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Triphosphine-Ligated Copper Hydrides for CO_2 Hydrogenation: Structure, Reactivity, and Thermodynamic Studies

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 Placeholder

ABSTRACT: The copper(I) triphosphine complex $LCu(MeCN)PF_6$ (L = 1,1,1-tris(diphenylphosphinomethyl)ethane), which we recently demonstrated is an active catalyst precursor for hydrogenation of CO_2 to formate, reacts with H_2 in the presence of a base to form a cationic dicopper hydride, $[(LCu)_2H]PF_6$. $[(LCu)_2H]^+$ is also an active precursor for catalytic CO_2 hydrogenation, with equivalent activity to that of $LCu(MeCN)^+$, and therefore may be a relevant catalytic intermediate. The thermodynamic hydricity of $[(LCu)_2H]^+$ was determined to be 41.0 kcal/mol by measuring the equilibrium constant for this reaction using three different bases. $[(LCu)_2H]^+$ and the previously reported dimer $(LCuH)_2$ can be synthesized by the reaction of $LCu(MeCN)^+$ with 0.5 and 1 equivalent of $KB(O^iPr)_3H$, respectively. The solid-state structure of $[(LCu)_2H]^+$ shows three-fold symmetry about a linear Cu-H-Cu axis and significant steric strain imposed by bringing two LCu^+ units together around the small hydride ligand. $[(LCu)_2H]^+$ reacts stoichiometrically with CO_2 to generate the formate complex $LCuO_2CH$ and the solvento complex $LCu(MeCN)^+$. The rate of the stoichiometric reaction between $[(LCu)_2H]^+$ and CO_2 is dramatically increased in the presence of bases that coordinate strongly to the copper center, *e.g.* DBU and TMG. In the absence of CO_2, the addition of a large excess of DBU to $[(LCu)_2H]^+$ results in an equilibrium that forms $LCu(DBU)^+$ and also presumably the mononuclear hydride LCuH, which is not directly observed. Due to the significantly enhanced CO_2 reactivity of $[(LCu)_2H]^+$ under these catalytically relevant conditions, LCuH is proposed to be the catalytically active metal hydride.

INTRODUCTION

The catalytic hydrogenation of CO_2 could play a central role in the production of renewable, carbon-based fuels and feedstocks.[1-4] The identification of first-row transition metal hydrides that can react favorably with CO_2 is crucial to developing alternatives to expensive noble-metal catalysts, thereby making this process more economically viable. In a typical catalytic cycle, CO_2 hydrogenation involves the reaction of a transition metal catalyst with hydrogen to form a metal-hydride intermediate and subsequent transfer of the hydride to CO_2 to produce formate. The favorability of each of these steps, which can significantly affect the overall catalytic activity, is a function of the thermodynamic stability of the metal-hydride bond. Because CO_2 is a relatively inert substrate, and because first-row transition metals typically form less reactive metal-hydride bonds than their second- and third-row analogues, the use of first-row metal complexes in catalytic CO_2 hydrogenation has historically been quite limited. Before 2010, the only examples were in reports by Inoue *et al.*,[5,6] Evans *et al.*,[7] and Jessop *et al.*[8] Since that year, and the report by Beller *et al.* of a tetraphosphine-ligated iron catalyst with relatively high activity,[9] many additional catalysts have been reported, with most based on iron[10-16] and a smaller number based on cobalt.[17-20] A crucial component in catalyst discovery and development has been the characterization of metal hydride species and their reactivity. The thermodynamic hydride donor abilities of many first-row metal hydrides have been studied, most extensively those of nickel[21-33] and cobalt,[34-38] and more recently of several iron complexes.[14,39-42] These properties have been used to guide catalyst development, especially for the hydrogenation of CO_2.[14,19,20,33,40-42] However, no comparable data has been reported for copper hydrides.

Copper hydrides are widely used reagents and catalysts in organic synthesis.[44] They have been utilized most notably for the selective reduction of carbonyl compounds,[45,46] although they catalyze numerous other reactions, such as the semihydrogenation[47,48] or hydroalkylation[49,50] of alkynes and the hydroboration[51] and hydroamination[52,53] of alkenes. The often-exceptional selectivity of these reactions is controlled in large part by the nature of the copper hydride intermediates. Hexameric complexes are most common with monodentate phosphine ligands, such as Stryker's reagent, $[(PPh_3)CuH]_6$.[54-58] With polydentate phosphines or with NHC ligands, lower-nuclearity structures can be obtained.[58-63] Although all of these complexes are multinuclear in the solid state, their speciation in solution is often unclear.[64-68] Even when the isolated complex is well characterized, the chemistry during catalysis can be more complex, with important implications for catalytic activity and selectivity.[69]

Several copper hydrides have been shown to react stoichiometrically with CO_2 to produce copper formates.[59,62-63,70-73] Some species are highly active catalysts for CO_2 reduction when used in conjunction with stoichiometric borane[74-76] or silane[77-79] reagents. Replacement of these high-energy reductants with hydrogen would be significantly more practical for applications in energy storage and fuel production. Hydrogenation of CO_2 using molecular copper catalysts has been demonstrated only very recently. Watari, Ikariya, and coworkers reported that a number of simple copper salts catalyze the hydrogenation of CO_2 to formate in the presence of strong organic bases.[80] The catalytic activity was found to vary considerably with the copper precursor and the base, but the active catalytic species were not identified. In an independent study, we showed that the well-defined, triphosphine-ligated complex $LCu(MeCN)^+$ is a more active catalyst precursor for CO_2 hydrogenation.[81] Spectroscopic monitoring of the reaction revealed mechanistic information including the catalyst resting state and two important roles for the base in promoting catalysis. However, no hydride species was observed throughout the reaction, and, therefore, the identity of the active species that reacts with CO_2 was not determined. Herein, we present studies of a series of triphosphine-ligated copper hydrides that are plausible catalytic intermediates, including a novel cationic dicopper hydride, $[(LCu)_2H]^+$, a previously-reported dimer, $(LCuH)_2$, and a transient mononuclear hydride, LCuH. In addition, we report the measurement of the thermodynamic hydride donor ability, or hydricity, of $[(LCu)_2H]^+$. These studies represent the first such measurement for a copper hydride and demonstrate the thermodynamic favorability of using copper hydrides for CO_2 hydrogenation. Finally, we report the stoichiometric and catalytic reactivity of $[(LCu)_2H]^+$ with CO_2 and discuss the implications for the catalytic mechanism, including an unusual role for the base in promoting these reactions.

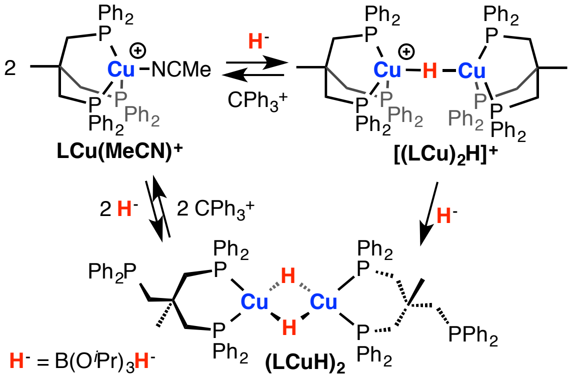
RESULTS

Syntheses of Copper Hydrides $[(LCu)_2H]^+$ and $(LCuH)_2$. The reaction of $LCu(MeCN)PF_6$[82] (L = 1,1,1-tris(diphenylphosphinomethyl)ethane) with 0.5 equivalents of $KB(O^iPr)_3H$ in MeCN formed a colorless, cationic dicopper hydride, $[(LCu)_2H]^+$**,** which was isolated cleanly in 74% yield after workup. $[(LCu)_2H]^+$ is somewhat thermally unstable under a nitrogen atmosphere in the solid state and even more so in solution, forming small but noticeable amounts of Cu^0, H_2, and the bis-ligated complex $Cu(L)_2^+$ within several hours. This decomposition is inhibited at -35 °C or under an H_2 atmosphere.

Addition of excess $KB(O^iPr)_3H$ to $LCu(MeCN)^+$ or of slightly more than 0.5 equivalents of $KB(O^iPr)_3H$ to $[(LCu)_2H]^+$ in THF or MeCN gave $(LCuH)_2$, (Scheme 1, top right), which was previously reported by Goeden *et al.* as the product of hydrogenolysis of $(CuO^tBu)_4$ in the presence of L.[59] $(LCuH)_2$ is a neutral, dimeric species, in which two hydrides bridge the two copper centers. Goeden *et al.* noted the thermal instability of $(LCuH)_2$ in solution and characterized it at -40 °C. We similarly find that $(LCuH)_2$ is significantly less thermally stable than $[(LCu)_2H]^+$, decomposing at room temperature in THF to give a black precipitate and free L. Addition of a stoichiometric amount of CPh_3BF_4 to a MeCN solution of $[(LCu)_2H]^+$ or suspension of $(LCuH)_2$ resulted in clean conversion back to $LCu(MeCN)^+$.

Spectroscopic and Structural Characterization of $[(LCu)_2H]^+$ and $(LCuH)_2$. Only a single set of ligand resonances is observed in the ^1H and ^{31}P NMR spectra of $[(LCu)_2H]^+$, indicating that the triphosphine ligands of the copper centers are magnetically equivalent, with κ^3 binding of each ligand. The PF_6^- anion also appears as a septet in the ^{31}P NMR spectrum and integrates to one-sixth of the signal for the triphosphine ligands, as expected for a dicopper cation. The hydride and phosphine resonances in $[(LCu)_2H]^+$ are both broadened at room temperature, likely due to the adjacent I = 3/2 Cu nuclei. The observed broadening obscures P-H coupling, even at low temperature.

Scheme 1. Synthesis of Copper Hydrides



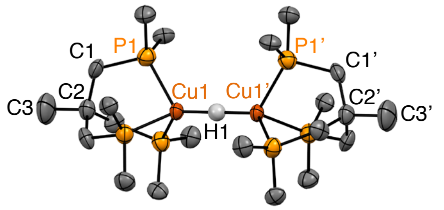


Figure 1. X-ray structure of the cationic dicopper unit in $[(LCu)_2H]PF_6$. Thermal ellipsoids are drawn at the 30% probability level. For clarity, only the *ipso* carbon of each phenyl substituents is shown, and hydrogen atoms, other than the hydride, have been omitted. Selected bond lengths (Å) and angles°: Cu1-Cu1’, 3.044(4); Cu1-H1, 1.522(2); Cu1-P1, 2.28(5); P1-C1, 1.86(5); C1-C2, 1.556(7); P1-Cu1-P1’, 91.3(2); P1-Cu1-H1’124.4(1); C2-C1-P1, 111(2); C1-P1-Cu1, 110(2).

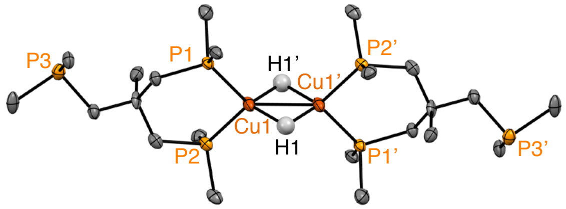


Figure 2. X-ray structure of $(LCuH)_2(MeCN)$. Thermal ellipsoids are drawn at the 30% probability level. For clarity, only the *ipso* carbon of each phenyl substituent is shown, and the solvent molecules and hydrogen atoms are omitted, other than the hydrides. Only the major disordered component is shown. Selected bond lengths (Å) and angles°: Cu1-H1, 1.63(3); Cu1-P1, 2.228(1); Cu1-P2, 2.234(4); Cu1-Cu1’, 2.3687(7); P1-Cu1-P2, 100.8(1); P1-Cu1-H1, 117(1); P2-Cu1-H1, 108(1).

The hydride resonance in $[(LCu)_2H]^+$ appears at a shift of -1.46 ppm in the ^{1}H NMR spectrum and integrates to the expected 0.5 H per copper. The ^{31}P chemical shift appears at -20.8 ppm, very similar to the shift of -21.0 ppm reported by Goeden *et al.* for the copper-coordinated phosphines of $(LCuH)_2$ at -40 °C in toluene-d_8.[59] We observe a different shift for $(LCuH)_2$, such that the two species can be easily distinguished by their ^{31}P NMR resonances. At room temperature, toluene-d_8 solutions of $(LCuH)_2$ show a broad singlet at -18.4 ppm, and in THF-d_8 the same signal is observed at -18.7 ppm. The chemical shift of this signal is temperature-dependent, shifting upfield to -19.4 ppm at -40 °C, but remains considerably downfield of the previously reported chemical shift of -21.0 ppm. In addition to the broad resonance for the copper-coordinated phosphines, we observe two sharp peaks at -27.0 and -27.8 ppm for the dangling phosphine arms of $(LCuH)_2$ in toluene-d_8 at -40 °C, which were previously reported at -28.9 and -29.7 ppm. At room temperature, these peaks are nearly coalesced and shift downfield to approximately -25.0 ppm, overlapping with the signal for free ligand, which forms from thermal decomposition of $(LCuH)_2$.

The solid-state structure of $[(LCu)_2H]^+$ as determined by X-ray crystallography (Figure 1) is consistent with the spectroscopic data, showing a hydride ligand sandwiched between two equivalent copper centers with κ^3-coordinated triphosphine ligands. The unit cell contains three independent dicopper cations. Only one-sixth of each cation is unique due to overall D_3 molecular symmetry, as the three arms of each ligand are related by crystallographically imposed three-fold rotational symmetry about the Cu-H-Cu axis, and the two copper centers are related by perpendicular two-fold rotation axes. The Cu-Cu distances in the individual cations are 3.044(4), 3.097(6), and 3.096(6) Å, giving an average Cu-Cu distance of 3.08(3) Å. In two of the dicopper cations, the hydride atoms were located from the Fourier difference map equidistant between the copper centers, along the Cu-Cu axis. The third was placed by analogy at the same site between the copper centers of the third cation. The Cu-H distances for all three hydrides were allowed to refine freely in subsequent refinements. With the caveat that these hydrogen atom positions cannot be determined accurately by X-ray crystallography, the hydride in each molecule appears to be equidistant between each copper along the Cu-H-Cu axis, with Cu-H distances of 1.522(2), 1.548(3), and 1.548(3) Å for the three dicopper cations in the unit cell.

The phosphines on the two different ligands are very nearly eclipsed, with average P-Cu-Cu-P torsion angles of 9.6°. The eclipsed conformation appears to be the result of a steric effect. The phenyl substituents on each ligand are brought into close contact by their convergence around the small hydride ion, and the eclipsed conformation allows them to interpenetrate to relieve this strain; they would clash further if the triphosphine ligands were staggered. The copper centers in $[(LCu)_2H]^+$ show a distinct distortion from tetrahedral geometry. The P-Cu-P angles of 93.6(1)° are compressed and the P-Cu-H angles of 122.7(8)° are elongated relative to the 109.5° for an ideal tetrahedral metal center.[83]

The neutral copper hydride dimer $(LCuH)_2$ is insoluble in MeCN; when synthesized by reaction of $LCu(MeCN)^+$ with $KB(O^iPr)_3H$ in MeCN, $(LCuH)_2(MeCN)$ precipitates cleanly as a yellow crystalline solid. A single crystal grown in this way was studied by X-ray crystallography, as shown in Figure 2. The resulting structure is similar to that previously reported for $(LCuH)_2(THF)$,[59] except that a minor disordered component is observed in the newer structure. The major component of $(LCuH)_2$ has inversion symmetry centered around the Cu_2H_2 diamond core. The disordered position represents a diastereomeric form of the dimer, in which the positions of the copper centers, the hydrides, and the phenyl groups are largely unchanged. However, the phosphorous atoms and the carbon atoms in the tris(phosphinomethyl)ethane backbone of one of the two triphosphine ligands are inverted, oriented in the opposite direction from the major isomer. Effectively, while the majority of the molecule retains its inversion symmetry, the backbones of the two ligands adopt localized C_s mirror symmetry. These two isomeric forms of $(LCuH)_2$ explain the observation of two resonances for the dangling phosphines in the ^{31}P NMR spectrum of $(LCuH)_2$. The signals do not represent inequivalent phosphines within a single dimeric structure, but rather two distinct structures. Refinement of the disorder in the crystal structure suggested that the major component represents 85.9% of the structure, corresponding to a 6:1 ratio of the two isomers, compared to the approximately 2:1 ratio observed by ^{31}P NMR spectroscopy. The difference is potentially due to packing effects in the crystal.

H_2 Heterolysis Reactions and Hydricity Measurements of $[(LCu)_2H]^+$. $LCu(MeCN)^+$ reacts with strong bases under 1 atm H_2 to give $[(LCu)_2H]^+$ in reversible equilibria (Scheme 2). The equilibrium constants for these reactions were measured in MeCN and found to depend on the strength of the base, as expected for heterolysis of H_2. These equilibria afforded a measure of the thermodynamic hydride donor ability, or hydricity ($\Delta G°_{H^-}$), of $[(LCu)_2H]^+$, which can be calculated from the equilibrium constant for the H_2 heterolysis reaction and the pK_a of the protonated base (see the discussion). The equilibrium constants were determined by ^1H and ^{31}P NMR spectroscopy for CD_3CN solutions of $LCu(MeCN)^+$ (5-10 mM) and equimolar amounts of base. Equilibrium constants for these reactions and hydricity values calculated from these values are summarized in Table 1.

No hydride formation was observed when using NEt^iPr_2 or NEt_3 (pK_a $[BH]^+$ 18.8), TMG (1,1,3,3-tetramethylguanidine, pK_a $[BH]^+$ 23.4), or DBU (1,8-diazabicycloundec-7-ene, pK_a $[BH]^+$ 24.3),[85] which are therefore absent from Table 1. The lack of an observed reaction under these conditions suggests $K_{eq} << 1$ M^{-1} atm^{-1}, and therefore, using the pK_a of DBU, $\Delta G°_{H^-} < 43$ kcal/mol. Reactions of $LCu(MeCN)^+$ with one atm H_2 in the presence of one equivalent of the strongly basic, non-coordinating phosphazenes $P_1{}^tBu(pyrr)$ (pK_a $[BH]^+$ 28.4, Table 1, entry 1) and $P_1{}^tBu(dma)$ (pK_a $[BH]^+$ 27.0 , Table 1, entry 2) or the bulky guanidine ^tBuTMG (pK_a $[BH]^+$ 26.5, Table 1, entry 7) showed slow formation of $[(LCu)_2H]^+$, along with the corresponding conjugate acids. No other products or byproducts were observed in these reactions. The ratios of $[[(LCu)_2H]^+]/[LCu(MeCN)^+]^2$ and $[BH^+]/[B]$ increased in parallel before stabilizing after approximately 1.5 weeks, indicating the reaction had reached equilibrium. The equilibrium constants measured for these reactions correspond to $\Delta G°_{H^-}$ values of 41.2 ± 0.6, 40.9 ± 0.3 kcal/mol, and 41.0 ± 0.5 kcal/mol. To verify reproducibility and reversibility, the H_2 heterolysis reaction was run with varied stoichiometry (Table 1, entries 2, 4, and 5) and in reverse (entry 6) as detailed in Table 1 and in the SI. These reactions gave values for $\Delta G°_{H^-}$ that are identical within experimental uncertainty, confirming that these values are derived from true equilibria rather than incomplete reactions. Altogether, combining the data from all reactions with a measurable K_{eq}, the hydricity of $[(LCu)_2H]^+$ is calculated to be $\Delta G°_{H^-} = 41.0 \pm 0.5$ kcal/mol, for which the reported uncertainty is two standard deviations.

Stoichiometric Reactions of $[(LCu)_2H]^+$ with CO_2. We investigated the reaction of $[(LCu)_2H]^+$ with CO_2, as summarized in Scheme 2, bottom. With 1 atm CO_2, this reaction is quite slow, taking approximately 4 days to reach completion. The only product observed in solution is $LCu(MeCN)^+$. The formate product precipitates as the mononuclear complex $LCuO_2CH$, which is largely insoluble in MeCN at ambient temperatures. X-ray quality single crystals grown directly from the reaction solution yielded a structure identical to that originally reported for $LCuO_2CH$.[84] The formation of this product from CO_2 even at low temperature and pressure is consistent with the favorability predicted by the hydricity value (see the discussion). However, the rate of CO_2 reactivity was significantly slower than expected for a catalytically active intermediate.

Scheme 2. Formation and CO_2 Reactivity of $[(LCu)_2H]^+$

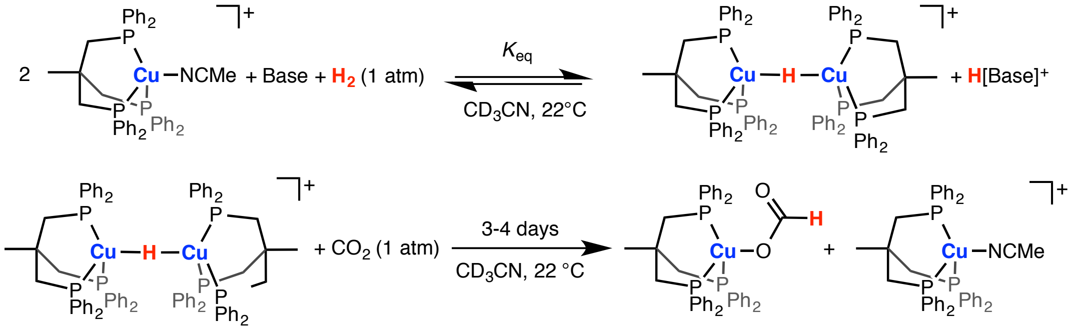


Table 1. Equilibrium Constants for H_2 Heterolysis Reactions and Hydricity Values Calculated for $[(LCu)_2H]^+$ in CD_3CN.

Entry	M^+/M_2H^+	P_{H2} (atm)	Base/H[Base]$^+$	pK_a(H[Base]$^+$)	K_{eq} (M^{-1} atm^{-1})	$\Delta G°_{H^-}$ (kcal/mol)
1	M^+	1.0	$P_1{}^t$Bu(pyrr)[c]	28.4[d]	450 ± 230	**40.9 ± 0.3**
2	M^+	1.7	$P_1{}^t$Bu(pyrr)[c]	28.4[d]	595	**41.0**
3	M^+	1.0	$P_1{}^t$Bu(dma)[b]	27.0[d]	32 ± 30	**41.2 ± 0.6**
4	M^+	1.7	$P_1{}^t$Bu(dma)[b]	27.0[d]	17	**40.9**
5	M^+	1.0	$P_1{}^t$Bu(dma)[b] (0.5 equiv)	27.0[d]	37	**41.3**
6	M_2H^+	1.0	H[$P_1{}^t$Bu(dma)]$^{+b}$	27.0[d]	52	**41.5**
7	M^+	1.0	^{t}BuTMG[a]	26.5[e]	7.3 ± 5.3	**41.0 ± 0.5**

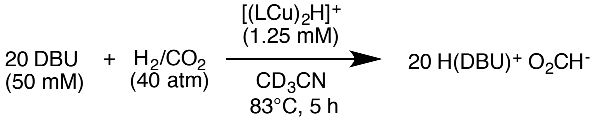
All data are for reactions at 22 ± 3 °C using 5-10 mM Cu^+ in CD_3CN. [a] ^{t}BuTMG = 2-*tert*-Butyl-1,1,3,3-tetramethylguanidine. K_{eq} and $\Delta G°_{H^-}$ values with reported uncertainties are the averages of three experiments each, and uncertainties are reported as two standard deviations. [b] $P_1{}^t$Bu(dma) = *tert*-Butylimino-tris(dimethylamino)phosphorane. [c] $P_1{}^t$Bu(pyrr) = *tert*-Butylimino-tris(pyrrolidino)phosphorane. [d] pK_a values taken from ref 85. [e] pK_a value taken from ref 81.

Use of $[(LCu)_2H]^+$ as a Catalyst Precursor for CO_2 Hydrogenation. To assess whether $[(LCu)_2H]^+$ was a viable catalytic intermediate, it was tested as a catalyst precursor (Scheme 3). A CD_3CN solution of $[(LCu)_2H]^+$ (1.25 mM) and DBU (50 mM) was degassed and charged with 40 atm H_2/CO_2, then heated to 83°C. The reaction progress was monitored *in operando* by ^{1}H NMR spectroscopy in a setup identical to our previously reported reactions using LCu(MeCN)$^+$ as a catalyst.[81] The reaction progress is shown in Figure 3. Clean and essentially complete conversion to H[DBU]O_2CH was observed within 5 hours, indicating that $[(LCu)_2H]^+$ is an active catalytic precursor. In fact, the catalytic performance, including the rate of formate production and the species observed in solution, was essentially indistinguishable from reactions using LCu(MeCN)$^+$ as a catalyst precursor.[81] The initial catalyst resting state was the base adduct, LCu(DBU)$^+$, and converted over time to $LCuO_2CH$ as the reaction progressed, with a concomitant decrease in catalytic activity. Because the calculation of the TOF and TON values depend on the catalyst concentration, in this case they are reported relative to the LCu(DBU)$^+$ concentration of 2.5 mM, rather than the starting concentration of 1.25 mM for $[(LCu)_2H]^+$. This gives an initial TOF of 7.5 h^{-1}, equivalent to the TOF measured using LCu(MeCN)$^+$ as a catalyst precursor.

Stoichiometric Reactivity of $[(LCu)_2H]^+$ in the Presence of DBU and Other Bases. In the catalytic reaction, complete conversion from $[(LCu)_2H]^+$ to LCu(DBU)$^+$ was evident in the first spectrum following gas addition. This result suggested that $[(LCu)_2H]^+$ reacts with CO_2 much faster under catalytic conditions than in the stoichiometric studies described above. The dramatically increased rate suggested that either the presence of H_2 or the presence of the base altered the rate of CO_2 insertion. Accordingly, we investigated the effect of added base on the stoichiometric reaction of $[(LCu)_2H]^+$ with CO_2.

The addition of 10 equivalents of DBU (5 equivalents per Cu) led to a dramatic increase in the rate of the reaction of $[(LCu)_2H]^+$ with CO_2. The reaction was complete within 15 minutes, and LCu(DBU)$^+$ was the only copper species observed by ^{1}H and ^{31}P NMR spectroscopy, indicating that the formate was an outer-sphere anion (Scheme 4, top). The formate peak was observed at 8.6 ppm, also consistent with an outer-sphere anion, yet it was broadened, indicating exchange between $LCuO_2CH$ and LCu(DBU)$^+$ near the NMR timescale, as observed during catalysis. A similar rate enhancement for the reaction of $[(LCu)_2H]^+$ with CO_2 was observed when using a 20-fold excess of TMG. However, much slower CO_2 reactivity was observed when using ^{t}BuTMG: the hydride was not consumed until after 5 hours when using this base.

Scheme 3. CO_2 Hydrogenation using $[(LCu)_2H]^+$



$$\underset{(50\ mM)}{20\ DBU} + \underset{(40\ atm)}{H_2/CO_2} \xrightarrow[\substack{CD_3CN \\ 83°C,\ 5\ h}]{\substack{[(LCu)_2H]^+ \\ (1.25\ mM)}} 20\ H(DBU)^+\ O_2CH^-$$

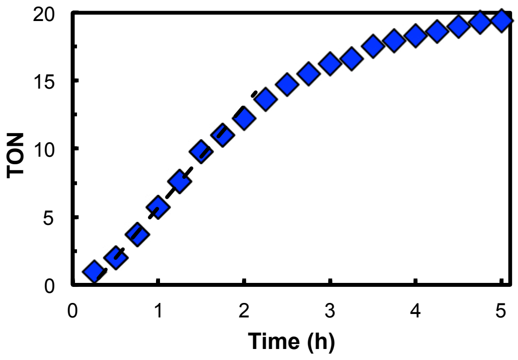
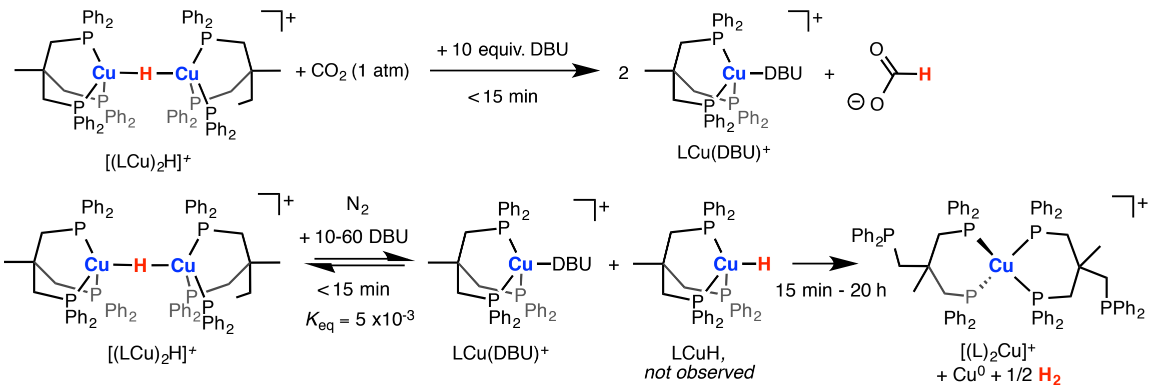


Figure 3. Progress for CO_2 hydrogenation using $[(LCu)_2H]^+$ as a catalyst precursor. Reaction conditions are indicated in Scheme 3. TON defined as mol $[HCO_2^-]$/mol [LCu(DBU)]$^+$ as determined by NMR spectroscopy. The initial linear region (dashed line) gives an initial TOF (TON/h) of 7.5 h^{-1}.

Scheme 4. Reactions of $[(LCu)_2H]^+$ in the presence of excess DBU



In the absence of CO_2, addition of excess DBU to $[(LCu)_2H]^+$ led to a color change from colorless to pale yellow and the immediate appearance of $LCu(DBU)^+$ in the ^1H and ^{31}P NMR spectra, followed by slow formation of the bis-ligated copper(I) complex $[Cu(L)_2]^+$. The latter species appeared in trace amounts after 10 min and steadily grew in over the next 20 h. A small amount of hydrogen became visible after 1 hr in the ^1H NMR spectrum. A black precipitate was also formed on the same timescale as $[Cu(L)_2]^+$. The amount of $LCu(DBU)^+$ that was formed and the rate of decomposition to $[Cu(L)_2]^+$ both increased with a greater excess of added DBU, consistent with the formation of $LCu(DBU)^+$ and a new (unobserved) hydride species in a rapid equilibrium, followed by slow decomposition to give Cu^0, $[Cu(L)_2]^+$, and H_2. Under the assumption that the unobserved hydride is a mononuclear species that forms in a 1:1 stoichiometry with $LCu(DBU)^+$ (Scheme 4, bottom) and with NMR features that overlap with those of $[(LCu)_2H]^+$, K_{eq} for the equilibrium in Scheme 4 was calculated to be $(4.8 \pm 3.3)x10^{-3}$ from the initial ^{31}P spectra of reactions using approximately 10-60 equiv DBU relative to $[(LCu)_2H]^+$. This equilibrium constant corresponds to a $\Delta G°$ value of 3.2 ± 0.2 kcal/mol for the formation of $LCu(DBU)^+$ and LCuH from $[(LCu)_2H]^+$ and DBU, as shown in Table 2.

Table 2. Equilibrium Data for DBU-promoted Decomposition of $[(LCu)_2H]^+$ into $LCu(DBU)^+$ and LCuH in CD_3CN.

Entry	Equiv. DBU	K_{eq} $(x10^{-3})$	$\Delta G°$ (kcal/mol)
1	10	4.9	**3.2**
2	10	3.3	**3.4**
3	20	7.5	**2.9**
4	36	3.6	**3.4**
5	54	4.6	**3.2**
Average		4.8 ± 3.3	**3.2 ± 0.2**

All data are for reactions at ambient temperatures using 1.5-2.5 mM $[(LCu)_2H]^+$ in CD_3CN. See SI for details of the calculations.

DISCUSSION

Hydricity of $[(LCu)_2H]^+$ and Implications for CO_2 Hydrogenation. For efficient catalysis, the energies of the catalytic intermediates need to be balanced. In the context of CO_2 hydrogenation, a metal hydride must be sufficiently reactive to transfer a hydride to CO_2 but stable enough to be regenerated efficiently using hydrogen and a base. This thermodynamic balance can be conveniently assessed by quantifying the hydricity value, or $\Delta G°_{H^-}$, of the metal hydride.[23] The hydricity is defined as the free energy required to cleave the metal-hydride bond heterolytically, forming free hydride and a metal cation (eq 1 in Scheme 5). A lower hydricity (corresponding to a more positive value of $\Delta G°_{H^-}$) indicates that the M-H species is a poorer hydride donor and, equivalently, that the free metal ion is a better hydride acceptor. The thermodynamic favorability of hydride transfer from a metal hydride to CO_2 can be evaluated by comparing the hydricity of the metal species to that of formate, which has been estimated to be 44 kcal/mol in MeCN.[21-23,86] Because the transfer of a hydride to CO_2 (eq 2) is the reverse of the hydricity half-reaction for formate, the overall reaction, hydride transfer from a metal to CO_2 (eq 3), will be favorable only if the hydricity of the M-H species is less than 44 kcal/mol.

Scheme 5. Favorability of H^- transfer from M^+ to CO_2

Reaction	ΔG° (kcal/mol)	
$M\text{-}H \longrightarrow M^+ + H^-$	ΔG_{H^-}	(1)
$H^- + CO_2 \longrightarrow HCO_2^-$	- 44	(2)
$M\text{-}H + CO_2 \longrightarrow M^+ + HCO_2^-$	$\Delta G°_{H^-}$ - 44	(3)

The hydricity value also determines the favorability of regenerating a hydride from the free metal ion using H_2 and a base, shown for the case of $[(LCu)_2H]^+$ in Scheme 6. The reverse of this H_2 heterolysis equilibrium (eq 4) can be combined with the hydride-donor ability of H_2 (eq 5), and the strength of the base (eq 6) in a thermodynamic cycle yielding the hydricity half-reaction for the metal hydride (eq 7).[23]

The free energy of eq 5 has been estimated to be 76 kcal/mol in MeCN.[23] The equilibrium constant (K_{eq}) for regenerating a metal hydride in MeCN can therefore be calculated if its hydricity and the pK_a of the protonated base are known. Alternatively, if the hydricity is not known, the thermodynamic cycle in Scheme 6 can be used to calculate it from equilibration of the H_2 heterolysis reaction in MeCN with a base of known strength. The equation for the hydricity calculation in that case is given in eq 8.[87-89]

Scheme 6. Thermodynamic cycle relating hydricity and H_2 heterolysis equilibria.

Reaction			ΔG° (kcal/mol)	
$[(LCu)_2H]^+ + H[Base]^+ + 2\,MeCN$	$\rightarrow$	$2\,LCu(MeCN)^+ + Base + H_2$	$1.364\log K_{eq}$	(4)
H_2	$\rightarrow$	$H^+ + H^-$	76	(5)
$Base + H^+$	$\rightarrow$	$H[Base]^+$	$-1.364\,pK_{a(BH+)}$	(6)
$[(LCu)_2H]^+ + 2\,MeCN$	$\rightarrow$	$2\,LCu(MeCN)^+ + H^-$	$\Delta G^\circ_{H^-}$	(7)

$$\Delta G^\circ_{H^-} = 1.364\log K_{eq} - 1.364\,pK_{a(BH+)} + 76 \qquad (8)$$

We determined the hydricity of the dicopper hydride cation $[(LCu)_2H]^+$ by measuring the equilibrium constants for its formation from $LCu(MeCN)^+$ *via* H_2 heterolysis. These reactions formed $[(LCu)_2H]^+$ only in the presence of strong bases (pK_a $[BH]^+ > 26$). The equilibrium constants gave a consistent value of $\Delta G^\circ_{H^-} = 41.0 \pm 0.5$ kcal/mol for $[(LCu)_2H]^+$. This value is in a relatively advantageous range for CO_2 hydrogenation. It is 3 kcal/mol less positive than that of formate, which provides sufficient but not excessive driving force for the reaction with CO_2. A greater hydricity (lower $\Delta G^\circ_{H^-}$) would provide even more of a driving force, which might lead to a faster reaction at room temperature. This change might be achieved by increasing the donor strength of the phosphines on the triphosphine ligand. However, very low values of $\Delta G^\circ_{H^-}$ correspond to more reactive species that can be difficult to regenerate in a catalytic cycle.

Structural Characterization of $[(LCu)_2H]^+$. Although the chemistry of multinuclear copper hydrides is extensive, $[(LCu)_2H]^+$ is one of only two structurally-characterized cationic dicopper hydrides containing phosphine ligands.[72] The most notable structural features in $[(LCu)_2H]^+$ are its apparently linear Cu–H–Cu unit, the long Cu–Cu distance within this unit, and the eclipsed arrangement of the phosphines around this axis. All of these features appear to be related to the steric pressure imposed by bringing two copper-triphosphine units together around one small hydride ligand. Many multicopper(I) clusters show very short intermetallic distances that have been attributed to a direct attractive (cuprophilic) interaction between the copper centers or to three-center, two-electron bonding; in other cases, the short distances are simply a result of the geometric constraints imposed by the ligand bridging the metal centers.[90-93] Whether due to these steric or electronic effects, short Cu–Cu distances are ubiquitous in copper hydrides, making the long Cu–Cu distance of >3 Å in $[(LCu)_2H]^+$ unique. All structurally-characterized copper hydrides, except for $[(LCu)_2H]^+$, contain at least one Cu–H–Cu unit with a Cu–Cu distance of 2.89 Å or shorter,[94] with most having a Cu–Cu distance in the range of 2.4-2.6 Å.

Considering that truly linear M–H–M groups are quite rare,[95-97] and no other examples exist among copper hydrides, it is possible that the apparent position of the hydride in $[(LCu)_2H]^+$ is actually the average of several disordered structures with bent geometries. There is precedent for this phenomenon in the structures of other dinuclear hydrides.[98-101] However, the long Cu–Cu distance in this complex probably precludes the attractive interactions between the metal centers that would lead to a bent geometry. In any case, X-ray diffraction techniques cannot resolve this issue.

Comparison of Cationic and Neutral Copper Hydrides. The cationic nature of $[(LCu)_2H]^+$ is unusual among copper hydrides and probably attenuates its hydricity. Most known copper hydrides are neutral species and are likely even stronger hydride donors. Three other cationic dicopper hydrides have been reported: two are N-heterocyclic carbene (NHC) complexes, $[(IPrCu)_2H]^+$ and the very similar $[(SIPrCu)_2H]^+$.[50,62] The third, $[(dpmppm\text{-}Cu)_2H]^+$, is a tetraphosphine complex reported by Tanase and coworkers, in which each copper center is coordinated to three phosphines and the bridging hydride (dpmppm = *meso*-bis[(diphenylphosphinomethyl)phenylphosphino]methane).[72] This complex is thus quite analogous to $[(LCu)_2H]^+$. The Cu–*H* ^{1}H NMR chemical shifts for all of the known cationic CuH species are upfield relative to neutral copper hydrides, which have positive chemical shifts.[102] The average Cu–H distances of 1.54 Å in $[(LCu)_2H]^+$ are also shorter than the distances in $(LCuH)_2$ (1.66 and 1.81 Å),[59] consistent with a more electron-deficient hydride ligand. The Cu–H distances are intermediate between those in the other cationic species $[(dpmppm\text{-}Cu)_2H]^+$ (1.62 Å) and $[(IPr)Cu]_2H^+$ (1.45 Å). However, its Cu–Cu distance of 3.08 Å is significantly longer than those of $[(dpmppm\text{-}Cu)_2H]^+$ (2.7948(7) Å) and $[(IPr)Cu]_2H^+$ (2.533(2) Å), which have distinctly bent Cu–H–Cu angles of 120˚ and 122˚, respectively.

Interestingly, Lalic and coworkers demonstrated that the cationic $[(NHC\text{-}Cu)_2H]^+$ complexes showed markedly lower reactivity towards other electrophiles than their corresponding neutral hydrides, $[(IPr)CuH]_2$ and $[(SIPr)CuH]_2$.[50] Nevertheless, all of the known cationic dicopper hydrides react with CO_2 to produce formate complexes. The reaction of $[(\text{dpmppm-Cu})_2H]^+$ with CO_2 was described as slow, although it proceeded largely to completion in < 1 day, making it more rapid than the reaction of $[(LCu)_2H]^+$ with CO_2. A *di*cationic *tri*copper hydride with diphosphine (dcpm) ligands has also been reported. Its CO_2 reactivity was not specifically reported, but it is stable to protic solvents and even air.[103] This stability is remarkable for a copper hydride complex and indicates that coordination of a third cationic copper center to a hydride ligand results in a dramatic loss of reactivity.

The decreases in reactivity upon coordinating each additional copper center are due in part to the Lewis acidity of the metal ion and in part to the steric shielding provided by the additional metal-ligand fragment. The former is a thermodynamic effect and should be reflected in the hydricity, while the latter is purely kinetic and would have no effect on the hydricity. We have attempted to measure the hydricity of $(LCuH)_2$ for a quantitative comparison between well defined and analogous cationic and neutral species, but its thermal decomposition prevents the establishment of equilibria required for such thermodynamic measurements.

Stoichiometric Reactivity of $[(LCu)_2H]^+$ with CO_2. Given the hydricity of 41.0 kcal/mol measured for $[(LCu)_2H]^+$ and the hydricity of 44 kcal/mol for formate, the reaction of $[(LCu)_2H]^+$ with CO_2 is predicted to be favorable by 3 kcal/mol. At room temperature, $[(LCu)_2H]^+$ does react with 1 atm CO_2, yielding the inner-sphere formate complex $LCuO_2CH$. However, the reaction is quite slow, taking ~3-4 days for complete conversion. Surprisingly, the rate of reaction is dramatically increased in the presence of excess base. In the presence of 10 equivalents of DBU or TMG, $[(LCu)_2H]^+$ reacts with CO_2 in less than 15 min, yielding two equivalents of the base adduct $LCu(DBU)^+$ or $LCu(TMG)^+$ and an outer-sphere formate anion. In the presence of the bulky base ^{t}BuTMG, the reaction rate is increased to a lesser degree, reaching completion after 5 h. We previously showed that DBU and TMG bind readily to the copper centers, whereas ^{t}BuTMG binds only very weakly.[81] Because ^{t}BuTMG is a much stronger base but a much weaker ligand, these results indicate that the increased CO_2 reactivity with DBU and TMG is related to the coordinating nature of these bases, rather than their basicity.

A plausible explanation for the enhanced CO_2 reactivity in the presence of DBU is that the base binds to one of the copper centers in $[(LCu)_2H]^+$, breaking up the dinuclear structure and forming both $LCu(DBU)^+$ and a more active, mononuclear copper hydride species, LCuH (eq 9). LCuH reacts with CO_2 much faster than $[(LCu)_2H]^+$ does, forming $LCuO_2CH$ as the initial product (eq 10), followed by rapid substitution of DBU for the formate ligand to produce a second equivalent of $LCu(DBU)^+$ and free formate (eq 11).

$$[(LCu)_2H]^+ + DBU \rightarrow LCuH + LCu(DBU)^+ \qquad (9)$$

$$LCuH + CO_2 \rightarrow LCuO_2CH \qquad (10)$$

$$LCuO_2CH + DBU \rightarrow LCu(DBU)^+ + {}^-O_2CH \qquad (11)$$

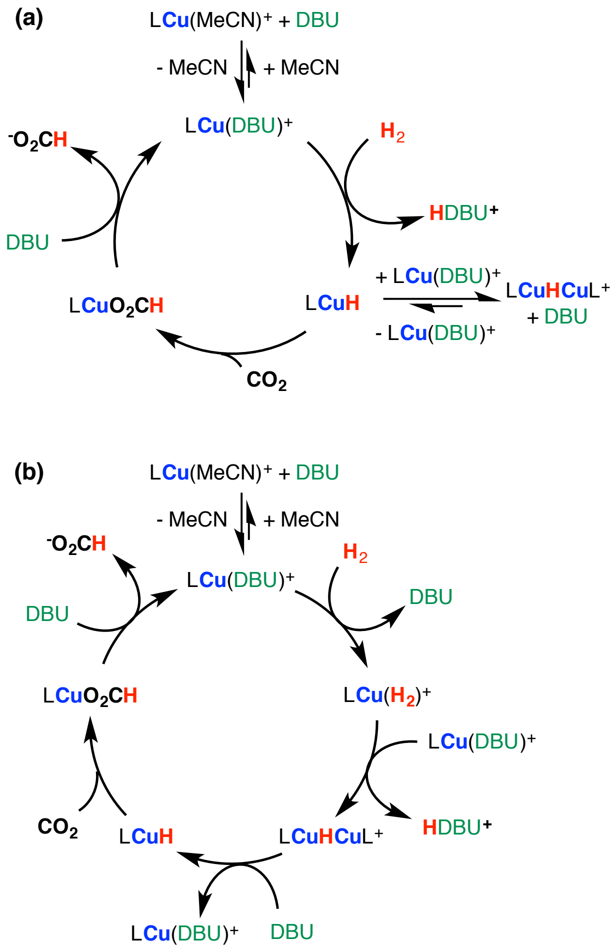
In support of this mechanism, we observe the formation of $LCu(DBU)^+$ in an unfavorable equilibrium upon the addition of excess DBU to $[(LCu)_2H]^+$ in the absence of CO_2. Slow decomposition to $[Cu(L)_2]^+$ and a black precipitate is observed on a longer timescale. We propose that the mononuclear hydride that is presumably formed in this reaction is not observed because its ^{31}P NMR spectral features are similar to and overlap with those of $[(LCu)_2H]^+$, which remains the major copper-containing species in solution and is structurally similar to the trigonally symmetric LCuH. The ^1H NMR resonances for LCuH could be obscured by those of $[(LCu)_2H]^+$ or of DBU, which is present in a large excess. $(LCuH)_2$, which could form from dimerization of LCuH, has distinct ^{31}P NMR resonances that are not observed. The reaction of LCuH with $LCu(DBU)^+$ (the reverse of eq 9) is thus apparently faster than dimerization of LCuH. Likewise, no precipitate or $[Cu(L)_2]^+$ is observed in the presence of CO_2, indicating that the reaction of LCuH with CO_2 is faster than its self-decomposition. Using the assumptions that LCuH is formed in a 1:1 stoichiometry with $LCu(DBU)^+$ and that its ^{31}P NMR resonance is overlapped with that of $[(LCu)_2H]^+$, we have estimated an equilibrium constant for the DBU-promoted dissociation of $[(LCu)_2H]^+$, $K_{\text{diss}} \approx (4.8 \pm 3.3) \times 10^{-3}$, corresponding to a $\Delta G°$ value of 3.2 ± 0.2 kcal/mol for this reaction. These studies indicate that $LCu(DBU)^+$, $[(LCu)_2H]^+$, and LCuH are the copper-containing species present at appreciable concentrations under catalytic conditions.

Implications for the Catalytic Mechanism. We previously proposed a simple mechanism for catalysis involving (a) heterolytic H_2 cleavage by the copper-base adduct $LCu(DBU)^+$ to form an unobserved copper hydride and protonated base, (b) CO_2 insertion into the copper-hydride bond to form a formate complex, and (c) displacement of the formate by DBU to regenerate $LCu(DBU)^+$.[81] Two of the catalytic intermediates have been directly observed through our *in operando* NMR studies. Whether $LCu(MeCN)^+$ or $[(LCu)_2H]^+$ was used as the catalyst precursor, the base adduct $LCu(DBU)^+$ was the only copper-containing species observed in the initial spectra. With greater reaction time and conversion, $LCuO_2CH$ became the predominant copper species. These two intermediates are in rapid equilibrium at the reaction temperature of 83 °C. The rapid exchange between DBU and formate keeps the catalyst active and soluble, whereas the formate complex is insoluble in MeCN on its own.

The remaining steps in our previously proposed catalytic cycle involve the formation and CO_2 reactivity of a transient copper hydride. Any of the three copper hydrides identified in this study could plausibly be the intermediate that reacts with CO_2. $[(LCu)_2H]^+$ can be formed under H_2 and is thermodynamically well suited to CO_2 hydrogenation. The rate, conversion, and species observed in solution for reactions using $[(LCu)_2H]^+$ as a precatalyst were identical to those in our previous studies, where $LCu(MeCN)^+$ was used as the catalyst precursor.[81] The identical performance of the two catalyst precursors is consistent with $[(LCu)_2H]^+$ being an accessible intermediate but does not necessarily indicate that it is the CO_2-reactive hydride. On the contrary, the stoichiometric reaction of $[(LCu)_2H]^+$ with CO_2 is too slow to be catalytically relevant, as discussed above. Instead, our stoichiometric studies suggest that binding of DBU to the dicopper complex forms an unobserved mononuclear hydride, LCuH, that is much more reactive.

Goeden *et al.* previously prepared the dimeric hydride complex $(LCuH)_2$ and showed that it reacted with CO_2,[59] making it another potential intermediate. However, $(LCuH)_2$ presumably forms from dimerization of LCuH, and there is no reason to suspect that dimerization assists its reaction with CO_2, or that it occurs at all under catalytic conditions. On the contrary, mononuclear copper hydrides are often believed to be the active intermediates in solution even when the structurally characterized complexes are polynuclear.[64-67] Notably, Stryker and coworkers studied $(LCuH)_2$ as a catalyst for the hydrogenation of ketones and found a half-order dependence on $[(LCuH)_2]$, indicating that the dimer dissociated to form a more reactive mononuclear hydride.[65] Moreover, our equilibrium studies suggest that recombination of LCuH with $LCu(DBU)^+$ to make $[(LCu)_2H]^+$ outcompetes the dimerization of LCuH. The factors disfavoring dimerization will be especially significant under catalytic conditions, where the concentration of LCuH is very small and vastly exceeded by the concentration of $LCu(DBU)^+$. In addition, we have found that $(LCuH)_2$ is soluble in benzene and THF but insoluble in MeCN; in contrast, no catalytic CO_2 hydrogenation is observed in benzene or THF, but catalysis occurs in MeCN. Therefore, we believe it is unlikely that $(LCuH)_2$ is an active intermediate, or even present in appreciable concentrations. For these reasons, we propose that the CO_2-reactive hydride is LCuH.

Scheme 7. Potential Catalytic Mechanisms.



Pathways for H_2 Activation and Hydride Formation. The remaining mechanistic questions center around the pathways for forming LCuH from $LCu(DBU)^+$ and H_2. Our previous studies suggested that the coordinated base within $LCu(DBU)^+$ remains bound and is intimately involved in the H_2 activation and hydride formation step(s).[81] Two plausible scenarios consistent with the available data are shown in Scheme 7, where the key distinction is whether $[(LCu)_2H]^+$ lies on the catalytic cycle, or whether it is formed in an unproductive, off-cycle equilibrium. Scheme 7(a) shows a simple modification to our originally proposed mechanism, where LCuH is formed in a bimolecular reaction of H_2 with $LCu(DBU)^+$. In this case, the formation of $[(LCu)_2H]^+$ is an off-cycle equilibrium caused by binding of the resting state $LCu(DBU)^+$ to the transient hydride. In Scheme 7(b), $[(LCu)_2H]^+$ is formed first from H_2 heterolysis and subsequently reacts with DBU to yield LCuH and $LCu(DBU)^+$. In both cases, coordination of DBU to $[(LCu)_2H]^+$ is essential to generating the active hydride and promoting catalysis. In Scheme 7(a), $[(LCu)_2H]^+$ is off-pathway, and DBU binding pushes the catalyst back on-cycle. In Scheme 7(b),

$[(LCu)_2H]^+$ is an essential intermediate, but DBU binding is still necessary to pushing the cycle forward. We cannot distinguish between the two mechanistic possibilities in Scheme 7 without a more detailed knowledge of the mechanism of H_2 activation and hydride formation. Kinetic studies that address this issue are underway.

SUMMARY AND CONCLUSIONS

To identify potential intermediates in the copper-catalyzed hydrogenation of CO_2, we have synthesized and characterized two isolable copper hydrides and uncovered evidence for the existence of one other transient species, all using the same triphosphine ligand. All of these complexes are potential catalytic intermediates. We have measured the thermodynamic hydricity of one of these hydrides, $[(LCu)_2H]^+$, which is the first such measurement reported for a copper hydride. The value, $\Delta G^\circ_{H^-}$ = 41.0 kcal/mol, indicates that $[(LCu)_2H]^+$ is a powerful hydride donor and energetically well suited to CO_2 hydrogenation. The cationic character of $[(LCu)_2H]^+$ is somewhat unusual for copper hydrides. Neutral copper hydrides are more common and are expected to be even stronger donors. The thermodynamic data therefore suggest that copper hydrides have been largely overlooked as potential catalysts for CO_2 hydrogenation.

Despite the thermodynamic favorability for the reaction of $[(LCu)_2H]^+$ with CO_2, the mononuclear complex LCuH appears to be the reactive intermediate under catalytic conditions. The formation of LCuH from $[(LCu)_2H]^+$ involves coordination of a base to break up the dinuclear structure of $[(LCu)_2H]^+$, for which we have estimated an equilibrium constant of 4.8 x10^{-3}. We have previously shown that coordination of the base to Cu^+ is essential for at least two other roles in catalysis: promoting H_2 activation and displacing formate from the inactive formate complex $LCuO_2CH$. The results in this study suggest that the base plays a third direct role in the catalytic cycle, forming the active intermediate LCuH from the less active $[(LCu)_2H]^+$. As with the other two roles for the base, this third role is dependent on its ability to coordinate to copper, explaining why bases that can coordinate strongly, particularly DBU, are more active in catalysis.

ASSOCIATED CONTENT

Experimental procedures, characterization of compounds, NMR spectra, reaction data for equilibrium studies. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*aaron.appel@pnnl.gov

Notes

The authors declare no competing financial interest

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(83) This distortion is characteristic of four-coordinate complexes with the triphosphine ligand, in which there are mismatched M-P and C-C distances on opposite sides of the six-membered metallocyclic rings. However, the distortion in $[(LCu)_2H]^+$ is pronounced even compared to most other copper(I) complexes with this ligand. The angles in $[(LCu)_2H]^+$ are more similar to $LCu(X)^+$ complexes with bulky apical (X) ligands such as diphenylbenzylphosphine (P-Cu-P, 93.1°; P-Cu-X, 123.0°) and dicyclohexylphosphine (P-Cu-P, 93.3°; P-Cu-X, 122.8°)[82] than the sterically unhindered acetonitrile ligand in $LCu(MeCN)^+$ (P-Cu-P, 95.6°; P-Cu-X, 121.2°). The Cu-P distances in $[(LCu)_2H]^+$ are 2.292 Å, in the middle of the range of 2.269 to 2.342 Å for other (κ^3-L)CuX complexes, longer than the average Cu-P distances in complexes with weakly donating, weak-field ligands such as formate (Cu-P: 2.272 Å)[84] and acetonitrile (Cu-P: 2.269 Å)[82] but shorter than complexes with more electron-rich, strong-field donors such as dicyclohexylphosphine (Cu-P: 2.311 Å).[82]

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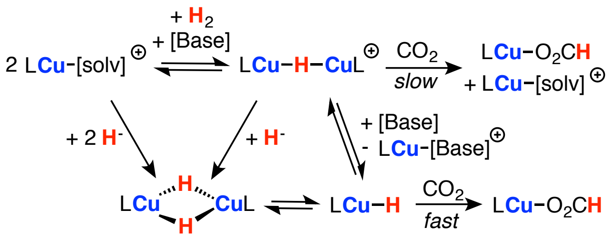
TOC Graphic:



2 LCu–[solv]⊕
+ H2
+ [Base]
LCu–H–CuL⊕
CO2
slow
LCu–O2CH
+ LCu–[solv]⊕
+ 2 H-
+ H-
+ [Base]
- LCu–[Base]⊕
LCu
H
H
CuL
LCu–H
CO2
fast
LCu–O2CH