A highly active copper catalyst for the hydrogenation of Carbon Dioxide to formate under ambient conditions

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Carbon dioxide (CO_2) can be an important reactant which can be used for the syntheses of varied types of industrially important chemicals. Hence, investigation concerning with the conversion of CO_2 into valuable energy-relevant chemicals is an important and current topic in molecular catalysis. 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 underdeveloped. Copper(I) complexes containing 1,1′-bis(di-*tert*-butylphosphino) ferrocene ligand were found to promote the catalytic hydrogenation of CO_2 to formate in the presence of DBU as the base where catalytic conversion of CO_2 *via* hydrogenation using *in situ* gaseous H_2 (granulated tin metal and concentrated HCl) 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, we report an efficient copper(I) complex based catalyst [CuI(dtbpf)] to achieve ambient-pressure CO_2 hydrogenation catalysis for generating formate salt (HCO_2^-) with turnover number (TON) values of 326 to 1.065 x 10^5 in 12 to 48 h of reaction at 25°C to 80°C. Outstanding catalytic performance makes [CuI(dtbpf)] a potential candidate for realizing the large-scale production of formate by CO_2 hydrogenation.

Introduction

Currently worldwide attention is focused on the utilization of carbon dioxide as versatile chemical feedstock for the syntheses of many important chemicals, *viz.* formic acid, methanol, urea, carbonates, and so on.[1] Of these, the hydrogenation of CO_2 to formic acid or formate holds a key position. Currently, most of the formic acid in industry is produced by the hydrolysis of methyl formate or formamide.[1c] Alternatively, the hydrogenation of CO_2 can also yield formic acid and hence can be considered a valuable chemical method for H_2 storage.[2] The essential condition for the hydrogenation of CO_2 requires the activation of both H_2 and CO_2 at the same time. This makes this reaction challenging because both H_2 and CO_2 are extremely kinetically stable in nature.[3] Hence, researchers have developed noble metal based compounds comprising of Ru[4], Rh[5], Ir[2b,6], Pd[7], Pt[8], Re[9], and Au[10] which act as efficient catalysts for the hydrogenation of CO_2.[4-10] 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.[4-10] 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[11], Co[12], Ni[13], Cu[14], and Mn[15] 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,[16] for which mechanistic studies have revealed that this reaction occurs primarily through hydrogenation of the CO_2, rather than CO, in $CO_2/CO/H_2/H_2O$ mixtures.[17] Moreover, homogeneous copper phosphine and carbene complexes are highly efficient catalysts for the reduction of CO_2 to CO,[18] hydroboration of CO_2 to form boryl formates,[19] and hydrosilylation of CO_2 to form silyl formates.[20] 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 favorable 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

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formates.[21] However, this CO_2 reactivity has remained stoichiometric because the copper formate products generally do not turn over when using hydrogen, rather than silanes or boranes, as the source of hydride. Very recently, Ikariya and co-workers showed that simple copper(I) and -(II) salts can catalyze the hydrogenation of CO_2 to formate in the presence of a suitable base.[22] The active catalyst species was not identified; in fact, the addition of carbene or phosphine ligands was found to impede catalysis. However, the bicyclic amidine base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was reported to have a distinct and unusual ability to promote turnover, even compared with very similar bases. No explanation for the effect of DBU was given, although a base-coordinated $[(DBU)_2CuI]$ complex was synthesized, characterized, and shown to be an active catalyst precursor. In 2013 Appel *et al.*[14a] reported triphosphine-ligated copper(I) complex $[LCu(MeCN)]PF_6$ for CO_2 hydrogenation in the presence of DBU. $[(LCu)_2H]^+$ is also an active precursor for catalytic CO_2 hydrogenation, with equivalent activity to that of $LCu(MeCN)^+$, and therefore may be a relevant catalytic intermediate.[14b] Also, Bertrand *et al.*[14c] reported the ability of stable copper hydride complexes to work in tandem with classical Lewis pairs for the catalytic reduction of CO_2 to formate using H_2. 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 carbon monoxide, and formate has possible use as a hydrogen energy carrier.[23]

$$CO_2 + H_2 + \text{base} \xrightarrow{[\text{CuI(dtbpf)}]} [\text{base-H}]^+[HCO_2]^-$$

Scheme 1. Catalytic hydrogenation of CO_2 to formate.

Our current studies of copper-catalyzed CO_2 hydrogenation are focused on using well-defined copper complexes that not only create stable catalyst but also facilitate investigation of the catalytic mechanism. Herein, we show that the 1,1′-bis(di-*tert*-butylphosphino) ferrocene (dtbpf)-ligated copper(I) complex [CuI(dtbpf)], is an effective catalyst for the reduction of CO_2 to formate using hydrogen and a base, with higher activity and thermal stability previous reported systems.[14,22] To the best of our knowledge, this investigation describes the first CO_2 hydrogenation catalyst based on ferrocenyl diphosphine copper complex at room temperature.

Experimental section

Materials and Physical Measurements

All the synthetic manipulations were performed under ambient condition. The solvents were dried and distilled before use following the standard procedures. Copper(I) iodide, Copper(I) chloride, Copper(I) bromide and 1,1′-bis(di-tert-butylphosphino) Ferrocene, Granulated tin metal 99.9%, concentrated HCl, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 4-(dimethylamino)pyridine (DMAP), Triethylamine 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.

Syntheses of the complexes [CuBr(dtbpf)] and [CuI(dtbpf)]

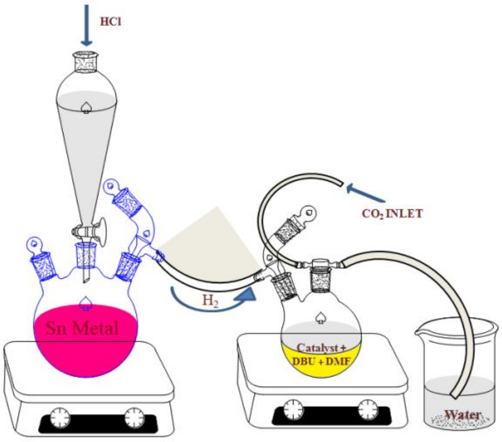
These complexes were prepared by our earlier reported method.[24]

[CuBr(dtbpf)] : Yield: (0.432 g, 70%). Anal. Calc. for $C_{26}H_{44}BrP_2CuFe$: C, 50.56; H, 7.13. Found: C, 50.88; H, 7.15. IR(cm^{-1}, KBr): ν = 3420, 3100, 3080, 2940, 2920, 2890, 2860, 2360, 2340, 2120, 1720, 1470, 1453, 1380, 1360, 1302, 1180, 1150, 1060, 1040, 938, 898, 850, 829, 810, 740, 630, 601, 580, 548, 490, 471, 440. ^1H NMR (δ ppm, 400 MHz, $CDCl_3$, 298K): δ 5.27 (s, 4H, C_5H_4), 4.44 (s, 4H, C_5H_4), 1.31 (m, 36H, CH_3). $^{31}P\{^1H\}$: δ 36.04 (s) (sharp).

[CuI(dtbpf)] : Yield: (0.531 g, 80%). Anal. Calc. for $C_{26}H_{44}IP_2CuFe$: C, 46.98; H, 6.62. Found: C, 47.02; H, 6.85. IR (cm^{-1}, KBr): ν = 3410, 3098, 2940, 2880, 1640, 1455, 1390, 1360, 1180, 1160, 1040, 940, 815, 591, 540, 491, 460, 438. ^1H NMR (δ ppm, 400 MHz, $CDCl_3$, 298K): δ 4.41 (s, 4H, C_5H_4), 4.40 (s, 4H, C_5H_4), 1.46 (m, 36H, CH_3). $^{31}P\{^1H\}$: δ 19.85 (s) (sharp).

General Procedure For Hydrogenation

A 100 mL two neck round-bottom (RB) flask was charged with dimethylformamide (5.0 mL) and base (10 mmol), and catalyst (0.02 mmol). This two neck round-bottom was connected to three neck round-bottom (RB) containing granulated tin metal through tube. Concentrated HCl was added to three neck round-bottom (RB) containing granulated tin metal in part wise to generate H_2 gas in-situ and this generate H_2 gas was passed to 100 mL two neck round-bottom (RB) flask through tube. This mixture was bubbled with CO_2(g) for 12 h keeping the two neck round-bottom RB in a magnetic stirring bar at room temperature and stirred vigorously. After the reaction, the solvent was removed completely by evaporation. The resulting oily residue was dissolved in $CDCl_3$ and ^1H NMR and ^{13}C spectra was recorded. The resulting product formate obtained after 12 h of reaction which was calculated from the integration values of the formate peak ($HCOO^-$) relative to an internal standard peak of dimethylformamide (DMF). A picture of the typical reaction setup is provided below.



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Results and discussion

[CuI(dtbpf)] was synthesized in good yield following our earlier reported method (Fig. 1).[24] We have screened the influence of various solvents, catalyst loadings, bases and reaction times on the reaction that identify key aspects of the catalytic system, including a base-promoted mechanism for H_2 activation that is distinct from known iron[11] and cobalt-based catalysts.[12] These results demonstrate that copper complexes can be active catalysts for CO_2 hydrogenation and identify reaction conditions that can potentially be used to promote catalysis with other copper complexes. Preliminary the catalytic hydrogenation of CO_2 was examined by using Cu catalysts and DBU as the base at 25°C with 1 atm CO_2/H_2.

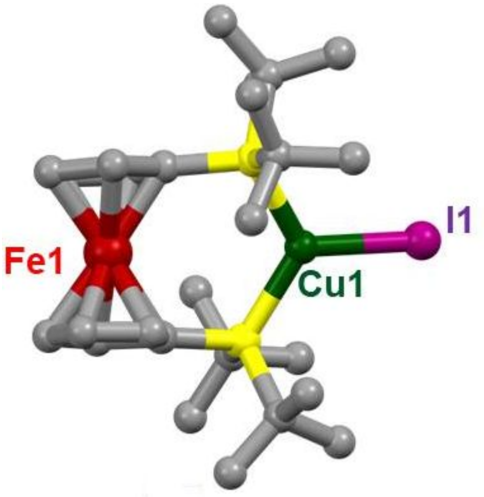

Fig. 1. Molecular Structure of [CuI(dtbpf)].

Table 1. Catalytic hydrogenation of CO_2 to formate.[a]

Entry	Catalyst	Base	Time	Yield [%][b]	TON[c]
1.	none	DBU	12h	0	-
2.	dtbpf	DBU	12h	0	-
3.	CuCl	DBU	12h	11	119
4.	CuBr	DBU	12h	14	152
5.	CuI	DBU	12h	12	130
6.	[CuI(dtbpf)]	DBU	12h	30	326
7.	[CuBr(dtbpf)]	DBU	12h	20	217

[a]Reaction conditions: catalyst (0.02 mmol), DBU (10 mmol), Dimethylformamide (5.0 mL), CO_2 (1 atm), H_2 (1 atm), 25°C, 12 h. [b]Molar ratio of the product/initial DBU determined by ^{1}H NMR spectroscopy. [c]Mole of formate/mole of catalyst.

The reaction was conducted with a base/Cu catalyst ratio of 500 in DMF under 1 atm of both CO_2 and H_2 for 12 h (See Fig. S1, ESI†). Table 1 summarizes the catalytic activity represented by the formate yield based on the initial molar amount of DBU, as well as the TON. It can be seen that without a copper source, no reaction operate (Table 1, entry 1). Also, no reaction occurred in the presence of isolated dtbpf ligand (entry 2). Table 1 shows the generation of formate from CO_2 (1 atm) and H_2 (1 atm) at room temperature in the presence of CuX (X= Cl, Br, I) as well as complexes [CuBr(dtbpf)] and [CuI(dtbpf)] (Table 1, entries 3-7). Various solvents such as DMF, THF, CH_3CN, DME, CH_3OH, Toluene, 2-propoanol and 1,4-dioxane can be used in the reaction. However, DMF is the preferred solvent (See Table S1, ESI†). We have also studied the influence of various bases such as DBU, TBD, DAMP, DBN, and NEt_3 on the [CuI(dtbpf)] catalysed CO_2 hydrogenation reaction.

Table 2. [CuI(dtbpf)]-catalyzed hydrogenation of CO_2 with organic bases.[a]

Entry	Base	Yield [%][b]	TON[c]
1.	NEt_3	<1	<1
2.	DBU	30	326
3.	TBD	5	54
4	DMAP	<1	<1
5.	DBN	<1	<1

[a]Reaction conditions: catalyst (0.02 mmol), DBU (10 mmol), Dimethylformamide (5.0 mL), CO_2 (1 atm), H_2 (1 atm), 25°C, 12 h. [b]Molar ratio of the product/initial DBU determined by ^{1}H NMR spectroscopy. [c]Mole of formate/mole of catalyst.

As shown in Table 2, the bases such as NEt_3, TBD, DAMP, and DBN (entries 1, 3, 4, and 5) reduced the catalytic efficiency in comparison to DBU (entry 2). This indicates that DBU is the most effective base for CO_2 hydrogenation reaction. Based on these experimental results, DBU was further employed as base for hydrogenation of CO_2 in the following experiments (Table 3). Further improvement in the catalytic efficiency was successfully achieved using the [CuI(dtbpf)]/DBU system. As shown in Table 3, TONs reached 1043 after prolonging the reaction time to 48 h (entry 5) (See Fig. S2, ESI†). While the optimal temperature was found to be 80°C at a pressure ratio of CO_2/H_2 = 1/1 atm, a temperature over 100 °C resulted in lower catalytic activity, possibly due to deposition of catalytically inactive copper metals during the hydrogenation (entry 6).

Table 3. Hydrogenation of CO_2 with the [CuI(dtbpf)]/DBU system.[a]

Entry	P(CO_2/H_2) [atm]	Catalyst (mmol)	T [°C]	t [h]	Yield [%][b]	TON[c]
1.	1/1	0.02	25	12	30	326
2.	1/1	0.02	40	12	50	543
3.	1/1	0.02	60	12	65	706
4.	1/1	0.02	80	12	90	978
5.	1/1	0.02	80	48	96	1043
6.	1/1	0.02	100	48	70	760
7.	1/1	0.002	25	12	40	4347
8.	1/1	0.0002	25	12	50	5434
9.	1/1	0.002	80	48	97	1.054 x10^4
10.	1/1	0.0002	80	48	98	1.065 x 10^5
11.	1/1	0.02[d]	80	12	24	552

[a]Reaction conditions: catalyst, DBU (10 mmol), Dimethylformamide (5.0 mL). [b]Molar ratio of the product/initial DBU determined by ^{1}H NMR spectroscopy. [c]Mole of formate/mole of catalyst. [d]CuI

Further lowering the catalyst loading by order of magnitude (entry 7-10) afforded TON up to 1.065 x 10^5. The product can be isolated with a 98% yield as hygroscopic white granules grown from the reaction mixture at 80°C. The above system has been tested using a 1:1 mixture of CO_2:H_2 at 1 atm total pressure (Table 4). The obtained results are nearly the same as compared to our system. In the proposed hydrogenation mechanism described in Fig. 3 had been supported by NMR spectroscopy (See Fig. S1–S5, ESI†). Firstly $[(dtbpf)Cu(DBU)]^+$ complex is formed upon dissolving [CuI(dtbpf)] in a solution with DBU. Association and deprotonation of H_2 presumably forms copper hydride, [(dtbpf)CuH], that is apparently a transient, steady-state intermediate which is observed over the course of the reaction (See Fig. S3, ESI†). We have successfully isolated [(dtbpf)CuH] independently by passing *in-situ* generate H_2 gas over the solution of [CuI(dtbpf)] in CH_3OH:CH_3CN for 12 hour (See ESI†). Reaction of [(dtbpf)CuH] with CO_2 forms the κ^1-coordinated formate complex, [(dtbpf)CuO_2CH] as previously reported.[14,20] The formate ligand then rapidly displaced by excess DBU, facilitating turnover and generating the free formate product. As the reaction proceeds and the available $HDBU^+$ is depleted, the major species observed in solution shifts from $[(dtbpf)Cu(DBU)]^+$ to [(dtbpf)CuO_2CH]. The formate complex is soluble in DMF in the absence of a coordinating base and precipitates from solution once the reaction approaches completion. The observation of $[(dtbpf)CuDBU]^+$ at the initial stage suggested that the rate limiting step in the reaction is hydride formation. The superior catalytic performance using DBU implies that the catalytic cycle should be driven by the facile formation of thermodynamically stable $[DBU\text{-}H]^+[HCO_2]^-$ and that DBU can promote the heterolytic splitting of H_2 bound to the Cu center to afford copper hydride complex.

Table 4. **Catalytic conversion of CO_2 with H_2 to formate with [CuI(dtbpf)]/DBU system.**[a]

Entry	Catalyst loading	P (atm)	T [°C]	t [h]	TON[b]
1.	0.02	1	25	12	347
2.	0.02	1	80	12	989
3.	0.02	1	80	48	1054
4.	0.002	1	25	12	4673
5.	0.002	1	80	12	8695
6.	0.002	1	80	48	1.065×10^4
7.	0.0002	1	25	12	5.652×10^4
8.	0.0002	1	80	12	6.521×10^4
9.	0.0002	1	80	48	1.065×10^5

[a]Reaction conditions: 1:1 CO_2:H_2, catalyst, DBU (10 mmol), Dimethylformamide (5.0 mL).

[b]Mole of formate/mole of catalyst.

Also, in ^{13}C NMR, the signal corresponding to the amidine carbon in coordinated DBU (162.5 to 163.0 ppm) was clearly shifted to a lower magnetic field compared with that in free DBU (159.7 ppm) in $CDCl_3$. This indicates that the amidine unit maintains rigid coordination in solution. It should be noted that the *in situ* generated active catalyst [(dtbpf)CuH] showed better catalytic properties compared to previously reported copper(I) and -(II) based catalytic systems.[14,20,22] In the catalyst presented herewith, DBU acts as supporting ligand to the larger P-Cu-P bite angle Cu(I) catalyst during the reaction, which imposes positive effect on the hydrogenation of CO_2.[23] To gain further insight into possible mechanistic pathways of the catalyst systems, detailed ^{31}P NMR experiments were conducted. The ^{31}P NMR spectrum of reaction mixture for a representative CO_2 hydrogenation using DBU results in distinctive four sharp resonances centred at 28.21, 49.47, 62.62 and 77.64 ppm (See Fig. S6-S7, ESI†). At 28.2 ppm resonance for coordinated dtbpf ligand remained in the solution after the catalytic experiment. This chemical shift was within the range and is comparable to that of the chelating dtbpf ligand.[25] Major signals can be observed around 49.47, 62.62 and 77.64 ppm. Additional HR-ESI-MS studies prior to catalysis revealed, in accordance to the $^{31}P\{^1H\}$-NMR spectra, a distinctive

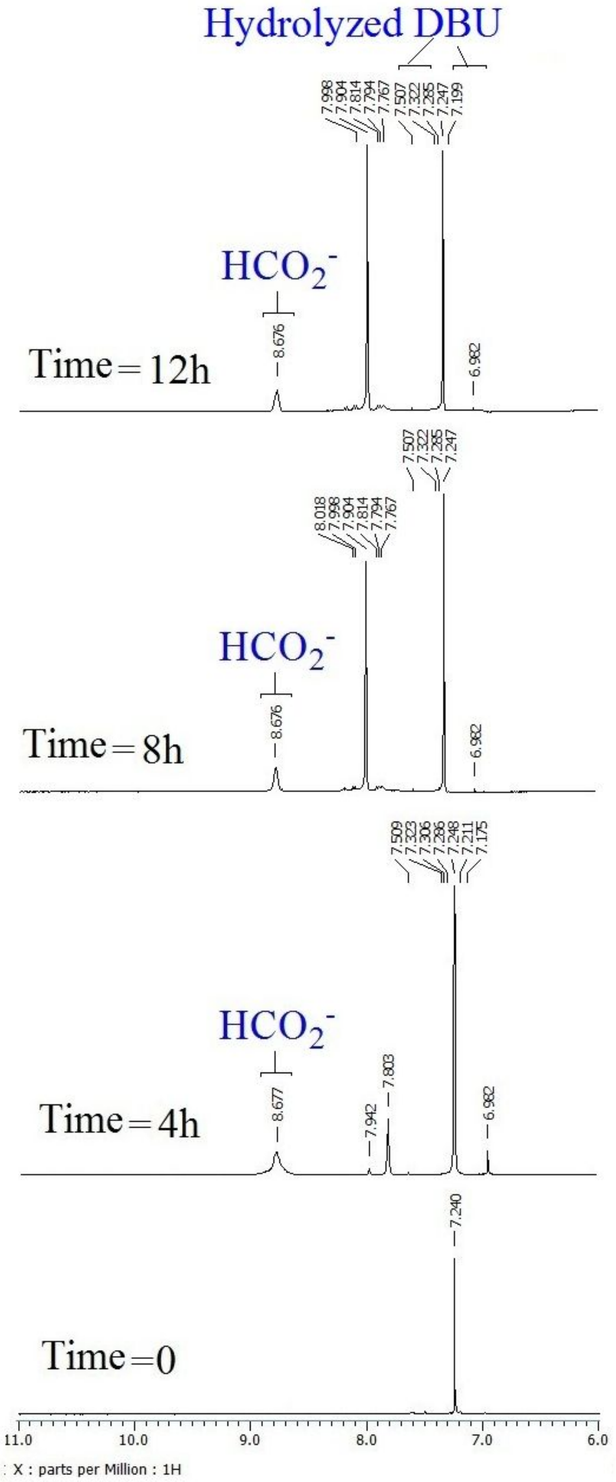

Fig. 2. Time-resolved ^1H NMR spectra for a representative CO_2 hydrogenation using DBU. Conditions: 1.0 atm H_2/CO_2, 25°C, [CuI(dtbpf)] (0.02 mmol), DBU (10 mmol), in 5 mL DMF (Table 3, entry 5). The region from 6.0 to 11 ppm showing formate and catalyst 1,1′-bis(di-*tert*-butylphosphino) ferrocene signals is shown, and diagnostic peaks are labeled. Spectra were acquired at room temperature

formation of a single molecular species with a mass peak of 537.46 m/z, resembling the [Cu(dtbpf)]-fragment (See Fig. S8, ESI†). After catalysis HR-ESI-MS measurement was performed, revealing the formation of several compounds with a distinctive peak at 689.49 m/z (See Fig. S9, ESI†).

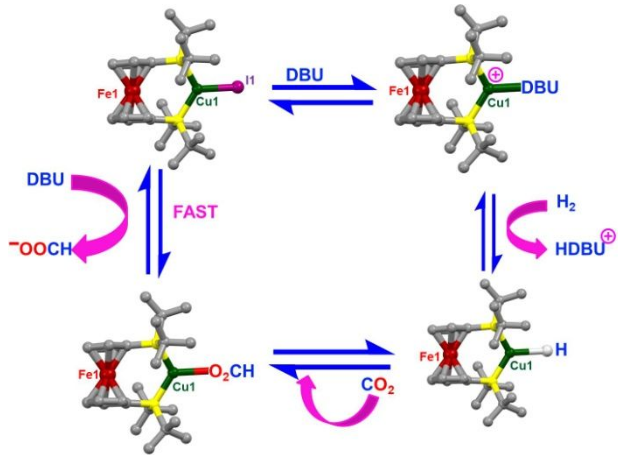

Fig. 3. Plausible mechanism for the hydrogenation of CO_2 catalyzed by the [CuI(dtbpf)]/[CuBr(dtbpf)]complex.

Conclusions

In summary, we have developed a new highly active catalyst, [(dtbpf)CuI], which catalyzes the hydrogenation of CO_2 to formate. Contrary to other first-row transition metal complexes bearing complicated ligands, the [(dtbpf)CuI]/DBU system promotes the formation of formate salt without the addition of extra ligands. Particularly, our understanding of the new DBU-coordinated complex strongly supports the fact that DBU plays a dual role 1) it stabilizes the Cu catalyst under the reaction conditions and 2) traps formic acid by acting as a base. This feature opens up new avenues for the utilization of Cu(I) complexes as catalysts for hydrogenation reaction. To develop more efficient Cu catalysts, mechanistic investigations of the hydrogenation system and new designs of Cu-based complexes are currently in progress in our laboratory.

Acknowledgements

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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**, 12936-12973; (*b*) J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, *Angew. Chem. Int. Ed.* 2016, **55**, 7296-7343; (*c*) J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, *Angew. Chem.* 2016, **128**, 7416-7467; (*d*) A. Ávarez, A. Bansode, A. Urakawa, A. V. Bavykina, T. A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, *Chem. Rev.* 2017, **117**, 9804-9838.

2 (*a*) T. C. Johnson, D. J. Morris, M. Wills, *Chem. Soc. Rev.* 2010, **39**, 81-88; (*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**, 383-388; (*c*) Q. Y. Bi, X. L. Du, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *J. Am. Chem. Soc.* 2012, **134**, 8926-8933; (*d*) Z. L. Wang, J. M. Yan, Y. Ping, H. L. Wang, W. T. Zheng, Q. Jiang, *Angew. Chem. Int. Ed.* 2013, **52**, 4406-4409; (*e*) Z.-L. Wang, J.-M. Yan, Y. Ping, H.-L. Wang, W.-T. Zheng, Q. Jiang, *Angew. Chem.* 2013, **125**, 4502–4505; (*f*) D. Mellmann, P. Sponholz, H. Junge, M. Beller, *Chem. Soc. Rev.* 2016, **45**, 3954-3988.

3 (*a*) J. Graciani, K. Mudiyanselage, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J. Hrbek, J. F. Sanz, J. A. Rodriguez, *Science* 2014, **345**, 546-550; (*b*) S. Kattel, P. J. Ramirez, J. G. Chen, J. A. Rodriguez, P. Liu, *Science* 2017, **355**, 1296-1299.

4 (*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**, 7278-7282; (*c*) T. Schaub, R.A. Paciello, *Angew. Chem.* Int. Ed. 2011, **123**, 7416-7420; (*d*) S. Bontemps, L. Vendier, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* 2012, **51**, 1671-1674; (*e*) S. Bontemps, L. Vendier, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* 2012, **124**, 1703-1706; (*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**, 1028-1031; (*h*) R. Kuriki, K. Sekizawa, O. Ishitani, K. Maeda, *Angew. Chem. Int. Ed.* 2015, **54**, 2406-2409; (*i*) R. Kuriki, K. Sekizawa, O. Ishitani, K. Maeda, *Angew. Chem. Int. Ed.* 2015, **127**, 2436-2439; (*j*) J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah, G. K. S. Prakash, *J. Am. Chem. Soc.* 2016, **138**, 778-781; (*k*) K. Rohmann, J. Kothe, M. W. Haenel, U. Englert, M. Holscher, W. Leitner, *Angew. Chem. Int. Ed.* 2016, **55**, 8966-8969; (*l*) K. Rohmann, J. Kothe, M.W. Haenel, U. Englert, M. Hçlscher, W. Leitner, *Angew. Chem.* 2016, 128, 9112-9115; (*m*) Z. Li, T.M. Rayder, L. Luo, J.A. Byers, C. Tsung, *J. Am. Chem. Soc.* 2018, **140**, 8082-8085; (*n*) C.A. Huff, M.S. Sanford, *ACS Catal.* 2013, **3**, 2412-2416; (*o*) A. Weilhard, M. I. Qadir, V. Sans, J. Dupont, *ACS Catal.* 2018, **8**, 1628-1634.

5 (*a*) F. Hutschka, A. Dedieu, M. Eichberger, R. Fornika, W. Leitner, *J. Am. Chem. Soc.* 1997, **119**, 4432-4443; (*b*) A. Anaby, M. Feller, Y. Ben-David, G. Leitus, Y. Diskin-Posner, L.J. Shimon, D. Milstein, *J. Am. Chem. Soc.* 2016, **138**, 9941-9950; (*c*) Q. Qian, J. Zhang, M. Cui, B. X. Han, *Nat. Commun.* 2016, **7**, 11481.

6 (*a*) R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* 2009, **131**, 14168-14169; (*b*) T.J. Schmeier, G.E. Dobereiner, R.H. Crabtree, N. Hazari, *J. Am. Chem. Soc.* 2011, **133**, 9274-9277; (*c*) C. Liu, J. Xie, G. Tian, W. Li, Q.L. Zhou, *Chem. Sci.* 2015, **6**, 2928-2931; (*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**, 17747-17750; (*e*) R. Kanega, N. Onishi, D.J. Szalda, M.Z. Ertem, J.T. Muckerman, E. Fujita, Y. Himeda, *ACS Catal.* 2017, **7**, 6426-6429; (*f*) A. Kumar, S. Semwal, J. Choudhury, *ACS Catal.* 2019, **9**, **3**, 2164-2168.

7 K. Mori, T. Sano, H. Kobayashi, H. Yamashita, *J. Am. Chem. Soc.* 2018, **140**, 8902-8909.

8 (*a*) X. Zhang, G. Liu, K. Meiwes-Broer, G. Gantefor, K. Bowen, *Angew. Chem. Int. Ed.* 2016, **55**, 9644-9647; (*b*) X. Zhang, G. Liu, K.-H. Meiwes-Broer, G Ganteför, K. Bowen, *Angew. Chem. Int. Ed.* 2016, **128**, 9796-9799.

9 Y. Jiang, O. Blacque, T. Fox, H. Berke, *J. Am. Chem. Soc.* 2013, **135**, 7751-7760.

10 Q. Liu, X. Yang, L. Li, S. Miao, Y. Li, Y. Q. Li, X. Wang, Y. Huang, T. Zhang, *Nat. Commun.* 2017, **8**, 1407.

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11 (*a*) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem., Int. Ed.,* 2010, **49**, 9777–9780. (*b*) R. Langer, Y. Diskin-Posner, G. Leitus, L.J. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* 2011, **50**, 9948-9952; (*c*) R. Langer, Y. Diskin-Posner, G. Leitus, L.J.W. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* 2011, **123**, 10122-10126; (*d*) C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* 2012, **134**, 20701-20704; (*e*) Y. Zhang, A.D. Maclntosh, J.L. Wong, E.A. Bielinski, P.G. Williard, B.Q. Mercado, N. Hazari, W.H. Bernskoetter, *Chem. Sci.* 2015, **6**, 4291-4299.

12 (*a*) C. Federsel, C. Ziebart, R. Jackstell, W. Baumann and M. Beller, *Chem.-Eur. J.,* 2012, **18**, 72-75; (*b*) M.S. Jeletic, M.T. Mock, A.M. Appel, J.C. Linehan, *J. Am. Chem. Soc.* 2013, **135**, 11533-11536; (*c*) J. Schneidewind, R. Adam, W. Baumann, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* 2017, **56**, 1890-1893; (*d*) J. Schneidewind, R. Adam, W. Baumann, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* 2017, **129**, 1916-1919.

13 (*a*) C.-C. Tai, T. Chang, B. Roller and P. G. Jessop, *Inorg. Chem.,* 2003, **42**, 7340–7341; (*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**, 14244-14250; (*c*) S.A. Burgess, A.J. Kendall, D.R. Tyler, J.C. Linehan, A.M. Appel, *ACS Catal.* 2017, **7**, 3089-3096; (*d*) B.G. Schieweck, N.F. Westhues, J. Klankermayer, *Chem. Sci.,* 2019, **10**, 6519-6523.

14 (*a*) C. M. Zall, J.C. Linehan, A.M. Appel, *ACS Catal.* 2015, **5**, 5301-5305; (*b*) C. M. Zall, J.C. Linehan, A.M. Appel, *J. Am. Chem. Soc.* 2016, **138**, 9968-9977; (*c*) E.A. Romero, T. Zhao, R. Nakano, X. Hu, Y. Wu, R. Jazzar, G. Bertrand, Nat. Cat. 2018, 1, 743-747.

15 (*a*) F. Bertini, M. Glatz, N. Gorgas, B. Stoeger, M. Peruzzini, L. F. Veiros, K. Kirchner, L. Gonsalvi, *Chem. Sci.* 2017, **8**, 5024-5029; (*b*) S. Kar, A. Goeppert, J. Kothandaraman, G. K. S. Prakash, *ACS Catal.* 2017, **7**, 6347-6351; (*c*) A. Dubey, L. Nencini, R.R. Fayzullin, C. Nervi, J.R. Khusnutdinova, *ACS Catal.* 2017, **7**, 3864-3868.

16 (*a*) G.C. Chinchen, P.J. Denny, J.R. Jennings, M.S. Spencer, K.C. Waugh, *Appl. Catal.* 1988, **36**, 1-65; (*b*) D.R. Palo, R.A. Dagle, J.D. Holladay, *Chem. Rev.* 2007, **107**, 3992-4021.

17 (*a*) Y.-F. Zhao, Y. Yang, C. Mims, C.H.F. Peden, J. Li, D. Mei, *J. Catal.* 2011, **281**, 199-211; (*b*) Y. Yang, C.A. Mims, D.H. Mei, C.H.F. Peden, C.T. Campbell, *J. Catal.* 2013, **298**, 10-17.

18 (*a*) D.S. Laitar, P. Müller, J.P. Sadighi, *J. Am. Chem. Soc.* 2005, **127**, 17196-17197; (*b*) C. Kleeberg, M.S. Cheung, Z. Lin, T. B. Marder, *J. Am. Chem. Soc.* 2011, **133**, 19060-19063.

19 R. Shintani, K. Nozaki, *Organometallics* 2013, **32**, 2459-2462.

20 (*a*) K. Motokura, D. Kashiwame, A. Miyaji, T. Baba, *Org. Lett.* 2012, **14**, 2642-2645; (*b*) L. Zhang, J. Cheng, Z. Hou, *Chem. Commun.* 2013, **49**, 4782-4784; (*c*) K. Motokura, D. Kashiwame, N. Takahashi, A. Miyaji, T. Baba, *Chem.-Eur. J.* 2013, **19**, 10030-10037.

21 (*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.

22 R. Watari, Y. Kayaki, S.-I. Hirano, N. Matsumoto, T. Ikariya, *Adv. Synth. Catal.* 2015, **357**, 1369-1373.

23 (*a*) S. Enthaler, J. von Langermann, T. Schmidt, *Energy Environ. Sci.* 2010, **3**, 1207-1217; (*b*) M. Grasemann, G. Laurenczy, *Energy Environ. Sci.* 2012, **5**, 8171-8181.

24 M. Trivedi, G. Singh, A. Kumar, N.P. Rath, *Dalton Trans.* 2015, **44**, 20874-20882.

25 T.J. Colacot, S. Parisel, in *Ferrocenes: Ligands, Materials and Biomolecules*, ed. P. Štěpnička, John Wiley & Sons, Ltd, West Sussex, 2008, pp. 117–140.

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Graphical Abstract: Synopsis and Pictogram

Catalytic conversion of CO_2 *via* hydrogenation using *in-situ* gaseous H_2 (granulated tin metal and concentrated HCl) to produce formate salt (HCO_2^-) at the turnover number (TON) value of 326 to 1.065 x 10^5 in 12 h to 48h of reaction at 25°C to 80°C has been reported.