

A simple route to highly active ruthenium catalysts for formylation reactions with hydrogen and carbon dioxide

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Abstract

A simple route to ruthenium catalysts suitable for formamide production from amines, hydrogen and carbon dioxide is reported. The formylation of 3-methoxypropylamine has been employed as a test reaction. Highly active and selective ruthenium based catalysts were formed in situ under reaction conditions from solid RuCl_3 in the presence of triphenylphosphine (PPh_3) and 1,2-bis(diphenylphosphino)ethane. While RuCl_3 does not catalyze the reaction effectively, the addition of phosphines led to nearly five-fold increase in rate. The achieved turnover frequencies are comparable to those of synthesized reference Ru-phosphine complexes. As a consequence of the high activity only very small amounts (~ 300 ppm) of both RuCl_3 and the phosphine are necessary to catalyze effectively the formylation reaction. Despite the very low concentration of the Ru complex, the structure of the in situ formed active complex was elucidated by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Both indicated similar local structure for the in situ formed complex and a Ru-reference complex after reaction.

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Keywords: Formylation of amines; 3-Methoxypropylamine; Ruthenium chloride; Phosphines; X-ray absorption spectroscopy; EXAFS

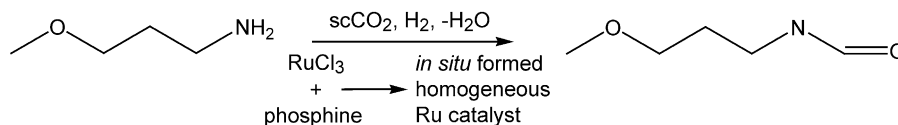
1. Introduction

The simultaneous use of carbon dioxide in chemical synthesis as C1-building block and as solvent is an attractive strategy for green chemistry. Toxic chemicals such as phosgene and carbon monoxide as well as environmentally harmful organic solvents can be potentially replaced [1–4]. One interesting route is the formylation of amines with hydrogen and carbon dioxide in the presence of ruthenium phosphine complexes [2,5,6]. For example the ruthenium catalyzed synthesis of dimethylformamide from dimethylamine, H_2 and CO_2 showed good results in homogeneous and heterogeneous catalysis [3,7,8]. Apart from dimethylamine, also other amines such as propylamine [9,10], diethylamine [11] and morpholine [12,13] have been investigated. Up to now the homogeneous catalysts were prepared directly or using complexes like $\text{RuH}_2(\text{P}(\text{CH}_3)_3)_4$, $\text{RuCl}_2(\text{P}(\text{CH}_3)_3)_4$,

$\text{RuH}_2(\text{P}(\text{C}_6\text{H}_5)_3)_4$ and $\text{RuCl}(\text{O}_2\text{CCH}_3)(\text{P}(\text{CH}_3)_3)_4$ [9,14,15] or the in situ formation of the active complexes from $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2$, $\text{RuCl}_2(\text{DMSO})_4$, and $[\text{RuCl}_2(\text{COD})]_n$ [16]. However, the use of a simple ruthenium salt, RuCl_3 , in the presence of phosphine ligands has not been reported and tested in the solventless formylation of amines using carbon dioxide as C1-synthesis block. To our knowledge the only studies hinting toward this direction are the formylation of amines in hexane in the presence of a $\text{RuCl}_3\text{-PPh}_3\text{-THF}$ solution covered in the patent of Kiso and Saeki [17] and the synthesis of formic acid in the presence of $\text{RuCl}_3/\text{PPh}_3$ in ethanol/water [18].

Here we show that highly active Ru catalysts can be prepared in situ by adding a suitable phosphine, 1,2-bis(diphenylphosphino)ethane (dppe) or triphenylphosphine (PPh_3), to the reaction mixture containing RuCl_3 as pre-catalyst. We investigated this simple in situ preparation of the catalyst using the formylation of 3-methoxypropylamine as a test reaction. It is shown that the catalytic performance of the in situ generated homogeneous catalysts is compa-

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Scheme 1. Formylation of 3-methoxypropylamine with hydrogen, “supercritical” carbon dioxide and in the presence of highly active and selective ruthenium catalysts.

able to that of $\text{RuCl}_2(\text{dppe})_2$ and $\text{RuCl}_2(\text{PPh}_3)_3$ reference complexes. Both strategies lead to highly active and virtually 100% selective catalysts. Inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy were applied to gain information concerning concentration and structure of the catalyst formed in situ from RuCl_3 and the phosphine.

2. Experimental

The formylation of 3-methoxypropylamine (mpa, Scheme 1) was chosen as a test reaction. The reaction was carried out in a temperature controlled 500 ml high pressure stainless-steel autoclave with a dosing system for gases [19]. In a typical procedure, mpa and the catalyst (50 μmol Ru, for RuCl_3 additionally the corresponding stoichiometric amount of phosphine) were filled into the reactor before closing and flushing with hydrogen. The reactor was then filled with hydrogen and adjusted at 100 °C to a pressure of 80 bar. Then 100 g carbon dioxide was added resulting in a total pressure of 220 bar at 120 °C. The stirring rate was fixed at 300 min^{-1} . After a certain reaction time, the reactor was cooled down and depressurized by opening the outlet valve. The reaction mixture was made up of two phases, a dense liquid phase containing the reactant amine and the products (formamide and water) and a less dense “supercritical” carbon dioxide phase. The reaction mixture was analyzed with a gas chromatograph (HP-6890) equipped with a HP-5 capillary column (30 m \times 0.32 mm \times 0.25 μm) and a flame ionization detector (FID). Product identification was achieved with a gas chromatograph (HP-6890) coupled to a mass spectrometer (HP-5973).

The X-ray absorption spectroscopy studies were performed at beamline X1 at HASYLAB (DESY). A Si(3 1 1) double-crystal monochromator was used and higher harmonics were effectively removed by detuning of the crystals to 70% of the maximum intensity. Additional experiments were performed at SNBL (ESRF, Grenoble). EXAFS spectra were taken in the step-scanning mode around the Ru K-edge (22,117 keV) between 21,900 and 22,800 eV using a RuCl_3 pellet as reference. Due to the low concentration of ruthenium, a transmission EXAFS cell with a long path length of 4 cm was constructed. The cross section was 6 mm \times 1 mm and the volume about 2 ml. The raw data were energy calibrated (Ru K-edge energy of RuCl_3 : 22,120 eV [20], first inflection point), background corrected and normalized us-

ing the WINXAS 3.0 software [21]. Fourier transformation for EXAFS data was applied to the k^1 -weighted functions in the interval $k = 3 - 12.5 \text{ \AA}^{-1}$ for the EXAFS data. Data fitting was performed in R-space. Typical deviations in coordination number are ± 0.5 and for the distance $\pm 0.02 \text{ \AA}$.

Safety note: the experiments described in this paper involve the use of high pressure and require equipment with the appropriate pressure rating.

3. Results and discussion

RuCl_3 used as pre-catalyst showed only low activity with a conversion of 12% and a turnover frequency (TOF) of 19 h^{-1} under standard reaction conditions as denoted in Fig. 1. After adding dppe the activity of the in situ formed catalyst increased affording a TOF of 90 h^{-1} and a conversion of 95%. Similar catalytic performance was observed when adding PPh_3 instead of dppe (Fig. 1). The catalytic behavior of the homogeneous catalysts $\text{RuCl}_2(\text{dppe})_2$ and $\text{RuCl}_2(\text{PPh}_3)_3$ used as references was in the same range. The selectivity to the corresponding formamide was in all reactions 100%. Thus, this in situ generation provides a very simple and cheap procedure for preparing highly active homogeneous Ru-catalysts. To confirm the formation of complexes acting as homogeneous catalysts formed from RuCl_3 and dppe or PPh_3 , first the Ru-concentration in the reaction mixtures after filtration and centrifugation was quantified with ICP-OES and second, pertinent tests according to Sheldon et al. [22] were performed. That is, the reaction was stopped after a

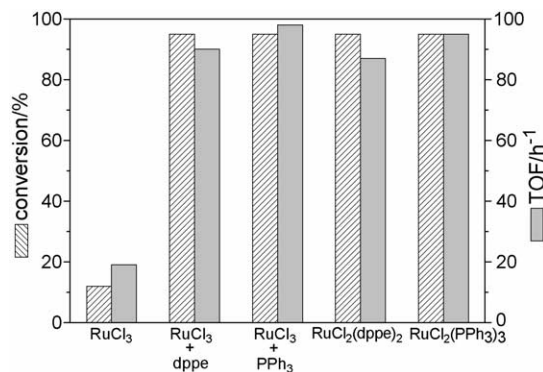


Fig. 1. Comparison of performance of catalysts generated in situ from $\text{RuCl}_3 + \text{dppe}$ or PPh_3 and related homogeneous reference catalysts $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuCl}_2(\text{dppe})_2$ in the formylation of mpa. Selectivity to formamide was 100% in all cases. Reaction conditions: 100 mmol mpa, 50 μmol Ru catalyst, 100 g CO_2 , 120 °C, total pressure 220 bar, 20 h.

certain time, the reaction mixture filtered off and checked, whether the catalytic reaction could be continued after this procedure. No significant loss of activity could be observed. This corroborated that all Ru-complexes formed were dissolved in the amine rich phase. After 3 h of reaction time, 49% of the amine was converted with the catalyst $\text{RuCl}_3 + \text{dppe}$. Only about 300 ppm ruthenium was present in the reaction mixture. After filtration and continuation of the reaction for a total time of 20 h, the conversion reached 90%. In an experiment without filtration, virtually the same conversion (88%) was found after 20 h, which proved that the ruthenium based complex is a homogeneous catalyst formed in situ under reaction conditions. Note that the conversion of $\text{RuCl}_3 + \text{PPh}_3$ after 3 h was 25% compared to 49% for the $\text{RuCl}_3 + \text{dppe}$ system.

This is in line with literature, where dppe complexes were found to be more active than monophosphine complexes [8] and also supports our hypothesis that Ru-phosphine complexes are the active component.

To gain some information about the structure of the in situ formed Ru-complexes, the product mixtures were investigated by XANES and EXAFS with an appropriate stainless-steel cell constructed for transmission experiments. Due to the low Ru-concentration in the product mixture a long path length cell was used (4 cm) that allows structural identification even at low concentrations. This shows that the structure of Ru-phosphine complexes can be identified even at low concentration. Studies on the local structure of ruthenium in systems with such low concentration of the target species are difficult to perform by means of any other techniques [23]. EXAFS spectra can be principally taken in two different modes: fluorescence detection or in transmission mode. Whereas Fiddy et al. [24] proposed the use of fluorescence detection it seemed here that also transmission EXAFS is applicable. Both the Ru K-edge and Rh K-edge are at rather high energies so that the absorption at an energy of 22 keV is only $\mu d = 0.08$. At 300 ppm of Ru an edge jump of 1.5 was found, leading to sufficient signal/noise ratio.

Fig. 2 shows the XANES region of the catalysts $\text{RuCl}_3 + \text{dppe}$ and the references RuCl_3 , $\text{RuCl}_2(\text{dppe})_2$ and $\text{RuCl}_2(\text{PPh}_3)_3$. Upon dppe addition the spectrum of RuCl_3 changed significantly. From these changes and the comparison of the near-edge structure of the in situ formed complex and the Ru-phosphine reference complexes, $\text{RuCl}_2(\text{dppe})_2$ and $\text{RuCl}_2(\text{PPh}_3)_3$, we infer that the local structure of the in situ formed complex is similar to $\text{RuCl}_2(\text{PPh}_3)_3$ after reaction. Fig. 3 shows the corresponding k^1 -weighted Fourier transformed EXAFS spectra. All catalysts exhibit a backscattering peak at 1.8 and 2.5 Å, RuCl_3 contains a supplementary peak at 3.25 Å. The peaks are slightly shifted to lower R values, because the spectra are not corrected for the phase shift. The backscattering contribution of RuCl_3 and $\text{RuCl}_2(\text{dppe})_2$ at 2.5 Å is much smaller than that of $\text{RuCl}_3 + \text{dppe}$ and $\text{RuCl}_2(\text{PPh}_3)_3$. The Fourier transformed spectra were fitted with Ru–Cl and Ru–P shells calculated by FEFF 6.0 [25].

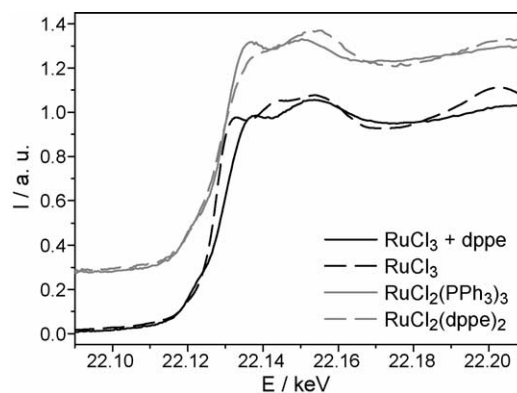


Fig. 2. X-ray absorption near edge structure at the Ru K-edge of RuCl_3 , $\text{RuCl}_3 + \text{dppe}$, $\text{RuCl}_2(\text{dppe})_2$ and $\text{RuCl}_2(\text{PPh}_3)_3$, all spectra were taken from the liquid product mixture.

The structural data obtained for $\text{RuCl}_2(\text{PPh}_3)_3$ are in good accordance with [26], three different Ru–P bond lengths (2.23, 2.37, and 2.41 Å) and two Ru–Cl bond lengths (2.387 and 2.388 Å) were reported (Table 1). Only one Ru–P distance, 2.22 Å, and one contribution at higher values at 2.93 Å, was found in our studies (Table 2). This originates from the fact that we measured the catalyst dissolved in the reaction mixture. A Ru–P distance of 2.32 Å was found in $\text{RuCl}_2(\text{dppe})_2$ in the reaction mixture that is also documented in [27]. With a Ru–P bond length of 2.27 Å and a contribution at 2.82 Å, $\text{RuCl}_3 + \text{dppe}$ shows a local structure that is similar to $\text{RuCl}_2(\text{PPh}_3)_3$ in solution. The excess of chloride ligands in the $\text{RuCl}_3 + \text{dppe}$ system may trigger more that structure and lead to the formation of dimers, which could explain the contribution at higher R -values. Note that the EXAFS fit only resulted in a Ru–P shell and no Ru–Cl contribution as in Refs. [28,29] was found. This may be due to the similar distance of Ru–P and Ru–Cl in the formed complexes. However, the Ru–P distance is usually shorter than the Ru–Cl distance [28,29], indicating the formation of phosphine complexes. Note that one of the limitations of EXAFS is that it is an averaging technique. We can assume that several species will exist in solution, and these are averaged by the EXAFS technique.

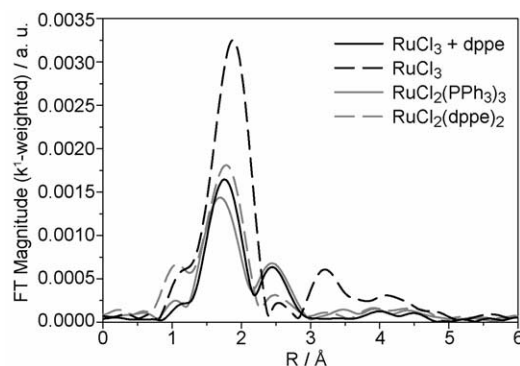


Fig. 3. The corresponding Fourier transformed EXAFS spectra (k^1 -weighted) at the Ru K-edge of RuCl_3 , $\text{RuCl}_3 + \text{dppe}$, $\text{RuCl}_2(\text{dppe})_2$ and $\text{RuCl}_2(\text{PPh}_3)_3$.

Table 1
Structural data from X-ray diffraction of Ru-phosphine-complexes as reported in literature

Compound	Bond lengths (Å)		Bond angles (°)		Reference
RuCl ₂ (PPh ₃) ₃	Ru–P(1)	2.374	P(1)–Ru–P(2)	156.4	[26]
	Ru–P(2)	2.412	P(1)–Ru–P(3)	101.1	
	Ru–P(3)	2.230	P(2)–Ru–P(3)	101.4	
	Ru–Cl(1)	2.387			
	Ru–Cl(2)	2.388			
RuCl ₂ (dppm) ₂	Ru–P(1)	2.340	P(1)–Ru–P(2)	71.39	[32]
	Ru–P(2)	2.367			
	Ru–Cl	2.426			
RuCl ₂ (dppe) ₂	Ru–P(1)	2.389	P(1)–Ru–P(2)	82.1	[27]
	Ru–P(2)	2.369			
	Ru–Cl	2.436			
RuBrCl(dppe) ₂	Ru–P(1)	2.388	P(1)–Ru–P(2)	81.43	[33]
	Ru–P(2)	2.362			
	Ru–Cl	2.432			
	Ru–Br	2.496			
RuCl ₂ (dppp) ₂	Ru–P(1)	2.416	P(1)–Ru–P(2)	86.79	[34]
	Ru–P(2)	2.441			
	Ru–Cl	2.435			

dppm: bis(diphenylphosphino)methane; dppe: 1,2-bis(diphenylphosphino)ethane; dppp: 1,3-bis(diphenylphosphino)propane.

Table 2
Structural data extracted from EXAFS spectra of different phosphino complexes as solid and in the liquid phase

Catalyst	Ru–P			Ru–Cl and Ru–Ru		
	<i>N</i>	<i>R</i> (Å)	$\Delta\sigma^2$ (Å ²)	<i>N</i>	<i>R</i> (Å)	$\Delta\sigma^2$ (Å ²)
RuCl ₂ (PPh ₃) ₃ ^a	1.0	2.23	0.0025	2.3	2.44	0.0027
	2.0	2.38	0.0025			
RuCl ₂ (dppe) ₂ ^a	4.0	2.29	0.0013	2	2.42	0.0006
RuCl ₂ (PPh ₃) ₃ ^b	3.0	2.24	0.0048	2	2.93	0.0060
RuCl ₂ (dppe) ₂ ^b	3.6	2.32	0.0063	–	–	–
RuCl ₃ + dppe ^b	3.9	2.27	0.0046	2	2.82	0.0091

N: coordination number; *R*: distance of the corresponding neighbour, $\Delta\sigma^2$: Debye–Waller factor.

^a Solid catalyst.

^b Liquid solution measured after reaction with 3-methoxypropylamine (mpa).

Nevertheless, the XANES and EXAFS data show that the structure of the in situ formed complex of the RuCl₃ + dppe mixture is similar to RuCl₂(PPh₃)₂ after reaction. In the next step, it would be desirable to identify the hydrido species in more detail, which is known to be easily formed in the presence of hydrogen [30,31].

Finally, it seems likely that the extension of the in situ catalyst preparation to other transition metals and other phosphines may provide catalysts with even higher efficiency than those shown in this work. A systematic study towards this aim could be rewarding.

4. Conclusions

The in situ generation of highly active catalysts from solid RuCl₃ and a suitable phosphine (dppe or PPh₃) for the formylation of 3-methoxypropylamine from hydrogen and carbon dioxide was demonstrated by catalytic measurements combined with X-ray absorption spectroscopy and ICP-OES. The

activity and the structure of the formed catalyst is similar to RuCl₂(PPh₃)₃. The use of this simple method for catalyst preparation may open new possibilities for high-throughput screening and lead to more economical and greener formylation processes requiring only very low amount of easy to prepare catalyst.

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