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The effects of pH on the molecular distribution of water soluble ruthenium(II) hydrides and its consequences on the selectivity of the catalytic hydrogenation of unsaturated aldehydes

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Abstract

The effect of pH on the formation and equilibrium distribution of the water soluble ruthenium hydrides $[HRuCl(TPPMS)_2]_2$, $[HRuCl(TPPMS)_3]$ and $[H_2Ru(TPPMS)_4]$ (TPPMS=(3-sulfonatophenyl)diphenylphosphine sodium salt) was studied in aqueous solution by pH-potentiometric and ^1H and ^{31}P NMR methods. Depending on the pH, $[RuCl_2(TPPMS)_2]_2$ and its hydrido-derivatives hydrolyse extensively, giving rise to formation of hydroxo-ruthenium complexes. It was established that at pH$\leq$3.3 the dominant ruthenium(II) species was $[HRuCl(TPPMS)_3]$, while at pH$\geq$7 it was $[H_2Ru(TPPMS)_4]$. While $[HRuCl(TPPMS)_3]$ catalyzed the slow, selective hydrogenation of the C=C bond in *trans*-cinnamaldehyde, $[H_2Ru(TPPMS)_4]$ was found an active and selective catalyst for C=O reduction. Consequently, the selectivity of the hydrogenation of *trans*-cinnamaldehyde could be completely inverted by minor changes in the solution pH, shifting the equilibrium between $[HRuCl(TPPMS)_3]$ and $[H_2Ru(TPPMS)_4]$.

1. Introduction

Water soluble tertiary phosphine complexes of the platinum group metals play a central role in aqueous organometallic catalysis [1–5]. The highest number of such complexes were prepared with sulfonated ligands, especially the sodium salts of (3-sulfonatophenyl)diphenylphosphine (TPPMS) and tris(3-sulfonatophenyl)phosphine (TPPTS). Some of them show valuable catalytic activity in aqueous solutions or in aqueous/organic biphasic systems, such as $[RhCl(TPPTS)_3]$ in hydroformylation of 1-propene [6] or $[RuCl_2(TPPMS)_2]_2$ in hydrogenation of biological membranes [7]. Under the conditions of preparation and catalytic applications of the complexes in aqueous systems there is an ample possibility of water interacting with the starting material, catalytic intermediates or products of the catalyzed reactions. For example, $[HRh(TPPTS)_4]$ could not be obtained by methods of the preparation of $[HRh(PPh_3)_4]$, instead $[Rh(OH)(TPPTS)_3]$ was obtained [8]. It was also shown that in case of $[RhCl(TPPTS)_3]$ [9] and $[RhCl(PTA)_3]$ (PTA=1,3,5-triaza-7-phosphaadamantane) [10] the phosphine ligand was catalytically oxidized by water probably through intermediate formation of Rh(I)-hydroxo species. Intermediate formation of hydrido-hydroxo-Pd(II) derivatives may be operative in the $[Pd(TPPMS)_4]$-catalyzed telomerization of butadiene with water [11]. Formation of transition metal hydrides via heterolytic splitting of H_2 is accompanied by proton production, such as in (1), and these reactions are assisted by the strong solvation

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of H^+ [12]:

$$[RuCl_2(TPPMS)_2]_2 + 2H_2 \rightleftharpoons [HRuCl(TPPMS)_2]_2 + 2H^+ + 2Cl^- \quad (1)$$

It is also well documented, that several molecular hydrides undergo acid dissociation in aqueous solution [13], the classical example being $[HCo(CO)_4]$, a strong acid itself [14]. All the mentioned reactions should be strongly influenced by $[H^+]$ in the appropriate pH range, and it is most surprising that the formation and distribution of hydrido- and hydroxo-complexes, and their effects on catalysis as a function of pH has not been quantitatively addressed in aqueous organometallic chemistry, apart from a few early attempts in carbonyl chemistry [13,14].

Selective hydrogenation of α,β-unsaturated aldehydes generated much interest in homogeneous catalysis because of the synthetic value of the corresponding allylic alcohols. However, there are only a few catalytic systems which favor C=O reduction over C=C hydrogenation [15–23]. Recent procedures use phase-separable homogeneous catalysts. *Trans*-cinnamaldehyde, crotonaldehyde and citral were reduced with outstanding selectivity to the unsaturated alcohol by hydrogen transfer from aqueous sodium formate solution with $[RuCl_2(TPPMS)_2]_2$+ TPPMS [18,19] and with $[RuCl_2(PTA)_4]$ [20] catalysts. An in situ generated catalyst (from $RuCl_3$ and excess TPPTS) was highly selective in hydrogenation of *trans*-cinnamaldehyde and 3-methyl-2-butenal (prenal) in solutions kept at pH 7 using phosphate buffer [21]. Somewhat contradictory to the latter finding, the hydrogenation of prenal catalyzed by $[H_2Ru(TPPTS)_4]$ produced a considerable amount of the fully saturated product (23% 3-methylbutanol at 100% conversion of prenal) [22]. In reduction of cinnamaldehyde, several Ru(II)–TPPMS and Os(II)–TPPMS complexes afforded 54–100% selectivity to cinnamyl alcohol [23], while $[HRu(CO)Cl(TPPMS)_3]\cdot 2H_2O$ and $[HRu(CO)Cl(TPPTS)_3]\cdot nH_2O$ proved unselective in the same reaction [24].

It can be reasonably concluded from the data and observations in the literature, that the distribution of the various hydrido and hydroxo molecular species potentially formed from a catalyst precursor under conditions of a catalyzed process is decisively influenced by the solution pH, and that the catalytic activity and selectivity in the overall reaction can be sensitive to this molecular distribution. Based on pH-potentiometric, NMR and catalytic hydrogenation measurements, here we report changes in the equilibrium distribution of $[HRuCl(TPPMS)_2]_2$, $[HRuCl(TPPMS)_3]$ and $[H_2Ru(TPPMS)_4]$ formed from $[RuCl_2(TPPMS)_2]_2$ in the presence of excess TPPMS as a function of the pH, accompanied by dramatic changes of the selectivity in cinnamaldehyde hydrogenation. To our knowledge, no similar studies have previously been reported in aqueous organometallic chemistry.

2. Experimental

2.1. Materials

All commercial reagents were of the highest available quality and checked by NMR, GC or HPLC methods before use. TPPMS [25,26] and $[RuCl_2(TPPMS)_2]_2$ [23,26] were prepared by using known procedures. $[HRuCl(TPPMS)_2]_2$ [23], $[HRuCl(TPPMS)_3]$ [27,28], and $[H_2Ru(TPPMS)_4]$ [29] were identified in solution by their ^1H and ^{31}P NMR spectra (Bruker WP 360 SY instrument, 20% D_2O in H_2O, 50°C). $[HRuCl(TPPMS)_2]_2$ δ (ppm) ^1H-8.9 (td, *J*(P-H) 36 Hz, *J*(H-H) 8 Hz), ^{31}P 51.6 (s, br); $[HRuCl(TPPMS)_3]$ δ (ppm) ^1H-18.0 (q, *J*(P-H) 21 Hz), ^{31}P 59.0 (s, br); $[H_2Ru(TPPMS)_4]$ δ (ppm) ^1H-10.3 (pseudo quartet, *J*(P-H) 34 Hz), ^{31}P 42.5 (s), 53.2 (s).

2.2. pH-potentiometric measurements

The experimental setup (Fig. 1) includes a thermostatted reactor (**a**) equipped with inlets for Ar or H_2 (**e**) and for KOH solution, a magnetic stirrer and a Radiometer ABU 91 autoburette (**d**) controlled by a PC (**c**); control software was developed by one of us: A.Cs.B.). Continuous pH measurements (**b**) were done inside the reactor using a Radelkis OP-0808P combined glass electrode which was calibrated against 0.05 M potassium hydrogen phtalate. In order to provide sufficient ionic strength 0.2 M KCl was used as solvent. Doubly distilled, deoxygenated water and carbonate-free 0.2 M KOH was used throughout. With this setup, a reaction, accompanied by proton production, can be run at constant pH by delivering an

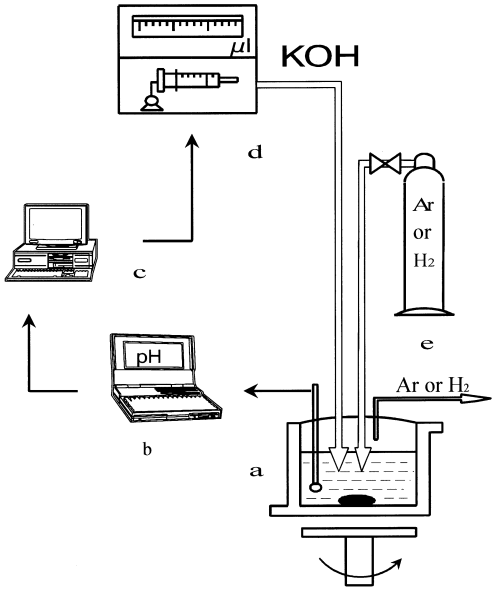


Fig. 1. Equipment for the pH-metric studies and measurements of the proton production.

appropriate volume of KOH solution to neutralize the liberated acid (pH-stat function of the autoburette). The extent of proton production is calculated from the volume of base solution. Alternatively, the pH changes can be monitored in time.

In a typical measurement, 10 ml of 0.2 M KCl was purged with argon for 15 min in the reactor vessel at 60°C, and its pH was adjusted with HCl or KOH to the required value in the 2–12 range. 40 mg (0.04 mmol Ru) $[RuCl_2(TPPMS)_2]_2$ and 50 mg (0.12 mmol) TPPMS were added as solids, and dissolved in a few seconds, under argon at 60°C. After equilibration the gas was changed for H_2, and further KOH was added until a new pH equilibrium was reached. Samples for NMR measurements were prepared the same way but the solvent contained 20% D_2O. The distribution of the three ruthenium(II) hydrides was calculated from the integrated intensities of the appropriate ^1H and ^{31}P NMR signals.

2.3. *Catalytic hydrogenation of trans-cinnamaldehyde*

A mixture of 3 ml of 0.2 M KCl, buffered with $Na_2HPO_4/NaH_2PO_4/HCl$, and 5 ml of chlorobenzene was purged at room temperature with H_2 for 15 min in a three-necked flask equipped with gas inlet and a reflux condenser. 10 mg (0.01 mmol) of $[RuCl_2(TPPMS)_2]_2$ and 12 mg (0.03 mmol) TPPMS were dissolved in this solution and the flask was brought to 80°C by immersing it into an oil bath. The characteristic purple color of $[HRuCl(TPPMS)_3]$ or yellow color of $[H_2Ru(TPPMS)_4]$ developed in about 2 min, at this point 50 μl (0.4 mmol) of cinnamaldehyde was added and the mixture was stirred further vigorously. Samples were withdrawn periodically from the organic phase and analyzed by gas chromatography (Chrom 5, Carbowax 20 M, 2 m packed column, 200°C).

3. Results

Dissolution of $[RuCl_2(TPPMS)_2]_2$ in water under an argon atmosphere at constant pH was accompanied by fast proton production. Hydrogenation of the equilibrated solution resulted in further generation of acid. The extent of proton production relative to the amount of ruthenium present, calculated from the volume of consumed 0.2 M KOH solution, is shown in Fig. 2 for both processes.

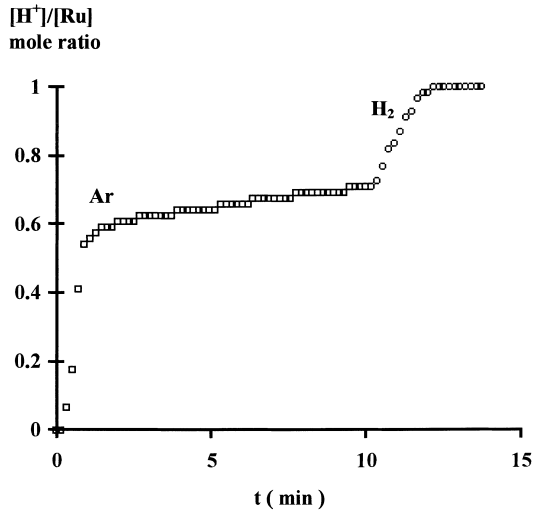


Fig. 2. Proton production upon dissolution under argon (□) and on subsequent hydrogenation (○) of $[RuCl_2(TPPMS)_2]_2$ at pH=6, as a function of reaction time. [Ru]=4.1×10^{-3} M, [TPPMS]=12.5×10^{-3} M, 0.2 M KCl, 60°C, P_{total}=1 bar.

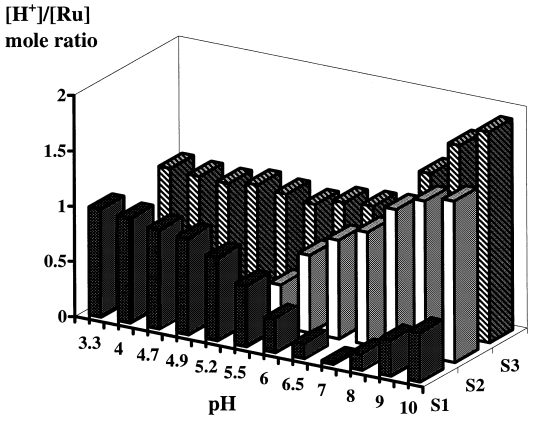


Fig. 3. Proton production upon dissolution under argon (S2) and on subsequent hydrogenation (S1) of $[RuCl_2(TPPMS)_2]_2$, as a function of pH. S3 is the sum of S1 and S2. [Ru]=4.1×10^{-3} M, [TPPMS]=12.5×10^{-3} M, 0.2 M KCl, 60°C, P_{total}=1 bar.

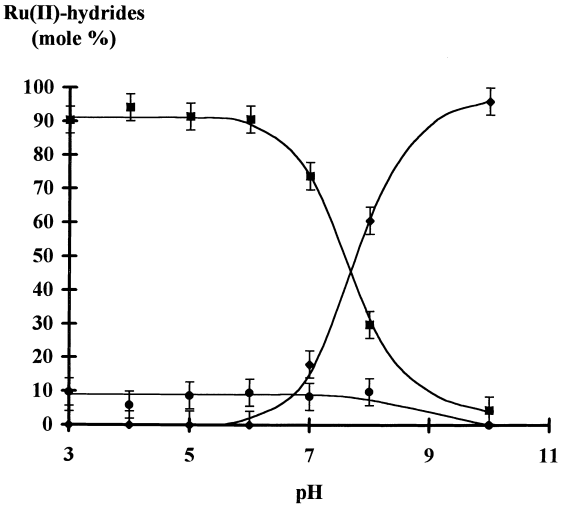
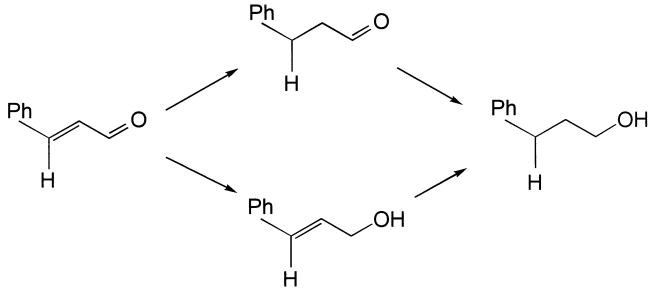


Fig. 4. Distribution of water-soluble ruthenium(II)-hydrides as a function of pH, based on the avarage of ^1H and ^{31}P NMR integrated intensities. ■ $[HRuCl(TPPMS)_3]$, ◆ $[H_2Ru(TPPMS)_4]$, ● $[HRuCl(TPPMS)_2]_2$. [Ru]=2.4×10^{-2} M, [TPPMS]=7.2×10^{-2} M, 0.2 M KCl, 50°C, H_2, P_{total}=1 bar.

The proton production upon dissolution and upon further hydrogenation, and also their sum for the two reactions, was strongly dependent on pH (Fig. 3). In acidic solutions (pH≤3.3) there was no proton generation on dissolution, however, hydrogenation resulted in production of H^+ equimolar to Ru(II). In these cases the color of the final, hydrogenated solutions was purple and the UV-Vis spectrum was identical to that of $[HRuCl(TPPMS)_3]$ in 0.1 M HCl [27]. With increasing pH the amount of protons produced in the hydrogenation step decreased and was practically zero at pH 7. At the same time, however, the amount of protons, generated in the dissolution step, increased to the same extent, so that the overall $[H^+]$:[Ru] ratio remained 1:1. In basic solutions, a small extent of proton production was observed again, followed by more acid generation in the hydrogenation step, and the overall $[H^+]$:[Ru] ratio approached 2:1 at pH 10. At pH≥7 the solutions displayed an intense yellow color. In order to establish the distribution of the molecular hydride species, the final, hydrogenated samples were subjected to ^1H and ^{31}P NMR measurements at 50°C. The distribution of $[HRuCl(TPPMS)_2]_2$, $[HRuCl(TPPMS)_3]$, and $[H_2Ru(TPPMS)_4]$, calculated from the integrated intensities of the respective ^1H and ^{31}P resonances, is shown in Fig. 4.

Hydrogenation of *trans*-cinnamaldehyde (Scheme 1) was investigated at 80°C in a water/chlorobenzene two-phase system, in which the pH of the aqueous phase was kept constant by using sodium phosphate



Scheme 1. Catalytic hydrogenation of *trans*-cinnamaldehyde.

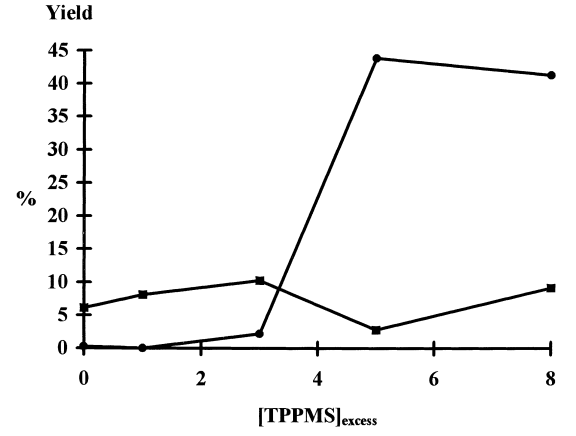


Fig. 5. Effect of the excess of TPPMS on the product distribution in hydrogenation of *trans*-cinnamaldehyde with $[RuCl_2(TPPMS)_2]_2$ and TPPMS as catalyst precursors at pH=4.4. ● cinnamyl alcohol, ■ dihydrocinnamaldehyde. [cinnamaldehyde]=0.08 M in 5 ml chlorobenzene, [Ru]=3.4×10^{-3} M in 3 ml 0.2 M phosphate buffer, 0.2 M KCl, H_2, 80°C, P_{total}=1 bar.

buffer. The product distribution obtained in 4 h reaction time was determined both as a function of TPPMS excess at constant pH (Fig. 5) and as that of the solution pH at constant $[TPPMS]_{tot}$ (Fig. 6). It could be concluded that formation of cinnamyl alcohol was favored by high ligand excess, although the C=C reduction could not be eliminated completely. Conversely, below pH 5, there was a slow but selective formation of the saturated aldehyde which stopped entirely in solutions of pH higher than 7, giving way to exclusive formation of the unsaturated alcohol.

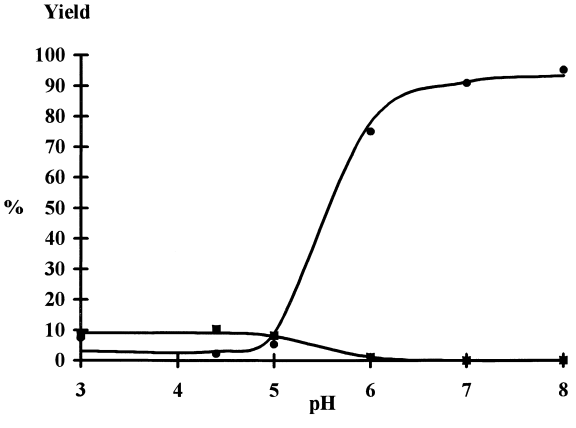


Fig. 6. Effect of pH on the product distribution in hydrogenation of *trans*-cinnamaldehyde with $[RuCl_2(TPPMS)_2]_2$ and TPPMS as catalyst precursors. ● cinnamyl alcohol, ■ dihydrocinnamaldehyde. [cinnamaldehyde]=0.08 M in 5 ml chlorobenzene, [Ru]=3.4×10^{-3} M, [TPPMS]=10.3×10^{-3} M in 3 ml 0.2 M phosphate buffer, 0.2 M KCl, H_2, 80°C, P_{total}=1 bar.

4. Discussion

4.1. Molecular distribution of ruthenium(II) hydrides in aqueous solution as a function of pH

Under the conditions of our pH-static measurements, $[RuCl_2(TPPMS)_2]_2$ dissolved in 0.2 M aqueous KCl with proton production, the amount of which strongly depended on the pH. Hydrogenation of the equilibrated solutions led to further proton production, similarly pH-dependent. These findings can be rationalized by considering the following reactions:

$$1/2[RuCl_2(TPPMS)_2]_2 + H_2O \rightleftharpoons 1/2[Ru(OH)Cl(TPPMS)_2]_2 + H^+ + Cl^- \quad (2)$$

$$1/2[RuCl_2(TPPMS)_2]_2 + 2H_2O \rightleftharpoons 1/2[Ru(OH)_2(TPPMS)_2]_2 + 2H^+ + 2Cl^- \quad (3)$$

$$1/2[RuCl_2(TPPMS)_2]_2 + H_2O + TPPMS \rightleftharpoons [Ru(OH)Cl(TPPMS)_3] + H^+ + Cl^- \quad (4)$$

$$1/2[RuCl_2(TPPMS)_2]_2 + 2H_2O + TPPMS \rightleftharpoons [Ru(OH)_2(TPPMS)_3] + 2H^+ + 2Cl^- \quad (5)$$

Reactions (2)–(5) represent the hydrolytic equilibria of the ruthenium complexes. Unfortunately, the ^{31}P NMR spectra show only very broad resonances and we do not have a structural identification of the supposed hydroxo-derivatives. However, their formation can be inferred from the amount of proton production and by analogy to $[Ru(OH)Cl(PPh_3)_2(H_2O)]_2$ and to $[Ru(OH)Cl(PPh_3)_2(H_2O)_2]$ [30]. Attempts to crystallize these compounds proved so far unsuccessful. Independent of the actual molecular form of the hydrolyzed products, the reactions seem to be reversible, and no proton production is observed upon dissolution of $[RuCl_2(TPPMS)_2]_2$ at pH$\leq$3.3. On the other hand, reactions (2) and/or (4) go to completion at pH 7, and at pH 10 already about 50% of all ruthenium is in the form of dihydroxo compound(s) formed in reactions (3) and/or (5).

Reaction of the starting Ru-complex with H_2 and TPPMS proceeds with heterolytic splitting of hydrogen (reactions 6 and 7) [23], analogous to the reaction of $[RuCl_2(PPh_3)_3]$ [31].

$$1/2[RuCl_2(TPPMS)_2]_2 + H_2 \rightleftharpoons 1/2[HRuCl(TPPMS)_2]_2 + H^+ + Cl^- \quad (6)$$

$$1/2[RuCl_2(TPPMS)_2]_2 + H_2 + TPPMS \rightleftharpoons [HRuCl(TPPMS)_3] + H^+ + Cl^- \quad (7)$$

It is well known, that in benzene solution, formation of $[HRuCl(PPh_3)_3]$ from $[RuCl_2(PPh_3)_3]$, which is a prerequisite for high catalytic activity, requires the presence of a base (proton sponge) [31]. Conversely, in aqueous solutions the above hydrides are formed spontaneously, due to the Bronsted basicity and high solvation power of water. According to the data of Figs. 3 and 4, reactions (6) and (7) take place in acidic solutions leading to the formation of the well-known hydrides, $[HRuCl(TPPMS)_2]_2$ [23], and $[HRuCl(TPPMS)_3]$ [27,28], without prior hydrolysis. However, the same hydrides can also be formed from the products of hydrolysis (Eqs. (8) and (9); not all possible reactions are shown):

$$1/2[Ru(OH)Cl(TPPMS)_2]_2 + H_2 \rightleftharpoons 1/2[HRuCl(TPPMS)_2]_2 + H_2O \quad (8)$$

$$[Ru(OH)Cl(TPPMS)_3] + H_2 \rightleftharpoons [HRuCl(TPPMS)_3] + H_2O \quad (9)$$

In neutral and basic solutions, formation of $[H_2Ru(TPPMS)_4]$ is observed. As shown in Fig. 4, the conversion of $[HRuCl(TPPMS)_3]$ to $[H_2Ru(TPPMS)_4]$ takes place predominantly in the $7 \leq pH \leq 8$ range where the two hydrides exist together. Therefore, a direct reaction can be reasonably assumed (Eq. (10)):

$$[HRuCl(TPPMS)_3] + H_2 + TPPMS \rightleftharpoons [H_2Ru(TPPMS)_4] + H^+ + Cl^- \quad (10)$$

In principle, we can also assume the formation of monomeric and dimeric hydrido-hydroxo-ruthenium complexes which are similar to the known $[HRu(OH)(PPh_3)_2(H_2O)]_2$ and $[HRu(OH)(PPh_3)_2(H_2O)]$ [30], especially in basic solutions. Hydrogenation of a plausible $[HRu(OH)(TPPTS)_3]$ complex would also lead to formation of $[H_2Ru(TPPMS)_4]$. Although the existence and reactions of such hydrido-hydroxo-ruthenium(II) species may well contribute to the overall equilibria, at the moment we do not have experimental evidence which would allow further discussion. However, it is important to note, that formation of the hydrides from hydroxo-ruthenium(II) species (such as in reactions 8 and 9) is accompanied with no further proton production. This is in accord with the experimental finding (Fig. 3) that the combined amount of protons formed in the dissolution (hydrolysis) and the hydrogenation steps is constant ($[H^+]$:[Ru]=1:1), up until the onset of formation of $[H_2Ru(TPPMS)_4]$ around pH 7.

Two further remarks should be given here. In all the reactions (2)–(7) ^{31}P NMR showed no signals of the starting $[RuCl_2(TPPMS)_2]_2$, i.e. the presence of 0.2 M KCl, necessary to provide sufficient ionic strength for precise pH-metric measurements, did not influence the above equilibria significantly. In accord with this conclusion, the rate and hydrogenation of *trans*-cinnamaldehyde was not affected by the addition of KCl (see later). Similarly, protonation of TPPMS need not be considered, since it was shown [27,32] to take place only to a negligible extent in the acidity range used here.

The most important conclusion from these combined pH-potentiometric and NMR measurements is that under our conditions, in acidic solutions the major ruthenium species is $[HRuCl(TPPMS)_3]$, while in basic solutions it is $[H_2Ru(TPPMS)_4]$. It is also important to note that our measurements were done under pH-static conditions. In the absence of a suitable buffer (or a pH-stat), the solutions made with plain water become considerably acidic (pH≈3–4), owing to the hydrolytic and hydrogenation equilibria discussed above and the molecular distribution will correspond to the actual pH.

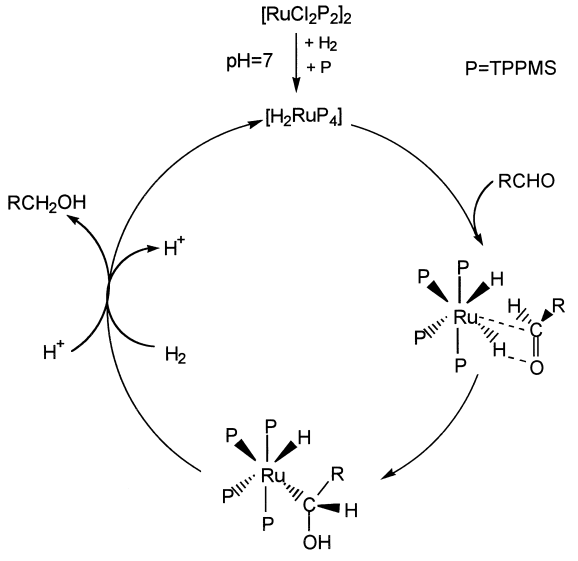
4.2. *Catalytic hydrogenation of trans-cinnamaldehyde*

Trans-cinnamaldehyde was catalytically reduced in a water(0.2 M KCl)/chlorobenzene two-phase system under mild conditions (80°C, 1 bar total pressure). The presence of KCl provided a fairly constant ionic strength, and was also important to provide a constant ionic environment in order to avoid changes in the hydrogenation rate and selectivity due to cations

[33,34]. Reactions were generally run for 4 h, during which 10–95% conversion of the starting compound was achieved. Under such conditions the product mixture contained 3-phenylpropanal (dihydrocinnamaldehyde) and 3-phenylpropenol (cinnamyl alcohol), while formation of the fully saturated product (3-phenylpropanol) was negligible. Figs. 5 and 6 show the product distribution of *trans*-cinnamaldehyde hydrogenation as a function of TPPMS ligand excess and as a function of the pH, respectively. It can be seen, that depending on these two variables, the reaction can be selective either towards the formation of the unsaturated alcohol or towards hydrogenation of the C=C bond! In addition, the selectivity can greatly vary as a result of minor changes in the pH. For example, in the presence of three equivalents of excess TPPMS, a slow but highly selective hydrogenation of cinnamaldehyde to dihydrocinnamaldehyde took place at pH 4.4. With the same reaction mixture, but at pH 6.0, the reaction was approximately eight times faster, producing almost exclusively cinnamyl alcohol (complete selectivity was achieved at pH$\geq$7). In unbuffered reaction mixtures with negligible ionic strength, changes of this magnitude in the pH can occur due to the presence of minor contaminants of the substrates or to metal ion hydrolysis. We reason that the latter effect may have caused the rather low selectivities observed in hydrogenation of unsaturated aldehydes catalyzed with $[RuCl_2(TPPMS)_2]_2$ [23], $[RuCl_2(TPPTS)_2]_2$ and $[H_2Ru(TPPTS)_4]$ [22] precatalysts. On the other hand, when appropriate pH conditions are provided for the exclusive presence of $[HRuCl(TPPMS)_3]$, then selective reduction of the C=C, and with $[H_2Ru(TPPMS)_4]$, the selective hydrogenation of the C=O bond of unsaturated aldehydes can be achieved. This is in accord with the observed high selectivities towards formation of the unsaturated alcohols, observed in reduction of unsaturated aldehydes with hydrogen transfer in aqueous sodium formate solutions [18,19]. In those cases the pH varied between 7.8–9.2 during the catalytic runs [19].

4.3. *Remarks on the mechanism of cinnamaldehyde hydrogenation*

From our limited set of kinetic data the most remarkable observation is that the exclusive C=O reduction of *trans*-cinnamaldehyde takes place in the presence of a relatively high excess of TPPMS, i.e. with $[H_2Ru(TPPMS)_4]$ as the true catalytic species (Figs. 5 and 6). This observation excludes both a dissociative and a straightforward associative mechanism.



Scheme 2. Possible intermediates in catalytic hydrogenation of *trans*-cinnamaldehyde.

We assume that direct interaction of $[H_2Ru(TPPMS)_4]$ and *trans*-cinnamaldehyde as depicted on Scheme 2, leads to formation of a hydroxyalkyl species. The unsaturated aldehyde product is formed either via reductive elimination or by protonation and a further reaction with H_2 regenerates $[H_2Ru(TPPMS)_4]$. This mechanism is close to the one suggested in [33,34] in order to rationalize the effect of added cations, but differs from the one in [23] in that the formation of an intermediate with an O-bonded aldehyde is not presumed. The origin of selective C=O reduction, therefore, lies in the possibility of a hydrogen-bonding assisted protonation of the carbonyl oxygen, accompanied by simultaneous Ru–C bond formation. At the same time, coordination of the C=C bond, a prerequisite for its hydrogenation, is prevented by the coordinative saturation of $[H_2Ru(TPPMS)_4]$. When the pH conditions make the formation of $[HRuCl(TPPMS)_3]$ predominant, C=C hydrogenation also becomes possible but as observed in [32] with $[HRuCl(PPh_3)_3]$ requires dis-

sociation of a phosphine ligand; this is reflected in the slow but selective hydrogenation of cinnamaldehyde to dihydrocinnamaldehyde.

5. Conclusions

The distribution of potentially catalytic intermediate molecular species in aqueous organometallic reactions can be influenced to a great extent by variations in solution pH. This, in turn, may manifest itself in dramatic changes in reaction rates and selectivities. This is convincingly illustrated by the effects of pH on the rate and selectivity in hydrogenation of cinnamaldehyde, catalyzed by $[RuCl_2(TPPMS)_2]_2$ and the various hydride species which may form in solutions of various different pH.

Acknowledgements

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