Communication

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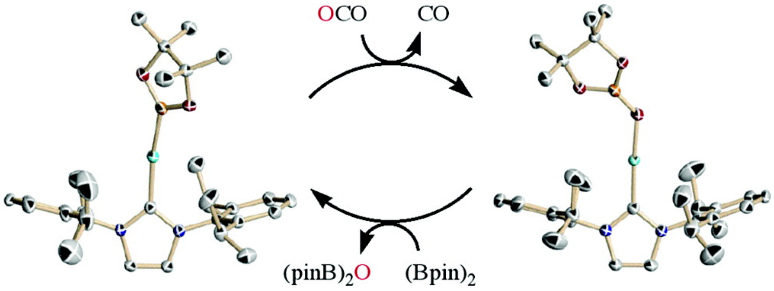

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Efficient Homogeneous Catalysis in the Reduction of CO_2 to CO

David S. Laitar, Peter Müller, and Joseph P. Sadighi*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge Massachusetts 02139

Received September 28, 2005; E-mail: jsadighi@mit.edu

Nature uses carbon dioxide, on a massive scale, as a one-carbon building block for the synthesis of organic molecules.[1] An important pathway for the consumption of CO_2 is its reduction to CO by the enzyme acetyl-CoA synthase/CO dehydrogenase (ACS−CODH).[2] Due to the large energy input required to generate it from CO_2, CO is produced industrially from fossil fuels.[3] Even with strong reducing agents, however, overcoming the O═CO bond enthalpy of 532 kJ/mol[4] often presents kinetic difficulties.[5,6]

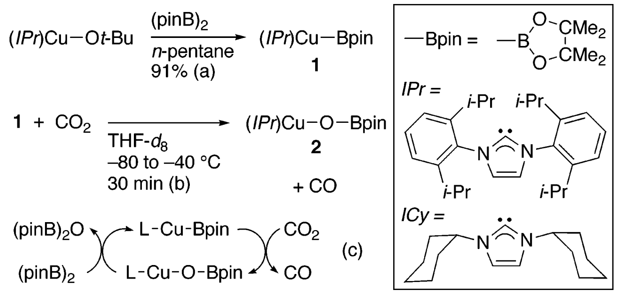
Certain metal complexes abstract oxygen readily from CO_2,[7] but the resulting metal−oxygen bonds are necessarily strong, and catalytic turnover is rare.[8] Photolytic[9] and photocatalytic[10] approaches show promise, and synthetic electrocatalysts have achieved impressive yields and selectivities in the reduction of CO_2 to CO.[11] However, the chemical processes involved are obscure, making it difficult to improve these systems by design, and CODH remains notably the most efficient catalyst for this reduction.[12] We report herein that a new carbene-supported copper(I) boryl complex abstracts oxygen from CO_2 and undergoes subsequent turnover readily. Using an easily handled diboron reagent as the net oxygen acceptor,[13] these key steps permit unprecedented turnover numbers and frequencies for the chemical reduction of CO_2 to CO in a homogeneous system.

While exploring the chemistry of organocopper(I) complexes supported by N-heterocyclic carbene (NHC) ligands,[14] we sought to synthesize a copper(I) boryl complex and explore its reactivity toward CO_2. Metal boryls often display distinctive reactivity,[15] catalyzing a number of remarkable transformations.[16] Although C−B bond-forming reactions have been achieved using diboron compounds with catalytic[17a] or stoichiometric[17b] copper(I), well-defined copper boryl complexes have not been described.

The known (*IPr*)Cu(O*t*-Bu) reacts rapidly with bis(pinacolato)-diboron (pinB−Bpin), forming a product identified as (*IPr*)Cu(Bpin) (**1**, Scheme 1) by ^{1}H and ^{11}B NMR spectroscopy. Diffusion of hexane vapor into a concentrated solution of **1** in toluene, carried out at −40 °C to avoid thermal decomposition,[18] produces single crystals suitable for analysis by X-ray diffraction. The resulting structure (Figure 1a) shows a monomeric, nearly linear coordination geometry with a Cu−B distance of 2.002(3) Å.

Complex **1** reacts with CO_2 under atmospheric pressure in C_6D_6 solution, quantitatively forming a new complex within minutes. The resonance for **1** in the ^{11}B NMR spectrum, a broad singlet at 41.7 ppm, is replaced by a singlet at 21.8 ppm, indicative of boron bound to three oxygen atoms.[19] Single crystals of this new copper complex are grown by diffusion of hexane vapor into a concentrated toluene solution. The X-ray crystal structure (Figure 1b) reveals the product to be (*IPr*)Cu(OBpin) (**2**): The copper boryl complex abstracts oxygen from CO_2, implying the release of CO as the byproduct.

Scheme 1 ^{a}



^{a} Isolated yield, contains some **2** (5 mol % by ^{11}B NMR); (b) reaction is complete in <10 min at ambient temp; (c) L = *IPr* or *ICy*.

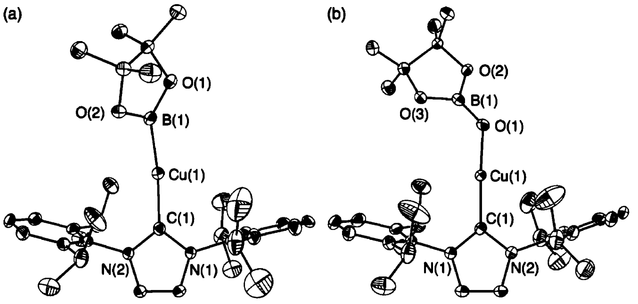


Figure 1. X-ray crystal structures, shown as 50% thermal ellipsoids, of boryl complex $\mathbf{1}\cdot C_6H_{14}$ (a), and borate $\mathbf{2}\cdot C_7H_8$ (b). Hydrogen atoms (calcd) and solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg), (a): Cu(1)−B(1) 2.002(3), Cu(1)−C(1) 1.937(2), C(1)−N(1) 1.363(3), C(1)−N(2) 1.363(3), C(1)−Cu(1)−B(1) 168.07(16), N(1)−C(1)−N(2) 102.97(18); (b): Cu(1)−O(1) 1.8096(16), O(1)−B(1) 1.306(3), Cu(1)−C(1) 1.857(2), C(1)−N(1) 1.355(3), C(1)−N(2) 1.364(3), C(1)−Cu(1)−O(1) 174.85(10), B(1)−O(1)−Cu(1) 133.61(16), N(1)−C(1)−N(2) 103.09(18).

To confirm the formation of CO, ^{13}C-labeled CO_2 is introduced to a resealable NMR tube containing a solution of **1** in THF-d_8 at −80 °C. After 30 min of gradual warming, analysis by ^{11}B (Figure 2a) and ^{1}H NMR spectroscopy at −40 °C indicates complete conversion of **1** to **2**. The sole labeled products visible in the ^{13}C NMR spectrum (Figure 2b) are ^{13}CO (*δ* 184 ppm) and an adduct (*δ* 164 ppm) formed reversibly from CO and borate **2**.[20]

Treatment of **2** in C_6D_6 solution with pinB−Bpin smoothly regenerates **1**, forming the stable byproduct pinB−O−Bpin,[21] over a reaction time of about 20 min. The success of this turnover step closes a catalytic cycle for the deoxygenation of CO_2. Addition of a THF solution of (*IPr*)Cu(O*t*-Bu) to a 100-fold excess of pinB−Bpin under an atmosphere of CO_2 results in the complete conversion of pinB−Bpin to pinB−O−Bpin within 20 h at ambient temperature, as judged by ^{11}B NMR analysis of an aliquot from the reaction mixture (Figure 3a). When labeled CO_2 is used as the limiting reagent, in the presence of ca. 2 mol % of precatalyst **1**, the ^{13}C NMR spectrum indicates complete consumption of CO_2, with CO representing the sole significant product (Figure 3b).

In the absence of copper catalyst, under otherwise identical conditions, no pinB−O−Bpin is detected, demonstrating that the diboron compound by itself is kinetically unable to reduce CO_2 to any observable extent. Control reactions run using copper precatalyst and pinB−Bpin in the absence of CO_2 (under an atmosphere

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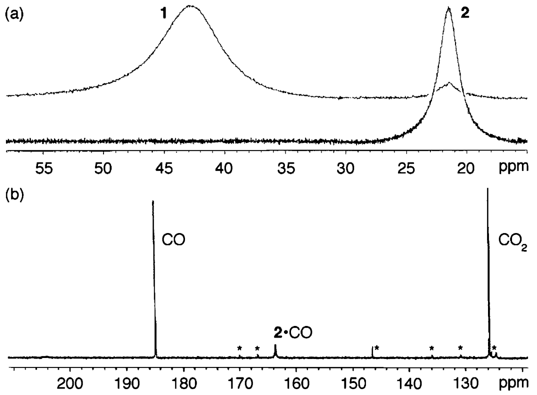

Figure 2. (a) ^{11}B NMR spectra before and after reaction with CO_2: **1** (containing 5% **2**) and **2**; (b) ^{13}C NMR spectrum after reaction of **1** with excess $^{13}CO_2$ (THF-d_8, −80 to −40 °C, 30 min); * denotes ligand-derived resonances; solvent and aliphatic resonances omitted for clarity.

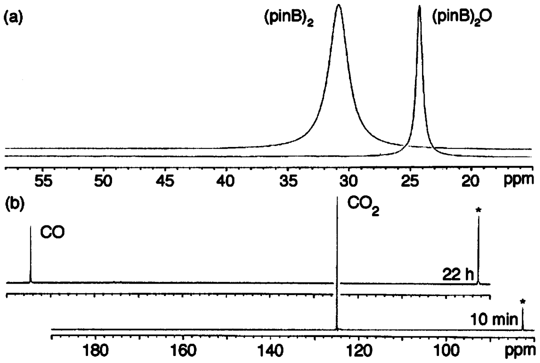

Figure 3. (a) ^{11}B NMR spectra showing conversion of pinB−Bpin to pinB−O−Bpin by catalytic reduction of CO_2 (excess CO_2, 1 mol % **1**, ambient temp, THF-d_8, 20 h); (b) ^{13}C NMR spectra, offset for clarity, before and after catalytic reduction of $^{13}CO_2$ to ^{13}CO (excess pinB−Bpin, ca.. 2 mol % **1**, ambient temp, THF-d_8); * denotes pin (Me_2**C**O)$_2$ resonance.

of argon or even dry air) show, at most, stoichiometric formation of pinB−O−Bpin with respect to copper. Thus, oxidation of pinB−Bpin by adventitious air does not contribute significantly to the formation of pinB−O−Bpin under these conditions, and essentially all conversion observed in the catalytic reactions results from the deoxygenation of CO_2.

Considerably higher turnover numbers are achieved at higher reaction temperatures. Turnover of pinacolborate **2** presumably occurs much more rapidly; the boryl complex **1**, generated in situ, is sufficiently stable toward decomposition to react productively with CO_2. The reduction of CO_2 at 100 °C, using 0.1 mol % (*IPr*)-Cu(O*t*-Bu) precatalyst, results in complete conversion of pinB−Bpin to pinB−O−Bpin after 20 h, corresponding to 1000 catalytic turnovers per copper.

To achieve more rapid catalytic turnover under mild conditions, the bulky *IPr* was replaced by the less sterically demanding *ICy* (1,3-dicyclohexylimidazol-2-ylidene) as a supporting ligand for copper. The complex (*ICy*)Cu(Bpin), generated in situ, is more prone to thermal decomposition than **1**, and catalytic reactions of CO_2 with pinB−Bpin using 1 mol % (*ICy*)Cu(O*t*-Bu) display only 81% conversion at ambient temperature, with visible precipitation of copper metal after less than 1 h. However, when the reaction is run at 0 °C for 30 min and then at ambient temperature for 30 min, complete conversion of pinB−Bpin to pinB−O−Bpin is observed. This turnover frequency, corresponding to 100 turnovers within 1 h, is dramatically higher than that achieved using the *IPr* supporting ligand.

In summary, we have achieved the catalytic reduction of CO_2 to CO in homogeneous solution, with high turnover numbers and frequencies, depending on the reaction conditions and supporting ligand. Both the oxygen abstraction and the catalyst turnover involve well-defined reactants and products, facilitating further study and pointing the way to future advances in catalytic reactions of CO_2.

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Supporting Information Available: All experimental procedures; complete ref 3; structural parameters for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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