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Tetranuclear thiocyanato-bridged copper(I) catalyst for the hydrogenation of Carbon Dioxide to formate under mild conditions

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The hydrogenation of carbon dioxide(CO_2) with a base to produce formate salts offers a method for storing hydrogen in an energy dense solid. This stored hydrogen (H_2) can be released later by acidifying the formate salts, or formic acid can be utilized directly in fuel cells. However, this process relies on catalytic CO_2 hydrogenation, which ideally should employ a catalyst made from an abundant earth metal. Recent research on molecular catalysts has led to improved rates for conversion of CO_2 to energy-rich products such as formate, but the catalysts based on first-row transition metals is under development. Copper(I) complexes containing 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene ligand were found to promote the catalytic hydrogenation of CO_2 to formate in the presence of NaOH/KOH as the base where catalytic conversion of CO_2 *via* hydrogenation using H_2 to produce valuable energy-relevant chemicals and therefore is a promising safe and simple strategy to conduct reactions under ambient pressure at room temperature. Aiming to this goal, herein we report an efficient copper(I) complex $[Cu_4(\kappa^2\text{-PCP}^{t\text{-Bu}})_2(\mu_2\text{-SCN})_4]$ as catalyst to achieve ambient-pressure CO_2 hydrogenation to generate metal formate ($HCO_2^-M^+$) with turnover number (TON) values of 108 to 23040 in 3 to 24 h of reaction at 25°C to 60°C. This outstanding catalytic performance makes $[Cu_4(\kappa^2\text{-PCP}^{t\text{-Bu}})_2(\mu_2\text{-SCN})_4]$ a potential candidate for realizing the large-scale production of metal formate by CO_2 hydrogenation.

Introduction

Global attention is currently directed towards the use of carbon dioxide (CO_2) as a versatile chemical feedstock for synthesizing various important chemicals, such as formic acid, methanol, urea, and carbonates, and so on.[1] Among these processes, the hydrogenation of CO_2 to produce formic acid or formate is particularly significant. At present, the majority of industrial formic acid is generated through the hydrolysis of methyl formate or formamide.[1c] CO_2 hydrogenation in the presence of base (e.g. NaOH, KOH) typically leads to formate salts (e.g. sodium/potassium formate) which can be used to store hydrogen in an energy dense solid (Scheme 1).[2-6] These formate salts can be used as hydrogen storage materials with hydrogen and CO_2 release upon acidification of the compounds.[7] The development of the homogeneous CO_2 hydrogenation has made significant progress in the past 30 years and has been well documented in the literature.[5, 8-14]

$$CO_2 + H_2 \xrightarrow[KOH/NaOH]{[Cu_4(\kappa^2\text{-PCP})_2(\mu_2\text{-SCN})_4]} [HCO_2]^-M^+ + H_2O$$

Scheme 1. CO_2 hydrogenation to produce formate salts

Several reports have employed homogeneous catalysts based on precious metals, including Ru[8], Rh[9], Ir[2b,10], Pd[11], Pt[12], Re[13], and Au[14] for the hydrogenation of CO_2.[8-14] The formation of metal hydride (M-H) through the interaction between the noble metal and H_2 is vital for these catalytic processes, so that, CO_2 can be inserted into the M-H bond.[8-14] In contrast, the use of abundant and inexpensive first-row metal complexes in catalytic CO_2 hydrogenation is quite limited and sporadic examples with Fe[15], Co[16], Ni[17], Cu[18], and Mn[19] based catalysts have been reported in literature. The greater abundance and lower cost of first-row transition metals would make them better suited to the large-scale production of fuels, if they could be made sufficiently active as catalysts. There are reasons to believe that copper complexes could behave as an effective catalyst in CO_2 hydrogenation. For instance, copper dispersions on ZnO/Al_2O_3 are widely used in the industrial conversion of syngas to methanol,[20] for which mechanistic studies have revealed that this reaction occurs primarily through hydrogenation of the CO_2, rather than CO, in

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$CO_2/CO/H_2/H_2O$ mixtures.[21] Moreover, homogeneous copper phosphine and carbene complexes are highly efficient catalysts for the reduction of CO_2 to CO,[22] hydroboration of CO_2 to form boryl formates,[23] and hydrosilylation of CO_2 to form silyl formates.[24] Despite these reports, the copper-catalyzed hydrogenation of CO_2 to formic acid, which is more relevant to the production of renewable fuels, has long remained elusive. The reaction is thermodynamically favourable in organic solvents with the addition of a suitable base. Copper hydrides can be formed from hydrogen in the presence of a base, and some have been shown to react stoichiometrically with CO_2 to produce formates.[25] However, this CO_2 reactivity has remained stoichiometric because the copper formate products generally do not turn over when using hydrogen, rather than silanes or boranes, as the source of hydride. The catalytic hydrogenation of CO_2 to formate (HCO_2^-) (Scheme 1), is promising for the large-scale fixation of CO_2, because such hydrogenation could substitute conventional methods using CO, and formate has possible use as a hydrogen energy carrier.[25] 1,2-Bis(di-*tert*-butylphosphinomethyl)-benzene($PCP^{t\text{-}Bu}$), a symmetrical diphosphine ligand, has become a role model for achieving the alkoxycarbonylation of various unsaturated compounds. Palladium complexes provide the basis for the first step in the commercial (Alpha) production of methyl methacrylate as well as very high selectivity to linear esters and acids from terminal or internal double bonds.[26] The design and development of highly active and effective systems comprising of non-precious transition metals still remain largely subtle. Recently, our group has made efforts to design well-defined and stable copper-based catalysts that can be used in hydrogenation of CO_2.[27] Our current studies of copper-catalyzed CO_2 hydrogenation are focused on using well-defined copper complex that not only create stable catalyst but also facilitate investigation of the catalytic mechanism. Herein, we demonstrates that the $PCP^{t\text{-}Bu}$ ligated copper(I) complex, $[Cu_4(\kappa^2\text{-}PCP^{t\text{-}Bu})_2(\mu_2\text{-}SCN)_4]$, is an effective catalyst for the reduction of CO_2 to formate using hydrogen, and a base, with higher activity and thermal stability compare to the previously reported systems.[18,26] To the best of our knowledge, this investigation describes the first CO_2 hydrogenation catalyst based on $PCP^{t\text{-}Bu}$ copper complex at room temperature.

Experimental section

Materials and Physical Measurements

All the synthetic works were performed under argon atmosphere. The solvents were dried and distilled before use following the standard procedures. Copper(I) thiocyanide, ligand $PCP^{t\text{-}Bu}$, sodium hydroxide, potassium hydroxide, H_2 and CO_2 (≥99.999%) were used as received. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL AL-400 FTNMR using tetramethylsilane and phosphoric acid as an internal standard for ^1H; ^{13}C and ^{31}P NMR, respectively. HR-MS spectra were recorded on electrospray mass spectrometer.

Synthesis of the complex $[Cu_4(\kappa^2\text{-}PCP^{t\text{-}Bu})_2(\mu_2\text{-}SCN)_4]$(1)

$PCP^{t\text{-}Bu}$ (394 mg, 1 mmol) was added slowly to a solution of CH_3OH (15 mL) and CH_2Cl_2 (15 mL) containing copper(I) thiocyanate (484 mg, 4 mmol). The resulting solution was refluxed for 12 h and then filtered and saturated with hexane and left for slow evaporation. Yellow colour crystals suitable for single crystal data collection were isolated after one week. Yield: (223 mg, 70%). Anal. Calc. for $C_{52}H_{88}N_4P_4S_4Cu_4$(%): C, 48.91; H, 6.89; N, 4.39; S, 10.03. Found: C, 48.96; H, 6.98; N, 4.46; S, 10.11. IR(cm^{-1}, KBr): ν = 3413, 2966, 2847, 2181, 2112, 1642, 1404, 1278, 1082, 1012, 865, 795, 669, 607, 537. ^1H NMR (δ_{ppm}, 400 MHz, $CDCl_3$, 298K): δ 7.33-7.30 (m, 4H), 7.18-7.15 (m, 4H), 3.28-3.26 (t, 8H, CH_2), 1.26 (m, 72H, CH_3). $^{31}P\{^1H\}$: δ25.21 (s) (sharp). UV/Vis: λ_{max} (ε[dm^3 mol^{-1} cm^{-1}]) = 234(7145), 380 (13369). HR-ESI-MS (m/z): Calcd: 1275.58. Found: 1277.71 $[M+2]^+$.

X-ray structure determination

The data for complex **1** was collected from a single crystal on a XtaLAB Synergy, Single source at home/near, HyPix four-circle diffractometer with a micro-focus sealed X-ray tube using a mirror as monochromator and a HyPix detector. The data for complex **1** was integrated with CrysAlisPro and a multi-scan absorption correction using SCALE3 ABSPACK was applied.[28] The diffractometer used Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing with SHELXT and refined by full-matrix least-squares methods against F^2 using SHELXL.[29-30] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Small and weak diffraction quality of the crystal evenafter prolonged exposure time is due to crystallinity issue. However, the structure was determined and refined properly.

General procedure for hydrogenation

In an argon flow inside 100 mL RB flask, the complex **1** (0.01, 0.01, 0.02, 0.002, or 0.0002 mmol), NaOH/KOH in 10 mL water (4.8 mmol) and tetrahydrofuran (THF) solvent (5 mL) were added to it and immediately close the 100 mL RB flask. The H_2 and CO_2 gas was then purged inside the RB flask at 1 atm pressure. The reaction mixture was then stirred with a magnetic stirrer for 30 minutes (600 rpm) and subsequently placed in a preheated oil bath. After heating for a given period of time, the RB flask was cooled down to room temperature. We have found a solution with two distinct layers and separated them with the help of centrifuge. A known amount of mesitylene was added as an internal standard to the top layer which was then analyzed by ^1H and ^{13}C NMR. Further, a known amount of imidazole was added to bottom aqueous layer as an internal standard, followed by ^1H and ^{13}C NMR analysis. Yields were determined through ^1H NMR from integration ratios (relaxation delay = 10 seconds).

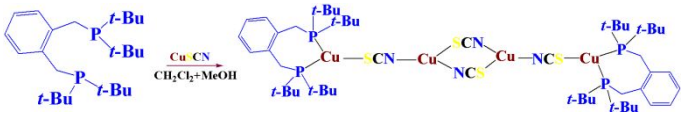
Procedure for recycling study

In an argon-filled RB flask, the complex **1** (0.002 mmol), NaOH/KOH in 10 mL water (4.8 mmol) and tetrahydrofuran (THF) solvent (5 mL) were added to it and immediately close the 100 mL RB flask. The H_2 and CO_2 gas was then purged

inside the RB flask at 1 atm pressure. The reaction mixture was then stirred with a magnetic stirrer for 30 minutes (600 rpm) and subsequently placed in a preheated oil bath. After heating for a given period of time (12 h), the RB flask was cooled down to room temperature. Upon opening the 100 mL two-neck RB flask inside an argon flow, a solution with two distinct layers was obtained. After transferring the whole solution in a centrifuge tube, the two layers were separated. The bottom layer was washed with additional 2 mL of THF, and the combined organic layer was transferred to another 100 mL two-neck RB flask and used directly for the next cycle. Meanwhile, a known amount of imidazole was added to bottom aqueous layer as internal standard, followed by its analysis by ^{1}H and ^{13}C NMR with $CDCl_3$ as the deuterated solvent. Yields were determined through ^{1}H NMR from the integration ratios of imidazole aromatic peaks with formate proton peak.

Results and discussion

$[Cu_4(\kappa^2\text{-}PCP^{t\text{-}Bu})_2(\mu_2\text{-}SCN)_4]$ was synthesized in good yield by the reaction of CuSCN with the ligand 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene in a dichloromethane: methanol mixture (50:50 *v/v*) at a 4:1 molar ratio under reflux condition (Scheme 2). This complex was hygroscopic solid,



Scheme 2. Synthesis route for complex **1**.

exhibiting solubility in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and various halogenated solvents and fully characterized by IR, UV-Vis, ^{1}H, and ^{31}P NMR spectroscopies (see Fig. S5-S9, ESI). The band associated with bridging SCN group appeared at 2112 cm^{-1} in **1** which is in good agreement with the literature values for the bridging thiocyanate group.[27] In the ^{1}H NMR spectra of the tetranuclear copper complex **1** displayed a multiplet in the range of δ 1.26 ppm corresponding to the *t*-butyl protons of the $PCP^{t\text{-}Bu}$ ligand. The methylene protons of PCP ligand were observed as a triplet at δ 3.26 to 3.28 ppm (See Fig. S6, ESI).[26,31] The $^{31}P\{^{1}H\}$ NMR spectra of complex **1** shows a single resonance at δ 25.21 ppm which corresponded to the phosphorus centers of 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene ligand and suggests that both the phosphorus centers were chemically equivalent (See Fig. S7, SI). The electronic absorption spectrum of **1** in methylenedichloride solution exhibits absorption bands between 234 nm and 380 nm (See Fig. S8, ESI). The absorption band in 380 nm is ascribed to the d-d transition and the higher-energy band has been assigned to intraligand charge transfer.[27] Complex **1** crystallizes in the monoclinic system with $P2_1/n$ space group. Complex **1** revealed to have a centrosymmetrical dimeric unit with the two thiocyanate groups bridging the two copper atoms (Fig. 1). The crystal structural analysis of complex **1,** reveals the tetranuclear structure which produces an 18-electron configuration at each copper without the need for any metal-metal bonds. The trigonal coordination around the copper atoms is defined by two P atoms of the chelating 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene ligand [Cu-P bond lengths = 2.236(2) Å and 2.253(2) Å] and two thiocyanate groups. The P1-Cu-P2 bite angle is 116.07(10)°, which is larger than those found in analogous complexes based on 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene ligand. The other coordination bond angles in **1** are rather distorted [P(1)-Cu(1)-S(1) = 114.51(10)°, P(2)-Cu(1)-S(1)= 129.36(10)°, $N(2)^{\#1}$-Cu(2)-N(1) =132.4(4)°, $N(2)^{\#1}$-Cu(2)-S(2)= 109.5(3)°, N(1)-Cu(2)-S(2)= 118.1(3)°]. This is because of the strained four-membered $Cu_2(SCN)_2$ ring and due to steric hindrance of the $PCP^{t\text{-}Bu}$ ligand. The Cu-S, Cu-N and Cu-P bond distances are 2.236(2)-2.253(2) Å, 1.878(10)-1.883(8) Å and 2.236(2)-2.253(2) Å, respectively and are comparable with other derivatives with 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene.[31] The S-C-N bond angle is 178.8(12)°-179.5(10)° which confirmed that thiocyanate groups are linearly coordinated to each copper atom. The S-C and C-N bond distances fall in the range of 1.623(11)Å-1.651(14) Å and 1.170(11)Å-1.179(13) Å, respectively. These distances are within the reported range. Crystal packing in complex **1** is stabilised by C-H···S hydrogen bond interactions (See S-10, ESI). The contact distances for C-H···S interactions are in the range of 2.970 Å.[32]

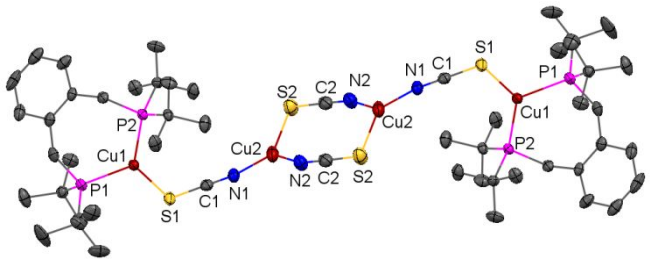


Fig. 1. Molecular structure of complex $[Cu_4(\kappa^2\text{-}PCP^{t\text{-}Bu})_2(\mu_2\text{-}SCN)_4]$ (**1**).

The influence of solvents, catalyst loadings, bases, and reaction times are crucial factors in any catalytic system. Similarly, the presence of different metal in different catalytic systems also plays a crucial role in catalytic outcomes. For example, it is noted that the outcome of the copper complex-catalyzed base-promoted H_2 activation reaction, is differ from iron and cobalt-based catalytic systems.[33,34] The reactions were run in THF solution containing Cu-complex **1**, NaOH/KOH dissolve in water as a base to trap the product generated by the CO_2 hydrogenation under 1 atm of both CO_2 and H_2 for 3 h (Scheme 1). Several control experiments were run initially to determine the extent of background reaction in the absence of a catalyst (Table 1). The product ($HCO_2^-Na^+$) is not isolated in the absence of copper catalyst or in the presence of $PCP^{t\text{-}Bu}$ ligand (entries 1 and 2, respectively). Entry 3 shows that CuSCN afforded low product yield compare to copper catalyst **1**, and thus suggested no rate acceleration. Although the hydrogenation of CO_2 was performed in different solvents such as THF, acetonitrile (ACN), methanol (MeOH), toluene, 2-

propanol, N-Methyl-2-Pyrrolidone (NMP). The catalytic activity of the complex **1** was found to be the highest in THF. Apart from these, the effect of bases such as NaOH and KOH were also examined on the copper complex **1** catalyzed hydrogenation of CO_2 (Table 1). However, the generation of formate salt took place in case of copper complex **1** (Table 1, entries 3, 4) under 1 atm of H_2 and CO_2 at room temperature. The reactions were conducted in a THF/H_2O biphasic system (5/10 mL; v/v), which allows for efficient recovery of the catalyst.

Table 1. Catalytic Hydrogenation of CO_2 to Formate[a]

Entry	Catalyst	Base	Time	Yield(%)[b]	TON[c]
1.	none	NaOH	3h	0	0
2.	$PCP^{t\text{-}Bu}$	NaOH	3h	0	0
3.	CuSCN	NaOH	3h	5	24
4.	Complex **1**	NaOH	3h	30	144
5.	Complex **1**	KOH	3h	40	192

[a]All experiments were done in triplicate. conditions: catalyst (0.01 mmol), NaOH/KOH (4.8 mmol) in 10 mL water, THF (5.0 mL), CO_2 (1 atm), H_2 (1 atm), 25°C. [b]Yield of formate product was determined in relation to amount of NaOH added by ^{1}H NMR spectroscopy using mesitylene as an internal standard. [c]Mole of formate/mole of catalyst.

The NaOH solution afforded 30% of HCOONa with TON of 144 in 3h upon hydrogenation in presence of 0.01 mmol of copper complex **1** (Table 1, entry 3). It is important to mention that in the reaction mixture, aqueous layer contained HCOONa and the organic layer contained the catalyst, thus allowing for easy recycling. From the insight of these observations, KOH solution was hydrogenated under 1 atm of H_2 and CO_2 with complex **1** with TON of 192 (Table 1, Entry 4). As presented in Table 2, a TON value of 108 to 144 was achieved on extending the reaction time to 24 h (Table 2, entries 3 and 4). The optimal temperature was found to be 60°C at 1 atm pressure of H_2 and CO_2. Raising the reaction temperature to 100°C resulted in lower catalytic activity, which may be attributed to the deposition of catalytically inactive copper metal during the reaction (Table 2, entries 3&4)

Table 2. Hydrogenation of CO_2 with 1/MOH system [Where M= Na, K].[a]

Entry	Base	Catalyst (mmol)	T [°C]	t [h]	Yield [%][b]	TON[c]
1.	NaOH	0.02	60	12	60	144
2.	KOH	0.02	60	12	90	216
3.	NaOH	0.02	100	24	45	108
4.	KOH	0.02	100	24	60	144
5.	NaOH	0.002	25	12	29	696
6.	NaOH	0.0002	60	12	65	15600
7.	KOH	0.002	25	12	40	960
8.	KOH	0.0002	60	12	96	23040
9.	KOH	0.002[d]	60	12	36	864

[a]All experiments were done in triplicate. conditions: catalyst (0.02/0.002/0.0002 mmol), NaOH/KOH (4.8 mmol) in 10 mL water, THF (5.0 mL), CO_2 (1 atm), H_2 (1 atm), 60°C. [b]Yield of formate product was determined in relation to amount of NaOH/KOH added by ^{1}H NMR spectroscopy using mesitylene as an internal standard. [c]Mole of formate/mole of catalyst.[d]CuSCN

Further lowering the catalyst loading from 0.002 mmol to 0.0002 mmol (Table 2, entries 5-8, (See S11–S16, ESI) gave TON values of up to 23040. A comparison of the catalytic results with other catalysts that have been reported in literature is given in Table 3. ^{1}H, 2D COSY NMR (Fig. S16, ESI) was performed to investigate the eventual correlation between $H_{formate}$ and $H_{imidazoline}$ but nothing could be observed. Therefore, the signal at 8.78 ppm corresponds to the formate complex. The hydrogenated product can be isolated with a 29 to 96% yield as white deliquescent powder grown from the reaction mixture at 60°C. Compared to HCOONa, the formation of HCOOK was faster (TON 15600 to 23040; Table 2, entries 6&8). The improved rate can be explained by the higher standard enthalpy of formation of HCOOK (−679.7 kJ/mol) compared to HCOONa (−666.5 kJ/mol), which facilitates the release of the formate group from the catalytic resting state. From the hydrogenation products yields and TONs, catalyst **1** is found to be the most suitable for hydrogenation in KOH. Finally, the recycling experiments were performed by using the biphasic solvent system (See S1, ESI) of the catalytic reaction mixture and noticed that catalyst **1** was recyclable up to the two cycles without noticing any significant loss in the catalytic activity under our established protocol (See S17, ESI). As even after four cycles over, 90% HCOOK yield was obtained with catalyst **1**. Thereby, suggesting that catalyst **1** is an efficient and robust catalyst for the investigated hydrogenation reaction. The homogeneity of the CO_2 hydrogenation reaction for **1** was evaluated. The use of mercury as a poison in the catalytic reaction checks the sensitivity of the metal catalyst. In the presence of mercury Wherein, mercury suppresses the reactivity of the metal complex as it amalgamates on the surface, making the metal complex unavailable for catalysis. The TON of the **1** after the exposure to the poison is shown in Fig. 2. The difference in TON with and without the poisoning suggests that the reaction is carried out *via* a homogenous approach. The most plausible CO_2 hydrogenation reaction mechanism is illustrated in Fig. 3.

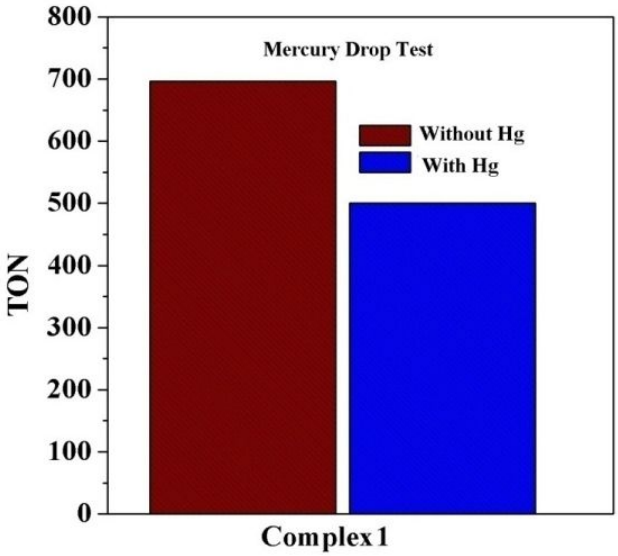


Fig. 2. Homogeneity test during hydrogenation of CO_2 using complex **1**. General reaction conditions: 0.002 mmol copper catalyst (complex **1**), 0.70 mmol elemental Hg, 4.8 mmol NaOH in 10 mL H_2O and 5 mL THF, 1 atm of H_2:CO_2 (1:1), 60°C, 12 h. TON is based on ^{1}H NMR analysis with imidazole as an internal standard.

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Table 3. Homogeneous copper catalysts reported in literature for CO_2 hydrogenation to formate.

Entry	Pre-catalyst	Solvent	Base	Additives	CO_2/PH_2 (bar)	T/°C	TOF/(h^{-1})	TON	Ref.
1.	$Cu(OAc)_2.H_2O$/DBU	1,4-dioxane	DBU	-	40/40	100	-	167	35
2.	$LCu(MeCN)PF_6$	CH_3CN	DBU	-	20/20	140	25	500	18a
3.	$[(L^1Cu)_2H]PF_6$	CH_3CN	DBU	-	20/20	83	7.5	-	18b
4.	Cyclic alkyl amino carbene based copper hydride complex in combination with Lewis pairs DBU/$B(C_6F_5)_3$	THF	DBU	-	15/45	100	-	1881	18c
5.	[CuI(dtbpf)]	DMF	DBU	-	1/1	80	-	1.065×10^5	27b
6.	$[Cu_2(\mu\text{-}I)_2(\kappa^1\text{-}PCP^{t\text{-}Bu})]$	1,4-dioxane	DBU	-	1/1	80	-	8700	27a
7.	*trans*-[(tBu-PNP)Fe(H)$_2$(CO)]	H_2O/THF	NaOH	-	3.33/6.66	30	788(5)	156	15b
8.	*trans*-[(tBu-PNP)Fe(H)$_2$(CO)]	H_2O/THF	-	$NaHCO_3$	-/8.3	80	320(16)	-	15b
9	$[Cu_4(\kappa^2\text{-}PCP^{t\text{-}Bu})_2(\mu_2\text{-}SCN)_4]$	H_2O/THF	NaOH	-	1/1	60	1300	15600	This work
10	$[Cu_4(\kappa^2\text{-}PCP^{t\text{-}Bu})_2(\mu_2\text{-}SCN)_4]$	H_2O/THF	KOH	-	1/1	60	1920	23040	This work

The reaction mechanism was supported by NMR spectra. A copper hydride species [Cu]-H is generated from complex **1**. Subsequent CO_2 insertion into the [Cu]-H bond furnishes the Cu formate complex. NMR spectra revealed the appearance of a peak at 8.78 ppm in the ^{1}H NMR spectrum and a signal at 167 ppm in the ^{13}C NMR spectrum (Fig. S14-S15).

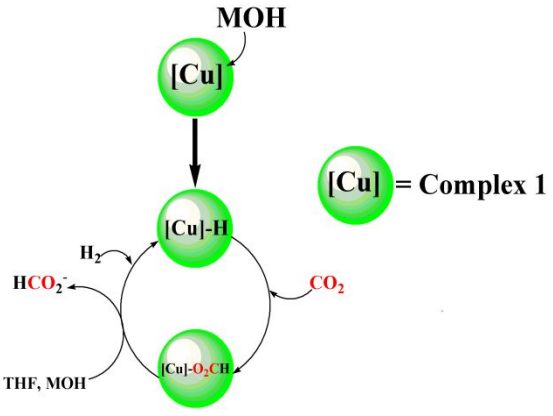

Fig. 3. Plausible mechanism for the hydrogenation of CO_2 catalyzed by the $[Cu_4(\kappa^2\text{-}PCP^{t\text{-}Bu})_2(\mu_2\text{-}SCN)_4]$ complex.

Attempts to characterize the hydride complex by NMR spectroscopy failed, probably because of conversion of hydride to formate or poor solubility of this hydride complex under the reaction conditions. The [Cu]-H is regenerated by the activation of H_2 with the concomitant release of formate through the aid of the base.

Conclusions

In summary, we have developed a highly active copper catalyst, $[Cu_4(\kappa^2\text{-}PCP^{t\text{-}Bu})_2(\mu_2\text{-}SCN)_4]$ (**1**), which catalyzes the hydrogenation of CO_2 to formate. Furthermore, this synthesize complex was evaluated as catalyst for the hydrogenation of CO_2 to formate, demonstrating their potential applicability in CO_2 conversion processes. Contrary to other first-row transition metal complexes bearing complicated ligands, the examined copper complex **1**//MOH system promotes the formation of formate salt without the addition of extra ligands. Under optimized reaction conditions, using 0.0002 mmol catalyst **1**, an exceptional TON of 23040 was achieved. This unprecedented activity of catalyst **1**, not only surpasses the catalytic outcome of the existing catalytic systems having first

row transition metals, but also established catalysts based on precious transition metals. Ongoing mechanistic studies and the design of next-generation Cu-based catalysts are expected to further enhance performance and broaden the scope of this promising catalytic platform.

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Notes and references

1 (*a*) W. Wang, Y. Himeda, J. T. Muckerman, G. F. Manbeck, E. Fujita, *Chem. Rev.* 2015, **115**, 12936; (*b*) J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, *Angew. Chem. Int. Ed.* 2016, **55**, 7296; (*c*) J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, *Angew. Chem.* 2016, **128**, 7416; (*d*) A. Ávarez, A. Bansode, A. Urakawa, A. V. Bavykina, T. A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, *Chem. Rev.* 2017, **117**, 9804;(*e*) S. Nagireddi, J.R. Agarwal, D. Vedapuri, *ACS Eng. Au*, 2024, **4**, 1, 22; (*f*) M.M. Ramirez-Corredores, *npj Mater. Sustain.* 2025, **2**, 35; (*g*) Z. Song, D. Han, M. Yang, J. Huang, X. Shao, H. Li, *Applied Surface Science* 2023, **607**, 155067.

2 (*a*) T.C. Johnson, D.J. Morris, M. Wills, *Chem. Soc. Rev.* 2010, **39**, 81; (*b*) J. F. Hull, Y. Himeda, W. H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman, E. Fujita, *Nat. Chem.* 2012, **4**, 383; (*c*) Q. Y. Bi, X. L. Du, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *J. Am. Chem. Soc.* 2012, **134**, 8926; (*d*) Z. L. Wang, J. M. Yan, Y. Ping, H. L. Wang, W. T. Zheng, Q. Jiang, *Angew. Chem. Int. Ed.* 2013, **52**, 4406; (*e*) Z.-L. Wang, J.-M. Yan, Y. Ping, H.-L. Wang, W.-T. Zheng, Q. Jiang, *Angew. Chem.* 2013, **125**, 4502; (*f*) D. Mellmann, P. Sponholz, H. Junge, M. Beller, *Chem. Soc. Rev.* 2016, **45**, 3954.

3 G.A. Filonenko, D. Smykowski, B.M. Szyja, G. Li, J. Szczygieł, E.J.M. Hensen, E.A. Pidko, *ACS Catal.* 2015, **5**, 1145.

4 K. Sordakis, A.F. Dalebrook, G. Laurenczy, *ChemCatChem* 2015, **7**, 2332.

5 W.-H. Wang, Y. Himeda, J.T. Muckerman, G.F. Manbeck, E. Fujita, *Chem. Rev.* 2015, **115**, 12936.

6 Q. Liu, L. Wu, S. Gülak, N. Rockstroh, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* 2014, **53**, 7085.

7 S. Siek, D.B. Burks, D.L. Gerlach, G. Liang, J.M. Tesh, C.R. Thompson, F. Qu, J.E. Shankwitz, R.M. Vasquez, N.S. Chambers, G.J. Szulczewski, D.B. Grotjahn, C.E. Webster, E.T. Papish, *Organometallics* 2017, **36**, 1091.

8 (*a*) Y. Musashi, S. Sakaki, *J. Am. Chem. Soc.* 2000, **122**, 3867-3877; (*b*) T. Schaub, R.A. Paciello, *Angew. Chem. Int. Ed.* 2011, **50**, 7278; (*c*) T. Schaub, R.A. Paciello, *Angew. Chem.* Int. Ed. 2011, **123**, 7416; (*d*) S. Bontemps, L. Vendier, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* 2012, **51**, 1671; (*e*) S. Bontemps, L. Vendier, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* 2012, **124**, 1703; (*f*) S. Moret, P. J. Dyson, G. Laurenczy, *Nat. Commun.* 2014, **5**, 4017; (*g*) N.M. Rezayee, C.A. Huff, M.S. Sanford, *J. Am. Chem. Soc.* 2015, **137**, 1028; (*h*) R. Kuriki, K. Sekizawa, O. Ishitani, K. Maeda, *Angew. Chem. Int. Ed.* 2015, **54**, 2406; (*i*) R. Kuriki, K. Sekizawa, O. Ishitani, K. Maeda, *Angew. Chem. Int. Ed.* 2015, **127**, 2436; (*j*) J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah, G. K. S. Prakash, *J. Am. Chem. Soc.* 2016, **138**, 778; (*k*) K. Rohmann, J. Kothe, M. W. Haenel, U. Englert, M. Holscher, W. Leitner, *Angew. Chem. Int. Ed.* 2016, **55**, 8966; (*l*) K. Rohmann, J. Kothe, M.W. Haenel, U. Englert, M. Hçlscher, W. Leitner, *Angew. Chem.* 2016, 128, 9112; (*m*) Z. Li, T.M. Rayder, L. Luo, J.A. Byers, C. Tsung, *J. Am. Chem. Soc.* 2018, **140**, 8082; (*n*) C.A. Huff, M.S. Sanford, *ACS Catal.* 2013, **3**, 2412; (*o*) A. Weilhard, M. I. Qadir, V. Sans, J. Dupont, *ACS Catal.* 2018, **8**, 1628; (p) B. Gao, Z. Wen, Y. Wang, D. Chen, B. Yang, T. Ishihara, L. Guo, *ChemCatChem* 2024, **16**, e202400814.

9 (*a*) F. Hutschka, A. Dedieu, M. Eichberger, R. Fornika, W. Leitner, *J. Am. Chem. Soc.* 1997, **119**, 4432; (*b*) A. Anaby, M. Feller, Y. Ben-David, G. Leitus, Y. Diskin-Posner, L.J. Shimon, D. Milstein, *J. Am. Chem. Soc.* 2016, **138**, 9941; (*c*) Q. Qian, J. Zhang, M. Cui, B. X. Han, *Nat. Commun.* 2016, **7**, 11481.

10 (*a*) R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* 2009, **131**, 14168; (*b*) T.J. Schmeier, G.E. Dobereiner, R.H. Crabtree, N. Hazari, *J. Am. Chem. Soc.* 2011, **133**, 9274; (*c*) C. Liu, J. Xie, G. Tian, W. Li, Q.L. Zhou, *Chem. Sci.* 2015, **6**, 2928; (*d*) B. An, L. Zeng, M. Jia, Z. Li, Z. Lin, Y. Song, Y. Zhou, J. Cheng, C. Wang, W.B. Lin, *J. Am. Chem. Soc.* 2017, **139**, 17747; (*e*) R. Kanega, N. Onishi, D.J. Szalda, M.Z. Ertem, J.T. Muckerman, E. Fujita, Y. Himeda, *ACS Catal.* 2017, **7**, 6426; (*f*) A. Kumar, S. Semwal, J. Choudhury, *ACS Catal.* 2019, **9**, **3**, 2164.

11 K. Mori, T. Sano, H. Kobayashi, H. Yamashita, *J. Am. Chem. Soc.* 2018, **140**, 8902.

12 (*a*) X. Zhang, G. Liu, K. Meiwes-Broer, G. Gantefor, K. Bowen, *Angew. Chem. Int. Ed.* 2016, **55**, 9644; (*b*) X. Zhang, G. Liu, K.-H. Meiwes-Broer, G Ganteför, K. Bowen, *Angew. Chem. Int. Ed.* 2016, **128**, 9796.

13 Y. Jiang, O. Blacque, T. Fox, H. Berke, *J. Am. Chem. Soc.* 2013, **135**, 7751.

14 (*a*) Q. Liu, X. Yang, L. Li, S. Miao, Y. Li, Y. Q. Li, X. Wang, Y. Huang, T. Zhang, *Nat. Commun.* 2017, **8**, 1407; (*b*) R. Bhardwaj, J. Choudhury, *Chemistry an asian journal*, 2025, **20**, e202401327; (*c*) J. Choudhury, R. Bhardwaj, S.K. Mandal, *Acc. Chem. Res.* 2024, **57**, 2859.

15 (*a*) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem., Int. Ed.,* 2010, **49**, 9777. (*b*) R. Langer, Y. Diskin-Posner, G. Leitus, L.J. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* 2011, **50**, 9948; (*c*) R. Langer, Y. Diskin-Posner, G. Leitus, L.J.W. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* 2011, **123**, 10122; (*d*) C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* 2012, **134**, 20701; (*e*) Y. Zhang, A.D. MacIntosh, J.L. Wong, E.A. Bielinski, P.G. Williard, B.Q. Mercado, N. Hazari, W.H. Bernskoetter, *Chem. Sci.* 2015, **6**, 4291; (*f*) D. Tocqueville, F. Crisanti, J. Guerrero, E. Nubret, M. Robert, D. Milstein, N. von Wolff, *Chem. Sci.,* 2022,**13**, 13220; (*g*) M. Liu, Y. Ye, J. Ye, T. Gao, D. Wang, G. Chen, Z. Song, *Magnetochemistry* 2023, **9**, 110;(*h*) M. Liu, T. Yu, R. Huang, W. Qi, Z. Heb, R. Su, *Catal. Sci. Technol.,* 2020,**10**, 3515.

16 (*a*) C. Federsel, C. Ziebart, R. Jackstell, W. Baumann and M. Beller, *Chem.-Eur. J.,* 2012, **18**, 72; (*b*) M.S. Jeletic, M.T. Mock, A.M. Appel, J.C. Linehan, *J. Am. Chem. Soc.* 2013, **135**, 11533; (*c*) J. Schneidewind, R. Adam, W. Baumann, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* 2017, **56**, 1890; (*d*) J. Schneidewind, R. Adam, W. Baumann, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* 2017, **129**, 1916;(*e*) W. Yao, G. Olajide, C.M. Boudreaux, M.M. Wysocki, M.K. Ahmed, F. Qu, T. Szilvási, E.T. Papish, *Organometallics* 2024, **43**, 1447.

17 (*a*) C.-C. Tai, T. Chang, B. Roller and P. G. Jessop, *Inorg. Chem.,* 2003, **42**, 7340; (*b*) R.C. Cammarota, M.V. Vollmer, J. Xie, J. Ye, J.C. Linehan, B.A. Burgess, A.M. Appel, L. Gagliardi, C.C. Lu, *J. Am. Chem. Soc.* 2017, **139**, 14244; (*c*) S.A. Burgess, A.J. Kendall, D.R. Tyler, J.C. Linehan, A.M. Appel, *ACS Catal.*

2017, **7**, 3089; (*d*) B.G. Schieweck, N.F. Westhues, J. Klankermayer, *Chem. Sci.,* 2019, **10**, 6519.
18 (*a*) C.M. Zall, J.C. Linehan, A.M. Appel, *ACS Catal.* 2015, **5**, 5301; (*b*) C. M. Zall, J.C. Linehan, A.M. Appel, *J. Am. Chem. Soc.* 2016, **138**, 9968; (*c*) E.A. Romero, T. Zhao, R. Nakano, X. Hu, Y. Wu, R. Jazzar, G. Bertrand, *Nat. Cat.* 2018, **1**, 743.
19 (*a*) F. Bertini, M. Glatz, N. Gorgas, B. Stoeger, M. Peruzzini, L. F. Veiros, K. Kirchner, L. Gonsalvi, *Chem. Sci.* 2017, **8**, 5024; (*b*) S. Kar, A. Goeppert, J. Kothandaraman, G. K. S. Prakash, *ACS Catal.* 2017, **7**, 6347; (*c*) A. Dubey, L. Nencini, R.R. Fayzullin, C. Nervi, J.R. Khusnutdinova, *ACS Catal.* 2017, **7**, 3864;(*d*) S. Kostera, S. Weber, M. Peruzzini, L.F. Veiros, K. Kirchner, L. Gonsalvi, *Organometallics* 2021, **40**, 1213.
20 (*a*) G.C. Chinchen, P.J. Denny, J.R. Jennings, M.S. Spencer, K.C. Waugh, *Appl. Catal.* 1988, **36**, 1; (*b*) D.R. Palo, R.A. Dagle, J.D. Holladay, *Chem. Rev.* 2007, **107**, 3992.
21 (*a*) Y.-F. Zhao, Y. Yang, C. Mims, C.H.F. Peden, J. Li, D. Mei, *J. Catal.* 2011, **281**, 199; (*b*) Y. Yang, C.A. Mims, D.H. Mei, C.H.F. Peden, C.T. Campbell, *J. Catal.* 2013, **298**, 10.
22 (*a*) D.S. Laitar, P. Müller, J.P. Sadighi, *J. Am. Chem. Soc.* 2005, **127**, 17196; (*b*) C. Kleeberg, M.S. Cheung, Z. Lin, T. B. Marder, *J. Am. Chem. Soc.* 2011, **133**, 19060.
23 R. Shintani, K. Nozaki, *Organometallics* 2013, **32**, 2459.
24 (*a*) K. Motokura, D. Kashiwame, A. Miyaji, T. Baba, *Org. Lett.* 2012, **14**, 2642; (*b*) L. Zhang, J. Cheng, Z. Hou, *Chem. Commun.* 2013, **49**, 4782; (*c*) K. Motokura, D. Kashiwame, N. Takahashi, A. Miyaji, T. Baba, *Chem.-Eur. J.* 2013, **19**, 10030.
25 (*a*) B. Beguin, B. Denise, R.P.A. Sneeden, *J. Organomet. Chem.* 1981, **208**, C18-C20; (*b*) G.V. Goeden, J.C. Huffman, K.G. Caulton, *Inorg. Chem.* 1986, **25**, 2484-2485; (*c*) C.M. Wyss, B.K. Tate, J. Bacsa, T.G. Gray, J.P. Sadighi, *Angew. Chem., Int. Ed.* 2013, **52**, 12920-12923; (*d*) N.P. Mankad, T.G. Gray, D.S. Laitar, J.P. Sadighi, *Organometallics* 2004, **23**, 1191-1193; (*e*) K. Nakamae, B. Kure, T. Nakajima, Y. Ura, T. Tanase, *Chem.-Asian J.* 2014, **9**, 3106-3110; (*f*) T.-A.D. Nguyen, B.R. Goldsmith, H.T. Zaman, G. Wu, B. Peters, T.W. Hayton, *Chem.-Eur. J.* 2015, **21**, 5341-5344.
26 J Vondran, M.R.L. Furst, G.R. Eastham, T. Seidensticker, D.J. Cole-Hamilton, *Chem. Rev.* 2021, **121**, 6610.
27 (*a*) M. Trivedi, A. Kumar, A. Husain, N.P. Rath, *Inorg. Chem.* 2021, **60**, 4385; (*b*) K. Chaudhary, M. Trivedi, D.T. Masram, A. Kumar, G. Kumar, A. Husain, N.P. Rath, *Dalton Trans.*, 2020, **49**, 2994.
28 Rigaku Oxford Diffraction, CrysAlisProSoftw. Syst. version 1.171.43.106a, 2024, Rigaku Corporation, Oxford, UK.
29 G.M. Sheldrick, SHELXT–Integrated space-group and crystal-structure determination. *Acta Cryst.* 2015, **A71**, 3.
30 G.M. Sheldrick, Crystal structure refinement with SHELXL. *ActaCryst.* 2015, **C71**, 3.
31 (*a*) T. Fanjul, G. Eastham, J. Floure, S.J.K. Forrest, M.F. Haddow, A. Hamilton, P.G. Pringle, A.G. Orpen, M. Waugh, *Dalton Trans.*, 2013, **42**, 100; (*b*) A.A.N. Magro, L.-M. Robb, P.J. Pogorzelec, A.M.Z. Slawin, G.R. Eastham, Cole- D.J. Hamilton, *Chem. Sci.,* 2010, **1**, 723.
32 G.R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, 1999.
33 (*a*) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P.J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 9777; (*b*) R. Langer, Y. Diskin-Posner, G. Leitus, L.J. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* 2011, **50**, 9948; (*c*) R. Langer, Y. Diskin-Posner, G. Leitus, L.J.W. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* 2011, **123**, 10122; (*d*) C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* 2012, **134**, 20701; (*e*) Y. Zhang, A.D. MacIntosh, J.L. Wong, E.A. Bielinski, P.G. Williard, B.Q. Mercado, N. Hazari, W.H. Bernskoetter, *Chem. Sci.* 2015, 6, 4291.
34 (*a*) C. Federsel, C. Ziebart, R. Jackstell, W. Baumann, M. Beller, *Chem.-Eur. J.*, 2012, **18**, 72; (*b*) M.S. Jeletic, M.T. Mock, A.M. Appel, J.C. Linehan, *J. Am. Chem. Soc.* 2013, **135**, 11533; (*c*) J. Schneidewind, R. Adam, W. Baumann, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* 2017, **56**, 1890; (*d*) J. Schneidewind, R. Adam, W. Baumann, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* 2017, **129**, 1916; (*e*) J. Choia, Y. Lee, *Inorg. Chem. Front.* 2020, **7**, 1845.
35 R. Watari, Y. Kayaki, S. I. Hirano, N. Matsumoto, T. Ikariya, *Adv. Synth. Catal.* 2015, **357**, 1369.

Data Availability Statement

The authors declare that the data supporting this article have been included as part of the Supplementary Information.