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Copper-Catalyzed Formic Acid Synthesis from CO_2 with Hydrosilanes and H_2O

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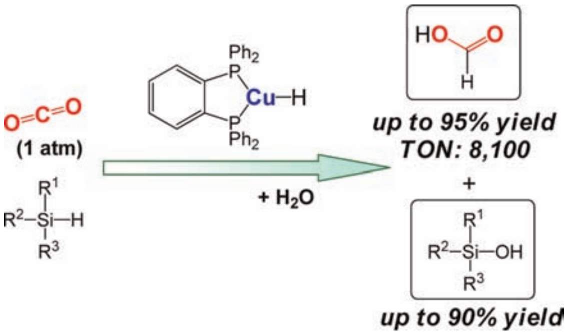
ABSTRACT

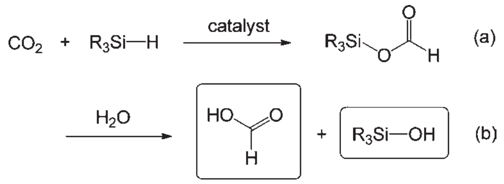


A copper-catalyzed formic acid synthesis from CO_2 with hydrosilanes has been accomplished. The $Cu(OAc)_2 \cdot H_2O$—1,2-bis(diphenylphosphino)benzene system is highly effective for the formic acid synthesis under 1 atm of CO_2. The TON value approached 8100 in 6 h. The reaction pathway was revealed by in situ NMR analysis and isotopic experiments.

The utilization of CO_2 as a renewable chemical feedstock has received much attention.[1] Reduction of CO_2 to formic acid is an attractive transformation reaction. Various highly active metal catalysts have been reported for the hydrogenation of CO_2 with H_2.[2] Because the reaction of CO_2 and H_2 to HCOOH is thermodynamically unfavorable, addition of a base, such as KOH, is necessary to promote the reaction. As a result, the hydrogenation product becomes a stable formate salt.

Reduction of CO_2 with hydrosilane is an alternative methodology to synthesize formic acid. Several hydrosilanes, such as polymethylhydrosiloxane (PMHS), are cheap, easy to handle, and readily available as byproducts of the silicone industry.[3] The reaction of CO_2 and hydrosilane proceeds exothermically, giving silyl formate as a product (Scheme 1a). Silyl formate could be easily decomposed to formic acid by addition of H_2O (Scheme 1b).[4] This reaction pathway is a simple approach to formic acid from CO_2. Several reaction systems using transition metals, such as Ir,[5] Ru,[6] Zr,[7] and an organocatalyst[8] have been reported for the hydrosilylation of CO_2. However, to the best of our knowledge, the one-pot synthesis of formic acid from CO_2 and hydrosilane has been scarcely reported.

Scheme 1. (a) Hydrosilylation of CO_2 and (b) Hydrolysis of Silyl Formate



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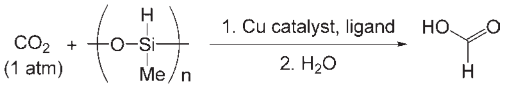
The hydrolysis of silyl formate affords silanol as a coproduct. Recently, significant efforts have been devoted to the oxidation of hydrosilanes to silanols[9] because of the highly utility of the oxidation products for silicon-based polymers[10] and organic donors.[11] The above formic acid synthesis procedure through consecutive hydrosilylation/hydration enables oxidation of hydrosilanes to the useful silanols.

Herein, we report a copper-catalyzed formic acid synthesis from CO_2, hydrosilanes, and H_2O through the consecutive hydrosilylation of CO_2 and hydrolysis of silyl formate. PMHS can be used as a hydrosilane. Furthermore, oxidation of aromatic, aliphatic, and alkoxy hydrosilanes to silanols using CO_2 as an oxidant is demonstrated.

A copper hydride complex having a 1,2-bis(diphenylphosphino)benzene (**1**) ligand has been reported as a new, active reduction catalyst for organic carbonyl compounds.[12,13] First, we examined the reaction of 1 atm of CO_2 in the presence of PMHS, $Cu(OAc)_2 \cdot H_2O$, and ligand **1**. An excess amount of CO_2 compared with the hydrosilane was used in a balloon apparatus. As shown in Table 1, entry 1, the hydrosilylation was complete within 4 h. Next, H_2O was added, and the reaction mixture was allowed to further react at room temperature for 1 h, affording 91% yield of formic acid. Hydrosilylation did not proceed at all in the absence of $Cu(OAc)_2 \cdot H_2O$ or ligand **1** (entries 2 and 3). The product was not obtained under Ar atmosphere instead of CO_2 (entry 5). In the $Cu(OAc)_2 \cdot H_2O$–**1** system, the formic acid yield increased to 95% at 60 °C (entry 6). Other phosphine ligands were not effective under the reaction conditions (entries 7 and 8).

Table 1. Formic Acid Synthesis from CO_2 with PMHS[a]

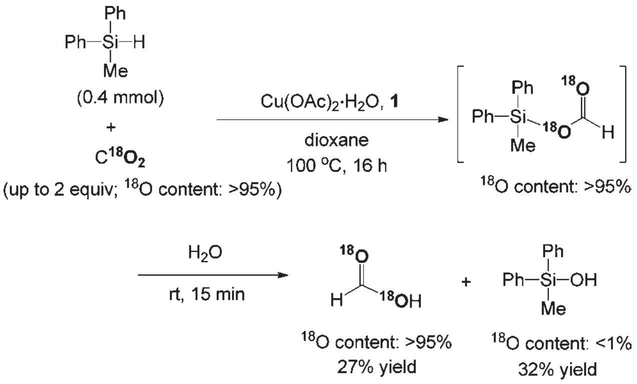


entry	catalyst	ligand	conv of Si–H[b] (%)	yield[b] (%)
1	$Cu(OAc)_2 \cdot H_2O$	**1**	>99	91
2	$Cu(OAc)_2 \cdot H_2O$	none	11	0
3	none	**1**	8	0
4	none	none	19	0
5[c]	$Cu(OAc)_2 \cdot H_2O$	**1**	17	0
6[d]	$Cu(OAc)_2 \cdot H_2O$	**1**	96	95
7[d]	$Cu(OAc)_2 \cdot H_2O$	dppp[e]	30	18
8[d]	$Cu(OAc)_2 \cdot H_2O$	PPh_3[f]	<1	trace

[a] Reaction conditions: CO_2 (1 atm, balloom), PMHS (Si–H: 1.0 mmol), Cu catalyst (5.0×10^{-3} mmol), ligand (7.5×10^{-3} mmol), 1,4-dioxane (2.0 mL), 100 °C, 4 h. After the hydrosilylation, H_2O (0.2 mL) was added, and the mixture was stirred at rt for 1 h. [b] Determined by ^1H NMR using an internal standard. Based on Si–H. Conv of Si–H was measured before the addition of H_2O. [c] Under 1 atm of Ar. [d] 60 °C, 30 min. [e] 1,3-Bis(diphenylphosphino)propane. [f] 1.5×10^{-2} mmol of PPh_3.

To confirm the reaction pathway shown in Scheme 1, ^1H NMR analysis was conducted (Figure S5, Supporting Information). After the reaction of PMHS with CO_2 in the presence of the Cu catalyst, a signal assignable to Si-*H* of PMHS at 4.7 ppm disappeared and a broad signal assignable to Si-OC(O)*H* appeared at 8.1 ppm. The methyl group connected to the Si atom was shifted to 0.4 ppm from 0.2 ppm. Then, addition of H_2O to the reaction mixture allowed formation of formic acid (*H*COOH, 8.0 ppm) and the silyl formate signals (8.1 and 0.4 ppm) disappeared. GC–MS analysis also revealed the formation of formic acid.

Scheme 2. Copper-Catalyzed Reaction of Diphenylmethylsilane with $C^{18}O_2$



Transformation of CO_2 to formic acid through silyl formate was confirmed by the reaction using $C^{18}O_2$ and $^{13}CO_2$. Scheme 2 shows the results of the reaction using $C^{18}O_2$. The reaction of diphenylmethylsilane with $C^{18}O_2$ afforded diphenylmethylsilyl formate with >95% of ^{18}O content: m/z [M^+]: 246, [$M^+ - CH_3$]: 231 (100), 229 (4.4), 227 (<1.0) (Figure S1, Supporting Information). The successive hydrolysis of the silyl formate proceeded by addition of H_2O, giving formic acid with >95% of ^{18}O

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content: m/z [M^+]: 50, [$M^+ - {}^{18}OH$]: 31, and diphenylmethylsilanol with $<1\%$ of ^{18}O (Figure S2 and S3, Supporting Information). This result indicates that all the oxygen atoms in the formic acid product originated from CO_2. The use of $^{13}CO_2$ instead of $C^{18}O_2$ afforded formic acid with $>95\%$ of ^{13}C content: m/z [M^+]: 47, [$M^+ - OH$]: 30 (Figure S4, Supporting Information). Thus, the carbon atom of CO_2 is also incorporated into the formic acid.

The present system was applicable to 50 mmol scale synthesis of formic acid from CO_2. The reaction of 50 mmol of Si–H in PMHS occurred in the presence of 5 μmol of Cu catalyst under 1 atm of CO_2 to afford an 81% yield of formic acid (eq S1, Supporting Information). The TON (turnover number) value was calculated to be 8100 (reaction time: 6 h). This value is much higher than those of reported catalysts for hydrosilylation of CO_2, such as $RuCl_3 \cdot nH_2O$[6a] and $Ru_2Cl_5(MeCN)_7$,[6a] as shown in Table 2.

It has been reported that the reaction between $Cu(OAc)_2 \cdot H_2O$ and PMHS in the presence of **1** affords the Cu(I)–hydride complex having ligand **1**.[12] In order to clarify the formation of the Cu(I)–H species and the catalytic CO_2 hydrosilylation pathway, in situ NMR analysis was conducted in the presence of $Cu(OAc)_2 \cdot H_2O$, **1** (1.5 equiv), and PMHS (22 equiv of Si–H to Cu) in benzene-d_6 solution.[14] After the reaction at room temperature, new signals appeared in the ^1H NMR spectrum at 1.42 and 3.57 ppm (Figure S6, Supporting Information). These signals are assignable to the reported **1**–Cu(I)–H complex and a presumed analogue of Stryker's reagent,[12] respectively, indicating the formation of Cu(I)–H complexes having ligand **1**. The NMR sample was then treated with $^{13}CO_2$ at room temperature. The intensity of these Cu(I)–H signals decreased, indicating a reaction between Cu–H and CO_2. Figure 1 shows the $^{13}C\{^1H\}$ NMR spectra of the solution before and after the addition of $^{13}CO_2$. After the addition of $^{13}CO_2$, new signals appeared immediately at 124, 159, and 168 ppm, which were assigned to CO_2, Si–OC(O)-H product, and a copper formate complex,[15] respectively (Figure 1b). After 10 min, the signals of CO_2 and the copper formate disappeared, whereas the signal of the Si–OC(O)H increased (Figure 1c). This result indicates the formation of silyl formate from CO_2 through the copper formate complex. Additionally, a new signal appeared at 169 ppm which is assignable to another copper formate complex.

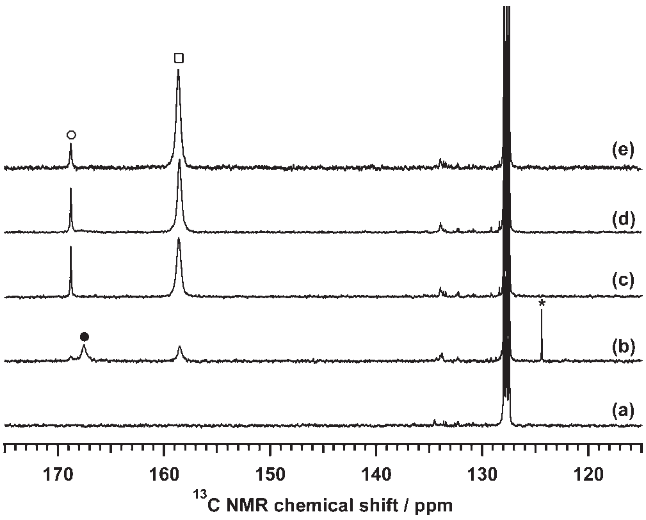

Figure 1. $^{13}C\{^1H\}$ NMR spectra of the reaction between $^{13}CO_2$ and PMHS in the presence of the copper catalyst. Reaction conditions: $Cu(OAc)_2 \cdot H_2O$ (Cu: 5.0×10^{-2} mmol), **1** (7.5×10^{-2} mmol), PMHS (Si–H: 1.1 mmol), and benzene-d_6 (1.5 mL), Ar, rt, 1 h. Then, 0.4 mL of the reaction mixture was transferred to the NMR tube under Ar. After the measurement of the spectrum (a), the sample was treated with $^{13}CO_2$ at room temperature. Spectra b–e are (b) 2, (c) 10, (d) 20, and (e) 60 min after the treatment with $^{13}CO_2$. The spectra in b–e show the conversion of $^{13}CO_2$ (*) to silyl formate (□) thorough copper formates (●, ○).

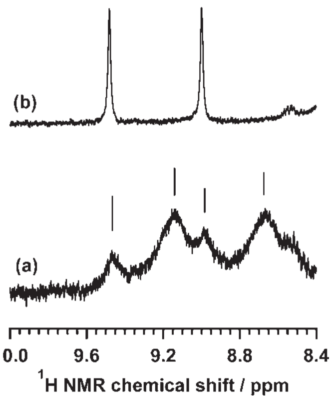

Figure 2. ^1H NMR spectra of the reaction between $^{13}CO_2$ and PMHS in the presence of the copper catalyst (a) 5 and (b) 180 min after treatment with $^{13}CO_2$. Reaction conditions are shown in Figure 1.

Table 2. List of Catalysts for Hydrosilylation of CO_2

catalyst	CO_2 (atm)	time (h)	TON	ref
$Cu(OAc)_2 \cdot H_2O$	1	6	8100	this work
$RuCl_3 \cdot nH_2O$	69–87	20	980	6a
$Ru_2Cl_5(MeCN)_7$	14	2×10^a	4619^a	6a
$[N(PPh_3)][HRu_3(CO)_{11}]$	50	24	292	6c
$RuCl_2(PPh_3)_3$	30	20	14	6d
$[RuH_2(PMe_3)_4]$	200–220		62	6f
N-heterocyclic carbene[b]	1	72	1840	8
zirconium complex[c]	1	1.5	225	7
[Ir(CN)(CO)(dppe)]	1		2.3	5

[a] Total TON value is reported during the 10 times reuse experiment. [b] For methanol synthesis. [c] For methane synthesis.

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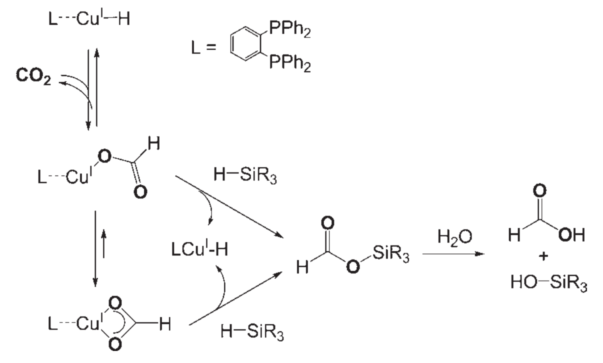
(14) The copper-catalyzed hydrosilylation of CO_2 effectively proceeded in benzene solvent as well as 1,4-dioxane.

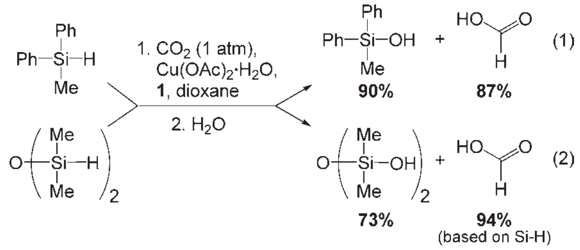
(15) The ^{13}C chemical shift of a previously reported Cu(I) formate complex was 168.5ppm; see: Lang, H.; Shen, Y.; Rüffer, T.; Walfort, B. *Inorg. Chim. Acta* **2008**, *361*, 95.

Scheme 3. Proposed Catalytic Reaction Pathway



After 60 min, the second copper formate decreased and the Si–OC(O)H species increased (Figure 1e). This result indicates that both of these copper formate species are intermediates to the silyl formate product. The formation of two copper formates is also supported by the ^{1}H NMR analysis: the sample after the addition of $^{13}CO_2$ showed two broad doublet signals centered at 8.9 and 9.2 ppm with ^{13}C–H coupling constants of 191.0 and 192.3 Hz, respectively (Figure 2a).[16] These coupling constant values are comparable to the reported Rh formate species (204.6 Hz).[2e] After 180 min, only one, sharp doublet signal centered at 9.2 ppm (192.3 Hz) was observed (Figure 2b).[17] The correlation between the ^{1}H NMR doublet resonance and the ^{13}C NMR signal at 169 ppm was confirmed by ^{13}C–^{1}H correlation spectroscopy analysis (Figure S8, Supporting Information). On the basis of these results, these two copper formates are suggested to be an unstable and reactive monodentate [Cu(η^1-OCHO)] species and a relatively stable bidentate [Cu(η^2-OCHO)] complex. The proposed reaction pathway involving two copper formates is shown in Scheme 3. As shown in Figure 1, the ^{13}C NMR signal of the monodentate species rapidly disappeared due to the CO_2 consumption and thermodynamic equilibrium. The formation of two equilibrium Rh formate species was also reported.[2e] The monodentate Rh formate species was also detectable only under high pressure CO_2.[2e]

The high utility of the silanols, the coproduct of the formic acid synthesis, encouraged us to examine the transformation of several hydrosilanes to silanols with the Cu catalyst using CO_2 as an oxidant. Diphenylmethylsilane reacted with CO_2 to afford 90% yield of the corresponding silanol accompanied by 87% yield of formic acid (eq 1).[18] Oxidation of tetramethyldisiloxane also proceeded, affording 73% yield of disilanol and 94% yield of formic acid (eq 2). The reaction of triethylsilane and triethoxysilane also occurred. The results are summarized in Table S1 (Supporting Information). Unfortunately, this catalyst system is not applicable toward hydrosilanes having carbon–carbon double bond and alkylchloride functions due to side reactions, such as hydrogenation.



In summary, this study has provided the first copper-catalyzed formic acid synthesis from CO_2.[19] The $Cu(OAc)_2 \cdot H_2O$–**1** system is highly effective for the formic acid synthesis under 1 atm of CO_2. The catalytic reaction pathway was revealed by in situ NMR analysis and isotopic experiments using $C^{18}O_2$ and $^{13}CO_2$. Several hydrosilanes were converted to the corresponding silanols in high yields accompanied by formic acid.

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Supporting Information Available. Experimental details and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Two broad singlet signals at 9.0 and 9.2 ppm were detected by ^{1}H NMR analysis after treatment with $^{12}CO_2$.

[17] In proton-coupled ^{13}C NMR analysis, a doublet signal centered at 169 ppm with a ^{13}C–H coupling constant of 192.4 Hz was observed (Figure S7, Supporting Information), indicating the carbon atom has a single, directly bonded H (formate species).

[18] The yields of formic acid and silanol from $C^{16}O_2$ are much higher than those of the reaction of $C^{18}O_2$ shown in Scheme 2, because a large excess of $C^{16}O_2$ could be used in the balloon.

[19] Formic acid derivatives (formamides) have been made via formic acid by CO_2 hydrogenation with heterogeneous and homogeneous copper catalysts; see: (a) Farlow, M. W.; Adkins, H. *J. Am. Chem. Soc.* **1935**, *57*, 2222. (b) Haynes, P.; Slaugh, L. H.; Kohnle, J. F. *Tetrahedron Lett.* **1970**, *11*, 365.

The authors declare no competing financial interest.