PhD Thesis

Synthesis of water-soluble Ru(II)- and Rh(I)-phosphine complexes and their application in biphasic catalysis

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1. Introduction and objectives

The ideal catalyst is selective, active under mild conditions and it's easy to separate from the products what allows its repeated use in catalytic processes. The first two features are more typical of homogeneous catalysts, conversely the latter is the main advantage of heterogeneous catalysts. Scientists all over the world try to combine the advantages of the two different types of catalysts.

One of the options to solve this problem is dissolving the catalyst in a solvent (for example in water) in which the organic substrate is very slightly soluble or insoluble. The catalytic reaction only occurs when using intense stirring, then setting aside the reaction mixture gives the opportunity to separate the phases. In the ideal case the organic phase contains the product(s) and the aqueous phase contains the catalyst. The foundations of aqueous-organic biphasic catalysis were developed at the Department of Physical Chemistry at University of Debrecen. It was shown that the water-soluble analogue of the widely used Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, i.e $[RhCl(m\text{tppms-Na})_3]$ was active in the hydrogenation of unsaturated carboxylic acids in water. Many hydrogenation reactions were examined using $[RhCl(PPh_3)_3]$ in organic solutions or $[RhCl(m\text{tppms-Na})_3]$ in water, but only a limited number of studies compared the catalytic properties of the mono- and the biphasic systems. The reduction of sorbic acid (*trans-trans*-hexa-2,4-dienoic acid) has important practical aspects, because the partially saturated derivatives and their esters are utilized by the cosmetics industry. *One of the aims of my work was to study the reaction conditions which can lead to increase the amount of 2-hexenoic acid in the reaction using Rh(I)-triphenylphosphine complexes.*

Triphenylphosphine and their derivatives are air-sensitive. In contrast, the tricyclic phosphine, 1,3,5-triaza-7-phosphaadamantane (pta), developed as a flame retardant compound, is air-stable so use of inert atmosphere is not necessary. Another important difference is, that triaryl and trialkyl phosphines can form phosphonium salts in reaction with alkyl halides, while pta undergoes N-alkylation. The sulphonated triphenylphosphines form phosphonium salts with unsaturated carboxylic acids, too, which raises the question, *whether pta and activated olefins yield phosphonium salts or not.*

Several of N-alkylated pta derivatives are known, but just a few of them contain groups in their side-chain which are suitable for further functionalization. *In my work I prepared some new N-alkylated (positively charged) pta derivatives and studied their interactions with the negatively charged* m*tppms ion.*

Mono- and binuclear Ru(II)-complexes have been synthesized with pta derivatives. Both the well-known *trans*-$[RuCl_2(pta)_4]$ and $[RuCl_2(dmso)_4]$ are light-sensitive and *this indicated the necessity to study the photoinduced changes of* $[RuCl_2(dmso)_2L_2]$ *(L = pta or its N-alkylated*

derivatives) synthesised during this work. Another aim was to investigate the catalytic activity of these new complexes in the reduction of aldehydes and redox isomerisation of allylic alcohols.

2. Applied experimental techniques

The ligands and their complexes were prepared under inert atmosphere via Schlenk-techniques. All catalytic experiments were carried out in the absence of air. In the case of elevated hydrogen pressures (2-10 bar) heavy-walled glass tube reactors were applied.

Identification of the new complexes was carried out by multinuclear (^{1}H-, ^{13}C-, ^{31}P-, and ^{19}F-) NMR spectroscopy on a BRUKER DRX 360 and a BRUKER AVANCE DRX 300 equipment. The redox isomerization reactions of the water-soluble allylic alcohols were followed by ^{1}H-NMR spectroscopy.

The ESI-MS experiments were carried out using BRUKER BioTOF II ESI-TOF and VG Autospec mass spectrometers. Elementary analyses were done on an Elementar Vario Micro (CHNS) equipment.

Single-crystal X-ray diffraction data were collected on an Enraf Nonius MACH3 four-circle diffractometer with Dr. Attila Bényei's collaboration. The structures of $[RuCl_3(pta\text{-}H)_3]Cl_2$ and $[(pta)_3Ru(\mu\text{-}Cl)_3Ru(pta)_3]Cl$ were determined by Dr. Sonia Manas (University of Almeria, Spain) on a Bruker APEX CCD diffractometer.

IR spectra were recorded on a Perkin Elmer Instruments Spectrum One FT-IR spectrometer equipped with Universal ATR Sampling Accessory.

The reaction mixtures were analyzed on HEWLETT-PACKARD 5890 Series II and Agilent 7890A type gas chromatographs using Chrompack WCOT Fused Silica 30 m×32 μm and CP WAX52CB columns.

The photochemical experiments were carried out in a photoreactor developed at the University of Almeria (Spanish Patent: P200200835 ES 2206017 A1 2004.) equipped with 150 W power halogen light source. At the University of Debrecen the solutions were thermostated and stirred in a reaction vessel illuminated by 150 W power halogen lamp (Osram, 64640HLX).

The pH of the solutions was determined by a Radelkis OK-117 pH meter. The UV-VIS spectra were recorded on a Jasco V-650 spectrophotometer.

List of abbreviations

Cinnamaldehyde: (2E)-3-phenylprop-2-enal

Cinnamylalcohol: (2E)-3-phenylprop-2-en-1-ol

Cp: cyclopentadienyl

dmso: dimethyl sulfoxide

Fumaric acid: *trans*-butenedioic acid

Hydrocinnamaldehyde: 3-phenylpropionaldehyde

Malic acid: *cis*-butenedioic acid

PPh_3: triphenylphosphine

Sorbic acid: *trans-trans*-hexa-2,4-dienoic acid

THF: tetrahydrofuran

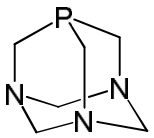
TOF: turnover frequency (h^{-1})

(*m*tppms-Na): Sodium diphenylphosphinobenzene-3-sulfonate

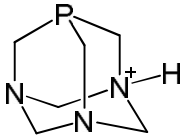
(*m*tppts Na_3): Na salt of tris(3-sulfophenyl)phosphine

$C_{10}H_{14}$: *p*-cymene (1-methyl-4-isopropylbenzene)

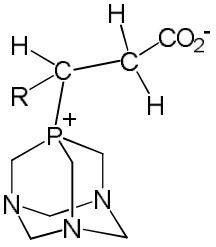
Phospha-urotropines



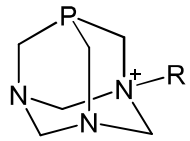
pta: 1,3,5-triaza-7-phosphatricylo-[3.3.1.1]decane



pta-H: 1-azonia-3,5-diaza-7- phosphatricylo -[3.3.1.1]decane



pta-Bor: R = COOH
pta-Glut: R = CH_2COOH



pta-Me: R = $-CH_3$

pta-Ethyl: R = $-CH_2-CH_3$

pta-Propyl: R= $-(CH_2)_2-CH_3$

pta-Butyl: R = $-(CH_2)_3-CH_3$

pta-Hexyl: R = $-(CH_2)_5-CH_3$

pta-Bn: R = $-CH_2C_6H_5$

pta-EtOH: R = $-CH_2-OH$

pta-EtOAc: R = $-CH_2-CO_2-CH_2-CH_3$

3. New scientific results

I. Hydrogenation of sorbic acid in mono- and biphasic systems with $[RhCl(PPh_3)_3]$ and its water soluble derivative

Hexanoic acid had been reported in the literature as the only product resulting from the hydrogenation of sorbic acid in benzene catalyzed by $[RhCl(PPh_3)_3]$. It was shown in this work that under conditions presented in *Table 1*. *trans*-hex-2-enoic acid is also formed in significant quantities.

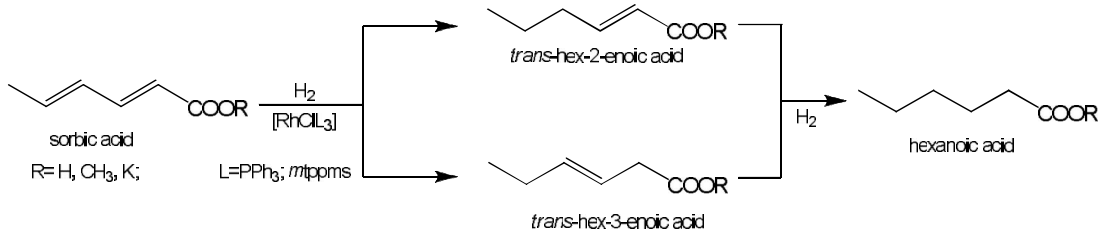


Figure 1.: Hydrogenation of sorbic acid

According to the literature in hydrogenation of dienoic carboxylic acids with isolated C=C bonds, water increases the selectivity towards monoolefinic products (*Figure 1*).

In the case of sorbic acid, containing conjugated C=C bonds, the observation was contradictory. The experiments presented here showed that addition of water decreased both the conversion and the selectivity (*Table 1.)*

Table 1. Hydrogenation of sorbic acid by $[RhCl(PPh_3)_3]$ in ethyl acetate

V_{Water} / V_{EtOAc}	conversion (%)	products (%)		
		***trans*-hex-2-enoic acid**	***trans*-hex-3-enoic acid**	**hexanoic acid**
0	**51**	**36**	**1**	**14**
1	**20**	**8**	**1**	**11**

0,01 mmol catalyst in 5 mL EtOAc, T = 40 °C, t = 1 h, [subs.]/[cat.] = 18, $p(H_2)$ = 1 bar

Independent experiments proved that *trans*-hex-3-enoic acid underwent a much faster hydrogenation than *trans*-hex-2-enoic acid, consequently hexanoic acid appearing at the beginning of the reactions is formed on this route.

The unfavorable effect of water can be interpreted as follows. Sorbic acid becomes partially deprotonated, and not only the olefinic but also the carboxylate group becomes temporarily coordinated to the Rh(I)-ion.

This assumption is supported by the fact that the water content of ethyl acetate influences significantly the hydrogenation of acids and the respective esters. Acids containing carboxylic ions

capable of forming coordination bonds (sorbic acid, 2- and 3-hexenoic acid) undergo slower hydrogenation than their respective ester derivatives (*Table 2.).*

Table 2.: Effect of water on the hydrogenation of sorbic acid and its methyl-ester

substrate	conversion (%)	products (%)		
		trans*-hex-2-enoic acid / *ester	***trans*-hex-3-enoic acid / *ester***	**hexanoic acid/*ester***
sorbic acid	**51**	**36**	**1**	**14**
sorbic acid metylester	***70***	***39***	***trace***	***31***

0,01 mmol [$RhCl(PPh_3)_3$] catalyst in 5 ml EtOAc, t = 1 h, T = 40 °C, [subs.]/[cat.]=18; 5 ml water; $p(H_2)$ = 1 bar

It was found that hydrogenation of sorbic acid dissolved in ethyl acetate by [$RhCl(PPh_3)_3$] showed almost identical conversion and selectivity to reduction of K-sorbate by [RhCl(*m*tppms--Na)$_3$].

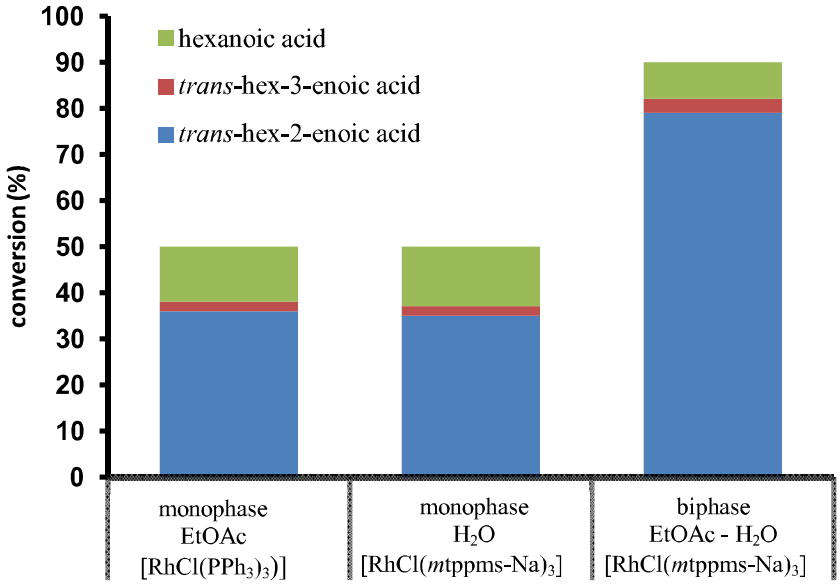


Figure 2: Comparison of the mono- and biphasic systems

t = 1 h; T = 40 °C; n_{Ru} = 0.01 mmol; [subs.]/[cat.] = 18; $p(H_2)$ = 1 bar;
$V_{monophase}$ = 5mL EtOAc or 5mL H_2O; $V_{biphase}$ = 5 ml EtOAc + 5mL H_2O

Experiments were also carried out in biphasic systems. While in ethyl acetate [$RhCl(PPh_3)_3$] did not catalyse the hydrogenation of aqueous K-sorbate at all, sorbic acid hydrogenation in aqueous-organic biphasic system by [RhCl(*m*tppms-Na)$_3$] was faster than in both monophasic reactions (*Figure 2.*).

The selectivity for *trans*-hex-2-enoic acid also increased. A possible explanation for this is that the *trans*-hex-2-enoic acid finds a temporary shelter from hydrogenation in the organic phase until the much more reactive sorbic acid disappears.

II. 1,3,5-triaza-7-phosphaadamantane (pta) derivatives

1./ Reaction with acids

1.1. Reaction with unsaturated carboxylic acids

a./ It was shown for the first time, that in aqueous media maleic anhydride, maleic- and glutaconic acids undergo addition to the P-atom of pta with their double bonds. The identification of the phosphonium salts were carried out by ^{1}H-, ^{31}P-, ^{13}C-NMR spectroscopy and their composition were determined by elemental analysis.

The molecular structures of the zwitterionic compounds in solid-state were confirmed by single crystal X-ray diffraction (*Figure 3*).

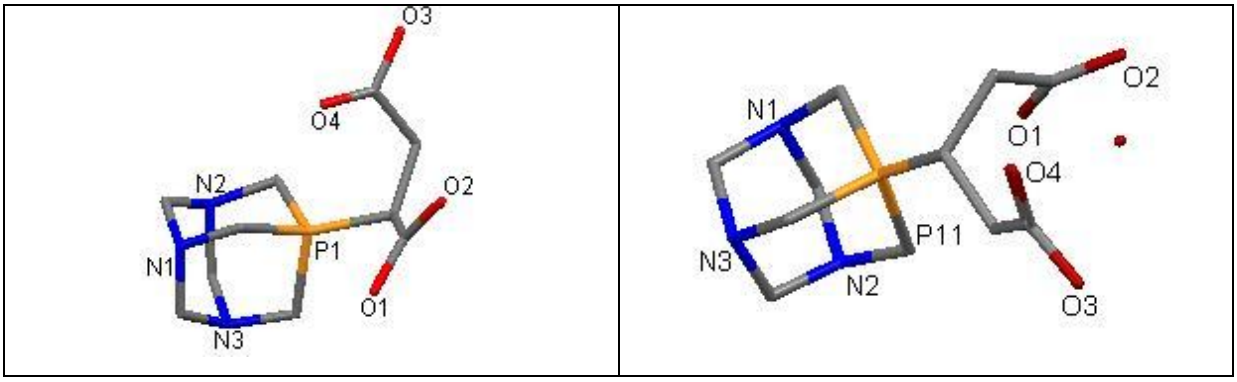


Figure 3:*Phosphonium salts of pta formed with maleic and glutaconic acids*

It was shown that with maleic acid the addition was complete already in 3 hours, however when it was replaced with its isomer, fumaric acid - the reaction reached only 20 % conversion after one week.

It was pointed out, that the N-alkylated and the N-protonated derivates of pta cannot form phosphonium salts neither with anhydrides nor with acids. Theoretical calculations (density functional theory [DFT] method with B3LYP functional and 6-31g*(d), 6-311+g**(d,p) basis set) proved that the formation of quaternary nitrogen reduce the electron density of phosphorous atom, therefore the formation of P-C bond becomes unfavorable.

b./ The coordination polymer formed in the reaction of $Ag(CF_3SO_3)$ with the adduct of pta and glutaconic acid is not light-sensitive. Remarkably, Ag(I) ions of the polymers are coordinated not only to the N- or O-atoms of phosphonium salt, but silver-silver bonds also can be detected. (*Figure 4*).

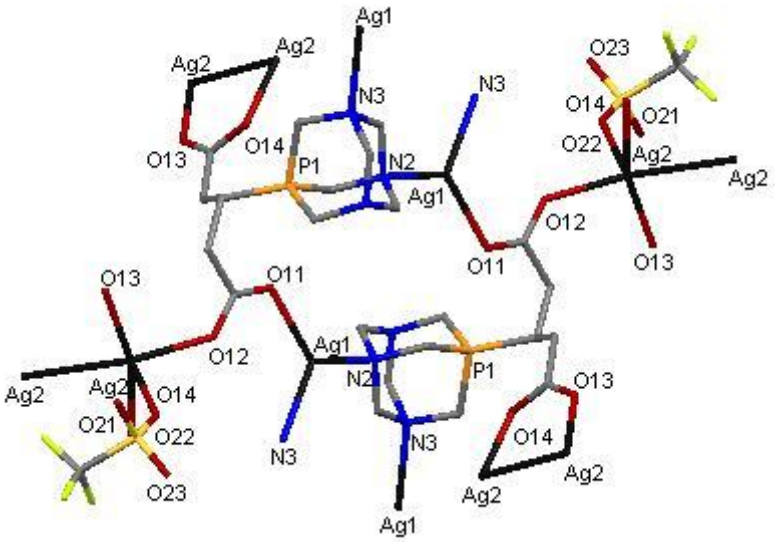


Figure 4: Structure of silver ions and phosphonium salts of pta with glutaconic acid

1.2. Reaction with *cc*. HBr

It is generally accepted, that only one of the three nitrogen atoms of pta can be protonated. In my work it was proved, that the treatment of pta with *cc*. HBr leads to the triply protonated (pta-H_3)Br_3. Solid state structure of this compound was also determined.

It was well-known, that the ring system of pta can be opened with *cc*. HBr treatment, but the structure of (P{CH_2NH_3}$_3$)Br_3 or its oxidized form were not determined previously. The latter salt was separated and characterized by single X-ray diffraction (*Figure 5*).

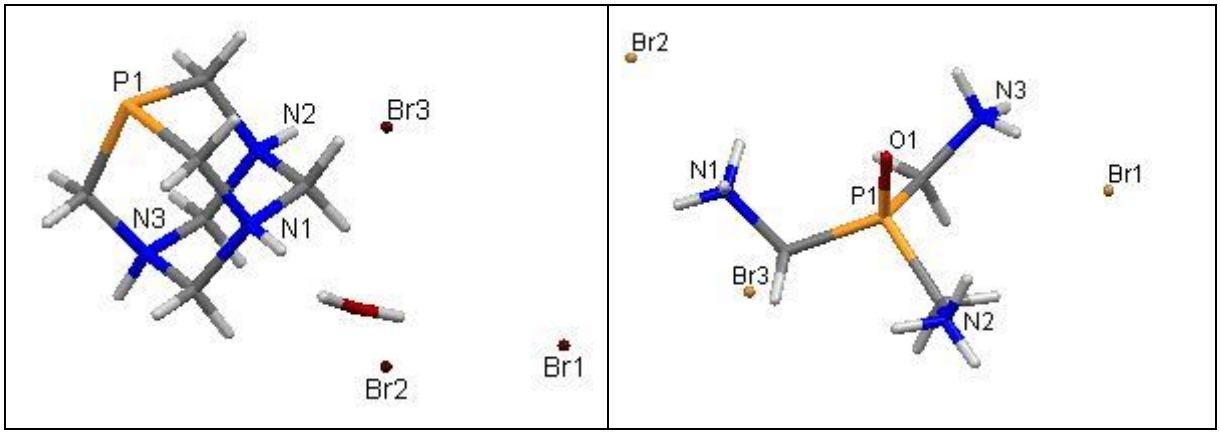


Figure 5: Structure of (pta-H_3)Br_3*H_2O and (O=P{CH_2NH_3}$_3$)Br_3

2./ N-alkylated phospha-urotropin derivatives

2.1. Reaction with alkyl halides

Four new, N-alkylated phospha-urotropin derivatives were synthesized from the reaction of pta with appropriate alkyl halides (hexyl bromide, 1,4-dibromobutane, 2-bromoacetic acid ethyl ester, 2-hydroxyethyl bromide) (*Figure 6.*).

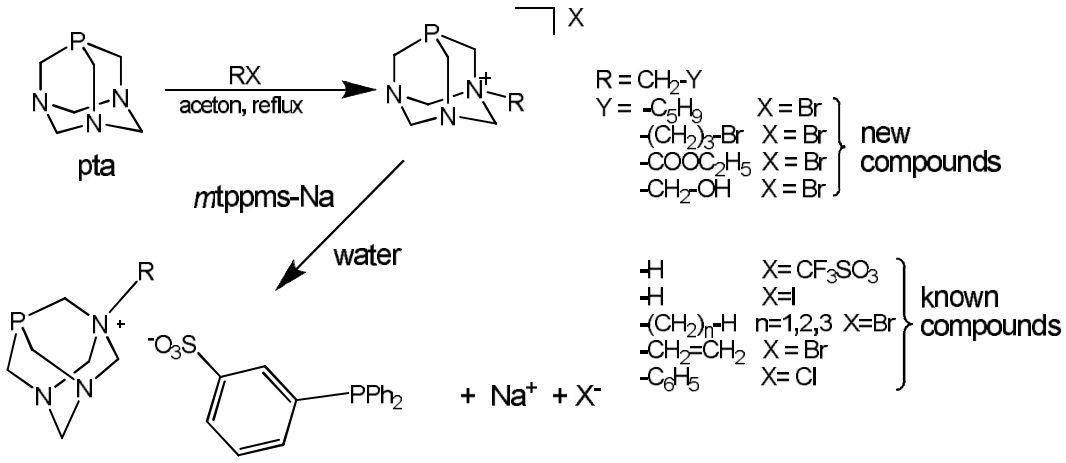


***Figure 6*:** N-alkylated pta derivatives

The identification of the new compounds was carried out by ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy and by elemental analysis. Solid state structure of three of them (R = CH_2CH_2OH, C_4H_9Br, $CH_2COOC_2H_5$) were determined by single crystal X-ray diffraction.

Spontaneous resolvation was observed in the case of (pta-R)Br (R = 4-bromobutyl) according to its X-ray diffraction structure. It was determined, that pseudochiral N-alkylated pta formed a chiral lattice with a bromide counter ion. The space group of the crystal is chiral ($P2_12_12_1$ No. 19) and Z'=1, so the asymmetric unit contains only one ion pair. It implies that an enantiomorph crystal conglomerate was obtained. Both enantiomeric forms were isolated and their conformation was determined by single crystal X-ray diffraction (*Figure 7*).

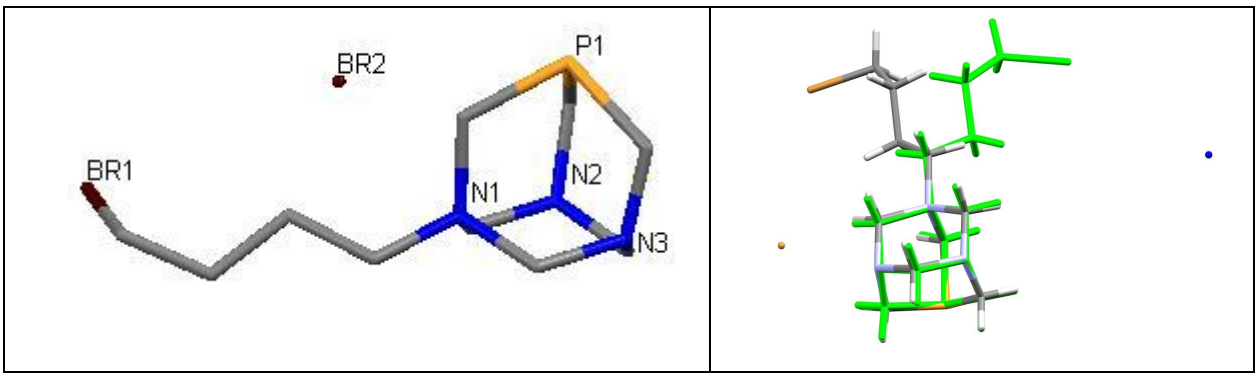


***Figure 7*:** Structure of (4-bromobutyl-pta)Br

I observed the same phenomenon while working with N-alkylated derivative, prepared from 2-bromoacetic acid ethyl ester.

It was confirmed, that alkylation of pta with 1,4-dibromobutane did not lead to a bisphosphine product, even using large excess of the phosphine. However, using 1,4-bis-chloromethylbenzene and a twofold excess of pta yielded the corresponding bisphosphine (*Figure 8.*).

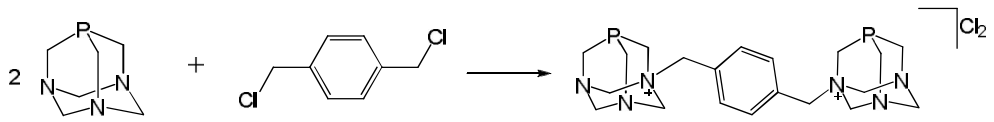


Figure 8: Preparation of a water-soluble bisphosphine

Alkylation of pta with benzyl chloride was carried out according to the literature. The single crystals of N-benzylated derivatives were obtained from both aqueous and methanolic solutions.

2.2. Water-soluble phosphine ion-pairs

Adding anequimolar amount of *m*tppms-Na to the aqueous solution of both new and known (pta-R)X compounds (shown in Figure 4) resulted in white precipitates, when R = butyl, 4-bromobutyl, hexyl and benzyl. The structure of (pta-R)(*m*tppms) organic salts was determined by X-ray crystallography (*Figure 9.*).

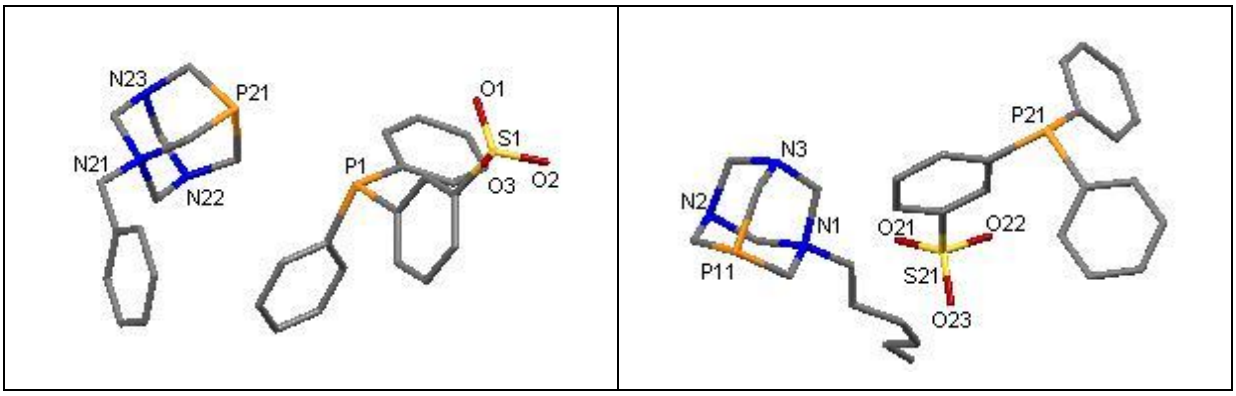


Figure 9: Structure of (pta-R)(*m*tppms) salts (R = Bn, C_4H_9Br)

III. Synthesis of Ru(II)-complexes containing phosphatriazaadamantane and its derivatives

1.Source of Ru: [{(η^6-$C_{10}H_{14}$)$RuCl_2$}$_2$]

1.1. Reactions with (pta-R)(*m*tppms) salts

The first synthesis of [(η^6-$C_{10}H_{14}$)RuCl(pta-Bn)(*m*tppms)]Cl has been described in this work. In the first step of the stepwise complex formation [(η^6-$C_{10}H_{14}$)$RuCl_2$(pta-Bn)]Cl was obtained in the reaction of (pta-Bn)Cl and [{(η^6-$C_{10}H_{14}$)$RuCl_2$}$_2$]. Then a methanolic solution of this compound and an equivalent amount of *m*tppms-Na was refluxed to yield [(η^6-$C_{10}H_{14}$)RuCl(pta-Bn)(*m*tppms)]Cl containing two different phosphine ligands. The molecular structure was not determined for this compound by single crystal X-ray diffraction, however it was obtained for [(η^6-$C_{10}H_{14}$)$RuCl_2$(pta--Bn)]Cl.

A one-step synthesis of [(η^6-$C_{10}H_{14}$)RuCl(pta-Bn)(*m*tppms)]Cl by refluxing (pta-Bn)(*m*tppms) and [{(η^6-$C_{10}H_{14}$)$RuCl_2$}$_2$] in methanol was also found possible (concentrations of the reactants: [Ru] = [pta-Bn] = [*m*tppms]) (*Figure 10.*).

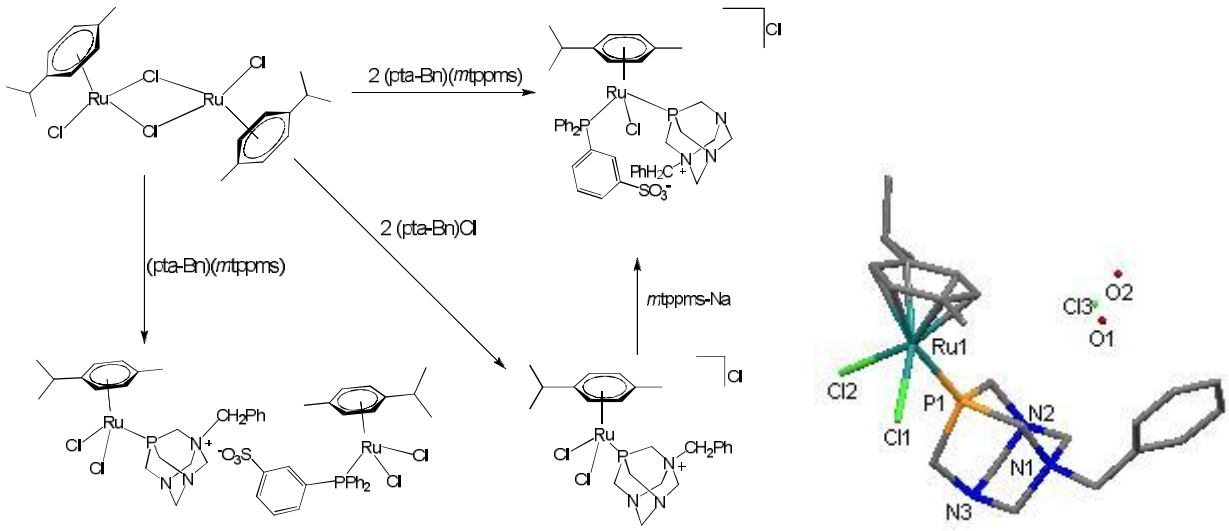


Figure 10: Half-sandwich Ru(II) complexes containing water soluble phosphine ion pairs

The reaction of [{(η^6-$C_{10}H_{14}$)$RuCl_2$}$_2$] and equimolar (pta-Bn)(*m*tppms) resulted in formation of [(η^6-$C_{10}H_{14}$)$RuCl_2$(*m*tppms)]$^-$ and [(η^6-$C_{10}H_{14}$)$RuCl_2$(pta-Bn)]$^+$ ions known from the literature. At room temperature or at reflux this solution did not change its composition. Similar reactions were carried out using (pta-Butyl)(*m*tppms) and (pta-Hexyl)(*m*tppms) salts producing slightly water soluble [(η^6-$C_{10}H_{14}$)$RuCl_2$(pta-R)][(η^6-$C_{10}H_{14}$)$RuCl_2$(*m*tppms)] salts.

1.2. Reaction with {(pta)-CH_2-C_6H_4-CH_2-(pta)}Cl_2

Reaction of the chloride salt of {(pta)-CH_2-C_6H_4-CH_2-(pta)} with equimolar [{(η^6--$C_{10}H_{14}$)$RuCl_2$}$_2$] resulted in a binuclear complex, where two [{(η^6-$C_{10}H_{14}$)$RuCl_2$}$_2$] units are linked by the phosphine as a bridging ligand (*Figure 11.*). The composition and the structure of this complex was proved by elemental analysis and ^{1}H-, ^{13}C-, ^{31}P-NMR and ESI-MS, respectively.

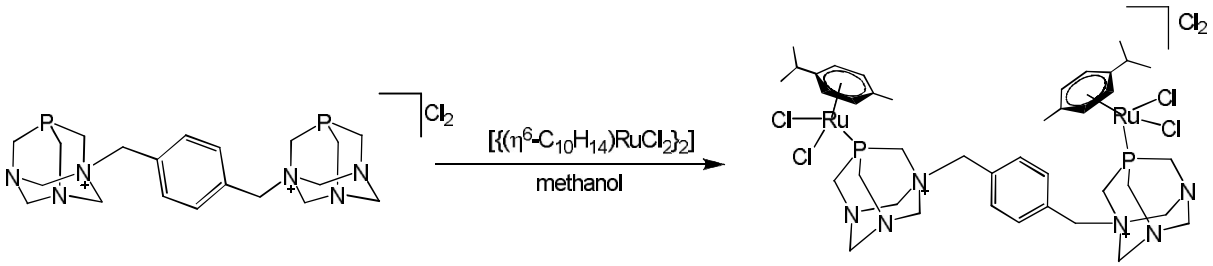


Figure 11: Synthesis of binuclear Ru(II)-complex

It was also shown that the same product was formed even when the ligand was present in large excess, i.e. no mononuclear complex was detected in the reaction mixture.

2. Ru-source: [$RuCl_2(PPh_3)_3$]

The [$RuCl_2(H_2O)(pta)_3$], only produced in situ in previous works, was obtained in crystalline form. The compound yielded by ligand exchange between [$RuCl_2(PPh_3)_3$] and pta was characterized in detail; its structure was determined by multinuclear NMR and ESI-MS, while its composition was assessed by elemental analysis. One nitrogen atom of each phosphine ligand of [$RuCl_2(H_2O)(pta)_3$] complex is protonated in 0.1 M HCl solution. The resulting [$RuCl_3(pta\text{-}H)_3$]Cl_2 was separated as single crystals and its structure analyzed (*Figure 12.*). The structure of $[RuCl_3(pta\text{-}H)_3]^{2+}$ cation is a distorted octahedron similar to the case of $[RuCl_3(pta\text{-}Me)_3]^{2+}$ known from the literature: P_{trans}-Ru-P_{trans} is nonlinear (bond angle 166.145°) and the bond distances between Ru-P_{trans} (2.335 Å) are higher than between Ru-P_{cis} (2.223 Å). Cl4 and Cl5 chloride ions are half occupied therefore there are five halogen ions per Ru(II) ion in the unit cell.

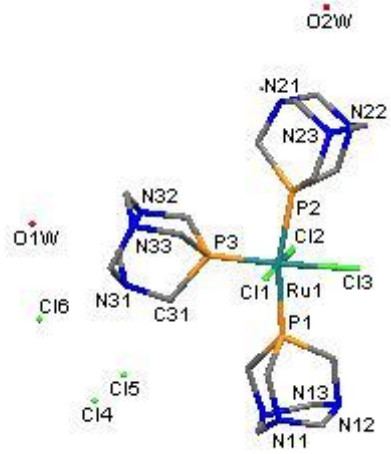


Figure 12: Structure of $[RuCl_3(pta\text{-}H)_3]Cl_2$

UV-VIS and ^{31}P-NMR analyses proved that $[RuCl_2(H_2O)(pta)_3]$ is able to coordinate one more pta in aqueous solution (the reaction was carried out protected from light as the complex is photosensitive) resulting in the formation of the known *trans*-$[RuCl_2(pta)_4]$. Synthesis of consistent products was unsuccessful in the case of other water-soluble phosphines like Na(*m*tppms), (pta--Me)CF_3SO_3, (pta-Bn)Cl.

3. Ru source: $[RuCl_2(dmso)_4]$

3.1. The synthesis of *cis-cis-trans*-$[RuCl_2(dmso)_2L_2]$ complexes (L = pta, (pta-Me)CF_3SO_3, (pta--Bn)Cl)

In chloroform solutions, room temperature is sufficient to substitute *trans* positioned dmso ligands of $[RuCl_2(dmso)_4]$ with pta (*Figure 13*) . *Cis-cis-trans*-$[RuCl_2(dmso)_2(pta)_2]$ can also be produced when the reaction partners are dissolved in water. In this environment not only pta can replace two dmso ligands, but also its N-metyl (pta-Me) and N-benzyl (pta-Bn) derivatives undergo such reaction. This behavior is surprising since there is no literatural data on charged Ru(II)-dmso complexes. The compounds produced were characterized by ^{1}H-, ^{31}P-, ^{13}C-NMR- and ESI-MS spectroscopy. Their composition was proved by elemental analysis.

UV-VIS spectroscopy proved that $[RuCl_2(dmso)_2(pta)_2]$ is the only product when the ratio of [pta] to [Ru] is less or equal than 2, but higher ligand ratios and longer reaction times lead to incorporation of an additional phosphine to Ru(II) ion.

The reaction product in chloroform is the known *trans*-$[RuCl_2(pta)_4]$, while in water it is the previously unknown $[Ru(H_2O)_2(pta)_4]^{2+}$.

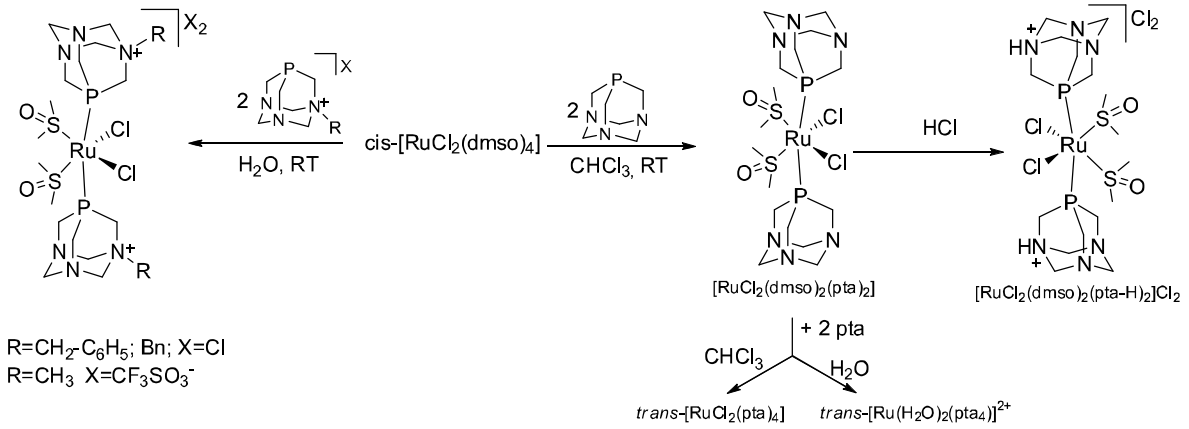


Figure 13: Synthesis of Ru(II)-dmso-complexes

We have shown that one nitrogen atom of each coordinated phosphine of $[RuCl_2(dmso)_2(pta)_2]$ can be protonated in aqueous solution and this protonation occurs at lower pH values (pK = 3.40) than in the case of the free ligand (pK = 5.63 - 6.0).

Cis-cis-trans-$[RuCl_2(dmso)_2(pta)_2]$, its protonated form *cis-cis-trans*-$[RuCl_2(dmso)_2(pta\text{-}H)_2]Cl_2$ and *cis-cis-trans*-$[RuCl_2(dmso)_2(pta\text{-}Me)_2](CF_3SO_3)_2$ were produced as single crystals and their structure was determined (*Figure 14.*).

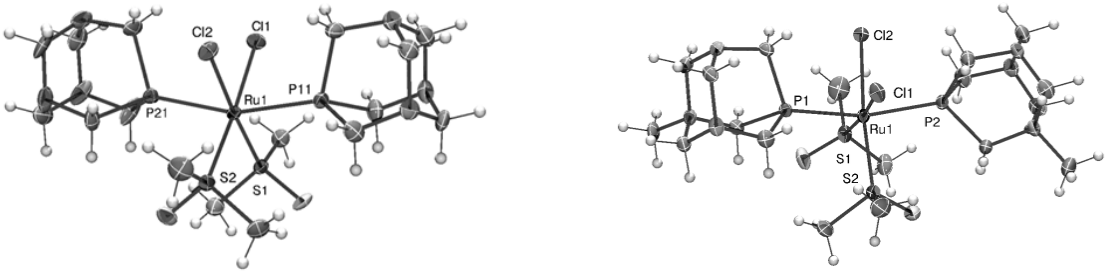


Figure 14: The structure of $[RuCl_2(dmso)_2(pta)_2]$ and $[RuCl_2(dmso)_2(pta\text{-}Me)_2](CF_3SO_3)_2$

Only $RuCl_2P_2S_2$ crystals, where P2 or S2 unit means bidentate ligands, were previously described in the literature. The specialty of the three crystal structures presented here is that only monodentate ligands are coordinated to the metal ion. Similarly to *trans*-$[RuCl_2(pta)_4]$ P-Ru-P angles differ substantially from 180°.

3.2. Photoconversion of *cis-cis-trans*-$[RuCl_2(dmso)_2L_2]$ complexes

It was observed that in aqueous solution $[RuCl_2(dmso)_2(pta)_2]$ exposed to visible light in the presence of an equivalent amount of pta transforms to a compound containing three chloride bridges.

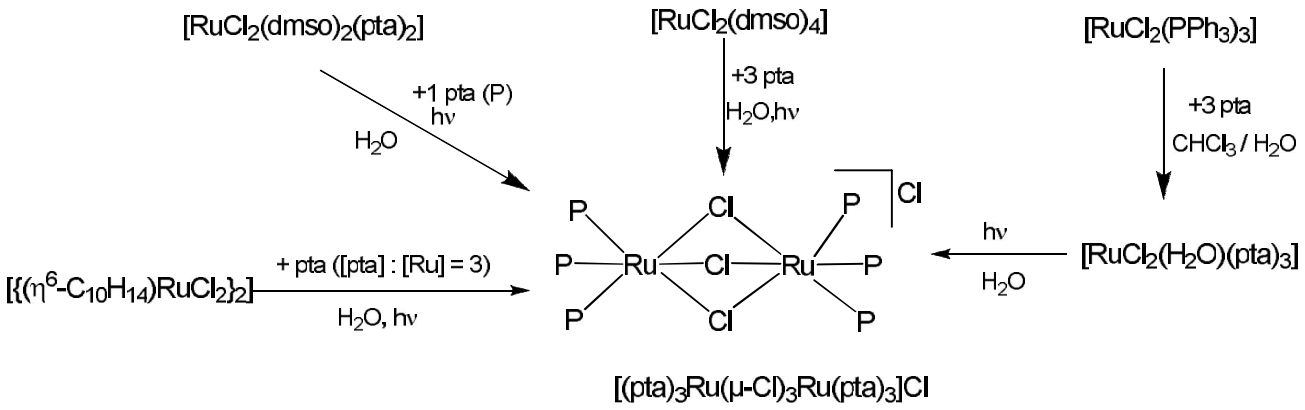


Figure 15: Synthesis of binuclear Ru(II)-pta complex

It was shown that $[(pta)_3Ru(\mu\text{-}Cl)_3Ru(pta)_3]Cl$ can also be synthesised by illumination of the following aqueous solution (*Figure 15*):

a./ $[RuCl_2(dmso)_4]$ and 3 equivalent pta

b./ $[\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$ and 6 equivalent pta

c./ *trans*-$[RuCl_2(pta)_4]$ and any of the water-soluble Ru(II)-sources $\{[RuCl_2(dmso)_4]$ or $[\{(\eta^6\text{-}C_{10}H_{14})RuCl_2\}_2]\}$ in quantity resulting [Ru]:[pta] = 1:3

d./ $[RuCl_2(H_2O)(pta)_3]$

e./ $[(dmso)_3Ru(\mu\text{-}Cl)_3RuCl(dmso)_2]$ and 6 equivalent pta.

^{1}H-, ^{13}C- and ^{31}P- NMR, ESI-MS, and elemental analysis data support the composition of the newly synthesised $[(pta)_3Ru(\mu\text{-}Cl)_3Ru(pta)_3]Cl$. The complex was also separated as single crystal and its structure analysed (*Figure 16.*). Aqueous solutions of $[(pta)_3Ru(\mu\text{-}Cl)_3Ru(pta)_3]Cl$ are also photosensitive and in the presence of two equivalent pta the dinuclear complex transforms to *cis*-$[RuCl_2(pta)_4]$ and *cis*-$[RuCl(H_2O)(pta)_4]^+$ known from the literature.

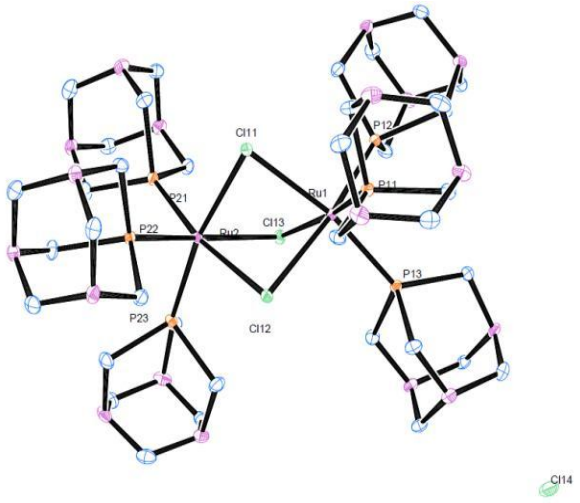


Figure 16: The structure of $[(pta)_3Ru(\mu\text{-}Cl)_3Ru(pta)_3$

IV. Catalytic properties of Ru(II)-complexes containing phosphatriaazadamantane (or its derivatives)

1./ Reduction of aldehydes with Na-formate in the presence of Ru(II)-pta catalysts

It was shown that the reduction of benzaldehyde with Na-formate is catalysed more efficiently by $[RuCl_2(H_2O)(pta)_3]$ presented here than with *trans*-$[RuCl_2(pta)_4]$ described in the literature.

It was observed that the activity of *trans*-$[RuCl_2(pta)_4]$ decreased upon irradiation because it transformed to less efficient *cis*-$[RuCl(H_2O)(pta)_4]$ and *cis*-$[RuCl_2(pta)_4]$ complexes. The yield of benzyl alcohol is even lower in the presence of *cis-cis-trans*-$[RuCl_2(dmso)_2L_2]$ {L = pta, (pta-Bn)Cl, (pta-Me)(CF_3SO_3)} complexes (*Table 3.*).

Phosphine-free $[RuCl_2(dmso)_4]$ and $[(dmso)_3Ru(\mu\text{-}Cl)_3RuCl(dmso)_2]$ complexes do not catalyse the reaction (*Table 3.*).

***Table 3*: Reduction of benzaldehyde and cinnamaldehyde with Na-formate**

catalyst	benz-aldehyde	*trans*-cinnamaldehyde			
	benzyl-alcohol (%)	conversion (%)	cinnamyl alcohol (%)	Hydrocinnam-aldehyde (%)	3-phenyl-propanol (%)
trans-$[RuCl_2(pta)_4]$	92	30	30	-	-
"in-situ" cis-$[RuCl(H_2O)(pta)_4]$ and cis-$[RuCl_2(pta)_4]$*	85	33	24	5	3
$[RuCl_2(H_2O)(pta)_3]$	99	55	55	-	-
$[(pta)_3Ru(\mu\text{-}Cl)_3Ru(pta)_3]^+$	25	5	5	-	-
$[RuCl_2(dmso)_4]$	0	0	-	-	-
$[(dmso)_3Ru(\mu\text{-}Cl)_3RuCl(dmso)_2]$	0	0	-	-	-
cis-cis-trans-$[RuCl_2(dmso)_2(pta)_2]$	71	34	16	7	11
cis-cis-trans-$[RuCl_2(dmso)_2(pta\text{-}Bn)_2]^{2+}$	68	33	28	2	3
cis-cis-trans-$[RuCl_2(dmso)_2(pta\text{-}Me)_2]^{2+}$	78	40	36	2	2

0.0625 mmol catalyst in 5 ml 5 M NaHCOO solution, t = 3 h, T = 80 °C, 5 mL chlorobenzene a./ 4.92 mmol benzaldehyde; b./ 3.96 mmol cinnamaldehyde; * These compounds are formed from aqueous *trans*- $[RuCl_2(pta)_4]$ upon20 min irradiation

The latter compounds are ineffective at reducing cinnamaldehyde, too. $[RuCl_2(H_2O)(pta)_3]$, characterized in this work, was the most active catalyst with respect to conversion and selectivity. The order of activity of the other Ru-pta complexes (from high to low) is $[RuCl_2(dmso)_2(pta\text{-}Me)_2]^{2+} > [RuCl_2(dmso)_2(pta)_2] > [RuCl_2(dmso)_2(pta\text{-}Bn)_2]^{2+} > [RuCl_2(pta)_4]$. Since the reduction of cinnamaldehyde could lead to several different compounds the selectivity of the reactions was also examined.

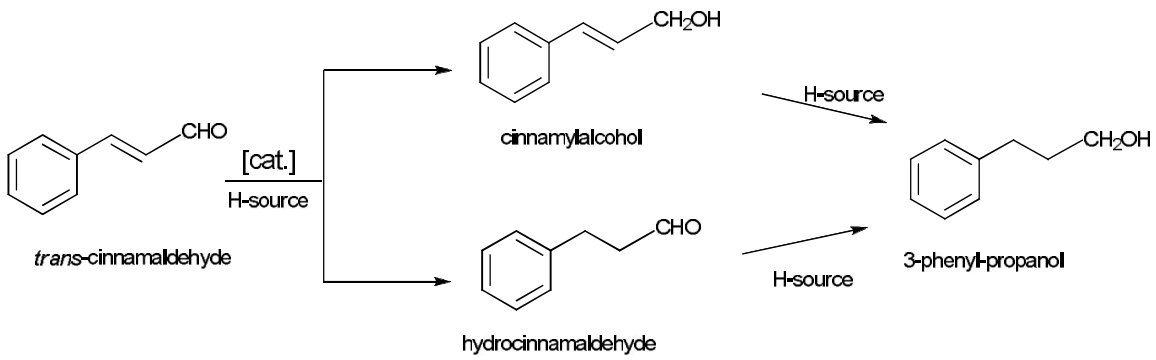


Figure 17.: Hydrogenation of cinnamaldehyde

It was shown that dmso-containing Ru(II)-pta complexes slightly facilitate the formation of dydrocinnamaldehyde and 3-phenyl-propanol in addition to cinnamyl alcohol.
The same applies to *cis*-$[RuCl(H_2O)(pta)_4]^+$ and *cis*-$[RuCl_2(pta)_4]$ complexes generated by irradiating of *trans*-$[RuCl_2(pta)_4]$.

2./ Hydrogenation/isomerisation of allylic alcohols with $[RuCl_2(dmso)_4]$ catalyst and its water-soluble phosphine-substituted derivatives.

It was established that aqueous $[RuCl_2(dmso)_4]$ can catalyse the isomerisation of 1-octane-3-ol to ketone only in the presence of different hydrogen sources. Besides octane-3-on, low amounts of the hydrogenated product, octane-3-ol are also formed under a hydrogen atmosphere of 1 bar pressure (*Figure 18*).

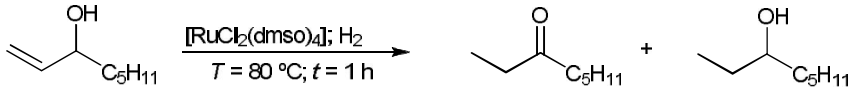


Figure 18.: Transformation of 1-octene-3-ol

The magnitude of transformation and the ratio of hydrogenated products could be increased by addition of water-soluble sulphonated triphenylphosphines (*m*tppms, *m*tppts) to the solutions.

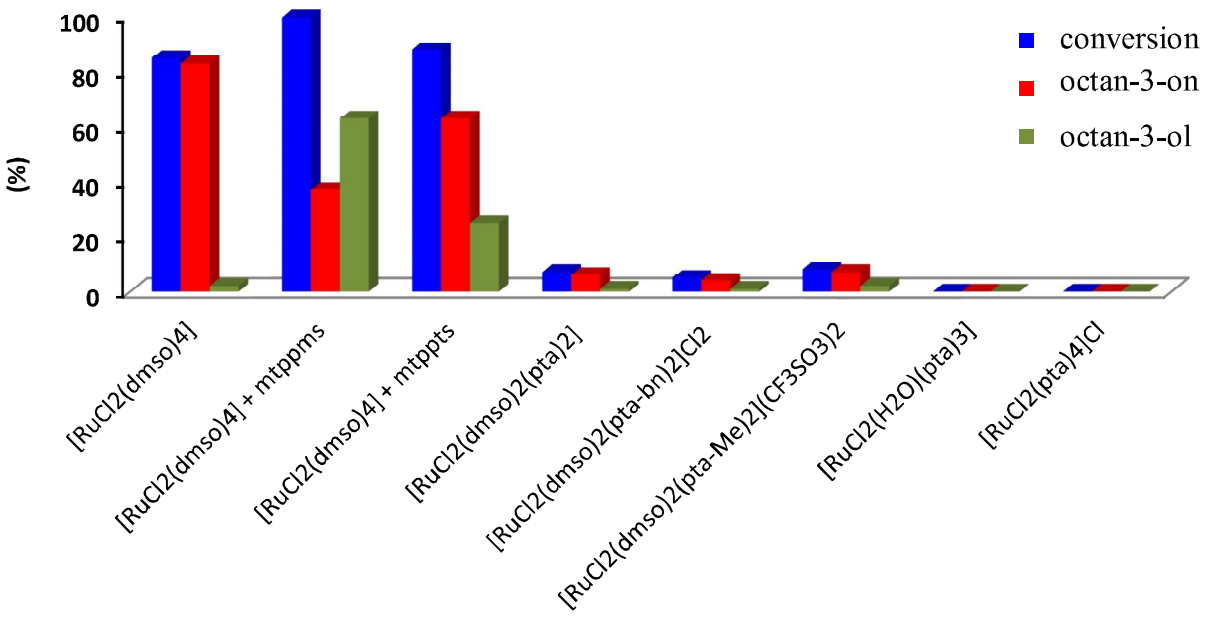


Figure 19: Redox isomerisation of 1-octene-3-ol with Ru(II)-dmso complexes

0,01 mmol catalyst in 3 mL water, 0,5 mmol 1-octen-3-ol in 1 mL toluene,
$p(H_2)$ = 1 bar, T = 80 °C, t = 1 h, [P]:[Ru] = 2 (P = *m*tppms, *m*tppts)

The efficiency of $[RuCl_2(dmso)_2(L)_2]$ complexes is low and the reaction is not catalysed at all by *trans*-$[RuCl_2(pta)_4]$ and $[RuCl_2(H_2O)(pta)_3]$.

Using an equivalent amount of Na-formate instead of hydrogen gas octane-3-on is formed exclusively with $[RuCl_2(dmso)_4]$ catalyst.

Under circumstances presented for *Figure 19* the transformation is complete for 1-heptene-3-ol and 1-hexene-3-ol but the conversion (while preserving selectivity) slightly decreases with the shortening of the carbon chain of allylic alcohols.

It was found that reduction of ketones did not occur not even upon elevation of formate concentration. It was determined from the temperature dependence of the reaction that below 50 °C it was very slow, quasi undetectable.

Aqueous solutions containing $[RuCl_2(dmso)_4]$ could be used repeatedly after its separation from the reaction products, but the activity of the catalyst dropped to half of the original value in the second cycle. In the phosphine-containing systems, saturated alcohol is also formed besides the isomerised reaction product.

The *"in situ"* catalyst formed in the reaction of $[RuCl_2(dmso)_4]$ with *m*tppms slightly favors reduction over isomerisation.

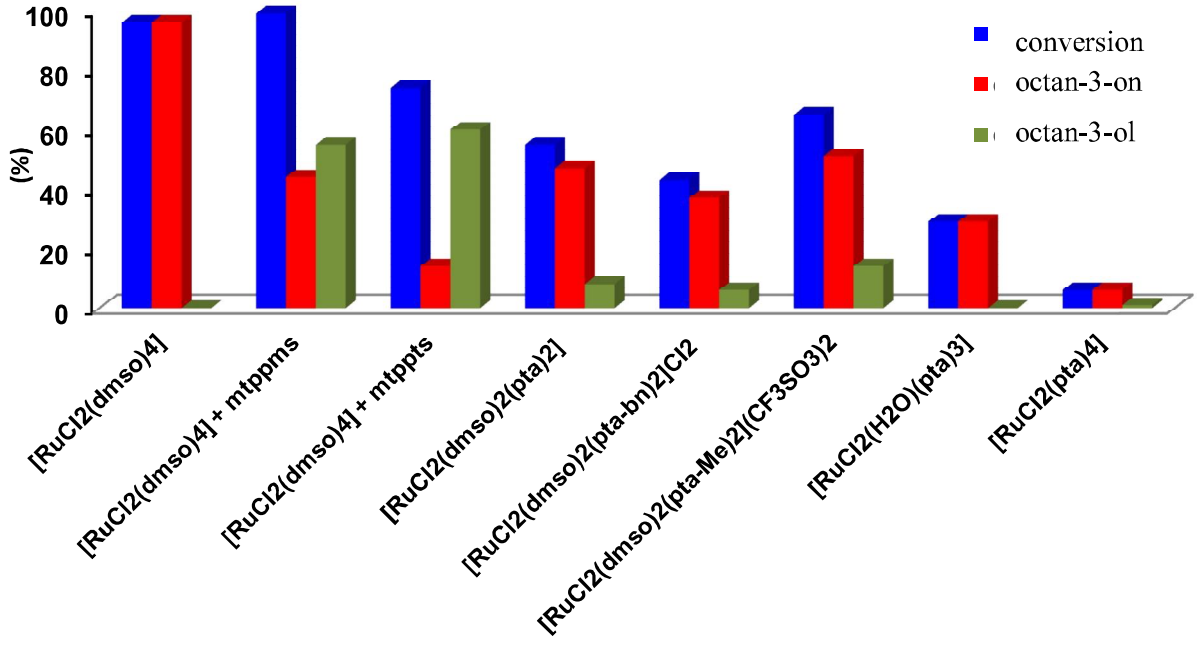


Figure 20: Isomerisation and hydrogenation of 1-octene-3-ol whit Na-formate

0,01 mmol catalyst in 3 mL water, 0,5 mmol 1-octen-3-ol in 1 mL toluene, n_{NaHCOO} = 0,5 mmol, T = 80 °C, t = 1 h, [P]:[Ru] = 2 (P = *m*tppms, *m*tppts)

In can be completed that $[RuCl_2(dmso)_2(L)_2]$ complexes do not meet the performance of $[RuCl_2(dmso)_4]$ catalyst either in the field of selectivity in conversion, but they are much more efficient than the dmso-free $[RuCl_2(H_2O)(pta)_3]$ and the poorly catalysing *trans*-$[RuCl_2(pta)_4]$ (*Figure 20.*).

4. Publikációs lista/List of Publications

A témához kapcsolódó közlemények/Papers related to the dissertation:

[1] ***A. Udvardy, Á. Kathó,***

Hydrogenation of sorbic acid in mono- and biphasic systems catalyzed by Rh(I)- phosphine complexes

React. Kin. Catal. Let. 95 (2008) 81-87

[2] ***A. Udvardy, A. Cs. Bényei, Á. Kathó,***

The dual role of *cis*-[$RuCl_2(dmso)_4$] in the synthesis of new water-soluble Ru(II)–phosphane complexes and in the catalysis of redox isomerization of allylic alcohols in aqueous–organic biphasic systems

J. Organomet. Chem. 717 (2012) 116-122

[3] ***A. Udvardy, P. Juhász, A. Cs. Bényei, Á. Kathó,***

Two in one: Charged tertiary phosphines held together by ionic or covalent interactions as bidentate phosphorus ligands for synthesis of half-sandwich Ru(II)-complexes.

Polyhedron, 60 *(2013)* 1-9

A témához szorosan nem kapcsolódó közlemény

[1] ***K. Voronova, M. Purgel, A. Udvardy, A. Cs. Bényei, Á. Kathó, F. Joó,***

Hydrogenation and redox isomerization of allylic alcohols catalysed by a new water-soluble Pd-salan complex (*Organometallics,* közlésre elfogadva, http://dx.doi.org/10.1021/om400555u)

Az értekezéshez nem kapcsolódó közlemények:

[1] ***S. Berényi, Zs. Gyulai, A. Udvardy, A. Sipos***

One-pot *N*-dealkylation and acid-catalyzed rearrangement of morphinans into aporphines

Tetrahedron Lett. 51 (2010) 1196-1198

[2] ***A. Udvardy, Zs. Gyulai, A. Sipos***

Extensive study of the autooxidation products of apomorphine and its pharmacologically active derivatives

J. Mol. Struct. 1002 (2011) 37-44

[3] ***Zs. Gyulai, A. Udvardy, A. Cs. Bényei, J. Fichna, K. Gach, M. Storr, G. Tóth, S. Antus, S. Berényi, A. Janecka, A. Sipos***

Synthesis and Opioid Activity of Novel 6-ketolevorphanol Derivatives

Med. Chem. 9 (2013) 1-10

[4] ***A. Sipos, A. Udvardy, A. Cs. Bényei, S. Berényi***

The first synthesis of 3-deoxyoripavine and its utilization in the preparation of 10-deoxyaporphines and cyprodime *C. Eur. J. Chem, 11(8), (2013) 1278-1285*

[5] ***A. Udvardy, A. Sipos***

Salutaridine and its derivatives as thebaine-equivalents in the synthesis of aporphines

C. Eur. J. Chem. elfogadva Ms. No. CEJC-D-13-00059R2

Előadások/Lectures:

[1] ***Udvardy A., Kathó Á.***

Szorbinsav hidrogénezése Rh- és Ru- komplexekkel

XLII. Komplexkémiai Kollokvium, 2007. május 23-25. Mátrafüred

[2] ***Juhász P., Udvardy A., Bertók Á., Kathó Á.***

Foszfatriazaadamantán származékok Ru-komplexeinek előállítása és katalitikus alkalmazása

XLIII. Komplexkémiai Kollokvium, 2008. május 28-30. Siófok

[3] ***Udvardy A., Kathó Á.***

Szorbinsav hidrogénezése Rh- és Ru- komplexekkel

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[4] ***Bertók Á., Udvardy A., Kathó Á.***

Semleges és kationos félszendvics Ru(II) komplexek előállítása és katalitikus alkalmazásai

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[5] ***Udvardy A., Bényei A. Cs., Kathó Á.***

Vízoldható foszfinokat tartalmazó Ru(II)-dmso komplexek képződése és katalitikus tulajdonságai

XLV. Komplex Kémiai Kollokvium 2010. május 26-28. Mátraháza

[6] ***Udvardy A., Kathó Á.***

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[7] ***Udvardy A., Kathó Á.***

Fotokémiai reakciók vízoldható foszfinokat tartalmazó Ru-dmso komplexekkel

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[8] ***Kathó Á., Bertók Á., Udvardy A., Szatmári I., Papp G., Torma K., S. Basu, Voronova K., Horváth H, Henrietta, A. Almássy, Czégéni Cs. E., Ősz K., Horváth H., Csajbók É., Joó F.:***

Klórozott szénhidrogének reduktív dehalogénezése

MKE 1, Nemzeti Konferencia, 2011. május 22-27, Sopron

[9] ***A. Sipos, V. Stempfer, A. Udvardy, A. Cs. Bényei, H. Schmidhammer, G. Viola***

Synthesis, structural characterization and antiproliferative activity of new noscopine derivatives

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[10] **A. Udvardy, A. Cs. Bényei, Á. Kathó:**

cis-[$RuCl_2(dmso)_4$]: Only a Ru(II)-source for synthesis of water-soluble Ru-phosphane complexes?

XLVII. Komplexkémiai Kollokvium, 2012. május 23-28. Mátrafüred

[11] **F. Joó, Cs. E. Czégéni, G. Papp, H. Horváth, K. Voronova, A. Udvardy, Á. Kathó**

Organometallic catalysis in water: an old wine in new bottle?

XXV. International Conference on Organometallic Chemistry, Lisboa, Portugal, 2012

[12] **Nagy E., Udvardy A., Kathó Á.**

N-Alkil-1,3,5-triaza-7-foszfaadamantán Ru(II)-komplexei és alkalmazásuk homogén és heterogén katalizátorként

XXXV. Kémiai Előadói Napok, 2012. október 29-31. Szeged

[13] **Horváth H., Szikszai D., Udvardy A., Joó F., Kathó Á.**

Alkinek katalitikus hidrogénezése új, vízoldható foszfint tartalmazó Ir(I)-karbén komplexekkel

XXXV. Kémiai Előadói Napok, 2012. október 29-31. Szeged

[14] **Nagy E., Udvardy A., Kathó Á.**

N-Alkil-1,3,5-triaza-7-foszfaadamantán Ru(II)-komplexei és alkalmazásuk homogén és heterogén katalizátorként

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Poszterek/Posters:

[1] ***A. Udvardy, Á. Kathó***

Hydrogenation of sorbic acid catalyzed by Rh- and Ru phosphine complexes

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[2] ***Á. Kathó, P. Juhász, A.Udvardy***

Synthesis and Catalytic Properties of Ru(II)-Arene Complexes of Alkylated Phosphatriazaadamantanes

Advances of Organic Chemistry, Smolenice, Slovak Republic, September 16-20, 2007.

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Phosphatriazaadamantane derivatives and their Ru-complexes in catalysis

16th Int. Symp. Hom. Catal., Florence, Italy 2008. Book of Abstracts, P-297.

[4] ***A. Udvardy, A. Cs. Bényei, Á. Kathó***

Formation and catalytic properties of Ru(II)-dmso complexes containing water-soluble phosphine ligands

10th International Symposium on Applied Bioinorganic Chemistry, Debrecen, Hungary 25 - 28 September, 2009.

[5] ***Á. Bertók, A. Udvardy, Á. Kathó*:**

Neutral and cationic half-sandwich Ru(II)-complexes with water-soluble phosphine ligands

10th International Symposium on Applied Bioinorganic Chemistry, Debrecen, Hungary 25 - 28 September, 2009.

[6] ***A. Sipos, A.Udvardy, Á. Kathó, S. Antus, S. Berényi***

Transition Metals in the Synthesis of 10-Deoxyaporphines

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[7] ***Á. Bertók, A. Udvardy, Á. Kathó***

Neutral and cationic half-sandwich Ru(II)-complexes with water-soluble phosphine ligands

5th Flash Conference of ERA-Chemistry „Big Task Of Water - Building And Destroying Molecules In Water" Frauenwörth, Germany18 - 22 October, 2009.

[8] ***A. Udvardy, A. Cs. Bényei, Á. Kathó***

Formation and catalytic properties of Ru(II)-dmso complexes containing water-soluble phosphine ligands

5th Flash Conference of ERA-Chemistry „Big Task Of Water - Building And Destroying Molecules In Water" Frauenwörth, Germany18 - 22 October, 2009.

[9] ***Á. Bertók, A. Udvardy, Á. Kathó***

Neutral and cationic half-sandwich Ru(II)-complexes with water-soluble phosphine ligands

2od Simposio Latinoamericano de Química de Coordinación y Organometálica, Maracaibo, Venezuela, 2009.

[10] ***A. Udvardy, A. Cs. Bényei, Á. Kathó***

Formation and catalytic properties of Ru(II)-dmso complexes containing water-soluble phosphine ligands

17th International Symposium on Homogeneous Catalysis (ISHC-17), Poznań, Poland, July 4th to 9th, 2010

[11] ***A. Udvardy, E. Nagy, Á. Kathó*:**

Ru(II)-complexes of N-alkyl-1,3,5-triaza-7-phosphaadamantane as homogenous and heterogenized catalyst

18th International Symposium on Homogeneous Catalysis Toulouse, France, 2012.

Book of Abstracts, P123

[12] ***A. Udvardy, E. Nagy, Á. Kathó***

Ru(II)-complexes of N-alkyl-1,3,5-triaza-7-phosphaadamantane as homogenous and heterogenized catalyst

XVIII. Nemzetközi Vegyészkonferencia, Félixfürdő, 2012. november 22-25. Erdély 2012.

Köszönetnyilvánítás

A munka az OTKA 101372, TÁMOP-4.2.1/B-09/1/KONV-2010-0007, TÁMOP-4.2.2/B-10/1/KONV-2010-0024, és a TÁMOP-4.2.2.A-11/1/KONV-2012-0043 számú ENVIKUT projekt keretében, az Európai Unió támogatásával, az Európai Szociális Alap társfinanszírozásával valósult meg.