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Aqueous phase carbon dioxide and bicarbonate hydrogenation catalyzed by cyclopentadienyl ruthenium complexes

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The water-soluble ruthenium(II) complexes [Cp′RuX(PTA)$_2$]Y and [CpRuCl(PPh$_3$)(mPTA)]OTf (Cp′ = Cp, Cp*, X = Cl and Y = nil; or X = MeCN and Y = PF$_6$; PTA = 1,3,5-triaza-7-phosphaadamantane; mPTA = 1-methyl-1,3,5-triaza-7-phosphaadamantane) were used as catalyst precursors for the hydrogenation of CO$_2$ and bicarbonate in aqueous solutions, in the absence of amines or other additives, under relatively mild conditions (100 bar H$_2$, 30–80 °C), with moderate activities. Kinetic studies showed that the hydrogenation of HCO$_3{}^-$ proceeds without an induction period, and that the rate strongly depends on the pH of the reaction medium. High-pressure multinuclear NMR spectroscopy revealed that the ruthenium(II) chloride precursors are quantitatively converted into the corresponding hydrides under H$_2$ pressure. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: catalysis; hydrogenation; carbon dioxide hydrogenation; ruthenium; water-soluble phosphines; cyclopentadienyl complexes

INTRODUCTION

The artificial fixation of carbon dioxide is an important chemical and environmental problem. CO$_2$ is widely available in the atmosphere and its conversion into useful organic C$_1$ building blocks such as methanol or formate remains a great challenge. The main contributions to the field by different groups have been described in an excellent review.[1] Several platinum metal group complexes have been shown to catalyze the hydrogenation of CO$_2$ to formic acid under both conventional and supercritical conditions, and in particular, some ruthenium complexes have been found to be highly active for this process.[2,3] [(η^6-arene)RuCl$_2$]$_2$ (arene = benzene, *p*-cymene) complexes have been used as catalyst precursors together with various ligands in the hydrogenation of CO$_2$ in organic solvents[4] and in water.[5] The possibility of recycling catalysts in aqueous–organic biphasic systems and the fact that aqueous solutions are environmentally benign provide a driving force for industrial application.[6] Homogeneous catalysis in aqueous solutions requires water-soluble catalysts, and in the hydrogenation of CO$_2$, rhodium and ruthenium-based complexes dominate, which employ water soluble phosphine ligands such as mono- and trisulfonated triphenylphosphine (TPPMS and TPPTS, respectively), P(CH$_2$OH)$_3$, P(CH$_2$CH$_2$CH$_2$OH)$_3$, P(CH$_2$CH$_2$CN)$_3$ and PTA (1,3,5-triaza-7-phosphaadamantane).

In previous aqueous catalytic systems, additives, such as organic amines, were usually required to obtain significant turnover frequencies (TOFs), although in the case of CO$_2$ hydrogenation it has been suggested that the role of added

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organic amines is to shift the pH of the reaction in favor of the formation of bicarbonate, which is suggested to be the reactive species.[7,8] As additives lower the general applicability of catalytic protocols in aqueous solutions and result in waste products, there is an interest in developing additive-free protocols. Several amine-free aqueous catalytic systems have been reported in the literature where significant TOFs have been achieved by performing the reactions in slightly basic aqueous solutions.[9,10] In the case of CO_2 hydrogenation, the most favorable pH for the reaction can relatively easily be adjusted by the addition of bicarbonate to the reaction mixture.

The cationic $[(\eta^6\text{-}p\text{-cymene})RuCl(PTA)_2]BF_4$ as well as the neutral $[(\eta^6\text{-}p\text{-cymene})RuCl_2(TPPTS)]$ and $[(\eta^6\text{-}p\text{-cymene})RuCl_2(PTA)]$ complexes have been used as precatalysts for the hydrogenation of various substrates,[11,12] including CO_2 hydrogenation.[5] A common feature of these complexes is that under the reaction conditions they are readily converted into the active catalytic species by loss of the coordinated arene, in turn needing long induction periods and leading to inactive polymetallic thermodynamic sinks, which hamper high catalytic performance and prevent recycling.

We have been interested for some years in the applications of arene and cyclopentadienyl Ru complexes bearing the water-soluble monodentate phosphine PTA in selective hydrogenation reactions,[9,13] and in medicinal applications,[11,12,14–17] and recently extended these studies to other transition metals[18,19] and ligand modifications to observe their implications in catalysis;[20–23] the various aspects of PTA chemistry have been recently reviewed.[24] Under hydrogenation conditions, (pentamethyl) cyclopentadienyl Ru PTA complexes usually showed higher stability than the corresponding arene complexes, thus they are reasonable candidates as catalysts for CO_2 hydrogenation.

Herein, we report results on the hydrogenation of CO_2 and bicarbonate in aqueous solutions, in the absence of amines or other additives, under relatively mild conditions (100 bar H_2, 30–80 °C) in the presence of catalytic amounts of the water-soluble ruthenium(II) complexes $[Cp'RuX(PTA)_2]Y$ and $[CpRuCl(PPh_3)(mPTA)]OTf$ ($Cp' = Cp$, Cp^*, $X = Cl$ and $Y = \text{nil}$; or $X = MeCN$ and $Y = PF_6$; PTA = 1, 3, 5-triaza-7-phosphaadamantane; mPTA = 1-methyl-1,3,5-triaza-7-phosphaadamantane), together with kinetic data obtained by multinuclear high-pressure NMR techniques.

EXPERIMENTAL

General information

All synthetic procedures were carried out using standard Schlenk glassware under an inert atmosphere of dry nitrogen. The ligands PTA,[25] mPTA[26] and the ruthenium complexes $[CpRuCl(PTA)_2]$ (**1**), $[Cp^*RuCl(PTA)_2]$ (**2**), $[CpRu(MeCN)(PTA)_2](PF_6)$ (**3**), $[Cp^{*\prime}Ru(MeCN)(PTA)_2](PF_6)$ (**4**) and $[CpRu(PPh_3)(mPTA)Cl]$ (**5**) were prepared as described in the literature.[11,12,27,28] All subsequent manipulations were carried out under oxygen-free conditions using standard Schlenk techniques with N_2, H_2 or CO_2 protective gases, as appropriate. Doubly distilled water was used throughout. D_2O (99.9%), D_2 (99.9%), Na_2CO_3 and $NaHCO_3$ (99% enriched in ^{13}C) were purchased from Cambridge Isotope Laboratories. Na_2CO_3, $NaHCO_3$ and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (TSPSA) were obtained from Fluka and used as received. H_2 and CO_2 were acquired from Carbagas and ruthenium(III) chloride was purchased from Johnson Matthey. ^1H, ^{13}C, ^2H and ^{31}P NMR spectra were recorded on a Bruker DRX400 NMR instrument in D_2O or $D_2O–H_2O$ mixtures. Pressurized samples were studied using medium pressure sapphire NMR tubes (up to 100 bar). Chemical shifts are referenced to 3-(trimethylsilyl)-1-propanesulfonic acid Na-salt (TSPSA, Fluka) and 85% H_3PO_4.

Hydrogenation experiments

A medium-pressure sapphire NMR tube (o.d. 10 mm) was used as a reactor. Under an N_2 atmosphere, the appropriate catalyst (9×10^{-6} mol), $NaHCO_3$ enriched in ^{13}C (99%) (16.8 mg, 0.2×10^{-3} mol), H_2O (1.6 ml) and D_2O (0.4 ml) were loaded into the sapphire tube. The tube was pressurized with H_2 (100 bar). The tube was shaken at the desired temperature (295–353 K) using equipment built in-house for this purpose. The reaction was monitored by ^1H and ^{13}C NMR spectroscopy and the integral of the formate C and H signals, as well as the integral of the CO_2 and CO_3^{2-}/HCO_3^- signal, were determined. The spectra were fitted with WINNMR, GNMR 4.0 and NMRICMA/MATLAB programs on PC (nonlinear least square fit to determine the spectral parameters; the differences between the measured and calculated spectra were minimised). The initial rates and turnover frequencies (= mol formate mol catalyst^{-1} h^{-1}) were calculated by nonlinear least squares fits of the experimental data from the initial part of the reactions. The overall activation enthalpy was determined in the temperature range $T = 295–353$ K in 1.0 M $NaHCO_3$ solutions.

Study of the pH effect on the hydrogenation

In the alkaline pH range (8.3–11.8), an appropriate mixture of Na_2CO_3 and $NaHCO_3$ was used to obtain a solution of the desired pH while keeping the total initial carbonate + bicarbonate concentration constant. In this pH range there is a fast exchange (on the NMR time scale) between carbonate and bicarbonate, therefore an average ^{13}C NMR shift can be determined and related to the pH, and a calibration curve of the pH vs chemical shift was measured. In order to prepare solutions with pH < 8.3, the reaction mixture was placed in a sapphire tube and pressurized with CO_2. The CO_2 pressure required to obtain a specific pH and the required concentration of $NaHCO_3$ were calculated using the pK values of carbonic acid p$K_1 = 6.35$, p$K_2 = 10.33$ (at 298 K) taken from the literature.[29] ^{13}C NMR spectra were recorded before addition of H_2 and the absolute intensities of the separate HCO_3^- and CO_2 signals (slow exchange on the

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NMR time scale in this pH range) were used to determine the total initial carbon concentration and to calculate the pH.

RESULTS AND DISCUSSION

Complexes **1–5**, shown in Fig. 1, were tested as catalysts for CO_2 or bicarbonate reduction in the pH range from 5.30 to 10.54 and in the temperature range from 30 to 80 °C. The reactions were followed by ^{13}C NMR spectroscopy; next to the resonance of $NaH^{13}CO_3$ at 160 ppm, a signal corresponding to $[HCOO]^-$ appears ($\delta = 171$ ppm, $^1J_{CH} = 195$ Hz) together with the appearance of the ^{13}C resonance of $[DCOO]^-$ ($\delta = 170.8$ ppm, $^1J_{CD} = 32$ Hz). Catalytic deuterium exchange between H_2, D_2O and the formate observed here is frequently encountered, since ruthenium–phosphine complexes often catalyze H–D exchange in water.[30,31] In general, at high pH values low turnover frequencies for **1** and **2** were observed, see Table 1. Complex **1** was found to require temperatures above 50 °C in order to efficiently catalyze the hydrogenation of bicarbonate to formate, and long reaction times were required in order to achieve significant conversions, decreasing the overall TOFs. The best value for initial TOF (h^{-1}) using **1** (5.16) was obtained at 80 °C under slightly basic pH (7.9) conditions, although almost complete conversion required long reaction time (ca. 12 h). Under these conditions, the fastest reaction rate using **1** was measured as 1.83×10^{-4} s^{-1} (Table 2). It was already reported that in water **1** is quantitatively converted at first into the corresponding aquo complex $[CpRu(H_2O)(PTA)_2]Cl$ (**6**) and then, under a pressure of hydrogen, into the corresponding monohydrido complex $[CpRu(H)(PTA)_2]$ (**7**).[11,12] The synthesis of **7** was also reported by Frost and coworkers.[32] When used as a catalyst for the hydrogenation of unsaturated organic substrates, the Cp ring in **7** does not dissociate, in contrast to that observed for arene complexes such as $[Ru(p\text{-cymene})Cl_2(PTA)]$, $[Ru(\eta^6\text{-benzene})Cl(PTA)_2]^+$ and $[Ru(\eta^6\text{-benzene})Cl_2(PTA)]$, giving either Ru hydrido-clusters of the kind $[Ru_4H_x(\eta^6\text{-benzene})_4]^{2+}$ ($x = 4$, 6) or arene-free PTA complexes such as $[RuCl_2(PTA)_4]$, albeit at slower rate than the active $[Ru(\eta^6\text{-arene})(H)(PTA)_2]^+$. We have verified that, also under the conditions of this study, complex **7** is formed, as observed from the singlet at −21.38 ppm in the $^{31}P\{^1H\}$NMR spectrum, or alternatively a doublet centered at same chemical shift in the ^{31}P NMR spectrum, or a triplet at −14.96 ppm ($^2J_{HP}$ 35.3 Hz, ^1H NMR, D_2O). No evidence for other hydrido- or PTA-containing species was observed, in agreement with the lack of induction period in the formation of formate, as shown in Fig. 2.

In contrast, **2** was found to be active at temperatures as low as 25 °C (see Tables 1 and 2). At moderate temperatures (50 °C) and pH 8.14 faster formation of formate (TOF = ca. 17 h^{-1}) was observed as expected. A study of the pH dependence showed that decreasing the pH from 8.14 to 5.6 increased the rate two-fold at 30 °C, whereas at high pH (>10), high temperatures were required to achieve significant TOFs. As for **1**, exposure of **2** to a pressure of hydrogen in D_2O revealed the formation of the monohydrido species $[Cp^*Ru(H)(PTA)_2]$ (**8**), which were previously identified by HP NMR techniques.[11,12]

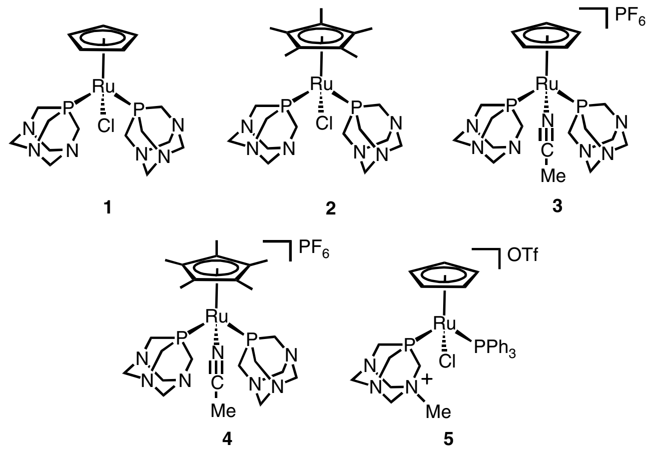

Figure 1. Catalyst precursors used in the present study.

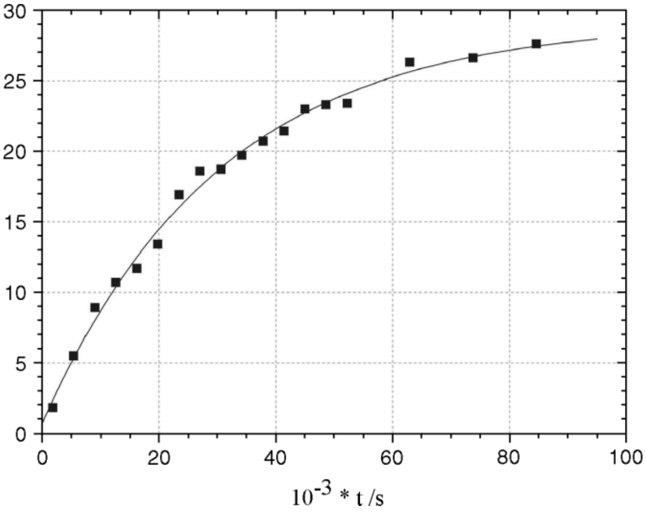

Figure 2. Typical concentration–time profile of $HCOO^-$ formation at 353 K, monitored *in situ* by ^1H and ^{13}C NMR spectroscopy. Initial conditions: $[NaH^{13}CO_3] = 0.030$ M, pH = 8.40, $P(CO_2) = 0$ bar, $P(H_2) = 100$ bar, $[CpRu(PTA)_2Cl] = 0.0045$ M.

We reasoned that complexes such as **3** and **4** bearing a labile neutral MeCN ligand in place of the chloride ligand could prove more active than **1** and **2**. The complexes were therefore tested at a few selected temperatures and pH, under the same reaction conditions as for **1** and **2**. It was observed that, while **3** was less active than **1** under comparable conditions (TOF = 0.5 h^{-1} at pH 8.14, 80 °C), **4** was slightly more active (TOF = 20 h^{-1}) than **2** when the pH was raised from 8.14 to 10.54. The TOFs of **2** and **4** were comparable to those obtained for the system $[(\eta^6\text{-}C_6H_6)RuCl_2]_2 + 4$ PTA (TOF = 22 h^{-1}).[5]

Table 1. Catalyst screening for aqueous hydrogenation of bicarbonate catalyzed by **1** and **2** at different values of pH and temperature[a]

Catalyst	T (°C)	pH	Percentage conversion	Time (h)	Initial TOF (h^{-1})
1	50	10.54	3	14	0.04
	50	7.87	27	3	1.2
			80	24	
	50	5.94	41	3	1.56
			80	24	
	65	7.87	65	3	4.5
			69	12	
	80	10.54	5	26	0.05
	80	9.46	20	3	1.4
			48	20	
	80	7.87	75	3	5.2
			94	12	
2	25	10.2	12.5	11	1.0
	25	9.4	38	5	7.4
	25	6.24	45	5	12.1
	30	9.46	5	3	0.4
			16	13	
	30	8.14	36	3	2.3
			82	24	
	30	5.60	64	3	5.0
			96	24	
	50	9.46	50	3	3.9
			66	5.5	
	62	10.3	52	5	11.4
	80	12.2	54	5	16.0

[a] Conditions provided in the Experimental section. Turnover frequencies were calculated by nonlinear least squares fits of the experimental data from the initial part of the reactions.

Table 2. Pseudo-first-order rates for the aqueous hydrogenation of bicarbonate catalyzed by **1** and **2** at different values of pH and temperature[a]

Catalyst	T (°C)	pH	$10^4 k_{obs}$ (s^{-1})
1	50	7.87	0.36
		5.94	0.51
	65	7.87	0.88
	80	10.1	0.13
		9.46	0.48
		9.00	0.33
		7.87	1.83
2	25	10.20	0.02
		9.40	0.17
		6.24	0.17
	30	9.46	0.16
		8.90	0.42
		8.14	0.43
	50	9.46	1.38
		8.14	5.16
	62	10.3	0.17
	80	10.54	0.22
		9.30	3.62
		9.05	1.38
		8.40	15.8

[a] Conditions provided in the Experimental section.

Table 3. Kinetic parameters for CO_2/HCO_3^- reduction: activation enthalpies and entropies. The overall activation enthalpy was determined in the temperature range $T = 295–353$ K in 1.0 M $NaHCO_3$ solutions

Catalyst	**1**	**2**
ΔH, kJ mol^{-1}	$+46.9 \pm 2.3$	$+60.1 \pm 1.9$
ΔS, J mol^{-1} K^{-1}	$+0.5 \pm 0.3$	$+3 \pm 2$

In addition, the water-soluble mixed phosphine complex **5** was evaluated as a catalyst for bicarbonate reduction. Complex **5** gave modest initial TOFs under all tested conditions, ranging from 1.2 h^{-1} (pH 8.14, 30 °C) to 10.3 h^{-1} (pH 9.05, 80 °C). Increasing the pH further resulted in a lower TOF 4.0 h^{-1} (pH 9.90, 80 °C).

Activation parameters were obtained by Eyring plots of $\ln(k_{obs}/T)$ against $1/T$ (Fig. 3). Table 3 shows the calculated apparent activation energies. These values reflect the temperature sensitivity of the whole reactions and there was not enough information to separate the global values for the elementary steps (formation of the catalytically active species, hydrogen activation, hydride transfer to bicarbonate, etc.) that have major contributions to the activation energy. For comparison, the apparent activation energy of the hydrogenation of bicarbonate with $[RuCl_2(PTA)_4]$ was found to be 86 kJ.mol^{-1},[7,8] and for the $[RhCl(TPPTS)_3]$-catalyzed hydrogenation of CO_2 in $H_2O–HNMe_2$ mixtures a much lower value, $E_a = 25$ kJ mol^{-1}, was determined.[7] The entropy contributions seem to be modest, as values close to isoentropic reactions were obtained.

CONCLUSIONS

All complexes used in this study were found to be moderately active in the hydrogenation of bicarbonate. Almost complete conversions were obtained using chloride complex **1** at 80 °C (pH 7.8, 12 h) and **2** at 50 °C (pH 8.14, 5.5 h). As for the Ru-arene complexes, such as $[Ru(\eta^6\text{-arene})Cl_2(PTA)]$ and $[Ru(\eta^6\text{-arene})Cl(PTA)_2]$, the catalytically active species can be proposed as corresponding to monohydride species. The complexes screened appear to be more stable under the conditions used as compared with the η^6-arene analogs.

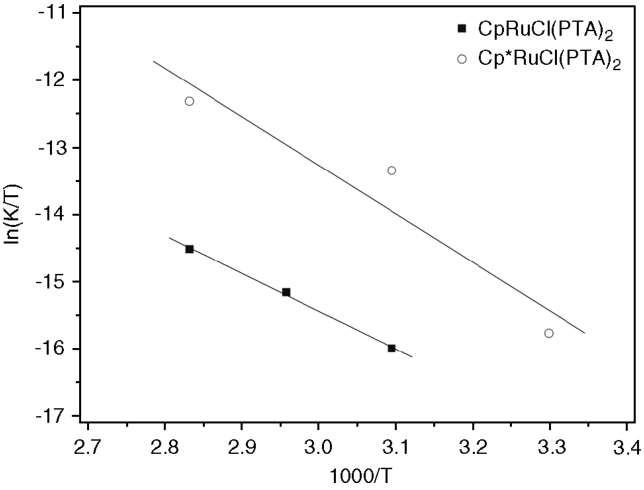

Figure 3. Eyring plots for HCO_3^- reduction in the presence of **1** and **2**.

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