

Reactivity of a Dihydrodiboreane with CO: Coordination, Insertion, Cleavage and Spontaneous Cyclic Alkyne Formation

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Abstract: Under a CO atmosphere the dihydrodiboreane [(cAAC)HB=BH(cAAC)] underwent coordination of CO concomitant with reversible hydrogen migration from boron to the carbene carbon atom, as well as reversible CO insertion into the B=B bond. Heating of the CO-adduct resulted in two unusual cAAC ring-expansion products, one presenting a B=C bond to a six-membered 1,2-azaborinane-3-ylidene, the other an unprecedented nine-membered cyclic alkyne resulting from reductive cleavage of CO and spontaneous C≡C triple bond formation.

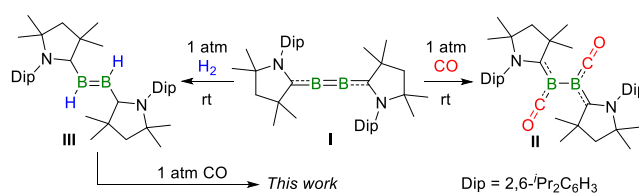
Thanks to the diverse arrangements of their filled and empty frontier *d*-orbitals, transition metals (TM) excel at binding and activating a vast range of small molecules, including CO and H₂.^[1] Being a strong σ -donor and π -acceptor, the carbonyl ligand is ideally adapted to the stabilization electron-rich metal centers,^[2] yet sufficiently labile to allow ligand substitution, a property that makes TM carbonyl complexes particularly well-suited to catalysis.^[3] Beyond its function as a labile yet stabilizing ligand, CO also plays a major role as a chemical feedstock in the TM-catalyzed conversion of syngas (H₂ + CO) to useful hydrocarbons or alcohols,^[4] by complete or partial reduction of CO, respectively.

In contrast, CO proves rather reluctant to bind to p-block elements because of their general inability to engage in π -backbonding. Mono-, di- and tricarbonyls of p-block elements have been identified in reactions of element atoms with CO in solid noble gas matrices.^[5] Similarly, most CO adducts of boranes, in which CO acts purely as a σ -donor, may only be generated and spectroscopically characterized at low temperature,^[6] and only a couple are sufficiently stable to have been structurally characterized.^[7]

In the last decade, however, it has become increasingly clear that main group compounds can be electronically tuned to mimic the behavior of TM complexes.^[8] Some frustrated Lewis pairs (FLPs), for example, have been shown to activate CO or H₂.^[9] The {B(C₆F₅)₃⋯P(^tBu)₃} pair, in particular, reacted stoichiometrically with syngas to effect complete CO cleavage and insertion of a CO-derived CH₂ unit into a B–aryl bond.^[10] Highly Lewis acidic pentaphenylborole (BC₄Ph₅) was found to coordinate CO at boron before undergoing CO insertion into the borole ring.^[11] This borole was also found to undergo H₂ addition to the two endocyclic carbon atoms adjacent to boron.^[12] More

recently unsymmetrical diboranes have also started to show some promise for TM-free H₂ and CO activation.^[13]

Advances in ligand design have enabled the isolation of numerous electron-rich, low-valent main group species that are capable of activating a wide variety of small molecules.^[14] Only a handful of these compounds, however, have been reported to activate both CO and H₂. Among these are the cyclic and acyclic (alkyl)(amino)carbenes (cAACs and aAACs), in which the ylidenic carbon atom undergoes facile addition of H₂^[15] as well as CO binding to afford the aminoketene product.^[16] A bulky diarylgermylene reported by Power and co-workers was shown to undergo H₂ addition as well as double CO insertion/coupling into both a Ge–C and an aryl–isopropyl bond of the ligand.^[17] In the area of low-valent boron chemistry the dicoordinate cAAC-supported aminoborylene reported by Stephan and Bertrand was shown to add H₂ across the B–C_{cAAC} bond and coordinate CO.^[18]



Scheme 1. Reactivity of diboracumulene I with CO and H₂.

In the last few years, our group has greatly expanded the reactivity scope of CO with low-valent boron compounds. Using first-row transition metal borylene precursors, we have reported several examples of base-triggered borylene-carbonyl coupling reactions,^[19] the reductive coupling of a borylene to two CO ligands at chromium,^[20] as well as the complete cleavage of CO at an iron(0) bis(borylene) complex upon coordination of a cAAC ligand.^[21] Addition of strong σ -donor π -acceptor ligands (cAAC, CO, RNC) to iron and manganese borylene carbonyls provided facile routes to tricoordinate CO-stabilized metal-free borylenes.^[22] Furthermore, CO was found to coordinate to N-heterocyclic carbene (NHC)-supported B≡B triple bonds and subsequently undergo fourfold reductive insertion of CO to yield bicyclic bis(boralactones).^[23] In contrast, the reaction of CO with the cAAC-supported diboracumulene I stopped at the stable bis(boraketene) II (Scheme 1).^[23b] Compound I was also shown to undergo facile addition of H₂ across the B–B multiple bond to yield dihydrodiboreane III (Scheme 1).^[24] Herein we report the subsequent coordination, insertion and CO-splitting reactivity of III with CO.

Stirring a deep blue solution of III in pentane under an atmosphere of dry CO at room temperature resulted in the

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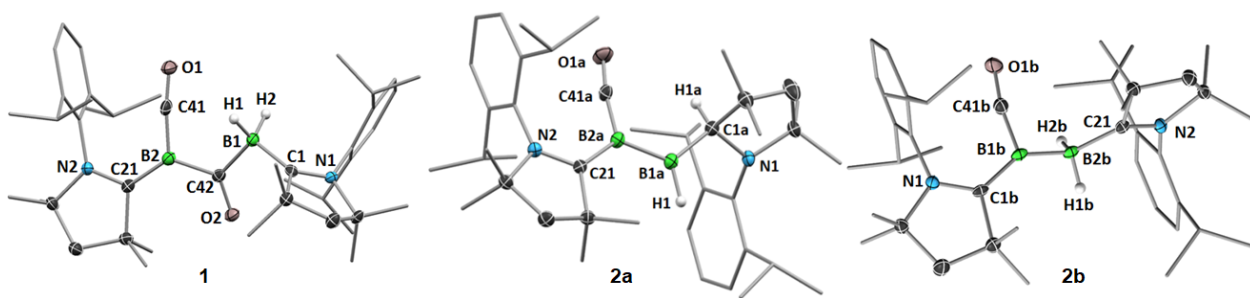
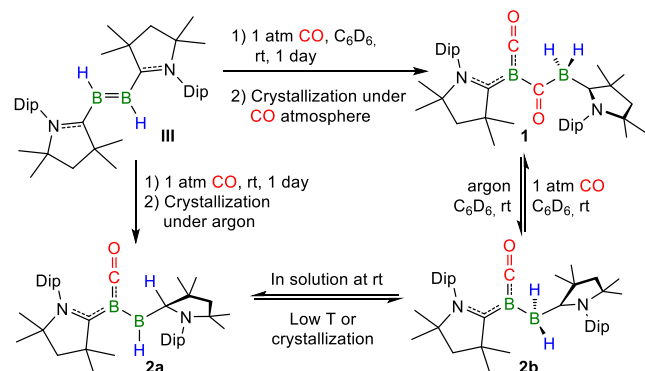


Figure 1. Crystallographically determined solid-state structures of **1**, **2a** and **2b**. The latter two structures are superimposed in the asymmetric unit in a 85:15 ratio. Atomic displacement ellipsoids depicted at 50% probability level and omitted for ligand periphery. Hydrogen atoms omitted except for boron- and C1a-bound hydrogens. Selected bond lengths for **1** (Å): C21–B2 1.506(2), B2–C41 1.475(2), O1–C41 1.1530(19), B2–C42 1.605(2), C42–O2 1.2512(18), B1–C42 1.637(2), B1–H1 1.136(17), B1–H2 1.153(18), B1–C1 1.594(2).

formation of an orange precipitate. The product was recrystallized by gentle warming into solution followed by slow cooling under a CO atmosphere to provide compound **1** in 50% yield. The ^{11}B NMR spectrum of **1** showed two 1:1 resonances, a singlet at -9.8 ppm and a BH_2 triplet at -17.4 ppm. The $^{13}\text{C}\{^1\text{H}, ^{11}\text{B}\}$ NMR spectrum displayed two distinct $\text{C}_{\text{carbene}}$ resonances at 239.1 and 211.5 ppm, as well as two C_{CO} resonances confirmed by a ^{13}C labelling experiment, one at 283.1, assigned to a diboraketone moiety, and the other at 229.8 ppm, assigned to a boraketene moiety.



Scheme 2. Room-temperature reactivity of **III** with CO.

An X-ray crystallographic experiment showed **1** to be a bis(cAAC)-stabilized 1-boraketene-1-dihydroboryl-methanone (Fig. 1), in which the original B=B bond has been entirely cleaved to insert a $\mu^2\text{-C=O}$ fragment. The entire $(\text{OC})\text{B}(\mu^2\text{-CO})\text{B}$ core of the molecule is nearly planar and in conjugation with the π -system of the boraketene-bound cAAC ligand. The cAAC ligand bound to the sp^3 -hybridized BH_2 moiety is tilted by ca. 75° out of the $(\text{OC})\text{B}(\text{CO})\text{B}$ plane and acts as a pure σ -donor (B1–C1 1.594(2) Å). The boraketene moiety shows strong π -backbonding to both the cAAC and CO ligands (B2–C21 1.506(2), B2–C41 1.475(2) Å) similar to that observed in bis(boraketene) **II** (avg. B– C_{cAAC} 1.514(2), B– C_{CO} 1.477(2) Å).^[23b] The central carbonyl moiety (C42–O2 1.2512(18) Å) is bound to both boron atoms via single bonds (1.637(2), 1.605(2) Å), making **1** the first structurally characterized diboraketone. Compound **1** displayed a broad $\nu(\text{B-H})$ absorption at 2335 cm^{-1} and two very intense $\nu(\text{C=O})$ IR stretches at 1984 and 1972 cm^{-1} , ca. 50 cm^{-1} higher than that of **II**.^[23b] This reflects the higher degree of electronic delocalization over the planar

$(\text{cAAC})(\text{BCO})(\mu^2\text{-CO})$ π -framework in **1** than in **II**, in which the two $(\text{cAAC})(\text{BCO})$ moieties are mutually orthogonal.

When **1** was subjected to vacuum or recrystallized under argon rather than a CO atmosphere, NMR spectroscopic analysis revealed an entirely different compound, **2**, displaying two 1:1 ^{11}B NMR resonances, one at 53.5 ppm, characteristic of an sp^2 borane moiety, the other at -18.4 ppm, indicative of a boraketene moiety. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum presented a single cAAC carbene resonance at 210.4 ppm and one boron-bound atom CO resonance at 214.4 ppm. X-ray crystallographic analyses of **2** repeatedly showed mixtures of two regioisomers superimposed within the same asymmetric unit in varying ratios (Fig. 1, for overlay see Fig. S24). The minor regioisomer, **2b** (5–15%), is a bis(cAAC)-stabilized (dihydroboryl)boraketene. The major regioisomer, **2a** (85–95%), is a cAAC-supported boraketene bound to a sp^2 -hybridized hydroborane moiety bearing a C1-protonated cAAC ligand (B1a–C1a 1.590(3); N1–C1a 1.481(2) Å). Because of bond restraints, which had to be applied to model the crystallographic superposition of **2a** and **2b**, further structural discussion is precluded. A solid-state IR spectrum showed two distinct $\nu(\text{C=O})$ stretches at 1921 and 1962 cm^{-1} displaying a ca. 1:4 intensity ratio. The band at 1921 cm^{-1} , similar to that of **II** (1928 cm^{-1})^[23b] is attributable to isomer **2b**, the $(\text{cAAC})(\text{BCO})$ π -framework of which resembles that of the two non-conjugated moieties of **II**. The second absorption, ca. 40 cm^{-1} higher, is attributable to isomer **2a**, in which the π -electron density is further delocalized into the empty p -orbital of the sp^2 -hybridized BH fragment. The relative intensities of the two bands approximately reflect the ratio of **2a** and **2b** observed by X-ray diffraction analysis.

Based on ^{11}B NMR data, **2a** was the only isomer present upon redissolution of crystalline samples at room temperature. While the ^{13}C NMR resonance of the protonated C1a carbon atom could not be identified even by recording ^{11}B -decoupled spectra, the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum showed a broad 2H resonance at 4.97 ppm (fwhm ≈ 23 Hz), which did not correlate with any ^{13}C NMR resonance in HSQC or HMBC experiments. Both observations point to a fast exchange between the hydrogen atoms attached to B1a and C1a on the NMR time scale and, together with the solid-state data, suggest the existence of an equilibrium between **2a** and **2b**. At -60°C in $\text{d}_8\text{-thf}$ the ^{11}B NMR

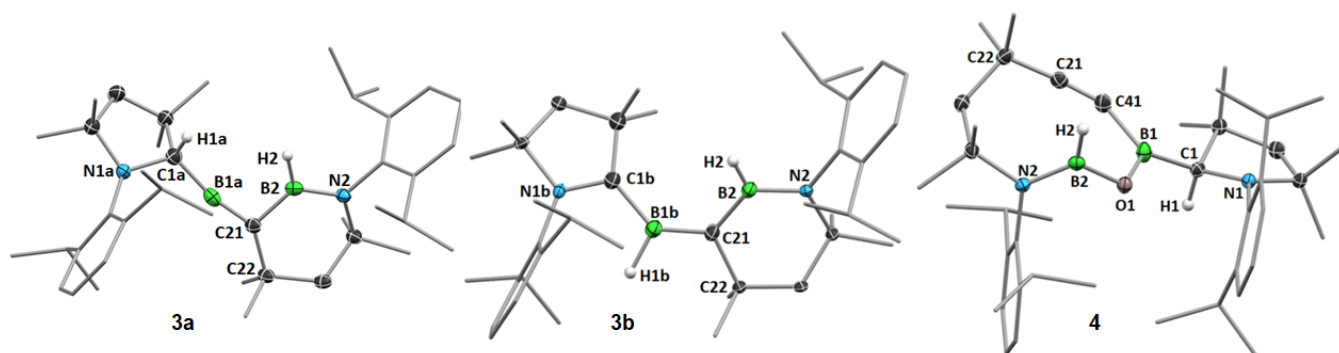
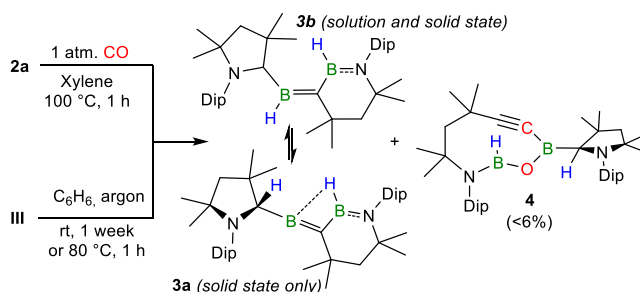


Figure 2. Crystallographically determined solid-state structures of **3a** (from an X-ray structure refined with **3a** as the sole isomer, present in >95%), **3b** (from an X-ray structure displaying a **3a:3b** ratio of 24:76) and **4**. Atomic displacement ellipsoids depicted at 50% probability level and omitted for ligand periphery. Hydrogen atoms omitted except for those on B1b, B2 and C1. Selected bond lengths (Å) and angles (°): **3a**: N2–B2 1.409(4), B2–H2 1.07(3), C21–B2 1.543(4), B1a–C21 1.361(4), B1a···H2 2.43(3), B1a–C1a 1.543(4), N1a–C1a 1.460(3), C21–B1a–C1a 167.9(3), B1a–C21–B2 99.8(2), B1a–C21–C22 120.5(2), B2–C21–C22 139.5(3); **3b**: N2–B2 1.421(5), B2–H2 1.12(4), C21–B2 1.532(6), B1b–C21 1.469(7), B1b–H1b 1.02(5), B1b–C1b 1.582(8), N1b–C1b 1.319(16), C21–B1b–C1b 132.5(5), B1b–C21–B2 128.0(4), B1b–C21–C22 115.0(4), B2–C21–C22 116.9(3); **4**: N2–B2 1.4069(17), B2–O1 1.4187(16), B2–H2 1.090(13), O1–B1 1.3588(16), B1–C1 1.599(2), B1–C41 1.5564(19), C41–C21 1.2101(18), B1–C41–C21 148.26(12), C41–C21–C22 174.82(13).

resonance of the sp^2 borane moiety of **2a** (53 ppm) had disappeared and been replaced by a broad resonance around –25 ppm, attributed to the BH_2 moiety of **2b**, concomitant with an upfield shift of the boraketene resonance from –18 to –20 ppm.^[25] The corresponding 1H NMR spectrum also showed a significant upfield shift of the broad BH resonance to ca. 3.2 ppm, typical for an sp^3 dihydroborane. While these observations provide qualitative proof of the existence of an equilibrium between **2a** and **2b**, partial crystallization of **2b** from the solvent during low temperature NMR recording prevented quantitative analysis of this equilibrium.



Scheme 3. Thermally-induced cAAC ring-expansion of **2**.

In solution under an atmosphere of CO, compound **2a** was found to convert rapidly back to **1** (Scheme 2).^[26] Under an atmosphere of argon, however, NMR spectroscopic monitoring over several days at room temperature revealed the slow transformation of **2a** into a new species, **3**, characterized by two broad $^{11}B\{^1H\}$ NMR resonances at 39.1 (fwhm \approx 670 Hz) and 31.7 ppm (fwhm \approx 480 Hz), and a deep red coloration. Full conversion to **3** in ca. 94% selectivity based on NMR spectroscopic data was achieved by heating a benzene solution of **2a** for 1 hour at 80 °C. Conversely, **3** could be obtained from direct heating of **III** at 110 °C in xylene under an atmosphere of CO. Interestingly, the solid-state IR spectrum of **3** displayed no $\nu(C=O)$ stretches and showed a broad $\nu(B-H)$ absorption at 2459 cm^{-1} .

Removal of volatiles, extraction with benzene and recrystallization from pentane yielded red crystals of **3** suitable for X-ray crystallographic analysis. Similarly to compound **2**, the asymmetric unit of **3** always contained two superimposed regioisomers, **3a** and **3b** (Fig. 2). Compounds **3a** and **3b** share a

six-membered 1,2-azaborinane-3-ylidene heterocycle resulting from the insertion of a BH moiety into the C–N bond of a cAAC ligand, and bound via C21 to either a sp -hybridized boron center (C21–B1–C1 $167.9(3)^\circ$) bearing a C1-protonated cAAC ligand (**3a**) or an sp^2 -hybridized BH moiety ($\Sigma(B1b) = 360.9(2)^\circ$) supported by a neutral cAAC ligand (**3b**). The B1b–C1b bond length in **3b** (1.582(8) Å) indicates a purely σ -donating cAAC ligand whereas the protonated C1a atom in **3a** is clearly sp^3 -hybridized (B1a–C1a 1.543(4), N1a–C1a 1.460(3) Å). The B1b–C21 bond in **3b** (1.469(7) Å) is within the range of B=C double bonds but still ca. 0.1 Å longer than the corresponding B1a–C21 bond in isomer **3a** (1.361(4) Å). The structures of **3a** and **3b** are reminiscent of linear and base-stabilized alkylidene boranes, respectively, which were first characterized in 1989.^[27] Berndt's diborylmethylene durylborane, for example, displays a B=C double bond distance of 1.374(8) Å, while that of its diethyl ether adduct is substantially longer (1.431(8) Å),^[27b] similarly to the B1=C21 distances in **3a** and **3b**, respectively, within the estimated standard deviations. The unusual B1–C21–B2 angle in **3a** ($99.8(2)^\circ$) and the significant deviation of C1–B1–C21 from linearity ($167.9(3)^\circ$) are most likely the result of a B–H agostic interaction between B1 and the B2–H2 σ -bond (B1···H2 2.43(3) Å), which stabilizes the highly electron-deficient B1 center. A similar α -agostic distortion was observed in other (alkyl)(boryl)methylene boranes presenting B–C–B angles of 104.3° and $98.1(5)^\circ$,^[28] while $[(Me_2B)(Me)C=BMe]$ was predicted to display an even more acute α -agostic distortion of 91° .^[28a] Upon redissolution of a crystalline sample of **3a/b**, isomer **3b** was always the only species observed by NMR spectroscopy from –100 to +60 °C (Figs. S16–S18), suggesting that tautomerization may be a result of crystallization and packing forces. Calculations enabled the assignment of the ^{11}B NMR resonance at 39.1 ppm to the endocyclic boron atom and that at 31.7 ppm to the cAAC-supported boron center.^[25] The corresponding BH protons appeared as broad resonances at 5.20 and 4.85 ppm, respectively, in the 1H NMR spectrum. A $^{13}C\{^1H,^{11}B\}$ NMR experiment showed C_{carbene} and $C_{\text{alkylidene}}$ resonances at 225.5 and 151.7 ppm, respectively. The latter is close to the B=C α B resonances observed in a series of (aryl)(boryl)methylene boranes around 165 ppm.^[28a] While borane- and diborane-induced ring-expansion reactions of NHCs are now well-documented^[29] and their mechanism thoroughly investigated,^[30] the activation barriers of analogous reactions

involving cAACs had been predicted to be too high.^[30a] Radius and Marder only recently reported the first examples of such cAAC ring-expansion reactions by insertion of (aryl)catecholboranes and AlH₃ into the endocyclic C-N bond.^[31] The formation of **3** thus confirms once more that the cAAC framework, although more inert than that of NHCs, is not immune to such reactions.^[32]

To analyze the bonding between B1b and the 1,2-azaborinane-3-ylidene heterocycle we performed theoretical calculations on **3b** at the M05-2X/def2-SVP level (see Supporting Information for computational details, Fig. S27). The HOMO of **3b** consists mainly of the B1b=C21 π bond and some π -antibonding between N1b and C1b, as well as N2 and B2 (Fig. 3). The seeming delocalization of the B=C π -electron density into the adjacent B2- and C1b-p(π) atomic orbitals appears not be very significant in view of i) the rather long B1b–C1b distance (1.582(8) Å in the solid-state structure) and ii) the π -donating endocyclic N2 atom adjacent to B2. The HOMO-7 corresponds to the σ -bond between the six-membered heterocycle and B1b, whereas the HOMO-8 essentially shows the σ -donor bond between the cAAC and B1b (Fig. S28). These results and the fact that the triplet state of the free 1,2-azaborinane-3-ylidene is 11.2 kcal·mol⁻¹ lower in energy than the singlet state (Fig. S29) show that **3b** is indeed a cAAC-stabilized alkylidene borane rather than a bis(carbene)-stabilized borylene as it may seem at first glance.

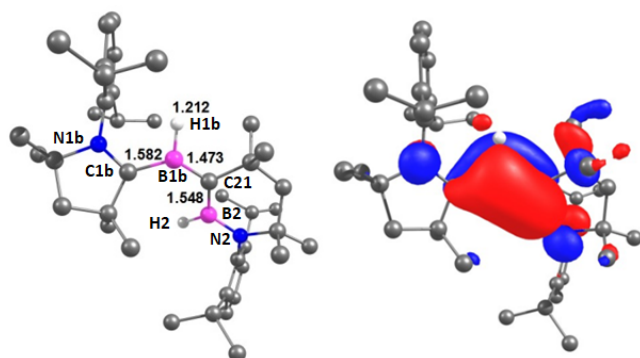


Figure 3. Optimized geometry of **3b** (left: bond lengths in Å) and HOMO right: (-5.815 eV) at the M05-2X/def2-SVP level.

During the purification of **3**, a colorless solid was isolated in ca. 6% yield by washing the crude reaction product with benzene. X-ray crystallographic analysis identified this minor product as compound **4**, a 1,3,2,9-oxazadiborocyclonon-6-yne (Fig. 2). Both boron centers in **4** are sp²-hybridized borane units bridged by the CO-derived oxygen atom. B1 further coordinates to a C1-protonated cAAC ligand and an alkynyl unit resulting from the coupling of the CO-derived carbon atom with the former carbenoid carbon of a ring-opened cAAC ligand. B2 further bears a hydride and coordinates to the amino moiety of the ring-opened cAAC ligand. Though the newly formed C41≡C21 triple bond does not present altogether linear bonding because of ring strain (C41–C21–C22 174.82(13); C21–C41–B1 148.26(12)°) the C41–C21 distance of 1.2101(18) Å confirms that this is indeed a C≡C triple bond. Concerted insertion-homocoupling reactions of CO at d- and f-block metal complexes have been known for some time,^[33] but there are only a handful of examples of metal-templated C≡C triple bond formation from the reductive coupling of CO.^[34] There is, to our knowledge, only one other example of

alkyne formation from fully cleaved CO at a low-valent main group compound, recently published by Scheschke and co-workers.^[35] The authors reported that under an atmosphere of CO a lithium triaryldisilenide-promoted reductive CO cleavage occurs, with formation of both a C=C double and C≡C triple bond, the carbon atoms of which all derive from CO. In contrast to these reports, however, which all involve reductive CO homocoupling, the C≡C bond in **4** results from coupling of CO with another donor ligand. While **4** was never isolated in sufficient amounts and purity to provide more than ¹¹B NMR spectroscopic data (δ = 30.2 ppm, fwhm{¹H} \approx 890 Hz; δ = 40.2 ppm, fwhm{¹H} \approx 980 Hz), its formation in up to 6% yield proved reproducible. Since heating isolated **3** under a CO atmosphere did not result in conversion to **4**, the latter likely derives directly from **2**.^[32]

To conclude, we have shown that the cAAC-supported dihydrodiborene **III** displays a rich reaction chemistry towards molecular CO, including adduct formation, reversible CO insertion into the B-B bond and unusual cAAC ring-expansion reactions yielding two novel heterocyclic products: i) a cAAC-supported 1,2-azaborinane-3-ylidene hydroborane (**3**) and ii) a unique 1,3,2,9-oxazadiborocyclonon-6-yne heterocycle (**4**), the formation of which requires a complex interplay of cAAC ring-expansion by borylene insertion, complete CO cleavage and C≡C bond formation involving the CO-derived carbon atom. While **4** is only a minor reaction product, it provides a tantalizing glimpse at the untapped potential of low-valent boron species for small-molecule activation, and further broadens the scope of cAAC non-innocence.

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Keywords: CO activation • diborene • ring-expansion • insertion • cyclic (alkyl)(amino)carbene

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- [25] For calculated ^{11}B NMR shifts of **2b**, **3a** and **3b** at B3LYP/6-311G(d) level see Supporting Information Fig. S26.
- [26] Preliminary calculations on the mechanism of formation of **1** and **2a/b** from **III**, the reversible CO addition/removal between **2a/b** and **1**, and the reversible hydrogen shift between **2a** and **2b** revealed a highly complex picture beyond the scope of this communication. We will report on the results of a computational full mechanism in due course.
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