Formation and Characterization of Water-Soluble Hydrido-Ruthenium(II) Complexes of 1,3,5-Triaza-7-phosphaadamantane and Their Catalytic Activity in Hydrogenation of CO_2 and HCO_3^- in Aqueous Solution

Gábor Laurenczy,*,[†] Ferenc Joó,[‡,§] and Levente Nádasdi*,[†,§]

Institute of Inorganic and Analytical Chemistry, University of Lausanne, BCH,
CH-1015 Lausanne-Dorigny, Switzerland and Institute of Physical Chemistry, University of Debrecen,
and Research Group of Homogeneous Catalysis of the Hungarian Academy of Sciences,
H-4010 Debrecen, P.O. Box 7, Hungary

Received February 23, 2000

The water-soluble tertiary phosphine complex of ruthenium(II), $[RuCl_2(PTA)_4]$, (PTA = 1,3,5-triaza-7-phosphaadamantane) was used as catalyst precursor for hydrogenation of CO_2 and bicarbonate in aqueous solution, in the absence of amine or other additives, under mild conditions. Reaction of $[RuCl_2(PTA)_4]$ and H_2 (60 bar) gives the hydrides $[RuH_2(PTA)_4]$ (at pH = 12.0) and $[RuH(PTA)_4X]$ ($X = Cl^-$ or H_2O) (at pH = 2.0). In presence of excess PTA, formation of the unparalleled cationic pentakis-phosphino species, $[HRu(PTA)_5]^+$, was unambiguously established by ^1H and ^{31}P NMR measurements. The same hydrides were observed when $[Ru(H_2O)_6][tos]_2$ (tos = toluene-4-sulfonate) reacted with PTA under H_2 pressure. The rate of CO_2 hydrogenation strongly depends on the pH. The highest initial reaction rate (TOF = 807.3 h^{-1}) was determined for a 10% HCO_3^-/90% CO_2 mixture (pH = 5.86), whereas the reduction was very slow both at low and high pH (CO_2 and Na_2CO_3 solutions, respectively). ^1H and ^{31}P NMR studies together with the kinetic measurements suggested that HCO_3^- was the real substrate and $[RuH(PTA)_4X]$ the catalytically active hydride species in this reaction. Hydrogenation of HCO_3^- showed an induction period which could be ascribed to the slow formation of the catalytically active hydride species.

Introduction

CO_2 is widely available in the atmosphere, and its conversion into useful organic C_1 building blocks such as methanol or formate is a great challenge for chemistry.[1−3] The first homogeneously catalyzed synthetic CO_2 reductions were reported only in the late 1960s and early 1970s.[4] Recently several platinum metal complexes were shown to catalyze the hydrogenation of CO_2 to formic acid under both sub- and supercritical conditions, and some ruthenium complexes have been found highly active in this process. In the synthesis of dimethylformamide from CO_2, H_2, and trimethylamine, Jessop and coworkers achieved turnover frequencies (TOF) up to 7200 h^{-1} using $[RuCl_2(PMe_3)_4]$ as catalyst in sc.CO_2 as solvent[5,6] while Baiker[7] et al. used a $[RuCl_2(dppe)_2]$ catalyst [dppe = $Ph_2P(CH_2)_2PPh_2$] for the hydrogenation of CO_2 in the presence of dimethylamine with an extremely high TOF of 360000 h^{-1}.

Since the discovery of water soluble phosphines, extensive studies have been carried out to employ their transition metal-complexes in aqueous/biphasic catalytic processes.[8−10] The possibility of catalyst recycling in water/organic biphasic systems and the fact that aqueous solutions are environment-friendly reaction media constitute the main driving force for industrial application.[11]

Tris(*m*-sulfophenyl)phosphine (TPPTS) complexes of rhodium(I) and ruthenium(II) proved to be catalytically active for hydrogenation of CO_2 in aqueous systems.[12] In the presence of organic amines a TOF of 1365 h^{-1} was detected using $[RhCl(TPPTS)_3]$ at room temperature and 40 bar total pressure while TOF = 7260 h^{-1} was established at 354 K. Under the same conditions, the analogous ruthenium complex, $[RuCl_2(TPPTS)_3]$, showed inferior catalytic activity (TOF = 6 h^{-1}). No hydrogenation products were detected in the absence of organic amines or alcohols. $[PdCl_2(TPPTS)_2]$ showed no activity; however, $PdCl_2$ was an active catalyst (TOF 530 h^{-1}) in aqueous

---

* To whom correspondence should be addressed. Phone: +4121 692 3858. Fax: +4121 692 3865. e-mail: Gabor.Laurenczy-Batta@icma.unil.ch.

[†] University of Lausanne.

[‡] University of Debrecen.

[§] Research Group of Homogeneous Catalysis of the Hungarian Academy of Sciences.

(1) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207−2221.

(2) Walther, D.; Rubens, M.; Rau, S. *Coord. Chem. Rev.* **1999**, *182*, 67−100.

(3) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155−174.

(4) Volpin, M. E.; Kolomnikov, I. S.; Lobeeva, T. S. *Izv. Akad. Nauk. SSR, Ser. Khim.* **1969**, 2084. (b) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1972**, *46*, C58−C60.

(5) Yessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231−233

(6) Yessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259−272

(7) Kröcher, O.; Köppel, R. A.; Baiker, A. *J. Chem. Soc., Chem. Commun.* **1997**, 453−454.

(8) Papadogianakis, G.; Sheldon, R. A. In *Catalysis*; A Special Periodical Report (Spivey, J. J., Senior Reporter); The Royal Society of Chemistry: London, 1999; Vol. 13.

(9) Cornils, B.; Herrmann, W. A., Eds. *Aqueous-Phase Organometallic Catalysis, Concepts and Applications*; Wiley-VCH: Weinheim, 1998.

(10) Joó, F.; Kathó, Á. *J. Mol. Catal. A* **1997**, *116*, 3−26.

(11) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal. A* **1995**, *104*, 17−85.

(12) Gassner, F.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1465−1466. (b) Leitner, W.; Dinjus, E.; Gassner, F. In *Aqueous-Phase Organometallic Catalysis, Concepts and Applications*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 1998; pp 486-498.

10.1021/ic000200b CCC: \$19.00

KOH solution[13a] and the presence of water similarly increased the rate of CO_2 reduction with catalysts prepared in situ from $RuCl_3$ and PPh_3.[13b]

$[RuCl_2(PMe_3)_4]$ proved highly active in CO_2 reduction under supercritical conditions.[5,6] The air-stable tertiary phosphine 1,3,5-triaza-7-phosphaadamantane[14] (PTA) can be regarded as a water-soluble analogue of PMe_3 as based on its small size (cone angle = 102°) and electronic properties.[15,16] Catalytic properties of several Ru(II) and Rh(I) complexes of PTA in aqueous solutions were extensively investigated[17−20] by Darensbourg and Joó. $[RuCl_2(PTA)_4]$ was found only slightly reactive under atmospheric pressure of H_2; however, it actively catalyzed the selective reduction of unsaturated aldehydes to unsaturated alcohols.[17,18] No attempts were made to identify hydrido complexes in these reactions. In contrast to $[RuCl_2(PTA)_4]$, $[RhCl(PTA)_3]$ is an efficient catalyst in the hydrogenation of olefins.[17,19−21] The mechanism and the selectivity of these hydrogenations can be strongly influenced by the pH of the solution. For example, with $[RuCl_2(TPPMS)_2]$ as catalyst for the reduction of unsaturated aldehydes in biphasic systems, the reaction was selective for $C{=}C$ reduction at low pH while in alkaline solution selective hydrogenation of the aldehyde function was observed.[22] This opposite selectivity could be explained by the effect of pH on the formation and on the distribution of the various hydridoruthenium(II) species.[23]

The apparent similarity of PTA to PMe_3 prompted the investigation of the catalytic activity of $[RuCl_2(PTA)_4]$ in hydrogenation of CO_2 in aqueous solutions. As part of a thorough kinetic study of the reaction, the pH-dependence of the reaction rate was determined in detail. To identify the catalytically active species, extensive multinuclear NMR studies were carried out to detect and characterize the hydrides formed from $[RuCl_2(PTA)_4]$ under H_2 pressure. We have already reported some preliminary results elsewhere.[24]

Experimental Section

All manipulations were done 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.

Reagents. D_2O (99.9%), D_2 (99.9%), and $NaHCO_3$ 99% enriched in ^{13}C were purchased from Cambridge Isotope Laboratories. Na_2CO_3, $NaHCO_3$, $NaHCO_2$, NaOH, HCOOH, HCHO, tetrakis(hydroxymethyl)-phosphonium chloride (80% aqueous solution), urotropine, and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (TSPSA) were the products of Fluka and used as received. H_2 and CO_2 were acquired from Carbagas-CH. Ruthenium(III) chloride was purchased from

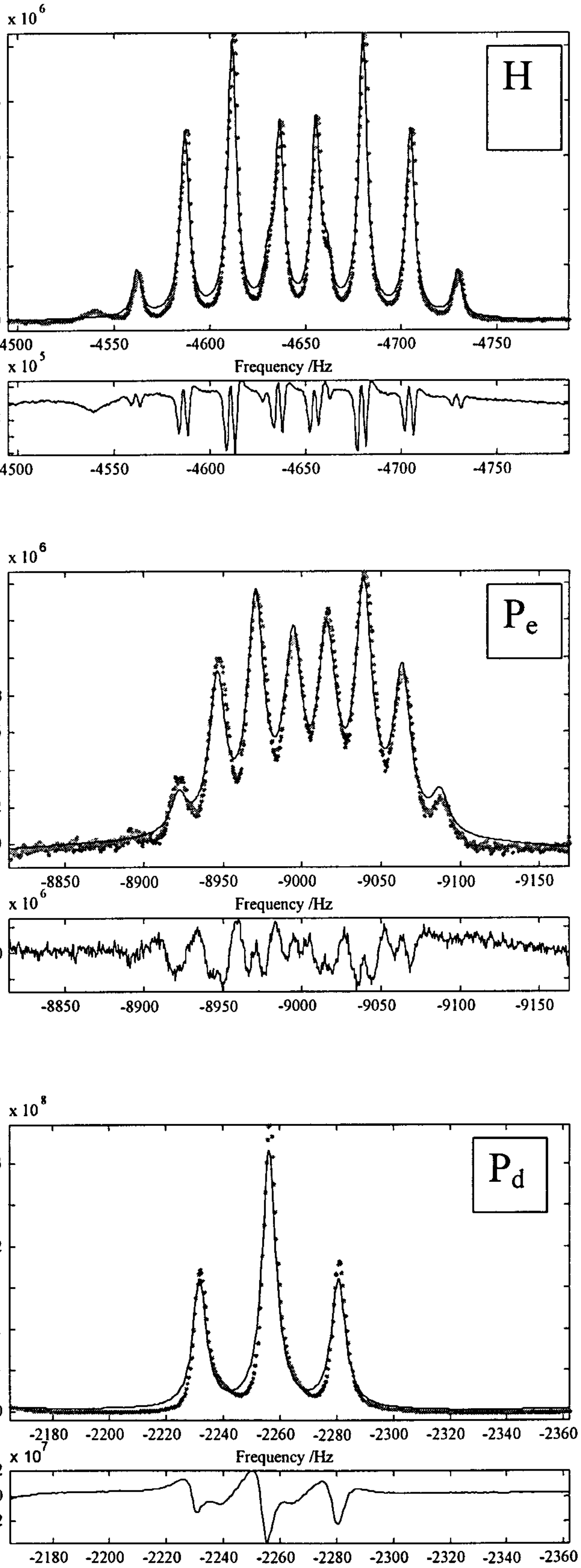


Figure 1. The measured and the calculated ^1H (top) and $^{31}P\{^1H\}$ (middle and bottom) NMR spectra of $[RuH(PTA)_5]^+$ (the differences between the measured and calculated intensities are shown below the spectra).

---

(13) Kudo, K.; Sugita N.; Takezaki, Y. *Nihon Kagaku Kaishi* **1977**, 302. (b) Zhang, J. Z.; Li, Z.; Wang, H.; Wang, C. Y. *J. Mol. Catal. A* **1996,** *112*, 9−14.

(14) Daigle, D. J.; Pepperman A. B.; Vail S. R. Jr. *J. Heterocycl. Chem.* **1974**, *17*, 407.

(15) Daigle, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1975**, *14*, 1217−1218. (b) Delerno, J. R.; Trefonas, L. M.; Darensbourg, M. Y.; Majeste, R. J. *Inorg. Chem.* **1976**, *15*, 816−819.

(16) Alyea, E. C.; Fisher, K. J.; Foo, S.; Philip, B. *Polyhedron* **1993**, *12*, 489−492.

(17) Darensbourg, D. J.; Joó, F.; Kannisto, M.; Kathó, Á.; Reibenspies, J. H. *Organometallics* **1992**, *11*, 1990−1993.

(18) Darensbourg, D. J.; Joó, F.; Kannisto, M.; Kathó, Á.; Reibenspies, J. H.; Daigle, D. J. *Inorg. Chem.* **1994**, *33*, 200−208.

(19) Darensbourg, D. J.; Stafford, N. W.; Joó, F.; Reibenspies, J. H. *J. Organomet. Chem.* **1996**, *488*, 99−108.

(20) Joó, F.; Nádasdi, L.; Bényei, A. Cs.; Darensbourg, D. J. *J. Organomet. Chem.* **1996**, *512*, 45−50.

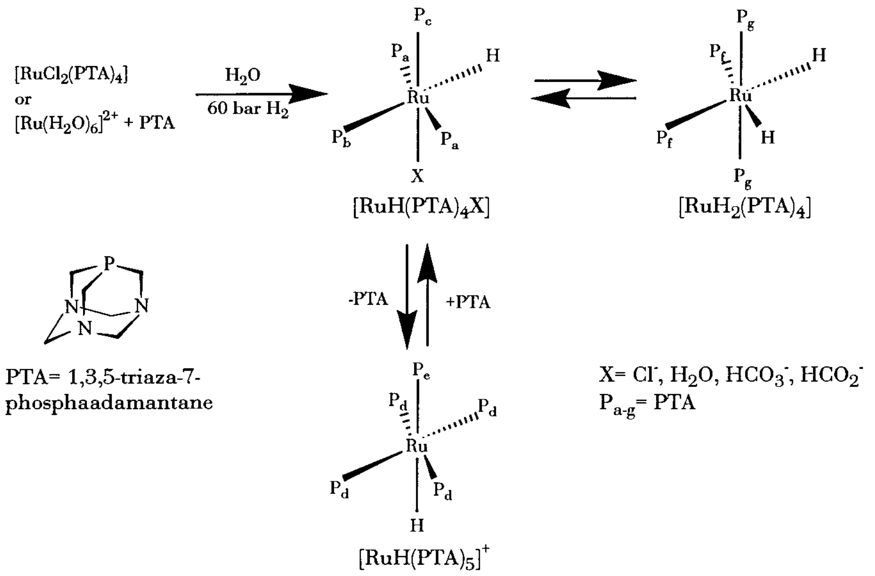
(21) Nádasdi, L.; Joó, F. *Inorg. Chim. Acta* **1999**, *293*, 218−222.

(22) Joó, F.; Kovács, J.; Bényei, A. Cs.; Kathó, Á. *Angew. Chem., Int. Ed.* **1998**, *37*, 969−970.

(23) Joó, F.; Kovács, J.; Bényei, A. Cs.; Kathó, Á. *Catal. Today* **1998**, *42*, 441−448.

(24) Joó, F.; Laurenczy, G.; Nádasdi, L.; Elek, J. *J. Chem. Soc., Chem. Commun.* **1999**, 971−972. (b) Joó, F.; Laurenczy, G.; Karády, P.; Elek, J.; Nádasdi, L.; Roulet, R. *Appl. Organomet. Chem.* **2000**, *14*, 1−3.

Scheme 1. Hydride Formation from $[RuCl_2(PTA)_4]$, $[Ru(H_2O)_6][TOS]_2$, and PTA under Hydrogen Pressure in Aqueous Solutions ($C(Ru) = 50$ mM, $P(H_2) = 60$ bar)



Johnson Matthey. PTA,[25] $[Ru(H_2O)_6][tos]_2$,[26] and $[RuCl_2(PTA)_4]$[18] were prepared as described in the literature.

Instrumentation. The reactions were carried out in medium-pressure sapphire NMR tubes[27,28] (pressure < 120 bar) and were followed by NMR spectroscopy. ^1H, ^2H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AC 200, AM 360, and DRX 400 NMR spectrometers. TSPSA and phosphoric acid were used as reference for the ^1H and ^{31}P NMR measurements, respectively. The spectra were fitted with WIN-NMR, GNMR 4.0, and NMRICMA/MATLAB programs on PC (nonlinear least-squares fit to determine the spectral parameters; the differences between the measured and calculated spectra are shown in Figure 1).

Equilibrium Studies. 27.6 mg (5.0×10^{-5} mol) of $[Ru(H_2O)_6][tos]_2$ was dissolved in 0.2 mL of water in a 5 mm diameter medium-pressure sapphire NMR tube. A 235.5 mg amount of PTA (1.5 mmol) was dissolved in 2 mL of water ($c_{PTA} = 0.75$ M) in a separate Schlenk tube, and the pH was adjusted to 6.0 with *p*-toluenesulfonic acid. Amounts of 0.20, 0.33, or 0.40 mL of this PTA solution together with 0.1 mL of D_2O (lock) were added to the solution of $[Ru(H_2O)_6][tos]_2$ in the NMR tube ($[PTA]/[Ru] = 3$, 5, or 6, respectively) which was subsequently pressurized with 60 bar of H_2. ^2H NMR experiments were carried out in D_2O solutions under 60 bar of D_2.

Catalytic Hydrogenation. In a typical reaction 4.3 mg (5.4×10^{-6} mol) of $[RuCl_2(PTA)_4]$, 134.4 mg (1.6×10^{-3} mol) of $NaHCO_3$, 33.6 mg (4.0×10^{-4} mol) of $NaHCO_3$ enriched in ^{13}C, and 1.80 mL of water were introduced under nitrogen atmosphere into a 10 mm medium-pressure sapphire NMR tube. A 200 μL amount of a 0.1 M D_2O solution of TSPSA ($c = 0.01$ M) was added to the mixture as internal standard. After the dissolution of all solids, H_2 of the desired pressure was admitted. The tube was placed onto a laboratory shaker (300 rpm) and thermostated to 323.0 ($\pm$0.1) K. The reactions were followed in situ, the concentrations of HCO_2^-, CO_3^{2-}/HCO_3^-, and CO_2 were determined from integration of the corresponding ^{13}C and ^1H NMR signals. The initial rates and turnover frequencies (TOF = mol formate/mol catalyst/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 ($pH_2 = 60$ bar, $pCO_2 = 0$ bar, $c_{catalyst} = 2.62 \times 10^{-3}$ M).

To prepare solutions with pH < 8.3, the reaction mixture was placed in a sapphire tube and pressurized with 10−60 bar of CO_2. The CO_2 pressure required for obtaining a specific pH and the actual concentration of $NaHCO_3$ required to keep the total carbon concentration constant (1 M) were calculated using the p*K* values of carbonic acid $pK_1 = 6.35$, $pK_2 = 10.33$ (at 298 K) taken from the literature.[29] ^{13}C NMR spectra were recorded before the admission of H_2, and the absolute intensities of the separate HCO_3^- and CO_2 signals (slow exchange on the NMR time scale in this pH range) were used to confirm the total initial carbon concentration and to calculate the pH.

Results and Discussion

When a neutral aqueous solution of $[RuCl_2(PTA)_4]$ is pressurized with H_2, the originally orange-yellow solution slowly turns almost colorless and two hydride signals appear in the hydride region of the ^1H NMR spectra.

At room temperature the formation of these species is slow, and several hours are required to attain equilibrium spectra. In alkaline conditions (pH = 12.0), the tetrakis-phosphinoruthenium(II) dihydride complex, $[RuH_2(PTA)_4]$ (Scheme 1) is the only hydride present [^1H NMR: multiplet at −11.40 ppm, $J(H-P_g) = 30.5$ Hz, $J(H-P_f) = 27.3$ Hz, ^{31}P NMR: triplet of triplets at −21.1 ppm (P_f), $J(P_f-P_g) = 23.0$ Hz, a multiplet at −28.2 ppm (P_g); $^{31}P\{^1H\}$ NMR: two triplets at −21.1 ppm (P_f) and −28.2 ppm (P_g), $^1H\{^{31}P\}$ NMR: singlet at −11.40 ppm]. In this complex the phosphorus and hydride nuclei represent an AA′MM′XX′ spin system. In acidic solution (pH = 2.0) the tetrakis-phosphinoruthenium(II) monohydride $[RuH(PTA)_4X]$ ($X = H_2O$ or Cl^-) is the major hydride species (traces of $[RuH_2(PTA)_4]$), [^1H NMR: doublet of quartets at −8.31 ppm, $J(H-P_a) = 27.5$ Hz, $J(H-P_b) = 86.5$ Hz, $J(H-P_c) = 27.1$ Hz; ^{31}P NMR four overlapped triplets at −5.25 ppm (P_c), $J(P_b-P_c) = 19.0$ Hz, $J(P_a-P_c) = 32.5$ Hz, four overlapped doublets at −39.75 ppm (P_a), $J(P_a-P_b) = 22.4$ Hz and a multiplet at −48.6 ppm (P_b); $^{31}P\{H\}$ NMR: doublet of triplets at −5.25 ppm (P_c), doublet of doublets at −39.75 ppm (P_a), and doublet of triplets at −48.6 ppm (P_b), respectively]. The stability of these Ru−PTA hydrides is lower than that of the analogous TPPMS or TPPTS derivatives and the mole fraction of Ru in $[RuH(PTA)_4X]$ and/or $[RuH_2(PTA)_4]$ does not exceed 0.05 at 25 °C and 80 bar H_2 pressure. The rest of $[RuCl_2(PTA)_4]$ remains unreacted. Similar results were obtained in the formation of the dihydrogen complex $[Ru(H_2O)_5(H_2)]^{2+}$ from $[Ru(H_2O)_6]^{2+}$

---

(25) Daigle, D. J. *Inorg. Synth.* **1998**, *32*, 40−45.
(26) Bernhardt, P.; Biner, M.; Ludi, A. *Polyhedron* **1990**, *9*, 1095−1097.
(27) Horváth, I. T.; Millar, J. M. *Chem. Rev.* **1991**, *91*, 1339−1351.
(28) Cusanelli, A.; Frey, U.; Richens, D. T.; Merbach, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 5265−5271.
(29) *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, 1997.

under 40 bar H_2 pressure (the formation constant $K = 4$ kg mol^{-1}),[30] while [RuH(TPPMS)$_3$Cl] and [RuH$_2$(TPPMS)$_4$] form quantitatively from [RuCl$_2$(TPPMS)$_2$] and TPPMS under atmospheric hydrogen in aqueous solution.[23] Darensbourg and coworkers found a similar color change from orange to light yellow when [RuCl$_2$(PTA)$_4$] was treated with aqueous sodium formate at 333 K and observed a hydride signal at −18.4 ppm in the ^{1}H spectrum;[18] this signal, however, was not detected in our system under H_2 pressure.

In contrast to the bulky sulfonated triphenylphosphine derivatives (TPPMS or TPPTS), the PTA ligand proved small enough to form [RuH(PTA)$_5$]$^+$ when [Ru(H$_2$O)$_6$][tos]$_2$ and a 5-fold excess of PTA was reacted under H_2 (Figure 1) [^{1}H NMR: doublet of quintets at −11.62 ppm, J(H−P$_d$) = 24.2 Hz, J(H−P$_e$) = 68.5 Hz, ^{31}P NMR: doublet of doublets at −51.00 ppm (P$_d$), J(P$_d$−P$_e$) = 24.7 Hz, doublet of quintets at −55.63 ppm (P$_e$); ^{31}P{H}: doublet at −51.00 ppm (P$_d$) and quintet at −55.63 ppm (P$_e$)]. The experimental and calculated ^{1}H (top) and ^{31}P-{H} (middle and bottom) NMR spectra of [RuH(PTA)$_5$]$^+$ are shown on Figure 1; the agreement of experimental and calculated spectra are shown as the difference of the two below each spectrum.

Several water-soluble hydridoruthenium(II) derivatives with various phosphine ligands have been described in the literature,[23,31−33] however, no structure of a ruthenium(II)−PTA-hydride was unambiguously determined prior to this study. In addition, while formation of [RuH(PTA)$_4$X] and [RuH$_2$(PTA)$_4$] could be expected by analogy to similar complexes with PPh$_3$, TPPMS, or TPPTS ligands, the existence of a pentakisphosphino derivative, [RuH(PTA)$_5$]$^+$, is completely unprecedented in aqueous organometallic chemistry. The hydridorhodium(I) complexes formed from [RhCl(PTA)$_3$] and analogous derivatives are more stable and can be prepared in high yield without the need of elevated H_2 pressure. Recently [RhH(mtpa$^+$I$^-$)$_4$](H$_2$O) (mtpa$^+$I$^-$ = 1-methyl-1-azonia-3,5-diaza-7-phosphaadamantane) was prepared by Pruchnik et al. and characterized by X-ray diffraction and NMR measurements.[34]

In aqueous solution [RuCl$_2$(PTA)$_4$] catalyzed the hydrogenation of CO_2 under mild conditions (298 K, 20 bar CO_2, 60 bar H_2) with low activity; turnover frequencies up to 0.24 h^{-1} were obtained. No additives, such as dimethylamine or methanol were used for the reduction. In situ ^{1}H and ^{13}C NMR measurements confirmed that no products other than HCO_2^- form during the reaction. Detailed kinetic investigations were carried out at 323 K. At this temperature the maximum activity (TOF 1.81 h^{-1}) was achieved in 2 h under 60 bar CO_2 and 60 bar H_2. There was no measurable difference in the reaction rate when D_2 was used instead of H_2. The relatively low activity of [RuCl$_2$(PTA)$_4$] in hydrogenation of aqueous CO_2 was considerably increased when the pH was adjusted so that most of the CO_2 was present as HCO_3^- (TOF = 24.5 h^{-1}).

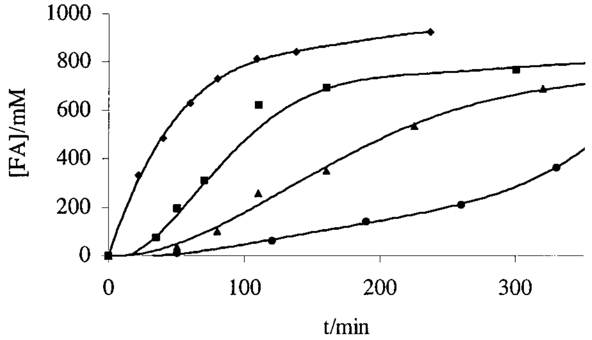


Figure 2. Formation of HCO_2^- (FA) as a function of time at different temperatures; ● = 323 K, ▲ = 333 K, ■ = 343 K, ◆ = 353 K, C(Ru) = 2.61 mM, C(NaHCO$_3$) = 1 M, P(H$_2$) = 60 bar.

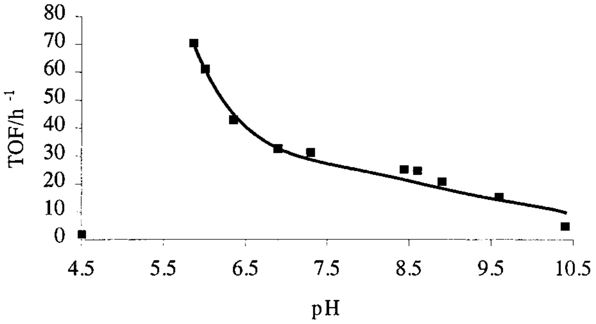


Figure 3. The rate of formation of HCO_2^- as a function of pH; C(Ru) = 2.61 mM, C_0(CO$_2$ + NaHCO$_3$) = 1 M, P(H$_2$) = 60 bar, T = 323 K.

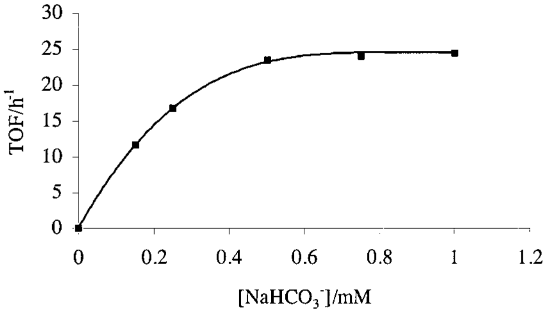


Figure 4. The rate of formation of HCO_2^- as a function of bicarbonate concentration; C(Ru) = 2.61 mM, P(H$_2$) = 60 bar, T = 323 K.

Both at 298 and 323 K, the catalytic reactions started with an induction period (Figure 2). However, the induction period diminished with increasing temperature, and at 353 K it could not be observed. In contrast to [RuCl$_2$(PTA)$_4$], [RuCl$_2$(TPPMS)$_2$], [RhCl(TPPMS)$_3$], and [RhCl(TPPTS)$_3$] did not show a significant induction period in hydrogenation of CO_2 in similar systems.[25] A possible explanation of this induction period may be the slow ligand-exchange on [RuCl$_2$(PTA)$_4$] resulting in the slow formation of the catalytically active Ru(II) hydride species. Similar low rates were determined in aqueous systems for the reactions of [Ru(H$_2$O)$_6$][tos]$_2$ with different ligands[35] such as CO, acetonitrile,[36] and ethene,[37] where detailed kinetic studies confirmed the dissociative activation mechanism for ligand exchange.

The influence of pH on the rate of hydrogenation of CO_2 is shown on Figure 3. The pH was regulated by varying the CO_2 pressure in the CO_2/HCO_3^-/CO_3^{2-} reaction system (see Experimental Section). This way there was no need for the use of amines or other organic bases. The activity of the catalyst increased with increasing [H$^+$] and, conversely, it was close to

---

(30) Aebischer, N.; Frey, U.; Merbach, A. *J. Chem. Soc., Chem. Commun.* **1998**, 2303−2304.

(31) Tóth, I. Z.; Joó, F.; Beck, M. T. *Inorg. Chim. Acta* **1980**, *42*, 153−161.

(32) López-Linares, F.; Gonzalez, M. G.; Páez, D. E. *J. Mol. Catal. A* **1999**, *145*, 61−68.

(33) Fache, E.; Santini, C.; Senocq, F.; Basset, J. M. *J. Mol. Catal.* **1992**, *72*, 331−336.

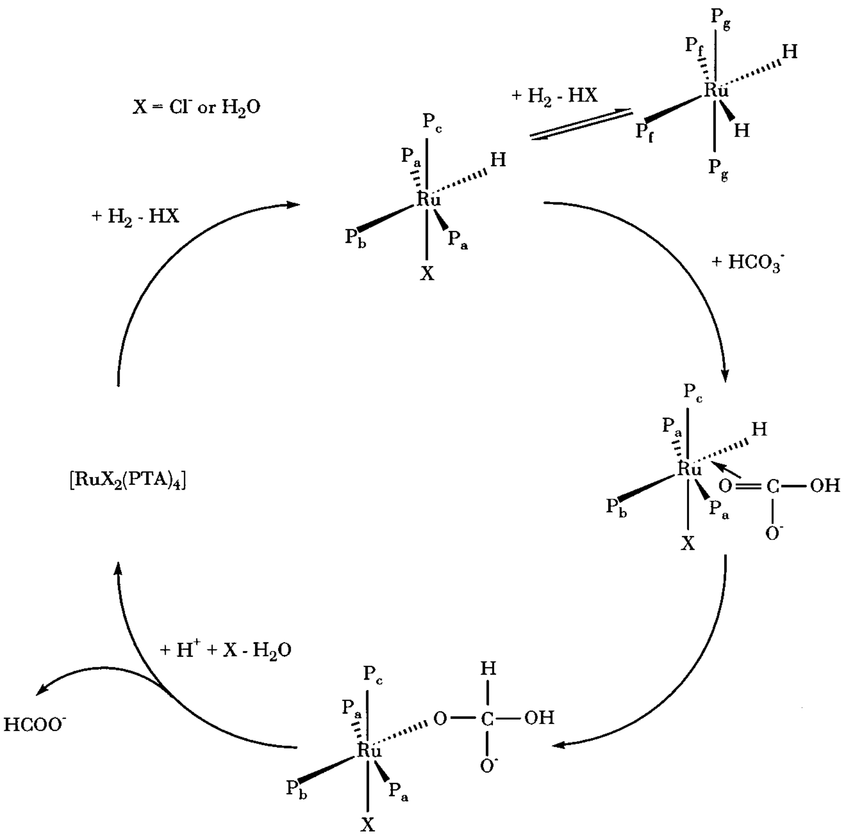
(34) Pruchnik, F. P.; Smoleñski, P.; Gałdecka, E.; Gałdecki, Z. *Inorg. Chim. Acta* **1999**, *293*, 110−114.

(35) Aebischer, N.; Sidorenkova, E.; Ravera, M.; Laurenczy, G.; Osella, D.; Weber J.; Merbach, A. *Inorg. Chem.* **1997**, *36*, 6009−6020.

(36) Aebischer, N.; Churlaud, R.; Dolci, L.; Frey U.; Merbach, A. *Inorg. Chem.* **1998**, *37*, 5915−5924.

(37) Laurenczy, G.; Merbach, A. *J. Chem. Soc., Chem. Commun.* **1993**, 187−189.

Scheme 2. The Proposed Mechanism of Hydrogenation of Bicarbonate to Formate in Presence of $[RuCl_2(PTA)_4]$ Precursor in Aqueous Solution



zero in strongly alkaline solutions. At 353 K, in the absence of carbon dioxide ($P_{\mathrm{hydrogen}} = 60$ bar, pH = 8.3) the highest initial turnover frequency was 345.7 h^{-1} while in case of 10% HCO_3^-/ 90% CO_2 it was found to be TOF = 807.3 h^{-1}. Although this value is far from those observed in supercritical systems, it compares favorably with most catalysts' activity under subcritical solutions.[12b,13b] Note that the reaction rate dramatically dropped when all bicarbonate was converted to formate; however, it did not become zero: the residual rate was close to the value (TOF 1.81 h^{-1}) observed in pure CO_2/H_2O. It is appropriate to compare these findings with those of Leitner et al.[12] who used $[RhCl(TPPTS)_3]$ as catalyst for CO_2 reduction in aqueous systems with various amines as auxiliary bases and also observed that the final concentration of formate never exceeded that of the amine. (However, in nonprotic solvents or in sc.CO_2 a ratio of formate/amine > 1 was, indeed, achieved.[5-7])

To explore the mechanism of the catalytic process, the influence of the catalyst concentration (Supporting Information, Figure S3), substrate concentration (Figure 4), and hydrogen pressure (Figure 5) on the reaction rate of hydrogenation of CO_2/ HCO_3^- was studied in detail. The rate of formation of HCO_2^- as a function of $[RuCl_2(PTA)_4]$ concentration was found to be first order with respect to [Ru(II)] {slope = 11.41 ([product]/ M) × ([catalyst]/M)$^{-1}$ h^{-1}}, leveled off with increasing $[HCO_3^-]$ and varied with a slightly nonlinear pattern with H_2 pressure. In the absence of $[RuCl_2(PTA)_4]$ there was no measurable formation of HCO_2^-.

An overall composite activation enthalpy of 86 kJ mol^{-1} can be calculated from the Arrhenius plot of the temperature dependence of the reaction rate. This value is substantially higher than those obtained in hydrogenation of CO_2 in aqueous solution with $[RhCl(TPPTS)_3]$ (25 kJ mol^{-1}),[12] with $K[Ru^{III}(EDTA\text{-}H)\text{-}Cl]\cdot 2H_2O$ (31 kJ mol^{-1})[38] or in reduction of HCO_3^- with heterogeneous Pd catalyst (25 kJ mol^{-1}).[39] On the basis of the findings described above, we assume that in our system the real substrate of the hydrogenation is the bicarbonate anion, which is in agreement with the low rate measured in acidic aqueous CO_2 solutions. In similar aqueous systems, like in the studies of Leitner et al., the main role of amine additives can be to increase $[HCO_3^-]$. The beneficial effect of some water, observed in hydrogenation of CO_2 in organic systems,[40] might also be interpreted by the formation of bicarbonate.

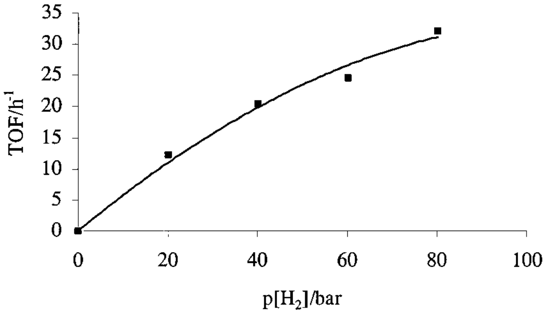


Figure 5. The rate of formation of HCO_2^- as a function of hydrogen pressure; C(Ru) = 2.61 mM, $C(NaHCO_3)$ = 1 M, pH = 8.30, T = 323 K.

The suggested catalytic cycle of HCO_3^- hydrogenation with $[RuCl_2(PTA)_4]$ as precatalyst in aqueous solution is shown in Scheme 2. $[RuCl_2(PTA)_4]$ forms $[RuH(PTA)_4X]$ (X = Cl^- or

---

[38] Taqui Khan, M. M.; Halligudi, S. B.; Shukla, S. *J. Mol. Catal.* **1989**, *57*, 47−60.

[39] Stalder, C.J.; Chao, S.; Summers, D. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 6318−6320.

[40] Inoue, Y.; Izumida, H.; Sasaki, Y.; Hashimoto, H. *Chem. Lett.* **1976**, 863−864. (b) Wiener, H.; Blum, J.; Fleichenfeld, H.; Sasson, Y.; Zalmanov, N. *J. Catalysis* **1988**, *110*, 184−190.

H_2O) and $[RuH_2(PTA)_4]$ in aqueous sodium bicarbonate solution under 20−80 bar H_2. According to the NMR measurements, the mole fraction of the monohydrido complex among the hydrides increases with decreasing pH, i.e., with increasing CO_2 pressure. In the presence of excess PTA, $[RuH(PTA)_5]^+$ can also form under hydrogen pressure; however, addition of excess PTA slows down the reaction. Therefore, it is highly probable that $[RuH(PTA)_4X]$ is the active species in the catalytic cycle. Bicarbonate then replaces X in $[RuH(PTA)_4X]$, and internal rearrangement within the resulting $[RuH(PTA)_4(HCO_3)]$ affords the formato-intermediate $[Ru(PTA)_4(HCO_2)]^+$. This would then release the product HCO_2^- with simultaneous coordination of X, followed by reaction with H_2 to regenerate the catalytically active $[RuH(PTA)_4X]$.

In their elegant mechanistic study on the hydrogenation of CO_2 to formic acid with a $[Rh(NBD)(PMe_2Ph)]BF_4$ catalyst, Tsai and Nicholas[41] obtained convincing evidence for the formation of both monodentate and bidentate formato-rhodium intermediates $[RhH(P)_3S(O_2CH)]^+$ and $[RhH(P)_2S(O_2CH)]^+$, respectively; in fact the latter resulted in a fairly stable, unproductive “shunt” in the catalytic cycle. Although we were unable to detect similar bicarbonato- or formato-intermediates of the above catalytic cycle (Scheme 2), the experimental findings are in accordance with the proposed mechanism. Namely, the induction period and the high overall activation enthalpy characterizing the reaction may be the consequence of the slow reaction of the precursor with H_2 to form the catalytically active Ru hydride. However, it is clear that further studies are needed to detect the reaction intermediates.

Conclusions

$[RuCl_2(PTA)_4]$ precursor shows moderate activity in hydrogenation of CO_2 in aqueous conditions; however, the rate increases considerably if HCO_3^- is added as substrate. No further additive (e.g., amine) is needed for an efficient reduction, the pH can be regulated through the CO_2/HCO_3^- buffer by varying the CO_2 pressure. Slightly acidic/neutral conditions are beneficial for the reaction rate as a compromise between increased concentration of the catalytically active Ru hydride and the highest available concentration of $[HCO_3^-]$. It seems that the main role of amines used in earlier studies is in the shift of pH in favor of the formation of bicarbonate. In the $[RuCl_2(PTA)_4]$ + PTA + H_2 system three hydride species, namely $[RuH(PTA)_4X]$ (X = Cl^- or H_2O), $[RuH_2(PTA)_4]$, and $[RuH(PTA)_5]^+$, were characterized, of which $[RuH(PTA)_4X]$ is thought to be the active catalyst in the bicarbonate reduction.

Acknowledgment. This work was supported by the Office Fédéral de l’Education et de la Science, Suisse (OFES C98.0011) and by the National Research Foundation of Hungary (OTKA T029934 and F023159). N.L. is grateful for an OFES fellowship. This research is part of the collaboration within the COST Action D10/0001 Working Group.

Supporting Information Available: Calibration curve of the ^{13}C NMR chemical shift of the HCO_3^-/CO_3^- in the fast-exchange domain as a function of pH (Figure S1). ^1H NMR spectra of the three Ru hydrides: $[RuH(PTA)_5]^+$, $[RuH(PTA)_4X]$, and $[RuH_2(PTA)_4]$ (Figure S2). The rate of formation of HCO_2^- as a function of $[RuCl_2(PTA)_4]$ concentration (Figure S3). This material is available free of charge via Internet at http://pubs.acs.org.

IC000200B

---

(41) Tsai, J. C.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117−5124.