The Effect of pH on the Reactions of Catalytically Important Rh^I Complexes in Aqueous Solution: Reaction of $[RhCl(tppms)_3]$ and *trans*-$[RhCl(CO)(tppms)_2]$ with Hydrogen (TPPMS = *mono*-sulfonated triphenylphosphine)

Ferenc Joó,*[a, b] József Kovács,[b] Attila Cs. Bényei,[a] Levente Nádasdi,[b, c] and Gábor Laurenczy[c]

Abstract: Hydrolysis and hydrogenation of $[RhCl(tppms)_3]$ (**1**) and *trans*-$[RhCl(CO)(tppms)_2]$ (**2**) was studied in aqueous solutions in a wide pH range ($2 < pH < 11$) in the presence of excess TPPMS (3-diphenylphosphinyl-benzenesulfonic acid sodium salt). In acidic solutions hydrogenation of **1** yields a mixture of *cis-mer-* and *cis-fac*-$[RhClH_2(tppms)_3]$ (**3a**,**b**) while in strongly basic solutions $[RhH(H_2O)(tppms)_3]$ (**4**) is obtained, the midpoint of the equilibrium between these hydride species being at pH 8.2. The paper gives the first successful ^1H and ^{31}P NMR spectroscopic characterization of a water soluble rhodium(I)-monohydride (**4**) bearing only *monodentate* phosphine ligands. Hydrolysis of **2** is negligible below pH 9 and its hydrogenation results in formation of $[Rh(CO)H(tppms)_3]$ (**5**), which is an analogue to the well known and industrially used hydroformylation catalyst $[Rh(CO)H(tppts)_3]$ (**6**) (TPPTS = 3,3′,3″-phosphinetriyltris(benzenesulfonic acid) trisodium salt). It was shown by pH-potentiometric measurements that formation of **5** is strongly pH dependent in the pH 5–9 range; this gives an explanation for the observed but previously unexplained pH dependence of several hydroformylation reactions. Conversely, the effect of pH on the rate of hydrogenation of maleic and fumaric acid catalyzed by **1** in the $2 < pH < 7$ range can be adequately described by considering solely the changes in the ionization state of these substrates. All these results warrant the use of buffered (pH-controlled) solutions for aqueous organometallic catalysis.

Keywords: biphasic catalysis · hydrides · hydroformylation · hydrogenation · rhodium

Introduction

Catalysis by water soluble phosphine complexes in aqueous solutions[1] and in aqueous–organic two-phase systems[2] has developed into a most successful way for product isolation and catalyst recycling both on the laboratory and industrial scale.[3–7] Of the several versions of liquid–liquid biphasic catalysis based on the use of immiscible organic[8] (among them fluorous[9, 10]) or ionic[11, 12] liquids and supercriticial fluids,[13, 14] only the Shell higher olefin process[15] (SHOP) is currently in large scale operation while there are at least six industrial processes using aqueous–organic biphasic technology.[5–7, 16, 17] Due to its elegant simplicity, the Ruhrchemie–Rhône Poulenc (RCH-RP) propene hydroformylation process[6, 17] is unquestionably the benchmark and clearest example of the operational, environmental and economical advantages made possible by conducting a large scale reaction in an aqueous–organic two-phase system. The key to the success of this process was the use of a highly hydrophylic rhodium catalyst, $[Rh(CO)H(tppts)_3]$ (**6**) containing the TPPTS **7** (3,3′,3″-phosphinetriyltris(benzenesulfonic acid) trisodium salt) ligand. This important achievement triggered an immense effort of research into aqueous organometallic catalysis which resulted in detailed mechanistic description of several important processes such as olefin hydroformylation,[18] hydrogenation,[19] ring opening metathesis polymerization[20] or vinylic/allylic substitutions.[21]

For an excellent performance in homogeneous organic reactions the catalysts have to be solubilized in aqueous mixtures, which usually translates into ligand modification. Two notable representatives of the ever-growing family of water soluble phosphine ligands[16, 19] are the *mono*-sulfonated triphenylphosphine, TPPMS, **8** (3-diphenylphosphinyl-benze-

[a] Prof. F. Joó, Dr. A. Cs. Bényei
Institute of Physical Chemistry, University of Debrecen
4010 Debrecen, P.O. Box 7 (Hungary)
Fax: (+36) 52-512915
E-mail: jooferenc@tigris.klte.hu

[b] Prof. F. Joó, Dr. J. Kovács, Dr. L. Nádasdi
Research Group of Homogeneous Catalysis
Hungarian Academy of Sciences, 4010 Debrecen (Hungary)

[c] Dr. L. Nádasdi, Dr. G. Laurenczy
Institute of Inorganic and Analytical Chemistry
University of Lausanne, 1015 Lausanne-Dorigny (Switzerland)

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nesulfonic acid, sodium salt[22]) and TPPTS, **7**.[3, 23] It is often assumed that in aqueous–organic two-phase reactions water simply gives a liquid phase which dissolves the catalyst and that nothing else happens. Several observations show this is not the case.[24] For example, Delmas et al. observed that the biphasic hydroformylation of 1-octene catalyzed by $[RhCl(cod)]_2$+**7** (COD = 1,5-cyclooctadiene) proceeded with a higher rate at pH 10 than at pH 7.[25] Yan et al. have determined a maximum in the rate and selectivity of 1-hexene hydroformylation at pH 7 using a catalyst prepared in situ from $RhCl_3$ and $P[C_6H_4\text{-}4\text{-}O(CH_2CH_2O)_6H]_3$.[26] A similar rate increase with increasing pH was found by Mieczynska et al. in hydrogenation and hydroformylation of unsaturated alcohols catalyzed by [Rh(acac)(CO)$_2$]+PNS (PNS = $Ph_2PCH_2CH_2CONHC(CH_3)_2CH_2SO_3Li$).[27] We suggested earlier that in hydrogenation of $[RhCl(tppms)_3]$ (**1**) in water a $[RhH(tppms)_{3\,or\,4}]$ monohydrido-species was formed instead of $[RhClH_2(tppms)_3]$ (**3**) as the primary product of oxidative addition.[28a] A similar effect was invoked also in case of hydrogenations catalyzed by $[RhCl(pta)_3]$ in aqueous solutions (PTA = 1,3,5-triaza-7-phosphaadamantane).[28b, c] However, we were unsuccessful in characterizing the supposed $[RhHP_{3\,or\,4}]$ species (P = **8** or PTA) by NMR spectroscopy. Formation of a similar rhodium(I) monohydride was proposed by Leitner et al. in the $[RhCl(tppts)_3]$-catalyzed hydrogenation of CO_2 in the presence of amines—again without a direct NMR evidence.[29] On the other hand, hydrogenation of $[RuCl_2(tppms)_2]_2$ (in the presence of excess TPPMS) at *controlled* pH at several points in the $1 < pH < 12$ range together with ^1H and ^{31}P NMR measurements revealed that the midpoint of the equilibrium shown in Equation (1) was around pH 6 and it could be easily shifted each way by the addition of acid or base.[30] This led to very pronounced changes in the rate and selectivity of hydrogenation of unsaturated aldehydes[30, 31] as well as of aqueous bicarbonate.[32]

$$[RuClH(tppms)_3] + H_2 + TPPMS \rightleftharpoons [RuH_2(tppms)_4] + H^+ + Cl^- \qquad (1)$$

The purpose of this paper is to describe the effects of varying pH on the hydridorhodium(I) complexes formed in aqueous solutions from $[RhCl(tppms)_3]$ (**1**) and $[RhCl(CO)(tppms)_2]$ (**2**) and to relate the changes in the reactivity of these complexes to their catalytic performance. Compound **1** is a water soluble analogue of the Wilkinson's catalyst, $[RhCl(PPh_3)_3]$ (**9**); properties of the latter in organic solvents are known in very fine detail.[19, 33] Similarly, **2** is the precursor of $[Rh(CO)H(tppms)_3]$ (**5**) analogous to the important hydroformylation catalyst $[Rh(CO)H(tppts)_3]$ (**6**). Some information regarding the hydride species formed from $[RhCl(tppts)_3]$ (**10**) in neutral and strongly acidic solutions is available from the work of Larpent and Patin,[34] however, despite several efforts rhodium(I) hydrides in *basic* aqueous solutions have not been characterized before. Also, Horváth has shown that in water **6** is less prone to phosphine dissociation than $[Rh(CO)H(PPh_3)_3]$ (**11**) in toluene, supposedly due to a network of hydrogen bonds and cation binding between the nine sulfonate groups.[35] Such *indirect* effects of the aqueous phase are outside the scope of the present study.

Abstract in Hungarian: *A $[RhCl(tppms)_3]$ (**1**) és transz-$[RhCl(CO)(tppms)_2]$ (**2**) komplexek hidrolízisét és hidrogénezését tanulmányoztuk vizes oldatban, széles pH tartományban ($2 < pH < 11$), TPPMS feleslegben (TPPMS = 3-difenilfoszfinil-benzolszulfonsav nátrium só). Savas oldatban **1** hidrogénezésekor cisz-mer- és cisz-fac-$[RhClH_2(tppms)_3]$, **3a**, **b** képződik, míg erősen lúgos oldatban $[RhH(H_2O)(tppms)_3]$ (**4**) alakul ki. E két, egymással egyensúlyban képződő komplex koncentrációja pH 8.2 esetén azonos. Dolgozatunkban elsőként adjuk meg egy kizárólag egyfogú foszfin ligandumot tartalmazó monohidridoródium(I) komplex **4** ^1H és ^{31}P NMR jellemzőit. **2** hidrolízise pH 9 alatt elhanyagolható mértékű, hidrogénezése során pedig $[Rh(CO)H(tppms)_3]$ (**5**) képződik, ami a jól ismert $[Rh(CO)H(tppts)_3]$ (**6**) ipari hidroformilező katalizátor analógja (TPPTS = 3,3′,3″-foszfintriil-benzolszulfonsav nátrium só). pH-potenciometrikus mérésekkel kimutattuk, hogy a pH 5–9 tartományban **5** képződése erősen pH-függő, ami magyarázatot ad több hidroformilezési folyamat korábban is észlelt de mindeddig nem értelmezett pH-függésére. Ugyanakkor, bár a maleinsav és fumársav **1** által katalizált hidrogénezésének sebessége a $2 < pH < 7$ tartományban szintén erősen függ a pH-tól, ezt a jelenséget kellően értelmezhetjük kizárólag e szubsztrátumok ionizációs állapotának megváltozásával. Mindezen eredmények arra figyelmeztetnek, hogy a vizes közegű fémorganikus katalízisben állandó pH-jú (pufferelt) oldatokat kell használni.*

Results and Discussion

Reaction of 1 and molecular hydrogen: When **1** was dissolved under argon in water with an orange color in acidic and with a red color in basic solutions (30 °C, 0.2 M KCl was used to provide sufficient ionic strength for pH measurements) a certain amount of H^+ was produced, this amount being a function of the actual pH of the solution. Upon admission of H_2 the color of the solutions turned yellow independent of the pH and this was accompanied by a second stage of proton liberation. We have followed these reactions by using a pH-potentiometric apparatus for automatic compensation of any acidification (see Experimental Section). The actual time course of both proton producing processes at a constant pH 10 is shown on Figure 1. The first step can be ascribed to the hydrolysis of the complex under an argon atmosphere, yielding $[Rh(OH)(tppms)_3]$ (**12**) while the second one indicates a heterolytic fission of H_2 with concomitant proton formation. Hydrogenation of **1** was investigated at several *constant* pH values in the $2 < pH < 11$ range; the results are summarized on Figure 2. It can be seen, that hydrolysis does not take place at all at pH 2, and its extent is less than 10% at pH 4 (front set of bars). Interestingly, even in strongly basic solutions (pH 11) the amount of protons formed is only about 35% relative to rhodium. Herrmann et al. have shown that **10** gives $[Rh(OH)(tppts)_3]$ (**13**) with 70–90% isolated yield upon standing of its aqueous solution at room temperature.[36] In our case, incomplete hydrolysis of **1** can be explained

0947-6539/01/0701-0194 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 1

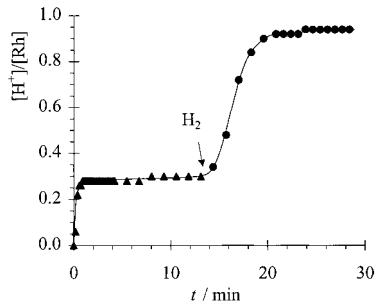


Figure 1. Time course of proton production upon dissolution and hydrogenation of $[RhCl(tppms)_3]$ (**1**) in aqueous solution at pH 10. $[\mathbf{1}] = 1.8 \times 10^{-3}$ M, $[\mathbf{8}] = 5.4 \times 10^{-3}$ M, [KCl] = 0.2 M, 0.1 MPa Ar or H_2, $T = 30\,^{\circ}C$.

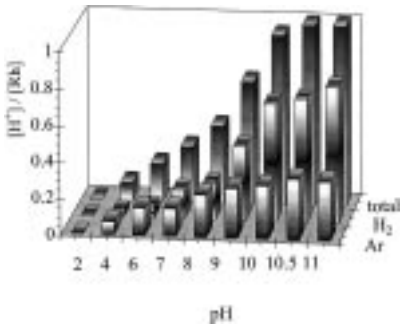


Figure 2. Proton production upon hydrolysis (Ar) and hydrogenation of $[RhCl(tppms)_3]$ (**1**) at various constant pH in the $2 < pH < 11$ range. $[\mathbf{1}] = 1.8 \times 10^{-3}$ M, $[\mathbf{8}] = 5.4 \times 10^{-3}$ M, [KCl] = 0.2 M, 0.1 MPa Ar or H_2, $T = 30\,^{\circ}C$.

considering the presence of a 1000 times excess of Cl^- over Rh. However, the presence of **12** in these solutions was confirmed by ^{31}P NMR data[37] although the spectra are not well resolved probably due to the exchange with the excess of **8**. Due to the ligand excess ([**8**]:[**1**] = 3) formation of $[Rh(OH)(tppms)_2]_2$ need not be considered.

Replacement of the argon atmosphere by hydrogen results in further proton production in the $4 < pH < 11$ range, on top of that observed in the hydrolysis process. The middle set of bars on Figure 2 represents this additional proton production, while the back set shows the combined amount of protons produced upon dissolution *and* hydrogenation. It should be emphasized that **1** *does* react with H_2 at pH 4 but this reaction is not accompanied by proton production. On the other extreme, a stoichiometric amount of H^+ is formed in the reaction of **1** and H_2 at pH 10. Based on these results combined with spectroscopic evidence (see below), the processes taking place in aqueous solutions of **1** under argon and hydrogen can be represented by Equations (2) – (5):

$$[RhCl(tppms)_3]\ (\mathbf{1}) + H_2O \rightleftharpoons [Rh(OH)(tppms)_3]\ (\mathbf{12}) + Cl^- + H^+ \quad (2)$$

$$[RhCl(tppms)_3]\ (\mathbf{1}) + H_2 \rightleftharpoons [RhClH_2(tppms)_3]\ (\mathbf{3a}, \mathbf{b}) \quad (3)$$

$$[RhClH_2(tppms)_3]\ (\mathbf{3a},\mathbf{b}) + H_2O \rightleftharpoons [RhH(H_2O)(tppms)_3]\ (\mathbf{4}) + Cl^- + H^+ \quad (4)$$

$$[Rh(OH)(tppms)_3]\ (\mathbf{12}) + H_2 \rightleftharpoons [RhH(H_2O)(tppms)_3]\ (\mathbf{4}) \quad (5)$$

Oxidative addition of H_2 to **1** as in Equation (3) gives the dihydridorhodium(III) complex, $[RhClH_2(tppms)_3]$ (**3**) in an "electroneutral" reaction, as no ions are formed during the reaction. One proton is produced in the hydrolysis of **1** [Eq. (2)] and in the dehydrochlorination of **3** [Eq. (4)], the latter reaction yields the monohydridorhodium(I) species, $[RhH(H_2O)(tppms)_3]$ (**4**). The same monohydride is produced in the reaction of $[Rh(OH)(tppms)_3]$ (**12**) with H_2 [Eq. (5)]; however, this reaction is again electroneutral. For this reason the front set of bars on Figure 2 directly gives the relative amount of **12** at the indicated pH on the mol fraction scale, and the back set shows the same for **4**.

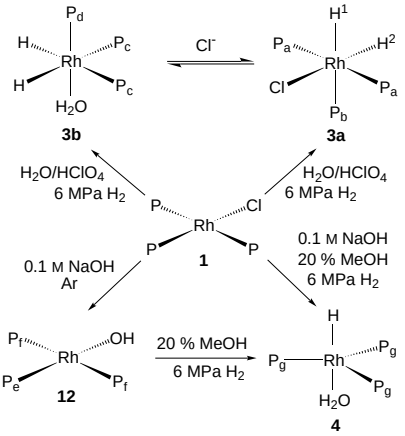
Reductive elimination of HCl from various transition metal compounds is a well known process often used to obtain highly reactive low valent complexes.[38] Compounds of the general formula $[RhClH_2(PR_3)_3]$ readily undergo such dehydrochlorination upon addition of a base such as Et_3N or alkali; this was frequently applied for generation of active catalysts for ketone reduction ($PR_3 = PPh_3$ and various optically active tertiary phosphines).[39] The procedure for the preparation of $[HRh(PPh_3)_4]$ also calls for the use of KOH.[40] However, one should consider that the reductive elimination of HCl is a reversible process and in a one-phase procedure it is retarded by the H^+ and Cl^- produced. Extraction of HCl, for example as $[Et_3NH]^+Cl^-$ into a separate aqueous phase,[41a] or using an aqueous alkali such as 40 % *w*/*w* NaOH[41b] shifts the reaction completely towards dehydrochlorination. Even with no added base water as solvent facilitates processes such as in Equations (2) and (4) due to the strong solvation of ions, especially that of H^+.

Notably we have made several attempts to isolate $[HRh(tppms)_4]$ in solid form. Both the direct synthesis[40] and the generally applicable TPPMS/PPh_3 metathesis[22, 42] methods failed and at best yielded a mixture of rhodium hydrides based on the several absorptions in the hydride stretching region of the infrared spectrum. In a similar attempt $[HRh(tppts)_4]$ could also not be prepared.[36a]

The strength of our novel potentiometric approach is its capabilility of indicating the pH boundaries within which a certain species exists as an appreciable or even major component of the reaction mixture. With a few exceptions[30, 31] metal ion hydrolysis in homogeneous or biphasic aqueous organometallic catalysis has been neglected so far and the formation of hydroxo-complexes was addressed only by preparative methods.[36] Only a few studies describe the effect of pH variation on the kinetics of hydrogenation[28, 43, 44] and hydroformylation[25–27] reactions. Quantitative measurements of proton production (or consumption) at several *constant* pH values in the widest possible pH range, as shown above, provide important additional information on the "pH window" for the formation of catalytically important complexes. On the other hand these pH-static hydrogenations can only give an estimate regarding the chemical composition of such species, not to mention structural information.

Characterization of the hydride species at various pH values by ^1H and ^{31}P NMR spectroscopy: When **1** and a two-fold excess of **8** was dissolved in water containing $HClO_4$ (0.1 M) and pressurized with 6 MPa of H_2, the originally deep orange solution turned light yellow. With multinuclear NMR spectroscopy under medium gas pressure we observed the quantitative formation of two rhodium-dihydride species,

cis-mer-$[RhClH_2(tppms)_3]$ (**3a**) (23%) and *cis-fac*-$[RhH_2X(tppms)_3]$ (**3b**) (77%, $X = H_2O$ or Cl^-) as shown in Scheme 1.[45] Addition of three equivalents NaCl to the reaction mixture resulted in an increase of the proportion of the *cis-mer*-dihydride (up to 50%), while a ten-fold excess of chloride shifted significantly the equilibrium further towards the formation of **3a** (88%). Although solely on the basis of ^1H and ^{31}P NMR spectra it is not possible to discriminate between $X = H_2O$ or $X = Cl^-$ as the ligand in axial position in these complexes, such an effect of excess chloride suggests the coordination of a chloride ion in **3a**, and a water molecule in **3b**. These data are in good agreement with those observed by Larpent et al.[34] for the analogous Rh-TPPTS hydrides under similar conditions in strongly acidic solutions.



Scheme 1. Hydrolysis and hydrogenation equilibria in the aqueous solution of $[RhCl(tppms)_3]$ (**1**) under argon or hydrogen. P = TPPMS (**8**).

In contrast to the above findings, completely different NMR spectra were recorded using a strongly basic (0.1M NaOH) aqueous solution of **1**, although a similar color change to light yellow was observed upon addition of 6 MPa H_2. Both in the ^1H and ^{31}P NMR spectra only broad signals were observed in the temperature range of 2–90 °C which may be due to fast exchange with the solvent and excess TPPMS. However, in solutions containing 20% *v*/*v* methanol the signals sharpened and well resolved spectra could be obtained. At pH 13.0 the only species, formed in quantitative yield was the *mono*hydride: $[RhH(H_2O)(tppms)_3]$ (**4**) containing the hydride, aqua, and the three phosphine ligands in a trigonal bipyramidal geometry (Scheme 1). Oxidation of TPPMS to phosphine oxide was always observed in strongly basic solutions, however its extent usually did not exceed 10% of all phosphorus which means that there was enough free TPPMS left if needed for a *tetrakis*-phosphine species.[40, 47, 48] However, the ^1H and ^{31}P NMR spectra[46] clearly show that such a compound is not formed; the instability of the putative $[HRh(tppms)_4]$ complex is also indicated by the failed attempts of its preparation and can be ascribed to the large steric demand of the *meta*-sulfonated triphenylphosphine ligand.

As mentioned earlier, the existence of a species, such as **4**, has been inferred before from various observations, however, well resolved ^1H NMR spectra of such compounds have never been obtained.[28, 29] Thus this paper gives the first direct evidence for the formation of rhodium(I)-monohydride in aqueous solutions containing only *monodentate* phosphine ligands. Part of the difficulties of obtaining well resolved spectra in basic aqueous solutions is caused by a hydride exchange with the solvent; indeed, we have observed a fast H–D exchange in solutions of **1** in D_2O under moderate H_2 pressure (2 MPa) which is markedly accelerated upon increasing the pH.[49]

The acidity of hydrido transition metal complexes is an important question of chemical bonding and homogeneous catalysis, however, only a few acid dissociation constants (pK_a) are known for rhodium complexes in aqueous solutions.[50] **3a**, **b** yields **4** with concomitant HCl loss, that is not in a simple acid deprotonation process; therefore it cannot be characterized by a single pK_a. Nevertheless, our pH-potentiometric measurements establish that under the particular experimental conditions used the pH at which **3** and **4** are present in 50:50 molar ratio is equal to pH 8.2, showing the thermodynamic acidity of **3a**,**b** being close that of $[Rh_{13}(CO)_{24}H_2]^{3-}$.[50]

Hydrogenation of maleic and fumaric acid as a function of pH with 1 as a catalyst precursor: In order to study possible effects of the change in the catalyst's composition brought about by changes in the pH we studied the hydrogenation of maleic and fumaric acids in a wide pH range. Initial rates of hydrogen uptake at 60 °C were determined by gas volumetry; results are shown on Figures 3 and 4. The Figures also show the molar distribution a) of the undissociated (H_2A) and deprotonated (HA^- and A^{2-}) forms of the substrate acids as a function of pH, calculated with acid dissociation constants taken from the literature.[51]

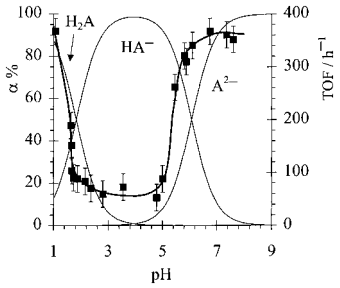


Figure 3. The effect of pH on the initial rate of hydrogenation of maleic acid (MA) catalyzed by $[RhCl(tppms)_3]$ (**1**) in aqueous solution. $[\mathbf{1}] = 1.0 \times 10^{-3}$ M, $[MA] = 5.0 \times 10^{-2}$ M, $T = 60$ °C, $p_{total} = 0.1$ MPa. The calculated distribution (α%) of nondissociated (H_2A) and dissociated (HA^-, A^{2-}) maleic acid is also shown.

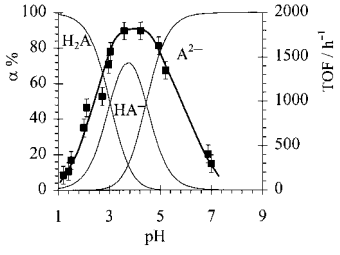


Figure 4. The effect of pH on the initial rate of hydrogenation of fumaric acid (FA) catalyzed by $[RhCl(tppms)_3]$ (**1**) in aqueous solution. $[\mathbf{1}] = 5.2 \times 10^{-4}$ M, $[FA] = 5.0 \times 10^{-2}$ M, $T = 60$ °C, $p_{total} = 0.1$ MPa. The calculated distribution (α%) of nondissociated (H_2A) and dissociated (HA^-, A^{2-}) fumaric acid is also shown.

0947-6539/01/0701-0196 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 1

The most striking feature of these graphs is in that while the rate of maleic acid hydrogenation goes through a deep *minimum* with increasing pH, the case of fumaric acid is just the opposite and a sharp *maximum* is seen. Both extrema coincide with the highest concentration of the HA^- form of the acids. It is an intriguing question why the monoanion of maleic acid reacts sluggishly in contrast to the monoanion of fumaric acid which was found an extremely reactive substrate; presently we do not have the answer. However, it can be also seen from the Figures, that most of the changes in the rate of these hydrogenations occur below pH 6–7 where the majority of rhodium is present as dihydride **3**, and that there is no significant further change in the hydrogenation rate upon increasing the relative amount of monohydride **4** by raising the pH to 7–10. It can be concluded therefore that in case of these substrates the dihydride $\rightleftharpoons$ monohydride equilibrium has little or no influence on the overall rate of the hydrogenation. Interestingly in line with the known higher reactivity of Wilkinson's catalyst towards *cis*-olefins, maleate esters are reduced faster by **9** in organic solvents than the corresponding fumarates.[33] This general trend is also observed with **1** in strongly acidic and strongly basic aqueous solutions, that is with the H_2A and A^{2-} forms of the substrates. In sharp contrast to this, the monoanion, HA^- formed from the *trans*-olefinic acid is reduced about seven times faster than the corresponding *cis*-isomer. In this case the effect of pH can be linked to the changes caused in the ionization state of the substrates. This conclusion agrees with that of Andersson et al. who studied the hydrogenation of acetamidoacrylic acid catalyzed by a water soluble cationic bisphosphine complex, $[Rh(bdppts)(nbd)]^+$ (BDPPTS = tetrasulfonated 1,4-*bis*-(diphenylphosphinyl)butane, NBD = norbornadiene). They have found that the reaction proceeded with the same mechanism both in organic and aqueous solvents and the pH effects on the rate in aqueous solution were ascribed solely to the dissociation/protonation of the substrate.[42]

Reaction of 2 with molecular hydrogen: In striking contrast to Vaska's compound, *trans*-$[IrCl(CO)(PPh_3)_2]$, the analogous rhodium complex *trans*-$[RhCl(CO)(PPh_3)_2]$ (**14**) does not form the corresponding dihydride in benzene or toluene solutions at 20 °C and 0.1 MPa hydrogen, although it catalyzes slow hydrogenation of olefins and aldehydes under more harsh conditions.[33] Compound **2**,[52a,b] the water soluble analogue of **14**,[52c,d] has been known for quite some time, although it has only now been characterized by NMR spectroscopy; the data confirm its *trans*-geometry.[53] In order to obtain detailed data on the possible effects of a base on reactions of this carbonyl complex similar to **1**, **2** was hydrogenated in several solutions of constant pH using a ligand excess ([**8**]:[**2**] = 3). The golden yellow solutions of **2** did not show any change when stirred under H_2 at pH 3 but turned significantly to deeper yellow at pH 10.5 and in sufficiently basic solutions proton production was observed by pH potentiometry. The detailed results concerning proton formation in these solutions are presented on Figure 5.

Two features are apparent on Figure 5 especially in comparison with Figure 2. First, there is virtually no hydrolysis of **2** below pH 9 and even at pH 10 its extent is only about

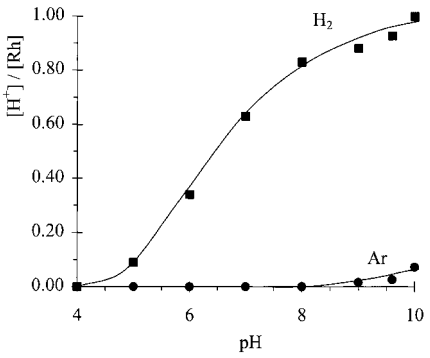
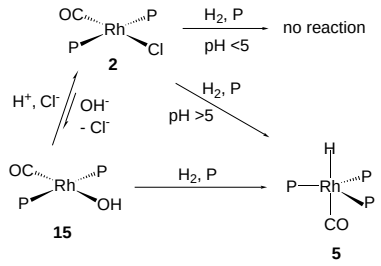


Figure 5. Proton production upon hydrolysis and hydrogenation of *trans*-$[RhCl(CO)(tppms)_2]$ (**2**) at various constant pH in the $4 < pH < 10$ range. $[\mathbf{2}] = 2.4 \times 10^{-3}$ M, $[\mathbf{8}] = 7.2 \times 10^{-3}$ M, 0.1 MPa Ar or H_2, $T = 35$ °C.

5 %. Therefore practically the total amount of proton production can be ascribed to the formation of **5** in a direct reaction of **2** with hydrogen. The second, even more important observation, is in that monohydride **5** is not formed in appreciable quantities at pH ≤ 5 but is formed in yields > 90 % at pH ≤ 9. These reactions are summarized in Scheme 2.



Scheme 2. Hydrolysis and hydrogenation equilibria in aqueous solution of *trans*-$[RhCl(CO)(tppms)_2]$ (**2**) under argon or hydrogen. P = TPPMS (**8**).

It was not possible to record useful NMR spectra of $[Rh(CO)(OH)(tppms)_2]$ (**15**) due to its low solubility even in strongly basic solutions. However, at pH 10 finely resolved spectra were obtained for **5** which was fully characterized by ^1H, ^{31}P, and ^{13}C NMR spectroscopy.[54] We note that ^{13}C-enriched **2** was not formed in measurable ratios when an aqueous solution of **2** was placed under ^{13}CO at room temperature—obviously the exchange is very slow—but could be obtained in quantitative yield in the fast reaction of **1** and ^{13}CO in methanol. The NMR data obtained by us for **5** are very close to the corresponding parameters[35, 36, 48, 52d] determined for **6** (or **11**) and are consistent with a trigonal-bipyramidal structure of **5** with the three TPPMS ligands in the equatorial plane. This structural correspondence gives further evidence to the general observation that there are only minor differences in the chemical properties of **7** and **8** and complexes thereof.

The observed effect of pH on the formation of **5** (together with the similarity of complexes of **7** and **8**) explains the results of Delmas et al.[25] who found a substantial increase in the rate of hydroformylation of 1-octene with **6** on an increase in the pH from 7 to 10, despite proton is *not* involved in the catalytic reaction. Such a rise in the pH should indeed result in a higher concentration of **6** and consequently in that of the

real catalytic species, [Rh(CO)H(tppts)$_2$], formed from **6** by phosphine dissociation. It is apparent from the NMR data that the effects of pH on hydrogenation of **1** and **2** bear no connection to the presence of sulfonate substituent(s) in the ligands. Therefore it seems reasonable to assume that similar pH effects are responsible for the rate increase in the hydroformylation and hydrogenation experiments of Yan et al.[26] and Mieczýnska et al.[27] where the tertiary phosphine ligands in the [Rh(CO)HP$_3$] catalyst carry poly(ethene glycol)- and alkylsulfonato-type substituents, respectively.

Conclusion

We have characterized some important protic equilibria of water soluble hydroxo- and hydridorhodium complexes including the first NMR characterization of a long anticipated Rh(I)-monohydride, [RhH(H$_2$O)(tppms)$_3$], in basic aqueous solution. It is shown that applying water in homogeneous or aqueous–organic biphasic systems for organometallic catalysis can be by no means regarded as using just another inert (innocuous) solvent. The molecular state of catalytically important transition metal complexes may be strongly influenced by the solution pH and this effect explains seemingly unreasonable kinetic features of such important reactions as hydrogenation and hydroformylation. A systematic study of the effect of pH and the use of buffered aqueous solutions of the appropriate pH in case of synthetically useful processes may bring gratifying results and, in fact, is a must in aqueous organometallic catalysis.

Experimental Section

All manipulations were done under an inert atmosphere (argon, N_2 or H_2) using conventional Schlenk techniques.

Instrumentation: Hydrogenations at controlled pH were carried out in a magnetically stirred, jacketed reactor equipped with a Radelkis OP-0808P combined glass-Ag/AgCl electrode, gas inlet/outlet, a capillary inlet for base delivery and a sampling port closed by a rubber septum.[30] If required, an ABU 91 autoburette (Radiometer) supplied 0.2 M KOH into the reactor to keep the pH constant. The autoburette was controlled by a PC used also for data collection. The amount of H^+ produced in the reaction was calculated from the known volume and exact concentration of base. Medium pressure ($p < 12$ MPa) NMR measurements were carried out using sapphire NMR tubes[55] and the ^{1}H, ^{13}C, and ^{31}P NMR spectra were collected by Bruker AC200, AM360 and DRX400 NMR spectrometers. ^{1}H, ^{13}C, and ^{31}P NMR spectra are referenced to 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (TSPSA, Fluka), to internal or external solvent peaks and 85% phosphoric acid, respectively. The spectra were fitted with WINNMR, GNMR 4.0, and NMRICMA/MATLAB programs on a PC. Infrared spectra were recorded on a PE Paragon 1000 PC FTIR spectrometer in KBr discs. For hydrogen uptake measurements a constant pressure gas-volumetric apparatus was used temperature controlled to $\pm 0.1\,^{\circ}$C by a Julabo F25 ultrathermostat/circulator.

Reagents: All solvents were purified by distillation and carefully deaerated before use. Doubly distilled water was used throughout. TPPMS (**8**) was prepared by sulfonation of PPh$_3$, and compounds **1** and **2** by phosphine metathesis in **9** and in *trans*-[RhCl(CO)(PPh$_3$)$_2$] using tetrahydrofuran solutions as described earlier.[22, 42] The purity of the products was routinly checked by NMR[53] and by FTIR spectroscopy [KBr, **2**: $\nu = 1980$ cm^{-1} (C=O, vs) and absence of TPPMS oxide, $\nu = 1120$ cm^{-1} (P=O, s) in both **1** and **2**]. D$_2$O (99.9%) was purchased from Cambridge Isotope Laboratories. H_2, N_2, and Ar were acquired from Carbagas-CH or from Messer (Hungary). Rhodium(III) chloride was purchased from Pressure Chemicals. Maleic and fumaric acids were supplied by Aldrich and were recrystallized from aqueous ethanol. Other reagents (Na_2HPO_4, NaH_2PO_4, $HClO_4$) obtained from Fluka and Aldrich were used as received.

Acknowledgement

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.

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[46] Complex **4**: ^{1}H (200.13 MHz, 66 % H_2O/17 % D_2O/17 % MeOH, 25 °C): $\delta = -9.93$ (q, $^{2}J(H,P_g) = 13.4$ Hz); ^{31}P (81.01 MHz, 66 % H_2O/17 % D_2O/17 % MeOH, 25 °C): $\delta = 40.8$ (d, $^{1}J(P_g,Rh) = 156.3$ Hz, 3 P); $^{31}P\{^{1}H\}$: $\delta = 40.8$ (d, $^{1}J(P_g,Rh) = 156.3$ Hz).
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[53] Complex **2**: ^{31}P NMR (146 MHz, 80 % H_2O/20 % D_2O, 25 °C): $\delta = 30.5$ (d, $^{1}J(P,Rh) = 127$ Hz). For ^{13}C enrichment, **1** was reacted with ^{13}CO (0.1 MPa in MeOH followed by evaporation to dryness. The residue was taken up in 80 % H_2O/20 % D_2O. ^{13}C (50.32 MHz): $\delta = 186.4$ (d, $^{1}J(C,Rh) = 68$ Hz).
[54] Complex **5**: all NMR measurements in 80 % H_2O/20 % D_2O at 40 °C. ^{1}H (200.13 MHz): $\delta = -9.49$ (dq, $^{2}J(H,P) = 13.8$ Hz, $^{2}J(H,C) = 38.2$ Hz); $^{1}H\{^{31}P\}$ (400.03 MHz): $\delta = -9.49$ (d, $^{2}J(H,C) = 38.2$ Hz; $^{1}H\{^{13}C\}$: $\delta = -9.49$ (q, $^{2}J(P,H) = 13.8$ Hz); ^{13}C (50.32 MHz): $\delta = 206.0$ (ddq, $^{1}J(C,Rh) = 53.9$ Hz, $^{2}J(C,P) = 10.4$ Hz, $^{2}J(H,C) = 38.2$ Hz); $^{13}C\{^{1}H\}$: $\delta = 206.0$ (dq); ^{31}P(161.93 MHz): $\delta = 41.2$ (br d, $^{1}J(P,Rh) = 155.0$ Hz); $^{31}P\{^{1}H\}$ $\delta = 41.2$ (dd, $^{1}J(P,Rh) = 155.0$ Hz, $^{2}J(P,C) = 10.4$ Hz).
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Received: April 14, 2000 [F2428]