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In the presence of simple  $Rh_2(OAc)_4$  and  $K_2CO_3$ , the hydrosilylation of  $CO_2$  (1 atm) with various hydrosi-

lanes efficiently proceeded to afford the corresponding silyl formates in moderate to high yields (53-90%

yields). By using the dimethylphenylsilyl formate produced by the hydrosilylation, formamides, formic

acid, and a secondary alcohol (via an aldehyde) could be synthesized by the reaction with various nucleo-

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# Catalytic synthesis of silyl formates with 1 atm of $CO_2$ and their utilization for synthesis of formyl compounds and formic acid

## Shintaro Itagaki, Kazuya Yamaguchi, Noritaka Mizuno\*

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

### A R T I C L E I N F O

### ABSTRACT

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### 1. Introduction

Although energy from fossil fuels makes an invaluable contribution to the quality of our lives, we are now facing serious environmental problems, e.g., global warming caused by  $CO_2$  from (over)use of fossil fuels. The increased concern for such serious problems has put pressure on the society to reduce and reuse  $CO_2$ . The catalytic transformation of  $CO_2$  as a renewable C1 building block is an attractive alternative [1–4]. To date, several procedures for the transformation of  $CO_2$  have been reported. For example, (i) chemical fixation of  $CO_2$  promoted by reactive substrates such as epoxides, alcohols, amines, and alkynes to form new C–O, C–N, and C–C bonds has been achieved by using several transition metal, acid, and/or base catalysts [5–8] and (ii)  $CO_2$  has chemically, electrochemically, or photo-electrochemically been reduced to useful C1 chemicals such as formic acid, formaldehyde, methanol, methane, and CO [9–11].

Hydrosilanes are readily available, easy-to-handle, nontoxic, and inexpensive reducing agents [12,13], and the reduction of  $CO_2$  with hydrosilanes to produce silyl formates [14–21], formaldehyde [22], methoxysilanes [23–25], and methane [26,27] is thermodynamically favorable. In particular, methoxysilanes [23–25] and methane [26] have been obtained in 1 atm of  $CO_2$ . Moreover, Cantat and co-workers have recently reported the direct synthesis

of formamides from amines, hydrosilanes, and CO<sub>2</sub> using nitrogen bases or N-heterocyclic carbenes in 1 atm of CO<sub>2</sub> [28,29]. In con-

trast, conventional synthesis of formamides by the reduction of CO<sub>2</sub>

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with H<sub>2</sub> requires high temperatures ( $\geq$ 75 °C) and high pressures  $(\geq 60 \text{ atm})$  [30–40]. Among the above-mentioned CO<sub>2</sub> reduction products, silyl formates are one of the most attractive compounds because they can potentially be utilized as valuable synthons, which will provide new routes for synthesis of a wide range of value-added chemicals from CO<sub>2</sub>. For example, silyl formates can be converted into formic acid by simple hydrolysis [41,42]. In addition, it is expected that silyl formates can be regarded as "formyl synthons" due to their strong Si-O bonds and that various kinds of carbonyl compounds can possibly be synthesized by the reaction with the corresponding nucleophiles. However, the synthesis of silyl formates from CO<sub>2</sub> itself generally requires high pressure of CO<sub>2</sub> (≥3 atm) (Table S1) [14–20]. In contrast, Sattler and Parkin quite recently realized the hydrosilylation of 1 atm of CO<sub>2</sub> using [Tris(2pyridylthio)methyl]zinc hydride [21]. In addition, Motokura et al. recently reported that the in situ-prepared Cu(I)-hydride complex can act as an efficient homogeneous catalyst for the reduction of CO<sub>2</sub> (1 atm) with hydrosilanes and that silvl formates are intermediates for the reduction [42].

In this paper, we report two important findings. Firstly, we demonstrate that the hydrosilylation of  $CO_2$  can be realized in 1 atm of  $CO_2$  using simple  $Rh_2(OAc)_4$  (OAc = acetate) and inorganic bases (Scheme 1). Secondly, we report the utilization of silyl formates for synthesis of various carbonyl compounds, that

<sup>\*</sup> Corresponding author. Tel.: +81 3 5841 7272; fax: +81 3 5841 7220. *E-mail address:* tmizuno@mail.ecc.u-tokyo.ac.jp (N. Mizuno).

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Scheme 1. Synthesis of silyl formates and their utilization.

is, a one-pot synthesis of various carbonyl compounds from CO<sub>2</sub> through hydrosilylation followed by reactions with various nucleophiles such as amines, water, and the Grignard reagent (Scheme 1).

### 2. Experimental

### 2.1. General

GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a TC-5 capillary column. Mass spectra were recorded on Shimadzu GCMS-QP2010 equipped with an InertCap 5 MS/Sil capillary column at an ionization voltage of 70 eV. Liquid-state NMR spectra were recorded on JEOL JNM-EX-270. HPLC analyses (for determination of formic acid) were performed on a Shimadzu Prominence system with a RID detector (Shimadzu RID 10A) equipped with a Shodex RSpak KC-811 column  $(8.0 \text{ mm ID} \times 300 \text{ mm length})$ . <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured at 270 and 67.8 MHz, respectively. Rh<sub>2</sub>(OAc)<sub>4</sub> was obtained from Wako Pure Chemical Industries (Cat. No. 180-01151) and used as received. Other metal salts and complexes, bases, and the Grignard reagents of phenylmagnesium bromide (PhMgBr) were obtained from Wako Pure Chemical Industries, Kanto Chemical, TCI, or Aldrich (reagent grade) and used as received. Hydrosilanes and amines were obtained from TCI and purified by distillation with CaH<sub>2</sub> before the use. Acetonitrile was purified by The Ultimate Solvent System (Glass Contour Company) [43]. Other solvents were obtained from Wako Pure Chemical Industries and Kanto Chemical. All hydrosilanes and solvents were stored over molecular sieve 3A 1/16 (Kanto Chemical), which was pretreated at 300 °C under vacuum [44], and handled in a glove box under Ar (O<sub>2</sub> < 1.0 ppm,  $H_2O < 1.0 \text{ ppm}$ ).

### 2.2. Typical procedure for hydrosilylation of CO<sub>2</sub>

Into a Schlenk tube (volume: 40 mL) were successively placed  $Rh_2(OAc)_4$  (0.25 mol%),  $K_2CO_3$  (0.5 mol%), internal standard (biphenyl), and a Teflon-coated magnetic stir bar. In a glove box under Ar, dimethylphenylsilane (**1a**, 1 mmol) and acetoni-trile (2 mL) were added. Then, the Ar gas in the Schlenk tube was replaced with 1 atm of CO<sub>2</sub>, and the mixture was vigorously stirred at 50 °C for 2 h. The conversion and the yield of the products were determined by GC analysis. The silyl formates were identified by means of GC mass and <sup>1</sup>H and <sup>13</sup>C NMR (see the Supporting Information).

### 2.3. Typical procedure for formylation of amines

After the hydrosilylation of  $CO_2$  with **1a** was completed, piperidine (**4a**, 1 mmol) was added to the reaction solution of dimethylphenylsilyl formate (**2a**) and the reaction mixture was vigorously stirred at 50 °C for 1 h. The conversion and the yield of the products were determined by GC and <sup>1</sup>H NMR analyses. The formamides were confirmed by the comparison of their GC retention times and GC mass spectra. A typical procedure for isolation of formamides is as follows: After the hydrosilylation of  $CO_2$  with **1a**  was completed, acetonitrile was removed by evaporation, followed by addition of *n*-hexane (2 mL). Catalysts ( $Rh_2(OAc)_4$  and  $K_2CO_3$ ) were insoluble in *n*-hexane and separated by filtration. Then, **4e** (1 mmol) was added to the filtrate, and the mixture was vigorously stirred at 50 °C for 1 h. *n*-Hexane was evaporated, and white precipitates obtained were washed with *n*-hexane and extracted with toluene. Evaporation of toluene afforded analytically pure *N*benzylformamide (**5e**, 35% yield).

### 2.4. Procedure for synthesis of formic acid

After the hydrosilylation of CO<sub>2</sub> with **1a** was completed, water (5 mmol) was added to the reaction solution of **2a** and the reaction mixture was vigorously stirred at room temperature for 0.5 h. The conversion and the yield of the products were determined by GC and <sup>1</sup>H NMR analyses. Formic acid was confirmed by the comparison of its HPLC retention time and <sup>1</sup>H and <sup>13</sup>C NMR spectra. A procedure for isolation of formic acid is as follows: After the hydrosilylation of CO<sub>2</sub> with **1a** was completed, acetonitrile was removed by evaporation, followed by addition of *n*-hexane (2 mL). Catalysts (Rh<sub>2</sub>(OAc)<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub>) were insoluble in *n*-hexane and separated by filtration. Then, water (5 mmol) was added to the filtrate, and the mixture was vigorously stirred at 50 °C for 0.5 h. Formic acid was extracted with water (0.91 mL) and further washed with *n*-hexane, affording an aqueous solution of formic acid (0.66 M).

### 2.5. Procedure for synthesis of benzhydrol

The reaction mixture of **2a** was evaporated, followed by the addition of THF (1 mL) in a glove box under Ar. Then, the THF solution of PhMgBr (1.10 M, 2 mL) was added to the THF solution of **2a**. After being stirred at room temperature for 1 h, the resulting mixture was quenched by the addition of  $H_2O(0.5 \text{ mL})$ . The conversion and the yield of the products were determined by GC analysis. The products were confirmed by the comparison of their GC retention times and GC mass spectra. Benzhydrol was isolated by a similar procedure to that for formamides.

### 3. Results and discussion

# 3.1. Effects of metal catalysts, bases, and solvents on the hydrosilylation of CO<sub>2</sub> with dimethylphenylsilane

Initially, the hydrosilylation of  $CO_2$  with **1a** was carried out in the presence of catalytic amounts of various metal salts (e.g.,  $Rh_2(OAc)_4$ , AgOAc,  $Pd(OAc)_2$ ,  $Cu(OAc)_2 \cdot H_2O$ ,  $Ru(acac)_3$ (acac = acetylacetonato),  $Pt(acac)_2$ ,  $AuBr_3$ ,  $IrCl_3 \cdot H_2O$ , 0.5 mol%) and K<sub>2</sub>CO<sub>3</sub> (0.5 mol%) (Table 1). No reaction proceeded in the absence of metal salts. Among the metal salts examined, only Rh<sub>2</sub>(OAc)<sub>4</sub> showed the high catalytic activity and selectivity for the hydrosilylation; for example, when the hydrosilylation was carried out with Rh<sub>2</sub>(OAc)<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub> under the conditions described in Table 1, the corresponding silvl formate **2a** was obtained in 90% yield (Table 1, entry 1). In this case, the turnover frequency was 90 h<sup>-1</sup>, and the turnover number reached up to 180 (see Table S1 for comparison). Other rhodium complexes such as [RhCl<sub>2</sub>Cp<sup>\*</sup>]<sub>2</sub>  $(Cp^* = pentamethylcyclopentadienyl), [Rh(cod)Cl]_2 (cod = 1,5$ cyclooctadiene), and  $Rh(PPh_3)_3Cl$  (PPh<sub>3</sub> = triphenylphosphine) were almost inactive (Table 2), while these complexes are reported to be active for dehydrosilylation of alcohols [45] and hydrosilylation of alkenes and alkynes [46,47].

As shown in Table 3, kinds of bases were also crucial for the hydrosilylation of  $CO_2$  with **1a**. Inorganic O-donor bases such as  $K_2CO_3$ ,  $Cs_2CO_3$ ,  $K_3PO_4$ , and KOt-Bu (*t*-Bu = *tert*-butyl) were suitable for the present  $Rh_2(OAc)_4$ -catalyzed hydrosilylation, while

Table 1	
Hydrosilylation of $CO_2$ with <b>1a</b> using various metal salts. <sup>a</sup>	

Entry	Catalyst	Conv. (%)	Yield (%)	
			2a	3a
1	$Rh_2(OAc)_4$	>99	90	8
2	AgOAc	1	nd	nd
3	$Pd(OAc)_2$	22	<1	10
4	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	6	nd	4
5	Ru(acac)₃	4	<1	2
6	Pt(acac) <sub>2</sub>	12	nd	4
7	AuBr <sub>3</sub>	6	nd	6
8	IrCl <sub>3</sub> .nH <sub>2</sub> O	18	5	5
9	None	1	nd	nd

<sup>a</sup> Reaction conditions: Catalyst (metal: 0.5 mol),  $K_2CO_3$  (0.5 mol), 1a (1 mmol),  $CH_3CN$  (2 mL),  $CO_2$  (1 atm),  $50 \circ C$ , 2 h. Conversions and yields were based on 1a and determined by GC analysis using biphenyl as an internal standard. nd = not detected. 3a = 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane.

### Table 2

Hydrosilylation of CO<sub>2</sub> with **1a** using various Rh-based catalysts.<sup>a</sup>

Entry	Catalyst	Conv. (%)	Yield (%)	
			2a	3a
1	Rh <sub>2</sub> (OAc) <sub>4</sub>	>99	90	8
2	RhCl <sub>3</sub> .nH <sub>2</sub> O	7	<1	2
3	[RhCl <sub>2</sub> Cp*] <sub>2</sub>	10	<1	5
4	[Rh(cod)Cl] <sub>2</sub>	5	nd	2
5	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl	16	8	6
6	$[Rh(CO)_2Cl]_2$	3	nd	<1
7	Rh <sub>6</sub> (CO) <sub>16</sub>	2	nd	<1

<sup>a</sup> Reaction conditions: Catalyst (metal: 0.5 mol%), base (0.5 mol%), **1a** (1 mmol), CH<sub>3</sub>CN (2 mL), CO<sub>2</sub> (1 atm), 50 °C, 2 h. Conversions and yields were based on **1a** and determined by GC analysis using biphenyl as an internal standard. nd = not detected. **3a** = 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane.

organic N-donor bases such as triethylamine ( $Et_3N$ ) and 1,8diazabicyclo[5.4.0]undec-7-ene (DBU) were not effective (Table 3). Among the solvents examined, acetonitrile was the best solvent for the present hydrosilylation (Table 4). Therefore, the hydrosilylation reactions were hereafter carried out with  $Rh_2(OAc)_4$  and  $K_2CO_3$  in acetonitrile.

### 3.2. Hydrosilylation of CO<sub>2</sub> with various hydrosilanes

Next, the scope of the present  $Rh_2(OAc)_4$ -catalyzed hydrosilylation of  $CO_2$  (1 atm) was investigated for a range of structurally diverse hydrosilanes (Table 5). The reaction efficiently proceeded even in 1 atm of  $CO_2$ , and the corresponding silv formates were

#### Table 5

Transformation of various silanes to silyl formates using  $Rh_2(OAc)_4$  and  $K_2CO_3$ .<sup>a</sup>

R₃SiH	+	CO <sub>2</sub>	KI <sub>2</sub> (OAC) <sub>4</sub> K <sub>2</sub> CO <sub>3</sub>	R <sub>3</sub> Si	+	R <sub>3</sub> SiOSiR <sub>3</sub>
1		1 atm		2		3

a	bl	le	3	

### Hydrosilylation of $\mathrm{CO}_2$ with $\mathbf{1a}$ using various bases.^a

Entry	Catalyst	Conv. (%)	Yield (%)	
			2a	3a
1	K <sub>2</sub> CO <sub>3</sub>	>99	90	8
2	Cs <sub>2</sub> CO <sub>3</sub>	>99	90	8
3	K <sub>3</sub> PO <sub>4</sub>	>99	77	23
4	KOt-Bu	94	81	13
5	DBU	15	4	11
6	Et₃N	3	nd	3
7	None	<1	nd	nd

<sup>a</sup> Reaction conditions: Rh<sub>2</sub>(OAc)<sub>4</sub> (0.25 mol%), base (0.5 mol%), **1a** (1 mmol), CH<sub>3</sub>CN (2 mL), CO<sub>2</sub> (1 atm), 50 °C, 2 h. Conversions and yields were based on **1a** and determined by GC analysis using biphenyl as an internal standard. nd = not detected. **3a** = 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane.

Table 4	
Effect of solvents on the hydrosilylation of CO <sub>2</sub> with <b>1a</b> .	a

Entry	Solvent	Conv. (%)	Yield (%)		
			2a	3a	
1	CH₃CN	>99	90	8	
2	Acetone	43 <sup>b</sup>	35	6	
3	1,4-Dioxane	<1	nd	<1	
4	THF	<1	nd	<1	
5	1,2-Dichloroethane	<1	nd	<1	
6	<i>n</i> -Hexane	<1	nd	nd	

<sup>a</sup> Reaction conditions:  $Rh_2(OAC)_4$  (0.25 mol%),  $K_2CO_3$  (0.5 mol%), **1a** (1 mmol), solvent (2 mL),  $CO_2$  (1 atm), 50 °C, 2 h. Conversions and yields were based on **1a** and determined by GC analysis using biphenyl as an internal standard. nd = not detected. **3a** = 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane.

<sup>b</sup> The hydrosilylation of acetone proceeded (2% yield).

obtained in moderate to high yields (53–90% yields, except for triisopropylsilane, **1h**). The transformation of dimethylphenylsilane derivatives (**1a–1d**) with electron-donating as well as electronwithdrawing *para*-substituents efficiently proceeded to attain high yields of the corresponding substituted silyl formates for 2 h (84–90% yields, Table 5, entries 1–4), though the reactivities were slightly different. The catalytic activity of  $Rh_2(OAc)_4/K_2CO_3$  for the hydrosilylation of  $CO_2$  with dimethylphenylsilane derivatives (**1a–1c**) increased in the order of **1b** (*p*-OMe, 0.78) < **1a** (*p*-H, 1.00) < **1c** (*p*-Cl, 1.67), where the values in the parentheses are the conversion ratios for competitive hydrosilylation (at 50 °C for 30 min), and the conversion of **1a** is taken as unity. This order suggests formation of a negatively charged transition state. The steric effect of substrates was very significant. The hydrosilylation with relatively bulky hydrosilanes such as diphenylmethylsilane (**1e**),

•		2	3					
Entry	Substrate			Temp. [°C]	Time [h]	Conv. [%]	Yield [%]	
							2	3
1	Me	X = H	1a	50	2	>99	90	8
2	х— У— ѕі—н	X=OMe	1b	50	2	97	84	13
3		X = Cl	1c	50	2	>99	85	12
4	IVIE	$X = CF_3$	1d	50	2	>99	87	13
5	Ph <sub>2</sub> MeSiH		1e	50	24	99	83	11
6	Ph <sub>3</sub> SiH		1f	70	24	88	53	nd <sup>b</sup>
7	Et₃SiH		1g	70	12	>94	72	10
8	<i>i</i> -Pr₃SiH		1h	80	24	<1	nd	nd

<sup>a</sup> Reaction conditions: Rh<sub>2</sub>(OAc)<sub>4</sub> (0.25 mol%), K<sub>2</sub>CO<sub>3</sub> (0.5 mol%), silane (1 mmol), CH<sub>3</sub>CN (2 mL), CO<sub>2</sub> (1 atm). Conversions and yields were based on silanes and determined by GC analysis using biphenyl as an internal standard. nd = not detected.

<sup>b</sup> The corresponding disiloxane (**3f**) was possibly formed but could not be detected by GC because of the low solubility in any solvents.

### Table 6

One-pot synthesis of formamides from CO<sub>2</sub>, **1a**, and nucleophiles (amines and aniline).<sup>a</sup>



<sup>a</sup> *Reaction conditions*: (i) Rh<sub>2</sub>(OAc)<sub>4</sub> (0.25 mol%), K<sub>2</sub>CO<sub>3</sub> (0.5 mol%), **1a** (1 mmol), CH<sub>3</sub>CN (2 mL), CO<sub>2</sub> (1 atm), 50 °C, 2 h; (ii) nucleophile (1 mmol), 50 °C. Yields were based on **1a** and determined by GC and <sup>1</sup>H NMR analyses. Consequently, **1a** was quantitatively converted into **3a** in all cases.

triphenylsilane (**1f**), and triethylsilane (**1g**) required longer reaction times and/or a higher reaction temperature (70 °C) to attain the corresponding silyl formates in moderate to high yields (84–90% yields, Table 5, entries 5–7). The reaction with **1h** hardly proceeded likely due to the steric hindrance of the isopropyl groups (Table 5, entry 8).

# 3.3. Reaction of dimethylphenylsilyl formate with various nucleophilic reagents

Finally, we turned out our attention to the reaction of the silyl formate (**2a**, produced through the hydrosilylation of  $CO_2$ ) with various nucleophilic reagents. The overall conversion of  $CO_2$  to carbonyl compounds was accomplished as a one-pot procedure by a simple addition of nucleophilic reagents to the reaction solution

after the hydrosilylation of  $CO_2$  with **1a** was completed. Various kinds of nucleophilic reagents such as common amines, aniline, water, and the Grignard reagent could be utilized to produce the corresponding formyl compounds and/or formic acid.

In the case of common amines and aniline, a silyl formate **2a** could act as a "formyl synthon" to produce the corresponding formamides with co-production of formic acid (Table 6). We confirmed that formic acid is co-produced through the reactions in Scheme 2.

It is noted that the reaction of amines with "methyl formate" hardly proceeded under the conditions described in Table 6 [48]. Various kinds of amines could be utilized as nucleophiles, and total yields of formamides (**5a–5g**) and formic acid based on **1a** were high in all cases (86–91% yields). Secondary amines including aliphatic (**4a** and **4b**) and benzylic (**4c**) ones could be converted



Scheme 2. The reaction of 2a with amines to produce formamides and formic acid.



**Scheme 3.** Synthesis of formic acid from **1a**, CO<sub>2</sub>, and water. After the hydrosilylation of CO<sub>2</sub> with **1a** under the conditions described in Table 1 was completed, water (5 mmol) was added to the reaction solution, and then the mixture was stirred at room temperature for 0.5 h. Consequently, **1a** was mainly converted into dimethylphenylsilanol (77% yield based on **1a**).



**Scheme 4.** Synthesis of benzhydrol from **1a**,  $CO_2$ , and PhMgBr. After the hydrosilylation of  $CO_2$  with **1a** under the conditions described in Table 1 was completed, the solvent was removed by evaporation, followed by the addition of THF (1 mL). Then, the THF solution of PhMgBr (1.10 M, 2 mL) was added to the reaction mixture and stirred at room temperature for 1 h. Consequently, **1a** was mainly converted into dimethylphenylsilanol (84% yield based on **1a**).

into *N*,*N*-disubstituted formamide derivatives (Table 6, entries 1–3). An aliphatic primary amine (**4d**) also gave the corresponding *N*-alkyl formamide (Table 6, entry 4). In the case of primary benzylic amines (**4e**–**4g**), the electronic effect of substituents was not significant, and the formylation efficiently proceeded, giving the corresponding formamides (Table 6, entries 5–7). The formylation of relatively less nucleophilic aniline (**4h**) also proceeded to give *N*-phenylformamide, while a longer reaction time (**18** h) was required in comparison with common amines (1–4h) (Table 6, entry 8).

Besides amines and aniline, water could act as a nucleophile [41,42]; the addition of water to the solution containing **2a** yielded formic acid in 90% yield (Scheme 3). The reaction of **2a** with the Grignard reagent produced the corresponding secondary alcohol, while the Grignard reaction of  $CO_2$  generally produces the corresponding carboxylic acid. When the reaction of **2a** with two equivalents of the Grignard reagent of PhMgBr was carried out, benzhydrol was obtained in 77% yield (Scheme 4). In this case, a silyl formate **2a** would also act as a formyl synthon to form benzaldehyde proceeds to give benzhydrol as a final product.

### 4. Conclusion

In summary, we reported herein two important and interesting findings of the efficient hydrosilylation of  $CO_2$  and the utilization of silyl formates. A simple combination of  $Rh_2(OAc)_4$  and inorganic O-donor bases efficiently promoted hydrosilylation of  $CO_2$  under mild conditions (1 atm, 50–70 °C). Various kinds of hydrosilanes could be utilized for the present hydrosilylation. The silyl formate produced through the hydrosilylation of  $CO_2$  could be utilized for synthesis of

value-added products. The reaction of the silyl formate with amines (including aniline) produced the corresponding formamides and formic acid. Water and the Grignard reagent could also be utilized as nucleophilic reagents to react with the silyl formate, producing formic acid and the corresponding secondary alcohol (via an aldehyde), respectively.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.10.014.

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