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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

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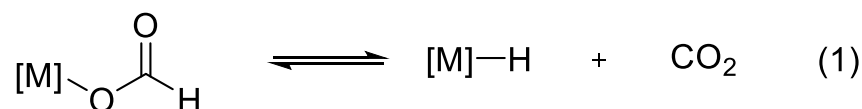
Keywords : Copper, Copper formate, Phenanthroline, Copper hydride, CO₂ insertion, Formic acid, Catalysis, Crystal structure

ABSTRACT: Formate complexes of copper(I) are rare. We report here the synthesis, characterization, and crystal structure of the simple tricoordinate [(phen*)Cu^I(κ¹-O₂CH)] (**1**) supported with the bulky phenanthroline ligand 2,9-di-terbutyl-1,10-phenanthroline (phen*). Complex **1** decarboxylates at 100°C to give H₂ and Cu(0) deposit with free phen*. To ensure that the degradation process goes through the hypothetical hydride [(phen*)CuH], Lewis acidic boron BR₃ compounds (R = C₆F₅, Et) or organic scavengers have been introduced to trap it. In most case degradation occurs except with B(C₆F₅)₃ that give the cationic complex [{"(phen*)Cu}₂(μ-HCO₂)][(HCO₂)B(C₆F₅)₃] (**2**) which has been crystallized. While **1** does not react with CS₂ when heated, it undergoes under 1 atm of ¹³CO₂, 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 storage¹⁰⁻¹⁵ to reduction chemistry.¹⁶⁻¹⁹

For example, in stark contrast to the stable carboxylate complexes [M](O₂CR) (R = alkyl), decarboxylation of the [M](O₂CH) species (Eq. 1) is much easier and is a classical reaction in the catalytic decomposition of formic acid (HCO₂H) into H₂ and CO₂.^{12,13,20}



These complexes also proved crucial intermediates in reductive chemistry by promoting hydrogen transfer reactions and CO₂ release especially when using liquid hydrogen surrogates such as HCO₂H,

HCO₂H–NEt₃, or solid sources containing the formate ion HCO₂⁻.^{21–27} At last, the utility of such complexes has been highlighted in the redox transformation of CO₂ and carbonyl molecules to methanol as well as in promoting the isomerization of methyl formate (HCO₂Me) into acetic acid.^{28–30} Easily obtained from different routes, mainly substitution reaction from halide derivatives with formate ion, reaction of HCO₂H with compounds involving hydrogen-sensitive [M]–R bonds (R = H, NR₂, R) species, or insertion of CO₂ 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 CO₂ 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}, [(η⁵-C₅H₄SiMe₃)₂Ti](C≡CSiMe₃)₂⁴⁵ or nitrogenated molecules as ancillary ligands.^{31,32} In the latter case, only one has been reported, the mixed-N,P-phosphane complex [(P(C₆H₂CH₂NMe₂-2)₃Cu(O₂CH)]³¹ which has been structurally characterized.

We report the synthesis and full characterization of the complex [(phen*)Cu(η¹-O₂CH)] (**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 ¹³CO₂. **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^tBu)] was prepared by addition of 1 equiv. ^tBuOK on a suspension of CuI in THF according to the literature procedure.⁴⁹ ¹H NMR (benzene-*d*₆): δ 1.32 (s, ^tBu). ¹³C{¹H} NMR (benzene-*d*₆): δ 72.7 C-(Me), 35.8 (Me). Being thermally unstable, [Cu(O^tBu)] 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 ¹H NMR were referenced to solvent impurities and are given in ppm. All the spectra were recorded at 25 °C.

Synthesis of [(phen*)Cu(κ¹-O₂CH)] (1**)** : [Cu(O^tBu)] (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(O₂CH)_{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, CO₂H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 2H), 1.76 (s, 18H). {¹³C} 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 CO₂H not seen*). IR data (ν cm⁻¹) : 2962 (w), 2783 (w), 2696 (w), 1620 (s, CO₂), 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-κ²-O₂CH)] [HCO₂B(C₆F₅)₃] (2) : A J. Young NMR tube was filled with **1** (7 mg, 0.017 mmol), B(C₆F₅)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 ¹H NMR spectra were carried out. {¹H} NMR (400 MHz, THF-*d*₈, δ/ppm) 8.60 (d, $J = 8.6$ Hz, 4H), 8.43 (s, 1H, HCO₂B), 8.19 (s, 1H, [Cu]₂(μ-O₂CH), 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(C₆F₅)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 ¹H NMR spectra of the clear light yellow solution indicated the release of free ligand with the formation of dark-red precipitate.

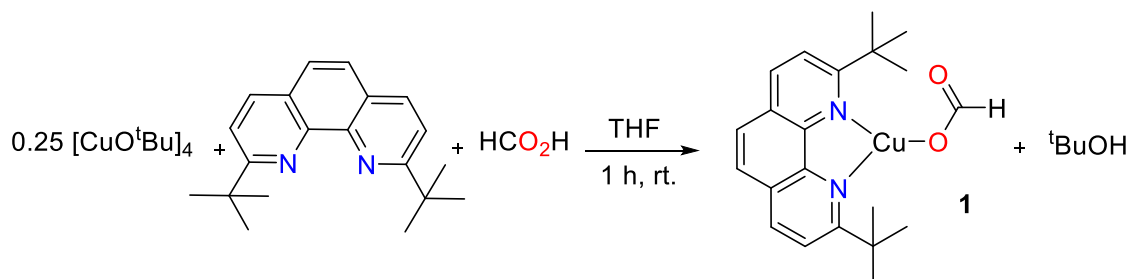
Thermal reaction of 1 with BR₃ (R = C₆F₅, Et₃) and Et-NCO, and phenylacetylene : In a J. Young NMR tube, **1** (1 equiv.) was dissolved in THF-*d*₈ (0.5 ml) and BR₃ (1 equiv.) or Et-NCO (2 equiv.) or phenylacetylene (1 equiv.) were added. The reaction mixture was heated at 60 °C and monitored at different times by ¹H 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 HCO₂H (18 μL, 0.48 mmol). At $t = 0$, the ¹H NMR spectra was recorded before the tube was immersed in an aluminium heating tube-plate at 100 °C. The reactions were then monitored by ¹H NMR every 15 min to see the evolution of H₂ (at 4.59 ppm in THF-*d*₈) and the disappearance of HCO₂H. When all the acid has disappeared, the gas phase was analyzed by GC analysis for detection of CO₂ and H₂ (see SI).

Result and discussion

Synthesis and characterization of [(phen*)Cu(κ¹-O₂CH)] (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(O₂CH)] (**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 CO₂³² 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 ^tBu groups and because all the [(phen*)CuX] (X = Cl, F, OTf) or [(phen*)Cu(L)]⁺ (L = CO, Me₂CO) 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(O₂CH)] (**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 ¹³C{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 δ = 8.2, a values quite downfield compared to the other [Cu^I(O₂CH)] 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 ¹³C{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 ν_{asym}(CO₂) stretching mode of the coordinated formate. This values is close to those reported for example in the complexes [(triphos)Cu₂O₂CH] (1620 cm⁻¹),⁴¹ [Cu(PPh₃)₂O₂CH].EtOH (1607 cm⁻¹),⁴² the phosphane [(P(C₆H₂CH₂NMe₂-2)₃)CuO₂CH] (1607 cm⁻¹),³¹ and [LCu₂(μ-HCO₂)](ClO₄)₂ (L = (N,N'-Me₂-C₆H₁₂N₃)CH₂(C₃HN₂)(N,N'-Me₂-C₆H₁₂N₃)) (1570 cm⁻¹)³² (see SI).

Single crystals of [(phen*)Cu^I(κ¹-O₂CH)_{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.

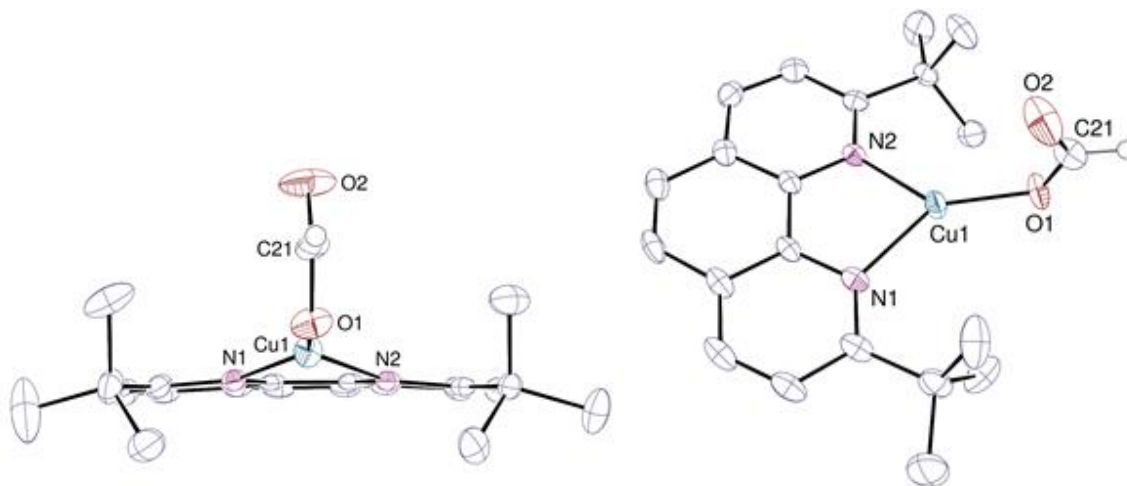


Figure 1. Two views of the crystal structure of complex **1'**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted except for that of formate. The minor iodide component is not shown. Selected bond distances (Å) and angles (deg): Cu1–O1 1.883(3), Cu1–N1 2.029(3), 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 κ¹-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(κ¹-O₂CH)] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) (1.848(2) Å)⁴³ and [(CAAC₁)Cu(κ¹-O₂CH)] (CAAC₁ = cyclic(alkyl)(amino)carbene) (1.863 Å),⁴⁴ but smaller than that found in the tetracoordinate phosphane compound [(P(C₆H₂CH₂NMe₂-2)₃)Cu(κ¹-O₂CH)] (2.041(2) Å).³¹ Unlike in the IPr-ligated copper formate⁴³ 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 CO₂ and H₂, leaving free phen* after 7 h at 60 °C (see SI). However, the CO₂ release suggested the presence of a transient Cu–H species, so we attempted to trap it with reactive groups such as BEt₃, B(C₆F₅)₃, Et–NCO, or phenylacetylene, following recent works.⁵⁴ For instance, we recently trapped the transient [(P₃N)CuH] hydride with B(C₆F₅)₃ as the unusual but stable triethylborohydride copper complex [(P₃N)Cu(μ -H-BEt₃)] (P₃N = N,N'-(2,4,6-C₆H₂Me₃)₂C₃H₆N₂C).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 CO₂.⁴³ 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 identified⁵⁵ and in the presence of phenylacetylene, we observed immediate greenish solution and phen* decoordination. With BEt₃, **1** degraded instead of forming a copper borohydride. Only with B(C₆F₅)₃, we isolated light orange crystals of the complex [{(phen*)Cu}₂(μ -O₂CH)][(HCO₂- κ^1)B(C₆F₅)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 [(HCO₂)B(C₆F₅)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 -O₂CH)].⁵³ The ¹H NMR spectrum of **2** in THF-*d*₈ revealed two broad ¹H 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 C₆F₅ moiety and B center in ¹⁹F NMR and ¹¹B NMR (see SI).

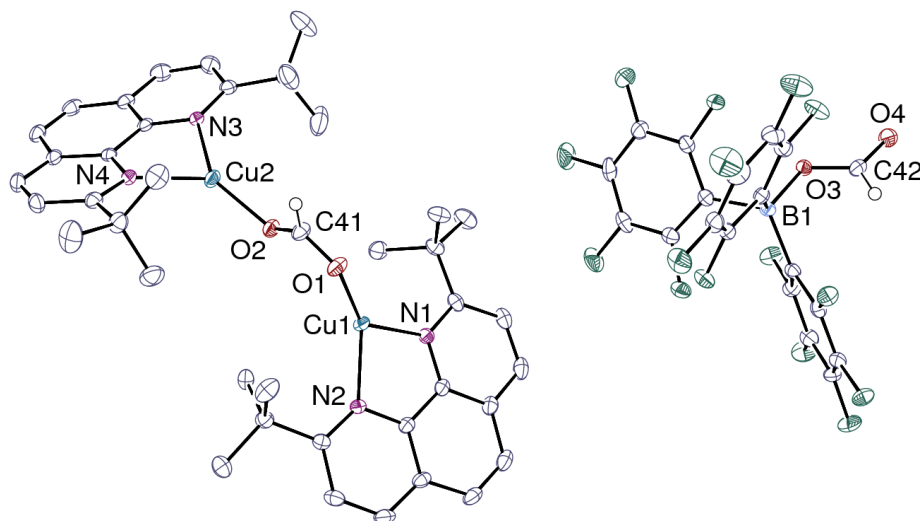


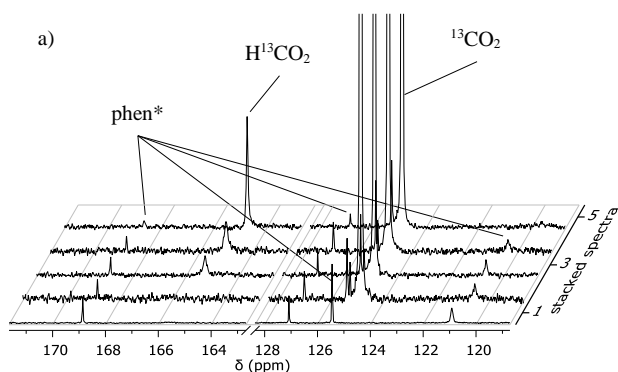
Figure 2. View of the crystal structure of complex **2**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted except for that of formate. Selected bond distances (Å) and angles (deg): Cu1–O1 1.9116(13), Cu1–N1 2.0508(15), Cu1–N2 2.0458(15), Cu2–O2 1.9260(13), 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).

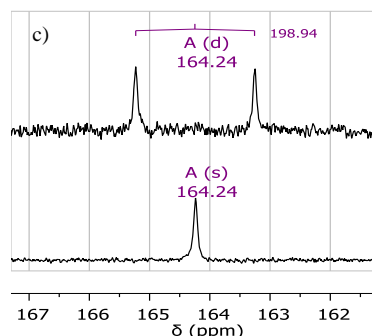
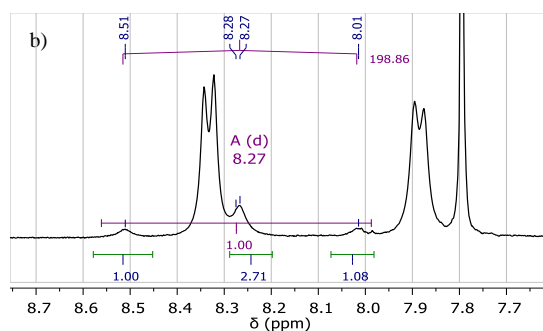
Stoichiometric reaction with $^{13}\text{CO}_2$

Guan *et al* reported in 2016 that decarboxylation of the nickel formate [(POCOP)Ni(κ^1 -O₂CH)] (POCOP = {2,6-(R₂PO)₂C₆H₃}; R = ^tBu, ⁱPr) in the presence of CS₂ gave the stable dithioformate [(POCOP)Ni(S₂CH)] derivative through the transient formation of the nickel hydride species.¹⁸ CS₂ being more reactive than CO₂ 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 CS₂ 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 $^{13}\text{CO}_2$ (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 CO₂. A J-Young NMR tube containing a THF-*d*₈ solution of **1** was pressurized with 1 atm $^{13}\text{CO}_2$ and heated at 60 °C for *ca* 4 h. ¹H and ¹³C NMR monitoring did not show degradation of the starting complex, but evidenced slow replacement of the unlabeled HCO₂ with H¹³CO₂. Enrichment of the formate anion in ¹³C supports the initial decarboxylation of **1** into the putative hydride [(phen*)Cu–H] that would immediately trap $^{13}\text{CO}_2$ to give the ¹³C-labeled formate derivative **1***. The evolution of **1** into **1*** is confirmed by ¹³C NMR. Indeed, while the formate carbon atom of **1** is not detected, the {¹H}¹³C NMR spectra showed a singlet at $\delta = 164.65$ (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 ¹³C NMR spectrum (20 % isotopic enrichment, IE, by ¹H NMR integration after 4h30) (Fig. 3c). The ¹H 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 ¹³C atom during the exchange process, and with a constant $J = 198$ Hz identical to that obtained for the C atom of the coordinated H¹³CO₂ ion in the ¹³C spectrum (Fig. 3c, top). Continuous heating of the reaction for 3 more hours enhanced the ¹³C enrichment (30 % IE) along with the degradation of **1** observed by the formation of free phen*.

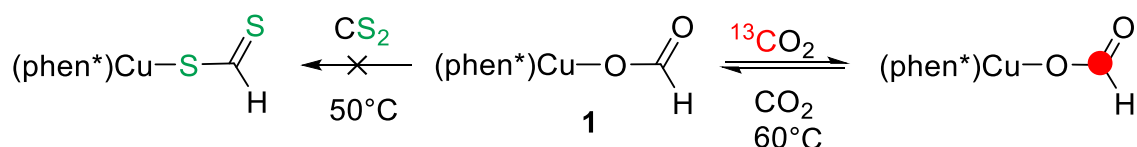
Figure 3. 3a- {¹H}¹³C NMR spectrum showing the increase with time of the H¹³CO₂ signal at 164 ppm (the signal increases from top to down). 3b- ¹H NMR signal of the H¹²CO₂ ligand of **1** which is split in the labelled analogue **1***. 3c- Singlet signal (bottom) in ¹³C NMR spectrum and doublet signal (top) in {¹H}¹³C NMR of H¹³CO₂ in **1***.





The ^1H - ^{13}C HSQC (heteronuclear single quantum coherence) analysis evidences the correlation between the labelled carbon of the formate ion ($\delta = 164.24$) and its neighboring proton ($\delta = 8.28$) (see SI). These observations provide solid proof for a successful $^{12}\text{CO}_2/^{13}\text{CO}_2$ exchange in $[(\text{phen}^*)\text{Cu}(\text{O}_2\text{CH})]$, 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

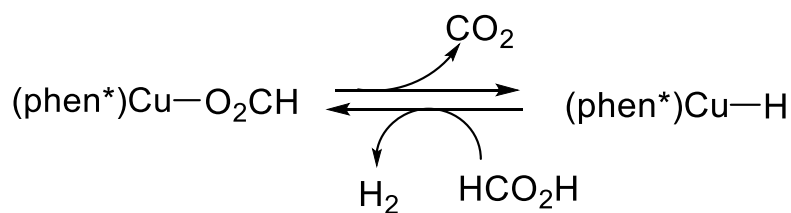
Scheme 2. Reactions of **1** with CS_2 and $^{13}\text{CO}_2$ at 50 and 60 °C, respectively.



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 selectivity¹² 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 ($\text{Cu}(\text{OAc})_2$, $\text{Cu}(\text{acac})_2$, $\text{Cu}(\text{O}_2\text{CH})_2$, $\text{Cu}(\text{NO}_3)_2$, CuCl_2 , CuO , CuCl , CuI , $\{\text{CuH}(\text{PPh}_3)\}_6$) in solution in $\text{HCO}_2\text{H}/\text{Et}_3\text{N}$ displayed a very low catalytic activity⁶⁴ 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 $[\text{Cu}_6(\mu^3\text{-H})_2(\text{L})_3(\text{BNC})_4][\text{PF}_6]_4$, involving a linear tetradentate phosphine ($\text{L} = \text{meso-Ph}_2\text{PCH}_2\text{P}(\text{Ph})(\text{CH}_2)_4\text{P}(\text{Ph})\text{-CH}_2\text{PPh}_2$), showed low catalytic activity for H_2 release from HCO_2H at 70°C in acetonitrile solution with $t\text{BuNC}$ and NEt_3 additives.⁶⁶ At last, in 2023, O'Hair *et al.* revealed that the mononuclear cuprate hydride anions $[(\text{X})\text{CuH}]^-$ ($\text{X} = \text{H}^-$, O_2CH^- , BH_4^- and CN^-) reacted in the gas-phase with formic acid to release H_2 with formation of the formate $[(\text{X})\text{Cu}(\text{O}_2\text{CH})]^-$ compound. The latter decarboxylates readily *via* collision-induced dissociation to regenerate the initial copper hydride.⁶⁷

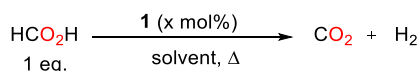
Scheme 3. The dehydrogenation of formic acid with **1**.



The dynamic exchange process of **1** under CO₂ 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 CO₂, it should also react quickly with the liquid acid HCO₂H, 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 ¹H NMR spectra and GC analysis (gas chromatography analysis) and the consumption of HCO₂H was followed by ¹H NMR with mesitylene as internal standard. The appearance and evolution of H₂ was detected at δ = 4.59 ppm in ¹H NMR, along with the diminution of the signals of HCO₂H (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- <i>d</i> ₈	100	16	0
2	10	THF- <i>d</i> ₈	100	2,5	100 ^{b,c}
3	5	THF- <i>d</i> ₈	100	3 8	27 90 ^c
4	1	THF- <i>d</i> ₈	100	15	40 ^c
5	5	THF- <i>d</i> ₈	80	4	4
6	5	THF- <i>d</i> ₈	60	15	0
7	14	MeCN-	60	15	0
8	5	MeCN- <i>d</i> ₃	100	8	0

^a Conversions measured by ¹H 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 ¹H NMR spectra of a THF-*d*₈ solution of **1** (10 mol%) containing 18 μL of HCO₂H evidenced the selective release of H₂ and no trace of CO was detected by GC analysis. In the absence of **1**, HCO₂H 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 HCO₂H (Fig. 4). At first (t = 0), the phen* signals of **1** in the HCO₂H-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 HCO₂H, which was not dehydrogenated (see SI).

Decomposition of HCO₂H 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 HCO₂H (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 HCO₂H into CO₂ and H₂ without the requirement of any base or additives. No additive is needed to promote the catalysis, because **1** spontaneously releases CO₂ 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 H₂. 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 NEt₃ and which displayed TOFs lower than 1 h⁻¹ at 95 °C.^{13,64,65} The species [Cu(NCMe)₄][PF₆] in acetonitrile and in the presence of various phosphine ligands and additives (tBuNCNEt₃) at 70 °C, showed greater activities in the decomposition of HCO₂H 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 10⁵,⁶⁸ and the most efficient complexes are currently based on noble metals (Ru and Ir), with TON values exceeding 10⁶.^{12,69} For example, Williams and coworkers in 2016 and Li *et al* in 2015, reported a binuclear iridium(III) and two organometallic mononuclear (C₅Me₅)Ir(III) catalysts exhibiting, at 90 °C, TOF of 2.28 × 10⁵ h⁻¹ (TON = 2.16 × 10⁶) and 4.88 × 10⁵ h⁻¹ (TON = 2.4 × 10⁶ 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(O₂CH)] (**1**) in the decomposition of formic acid, and it generated H₂ and CO₂. 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 ¹³C NMR, which revealed the steady increase of the ¹³CO₂H signal during dynamic isotopic exchange with ¹³CO₂.

Figure 4. ^1H 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).

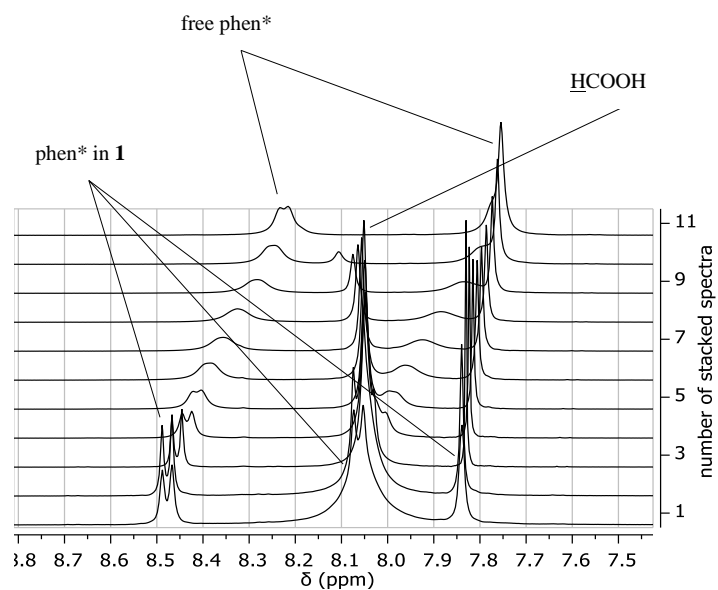
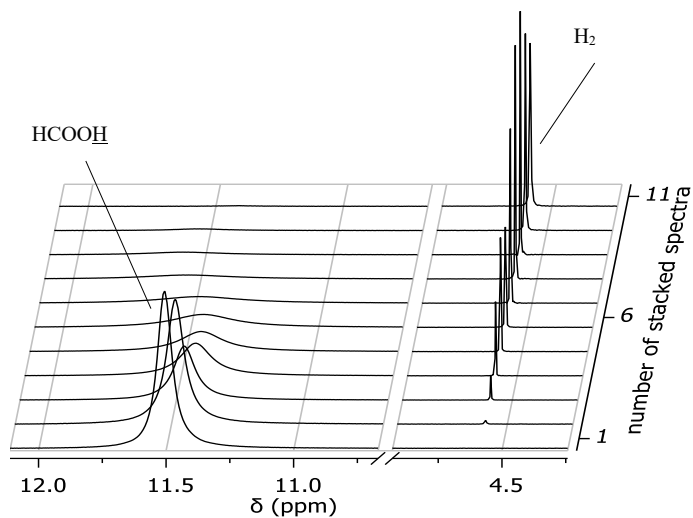


Figure 5. ^1H NMR spectrum showing disappearance of the acidic signal of formic acid and concomitant release of H_2 . Spectrum were recorded every 15 min (total reaction time, 2h30).



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.

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

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