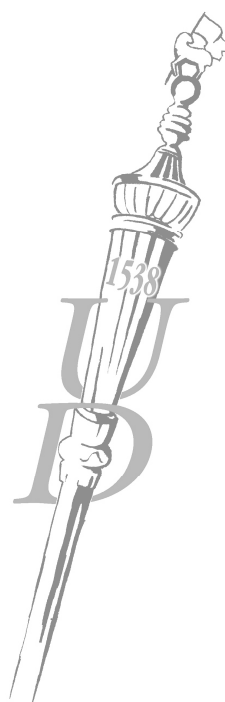


PhD Theses

**Catalytic application of Ru(II) and Rh(I) phosphine complexes
in liquid-liquid and solid-liquid systems**

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I. Introduction and objectives

In the past few decades, the investigation of water-soluble transition metal complexes played an important role in homogeneous catalysis. Most complexes with phosphine ligands were investigated in detail. A large number of water-soluble organic phosphine ligands and their transition metal complexes have been prepared and used as catalyst in aqueous solutions.

It is economically important to recover the noble metal complexes efficiently after the reaction. Since transition metal catalysts can be really expensive, there is an aim to recover the organometallic catalysts and use them in another catalytic reaction. Several methods were tried, one of the best methods was the two-liquid phase homogeneous catalysis, in which the catalyst is dissolved in one phase and the substrate and the product(s) are dissolved in the other. Thus, after the catalytic reaction, the catalyst is easily recovered. According to another successful method, the catalyst is anchored on the surface of a solid support; these heterogenized homogeneous catalysts are easy to separate from the reaction mixture.

In some cases it is very important, that in the course of the reaction, where more than one products can be formed, only one of them is produced. The selective catalytic reactions have a great importance; for example in the pharmaceutical industry it is often required, that only one of the possible stereoisomers is produced, and the other one, which in most cases is harmful, does not appear even in small amounts.

Hydrogenation reactions catalyzed by water soluble phosphine complexes of rhodium and ruthenium have been examined thoroughly by our research group in the last few decades. The main aim of our work was the preparation of water-soluble complexes, capable of selectively catalyze some hydrogenation reactions.

Some of the most widely examined water-soluble ligands are the sulfonated triphenyl-phosphines; during my work the *mtppms* = 3-phenylphosphinyl-benzenesulfonic acid sodium salt was examined. The structure of this ligand is shown in Fig 1. Pta = 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane is also a well-known water-soluble phosphine ligand, and other water-soluble derivatives, such as methyl-pta-iodide (Me-pta⁺I⁻) and benzyl-pta-chloride (Bzl-pta⁺Cl⁻) are also known. These two ligands were also investigated by me in detail (Fig 1.).

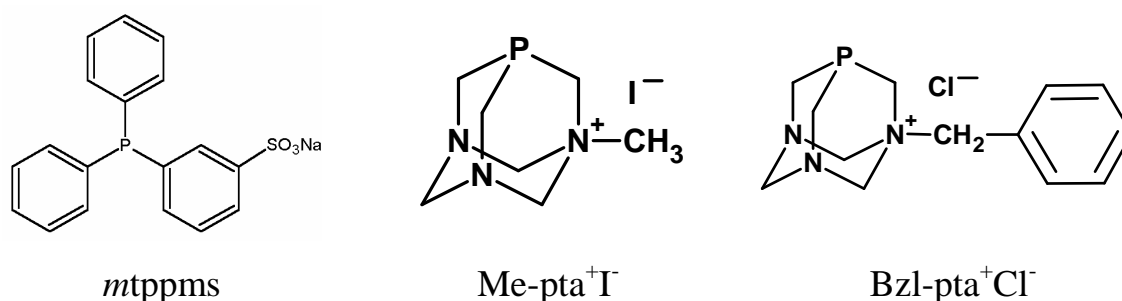


Fig 1. The applied ligands

The ruthenium and rhodium complexes of the *mtppms* were prepared and used in various catalytic systems by several research groups. My major aim was to investigate the hydrogenation of alkynes with [$\{\text{RuCl}_2(\text{mtppms})_2\}_2$] in water/organic biphasic systems. The effect of iodide excess on the catalytic property of this catalyst was also studied. Selectivity was elucidated with the application of different pH values and H₂ pressures.

Furthermore, my goals were to anchor [$\{\text{RuCl}_2(\text{mtppms})_2\}_2$] and [$\text{RhCl}(\text{mtppms})_3$] complexes on the surface of different ion-exchangers and to investigate the catalytic properties of the obtained heterogenized homogeneous catalysts.

The preparation and characterization of Ru(II) and Rh(I) complexes of pta derivatives (Me-pta⁺I⁻ and Bzl-pta⁺Cl⁻), and the use of these new

complexes for the hydrogenation of different substrates in water/organic biphasic systems were also among my aims.

II. Applied experimental techniques

The low-pressure (1 bar) experiments were carried out in a gas burette, whereas in the case of higher pressures (10 bar) special pressure resistant glass tube reactors were applied. With the immobilized catalysts the reactions were carried out in the H-Cube hydrogenation reactor, which is a flow-through minireactor, developed by the Thales Nanotechnology Inc. The prepared catalysts were filled into a cartridge (CatCart) by the mentioned company.

The reaction mixtures from the hydrogenation of the alkynes (phenylacetylene, diphenylacetylene, 1-phenyl-prop-1-yne, 1-phenyl-but-1-yne) and the trans-cinnamaldehyde were analysed on HP5890 Series II type gas chromatograph (Column: Chrompack WCOT Fused Silica 30m×0.32mm, CP WAX52CB).

The hydrogenation of styrene-4-sulphonic acid sodium salt was followed by ¹H-NMR spectroscopy with Bruker Avance 360 device. Data processing was made by Bruker WinNMR software package. To characterise and determine the pta derivatives and their Ru(II) and Rh(I) complexes ¹H- and ³¹P-NMR spectroscopies were used. Elemental analysis by combustion was examined in the Department of Pharmaceutical Chemistry of the University of Szeged. ICP-OES measurement were carried out in the laboratory of Analab Ltd., Debrecen.

III. New scientific results

1. It was shown, that the $[\{\text{RuCl}_2(\text{mtppps})_2\}_2]$ complex catalyses the hydrogenation of phenylacetylene in aqueous/organic biphasic systems. In alkene/alkyne mixtures, alkynes are preferentially hydrogenated.

The hydrogenation of phenylacetylene with $[\{\text{RuCl}_2(\text{mtppps})_2\}_2]$ proceeded with good yield in aqueous/organic biphasic systems both in acidic and in basic media. The hydrogen uptake is slower with phenylacetylene than with styrene-4-sulphonic acid sodium salt, but in hydrogenations of these two substrates together, the phenylacetylene is reduced first.

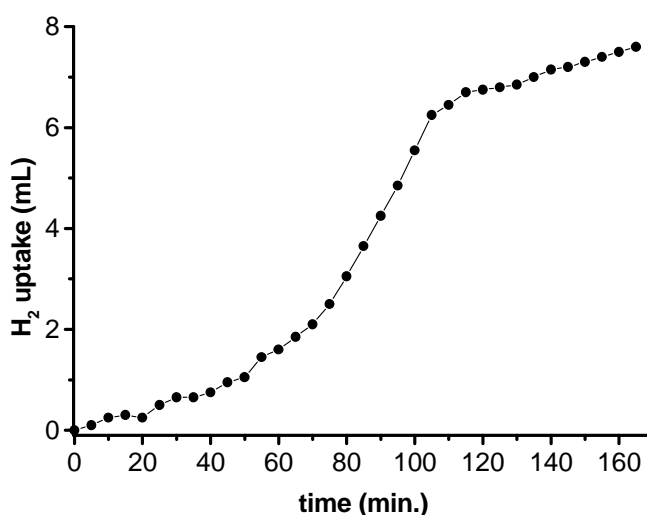


Fig 2. The effect of the addition of phenylacetylene on the hydrogenation of sulphostyrene

6.6 mg (6.79×10^{-3} mmol) $[\{\text{RuCl}_2(\text{mtppps})_2\}_2]$, 8.1 mg (2.03×10^{-2} mmol) *mtppps*, 103.1 mg (0.5 mmol) $\text{CH}_2=\text{CHC}_6\text{H}_4\text{SO}_3\text{Na}$, 2 mL 0.1 M HCl solution, at the 110. minute 1 mL 0.5 M phenylacetylene chlorobenzene solution, $T=50^\circ\text{C}$

The hydrogenation of 4-sulphostyrene started only after an induction period, but then proceeded with rather high rate. Addition of phenylacetylene reduced the rate of the hydrogen uptake.

2. It was confirmed, that the hydrogenation of internal alkynes (diphenylacetylene, 1-phenyl-prop-1-yne, 1-phenyl-but-1-yne) is significantly influenced by the pH.

In the hydrogenation of diphenylacetylene, the cis-stilbene appeared almost exclusively in acidic media, but in basic solutions the trans-stilbene and the diphenylethane appeared as major products with a higher conversion than what was reached in acidic solutions (Fig 3).

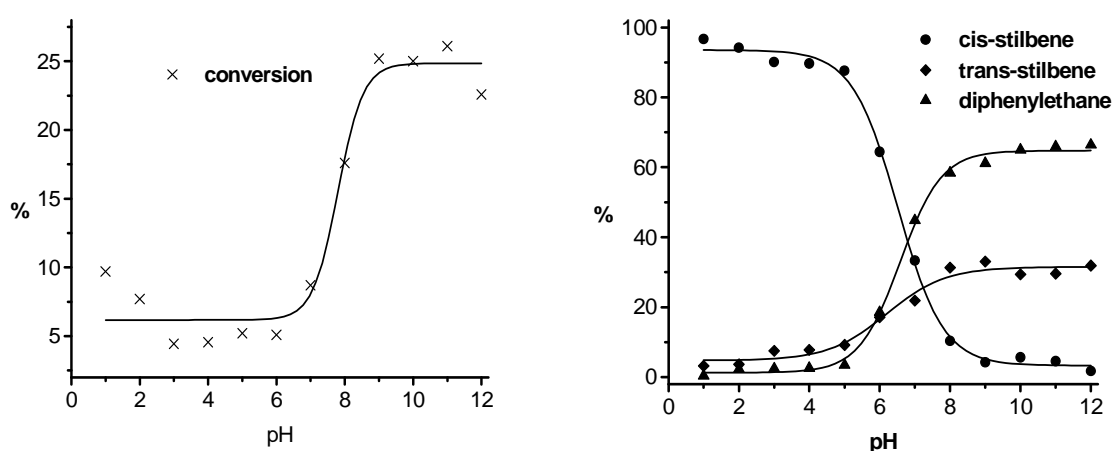


Fig 3. Hydrogenation of diphenylacetylene with $[\{RuCl_2(mtppps)_2\}_2]$ in aqueous/organic biphasic systems

$$n_{cat}=6.8 \times 10^{-3} \text{ mmol}, n_{substrate}=0.5 \text{ mmol}, V_{0.2 \text{ M phosphate buffer}}=2 \text{ mL}, V_{toluene}=1 \text{ mL}, p(H_2)=1 \text{ bar}, T=50 \text{ }^\circ\text{C}, t=3 \text{ h}$$

Similar to the case of diphenylacetylene, the hydrogenation of 1-phenyl-prop-1-yne and 1-phenyl-but-1-yne depends on the pH. In acidic solutions the cis- and trans-products appear mainly, whereas the products were trans-1-phenyl-prop-1-ene, trans-1-phenyl-but-1-ene, propylbenzene and butylbenzene in basic solutions. In the case of these two substrates, migration of the carbon-carbon double bond can occur, thus other isomers can appear.

3. It was proved, that the presence of iodide excess accelerates the hydrogenation of diphenylacetylene, and pH also plays a dominant role in the product distribution and conversion.

Hydrogenation of diphenylacetylene in the presence of iodide proceeded with a good yield. In acidic media the cis-stilbene appeared almost exclusively, furthermore the conversion was much higher, than in the systems without iodide. In basic media the products were trans-stilbene and the diphenylethane. Nevertheless, both the cis and trans products appeared at pH 9-10, thus in the presence of iodide, the cis/trans product switch shifts to higher pH (Fig 4).

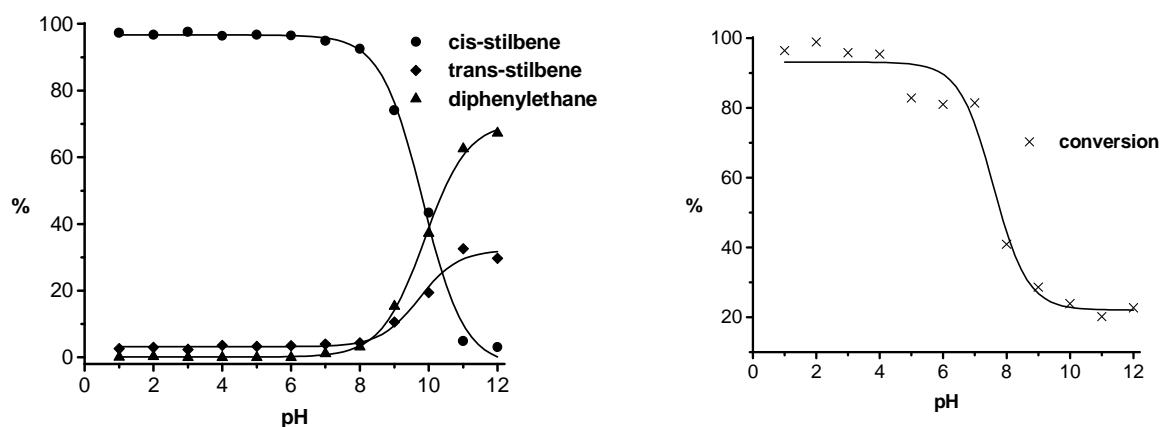
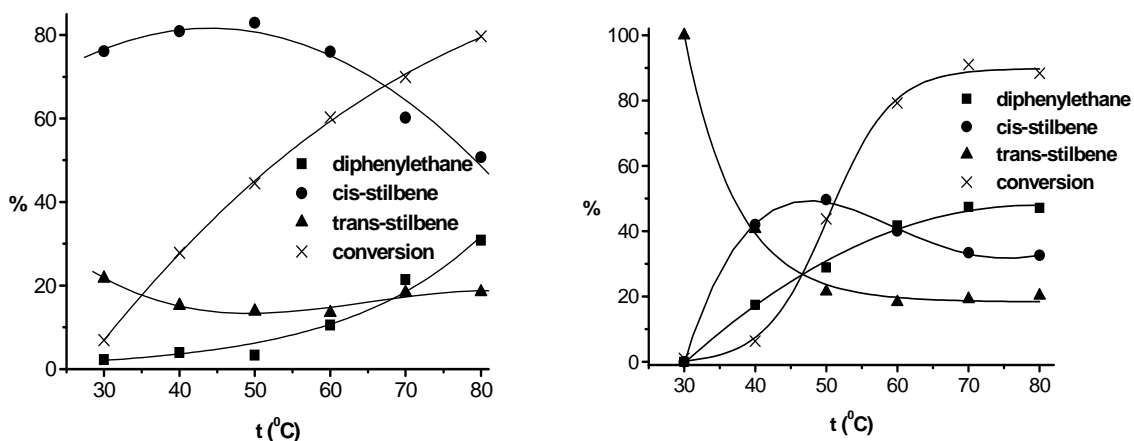


Fig 4. Hydrogenation of diphenylacetylene in the presence of iodide with $[\{RuCl_2(mtppms)_2\}_2]$ in aqueous/organic biphasic systems
 $n_{cat}=6.8 \times 10^{-3}$ mmol, $n_{substrate}=0.5$ mmol, $V_{0.2 \text{ M phosphate buffer}}=2$ mL, $V_{toluene}=1$ mL,
 $n_{NaI}=10 \cdot n_{cat}$, $p(H_2)=1$ bar, $T=50^\circ C$, $t=3$ h

4. It was established, that homogeneous phosphine complexes anchored on the surface of ion-exchangers also catalyse the hydrogenation of acetylenes.

$[\{RuCl_2(mtppms)_2\}_2]$ and $[RhCl(mtppms)_3]$ complexes were immobilized on different ion-exchangers (DEAE-Molselect, QAE-Sephadex, QAE-Lewatit). The anchored $[\{RuCl_2(mtppms)_2\}_2]$ complex catalysed the

hydrogenation of alkynes and the reduction was selective to the cis product (Fig 5). The immobilized $[\text{RhCl}(\text{mtppps})_3]$ complex also catalysed the hydrogenation of alkynes (Fig 5), but this catalyst, as most rhodium complexes, is a good catalyst for alkene hydrogenation, thus the saturated diphenylethane was the major product.



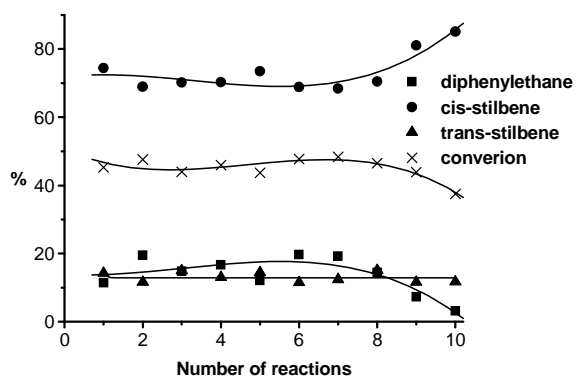
$[\{\text{RuCl}_2(\text{mtppps})_2\}_2]/\text{Molselect}$
catalyst

$[\text{RhCl}(\text{mtppps})_3]/\text{Molselect}$ catalyst

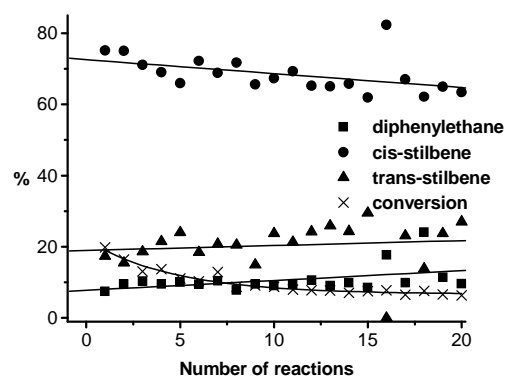
*Fig 5. The temperature dependence for the hydrogenation of diphenylacetylene in the H-Cube hydrogenation device
Substrate: 0.1 M diphenylacetylene solution, solvent: toluene:ethanol=1/1, eluent: 96 % ethanol, $p(\text{H}_2)=30$ bar*

5. It was determined, that a cartridge is able to catalyse the hydrogenation reactions several times. These immobilized complexes are reusable with no significant loss in activity.

Several catalyst-containing cartridges were applied for hydrogenation reactions in many runs. Neither $[\{\text{RuCl}_2(\text{mtppps})_2\}_2]$ immobilized on DEAE-Molselect, nor $[\text{RhCl}(\text{mtppps})_3]$ anchored on QAE-Lewatit lost its activity and selectivity after many reactions. This behaviour is shown in Fig 6.



$[\{\text{RuCl}_2(\text{mtppps})_2\}_2]/\text{Molselect}$ catalyst



$[\{\text{RuCl}_2(\text{mtppps})_2\}_2]/\text{Lewatit}$ catalyst

Fig 6. Investigation of stability of anchored complexes
 Substrate: 0.1 M diphenylacetylene solution, solvent: toluene/ethanol=1/1,
 eluent: 96 % ethanol

6. It was determined, that there is no significant difference in the turnover frequencies of the catalyst in different reaction systems (homogeneous, heterogeneous suspension and heterogenous flow systems).

Hydrogenation of diphenylacetylene was examined in the H-Cube hydrogenation device and in pressure-resistant glass equipment in suspension. The catalytic activity was compared with the results obtained in homogeneous systems and the data are summarized in Table 1. It can be seen, that the TOF values in the different systems do not differ significantly from each other. Nevertheless, the carbohydrate-based ion-exchangers (QAE-Sephadex, DEAE-Molselect) were more active than the catalysts anchored catalysts on styrene-divinylbenzene copolymers (QAE-Lewatit).

Table 1. The comparison of the different hydrogenation methods

Catalyst	TOF (h ⁻¹)		
	Suspension	H-Cube	Homogeneous system
Ru-tppms/DEAE-Molselect	10.0	7.3	6.6
Ru-tppms/QAE-Sephadex	12.8	10.8	
Ru-tppms/QAE-Lewatit	8.4	2.8	
Reaction conditions	50 °C, p(H ₂)=10 bar Solvent: toluene/ethanol =1/1	50 °C p(H ₂)=30 bar Solvent: toluene/ethanol =1/1 Eluent: 96 % ethanol	50 °C p(H ₂)=1 bar Solvent: water/toluene =2/1 pH=10

7. Several new Ru(II) and Rh(I) complexes of *Bzl-pta*⁺*Cl*⁻ and *Me-pta*⁺*I*⁻ were prepared, and their structures were elucidated.

[RuCl₂(H₂O)(Bzl-pta)₃]Cl₃, [RuI₂(H₂O)(Me-pta)₃]I₃, [RhI(Me-pta)₃]I₃ and [{RhI₂(Me-pta⁺)₂}] were synthesized from RuCl₃×3H₂O and RhCl₃×3H₂O in the presence of an excess of the corresponding ligand in 96 % ethanol at reflux temperature. In the case of the *Me-pta*⁺*I*⁻ NaI excess was applied. The compositions of the complexes were determined by elemental analyses (combustion and ICP-OES methods), and the structures were characterised by ³¹P-NMR measurements.

8. It was established, that $[RuCl_2(H_2O)(Bzl-pta)_3]Cl_3$, $[RuI_2(H_2O)(Me-pta)_3]I_3$ and $[RhI(Me-pta)_3]I_3$ catalyse the hydrogenation of phenylacetylene; with the rhodium complex, the hydrogenation of diphenylacetylene proceeded, too.

$[RuCl_2(H_2O)(Bzl-pta)_3]Cl_3$ and $[RuI_2(H_2O)(Me-pta)_3]I_3$ complexes catalyse the hydrogenation of phenylacetylene, and the pH has a great influence on the reaction (Fig 7). In acidic solutions 8-10 % conversions were reached, but in basic media (pH=10-12) the conversion got up to 30 %. The reduction was selective to styrene, this was the main product (around 80 %). The activity of the $[RhI(Me-pta)_3]I_3$ complex was much higher; although in acidic solutions the conversion was still low, but in basic media it increased up to 100 %. Hydrogenation of diphenylacetylene and 1-phenyl-prop-1-yne took place only with the Rh catalyst, at high pH (pH=10-12).

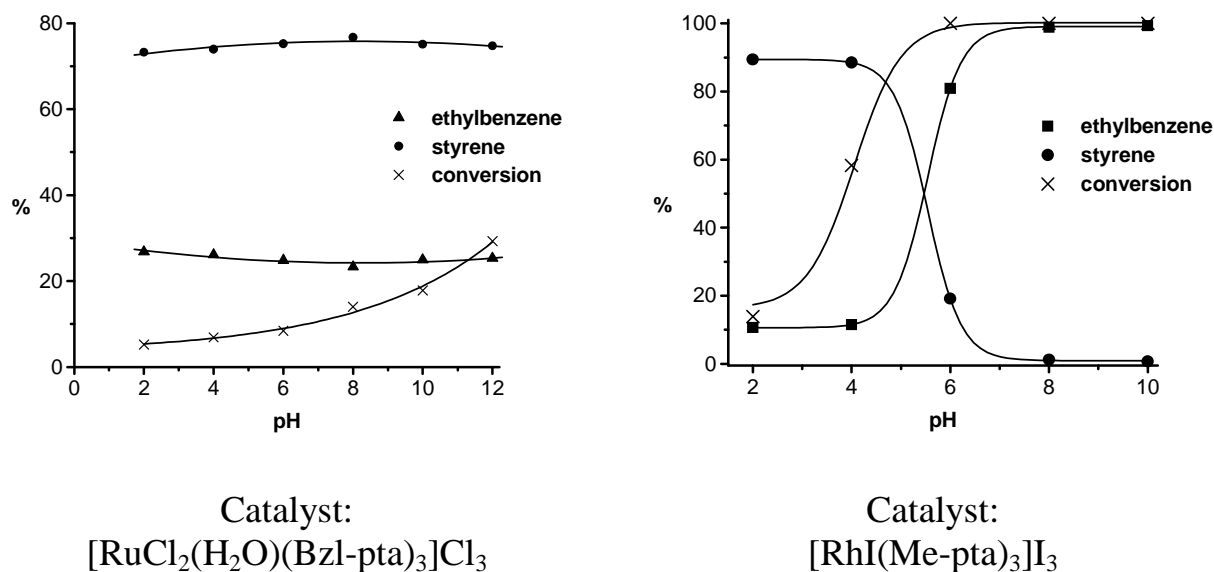


Fig 7. Hydrogenation of phenylacetylene with complexes of pta derivatives
 $n_{cat}=9.5 \times 10^{-3}$ mmol, $n_{substrat}=0.25$ mmol, $V_{0.2 \text{ M phosphate buffer}}=2$ mL, $V_{toluene}=1$ mL,
 $T=80$ °C, $p(H_2)=10$ bar, $t=3$ h

9. It was demonstrated, that $[\text{RuCl}_2(\text{H}_2\text{O})(\text{Bzl-pta})_3]\text{Cl}_3$, $[\text{RuI}_2(\text{H}_2\text{O})(\text{Me-pta})_3]\text{I}_3$ and $[\text{RhI}(\text{Me-pta})_3]\text{I}_3$ catalyse the hydrogenation of *trans*-cinnamaldehyde.

The Rh-based complex was much more active in this case too, than the Ru ones, and higher conversions were reached at higher pH. In addition, $[\text{RuCl}_2(\text{H}_2\text{O})(\text{Bzl-pta})_3]\text{Cl}_3$ and $[\text{RuI}_2(\text{H}_2\text{O})(\text{Me-pta})_3]\text{I}_3$ complexes selectively produced the cinnamyl alcohol, thus the carbon-oxygen double bond was hydrogenated. The $[\text{RhI}(\text{Me-pta})_3]\text{I}_3$ complex hydrogenated first the carbon-carbon double bond, but in basic solutions hydrogenation of the aldehyde function took place too, and the fully saturated hydrocinnamyl alcohol appeared as main product.

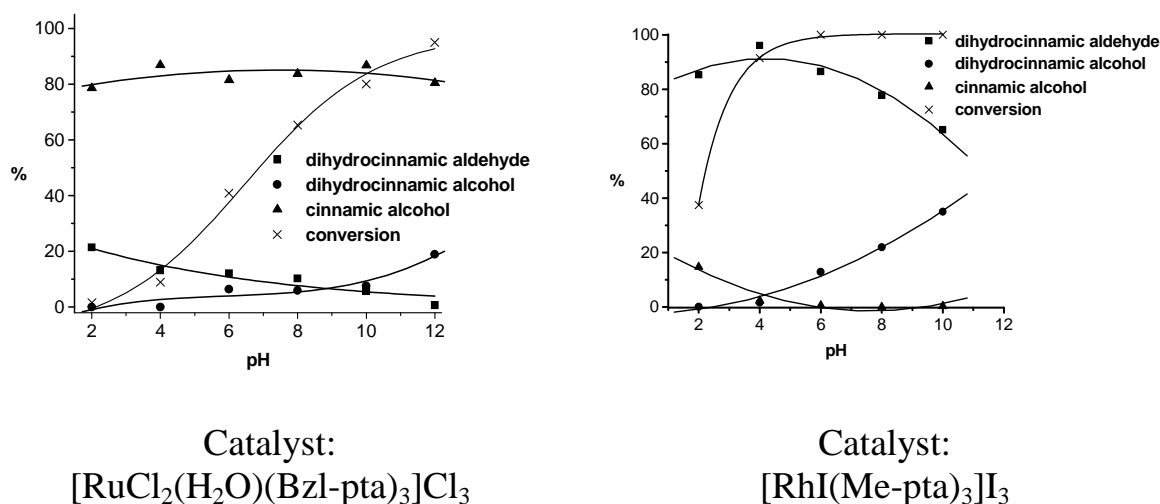


Fig 8. Hydrogenation of *trans*-cinnamaldehyde with complexes of pta derivatives

$n_{\text{cat}}=9.5 \times 10^{-3}$ mmol, $n_{\text{substrate}}=0.25$ mmol, $V_{0.2 \text{ M phosphate buffer}}=2$ mL, $V_{\text{toluene}}=1$ mL, $T=80$ °C, $p(\text{H}_2)=10$ bar, $t=3$ h

10. Under a hydrogen atmosphere, $[RhI(Me-pta)_3]I_3$ catalyse the hydrogenation of oct-1-ene-3-one, while under argon, redox isomerization to octan-3-one is observed.

In hydrogen atmosphere (1 bar and 10 bar H_2 pressure) $[RhI(Me-pta)_3]I_3$ catalyse the hydrogenation of oct-1-ene-3-ol. In acidic media the hydrogen uptake was slower, but in neutral and basic solutions almost 100 % conversion was reached, with octan-3-ol as sole product. Under argon the isomerization took place to octan-3-one.

List of publications

Articles connected to the topic of this thesis:

1. H. H. Horváth, F. Joó, Stereoselective Homogeneous Catalytic Hydrogenation of Disubstituted Alkynes in Aqueous-Organic Biphasic Media, *React. Kinet. Catal. Lett.*, **85** (2005) 355-360
2. H. H. Horváth, G. Papp, Cs. 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.*, **8** (2007) 442-446

Posters and oral presentations at conferences:

1. Ferenc Joó, Henrietta Horváth, Selective hydrogenation of alkynes in aqueous-organic biphasic systems, *Knowledge-based Materials and Technologies for Sustainable Chemistry* (Tallin, 2005)
2. Henrietta Horváth, Homogeneous hydrogenation of acetylenes in biphasic systems, *First Year Acquachem Meeting* (Lisszabon, 2005)
3. Henrietta H. Horváth, Ferenc Joó, Selective catalytic hydrogenation of disubstituted alkynes, *XVI. FECHM Conference on Organometallic Chemistry* (Budapest, 2005)

4. Horváth H. Henrietta, Joó Ferenc, Catalytic properties of ionic Ru(II)- and Rh(I) complexes in aqueous/organic biphasic systems and on ion-exchanger supports (in Hungarian), *XLII. Komplexkémiái Kollokvium* (Mátrafüred, 2007)

5. Henrietta H. Horváth, Péter Juhász, Ferenc Joó, Ágnes Kathó, Synthesis and Catalytic Properties of Rh(I) and Ru(II) Complexes of Alkylated Phosphotriazaadamantanes, *3rd International Conference on Green and Sustainable Chemistry* (Delft, 2007)