CO$_2$ Binding and Splitting by Non-Polar Multiple Bonds

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Abstract: *CO$_2$ is found to undergo room-temperature, ambient-pressure reactions with two species containing boron-boron multiple bonds, leading to incorporation of either one or two CO$_2$ molecules. In one case, a thermally-unstable intermediate was structurally characterized, indicating the operation of an initial 2+2 cycloaddition mechanism in the reaction.*

It is widely believed that CO$_2$ has massive implications for climate change, hence a thriving research field has been built around its chemical modification. Even a cursory glance at the literature of chemical CO$_2$ activation shows the clear prominence of strongly polar systems as reagents and catalysts of choice for this process,[1] as could be expected given the polar C=O bonds of the molecule. While CO$_2$-binding species can be based on a wide range of elements from throughout the periodic table, main-group species suitable for this task are attracting growing interest as cheaper and environmentally benign alternatives to metal-containing systems.[2] Particularly notable in this field are frustrated Lewis pairs (FLPs),[3] whose combination of nucleophilic and electrophilic sites are well-suited to combine with the carbon and oxygen atoms of CO$_2$, respectively (Figure 1A). Another common mechanism of main-group-based CO$_2$ activation is the (initial) 2+2 cycloaddition of one C=O bond of CO$_2$ with another E-E multiple bond, e.g. P=N (i.e. the Aza-Wittig reaction), Si=O, Si=N, Ge=O, Sn=O, and B=N bonds (Figure 1B).[4]

To our knowledge, no CO$_2$ fixation or activation has been observed by solely utilizing a nonpolar multiple bond, despite the fact that a range of highly reactive compounds with E-E multiple bonds are known.[5] However, in 2011 Kato and Baceiredo reported[6] the reaction of CO$_2$ with a disilyne bisphosphine adduct, a compound thought to possess some multiple bonding character between its two silicon atoms despite the clearly non-planar geometry around the silicon atoms.

Herein we present fixation and splitting reactions of CO$_2$ through its interaction with distinctly non-polar multiple bonds of two significantly different diboron species:[5c,d,e] a doubly base-stabilized diborene[5,7] with tricoordinate boron atoms and a B=B double bond, and a linear diboryne species bearing strongly π-acidic cyclic (alkyl)(amino)carbene (CAACs) donors,[8] effectively a diboracumulene[9] species with a B-B bond order between two and three. Interestingly, in the reaction of CO$_2$, we were also able to isolate the thermally unstable 2+2 (C=O + B=B) cycloaddition product, which slowly undergoes cleavage of one C=O bond. The apparently facile reaction of CO$_2$ with B-B multiply bound species is attributed to the high reactivity of the latter, which is able to overcome the lack of polarity in the bond and effect the initial cycloaddition step.

A. CO$_2$ activation via frustrated Lewis pairs
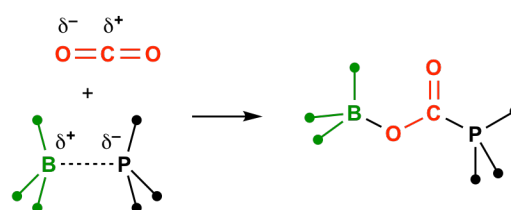
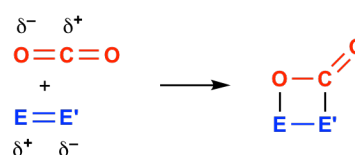### B. CO$_2$ activation via polar multiple bonds

Figure 1. Generalized depiction of the major modes of activation of CO$_2$ by main-group compounds.

Dibromodiborenes (L(Br)B=B(Br)L), very few of which exist in the literature,[10,11] were chosen as candidates for CO$_2$ binding due to their sterically unhindered B=B bonds and thus presumed high reactivity. Upon treatment with one atmosphere of CO$_2$ at room temperature, after 7 min the ^{11}B NMR spectroscopic signal of diborene **1**[10] (δ_B 20) was found to have completely disappeared, replaced by two broad signals (δ_B ca. 0, −10). Removal of the solvent from this mixture and extraction of the residue into hexane provided a solution from which orange crystals (**2**) were grown. The solid-state structure of **2** (Figure 2, middle) confirms the combination of the diborene **1** with CO$_2$ to form a dibora-β-lactone structure in which the two boron atoms form a slightly puckered four-membered B-B-C-O ring with one carbon and one oxygen atom of the CO$_2$ unit. The remaining oxygen atom is part of a carbonyl group with a short C-O distance of 1.20(1) Å but a relatively wide O-C-B angle (136.2(8)°). Interestingly, the endocyclic B-B-C angle is strongly acute (73.7(8)°). The NHC and Br groups are each oriented in a *trans* fashion with respect to the ring.

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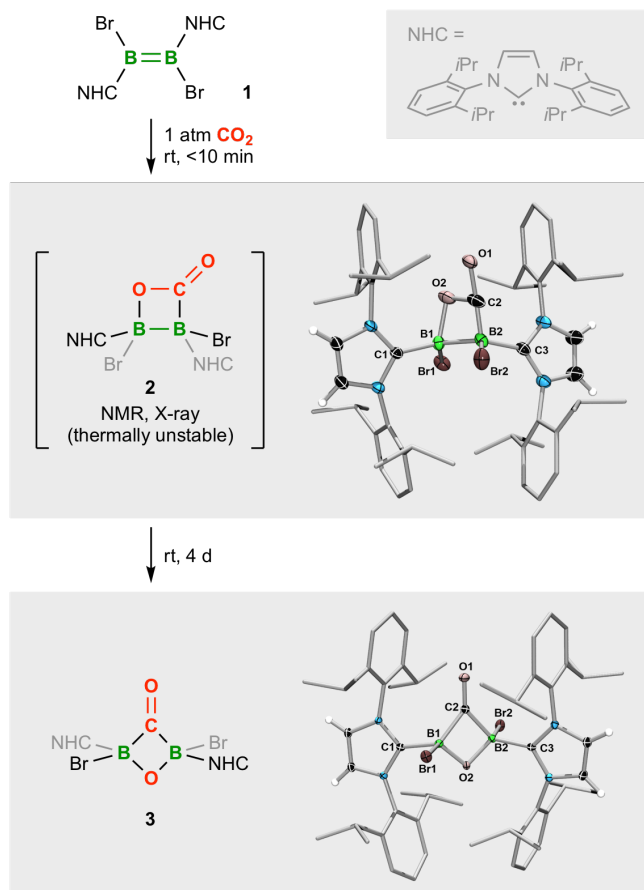
Figure 2. Products of the reaction of diborene **1** with CO$_2$ and their crystallographically derived structures. Ellipsoids shown at the 50% probability level. Some ellipsoids and most hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°) for **2**: B1-B2 1.80(2), B2-C2 1.69(2), C2-O1 1.20(1), C2-O2 1.346(9), B1-O2 1.49(2); B1-B2-C2 73.7(8), B2-C2-O1 136.2(8), O1-C2-O2 124.5(7). For **3**: B1-O2 1.436(2), B2-O2 1.445(2), B1-C2 1.642(2), B2-C2 1.641(3), C2-O1 1.212(2); B1-O2-B2 95.5(1), B1-C2-B2 81.0(1).

Unfortunately, however, dibora-β-lactone **2** could not be isolated in quantity or fully characterized due to its thermal instability, as this compound selectively proceeds to form a new species even in the solid state. This species can be selectively prepared in an 81% yield by stirring a solution of **1** under a CO$_2$ atmosphere for 4 d at rt, followed by removal of solvent, washing with hexane and drying. This new compound, **3**, was also structurally characterized (Figure 2, bottom), showing it to be an isomer of **2** in which one of the C-O bonds has been completely cleaved. The resulting compound is a C_2-symmetric "dibora" analogue of an oxetan-3-one (i.e. a 2,4-diboraoxetan-3-one) in which the two boron atoms are not directly bound but bridged by a single oxygen atom, forming a four-membered B-C-B-O ring. The low precision of the structure of **2** precludes detailed comparison with that of **3**, however, the NHC and Br groups of the latter are similarly *trans*-oriented with respect to the four-membered ring. In contrast to that of **2**, the four-membered ring of **3** is almost perfectly planar. The carbonyl C=O distance (1.212(2) Å) is slightly shorter than those of conventional organic ketones, but slightly longer than those of

structurally-characterized examples of the analogous organic compounds oxetan-3-ones (avg. 1.192 Å, nine examples).[12] The C=O distance of **3** is, however, significantly shorter than that of our previously-published diboryne monocarbonyl (1.249(2) Å), which is lengthened due to π-donation from the strongly π-donating, multiply-bound B$_2$ unit.[13]

Compound **3** exhibits a signal at δ_B 7.0 in its ^{11}B NMR spectrum, and a strongly downfield-shifted quaternary carbon signal at δ_C 278.7 attributable to a diboracarbonyl (B$_2$C=O) carbon nucleus. Although the carbonyl carbon signal of our previously-published diboryne monocarbonyl[13] was not found in its ^{13}C{^{1}H} NMR spectrum, a previously-reported carborane with an exocyclic B$_2$C=O group showed a downfield carbonyl ^{13}C NMR signal at δ_C 205.[14] However, the comparability of this complex with **3** is limited, as the former contains a definitive (albeit nonclassical) B-B bond, while **3** does not. The IR spectrum of **3** contains a distinct signal at 1706 cm^{-1}, attributable to the C=O stretch, which lies in the same region as literature-known aliphatic ketones.[15] It should also be noted that two other dibromodiboranes were tested with CO$_2$, namely [L(Br)B=B(Br)L] (L = 1,3-bis(2,6-diethylphenyl)imidazolin-2-idene, 1,3-bis(2,6-di*iso*propylphenyl)imidazolin-2-idene), both containing NHC ligands with saturated backbones. In marked contrast to **1**, these diborenes did not react with CO$_2$ at room temperature, and upon heating to 60 ºC led only to intractable mixtures.
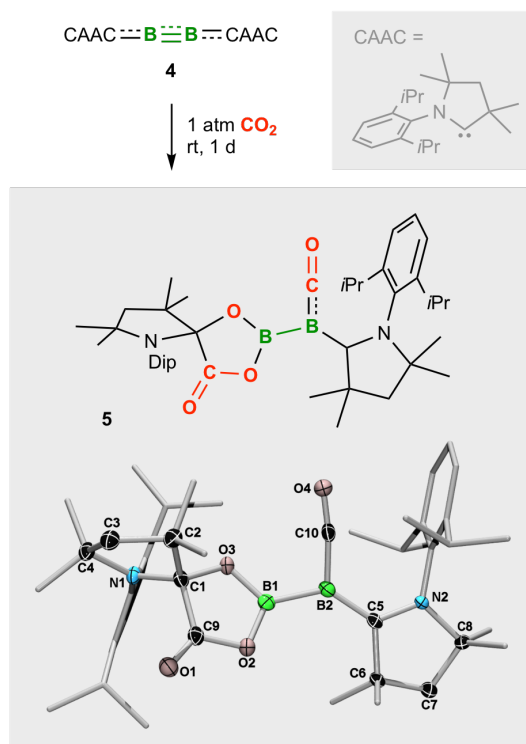

Figure 3. Product of the reaction of diboracumulene **4** with CO$_2$ and its crystallographically derived structure. Ellipsoids shown at the 50% probability level. Some ellipsoids and most hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): B1-B2 1.660(4), B1-O2 1.417(3), B1-O3 1.380(2), C9-O1 1.202(3), C9-O2 1.366(3), B2-C10 1.466(3), C10-O4 1.157(2), B2-C5 1.497(3); B2-C10-O4 171.6(2).
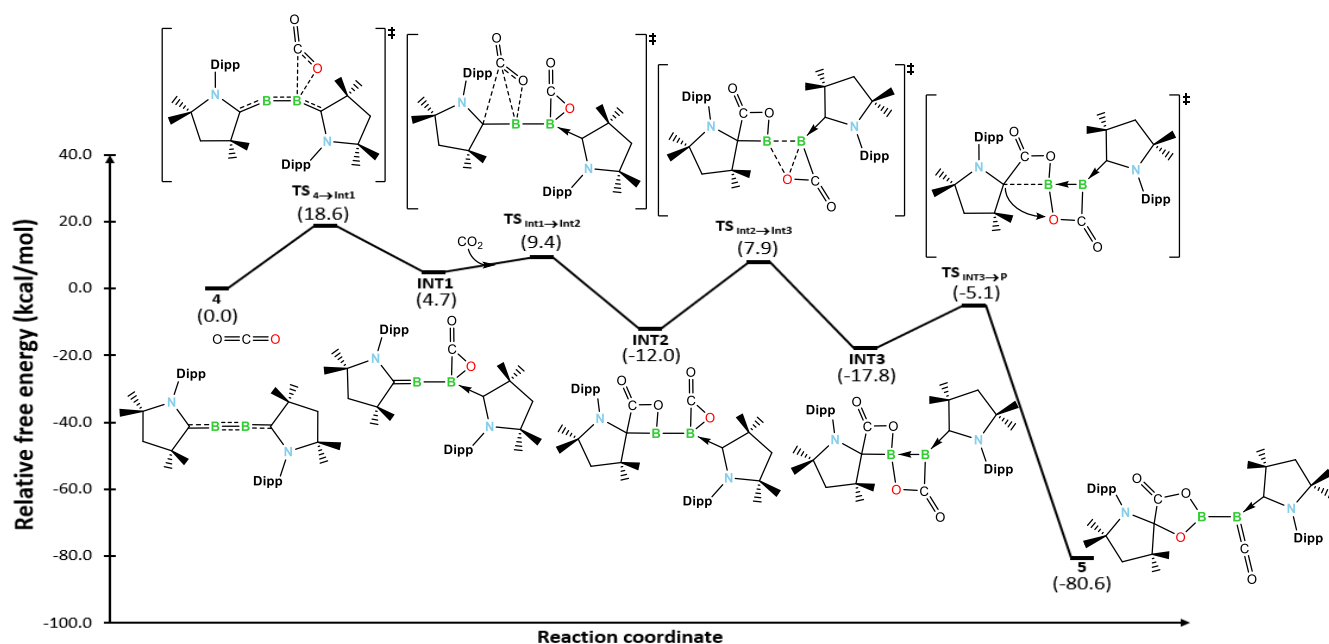
Figure 4. Calculated reaction mechanism of the diboracumulene **4** with CO_2 on the level of a combined semi-empirical-DFT approach.

The diboryne **4**[9] (Figure 3) – also describable as an electron-deficient diboracumulene – has emerged as one of the most reactive members of the diboryne family, presumably due to its strongly π-acidic CAAC donors. Accordingly, we also attempted the reaction of **4** with CO_2. Stirring a purple solution of **4** at room temperature and under an atmosphere of CO_2 resulted in a color change to orange, from which yellow crystals were obtained after workup. This compound, **5** (Figure 3), was found to have two broad ^{11}B NMR signals (δ_B 43.2, –27.1), the former being more broad than the latter, both significantly upfield from that of precursor **4** (δ_B 80). The ^{13}C NMR spectrum of **5** showed low-field signals at δ_C 172.0, 210.4 and 218.2, the former corresponding to a standard carboxyl carbon nucleus of an ester group. The solid-state structure of **5**, shown in Figure 3, explains the two signals observed in the ^{11}B NMR spectrum, with one boron atom effectively a part of a boronate ester group, the other being akin to a CO-bound monovalent borylene species.[16] The structure also indicates that two CO_2 molecules have been combined with **4** to form **5**, one of which has been split to form a boron-bound CO unit. The remaining oxygen atom is incorporated into a spiro system containing one boron atom, one carboxyl group, one oxygen atom and the former carbene carbon atom of the CAAC fragment.

This structure allows us to assign the high-field ^{11}B NMR shift (δ_B –27.1) of **5** to the tricoordinate, monovalent boron center, given the precedence of high-field shifts of CO-bound borylene species, e.g. [DurB(CO)(CAAC)] (δ_B –13.4; Dur = 2,3,5,6-tetramethylphenyl)[17] and [TpB(CO)(CNDip)] (δ_B –28; Tp = 2,6-di(2,4,6-tri*iso*propylphenyl), Dip = 2,6-di*iso*propylphenyl).[18] This shift is also reminiscent of that of the 1,2-bis(borylene) species [(CAAC)(OC)BB(CO)(CAAC)] (δ_B –22),[19] as well as other compounds containing the monovalent [-B(CO)(CAAC)] fragment.[20] The C-O (1.157(2) Å) and B-C (1.466(3) Å) distances of **5** are similar to those of comparable [B(CO)(CAAC)]-containing compounds, as exemplified by [DurB(CO)(CAAC)] (C-O: 1.158(2); B-C: 1.469(2) Å)[17] Strong, sharp signals at 1987 and 1777 cm^{-1} were found in the solid-state IR spectrum of **5**. Similar

to that of **3**, the band at 1777 cm^{-1} can be assigned to the carboxyl C=O double bond of **5**, while the band at 1987 cm^{-1} can be comfortably assigned to the stretching mode of the boraketene C=O unit. This signal is found in a similar range as the CO stretching bands of (terminal) dicarbonyl adducts of diborynes (1928, 1929 cm^{-1}),[19] as well as two other compounds comprising the (CAAC)B(CO) fragment bound through their boron atom to another boron-containing group (1921, 1962 cm^{-1}).[20]

Given the unusual structure of compound **5** and its implication of C=O bond cleavage, we performed DFT calculations to investigate the reaction mechanism of its formation. Although we attempted this using various routes (for example, direct [2+2] cycloaddition, or O→B coordination followed by a nucleophilic attack to obtain the dibora–β–lactone as the presumed intermediate) we failed to describe the cycloaddition step across a C^{CAAC}-B bond. Our proposed mechanism (see Figure 4) considers an initial CO_2 [2+1] cycloaddition at one boron atom, through $TS_{4\rightarrow INT1}$ ($\Delta G^{\ddagger}$ = 18.6 kcal·mol^{-1}), leading to the epoxide **INT1**, which is an endergonic step (4.7 kcal·mol^{-1}). This induces the adoption of a greater double–bond character in the other C^{CAAC}-B bond, thus, the second carbon dioxide promptly attacks the free boron in a similar manner, via transition state $TS_{INT1\rightarrow INT2}$ ($\Delta G^{\ddagger}$ = 4.7 kcal·mol^{-1}), which forms not a three- but a four-membered ring and a C–C bond (**INT2**). This exergonic step stabilizes the system by –16.7 kcal·mol^{-1}. The boraepoxide ring then undergoes a ring expansion transferring the oxygen from one boron to the other via $TS_{INT2\rightarrow INT3}$ ($\Delta G^{\ddagger}$ = 19.9 kcal·mol^{-1}). The resulting double-spiro compound, **INT3**, is located –5.8 kcal·mol^{-1} lower in energy than the previous intermediate. A facile C^{CAAC}–B bond cleavage ($TS_{INT3\rightarrow 5}$; $\Delta G^{\ddagger}$ = 12.7 kcal·mol^{-1}) is then accompanied by the C^{CAAC} atom binding the endocyclic oxygen atom of the nearby diboralactone ring, forming the energetically-favorable planar five–membered ring and boraketene units of the final structure **5**. In sum, this is a very exergonic reaction (–80.6 kcal·mol^{-1}), with the overwhelming majority of the stabilization arising from the final step (**INT3** to **5**).

The mild fixation and splitting of CO_2 by nonpolar multiple bonds reported herein is an unusual reactivity pattern for this substrate, which, thanks to its polar C=O bonds, tends to react much more easily with strongly polar or charged reagents. The combination of two CO_2 molecules with diboracumulene **4**, with accompanying boron-carbon bond cleavage, suggests that the carbene carbon atoms of **1** and **4** may assist in the fixation process.

Acknowledgements

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