[Review Paper]

Carbon Dioxide to Organic Compounds Assisted by Silanes: Successive Transformation of Silyl Formate to Various Products

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This review paper summarizes the recent advances in the transformation of silyl formate to various organic compounds using one-pot processes. Silyl formate can be synthesized from CO₂ and hydrosilane via hydrosilylation. Recently, many catalysts have been developed for CO₂ conversion to silyl formate, resulting in the increasing importance of further conversion of silyl formate. A number of conversion reactions of silyl formate are introduced, including hydration, ester formation, amide formation, salt production, carbon-carbon bond formation, and metal carbonyl complex formation. These reactions smoothly proceed because of the high reactivity and electrophilicity of silyl formate. In some cases, the scope of the reaction partners, such as alcohols and amines, will also be discussed.

Keywords
Silyl formate, Carbon dioxide, Hydrosilane, Amine, Alcohol

1. Introduction

Utilization of carbon dioxide (CO₂) as a feedstock for the production of various chemicals is an important goal for environmental protection and sustainable development¹). Hydrosilylation of CO₂ with hydrosilane to silyl formate is a recently established catalytic reaction²). One of the advantages of the hydrosilylation of CO₂ is thermodynamically favorability compared with CO₂ hydrogenation with H₂³). For example, the reaction between CO₂ and hydrosilane (Me₃SiH) is predicted to be an exothermic reaction (ΔE = −57.2 kJ/mol)³), whereas the reaction with H₂ to formic acid is usually endothermic reaction without base additives. To date, a variety of metal complex and nonmetal catalysts for CO₂ hydrosilylation have been reported, with most of these systems selectively affording silyl formate with high yield under mild reaction conditions such as 1 atom of CO₂⁴). Encouraged by the rapid establishment of the CO₂ hydrosilylation system, many research groups have examined further transformation of silyl formate to a variety of useful chemical compounds.

Further reduction of silyl formate to methoxysilane has been examined using the same catalyst for CO₂ hydrosilylation (Scheme 1(c)). The reaction of three Si–H groups with a single CO₂ molecule affords methoxysilane and disiloxane through the formation of a silyl acetal (Scheme 1(b)). The obtained methoxysilane can be converted to methanol easily by hydration. Ying and co-workers reported an N-heterocyclic carbene catalyst for the hydrosilylation of CO₂ with methoxysilane as a major product⁴a). Almost all of the CO₂ was converted to methoxysilane and a small amount of CH₂(OSiR₃)₂ was detected during the initial stage of the reaction. Reduction of methoxysilane with additional hydrosilane afforded methane and siloxane (Scheme 1(d)). The frustrated Lewis pair, B(C₆F₅)₃/2,2,6,6-tetramethylpiperidine, and hydrogen reacted with CO₂ in the presence of hydrosilane⁴b). The CO₂ molecule was gradually reduced, finally forming methane. Formatoborane formation from CO₂ and the frustrated Lewis pair was determined to be the rate-limiting step.

Scheme 1 Reduction Pathway of CO₂ to Silyl Formate (a), Bis(silyl)acetal (b), Methoxysilane (c), and Methane (d)

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determining step in this reaction system. A tethered Ru-S complex was also reported as a highly selective catalyst for CO₂ reduction to bis(silyl)acetal (Scheme 1(b))⁴c. Heterolytic splitting of the Si-H bond at the Ru-S site occurred to yield an active cationic Si species, which showed high reactivity toward CO₂ to afford reduced products. This chemoselectivity is highly sensitive to temperature, with a 96 % selectivity for bis(silyl)acetal at 80 °C and 69 % selectivity for methoxysilane at 150 °C in the presence of excess hydrosilane.

Another example of the reductive functionalization of CO₂ is formamide synthesis (Scheme 2). Cantat and co-workers reported organic strong base-catalyzed formamide synthesis from CO₂, amines, and hydrosilanes⁵. Usually in these reaction systems, excess reducing agents and hydrosilane are used for complete conversion of the amine substrate. Based on the mechanism of the formylation of CO₂, the use of silyl formate as a formylating agent of amines is potential reaction route that could decrease the need for hydrosilane in the overall reaction.

In this review, we will focus on the potential usefulness of silyl formate as a highly reactive and readily available precursor for the production of various chemicals. Scheme 3 shows the successive transformation of silyl formate synthesized from CO₂ and hydrosilane. Silyl formate can be easily converted to formic acid by simple hydration. Based on the activated formate structure of silyl formate, formylation can also proceed with various reaction partners, including amines and alcohols. Additionally, carbon-carbon bond formation and metal-carbonylation can also occur with silyl formate.

2. Hydration to Formic Acid

Silyl formate is easily hydrated to yield formic acid, affording silanol as a co-product which is also usable for silicon-based polymer synthesis⁶ and as a coupling reaction partner⁷. On the other hand, additional energy input is necessary for the production of formic acid from formic acid salt which is a general product of the hydrogenation of CO₂ with H₂ using equimolar amount of base. Mizuno and co-workers reported the efficient hydrosilylation of CO₂ using Rh₂(OAc)₄ and K₂CO₃ catalyst system (Scheme 4)⁸. After the reaction, the addition of a slight excess of water afforded a 90 %

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**Scheme 2** Formamide Synthesis from CO₂, Amine, and Hydrosilane

**Scheme 3** Successive Transformations of Silyl Formate to Various Chemicals
yield of formic acid along with the corresponding silanol. The Ni-catalyzed hydrosilylation of CO$_2$ with alkylsilanes followed by hydration to yield formic acid was also reported$^9)$. For triethylsilyl formate, the hydration reaction effectively occurred to afford formic acid in 88 % yield (Scheme 5).

The copper-bisphosphine complex showed high catalytic activity for the hydrosilylation of CO$_2$ with various hydrosilane substrates$^{10,11)}$. Figure 1 summarizes the one-pot transformation of CO$_2$ and various hydrosilanes to afford formic acid and silanol promoted by the Cu-dppbz complex$^{10)}$. Aromatic silanes, including diphenylmethylsilane, were readily converted to the corresponding silanol and formic acid in 90 % and 87 % yields, respectively. The reaction occurred for triethylsilane and triethoxysilane with good to moderate yields of the target products. Tetramethyldisiloxane easily reacts with CO$_2$ and H$_2$O to form silanol and formic acid, achieving 94 % yield based on Si-H group.

Hydrosilylation of CO$_2$ proceeded in the presence of simple salt catalysts, such as Cs(HCOO) and K$_2$CO$_3^{12)}$. Scheme 6 shows the hydrosilylation of CO$_2$ using simple salts and successive hydration to formic acid. After the addition of water, formic acid was obtained in 65 % and 58 % yield for Cs(HCOO) and K$_2$CO$_3$, respectively.

Isotopic experiments revealed important information regarding the reaction pathway. Buchmeiser and co-workers reported a Pt nanoparticle catalyst for the

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**Scheme 4** Rh and Base Combined System for CO$_2$ Hydrosilylation-hydration Sequence

**Scheme 5** Ni and Et$_3$B Combined System for CO$_2$ Hydrosilylation-hydration Sequence

**Scheme 6** Simple Salt Catalyst System for CO$_2$ Hydrosilylation-hydration Sequence

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**Fig. 1** Formic Acid Synthesis through Cu-catalyzed Hydrosilylation of CO$_2$ and Successive Hydration along with Silanol/Disiloxane Production
after the reaction of $^{13}$CO$_2$, the addition of D$_2$O afforded H$^{13}$CO$_2$D as the main product (Scheme 7). This clearly indicated that (i) conversion of the carbon atom of CO$_2$ to formic acid and (ii) the hydride of hydrosilane is selectively inserted in the formyl group. More detailed information was obtained from the reaction using C$^{18}$O$_2$. The Cu-dppbz complex readily promoted the hydrosilylation of C$^{18}$O$_2$ to silyl formate with two $^{18}$O atoms (Scheme 8). Silyl formate was further converted to formic acid in the presence of H$_2^{16}$O with its two $^{18}$O atoms remaining intact. The $^{18}$O content in the silanol was negligible. These results suggest that all oxygen atoms contained in the resulting formic acid originated from CO$_2$ and the hydration occurred through nucleophilic attack of H$_2$O on the Si atom followed by proton transfer to an oxygen atom of silyl formate from H$_2$O.

Hydroborylation is another reductive conversion method of CO$_2$. Shintani and co-workers reported the Cu/N-heterocyclic carbene-catalyzed hydroborylation of CO$_2$ (14). The reaction proceeded under mild reaction conditions of 35 °C and 1 atm of CO$_2$. After quenching the reaction mixture with HCl aq., yield as high as 85 % yield for formic acid were obtained (Scheme 9).

3. Reaction with Alcohols to Afford Alkyl and Phenyl Formate

García and co-workers reported the reaction between silyl formate and alcohols in the presence of HBF$_4$ (9). After the Ni-catalyzed hydrosilylation of CO$_2$ with triethylsilane, alcohol and HBF$_4$ addition afforded alkyl formate and fluorosilane. **Table 1** summarizes the scope of alcohols that were used for the alkyl formate synthesis. Linear and branched alcohols both showed
good reactivity with silyl formate. In all cases, the corresponding alkyl formates were obtained in yields of >80 % within 1 h. The reaction also occurred with phenol and benzyl alcohol. The transformation reaction is driven by fluorosilane formation as the high affinity of F and Si easily cleaves the Si–O bond of silyl formate. Phenyl formates are generally synthesized by Pd or Lewis acid-catalyzed reaction systems(5). The present system from silyl formate shows advantages for short reaction time and high product yield.

Without alcohols additions, ethyl formate was detected with triethoxysilane as a reducing agent of CO₂. After the Zn-catalyzed hydrosilylation of CO₂ with triethoxysilane, the addition of aqueous HCl afforded ethyl formate via decomposition of the ethoxy group (Scheme 10)(6).

4. Reaction with Potassium Fluoride to Yield Potassium Formate

Si–O bond cleavage using the strong bonding phenomena of Si–F can also be applied to the transformation of silyl formate to yield potassium formate. After the Ni-catalyzed hydrosilylation of CO₂ with triethylsilane, potassium fluoride was added to the reaction mixture containing silyl formate. Potassium formate was detected with an 85 % yield after 15 min in the resulting solution (Scheme 11)(9). Similar to alkyl formate synthesis (Table 1), triethylfluorosilane was formed as a by-product.

5. Reaction with Amines to Afford Formamide and Carbamate

As previously mentioned, silyl formate is highly reactive toward protonic substrates such as water and alcohols. Therefore, it is expected that silyl formate would also be reactive toward amines. The reaction of CO₂ with amines and excess reducing agents, including H₂ and hydrosilane, afforded formamide in a one-pot process(5). Successive addition of an equimolar amount of primary and secondary amines to silyl formate, generated by the reaction of CO₂ and hydrosilane, afforded both formamide and formic acid. Table 2 summarizes the results of the reaction between dimethylphenylsilyl formate and equimolar amines, as reported by Mizuno and co-workers(8). Various aliphatic and aromatic amines reacted with silyl formate to afford the corresponding formamide and formic acid in yield of approximately 40 % and 50 %, respectively. Formamide formation afforded equimolar amounts of silanol, which reacted with other silyl formate to yield formic acid.

| Amine              | t [h] | Amide yield [%] | Formic acid yield [%] |
|--------------------|------|-----------------|-----------------------|
| Morpholine         | 1    | 43              | 43                    |
| n-BuNH₂            | 4    | 40              | 50                    |
| Ph–CH₂(NH₂)H       | 1    | 47              | 40                    |
| n-OctylNH₂         | 1    | 46              | 45                    |
| PhCH₂NH₂           | 1    | 42              | 47                    |
| m-Cl–PhCH₂NH₂      | 1    | 43              | 45                    |
| p-MeO–PhCH₂NH₂     | 1.5  | 40              | 47                    |
| PhNH₂              | 18   | 34              | 33                    |
This is the underlying mechanism for the formation of an almost equal yield of the two products in Table 2. On the other hand, the reaction of triethylsilyl formate and primary amines yielded 80% of formamide with a 5-6% yield of formic acid (Table 3)\(^9\). This indicates that the different functional groups on the Si atom may affect the reactivity of silyl formate with amines. The reaction of triethylsilyl formate with secondary amines afforded formamide and silyl carbamate (Table 4).

Generally, acid or base catalyst is necessary for the production of formamide from amines and formic acid\(^{17}\). High reactivity of silyl formate enables the efficient formamide synthesis without catalyst.

Other reaction systems for the successive addition of amines to silyl formate involve Zn\(^{16}\) and Pt-catalyzed hydrosilylation\(^{13}\). Scheme 12 shows the results of the reaction with dimethylamine and the corresponding formamide (DMF) formation detected via NMR\(^{16}\). Borylformate was also reactive with amines to yield formamide with the corresponding formamides produced in 81-98% yields in the presence of 1.5 molar equivalents of triethylamine (Scheme 13)\(^{14}\).

### 6. Carbon–carbon Bond-formation Using Silyl Formate

Several carbon–carbon bond-formation reactions using silyl formate have been reported. The reaction

\[ \text{CO}_2 + \text{Et}_3\text{SiH} \xrightarrow{\text{Ni complex}} \text{Et}_3\text{B} \]

\[ \begin{align*}
\text{O} & \quad \text{H} \\
\text{SiEt}_3 & \quad \text{Amine (1 mmol)}
\end{align*} \]

\[ \begin{align*}
\text{O} & \quad \text{H} \\
\text{SiEt}_3 & \quad \text{Amine (1 mmol)}
\end{align*} \]

\[ 80^\circ \mathrm{C}, \tau \mathrm{h} \]

| Amine            | \( t[\text{h}] \) | Amide yield [%] | Formic acid yield [%] |
|------------------|------------------|-----------------|------------------------|
| PhCH\(_2\)NH\(_2\) | 6                | 80              | 5                      |
| Cyclohexyl-NH\(_2\) | 4               | 83              | 6                      |
| Et-CH(NH\(_2\))CH\(_3\) | 4      | 85              | 6                      |

### Table 3

Synthesis of Amide and Formic Acid from Primary Amine and Silyl Formate after Ni-catalyzed Hydrosilylation of CO\(_2\)

\[ \text{CO}_2 + \text{Et}_3\text{SiH} \xrightarrow{\text{Ni complex}} \text{Et}_3\text{B} \]

\[ \begin{align*}
\text{O} & \quad \text{H} \\
\text{SiEt}_3 & \quad \text{Amine (1 mmol)}
\end{align*} \]

\[ \begin{align*}
\text{O} & \quad \text{H} \\
\text{SiEt}_3 & \quad \text{Amine (1 mmol)}
\end{align*} \]

\[ 80^\circ \mathrm{C}, \tau \mathrm{h} \]

| Amine            | \( t[\text{h}] \) | Amide yield [%] | Formic acid yield [%] |
|------------------|------------------|-----------------|------------------------|
| (PhCH\(_2\))\(_2\)NH | 5                | 47              | 8                      | 33                     |
| Pyrrolidine      | 6                | 52              | 5                      | 29                     |

### Table 4

Synthesis of Amide and Formic Acid from Secondary Amine and Silyl Formate after Ni-catalyzed Hydrosilylation of CO\(_2\)

\[ \text{CO}_2 + \text{Et}_3\text{SiH} \xrightarrow{\text{Ni complex}} \text{Et}_3\text{B} \]

\[ \begin{align*}
\text{O} & \quad \text{H} \\
\text{SiEt}_3 & \quad \text{Amine (1 mmol)}
\end{align*} \]

\[ \begin{align*}
\text{O} & \quad \text{H} \\
\text{SiEt}_3 & \quad \text{Amine (1 mmol)}
\end{align*} \]

\[ 80^\circ \mathrm{C}, \tau \mathrm{h} \]

| Amine            | \( t[\text{h}] \) | Amide yield [%] | Formic acid yield [%] | Carbamate yield [%] |
|------------------|------------------|-----------------|------------------------|----------------------|
| (PhCH\(_2\))\(_2\)NH | 5                | 47              | 8                      | 33                   |
| Pyrrolidine      | 6                | 52              | 5                      | 29                   |

Scheme 12 Zn-catalyzed Hydrosilylation of CO\(_2\) and Successive Formamide Formation

\[ \text{CO}_2 + \text{Et}_3\text{SiH} \xrightarrow{\text{[Zn(OEt\(_2\)]}} \text{Me}\(_2\text{NH} \]

\[ \text{TON}=10^7, \text{TOF}=2.9 \text{ h}^{-1} \]

Scheme 13 Cu-catalyzed Hydroborylation and Successive Formamide Formation

\[ \text{CO}_2 + \text{H}(\text{pin}) \xrightarrow{\text{Cu(O)(pin)(Ph)}} \text{Et}_3\text{B} \]

\[ \text{TON}=10^7, \text{TOF}=2.9 \text{ h}^{-1} \]

\[ \text{HN}(\text{pin}) \]

\[ \text{TON}=10^7, \text{TOF}=2.9 \text{ h}^{-1} \]

\[ 81-98\% \]
between silyl formate and a Grignard reagent, PhMgBr, afforded diphenylmethanol in a 77% yield along with a silanol (Scheme 14). The nucleophilic attack and further reduction of silyl formate was facilitated by the nucleophilicity of PhMgBr.

Another interesting result was reported involving the reaction of CO₂, silane, and benzene to form benzoic acid 18). The reaction of CO₂ with the silyl cation formed from [Ph₃C][B(C₆F₅)₄] and triethylsilane afforded a cationic silylated benzoic acid intermediate (Scheme 15). The key reaction step in this scheme was the electrophilic activation of CO₂ by the silyl cation to afford the silylated CO₂ cation. The detailed reaction mechanism indicated that the neutral silyl formate was not an intermediate, however, but the cation with a similar structure participated in its place. Hydration of the cationic intermediate afforded benzoic acid in a 51% yield. Deprotonation of the cation using 2,4,6-trimethylpyridine resulted in an 11% yield of the corresponding silyl ester.

7. Reaction with Iridium Hydride to Ir(CO) Complex

The formation of Ir carbonyl complex ([Ir(CO)]_n, Ir = Ir²⁺ with pincer ligand (2,6-[OP(tBu)₂]₂C₆H₃) [B(C₆F₅)₄]⁻ from Ir hydride complex ([Ir_H]), R₃Si_H, and CO₂ has been reported by Brookhart and co-workers 19). When moderately bulky hydrosilanes such as Et₃SiH, iPrMe₂-SiH, and Ph₂SiH were used as the reductant of CO₂ with [Ir-H], R₃Si-H, and CO₂ has been reported by Brookhart and co-workers 19). When moderately bulky hydrosilanes such as Et₃SiH, iPrMe₂-SiH, and Ph₂SiH were used as the reductant of CO₂ with [Ir-H], a small amount of [Ir(CO)] was detected by ³¹P NMR (nuclear magnetic resonance) measurement. The reaction mechanism of the formation of [Ir(CO)] was verified by using Ir dihydride ([Ir(H₂)]) as a model compound of the active species during the [Ir-H]-catalyzed CO₂ reduction and H¹³COOMe as a model compound of silyl formate (Scheme 16).

[Ir(H₂)] reacted with the excess amount of H¹³COOMe and then generated the [Ir¹³CO)] and MeOH. Ir monohydride SiEt₃ complex [Ir(H)(SiEt₃)], which was in equilibrium with [Ir(H₂)] during the CO₂ reduction by R₃Si-H⁻²⁰, also generated the [Ir¹³CO)] and MeOH on the same reaction condition. Based on the results of this experiment, [Ir(H₂)] was considered to be initially converted into the [Ir(H)(¹³COOMe)], then, intramolecular hydride reduction was presumed to be occurred to form the [Ir¹³CO)]. During the CO₂ reduction by R₃Si-H and [Ir-H], [Ir(CO)] seems to be generated from the active species such as [Ir(H₂)] and silyl formate as the first reduced form of CO₂ (Scheme 17).

Overall CO₂ reduction reaction mechanism using hydrosilane and Ir catalyst is shown in Scheme 18. The use of a proper hydrosilane as the reducing agent will achieve the selective [Ir(CO)] formation. It is expected that several metal carbonyl complexes could be synthesized from CO₂, hydrosilane, and metal (hydride) complex.
8. Conclusion

This review summarizes the recent progress in transformations of silyl formate to form various chemicals. Silyl formate was synthesized from CO₂ and hydrosilane and further converted using water or functional molecules in one-pot syntheses. The reaction between silyl formate and water proceeded quantitatively to afford formic acid and several isotopic experiments were performed to determine the reaction pathway. The reaction with alcohols or amines afforded the corresponding formyl esters and formamides in good to excellent yields. Additionally, the electrophilicity of silyl formate facilitated reactions with nucleophilic compounds, including PhMgBr and benzene, to afford organic products via carbon–carbon bond formation. With the development of novel catalytic reaction systems for the hydrosilylation of CO₂, the significance of silyl formate and its derivatives for new transformations will continue to increase.

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要  旨
二酸化炭素とヒドロシランからのジ酸シリル生成を経由する二酸化炭素の有機化合物への転換反応

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本稿では二酸化炭素とヒドロシランの反応によって生成したジ酸シリルからのワンボットでの有機化合物への変換反応を取り上げる。近年、二酸化炭素とヒドロシランからのジ酸シリル合成に高活性を示す触媒の報告が増えており、この技術の確立に伴い、得られるジ酸シリルからの転換反応開発の重要性も増している。そこで、ジ酸シリルを原料とする反応として、

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