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COMMUNICATION

Selective CO₂ Splitting by Doubly Reduced Aryl Boranes to Give CO and [CO₃]²⁻

Esther von Grotthuss, Sven E. Prey, Michael Bolte, Hans-Wolfram Lerner, and Matthias Wagner*

Abstract: Alkali metal salts M₂[**1**] (M = Li, Na) of doubly reduced 9,10-dimethyl-9,10-dihydro-9,10-diboraanthracene (**1**) instantaneously add the C=O bond of CO_2 across their boron centers to furnish formal [4+2]-cycloadducts M₂[**2**]. If only 1 equiv of CO_2 is supplied, these products are stable. In the presence of excess CO_2, however, C–O-bond cleavage occurs and an O^{2-} equivalent is transferred to CO_2 to furnish CO and $[CO_3]^{2-}$. With M = Li, Li_2CO_3 precipitates and the neutral **1** is liberated such that it can be reduced again to establish a catalytic cycle. With M = Na, $[CO_3]^{2-}$ remains coordinated to both boron atoms in a bridging mode (Na₂[**4**]). A mechanistic scenario is proposed, based on isolated intermediates and model reactions.

The exhaust gas CO_2 has long been neglected as a ubiquitous and potentially valuable C_1 building block for chemical synthesis. Today, however, this situation is dramatically changing, driven by the general awareness that fossil oil and gas are limited resources and that the accumulation of CO_2 in the earth's atmosphere significantly contributes to climate change.[1] Conversion of the thermodynamically stable CO_2 molecule into useful chemicals requires the input of energy and reduction equivalents. As an additional challenge, high-pressure conditions are only avoidable with the help of carefully designed catalysts.

Prospective technologies for the renewable production of organic compounds from CO_2 are often based on the heterogeneous $CO_2 \rightarrow CO$ electroreduction at metal surfaces and nanoparticles (*e.g.*, Cu, Ag, Au),[2-4] Bi-modified glassy carbon cathodes,[5] or metal-organic frameworks.[6] Common obstacles include high electrode overpotentials, low energetic efficiencies, rapid deactivation of the systems, and poor product selectivities.[3] The one-electron reduction of CO_2 occurs only at very cathodic potential values, mainly because of the energy penalty associated with bending of the linear molecule upon electron uptake to furnish the $[CO_2]^{\cdot-}$ radical. Correspondingly, the bent $[CO_2]^{\cdot-}$ is predisposed to accept a second electron.[1a] Some transition-metal compounds can act as nucleophiles toward CO_2 molecules and thereby transfer two electrons simultaneously onto the substrate, which is afterwards stabilized through π backbonding (see below). Indeed, several metal complexes exist that are capable of achieving the $CO_2 \rightarrow CO$ reduction under mild conditions, albeit not always in a catalytic fashion.[7-10]

Since the advent of frustrated Lewis pair (FLP) chemistry, increasing efforts have been devoted to the replacement of transition-metal catalysts by appropriate combinations of main-group Lewis acids and bases. In the context of CO_2 activation, a plethora of capture products such as $R_3P–C(O)–O–BR'_3$ are nowadays known. Follow-up reactions with various reducing agents have been studied and the palette of obtainable compounds encompasses CO, HC(O)OH, H_3COH, and CH_4.[11] Despite these impressive achievements, examples of catalytic CO_2 reductions with FLPs are still scarce and often require drastic reaction conditions, extended periods of time, as well as rather expensive hydride donors (*e.g.*, $HB(OR)_2$, $HSiR_3$). The reduction products are mainly obtained in the form of organyloxyboranes and -silanes (*e.g.*, $H_3CO–B(OR)_2$) and the released O atoms appear incorporated in dibor- or disiloxanes (*e.g.*, $(RO)_2B–O–B(OR)_2$).[11]

In the quest for more atom economic main-group reduction catalysts, arylboranes with two cooperating boron centers and the ability to accept two electrons from an electropositive metal or a negative electrode bear particular promise. In 2010, our group reported the activation of C(sp)–H ([**B**]²⁻) and C=O ([**C**]²⁻) bonds by the doubly reduced 9,10-dihydro-9,10-diboraanthracene [**A**]²⁻ (Scheme 1a).[12, 13] Later we also succeeded in the cleavage of H_2 on the [**A**]²⁻ platform and proposed a concerted addition of the H_2 molecule to the two
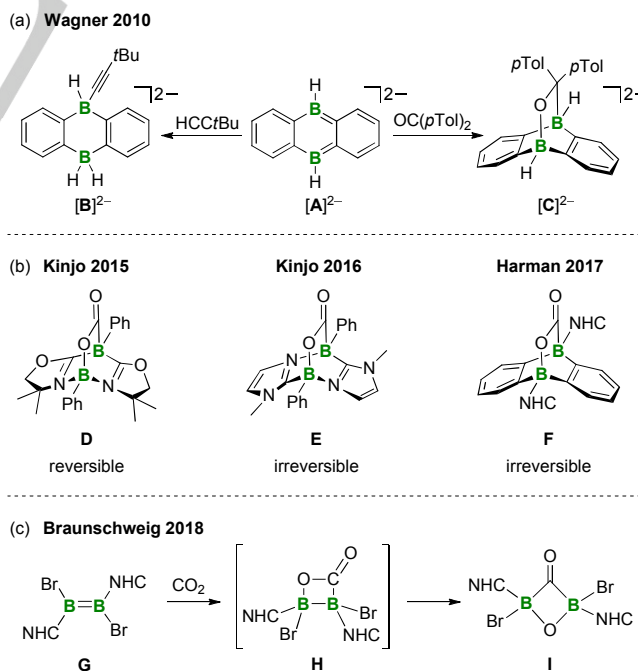

Scheme 1. (a) Activation of C(sp)–H and C=O bonds by a doubly reduced 9,10-dihydro-9,10-diboraanthracene ([**A**]²⁻). (b) Cycloaddition products of CO_2 with neutral boron-containing heterocycles (**D-F**). (c) Reaction of the diborene **G** with CO_2 to furnish **I** *via* **H**. NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

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Supporting information for this article (including all experimental procedures together with further spectroscopic, crystallographic, and computational details) is available on the WWW under http://...

boron atoms.[14] In the meantime, related systems have been disclosed by Kinjo[15, 16] and Harman[17] and shown to add CO_2 through one of its C=O bonds (**D**-**F**; Scheme 1b). Even under a CO_2 atmosphere no further transformation took place. Braunschweig et al. encountered a different situation when they treated the diborene **G** with CO_2 (Scheme 1c).[18] As a thermally unstable primary intermediate, they observed the dibora-β-lactone **H**, which rearranged with CO_2 splitting to form the isomeric 2,4-diboraoxetan-3-one **I**.

Herein, we report that reactions of CO_2 with alkali metal salts M_2[**1**] (M = Li, Na; cf. Scheme 2) do not stop at the stage of **F**-type cycloadducts, but proceed further to furnish CO and O^{2-} equivalents. Contrary to the stoichiometric system **G**-**I**, however, CO is released and the O^{2-} equivalent transferred to CO_2 with formation of $[CO_3]^{2-}$. The reaction is quantitative and the scaffold of **1** remains fully intact, which renders the system catalytic.

Stirring of the known **1**[19] in THF over lithium or sodium metal quantitatively provides the respective M_2[**1**] salts. Exposure of a red solution of Li_2[**1**] in [D_8]THF to excess CO_2 resulted in an immediate decolorization (room temperature, 1 atm). After an induction period of several minutes, gas evolution set in, accompanied by the formation of a colorless precipitate (Scheme 2). An NMR spectroscopic investigation of the supernatant after 30 min revealed the selective and quantitative conversion of Li_2[**1**] to **1**. A solution of the precipitate in D_2O
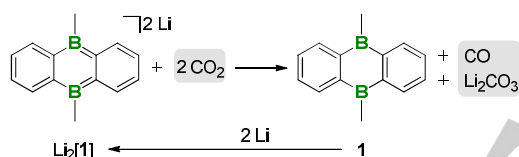
Scheme 2. Highly selective transformation of CO_2 to CO and Li_2CO_3 with lithium metal and **1** as the redox catalyst (THF, room temperature, 1 atm).

showed only one resonance in the $^{13}C\{^1H\}$ and one in the ^7Li NMR spectrum (δ = 167.7 and 0.11 ppm, respectively). Moreover, the precipitate gave rise to a prominent IR stretch at 1435 cm^{-1} with a shoulder at higher wavenumbers. These values are in accordance with corresponding data recorded on commercial samples of Li_2CO_3. On a preparative scale, Li_2[**1**] and CO_2 gave Li_2CO_3 in yields of 83%. When the reaction was carried out in a sealed NMR tube, also the resonances of newly formed CO ($\delta(^{13}C)$ = 184.9 ppm[20]) and residual CO_2 ($\delta(^{13}C)$ = 125.7 ppm[21]) were detected. Further evidence for the formation of CO was gathered from a chemical analysis technique based on the reduction of colorless, aqueous $PdCl_2$ to black Pd metal.[22] In conclusion, 1 equiv of Li_2[**1**] transforms 2 equiv of CO_2 into 1 equiv of CO and 1 equiv of Li_2CO_3. Importantly, the reaction can also be performed in a catalytic fashion: as a proof of principle, we have treated the **1**-containing supernatant first with lithium metal, then with CO_2, and harvested a second crop of Li_2CO_3/CO.

Given that the rate of H_2 activation with M_2[**A**] salts is significantly influenced by the choice of the counter cation M^+,[14] the CO_2 reduction was next repeated with the green-colored Na_2[**1**]. An X-ray crystal-structure analysis of the polymeric inverse sandwich complex [$Na_2(thf)_3$][**1**] is shown in Figure 1 (av.

Na···COG = 2.268 Å; COG: centroid of the B_2C_4 ring). Upon addition of CO_2, decolorization of the solution and CO evolution occurred as before, but no Na_2CO_3 precipitated and the reaction mixture also contained no free **1**. Rather, the ^{11}B NMR spectrum was characterized by a broad resonance at 2.7 ppm, indicating tetracoordinate boron nuclei.[23] In line with that, the three signals observed in the ^1H NMR spectrum [7.25 (4H), 6.71 (4H), 0.31 (6H) ppm] and the corresponding ^{13}C resonances were considerably shifted upfield compared to those of **1**. An additional ^{13}C signal appeared at δ = 163.5 ppm and the IR spectrum of the product contained two strong stretches in the carbonyl region ($\tilde{\nu}$ = 1399, 1523 cm^{-1}). Taken together, the spectroscopic results indicated the presence of a symmetric diadduct of **1**, which was finally identified as the $[CO_3]^{2-}$ complex Na_2[**4**] by X-ray crystallography. The thf-solvated salt forms C_1-symmetric tetramers [$Na_8(thf)_{14}$][**4**]$_4$ in the solid state (see the Supporting Information). The bicyclo[3.2.2] ion [**4**]$^{2-}$ acquires its negative charges from a bridging $[CO_3]^{2-}$ ion (Figure 1). The average lengths of the formal C=O double and C–OB single bonds are 1.252 Å and 1.302 Å, respectively,[24] with an unstrained O–C–O bond angle of 123°. The comparatively large spread of the individual B–O bond lengths (1.600(8)-1.646(8) Å) indicates a soft bonding potential. Together with the large average B–O bond length of 1.626 Å,[25] this points toward a weak interaction. Consequently, the extra thermodynamic driving force provided by the higher lattice energy of Li_2CO_3 vs Na_2CO_3 (ΔU_{POT} = 2523 vs 2301 kJ mol^{-1})[26] suffices to cause the precipitation of the former while the latter remains coordinated to the ditopic Lewis acid **1**.

We next treated M_2[**1**] (M = Li, Na) with only 1 equiv of CO_2. The bicyclo[2.2.2] adducts M_2[**2**] formed quantitatively (Scheme 3a).[27] Na_2[**2**] gives rise to two ^{11}B NMR signals: a broad one at δ = 2.0 ppm, similar to the $[CO_3]^{2-}$ adduct Na_2[**4**], is assignable to the BO atom. A sharp one at δ = –14.6 ppm corresponds to the boron center attached to the carbonyl carbon atom. The carbonyl ^{13}C resonance (δ = 219.9 ppm; cf. **F**: 198.4 ppm) is
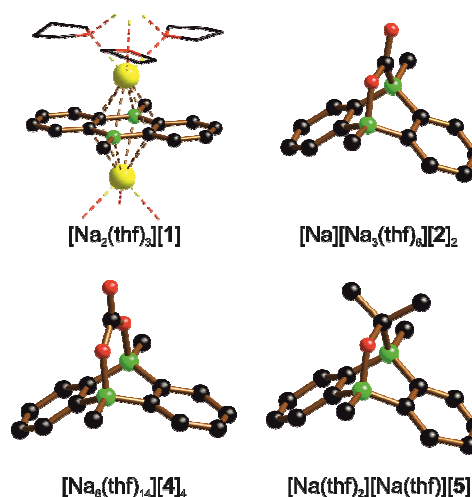

Figure 1. Molecular structures of [$Na_2(thf)_3$][**1**], [Na][$Na_3(thf)_6$][**2**]$_2$, [$Na_8(thf)_{14}$][**4**]$_4$, and [$Na(thf)_2$][$Na(thf)$][**5**] in the solid state. Na$^+$ cations and coordinating thf molecules are only shown for [$Na_2(thf)_3$][**1**]; all CH atoms are omitted for clarity.

broadened almost beyond detection due to the effect of the boron quadrupole moment. According to the overall numbers and patterns of the ^1H and ^{13}C NMR signals, $[2]^{2-}$ possesses average C_s symmetry in solution. The NMR data of $Li_2[2]$ are essentially the same as those of $Na_2[2]$. Single crystals of $[Na][Na_3(thf)_6][2]_2$ grew directly from the reaction mixture. Its solid-state structure contains two crystallographically independent $[2]^{2-}$ ions with identical geometric parameters within experimental error (Figure 1). The B–O bond length of $[2]^{2-}$ (av. 1.589 Å) lies between that of Harman's neutral derivative **F** (1.509(2) Å) and that of the $[CO_3]^{2-}$ adduct $[Na_8(thf)_{14}][4]_4$ (av. 1.626 Å). The formal C–O single bond of the CO_2 bridge in $[2]^{2-}$ (av. 1.319 Å) is longer by 0.053 Å than the C=O double bond (av. 1.266 Å). The primary C=O-activation step is reminiscent of common [4+2]-cycloaddition reactions across the two central carbon atoms of anthracene,[28] an isoelectronic analog of $[1]^{2-}$. Alternatively, one can view the $[1]^{2-}$ ion as containing ambiphilic boron centers, which concertedly act on the substrate as a frustrated B^{+I}/B^{+III} Lewis pair (see the resonance form $M_2[1]^*$ in Scheme 3a).[16] Analogous to the μ-$[CO_3]^{2-}$ adduct $Na_2[4]$, the primary product $Na_2[2]$ may be described as featuring a $[CO_2]^{2-}$ dianion, simultaneously bonded to the two boron atoms of neutral **1**.

When $M_2[2]$ was put under a blanket of CO_2 ($[D_8]THF$, room temperature, 1 atm), we obtained the same product mixtures as before when we had treated $M_2[1]$ directly with excess CO_2, which confirmed the role of $M_2[2]$ as an intermediate in the CO_2-reduction sequence. The elongated B–O bond likely constitutes the weak link of $[2]^{2-}$ and the site of attack of a second CO_2 molecule, which reacts through the insertion of one C=O bond. A plausible mechanism of this insertion involves an equilibrium in which ring-opening occurs through B–O bond heterolysis. The transient intramolecular B/O-FLP could activate the substrate CO_2 in the usual manner to afford compound $M_2[3]$ (Scheme 3a). Its $[R_3B–O–C(O)–O–C(O)–BR_3]^{2-}$ fragment has a structural analog in the mixed carboxylic-carbonic anhydrides (MCCAs) $R_3C–O–C(O)–O–C(O)–CR_3$,[29] which often suffer from low stability. In the case of $[3]^{2-}$, decomposition is even too rapid to allow an NMR-spectroscopic characterization. The molecular structure of this putative intermediate was therefore investigated by quantum-chemical calculations. The computed dianion $[3^c]^{2-}$ represents a local minimum on the energy surface (Figure 2). Regarding the release of CO, the most noteworthy structural peculiarity lies in the pronounced difference between the two $C(sp^2)$–O bond lengths within the central C–O–C unit: the one belonging to the CO_3 moiety is 1.357 Å, whereas the one belonging to the CO_2 fragment amounts to 1.437 Å. We therefore assume that the latter heterolytically dissociates in the course of the subsequent reaction step, whereupon a species is formed, which contains an η^1-coordinated $[CO_3]^{2-}$ ligand on one boron atom and a CO ligand on the other. Ample precedence exists for R_3B–CO complexes and association/dissociation equilibria with their free components R_3B/CO.[30] In this vein, loss of CO should readily occur also in the present situation and the generated Lewis-acidic B center can subsequently bind to the $[CO_3]^{2-}$ ligand to give the μ-complex $M_2[4]$, which persists in the case of M = Na, but dissociates in the case of M = Li. We note that the mechanistic scenario outlined in Scheme 3a is strikingly similar to the CO_2-activation reaction mediated by the transition-
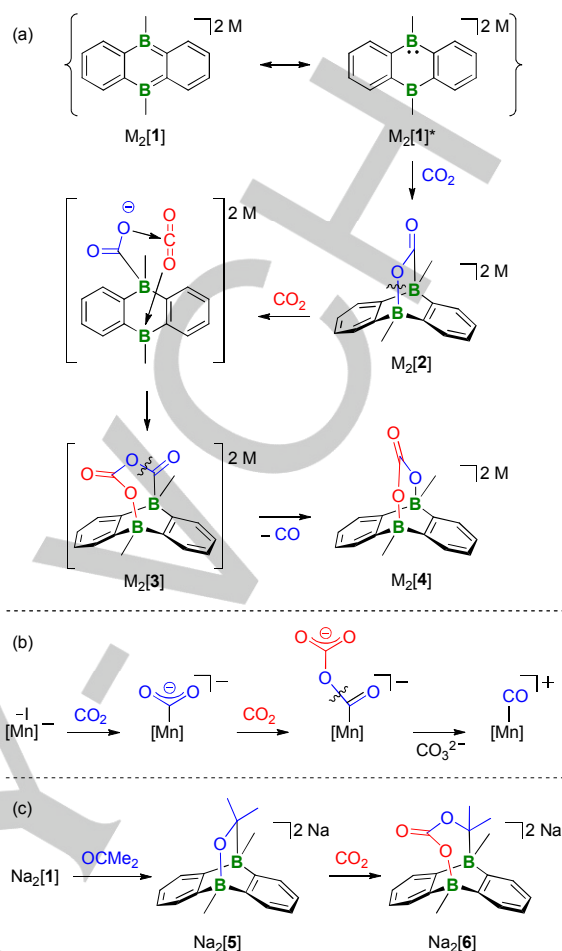
Scheme 3. (a) Proposed mechanism for the reaction of $M_2[1]$ (M = Li, Na) with CO_2. (b) Related transformation mediated by the anionic *fac*-$[Mn^{-I}(CO)_3(bis^{-Me}NHC)]^-$ complex containing a methylene bis(*N*-methylimidazol-2-ylidene) ligand. (c) Stable model complex $Na_2[6]$ of the putative intermediate $Na_2[3]$, obtained by treatment of $Na_2[1]$ with acetone and then with CO_2.

metal complex *fac*-$[Mn^{+I}(CO)_3(bis^{-Me}NHC)Br]$ with a chelating methylene bis(*N*-methylimidazol-2-ylidene) ligand (Figure 3b):[10] In the course of the catalytic cycle, the metal-centered HOMO of an electrogenerated $[Mn^{-I}]^-$ intermediate nucleophilically attacks an incoming CO_2 molecule and forms a $[Mn^{+I}–CO_2]^-$ anion, which subsequently chains up with a second equivalent of CO_2. Finally, $[CO_3]^{2-}$ dissociates from the complex to leave a $[Mn^{+I}–CO]^+$ cation behind.

In order to gain further proof for the intermediacy of $Na_2[3]$, we decided to replace the carbonyl group marked in blue in Scheme 3a by a CMe_2 group, which should be less easily extricable than CO. The addition of 1 equiv of acetone to $Na_2[1]$ gave
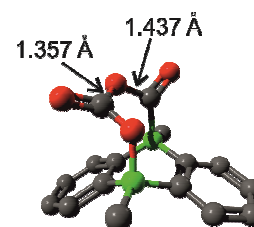

Figure 2. Calculated structure of $[3^c]^{2-}$ at the PBE0D/TZVP level of theory with the SMD polarized continuum model for solvation in THF.

Na$_2$[**5**] in a clean reaction (Scheme 3c). X-ray crystallography on [Na(thf)$_2$][Na(thf)][**5**] (Figure 1) revealed a B–O bond length of 1.562(6) Å, which is shorter by 0.027 Å than that of [Na][Na$_3$(thf)$_6$][**2**]$_2$, but still longer by 0.053 Å than that of Harman's CO$_2$-inert adduct **F**. Upon exposure to CO$_2$ (room temperature, 1 atm), Na$_2$[**5**] was converted further to Na$_2$[**6**] (Scheme 3c). The NMR spectra of this product are in line with the uptake of 1 equiv of CO$_2$: (i) all ^{1}H, ^{11}B, and ^{13}C{^{1}H} resonances were shifted compared to the starting material Na$_2$[**5**], but the signal patterns remained compatible with a bridged derivative of **1** with average C_s symmetry. (ii) A new ^{13}C{^{1}H} resonance appeared at $\delta = 159.1$ ppm, which we assign to the carbonyl carbon atom of the activated CO$_2$ molecule (cf. the [CO$_3$]$^{2-}$ signal of Na$_2$[**4**] at $\delta = 163.5$ ppm). (iii) The IR spectrum of Na$_2$[**6**] (but not of Na$_2$[**5**]) contains strong absorption bands at $\tilde{\nu} = 1358$ and 1397 cm^{-1}, in the typical region of C=O stretches. Notably, even if the reaction was carried out in a sealed NMR tube, no resonance of CO could be detected. This result strongly indicates that the CO released in the course of the reaction between M$_2$[**1**] and CO$_2$ indeed originates from the first incorporated molecule of CO$_2$.

To conclude, the presence of 9,10-dimethyl-9,10-dihydro-9,10-diboraanthracene (**1**) as a redox catalyst enables the clean reduction of CO$_2$ with lithium metal under ambient conditions and with selective formation of CO and Li$_2$CO$_3$ (the main products of the corresponding uncatalyzed reaction are Li$_2$O and elemental carbon[31]). Notwithstanding the relevance of Li$_2$CO$_3$ for the chemical and pharmaceutical industry,[32] it would be desirable to prepare also Na$_2$CO$_3$ in the same way. The reaction currently stops at the stage of an isolable Na$_2$CO$_3$–**1** aggregate, but our system offers multiple options to promote the release of Na$_2$CO$_3$, e.g., by adjusting the steric demand of the boron-bonded substituents.

Keywords: boron • CO$_2$ activation • electrocatalysis • main-group ambiphile • reduction

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COMMUNICATION

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Two in one sweep: A doubly reduced 9,10-diboraanthracene splits CO_2 quantitatively and under ambient conditions to give CO and carbonate ions. If lithium metal is used as the reducing agent, Li_2CO_3 precipitates from the reaction mixture and the CO_2 reduction process becomes catalytic.
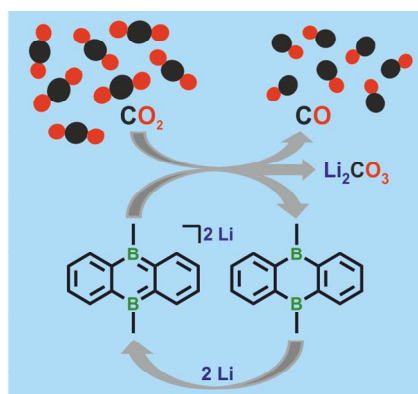
E. von Grotthuss, S. E. Prey, M. Bolte, H.-W. Lerner, and M. Wagner*

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Selective CO_2 Splitting by Doubly Reduced Aryl Boranes to Give CO and $[CO_3]^{2-}$