Classical and non-classical phosphine-Ru(II)-hyidrides in aqueous solution: Many, various, and useful.[1]

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[1] This paper is dedicated to Professor David J. Cole-Hamilton, an outstanding scientist and a long-time friend on the occasion of his 65th birthday. David was one of the pioneers of applying organometallic catalysts in aqueous solutions and in biphasic systems, a most fruitful idea what has been later very successfully extended into homogeneous catalysis in biphasic combinations of new alternative solvents such as supercritical fluids and ionic liquids.

1. Introduction

Ruthenium(II) complexes with various phosphine ligands play important role in homogeneous catalysis. Hydrogenation of various substrates (alkenes[1,2], alkynes[3], aldehydes[4-7], ketones[6], aromatics,[8,9] CO_2,[10,11] etc.) may be the best examples but Ru(II)-complexes catalyze many other reactions (H-transfer[12], H-D exchange[13], isomerization[1,14], alkene and alkyne metathesis,[15] etc.). It is not surprising therefore that much effort has been devoted to apply Ru(II)-based catalysts also in aqueous organometallic catalysis.[16-18] In most cases solubilization of such catalysts in water was achieved by ligands having certain number of sulfonate groups generally with sodium cations. Although the main drive for using water-soluble catalysts in biphasic systems is in the recovery of the expensive catalysts and isolation of the valuable products by phase separation,[16-19] the aqueous medium may also significantly influence the properties of the transition metal complexes relative to those of their analogues in organic solvents.

The monosulfonated triphenylphosphine (*m*tppms; sodium 3-diphenylphosphinobenzenesulfonate) was introduced into coordination chemistry in 1958 and studies on the stabilities of its metal complexes played significant role in shaping the concept of the „Ahrland-Chatt triangle".[20] The use of *m*tppms in catalysis[2] started in 1973 when it was applied for stabilization of low-valent transition metal ions and for synthesis of water-soluble analogues of active hydrogenation catalysts such as $[RhCl(PPh_3)_3]$ and $[RuHCl(PPh_3)_3]$. $[RuHCl(mtppms)_3]$ (**1**) was first obtained in pure form via ligand exchange in $[RuHCl(PPh_3)_3]$ by Borowski, Cole-Hamilton and Wilkinson in 1978 who characterized it by using infrared and NMR spectroscopies and found a broad hydride resonance in aqueous solution at $\delta_H = -18.8$ ppm.[1] Broadness of this resonance was rationalized either by slow interchange of the *m*tppms ligands in the coordination sphere of ruthenium(II) or by dissociation of a phosphine

ligand leading to formation of [RuHCl(H_2O)(*m*tppms)$_2$] and subsequent interchange of free and coordinated *m*tppms. Nevertheless, based on the ^{31}P NMR spectum it was concluded that phosphine dissociation did not occur. Another interesting observation disclosed in this pioneering article was that at elevated temperatures the originally red aqueous solutions of **1** reacted with H_2 resulting in pale yellow solutions which were active in biphasic hydrogenation and isomerization of hex-1-ene. The nature of the hydride species likely to act as catalyst in these yellow solutions was not investigated.

Reaction of $RuCl_3$.aq and *m*tppms in refluxing ethanol yielded a light brown complex which was originally formulated[2(d)] as [$RuCl_2$(*m*tppms)$_2$] but later identified by Sánchez-Delgado et al. as [{$RuCl_2$(*m*tppms)$_2$}$_2$] (**2**).[21] Uv-visible measurements on hydrogenation of this compound in 0.1 M HCl aqueous solutions under 1 bar H_2 in the presence of increasing amounts of *m*tppms indicated formation of [RuHCl(*m*tppms)$_3$] (no NMR data).[2(d)] Conversely, refluxing a suspension of **2** under H_2 in wet thf (5 %v/v H_2O; thf = tetrahydrofurane) afforded [{RuHCl(*m*tppms)$_2$}$_2$] (**3**) (δ_H = − 8.7 ppm (td), $^2J_{PH}$ = 38 Hz).[21]

Basset et al. synthesized similar Ru(II)-phosphine complexes using trisulfonated triphenylphosphine (*m*tppts; trisodium 3,3',3''-phosphinetriylbenzenesulfonate)[22] ligand via ligand exchange in thf/water mixtures (6/1 v/v).[4] [RuHCl(*m*tppts)$_3$] (**4**) and [RuH_2(*m*tppts)$_4$] (**5**) were obtained from [RuHCl(PPh_3)$_3$] and [RuH_2(PPh_3)$_4$], respectively, while [{$RuCl_2$(*m*tppts)$_2$}$_2$] (**6**) was a product of the reaction of [$RuCl_2$(PPh_3)$_3$] and *m*tppts.[4(a)] [RuHI(*m*tppts)$_3$] (**7**) was isolated from the reaction of **4** and NaI. In aqueous solutions **4** reacted with H_2 in the presence of an excess of *m*tppts to yield **5.**[4(a)]

Based on the spectral data a fluxional distorted bipyramidal structure was assigned to [RuHCl(*m*tppts)$_3$] (**4**) (δ_H = − 18.5 ppm (q), $^2J_{PH}$ = 25 Hz). For [RuH_2(*m*tppts)$_4$] (**5**) a complicated signal with four intense merging line centered around δ_H = − 10.5 ppm was observed with an apparent coupling constant of approximately 35 Hz. This compound was

assumed a dihydride. It is of interest, that a minor species was also detected ($\delta_H = -17.7$ ppm (q), $^2J_{PH} = ca.$ 25 Hz). It was suggested that this species was the *aquo* complex $[RuH_2(H_2O)(m\text{tppts})_3]$ (**8**) arising from dissociation of the triply charged phosphine ligand in the highly polar solvent. $[RuHI(m\text{tppts})_3]$ (**7**) showed only one hydride signal ($\delta_H = -15.4$ ppm (q), $^2J_{PH} = ca.$ 25 Hz) and its structure was taken analogous to that of $[RuHCl(m\text{tppts})_3]$.

Hernandez and Kalck prepared $[RuHCl(m\text{tppts})_3]$ (**4**) both by ligand exchange in $[RuHCl(PPh_3)_3]$ and by the reaction of $[\{RuCl_2(m\text{tppts})_2\}_2]$ (**6**), H_2 and *m*tppts under 20-35 bar H_2.[6] The reported hydride signal for $[RuHCl(m\text{tppts})_3]$ was $\delta_H = -18.6$ ppm (q), $^2J_{PH} = ca.$ 25 Hz. $[RuH_2(m\text{tppms})_4]$ (**5**) was obtained by $NaBH_4$ reduction of $RuCl_3$.aq/*m*tppts, or $[\{RuCl_2(m\text{tppts})_2\}_2]$/*m*tppts or $[RuHCl(m\text{tppts})_3]$/*m*tppts at room temperature. In ^{1}H NMR a pseudo-quartet was observed at – 10.6 ppm due to an overlap of signals.

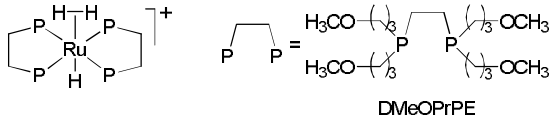
It is very important to mention that in all the above investigations no attention was paid to the pH of the NMR samples and all spectra were recorded under atmospheric hydrogen pressure.

Since the seminal discovery of the first dihydrogen complexes[23] by Kubas and co-workers in 1984, much attention is focussed on such complexes both from structural, stability and reactivity viewpoints.[23(b),24-29] One distinctive feature of complexes containing coordinated dihydrogen (often termed as non-classical hydrides) is in that acid base dissociation of the η^2-H_2 ligand can lead to formation of „classical" M-H hydride species without changing the oxidation state of the metal ion.[30-35]

Although the number of well-characterized dihydrogen complexes is high, only a few of them were observed and studied in aqueous media.

In acidic aqueous solutions $[Ru(H_2O)_6]^{2+}$ was shown by Merbach and coworkers to react with H_2 under 40-100 bar hydrogen pressure to yield $[Ru(\eta^2\text{-}H_2)(H_2O)_5]^{2+}$ ($\delta_H = -7.68$ (s) ppm).[36] On prolonged reaction in D_2O $[Ru(\eta^2\text{-}HD)(H_2O)_5]^{2+}$ and dissolved HD was also

detected by NMR spectroscopy. The longitudinal relaxation time, T_1 of the ^{1}H NMR signal of η^2-H_2 at 400 MHz was found 55.7 ms (296.4 K) and 67.1 ms (321.7 K) characteristic for a bound dihydrogen.

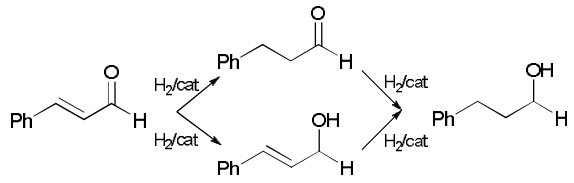


Scheme 1. Structure of *trans*-[RuH(η^2-H_2)(DMeOPrPE)$_2$]$^+$

The water-soluble *trans*-[RuH(η^2-H_2)(DMeOPrPE)$_2$]$^+$ (Scheme 1) was prepared by Tyler and coworkers by hydrogenation (25 bar H_2) of *trans*-[$RuCl_2$(DMeOPrPE)$_2$] in aqueous solution buffered to pH 7 (δ_{HH} = − 6.6 (s, br) ppm; δ_H = − 11.4 ppm (quint), $^2J_{PH}$ = 20 Hz, consistent with a *cis* P-H coupling).[37] The ^{1}H T_1(253.1 K) value of the H_2 resonance was determined to be 21.1 ms at 500 MHz. The complex also underwent H/D exchange.

Süss-Fink and coworkers have found that two of the three NMR signals of $[H_6Ru_4(C_6H_6)_4]^{2+}$ in the hydride region at 153.1 K showed T_1 values in the range 200-300 ms, however, the resonance at δ_H = -17.33 pp exhibited a T_1 value of only 34 ms.[8] The non-classical hydride nature of this water-soluble hydrido-ruthenium cluster was also supported by single crystal X-ray structure determination.

Formation and distribution of the various hydrido-Ru(II)-*m*tppms species in aqueous solutions is strongly influenced by the pH. With combined pH-potentiometric and NMR (^{1}H, ^{31}P) measurements we established that the major species below pH 7 was [RuHCl(*m*tppms)$_3$] (**1**) while the dominant species above pH 8 was thought to be [RuH_2(*m*tppms)$_4$].[38] Stoichiometric proton liberation accompanying hydrogenation of **2** also showed that **3** and [RuH_2(*m*tppms)$_4$] were formed via heterolytic activation of H_2. This may imply the intermediate role of molecular hydrogen complexes as was demonstrated in case of [$RuCl_2$(dppe)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$).[30(a)]



Scheme 2. Hydrogenation of cinnamaldehyde

Hydrogenation of *trans*-cinnamaldehyde ((2*E*)-3-phenylprop-2-enal) (Scheme 2) became a prototype reaction to test the selectivity of catalysts in biphasic hydrogenations of α,β-unsaturated aldehydes to allylic alcohols . When **2** + *m*tppms was used as catalyst at atmospheric H_2 pressure as a function of the pH it was found that selectivity parallelled the distribution of Ru(II)-hydrides: below pH 5 mostly hydrogenation of the –C=C– double bond (formation of 3-phenylpropanal) occured while above pH 6 a fast and selective reduction of the aldehyde function (formation a cinnamyl alcohol) took place.[38,39] These results were in agreement with those of Grosselin et al.[7] but were at variance with the findings that cinnamaldehyde could be selectively hydrogenated to cinnamyl alcohol in slightly acidic solutions at 20 bar H_2 pressure,[6] so we decided to study the effect of hydrogen pressure on the selectivity of the reaction. Indeed, at pH 3.04 and 1 bar H_2 the product was a 61:39 mixture of cinnamyl alcohol and 3-phenylpropanal, however, the selectivity increased to 93:7 by increasing the hydrogen pressure to 8 bar.[39]

It is of interest that **2** is a very active catalyst of the H/D exchange between H_2O and D_2O and the reaction rate depends to a great extent on the pH of the solutions.[13] Similarly, there are significant pH effects on the aqueous-biphasic redox isomerization of allylic alcohols catalyzed by **2**.[14]

It could be reasoned that the pronounced effects of the solution pH and H_2 pressure (concentration of dissolved H_2) on the rate and selectivity of the above reactions indicated changes in the catalytic species, conceivably Ru(II)-hydrides. Theoretical calculations also

showed unlikely the presence of [RuH_2(*m*tppms)$_4$] in aqueous solutions and suggested the formation of [$RuH_2(H_2O)$(*m*tppms)$_3$] .[40] Therefore we decided to systematically determine the composition and structure of the various hydrido-Ru(II)-*m*tppms species formed under H_2 in acidic or basic aqueous solutions, at atmospheric as well as at elevated pressures. These measurements were complemented by investigations on the Ru(II) hydrides formed in aqueous sodium formate solutions. Below we report the results of theses studies.

2. Experimental

Monosulfonated triphenylphosphine (*m*tppms),[41] [{$RuCl_2$(*m*tppts)$_2$}$_2$] [41(a)] and [$Ru(H_2O)_6$](tos)$_2$[42] (tos=tosylate, *4*-toluenesulfonate) were obtained by literature methods. All reagents and solvents were commercial products of highest purity supplied by Sigma-Adrich, VWR International, and Merck. D_2O and $NaH^{13}CO_2$ were purchased from Sigma-Adrich. Gases (Ar, N_2, H_2) were supplied by Messer and Linde. pH of the solutions was adjusted by using 0.2 M phosphate buffer. Doubly distilled water was used throughout.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AV360, Bruker AV400 and Bruker DRX400 NMR spectrometers and referenced to solvent peaks as well as to DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt) and phosphoric acid, respectively. *J* values are given in Hz. To prevent H/D exchange, D_2O or other deuterated solvents for locking purposes were in many cases used in closed capillaries. Samples above atmospheric but below 10 bar total pressure were prepared in Wilmad® quick pressure valve tubes, while those at higher H_2 pressures were studied in 10 mm medium-pressure sapphire NMR tubes as described earlier. The longitudinal relaxation time (T_1) was determined by *t1ir* (inversion-recovery experiment) and the transversal relaxation time (T_2) was established using the *cpmg* (Carr-Purcell-Meiboom-Gill) pulse sequence. The *cosyqf* and the *zgigcw* (inverz gated

decoupling) pulse sequence was used to determine the structure of *trans*-$[RuH_2(HCOO)(m\text{tppms})_3]$.

3. Results

3.1 Formation of water-soluble Ru(II)-hydrides in acidic aqueous solutions

Characteristic NMR parameters of the water-soluble Ru(II)-hydrido-phosphine complexes involved in this study are given in Table 1 while the structures of these compounds based on NMR measurements are shown in Scheme 3. Coupling constants are given only in Table 1. In aqueous solutions all complexes showed broad overlapping δ_H resonances in the aromatic reagion. Therefore in the discussion we refer mainly to the proton resonances in the hydride region. Table 1 and Scheme 3 are followed by the description of the formation and properties of the individual complexes.

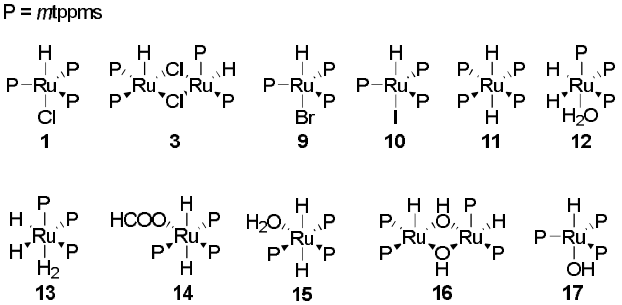
Table 1. Characteristic NMR parameters for Ru(II)-*m*tppms complexes in aqueous solutions

Compound	δ_H (ppm) hydride region	δ_P (ppm)	J_{PH}	J_{PP}
$[RuHCl(m\text{tppms})_3]$ (**1**)	-17,94(q)	60,2(br)	24,4	
$[\{RuHCl(m\text{tppms})_2\}_2]$ (**3**)	-8,71(t) -8,73(t)	52,3(d) 52,7(d)	38 38	38 38
$[RuHBr(m\text{tppms})_3]$[(a)] (**9**)	-16,7(q)	59,9(br)	25,4	
$[RuHI(m\text{tppms})_3]$[(b)] (**10**)	-15,0(q)	59,5(br)	24,6	
trans-$[RuH_2(m\text{tppms})_4]$[(c)] (**11**)	-7,7(quint)	57,2(s)	10	
cis-fac-$[RuH_2(H_2O)(m\text{tppms})_3]$ (**12**)	-10,4(td)	42,0(br) 58,0(br)	39 34	
$[RuH_2(\eta^2\text{-}H_2)(m\text{tppms})_3]$[(d)]	-7,2(br)	43,0(br)		

(**13**)		51,0(br)		
trans-[$RuH_2(HCOO)$(*m*tppms)$_3$][(e)] (**14**)	-19,2(td)	44,0(br) 79,2(t)	23 23	25
trans-[$RuH_2(H_2O)$(*m*tppms)$_3$] (**15**)	-17,7(td)	44,0(br) 77,1(t)	25 27	27
[{RuH(OH)(*m*tppms)$_2$}$_2$] (**16**)	-8,66(t) -8,68(t)	51,1(d) 51,8(d)	38 38	38 38
[RuH(OH)(*m*tppms)$_3$] (**17**)	-19,7(q)	58,5(br)	24	

1, **3**, **9**, **10**: δ_H(400Mhz; 0.1M phosphoric acid/10%CD_3OD; 333K; H_2O), δ_P(146MHz; 0.1M phosphoric acid/10%CD_3OD; 333K; H_3PO_4); **11**, **12**, **13**: δ_H(360MHz; 0.2M phosphate buffer, pH(for **11**)=3.01; pH(for **12**, **13**)=10,0/10%CD_3OD; 333K; H_2O), δ_P(146MHz; 0.2M phosphate buffer, pH(for **11**)=3.01; pH(for **12**, **13**)=10,0/10%CD_3OD; 333K; phosphate); **14**, **15**: δ_H(360MHz; H_2O/D_2O capillary; 300K), δ_P(146MHz; H_2O/D_2O capillary; 300K; H_3PO_4); **16**, **17**: δ_H(360MHz; EtOH/D_2O capillary; 300K; EtOH), δ_P(146MHz; EtOH/D_2O capillary; 300K; H_3PO_4)

(a) [Br^-] = 2M, (b) [I^-] = 2M, (c) p(H_2)>5bar, T_{1min} = 152ms (343K), (d) p(H_2)>5bar, T_{1min} = 18ms (367K), (e) δ_C(90MHz; H_2O/D_2O capillary; 300K) 174 (1 C, br t, coord. $HCOO^-$) J_{CP} 5.



Scheme 3. Structures of water-soluble Ru(II)-hydridophosphine complexes

(P = monosulfonated triphenylphosphine, *m*tppms)

3.1.1 [{RuHCl(mtppms)$_3$}$_2$]; (**3**)

Hydrogenation of [{RuCl$_2$(*m*tppms)$_2$}$_2$] (**2**) (0.051 M Ru) in 0.1 M phosphoric acid (containing 10% v/v CD_3OD) under 1 bar H_2 at 333K (in the absence of added *m*tppms and halide) led to the formation of the known[21,38] monohydride dimer [{RuHCl(*m*tppms)$_2$}$_2$]; the spectral parameters (Table 1) agree well with those determined by Sánchez-Delgado et al.[21] In the absence of further *m*tppms the compound did not show signs of bridge splitting on heating or under H_2 pressure up to 100 bar.

3.1.2 [RuHX(mtppms)$_3$]; X = Cl$^-$ (**1**), *Br$^-$* (**9**), *I$^-$* (**10**)

Under the conditions above, hydrogenation of **2** in the presence of 0.102 M NaCl resulted in a deep red solution with a well-resolved quartet ^{1}H NMR signal in the hydride region, δ_H = − 17.94 ppm (q). Under the same conditions with increasing amounts of chloride this quartet is gradually shifted to δ_H = − 17.63 ppm (2 M NaCl). In the presence of 2 M NaBr the colour of the final solution is deep bluish red while in 2 M NaI solutions it becomes purple. ^{1}H NMR spectra in these cases show resonances at δ_H = − 16.7 ppm (q) and δ_H = − 15.0 ppm (q), respectively. Considering also the ^{31}P NMR data (Table 1) it can be concluded that the solutions contained the monomeric Ru(II)-monohydrides [RuHX(*m*tppms)$_3$] (X = Cl$^-$, Br$^-$, I$^-$), respectively. **1** has already been characterised,[1,38] however, the bromo- and iodo-derivatives are new compounds. Interestingly, although all the hydride signals are well resolved, those for **1** and **9** are somewhat broad in contrast to the sharp and intensive resonance of [RuHI(*m*tppms)$_3$] (**10**). Conversely, ^{31}P{H} NMR spectra show only a broad signal for each compound at δ/ppm = 60.2 (Cl$^-$), 59.9 (Br$^-$) and 59.5 (I$^-$), respectively.

3.1.3 trans-[RuH_2(mtppms)$_4$]; (**11**)

When **2** was hydrogenated under acidic conditions (pH 3.01) in the presence of excess *m*tppms applying hydrogen pressure (>5 bar) a yellow solution was obtained. Solutions of [RuHCl(*m*tppms)$_3$] are deep red therefore this colour indicated formation of a new compound. Indeed, the ^{1}H NMR spectrum contained a well resolved quintet at $\delta_H = -7.7$ ppm (quint) while ^{31}P{H} NMR showed a singlet at $\delta_P = -57.2$ ppm; both refer to four equivalent phosphine ligands in the coordination sphere. The NMR spectra did not change up to 100 bar H_2 pressure. Integrated signal intensities in the hydride and aromatic region as well as those of the bound and free phosphorus signals showed a 2:1 hydride:ruthenium ratio. Such spectral data are in accord with formulating the species in solution as octahedral *trans*-[RuH_2(*m*tppms)$_4$]; such a species have not been observed earlier.

Distinguishing classical and non-classical transition metal hydrides is often based on the criterion of Crabtree et al.[33,43-45] According to this, complexes can be regarded as non-classical hydrides (complexes of molecular hydrogen) in case the minimum value of the hydride longitudinal relaxation time T_1 is less than 80 ms, while the characteristic value of T_1(min) for classical hydrides is higher than 150 ms (at 250 MHz). T_1(min) refers to the minimum of T_1 as a function of the temperature , however its experimental determination is not always possible, especially for aqueous solutions where the available „temperature window" is rather limited. Following Crabtree's suggestion, we determined T_1(min) from the plot of of lnT_1 and lnT_2 as the functions of 1/T in the 303-338 K range; intersection of the two straight lines (T_1=T_2) yielded T_1(min) = 152 ms. This allowed unambiguous formulation of the complex formed in acidic solutions under H_2 pressure as the classical dihydride: *trans*-[RuH_2(*m*tppms)$_4$]. It is important to mention that **11** ($\delta_H = -7.7$ ppm) is *not* the *m*tppms-containing analogue of [RuH_2(*m*tppts)$_4$] reported by Basset et al. ($\delta_H = -10.4$ ppm)[4(a)] and by Hernandez and Kalck ($\delta_H = -10.6$ ppm)[6] (see below).

3.2 Formation of water-soluble Ru(II)-hydrides in neutral or basic aqueous solutions

3.2.1 cis-fac-[$RuH_2(H_2O)(mtppms)_3$]; (**12**)

[RuH_2(*m*tppts)$_4$] was prepared earlier by ligand exchange[4(a)] in [$RuH_2(PPh_3)_4$] and atmospheric hydrogenation[4(a)] of [RuHCl(*m*tppts)$_3$] as well as by $NaBH_4$ reduction[6] of $RuCl_3$.aq/*m*tppts, [{$RuCl_2$(*m*tppts)$_2$}$_2$]/*m*tppts, or [RuHCl(*m*tppts)$_3$]. It is of interest, that in the latter three cases the conditions are basic, neutral in the ligand exchange process, and possibly slightly acidic in hydrogenation of [RuHCl(*m*tppts)$_3$] due to heterolytic splitting of H_2. Elemental analysis of the yellow solid agreed with that of a tetrakisphosphine complex. However, solution characterization was never unambiguous since the hydride resonance around $\delta_H = -10.5$ ppm was broad and not well resolved.

In our studies on the pH dependence of the formation of Ru(II)-hydrides we observed similar overlapping ^{1}H resonances (at -10.3 ppm) and based on analogy of *m*tppms- and *m*tppts-containing complexes assigned it to the species *cis*-[RuH_2(*m*tppms)$_4$].[j] In those measurements [{$RuCl_2$(*m*tppms)$_2$}$_2$] was hydrogenated in the presence of excess *m*tppms (Ru:P=1:6). When this reaction was now reinvestigated, it was found that at pH 10.0 the ^{31}P NMR spectrum of a solution with a Ru:P=1:3 ratio did not show the presence of free *m*tppms. Conversely, in solutions with Ru:P=1:4 or 1:5, the ratio of bound and free *m*tppms was 3:1 and 3:2, respectively. Based on these measurements we concluded that even in an excess of phosphine ligand the Ru-containing species was *cis-fac*-[$RuH_2(H_2O)$(*m*tppms)$_3$]. The hydride resonance can now be interpreted as a doublet of triplets with close coupling constants giving rise to a „pseudo quartet".

3.2.2 [$RuH_2(\eta^2$-$H_2)(mtppms)_3$]; (**13**)

Under slight H_2 pressure (>5 bar), basic (pH 10.0) aqueous solutions of $[\{RuCl_2(m\text{tppms})_2\}_2]$ + *m*tppms (Ru:P = 1:4) displayed an ^1H NMR spectrum containing only a rather broad singlet at $\delta_H = -7.2$ ppm. The spectrum was unchanged up to 100 bar H_2 and no fine structure could be resolved. From integrated intensities of the spectra it could be established, that the species in solution contained 4H and 3P per Ru. Using the NMR techniques described for *trans*-$[RuH_2(m\text{tppms})_4]$ (see *3.1.3*), the temperature dependence of T_1 and T_2 allowed the determination of $T_1(\text{min}) = 18$ ms. This value is characteristic for a dihydrogen complex and we suggest the species in basic solutions under H_2 pressure to be $[RuH_2(\eta^2\text{-}H_2)(m\text{tppms})_3]$. The broad singlet in ^1H NMR may indicate a fast site exchange of the four hydrogens. The same solutions under atmospheric H_2 contain *cis-fac*-$[RuH_2(H_2O)(m\text{tppms})_3]$ (see *3.2.1*) so formation of $[RuH_2(\eta^2\text{-}H_2)(m\text{tppms})_3]$ involves the replacement of an H_2O ligand at elevated H_2 pressures. Studies on similar H_2/H_2O exchanges showed such processes feasible, however, those measurements were made in thf or hexane solutions of W(0)-aqua complexes[46] or in CH_2Cl_2 solutions of Ru(II)-hydridotris(1-pyrazolylborate) complexes.[47] Although a water-soluble $[RuH(\eta^2\text{-}H_2)(PP)_2]$ (PP=chelating bisphosphine) complex is known[37], to our knowledge, $[RuH_2(\eta^2\text{-}H_2)(m\text{tppms})_3]$ is the first water-soluble molecular hydrogen complex of Ru(II) with monodentate phosphine ligands.

3.3 Formation of the water-soluble Ru(II)-hydrides trans-$[RuH_2(HCOO)(m\text{tppms})_3]^-$ (**14**) *and trans-$[RuH_2(H_2O)(m\text{tppms})_3]$* (**15**) *in aqueous formate solutions*

In addition to using H_2 of various pressures, biphasic hydrogenations can be achieved also by hydrogen transfer from aqueous sodium formate. In such a transfer hydrogenation reduction of cinnamaldehyde with **2** + *m*tppms catalyst we observed very selective formation of cinnamyl alcohol ((2*E*)-3-phenylprop-2-en-1-ol) with 3-phenylpropanal or the fully saturated

product, 3-phenylpropanol below the GC detection limit.[f] It was therefore of interest to establish the nature of the catalytic species in aqueous formate solutions.

Reactions of [{$RuCl_2$(*m*tppms)$_2$}$_2$] (0.042 M Ru), *m*tppms (0.17 M) with HCOONa (0.84 M) in a H_2O (D_2O capillary) under an argon atmosphere at 300 K temperature led to the appearance of two ^{1}H NMR signals in the hydride region. In the first few minutes of the reaction only the one at $\delta_H = -19.2$ppm (td) could be seen while the other at $\delta_H = -17.7$ ppm (td) grew in gradually in about 1 hour. Our earlier studies have shown that one has to consider the presence of formato complexes under such conditions. Therefore one of the compounds ($\delta_H = -19.2$ ppm) was assumed to be *trans*-[RuH_2(HCOO)(*m*tppms)$_3$]$^-$ while the other ($\delta_H = -17.7$ ppm) *trans*-[$RuH_2(H_2O)$(*m*tppms)$_3$] . ^{31}P-^{31}P COSY spectra revealed that *trans*-[RuH_2(HCOO)(*m*tppms)$_3$]$^-$ had $\delta_{P(A)} = 44.0$ ppm (s) and $\delta_{P(B)} = 79.2$ ppm (t), while *trans*-[$RuH_2(H_2O)$(*m*tppms)$_3$] displayed $\delta_{P(A)} = 44.0$ ppm (s) and $\delta_{P(B)} = 77.1$ ppm (t). Selective ^{31}P decoupling at 44 ppm and 79 ppm led to the replacement of the two triplets of doublets in ^{1}H NMR by two doublets and by two triplets, respectively. This unambigously showed the *trans-mer* coordination in the 'RhH_2(*m*tppms)$_3$' fragment of an octahedral complex. The resonance of coordinated formate in *trans*-[RuH_2(H^{13}COO)(*m*tppms)$_3$]$^-$ ($\delta_C = 174.0$ ppm, br; $^1J_{CH} = 195$ Hz) could be clearly distinguished from that of free H^{13}COO$^-$ ($\delta_C = 170.7$ ppm, $^1J_{CH} = 193$ Hz). In the ^{31}P NMR spectrum the resonance at 79.2 ppm brodened upon using H^{13}COONa and although the coupling did not lead to well resolved fine structure $^3J_{CP}$ could be estimated approximately 5 Hz what is in the range of $^3J_{CP}$ values of similar complexes. No similar line-broadening was observed on the ^{31}P NMR signal of the aquo complex (**15**). Altogether these measurements support our assumption that the two species prevailing in aqueous formate solutions are, indeed, **14** and **15**.

One question remains concerning the time course of the appearance of these complexes. According to the NMR data, in the early phase of the reaction that is at relatively

high formate concentration chloride is replaced entirely by formate. However, mixtures of [{$RuCl_2$(*m*tppms)$_2$}$_2$] and *m*tppms catalyze the decomposition of aqueous formate to yield H_2 and bicarbonate – the reaction is known to lead to equilibrium.[11] One reason for the coexistence of **14** and **15** in aged samples may be this decomposition of free formate. The reaction results in a buildup of some H_2 pressure in the NMR tube under which circumstances **15** is stabilized. Since aqueous HCOONa solutions are basic (with pH around 8) the conditions are very similar to those favouring the formation of *cis-fac*-[$RuH_2(H_2O)$(*m*tppms)$_3$] in formate-free solutions.

3.4 Formation of water-soluble Ru(II)-hydrides in alcoholic solutions

Heating of [$Ru(H_2O)_6$](tos)$_2$ in MeOH or EtOH under an argon atmosphere (1 bar) in the presence of *m*tppms (Ru:P=1:3) yielded deep orange solutions. These displayed ^{1}H and ^{31}P{^{1}H} NMR spectra closely resembling those of [RuHCl(*m*tppms)$_3$] (**1**) and [{RuHCl(*m*tppms)$_2$}$_2$] (**3**). However, these solutions do not contain chloride therefore we assume formation of a hydroxide-bridged dimer [{RuH(OH)(*m*tppms)$_2$}$_2$] (**16**; δ_H = − 8.66 ppm (t); − 8.68 ppm (t)) as well as that of the hydroxo monomer [RuH(OH)(*m*tppms)$_3$] (**17**; δ_H = − 19.7 ppm (q). The exact composition and structure of such chloride-free Ru(II)-hydride complexes together with their catalytic properties are under intense scrutiny in our laboratory.

4. Discussion

Ruthenium(II) hydrides are important catalysts or catalyst precursors in homogeneous hydrogenation attracting much attention.[12,48-51] [$RuH_4(PPh_3)_3$] was synthetized long before the discovery of η^2-H_2 complexes, and can be obtained by $NaBH_4$ reduction of [$RuCl_2(PPh_3)_3$] in benzene/methanol,[52] or by hydrogenation of [$RuHCl(PPh_3)_3$] in a benzene/50% NaOH aqueous biphasic system.[53] Note, that both methods apply strongly basic conditions. The

complex is characterized by a broad singlet hydride resonance (literature data for δ_H between − 7.0, and − 7.1 ppm). [12,45,52(c),54] It was one of the first compounds shown to contain a molecular hydrogen ligand and consequently reformulated as $[RuH_2(\eta^2\text{-}H_2)(PPh_3)_3]$.[45] As described above, the water-soluble analog, **13**, is also formed easily but is stable only in basic aqueous solutions under H_2 pressure. Despite the slight difference in the phosphine ligand and in the solvent, the hydride resonance (δ_H = − 7.2 br, s) and the T_1(min) (18 ms) of **13** are in good agreement with those of $[RuH_2(\eta^2\text{-}H_2)(PPh_3)_3]$ (T_1(min) = 30 ms).[45] Although $[RuH_2(\eta^2\text{-}H_2)(PPh_3)_3]$ was reported to undergo dimerization in benzene/ethanol,[54] aqueous solutions of **13** remained stable for longer times.

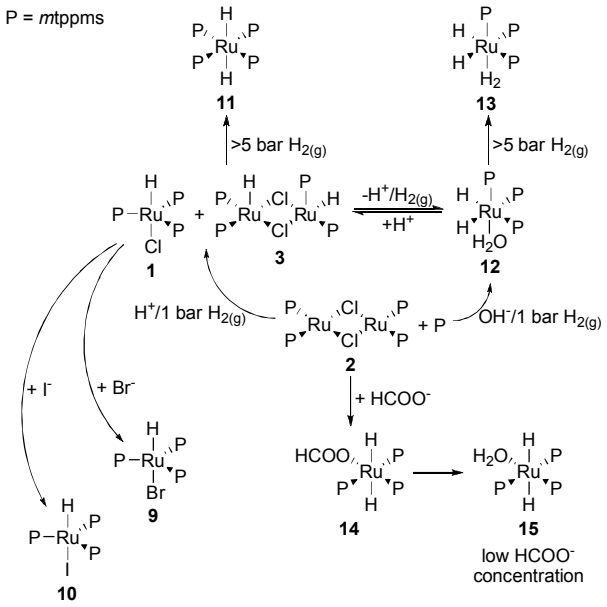
$[RuH_2(PPh_3)_4]$ was prepared in reduction of $[Ru(acac)_3]$ with Et_3Al[50] or by that of $RuCl_3$.aq with $NaBH_4$ in hot ethanol[55] in the presence of an excess of PPh_3. With no phosphine excess,[55] as well as in the reaction of $[RuCl_2(PPh_3)_3]$ with hot 2-propanol/KOH[12] or in that of $1/x[RuCl_2(COD)_x]/3PPh_3$ in hot 2-butanol/NaOH[49] $[RuH_2(PPh_3)_3]$ (δ= − 10.15 ppm[12,50,56]) was obtained. $[RuH_2(PPh_3)_4]$ readily looses one phosphine ligand in solution. Similarly, we have found that at 1 bar H_2 pressure in basic aqueous solutions **12** (δ= − 10.4 ppm) does not exchange its H_2O ligand for *m*tppms in slight excess of phosphine. Conversely, the tetrakisphosphine complex, **11** (δ= − 7.7 ppm), can be obtained in acidic aqueous solutions under H_2 pressure from $[\{RuCl_2(m\text{tppms})_2\}_2]$ and an excess of *m*tppms. The analogous *trans*-$[RuH_2(dppe)_2]$ (dppe=$Ph_2PCH_2CH_2PPh_2$) is characterized by δ_H = − 8.62 ppm, quintet, $^2J_{PH}$ 18 Hz.[30(c)]

In dilute solutions of $[RuH_2(m\text{tppts})_4]$, Basset et al observed a small intensity quartet in ^{1}H NMR at − 17.7 ppm and attributed it to a $[RuH_2(H_2O)(m\text{tppts})_3]$ species.[4(a)] In agreement with this suggestion, within this study we characterized **15** (δ_H − 17.7 ppm, td) which does not form in appreciable concentrations upon hydrogenation of

[{$RuCl_2$(*m*tppms)$_2$}$_2$] /*m*tppms in water but can be detected in dilute Na-formate solutions (see *3.3*).

DFT calculations led to the conclusion that the Ru(II)-dihydrides, such as [$RuH_2(PPh_3)_3$] are more active catalysts for aldehyde and ketone hydrogenations than the corresponding monohydrides, e.g. [$RuHCl(PPh_3)_3$].[12] Our findings give support to these calculations in that the changes in experimental conditions to favour the formation of the dihydrides **11**, **12** or **13** (increasing basicity or hydrogen pressure) dramatically increase the selectivity of the hydrogenation of unsaturated aldehydes towards formation of allylic alcohols.[j,m]

trans-Ru(II)-dihydrides are rare and in most cases contain bidentate phosphine ligands; to our knowledge *trans*-[RuH_2(*m*tppms)$_4$] (**11**) is the first such compound characterized with monodentate phosphine ligands in aqeuous solution. Formation of this complex already at slight H_2 pressure in contrast to the presence of [$RuHCl$(*m*tppms)$_3$] under atmospheric H_2 may be behind the remarkable change[39] in C=C vs. C=O selectivity in cinnamaldehyde hydrogenation upon increasing H_2 pressure from 1 to 8 bar.



Scheme 4. Formation and interconversion of Ru(II)-hydridophosphine species under various conditions

Formation and interconversion of the Ru(II)-hydrido-phosphine complexes in aqueous solution show considerable diversity – the relevant processes are summarized on Scheme 4. Our studies revealed the existence of rare species such as a trans-dihydrides (**11** and **15**) and a dihydrido-dihydrogen-Ru(II) complex (**13**) perfectly stable in aqueous solution. **11, 15** and **13** are all unique in the sense that the hitherto known similar complexes contained bidentate phosphine ligands. Formation of **12** from **2** is in accord with our earlier pH-potentiometric measurements[j] when in basic solutions and at 1 bar H_2 pressure heterolytic splitting of two H_2 molecules in two independent steps were observed to lead to a Ru(II)-dihydride then identified as $[RuH_2(mtppms)_4]$. The detailed structural studies described here have shown that under atmospheric hydrogen the prevalent dihydride is, indeed, **12**; its formation from **2** also requires release of 2 mol H^+ for each mol Ru(II). **12** readily converts to **13** upon increasing the H_2 pressure. Both H_2O (in **12**) and H_2 (in **13**) can be easily replaced by an aldehyde substrate. Alternatively, the aldehyde C=O can be hydrogenated by direct hydrogen transfer from **12** or **13** what can lead to selective formation of allylic alcohols.

Transfer hydrogenations in aqueous solutions or aqueous-organic biphasic systems often use Na-formate+H_2O as H-donor and such reactions are usually carried out in concentrated formate solutions.[5] According to our present results, in those solutions the prevalent Ru(II) species is **14**, while in dilute formate solutions **15** could be also observed. For the reasons disccussed above both are expected to be selective catalysts for the C=O hydrogenation of unsaturated aldehydes and, indeed, that is the case.

Although NMR measurements show the **1** to **9** and **1** to**10** reactions (Scheme 4) complete in 2 M NaBr and NaI solutions, respectively, we wanted to prepare chloride free

Ru(II)-hydrides in alcoholic solutions from $[Ru(H_2O)_6]^{2+}$ and *m*tppms. During such experiments we observed formation of hydrido-hydroxo complexes which showed interesting catalytic properties e.g. in aqueous-organic biphasic racemization of *(S)*-1-phenylethanol.[57] Presently these compounds are only partially characterized in solutions, and their ^{1}H- and ^{31}P-NMR parameters are different from those determined for Ru-hydrido-hydroxo complexes by Wilkinson, Cole-Hamilton and co-workers.[58] Due to their useful catalytic properties these compounds deserve further studies.

Conclusions

In this article we showed that in aqueous solution a plethora of classical and non-classical Ru(II)-hidrides can be formed from $[\{RuCl_2(m\text{tppts})_2\}_2]$ and *m*tppts depending on the pH and hydrogen pressure. Some of them have organosoluble analogs, such as e.g. $[RuHCl(PPh_3)_3]$ and $[RuH_2(\eta^2\text{-}H_2)(PPh_3)_3]$, others (e.g. **12** and **15**) were observed only in aqueous solutions. The easy interconversion of theses species with changing pH and H_2 pressure allows rationalization of changes in the rate and selectivity of certain reactions such as the hydrogenation of unsaturated aldehydes in aqueous systems.

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