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Comparison of Catalytic Properties of the Easily Interconvertible, Water-Soluble [RuHCl(CO)(*m*tppms-Na)$_3$] and [RuH(H$_2$O)(CO)(*m*tppms-Na)$_3$][BF$_4$]

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Abstract: The effect of the mobile interconversion of [RuHCl(CO)(*m*tppms-Na)$_3$] **1**, and [RuH(H$_2$O)(CO)(*m*tppms-Na)$_3$]$^+$ **2**, was studied in hydrogenation of phenylacetylene and cinnamaldehyde in aqueous–organic biphasic systems, as a function of the chloride concentration and the pH of the aqueous phase. Catalytic activity of the two complexes was also determined in homogeneous organic solvents without any additives. In the biphasic system, the rate of selective hydrogenation of phenylacetylene to styrene was strongly increased upon addition of NaCl, while the reaction of cinnamaldehyde slowed, with no change in product distribution. Both reactions responded with a rate decrease upon increasing the pH of the aqueous phase. It was concluded that hydrogenation of phenylacetylene was catalyzed by **1** with no chloride dissociation, while in the reduction of cinnamaldehyde, the aquo-complex **2** was the active catalytic species. Catalytic cycles were suggested to rationalize these findings.

Keywords: alkynes; aqueous-organic biphasic; chloride; cinnamaldehyde; hydrogenation; pH

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1. Introduction

Since its first synthesis in 1965 [1], [RuHCl(CO)(PPh$_3$)$_3$] [2,3] and its analogs containing a wide array of tertiary phosphines have proved to be excellent catalysts for various important organic transformations (hydrogenation of aldehydes and ketones [4,5], hydrosilylation [6], alkylation [7,8], arene C–H amidation [9], to name only a few). Alkyne substrates have been frequently studied, especially with regard to selective semi-hydrogenation to alkenes [10–12]. Although most of these reactions were carried out in anhydrous organic solvents, in several cases beneficial effects of small amounts of added water were observed [4].

With the aim of recovery and recycling of the expensive precious metal catalysts, several water-soluble tertiary phosphine ligands, including 3-diphenylphoshinobenzoic acid (*meta*-monosulfonated triphenylphosphine, *m*tppms-H) and (3,3′,3″-phosphinetriylbenzenesulfonic acid, *meta*-trisulfonated triphenylphosphine, *m*tppts-H$_3$) were prepared and applied, in most cases as their sodium salts, *m*tppms-Na [13] (Figure 1) and *m*tppts-Na$_3$ [13], respectively, to replace PPh$_3$ in known active homogeneous catalysts such as [RhCl(PPh$_3$)$_3$], [HRuCl(PPh$_3$)$_3$], and many others [14,15]. In line with these efforts, [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, and [RuHCl(CO)(*m*tppts-Na$_3$)$_3$] were also synthesized and used as catalysts of hydrogenation and hydroformylation in aqueous or aqueous-organic biphasic solvent systems [16–19].

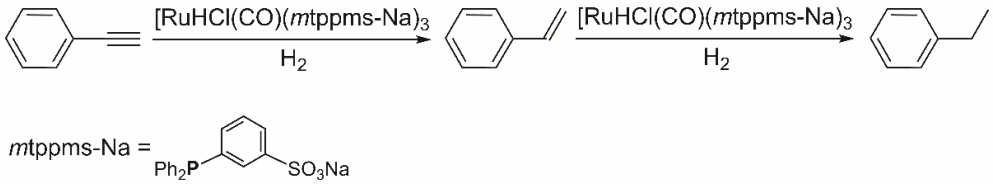

Figure 1. Hydrogenation of phenylacetylene.

Some time ago we observed that in aqueous solution [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, underwent facile chloride dissociation (Equation (1)).

$$[RuHCl(CO)(mtppms\text{-}Na)_3] + H_2O \rightleftharpoons [RuH(H_2O)(CO)(mtppms\text{-}Na)_3]^+ + Cl^- \quad (1)$$

This reaction was confirmed by ^{1}H- and ^{31}P{H}-NMR spectroscopy, and by synthesis of the resulting aqua-complex [RuH(H$_2$O)(CO)(*m*tppms-Na)$_3$]$^+$, **2** on an independent route; the cationic complex was isolated as its tetrafluoroborate salt [RuH(H$_2$O)(CO)(*m*tppms-Na)$_3$][BF$_4$] (**2**[BF$_4$]). While in purely aqueous solution **1** underwent complete dissociation to **2**; it is important to mention here, that in purely methanolic solution no such chloride dissociation of **1** was detected. However, in methanol–water mixed solvents the chloride-free complex was also detected by NMR measurements, in increasing concentration with increasing water content. For example, in H$_2$O/MeOD 1: 1 (v/v), already 70% of all Ru was present as **2** at 25.0 °C, together with 30 % of **1** [19].

Since in aqueous or aqueous–organic biphasic processes, the catalysis takes place in the presence of water, it seemed important to compare the catalytic activity and selectivity of **1** and **2**. Here we present our results on hydrogenation of phenylacetylene and cinnamaldehyde (CA) with the use of [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, and [RuH(H$_2$O)(CO)(*m*tppms-Na)$_3$][BF$_4$], **2**[BF$_4$] as catalysts.

2. Results and Discussion

2.1. Hydrogenation of Phenylacetylene

Since in aqueous solution [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, is fully converted to [RuH(H$_2$O)(CO)(*m*tppms-Na)$_3$]$^+$, **2**, for comparison of the catalytic activity of the two complexes methanol was used as solvent, in which both **1** and **2**[BF$_4$] are soluble but no chloride dissociation takes place from **1**. Hydrogenation of phenylacetylene was chosen as a test reaction (Figure 1), which can also be studied in aqueous-organic biphasic reaction systems in which the low solubility of phenylacetylene and its hydrogenated products in water prevent their accumulation in the aqueous phase.

2.1.1. Hydrogenation of Phenylacetylene in Homogeneous Organic Solution (MeOH)

The time course of phenylacetylene hydrogenation catalyzed by **1** and **2**, respectively, is shown on Figure 2. In both cases, it was established by gas chromatographic analysis of the reaction mixture that the exclusive product was styrene, with no formation of ethylbenzene. **1** was found a far more active catalyst (initial turnover frequency, TOF$_i$ = 29.3 h^{-1}), although eventually, the use of **2** also led to 100% conversion of phenylacetylene (TOF$_i$ = 4.4 h^{-1}).

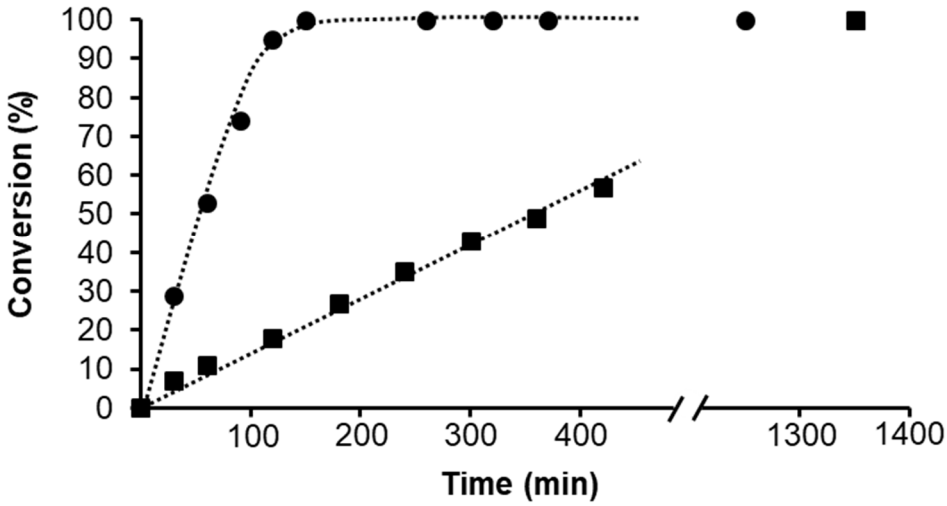

Figure 2. Time course of phenylacetylene hydrogenation in MeOH solution catalyzed by [RuHCl(CO)(*m*tppms-Na)$_3$], **1** (●) and [RuH(H$_2$O)(CO)(*m*tppms-Na)$_3$][BF$_4$], **2**[BF$_4$] (■) Conditions: [phenylacetylene] = 6.25 × 10^{-2} M, [Ru] = 1.25 × 10^{-3} M, *P*(H$_2$) = 1 bar, *T* = 60 °C. Analysis of the reaction mixture by gas chromatography.

Interestingly, hydrogenations catalyzed by [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, were not only faster than those with [RuH(H$_2$O)(CO)(*m*tppms-Na)$_3$][BF$_4$], **2**[BF$_4$] as the catalyst, but proceeded at a constant rate until the complete consumption of phenylacetylene. This zero-order dependence of the rate from the actual substrate concentration refers to a strong substrate-catalyst coordination, which is often found in alkyne hydrogenation [10,12]. Catalyzed hydration of phenylacetylene as a competing side-reaction was not detected by GC analysis of the organic phase.

2.1.2. Hydrogenation of Phenylacetylene in water–1,2-dichloroethane (1,2-DCE) Biphasic System

While the measurements on catalytic hydrogenation of phenylacetylene in homogeneous methanolic solutions provide data for comparison of the intrinsic catalytic activities of **1** and **2**, reactions in aqueous–organic biphasic systems allow the study of water-soluble additives, such as halides, as well as the effect of pH on the rates of reactions catalyzed by the mentioned complexes.

It is known that, in aqueous solution, **1** and **2** are in a dynamic equilibrium (Equation (1)), one which is governed by chloride concentration [19]. Therefore, first we studied the effect of chloride on hydrogenation of phenylacetylene. The reactions were carried out in mixtures of 1,2-dichloroethane and aqueous solutions of various sodium chloride concentration, and the results are shown on Figure 3. It is seen that the reaction rate increased with the increase of chloride concentration in the aqueous phase, levelling off at approximately [Cl$^-$] = 1 M. At this point, the actual rate was about three times higher than in the absence of chloride. Since, in purely aqueous solution, **1** reversibly dissociates to **2**, this increase of the hydrogenation rate with increasing chloride concentration can be attributed to increase of the mole ratio of **1** at the expense of the mole ratio of **2**. This finding is in accord with the results from the experiments with homogeneous methanolic solutions (Figure 2), where **1** proved to be significantly more active than **2** for the hydrogenation of phenylacetylene. Note that the consumption of the alkyne substrate was considerably lower in the biphasic system than with **1** in homogeneous solutions, reaching a maximum TOF = 7.5 h^{-1} at 1 M chloride concentration. Lower reaction rates are a common feature of biphasic reactions relative to homogeneous processes due to low substrate concentration in the catalyst-containing aqueous phase and hindered material transport between the phases [20].

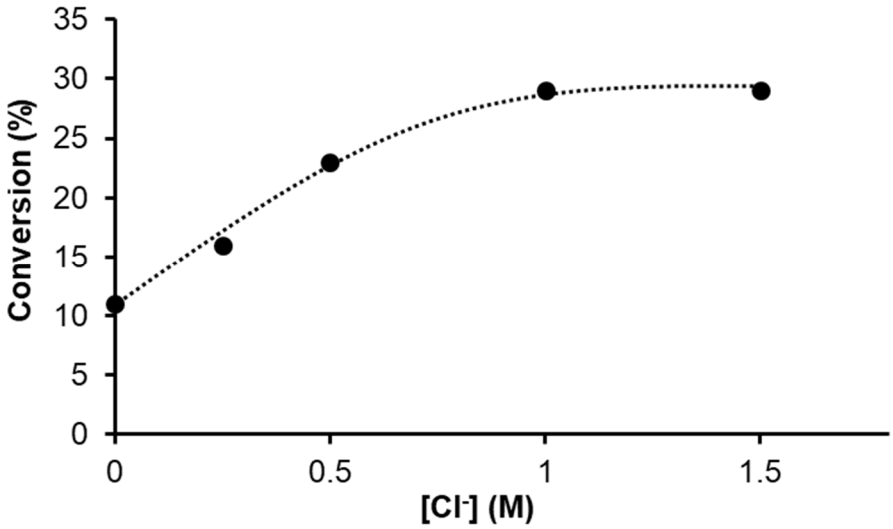

Figure 3. Conversion of phenylacetylene in hydrogenation catalyzed by [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, as a function of the concentration of added sodium chloride in a water–1,2-DCE biphasic system. Conditions: n(phenylacetylene) = 0.5 mmol, n(Ru) = 0.01 mmol, $P(H_2)$ = 1 bar, T = 60 °C, t = 2 h, V(aq. chloride solution) = 1 mL, V(1,2-DCE) = 1 mL. Analysis of the reaction mixture by gas chromatography.

Often an advantage of aqueous systems in organometallic catalysis is the possibility of influencings the reactions' rates or selectivity by proper selection of pH [11,21]. For this reason, we have also studied the biphasic hydrogenation of phenylacetylene in water–1,2-DCE biphasic solvent mixtures as a function of pH. The pH of the aqueous phase was adjusted with the use of 0.2 M phosphate buffer solutions. The results are reported in Figure 4, and show a retarding effect of increasing pH on the rate of phenylacetylene hydrogenation. Especially important is the pH = 7–11 range, in which the alkyne conversion dropped from 28% to 5%.

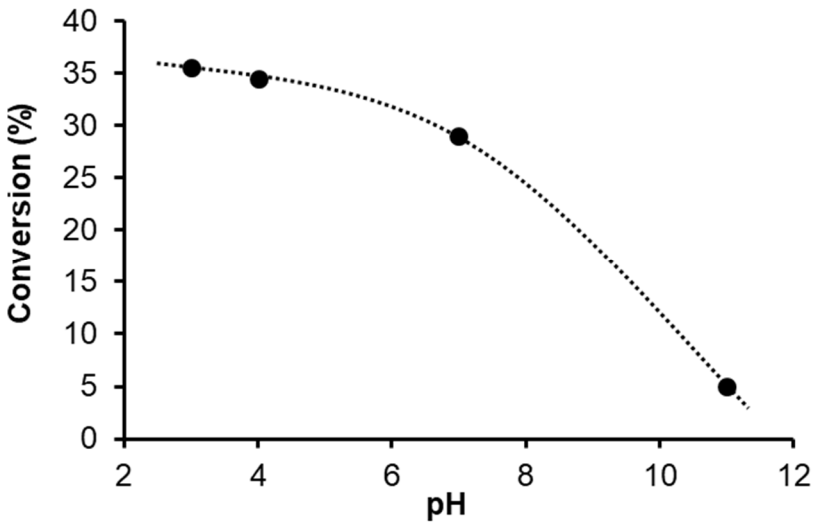

Figure 4. Conversion of phenylacetylene in hydrogenation catalyzed by [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, as a function of the pH of the aqueous phase in water–1,2-DCE biphasic systems. Conditions: n(phenylacetylene) = 0.5 mmol, n(Ru) = 0.01 mmol, $P(H_2)$ = 1 bar, T = 60 °C, t = 2 h, V(aq. phosphate buffer) = 1 mL, V(1,2-DCE) = 1 mL. Analysis of the reaction mixture by gas chromatography.

Due to its solubility in aqueous solutions in a wide pH range, it was possible to record $^{31}P\{^1H\}$-NMR spectra of **1** as a function of the pH in solutions of $9 \leq pH \leq 13$. No color

change or precipitation was observed in the solutions of various alkalinity. For preparation of the solutions, solid [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, was used, and it was assumed from earlier measurements [19] that it fully dissociated to [RuH(H_2O)(CO)(*m*tppms-Na)$_3$]$^+$, **2**, in pure water. As shown in Figure 5, the ^{31}P resonance shifted from 22.8 ppm to 17.7 ppm upon the change of pH from 9 to 13. In agreement with similar measurements in the literature [14,21], this change can be attributed to the acid dissociation of coordinated H_2O (Figure 6). Evaluation of the data with the use of the PSEQUAD program [22] resulted in an aqueous pK_a of 11.3 for acid dissociation of [RuH(H_2O)(CO)(*m*tppms-Na)$_3$]$^+$. Depending on the nature of the other ligands in the coordination sphere of a Ru^{2+}-aqua complex, pK_a values of the coordinated H_2O ligand span a wide range, as shown by selected examples: [Ru(H_2O)(NCMe)$_4$(P^{i}Pr$_3$)] (pK_a = 11.36) [23], in the Ru(II)-N-heterocyclic carbene complex; [RuCl(H_2O)(*p*-cymene)(NHC)]$^+$ (pK_a = 8.1; *p*-cymene = 4-isopropyltoluene, NHC = 1-butyl-3-methylimidazol-2-ylidene) [24], in [Ru(H_2O)(η^6-benzene)(bpy)]$^{2+}$ (pK_a = 7.2; bpy = 2,2′-bipyridine) [25]; and [Ru(H_2O)$_6$]$^{2+}$ (pKa = 5.89) [26], to mention only a few. The high pK_a = 11.3 of [RuH(CO)Cl(*m*tppms-Na)$_3$] is almost identical to that of [Ru(H_2O)(NCMe)$_4$(P^{i}Pr$_3$)] but is different from those of the arene-Ru^{2+} complexes and from that of [Ru(H_2O)$_6$]$^{2+}$ which contains only hard, O-donor aqua ligands. The important role of formation of aqua- and hydroxo-complexes of Ru^{2+} was also demonstrated in detail in redox isomerization of allylic alcohols [27].

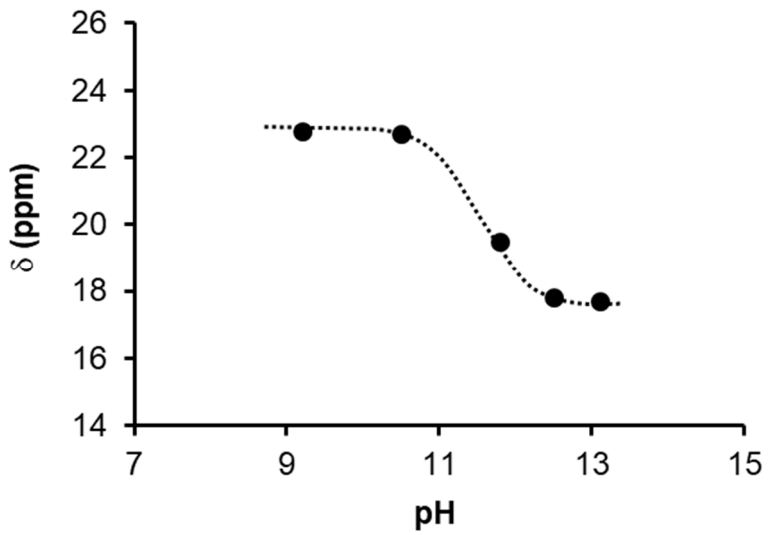

Figure 5. Chemical shift of the ^{31}P{^{1}H}-NMR resonance of [RuHCl(H_2O)(*m*tppms-Na)$_3$] in aqueous (D_2O) solution as a function of pH. Conditions: n(Ru) = 0.02 mmol, 0.5 mL D_2O, *T* = 298 K, argon atmosphere.

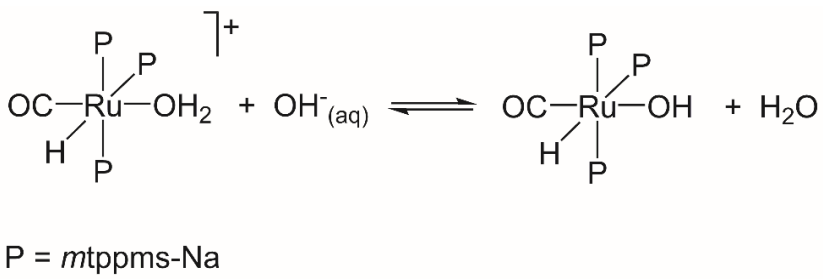

Figure 6. Acid dissociation of coordinated H_2O in [RuH(H_2O)(CO)(*m*tppms-Na)$_3$]$^+$.

Although the conditions of catalytic measurements (Figure 4) and pH-metric NMR titrations (Figure 5) are not exactly the same, it is safe to assume that it is the acid dissociation of **2**, depicted in Figure 6, that leads to the loss of catalytic activity.)

2.1.3. Mechanism of Phenylacetylene Hydrogenation in Aqueous–Organic Biphasic Solvent Mixtures Catalyzed by [RuHCl(CO)(mtppms-Na)$_3$], 1, or [RuH(H_2O)(CO)(mtppms-Na)$_3$]$^+$, 2

A possible mechanism of phenylacetylene hydrogenation catalyzed by **1** (X = Cl^-) is shown in Figure 7. It is also suggested that the same catalytic cycle (Figure 7) is operative with catalyst **2** (X = H_2O), with taking care of the charge of Ru(II)-complexes on replacement of a charged ligand (Cl^-) with a neutral one (H_2O). According to this catalytic cycle, the first step is substitution of a phosphine ligand (P) in (**A**) by the alkyne substrate leading to the alkyne complex **B**. Internal hydride migration to the coordinated alkyne affords an intermediate styryl-Ru(II) complex (**C**). Reaction of **C** with H_2 yields the free product (styrene), and re-coordination of P results in formation of **A**, closing the catalytic cycle. Hydrogen activation may take place in **C** via substitution of S (solvent, in this case: H_2O) by H_2 resulting in a putative Ru(H_2) dihydrogen complex in which the coordinated H_2 is able to protonate the Ru-C bond with simultaneous formation of a Ru-H bond [28–30]. According to earlier results, dihydrogen can be a better ligand for Ru(II) than H_2O [31], however, replacement of H_2O in **A** by OH^- due to acid dissociation of H_2O may hinder substitution [27]. This is in agreement with the observed decrease of the overall rate of phenylacetylene hydrogenation with the increase of pH. Strong alkyne coordination vs binding of styrene may explain the selectivity for alkyne semi-hydrogenation, and the zero-order hydrogenation rate dependence on alkyne concentration. The suggested cycle is also supported by detection of free phosphine by ^{31}P NMR spectroscopy in the reaction mixture. Similar observations were made by Torres et al. [32] and by Jia et al. [33], who studied the stoichiometric insertion reactions of phenylacetylene and other alkynes into the Ru-H bond in [RuHCl(CO)(PPh_3)].

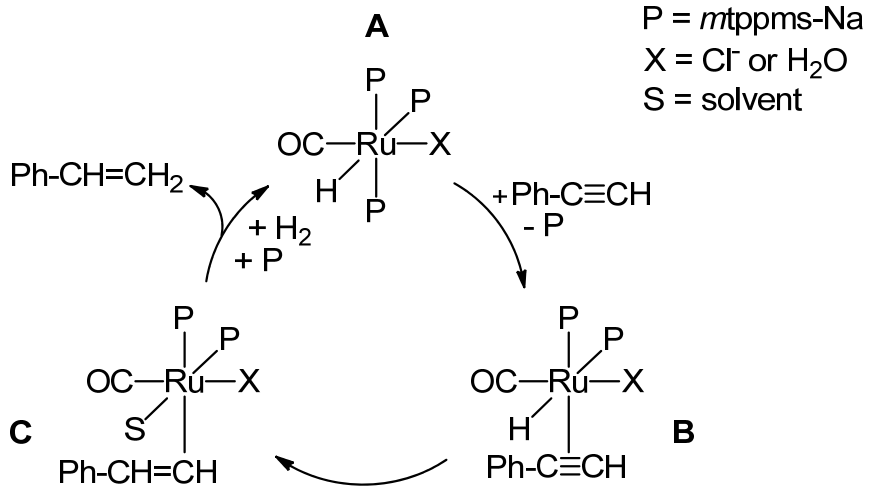

Figure 7. Suggested catalytic cycle of phenylacetylene hydrogenation catalyzed by [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, or [RuH(H_2O)(CO)(*m*tppms-Na)$_3$]$^+$, **2**.

2.2. Hydrogenation of Cinnamaldehyde

In addition to the saturated aldehyde and saturated alcohol products, hydrogenation of α,β-unsaturated aldehydes may yield allylic alcohols, which are important intermediates in the food and fragrance industry. For this reason we compared the catalytic activity and selectivity of [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, and [RuH(H_2O)(CO)(*m*tppms-Na)$_3$]$^+$, **2** in the hydrogenation of cinnamaldehyde (CA; 3-phenylprop-2-enal) (Figure 8).

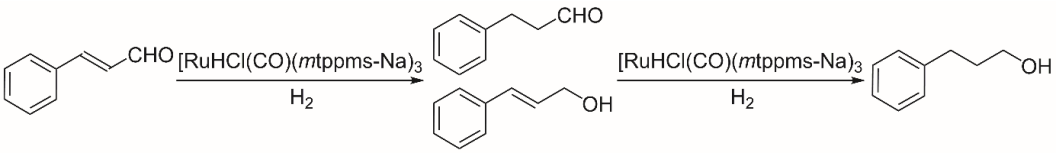

Figure 8. Hydrogenation of cinnamaldehyde.

2.2.1. Hydrogenation of Cinnamaldehyde in 2-Methoxyethanol

Homogeneous hydrogenation of cinnamaldehyde in a water-free organic solvent was carried out in 2-methoxyethanol, in order to prevent acetal formation (which took place in the methanol used above for hydrogenation of phenylacetylene).

It is seen from the results shown in Table 1, that with both catalysts the main product was the unsaturated alcohol (cinnamyl alcohol, 3-phenylprop-2-enol). Small amounts of the saturated aldehyde (hydrocinnamaldehyde: 3-phenylpropanal) were also detected. Formation of the fully hydrogenated product, 3-phenylpropanol was not observed. In contrast to the case of phenylacetylene hydrogenation, the two complexes did not show a remarkable difference in catalytic activity.

Table 1. Homogeneous hydrogenation of cinnamaldehyde with catalysts **1** and **2**, respectively, in 2-methoxyethanol solution.

	1	**2[BF$_4$]**
Conversion (%)	13	10.9
Cinnamyl alcohol (%)	11.8	10.7
3-Phenylpropanal	1.2	0.2
Selectivity (%)	90.8	98.2

Conditions: n(cinnamaldehyde) = 1.59 mmol, n(**1** or **2**[BF$_4$]) = 9.52×10^{-3} mmol, T = 80 °C, P(H$_2$) = 1 bar, t = 2 h, V(2-methoxyethanol) = 8 mL. Analysis of the reaction mixture by gas chromatography.

2.2.2. Hydrogenation of Cinnamaldehyde in Aqueous–Organic Biphasic System (Water–Toluene)

Depending on the chloride concentration in the catalyst-containing aqueous phase, [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, and [RuH(H$_2$O)(CO)(*m*tppms-Na)$_3$]$^+$, **2** may be present in various molar ratios (Equation (1)). This effect was studied in water–toluene mixtures (Figure 9).

The data in Figure 9 show that in hydrogenation of cinnamaldehyde, increased chloride concentrations in the aqueous phase decreased the conversion of the substrate. This is precisely the opposite effect than that observed in the case of phenylacetylene hydrogenation in aqueous–organic biphasic mixtures with the same catalyst. The main product was cinnamyl alcohol; e.g., in a 0.1 M chloride concentration it represented 60 % of all products. Interestingly, in water–toluene biphasic mixtures the fully saturated product, 3-phenylpropanol, too, was detected, although the reaction still showed moderate selectivity to cinnamyl alcohol (product distribution at 0.5 M [Cl$^-$]: cinnamyl alcohol 58%, 3-phenylpropanal 29%, 3-phenylpropanol 13%). We attribute the appearance of cinnamyl alcohol in the biphasic systems (in contrast to the homogeneous solutions), to the higher hydrogen pressure (10 bar vs. 1 bar) rather than to the difference in the temperature (60 °C vs 80 °C). These data also show that under biphasic conditions, hydrogenation of cinnamaldehyde with **1** as the catalyst was less selective than under homogeneous conditions (in 2-methoxyethanol), and that the selectivity changed only moderately with increasing chloride concentration. It should be added here that no side-reactions (such as e.g., Cannizaro reaction) were detected by gas chromatography.

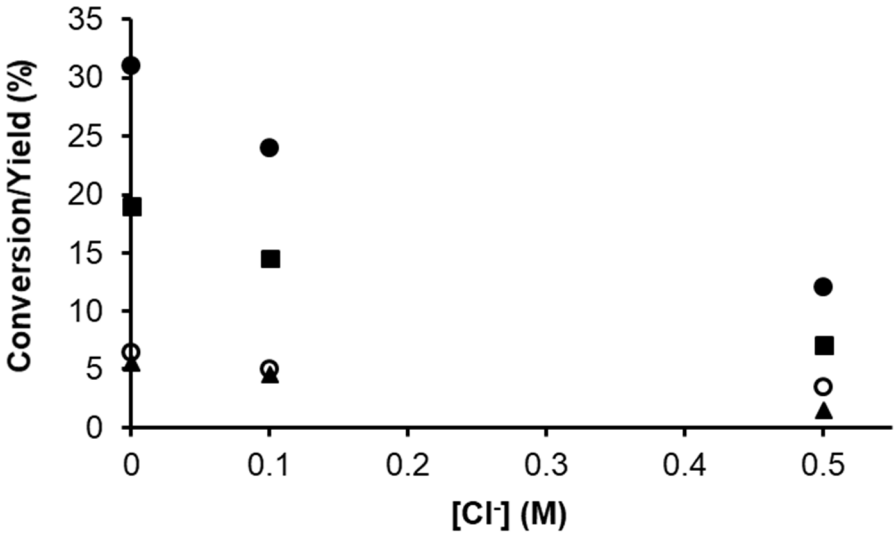

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Figure 9. Conversion and product yields in hydrogenation of cinnamaldehyde catalyzed by **1**, as a function of the concentration of added chloride in water-toluene biphasic system. (●:total conversion. ■:cinnamyl alcohol; ○:3-phenylpropanal; ▲:3-phenylpropanol) Conditions: n(cinnamaldehyde) = 0.5 mmol, n(Ru) = 0.01 mmol, $P(H_2)$ = 10 bar, T = 60°C, t = 2h, $V(H_2O)$ = 1 mL, V(toluene) = 1 mL. Analysis of the reaction mixture by gas chromatography.

Figure 10 shows the effect of pH of the aqueous phase on the conversion of cinnamaldehyde and the yields of the products. It is seen that the increase of pH resulted in a constant decrease of the conversion, and in basic solutions (around pH 11), the reaction practically stopped. In this case, however, there was no such sudden loss of activity other than that observed in hydrogenation of phenylacetylene in the range of $7 \leq pH \leq 11$. The major products were cinnamyl alcohol and 3-phenylpropanal, in 75% and 25%, respectively, both at pH 2 and 4, that is, the selectivity did not change with the increase of pH. Andriollo and co-workers made extensive studies on the hydrogenation of cinnamaldehyde. [17] In their investigations, more extreme conditions were used. At the lowest investigated temperature (80 °C) an initial turnover frequency of TOF = 1.2 h^{-1} was determined, while at 120 °C TOF = 16.2 h^{-1} could be obtained. In contrast, despite the lower temperature (60°C), a TOF of 31 h^{-1} can be calculated from the data of this paper (Figure 9) (in the absence of added chloride). The selectivities in both studies were in favor of cinnamyl alcohol. Nevertheless, the biphasic hydrogenation of cinnamaldehyde could not be made completely selective to any of the intermediates.

2.2.3. Mechanism of Cinnamaldehyde Hydrogenation Catalyzed by [RuHCl(CO)(mtppms-Na)$_3$], 1, in Aqueous–Organic Biphasic Solvent Mixtures

In order to reveal a possible interaction between [RuHCl(CO)(*m*tppms-Na)$_3$] and cinnamaldehyde, CA was added in increasing amounts to a solution of **1** in H_2O/CD_3OD = 50/50 V/V solvent mixture and the ^{1}H-NMR spectra were recorded under inert atmosphere. The results are shown in Figure 11.

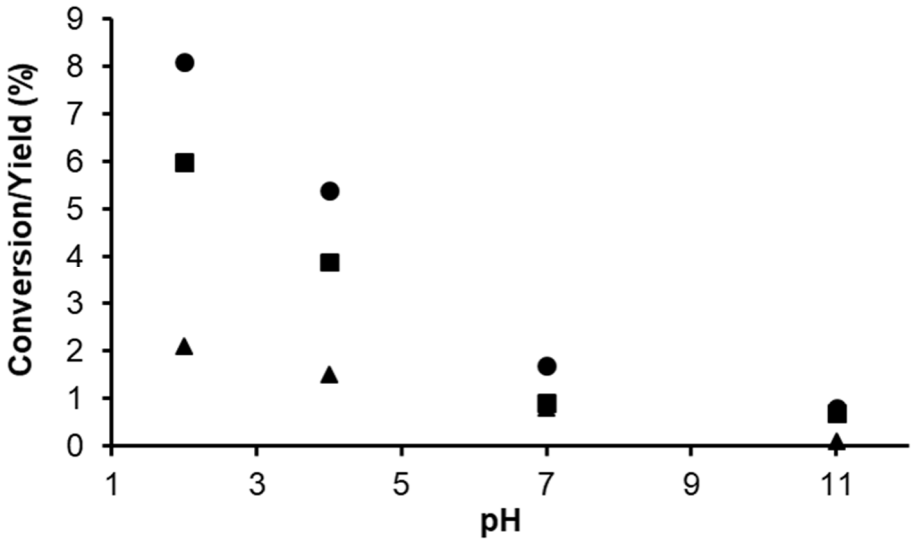

Figure 10. Conversion and product yields in hydrogenation of cinnamaldehyde catalyzed by **1**, as a function of the pH of the aqueous phase in water/toluene biphasic system (●:total conversion; ■:cinnamyl alcohol; ▲:3-phenylpropanal; o:3-phenylpropanol). Conditions: n(cinnamaldehyde) = 0.5 mmol, n(**1**) = 0.01 mmol, $P(H_2)$ = 10 bar, T = 60 °C, t = 2 h, V(aq. phosphate buffer) = 1 mL, V(toluene) = 1 mL. Analysis of the reaction mixture by gas chromatography.

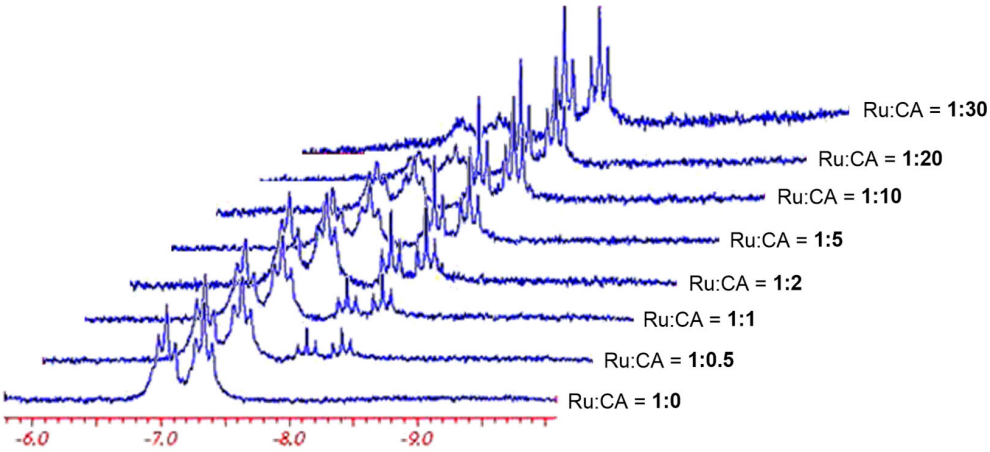

Figure 11. Effect of increasing amounts of cinnamaldehyde (CA) on the ^{1}H-NMR spectra (hydride region) of [RuHCl(CO)(*m*tppms-Na)$_3$] (**1**) solutions under argon at various [Ru]/[CA] ratios. Conditions: n(**1**) = 0.015 mmol, T = 298 K, 0.6 mL solvent (H_2O/CD_3OD = 50/50 V/V).

The most important finding is that, although the ^{1}H-NMR hydride signal was shifted by approximately 1 ppm, its multiplicity did not change. This means that the product retains one P atom in *trans*- and two P-atoms in *cis*-position relative to the hydride ligand. At the same time, ^{31}P-NMR measurements showed no free phosphine in these solutions. Conversely, an inhibiting effect of chloride was observed, which suggests that formation of the catalytically active Ru(II)-species involves chloride dissociation from **1**. Based on these findings we suggest the following catalytic cycle (Figure 12).

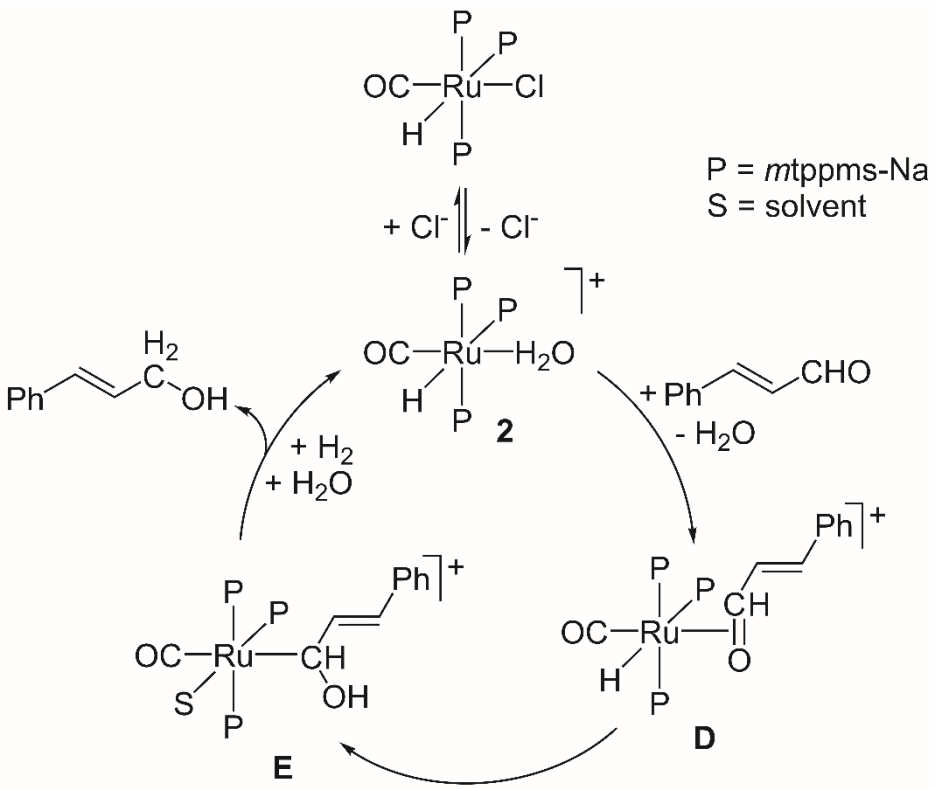

Figure 12. Suggested mechanism of cinnamaldehyde hydrogenation catalyzed by [RuHCl(CO)(*m*tppms-Na)$_3$], **1**.

According to this mechanism, chloride dissociation from **1** in the aqueous phase results in formation of **2**, which is the active catalytic species in the reaction. Replacement of H_2O in **2** by cinnamaldehyde results in the C=O π-coordinated intermediate, **D**, which yields the alkenol-Ru intermediate **E** via internal rearrangement. Reaction of **E** with H_2 in the aqueous solution gives back the aqua-complex **2** with simultaneous release of cinnamyl alcohol. It is stressed, however, that there is also a possibility of coordination of cinnamaldehyde via the C=C double bond, which would result in formation of the saturated adehyde product (3-phenylpropanal), similar to the previously discussed case of phenylacetylene hydrogenation (Figure 7). Increase of the pH of the aqueous phase resulted in the decrease of the conversion of cinnamaldehyde. This may be due to the deprotonation of **2** (Figure 6) resulting in formation of a Ru(II)-hydroxo complex which is less amenable to formation of **D** needed for providing the unsaturated alcohol product. Replacement of the anionic hydroxo ligand in an oxophylic Ru^{2+}-based complex by a neutral incoming ligand is difficult, which often leads to diminished catalytic activity. This is unambiguously shown in the recent paper of López-Sánchez et al. [34].

This suggested mechanism is in accord with the observed rate-decreasing effect of chloride and with the NMR investigations which showed no dissociation of *m*tppms-Na in the interaction of [RuHCl(CO)(*m*tppms-Na)$_3$] and cinnamaldehyde (Figure 11). At the same time, however, it brings up important questions. Perhaps the most important question regards the dissociation of a phosphine ligand in phenylacetylene hydrogenation, while in cinnamaldehyde reduction chloride dissociation is assumed to yield the substrate-containing intermediate. We cannot give a clear explanation for all these problems on the basis of the experimental results obtained so far. Determination of all important mechanistic details certainly requires more scrutiny.

3. Materials and Methods

3.1. Materials

[RuHCl(CO)(*m*tppms-Na)$_3$] [19], [RuH(H_2O)(CO)(*m*tppms-Na)$_3$][BF_4] [19] and *m*tppms-Na [14] were prepared as described in the literature. $RuCl_3 \times 3H_2O$ was a loan of Johnson Matthey (London, UK). Deuterated solvents were obtained from Cambridge Isotope Laboratories (Tewksbury, MA, USA). All other compounds were were obtained commercially and used as received from Sigma-Aldrich (St. Louis, MI, USA); VWR International (West Chester, PA, USA); and Molar Chemicals Kft. (Halásztelek, Hungary). Gases (Ar, N_2, H_2) were supplied by Linde Magyarország Zrt. (Répcelak, Hungary). Doubly distilled H_2O was used throughout, and all manipulations were done under inert atmosphere.

3.2. Methods

^{1}H-, ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker Avance 360 MHz or a Bruker DRX 400 NMR spectrometer (Bruker, Billerica, Massachusetts, USA). δ(H) and δ(P) in ppm are referenced to residual solvent peaks further referenced to external 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) sodium salt and 85 % H_3PO_4, respectively; coupling constants (*J*) in Hz.

The reaction of cinnamaldehyde (CA) with [RuHCl(CO)(*m*tppms-Na)$_3$] (**1**) at various [CA]/[Ru] ratios was followed by recording the ^{31}P{^{1}H}- and ^{1}H-NMR spectra (hydride region) of **1** under argon atmosphere. Conditions: n(**1**) = 0.015 mmol, T = 298 K, 0.6 mL solvent (H_2O/CD_3OD = 50/50 V/V). NMR parameters of the resulting aldehydo-Ru(II) complex: δ(^{1}H)= –7.93 ppm(td) $^2J_{HPd}$ = 99 Hz; $^2J_{HPt}$ = 24 Hz. δ(^{31}P{^{1}H}) = 47.7 ppm(d), $^2J_{PP}$ = 14 Hz; 20.3 ppm(t) $^2J_{PP}$ = 14 Hz.

The pH of the reaction mixtures was set by using 0.2 M phosphate buffer solutions. For NMR measurements in D_2O, the actual pH meter readings in D_2O (pH*) were corrected for H_2O by using pH = pH* + 0.44 [35].

Deprotonation of [RuH(H_2O)(CO)(*m*tppms-Na)$_3$]$^+$ was followed by ^{31}P{^{1}H}-NMR spectroscopy. The shift of ^{31}P-NMR signals as a function of the pH was evaluated by the PSEQUAD program [22] to yield the acid dissociation constant (pK_a) of **2**.

The catalytic activity of the complexes were described by their turnover frequencies TOF = (mol reacted substrate)(mol catalyst × h)$^{-1}$. Initial turnover frequencies (TOF$_i$) were calculated from conversions in the first 30–180 min of hydrogenations.

3.3. General Procedure of Hydrogenation Reactions

Hydrogenations at atmospheric pressure were carried out in Schlenk-vessels, whereas in the case of higher pressures (2–10 bar) thick-walled glass tube reactors were used.

To a hydrogen-filled Schlenk tube containing [RuHCl(CO)(*m*tppms-Na)$_3$] (12.6 mg; 0.01 mmol) or [RuH(H_2O)(CO)(*m*tppms-Na)$_3$][BF_4] (13.5 mg, 0.01 mmol) in 8 mL solvent was added phenylacetylene (1.0 mmol) or cinnamaldehyde (1.0 mmol). The reaction mixture was stirred under hydrogen at various temperatures and pH. The reactions were followed by gas chromatography (Hewlett-Packard 5890 Series II equipment: Agilent Technologies, Santa Clara, CA, USA), Carbowax 30M, split injection 1:50, *T*(injector) = 250 °C, *T*(FID detector) = 300 °C, oven temperature program: *T*(initial) = 60 °C, t(initial) = 6 min, ramp = 22 °C/min, *T*(final) = 200 °C, t(final) = 8 min); internal standard: naphthalene.

4. Conclusions

In this work, we have studied in two important reactions: the effect of the easy interconversion of [RuHCl(CO)(*m*tppms-Na)$_3$], **1**, and [RuH(H_2O)(CO)(*m*tppms-Na)$_3$]$^+$, **2**, in aqueous–organic biphasic systems, depending on the chloride concentration and the pH of the aqueous phase. Phenylacetylene underwent selective hydrogenation to styrene, while the reaction of cinnamaldehyde afforded a mixture of hydrogenated products. The rate of biphasic hydrogenation of phenylacetylene with use of a 1 M aqueous NaCl phase was three times higher relative to pure water. This led to the conclusion that under such conditions, the chloride ligand was retained in the catalytically active intermediates all

around the catalytic cycle. Conversely, in hydrogenation of cinnamaldehyde, chloride had a retarding effect on the reaction rate showing that the effective catalyst was the chloride-free $[RuH(H_2O)(CO)(m\text{tppms-Na})_3]^+$. With both catalysts, an increase of the pH of the aqueous phase decreased the rate of hydrogenation of both substrates, however, the selectivity was not affected.

The major conclusion of this study is that in aqueous or aqueous-organic biphasic catalysis, special attention has to be paid to the possible effects of water and water-soluble additives. Seemingly inert salts and buffer components may largely influence the rate and selectivity of the reactions via the modification of the catalytic species by promoting dissociation of ionic ligands or formation of hydroxo-complexes. For better or for worse, all this may result in largely altered catalytic properties of metal complexes used in synthesis.

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