



Water-soluble analogs of $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$ and their catalytic activity in the hydrogenation of carbon dioxide and bicarbonate in aqueous solution

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday in recognition of his outstanding contributions to organometallic chemistry and catalysis

Abstract

The new water-soluble ruthenium-nitrosyl complexes $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$ and $[\text{RuCl}_3(\text{NO})(\text{TPPTS})_2]$ were synthesized and characterized by IR, ^1H and ^{31}P NMR spectroscopies. The NO stretching frequencies, $\nu_{\text{NO}} = 1870 \text{ cm}^{-1}$ (TPPMS) and 1883 cm^{-1} (TPPTS) suggest a linear Ru–N–O arrangements. Reactions with OH^- yield the corresponding $[\text{RuCl}_3(\text{NO}_2)(\text{P})_2]$ derivatives, furthermore, $[\text{RuH}(\text{NO})(\text{P})_3]$ is formed with TPPMS or TPPTS, respectively, under 100 bar H_2 pressure. The new complexes are suitable precatalysts for the hydrogenation of carbon dioxide and/or bicarbonate in aqueous solutions up to a turnover frequency of 400 h^{-1} under relatively mild conditions (30 bar H_2 , 70°C).

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1. Introduction

The important physiological and environmental role of NO has generated an increased interest towards the properties and reactions of its metal complexes, especially in the case of the water-soluble ones [1]. In the early 1970s several nitrosyl complexes of ruthenium, containing also tertiary phosphine ligands, were prepared, however, the only water-soluble ruthenium compound of this type

described so far is $[\text{Ru}(\text{NO})_2(\text{TPPTS})_2]$ (TPPTS: tris(3-sulfonatophenyl)phosphine, trisulfonated triphenylphosphine) [2]. The ^{31}P NMR and IR spectroscopic characteristics of the TPPTS-containing derivative matched exactly those of the well characterized $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2]$ and therefore a similar distorted tetrahedral structure with linear Ru–N–O groups was postulated. One of the most studied nitrosylphosphine complex of ruthenium is $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$ which—among others—serves as a useful starting material for the preparation of various other Ru–NO complexes. For example the reduction of $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$ in refluxing

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ethanolic KOH in the presence of excess PPh_3 yields $[\text{RuH}(\text{NO})(\text{PPh}_3)_3]$, a catalyst of isomerization of olefins and hydrogenation of olefins, aldehydes and ketones [3–5]. The lack of data on the properties of analogous water-soluble Ru–NO compounds promoted us to investigate the preparation and reactions of $[\text{RuCl}_3(\text{NO})(\text{P})_2]$ -type complexes with the hydrophilic tertiary phosphine ligands TPPTS, (3-sulfonatophenyl)diphenylphosphine, monosulfonated triphenylphosphine (TPPMS) and 1,3,5-triaza-7-phosphaadamantane (PTA). $[\{\text{RuCl}_2(\text{TPPMS})_2\}_2]$ [6] and $[\text{RuCl}_2(\text{PTA})_4]$ [7] have already been studied as catalyst precursors for hydrogenation of olefins [8], aldehydes [9] and carbon dioxide [10,11] in homogeneous solutions or in aqueous/organic biphasic systems. The fixation of carbon dioxide is an important chemical and environmental question, and therefore we wished to assess the specific influence of the NO-ligand in the catalytic hydrogenation of CO_2 in aqueous systems.

2. Experimental

TPPMS [6], TPPTS [12] and PTA [13] were prepared according to the literature. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was a loan of Johnson Matthey, $\text{K}_2[\text{RuCl}_5(\text{NO})]$ was purchased from Alfa. *N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) was supplied by Aldrich. ^{13}C -enriched (99%) NaHCO_3 and D_2O (99.9%) were obtained from Cambridge Isotope Laboratories. Doubly distilled water was used throughout, and all manipulations were done in an inert atmosphere. ^1H and ^{31}P NMR spectra were recorded on Bruker WP 360 SY and DRX400 equipments in D_2O or $\text{D}_2\text{O}/\text{H}_2\text{O}$ mixtures. Pressurized samples were studied using a thick-wall glass NMR tube with a Teflon valve (Aldrich; up to 10 bar) or 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 , respectively. Infrared spectra were taken on a PE Paragon 1000 PC FT-IR spectrophotometer in KBr discs or as Nujol mulls. For the pH-potentiometric titrations, a radiometer ABU-90 autoburette was used, equipped with a combined Ag/AgCl-glass electrode (Radelkis OP-0808P) calibrated against 0.5 M potassium hydrogen phthalate.

2.1. Synthesis of $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$

2.1.1. Method I

TPPMS of 400 mg (1 mmol) was dissolved with magnetic stirring in 15 ml deaerated ethanol in a Schlenk flask under N_2 at room temperature. Then a solution of 193 mg (0.5 mmol) $\text{K}_2[\text{RuCl}_5(\text{NO})]$ in 3 ml water was added and the mixture was refluxed under N_2 for 90 min. After cooling to room temperature the yellow product was filtered, washed with a small amount of cold ethanol and dried in vacuo. Yield: 250 mg (52%). For $\text{C}_{36}\text{H}_{28}\text{Cl}_3\text{NO}_7\text{P}_2\text{S}_2\text{Na}_2\text{Ru}$ calculated (found): C (%), 44.76 (44.44); H (%), 2.92 (3.13%); N (%), 1.45 (1.52); Cl (%), 11.01 (11.37). ν_{NO} (KBr) = 1870 cm^{-1} . ^{31}P NMR: δ 13.6 ppm (s) ($\text{D}_2\text{O}/\text{DMSO}$, 1/1); 12.9 ppm (s) (CDCl_3).

2.1.2. Method II

TPPMS of 2.4 g (6 mmol) was dissolved with magnetic stirring in 45 ml deaerated ethanol in a Schlenk flask under N_2 at reflux temperature. A solution of 390 mg (1.5 mmol) $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in 5 ml ethanol was added, followed by 600 mg (3 mmol) of Diazald in 10 ml ethanol. The mixture was refluxed for 30 min and was worked up as above. Yield: 847 mg (58%). Found: C (%), 45.05; H (%), 3.22; N (%), 1.50; Cl (%), 11.10.

2.2. Synthesis of $[\text{RuCl}_3(\text{NO})(\text{TPPTS})_2]$

TPPTS of 627 mg (1 mmol) was dissolved with magnetic stirring in 15 ml deaerated ethanol in a Schlenk flask under N_2 at room temperature. Then a solution of 193 mg (0.5 mmol) $\text{K}_2[\text{RuCl}_5(\text{NO})]$ in 3 ml water was added and the mixture was refluxed under N_2 for 90 min. After cooling to room temperature the greenish yellow product was filtered and washed with a small amount of cold ethanol. Yield: 521 mg (76%). ν_{NO} (KBr) = 1883 cm^{-1} . ^{31}P NMR: δ 16.0 ppm (s) (D_2O).

2.3. Attempted synthesis of $[\text{RuCl}_3(\text{NO})(\text{PTA})_2]$

PTA of 79 mg (0.5 mmol) was dissolved with magnetic stirring in 7.5 ml deaerated ethanol in a Schlenk flask under N_2 at room temperature. Then a solution of 97 mg (0.25 mmol) $\text{K}_2[\text{RuCl}_5(\text{NO})]$ in 1.5 ml water was added and the mixture was refluxed under N_2 for

90 min. After cooling to room temperature the brown product was filtered and washed with a small amount of cold ethanol. Yield: 107 mg (78%; for the above formula). ν_{NO} (KBr) = 1854 cm^{-1} . No consistent elementary analysis data could be obtained. The product is very sparingly soluble in water and other ordinary solvents and was not investigated further.

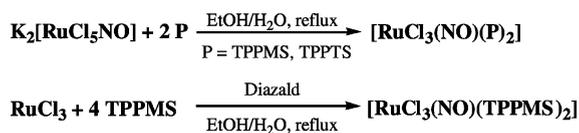
2.4. Hydrogenation experiments

The following procedure is typical. A medium pressure sapphire NMR tube (o.d. 10 mm) was used as a reactor. In this tube under an N_2 atmosphere, 5.41 mg (0.005 mmol) $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$, 6.26 mg (0.016 mmol) TPPMS, 91 mg (1.08 mmol) $\text{NaH}^{13}\text{CO}_3$ were dissolved in 1.80 ml H_2O + 0.20 ml D_2O together with 4.4 mg TSPSA (0.02 mmol). The reactor was filled with CO_2 up to the desired pressure, then 30 bar H_2 was added. The tube was securely placed on top of a laboratory shaker equipped with a controllable heating mantle to accommodate the reactor, and the reaction mixture was shaken at 70 °C. The reaction was followed by recording the ^1H NMR spectra of the solution in time, and comparing the integral of the formate C–H signal to that of TSPSA. In the pH variation studies, the actual pH was set by choosing the appropriate bicarbonate concentration and CO_2 pressure. The pH of the solution was calculated as $\text{pH} = \text{p}K_{\text{a}1} + \ln([\text{HCO}_3^-]/[\text{CO}_2])$, where $\text{p}K_{\text{a}1}$ is the first ionization constant of carbonic acid, 6.35 at 25 °C [14]. The actual $[\text{HCO}_3^-]/[\text{CO}_2]$ ratio was calculated from the ^{13}C NMR spectra taken at this temperature.

3. Results and discussion

3.1. Synthesis and properties of the water-soluble Ru–NO–phosphine complexes

The reaction of $\text{K}_2[\text{RuCl}_5(\text{NO})]$ with two equivalents of TPPMS or TPPTS yields well-defined complexes of the formula $[\text{RuCl}_3(\text{NO})(\text{P})_2]$. $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$ was also prepared in the direct reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, TPPMS and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) with equally good yield and purity (Scheme 1). These yellow compounds are well soluble in water. Their IR spectral parameters are close



Scheme 1. Synthesis of the water-soluble $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$ and $[\text{RuCl}_3(\text{NO})(\text{TPPTS})_2]$ complexes.

to that of $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$, i.e. $\nu_{\text{NO}} = 1870 \text{ cm}^{-1}$ (TPPMS), 1883 cm^{-1} (TPPTS) and 1875 cm^{-1} (PPh_3 , [15]), respectively. The ^{31}P NMR spectra display singlet resonances at δ 13.6 ppm (TPPMS, $\text{D}_2\text{O}/\text{DMSO}$: 1/1) and at 16.0 ppm (TPPTS, D_2O). These spectral features are consistent with an octahedral complex geometry, having the two phosphine ligands in *trans* position in the equatorial plane and the NO and one of the Cl^- ligands in axial positions. The ν_{NO} frequencies suggest a linear Ru–N–O arrangements. For $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$ this structure has been unequivocally established by single crystal X-ray diffraction [16] and this lends support to the structural conclusions regarding the TPPMS- and TPPTS-containing complexes, too.

At room temperature, $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$ and $[\text{RuCl}_3(\text{NO})(\text{TPPTS})_2]$ give stable aqueous solutions, but as expected, show the characteristic reaction [1] of linear nitrosyl complexes with OH^- . The pH-potentiometric titration of an aqueous solution of $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$ resulted in a typical S-shaped pH versus $[\text{OH}^-]$ curve with an inflexion point at pH = 8.3. Fig. 1 shows a pH-static titration

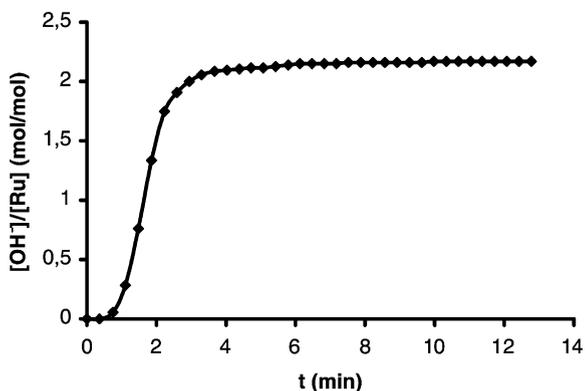
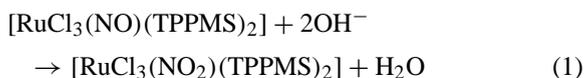


Fig. 1. Base consumption in the reaction of $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$ in dilute KOH solution. $[\text{Ru}] = 4.8 \text{ mM}$, $\text{pH} = 10.6$, $[\text{KCl}] = 0.2 \text{ M}$, $V = 10 \text{ ml}$, $T = 35 \text{ }^\circ\text{C}$.

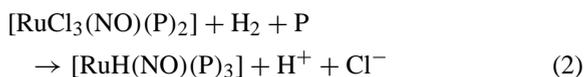
of $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$. In this experiment, the complex was dissolved in an aqueous KOH solution of pH 10.6, and any acid produced in its subsequent reactions was neutralized by the addition of a KOH solution of known concentration by an autoburette. It has been found that two equivalents of KOH per 1 mol of the Ru-complex was consumed, and it is conceivable therefore that it can be rendered to the nucleophilic addition of OH^- on the ruthenium-bound NO to yield a nitro-derivative (Eq. (1)).



Note, that the reaction is rapid; at room temperature the half time is about 1 min. Fig. 1 also shows that no noticeable further reactions happen in the next 10 min. It can be concluded from these results, that already in slightly basic solutions (approximately above pH = 8) the initial nitrosyl-complex is rapidly converted to the nitro-compound.

On prolonged heating at 70 °C in aqueous or ethanolic solutions $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$ and $[\text{RuCl}_3(\text{NO})(\text{TPPTS})_2]$ react with an excess of TPPMS and TPPTS, respectively, yielding strong green solutions showing a singlet ^{31}P resonance at 15.0 ppm (TPPMS) and 24.0 ppm (TPPTS). Uncharacterized green impurities have been observed in the preparation of $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$ [17,18]. The singlet ^{31}P signal observed by us is consistent with a trigonal bipyramidal structure and reduction by the added phosphine can lead to the formation of *mer*- $[\text{RuCl}(\text{NO})(\text{P})_3]$. This compound was not further investigated, although it may be an intermediate in the formation of the $[\text{RuH}(\text{NO})(\text{P})_3]$ complexes as indicated by the rapid colour change of the solutions from green to yellow under H_2 pressure together with the appearance of the characteristic NMR signals of $[\text{RuH}(\text{NO})(\text{P})_3]$ (vide infra).

In the presence of excess phosphine, the reaction of $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$ and $[\text{RuCl}_3(\text{NO})(\text{TPPTS})_2]$ with H_2 yields the corresponding hydrido-complexes (Eq. (2), P = TPPMS or TPPTS).



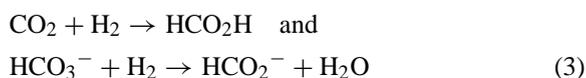
Thus, in phosphate buffer solutions of $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$ at pH = 6.0 and under 100 bar H_2 pressure a quartet hydride resonance was observed in

the ^1H NMR spectrum at $\delta = -6.8$ ppm with a coupling constant $^2J_{\text{P-H}} = 28$ Hz. Under similar conditions, the product of the hydrogenation of $[\text{RuCl}_3(\text{NO})(\text{TPPTS})_2]$ showed a similar quartet at $\delta = -6.9$ ppm ($^2J_{\text{P-H}} = 27$ Hz). The quartets collapse to singlets on phosphorus decoupling. Similarly, the doublet ^{31}P resonances at 62.4 ppm ($^2J_{\text{P-H}} = 27$ Hz) (TPPMS) and at 66.7 ppm ($^2J_{\text{P-H}} = 27$ Hz) (TPPTS) show up as singlets in the $^{31}\text{P}\{^1\text{H}\}$ spectra. These data are in excellent agreement with the ^1H NMR parameters of $[\text{RuH}(\text{NO})(\text{PPh}_3)_3]$ (CD_2Cl_2): $\delta = -6.6$ ppm (q, $^2J_{\text{P-H}} = 30$ Hz) [3,19]. Based on these findings, we suggest trigonal bipyramidal structures for the $[\text{RuH}(\text{NO})(\text{P})_3]$ complexes (P = TPPMS or TPPTS) with equatorial phosphines and axial hydride and nitrosyl ligands; in the solid state a similar, slightly distorted trigonal bipyramidal coordination geometry was confirmed in the case of $[\text{RuH}(\text{NO})(\text{PPh}_3)_3]$ by X-ray crystallography [20].

3.2. Hydrogenation of carbon dioxide and bicarbonate in aqueous solution

The hydrogenation of carbon dioxide is of great interest because of its possible use as a C1 source, and also due to environmental concerns [21]. Several very active homogeneous catalysts are known, including $[\text{RuCl}_2(\text{PMe}_3)_4]$ [22], but it was only recently, that CO_2 and HCO_3^- were reduced to formic acid and formate in fully aqueous solutions using $[\{\text{RuCl}_2(\text{TPPMS})_2\}_2]$ [10] and $[\text{RuCl}_2(\text{PTA})_4]$ [11] as catalysts. Furthermore, *mer*- $[\text{Mo}(\text{CO})\text{H}(\text{NO})(\text{PMe}_3)_3]$ and *mer*- $[\text{W}(\text{CO})\text{H}(\text{NO})(\text{PMe}_3)_3]$ showed rapid insertion of CO_2 into the M–H bond giving the corresponding formate-complexes [23,24] and these insertions were facilitated by the hydridic polarization of the M–H bond by the NO ligand. Therefore, it seemed interesting to study the catalytic properties of the water-soluble $[\text{RuH}(\text{NO})(\text{P})_3]$ complexes prepared in situ from $[\text{RuCl}_3(\text{NO})(\text{P})_2]$, H_2 and added phosphine, P = TPPMS or TPPTS.

Both $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$ and $[\text{RuCl}_3(\text{NO})(\text{TPPTS})_2]$ proved suitable catalyst precursors in the hydrogenation of carbon dioxide and bicarbonate (Eq. (3)).



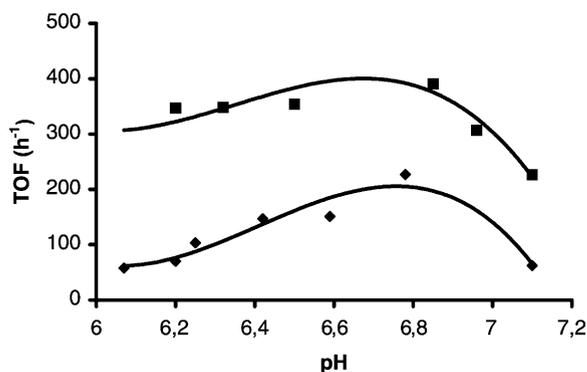


Fig. 2. Turnover frequency of the hydrogenation of $\text{CO}_2/\text{HCO}_3^-$ with $[\text{RuCl}_3(\text{NO})\text{P}_2]$ catalysts as a function of the pH, P = TPPMS (◆), TPPTS (■). $[\text{Ru}] = 2.6 \text{ mM}$, $[\text{P}] = 7.8 \text{ mM}$, $[\text{NaHCO}_3] = 0.54 \text{ M}$, $P_{\text{CO}_2} = 5\text{--}58 \text{ bar}$, $P_{\text{H}_2} = 30 \text{ bar}$, $T = 70^\circ \text{C}$.

Under typical experimental conditions ($[\text{Ru}] = 2\text{--}8 \text{ mM}$, $[\text{HCO}_3^-] = 0.1\text{--}0.9 \text{ M}$, $P_{\text{CO}_2} = 30 \text{ bar}$, $P_{\text{H}_2} = 30 \text{ bar}$, $T = 70^\circ \text{C}$) the catalytic activity of both complexes, expressed as mol product $(\text{mol Ru h})^{-1}$ (turnover frequency, TOF) were in the range of $50\text{--}400 \text{ h}^{-1}$. The rate of product formation proved first order dependent on both the catalyst concentration and the hydrogen pressure, and increased with increasing phosphine concentration levelling off at the $[\text{phosphine}]/[\text{Ru}]$ ratio of 6. This latter behaviour may be explained by the formation of the $[\text{RuH}(\text{NO})(\text{P})_3]$ complexes as the actual catalytic species. The effect of pH on the reaction rate is more complex (Fig. 2).

As can be seen with both complexes, the rate shows a maximum in the function of the pH and drops sharply above $\text{pH} = 7$, in as much that aqueous NaHCO_3 solutions ($\text{pH} = 8.31$ at 1 M) could not be hydrogenated when no CO_2 pressure was applied. This observation contrasts the case of the $[\{\text{RuCl}_2(\text{TPPMS})_2\}_2]$ [10] and $[\text{RuCl}_2(\text{PTA})_4]$ [11] catalysts which showed high activity for the hydrogenation of bicarbonate. It seems likely, that the deactivation is caused by the formation of the nitro-complexes $[\text{RuCl}_3(\text{NO}_2)(\text{TPPMS})_2]$ and $[\text{RuCl}_3(\text{NO}_2)(\text{TPPTS})_2]$ rapidly taking place in basic solutions (vide supra). This sets an upper pH limit of the use of the nitrosyl complexes for catalytic hydrogenation in aqueous solutions. On the other side of the maximum, increasing the pressure of CO_2 (with concomitant lowering of the pH) leads to gradually lower rates of hydrogenation. This effect points to the partic-

ipation of HCO_3^- rather than hydrated CO_2 in the catalytic cycle although we do not have direct evidence of the intermediates, and at this stage of the investigations further speculations on the reaction mechanism would be premature.

Several water-soluble Ru- and Rh-complexes have been shown earlier to catalyze the isotope exchange between H_2 and D_2O , as well as between D_2 and H_2O with high efficiency (TOFs up to 1250 h^{-1}) [25]. In the aqueous hydrogenation of $\text{CO}_2/\text{HCO}_3^-$ with the same catalysts, including, e.g. $[\{\text{RuCl}_2(\text{TPPMS})_2\}_2]$, the formation of large proportions of DCO_2^- was indicated by the characteristic splitting of the ^{13}C resonance at 170.7 ppm ($t, {}^1J_{\text{C-D}} = 30.5 \text{ Hz}$). It is noteworthy, that in the case of the nitrosyl complexes under study no formate deuteration was observed.

Under strictly identical experimental conditions ($[\text{Ru}] = 2.6 \text{ mM}$, $[\text{TPPMS}]$ or $[\text{TPPTS}] = 7.8 \text{ mM}$, $[\text{CO}_2] = 0.1 \text{ M}$, $[\text{NaHCO}_3] = 0.8 \text{ M}$, $P_{\text{H}_2} = 30 \text{ bar}$, $T = 70^\circ \text{C}$) the following specific activities (TOF) were observed: $[\text{RuCl}_3(\text{NO})(\text{TPPMS})_2]$, 102 h^{-1} ; $[\text{RuCl}_3(\text{NO})(\text{TPPTS})_2]$, 197 h^{-1} ; $[\{\text{RuCl}_2(\text{TPPMS})_2\}_2]$, 501 h^{-1} . This comparison shows, that of the three catalysts the NO-complexes are less active, although this activity is still fairly high for the homogeneously catalyzed CO_2 hydrogenations [22]. Based on this limited set of data the specific role of the NO ligand cannot be assessed. It is possible that the mechanisms of the HCO_3^- hydrogenations differ in the case of the $[\text{RuH}(\text{NO})(\text{P})_3]$ and $[\text{RuH}_2(\text{P})_4]$ (P = TPPMS or TPPTS) catalysts, formed from the nitrosyl complexes and $[\{\text{RuCl}_2(\text{TPPMS})_2\}_2]$, respectively. Further work to elucidate the reaction mechanism and to extend the scope of catalysis by the new water-soluble Ru-NO complexes is in progress.

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