

Efficient Homogeneous Catalysis in the Reduction of CO₂ 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 CO₂ 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 CO₂, CO is produced industrially from fossil fuels.³ Even with strong reducing agents, however, overcoming the O=CO bond enthalpy of 532 kJ/mol⁴ often presents kinetic difficulties.^{5,6}

Certain metal complexes abstract oxygen readily from CO₂,⁷ but the resulting metal–oxygen bonds are necessarily strong, and catalytic turnover is rare.⁸ Photolytic⁹ and photocatalytic¹⁰ approaches show promise, and synthetic electrocatalysts have achieved impressive yields and selectivities in the reduction of CO₂ 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 CO₂ 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 CO₂ 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 CO₂. 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 (*i*Pr)₃Cu(Ot-Bu) reacts rapidly with bis(pinacolato)-diboron (pinB–Bpin), forming a product identified as (*i*Pr)₃Cu(Bpin) (**1**, Scheme 1) by ¹H and ¹¹B 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 CO₂ under atmospheric pressure in C₆D₆ solution, quantitatively forming a new complex within minutes. The resonance for **1** in the ¹¹B 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 (*i*Pr)₃Cu(OBpin) (**2**): The copper boryl complex abstracts oxygen from CO₂, implying the release of CO as the byproduct.

To confirm the formation of CO, ¹³C-labeled CO₂ 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 ¹¹B (Figure 2a) and ¹H NMR spectroscopy at –40 °C indicates complete

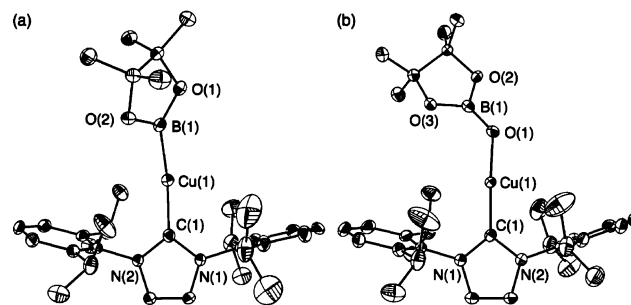
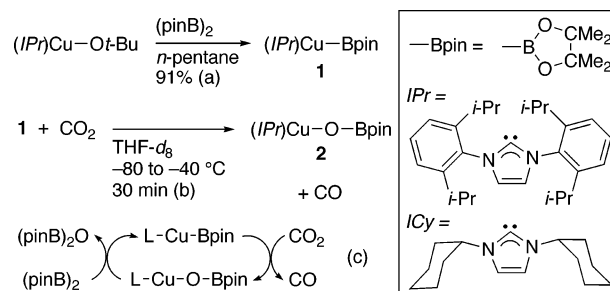
Scheme 1^a

Figure 1. X-ray crystal structures, shown as 50% thermal ellipsoids, of boryl complex **1**·C₆H₁₄ (a), and borate **2**·C₇H₈ (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).

conversion of **1** to **2**. The sole labeled products visible in the ¹³C NMR spectrum (Figure 2b) are ¹³CO (δ 184 ppm) and an adduct (δ 164 ppm) formed reversibly from CO and borate **2**.²⁰

Treatment of **2** in C₆D₆ 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 CO₂. Addition of a THF solution of (*i*Pr)₃Cu(Ot-Bu) to a 100-fold excess of pinB–Bpin under an atmosphere of CO₂ results in the complete conversion of pinB–Bpin to pinB–O–Bpin within 20 h at ambient temperature, as judged by ¹¹B NMR analysis of an aliquot from the reaction mixture (Figure 3a). When labeled CO₂ is used as the limiting reagent, in the presence of ca. 2 mol % of precatalyst **1**, the ¹³C NMR spectrum indicates complete consumption of CO₂, 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 CO₂ to any observable extent. Control reactions run using copper precatalyst and pinB–Bpin in the absence of CO₂ (under an atmosphere

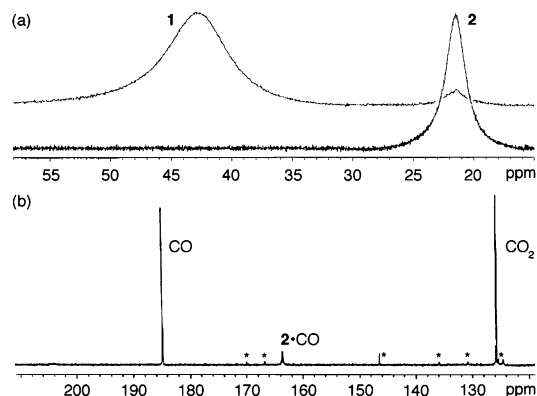


Figure 2. (a) ^{11}B NMR spectra before and after reaction with CO_2 : **1** (containing 5% **2**) and **2**; (b) ^{13}C NMR spectrum after reaction of **1** with excess $^{13}\text{CO}_2$ ($\text{THF}-d_8$, -80 to -40 $^\circ\text{C}$, 30 min); * denotes ligand-derived resonances; solvent and aliphatic resonances omitted for clarity.

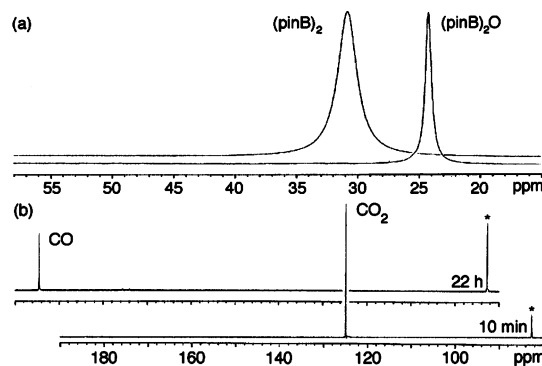


Figure 3. (a) ^{11}B NMR spectra showing conversion of pinB-Bpin to pinB-O-Bpin by catalytic reduction of CO_2 (excess CO_2 , 1 mol % **1**, ambient temp, $\text{THF}-d_8$, 20 h); (b) ^{13}C NMR spectra, offset for clarity, before and after catalytic reduction of $^{13}\text{CO}_2$ to ^{13}CO (excess pinB-Bpin, ca. 2 mol % **1**, ambient temp, $\text{THF}-d_8$); * denotes pin (Me_2CO) $_2$ 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 $^\circ\text{C}$, using 0.1 mol % (*iPr*)-Cu(*Or*-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(*Or*-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 $^\circ\text{C}$ 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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