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Towards a methanol economy based on homogeneous catalysis: methanol to H_2 and CO_2 to methanol

E. Alberico*[a,b] and M. Nielsen*[c,d]

The possibility to implement both the exhaustive dehydrogenation of aqueous methanol to hydrogen and CO_2 and the reverse reaction, the hydrogenation of CO_2 to methanol and water, may pave the way to a methanol based economy as part of a promising renewable energy system. Recently, homogeneous catalytic systems have been reported which are able to promote either one or the other of the two reactions under mild conditions. Here, we review and discuss these developments.

Introduction

More than 80% of the total worldwide energy consumption is today based on fossil fuels,[1] resulting in an increase of anthropogenic CO_2 in the atmosphere. Moreover, it is well known that oil sources are likely to be near-depleted by the end of this century if we maintain or increase the present rate of their consumption. Hence, there is an urgency to develop techniques for exploiting alternative energy resources such as wind, sunlight, and biomass in order to generate electricity and/or H_2, the latter being equivalent to chemically stored electrical energy. The capability of storing electricity is important because of the intermittent supply of most renewable energy sources.[2–4]

Hydrogen is an ideal fuel as its combustion releases energy and water as the sole by-product. However, mainly because of its physical and chemical properties, hydrogen is not an ideal energy vector: it is a gas with a limited volumetric energy density which, as fuel, especially in the field of automotive applications,

E. Alberico

Elisabetta Alberico obtained her degree in Chemistry (Laurea) from the University of Sassari, Italy, and her PhD under the supervision of Prof. Albrecht Salzer at the Rheinisch-Westfälische Technische Hochschule (RWTH), Aachen, Germany. Since 2001 she holds a permanent position as researcher at the Institute of Biomolecular Chemistry of the National Research Council in Sassari. She is currently a visiting researcher at the Leibniz Institute for Catalysis (LIKAT), Rostock, in the group of Prof. Matthias Beller. Her research interests are in the fields of organometallic chemistry, asymmetric homogeneous hydrogenation and transfer hydrogenation and application of catalytic methods to the synthesis of molecules endowed with biological activity.

M. Nielsen

Martin Nielsen obtained his PhD at Aarhus University in Denmark under the supervision of Prof. Karl Anker Jørgensen. He then worked as a postdoc on a Alexander von Humboldt Research Fellowship at the Leibniz Institute for Catalysis (LIKAT), Rostock, in the group of Prof. Matthias Beller. Hereafter, he moved to Harvard University, USA, where he did his next postdoc with Prof. Theodore A. Betley on a Danish Council for Independent Research Fellowship followed by a Marie Curie International Outgoing Fellowship. Currently, he is a senior researcher at the Technical University of Denmark. His research interests include catalysis and sustainable chemistry.

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[a] Istituto di Chimica Biomolecolare, CNR, tr. La Crucca 3, 07100 Sassari, Italy. E-mail: elisabetta.alberico@cnr.it
[b] Leibniz-Institut für Katalyse an der Universität Rostock, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany
[c] Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, USA
[d] Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Kemitorvet 207, 2800 Kgs. Lyngby, Denmark. E-mail: marnie@kemi.dtu.dk

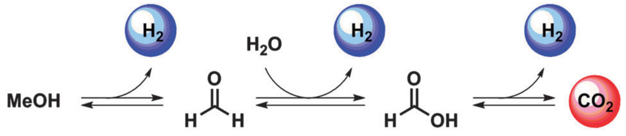
has to be either compressed at very high pressure (350–700 bars) or liquefied at very low temperature (−253 °C). It is flammable and can diffuse through several metals and materials.

The chemical storage of hydrogen in solid or liquid compounds from which it can be released as gas through a suitable (and ideally fully reversible) dehydrogenation reaction has been intensively investigated as a possibility to overcome some of these limitations.[5] Several criteria have to be considered when evaluating the potential of a chemical substance as hydrogen carrier, among others, its storage capacity (H_2 wt%), its volumetric hydrogen content (kg H_2 m^{-3} carrier) and the energy efficiency of the whole process of carrier hydrogenation–dehydrogenation, from hydrogen production to final hydrogen utilization. Methanol belongs to the broader class of liquid storage compounds which includes liquid organic hydrogen carriers (LOHC *i.e.* methylcyclohexane and *N*-ethylperhydrocarbazole),[6a] alcohols[6b–d] and formic acid.[6d,e] It is a key platform chemical for existing fuel and chemical infrastructures and contains 12.6% w/w hydrogen, which can be released through aqueous reforming.[7] Heterogeneous catalysts, which promote this reaction[7] and the reverse one, the conversion of CO_2 and H_2 to MeOH,[8] operate at high temperatures (>200 °C) and/or applied pressures (>25 bar). Indeed the high temperature required for dehydrogenation is one of the main factors which so far has made MeOH less suitable as energy carrier in the field of portable applications. Therefore, developing milder routes for these two conversions is highly desirable in order to reach a viable H_2 energy system based on a CO_2–MeOH cycle. Moreover, the carbon dioxide released in the process and from any other source might be hydrogenated back to methanol using hydrogen obtained from renewable sources, ideally from water electrolysis powered by solar energy, thus completing a carbon neutral cycle.

The advantages and limitations of a methanol based economy, how far this is from being implemented, especially in relation to technologies currently available for carbon dioxide capture and sequestration and water electrolysis for hydrogen production, have been reviewed in excellent monographs and articles and the reader is referred to them for an in-depth acquaintance with the topic.[9]

In this review we would like to draw the readers' attention to recent reports concerning the development and application of homogenous catalysts for MeOH dehydrogenation (≤95 °C and atmospheric pressure) and CO_2 hydrogenation to MeOH (≤145 °C and ≤60 bars) which are active under comparatively mild conditions.

Looking into the mechanism of a homogeneously catalysed CO_2/MeOH hydrogenation/dehydrogenation system, it becomes evident that a few organic intermediates must exist alongside this stepwise transformation. As shown in Scheme 1, the generally proposed MeOH dehydrogenation pathway by homogeneous catalysis commences with the formation of formaldehyde, which is then converted to formic acid promoted by a H_2O molecule. The final step is CO_2 production from formic acid. In each of these three steps, a H_2 molecule is liberated. The CO_2 hydrogenation pathway is envisioned to follow the reversed sequence of the same reaction steps.



Scheme 1 Schematic representation of the steps that constitute the reversible MeOH dehydrogenation and CO_2 hydrogenation promoted by homogeneous catalysts.

In the absence of water and in the presence of suitable catalysts, methanol may decompose to hydrogen and formaldehyde (the latter may further react to afford other products, depending on the catalyst and the reaction conditions) (eqn (1)) or be fully dehydrogenated to hydrogen and carbon monoxide (eqn (2)). The catalysts which were found able to promote such processes in the absence of a hydrogen acceptor in almost all cases were applied with much greater success to the dehydrogenation of ethanol and iso-propanol, the latter being often the substrate of choice to test new catalysts, because of the more favourable thermodynamics and the possibility of a higher operational temperature.[6b–d,10,11]

$$CH_3OH(l) \rightarrow H_2CO(g) + H_2(g) \qquad \begin{aligned} \Delta H^\circ_{298} &= 129.8\ \text{kJ mol}^{-1} \\ \Delta G^\circ_{298} &= 63.5\ \text{kJ mol}^{-1} \end{aligned} \tag{1}$$

$$CH_3OH(l) \rightarrow CO(g) + 2H_2(g) \qquad \begin{aligned} \Delta H^\circ_{298} &= 127.9\ \text{kJ mol}^{-1} \\ \Delta G^\circ_{298} &= 29.0\ \text{kJ mol}^{-1} \end{aligned} \tag{2}$$

Methanol dehydrogenation

Partial methanol conversion

The first examples of homogeneously catalysed methanol dehydrogenation were published approximately 30 years ago. However, because reactions were carried out in the absence of water, the possibility for the full conversion of methanol to CO_2 and three H_2 was precluded. Yet they will be briefly discussed here as they set the very early stage for future developments towards the successful sustainable production of hydrogen from alcohols.

Thermal decomposition of methanol. Early accounts on the thermal dehydrogenation of methanol with hydrogen evolution promoted by a homogeneous catalyst were reported by the groups of Saito,[12] Maitlis,[13] Shinoda[14] and Cole-Hamilton.[15] These reactions were carried out using ruthenium catalyst precursors modified by phosphines and other ancillary ligands. The dehydrogenation of methanol to formaldehyde and hydrogen (eqn (1)) is an endergonic and endothermic process, which becomes feasible under relatively mild conditions (65 °C, reflux) if the reaction is carried out in an open vessel from which hydrogen easily escapes the reaction medium due to its very limited solubility, thus shifting the equilibrium.

Saito could show that catalyst $[Ru(OAc)(Cl)(PEtPPh_2)_3]$, prepared *in situ* from $[Ru_2(OAc)_4(Cl)]$ and $PEtPPh_2$, is competent for the dehydrogenation of methanol to formaldehyde at reflux with an initial TOF of 0.96 h^{-1} and a total TON of 34 over 90 hour reaction time (Table 1, entry 1).[12a,c] An optimum of two equivalents of acetic acid to ruthenium is required to achieve this result as compared to TOF 0.60 h^{-1} without any. While formaldehyde was the only

Table 1 Active homogeneous catalysts for methanol thermal dehydrogenation

Entry	Catalyst (mmol)	MeOH (mL)	Additive (mmol)	T (°C)	Time (h)	H_2 (mmol)	Yield[a] (%)	TOF[b] (h^{-1})	TON[c]	Products	Ref.
1	$[Ru(OAc)(Cl)(PEtPPh_2)_3]$ 0.1	400	CH_3COOH 0.2	65	90	3.4	0.034	0.38	34	HCHO, $HCOOCH_3$, $H_2C(OCH_3)_2$	12*a* and *c*
2	$[Ru(Cl)_2(PPh_3)_3]$ 0.08	10	—	150	18	5.2	2.1	3.6	65	$HCOOCH_3$, $H_2C(OCH_3)_2$	13
3	$[Ru(H)_2(N_2)(PPh_3)_3]$ $1–5 \times 10^{-3}$	5	NaOH 5	150	2	[d]	[d]	6.4	12.8	n.r.	15
4	$[Ru(H)_2(PPh_3)_4]$ $1–5 \times 10^{-3}$	5	NaOH 5	150	2	[d]	[d]	7.5	15	n.r.	15
5	$RuCl_3{\cdot}3H_2O$ 1	200	MeONa 610	79	n.r.	—	—	1.68[e]	—	HCOONa	12*d*

n.r. not reported. [a] The yield is referred to methanol and is calculated assuming that each mmole of converted methanol has been dehydrogenated to formaldehyde and hydrogen. [b] Average TOF referred to overall reaction time. [c] TON is referred to hydrogen production. [d] Because a range of catalyst concentrations is given, it is not possible, based on reported TOF and TON, to estimate the amount of hydrogen evolved and yield thereof. [e] Initial TOF.

product in the early stage of the reaction, at higher conversion both methylformate (the product of a Tishchenko-like dimerization of formaldehyde) and dimethoxymethane (formaldehyde dimethyl acetal) could eventually be detected in solution. No carbon monoxide or methane contaminants were detected in the gas phase.

Almost at the same time Maitlis reported the dehydrogenation of methanol to methylformate and dimethoxymethane catalysed by $[Ru(Cl)_2(PPh_3)_3]$ at 150 °C achieving a total TON = 65 for hydrogen evolution over 18 hours, at which time activity ceased likely due to formation of inactive $[(PPh_3)_2Ru(CO)(\mu\text{-}H)(\mu\text{-}Cl)_2(CO)(PPh_3)_2]$, which was isolated from the reaction mixture (Table 1, entry 2).[13]

Cole-Hamilton showed that the rate of hydrogen evolution from methanol over 2 h at 150 °C could be greatly improved by performing the reaction in the presence of a 10 fold excess of base (NaOH) as to the catalyst when using preformed $[Ru(H)_2(N_2)(PPh_3)_3]$ (TOF = 6.4 h^{-1}, Table 1, entry 3) or $[Ru(H)_2(PPh_3)_4]$ (TOF = 7.5 h^{-1}, Table 1, entry 4).[15] Notably, $RuCl_3$ with no ancillary ligand is able to promote methanol dehydrogenation if sodium methoxide is added to the reaction mixture, thus showing the critical role played by the base.[12d] With 20% sodium methoxide the solution boiling point was raised from 65 °C to 79 °C bringing about an 84 fold increase of the initial turnover rate from 0.02 h^{-1} without base to 1.68 h^{-1} (Table 1, entry 5). The accelerating effect was however mostly ascribed to the high base concentration, since the catalytic activities at sodium methoxide concentrations below 5% (boiling point of the solution 66.8 °C) were far lower than those extrapolated from the Arrhenius plot.

Table 1 summarizes and compares the activity of complexes which were able to promote, although with poor activity, the thermal decomposition of methanol.

Other ruthenium based catalysts, namely $\{[Ru(SnCl_3)_5(PPh_3)](Et_4N)_3\}$,[16a] $\{Ru(SnCl_3)_2[P(OMe)_3]_3\}$,[16b] and $[(\eta^5\text{-}C_5H_5)Ru(SnF_3)(PPh_3)_2]$[16c–e] are also able to dehydrogenate methanol with liberation of hydrogen. These catalysts are not included in Table 1 as the main focus was, in these cases, on the production of acetic acid, or rather its methyl ester, from sole methanol, thus circumventing the use of iodide and carbon monoxide as otherwise required by the Monsanto process.

Decomposition of methanol by molecular photocatalysis. A few reports have appeared concerning the combined use of light and homogeneous metal catalysts based on rhodium, iridium, ruthenium and palladium to promote methanol dehydrogenation.[10] The ultimate goal here is to exploit sunlight as the energy source to pay for the thermodynamic cost of the alcohol dehydrogenation. In an early report it was shown that the combined use of either $[Rh(H)(PiPr_3)_3]$ or $[Rh(H)(CO)(PiPr_3)_2]$ and light could decompose methanol to hydrogen and carbon monoxide, although neither TOF nor TON were provided.[17] The reaction was performed using a 500 W tungsten halogen lamp in the presence of pyrex and water filters. Because methanol can react thermally with $[Rh(H)(PiPr_3)_3]$ to afford $[Rh(H)(CO)(PiPr_3)_2]$, the two catalysts must give rise to a similar catalytic cycle. It was suggested that light is required to dissociate CO from $[Rh(H)(CO)(PiPr_3)_2]$ (λ_{max} = 360 nm) which is formed during the catalytic cycle following formaldehyde decarbonylation and provide a vacant coordination site for a new alcohol molecule to bind. Also in the case of catalysts $[Ru(H)_2(N_2)(PPh_3)_3]$ and $[Ru(H)_2(PPh_3)_4]$ the rate enhancement observed in hydrogen evolution from methanol upon irradiation has been ascribed to the labilization of a coordinated ligand, more specifically to the release of dihydrogen from intermediate $[Ru(H_2)(H)_2(PPh_3)_3]$.[15] A more detailed study concerning methanol dehydrogenation was carried out using $[Pd_2(Cl)_2(dpm)_2]$ and *cis*$[Rh_2(Cl)_2(dpm)_2]$ (dpm = bis(diphenylphosphino)methane) which proved effective in promoting hydrogen evolution from a 9 : 1 MeOH/acetone solution at reflux under photoirradiation with a 400 high-pressure mercury lamp affording a maximum TOF of 156 and 130 h^{-1} respectively.[18] Neither catalyst was active in the dark and the presence of acetone, acting as sensitizer, boosted the activity of both. $[IrH(SnCl_3)_3]^{3-}$, either preformed or generated *in situ* under photoirradiation from $IrCl_3{\cdot}3H_2O$, $SnCl_2{\cdot}2H_2O$ and LiCl, could also catalyse the dehydrogenation of methanol to hydrogen (with trace amounts of methane) and formaldehyde dimethylacetal at reflux, upon exposure to a high pressure mercury lamp.[19]

Aqueous methanol dehydrogenation to hydrogen and carbon dioxide: methanol reforming

In 2013, the first examples of homogeneously catalysed complete methanol dehydrogenation to CO_2 and three molecules of H_2 were disclosed.[11]

$$CH_3OH(g) + H_2O(g) \rightarrow 3H_2(g) + CO_2(g) \quad \begin{array}{l} \Delta H^{\circ}_{298} = 53.3\ \mathrm{kJ\ mol^{-1}} \\ \Delta G^{\circ}_{298} = 0.6\ \mathrm{kJ\ mol^{-1}} \end{array} \tag{3}$$

$$CH_3OH(g) \rightarrow CO(g) + 2H_2(g) \quad \begin{array}{l} \Delta H^{\circ}_{298} = 94.6\ \mathrm{kJ\ mol^{-1}} \\ \Delta G^{\circ}_{298} = 29.3\ \mathrm{kJ\ mol^{-1}} \end{array} \tag{4}$$

$$H_2(g) + CO_2(g) \rightarrow CO(g) + H_2O(g) \quad \begin{array}{l} \Delta H^{\circ}_{298} = 41.1\ \mathrm{kJ\ mol^{-1}} \\ \Delta G^{\circ}_{298} = 28.4\ \mathrm{kJ\ mol^{-1}} \end{array} \tag{5}$$

Exhaustive methanol dehydrogenation is currently realized through steam reforming according to eqn (3) using heterogeneous catalysts which operate between 200 and 300 °C.[7a,b] Established catalysts fall into two main classes: copper-based and group 8–10 metal-based catalysts.[7c,d] Commercially available $CuO/ZnO/Al_2O_3$ is a catalyst formulation which belongs to the first class and highlights the constitutional elements of a competent heterogeneous catalyst: copper is the active metal, ZnO is a metal oxide which ensures active site segregation to prevent copper sintering at high temperatures and alumina provides a high surface support which increases copper dispersion and contributes minimizing sintering as well. Copper-based catalysts are highly active and selective for methanol steam-reforming and are outstandingly cost effective, but suffer from deactivation problems due to the sintering of metal particles above 300 °C and are pyrophoric. Palladium–zinc alloy-based catalysts are representative of the second class: its members enjoy improved thermal stability compared to the copper ones but, in general, are less active and, with the exception of those based on Pd– and Pt–metal alloy, can favour decomposition of methanol according to eqn (4), thus increasing the relative amount of CO contamination.

Lower operational temperatures are highly desirable, especially in view of the application of methanol as fuel in Reformed Methanol Fuel Cells (RMFC) for mobile applications: here methanol reforming takes place on board to directly fuel the cell with hydrogen. Because of the high temperature required by heterogeneous catalysts, the overall efficiency of state of the art devices does not exceed 40%. Furthermore high temperatures favour formation of CO[20] which, already at few ppm concentration, may poison the precious electrocatalyst at the cell anode. It should be mentioned that another possible source of CO contamination under the conditions of steam reforming is the reverse water gas shift reaction (eqn (5)).

A very first report concerning the possibility of applying an homogeneous catalyst to the thermal dehydrogenation of alcohols in the presence of water was published by Cole-Hamilton and relied on the use of $[Rh(bipy)_2]Cl$ as catalyst.[21] The rationale behind the use of water is the possibility to open a new decomposition path according to eqn (3) and Scheme 1, which is thermodynamically less demanding than simple dehydrogenation as to eqn (1) or (2). Reactions were carried out using a 95 : 5 v/v solution of alcohol/H_2O, in the presence of NaOH ($0.25–5 \times 10^{-3}$ mol) with $[Rh(bipy)_2]Cl$ (5×10^{-6} mol) at 120 °C in a closed system for 3 h. Alcohols other than methanol, such as ethanol, isopropanol and butane-2,3-diol, afforded almost a 100 fold higher rate of hydrogen production compared to methanol, which had a TOF = 7 h^{-1} (Table 2, entry 1). No detail though was provided for the gas- and liquid-phase composition of the system after reaction; however, in the case of ethanol, beside H_2 in the gas phase and ethanal and its condensation products in the liquid phase, CH_4 and CO_2 in a 1 : 1 ratio were detected (the latter after acid addition to the solution) showing the ability of the catalyst to promote intermediate aldehyde decarbonylation and formation of CO_2. 25 years later, almost at the same time, two groups, Grützmacher's[22] and Beller's,[23a] reported the efficient aqueous dehydrogenation of methanol to hydrogen and carbon dioxide below 100 °C promoted by homogenous ruthenium catalysts (Fig. 1, **1** and **2**, respectively), with almost no trace of CO contamination, setting the stage for a foreseeable application in RMFC. Very recently Milstein has shown that also ruthenium catalyst **3** (Fig. 1) is able to promote the same transformation.[24] A common feature of these catalysts is that they possess multidentate ligands which confer improved thermal stability to the resulting metal complexes while blocking three (like in **2** and **3**) or four (like in **1**) of the possible metal coordination sites; this is particular useful in order to hamper the possible decarbonylation of formaldehyde arising from methanol dehydrogenation.

Most importantly, the abstraction of hydrogen from the alcohol relies on a cooperative mechanism involving both the metal and the ligand, the latter being therefore termed "non-innocent".[25] Experimental evidence suggests that, when catalysed by such complexes, exhaustive dehydrogenation of methanol might proceed through three consecutive steps: dehydrogenation of methanol to hydrogen and formaldehyde (eqn (1)), dehydrogenation of the gem-diol arising from the reaction of formaldehyde with water (eqn (6)),[26] final dehydrogenation of the resulting formic acid to hydrogen and carbon dioxide (eqn (7)). This sequence is identical to the general reaction pathway shown in Scheme 1.[11]

$$CH_3OH(l) \rightarrow H_2CO(g) + H_2(g) \quad \begin{array}{l} \Delta H^{\circ}_{298} = 129.8\ \mathrm{kJ\ mol^{-1}} \\ \Delta G^{\circ}_{298} = 63.5\ \mathrm{kJ\ mol^{-1}} \end{array} \tag{1}$$

$$H_2CO(g) + H_2O(l) \rightarrow H_2(g) + HCOOH(l) \quad \begin{array}{l} \Delta H^{\circ}_{298} = -30.7\ \mathrm{kJ\ mol^{-1}} \\ \Delta G^{\circ}_{298} = -22.8\ \mathrm{kJ\ mol^{-1}} \end{array} \tag{6}$$

$$HCOOH(l) \rightarrow CO_2(g) + H_2(g) \quad \begin{array}{l} \Delta H^{\circ}_{298} = 31.6\ \mathrm{kJ\ mol^{-1}} \\ \Delta G^{\circ}_{298} = -31.8\ \mathrm{kJ\ mol^{-1}} \end{array} \tag{7}$$

$$CH_3OH(l) + H_2O(l) \rightarrow 3H_2(g) + CO_2(g) \quad \begin{array}{l} \Delta H^{\circ}_{298} = 130.7\ \mathrm{kJ\ mol^{-1}} \\ \Delta G^{\circ}_{298} = 8.9\ \mathrm{kJ\ mol^{-1}} \end{array} \tag{8}$$

The structure of ruthenium hydride $[K(dme)_2][RuH(trop_2dad)]$ (dme = dimethoxyethane, $trop_2dad$ = *N*,*N*′-bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1,4-diaminoethane) **1** has been confirmed by X-ray analysis. It is a 16-electron valence Ru(II) complex which catalyses

Table 2 Active homogeneous catalysts for methanol reforming

Entry	Catalyst (10^{-3} mmol; ppm to MeOH)	MeOH (mmol)	H_2O (mmol)	Solvent (mL)	Additive (mmol)	T (°C)	Time (h)	H_2 (mmol)	Yield[a] (%)	TOF[b] (h^{-1})	TON	Conv. (%)
1	$[Rh(bipy)_2]Cl$[c] 5; 45	111	27.8	—	NaOH 5	120	3	0.105	0.03	7	21	n.r.
2	$[K(dme)_2][RuH(trop_2dad)]$ **1**[d] 10; 500	2	2.6	THF 1	—	90	10	5.0	84.0	54	540	90
3	$[Ru(H)(Cl)(CO)(PNP^{iPr})]$ **2b**[e] 0.88; 1	890	222	—	KOH 320	91	576	311	11.6	613	353 409	[f]
4	$[Ru(H)(Cl)(CO)(PNP^{iPr})]$ **2b** 150; 150	890	222	—	KOH 320	91	24	231	26	64	192	[f]
5	$[Ru(H)(Cl)(CO)(PNP^{Ph})]$ **2a** 49.3; 250	198	111	—	NaOH 1	72	2	3.4	0.57	34	68	[f]
6	$[Fe(H)(BH_4)(CO)(PNP^{iPr})]$ **2c**[g] 1; 4.5	222	55.5	—	KOH 80	91	46	9.8	1.5	214	9834	[f]
7	$[Ru(H)(BH_4)(CO)(PNP^{Ph})]$ **2d**[h] 5; 22.5 $[Ru(H)_2(dppe)_2]$ 5; 22.5	222	55.5	Triglyme 4	—	93.5	192	42.8	6.4	22	4286	6.4
8	$[Ru(H)(Cl)(CO)(NNP^{tBu})]$ **3**[i] 5; 250	20	111	Toluene 2	KOH 40	100–105	648	131	72.8[j]	44	28 661[j]	79

n.r. not reported. [a] The yield is referred to methanol and is calculated assuming that each mmol of converted methanol has been fully dehydrogenated providing three mmoles of hydrogen. [b] The TOF is the average value measured over the entire reaction time. [c] Data extracted from ref. 21, Table 1, experiment performed in a closed vessel. [d] Data extracted from ref. 22, SI pag. 14, base-free experiment. [e] Data extracted from ref. 23*a*, SI pag. 21, long-term experiment with focus on catalyst stability. [f] Because no internal standard was used, it is not possible to provide conversions. For each experiment it is however possible to provide yields relative to the combined amount of water and base, which are the limiting reagent, according to supplementary equation 4 in ref. ref. 23*a*: entry 3, yield 27%; entry 4, yield 20%; entry 5, yield 1%; entry 6, yield 3.4%. [g] Data extracted from ref. 23*b*, Table 1, entry 11. [h] Data extracted from ref. 23*c*, SI pag. 6, long-term experiment. [i] Data extracted from ref. 24, SI pag. 2 Table S1. [j] The TON is the total one over three consecutive uses (recycling) of the organic phase containing the catalyst; likewise, the yield has been calculated based on the total amount of methanol, 3 × 20 mmol, used over the three experiments.

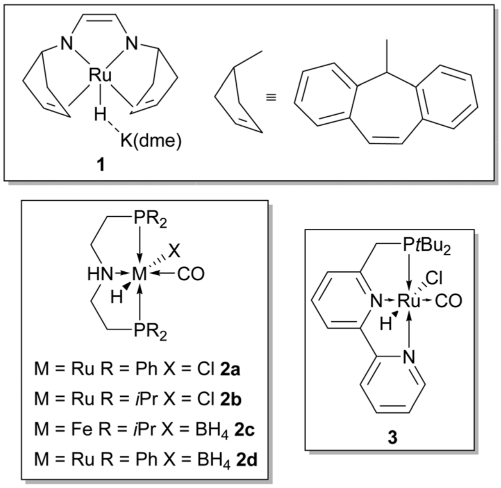
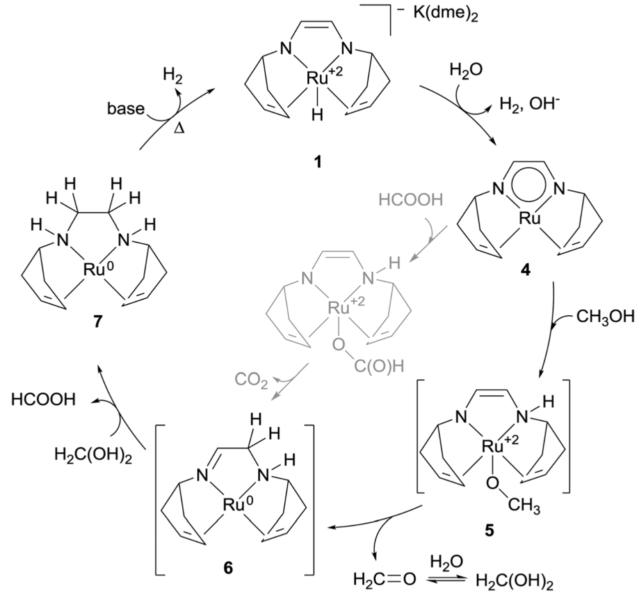


Fig. 1 Homogeneous catalysts which promote the aqueous dehydrogenation of methanol to hydrogen and carbon dioxide.

the reaction of methanol and water to afford H_2 and CO_2 below 100 °C without addition of exogenous base.[22] When the reaction was carried out in an open vessel at 90 °C in MeOH (2 mmol, 81 μL), H_2O (2.6 mmol, 47 μL), toluene (1 mmol, 110 μL as internal standard), and THF (1 mL) with **1** (10×10^{-3} mmol, 0.5 mol% to MeOH), a TON = 540 over 10 hours was achieved corresponding to an average TOF = 54 h^{-1} (each mole of hydrogen gas produced per mole of catalyst is considered as a turnover) (Table 2, entry 2). Neither formaldehyde nor its acetal were detected in solution, suggesting that attack of water may proceed on still coordinated formaldehyde and dehydrogenation of the acetal to formic acid be faster than that of methanol to formaldehyde, as predicted by DFT for primary alcohol dehydrogenation. Indirect evidence of the intermediacy of HCOOH was provided by the ability of **1** (0.01% mol) to decompose a 1 M solution of HCCOH in dioxane at 90 °C within minutes affording an initial turnover frequency of 24 000 h^{-1}. Based on the isolation and characterisation of some relevant intermediates and following investigation into their reactivity, the authors have suggested the catalytic cycle illustrated in Scheme 2. The hydride **1** does not react appreciably with alcohols but it does with H_2O (or carboxylic acid) to generate a very reactive neutral Ru species **4** (characterized by NMR), with release of one molecule of H_2 and one equivalent of base. This is therefore considered to be the first step of the catalytic cycle. Addition of the OH bond of a substrate molecule, either methanol (this case is illustrated in Scheme 2), gem-diol (arising from hydration of formaldehyde), or formic acid, across the Ru–N bond affords the enamido complex **5**. This activates the α-CH of the coordinated substrate which is then transferred to the ligand to give an imino–amino Ru(0) complex **6** after release of the dehydrogenation product. **6** can reiterate this process with a second substrate molecule to provide diamino complex **7** from which one equivalent of hydrogen is then released, aided by base and heat, to regenerate **1**. Intermediates **7** and its adduct with benzaldehyde have been synthesized *via* stoichiometric reactions and characterized by X-ray analysis. Species **4** and **6** are competent for dehydrogenation of either MeOH, formaldehyde gem-diol or formic acid (in Scheme 2 the dehydrogenation of formic acid as by **4** to afford **6** and CO_2 is shown in grey). This is an example of cooperative catalysis in which the ligand is both redox- and chemically active, supporting the metal shuttle between oxidation states 2 and 0 and adding the hydrogen



Scheme 2 Proposed catalytic cycle for the aqueous dehydrogenation of MeOH promoted by $[K(dme)_2][RuH(trop_2dad)]$ **1**.

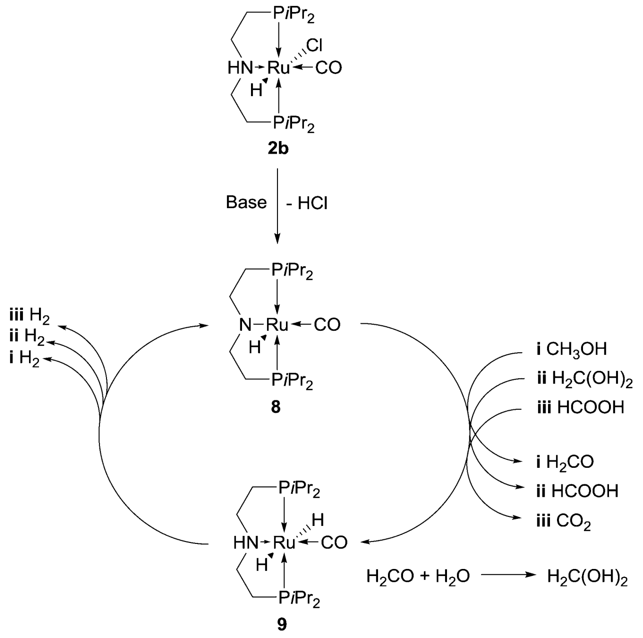
termini abstracted from the substrate which are then released as hydrogen gas.

Ruthenium catalysts $[Ru(H)(Cl)(CO)(PNP^R)]$ (PNP^R = bis[(2-diphenylphosphino)ethyl]amine if R = Ph; bis[(2-diisopropylphosphino)ethyl]amine if R = iPr) **2a** and **2b**, respectively supported by aliphatic PNP ligands, originally developed for ester hydrogenation[27a] (**2a**) and acceptorless dehydrogenation of alcohols other than methanol[27b,c] (**2b**), were identified as competent catalysts for the aqueous reforming of methanol under basic conditions.[23a] Several parameters were found to affect the activity and productivity of the catalysts: type and amount of base, temperature and water content. The reaction turned out to be favoured by a high base content with KOH as base of choice, high temperature and low water amount, yet activity was observed already at 75 °C at 0.1 M base concentration and even in the presence of 90% v/v of water. Under optimised conditions, neat MeOH (10 mL), KOH = 8 M, catalyst **2b** (1.58 μmol, 6.4 ppm), at 95 °C, an average TOF = 4723 h^{-1} was achieved over three hours. The evolved gas was pure hydrogen with almost no trace of CO contamination (below 1 ppm) while CO_2 was trapped as carbonate. By performing a longer term experiment in the presence of less base and a higher amount of catalyst (MeOH 8 mL, H_2O 2 mL, NaOH = 0.1 M, catalyst **2a** 49.3 μmol, 250 ppm, 72 °C) a steady-state condition was achieved within hours when CO_2 could escape the reaction medium and the expected H_2/CO_2 3 : 1 ratio was observed. Complex **2b** proved extremely robust as hydrogen evolution continued for three weeks affording a TON = 350 000 with an average TOF = 200 h^{-1} (using 1.0 ppm **2b** in a 9 : 1 ratio of $MeOH/H_2O$), measured over the last 24 h (Table 2, entry 3). Parallel to base consumption and the ensuing decrease of boiling temperature, in fact, a decrease in activity was observed.

Compound **2b** is merely a catalyst precursor which needs one equivalent of base to be converted into amido complex **8** (Scheme 3). The amido complex has been reported to react with iso-propanol or hydrogen gas to afford dihydride **9**:[27b] the protic hydrogen of the –OH moiety in the alcohol would add to the basic nitrogen of the ligand in **8** whereas the hydride of the α-CH would be transferred to the metal centre. It was therefore suggested that **8** and **9** are the two key species between which dehydrogenation of methanol, formaldehyde gem-diol(ate) and formate (which was detected in solution under catalytic-like conditions) occurs with ensuing hydrogen evolution.[23a]

DFT calculations have provided support to the proposed metal–ligand cooperative mechanism, highlighting the decisive role of the protic solvent, either water or methanol, in relaying a proton shuttle from the ligand nitrogen to the ruthenium hydride for the formation of a ruthenium dihydrogen complex from which hydrogen is eventually released.[28] However it has been suggested, based on calculations, that formate decomposition to hydrogen and carbon dioxide could take place through both inner- and outer-sphere mechanisms.[28b] According to the calculated free-energy landscape of the overall reaction, dehydrogenation of gemdiol(ate) has the lowest rate constant and dehydrogenation of formate the highest among the three steps,[28b] which is in line with the experimental observation that free formate, but neither formaldehyde nor gem-diolate, was observed in solution The actual rate of each step would however depend on the relative concentration of the species involved (''steady-state regime'').

The outer-sphere, cooperative mechanism does not require a change in the formal oxidation state of the central metal to trigger substrate reactivity and is hence open to 1st row transition metals. These metals usually prefer one-electron redox changes, making it more challenging to stabilise and maintain



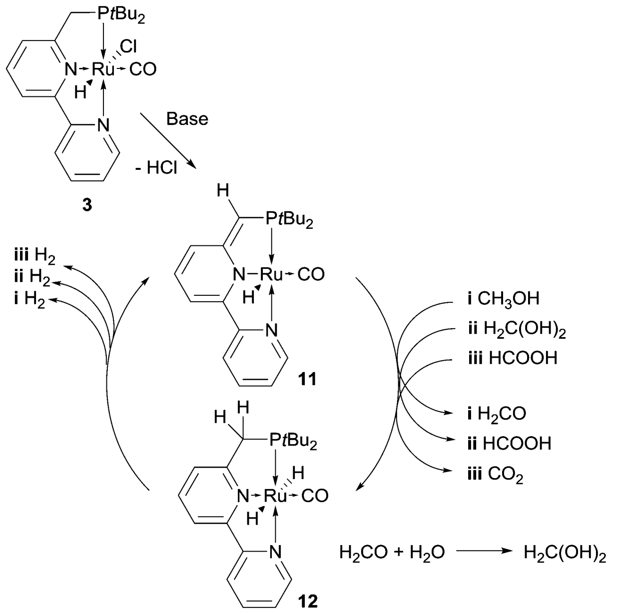
Scheme 3 Oversimplified proposed catalytic cycle for the aqueous dehydrogenation of MeOH promoted by $[Ru(H)(Cl)(CO)(PNP^{iPr})]$ **2b**.

the catalyst functionality, should the reaction proceed according to classical oxidative addition, insertion and reductive elimination. Indeed the analogous iron complex **2c** was synthesized and proved effective in aqueous methanol reforming.[23b,29] Under optimised conditions, $MeOH/H_2O$ 9/1 v/v (10 mL), KOH = 8 M, catalyst **2c** (4.18 μmol, 18.8 ppm to MeOH), at 91 °C, a TOF = 702 h^{-1} was achieved in the first hour, and a TON = 6270 over 43 hours. By adding 5 equivalents of free ligand to the solution it was possible to extend the catalyst lifespan over almost five days, affording, under otherwise identical conditions, a TON = 9184 (111 h) (Table 2, entry 6). Although based on a far cheaper and abundant metal, the iron system is clearly less active than the ruthenium one, as correctly anticipated by theoretical calculations.[28a] However if the turnover activity per unit cost, recently suggested by Crabtree as a further "green" parameter to judge a catalyst,[30] then the advantage brought about by iron is easily apparent and should stimulate further efforts towards the development of 1st row transition metal based catalysts.

One drawback associated with the use of catalysts **2** in methanol reforming is the need for a high base concentration. The role of the base is many-fold: on the one hand it allows, by means of the salt effect, to increase the operational temperature and thus both the thermodynamic driving force and the rate of reaction; it provides an additional free energy advantage because of the acid–base reaction with the generated CO_2; it is likely necessary to regenerate the catalytic active species from dormant resting states.[31] Furthermore, because free formate is actually detected in solution when using catalysts **2** under basic conditions, it was suspected that its dehydrogenation might be slow at low methanol conversion. Therefore it was envisioned that either the addition of a higher catalyst amount, of a second catalyst which had proved effective in formic acid decomposition or of a high-boiling solvent might contribute to achieve methanol reforming even in the absence of base. Indeed, after catalyst and solvent screening, it was found that the combined use of catalyst Ru–MACHO–BH_4 **2d**, which does not need an exogenous base to be activated, and $[Ru(H)_2(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane) **10**, in the presence of triglyme (MeOH 9 mL, H_2O 1 mL, triglyme 4 mL, **2d** 5 μmol, **10** 5 μmol) allows to dehydrogenate methanol at 93.5 °C with an average TOF = 93 h^{-1} over 7 hours.[23c] The catalyst system stayed active for 8 days affording an overall TON of 4286 (Table 2, entry 7). Interestingly the two catalysts operate in a synergistic manner, as their combined activity is superior to the sum of the activities displayed by each of them alone in the same transformation.

Very recently Milstein *et al.* have added catalyst **3** (Fig. 1) to those amenable to methanol reforming: under optimised conditions, MeOH 20 mmol, 0.8 mL, H_2O 111 mmol, 2 mL, toluene 2 mL, KOH 40 mmol, catalyst **3** 5×10^{-3} mmol, 250 ppm to MeOH, T_{set} = 115 °C (effective T = 100–105 °C), a 70% yield of hydrogen was achieved over 9 day reaction time, corresponding to an average TOF = 45 h^{-1}.[24] The base is necessary in order to generate the true catalytic species **11** from **3** (1 equivalent to the catalyst) and, according to the authors, to generate formate from methanol. In fact, while no hydrogen is produced from methanol in the absence of base, conversion of formic acid to hydrogen and CO_2 with the same catalyst is instead possible. Toluene is likely necessary to increase catalyst solubility as no activity was detected in the absence of an organic solvent. Furthermore, the presence of a biphasic system allows for the easy recovery and recycling of the catalyst: the organic phase of the experiment under optimised conditions was separated and used twice for the reforming of new batches of methanol, showing undiminished activity and affording, after an overall reaction time of almost 1 month, a remarkable TON of about 29 000 (Table 2, entry 8). Like in the cases of catalysts **1** and **2**, catalyst **3**, or rather its activated form **11** (Scheme 4), relies on ligand–metal cooperation to abstract hydrogen from the substrate, either methanol, formaldehyde gem diolate or formate.[25f] The dearomatised complex **11**, resulting from deprotonation at the pyridinylmethylenic carbon, can in fact regain aromatisation at the pyridine moiety by interacting with the substrate, adding a "proton-like" hydrogen to the side-arm of the ligand and a "hydride-like" hydrogen to ruthenium (Scheme 4). The resulting dihydride **12** then releases hydrogen.

Very recently Crabtree *et al.* have reported the acceptorless dehydrogenation of methanol using homogeneous iridium bis(N-heterocyclic) carbene catalysts: under optimised conditions (dry MeOH, 3 mL, KOH 6.7 M, [Ir] 1 μmol, 91 °C) using a bis(N-heterocyclic) carbene complex stabilised with CO ligands an overall TON of 2900 over 15 hours was achieved which could be increased to 8000 over 40 hours.[32] However, by measuring the relative amounts of HCOOK and K_2CO_3 produced, it turned out that only 5% of the converted MeOH had been exhaustively dehydrogenated to CO_2 (trapped as carbonate) and H_2, the rest being transformed into formate. Yet the catalysts are noteworthy



Scheme 4 Proposed key-intermediates in the aqueous dehydrogenation of MeOH promoted by **3**, through aromatisation–dearomatisation of the pyridine pincer based ligand.

in that they can operate in air with undiminished efficiency and rely on simpler and cheaper ancillary ligands as to catalyst **1–3**.

For the sake of comparison, selected data concerning the homogeneous catalysts able to promote aqueous reforming of methanol are collected in Table 2. For catalyst **2b**, two further experiments with a higher catalyst loading (Table 2, entries 4 and 5) are reported.

Comparison between data reported in Table 1 for methanol decomposition and in Table 2 for aqueous methanol dehydrogenation clearly show that ruthenium catalysts bearing ''non-innocent'' pincer ligands (Table 2) have proved so far more active in methanol dehydrogenation than those whose ancillary ligands are not directly involved in substrate transformation (Table 1). This is probably due to the higher energy demanding events taking place at the metal in the latter case, like labilisation of a coordinated ligand or change in the oxidation state which is not necessary for the former, or if so, like in the case of catalyst **1** developed by Grützmacher *et al.*, is supported by the ligand.[22]

Among homogeneous catalysts for aqueous methanol dehydrogenation, catalyst **2b** stands out for the high average TOF of 613 h^{-1} over 23 days (although the average TOF during the last 24 hours of the reaction was 200 h^{-1}, which is however still higher than the average TOF for catalysts **1** and **3**). Yet yield is quite limited if compared to those recorded with **1** and **3**: use of a higher catalyst loading serves to improve it although at the expenses of activity (TOF) (compare entries 3 and 4 in Table 2). Unlike others in Table 2, catalysts **2** do not require any added solvent to allow for better catalyst solubilisation and are tolerant of various methanol/water ratios. The robustness of aliphatic PNP pincer ruthenium catalysts has been further demonstrated in the dehydrogenation of higher alcohols, such as biomass derived ethanol[33] and glycerol,[34] a by-product of biodiesel production, selectively affording, in the last case, valuable lactic acid. Catalyst **2a** could be applied directly to industrial batches of bioethanol and glycerol with undiminished, if not superior, efficiency compared to solutions of the pure substrates.

The main drawback of catalysts **2** and **3** is the requirement of high base loads, whereas catalyst **1** operates smoothly without. At the present stage of development, it has been pointed out that the capturing of CO_2 from small and widespread sources may be technically feasible but economically prohibitive and CO_2 should be eventually captured from the atmosphere itself.[9b] On the other hand, the high base concentration required by catalysts **2** and **3** might be advantageously exploited to sequestrate CO_2 for its later recycle, for example by hydrogenation of the resulting bicarbonate to formate salts,[35] while awaiting for a fully reversible charge–discharge $CH_3OH \leftrightarrow CO_2$ process.

Aqueous methanol dehydrogenation actually combines three catalytic cycles running at the same time, each of which might require a different catalyst for optimal efficiency. Entry 7 in Table 2 shows the feasibility of such approach, without the need for catalyst confinement. The possibility of replacing precious metals with non-noble ones has been demonstrated with catalyst **2c**. Designing phosphorus-free ligands would help reducing catalyst cost further.

The activities and productivities of the homogeneous catalysts developed so far for methanol reforming lie far behind those required for practical applications and, at present, do not compare favourably with those achieved with supported metal catalysts.[36] Yet, they operate under milder conditions and are thus more selective (no CO contamination). In addition, the mechanism of a catalytic process promoted by a homogeneous catalysts is in general more easily disclosed and this opens the possibility to tailor an optimized catalyst by modifying its structural electronic and steric properties. This will certainly stimulate further intense effort to develop improved systems for methanol reforming.

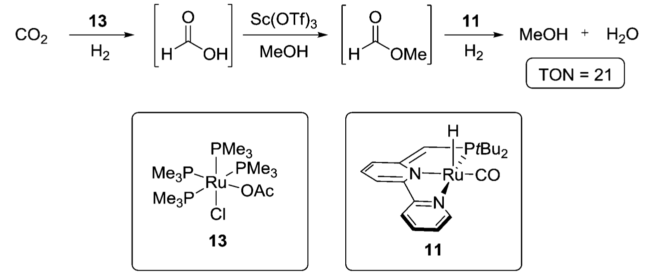
Carbon dioxide hydrogenation

Numerous reports have focussed on partial hydrogenation of CO_2, especially to formic acid, a topic which has been recently reviewed in depth by several authors[37] and readers are referred to them for detailed descriptions on this topic.

For selective reduction to $MeOH–H_2O$, activated hydrides such as boranes[38] or silanes[39] have usually been employed. However, examples of homogeneously catalysed reduction of CO_2 to $MeOH/H_2O$ using molecular H_2 as reducing agent have until recently remained elusive.[40] In this account, the direct hydrogenation of CO_2 to MeOH using H_2 as reductant and homogeneous catalysts will be discussed. In addition, procedures that employ CO_2-derivatives will be mentioned.

Sanford *et al.* presented the first successful example of homogeneous catalytic CO_2 hydrogenation to MeOH and H_2O in 2011.[41] This was achieved through cascade catalysis using a combination of three catalytic systems in order to accommodate the sequential reduction as illustrated in Scheme 5.

The first step is the hydrogenation of CO_2 to formic acid using catalyst **13**,[42] which is followed by a $Sc(OTf)_3$ catalysed esterification to methyl formate. Overall, it was found that, in a one-pot procedure, methyl formate could be formed from CO_2 with a TON of 40 after 16 hours at 135 °C. For the further hydrogenation of the ester to MeOH, complex **11**, one of Milstein's catalysts,[25a,f,43] was employed. This led to an optimised system, which produced MeOH with a TON of 2.5 after 16 hours at 135 °C under 30/10 bars of H_2/CO_2 pressure. A low CO_2 pressure was necessary in order to avoid inactivation of **11** due to covalent bond formation between CO_2 and the complex.[44] A further problem was the inactivation of **11** by



Scheme 5 Sanford approach to CO_2 hydrogenation to $MeOH/H_2O$ using a cascade catalytic system.

Sc(OTf)$_3$, which explained the low overall TON of CO$_2$ conversion to MeOH. These issues were partially circumvented by setting up a two-compartments system in which catalysts **13** and **11** are confined in one compartment, and Sc(OTf)$_3$ in the other. This led to an improved TON of 21.

The system described by Sanford *et al.* illustrates the possibility for homogeneous catalytic CO$_2$ hydrogenation. When comparing this procedure with the general hydrogenation approach shown in Scheme 1, catalyst **13** is responsible for the first reduction, Sc(OTf)$_3$ is present as a Lewis acid for activating formic acid to form methyl formate, and **11** promotes the other two reduction steps towards methanol. Therefore, developing a catalytic system capable of hydrogenating formic acid directly would allow to dispense with Sc(OTf)$_3$. Moreover, finding a catalyst that not only tolerates CO$_2$, but also effectively hydrogenates it all the way to MeOH is of obvious interest. This would allow to use a single catalyst for the whole procedure and to adjust more freely the applied CO$_2$ pressure.

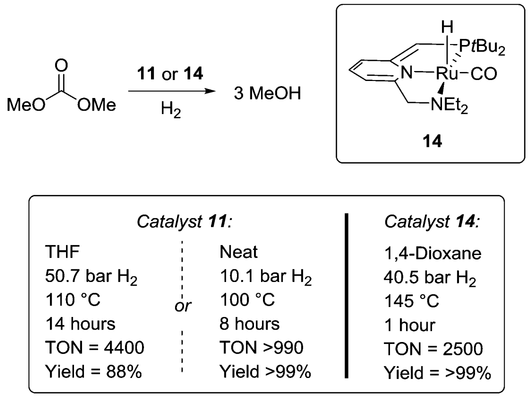
Almost simultaneously with Sanford, Milstein *et al.* showed that the CO$_2$-derivative dimethyl carbonate can be hydrogenated to MeOH using a single catalyst (Scheme 6).[45] Under optimised conditions, a TON of 4400 could be achieved using catalyst **11**, whereas a TON of 2500 was obtained with **14**. Yields of 88% and $>$99% were obtained, respectively. In addition, when using **11** as catalyst (0.01 mol%), the reaction could be performed neat at 100 °C under 10.1 bar of H$_2$ pressure leading to a quantitative yield of MeOH after 8 hours with a TON $>$ 990. Hence, this procedure represents a mild, solvent- and waste free procedure. However, the use of dimethyl carbonate reduces the overall gravimetric H$_2$ capacity of the system. In addition, no long term reactivity was provided.

A mechanism for the catalytic cycle has been proposed based on experimental evidence[45] and calculations.[46] All studies suggest methyl formate and formaldehyde as intermediates, which supports the general pathway shown in Scheme 1. There is, however, some dispute as to how rupture of the OCH$_3$ group on the resulting ruthenium alkoxide is mediated. One suggestion is that one hydrogen from the ligand arm is transferred to afford CH$_3$OH in a cooperative metal–ligand fashion. An alternative lower energy lying route has been put forward where a CH$_3$O group is actually transferred to the metal after transfer of the Ru–H hydride to the carbonyl group (Ru–H/Ru–OCH$_3$ metathesis).[46c]

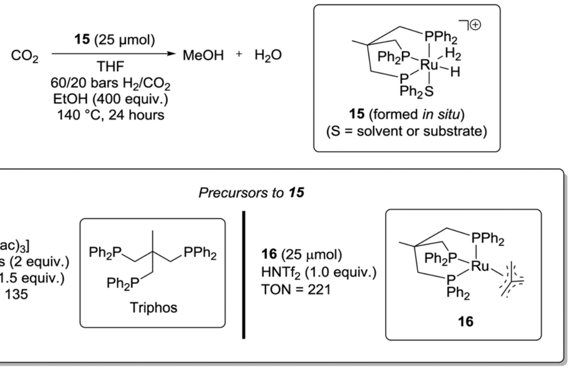
Ding *et al.* showed that **2a** (Fig. 1), is also capable of reducing carbonates to MeOH.[47] At 140 °C, a catalyst loading of 0.001–0.1 mol% suffices to form MeOH in 84–99% yield from a range of carbonate substrates. An impressive TON up to 87 000 and TOF of 1200 h^{-1} were obtained.

Another indirect approach, where CO$_2$ is initially transformed into an urea derivative before being hydrogenated to MeOH and amines, was also suggested by Milstein *et al.*[48] When using 2 mol% of catalyst **11**, yields up to 94% were obtained; however, with 1 mol% of **11** the yields did not exceed 63%, limiting the applicability of the system. Moreover, as opposed to the system shown in Scheme 6, using ureas as CO$_2$-derivatives inevitably creates undesired amine side products. Even if these amines became part of a cycle encompassing urea to MeOH–amine, they would still represent unnecessary ballast compared to the optimal CO$_2$–MeOH hydrogenation–dehydrogenation system.

In 2012, Klankermayer and Leitner *et al.* demonstrated for the first time that a single catalyst is capable of hydrogenating CO$_2$ to MeOH (Scheme 7).[49a] This was achieved by mixing the precursors of catalyst **15**[49b] in THF at 140 °C with 60/20 bars of pressurised H$_2$ and CO$_2$, respectively. In addition, EtOH (400 eq. with respect to **15**) and an acid additive (MSA or HNTf$_2$, 1.0–1.5 eq. with respect to **15**) were required in order to achieve TON values exceeding 10. The precursors of **15** can be either a mixture of [Ru(acac)$_3$] and triphos or **16**. When employing [Ru(acac)$_3$]/triphos a TON up to 135 could be achieved after 24 hours. With **16**, the TON could reach 221. Moreover, it was shown that the system was active for at least 3 days, demonstrating the robustness of the system. EtOH could be replaced by MeOH but at the expense of the efficiency. Under otherwise identical reaction conditions, TONs of 52 and 24 were observed after 24 hours with EtOH and MeOH, respectively. The role of the alcohol was suggested to be ester formation by reaction with formic acid. Using the double amount of ethanol did not result in an increased reaction rate, which the authors ascribed to the fact that ethyl formate formation is not rate-limiting.



Scheme 6 Milstein approach to hydrogenation of the CO$_2$-derivative dimethyl carbonate using either catalyst **11** or **14**.



Scheme 7 Klankermayer and Leitner approach to CO$_2$ hydrogenation to MeOH using a ruthenium–phosphine catalytic system. The stated equivalents are with respect to ruthenium.

However, the efficiency in the absence of an alcohol additive, under otherwise identical reaction conditions, was not reported.

Clear advantages of this system are that CO_2 is directly hydrogenated to MeOH and H_2O by a single catalyst and that the system is stable on the scale of days. As such, this system is a proof of principle that a single molecular organometallic complex can encompass all three hydrogenation steps. Moreover, avoiding THF as solvent would increase the gravimetric H_2 yield of the produced MeOH.

Two years later, Klankermayer and Leitner reported that the same system is capable of performing the full hydrogenation of CO_2 to MeOH without the need of an alcohol additive.[50a] In fact, the conditions that provides a TON of 221 in the presence of 400 equivalents of EtOH (Scheme 7, using **16**) gave a very similar TON of 228 without any alcohol additive. Using half the amount of **16** (12.5 μmol) led to an initial TOF of 79 h^{-1}, which is comparable to state-of-the-art heterogeneous Cu/ZnO catalysts.[51] Moreover, re-pressurising the reaction mixture with CO_2 and H_2 after 16 and 32 hours allowed for a total TON of 603 after 48 hours.

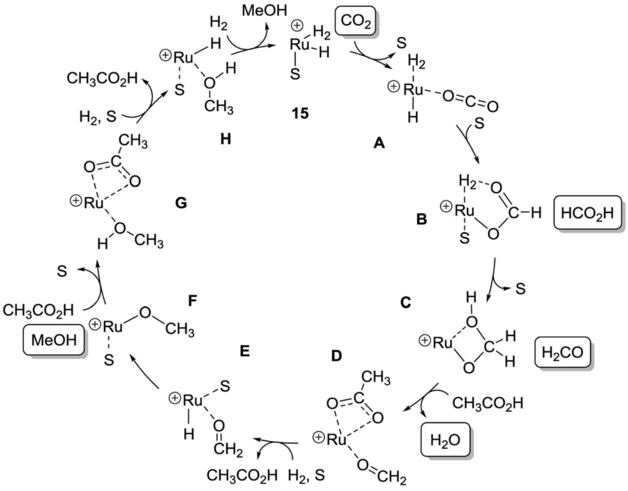
Exchanging THF with 2-MeTHF (2-methyltetrahydrofurane) led to a biphasic system, which allowed for easy separation of the aqueous product phase (H_2O and MeOH) from the organic phase containing the catalyst, though a small decrease in reactivity compared to THF was observed (TON of 186 after 24 hours). A total TON of 769 could be achieved after 4 cycles of CO_2 hydrogenation when using 12.5 μmol of **16**, showing the potential of this reaction system. However, the reactivity of the fourth cycle was merely 50% compared to the first cycle (TON of 110 compared to 247).

Due to the fact that this system represents the first example of a homogeneous catalytic system capable of catalysing the hydrogenation of CO_2 to MeOH, the mechanism proposed by Klankermayer and Leitner is of interest. The mechanistic aspects of all three hydrogenation steps were studied in depth by NMR and *in silico* experiments. Based on this, a very detailed mechanism was proposed, which is presented here in a highly simplified manner in Scheme 8 for the sake of brevity.

Initially, the solvent (S = THF) in **15** is replaced by CO_2 forming complex **A**. After migratory insertion of CO_2 into the ruthenium–hydride bond a solvent molecule coordinates to form **B**. It is proposed that a H_2 molecule is released and re-attached during this process. At this stage, the central CO_2-carbon atom has reached the oxidation state of formic acid.

A heterolytic cleavage of the Ru-bound H_2 followed by a hydride transfer to the carbon atom leads to **C**. To facilitate these events, a H_2 molecule is replacing the solvent and eventually detaches again (not shown). Moreover, the catalytic cycle has at this point reached the stage where the carbon atom has the oxidation state equivalent to that of formaldehyde.

Complex **C** is then converted to **D** by collapse of the ruthenium methanediolate to a ruthenium–formaldehyde adduct assisted by protonation by a carboxylic acid, which acts as proton shuttle. Acetic acid was used as model for the calculations in this instance. The presence of a **D** like intermediate was corroborated by *in situ* NMR studies. Furthermore, it was found that the acid-mediated path is energetically favoured over the water-assisted pathway and **D** represents a low energy intermediate for the formation of **E**. As for the step from **B** to **C**, intermediate **F** is formed from **E** *via* a transient bound H_2 (which replaces the solvent), and transfer of a hydride to the carbon atom, rendering it in the oxidation state of a methanol.



Scheme 8 Highly truncated representation of the Klankermayer and Leitner proposal for the mechanism of the total hydrogenation of CO_2 to MeOH and H_2O catalysed by **15** (shown without Triphos). Acetic acid is used to model a carboxylic unit. S = solvent (THF).

As for the collapse of methanediol (**C** to **E**), a low energy pathway towards **H** is found when introducing a carboxylic acid as assisting unit. Hence, intermediate **G** has a similar function for the **F** to **H** transformation as **D** has it for **C** to **E**. Finally, **15** is regenerated by ligation of H_2 and extrusion of MeOH.

As shown in the catalytic cycle, a single complex is proposed to perform all three hydrogenation stages. Moreover, both formic acid and formaldehyde were shown to be hydrogenated by **15**, supporting the notion of a single complex catalysed hydrogenation of CO_2 to MeOH.

Overall, an exergonic reaction is predicted by the calculations, which is in accordance with (reverse) eqn (8).

Because of the limited number of reports on direct hydrogenation of CO_2 to MeOH by a single molecular catalyst, the work by Klankermayer and Leitner represents a guideline for future studies in this area. Developing more active catalysts for this process is of obvious necessity in order to meet any demands for a practical application of hydrogen storage in a cycle CO_2–MeOH based on homogeneous catalysis. Furthermore, it would be interesting to test the activity of the Klankermayer and Leitner catalyst for the opposite directed reaction, MeOH dehydrogenation.

Complex **16** has also been shown to be active for the hydrogenation of dimethyl carbonate.[50b] Using 1 mol% and 1.5 equivalent of $HNTf_2$ under 50 bar H_2 at 140 °C in dioxane allowed for 99% conversion with 94% selectivity towards MeOH after 16 hours.

Conclusions

Very recently, methanol dehydrogenation to carbon dioxide and the reverse reaction catalysed by homogeneous catalysis have witnessed great progress. Whereas several efficient catalytic systems comprising a single catalyst have already been devised for the former reaction, only a single example of the latter has been published to date. Moreover, much more efficient systems need to be developed for both directions in order to approach practical applicability.

To date, there are no examples of any homogeneous catalytic system capable of catalysing both directions of the CO_2/MeOH cycle. Perhaps combining a system from the dehydrogenation direction that would work under the Klankermayer and Leitner system, such as the Grützmacher system, could show some insight to this intriguing endeavour.

Considering the sudden increase of homogeneous catalytic systems capable of performing MeOH dehydrogenation or CO_2 hydrogenation within the last very few years, it will be very interesting to follow the further developments to come in this area in the near future.

Acknowledgements

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