

Homogeneously catalysed reduction of carbon dioxide with silanes: a study on solvent and ligand effects and catalyst recycling

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This work is dedicated to Prof. Dr. Eckhard Dinjus on occasion of his 60th birthday.

Abstract

The ruthenium-catalysed hydrosilylation of CO₂ was studied with respect to the influences of the solvent present and different co-ligands used. Nitriles exhibit favourable properties as a solvent for this reaction. The catalytic activity of [RuCl(MeCN)₅]⁺[(*trans*)-RuCl₄(MeCN)₂][−] as pre-catalyst may be increased by additional phosphine ligand. Further N-donor substituents in the phosphine do not result in an increased activity. The homogeneous catalyst may be recycled effectively by a thermal separation of the reaction product. For this procedure, the catalytic activity kept constant during 10 runs.

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1. Introduction

Modern chemistry to an increasing extent requires new strategies for the resources-saving utilisation of raw materials, ecologically acceptable manufacturing methods, and innovative processes. These chemistry-specific aspects of sustainable research and technology are summarised by the term of green chemistry [1]. In this connection, it is looked for possibilities of using carbon dioxide as an inexpensive and widely available raw material for chemical syntheses [2–4]. One approach pursued aims at an alternative synthesis of monomer building blocks for silicones.

Recently, it was shown that the ruthenium-catalysed hydrosilylation of carbon dioxide provides synthetic access to such monomers [5]. Other examples for the hydrosilylation were previously reported [6–8]. Apart from its applicability to different substituted tertiary silanes, synthesis of potential D- and T-monomer building blocks by the reaction of secondary and primary silanes, respectively, was shown [5,9]. Similar to the technically established acetoxysilanes (H₃CCO₂)_nSiR_{4−n}, the formoxysilanes (HCO₂)_nSiR_{4−n}

accessible by this synthetic approach (Scheme 1) undergo a remarkably fast polycondensation to siloxane-type polymers that is already been induced by atmospheric humidity [5,10]. In comparison to conventional esterifications of formic or acetic acid derivatives, the essential advantage of the approach described here is that no salts are formed as by-products and no water needs to be separated after the reaction.

An important aspect to make this hydrosilylation route technically feasible is catalytic activity. The highest turn-over-number (TON; $n_{\text{substrate}}/n_{\text{metal}}$) and turn-over-frequency (TOF; after complete conversion; $n_{\text{substrate}}/(n_{\text{metal}} \times h)$) reported so far amount to 465 and 235 [5], respectively, which certainly is not sufficient. Here, the influence of the solvent on the activity of the catalytic system as well the influence of additional P- and P,N-donor ligands shall be described. Moreover, a procedure for catalyst recycling shall be presented.

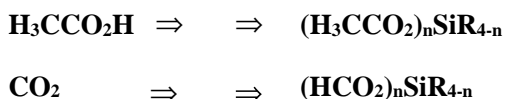
2. Experimental

2.1. Reagents

CO₂ was purchased from Linde (4.8) and used without further purification. PPh₃, PCy₃ and P(*i*-Pr)₃ were

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Scheme 1.

purchased from Strem Chemicals. Et₃SiH **1a** from Lancaster and Me₂PhSiH **1b** from Aldrich. The pre-catalyst Ru₂Cl₅(MeCN)₇ **4** was prepared according to the method developed earlier [5]. The hemilabile co-ligands (see Table 3) of the types R₂P(CH₂)_nCN and 2-[R₂P(CH₂)_m]C₅H₅N were prepared according to published procedures [11,12].

2.2. NMR spectra

The spectra were acquired on a Bruker AC 200 spectrometer (¹H NMR: 200.13 MHz; ¹³C NMR 50.32 MHz; ²⁹Si NMR: 39.76 MHz). Chemical shifts (δ) are given in ppm and were referenced to internal or external SiMe₄ (¹H, ¹³C, ²⁹Si), respectively.

2.3. General procedures

All manipulations were carried out under an atmosphere of dry argon. All solvents were dried and distilled before use according to literature procedures. They were stored under argon after distillation. Commercially available reagents were used as received and freshly degassed. Reactions under CO₂ pressure were performed in 80 cm³ stainless steel reactors equipped with manometer, thermo couple and magnetic stirrer. Yields of formoxysilanes were based on the corresponding starting silanes. By-products were identified by ¹H and ²⁹Si NMR spectroscopy. The reaction parameters are set to values, that establish conditions favourable to compare the experimental results. For example, when studying ligand effects, conditions are chosen for incomplete conversion without ligands.

2.4. Hydrosilylation with different solvents

RuCl₃·nH₂O (0.0990 g, 0.4 mmol) is dissolved or suspended in the specified quantity of the solvent (see Table 1). The solution or suspension is transferred to the reactor. Et₃SiH **1a** (4.65 g, 40.0 mmol) and CO₂ (27.4 g, 0.62 mol) are added. The delivered amount of CO₂ is measured as mass difference of the CO storage vessel. The reaction mixture is vigorously stirred at 373 K at a pressure ranging between 70 and 88 bar for 20 h. Unreacted CO₂ is carefully removed by stirring at 298 K. Values of conversion and selectivity are determined by ¹H NMR with a relative error of ±3%. Preparative purification may be carried out by removal of the volatile components in vacuum of less than 8 mbar at 298 K, followed by distillation affording Et₃Si(O₂CH) **2a** (b.p.: 428 K). ¹H NMR data (CDCl₃): 8.09 (s, 1H, O₂CH), 0.97 (m, 9H, CH₃), 0.77 (m, 6H, CH₂). ¹³C{¹H} NMR data

(CDCl₃): 160.9 (O₂CH), 6.2 (CH₃), 4.4 (CH₂). ²⁹Si{¹H} NMR data (CDCl₃): 27.6.

2.5. Hydrosilylation with different co-ligands

Analogous to the procedure described for the synthesis of **2a**, Ru₂Cl₅(MeCN)₇ **4** (0.0269 g, 0.0401 mmol), dissolved in 30 cm³ MeCN, the specified quantity of the co-ligand (see Tables 2 and 3), Me₂PhSiH **1b** (5.45 g, 40 mmol) and CO₂ (3.5 g, 80 mmol) were reacted at 313 K at a pressure of 8 bar for 20 h to afford Me₂PhSi(O₂CH) **2b** (b.p.: 367 K at 23 mbar). Yields as listed in Tables 2 and 3 are based ¹H NMR analyses of the raw product solutions. ¹H NMR data (CDCl₃, 298 K): 8.12 (s, ¹H, O₂CH), 7.65 (complex pattern, 2H, Ph), 7.43 (complex pattern, 3H, Ph), 0.63 (s, 6H, CH₃). ¹³C{¹H} NMR data (CDCl₃, 298 K): 160.8 (O₂CH), 134.8 (C_i), 133.5 (C_o), 130.4 (C_p), 128.0 (C_m), -1.7 (CH₃). ²⁹Si{¹H} NMR data (CDCl₃, 298 K): 14.2.

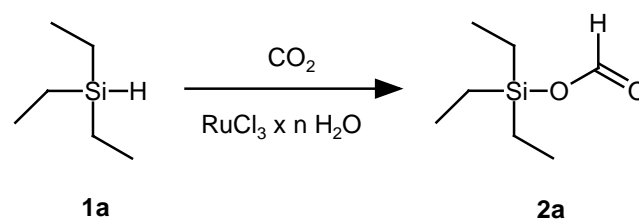
2.6. Hydrosilylation with catalyst recycling

In the same way as described for the synthesis of **2b**, Ru₂Cl₅(MeCN)₇ **4** (0.0269 g, 0.0401 mmol), dissolved in 10 cm³ MeCN, Me₂PhSiH **1b** (5.45 g, 40 mmol) and CO₂ (3.5 g, 80 mmol) were reacted at 353 K at a pressure of 14 bar for 2 h. After decompressing, the MeCN is removed at 298 K in vacuum (10 mbar). Further distillation affords analytically pure Me₂PhSi(OOCH) **2b**. The residue is taken up with another 30 cm³ MeCN to be transferred back into the reactor for the next hydrosilylation experiment. In this way, 10 successive experiments were performed. Yields of **2b** (**3b**) based ¹H NMR analyses were 98 (2), 97 (3), 96 (4), 96 (4), 95 (5), 94 (6), 92 (8), 91 (9), 91 (9), and 90% (10%). The total yield of isolated **2b** amounts to 66.61 g (369.5 mmol, 92.4%), corresponding to a TON of 4619.

3. Results

3.1. Investigation of solvent effects

RuCl₃·nH₂O is the simplest known pre-catalyst for the hydrosilylation of CO₂ to formoxysilanes [5]. It was to be found out whether solvents other than acetonitrile could be used in an economically efficient manner. Solvent dependency was studied using the reaction of Et₃SiH (**1a**) at



Scheme 2.

Table 1
Conversion and selectivity for the hydrosilylation of CO₂ with HSiEt₃ in different solvents^a

Entry	Solvents	Conversion (1a) (%)	Selectivity (2a) (%)	Selectivity (3a) (%)
1	–	13	0	56
2	MeCN	>99	91	9
3	MeCN ^b	>99	97	3
4	MeCN ^{b,c}	>99	98	2
5	MeCN ^{b,d}	99	98	2
6	MeCN ^{b,e}	30	66	34
7	C ₂ H ₅ CN	>99	88	12
8	PhC ₂ H ₄ CN	>99	83	17
9	Benzene ^f	6	0	47
10	Pyridine	3	0	>99
11	CH ₂ Cl ₂ ^g	23	0	17
12	Tetrahydrofuran	59	0	9
13	Propylene carbonate	24	0	87
14	HCONMe ₂	>99	0	98

^a General conditions: 4.65 g (40 mmol) HSiEt₃, 27.4 g (0.62 mol) CO₂, 99.0 mg (40 μmol) RuCl₃ hydrate, V_{MeCN} = 30 cm³, t = 20 h, T = 373 K; refer also to Section 2.

^b T = 373 K.

^c V_{MeCN} = 10 cm³.

^d V_{MeCN} = 1 cm³.

^e V_{MeCN} = 0.2 cm³.

^f 53% Et₃SiOH formed.

^g 83% Et₃SiCl formed.

100 °C as an example (Scheme 2). The results are listed in Table 1.

By the reaction of **1a** without solvent, formoxysilane **2a** is not formed, the main product of the reaction being Et₃SiOSiEt₃ (**3a**) (Table 1, entry 1). In nitriles **1a** is completely converted (entries 2, 7, 8). The selectivity for **2a** is between 83 and 91%. Generally, this finding allows the conclusion to be drawn that nitriles may be selected due to their boiling point to enable an easy separation of the reaction product. In benzene, pyridine, and dichloromethane, no **2a** is formed (entries 9–11). The product mixtures produced by the reactions in benzene and pyridine contain high amounts of unreacted **1a** in addition to 6 and 3% of **3a**, respectively.¹ In CH₂Cl₂ (entry 11), Et₃SiCl is the main product, probably as a result of the presence of the solvent.

In tetrahydrofuran, a remarkable reaction behaviour can be observed (entry 12). No **2a** is produced, but obviously a ring opening polymerisation of tetrahydrofuran takes place. Analysis of the raw product solution by ¹H NMR shows two broad resonances at 3.50 and 1.70 ppm (ratio 1/1) apart from the two multiplets of the methylene protons of tetrahydrofuran at 3.75 and 1.90 ppm (ratio 1/1). By measuring the same sample again after 10 days at 25 °C, a significantly increased intensity of the broad signals is found and the solution also exhibits a higher viscosity. This may be explained

¹ This result disagrees with the investigation performed by Koinuma et al., according to which the reaction of Et₂MeSiH in benzene with RuCl₂(PPh₃)₃ as catalyst yielded 14% Et₂MeSiOCHO. Refer to [8].

by a progressing polymerisation at this temperature, which has probably been initiated by a cationic silyl species, analogously as reported earlier by Hrkach and Matyjaszewski [13].

Although carbon dioxide is highly soluble in propylene carbonate (entry 13) and *N,N*-dimethylformamide (entry 14), no detectable amounts of **2a** are found. An insufficient solubility of the substrate under reaction conditions is assumed to be the reason. When the reactions are performed in an autoclave with a window, two liquid phases exist, the solvent phase with the dissolved catalyst and a second phase which after sampling was identified to be almost pure silane.

Further investigations focused on the influence of the absolute solvent amount on conversion and selectivity. In Table 1, entries 3–5, it is shown that the increasing substrate/solvent ratio in the concentration range of 0.75–40 mol l⁻¹ does not lead to any significant changes. Even with very little acetonitrile (entry 13), corresponding to a substrate concentration of 200 mol l⁻¹, 30% conversion with 66% selectivity to **2a** takes place. This indicates a potential role of nitriles as complex ligands in the intermediates of the catalytic cycle (see also below).

3.2. Influence of monodentate donor ligands

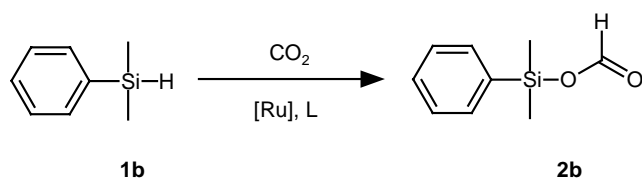
The complex [RuCl(MeCN)₅]⁺[(*trans*)-RuCl₄(MeCN)₂]⁻ (**4**) which in preliminary investigations was found to be an efficient catalyst for the hydrosilylation of CO₂ is synthesised from RuCl₃ [5]. Studies focused on whether the pre-catalyst **4** is suitable for forming in situ catalysts of higher activity with certain co-ligands. The experiments for the conversion of Me₂PhSiH (**1b**) into Me₂PhSiOCHO (**2b**) (Scheme 3) using monodentate nitrogen and phosphorus donor ligands are listed in Table 2.

To ensure a good comparability of the experiments, mild conditions (313 K) were selected. Under these conditions, without additional ligand, a rate of conversion into **2b** of 20% was reached, which corresponds to a TON of 80 (Table 2, entry 1). Addition of pyridine (entries 2, 3)

Table 2
Hydrosilylation of CO₂ with Me₂PhSiH using catalyst **4** with monodentate co-ligands^a

Entry	Ligand	Ligand/Ru	Yield 2b (%)	TON
1	–	0	20	80
2	Pyridine	1	12	59
3	Pyridine	2	2	9
4	P(<i>i</i> -Pr) ₃	0.33	84	420
5	P(<i>i</i> -Pr) ₃	1	86	432
6	P(<i>i</i> -Pr) ₃	2	73	366
7	PPh ₃	1	65	327
8	PPh ₃	2	20	102
9	PCy ₃	1	70	350

^a General conditions: 5.45 g (40 mmol) Me₂PhSiH **1b**, 3.5 g (0.08 mol) CO₂, 269.0 mg (40 μmol) Ru₂Cl₅(MeCN)₇ **4**, V_{MeCN} = 30 cm³, t = 20 h, T = 313 K; refer also to Section 2.



Scheme 3.

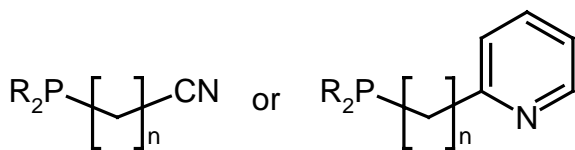
results in a partial deactivation of the catalyst. Contrary to this, the addition of phosphines generally allows for catalytic activities increased by up to a factor of 5.4 (entry 5). The TON varies between 327 and 432 with one equivalent $\text{P}(i\text{-Pr})_3$, PPh_3 or PCy_3 (entries 5, 7, 9). Remarkable is the fact that a non-stoichiometric amount of $\text{P}(i\text{-Pr})_3$, related to ruthenium, already is sufficient for reaching a high activity (entry 4). A ligand/ruthenium ratio of 2 does not lead to a further increase in activity (entries 6, 8).

These results reveal that a modification of the catalyst with phosphine ligands leads to increased catalytic activities under mild reaction conditions already. These findings are of particular interest to the reaction of temperature-labile silane derivatives with carbon dioxide.

3.3. Influence of hemilabile donor ligands

From mechanistic considerations, the dissociation or coordination of at least one ligand may be expected to offer or occupy the participating coordination sites at the ruthenium centre. To find out whether this can be achieved by using potential hemilabile coordinating ligands, investigations covered such ligands with a strong binding phosphine group and a more or less weak coordinating N-donor group in the backbone. The tested ligands differ in their basicity at the phosphorus, their distance between both donor groups, and their N-donor group, e.g. nitrile or 2-pyridyl (Scheme 4) [11,12].

Similar to the results discussed above (refer to Table 2), catalyst systems utilising basic phosphines with an equimolar P/Ru ratio (Table 3, entries 1–3, 6, 9) exhibit good activities. Also with $\text{Ph}_2\text{P}(\text{CH}_2)_6\text{CN}$ as co-ligand an effective catalyst is formed (entry 7). Higher P/Ru ratios result in a significantly decreased activity (entries 4, 5, 8, 11, 14, 17), even more than by use of monodentate phosphines (Table 2). Effects due to the presence of additional N-donor groups in the ligand backbone cannot be noted. For example, the addition of one equivalent of $\text{P}(i\text{-Pr})_3$ to pre-catalyst 4 (Table 2,



Scheme 4.

Table 3

Hydrosilylation of CO_2 with Me_2PhSiH using catalyst 4 with hemilabile co-ligands^a

Entry	Ligand	P/Ru	Yield 2b (%)	TON
1	$(i\text{-Pr})_2\text{P}(\text{CH}_2)_3\text{CN}$	1	84	419
2	$(i\text{-Pr})_2\text{P}(\text{CH}_2)_5\text{CN}$	1	86	430
3	$(i\text{-Pr})_2\text{P}(\text{CH}_2)_6\text{CN}$	1	79	397
4	$(i\text{-Pr})_2\text{P}(\text{CH}_2)_6\text{CN}$	2	17	87
5	$(i\text{-Pr})_2\text{P}(\text{CH}_2)_6\text{CN}$	4	6	33
6	$(i\text{-Pr})_2\text{P}(\text{CH}_2)_8\text{CN}$	1	79	394
7	$\text{Ph}_2\text{P}(\text{CH}_2)_6\text{CN}$	1	86	428
8	$\text{Ph}_2\text{P}(\text{CH}_2)_6\text{CN}$	2	3	14
9	$\text{Cy}_2\text{P}(\text{CH}_2)_3\text{CN}$	1	75	376
10	$2\text{-}[(i\text{-Pr})_2\text{P}]\text{C}_5\text{H}_5\text{N}$	1	62	310
11	$2\text{-}[(i\text{-Pr})_2\text{P}]\text{C}_5\text{H}_5\text{N}$	2	36	180
12	$2\text{-}[(i\text{-Pr})_2\text{PCH}_2]\text{C}_5\text{H}_5\text{N}$	1	26	129
13	$2\text{-}[(i\text{-Pr})_2\text{P}(\text{CH}_2)_6]\text{C}_5\text{H}_5\text{N}$	1	49	247
14	$2\text{-}[(i\text{-Pr})_2\text{P}(\text{CH}_2)_6]\text{C}_5\text{H}_5\text{N}$	2	6	31
15	$2\text{-}[(i\text{-Pr})_2\text{P}(\text{CH}_2)_7]\text{C}_5\text{H}_5\text{N}$	1	25	127
16	$2\text{-}[\text{Ph}_2\text{P}(\text{CH}_2)_6]\text{C}_5\text{H}_5\text{N}$	1	53	266
17	$2\text{-}[\text{Ph}_2\text{P}(\text{CH}_2)_6]\text{C}_5\text{H}_5\text{N}$	2	3	13

^a General conditions: 5.45 g (40 mmol) Me_2PhSiH **1b**, 3.5 g (0.08 mol) CO_2 , 269.0 mg (40 μmol) $\text{Ru}_2\text{Cl}_5(\text{MeCN})_7$ **4**, $V_{\text{MeCN}} = 30 \text{ cm}^3$, $t = 20 \text{ h}$, $T = 313 \text{ K}$; refer also to Section 2.

entry 5) leads to the same activity than it is reached with $(i\text{-Pr})_2\text{P}(\text{CH}_2)_5\text{CN}$ (Table 3, entry 2). Interestingly, ligands with pyridyl moieties may yield catalysts of excellent activity whereas pyridine as solvent causes a nearly complete deactivation.

3.4. Investigation of catalyst recycling

For processes utilising expensive catalysts for the synthesis of low-priced intermediates, recycling of the active transition metal or the active catalyst is of particular importance. In homogeneous catalysis established procedures are based on extraction or thermal separation of the products from the catalyst or benefit from multi-phase catalysis with modified homogeneous catalysts. Based on the example of the synthesis of **2b**, it was investigated whether a repeated use of the catalyst is possible after distillation of the reaction product. For this purpose, the following series of experiments was performed. Using the pre-catalyst **4**, the silane **1b** is reacted in acetonitrile solution. Next, the solvent is separated by distillation followed by the distillation of the product **2b**. The residue is suspended again in acetonitrile and re-used for the next conversion. The results of 10 successive experiments are represented in Fig. 1.

With this procedure, the by-product $\text{Me}_2\text{PhSiOSiMe}_2\text{Ph}$ (**3b**) is enriched, because it is not separated. However, product formation is not affected. During all experiments, no significant deactivation of the catalyst is found. From the added product distillates of all single experiments, **2b** is obtained in an analytical pure form with a total yield of 92%. With optimised reactions conditions used here, the TOF is 230 h^{-1} .

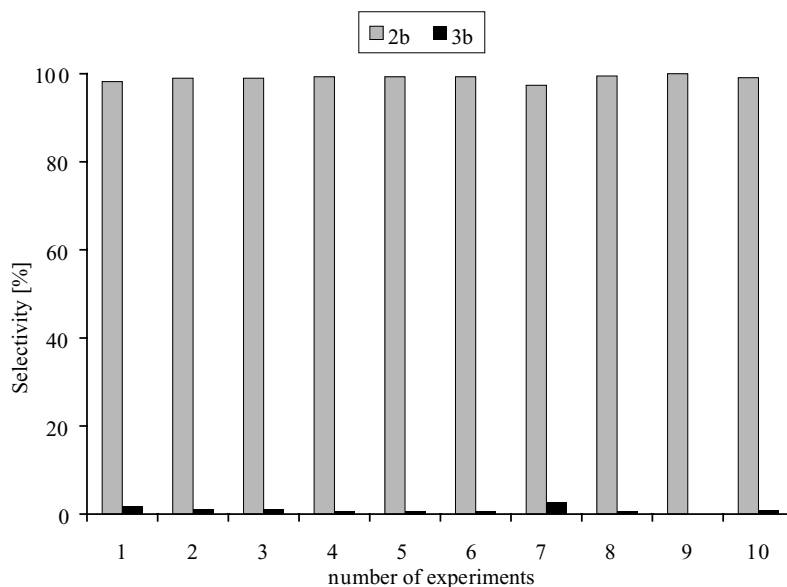


Fig. 1. Selectivities in successive experiments at 353 K (each 2 h) with catalyst recycling. The selectivities are determined based on the amount of newly formed **3b**. Conditions: 5.45 g (40 mmol) Me_2PhSiH **1b**, 3.5 g (0.08 mol) CO_2 , 269.0 mg (40 μmol) $\text{Ru}_2\text{Cl}_5(\text{MeCN})_7$ **4**, $V_{\text{MeCN}} = 10 \text{ cm}^3$, $t = 2 \text{ h}$, $T = 313 \text{ K}$; refer also to Section 2.

4. Conclusion

For the hydrosilylation of carbon dioxide nitriles were shown to be the preferred solvents. The catalytic activity of ruthenium catalysts effectively may be enhanced by additional certain phosphine ligands. Therefore in concluding studies preformed ruthenium phosphine complexes will be synthesised and compared to the activities of in-situ catalysts investigated in this work. It is also expected that even far better TON's as those of 4600 reached here will be achieved, if additional recycling processes are carried out.

Acknowledgements

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