

Catalyst Control of Selectivity in CO₂ Reduction Using a Tunable Heterobimetallic Effect

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S Supporting Information

ABSTRACT: A tunable bimetallic effect on product selectivity in catalytic CO₂ reduction was identified using *N*-heterocyclic carbene-ligated Cu complexes. While the monometallic Cu-only system catalyzes hydroboration of CO₂ with pinacolborane to produce formate exclusively, introducing a bimetallic effect with analogous Cu–Fe, Cu–W, and Cu–Mo catalysts produces mixtures of formate and CO. Within a series of isosteric catalysts, the selectivity of CO versus formate was controlled by tuning the electronic nature of the Cu/*M* pairing, with high selectivity for CO being achieved using a Cu–Mo catalyst.

Motivations ranging from environmental remediation to energy storage to chemical synthesis have driven intense research into CO₂ reduction catalysis.¹ While several catalytic approaches have proven successful in overcoming the kinetic barrier associated with activating the inert CO₂ molecule, achieving control over product selectivity remains underdeveloped. For example, several homogeneous catalyst designs have been identified for the reduction of CO₂ with oxophilic silane or borane reagents. Corresponding HCO₂[E],^{2–5} CO,⁶ H₂CO,^{7,8} H₃CO[E],^{9–13} or CH₄^{14–17} reduction products or mixtures thereof^{18–21} are observed ([E] = silyl or boryl), with the product selectivity being determined empirically rather than through rational design in most cases.

However, nature has evolved to achieve exquisite efficiency as well as selectivity control during biological CO₂ reduction, and apparently the nuclearities of the metalloenzymatic active sites play an important role (Figure 1). The monometallic Mo and W active sites of formic acid dehydrogenases²² interconvert CO₂ and formic acid selectively, while the heterobimetallic Ni/Fe²³ and Cu/Mo²⁴ active sites of the carbon monoxide dehydrogenases interconvert CO₂ and CO selectively. Although similar synthetic bimetallic effects have been identified in stoichiometric CO₂ reactions,^{25–28} bimetallic effects have rarely been studied systematically with respect to either reaction rate^{29–32} or product selectivity³³ in catalytic CO₂ reduction. Similar bimetallic cooperative effects may be important in heterogeneous CO₂ catalysis, where well-defined mechanistic understanding is more elusive.³⁴

Catalysts based on Cu ligated by *N*-heterocyclic carbenes (NHCs) provide a convenient testing ground for this phenomenon: monometallic (NHC)Cu catalysts for CO₂ reduction are well established,³⁵ and our group has developed the ability to synthesize heterobimetallic (NHC)Cu–[*M*]

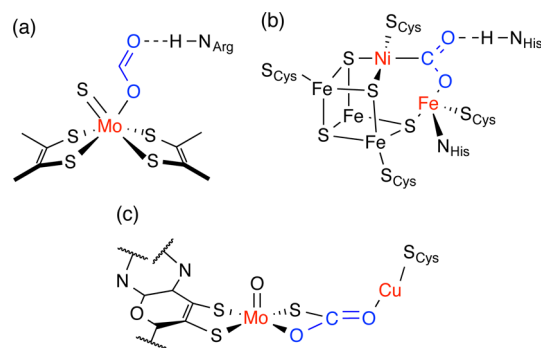


Figure 1. (a) Proposed monometallic CO₂ activation by a [Mo] formic acid dehydrogenase; proposed bimetallic CO₂ activation at the active sites of (b) [NiFe] and (c) [MoCu] carbon monoxide dehydrogenases.^{22–24}

complexes with tunable steric and electronic properties ([*M*] = metal carbonyl anion).³⁶ Previously, it was known that reagent control over CO₂ reduction selectivity could be achieved with a single monometallic (NHC)Cu catalyst (Figure 2a): use of H–[B] or H–[Si] reductants produced HCO₂[E] products selectively,^{3,4} while a [B]–[B] reductant produced CO

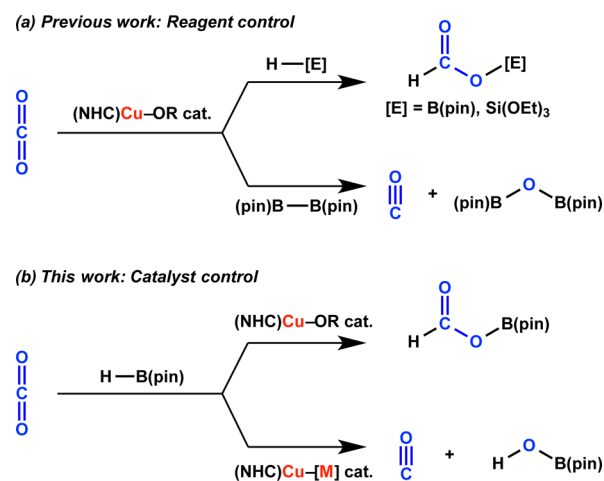


Figure 2. (a) Previously established reagent control of CO₂ reduction with (NHC)Cu catalysts.^{3,4,6} (b) Newly established catalyst control by introducing a heterobimetallic effect; [*M*] = metal carbonyl anion, NHC = *N*-heterocyclic carbene, pin = pinacolate.

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Table 1. Catalytic CO₂ Reduction Results with Pinacolborane (HBpin)^a

entry	catalyst	%conversion ^b	equiv of 1 ^c	equiv of 2 ^c	equiv of 3 ^c	CO/1 ^d
1	(IPr)CuFp	72 ± 15	3.0 ± 1.0	0	2.1 ± 0.5	~0.7:1
2 ^e	(IPr)CuOtBu	85	8.5	0	0	0
3	FpBpin	0	0	0	0	N/A
4	(IPr)CuWp	76 ± 14	1.8 ± 0.5	1.3 ± 0.3	2.3 ± 0.7	~2:1
5	(IPr)CuMp	73 ± 21	0.3 ± 0.3	0	3.5 ± 1.0	~12:1
6	(IMes)CuFp	92 ± 30	0	2.4 ± 1.7	3.4 ± 1.2	≥20:1
7	(IMes)CuWp	92 ± 4	0	n.d. ^f	n.d. ^f	≥20:1
8	(IMes)CuMp	82 ± 21	0	0	4.1 ± 1.0	≥20:1
9 ^g	(IPr)CuOtBu + FpBpin	96 ± 3	0	n.d. ^f	n.d. ^f	≥20:1

^aDetermined by ¹H NMR integration against an internal standard (mesitylene). ^bBased on HBpin. ^cBased on catalyst. ^dAssumes 1 equiv of CO per 2 and 1 equiv of CO per 3. ^eData from ref 4 (THF, 35 °C, 24 h). ^fNot determined due to peak overlap, but 2 and 3 were the only [Bpin]-containing products observed. ^gCatalyst loading of 10 mol % was used for each cocatalyst.

selectively.⁶ In this communication, we show that catalyst control over CO₂ reduction selectivity can be achieved with (NHC)Cu-[M] catalysts (Figure 2b): with a single H-[B] reductant, selectivity for CO versus HCO₂[B] can be controlled by tuning the heterobimetallic catalyst through the nature of the Cu/M pairing.

During our studies on heterobimetallic C-H borylation,³⁷ we proposed that pinacolborane, H-Bpin, is activated reversibly by (IPr)Cu-Fp (IPr = *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; Fp = FeCp(CO)₂) to yield small concentrations of the pair 0.5 [(IPr)Cu-H]₂ + Fp-Bpin.³⁸ We also noted that exposure of this mixture to CO₂ produced both the formate product, HCO₂Bpin (1), and a boron oxygenate, pinB-O-Bpin (3), even though (IPr)Cu-Fp itself does not react with CO₂.³⁹ Product 3 was presumed to result from CO₂ deoxygenation. (The direct product of CO₂ deoxygenation, HO-Bpin (2), if produced slowly would react with H-Bpin to generate 3 and H₂.) Upon further examination, we found that (IPr)Cu-Fp is a catalyst for CO₂ reduction by H-Bpin, converting 72% of the H-Bpin to a ~ 0.7:1 mixture of 3 and 1 under the conditions specified in Table 1 (Entry 1). At first, we presumed that these two products derived from separated monometallic catalysis by [(IPr)CuH]₂ and Fp-Bpin. Indeed, [(IPr)CuH]₂ is already known to quantitatively catalyze CO₂ reduction to formate using silane or borane reductants in different solvents (benzene, THF) and at different temperatures (25–100 °C);^{3,4} one relevant data point is presented in Table 1 (Entry 2). However, to our surprise, exposing Fp-Bpin to the same conditions did not produce 2 or 3 and, in fact, resulted in no reaction whatsoever (Table 1, Entry 3). Together, these results demonstrate that the deoxygenation of CO₂ by H-Bpin to produce CO requires both metal sites to be present and verifies the presence of a cooperative effect.

Seeking to better understand this bimetallic selectivity effect, we then tested other (IPr)Cu-[M] complexes as catalysts under the same conditions. Use of (IPr)Cu-Wp (Wp = WCp(CO)₃) resulted in 76% conversion of H-Bpin with ~2:1 CO/1

selectivity (Table 1, Entry 4). Use of (IPr)Cu-Mp (Mp = MoCp(CO)₃) resulted in 73% conversion of H-Bpin with ~12:1 selectivity for CO over 1 (Table 1, Entry 5). Because the Fp, Wp, and Mp fragments represent electronically distinct metal carbonyl species (relative nucleophilicities: [Fp]⁻, 7 × 10⁷; [Wp]⁻, 500; [Mp]⁻, 67),⁴⁰ this series of experiments demonstrates that CO₂ reduction selectivity can be controlled by electronically tuning the bimetallic pairing.

We then examined the sterically less hindered (IMes)Cu-[M] catalysts (IMes = *N,N'*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), which might be expected to give higher concentrations of the catalytically active (NHC)CuH/[M]-Bpin pairs. All three of the catalysts exhibited high selectivity for CO over 1 (Table 1, Entries 6–8). The corresponding monometallic precatalyst, (IMes)Cu-OtBu, is known to give high yields of formate during CO₂ reduction with silane or borane reagents.^{3,4}

We also note that evolution of CO in these reactions was detected by two methods: CO trapping with Cp*RuCl(PCy₃) to generate Cp*RuCl(PCy₃)(CO) according to the two-pot method recently used by Cummins (Figures S7–S8),⁴¹ and GC-MS analysis of the reaction headspace (Figure S11). However, we consider ¹H NMR integration of the nonvolatiles 2 and 3 relative to 1 to be the more accurate method for determining CO:1 selectivity. In some cases, individual yields of 2 and 3 were not determined due to their similar ¹H and ¹¹B NMR spectra. We were able to verify their peak assignments by exposing one of the catalytic mixtures featuring both 2 and 3 to additional H-Bpin after completion of the reaction: H₂ evolution was observed by ¹H NMR as the peaks for 2 shrank and the peaks for 3 grew in both ¹H and ¹¹B NMR (Figures S9–S10). Nonetheless, the resolution of 2 and 3 by ¹H NMR is highly dependent on spectral line widths, and sometimes we can only report overall conversion to 2 + 3.

Several observations lead us to a hypothetical mechanism. (1) Neither (NHC)Cu-Fp nor Fp-Bpin react with CO₂ independently, indicating that the CO₂ activating species must be

$[(\text{NHC})\text{Cu}-\text{H}]_2$. (2) Catalysis with $[(\text{NHC})\text{Cu}-\text{H}]_2$ produces **1** but does not result in decarbonylation to either **2** or **3**,⁴ indicating that the $[\text{M}]$ -Bpin species act as catalysts/precatalysts for the decarbonylation of **1**. (3) Catalytic reactions that give high selectivity for CO at full conversion contained large amounts of formate **1** at partial conversion. (4) Although **1** is known to be unstable toward isolation,⁴² Fp-Bpin (10 mol %) was added to a preformed $\sim 1:1$ mixture of (**2** + **3**)/**1** under N_2 , and no reaction was observed after 36 h. Replacing the N_2 atmosphere with a CO_2 atmosphere resulting in consumption of **1** and a $\sim 4:1$ mixture of (**2** + **3**)/**1** after 24 h; FpH was observed as a byproduct (Figure 3).

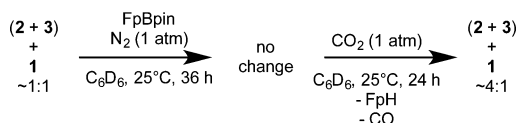


Figure 3. Observed decarbonylation activity of Fp-Bpin on formate **1**.

Collecting these observations together, a hypothetical mechanism is shown in Figure 4. Catalyst activation by HBpin

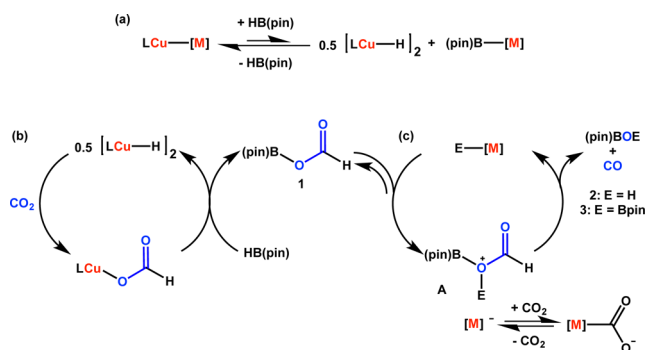


Figure 4. Hypothetical mechanism: (a) catalyst activation, followed by autotandem (b) CO_2 hydroboration, and (c) CO_2 -assisted formate decarbonylation. $\text{E} = \text{B}(\text{pin})$ for the first turnover and then H throughout. $\text{L} = \text{IPr}$ or IMes , $[\text{M}] = \text{Fp}$, Wp , or Mp , $\text{pin} = \text{pinacolate}$.

produces $0.5 [(\text{NHC})\text{CuH}]_2 + [\text{M}]\text{Bpin}$. An autotandem reaction then ensues. First, copper-catalyzed hydroboration converts CO_2 to **1**. Formate **1** is then decarbonylated through rate-determining electrophilic activation by $[\text{M}]-\text{E}$ ($\text{E} = \text{Bpin}$ in the first turnover and then H throughout). Transfer of E^+ to **1** initiates decarbonylation via intermediate **A**, but this reversible activation must be driven forward through sequestration of $[\text{M}]^-$ by CO_2 . Carboxylation of $[\text{Fp}]^-$ is known to be reversible,⁴³ and the acid-catalyzed decarbonylation of formate **1** through **A** is proposed in analogy to the known Brønsted or Lewis acid-catalyzed decarbonylation of formic acid itself.^{44,45}

Consistent with this proposal, within the series of isosteric IPr-ligated complexes (Table 1, Entries 1, 4–5), the rate of decarbonylation is apparently related to the lability of $[\text{M}]-\text{Bpin}$, following the $[\text{M}]^-$ leaving group ability of $[\text{Mp}]^- > [\text{Wp}]^- > [\text{Fp}]^-$ that also correlates with their relative $\text{p}K_a$ values.⁴⁰ Furthermore, catalysis with a 1:1 mixture of $(\text{IPr})\text{Cu}-\text{O}t\text{Bu} + \text{Fp}-\text{Bpin}$ (Table 1, Entry 9) gave higher selectivity for CO than did $(\text{IPr})\text{Cu}-\text{Fp}$, presumably because the metals need not be linked during productive catalysis and because the unfavorable catalyst activation equilibrium was bypassed, giving higher effective concentration of the decarbonylation catalyst (much like for all IMes catalysts, *vide supra*). At this time, we cannot rule

out that decarbonylation reactivity could also come from polarity inversion in the catalyst activation step yielding the pair, $(\text{NHC})\text{CuBpin} + [\text{M}]\text{H}$, of which $(\text{NHC})\text{CuBpin}$ is established as a catalyst for CO_2 deoxygenation.⁶ However, all experimental observations are consistent with the simpler mechanism shown in Figure 4. Further experiments to elucidate mechanistic information are ongoing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05692.

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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