CO2 / 13CO2 Dynamic Exchange in the Formate Complex [(2,9-(tBu) 2-phen)Cu(O2CH)] and Its Catalytic Activity in the Dehydrogenation of Formic Acid

Kieu Phung, Pierre Thuéry, Jean-Claude Berthet, Thibault Cantat

$CO_2/^{13}CO_2$ Dynamic Exchange in the Formate Complex [(2,9-(^{t}Bu)$_2$-phen)Cu(O_2CH)] and its Catalytic Activity in the Dehydrogenation of Formic Acid

Kieu Phung,[†] Pierre Thuéry,[†] Jean-Claude Berthet, [†]* and Thibault Cantat, [†]*
[†] Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif-sur-Yvette Cedex, France
*To whom correspondence should be addressed. E-mail: thibault.cantat@cea.fr

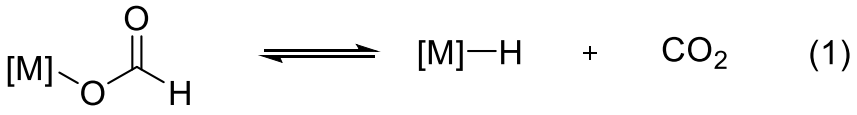
Keywords : Copper, Copper formate, Phenanthroline, Copper hydride, CO_2 insertion, Formic acid, Catalysis, Crystal structure

ABSTRACT: Formate complexes of copper(I) are rare. We report here the synthesis, characterization, and crystal structure of the simple tricoordinate [(phen*)$Cu^I(\kappa^1$-$O_2CH)$] (**1**) supported with the bulky phenanthroline ligand 2,9-di-terbutyl-1,10-phenanthroline (phen*). Complex **1** decarboxylates at 100°C to give H_2 and Cu(0) deposit with free phen*. To ensure that the degradation process goes through the hypothetical hydride [(phen*)CuH], Lewis acidic boron BR_3 compounds (R = C_6F_5, Et) or organic scavengers have been introduced to trap it. In most case degradation occurs except with $B(C_6F_5)_3$ that give the cationic complex [{(phen*)Cu}$_2$(μ-HCO_2)][(HCO_2)B(C_6F_5)$_3$] (**2**) which has been crystallized. While **1** does not react with CS_2 when heated, it undergoes under 1 atm of $^{13}CO_2$, a dynamic decarboxylation/carboxylation process that indicates transient formation of the hydride. The catalytic activity of complex **1** in the dehydrogenation of formic acid is revealed.

INTRODUCTION

In recent years, formate complexes have aroused considerable interest and a number of molecular species have been synthesized and isolated in the d- and f-transition metal as well as in non-metal series.[1–9] Their interest lies in their particular chemical behavior and reactivity, which have found application in coordination chemistry, catalysis, and in a number of areas ranging from energy storage[10–15] to reduction chemistry.[16–19]

For example, in stark contrast to the stable carboxylate complexes [M](O_2CR) (R = alkyl), decarboxylation of the [M](O_2CH) species (Eq.1) is much easier and is a classical reaction in the catalytic decomposition of formic acid (HCO_2H) into H_2 and CO_2.[12,13,20]



These complexes also proved crucial intermediates in reductive chemistry by promoting hydrogen transfer reactions and CO_2 release especially when using liquid hydrogen surrogates such as HCO_2H,

$HCO_2H{-}NEt_3$, or solid sources containing the formate ion HCO_2^-.[21–27] At last, the utility of such complexes has been highlighted in the redox transformation of CO_2 and carbonyl molecules to methanol as well as in promoting the isomerization of methyl formate (HCO_2Me) into acetic acid.[28–30] Easily obtained from different routes, mainly substitution reaction from halide derivatives with formate ion, reaction of HCO_2H with compounds involving hydrogen-sensitive [M]–R bonds (R = H, NR_2, R) species, or insertion of CO_2 into the [M]–H bond, formate complexes can be viewed as interesting synthons to generate transient or stable hydride complexes by decarboxylation,[30–32] provided that the CO_2 release is thermodynamically driven. At last, metal formates such as those of Cu(I) and Cu(II), Ag(I) and Au(I), have gained interest as new synthons in the deposition of thin metal films by chemical vapor deposition (CVD), spin-coating processes, *etc.*[33–35]

Although well documented for Cu(II),[36–40] copper(I) formate complexes are quite rare. Only a fistful have been reported with the Cu(I) ion coordinated with phosphine[41,42], carbene (NHC type)[43,44], $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti](C{\equiv}CSiMe_3)_2$[45] or nitrogenated molecules as ancillary ligands.[31,32] In the latter case, only one has been reported, the mixed-N,P-phosphane complex $[(P(C_6H_2CH_2NMe_2\text{-}2)_3)Cu(O_2CH)]$[31] which has been structurally characterized.

We report the synthesis and full characterization of the complex $[(phen^*)Cu(\eta^1\text{-}O_2CH)]$ (**1**), with the phen* = 2,9-di-terbutyl-1,10-phenanthroline ligand, and some aspects of its reactivity. We also describe our attempts to synthesize or capture the bulky monomeric hydride [(phen*)CuH], especially by its reversible insertion of labelled $^{13}CO_2$. **1** is also a rare example of a copper complex that catalyzes the dehydrogenation of formic acid.

EXPERIMENTAL SECTION

General considerations, unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques under Ar atmosphere or using a recirculating mBraun LabMaster DP inert atmosphere (Ar) glovebox, where all chemicals purchased from commercial suppliers were stored. Phen* has been prepared from modified published procedures.[46–48]

Commercial CuI was degassed and stored in the glove boxes. The yellow complex [Cu(O^{t}Bu)] was prepared by addition of 1 equiv. ^{t}BuOK on a suspension of CuI in THF according to the literature procedure.[49] ^{1}H NMR (benzene-d_6): δ 1.32 (s, ^{t}Bu). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 72.7 C-(Me), 35.8 (Me). Being thermally instable, [Cu(O^{t}Bu)] was stored in the fridge (-40°C) inside the glovebox. The 4 Å molecular sieves (Aldrich) were activated by drying under dynamic vacuum at 250 °C for 48 h prior to use. Mesitylene (Aldrich) was stored over activated 4 Å molecular sieves and used directly without further purification. Deuterated solvents (THF, benzene, acetonitrile) purchased from Eurisotop were dried over potassium or KH, distilled under vacuum and stored over 4 Å molecular sieves. Catalytic dehydrogenation reaction were performed in high-pressure New-Era NMR tubes to avoid potential explosion. NMR spectra were obtained using a Bruker AVANCE Neo 400 MHz spectrometer. Chemical shifts for ^{1}H NMR were referenced to solvent impurities and are given in ppm. All the spectra were recorded at 25 °C.

Synthesis of [(phen*)Cu(κ^1-O$_2$CH)] (1) : [Cu(O^{t}Bu)] (84.5 mg, 0.62 mmol) and phen* (180.7 mg, 0.62 mmol) were weighted in a 50 mL round bottom flask and dissolved in freshly distilled THF (20 mL). The resulted clear light brown mixture was stirred at room temperature for ~1 h and formic acid (27.6 µL, 0.62 mmol) was added. The solution immediately turned clear red. After 1 h stirring at room temperature, the solvent and volatiles were removed under vacuum. The residual dark-orange solid was washed with pentane (10 mL x 3) and dried under vacuum overnight. **1** was obtained as dark-orange solid (220.9 mg, 89 %). Orange crystals of $[(phen^*)Cu(O_2CH)_{0.8}I_{0.2}].(THF)_{0.5}$ (**1'**) were obtained by slow diffusion of pentane to a THF solution of **1** (containing KI).$\{^1H\}$ NMR 400 MHz, THF-d_8, δ/ppm): 8.41 (d, J = 8.4 Hz, 2H), 8.34 – 8.07 (s, 1H, CO_2H), 7.97 (d, J = 8.4 Hz, 2H), 7.81 (s, 2H), 1.76 (s, 18H).$\{^{13}C\}$ NMR (101 MHz, THF-d_8, δ/ppm): 168.86, 144.20, 137.58, 127.08, 125.45, 120.95, 120.91, 38.32, 30.03. (*carbon of CO_2H not seen*). IR data (ν cm^{-1}) : 2962 (w), 2783 (w), 2696 (w), 1620 (s, CO_2), 1612 (m), 1583 (w), 1550 (m), 1496 (s), 1477 (w), 1415 (w), 1392 (w), 1363 (m), 1327 (s), 1209 (w), 1136 (s), 923 (w), 860 (s), 754 (s),

650 (w), 615 (m). Elemental analysis for $C_{20}H_{24}CuN_2(HCO_2)_{0.8}I_{0.2}$, (M = 417.37 g/mol), found (theoretical) %: C, 59.43 (59.86); H, 6.02 (5.99); N, 6.92 (6.71).

[{(phen*)Cu}$_2$(μ-κ^2-O$_2$CH)][HCO$_2$B(C$_6$F$_5$)$_3$] (2) : A J. Young NMR tube was filled with **1** (7 mg, 0.017 mmol), $B(C_6F_5)_3$ (4.5 mg, 8.5 μmol, 0.5 equiv.) and THF-*d*$_8$ (0.5 ml) in the glovebox. The dark-orange mixture has turned yellow after 15 h at room temperature and the ^{1}H NMR spectra were carried out. {^{1}H} NMR (400 MHz, THF-*d*$_8$, δ/ppm) 8.60 (d, *J* = 8.6 Hz, 4H), 8.43 (s, 1H, *H*CO$_2$B), 8.19 (s, 1H, [Cu]$_2$(μ-O$_2$C*H*), 8.10 (d, *J* = 8.6 Hz, 4H), 8.01 (s, 4H), 1.65 (s, 35H). Single crystals of **2** were grown by slow diffusion of pentane into a THF solution of **1** and $B(C_6F_5)_3$ in the 1/1 ratio.

Thermal treatment of 1 : A J. Young NMR tube was filled with **1** (5 mg, 0.012 mmol) in solution in THF-*d*$_8$ (0.5 ml). The dark-orange suspension was heated at 50 °C for 5 h to result a clear orange solution and dark-red solid and continue at 60 °C for 7 h. At the end, the ^{1}H NMR spectra of the clear light yellow solution indicated the release of free ligand with the formation of dark-red precipitate.

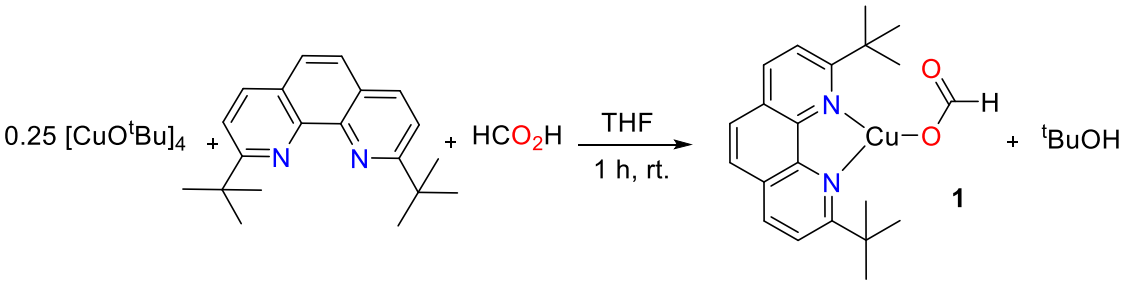
Thermal reaction of 1 with BR$_3$ (R = C$_6$F$_5$, Et$_3$) and Et-NCO, and phenylacetylene : In a J. Young NMR tube, **1** (1 equiv.) was dissolved in THF-*d*$_8$ (0.5 ml) and BR_3 (1 equiv.) or Et-NCO (2 equiv.) or phenylacetlyene (1 equiv.) were added. The reaction mixture was heated at 60 °C and monitored at different times by ^{1}H NMR (See SI).

General procedure for the catalytic dehydrogenation of formic acid (FA) : To an orange suspension of the formate complex **1** (x mol%) (x = 1, 5 or 10) in THF (0.5 mL) containing mesitylene as an internal standard (6.7 μL, 10 mol%), was syringed HCO_2H (18 μL, 0.48 mmol). At t = 0, the ^{1}H NMR spectra was recorded before the tube was immersed in an aluminium heating tube-plate at 100°C. The reactions were then monitored by ^{1}H NMR every 15 min to see the evolution of H_2 (at 4.59 ppm in THF-*d*$_8$) and the disappearance of HCO_2H. When all the acid has disappeared, the gas phase was analyzed by GC analysis for detection of CO_2 and H_2 (see SI).

Result and discussion

Synthesis and characterization of [(phen*)Cu(κ^1-O$_2$CH)] (1)

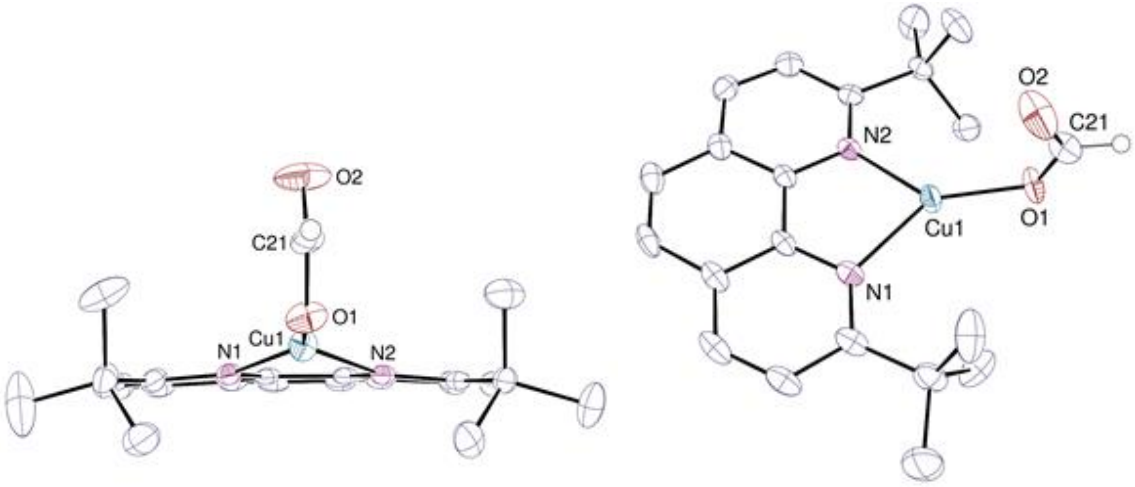
We recently considered the bulky phenanthroline ligand 2,9-*di*-terbutyl-1,10-phenanthroline (phen*) to prepare highly soluble copper mono-phenanthroline complexes that would be stable to ligand redistribution and prevent dimerization. With this ligand, synthesized by a modified procedure, we targeted to isolate the copper formate [(phen*)Cu^I(O$_2$CH)] (**1**) species which we hoped could thermally decarboxylate to afford a stable copper monohydride derivative which is yet inaccessible. Indeed, recent reduction of a dicopper(II) formate has been reported to generate spontaneous formation of a stable hexanuclear hydride copper(I) derivative by releasing CO_2[32] and such a decarboxylation process could be a promising entry to copper(I)-hydride complexes. We hypothesized this latter to be monomeric due to the congestion of the ^{t}Bu groups and because all the [(phen*)CuX] (X = Cl, F, OTf) or [(phen*)Cu(L)]$^+$ (L = CO, Me_2CO) derivatives reported so far are monomeric in the solid state.[46,50–52]



Scheme 1. Synthesis of the formate complex **1**.

Complex [(phen*)$Cu^{I}(O_2CH)$] (**1**) was readily obtained by addition of 1 equiv. of phen* to a THF solution of the yellow tetramer $[Cu(O^tBu)]_4$ (1 equiv.) and then by treatment with formic acid (1 equiv.) at room temperature. (Scheme 1) The change of color (yellow to orange) is immediate. After stirring 1 h at r.t. and then evaporation of the volatiles and washing of the residue with pentane, complex **1** was readily isolated in good yield (89 %) as a dark-orange solid. It has been characterized in solution by ^1H and $^{13}C\{^1H\}$spectra and in solid state by its infra-red spectrum and by elemental analysis. The ^1H NMR signal of the CH hydrogen atom of the formate anion appears as a broad singlet at $\delta = 8.2$, a values quite downfield compared to the other [$Cu^{I}(O_2CH)$] species (range 9.01–8.40 ppm)[31,41,43,44] and the signals of phen* are shifted downfield in comparison with those of the free ligand. The $^{13}C\{^1H\}$ NMR spectrum only evidences signals of phen* and the carbon atom of the formate is undetectable. The strong band at 1620 cm^{-1} in the infra-red spectrum is assigned to the $\nu_{asym}(CO_2)$ stretching mode of the coordinated formate. This values is close to those reported for example in the complexes [(triphos)Cu_2O_2CH] (1620 cm^{-1}),[41] [$Cu(PPh_3)_2O_2CH$].EtOH (1607 cm^{-1}),[42] the phosphane [$(P(C_6H_2CH_2NMe_2\text{-}2)_3)CuO_2CH$] (1607 cm^{-1}),[31] and [$LCu_2(\mu\text{-}HCO_2)](ClO_4)_2$ (L = (N,N'-Me_2-$C_6H_{12}N_3$)$CH_2(C_3HN_2)$(N,N'-Me_2-$C_6H_{12}N_3$)) (1570 cm^{-1})[32] (see SI).

Single crystals of [(phen*)$Cu^{I}(\kappa^1\text{-}O_2CH)_{0.8}I_{0.2}$].$(THF)_{0.5}$ (**1′**) could be grown in an NMR tube by slow diffusion of pentane into a crude THF mixture of **1** prepared in situ. The iodine atom presence in the crystal likely results from residual KI impurity contained in [$Cu(O^tBu)$], the latter being synthesized from treatment of CuI with KO^tBu. Views of the structure of **1′** determined by X-ray diffraction are shown in Fig. 1 with selected bond lengths and angles.



.

Figure 1. Two views of the crystal structure of complex **1′**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted except for that of formate. The minor iodide component is not shown. Selected bond distances (Å) and angles (deg): Cu1−O1 1.883(3), Cu1−N1 2.029(3), Cu1−N2 2.080(3), O1−C21 1.248(5), O2−C21 1.242(4); N1−Cu1−N2 83.44(10), N1−Cu1−O1 140.69(13); N2−Cu1−O1 135.23(12)

1′ is a monomeric, three-coordinate complex with the Cu ion ligated to the N1, N2 and O1 atoms in a distorted trigonal geometry, with the minor iodide component being close to the formate carbon atom. As in other reported carbene-copper complexes[43,44], the formate unit bonds to the copper center in an κ^1-coordination mode through one of the oxygen atoms, with a Cu1–O1 bond length of 1.883(3) Å, which is longer than in the 2-coordinate carbene species [(IPr)Cu(κ^1-O_2CH)] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) (1.848(2) Å)[43] and [($CAAC_1$)Cu(κ^1-O_2CH)] ($CAAC_1$= cyclic(alkyl)(amino)carbene)) (1.863 Å),[44] but smaller than that found in the tetracoordinate phosphane compound [$(P(C_6H_2CH_2NMe_2\text{-}2)_3)Cu(\kappa^1\text{-}O_2CH)$] (2.041(2) Å).[31] Unlike in the IPr-ligated copper formate[43] where the two C–O distances are distinct by 0.085 Å, there is no significant difference between the C21–O1 and

C21–O2 distances (1.248(5) Å, 1.242(4) Å, respectively), indicating charge delocalization over the carboxylic moiety. However, the formate ligand is not coordinated in chelating κ^2-fashion as shown by the long Cu1···O2 distance of 3.112(4) Å. The Cu–N distances are in the range of values found in [(phen*)CuX] complexes. In addition, steric hindrance due to the bulky tert-butyl substituents caused the copper center to deviate from the mean plane of the phen* by 0.520(2) Å. This typical coordination mode can also be observed in other [(phen*)CuX] (X = halide) copper complexes.[46,50,53] In the packing, centrosymmetric dimers are formed through π-stacking interactions [centroid···centroid distances, 3.5660(19)–4.1058(19) Å; dihedral angles, 0–7.40(15)°] and the distance between the phenanthroline mean planes reaches 3.412 Å].

Attempts to the copper monohydride [(phen*)Cu–H]

We tried to detect the [(phen*)Cu–H] complex by heating a solution of **1** in THF at 50 °C, but **1** decomposed slowly and released CO_2 and H_2, leaving free phen* after 7 h at 60 °C (see SI). However, the CO_2 release suggested the presence of a transient Cu–H species, so we attempted to trap it with reactive groups such as BEt_3, $B(C_6F_5)_3$, Et-NCO, or phenylacetylene, following recent works.[54] For instance, we recently trapped the transient [(P_3N)CuH] hydride with $B(C_6F_5)_3$ as the unusual but stable triethylborohydride copper complex [(P_3N)Cu(μ-H-BEt_3)] (P_3N = N,N′-(2,4,6-$C_6H_2Me_3$)$_2C_3H_6N_2C$).[54] In contrast, in the carbene series, [(IPr)Cu(OtBu)] underwent hydrosilylation to give the stable dimer [(IPr)CuH]$_2$, which easily converted to the monoformate derivative under 1 atm CO_2 [43]. Unfortunately, here, we did not obtain the expected hydride reaction products, but rather undetermined and intractable mixtures. For example, with EtNCO (4 h at 50 °C), no formation of the expected [Cu]-NCHOEt complex could be identified[55] and in the presence of phenylacetylene, we observed immediate greenish solution and phen* decoordination. With BEt_3, **1** degraded instead of forming a copper borohydride. Only with $B(C_6F_5)_3$, we isolated light orange crystals of the complex [{(phen*)Cu}$_2$(μ-O_2CH)][(HCO_2-κ^1)$B(C_6F_5)_3$] (**2**), indicating initial formate abstraction by the Lewis acidic boron center. A view of the structure of **2** determined by X-ray diffraction is represented in Fig. 2 with selected bond lengths and angles. The Cu–N distances are classical and similar to those found in **1'**. Of interest are the C–O bond lengths in the bridging and monodentate formate ligands of **2**. In the former entity, the two C–O distances are quite identical and similar to those found in the monodentate complex **1'** and suggest charge delocalization. In contrast, in the anionic moiety [(HCO_2)$B(C_6F_5)_3$]$^-$ the difference of 0.1 Å between the two C–O bonds likely reflects single and double bond character as in the species [(IPr)Cu(κ^1-O_2CH)].[53] The ^{1}H NMR spectrum of **2** in THF-d_8 revealed two broad ^{1}H NMR signals at 8.19 ppm and 8.43 ppm[56–58] for the copper and boron formate, respectively, along with up-field shifted signals for the C_6F_5 moiety and B center in ^{19}F NMR and ^{11}B NMR (see SI).

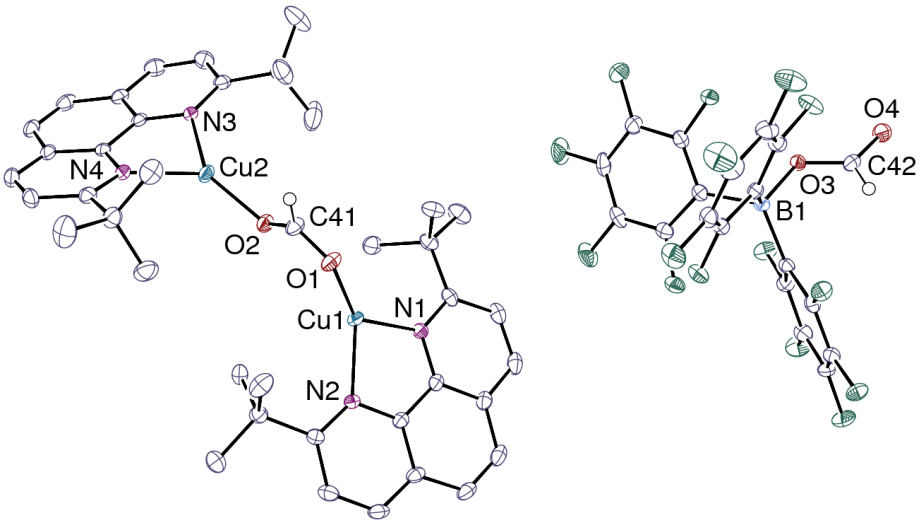


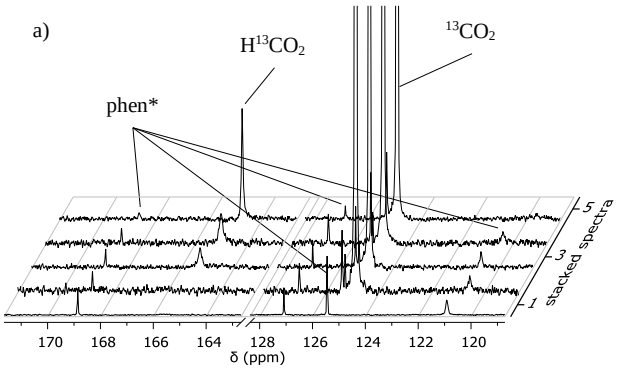
Figure 2. View of the crystal structure of complex **2**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted except for that of formate. Selected bond distances (Å) and angles (deg): Cu1−O1 1.9116(13), Cu1−N1 2.0508(15), Cu1−N2 2.0458(15), Cu2−O2 1.9260(13), Cu2−N3 2.0584(15), Cu2−N4 2.0585(15), ⟨Cu−N⟩ 2.053(5), O1−C41 1.245(2), O2−C41 1.251(2), B1−O3 1.513(2), O3−C42 1.301(2), O4−C42 1.207(2); N1−Cu1−N2 83.20(6), O1−Cu1−N1 135.82(6), O1−Cu1−N2 135.17(6), N3−Cu2−N4 82.85(6), O2−Cu2−N3 136.43(6); O2−Cu2−N4 137.44(6).

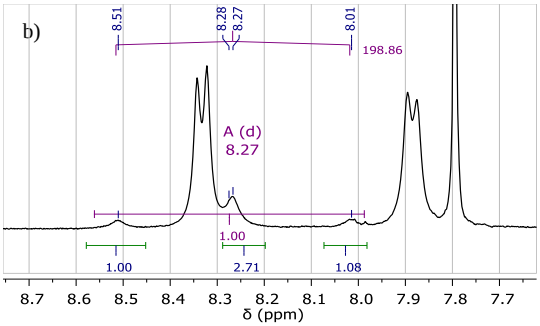
Stoichiometric reaction with $^{13}CO_2$

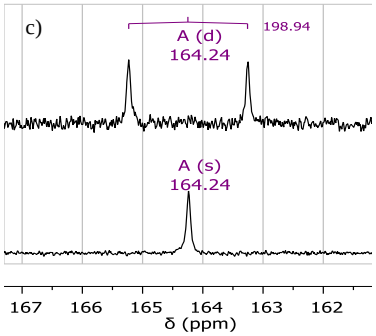
Guan *et al* reported in 2016 that decarboxylation of the nickel formate [(POCOP)Ni(κ^1-O_2CH)] (POCOP = {2,6-($R_2PO)_2C_6H_3$}; R = ^{t}Bu, ^{i}Pr) in the presence of CS_2 gave the stable dithioformate [(POCOP)Ni(S_2CH)] derivative through the transient formation of the nickel hydride species.[18] CS_2 being more reactive than CO_2 for the insertion reaction,[59,60] and because these authors claimed that the method could be applied to a wide variety of formate complexes of d-transition metals, we, therefore, attempted a similar reaction. Disappointingly, treatment of **1** with excess CS_2 in THF at room temperature did not afford the expected dithioformate (Scheme 2). The NMR spectra showed no evolution, and further warming at 50 °C for 3 h, only evidenced slow decomposition into free ligand and Cu black.

We thus changed our strategy to detect a potential active copper hydride intermediate by considering a dynamic isotopic exchange procedure with labeled $^{13}CO_2$ (Scheme 2). This method, recently developed with copper(I) catalysts to insert efficiently, in a single step, a carbon tag into carboxylate substrates without structural change, is based on reversible carboxylation and decarboxylation processes.[61] If working, such a method would be useful to access labeled formate anion from the corresponding labeled CO_2. A J-Young NMR tube containing a THF-d_8 solution of **1** was pressurized with 1 atm $^{13}CO_2$ and heated at 60 °C for *ca* 4 h. ^{1}H and ^{13}C NMR monitoring did not show degradation of the starting complex, but evidenced slow replacement of the unlabeled HCO_2 with $H^{13}CO_2$. Enrichment of the formate anion in ^{13}C supports the initial decarboxylation of **1** into the putative hydride [(phen*)Cu–H] that would immediately trap $^{13}CO_2$ to give the ^{13}C-labeled formate derivative **1***. The evolution of **1** into **1*** is confirmed by ^{13}C NMR. Indeed, while the formate carbon atom of **1** is not detected, the {^{1}H}^{13}C NMR spectra showed a singlet at δ = 164.65 (in the expected range for a formate anion) that grew up continuously with time (Fig. 3a). The signal appeared as a doublet with a coupling constant J = 198 Hz in the non-decoupled ^{13}C NMR spectrum (20 % isotopic enrichment, IE, by ^{1}H NMR integration after 4h30) (Fig. 3c). The ^{1}H NMR signal for the formate unit of **1** appears as a broad singlet at 8.28 ppm (Fig. 3b) that split by coupling with the ^{13}C atom during the exchange process, and with a constant J = 198 Hz identical to that obtained for the C atom of the coordinated $H^{13}CO_2$ ion in the ^{13}C spectrum (Fig. 3c, top). Continuous heating of the reaction for 3 more hours enhanced the ^{13}C enrichment (30 % IE) along with the degradation of **1** observed by the formation of free phen*.

Figure 3. 3a- {^{1}H}^{13}C NMR spectrum showing the increase with time of the $H^{13}CO_2$ signal at 164 ppm (the signal increases from top to down). 3b- ^{1}H NMR signal of the $H^{12}CO_2$ ligand of **1** which is split in the labelled analogue **1***. 3c- Singlet signal (bottom) in ^{13}C NMR spectrum and doublet signal (top) in {^{1}H}^{13}C NMR of $H^{13}CO_2$ in **1***.

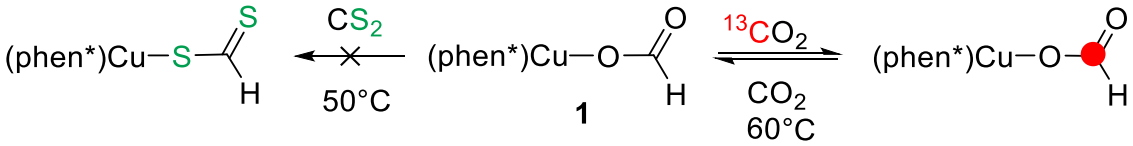






The ^{1}H-^{13}C HSQC (heteronuclear single quantum coherence) analysis evidences the correlation between the labelled carbon of the formate ion (δ = 164.24) and its neighboring proton (δ = 8.28) (see SI). These observations provide solid proof for a successful $^{12}CO_2/^{13}CO_2$ exchange in [(phen*)Cu(O_2CH)], and clearly suggest the involvement of a copper hydride as transient intermediate. In their investigations into the copper-catalyzed hydrosilylation of CO_2 to silyl formate,[62] Motokura *et al.* also reported the capture of CO_2 by a tricoordinated copper diphosphine hydride to give the corresponding formate, but the originated hydride was regenerated by reaction of the formate complex with a hydrosilane.[62]

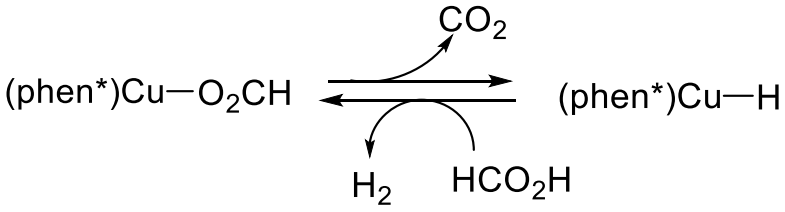
Scheme 2. Reactions of **1** with CS_2 and $^{13}CO_2$ at 50 and 60 °C, respectively.



Catalytic dehydrogenation of formic acid (FA)

H_2 is a clean and sustainable energy vector that can connect power generation plants and mobile end-users. Formic acid is a convenient liquid source and carrier of H_2, and its conversion to H_2 and CO_2 and back has been widely studied. Many soluble d-transition metal complexes can catalyze HCO_2H dehydrogenation (H_2 and CO_2 release) with high activity and selectivity[12] since Coffey's first report in 1967.[63] Most of the homogeneous catalysts are based on noble metals such as Ru, Rh, and Ir, but cheaper and more abundant metals are less explored, especially copper. The first Cu-catalyzed homogeneous systems for HCO_2H decomposition were reported only in 2014:. The Cu(I) and Cu(II) precursors ($Cu(OAc)_2$, $Cu(acac)_2$, $Cu(O_2CH)_2$, $Cu(NO_3)_2$, $CuCl_2$, CuO, CuCl, CuI, $\{CuH(PPh_3)\}_6$) in solution in HCO_2H/Et_3N displayed a very low catalytic activity[64] which was found dependent on the nature of the amine as confirmed later by a DFT study.[65] In 2019, the hexanuclear cationic copper hydride $[Cu_6(\mu^3\text{-}H)_2(L)_3(^tBNC)_4][PF_6]_4$, involving a linear tetradentate phosphine (L= meso-$Ph_2PCH_2P(Ph)(CH_2)_4P(Ph)CH_2PPh_2$), showed low catalytic activity for H_2 release from HCO_2H at 70°C in acetonitrile solution with ^tBuNC and NEt_3 additives.[66] At last, in 2023, O'Hair *et al* revealed that the mononuclear cuprate hydride anions $[(X)CuH]^-$ (X = H^-, O_2CH^-, BH_4^- and CN^-) reacted in the gas-phase with formic acid to release H_2 with formation of the formate $[(X)Cu(O_2CH)]^-$ compound. The latter decarboxylates readily *via* collision-induced dissociation to regenerate the initial copper hydride.[67]

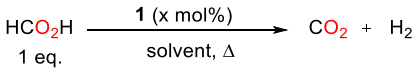
Scheme 3. The dehydrogenation of formic acid with **1**.



The dynamic exchange process of **1** under CO_2 suggested that it could be a rare copper catalyst for the dehydrogenation of formic acid. We reasoned that if the hydride intermediate could trap gaseous CO_2, it should also react quickly with the liquid acid HCO_2H, which was more abundant in the reaction medium (Scheme 3)..

Table 1 summarizes the catalytic activity of **1** under different reaction conditions. Gas evolution was measured by ^{1}H NMR spectra and GC analysis (gas chromatography analysis) and the consumption of HCO_2H was followed by ^{1}H NMR with mesitylene as internal standard. The appearance and evolution of H_2 was detected at δ = 4.59 ppm in ^{1}H NMR, along with the diminution of the signals of HCO_2H (Fig. 4 and 5).

Table 1. Optimization of the reaction conditions for the dehydrogenation of formic acid with complex **1**.



En-try	x (mol %)	Solvent	T (°C)	Time (h)	Conv. (%)
1	0	THF-d_8	100	16	0
2	10	THF-d_8	100	2,5	100 [b,c]
3	5	THF-d_8	100	3 8	27 90 [c]
4	1	THF-d_8	100	15	40 [c]
5	5	THF-d_8	80	4	4
6	5	THF-d_8	60	15	0
7	14	MeCN-d_3	60	15	0
8	5	MeCN-d_3	100	8	0

[a] Conversions measured by ^{1}H NMR against mesitylene (10 mol%) as internal standard.[b] TOF = 4 h^{-1}; [c] **1** is degraded

When heated to 100°C, which is a temperature favoring decarboxylation of **1** (see above), the ^{1}H NMR spectra of a THF-d_8 solution of **1** (10 mol%) containing 18 µL of HCO_2H evidenced the selective release of H_2 and no trace of CO was detected by GC analysis. In the absence of **1**, HCO_2H was not degraded (Entries 1-2). NMR monitoring of the dehydrogenation of formic acid and of the behavior of the catalyst **1** was recorded by following the aromatic signals of the phen* ligand concomitantly with the degradation of HCO_2H (Fig. 4). At first (t = 0), the phen* signals of **1** in the HCO_2H-THF-d_8 solution are shifted downfield (by 0.08–0.1 ppm) by comparison to those of pure **1** in THF-d_8, suggesting a possible interaction between **1** and the acid. During the course of the reaction, these signals slowly moved to lower frequencies (upfield shifted) and broadened. By the end of the reaction when almost all of the formic acid

has been consumed, the signal of free phen* emerged, reflecting decomposition of the catalyst **1**. Catalyst degradation was confirmed by further addition of HCO_2H, which was not dehydrogenated (see SI).

Decomposition of HCO_2H with a 10 mol% charge in **1** is complete after 2.5 h at 100 °C (Fig. 5). Decreasing the catalyst loading to 5 mol% increased the reaction time (total conversion after 8 h) whereas for a charge of 1 mol%, the catalyst is totally degraded after 15 h when only 40 % of the acid has been dehydrogenated (Entries 3-4).

The thermal input is of importance (Entries 3, 5–6). By reducing the temperature to 80 °C, a low conversion of HCO_2H (4 %) can be measured after 4 h, and below the boiling point of THF (66 °C), no reaction occurred. The influence of the solvent is also important and is highlighted by the distinct reactivity in THF and acetonitrile. The latter seems to completely prevent the dehydrogenation process at 0 °C or 100 °C (Entries 7–8).

Overall, these results underlined that complex **1** is reactive in the catalytic decomposition of HCO_2H into CO_2 and H_2 without the requirement of any base or additives. No additive is needed to promote the catalysis, because **1** spontaneously releases CO_2 under heating with formation of a transient hydride [Cu]–H that has sufficient hydride character to deprotonate formic acid and regenerate **1** with evolution of H_2. With a TOF of 4 h^{-1} (Entry 2) at 100 °C for a catalyst loading of 10 mol%, it is not very active. This activity is however superior to that reported for a variety of simple Cu(0), Cu(I) and Cu(II) precursors in presence of NEt_3 and which displayed TOFs lower than 1 h^{-1} at 95°C.[13,64,65] The species $[Cu(NCMe)_4][PF_6]$ in acetonitrile and in the presence of various phosphine ligands and additives (^{t}BuNC-NEt_3) at 70°C, showed greater activities in the decomposition of HCO_2H with reported TOFs in the range 10–240 h^{-1}.[66]

However, all these copper catalysts exhibit activities significantly lower than the TOF values of 5 000 – 10 000 h^{-1} required for an economically viable process.[12] Iron catalytic systems have TOFs of *ca* 10 000 h^{-1} and TONs of 10^5,[68] and the most efficient complexes are currently based on noble metals (Ru and Ir), with TON values exceeding 10^6.[12,69] For example, Williams and coworkers in 2016 and Li *et al* in 2015, reported a binuclear iridium(III) and two organometallic mononuclear (C_5Me_5)Ir(III) catalysts exhibiting, at 90 °C, TOF of 2.28×10^5 h^{-1} (TON = 2.16 10^6) and 4.88×10^5 h^{-1} (TON = 2.4 10^6 at 80°C), respectively.[70,71]

Conclusion

In conclusion, we synthesized a novel monoligated copper(I)-formate with a bulky substituted phenanthroline ligand (phen*), which provides solubility and stability. Such Cu(I)-formate species with simple nitrogen ligands are rare. We tested the catalytic activity of [(phen*)Cu(O_2CH)] (**1**) in the decomposition of formic acid, and it generated H_2 and CO_2. We could not detect or trap the hydride [(phen*)CuH] intermediate from decarboxylation of **1** with organic scavengers. However, we showed the transient formation of this hydride by ^{13}C NMR, which revealed the steady increase of the $^{13}CO_2H$ signal during dynamic isotopic exchange with $^{13}CO_2$.

Figure 4. ^{1}H NMR spectrum showing the aromatic signals of the phen* moiety of **1** (10 mol%) in the formic acid dehydrogenation catalysis. Spectrum were recorded every 15 min (total reaction time, 2h30).

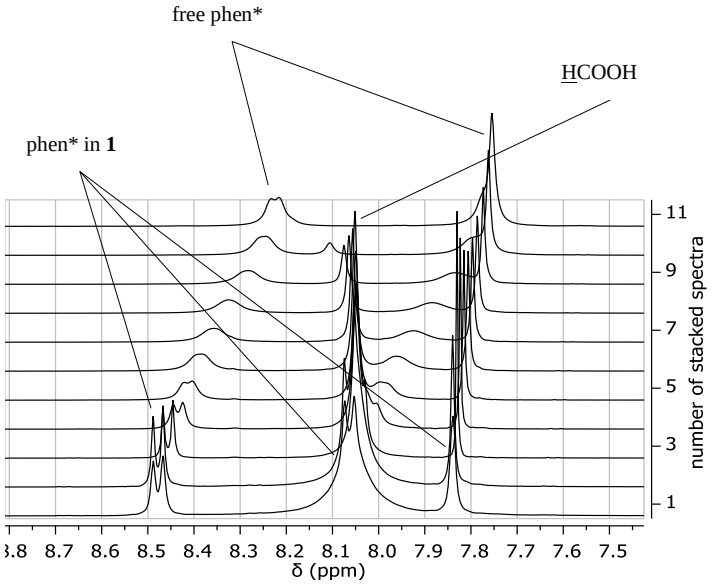
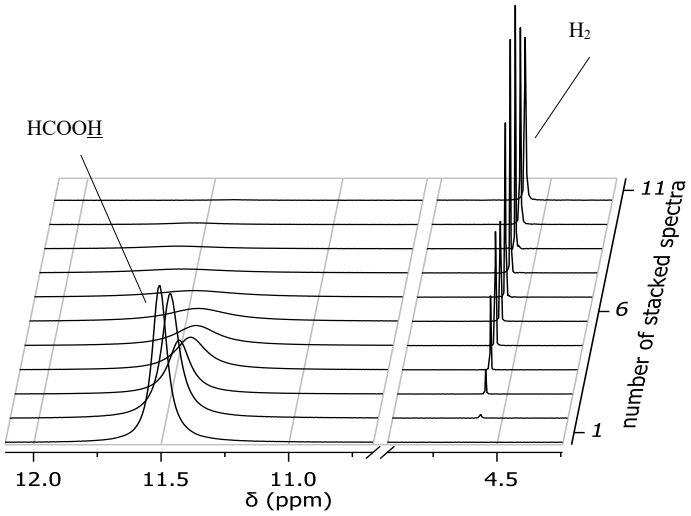


Figure 5. ^{1}H NMR spectrum showing disappearance of the acidic signal of formic acid and concomitant release of H_2. Spectrum were recorded every 15 min (total reaction time, 2h30).



ASSOCIATED CONTENT

Supporting Information : The Supporting Information is available free of charge on the ACS Publications website. Supplementary equations, experimental detailed and X-ray diffraction data are provided in the Supporting Information.

Accession Codes : CCDC 2278959 and 2278960 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*Emails: thibault.cantat@cea.fr and jean-claude.berthet@cea.fr
Fax: +33 1 6908 6640; Tel.: +33 1 6908 4338

Author Contributions

The manuscript was written with contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

For financial support of this work, we acknowledge CEA, CNRS, the University Paris-Saclay and the European Research Council (ERC Consolidator Grant Agreement no. 818260).

REFERENCES

(1) Kinzel, N. W.; Werlé, C.; Leitner, W. Transition Metal Complexes as Catalysts for the Electroconversion of CO_2 : An Organometallic Perspective. *Angew. Chem. Int. Ed.* **2021**, *60*, 11628–11686.
(2) Creutz, C.; Chou, M. H. Hydricities of d^6 Metal Hydride Complexes in Water. *J. Am. Chem. Soc.* **2009**, *131*, 2794–2795.
(3) Godou, T.; Chauvier, C.; Thuéry, P.; Cantat, T. Iron-Catalyzed Silylation of Alcohols by Transfer Hydrosilylation with Silyl Formates. *Synlett* **2017**, *28*, 2473–2477.
(4) Darensbourg, D. J.; Wiegreffe, P.; Riordan, C. G. Mechanistic Aspects of Decarboxylation Reactions of Group 10 Metal Formato Hydrido Tricyclohexylphosphine $[(PCy_3)_2M(H)O_2CH]$ Derivatives. *J. Am. Chem. Soc.* **1990**, *112*, 5759–5762.
(5) Merrifield, J. H.; Gladysz, J. A. Synthesis and Decarboxylation Mechanism of the Chiral Rhenium Formate (Eta-C_5H_5)Re(NO)(PPh_3)(OCHO). *Organometallics* **1983**, *2* (6), 782–784.
(6) Takao, S.; Takao, K.; Kraus, W.; Emmerling, F.; Scheinost, A. C.; Bernhard, G.; Hennig, C. First Hexanuclear U^{IV} and Th^{IV} Formate Complexes – Structure and Stability Range in Aqueous Solution. *Eur. J. Inorg. Chem.* **2009**, *2009*, 4771–4775.
(7) Chauvier, C.; Tlili, A.; Das Neves Gomes, C.; Thuéry, P.; Cantat, T. Metal-Free Dehydrogenation of Formic Acid to H_2 and CO_2 Using Boron-Based Catalysts. *Chem. Sci.* **2015**, *6*, 2938–2942.
(8) Chauvier, C.; Thuéry, P.; Cantat, T. Silyl Formates as Surrogates of Hydrosilanes and Their Application in the Transfer Hydrosilylation of Aldehydes. *Angew. Chem. Int. Ed.* **2016**, *55*, 14096–14100.
(9) Chauvier, C.; Imberdis, A.; Thuéry, P.; Cantat, T. Catalytic Disproportionation of Formic Acid to Methanol by Using Recyclable Silylformates. *Angew. Chem. Int. Ed.* **2020**, *59*, 14019–14023.
(10) Grasemann, M.; Laurenczy, G. Formic Acid as a Hydrogen Source – Recent Developments and Future Trends. *Energy Environ. Sci.* **2012**, *5*, 8171–8181.

(11) Mellmann, D.; Sponholz, P.; Junge, H.; Beller, M. Formic Acid as a Hydrogen Storage Material – Development of Homogeneous Catalysts for Selective Hydrogen Release. *Chem. Soc. Rev.* **2016**, *45*, 3954–3988.
(12) Guan, C.; Pan, Y.; Zhang, T.; Ajitha, M. J.; Huang, K. An Update on Formic Acid Dehydrogenation by Homogeneous Catalysis. *Chem. Asian J.* **2020**, *15*, 937–946.
(13) Iglesias, M.; Fernández-Alvarez, F. J. Advances in Nonprecious Metal Homogeneously Catalyzed Formic Acid Dehydrogenation. Catalysts **2021**, *11*, 1288–1307.
(14) Singh, T.; Jalwal, S.; Chakraborty, S. Homogeneous First-row Transition-metal-catalyzed Carbon Dioxide Hydrogenation to Formic Acid/Formate, and Methanol. *Asian J. Org. Chem.* **2022**, *11*, https://doi.org/10.1002/ajoc.202200330.
(15) Onishi, N.; Kanega, R.; Kawanami, H.; Himeda, Y. Recent Progress in Homogeneous Catalytic Dehydrogenation of Formic Acid. *Molecules* **2022**, *27*, 455, doi.org/10.3390/molecules27020455.
(16) Savourey, S.; Lefèvre, G.; Berthet, J.-C.; Thuéry, P.; Genre, C.; Cantat, T. Efficient Disproportionation of Formic Acid to Methanol Using Molecular Ruthenium Catalysts. *Angew. Chem. Int. Ed.* **2014**, *53*, 10466–10470.
(17) Wang, L.; Sun, H.; Zuo, Z.; Li, X.; Xu, W.; Langer, R.; Fuhr, O.; Fenske, D. Activation of CO_2, CS_2 , and Dehydrogenation of Formic Acid Catalyzed by Iron(II) Hydride Complexes. *Eur. J. Inorg. Chem.* **2016**, 5205–5214.
(18) Ma, Q.-Q.; Liu, T.; Adhikary, A.; Zhang, J.; Krause, J. A.; Guan, H. Using CS_2 to Probe the Mechanistic Details of Decarboxylation of Bis(Phosphinite)-Ligated Nickel Pincer Formate Complexes. *Organometallics* **2016**, *35*, 4077–4082.
(19) Liu, W.; Huang, H.; Ouyang, T.; Jiang, L.; Zhong, D.; Zhang, W.; Lu, T. A Copper(II) Molecular Catalyst for Efficient and Selective Photochemical Reduction of CO_2 to CO in a Water-Containing System. *Chem. Eur. J.* **2018**, *24*, 4503–4508.
(20) Al-Nayili, A.; Majdi, H. Sh.; Albayati, T. M.; Saady, N. M. C. Formic Acid Dehydrogenation Using Noble-Metal Nanoheterogeneous Catalysts: Towards Sustainable Hydrogen-Based Energy. *Catalysts* **2022**, *12*, 324-340.
(21) Wienhöfer, G.; Sorribes, I.; Boddien, A.; Westerhaus, F.; Junge, K.; Junge, H.; Llusar, R.; Beller, M. General and Selective Iron-Catalyzed Transfer Hydrogenation of Nitroarenes without Base. *J. Am. Chem. Soc.* **2011**, *133*, 12875–12879.
(22) Shen, R.; Chen, T.; Zhao, Y.; Qiu, R.; Zhou, Y.; Yin, S.; Wang, X.; Goto, M.; Han, L.-B. Facile Regio- and Stereoselective Hydrometalation of Alkynes with a Combination of Carboxylic Acids and Group 10 Transition Metal Complexes: Selective Hydrogenation of Alkynes with Formic Acid. *J. Am. Chem. Soc.* **2011**, *133*, 17037–17044.
(23) Broggi, J.; Jurčík, V.; Songis, O.; Poater, A.; Cavallo, L.; Slawin, A. M. Z.; Cazin, C. S. J. The Isolation of [Pd{OC(O)H}(H)(NHC)(PR_3)] (NHC = N-Heterocyclic Carbene) and Its Role in Alkene and Alkyne Reductions Using Formic Acid. *J. Am. Chem. Soc.* **2013**, *135*, 4588–4591.
(24) Zeng, M.; Li, L.; Herzon, S. B. A Highly Active and Air-Stable Ruthenium Complex for the Ambient Temperature Anti-Markovnikov Reductive Hydration of Terminal Alkynes. *J. Am. Chem. Soc.* **2014**, *136*, 7058–7067.
(25) Guo, S.; Yang, P.; Zhou, J. (Steve). Nickel-Catalyzed Asymmetric Transfer Hydrogenation of Conjugated Olefins. *Chem. Commun.* **2015**, *51*, 12115–12117.
(26) Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. *Chem. Rev.* **2015**, *115*, 6621–6686.
(27) Touge, T.; Nara, H.; Fujiwhara, M.; Kayaki, Y.; Ikariya, T. Efficient Access to Chiral Benzhydrols via Asymmetric Transfer Hydrogenation of Unsymmetrical Benzophenones with Bifunctional Oxo-Tethered Ruthenium Catalysts. *J. Am. Chem. Soc.* **2016**, *138*, 10084–10087.

(28) Li, Y.-N.; Ma, R.; He, L.-N.; Diao, Z.-F. Homogeneous Hydrogenation of Carbon Dioxide to Methanol. *Catal. Sci. Technol.* **2014**, *4*, 1498–1512.
(29) Kar, S.; Goeppert, A.; Prakash, G. K. S. Integrated CO_2 Capture and Conversion to Formate and Methanol: Connecting Two Threads. *Acc. Chem. Res.* **2019**, *52*, 2892–2903.
(30) Eberhardt, N. A.; Guan, H. Nickel Hydride Complexes. *Chem. Rev.* **2016**, *116*, 8373–8426.
(31) Lang, H.; Shen, Y.; Rüffer, T.; Walfort, B. Phosphane Copper(I) Formate Complexes Stabilized by Formic Acid and Acetic Acid through H···O···H Bridges. *Inorg. Chim. Acta* **2008**, *361*, 95–102.
(32) Lücken, J.; Auth, T.; Mozzi, S. I.; Meyer, F. Hexanuclear Copper(I) Hydride from the Reduction-Induced Decarboxylation of a Dicopper(II) Formate. *Inorg. Chem.* **2020**, *59*, 14347–14354.
(33) Mouche, M.-J.; Mermet, J.-L.; Romand, M.; Charbonnier, M. Metal—Organic Chemical Vapor Deposition of Copper Using Hydrated Copper Formate as a New Precursor. *Thin Solid Films* **1995**, *262*, 1–6.
(34) Grodzicki, A.; Łakomska, I.; Piszczek, P.; Szymańska, I.; Szłyk, E. Copper(I), Silver(I) and Gold(I) Carboxylate Complexes as Precursors in Chemical Vapour Deposition of Thin Metallic Films. *Coord. Chem. Rev.* **2005**, *249*, 2232–2258.
(35) Mokhtari, O.; Conti, F.; Saccon, R.; Bhogaraju, S. K.; Elger, G. Formic Acid and Formate Salts for Chemical Vapor Deposition of Copper on Glass Substrates at Atmospheric Pressure. *New J. Chem.* **2021**, *45*, 20133–20139.
(36) Casarin, M.; Corvaja, C.; Di Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F. One-Dimensional and Two-Dimensional Coordination Polymers from Self-Assembling of Trinuclear Triangular Cu(II) Secondary Building Units. *Inorg. Chem.* **2005**, *44*, 6265–6276.
(37) Barquín, M.; Cocera, N.; González Garmendia, M. J.; Larrínaga, L.; Pinilla, E.; Seco, J. M.; Torres, M. R. Acetato and Formato Copper(II) Complexes with 4,4′-Dimethyl-2,2′-Bipyridine and 5,5′-Dimethyl-2,2′-Bipyridine: Synthesis, Crystal Structure, Magnetic Properties and EPR Results. A New 1D Polymeric Water Chain. *Inorg. Chim. Acta* **2010**, *363*, 127–133.
(38) Di Nicola, C.; Garau, F.; Gazzano, M.; Guedes da Silva, M. F. C.; Lanza, A.; Monari, M.; Nestola, F.; Pandolfo, L.; Pettinari, C.; Pombeiro, A. J. L. New Coordination Polymers and Porous Supramolecular Metal Organic Network Based on the Trinuclear Triangular Secondary Building Unit $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}Pz)_3]^{2+}$ and 4,4′-Bypiridine. 1°. *Cryst. Growth Des.* **2012**, *12*, 2890–2901.
(39) Marchal, W.; Longo, A.; Briois, V.; Van Hecke, K.; Elen, K.; Van Bael, M. K.; Hardy, A. Understanding the Importance of Cu(I) Intermediates in Self-Reducing Molecular Inks for Flexible Electronics. *Inorg. Chem.* **2018**, *57*, 15205–15215.
(40) Fujita, W. Crystal Structures, and Magnetic and Thermal Properties of Basic Copper Formates with Two-Dimensional Triangular-Lattice Magnetic Networks. *RSC Adv.* **2018**, *8*, 32490–32496.
(41) Ghilardi, A. C.; Bianchini C.; Meli A.; Midollini S.; Orlandini A. *J. Organomet. Chem.* **1983**, 248, C13–C16.
(42) Bowmaker, G. A.; Hanna, J. V.; Healy, P. C.; Reid, J. C.; Rickard, C. E. F.; White, A. H. Crystal Structures and Vibrational and Solid-State (CPMAS) NMR Spectroscopic Studies in the Tris(Triphenylphosphine)-Copper(I) and -Silver(I) Formate Systems. *J. Chem. Soc., Dalton Trans.* **2000**, 5, 753–762.
(43) Zhang, L.; Cheng, J.; Hou, Z. Highly Efficient Catalytic Hydrosilylation of Carbon Dioxide by an N-Heterocyclic Carbene Copper Catalyst. *Chem. Commun.* **2013**, *49*, 4782–4784.
(44) Romero, E. A.; Zhao, T.; Nakano, R.; Hu, X.; Wu, Y.; Jazzar, R.; Bertrand, G. Tandem Copper Hydride–Lewis Pair Catalysed Reduction of Carbon Dioxide into Formate with Dihydrogen. *Nat. Catal.* **2018**, *1*, 743–747.

(45) Tuchscherer, A.; Shen, Y.; Jakob, A.; Mothes, R.; Al-Anber, M.; Walfort, B.; Rüffer, T.; Frühauf, S.; Ecke, R.; Schulz, S. E.; Gessner, T.; Lang, H. Lewis-Base Copper(I) Formates: Synthesis, Reaction Chemistry, Structural Characterization and Their Use as Spin-Coating Precursors for Copper Deposition. *Inorg. Chim. Acta* **2011**, *365*, 10–19.
(46) Pallenberg, A. J.; Koenig, K. S.; Barnhart, D. M. Synthesis and Characterization of Some Copper(I) Phenanthroline Complexes. *Inorg. Chem.* **1995**, *34*, 2833–2840.
(47) Dietrick-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P. Direct Synthesis of Disubstituted Aromatic Polyimine Chelates. *Tetrahedron Letters* **1982**, *23* (50), 5291–5294.
(48) Tianli, W.; Fei, C.; Jie, Q.; Yan-Mei, H.; Quing-Hua, F. Asymmetric Ruthenium-Catalyzed Hydrogenation of 2- and 2,9-Subtstituted 1,10-Phenanthrolines. *Angew. Chem. Int. Ed.* **2013**, 52, 7172–7176.
(49) Tsuda, T.; Hashimoto, T.; Saegusa, T. Cuprous Tert-Butoxide. New and Useful Metalation Reagent. *J. Am. Chem. Soc.* **1972**, *94*, 658–659.
(50) Gandhi, B. A.; Green, O.; Burstyn, J. N. Facile Oxidation-Based Synthesis of Sterically Encumbered Four-Coordinate bis(2,9-di-*tert*-butyl-1,10-phenanthroline)Copper(I) and Related Three-Coordinate Copper(I) Complexes. *Inorg. Chem.* **2007**, *46*, 3816–3825.
(51) Liu, Y.; Chen, C.; Li, H.; Huang, K.-W.; Tan, J.; Weng, Z. Efficient S_N2 Fluorination of Primary and Secondary Alkyl Bromides by Copper(I) Fluoride Complexes. *Organometallics* **2013**, *32*, 6587–6592.
(52) Green, O.; Gandhi, B. A.; Burstyn, J. N. Photophysical Characteristics and Reactivity of bis(2,9-di-*tert*-butyl-1,10-Phenanthroline)Copper(I). *Inorg. Chem.* **2009**, *48*, 5704–5714.
(53) Nitsch, J.; Kleeberg, C.; Fröhlich, R.; Steffen, A. Luminescent Copper(I) Halide and Pseudohalide Phenanthroline Complexes Revisited: Simple Structures, Complicated Excited State Behavior. *Dalton Trans.* **2015**, *44*, 6944–6960.
(54) Aloisi, A.; Crochet, E.; Nicolas, E.; Berthet, J.-C.; Lescot, C.; Thuéry, P.; Cantat, T. Copper–Ligand Cooperativity in H_2 Activation Enables the Synthesis of Copper Hydride Complexes. *Organometallics* **2021**, *40*, 2064–2069.
(55) English, L. E.; Horsley Downie, T. M.; Lyall, C. L.; Mahon, M. F.; McMullin, C. L.; Neale, S. E.; Saunders, C. M.; Liptrot, D. J. Selective Hydroboration of Electron-Rich Isocyanates by an NHC-Copper(I) Alkoxide. *Chem. Commun.* **2023**, *59*, 1074–1077.
(56) Voss, T.; Mahdi, T.; Otten, E.; Fröhlich, R.; Kehr, G.; Stephan, D. W.; Erker, G. Frustrated Lewis Pair Behavior of Intermolecular Amine/$B(C_6F_5)_3$ Pairs. *Organometallics* **2012**, *31*, 2367–2378.
(57) Zhao, T.; Hu, X.; Wu, Y.; Zhang, Z. Hydrogenation of CO_2 to Formate with H_2 : Transition Metal Free Catalyst Based on a Lewis Pair. *Angew. Chem. Int. Ed.* **2019**, *58*, 722–726.
(58) Ashley A. E.; Thompson A. L.; Dermot, O. Non-Metal-Mediated Homogeneous Hydrogenation of CO_2 to CH_3OH. *Angew. Chem. Int. Ed.* **2009**, *48*, 9839–9843.
(59) Butler, I. S.; Fenster, A. E. Activation of Carbon Disulphide by Transition Metal Complexes. *J. Organomet. Chem.* **1974**, *66*, 161–194.
(60) Pandey, K. K. Reactivities of Carbonyl Sulfide (COS), Carbon Disulfide (CS_2) and Carbon Dioxide(CO_2)with Transition Metal Complexes. *Coord. Chem. Rev.* **1995**, *140*, 37–114.
(61) Destro, G.; Loreau, O.; Marcon, E.; Taran, F.; Cantat, T.; Audisio, D. Dynamic Carbon Isotope Exchange of Pharmaceuticals with Labeled CO_2. *J. Am. Chem. Soc.* **2019**, *141*, 780–784.
(62) Motokura, K.; Kashiwame, D.; Takahashi, N.; Miyaji, A.; Baba, T. Highly Active and Selective Catalysis of Copper Diphosphine Complexes for the Transformation of Carbon Dioxide into Silyl Formate. *Chem. Eur. J.* **2013**, *19*, 10030–10037.
(63) Coffey, R. S. The Decomposition of Formic Acid Catalysed by Soluble Metal Complexes. *Chem. Commun.*, **1967**, *18*, 923-924.

(64) Scotti, N.; Psaro, R.; Ravasio, N.; Zaccheria, F. A New Cu-Based System for Formic Acid Dehydrogenation. *RSC Adv.* **2014**, *4*, 61514–61517.
(65) Correa, A.; Cascella, M.; Scotti, N.; Zaccheria, F.; Ravasio, N.; Psaro, R. Mechanistic Insights into Formic Acid Dehydrogenation Promoted by Cu-Amino Based Systems. *Inorg. Chim. Acta* **2018**, *470*, 290–294.
(66) Nakajima, T.; Kamiryo, Y.; Kishimoto, M.; Imai, K.; Nakamae, K.; Ura, Y.; Tanase, T. Synergistic Cu_2 Catalysts for Formic Acid Dehydrogenation. *J. Am. Chem. Soc.* **2019**, *141*, 8732–8736.
(67) Ma, H. Z.; Canty, A. J.; O'Hair, R. A. J. Near Thermal, Selective Liberation of Hydrogen from Formic Acid Catalysed by Copper Hydride Ate Complexes. *Dalton Trans.* **2023**, *52*, 1574–1581.
(68) Boddien, A.; Mellmann, D.; Gärtner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurenczy, G.; Ludwig, R.; Beller, M. Efficient Dehydrogenation of Formic Acid Using an Iron Catalyst. *Science* **2011**, *333*, 1733–1736.
(69) Sponholz, P.; Mellmann, D.; Junge, H.; Beller, M. Towards a Practical Setup for Hydrogen Production from Formic Acid. *ChemSusChem* **2013**, *6*, 1172–1176.
(70) Celaje J.; Lu Z.; Kedzie E. A Prolific Catalyst for Dehydrogenation of Neat Formic Acid. *Nat. Commun.* **2016**, 7, 11308–11314.
(71) Wang, Z.; Lu, S.-M.; Li, J.; Wang, J.; Li, C. Unprecedentedly High Formic Acid Dehydrogenation Activity on an Iridium Complex with an *N* , *N* ′-Diimine Ligand in Water. *Chem. Eur. J.* **2015**, *21*, 12592–12595.