CO₂ Binding and Splitting by Non-Polar Multiple Bonds

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Abstract: CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂-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 CO₂, respectively (Figure 1A). Another common mechanism of main-group-based CO₂ activation is the (initial) 2+2 cycloaddition of one C=O bond of CO₂ 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 CO₂ 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 CO₂ with a disilene 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 CO₂ through its interaction with distinctly non-polar multiple bonds of two significantly different diboron species,[6c,6d] a doubly base-stabilized diborene[5,7] with tricoordinate boron atoms and a B=B double bond, and a linear diborene 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 CO₂, 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 CO₂ 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. CO₂ activation via frustrated Lewis pairs

![Figure 1](image-url)

Figure 1. Generalized depiction of the major modes of activation of CO₂ by main-group compounds.

Dibromodiborenes (L(Br)=B(Br)L), very few of which exist in the literature,[6h,8,10,11] were chosen as candidates for CO₂ binding due to their sterically unhindered B-B bonds and thus presumed high reactivity. Upon treatment with one atmosphere of CO₂ at room temperature, after 7 min the $^{13}$B NMR spectroscopic signal of diborene 1[10] (δB 20) was found to have completely disappeared, replaced by two broad signals (δB 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 CO₂ 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 CO₂ 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 NHCl and Br groups are each oriented in a trans fashion with respect to the ring.

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of conventional organic ketones, but slightly longer than those of carbonyl C=O distance (1.212(2) Å) is slightly shorter than those 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). 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= unit.

Compound 3 exhibits a signal at δB 7.0 in its 11B NMR spectrum, and a strongly downfield-shifted quaternary carbon signal at δC 127.8 attributable to a diboracarbonyl (B=O) carbon nucleus. Although the carbonyl carbon signal of our previously-published diboryne monocarbonyl was not found in its 13C(H) NMR spectrum, a previously-reported carborane with an exocyclic B=O group showed a downfield carbonyl 13C NMR signal at δC 205. 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.

Unfortunately, however, dibora-ji-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 CO2 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 C2-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...
The diboryne \( \text{DurB(CO)(CAAC)} \) (Figure 3) – also describable as an electron-deficient diboraculene – has emerged as one of the most reactive members of the diboryne family, presumably due to its strongly rπ-acidic CAAC donors. Accordingly, we also attempted the reaction of \( \text{DurB(CO)(CAAC)} \) with \( \text{CO}_2 \). Stirring a purple solution of \( \text{DurB(CO)(CAAC)} \) at room temperature and under an atmosphere of \( \text{CO}_2 \) resulted in a color change to orange, from which yellow crystals were obtained after workup. This compound, \( \text{DurB(CO)(CAAC)} \) (Figure 3), was found to have two broad \( ^{13}\text{B} \) NMR signals (\( \delta_5 \) 43.2, -27.1), the former being more broad than the latter, both significantly upfield from that of precursor \( \text{DurB(CO)(CAAC)} \) (\( \delta_6 \) 80). The \( ^{13}\text{C} \) NMR spectrum of \( \text{DurB(CO)(CAAC)} \) showed low-field signals at \( \delta_\text{C} \) 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 \( \text{DurB(CO)(CAAC)} \), shown in Figure 3, explains the two signals observed in the \( ^{13}\text{B} \) NMR spectrum, with one boron atom effectively a part of a boronate ester group, the other being akin to the \( ^{13}\text{C} \) NMR signals (\( \delta_\text{C} \) 1987 and 1927 cm\(^{-1}\)) of comparable \( \text{DurB(CO)(CAAC)} \) fragments. Accordingly, we also attempted this using various routes (for example, direct \([2+2]\) cycloaddition, or \( \text{O} \rightarrow \text{B} \) coordination followed by a nucleophilic attack to obtain the dibora-\( \beta \)-lactone as the presumed intermediate) we failed to describe the cycloaddition step across a \( \text{CO}_2 \text{CAAC} \) bond. Our proposed mechanism (see Figure 4) considers an initial \( \text{CO}_2 \) \([2+1]\) cycloaddition at one boron atom, through \( \text{TS}_{\text{INT1}} \) (\( \Delta G^1 = 18.6 \text{ kcal-mol}^{-1} \)), leading to the epoxide \( \text{INT1} \), which is an endergonic step (4.7 kcal-mol\(^{-1}\)). This induces the adoption of a greater double–double bond character in the other \( \text{CO}_2 \text{CAAC} \) bond, thus, the second carbon dioxide promptly attacks the free boron in a similar manner, via transition state \( \text{TS}_{\text{INT1,INT2}} \) (\( \Delta G^2 = 4.7 \text{ kcal-mol}^{-1} \)), which forms a three- but a four-membered ring and a C–C bond (\( \text{INT2} \)). This exergonic step stabilizes the system by \(-16.7 \text{ kcal-mol}^{-1}\). The boraepoxide ring then undergoes a ring expansion transferring the oxygen from one boron to the other via \( \text{TS}_{\text{INT2,INT3}} \) (\( \Delta G^3 = 19.9 \text{ kcal-mol}^{-1} \)). The resulting double-spiro compound, \( \text{INT3} \), is located \(-5.8 \text{ kcal-mol}^{-1}\) lower in energy than the previous intermediate. A facile \( \text{CO}_2 \text{CAAC} \)-bond cleavage \( \text{TS}_{\text{INT3,INT4}} \) (\( \Delta G^4 = 12.7 \text{ kcal-mol}^{-1} \)) is then accompanied by the \( \text{CO}_2 \text{CAAC} \) atom binding the endocyclic oxygen atom of the nearby diboralactone ring, forming the energetically-favorable planar five–membered ring and boraketenone units of the final structure \( \text{INT5} \). In sum, this is a very exergonic reaction (\(-80.6 \text{ kcal-mol}^{-1}\)), with the overwhelming majority of the stabilization arising from the final step (\( \text{INT3 to INT5} \)).
The mild fixation and splitting of CO₂ 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 CO₂ 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.

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