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Hydrogenation of CO_2

Hydrogenation of Carbon Dioxide to Methanol by Using a Homogeneous Ruthenium–Phosphine Catalyst**

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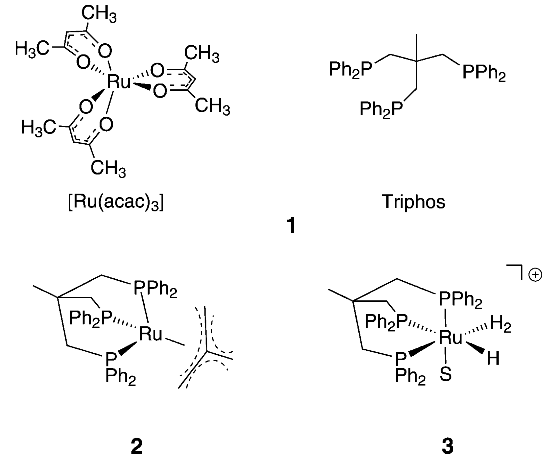
Dedicated to Professor David Milstein on the occasion of his 65th birthday

The increasing global energy consumption based on fossil resources and the entailed production of greenhouse gases demands for new strategies of carbon management. Additionally, the depletion of the world-wide oil, gas, and coal reserves stresses the need for alternative carbon sources for the production of fuels and chemicals. In this context, the sustainable use of carbon dioxide as carbon resource has been envisaged by chemists and chemical engineers for decades, and the field has seen a highly dynamic development recently.[1–3] The effective hydrogenation of carbon dioxide to methanol could contribute particularly strongly to the development of a low-carbon economy, where methanol serves as energy vector and offers a versatile entry into the chemical supply chain.[4]

The current production of methanol is based on syngas (CO/H_2) derived from fossil resources using heterogeneous catalysts at elevated temperatures and pressure.[4,5] Small amounts of CO_2 are added to the feedstock stream to balance the C/H ratio. The direct hydrogenation of only carbon dioxide to methanol using heterogeneous catalysts has been demonstrated and is investigated intensively for larger scale implementation.[6,7] In sharp contrast, the conversion of CO_2 with H_2 into CH_3OH using a single molecularly defined homogeneous catalyst remains as yet elusive. Catalytic reduction of CO_2 to the methanol stage has been achieved only with stoichiometric amounts of reducing agents, such as boranes or silanes.[8] In their seminal work on ruthenium(II) pincer complexes, Milstein et al. developed the first homogeneous catalysts that are able to hydrogenate carbonic acid derivatives and formates to methanol.[9] Based on these findings, indirect routes from carbon dioxide to methanol via a stepwise conversion of such intermediates were proposed. The principle feasibility of this approach was demonstrated recently by Huff and Sanford, where the hydrogenation of carbon dioxide to methanol could be accomplished in a cascade reaction with different homogeneous catalyst via formic acid and methyl formate intermediates.[10] The multicomponent catalytic system required a complex mixture of three different catalysts and partial incompatibility made a spatial separation of reaction steps essential resulting in a maximum turnover number (TON) of 21 equivalents of methanol per ruthenium center.

Herein, we describe the homogenously catalyzed hydrogenation of CO_2 to methanol using a homogeneous transition-metal catalyst system based on a single ruthenium phosphine complex. The starting point for our investigation was a recently established robust multifunctional ruthenium system, which provided an excellent catalyst for the hydrogenation of carboxylic acids and their derivatives to the corresponding alcohols.[11–13] It comprises an in situ system **1** composed of [Ru(acac)$_3$] and the tridentate ligand Triphos (Triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) in the presence of additional organic acid (Scheme 1).[11a] Mechanistic investigations suggested that species of type **3** comprising the facially coordinated tripodal ligand facilitate hydride transfer and protonolysis as key steps for the addition of hydrogen to the carboxylate functional group.[11b] In the



Scheme 1. Precursor complexes **1** and **2** used in combination with organic acids in the hydrogenation of formate ester and CO_2 to methanol and proposal for a tentative active species **3** (S = solvent or substrate).

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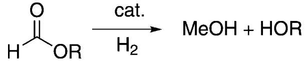
present study, the ruthenium(II)-complex [(Triphos)Ru(TMM)] **2** (TMM = trimethylenemethane) was also used as isolated direct precursor to such species in the presence of hydrogen and organic acids.[14] In a first set of experiments, both catalyst systems were tested in the hydrogenation of formate ester to liberate methanol (Table 1).

Table 1: Catalytic hydrogenation of formate esters.[a]



Entry	Cat.	Acid[b]	R	pH_2[c] [bar]	TON[d]
1	**1**[e]	MSA	Et	50	75
2	**1**[e]	MSA	Me	50	74
3	**2**	–	Et	30	5
4	**2**	MSA	Et	30	77

[a] Reaction conditions: ruthenium complex (25 μmol), substrate (2.5 mmol), THF (2 mL), 140 °C, 24 h. [b] 38 μmol (1.5 equiv) methanesulfonic acid (MSA). [c] At room temperature. [d] TON = mol MeOH/mol catalyst. [e] 50 μmol (2 equiv) Triphos.

The hydrogenation of ethyl formate occurred smoothly at 140 °C and moderate H_2 pressures using the catalyst system **1** and full conversion corresponding to a TON of 75 was obtained (Table 1, entry 1). Methyl formate was hydrogenated in an analogous manner giving only methanol as product with a TON of 74 (Table 1, entry 2). Using the isolated precursor complex **2** lead to TONs of 5 without and 77 with the acidic additive, further supporting structures of type **3** as active species in this catalytic transformation (Table 1, entries 3 and 4).

Ruthenium–phosphine transition-metal complexes are well-established for the hydrogenation of CO_2 to formic acid and its derivatives.[15] Interestingly, the addition of hydrogen to CO_2 with rhodium–phosphine catalysts has been rationalized on the basis of a similar hydride-transfer/protonolysis sequence, as suggested for the carboxylate reduction with **3**.[16] Furthermore, the insertion of CO_2 into the Ru–H hydride bond of $Ru(P_3)$ complexes has been described.[17] Encouraged by the combination of the results in Table 1 with these findings, the hydrogenation of carbon dioxide to methanol with catalyst systems **1** and **2** was approached. Ethanol was used as the alcohol component to tentatively stabilize the formate intermediate as ester, thus allowing any formed methanol to be directly identified in solution.Using **1** together with 2 equiv Triphos in ethanol/THF with 10 bar of CO_2 and 30 bar of H_2 at 140 °C for 24 h resulted in the formation of only very low quantities of methanol (Table 2, entry 1). However, with methanesulfonic acid (1.5 equiv) as additive, methanol was obtained with a TON of 52 (Table 2, entry 2). A slightly higher TON of 63 could even be achieved with **2** as compared to the in situ system **1**. Again, formation of methanol occurred with complex **2** in the presence of 1.5 equiv of MSA with much higher activity than without acid (Table 2, entries 3 and 4). In the corresponding NMR spectra (Table 2, entry 4), small amounts of formic acid, methyl formate, and ethyl formate could be detected, supporting the assumption of formate esters as intermediates. We note, however, that a stepwise reduction of CO_2 to methanol via the formate anion in the coordination sphere of the metal cannot be ruled out at this stage.

Table 2: Hydrogenation of carbon dioxide to methanol.[a]

$$CO_2 + 3\,H_2 \xrightarrow{\text{cat.}} MeOH + H_2O$$

Entry	Cat.	Acid[b]	Additive[c]	pH_2 [bar]	pCO_2 [bar]	TON[d]
1	**1**[e]	–	EtOH	30	10	2
2	**1**[e]	MSA	EtOH	30	10	52
3	**2**	–	EtOH	30	10	8
4	**2**	MSA	EtOH	30	10	63
5	–	MSA	EtOH	30	10	0
6	**1**[e]	MSA	EtOH	30	–	0
7	**1**[e]	MSA	$[D_4]$MeOH	30	10	24

[a] Reaction conditions: catalyst (25 μmol), THF (1.5 mL), 140 °C, 24 h. [b] 38 μmol (1.5 equiv) methanesulfonic acid. [c] 10 mmol. [d] TON = mmol MeOH/mmol catalyst. [e] 50 μmol (2 equiv) Triphos.

A series of control experiments confirmed the origin of the observed methanol from ruthenium-catalyzed CO_2 hydrogenation. No methanol was formed in the absence of CO_2 (Table 2, entry 6). Also the presence of acid alone did not lead to any detectably formation of CO_2 reduction products as expected (Table 2, entry 5). Most significantly, the formation of methanol from CO_2 was also unambiguously confirmed using deuterium-labeled MeOH as alcohol component (Table 2, entry 7) and experiments with $^{13}CD_3OD$ (see the Supporting Information). The incorporation of ^1H and ^{12}C from the gaseous reagents was clearly evident in the NMR spectroscopic analysis of the methanol in the reaction mixture. These experiments also confirm the technically important possibility of catalytic "breeding" of MeOH; however, the TON of 24 was slightly lower than in the case of ethanol as additive.

Using the in situ system from entry 2 of Table 2 as a starting point, a first screening of reaction variables was carried out to identify key parameters for future optimization

Table 3: Variation of reaction parameters in the catalytic hydrogenation of carbon dioxide to methanol.[a]

$$CO_2 + 3\,H_2 \xrightarrow{\text{cat.}} MeOH + H_2O$$

Entry	Cat.	Acid (equiv)[b]	t [h]	pH_2 [bar]	pCO_2 [bar]	TON[c]
1	**1**[d]	MSA (1.0)	24	30	10	39
2	**1**[d]	MSA (3.0)	24	30	10	30
3	**1**[d]	MSA (5.0)	24	30	10	25
4	**1**[d]	*p*-TsOH (1.5)	24	30	10	43
5	**1**[d]	MSA (1.5)	8	30	10	19
6	**1**[d]	MSA (1.5)	72	30	10	65
7[e]	**1**[d]	MSA (1.5)	24	30	10	46
8	**1**[d]	MSA (1.5)	24	60	20	135
9	**2**	$HNTf_2$ (1.0)	24	30	10	86
10	**2**	$HNTf_2$ (1.5)	24	30	10	77
11	**2**	$HNTf_2$ (3.0)	24	30	10	65
12	**2**	$HNTf_2$ (1.0)	24	60	20	221

[a] Reaction conditions: catalyst (25 μmol), THF (1.5 mL), EtOH (10 mmol), 140 °C. [b] Equivalents to catalyst. [c] TON = mmol MeOH/mmol catalyst. [d] 2 equiv Triphos. [e] 20 mmol EtOH added.

(Table 3). The TON increased from 19 after 8 h over 52 after 24 h to 65 after 72 h, demonstrating a significant catalytic activity even after prolonged reaction times (Table 3, entry 5,6). Doubling the amount of ethanol in the reaction mixture at constant total volume did not lead to an increased methanol formation, indicating that ethyl formate formation is not rate-limiting (Table 3, entry 7). Reduced TONs were observed both at lower and higher ratios of MSA (Table 3, entries 1–3), showing that only a slight excess of acid (1.5 equiv) is required for catalyst activation.[13b] Replacing MSA with *p*-toluenesulfonic acid resulted in a decreased TON of 43, suggesting that the counterion introduced through the acid may significantly affect the catalyst performance (Table 3, entry 4). Variation of the ligand-to-metal ratio in the in situ system **1** gave the best result using 2 equiv of Triphos per [Ru(acac)$_3$] (see the Supporting Information). Moreover, raising the carbon dioxide pressure to 20 bar and the hydrogen pressure to 60 bar increased the TON to 135 (Table 3, entry 8).

Using the isolated ruthenium complex **2** in combination with one equivalent of the acid bis(trifluoromethane)sulfonimide (HNTf$_2$) resulted in an improved TON of 86 in comparison to the experiment with MSA (Table 3, entry 9). This result further corroborates the assumption of cationic ruthenium complex **3** as catalytic active species and indicates the enhancing effect of weakly coordinating anions. The addition of 1.5 or 3 equivalents HNTf$_2$ slightly reduced the catalytic activity and a decreased TON of 77 and 65 could be obtained (Table 3, entry 10 and 11). Most significantly, raising the carbon dioxide pressure to 20 bar and the hydrogen pressure to 60 bar in the reaction with **2** and 1 equiv HNTf$_2$ resulted in a greatly increased TON of 221 (Table 3, entry 12), which is now well in the range of even the most active catalytic systems with reducing agents other than hydrogen.

In summary, the results of this study clearly demonstrate the possibility to hydrogenate carbon dioxide to methanol using a single homogeneous transition-metal catalyst under relatively mild reaction conditions. Studies on the active catalyst species and the detailed reaction mechanism are currently underway in our laboratories and will provide valuable information for rational tuning of catalyst activity.

Experimental Section

General procedure for the homogeneous hydrogenation of carbon dioxide to methanol: Under an argon atmosphere, catalyst **2** (0.025 mmol), bis(trifluoromethane)sulfonimide (0.025 mmol), and ethanol (10 mmol) were weighed into a Schlenk tube along with THF (1.5 mL). The yellow solution was transferred via cannula to a stainless steel autoclave under argon atmosphere. The autoclave was pressurized with carbon dioxide to 20 bar and then hydrogen was added up to a total pressure of 80 bar at room temperature. The reaction mixture was stirred and heated to 140 °C in an oil bath. After 24 h, the autoclave was cooled to 0 °C and then carefully vented. The resulting clear yellow solution was analyzed by ^{1}H NMR and gas chromatography. Turnover numbers (TONs) were found to be reproducible within ΔTON = ± 5 in two independent runs for selected experiments.

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