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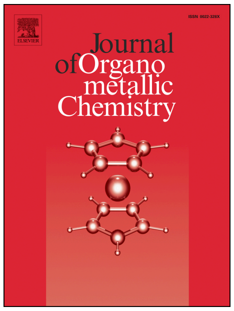

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Graphical Abstract

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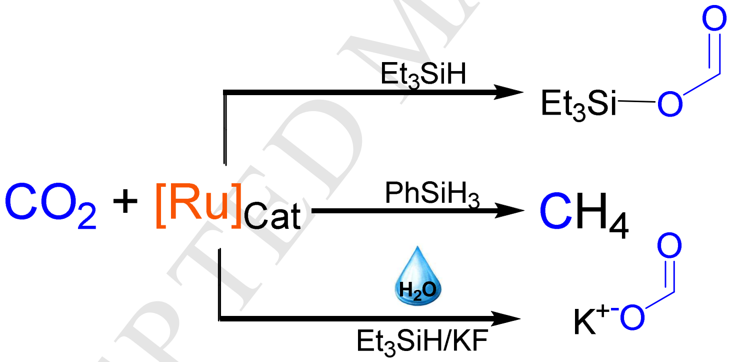

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Catalytic Reduction of CO_2 with Organo-Silanes using $[Ru_3(CO)_{12}]$

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Abstract

The reaction of carbon dioxide with Et_3SiH in the presence of catalytic amounts of $[Ru_3(CO)_{12}]$ as a catalytic precursor was achieved to produce silyl formate ($Et_3SiOCOH$) **1s** with a TON of 9 000. A similar reaction in the presence of KF yielded potassium formate (**8s**) in a one-pot protocol with high selectivity using water or MeCN as the solvent. In the current report the complete reduction of carbon dioxide to methane was achieved, with the use of a more reactive silane (phenylsilane). A catalytically relevant species was the ruthenium cluster $[H_4Ru_4(CO)_{12}]$. This is the second report on the hydrosilylation of carbon dioxide catalyzed by highly active and readily available ruthenium clusters and this is the first report of hydrosilylation of CO_2 to methane.

Key words: carbon dioxide; reduction; silane; formate; ruthenium; catalysis.

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Introduction

The increasing abundance of carbon dioxide in the atmosphere is currently one of the topics of great interest. Particularly, the use of this contaminant gas as a C1 source represents a challenge in the efficient production of high value-added materials and fuels.[1] CO_2 is a molecule with high thermodynamic stability and consequently low reactivity. Therefore, the use of catalytic methods is an attractive option for the activation of this gas.

Among all possible transformations of CO_2 to C1 or higher chemicals, the most attractive and promising reactions in terms of energy balance, catalyst performance, reusability, and scale-up perspective are hydrogenation to formate, methanol, or methane, reduction to CO and production of (poly)carbonate (**Figure 1**).[2]

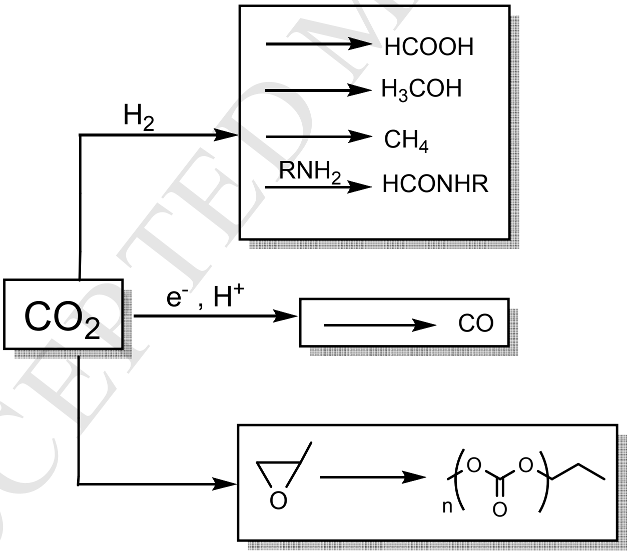

Figure 1. Possible transformations of CO_2

The hydrogenation methods are of particular interest since the corresponding products are more reactive than carbon dioxide and can be used as raw materials for the preparation of a

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wide variety of organic products or fuels. However, even when H_2 is highly reactive, it also represents a problem in terms of safe handling. Thus, the use of alternative hydrogenation procedures for carbon dioxide that replace H_2 with safer hydrogen sources such as organosilanes are desirable.

The hydrogenation of carbon dioxide to methane with silanes involves four steps. Silyl formate is the product of the first step, and two molecules of disiloxane are produced along with methane for the final step.[3,4] An important consideration for carbon dioxide hydrogenation using silanes is that the Si-H bond is relatively easy to activate. In the presence of a metal-containing catalyst, it produces an active hydride, ultimately yielding the formation of strong Si-O bonds. Based on our experience in carbon dioxide hydrosilylation using nickel catalysts,[5,6] we decided to expand this chemistry to the use of ruthenium catalytic precursors, particularly ruthenium clusters. In the literature there are reports of hydrosilylation of carbon dioxide with other metals such as Ir, Pt, Pd, Zr and Cu with high activity.[7–11]

We found that the use of simple ruthenium clusters in the hydrosilylation of CO_2 remains as a relatively un-explored area. There are many theoretical studies regarding carbon dioxide hydrogenation with metal clusters,[12–15] as well as experimental reports about carbon dioxide reduction with metal clusters.[16–26] some reports specifically deal with carbon dioxide hydrogenation using the ruthenium cluster $[Ru_3(CO)_{12}]$ and $H_{2(g)}$,[20,22] and just one report employed hydrosilylation.[27] Since the hydrosilylation protocols are safer and practical alternatives for hydrogenation, we present our findings on the hydrosilylation of carbon dioxide with a simple ruthenium cluster, which is 30 times more active than previously

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reported,[27] and the first report of complete reduction to methane with silanes using ruthenium.

Results and discussion

The catalytic hydrogenation of carbon dioxide with Et_3SiH using $[Ru_3(CO)_{12}]$ as a catalytic precursor was achieved. First, the reaction times of 1, 25, and 48 h were assessed, and the best conversion was achieved at 48 hours. The reaction was conducted using a 1 % load of $[Ru_3(CO)_{12}]$ relative to Et_3SiH. The reaction occurred at 80 °C in 1 atm of CO_2 and was monitored by GC-MS. The main hydrogenation product from CO_2 was the silyl formate (**1s**), which is a relevant product that can be used as a starting material for a wide variety of important products for industry and academia (**Figure 2**).

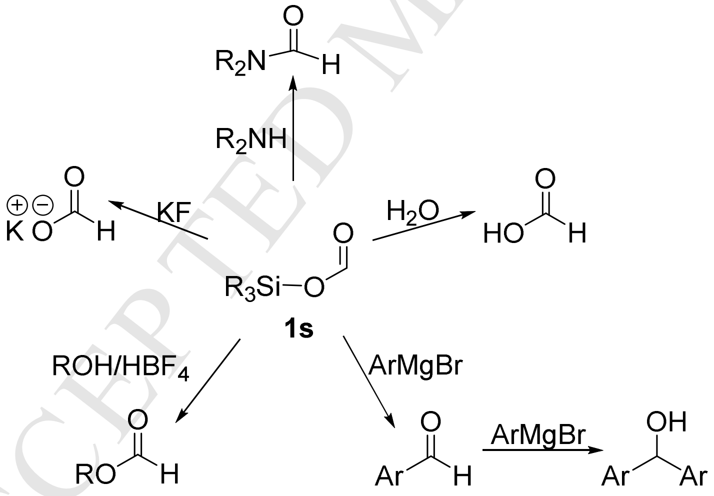

Figure 2. Some silyl formate applications

The polarity of different solvents such as MeCN, toluene, and MeOH was also assessed (**Table 1**). The only solvent where carbon dioxide was actually reduced was acetonitrile, with a 15 % conversion to **1s** (Entry 3). Clearly, the use of low-polarity solvents such as

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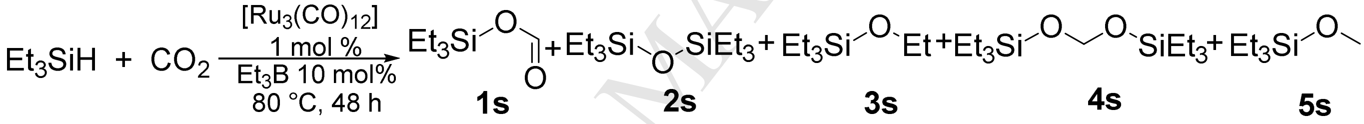
toluene does not allow the reaction, and the use of methanol produced the silane solvolysis to yield **5s**.

According to our previous results with nickel catalysts,[5] an important feature of this transformation is the strong dependence on the use of Et_3B as an additive to enhance the hydrogenation of carbon dioxide. Therefore, we initially used Et_3B, but in order to determine the actual need for this additive in the current reduction of CO_2, the reaction was also performed without Et_3B (**Table 2**, entry 2). To our surprise, the absence of this additive in the current case improved the conversion of **1s**, so we did not use it further.

Table 1. Reaction of CO_2 and Et_3SiH using $[Ru_3(CO)_{12}]^{a,b,c}$



Entry	Solvent	Conversion (%)					
		1s	**2s**	**3s**	**4s**	**5s**	**total**
1	MeOH	nd	6	nd	nd	93	99
2	Toluene	nd	nd	nd	nd	nd	0
3	MeCN	15	55	5	14	nd	89

a) nd: not detected, b) All yields were determined by GC-MS, using $Et_3SiOCOH$ as internal std, c) Reaction conditions: Et_3SiH (1.55 mmol), [Ru] (0.0155 mmol), Et_3B (0.155 mmol), CO_2 (1 atm), solvent (5 mL). 80 °C, 48 h.

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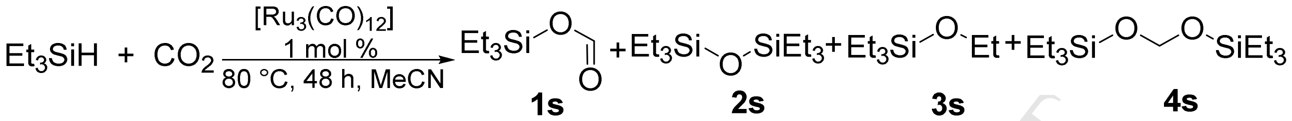
Table 2. The influence of Et_3B in CO_2 hydrogenation[a,b,c]



Entry	Et_3B	Conversion (%)				
		1s	2s	3s	4s	Total
1	10 mol%	15	55	5	14	89
2	--	29	10	nd	10	45

a) nd: not detected, b) All yields were determined by GC-MS, using $Et_3SiOCOH$ as internal std, c) Reaction conditions: Et_3SiH (1.55 mmol), [Ru] (0.0155 mmol), Et_3B (0.155 mmol), CO_2 (1 atm), solvent (5 mL). 80°C, 48 h.

We next carried out an assessment for a variety of mild temperatures and CO_2 pressure in order to obtain a higher conversion of carbon dioxide reduction to **1s**. Key results are presented in **Table 3**. The best conversion and selectivity to product **1s** takes place in 100 psi of carbon dioxide and at 80 °C (entry 2). Considering that $[Ru_3(CO)_{12}]$ is a well-known precursor of nanoparticles,[28–41] a mercury drop test was conducted to assess the homogeneity of the process (entry 8).[42, 35] As a result, no significant decrease in activity was observed, meaning this reaction is likely to be a homogeneous process.

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Table 3. Testing at different temperatures and pressures[a,b,c]

Entry	Conditions		Conversion (%)			
	Pressure (psi)	Temperature (°C)	1s	2s	4s	total
1	500	80	47	16	30	93
2	100	80	87	9	3	99
3	50	80	60	17	15	92
4	100	60	12	8	2	22
5	200	100	69	22	6	97
6	500	80	56	18	13	87
7	500	100	74	18	6	98
8a)	100	80	80	8	9	97

a) Hg drop test (0.309 mmol), b) all yields were determined by GC-MS, using $Et_3SiOCOH$ as internal std, c) Reaction conditions: Et_3SiH (3.1 mmol), [Ru] (0.031 mmol), MeCN (10 mL).

To investigate the catalyst load, the reaction was initially carried out with 1 mol % load of $[Ru_3(CO)_{12}]$, which was successfully reduced to 0.01 mol % with a TON of 9 000 (see Supporting Information). This ruthenium cluster was compared with other mononuclear

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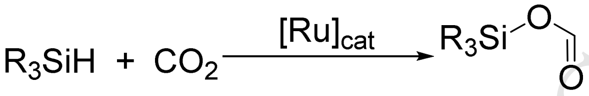
and dinuclear ruthenium catalytic precursors (see **Table 4**), and the use of $[Ru_3(CO)_{12}]$ represents the most active one reported for the hydrosilylation of CO_2.

Table 4. Reported catalysis of ruthenium for hydrosilylation of CO_2



Precatalyst	**Silane**	**Conditions** **T (°C) / P (psi) / T(h) / solv**	**TON**
$[Ru_3(CO)_{12}]$*	Et_3SiH	80 / 100/ 48 /MeCN	9 000
$[RuCl_3(MeCN)_3]$[43]	Me_2PhSiH	85 / 293/ 1½ /MeCN	485
$[RuCl_3{\cdot}n\mathrm{H2O}]$[44]	Me_2PhSiH	80 / 1028/ 20 / MeCN	91
$[Ru_2Cl_5(MeCN)_7]$[45]	Me_2PhSiH	80 / 205 / 20 / MeCN	970
$[RuH_2(PMe_3)_4]$[46]	$MeEt_2SiH$	90 / 2939 / 63 /$scCO_2$	62
$[RuCl_2(PPh_3)_3]$[47]	$MeEt_2SiH$	100 / 440 / 20 / benzene	14
$[\overset{\frown}{\mathrm{Ru\text{-}SAr}}(PR_3)]$[48]	Et_3SiH	80 / 73 / 4 / benzene	50
$[((Ph_3P)_2N)][HRu_3(CO)_{11}]$[27]	Et_3SiH	100 / 734 / 24 /CH_2Cl_2	292

*This work.

To identify some of the involved active species in the catalytic process, a reaction of Et_3SiH was carried out with $[Ru_3(CO)_{12}]$ following a reported procedure (**Scheme 1**).[49] However, we used acetonitrile instead of toluene, and the ^{1}H NMR spectrum of the crude reaction displayed three signals between -17 and -18.5 ppm. After purification by column

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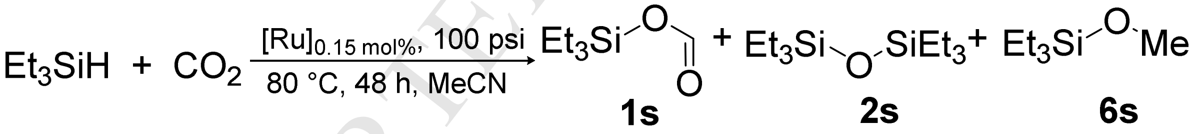
chromatography, only one hydride was recovered, which showed a signal at -17.8 ppm. This compound has been previously characterized as $[H_4Ru_4(CO)_{12}]$.[50] This is an air-stable cluster that can be handled in the open atmosphere.

$$4Et_3SiH + [Ru_3(CO)_{12}] \xrightarrow[80\ °C]{MeCN,\ 4\ h} [H_4Ru_4(CO)_{12}]$$

Scheme 1.

To find out if the cluster $[H_4Ru_4(CO)_{12}]$ was a catalytically relevant species, it was independently synthetized[51] and used. A comparison of its catalytic activity with that of $[Ru_3(CO)_{12}]$ is presented in **Table 5**.

Table 5. Catalytic activity using both ruthenium clusters[a,b]



Cluster	Conversion (%)			
	1s	2s	6s	Total
$[Ru_3(CO)_{12}]$	49	32	15	96
$[H_4Ru_4(CO)_{12}]$	47	29	21	97

a) all yields were determined by GC-MS, using $Et_3SiOCOH$ as internal std, b) Reaction conditions: Et_3SiH (3.1 mmol), [Ru] (0.0046 mmol), MeCN (10 mL).

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As shown in the table, both ruthenium clusters presented practically the same catalytic activity. Consequently, we established that [$Ru_4(H)_4(CO)_{12}$] was produced *in situ* and able to work as catalytic precursor. The silyl formate (**1s**) is a product of great industrial interest (**Figure 2**). However, some practical disadvantages are associated with it, such as complicated handling and tendency to be readily hydrolyzed. A practical alternative to overcome these inconveniences is the production of potassium formate by reacting the silyl formate with KF (**Figure 2**). Thus, to obtain potassium formate using a one-pot procedure, a similar reaction for the CO_2 reduction was conducted but with KF added from the beginning the reaction to yield potassium formate in a 75 % conversion (**Table 6**). Noteworthy, the ruthenium-free control reactions revealed no reaction at all.

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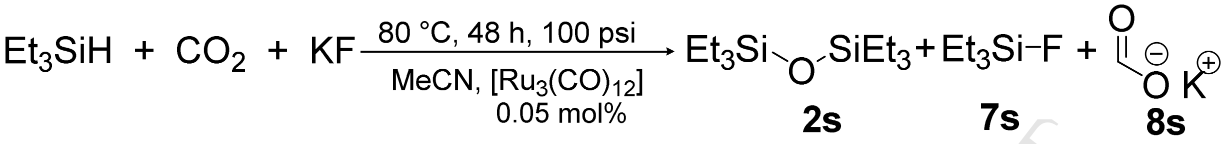
Table 6. Potassium formate obtained in one-pot procedure[a,b]



Entry	time (h)	Conversion (%)		
		2s	**8s**	**total**
1	48	24	75	99
2	24	26	73	99
3	13	20	74	94
4	5	23	67	90

a) all yields were determined by GC-MS, using $Et_3SiOCOH$ as internal std, b) Reaction conditions: Et_3SiH (3.1 mmol), KF (3.1 mmol), [Ru] (0.00155 mmol), MeCN (10 mL).

The product Et_3SiF (**7s**) thermodynamically directs the reaction due to the formation of a strong Si-F bond. This allowed for shorter reaction times to be considered (entries 2-4, **Table 6**), and the reaction time was decreased from 48 to 5 hours with good conversion to potassium formate (**8s**). To make this a green process, the reaction was tested in water as a solvent instead of MeCN, through which **8s** was successfully produced in 60% yield (**Scheme 2**).

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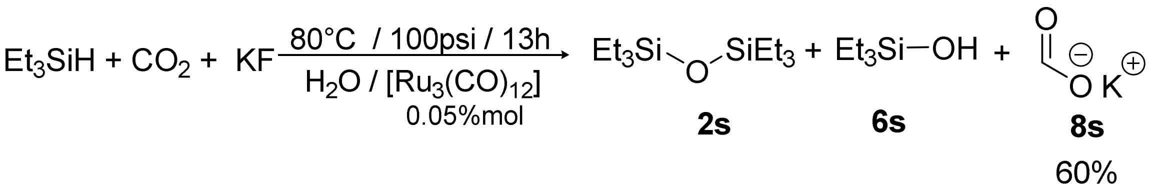

Scheme 2.

Using similar reaction conditions to those in in **Table 2** but with $PhSiH_3$ instead of Et_3SiH and the optimized catalyst load (0.05 mol%), the reaction was conducted and monitored by NMR and CG/MS. This reaction is presented in **Scheme 3**, for which a more active silane was used to obtain a complete reduction of CO_2 to methane. The product was characterized by ^1H and $^{13}C\{^1H\}$ NMR, including the use of isotopically labeled carbon dioxide ($^{13}CO_2$). The final gas mixture dissolved in C_6D_6 contained approximately 28% CH_4 (see Supporting Information section, **Figure S6**).

$$^{13}CO_2 \xrightarrow[\text{80°C, 48h, 100psi}\\ \text{MeCN}]{\text{Ph-SiH}_3\text{, Et}_3\text{B 10 mol\%}\\ [\text{Ru}_3(\text{CO})_{12}]\text{ 0.05 mol\%}} {}^{13}CH_4$$

Scheme 3.

CONCLUSIONS

The hydrosilylation of carbon dioxide was achieved by using $[Ru_3(CO)_{12}]$ and $[H_4Ru_4(CO)_{12}]$ as catalysts precursors. This is the second report on this topic and the first report for the complete reduction of CO_2 to methane using ruthenium and phenylsilane under relatively mild conditions. Also, it was possible to produce silyl formate with good yield and selectivity. Additionally, potassium formate was produced in water with good yield.

EXPERIMENTAL SECTION

General considerations. Unless otherwise stated, all processes were performed using an MBraun glovebox (<1 ppm H_2O and O_2) under an argon atmosphere (Praxair 99.998) or by using high-vacuum and standard Schlenk techniques under an argon atmosphere. Acetonitrile was dried and distilled over CaH_2, toluene was dried and distilled over sodium, methanol was dried and distilled from a solution of magnesium/iodine, and water was distilled and deoxygenated under an argon flow. Deuterated solvents for NMR experiments were purchased from Cambridge Isotope Laboratories. Triethylsilane (99% purity, Aldrich), carbon dioxide (99.998% purity, supplied by Praxair), phenylsilane (97% purity, Aldrich), triethylborane (95% purity, Aldrich), and triruthenium dodecacarbonyl (99% Aldrich) were used. All reagents for the catalytic reactions were loaded in the glove box. The GC-MS determinations were made using an Agilent 5975C system equipped with a 30-m DB-5MS capillary column (0.25 mm i.d.; 0.25 μm).

Reaction monitoring. The reaction was performed using a 50-mL Schlenk flask equipped with a Rotaflo valve and a magnetic stirring bar. It was loaded with 9.8 mg (0.015 mmol) of $[Ru_3(CO)_{12}]$, 180 mg (1.53 mmol) of Et_3SiH, 15.8 mg (0.153 mmol) of Et_3B, 5 mL of MeCN, and CO_2 atmosphere. All reagents were loaded in a glove box except CO_2, which was added using a double manifold gas/vacuum. The mixture was heated at 80 °C in a silicon oil bath for 1 h, and the reaction was then depressurized in a hood, opened under argon atmosphere, and analyzed by GC/MS. For further reaction time, the reaction mixture was pressurized again with CO_2 and heated at 80 °C. A sample was taken after 24 h and then after a total of 48 h.

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Reactivity of CO_2 with Et_3SiH catalyzed by $[Ru_3(CO)_{12}]$ in different solvents. The reaction was performed in a 50-mL Schlenk flask equipped with a Rotaflo valve and a magnetic stirring bar. The flask was loaded with 9.8 mg (0.015 mmol) of $[Ru_3(CO)_{12}]$, 180 mg (1.53 mmol) of Et_3SiH, 15.8 mg (0.153 mmol) of Et_3B, and 5 mL of MeCN, and then pressurized with CO_2. All the reagents were loaded in a glove box except CO_2, which was added using a gas/vacuum double manifold. The mixture was heated at 80 °C in a silicon oil bath for 48 h. This methodology was also done using toluene and MeOH instead of MeCN.

Use of different CO_2 pressures. The pressures were examined in a 100-mL stainless steel Parr autoclave, and the reactor was loaded with 19.6 mg (0.030 mmol) of $[Ru_3(CO)_{12}]$, 360 mg (3.06 mmol) of Et_3SiH, 10 mL of MeCN, and CO_2 at a desired pressure. Then, the reactor was heated at different temperatures for 48 h. After this time, the reactor was cooled to room temperature and depressurized in a hood. The final reaction mixture was analyzed by GC/MS.

Hg drop test. This reaction was performed as described for the previous reaction, but with the addition of 61.0 mg (0.306 mmol) of Hg and CO_2 at 100 psi followed by heating at 80 °C for 48 h. The reaction mixture was filtered on celite and analyzed by GC/MS.

Load of $[Ru_3(CO)_{12}]$. All reactions were performed in a 100-mL stainless steel Parr autoclave. The reactor was loaded with 360 mg (3.06 mmol) of Et_3SiH, 10 mL of MeCN, 100 psi of CO_2 , and 10.7 mg, 1.6 mg, or 1.0 mg (0.0167 mmol, $2.5x10^{3}$ mmol, $1.6x10^{-3}$ mmol respectively) of $[Ru_3(CO)_{12}]$. These amounts represent catalyst loads of 0.54, 0.08, and 0.05 mol %, respectively. Particularly for the reaction using 0.01 mol % catalyst, the reaction was carried out with 1.0 mg ($1.6x10^{-3}$ mmol) of [$Ru_3(CO)_{12}$], 1815 mg (15.64 mmol) of Et_3SiH, 10 mL of MeCN, and 100 psi of CO_2. All reactions were heated at 80 °C for 48 h, and the reaction mixtures where analyzed by GC/MS.

Identification of catalytic species. This reaction was carried out in a 50-mL Schlenk flask equipped with a Rotaflo valve and a magnetic stirring bar. The flask was loaded with 50.0 mg (0.078 mmol) of [$Ru_3(CO)_{12}$], 39.3 mg (0.338 mmol) of Et_3SiH, and 5 mL of MeCN, and the reaction was heated at 80 °C for 4 h. Then, the reaction was evaporated to dryness and purified by column chromatography in a glove box and carried out using silica and a mixture of THF/acetone as eluent. The product was identified as [$H_4Ru_4(CO)_{12}$][50] by a characteristic ^1H NMR peak at -17.8 ppm (22°C, 300 MHz, THF-d_8).

One-pot synthesis of potassium formate. The reaction was carried out in a 100-mL stainless steel Parr autoclave. The reactor was loaded with [$Ru_3(CO)_{12}$] (1.0 mg $1.6x10^{-3}$ mmol), Et_3SiH (360 mg 3.06 mmol), KF (179.8 mg, 3.06 mmol), 10 mL of MeCN or water, and CO_2 (100 psi), and heated at 80 °C for 13 h. When MeCN was used as the solvent, the final mixture was filtered over celite and analyzed by GC/MS, but when the reaction was performed in water, it was analyzed by ^1H NMR (22 °C, 300 MHz, D_2O) 8.40 ppm (KOC(O)-**H**). Isolated yield = 60%

CO_2 reduction with phenylsilane. A 100-mL stainless steel Parr autoclave was loaded with [$Ru_3(CO)_{12}$] (1.0 mg $1.6x10^{-3}$ mmol), $PhSiH_3$ (338.0 mg 3.06 mmol), Et_3B (61.2 mg, 0.31 mmol), 10 mL of MeCN, and CO_2 (100psi), and heated at 80°C for 48 h. Then, the reactor was cooled and depressurized while bubbling the gas into a Benzene-d_6. The reaction residue was analyzed by GC/MS, and gases were analyzed by ^1H and

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$^{13}C\{^1H\}$NMR in an NMR tube with a J. Young valve. ^1H NMR (22 °C, 300 MHz, Benzene-*d*$_6$): δ 0.52 ppm (CH_4). $^{13}C\{^1H\}$NMR (22 °C, 300 MHz, Benzene-*d*$_6$): δ 0.11 ppm (CH_4).

A similar experiment was made using $^{13}CO_2$.

Supporting Information available.

Relevant experimental data, NMR spectra and GC-MS determinations.

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Highlights

Catalytic Reduction of CO_2 with Organo-Silanes using $[Ru_3(CO)_{12}]$

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- ✓ Commercially available catalyst precursor and silanes
- ✓ Safe use of silanes as hydrogen sources
- ✓ Selective hydrogenation depending on the selected silane
- ✓ First report on the complete reduction of CO_2 to methane with silanes and ruthenium

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