COMMUNICATION

Insertion of carbon monoxide into asymmetric diborene to form oxaborirane

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The insertion of carbon monoxide (CO) into the asymmetric diborene concomitant with the B-O bond formation at ambient conditions gives an oxaborirane species. A similar insertion reaction with Isocyanide, the isoelectronic species of CO, generates azaboriridine derivatives.

The activation of carbon monoxide (CO) is of paramount significance in organometallic chemistry and may be introduced to the various substrates by carbonylation to produce fine chemical substances.[1] While the fixation and activation of CO are easily realized by transition metals benefiting from their empty and occupied d orbitals,[2] some main group species exhibiting metallomimetic reactivity are also known to react with CO under mild conditions.[3] Since the first isolation of N-heterocyclic carbene (NHC)-stabilized diborene and diboryne, by the groups of Robinson and Braunschweig,[4,5] a diversity of Lewis-base-stabilized B–B multiply bonded species have been synthesized, and their reactivity have been widely explored.[6] Among them, a few reactions with CO have been reported to date. Braunschweig et al. reported the binding and subsequent coupling of CO with NHC-stabilized diborynes (**I**, **II**) (Figure 1a).[7] Interestingly, the same reaction with cyclic (alkyl)(amino)carbene (CAAC)-stabilized diboracumulene (**III**) only affords the bis(boraketene) product, which does not react with CO further.[7] The same group demonstrated that depending on the reaction and recrystallization conditions, the reaction of dihydrodiborene (**IV**) with CO gives various products involving the CO-coordinated products accompanied by the hydrogen migration and the two CO-inserted product (Figure 1b).[8] The extant unsaturated B-B multiply bonded species capable of capturing CO are limited to the symmetric derivatives (**I-IV**), more than one CO is required to cleave the B–B unsaturated bond completely, and the insertion of single CO molecule into the B–B multiple bonds has not been achieved thus far. Herein, we report the complete scission of the asymmetric B=B bond by insertion of a single CO molecule to give an oxaborirane species.

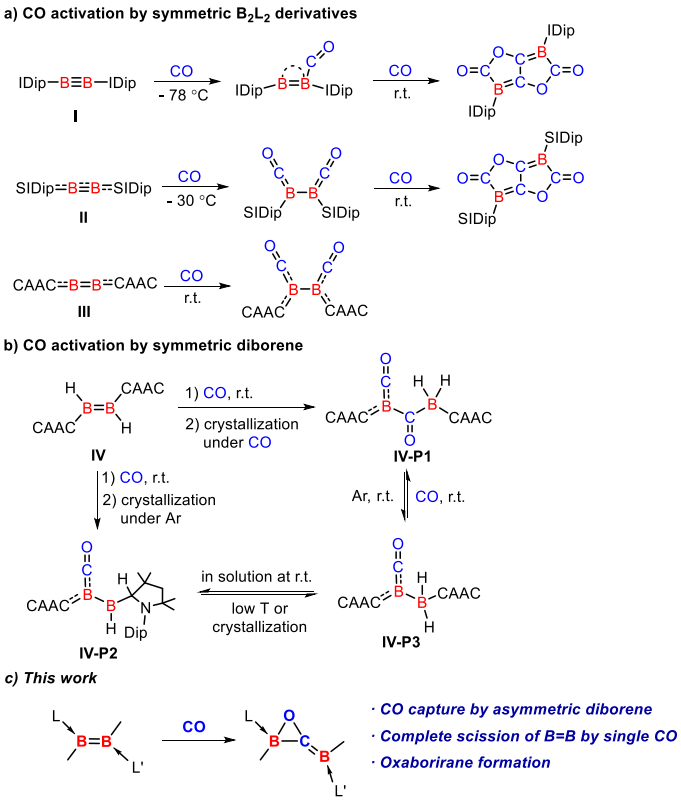

Figure 1. a) CO activation by diboryne and diboracumulene. b) CO activation by diborene. c) present work. IDip = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene, SIDip = 1,3-bis-(diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene, CAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene.

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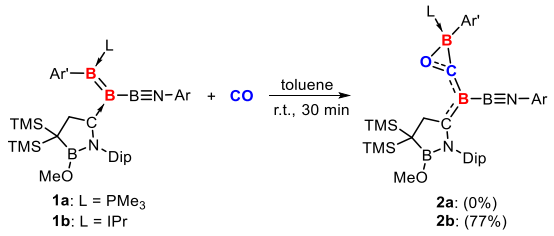
Very recently, we reported the synthesis of asymmetric diborenes **1a** and **1b** with extremely polarized B=B bonds and demonstrated that **1b** splits the N=N bond of both a diazo compound and diazirine to give an azadiboraallene species via the incorporation of an N atom in the B=B bond.[9] We envisaged that the unique chemical property of compound **1** may allow discovering a new reaction mode against other unsaturated molecules, which promoted us to investigate the reaction of **1** with CO. Exposure of the toluene solution of **1a** to CO atmosphere (1 atm) at room temperature led to an unidentified mixture with the observation of free PMe_3, indicating that the coordination ability of phosphine may not be strong enough to stabilize the product or involved-intermediates. By contrast, the reaction of **1b** with CO under the same conditions afforded a major product. After workup and recrystallization, compound **2b** was isolated as yellow crystals in 77% yield. The ^{11}B NMR spectrum of **2b** exhibits four signals at δ 40.5, 26.3, 2.8 and −14.7 ppm, that are assigned to MeO−*B*, *B*≡N, cAAC−*B* and IPr−*B* respectively, according to the calculated ^{11}B NMR chemical shifts (Table S2). Compound **2b** does not react further with CO even heating at 80 °C, which is notably different from the formation of **IV-P1** (Fig 1).



Scheme 1. Reactions of **1a** and **1b** with CO (Dip = 2,6-diisopropylphenyl, Ar = 4-bromo-2,6-diisopropylphenyl, TMS = trimethylsilyl, Ar' = 4-*tert*-butylphenyl, IPr = 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene).

Yellow single crystals of **2b** were obtained from the *n*-hexane solution at −5 °C. The solid-state molecular structure confirmed the insertion of CO into the B=B bond concomitant with the formation of a B−O bond to furnish a BCO three-membered ring, namely, an oxaborirane (Figure 2). The B2 and C22 atoms adapt nearly trigonal planar geometry (sum of the bond angles: B2 = 359.25°, C22 = 359.12°), indicating the sp^2-hybridized character. The bond length of C23−B2 (1.497(3) Å) is identical to that (1.497(7) Å) in **1b**, and comparable to the reported CAAC−B(CO)R bond in **IV-P1** (1.506(2) Å).[8] The distance of B2−C22 (1.500(3) Å) is longer than the typical B=C double bond species,[10] but significantly shorter than the B−C(=O) single bond in **IV-P1** (1.605(2) Å),[8] indicative of its partial multiple bond character. The C22−O1 bond length (1.338(3) Å) is remarkably shorter than the reported C(sp^3)−O(sp) bonds in the BCO three-membered rings (1.4573(18) Å, 1.441(2) Å),[11] but no BCO three-membered species with a C(sp^2)−O(sp) bond to compare. The distance of B1−O1 bond (1.549(3) Å) is significantly longer than the reported B(sp^3)−O(sp) bond in BCO three-membered rings (1.4780(19) Å, 1.482(2) Å).[11] It is noteworthy to mention that **2b** represents the first example of the formation of an oxaborirane by the reaction of diborene with CO.[11a, 12, 13]

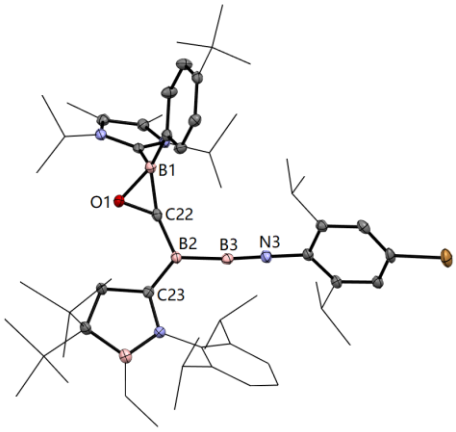


Figure 2. Solid-state structure of **2b**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

To reveal the electronic structure of **2b**, density functional theory (DFT) calculations were performed at the B3LYP-D3(BJ)/6-311G(d,p) level. The calculated frontier orbitals show that the highest occupied molecular orbital (HOMO) mainly corresponds to the π-bonding orbital over the C23−B2−C22 moiety, while the HOMO−1 comprises the in-plane B≡N π orbital with contributions from π orbitals of the aryl ring (Figure 3). The HOMO−2 is the combination of the σ-bonding orbitals of the B1−C22, B1−O1 and B2−C22 bonds and π orbitals of the aryl ring on B1. The LUMO is dominated by the p orbitals on the C23 and C22 atoms with a contribution of π-type orbital over the B−N bond in CAAC. Natural bond orbital (NBO) analysis shows that the Wiberg bond indexes (WBI) values of the C23−B2, B2−C22 and C22−O1 bonds are 1.25, 1.25 and 1.16, respectively, indicating their partial multiple bond characters. The WBI value of the O1−B1 bond is only 0.63, suggesting a weak bond interaction. These data are consistent with its structural features, illustrating the delocalization of electrons over the C23−B2−C22−O1 skeleton.

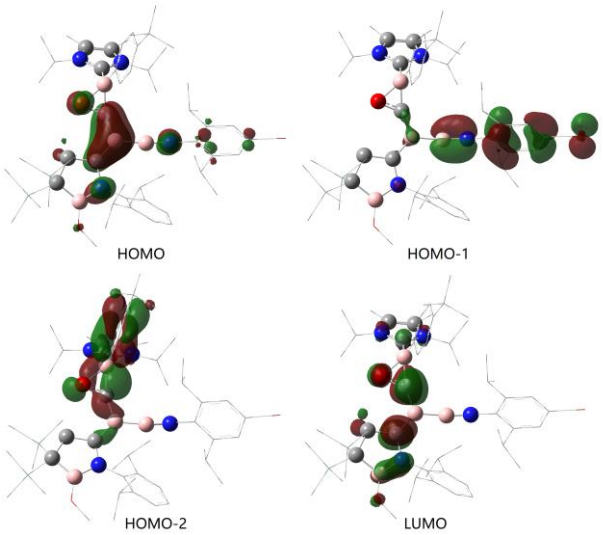


Figure 3. Frontier orbitals of **2b**.

The reaction mechanism for the activation of CO by **1b** was theoretically explored by using simplified model compound **1b'** at the B3LYP-D3(BJ)/6-31G(d) level (Figure 4). The reaction starts with the regio-selective coordination of CO to the electrophilic terminal sp^2 B atom of **1b'**[9] via **TS1** with a barrier of 8.7 kcal·mol^{-1}, leading to the zwitterionic intermediate **Int1**. Subsequent B–O bond formation proceeds via **TS2** with a barrier of 6.5 kcal·mol^{-1} to afford the oxaborirane derivative **2b'**.

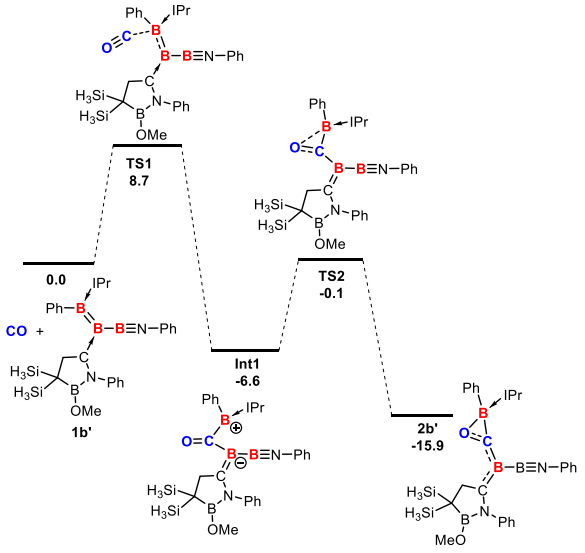
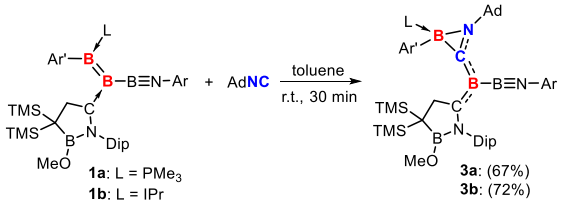


Figure 4. DFT-calculated free energy profile (kcal·mol^{-1}) for the proposed mechanism of the reaction between **1b'** and CO.

Given the fact that isocyanide is isoelectronic with CO, we speculated that compound **1** reacts with isocyanides to afford BCN three-membered ring species. To bear out the hypothesis, **1a** and **1b** were treated with one equivalent of 1-adamantyl isocyanide in toluene at room temperature. After workup, products **3a** and **3b** were gained in good yields (**3a**: 67%, **3b**: 72%). The ^{11}B NMR spectra show four signals at δ 38.6, 24.3, −0.4 and −20.5 ppm for **3a** and 38.0, 25.2, 0.0, and −20.2 ppm for **3b**, which are assigned to MeO–*B*, *B*≡N, cAAC–*B* and PMe_3–*B* (IPr–*B*), respectively. Notably, the isocyanide reacts selectively with the B=B bonds of **1a** and **1b** rather than the B≡N bonds.[14]



Scheme 2. Reactions of **1a** and **1b** with AdNC (Ar = 4-bromo-2,6-diisopropylphenyl, Ar' = 4-*tert*-butylphenyl, IPr = 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene, Ad = 1-adamantyl).

The X-ray diffraction analyses of **3a** and **3b** revealed the insertion of the C atom of isocyanide into the B=B bond accompanied by the B–N bond formation (Figure 5). The B2, C1 atoms in **3a** and **3b** and N1 atom in **3b** are nearly trigonal planar (sum of the bond angles: B2 = 359.67°, C1 = 359.98° for **3a**; B2 = 360°, C1 = 359.8°, N1 = 359.9° for **3b**), while the N1 atom in **3a** is slightly pyramidal (356.59°). The bond lengths of C2–B2 in **3a** (1.476(2) Å) and **3b** (1.480(9) Å) are slightly shorter than **2b** (1.497(3) Å), while the B2–C1 distances in **3a** (1.524(2) Å) and **3b** (1.536(10) Å) are slightly longer than **2b** (1.500(3) Å). The calculated frontier orbitals of **3a** are similar to those of **2b** (Figure 5). The HOMO mainly comprises the π-bonding orbital over the C2–B2–C1 moiety, while the HOMO−1 is dominated by the in-plane B≡N π orbital with contributions from π orbitals of the aryl ring. The HOMO−2 mainly corresponds to the σ-bonding orbitals of the B1–C1, B1–N1 and B2–C1 bonds and π orbitals of the aryl ring on B1. The LUMO is the p orbitals on the C2, C1 and N1 atoms with a contribution of π-type orbital over the B–N bond in CAAC. The WBI values of C2–B2, B2–C1 and C1–N1 bonds in **3a** are 1.32, 1.14 and 1.38 respectively, suggesting their partial multiple bond characters. The formation of compound **3** represents the rare construction of BCN three-membered ring, azaboriridine, by the reaction between B-B unsaturated species and isonitrile.[15,16]

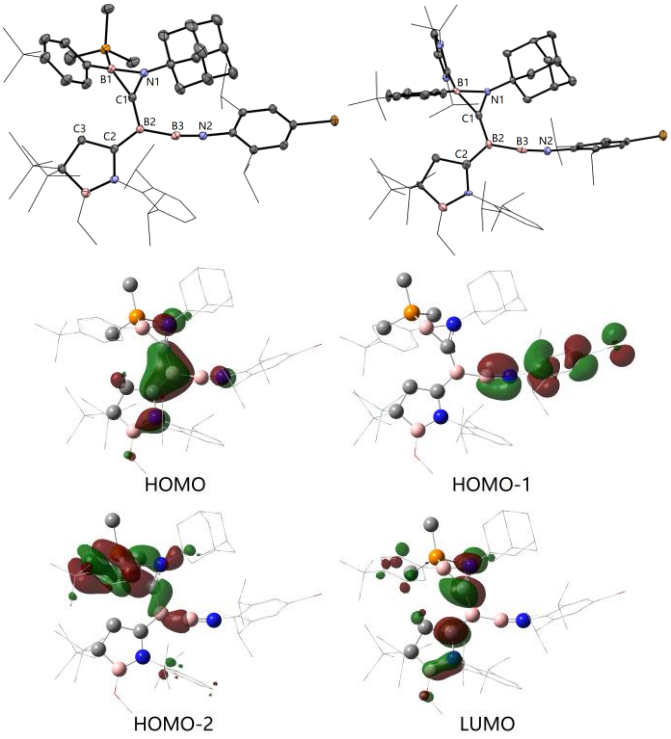


Figure 5. Solid-state structure of **3a** and **3b**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level (top). Frontier orbitals of **3a** (bottom).

In conclusion, we have demonstrated the complete scission of the B=B bond by CO and isonitriles. The controlled insertion of a single CO molecule into the

asymmetric B=B bond gave oxaborirane **2b** with BCO three-membered ring whereas employment of isocyanide produced azaboriridine featuring the BCN three-membered rings **3**. The DFT calculations indicate the delocalization of electrons over the C−B−C−O (**2b**) and C−B−C−N (**3**) skeletons.

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Conflicts of interest

The authors declare no conflict of interest.

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