



**Új, vízoldható Ru(II)-foszfin komplexek előállítása és
katalitikus alkalmazása**

Doktori (PhD) értekezés tézisei

Horváth Henrietta

**Synthesis and catalytic properties of new water-soluble
Ru(II)-phosphine complexes**

PhD thesis

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Introduction

Moisture-sensitive reagents are often used in organometallic chemistry thus the necessity of strictly anhydrous media for organometallic catalysis seemed, for a long time, to be an axiomatic issue. However, the widely used chlorinated hydrocarbons and aromatic solvents are harmful to the environment due to their volatility and toxicity therefore their replacement by environmentally friendly solvents is an immediate problem.

The most fruitful solution of this challenge would be the complete omission of solvents but that is, in most cases, not feasible. However, the use of “green” solvents, of which the most important are water, supercritical carbon dioxide and ionic liquids, attracts more and more interest.

Water is environmentally friendly, inexpensive, nonflammable and widely available. Besides, several reactions of biologically important substrates (e.g. carbohydrates) proceed almost exclusively in aqueous medium.

Recently, water is often used in biphasic reactions since it does not, or only to a slight extent, mix with most organic solvents. The reaction of water-immiscible substrates and the catalyst present in the aqueous medium occurs by intense stirring. The catalyst-containing aqueous phase can be easily separated from the organic phase, and can be reused in a new reaction.

The water-soluble analogs of almost all catalysts efficient in organic solvents have been synthesized. Of these Ru complexes are usually prepared by reacting RuCl_3 with the corresponding water-soluble phosphine.

The aim of my work was to study the applicability of other Ru sources. My research was focused on whether water-soluble compounds are formed in the reactions of well-known water-soluble phosphines and the easily available arene-containing Ru dimer $[(\text{arene})\text{RuCl}_2]_2$ or the polymer formed with cyclooctadiene $[\{\text{RuCl}(\text{cod})\}_n]$. If so, what are the catalytic properties of these complexes like in aqueous (monophasic) reactions of water-soluble substrates or in biphasic processes. A further aim was to investigate the difference in the behaviour of catalysts dissolved in organic and aqueous media, and to study how these influence the course and selectivity of catalytic processes.

The thesis is divided into three major parts. One involves the synthesis half-sandwich Ru complexes with water-soluble phosphine ligands and their use in catalysis – mainly in the hydrogenation of HCO_3^- in aqueous medium.

The other two parts mainly deal with the hydrosilylation reactions catalyzed by $[\text{RuHCl}(\text{CO})(\text{mtppps})_3]$ and $[\text{RuCl}(\text{CH}_3\text{CN})_4(\text{P}^i\text{Pr}_3)]^+$. The hydrolysis of these complexes was also studied as well as the catalytic properties of the chloro-, and the resulting aqua complexes in the hydrogenation and hydrosilylation of phenylacetylene.

Applied experimental techniques

The water soluble phosphines (pta, mtppps, mtppts, see *Fig. 1*) and the various Ru(II)-phosphine complexes were prepared under an inert atmosphere.

The identification of the new complexes was carried out by ^1H -, ^{13}C - and ^{31}P -NMR techniques (BRUKER DRX 360, BRUKER Avance 300 MHz) and by mass spectrometry (BRUKER BioTOF II ESI-TOF and VG Autospec). Elementary analyses (C, H, N) were done on a Perkin Elmer CHNS/O analyser at the Department of Inorganic Chemistry, University of Zaragoza. The formation of $[\text{RuCl}(\eta^6\text{-C}_{10}\text{H}_{14})(\text{pta})(\text{mtppts})]\text{Cl}$ complex was followed by UV-VIS spectroscopy on a Hitachi U2000 equipment. Single-crystal X-ray diffraction data were collected on a Enraf Nonius MACH3 or on a Bruker SMART APEX CCD diffractometer.

Atmospheric pressure hydrogenations were carried out in Schlenk-vessels, whereas in the case of higher pressures (2-10 bar) heavy-walled glass tube reactors or stainless steel reactors (10-100 bar) were applied. The formation of half-sandwich Ru hydrides and the reduction of HCO_3^- were studied in high pressure sapphire NMR tubes.

The hydrogenation of cinnamaldehyde and the hydrosilylation of phenylacetylene were followed by gas chromatography (HEWLETT-PACKARD 5890 Series II equipment). The hydrogenation of HCO_3^- was studied by ^{13}C NMR techniques while the hydrogenation of allyl-alcohol was investigated by ^1H -NMR spectroscopy.

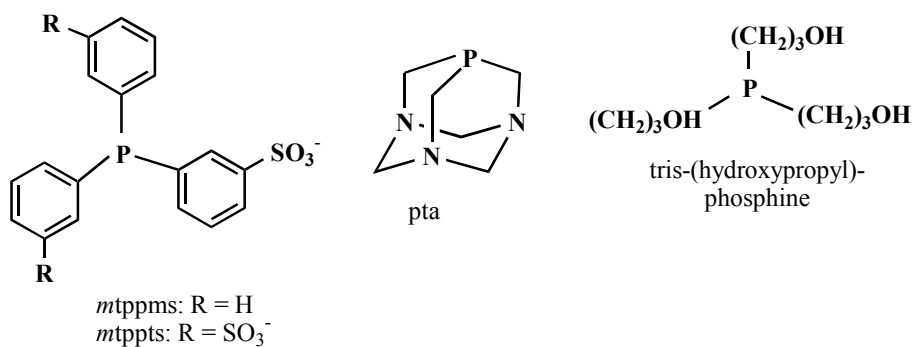


Figure 1.: The water-soluble ligands: *mtppps*, *mtppts* and *pta*

Abbreviations

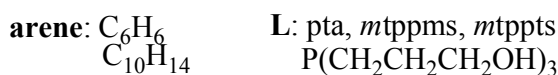
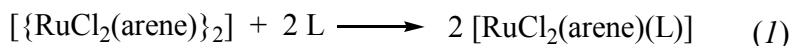
cod:	1,5 cyclooctadiene
C₁₀H₁₄:	<i>p</i> -cymene, (4-isopropyltoluene)
<i>mtppps</i>:	Na salt of diphenyl-(3-sulfophenyl)phosphine
<i>mtppps-gua</i>	guanidinium salt of diphenyl-(3-sulfophenyl)phosphine
<i>mtppts</i>:	Na salt of tris(3-sulfophenyl)phosphine
pta:	1,3,5-triaza-7-phosphaadamantane
PⁱPr₃:	triisopropyl-phosphine
PPh₃:	triphenylphosphine
TOF:	(Turnover Frequency): (reacted substrate)(catalyst x time) ⁻¹ , mol(mol·h) ⁻¹
HPz:	pyrazole
MeO-cellosolv:	2-methoxy-ethoxy-ethanol = diethyleneglycol-methyl-ether
THF:	tetrahydrofuran
ESI:	electron spray ionisation

New scientific results

I. Sixteen new Ru(II)-phosphine complexes have been synthesised in solid state and the molecular structure of five of them were determined by X-ray diffraction.

a./ Synthesis of phosphine-substituted water-soluble half sandwich Ru(II)-complexes

[RuCl₂(arene)(L)]-type complexes were prepared by refluxing the methanolic solution of the corresponding Ru dimer and the ligand for 6-24 hours under an inert atmosphere.



The mixed phosphine complex, [RuCl(η⁶-C₁₀H₁₄)(pta)(mtppts)]Cl, was synthesized by boiling [RuCl(η⁶-C₁₀H₁₄)(pta)] and an equivalent amount of mtppts in methanol for 5 hours.

The solid-state structures of [RuCl₂(η⁶-C₆H₆)(pta)]·H₂O and [RuCl₂(η⁶-C₆H₆)(mtppps-gua)] were determined by single crystal X-ray diffraction, and they were found to be similar to that of the known [RuCl₂(η⁶-C₁₀H₁₄)(pta)]·CH₂Cl₂.

b./ Synthesis of [RuHCl(CO)(mtppps)₃] and [RuH(H₂O)(CO)(mtppps)₃](BF₄)

[RuHCl(CO)(mtppps)₃] was obtained in a ligand exchange reaction between [RuHCl(CO)(PPh₃)₃] and mtppps carried out in THF/CHCl₃ mixture. In aqueous solution chloride dissociation occurred yielding [RuH(H₂O)(CO)(mtppps)₃]⁺. This complex was also prepared by an independent synthetic method as shown in Fig. 2.

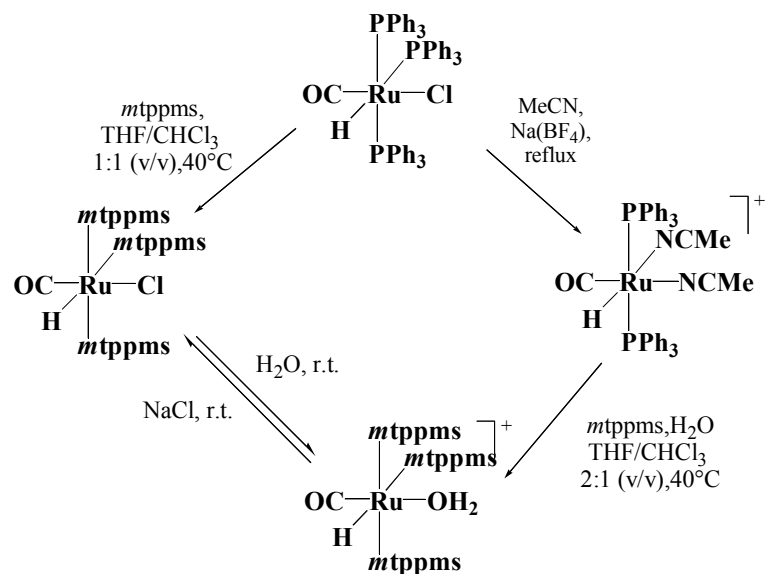


Figure 2.: Synthesis of $[\text{RuHCl}(\text{CO})(\text{mtppps})_3]$ and $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{mtppps})_3](\text{BF}_4)$

c./ Synthesis of $[\text{RuCl}(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)$ complex and its derivatives

Experimental methods of these complexes and reaction conditions are shown in Fig.

3.

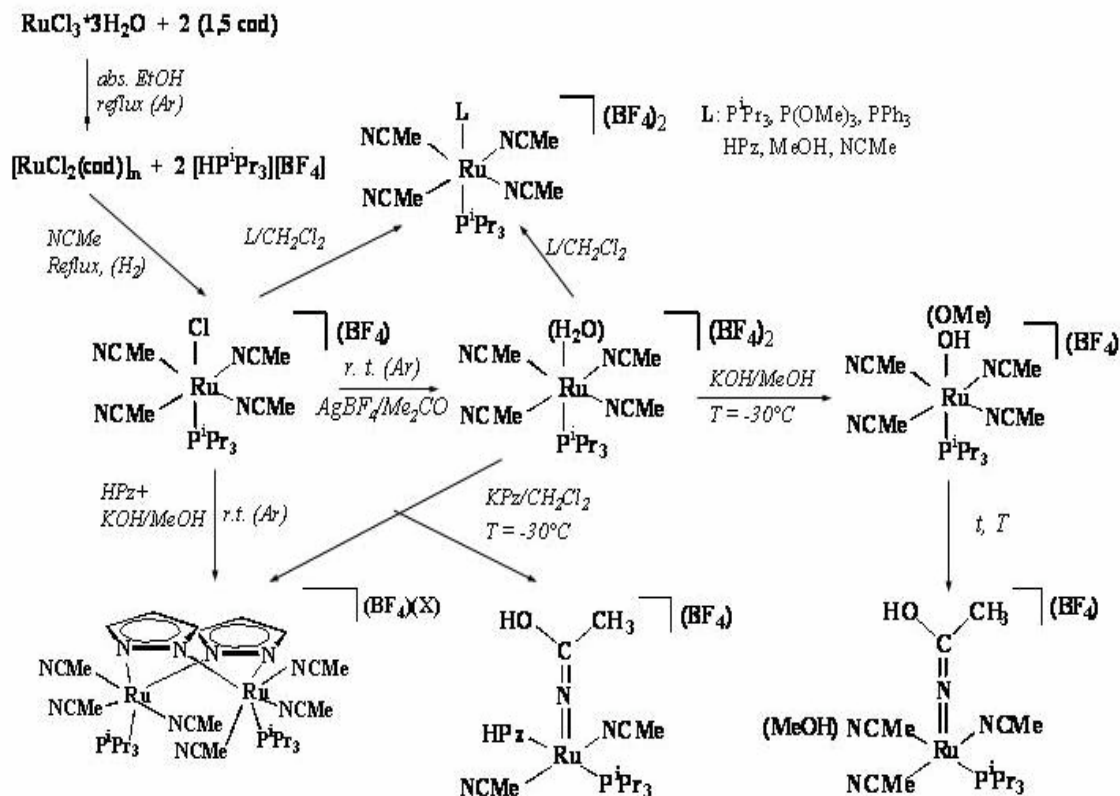
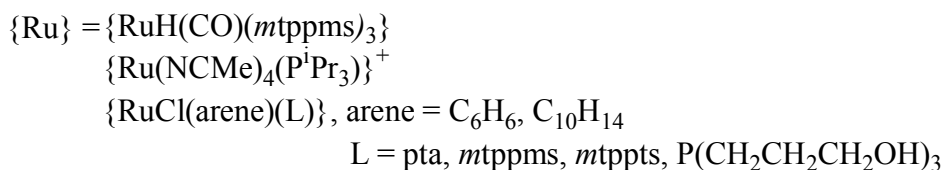
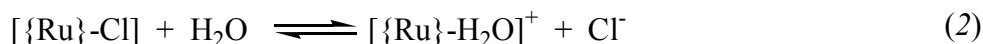


Figure 3.: Synthesis originating $[\{\text{RuCl}_2(\text{cod})\}_n]$ precursor

The solid-state structures of $[\text{RuCl}(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)$ $[\text{Ru}(\text{H}_2\text{O})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)_2$ and $[\text{Ru}(\text{NCMe})_4(\text{P}^i\text{Pr}_3)_2](\text{BF}_4) \cdot (\text{CHCl}_3)$ were also determined by single crystal X-ray diffraction.

II. Chloride dissociation equilibria of the complexes in aqueous solution

a./ ^{31}P -NMR studies proved the hydrolysis of chloro complexes.



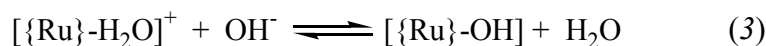
b./ Dissociation equilibrium constants of $[\text{RuHCl}(\text{CO})(\text{mtppps})_3]$ and $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{mtppps})_3](\text{BF}_4)$ complexes were determined.

The NMR spectra of aqueous solution of $[\text{RuHCl}(\text{CO})(\text{mtppps})_3]$ showed the presence of $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{mtppps})_3]^+$ as the major species. The spectra were recorded at various Cl^- concentrations, and the relative amounts of $[\text{RuHCl}(\text{CO})(\text{mtppps})_3]$ and $[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{mtppps})_3]^+$ were determined from the integrated intensities of the $^{31}\text{P}\{^1\text{H}\}$ -NMR signals, and the dissociation constant: $K = 9.8 \cdot 10^{-2} \text{ M}^{-1}$ was also calculated.

Similarly, the relative amounts of $[\text{Ru}(\text{H}_2\text{O})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)_2$ and $[\text{Ru}(\text{Cl})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)$ at different Cl^- concentrations were determined by titrating an aqueous solution of $[\text{Ru}(\text{H}_2\text{O})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)_2$ with NaCl solution. The dissociation constant was calculated using the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectral data and was found $K = 0.5 \text{ M}^{-1}$.

In CD_3OD methanolysis of $[\text{RuHCl}(\text{CO})(\text{mtppps})_3]$ but not of the $[\text{RuCl}(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)$ could also be detected.

c./ It was pointed out that the aqua complexes ($[\text{RuH}(\text{H}_2\text{O})(\text{CO})(\text{mtppps})_3]^+$, $[\text{Ru}(\text{H}_2\text{O})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)]^{2+}$) are converted to hydroxo complexes depending on the pH of the solution. The equilibrium constants of these processes were determined.



In solutions of $\text{pH} > 9$ the chemical shift of the phosphorous signals in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra changes gradually with the change in the pH. The chemical shift vs. pH curve is similar to that of pH potentiometric measurements. The equilibrium constants of eq. (3) were calculated from these data using the PSEQUAD software and these were found to be $\text{pK}_a=11.97$ for $[\text{RuH}(\text{H}_2\text{O})(\text{mtpms})_3](\text{BF}_4)$ and $\text{pK}_a= 11.36$ for $[\text{Ru}(\text{H}_2\text{O})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)_2$, respectively.

III. The reaction of $[\{\text{RuCl}_2(\text{arene})\}_2]$, water-soluble phosphines ($L = \text{pta}$, mtpms , mtppts) and H_2 was studied in aqueous solutions. Several hydrido complexes were indentified at $p = 10\text{-}100$ bars. Some of these complexes were detected also in the reaction with HCOONa .

Depending on the $[\text{L}]/[\text{Ru}]$ ratio, temperature, hydrogen pressure and the reaction time various hydrido complexes were formed of which the $[\text{RuH}(\text{arene})\text{L}_2]^+$ was the dominating species in all the cases.

Fig. 4 depicts the complexes formed in the reaction of $[\{\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)\}_2]$ and pta and their reactions with hydrogen.

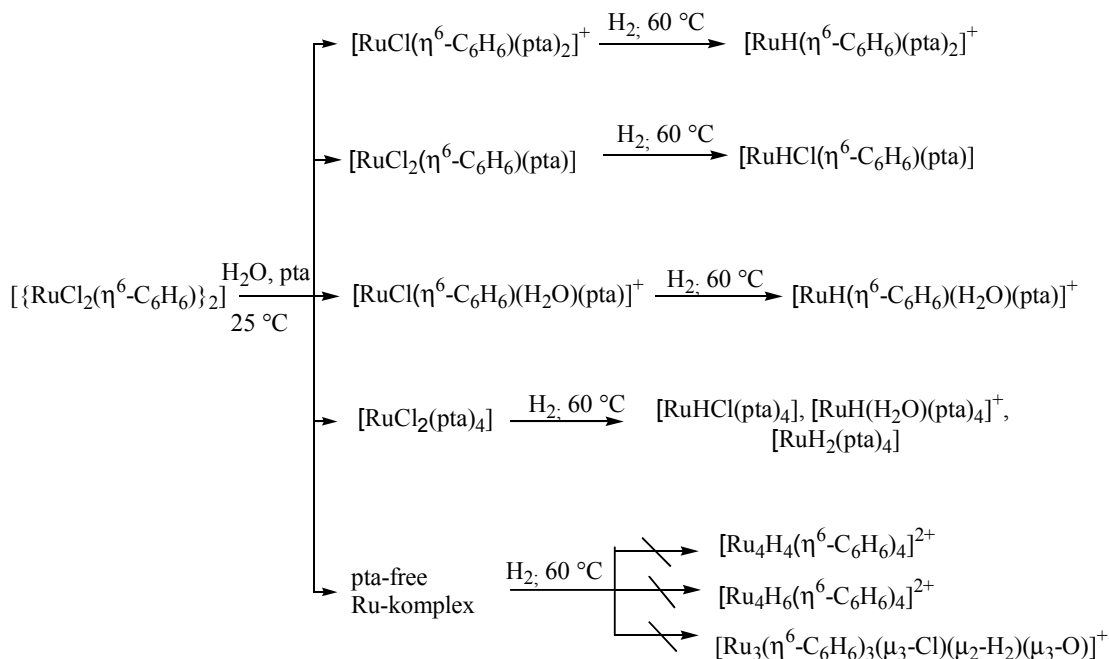


Figure 4: The complexes formed in the reaction of $[\{\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)\}_2]$ and pta and their reactions with hydrogen ($p = 100$ bar).

IV. The new water-soluble Ru(II)-phosphine complexes were used as catalysts for hydrogenation and hydrosilylation reactions.

a./ $[RuCl_2(arene)(L)]$ ($L = pta, mtppts$) formed in situ as well as the isolated $[RuCl_2(\eta^6-C_{10}H_{14})(pta)]$ showed catalytic activity in the hydrogenation of HCO_3^- in aqueous solution.

It was established that in the reaction catalyzed by $[(\eta^6-C_{10}H_{14})RuCl_2(pta)]$ both $HCOO^-$ and $DCOO^-$ were formed.



The turnover frequency (TOF) was determined by following the progress of the reactions by ^{13}C -NMR spectra. For the $[\{RuCl_2(\eta^6-C_6H_6)\}_2] + 4pta$ “in-situ” catalyst, at $p(H_2) = 100$ bar pressure, depending on the temperature and $[L]/[Ru]$ ratio, the TOF was found to be between 22 and 409 h^{-1} .

b./ Hydrogenation of cinnamaldehyde

The hydrogenation of cinnamaldehyde catalyzed by $[RuCl_2(\eta^6-C_{10}H_{14})(pta)]$ was studied in biphasic systems at various hydrogen pressures and temperatures, with and without the presence of $HCOONa$. It was established that hydrogenation occurs only at pressures higher than 10 bar and the main product was cinnamylalcohol.

The extent of hydrogenation significantly increases in the presence of small amounts of formate ($[HCOONa]/[R] = 2$) facilitating hydride formation, and, simultaneously, the reduction of $C=C$ bonds becomes preferred.

c./ It was proved that the catalytic activities of aqua and chloro complexes differ both in hydrogenation and hydrosilylation reactions in organic as well as in biphasic (aqueous/organic) systems.

The catalytic activities of $[RuHCl(CO)(mtppts)_3]$ and $[RuH(H_2O)(CO)(mtppts)_3]^+$ were studied in the hydrogenation and hydrosilylation of cinnamaldehyde and phenylacetylene.

In methanol and under atmospheric hydrogen pressure, both complexes catalyze the hydrogenation of phenylacetylene to styrene. The process catalyzed by $[RuHCl(CO)(mtppts)_3]$ is significantly faster than the one catalyzed by $[RuH(H_2O)(CO)(mtppts)_3]^+$ ($t_{1/2} \approx 50$ min and 400 min at 60 °C).

In methanol both catalysts mainly favour the formation of the unsaturated alcohol; in the reduction of cinnamaldehyde almost complete selectivity was observed, though the activity was slightly lower than that in the presence of $[\text{RuHCl}(\text{CO})(\text{mtppps})_3]$.

Of the five possible products in the hydrosilylation reactions of phenylacetylene (Fig. 5) mainly β -styryl silane (both *Z* and *E* isomers) and styrene are formed both in mono- and biphasic systems.

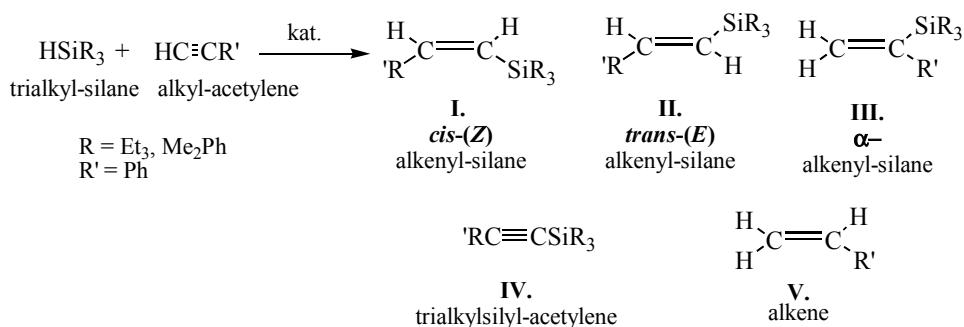


Figure 5.: Products of hydrosilylation

In MeO-cellosolv the chloro complex (no solvolysis occurs in this solvent) favours the formation of *Z*-styryl-silane, while the aqua complex primarily catalyzes the reduction of phenylacetylene with significantly less activity than the chloro complex does.

I have found in the same process in biphasic water-dichloroethane system, that:

- Both the quality and quantity of the hydrosilane have an effect on the catalysis: the reaction is faster with HSiMe_2Ph than with HSiEt_3 . The excess of silane primarily influences the reaction rate rather than the selectivity.
- The presence of air has no significant effect on the conversion or on the selectivity.
- The conversion decreases using a buffer of pH = 7.5 instead of water as an aqueous phase, however, the selectivity increases in favour of the *Z*-styryl-silane.
- Of the halides (Cl^- , Br^- , I^-) the highest conversion can be achieved in the presence of chloride. Increasing its concentration the selectivity also changes: the amount of *Z* isomer increases at the expense of *E*-styryl-silane.

The catalytic activities of $[\text{RuCl}(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)$ and $[\text{Ru}(\text{H}_2\text{O})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)_2$ were also compared in the hydrosilylation of phenylacetylene and the following conclusions should be noted:

- In 1,2-dichloro-ethane $[\text{Ru}(\text{H}_2\text{O})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)_2$ proved to be more active as a catalyst.
- Replacing 1,2-dichloro-ethane with acetone or THF the conversion significantly decreases. Though the main product is the *Z*-alkenyl-silane in all three solvents, its amount decreases in the order 1,2- dichloro-ethane > acetone > THF, and, at the same time the amount of styrene increases to almost 30 % in THF.
- In an aqueous-organic biphasic systems the ratio of reactants also has a significant effect on the selectivity. With a concentration ratio of phenylacetylene and HSiEt_3 approaching 1, the percentage of styrene in the product mixture increases. It is even more typical that at the same time the formation of *Z*-styryl-silane becomes dominant on the expense of the *E*-isomer. The conversion can be increased and the formation of styrene can be suppressed with the increase of temperature and use of HSiMe_2Ph instead of HSiEt_3 .

The role of the pH of the solution was pointed out regarding the hydrogenation of allyl alcohols in aqueous solution by $[\text{Ru}(\text{H}_2\text{O})(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)_2$. At atmospheric pressure the extent of hydrogenation of the compounds studied (allyl alcohol, geraniol, 1-octene-3-ol) is rather low. The reaction of 1-octene-3-ol, however, was accelerated when the catalyst was dissolved in a phosphate buffer of $\text{pH} = 7.5$ instead of water. Mainly isomerisation occurs: the amount of 3-octanone is 6.5 times higher than that of 3-octanol.

The results of my thesis throw light on the fact that in the hydrogenation and hydrosilylation processes catalyzed by chloro complexes not only $[\text{H}^+]$ but the concentration (and quality) of halides has influence on the conversion and selectivity of the reaction too.

Publikációs lista/List of Publications

A témához kapcsolódó közlemények/Papers related to the dissertation:

- [1] **H. Horváth, G. Laurenczy, Á. Kathó, J. Organomet. Chem. 689 (2004) 1036-1045**
Water-soluble (η^6 -arene)ruthenium(II)-phosphine complexes and their catalytic activity in the hydrogenation of bicarbonate in aqueous solution
- [2] **G. Papp, H. Horváth, Á. Kathó, F. Joó, Helvetica Chimica Acta, 88 (2005) 566-573**
Aqueous Organometallic Chemistry. Synthesis and Solution Equilibria of Trisodium Carbonylchlorotris[3-(diphenylphosphino- κP)benzenesulfonato]-hydridoruthenate(3-) ($[\text{RuH}(\text{Cl})(\text{CO})\{m\text{-(Ph}_2\text{P)-C}_6\text{H}_4\text{-SO}_3\text{Na}\}_3]$) and Trisodium Aquacarbonyltris[3-(diphenylphosphino- κP)benzenesulfonato]-hydridoruthenate(2-) Tetrafluoroborate(1-) ($[\text{RuH}(\text{CO})(\text{H}_2\text{O})\{m\text{-(Ph}_2\text{P)-C}_6\text{H}_4\text{-SO}_3\text{Na}\}_3][\text{BF}_4]$)

Előkészületben/In preparation:

- [1] **H. Horváth, G. Papp, F. Joó, Á. Kathó**
Comparison of catalytic properties of the easily interconvertible, water-soluble $[\text{RuHCl}(\text{CO})(\text{mtppms})_3]$ and $[\text{RuH}(\text{CO})(\text{H}_2\text{O})(\text{mtppms})_3]^+$
- [2] **H. Horváth, Á. Kathó, F. Joó, E. Sola, M. Martin**
Reactions of $[\text{RuCl}(\text{NCMe})_4(\text{P}^i\text{Pr}_3)](\text{BF}_4)$ in aqueous and organic media: synthetic, equilibrium and catalytic studies

Előadások/Lectures:

- [1] **Papp G., Horváth H., Kathó Á., Joó F.**
XXXIX. Komplexkémiai Kollokvium, 2004. május 26-28, Agárd-Gárdony
A $[\text{RuHCl}(\text{CO})(\text{mtppms})_3]$ komplex oldategyensúlyi viselkedése és katalitikus tulajdonságai
- [2] **Horváth H., Papp G., Joó F., Kathó Á.**
XXXIX. Komplexkémiai Kollokvium, 2004. május 26-28, Agárd-Gárdony
A $[\text{RuHCl}(\text{CO})(\text{mtppms})_3]$ és a $[\text{RuH}(\text{CO})(\text{H}_2\text{O})(\text{mtppms})_3]^+$ komplexek katalitikus tulajdonságainak összehasonlítása
- [3] **Kathó Á., Horváth H., Laurenczy G.**
XXXIX. Komplexkémiai Kollokvium, 2004. május 26-28, Agárd-Gárdony
Vízoldható foszfint tartalmazó félszendvics Ru-komplexek
- [4] **P. Csabai, M. Fekete, G. Papp, H. Horváth, Á. Kathó F. Joó**
Synthesis and catalytic properties of new water-soluble organometallic Ru(II)-complexes

Poszterek/Posters:

[1] **Á. Kathó, H. Horváth, G. Laurenczy**

13th International Symposium on Homogeneous Catalysis, September 3-7, 2002, Tarragona, Spain

Catalytic application of half-sandwich ruthenium complexes in aqueous solution

[2] **H. Horváth, Á. Kathó, G. Laurenczy**

3rd Swiss COST Chemistry Symposium, October 17-18, 2002, Basel, Switzerland

Hydrogenation with Ruthenium(arene)phosphine Catalysts in Water

Chimia, **56**, (2002), 413

[3] **Á. Kathó, H. Horváth, G. Laurenczy and F. Joó**

28th International Conference on Solution Chemistry, August 23-28, 2003, Debrecen, Hungary

Phosphine-substituted water-soluble (arene)Ru(II)-complexes

[4] **G. Papp, H. Horváth, Á. Kathó, F. Joó**

14th International Symposium on Homogeneous Catalysis, July 5-9, 2004, Munich

Solution equilibria and catalytic properties of $[\text{RuHCl}(\text{CO})(\text{mtppms})_3]$

[5] **H. Horváth, G. Papp, F. Joó, Á. Kathó**

14th International Symposium on Homogeneous Catalysis, July 5-9, 2004, Munich

Comparison of catalytic properties of the easily interconvertible, water-soluble $[\text{RuHCl}(\text{CO})(\text{mtppms})_3]$ and $[\text{RuH}(\text{CO})(\text{H}_2\text{O})(\text{mtppms})_3]^+$

[6] **H. Horváth, G. Papp, F. Joó, Á. Kathó**

7th Summer School on Green Chemistry, September 5-11, 2004, Venezia, Italy

Comparison of catalytic properties of the easily interconvertible, water-soluble $[\text{RuHCl}(\text{CO})(\text{mtppms})_3]$ and $[\text{RuH}(\text{CO})(\text{H}_2\text{O})(\text{mtppms})_3]^+$

[7] **H. Horváth, G. Papp, Á. Kathó, F. Joó**

Metamorphosis of the $[\text{RuHCl}(\text{CO})(\text{mtppms})_3]$ catalyst during the hydrosilylation of alkynes in aqueous-organic biphasic systems

Conf. on Knowledge-based Materials and Technologies for Sustainable Chemistry, Tallinn (2005)

Book of Abstracts, O44, p. 56