PhD Theses

Catalytically active Ru(II)-hydrides in aqueous solutions

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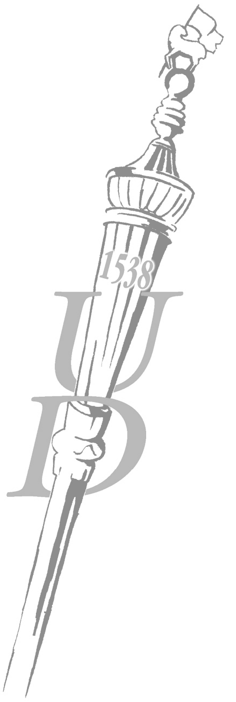

University of Debrecen
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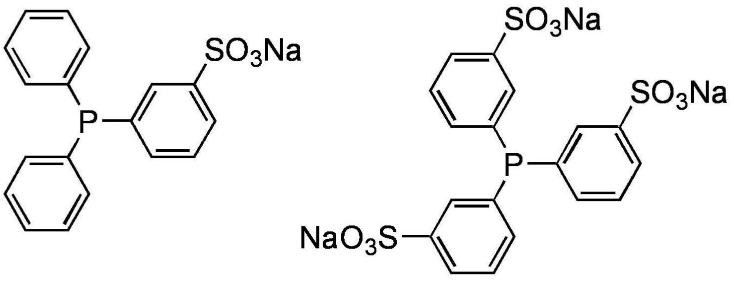
I. Introduction and objectives

The activity and selectivity of soluble homogeneous catalysts are the main advantages of homogeneously catalyzed processes. Separation of the catalysts from the products and substrates is a difficult step in most cases. It is the biggest problem of industrial applications of homogeneous catalysis.

More successful were those experiments where two non-miscible solvents were applied. One of the solvents dissolved the catalyst while the other one contained the substrate and products. Most of the important substrates are soluble in the organic phase and in this case the other phase can be an aqueous solution of the catalyst. For this purpose the catalyst needs to be water soluble. The easiest way to reach water-solubility is to increase the hydrofilic properties of ligands. Usually this is achieved by sulfonation. The compounds produced this way include, for example, sulfonated tertiary phosphines having good water-solubility. Accordingly, their transition metal complexes are water soluble, as well. Trisulfonated triphenylphosphine is applied in industry on a large scale. Conversely, the monosulfonated triphenylphosphine is mostly used in model reactions in the laboratory.



*m*tppms *m*tppts

Figure 1.: *Water soluble sulfonated phosphines.*

At the Department of Physical Chemistry, University of Debrecen several Ru(II) and Rh(I) complexes were synthesized by the use of *m*tppms. Primarily, this kind of complexes were used in hydrogenation of water soluble substrates and model substrates for example *trans*-cinnamaldehyde in aqueous-organic biphasic systems.

In several catalytic processes the active intermediate compounds are transition metal hydrides. These complexes can be transformed to each other by changing the circumstances. By this procedure in most cases the reaction selectivity is also changing, what has important implications for idustrial processes.

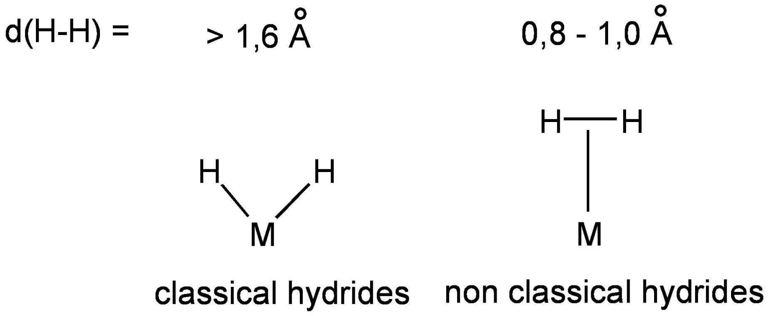


Figure 2.: *Classical and non-classical transitional metal hydrides.*

Depending on the conditions (solvent, H_2 pressure, pH, chloride concentration), the reaction of water-soluble Ru(II)-phosphine complexes with various hydrogen sources (H_2, silanes, HCOONa/H_2O) can yield various hydrides. Accordingly, these hydrides decisively influence the rate and selectivity of the catalytic reactions. The aim of my PhD work was the identification of these Ru(II)-hydrides, determination of their structure in solution and study of their catalytic properties.

II. Experimental techniques

For the structure determination of water-soluble Ru(II) complexes mostly NMR-techniques were used.

The NMR experiments were run on (^{1}H 360 MHz, ^{13}C 90 MHz, and ^{31}P 146 MHz) BRUKER AV 360, AC 200, DRX 400 and DRX 600 devices. Due to the fact that these complexes form in solution –in many cases under higher hydrogen pressure– NMR measurements under H_2 are needed. The medium-pressure (20-100 bar) experiments were carried out in sapphire NMR tubes at the Federal Polytechnic (EPFL) in Lausanne, Switzerland. The low-pressure (2-8 bar) measurements were done in commercial „Wilmad® quick pressure valve”-NMR tubes.

The products of hydrogenation and hydrosilylation reactions were analyzed by gas chromatography on a HP5890 GC (Chrompack carbowax column, split injection 1:100, FID detector).

III. New scientific results

*1. cis-[RuH$_2$(H$_2$O)(*m*tppms)$_3$] was identified in basic aqueous solution under atmospheric hydrogen pressure.*

I studied the reaction of [{RuCl$_2$(*m*tppms)$_2$}$_2$] with H$_2$ in basic aqueous solutions under atmospheric hydrogen pressure because some experimental results and theoretical calculations suggested that under such conditions the earlier established hydride structure: *cis*-[RuH$_2$(*m*tppms)$_4$] was not correct. Indeed, NMR titration measurements proved the *cis*-[RuH$_2$(H$_2$O)(*m*tppms)$_3$] composition. Consequently, in this solution three *m*tppms ligands coordinate to the Ru center.

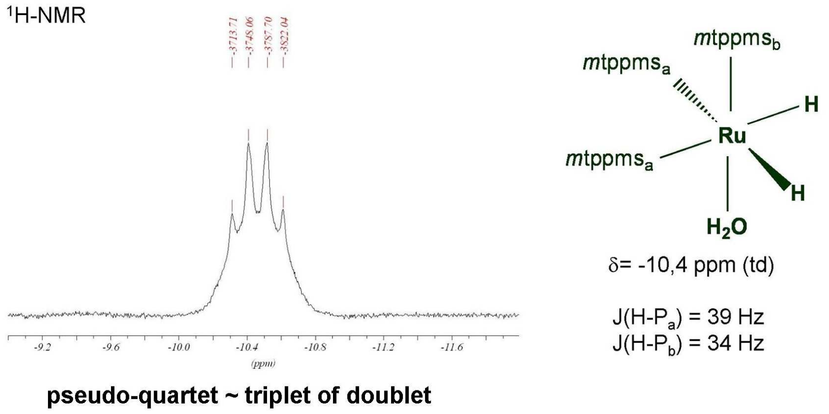


***Figure 3.**: Structure and ^{1}H-NMR spectrum of cis-[RuH$_2$(H$_2$O)(*m*tppms)$_3$] under 1 bar H$_2$. ([Ru] = 0,03M, 10 v/v% CD$_3$OD/H$_2$O)*

*2. It was established that the selectivity in the hydrogenation of trans-cinnamaldehyde with [{RuCl$_2$(*m*tppms)$_2$}$_2$] catalyst, changes with pressure.*

The hydrogenation of *trans*-cinnamaldehyde is a model reaction because the substrate contains both C=C and C=O double bonds. I carried this reaction out in aqueous-organic biphasic systems under higher pressure and acidic conditions. The results are shown on Fig. 4.

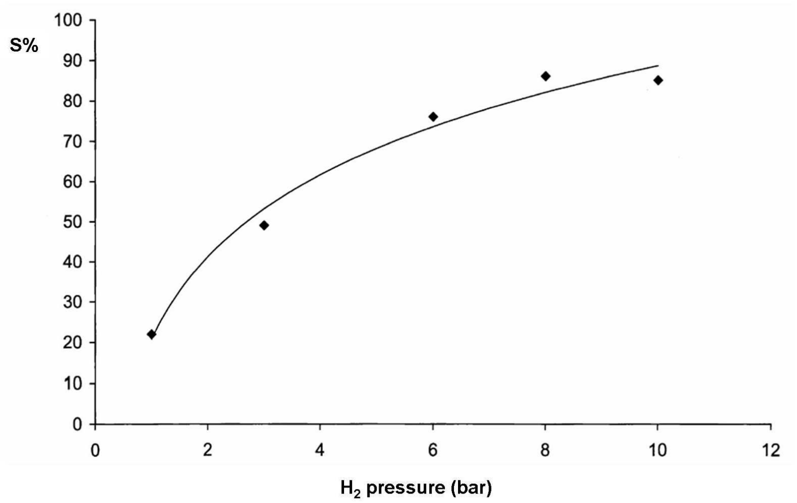


***Figure 4.**: Change of selectivity in hydrogenation of trans-cinnamaldehyde with [{$RuCl_2$(*m*tppms)$_2$}$_2$], pH = 3,04.*

[S% = 100x{(alcohol-aldehyde)/(alcohol+aldehyde)}]

This reaction under atmospheric hydrogen pressure was highly selective in the reduction of C=C double bond. However, the selectivity was changed in favour of the C=O hydrogenation with increasing pressure of H_2, thus giving a rare example of the change of chemoselectivity by pressure.

*3. The structure of trans-[RuH_2(m*tppms*)$_4$] was characterized by NMR spectroscopy in acidic aqueous solution under higher hydrogen pressure.*

The change of selectivity in hydrogenation of trans-cinnamaldehyde under higher pressure and other examples in the literature point to the formation of different Ru-hydrides under higher pressure than under atmospheric hydrogen.

I made ^{1}H and ^{31}P NMR measurements under low (2-8 bar) and medium (10-100 bar) hydrogen pressure (Fig. 5.).

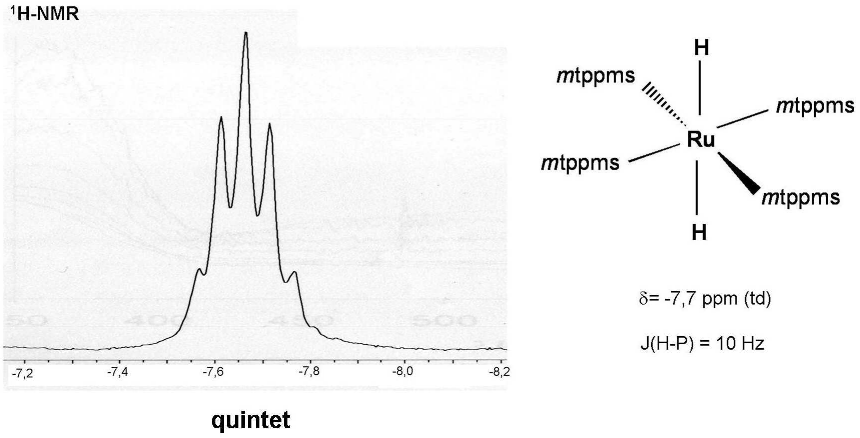


***Figure 5.**: Structure and ^{1}H-NMR spectrum of trans-[RuH$_2$(*m*tppms)$_4$] under 100 bar H$_2$. ([Ru] = 0,03M, 10 v/v% CD$_3$OD/H$_2$O)*

The ^{1}H-NMR signal is a regular quintet what means four equivalent phosphines in the coordination sphere. The integral of this signal shows the ratio of ruthenium and hydrides 1:2. The four phosphines are in one plane and the two hydrides are above and below this plane if we suppose an octahedral structure. The ^{31}P-NMR spectra is another evidence for the phosphines being equivalent, namely the signal of this complex is a relatively broad singlet and the proton decoupled signal is more narrow.

*4. The $T_{1(min)}$ of trans-[RuH$_2$(*m*tppms)$_4$] was determined as 152 ms.*

The structural assignment of transitional metal polyhydrides is possible by the determination of the temperature dependence of longitudinal (T_1) and transversal (T_2) relaxation times.

On the basis of this method I determined the relaxation times at various temperatures; the results are plotted on Fig. 6.

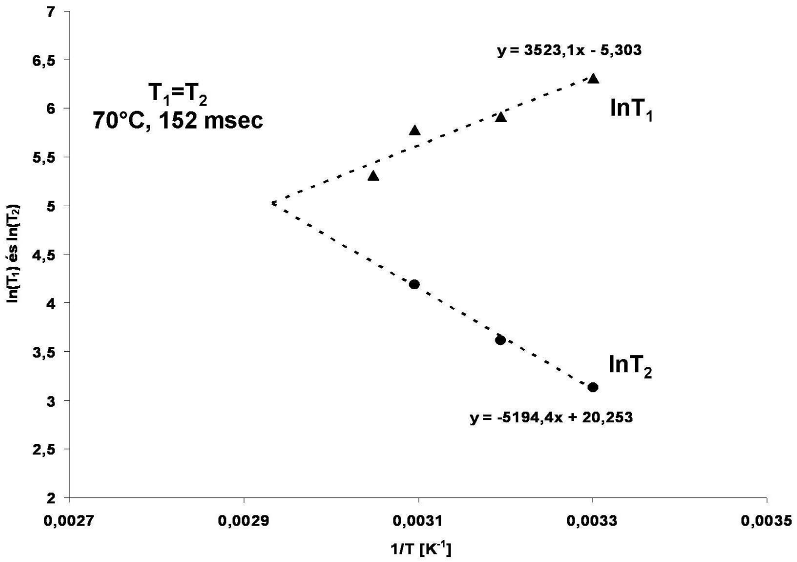


Figure 6.: *Determination of* $T_{1(min)}$ *[*$T_1=T_2$*] of trans-[*$RuH_2(mtppms)_4$*] (acidic solution pH=3,0).*

The $T_{1(min)}$ was found 152 ms namely, in acidic solution under 5-100 bar hydrogen pressure *trans*-[RuH_2(*m*tppms)$_4$] was generated.

5. It was established that under weakly basic conditions and at 5-100 bar hydrogen pressure [$RuH_2(H_2)(mtppms)_3$*] was the exclusive hydride species.*

The formation of various Ru(II)-hydrides at different pH under atmospheric pressure necessitated measurements under higher pressure and in basic solutions.

The ^{1}H and ^{31}P NMR measurements showed the formation of a new hydride species at 40-50°C, pH ~ 8, 100 bar H_2. Multiplicity of this new signal was not measurable but the integrals revealed the ratio of Ru:*m*tppms:H=1:3:4.

In this case too, I studied the influence of temperature on the relaxation times and determined the $T_{1(min)}$ (Fig. 7.).

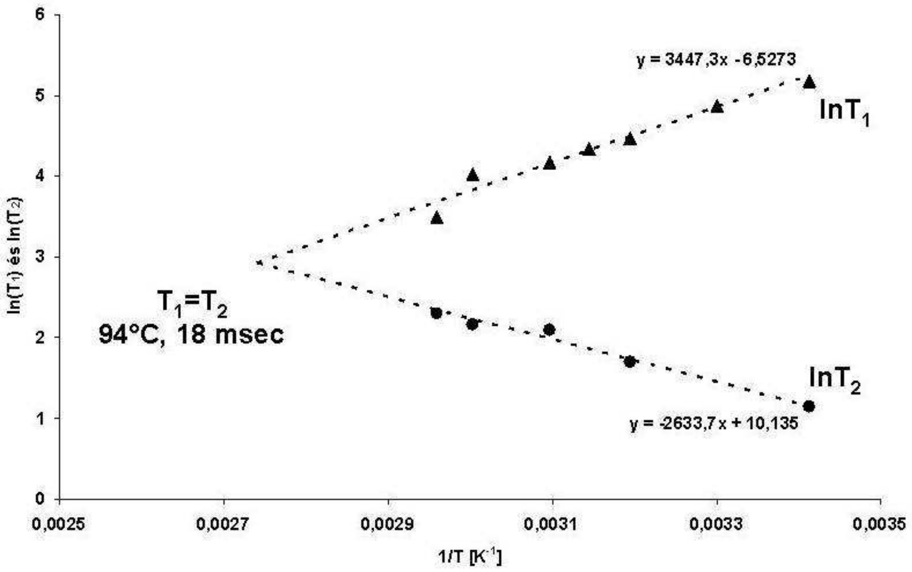


***Figure 7.**: Determination of $T_{1(min)}$ [$T_1=T_2$] of [$RuH_2(H_2)$(m*tppms)$_3$] (basic solution pH=8,0).*

The $T_{1(min)}$ was found 18 ms. This value agrees well with the $T_{1(min)}$ (30 ms) obtained for an analogous Ru(II)-complex [$RuH_2(H_2)(PPh_3)_3$].

The [$RuH_2(H_2)$(*m*tppms)$_3$] complex is one of the rare non-classical (η^2-H_2) hydrides observed so far in aqueous solution.

*6. Chloride dissociation of [RuHCl(CO)(*mtppms*)$_3$] was shown to have an important effect on the catalysis of aqueous-organic biphasic hydrogenation reactions.*

Earlier we studied the equilibrium of the chloro-Ru- and aqua-Ru-complexes obtained from [RuHCl(CO)(*m*tppms)$_3$] in aqueous solution. I determined the influence of this chloride dissociation in hydrogenation of phenylacetylene and *trans*-cinnamaldehyde in aqueous-organic biphasic systems with [RuHCl(CO)(*m*tppms)$_3$] as catalyst (Fig. 8.).

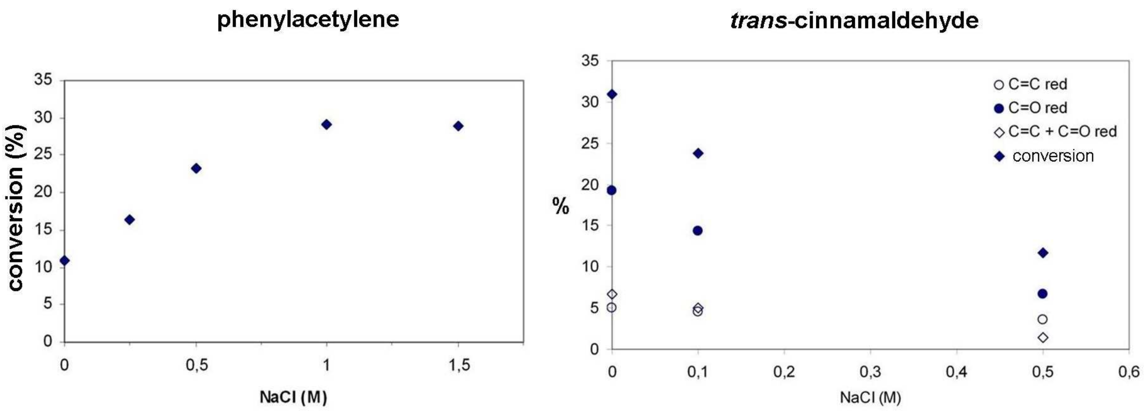


***Figure 8.**: The effect of chloride on the hydrogenation of phenylacetylene and trans-cinnamaldehyde.*

([Ru] = 0,01 M, [sub] = 0,5 M, p(H_2) = 1 bar, T = 333K, t = 2h, 1mL buffer pH=7,0 /1mL toluene)

A higher chloride concentration resulted in a higher conversion of phenylacetylene hydrogenation. The effect of chloride on the hydrogenation of *trans*-cinnamaldehyde was the opposite, namely, the conversion lowered on the increase of chloride concentration.

7. The adverse effect of chloride was rationalized by considering the coordination of phenylacetylene and trans-cinnamaldehyde.

I followed the reaction of the catalyst and *trans*-cinnamaldehyde by ^{1}H-NMR spectroscopy. A new hydride signal appeared in the spectra. Figure 9. shows these results.

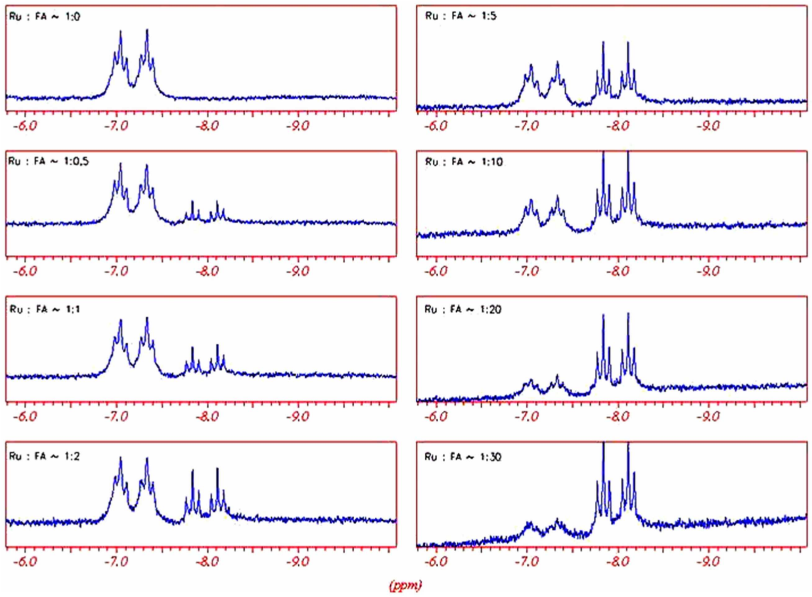


Figure 9.: *Reaction of [RuHCl(CO)(*mt*ppms)$_3$] and trans-cinnamaldehyde.*

*^{1}H NMR spectra; Ru = [RuHCl(CO)(*mt*ppms)$_3$], FA = trans-cinnamaldehyde*

[Ru] = 0,025 M T = 298 K, 0,6 mL solvent (50 v/v% CD_3OD/H_2O)

The aldehyde coordinates to the place of H_2O or Cl^-, and the water exchange is probably easier than that of chloride. Conversely, phenylacetylene coordinates into the place of one *m*tppms ligand in the coordination sphere (Fig. 9.).

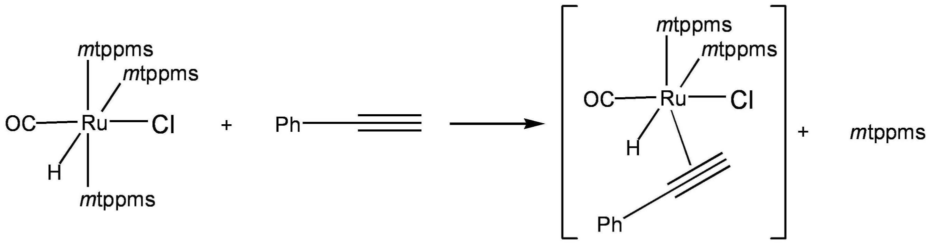


Figure 10.: *Formation of the intermediate complex in hydrogenation of phenylacetylene.*

The stability of that intermediate complex increases with an increase of the chloride concentration because it contains one coordinated chloride. After rearrangment and reaction with molecular hydrogen that complex collapses to yield the products.

8. It was established, that pH influenced the hydrogenation of trans-cinnamaldehyde and phenylacetylene in aqueous-organic biphysic system with $[RuHCl(CO)(m\text{tppms})_3]$ *catalyst the same way. Both reactions showed lower conversions of the substrate with increasing pH.*

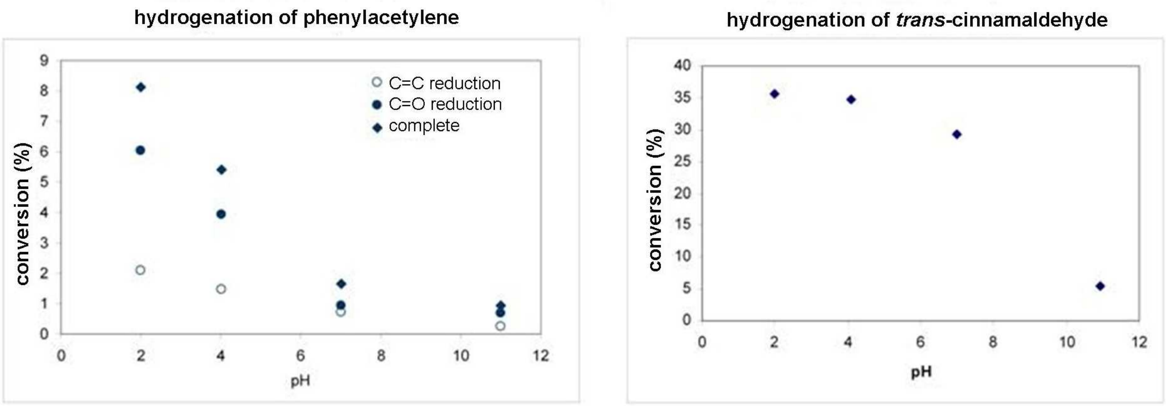


***Figure 11.**: Influence of pH in hydrogenation of trans-cinnamaldehyde and phenylacetylene.*

[Ru] = 0,01M, [sub] = 0,5 M, $p(H_2)$ *= 1 bar, T = 333K, t = 2h, 1mL buffer/1mL toluene*

The explanation of these results is in the deprotonation of $[RuH(H_2O)(CO)(m\text{tppms})_3]$. At higher pH the prevalent $[RuH(OH)(CO)(m\text{tppms})_3]$ complex is not an active catalyst of hydrogenation.

9. A strong effect of pH and chloride concentration in hydrosilylation of trans-cinnamaldehyde in aqueous-organic biphasic systems with $[RuHCl(CO)(m\text{tppms})_3]$ *catalyst was demonstrated.*

The [Ru-Cl] and the $[Ru\text{-}H_2O]$ complexes were the active catalysts in the hydrogenation of the C=O double bond in the reaction of *trans*-cinnamaldehyde. However, with both complexes the important parameter was the pH of the solutions (Fig. 12.).

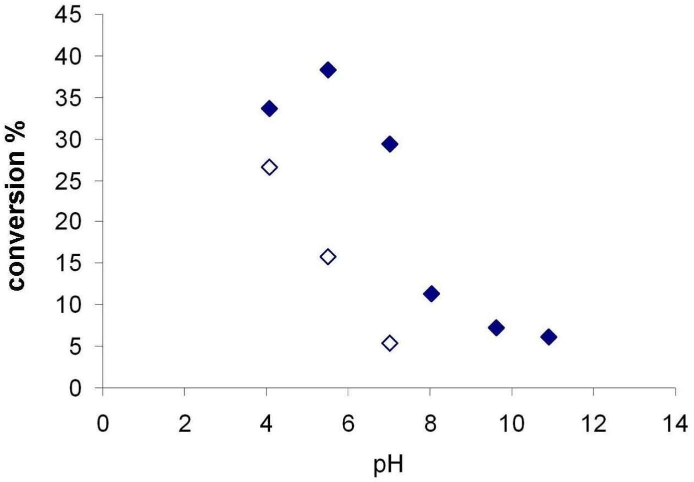


Figure 12.: *Effect of pH on hydrosilylation of trans-cinnamaldehyde.*
[cat] = 0,01 M, [sub] = 1 M, T = 333 K, t = 2 h, Ar, 1mL phosphate buffer / 1 mL toluene,
♦*: silylated cinnamaldehyde + cinnamyl alcohol (without Cl$^-$),* ◊*: silylated cinnamaldehyde + cinnamyl alcohol ([Cl$^-$] = 1 M)*

The catalytic activity of the aqua-complex as a function of pH followed a maximum curve (max.: pH ~ 5,5). Conversely, the activity of the chloro-complex decreased abruptly with an increase of the pH.

A new hydride species was detected in neutral and basic solutions in the absence of chloride. The new hydride was found to be [RuH$_2$(CO)(*m*tppms)$_3$], whith no catalytic activity in this system. Table 1. shows the distribution of various hydride species at suitable conditions in this system.

pH [Cl$^-$] / M	2,1	7,5	11,2
0,021	[RuH(H$_2$O)(CO)(*m*tppms$_3$] ~100%	[RuH$_2$(CO)(*m*tppms)$_3$] ~99%	[RuH$_2$(CO)(*m*tppms)$_3$] ~99%
0,521	[RuHCl(CO)(*m*tppms)$_3$] ~100%	[RuH$_2$(CO)(*m*tppms)$_3$] ~58% [RuHCl(CO)(*m*tppms)$_3$] ~42%	[RuH$_2$(CO)(*m*tppms)$_3$] ~99%
1,021		[RuH$_2$(CO)(*m*tppms)$_3$] ~28% [RuHCl(CO)(*m*tppms)$_3$] ~72%	

Table 1.: *Different hydrides from [RuHCl(CO)(mtppms)$_3$] – SiHMe$_2$Ph in aqueous solution.*

In addition, under basic conditions and at higher chloride concentrations [RuHCl(CO)(*m*tppms)$_3$] and [RuH$_2$(CO)(*m*tppms)$_3$] are in equlibrium. Finally, I characterized the active catalyst in this hydrosilylation reaction, as [RuH(H$_2$O)(CO)(*m*tppms)$_3$]; of course, any decrease of it's concentration as a consequence of increasing chloride concentrations results in lower catalytic activities.

*10. Optimal reaction conditions were established in single-phase hydrogenation of trans-cinnamaldehyde by hydrogen transfer from aqueous HCOONa with [{RuCl$_2$(*m*tppms)$_2$}$_2$] as catalyst.*

Both the conversion of the substrate and the selectivity towards C=O hydrogenation were 100% in H$_2$O/*i*-PrOH solution under mild conditions (30°C, 2 hour) with HCOONa as hydrogen source. I tried some other water-miscible organic solvents: acetone, methanol, methyl cellosolve. Application of these solvents was also succesful.

HCOOH/HCOONa mixtures could also be used as hydrogen source instead of HCOONa. In formic acid the reaction didn't proceed. The best conversions were observed when I used pure sodium-formate alone. The optimal ratios of [Ru]:[*m*tppms] and [sub]:[cat], were also determined: [Ru]:[*m*tppms]=1:6 and [sub]:[cat] = 200:1.

*11. The structure of trans-[RuH$_2$(HCOO)(*m*tppms)$_3$] was determined by 1D, 2D and selective decoupling NMR techniques.*

NMR experiments were perfomed in the [{RuCl$_2$(*m*tppms)$_2$}$_2$] / HCOONa / H$_2$O / *i*-PrOH system to explore the reaction between the complex and formate. I have established that a new hydride species is formed in solution, namely *trans*-[RuH$_2$(HCOO)(*m*tppms)$_3$].

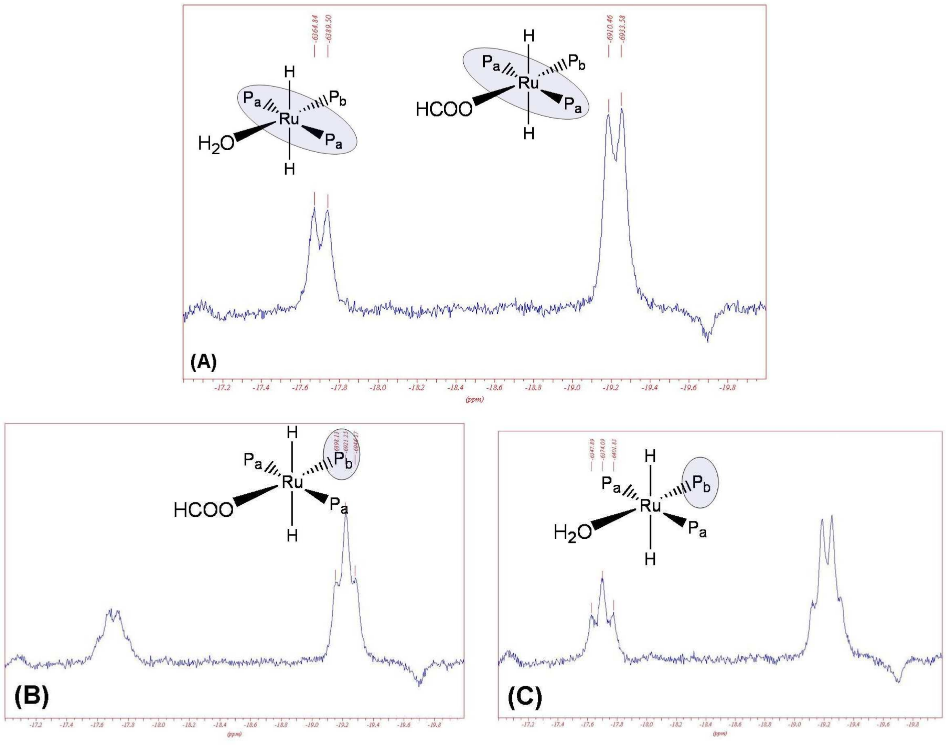


***Figure 13.**: Selective P-decoupled ^{1}H-NMR spectra; [Ru] = 0,042 M, [*m*tppms] = 0,17 M, [HCOONa] = 0,84 M; 0,6mL H$_2$O/i-PrOH=1/1; D$_2$O capillary (**A**: ^{1}H{^{31}P ~44ppm}; **B**: ^{1}H-NMR{^{31}P ~79ppm}; **C**: ^{1}H-NMR{^{31}P ~77ppm})*

This dihydride was characterized by various 1D, 2D (^{31}P-^{31}P COSY) and selective decoupling (Fig. 13.) NMR experiments.

Publikációs lista / List of publications

A doktori értkezéshez kapcsolódó publikációk / Articles connected to the topic of this thesis:

[1] G. Papp, J. Elek, L.Nádasdi, G. Laurenczy, F. Joó: Dramatic pressure effects on the selectivity of the aqueous/organic biphasic hydrogenation of trans- cinnamaldehyde catalyzed by water-soluble Ru(II)-tertiary phosphane complexes *Adv. Synth. Catal.* **2003**, *345*, 172-174 IF: [3.783]

[2] J. Elek, L. Nádasdi, G. Papp, G. Laurenczy, F. Joó: Homogeneous hydrogenation of carbon dioxide and bicarbonate in aqueous solution catalyzed by water-soluble ruthenium (II) phosphine complexes *Appl. Cat. A.* **2003**, *255*, 59-67 [IF: 2.825]

[3] G. Papp, H. Horváth, Á. Kathó, F. Joó: Aqueous Organometallic Chemistry. Synthesis and Solution Equilibria of Trisodium Carbonylchlorotris[3-(diphenylphosphino-κP)benzenesulfonato]-hydrido-ruthenate(3-) ($[RuH(Cl)(CO)\{m\text{-}(Ph_2P)\text{-}C_6H_4\text{-}SO_3Na\}_3]$) and Trisodium Aquacarbonyltris[3-(diphenylphosphino-κP)benzenesulfo-nato]-hydrido-ruthenate(2-) Tetrafluoroborate(1-) ($RuH(CO)(H2O)\text{-}\{m\text{-}(Ph_2P)\text{-}C_6H_4\text{-}SO_3Na\}_3] [BF_4]$) *Helv. Chim. Acta* **2005,** *88*, 566-573 [IF: 1.650]

[4], H. Horváth, G. Papp, Á. Kathó, F. Joó: Comparison of the catalytic properties of the easily interconvertible, water-soluble $[RuHCl(CO)(m\text{tppms})_3]$ and $[RuH(H_2O)(CO)(m\text{tppms})_3]^+$ in the hydrogenation of phenylacetylene and *trans*-cinnamaldehyde *J. Organometal. Chem.* közlésre előkészítve/prepared for publication

A doktori értkezéshez nem kapcsolódó publikációk / Articles not connected to the topic of this thesis:

[5] G. Papp, J. Kovács, A. Cs. Bényei, G. Laurenczy, L. Nádasdi, F Joó: (para-Diphenylphosphino)benzenesulfonic acid and its ruthenium(II) complexes: an old water soluble phosphine ligand in a new perspective. *Can. J. Chem.* **2001**, *79,* 635-641 [IF: 1.144]

[6] L. Kiss, G. Papp, F. Joó, S. Antus: Efficient synthesis of pterocarpans by Heck-oxyarylation in ionic liquids *Heterocyclic Communications* **2001**, *7,* 417-420 [IF : 0.352]

[7] I. Bak, G. Papp, T. Turoczi, L. Szendrei, M. Vecsernyes, F. Joo, A. Tosaki: The role of heme oxygenase related carbon monoxid in ischemic / reperfused hearts *Free Rad. Bio. Med*. **2002**, *33,* 639-648 [IF: 5.533]

[8] I. Bak, L. Szendrei, T. Turoczi, G. Papp, F. Joó, D. K. Das, J. de Leiris, P. Der, B. Juhasz, E. Varga, I. Bacskay, J. Balla, P. Kovacs, A. Tosaki: Heme oxygenase-1 related carbon monoxide production and ventricular fibrillation in isolated ischemic/reperfused mouse myocardium *FASEB Journal* **2003**, *17(14),* 2133-2135 [IF: 7.172]

[9] H. H. Horváth, G. Papp, C. Csajági, F. Joó: Selective catalytic hydrogenations in a microfluidics-based high throughput flow reactor on ion-exchange supported transition metal complexes. A modular approach to the heterogenization of soluble complex catalysts. *Catal. Commun.* **2007**, *8,* 442-446 [IF: 2.394]

[10] Á. Zsigmond, S. Undrala, F. Notheisz, G. Papp, F. Joó: New application of an anchored Ru(II)-N-heterocyclic carbene complex. *Catal. Lett.* **2007**, *115*, 163-168 [IF: 1.883]

Konferencia előadások és poszterek / Posters and oral presentations at conferences:

1. J. Kovács, G. Papp, F. Joó: Effect of pH on the Mechanism of the Hydrogenation of Unsaturated Aldehydes Catalyzed by Water Soluble Ruthenium Phosphine Catalysts
R.S.C. Inorganic Reaction Mechanisms Meeting 97, Debrecen, Book of Abstracts, P53 **1998**

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Abstr. 11th International Symposium on Homogeneous Catalysis, St. Andrews (Scotland), P.70 **1998**

3. F. Joó, L. Nádasdi, G. Papp, J. Elek, G. Laurenczy: Selective hydrogenations catalyzed by water-soluble ruthenium-phosphine complexes
12th Int. Symp. Hom. Catal. (ISHC-12) Stockholm, C5, Abstr. p. 35 **2000**

4. F. Joó, G. Papp, J. Kovács, A.Cs. Bényei, J. Elek, L. Nádasdi, G. Laurenczy: Formation and catalytic activity of hydrido-ruthenium(II) complexes with meta- and para-monosulfonated triphenylphosphine ligands
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5. G. Papp, F. Joó, J. Kovács, J. Elek: Selectivity as the fundamental principle of green chemistry. The Ru-catalyzed hydrogenation of unsatured aldehydes
83th Ann. Conf. Canadian Soc. Chem., Calgary (Canada), Abstr. No. 534 EN **2000**

6. G. Papp, F. Joó: Solution behaviour and catalytic properties of $RuHCl(CO)P_3$-type complexes
28th International Conference on Solution Chemistry, Hungary, Debrecen **2003**

7. G. Papp, H. Horváth, Á. Kathó, F. Joó: A $[RuHCl(CO)(\mathit{m}\mathrm{tppms})_3]$ komplex oldategyensúlyi viselkedése és katalitikus tulajdonságai
40. Komplexkémiai Kollokvium, Gárdony **2004**

8. Á. Kathó, J. Molnár, G. Papp, F. Joó: Effect of NaI on the aqueous/organic biphasic hydrogenation of cinnamaldehyde catalyzed by $[\{RuCl_2(m\text{tppms})_2\}_2]$
14th International Symposium on Homogeneous Catalysis, Munich, Germany, **2004**

9. H. Horváth, G. Papp, F. Joó, Á. Kathó: Comparison of the catalytic properties of the easily interconvertible, water-soluble $[RuHCl(CO)(m\text{tppms})_3]$ and $[RuH(CO)(H_2O)(m\text{tppms})_3]^+$
14th International Symposium on Homogeneous Catalysis, Munich, Germany, **2004**

10. G. Papp, H. Horváth, Á. Kathó, F. Joó: Solution equilibria and catalytic properties of $[RuHCl(CO)(m\text{tppms})_3]$
14th International Symposium on Homogeneous Catalysis, Munich, Germany, **2004**

11. P. Csabai, M. Fekete, G. Papp, H. Horváth, Á. Kathó, F. Joó: Synthesis and catalytic properties of new water-soluble organometallic Ru(II) complex
COST D30 Workshop, Tarragona, Spain,19-20th November, **2004**

12. Á. Kathó, J. Molnár, G. Papp, F. Joó: Effect of NaI on the hydrogenation of cinnamaldehyde catalyzed by $[RuCl_2(m\text{tppms})_2]_2$
First Year AQUACHEM Meeting, Lisbon, Portugal, 7-8th February, **2005**

13. F. Joó, H. H. Horváth, G. Papp: Hydrogenations on supported Ru(II)- and Rh(I)-complex catalyst using the H-CubeTM reactor
Microfluidic Based Hydrogenation Course, Thales Nanotechnology Inc., Budapest, Hungary; **2005**

14. F. Joó, H. H. Horváth, G. Papp: Hydrogenation of alkynes with soluble and immobilized catalysts
COST D30 Working Group 0001/03 meeting, Hungary, Debrecen, **2005**

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