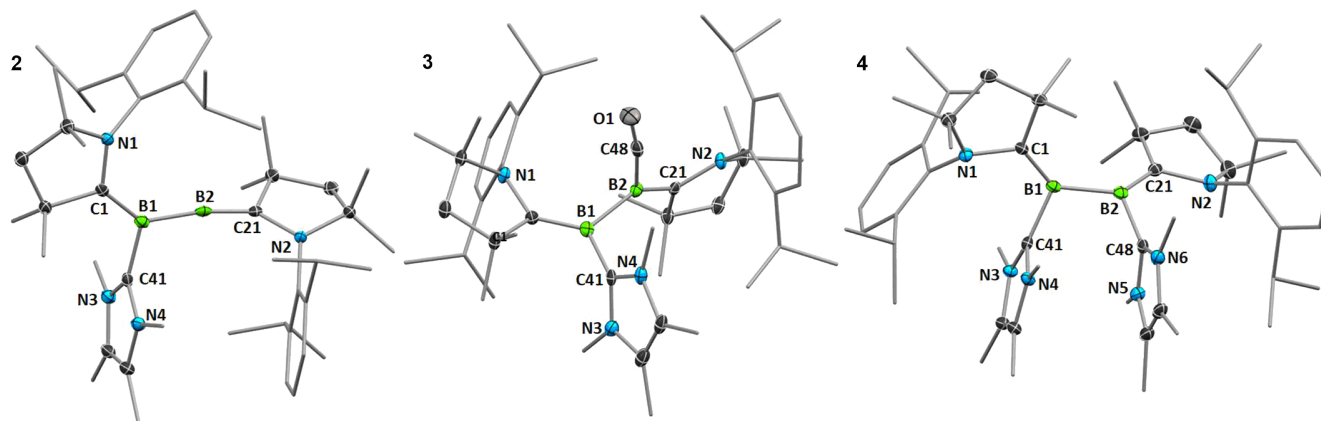
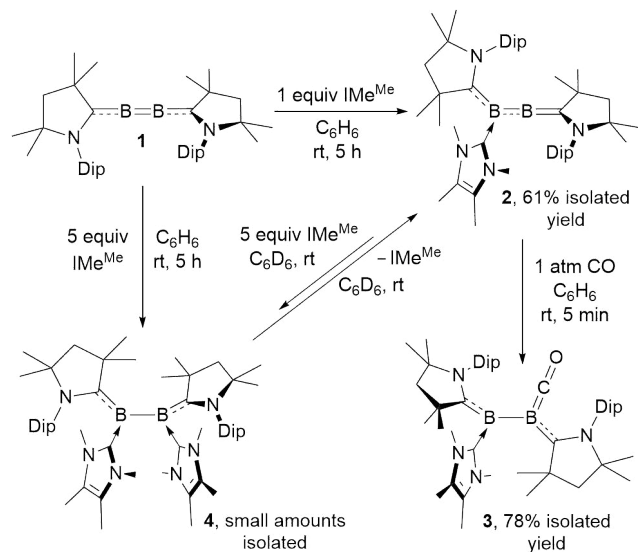


Figure 2. Crystallographically-derived molecular structures of compounds **2**, **3** and **4**. Thermal ellipsoids drawn at 50% probability level. Ellipsoids on the cAAC^{Me} and IMe^{Me} ligand periphery and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): **2** B1-B2 1.626(2), B1-C1 1.484(2), B2-C21 1.423(2), B1-C41 1.605(2), C21-B2-B1 167.09(13), $\Sigma\angle_{B1}$ 359.70(12); **3** B1-B2 1.755(2), B1-C1 1.4645(19), B2-C21 1.495(2), B1-C41 1.608(2), B2-C48 1.456(2), C48-O1 1.1698(16), B2-C48-O1 170.51(13), $\Sigma\angle_{B1}$ 357.96(12), $\Sigma\angle_{B2}$ 359.97(12); **4** B1-B2 1.804(2), B1-C1 1.4766(18), B2-C21 1.4778(19), B1-C41 1.6125(18), B2-C48 1.6174(19), $\Sigma\angle_{B1}$ 357.91(10), $\Sigma\angle_{B2}$ 358.33(11).

unsymmetrical sp²-sp² zerovalent diboron molecules, and is significantly more reactive than its symmetrical precursor for the activation of σ bonds.

Since a preliminary attempt to synthesize a phosphine adduct of the diboracumulene B₂(cAAC^{Me})₂ (**1**)²⁰ failed, our attention turned towards stronger σ donors such as NHCs. The addition of 1 equiv. IMe^{Me} (1,3-dimethylimidazol-2-ylidene) to **1** in benzene at room temperature led to a slow color change from deep blue to green (Scheme 1). After removal of volatiles and washing with pentane, compound **2** was isolated as a green solid in 61% yield. Compound **2** displays two broad ¹¹B NMR resonances, one highly deshielded at 126.4 ppm, 46 ppm downfield of that of **1**, indicating a very electron-poor boron atom, the other at 6.1 ppm, in the region typical for doubly base-stabilized borylenes.²¹ In the ¹H and ¹³C{¹H} NMR spectra, all cAAC^{Me} and IMe^{Me} ligand resonances are magnetically inequivalent, indicating a highly unsymmetrical compound.



Scheme 1. Adduct formation of **1** with donor ligands.

X-ray crystallographic analysis of single crystals of **2** obtained from benzene (Fig. 2) confirmed the binding of a single

IMe^{Me} ligand to one of the boron centers, which is now sp²-hybridized ($\Sigma\angle_{B1} = 359.7(12)^\circ$), the other boron remaining sp-hybridized with a slight bending to release steric strain (C21-B2-B1 167.09(13)°). The cAAC π -frameworks form an angle of ca. 75°, while the plane of the IMe^{Me} ring is arranged near-perpendicularly to the adjacent cAAC ring (ca. 94°). The B-C_{NHC} distance (1.605(2) Å) indicates a pure σ -donor interaction. Although structurally similar to Kinjo's sp-sp² allenic diborene **VIII**, compound **2** differs in that it bears a σ -donating IMe^{Me} (B1-C41 1.605(2) Å) and a strongly π -accepting cAAC^{Me} ligand (B1-C1 1.484(2) Å) at the sp²-hybridized B1 center, instead of two σ -donating PMe₃ ligands as in **VIII**.¹³ As a consequence, the π electron density at the B-B bond is strongly reduced, which leads to significant elongation, intermediate between a B-B single and double bond (**2**: 1.626(2); **VIII**: 1.560(4) Å), whereas the B-C_{cAAC} bond at the sp-hybridized B2 atom (1.423(2) Å) is virtually identical in length to the formal B=C double bond in **VIII** (1.424(4) Å).¹³ The delocalization of the π -electron density throughout the N1-C1-B1-B2-C21-N2 core results in hindered rotation about the B=C bonds and the magnetic inequivalence of all ligand resonances in the ¹H and ¹³C NMR spectra. The NMR spectra remained invariant up to 60 °C in C₆D₆, at which temperature compound **2** started to decompose (*vide infra*).

A C₆D₆ solution of **2** stirred for 5 min at room temperature under an atmosphere of CO turned red. The ¹¹B NMR spectrum showed quantitative conversion to compound **3**, which displays two new resonances, one at 10.0 ppm, corresponding to the B(cAAC^{Me})(IMe^{Me}) borylene center and slightly less shielded than that in compound **2** ($\delta_{11B} = 6.1$ ppm); the other at -18.1 ppm for the B(cAAC^{Me})(CO) boraketene center, similar to that of compound **VI** ($\delta_{11B} = -18.4$ ppm)¹⁵ or the bis(CO) adduct B₂(cAAC^{Me})₂(CO)₂ ($\delta_{11B} = -22.0$ ppm).²² Like **2**, the ¹H NMR spectrum of **3** presents two sets of unsymmetrical cAAC^{Me} ligand resonances, one of which is broadened by hindered rotation, as well as magnetically inequivalent IMe^{Me} methyl resonances, for which the backbone CH₃ groups display ⁵J_{IH-IH} coupling (⁵J = 0.5 Hz). X-ray crystallographic analysis of red single crystals of **3** confirmed the formation of the unsymmetrical IMe^{Me}-CO adduct, which displays a B-B single bond (1.755(2) Å) (Fig. 2). Overall, the structural fea-

tures of **3** are a mixture of the orthogonally arranged sp^2 -borylene moiety of **2** and the boraketenyli moiety of the symmetrical bis(CO) adduct $B_2(cAAC^{Me})_2(CO)_2$.²² The B-B bond length of 1.755(2) Å is typical of a single bond and the short B2-C_{CAAC} and B2-C_{CO} distances of 1.495(2) and 1.456(2) Å indicate strong π backbonding to both the cAAC^{Me} and CO ligand of the boraketenyli moiety. This is also borne out by the CO stretching frequencies ($\nu = 1912, 1895\text{ cm}^{-1}$), which are significantly lower than for free C≡O ($\nu = 2143\text{ cm}^{-1}$) and slightly lower than that in $B_2(cAAC^{Me})_2(CO)_2$ ($\nu = 1928\text{ cm}^{-1}$).²²

In order to obtain a bis(NHC) adduct of **1**, a benzene solution of compound **1** or **2** was stirred with 5 equiv. IMe^{Me} for 5 h at room temperature. After removal of volatiles, the orange reaction mixture was extracted with pentane, yielding small amounts of a new, red compound (**4**). The ¹¹B NMR spectrum of freshly isolated **4** showed a single broad ¹¹B NMR resonance at 14.4 ppm, slightly downfield from the borylene resonance of **2** ($\delta_{11B} = 6.1\text{ ppm}$), suggesting indeed the formation of a symmetrical bis(IMe^{Me}) adduct. The acquisition of a full NMR data set was, however, marred by its highly fluxional solution behavior and spontaneous re-dissociation into **2** and free IMe^{Me}.

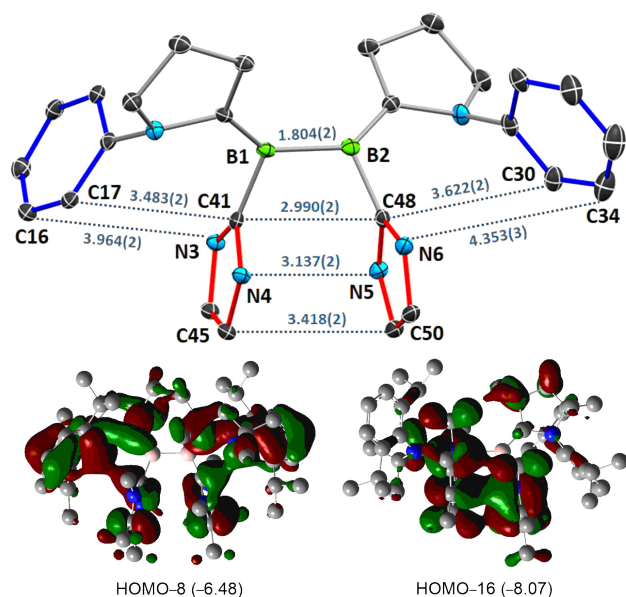


Figure 3. Top: Simplified view of the solid-state structure of **4** displaying the shortest IMe^{Me}-to-IMe^{Me} (red) and IMe^{Me}-to-Dip (blue) interactions as dotted lines with distances in Å. Thermal ellipsoids drawn at the 30% probability level. Methyl and isopropyl substituents and hydrogen atoms omitted for clarity. Bottom: Plots of the HOMO-8 and HOMO-16 of **4** at the B3LYP/6-311G(d) level showing π overlap between the staggered aromatic rings. Hydrogens omitted for clarity. Isovalue: 0.03. Energies (eV) given in brackets.

The X-ray crystallographic structure of **4** (Fig. 2) confirmed the formation of the symmetrical bis-IMe^{Me} adduct. Unlike the bis(CO) or bis(*t*BuNC) adducts of **1**, however, in which the two sp^2 boron moieties are orthogonal to each other, the planes of the two borylene moieties in **4** form an angle of only 52°, which brings the two IMe^{Me} rings into close proximity (C41...C48 2.990(2) Å) as shown in Fig. 3. Furthermore, unlike in compounds **2** and **3**, the Dip substituents of the cAAC ligands in **4** flank the adjacent IMe^{Me} ligands, also bringing

their ring systems into relatively close proximity (C41...C17 3.483(2); C48...C30 3.622(2) Å, Fig. 3). These distances and the staggered arrangement of the aromatic IMe^{Me} and Dip ring systems (see Fig. S20 in the Supporting Information) are typical of π -stacking interactions.²³ This ligand arrangement results in considerable steric strain, which leads to an unusually long B-B bond length of 1.804(2) Å. There are only a couple of examples of diboron(4) compounds with B-B bonds longer than 1.8 Å. These include a lithium-bound $[B_2(NXyl)_4]^{+}$ tetraanion (Xyl = 2,6-Me₂C₆H₃) with a B-B bond of 1.814(4) Å resulting from the strong steric repulsion of the four *o*-xylyl substituents,²⁴ and a titanium complex chelated by the $[(Me_2N)_2B_2(NDip)_2]^{2-}$ ligand with a B-B bridge of 1.800(2) Å elongated by the ring strain of the B₂N₂Ti metallacycle.²⁵ In compound **4**, this steric strain is probably at the origin of its lability and fluxional solution behavior.

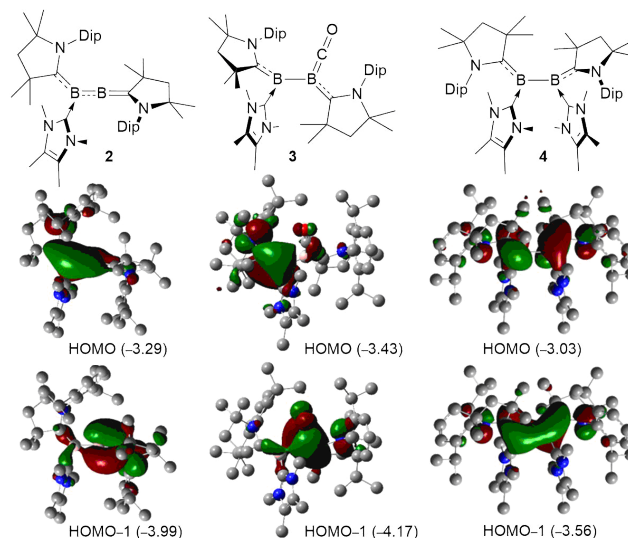


Figure 4. Plots of the HOMO and HOMO-1 of compounds **2** – **4** optimized at the B3LYP/6-311G(d) level. Hydrogen atoms omitted for clarity. Energies (eV) given in brackets.

The bonding situation in compounds **2** – **4** was analyzed by DFT calculations at the B3LYP/6-311G(d) level (Fig. 4). For the mono-IMe^{Me} adduct **2**, the HOMO essentially represents the π -bonding interaction between the sp -hybridized B2 atom and the C21 carbene carbon atom, while the HOMO-1 represents the borylene lone pair localized on the sp^2 -hybridized B1 atom, extending over the B1-C_{CAAC} π bond and, to a lesser degree, the B1-B2 π bond (Fig. 3). This contrasts with the unsymmetrical CO-IMe^{Me} adduct **3**, in which the HOMO and HOMO-1 are separately localized on each borylene moiety, displaying π backbonding to the cAAC^{Me} and CO ligands but no B-B π interaction. For the symmetrical bis-IMe^{Me} adduct **4** the HOMO is symmetrically distributed over each borylene moiety and displays a B-B π antibonding interaction. Interestingly, despite the extremely long B-B bond, and unlike the HOMO-1 of **3**, which shows negligible B-B π bonding, the HOMO-1 of **4** is a π -bonding MO extending over the C1-B1-B2-C21 core. From these calculations it seems that, despite its extreme length, the B-B bond in **4** does present some π -bonding character and that the lengthening is simply caused by the staggered configuration of the Dip and IMe^{Me} ligands. The orbital π interactions between these are visible in the plots of the HOMO-8 and HOMO-16 displayed in Fig. 3.

As expected, the unsymmetrical $sp-sp^2$ hybridization of **2** led

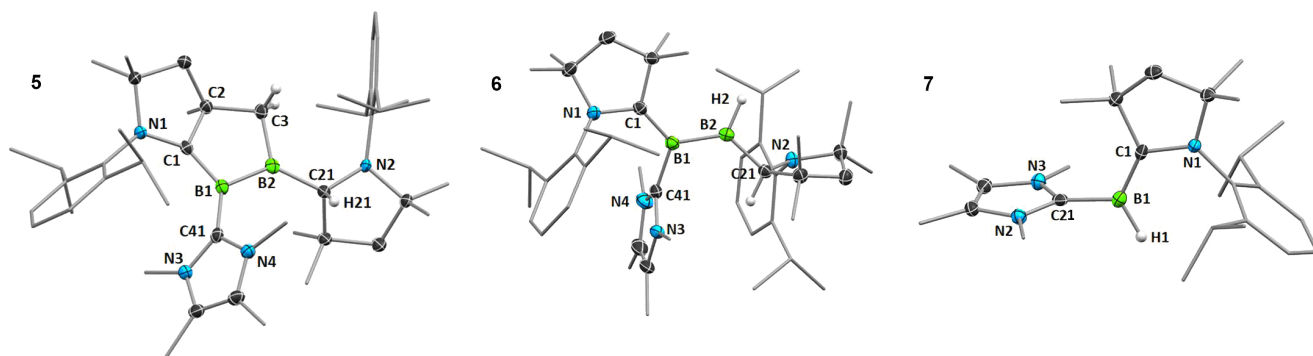
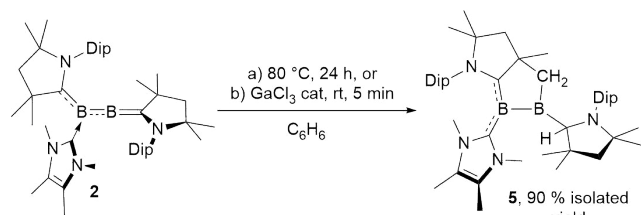


Figure 5. Crystallographically-derived molecular structures of compounds **5**, **6** and **7**. Thermal ellipsoids drawn at the 50% probability level. Ellipsoids on the cAAC and IMe^{Me} ligand periphery and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): **5** B1-B2 1.661(3), B1-C1 1.482(3), B2-C21 1.602(3), B1-C41 1.573(3), B2-C3 1.594(3), C1-N1 1.397(2), C21-N2 1.476(2), $\Sigma\angle_{B1}$ 359.78(17), $\Sigma\angle_{B2}$ 359.87(16); **6** B1-B2 1.655(2), B1-C1 1.488(2), B2-C21 1.609(2), B1-C41 1.600(2), B2-H2 1.134(16), C21-N2 1.4934(17), $\Sigma\angle_{B1}$ 359.55(12), B1-B2-C21 128.05(12); **7** B1-C1 1.447(2), B2-C21 1.582(2), B1-H1 1.120(17), C1-N1 1.4284(18), C1-B1-C21 119.27(14).

to an increased reactivity compared to **1**. This became apparent from its slow decomposition at room temperature in solution to a new species, compound **5**, which displays two broad ¹¹B NMR resonances at 91.4 and 9.4 ppm. Full conversion to **5** was achieved by heating a benzene solution of **2** at 80 °C for 24 hours or by the addition of a GaCl₃ catalyst, which led to an instant color change to yellow (Scheme 2).

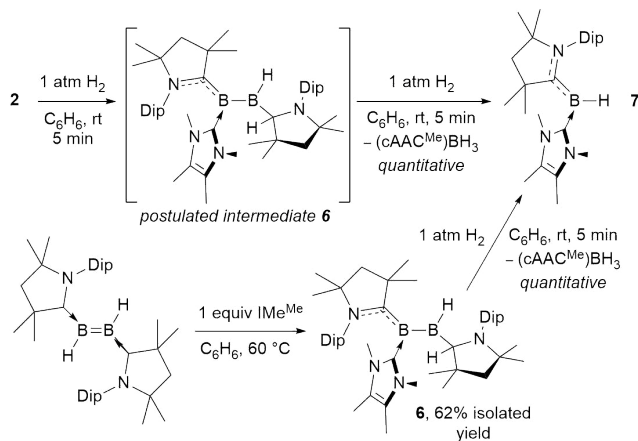


Scheme 2. Intramolecular C-H-activation of compound **2**.

X-ray crystallographic analysis revealed a bicyclic borylborylene structure (Fig. 5), resulting from the C-H activation of a β -methyl substituent on the cAAC^{Me} ligand of the sp² moiety of **2** by its highly nucleophilic sp-hybridized B2 atom, followed by 1,2-hydride migration from B2 to the adjacent cAAC^{Me} ligand, a process which is well-known in cAAC-supported hydroboranes.²⁶ The original C21 carbene carbon atom is now clearly sp³-hybridized (B2-C21 1.602(3), C21-N2 1.476(2) Å). Interestingly, the C₃N₂ ring of the IMe^{Me} ligand now forms an angle of only 57° with the plane of the sp² C1 atom, while the B-C_{NHC} bond is considerably shortened from 1.605(2) Å in **2** to 1.573(3) Å in **5**, which indicates some π backbonding to IMe^{Me}.

The increased nucleophilicity of **2** also became apparent in its reactivity toward H₂. While cumulene **1** undergoes slow room temperature hydrogenation over the course of one day to yield the *trans*-dihydrodiborene [(cAAC^{Me})BH]₂, which itself does not undergo further hydrogenation,¹⁴ compound **2** reacted quantitatively with H₂ (1 atm) within minutes to yield a 1:1 mixture of the mixed parent borylene **7** (doublet at δ_{11B} = 2.9 ppm, ¹J_{B-H} = 105.7 Hz) and (cAAC^{Me})BH₃ (quartet at δ_{11B} = -32.5 ppm, ¹J_{B-H} = 88 Hz,^{26a} Scheme 3). Borylene **7** could be isolated from this mixture in ca. 90% purity by the addition of one equiv. of cAAC^{Me}, which reacted with (cAAC^{Me})BH₃ to form (cAAC^{Me})BH₂(cAAC^{Me}-H),^{26a} which was removed by selective crystallization from hexanes. Analytically pure **7** was

independently obtained from the reduction of (cAAC^{Me})BHB₂²⁷ with KC₈ in the presence of IMe^{Me}. The solid-state structure of **7** (Fig. 5) is analogous to that of its cyanoborylene analogue (cAAC^{Me})(IMe^{Me})B(CN),²⁸ albeit with a slightly shorter B-C_{AAAC} bond (1.447(2) vs. 1.458(1) Å) as the hydride is a pure σ ligand, whereas CN is slightly π -acidic. The HOMO of **7** calculated at the B3LYP/6-311G(d) level essentially corresponds to the B1-C1 π bond, with a small π -bonding contribution from the B1-C21 bond and an antibonding C1-N1 interaction (see Fig. S24 in the Supporting Information).



Scheme 3. Twofold hydrogenation of **2** and isolation of the mono-hydrogenated intermediate **6**.

Although the hydrogenation of **2** occurred too rapidly to identify any reaction intermediates even at lower temperatures, we postulated that it proceeds via i) H₂ activation at the nucleophilic sp-hybridized B2 atom of **2**, followed by a 1,2-hydride shift from B2 to C21 to yield the intermediate borylborylene **6**, ii) 1,2-dihydrogen addition across the activated B-B bond of **6**, which leads to B-B bond cleavage and formation of borylene **7** and (cAAC^{Me}-H)BH₂, which readily tautomerizes to (cAAC^{Me})BH₃.^{26a} To corroborate this postulated mechanism, compound **6** was independently synthesized from the 1:1 reaction of IMe^{Me} and diborene (cAAC^{Me})₂B₂H₂²⁷ in benzene at 60 °C for 8 hours (Scheme 3). Compound **6** displayed two broad ¹¹B NMR resonances at 81.4 and 15.4 ppm, corresponding to the sp²-boryl and sp²-borylene moieties, respectively, the structure

being confirmed by X-ray crystallographic analysis (Fig. 4). Unlike its CO analogue **VI**,¹⁵ compound **6** does not co-crystallize with its sp²-sp³ tautomer, in which both hydrides are located on the boron atom of the boryl moiety and both cAAC^{Me} ligands are neutral. As expected, placing a benzene solution of **6** under an atmosphere of H₂ resulted in quantitative conversion to **7** and (cAAC^{Me})BH₃ within minutes at room temperature (Scheme 3), which strongly supports the hypothesis of it being an intermediate in the hydrogenation of **2** to **7**.

To conclude, we have demonstrated that the unsymmetrical zerovalent sp-sp² diboron compound **2** (B₂L^A₂L^B) provides a flexible platform for the synthesis of novel symmetrical B₂L^A₂L^B₂ and unsymmetrical B₂L^A₂L^BL^C zerovalent sp²-sp² diboron compounds with L^A, L^B and L^C being ligands of varying σ-donor and π-acceptor strength. Furthermore, we showed that the unsymmetrical nature of **2** greatly enhances the nucleophilicity of its sp-hybridized boron atom compared to its symmetrical precursor. This promotes spontaneous intramolecular C-H bond activation and facile twofold, B-B bond-cleaving H₂ addition. We are confident that the growing range of available unsymmetrical mono- and zerovalent diboron compounds will soon yield more fascinating reactivity, beyond that of their symmetrical counterparts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information includes synthetic methodologies, NMR, UV-vis and X-ray crystallographic characterization data of new compounds, and details of the computational methods and results. It is available free of charge on the ACS Publications website. Cif files of all crystallographic structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 1852438 (**2**), 1852437 (**3**), 1852442 (**4**), 1852439 (**5**), 1852441 (**6**) and 1852441 (**7**).

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Note

There are no competing interests to declare.

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SYNOPSIS TOC

Desymmetrization of a cyclic (alkyl)(amino)carbene (cAAC)-supported zerovalent diboron compound, $B_2(cAAC)_2$, by mono-adduct formation with a σ -donating N-heterocyclic carbene (NHC) yields a highly nucleophilic zerovalent $B_2(cAAC)_2(NHC)$ species, which readily forms symmetrical and unsymmetrical adducts with various donor ligands, and undergoes intramolecular C-H bond activation, as well as twofold hydrogenation with B-B bond cleavage to a novel parent borylene.

