ACS Catalysis
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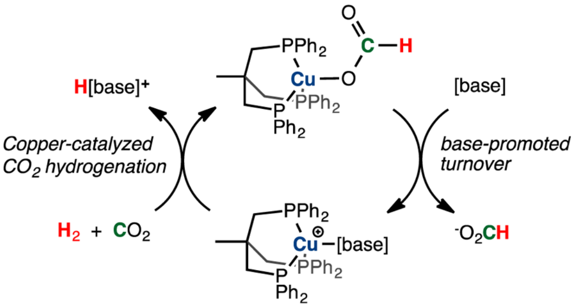
A Molecular Copper Catalyst for Hydrogenation of CO_2 to Formate

Christopher M. Zall, John C. Linehan, and Aaron M. Appel*

Pacific Northwest National Laboratory, P.O. Box 999, MS K2-57, Richland, Washington 99352, United States

Supporting Information

ABSTRACT: There is widespread interest in the hydrogenation of CO_2 to energy-rich products such as formate. However, first-row transition metal catalysts for the hydrogenation of CO_2 to formate remain rare. Copper complexes are widely used in the reduction of organic substrates, but their use in the catalytic hydrogenation of CO_2 has been limited. Here, we demonstrate that the copper(I) complex $LCu(MeCN)PF_6$ is an active catalyst for CO_2 hydrogenation in the presence of a suitable base. Screening of bases and studies of catalytic reactions by in operando spectroscopy revealed important and unusual roles for the base in promoting H_2 activation and turnover.



KEYWORDS: *CO_2, copper, hydrogenation, catalysis, H_2 activation, DBU*

The development of catalysts for efficient hydrogenation of CO_2 is an active area of research, with the potential to reduce our dependence on fossil resources for the production of chemical fuels and feedstocks. Catalysts that can convert the electrical energy from intermittent energy sources, such as wind and solar, into chemical fuels could provide a valuable energy storage mechanism by producing fuels during periods of excess supply that can be used during periods of excess demand.[1] When produced from the reduction of carbon dioxide, carbon-based fuels such as formic acid (usually trapped as formate)[2] and methanol[3] are attractive targets for energy storage, as these fuels have higher volumetric energy densities and can be stored and transported more efficiently and safely than hydrogen.[4] With an energy input of renewably generated H_2 or electricity, the overall cycle can, in principle, be carbon-neutral, as equal quantities of CO_2 are first taken up and then emitted over the life cycle of the fuel.[5]

Numerous transition-metal catalysts for CO_2 hydrogenation to formate have been developed over the previous few decades, with turnover numbers (TON, or mol formate per mol catalyst) easily exceeding 10^4 and turnover frequencies (TOF, or turnovers per unit time) in some cases greater than 10^4 h^{-1}.[6−8] The most active catalysts are typically complexes of either ruthenium or iridium. The greater abundance and lower cost of first-row transition metals would make them better suited to the large-scale production of fuels, if they could be made sufficiently active as catalysts. Several examples of first-row catalysts for CO_2 hydrogenation are now known, and in particular, complexes of Fe[9−15] and Co[16−19] have been shown to be quite active. There are reasons to believe that copper complexes should be effective in CO_2 hydrogenation. For instance, copper dispersions on ZnO/Al_2O_3 are widely used in the industrial conversion of syngas to methanol;[20,21] mechanistic studies have revealed that this reaction occurs primarily through hydrogenation of the CO_2, rather than CO, in these $CO_2/CO/H_2/H_2O$ mixtures.[22,23] Moreover, homogeneous copper phosphine and carbene complexes are highly efficient catalysts for the reduction of CO_2 to CO,[24,25] hydroboration of CO_2 to form boryl formates,[26] and hydrosilylation of CO_2 to form silyl formates.[27−29] These reactions are driven by the stoichiometric use of borane and silane reagents, and turnover is facilitated by the formation of strong B−O and Si−O bonds, the cleavage of weak B−H and Si−H bonds, or both. These high-energy reagents may be useful in the production of value-added chemicals, but they are impractical in the context of energy storage.

Molecular copper-catalyzed *hydrogenation* of CO_2 to formic acid, which is more relevant to the production of renewable fuels, has long remained elusive. The reaction is thermodynamically favorable in organic solvents with the addition of a base. Copper hydrides can be formed from hydrogen in the presence of a base, and some have been shown to react stoichiometrically with CO_2 to produce formates.[30−35] However, this CO_2 reactivity has remained stoichiometric because the copper formate products generally do not turn over when using hydrogen, rather than silanes or boranes, as the source of hydride. Very recently, Watari, Ikariya, and co-workers showed that simple copper(I) and -(II) salts can catalyze the hydrogenation of CO_2 to formate in the presence of a suitable base.[36] The active catalyst species was not identified; in fact, the addition of carbene or phosphine ligands was found to impede catalysis. However, the bicyclic amidine base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was reported to have a distinct and unusual ability to promote turnover, even compared with very similar bases. No explanation for the effect of DBU was given, although a base-coordinated $(DBU)_2CuI$

Received: July 30, 2015
Published: August 5, 2015

DOI: 10.1021/acscatal.5b01646
ACS Catal. 2015, 5, 5301−5305

complex was synthesized, characterized, and shown to be an active catalyst precursor.

Our current studies of copper-catalyzed CO_2 hydrogenation are focused on using well-defined copper complexes with chelating ligands that not only create stable catalysts but also facilitate investigation of the catalytic mechanism. Herein, we show that the triphosphine-ligated copper(I) complex $[LCu(MeCN)]^+$, **1**-MeCN, is an effective catalyst for the reduction of CO_2 to formate using hydrogen and a base, with higher activity and thermal stability than the previous system reported by Watari et al.[36] To the best of our knowledge, our report describes the first CO_2 hydrogenation catalyst based on a well-defined copper complex. We have screened several bases and conducted in operando spectroscopic studies that identify key aspects of the catalytic system, including a base-promoted mechanism for H_2 activation that is distinct from known iron- and cobalt-based catalysts. These results demonstrate that copper complexes can be active catalysts for CO_2 hydrogenation and identify reaction conditions that can potentially be used to promote catalysis with other copper hydride complexes.

Copper complexes with the triphos ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, or "L," were chosen for our CO_2 hydrogenation studies because the tridentate ligand stabilizes well-defined solvento[37] and hydrido[31] copper(I) species with low nuclearity. Notably, a dimeric copper hydride with this ligand has been shown to react with CO_2 to generate a copper(I) formate, although this reaction was not shown to be catalytic. Interestingly, this copper hydride was generated from hydrogenolysis of the Cu−O^{t}Bu bonds in $(CuO^tBu)_4$ in the presence of L. We envisioned that a similar activation of H_2 using the solvento complex **1**-MeCN and an added base could provide a renewable route to the copper hydride during catalysis. Preliminary catalytic reactions using DBU as the base were conducted at 80−140 °C with 40 atm H_2/CO_2. The results of these reactions are summarized in Table 1. As shown in Figure 1, the reactions at 100 and 120 °C in CD_3CN showed essentially complete conversion to $[H(DBU)]O_2CH$ within a few hours (using 5 mol % **1**-MeCN, relative to base, corresponding to TON values of ~20). At 140 °C and 1 mol % catalyst loading, nearly complete conversion to formate was observed after 2 h (96 TON, overall TOF 48 h^{-1}). At 140 °C and with 0.1 mol % catalyst loading, a TON value of 500 was obtained. The catalytic performance is therefore modest but encouraging. The TON values and the thermal stability are better than the copper catalyst reported by Watari et al. (TON 165 at 100 °C), demonstrating that the triphosphine ligand imparts stability to the catalyst. The TON and TOF values are similar to or better than many other first-row transition metal catalysts[9,12−14,17] but significantly lower than the most active such catalysts.[10,11,16,18]

Table 1. Catalytic Conversion of CO_2 and H_2 to Formate Using 1-MeCN and DBU in MeCN at 40 atm H_2/CO_2[a]

entry	$[LCu^+]$ (mM)	[DBU] (mM)	T (°C)	time (h)	TOF (h^{-1})	TON
1	2.5	50	80	6	2.9[b]	14[d]
2	2.5	50	100	4	8.1[b]	18[d]
3	2.5	50	120	3	18[b]	19[d]
4	0.25	25	140	2	48[c]	96[e]
5	0.05	50	140	20	25[c]	500[e]
6	2.5	0	140	20	N/A	~0[e]
7	0	50	140	20	N/A	~0[e]

[a] Reaction conditions: 1.5 mL MeCN, 40 atm 1:1 H_2/CO_2. [b] Initial TOF values, calculated from plots of initial reaction progress (Figure 1). [c] Overall TOF values: TON divided by the overall reaction time. [d] Mol formate/mol catalyst, calculated from the formate ^{1}H NMR integration relative to that of the catalyst. [e] Calculated from the formate integration relative to an internal standard of DMF.

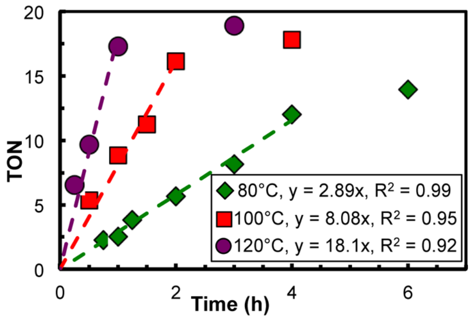
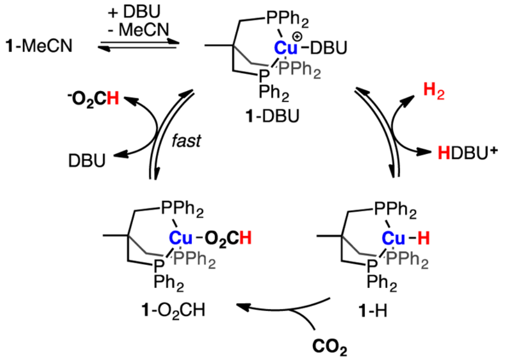


Figure 1. Initial reaction progress for catalytic hydrogenation of CO_2 at various temperatures (Table 1, entries 1−3). For each temperature, the best-fit line for the initial linear region is shown on the plot, and the equation for the fit is given in the legend.

To gain insight into the catalytic mechanism and facilitate screening of reaction conditions, we studied reactions at low pressures (1.8 atm) of H_2/CO_2 and 60 °C by NMR spectroscopy. Under these conditions, complete conversion to $[H(DBU)]O_2CH$ was observed, with an initial TOF of $(3.7 \pm 1.3) \times 10^{-2}$ h^{-1}. The NMR spectra for the reaction support the mechanism shown in Scheme 1.

Scheme 1. Proposed Catalytic Mechanism



The catalyst resting state throughout the early phases of the reaction is the base adduct, **1**-DBU, which is observed immediately upon dissolving **1**-MeCN in a solution with DBU. Association and deprotonation of H_2 presumably forms a copper hydride, **1**-H, that is apparently a transient, steady-state intermediate because no hydride is observed over the course of the reaction. Reaction of **1**-H with CO_2 forms the κ^1-coordinated formate complex, **1**-O_2CH. The formate ligand is rapidly displaced by excess DBU, facilitating turnover and generating the free formate product. As the reaction proceeds and the available DBU is depleted, the major species observed in solution shifts from **1**-DBU to **1**-O_2CH. The formate complex is largely insoluble in MeCN in the absence of a coordinating base and precipitates from solution once the reaction approaches completion.

The observation of **1**-DBU as the initial resting state suggested that hydride formation was rate-limiting. A conventional mechanism for hydride formation would involve association of H_2 to form a discrete $Cu(H_2)^+$ dihydrogen or dihydride complex, followed by deprotonation. With this mechanism, the use of stronger bases should drive the deprotonation step, resulting in increased rates. In addition, coordination of the base to the copper center should decrease the rates by preventing the association of H_2 to copper. Therefore, we predicted that using stronger, bulkier bases should increase the rates by increasing the favorability of hydride formation and leaving the copper coordination site open. A selection of bases was screened for this reaction (Table 2). We have determined the pK_a value for H[^{t}BuTMG]$^+$ to be 26.5 in MeCN (see SI). The pK_a values for the conjugate acids of the other bases are from Leito et al.[38]

Table 2. Turnover Frequencies for Low-Pressure Catalytic Hydrogenation of CO_2 to Formate Using Various Bases[a]

entry	base	pK_a (BH^+)	init TOF[b] (h^{-1}, × 10^{-2})	TON[c]
1	NEt_3	18.8[d]	N/A	N/A
2	TMG	23.4[d]	1.1 ± 0.6	>5[e]
3	DBU	24.3[d]	3.7 ± 1.3	20
4	TBD	26.0[d]	0.9 ± 0.6	>5[e]
5	^{t}BuTMG	26.5	0.4 ± 0.6	0.8[f]

[a] Reaction conditions: 2.5 mM **1**-MeCN, 50 mM base, 1.8 atm H_2/CO_2, 60 °C. [b] Initial TOF values, representing the average from at least three reactions, with uncertainty reported as two standard deviations. [c] Determined from integration of the formate ^{1}H resonance, relative to that of the catalyst. [d] pK_a values taken from ref 38. [e] These reactions were not followed to completion, but the reaction progress was linear with time through at least five turnovers. [f] From the average of three reactions with actual TON values between 0.13 and 1.7.

Surprisingly, there was no correlation between the pK_a and the catalytic rates. The rates instead correlated *with* the ability of the base to coordinate to the copper center. DBU, which gave the fastest catalytic rates, also binds most strongly, as revealed by separate experiments involving addition of the bases to **1**-MeCN: addition of a single equivalent of DBU to **1**-MeCN resulted in complete conversion to **1**-DBU. The sterically unhindered guanidines tetramethylguanidine and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TMG and TBD), which gave slower catalytic rates, also showed weaker binding equilibria: addition of 1 equiv of TMG or TBD to **1**-MeCN formed roughly 1:1 mixtures of **1**-MeCN and the corresponding base adduct. The bulky guanidine 2-*tert*-butyl-TMG (^{t}BuTMG), which showed very little binding to the copper center even with a 20-fold excess of base, gave the slowest initial rates. The rates for these reactions are inconsistent with a mechanism in which H_2 competes with the base for an open coordination site. Rather, they suggest that coordination of the base *assists* in hydride formation, possibly by prepositioning the base for efficient reaction with H_2 at the metal center.

The coordinating bases DBU, TMG, and TBD displace the formate ligand in **1**-O_2CH; when using these bases, the catalytic resting state was the corresponding base adduct, and the reactions were catalytic, showing linear reaction progress through at least several turnovers. However, reactions using ^{t}BuTMG, which does not displace the formate ligand, gave consistently low, often noncatalytic yields of formate. From the NMR spectra, the copper species converted from **1**-MeCN to the inactive formate complex, **1**-O_2CH, which precipitated. Thus, in addition to promoting the rates of reaction, coordination of the base to the copper center is actually crucial in achieving catalytic turnover. By substituting for the formate ligand, the coordinating bases keep the catalyst soluble and active throughout the reaction.

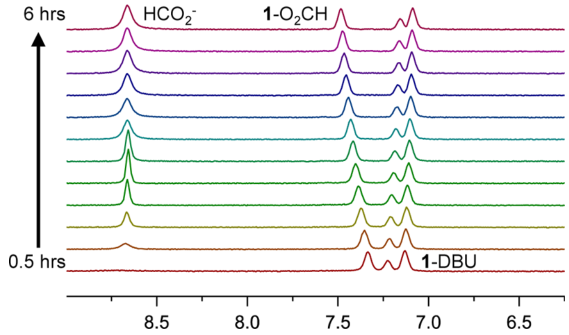


Figure 2. ^{1}H NMR spectra from 6.25 to 9.0 ppm for a reaction at 40 atm H_2/CO_2 and 83 °C (Table 3, entry 1), showing the change in the formate and catalyst resonances.

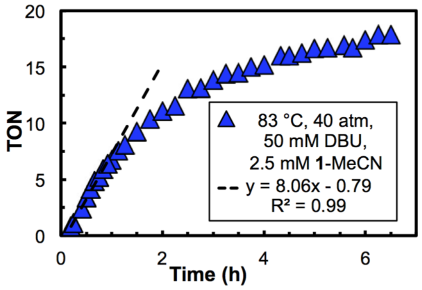


Figure 3. Progress for a representative reaction studied at 40 atm H_2/CO_2 and 83 °C by in operando NMR spectroscopy (Table 3, entry 1). The best fit to the initial linear region is shown.

To confirm that the catalytic behavior is the same at low and high pressures, we studied reactions at 40 atm H_2/CO_2 and 83 °C by in operando NMR spectroscopy. The ^{1}H NMR spectra for a representative reaction using DBU and 5 mol % **1**-MeCN at 83 °C are shown in Figure 2. The time profile for this reaction is shown in Figure 3. The catalyst species observed over the course of these high-pressure reactions were identical to those observed in the low-pressure reactions. The only notable difference was that the resonances for **1**-DBU and **1**-O_2CH appeared as a single set of peaks when monitored at 83 °C. The coalescence of these resonances, which are distinct at room temperature, indicates that the interconversion of the two species is rapid at elevated temperature, consistent with the proposed mechanism in Scheme 1. Results using different bases and concentrations are given in Table 3. Using 50 mM DBU, reactions went nearly to completion within 6.5 h, with an initial TOF of 8 ± 1 h^{-1} (Table 3, entry 1). Essentially identical TOFs were measured with higher base concentration (Table 3, entries 2 and 3). The apparent zero-order dependence on base is consistent with deprotonation of H_2 by the precoordinated base in **1**-DBU, rather than by free base. As with the low-pressure conditions, reactions using TBD and ^{t}BuTMG were significantly slower than those using DBU (Table 3, entries 4 and 5).

The major objective of this research was to evaluate the viability of molecular copper complexes as catalysts for the hydrogenation of CO_2. Our results demonstrate that the use of

Table 3. Results from Catalytic Reactions Studied by NMR spectroscopy in CD_3CN with 40 atm H_2/CO_2 at 83 °C[a]

entry	[LCu^+] (mM)	[base] (mM)	time (h)	TOF (h^{-1})[b]	TON[c]
1	2.5	50, DBU	6.5	8 ± 1	18.2
2	2.5	100, DBU	6.5	7.4	21.2
3	2.5	381, DBU	40	9.1	130
4	2.5	50, TBD	30	0.44	7.5
5	2.5	50, ^{t}BuTMG	20	0.75	2.7

[a] Catalytic conditions: 0.35−0.45 mL CD_3CN, 40 atm 1:1 H_2/CO_2, 83 °C. [b] TOF values determined from the initial linear regions of reaction profiles, as shown in Figure 2. [c] Determined from ^1H NMR integration of the formate resonance, relative to that of the catalyst.

chelating phosphines can yield stable and well-defined copper catalysts. In addition, we have shown that direct coordination of the base to the metal center can play at least two direct and unusual roles in promoting catalysis: activating H_2 and facilitating turnover. The role of the base in facilitating turnover involves simple, direct substitution of DBU for the coordinated formate ligand, regenerating the catalyst resting state from the inactive and insoluble **1**-O_2CH. This process is observed directly as a rapid equilibrium by NMR spectroscopy. The role of the base in facilitating hydride formation is more subtle. The zero-order dependence of the rate on [DBU], the correlation of the rates with the coordinating ability of the base, and the lack of a correlation with the pK_a of the base suggest that H_2 reacts directly with the base-coordinated catalyst resting state. This mechanism is distinct from the more conventional mechanisms involving formation of a Cu−H_2^+ complex that is subsequently deprotonated by free base. The difference is likely due to the instability of the hypothetical Cu−H_2^+ complex: σ-complexes of copper are exceptionally rare. The first intermolecular examples were reported only very recently,[39,40] and dihydrogen complexes of copper are essentially unknown. A bimolecular reaction between a highly unstable Cu−H_2^+ species and free base should be far less likely than the reaction of a stable Cu-[base]$^+$ adduct with free H_2, provided that the coordinated base is strong enough to efficiently deprotonate H_2. The unique effectiveness of DBU in this reaction is likely due to its nature as both a strong base and one that can bind strongly to form a stable adduct.

The details of the mechanism of H_2 activation in this case are unclear: the phosphine donors are labile, and the reaction may involve dissociation of one of the phosphines, coordination of H_2 to the vacated site, and subsequent deprotonation by the adjacent DBU. Alternatively, the reaction could involve a one-step σ-bond-metathesis-like addition of H_2 across the Cu−N bond in **1**-DBU. Yet another alternative is frustrated-Lewis-pair-like insertion of H_2 *between* the Lewis−acidic Cu and basic N; this seems less likely because the fastest rates are observed with the more coordinating (and therefore less "frustrated") bases. The nature of the active copper hydride intermediate is also unclear. We favor a mononuclear hydride, as shown in Scheme 1, but a dinuclear species is also plausible. Detailed mechanistic studies, including characterization of the copper hydride intermediates, are underway in our laboratories. These studies should enable the design of catalysts with improved performance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01646.

> Experimental details, additional reaction data, NMR spectra for catalytic reactions, studies of base binding to **1**-MeCN, pK_a measurement of H[^{t}BuTMG]$^+$ (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: aaron.appel@pnnl.gov.

Notes

The authors declare no competing financial interest

■ ACKNOWLEDGMENTS

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. Pacific Northwest National Laboratory is operated by Battelle for the US Department of Energy.

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