Highly active ruthenium complexes with bidentate phosphine ligands for the solvent-free catalytic synthesis of *N*,*N*-dimethylformamide and methyl formate

Oliver Kröcher, René A. Köppel and Alfons Baiker*

Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

Complexes of the type [$RuCl_2L_2$] [L = $Ph_2P(CH_2)_nPPh_2$ (n = 1–3), $Me_2P(CH_2)_2PMe_2$] are shown to be highly active and selective catalysts for the synthesis of formic acid derivatives from carbon dioxide, hydrogen and dimethylamine or methanol–triethylamine, respectively, without any additional solvent, affording at 373 K with [$RuCl_2(dppe)_2$] an extremely high turnover frequency (TOF) of 360 000 h^{-1} in *N*,*N*-dimethylformamide synthesis and a TOF of 830 h^{-1} in methyl formate synthesis.

Recently, carbon dioxide has gained renewed interest as an ideal source of carbon in synthetic chemistry because of its abundance, low cost and non-toxicity.[1,2] Among the possible valuable chemicals, special attention is given to formic acid and its derivatives like *N*,*N*-dimethylformamide [eqn. (1)] and methyl formate [eqn. (2)].[3,4]

$$CO_2 + H_2 + Me_2NH \rightarrow Me_2NC(O)H + H_2O \qquad (1)$$

$$CO_2 + H_2 + MeOH \rightarrow HC(O)OMe + H_2O \qquad (2)$$

The progress made up to 1995 in the homogeneously catalysed synthesis of *N*,*N*-dimethylformamide (dmf) and methyl formate from carbon dioxide has been reviewed recently.[3,4] Among various transition-metals investigated, ruthenium and rhodium complexes were found to exhibit high activity. Although remarkable efforts have been made to increase the activity of the catalytic complexes used, the turnover numbers (TON) and turnover frequencies (TOF) achieved remained realtively low.[3,4]

More recently, the use of [$RuCl_2(PMe_3)_4$] as a catalyst for the synthesis of formic acid, dmf and methyl formate from carbon dioxide, hydrogen and dimethylamine or methanol, respectively, has been reported by Jessop *et al.*[3,5] The application of supercritical carbon dioxide (sc-CO_2) as a solvent for hydrogen and the catalyst enabled the authors to produce dmf with overall rates of up to 10000 h^{-1} and methyl formate with overall rates of up to 55 h^{-1}. The use of sc-CO_2-soluble complexes was reported to be crucially important for achieving high activities. Although the process reported by Jessop *et al.* is far more efficient compared to the liquid-phase synthesis of dmf and methyl formate, overall reaction rates are still relatively low and the catalysts are sensitive to air, which impairs technical utilisation. The aim of our study was to find more active and stable catalysts for the synthesis of dmf and methyl formate, obviating these limitations.

Ruthenium complexes of the type [$RuCl_2L_2$], with L representing the chelating ligands dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2P(CH_2)_2PPh_2$ or dppp = $Ph_2P(CH_2)_3PPh_2$, were prepared,[6] which are easy to characterize, relatively cheap, and stable to water and air.

Table 1 lists the experimental conditions and the catalytic results obtained with the various ruthenium complexes for the synthesis of *N*,*N*-dimethylformamide and methyl formate, respectively. Note that catalytic results presented in Table 1 were confirmed by at least two repetitive experiments. Blank tests without catalyst performed repeatedly throughout the study revealed no catalytic activity.

The synthesis of dmf proceeded very rapidly at 373 K with up to 99% yield and always with 100% selectivity to dmf. Analysis of the gas phase by GC confirmed that no gaseous by-products (CO, CH_4) were formed. A TOF of 360 000 h^{-1} could be reached with [$RuCl_2(dppe)_2$], which is 36 times higher than that with [$RuCl_2(PMe_3)_4$], the best catalyst reported so far.[3,5] In an experiment using 110 g dimethylamine a maximum TON of 740 000 was achieved, which indicates the upper limit of the catalyst's lifetime under the conditions applied. Calculated on the basis of 1 g of ruthenium, 530 kg dmf can be produced within 2 h. Further improvement in TOF may be possible by optimizing the reaction parameters. High TOFs could also be reached with [$RuCl_2(dppm)_2$], whereas [$RuCl_2(dppp)_2$] exhibited much lower activity (Table 1).

The extremely high catalytic activity achieved with such *trans*-[$RuCl_2L_2$] complexes was not *a priori* expected, since the formation of a monohydride species was reported to be a prerequisite for catalytic activity for this type of hydrogenation

Table 1 Catalytic properties of ruthenium complexes in the production of *N*,*N*-dimethylformamide and methyl formate from CO_2[a]

Complex (μmol)	Reactant [additive] (mol)	t/h	Product	TON[b]	TOF[c]/h^{-1}
[$RuCl_2(PMe_3)_4$][d] (6.4)	Dimethylamine (3.80)	70.0	dmf	420 000	6 000
[$RuCl_2(dppe)_2$] (0.58)	Dimethylamine (2.44)	2.05	dmf	740 000	**360 000**
[$RuCl_2(dppe)_2$] (0.73)	Dimethylamine (0.78)	0.75	dmf	200 000	265 000
[$RuCl_2(dppm)_2$] (1.0)	Dimethylamine (0.72)	0.50	dmf	95 000	190 000
[$RuCl_2(dppp)_2$] (3.1)	Dimethylamine (0.72)	4.05	dmf	10 700	2 650
[$RuCl_2(dmpe)_2$] (8.7)	Dimethylamine (0.72)	15.0	dmf	30 000	2 000
[$RuCl_2(PMe_3)_4$][d,e] (2.9)	Methanol (0.08) [triethylamine] (0.030)	64.0	Methyl formate	3 500	55
[$RuCl_2(dppe)_2$] (3.8)	Methanol (0.74) [triethylamine] (0.370)	15.5	Methyl formate	12 900	**830**
[$RuCl_2(dppe)_2$][e] (2.3)	Methanol (0.74) [triethylamine] (0.074)	15.5	Methyl formate	10 100	650

[a] *Reaction conditions*: 500 ml stainless-steel autoclave equipped with magnetically coupled stirrer. Analysis: GC equipped with Supelco SPB-1 fused silica capillary column. $p(H_2)$ = 8.5 MPa, $p(CO_2)$ = 13.0 MPa, T = 373 K. [b] TON = mol product/mol complex. [c] TOF = TON h^{-1}. [d] Lit. data[3] for the hitherto best catalyst [$RuCl_2(PMe_3)_4$]. 300 ml autoclave. [e] T = 353 K.

catalyst.[5,7] No conversion of *trans*-[$RuCl_2L_2$] complexes to the corresponding monohydrides at normal pressure is described in the literature.[8,9] Despite this, [RuHCl(dppe)$_2$], identified by NMR, could be found in the reactor after pretreatment of [$RuCl_2$(dppe)$_2$] with 40 bar of hydrogen and dimethylamine, confirming monohydrides as key intermediates in the catalytic cycle. The monitored pressure in the reactor as well as the catalytic results indicated no further induction period after addition of carbon dioxide.

Jessop *et al.* investigated visually the phase behaviour in the reactor under comparable conditions for different reactants and additives. They found that a supercritical phase of carbon dioxide and hydrogen exists besides a liquid phase, highly swelled by dissolved gases.[5] Thus, high concentrations of carbon dioxide and possibly hydrogen could be assumed in the liquid-amine phase. Leitner *et al.* reported high concentrations of dissolved carbon dioxide in the liquid phase also under subcritical conditions.[10] Due to their insolubility in the sub- or super-critical carbon dioxide, the complexes *trans*-[$RuCl_2L_2$] are expected to operate in the liquid phase, which is also supported by the fact that the catalysts could only be found in the liquid-product mixture after reaction. Moreover, cleaning of the lower part of the autoclave was sufficient to exclude any activity in subsequent blank tests. Variations of the carbon dioxide partial pressure from super- to sub-critical conditions, using [$RuCl_2$(dppe)$_2$] as catalyst, resulted in a decrease of activity from 360 000 h^{-1} (8.5 MPa CO_2) to 150 000 h^{-1} (1.8 MPa CO_2), but no drastic activity drop was observed, indicating supercritical conditions not to be a necessary prerequisite for high catalytic activity.

Despite their similar solubility properties, the three related complexes [$RuCl_2$(dppm)$_2$], [$RuCl_2$(dppe)$_2$] and [$RuCl_2$(dppp)$_2$] exhibited substantially different activities, with [$RuCl_2$(dppp)$_2$] being far less active than [$RuCl_2$(dppm)$_2$] and [$RuCl_2$(dppe)$_2$] (Table 1). In order to compare the catalytic properties of these complexes, which are insoluble in sc-CO_2, with a complex soluble in the supercritical phase, [$RuCl_2$(dmpe)$_2$] [dmpe = $Me_2P(CH_2)_2PMe_2$] was prepared,[11] using bidentate methyl phosphine ligands instead of phenyl phosphine ligands. Interestingly, [$RuCl_2$(dmpe)$_2$] exhibited similar low activity to [$RuCl_2$(dppp)$_2$], suggesting a more pronounced influence of the phosphine ligands than of the catalysts solubility properties.

[$RuCl_2$(dppe)$_2$] was also tested for methyl formate synthesis at 353 K and exhibited a 12 times higher activity (TOF = 650 h^{-1}) than [$RuCl_2(PMe_3)_4$] (TOF = 55 h^{-1}) under comparable conditions. Increasing the triethylamine concentration and the temperature resulted in an even higher TOF of 830 h^{-1}, which is 15 times higher than the best previous results.[5] Analysis of the reaction mixture by ^{1}H NMR spectroscopy revealed the formation of an adduct of formic acid and triethylamine beside methyl formate. Methyl formate synthesis with our complexes is favourable compared to that with [$RuCl_2(PMe_3)_4$], because higher temperatures can be applied, which is crucial for an effective esterification of the initially formed formic acid.

In conclusion, we can state that ruthenium complexes with bidentate phosphine ligands exhibit much higher activity for the solvent-free synthesis of *N*,*N*-dimethylformamide (dmf) and methyl formate from carbon dioxide than hitherto reported catalytic systems.[3,5] The high concentrations of hydrogen and carbon dioxide in the liquid dimethylamine or methanol–triethylamine phase afford high concentrations of all reactants at the catalytic centres in an ideal reaction design. We have demonstrated that further improvements in the homogeneous hydrogenation of carbon dioxide are achievable not only by developing complexes soluble in the supercritical medium, but also by the utilisation of better suited ligands for this reaction in combination with a solvent-free reaction design.

References

1 B. Cornils and W. A. Herrmann, in *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, 1996, pp. 1048–1072.
2 T. Clifford and K. Bartle, *Chem. Ind.*, 1996, 449.
3 P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, **95**, 259.
4 W. Leitner, *Angew. Chem., Int. Ed. Engl.*, 1996, **34**, 2207.
5 P. G. Jessop, Y. Hsiao, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1996, **118**, 344.
6 R. Mason, D. W. Meek and G. R. Scollary, *Inorg. Chim. Acta*, 1976, **16**, L11.
7 E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, ed. R. J. H. Clark, Elsevier, Amsterdam, 1984.
8 J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 2605.
9 M. T. Bautista, E. P. Cappellani, S. D. Drouin, R. H. Morris, C. T. Schweitzer, A. Sella and J. Zubkowski, *J. Am. Chem. Soc.*, 1991, **113**, 4876.
10 W. Leitner, E. Dinjus and F. Gaßner, *J. Organomet. Chem.*, 1994, **475**, 257.
11 J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896.

Received, 3rd December 1996; Com. 6/08150I