THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (PhD)

Synthesis, heterogenization and catalytic applications of water-soluble Ru(II)-phosphine complexes

Evelin Bolyog-Nagy

Supervisor: Dr. Ágnes Kathó

UNIVERSITY OF DEBRECEN
DOCTORAL SCHOOL OF CHEMISTRY

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I. INTRODUCTION AND AIM OF THE WORK

One of the basic principles of green chemistry is to use alternative solvents (e.g. water) instead of organic solvents and to replace stoichiometric reaction with catalytic process. The properties of homogeneous catalysts are in many respects superior to heterogeneous variants, but sometimes the isolation and recirculation of homogeneous catalyst are difficult. A solution of this problem can be the preparation of solid-supported catalysts or use of biphasic catalysis.

Water-soluble metal complexes, which are used in aqueous-organic biphasic catalysis generally contain as ligand a phosphine with a polar group. But nowadays several research groups are studying the water-soluble complexes of 1,3,5-triaza-7-phosphaadamantane (pta). The water solubility of the ligand can be enhanced by quaternization of one of the ligand nitrogens with alkyl or benzyl halides (e.g with benzyl chloride, Bn-Cl).

This dissertation is focused on the synthesis of Ru(II)-complexes containing ~~of~~ pta or its *N*-alkylated derivatives for catalytic application in aqueous-organic two-phase chemical transformations. Furthermore, it was my goal to functionalize the Merrifield resin with pta and to react it with Ru(II)-precursors to produce supported half-sandwich Ru(II)-complexes.

The best known representative of Ru(II)-pta complexes is $[RuCl_2(\eta^6\text{-}C_{10}H_{14})(pta)]$, (abbreviated as RAPTA-C), exhibits promising antitumor properties. It has been reported in the literature that the $[RuCl_2(\eta^6\text{-}C_{10}H_{14})(pta\text{-}Bn)]Cl$ and *trans*-$[RuCl_2(pta)_4]$ complexes catalyzed the hydration of nitriles, which is a process of industrial importance. I planned to study the catalytic activity of *in situ* catalysts formed in reaction of various water soluble Ru(II)-precursors ($[\{RuCl_2(\eta^6\text{-}C_{10}H_{14})\}]_2$, $RuCl_3 \cdot H_2O$, $[RuCl_2(dmso)_4]$) and phosphines (pta, (pta-Bn)Cl).

Several $[RuCl_2(\eta^6\text{-}arene)P]$ complexes containing water-soluble phosphine (P) ligands have been found to promote the biphasic aqueous-organic isomerization of allyl alcohols to saturated ketones in the presence of a base. I wished to examine the catalytic activity of $[RuCl_2(\eta^6\text{-}C_{10}H_{14})(pta)]$ and $[RuCl_2(\eta^6\text{-}C_{10}H_{14})(pta\text{-}Bn)]Cl$ in this reaction in more detail and to clarify the role of the base. The $[RuCl_2(\eta^6\text{-}C_{10}H_{14})(m\text{tppms-Na})]$ containing monosulfonated triphenylphosphine (*m*tppms-Na) catalyzes the reduction of ketones from 2-propanol in the presence of KOH. But the presence of a strong base is not desirable for base-sensitive substrates. Thus, my aim was a) to investigate the catalytic activity of $[RuCl_2(\eta^6\text{-}C_{10}H_{14})(pta)]$ and $[RuCl_2(\eta^6\text{-}$

$C_{10}H_{14}$)(pta-Bn)]Cl in the reduction of oxo-compounds b) to work out a base-free method.

The [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(*m*tppms-Na)] containing monosulfonated triphenylphosphine (*m*tppms-Na) catalyzes the reduction of ketones from 2-propanol in the presence of KOH. But the presence of a strong base is not desirable for sensitive substrates. Thus, my aim was to investigate whether a) the said catalyst could be replaced by [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(P)] (pta; (pta-Bn)Cl) complexes b) the use of strong base during the reduction can be avoided.

1. EXPERIMENTAL SECTION

Most of the prepared ligands and complexes are oxygen-sensitive therefore the Schlenk technique was used for their preparation. Catalytic experiments were performed under inert atmosphere, except for the hydration reactions of nitriles.

To determine the structure of complexes multinuclear ^{1}H-, ^{13}C-, ^{31}P-NMR measurements were performed on BRUKER DRX 360 and BRUCKER DRX 400 devices. The product distribution of the catalytic reactions was determined on an Agilent 7890A gas chromatograph. The composition of the product mixture was calculated from the ratio of the areas under the signal based on the retention time of the corresponding standard materials. For the separation of allylic alcohols a Chrompack WCOT Fused Silica 30 m×0.32 mm CP WAX52CB column and for nitriles an OPTIMA 1 - 0.25 µm (30 m×0.32 mm) column was used. The redox isomerization of water-soluble allylic alcohols was followed by ^{1}H-NMR spectroscopy. The purity of the reaction products isolated in solid form was confirmed by elemental analysis, ESI-MS, ^{13}C- and ^{1}H-NMR spectroscopy.

BRUKER BioTOF II ESI-TOF and VG Autospec mass spectrometers were used for ESI-MS measurements and Elementar Vario Micro (CHNS) was used for elemental analysis. ICP measurements were performed on an Agilent ICP-OES 5100 instrument.

The X-ray diffraction structures were determined by Dr. Attila Bényei and Dr. Antal Udvardy on a Bruker-Nonius MACH3 four-circle single crystal diffractometer.

Infrared spectra were recorded on a Perkin Elmer Instruments Spectrum One FT-IR spectrometer with an ATR sampling, and UV spectra were recorded on an AnalytikJena SPECORD S600 spectrophotometer.

The pH of the solutions was determined an Orion 3Star pH meter.

III. LIST OF ABBREVIATIONS

Bn: benzyl

C$_{10}$H$_{14}$: *p*-cymene (4-isopropyltoluene; 1-methyl-4-isopropylbenzene)

dmso: dimethyl sulfoxide

ESI-MS: Electrospray Ionisation Mass Spectrometry

FT-IR: Fourier Transform Infrared Spectrometer

ICP-OES: inductively coupled plasma optical emission spectrometry

(***m*tppms-Na):** sodium salt of monosulfonated triphenylphosphine

NMR: Nuclear Magnetic Resonance

PPh$_3$: triphenylphosphine

pta: 1,3,5-triaza-7-phosphaadamantane;
1,3,5-triaza-7-phosphatricyclo[3.3.1.1]$^{3.7}$decane
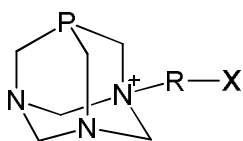
pta-Bn: benzyl-pta

pta-Me: methyl-pta

t: reaction time

T: temperature

TOF: turnover frequency, (mol reacted substrate)×(mol catalyst×time)$^{-1}$)
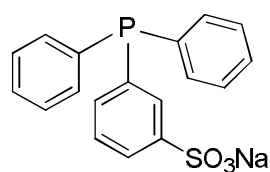
UV-vis: Ultraviolet–visible spectroscopy

Water-soluble phosphines used in this study:

pta: R = −

***m*tppms-Na**

pta-Me: R = CH$_3$

pta-Bn-X: X = H, *t*Bu, CH$_3$, NO$_2$, Cl

IV. NEW SCIENTIFIC ACHIEVEMENTS

1. Hydration of nitriles with Ru(II)-complexes

1.1. It was proved that the aqueous solution of $RuCl_3 \cdot 3H_2O$ in the presence of 5 equivalents of pta catalyzes the hydration of benzonitrile however, its activity does not reach the *trans*-[RuCl_2(pta)_4] known in the literature. *Mer-trans*-[RuCl_2(OH_2)(pta)_3] and [{Ru(pta)_3}_2(μ-Cl)_3]Cl are also active in hydration of benzonitrile. The efficiency of the latter three complexes can be increased by the addition of more equivalents of phosphine (pta or (pta-Bn)Cl).

1.2. The aqueous solution of commercially available [{RuCl_2(η^6-C_{10}H_{14})}_2] in the presence of 6 equivalents of (pta-Bn)Cl can catalyse the hydration of nitriles more efficiently than the [RuCl_2(η^6-C_{10}H_{14})(pta-Bn)]Cl described in the literature (*Figure 1*).
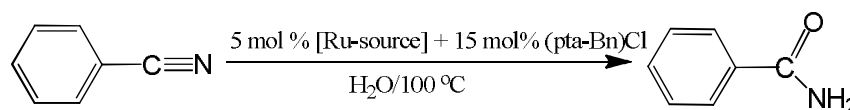
Figure 1: Hydration of benzonitrile to benzamide

The activity of [RuCl_2(η^6-C_{10}H_{14})(pta-Bn)]Cl can be increased in the presence of (pta-Bn)Cl and the resulting benzamide precipitates from the solution.

**1.3.** It was shown that the aqueous solution of [RuCl_2(dmso)_4] does not catalyze the hydration of benzonitrile even in the presence of 3 equivalents of *m*tppms-Na. But an active catalyst is formed when the aromatic phosphine is replaced by L=pta, (pta-Me)CF_3SO_3, (pta-Bn)Cl ligands. The (pta-Bn)Cl promotes most effectively this process and the observed efficiency is greater than the *cis-cis-trans*-[RuCl_2(dmso)_2(pta-Bn)_2]Cl_2.

1.4. It was proved that a) the aqueous solutions of [RuCl_2(dmso)_4] in the presence of 3 equivalents of (pta-Bn)Cl was more active than the *in situ* catalyst formed in the aqueous reaction of [{RuCl_2(η^6-C_{10}H_{14})}_2] and 6 equivalents of (pta-Bn)Cl. b) the catalyst can be used in five times without loss of activity (even in the eighth cycle the conversion rate is 70 %).

1.5. To understand the outstanding effect of (pta-Bn)Cl, *N*-alkylated pta derivatives were prepared using with R = *t*Bu-, CH_3-, NO_2-, Cl groups of *p*-substituted benzyl chloride (*Figure 2*).

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R = -*t*Bu; -NO$_2$; -CH$_3$, -Cl
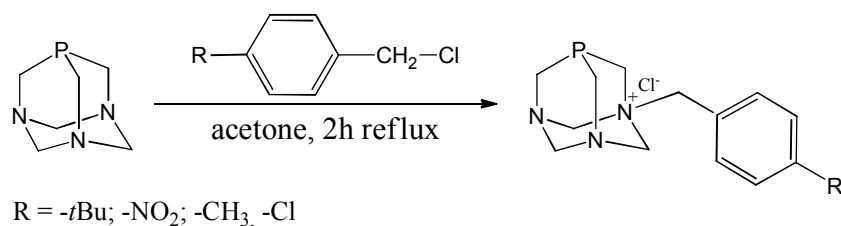
Figure 2: Preparation of variously substituted *N*-benzylated pta derivatives

Two of them are new compounds (R = CH$_3$, Cl) and their molecular structure was determined by X-ray diffration.
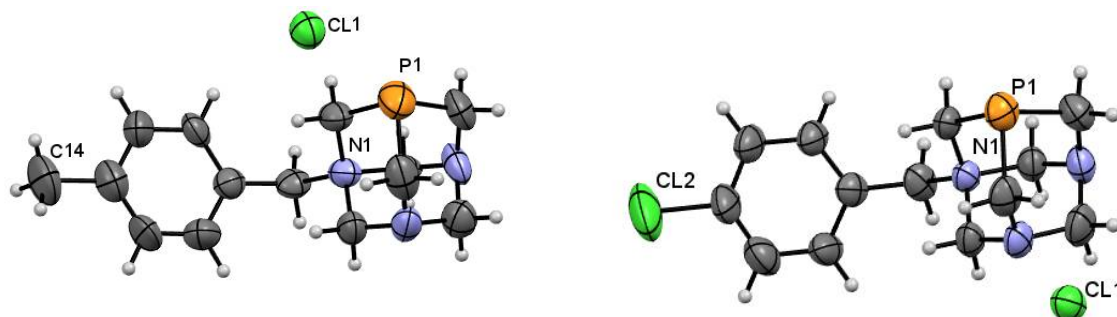
Figure 3: The molecular structures of [pta-CH$_2$-C$_6$H$_4$-*p*-CH$_3$]Cl and [pta-CH$_2$-C$_6$H$_4$-*p*-Cl]Cl

1.6. The scope of the hydration was also explored using *in situ* catalysts formed in the reactions of [RuCl$_2$(dmso)$_4$] (or [{RuCl$_2$(η^6-C$_{10}$H$_{14}$)}$_2$]) and 3 equivalents of (pta-Bn)Cl. It was found that most of the studied nitriles (except 2-pyridinecarbo- and acetonitrile) were successfully hydrated with both catalysts. *Table 1* shows the conversion values determined by gas chromatography and the yields of products isolated by ether extraction () and filtration {}.

Table 1: Hydration of nitriles with [(pta-Bn)Cl]:[Ru]=3 in aqueous solutions

Entry	Substrate	Ru=[RuCl$_2$(dmso)$_4$]	Ru=[{RuCl$_2$(η^6-C$_{10}$H$_{14}$)}$_2$]
1	Benzonitrile	99 (90) {42}	99 (80) {18}
2	4-Tolunitrile	99 (65) {64}	98 (91) {49}
3	4-Chlorophenyl-acetonitrile	98 {56}	96 {51}
4	4-Chlorobenzonitrile	98 (86) {59}	98 (68) {60}
5	4-(Trifluoromethyl)benzonitrile	95 (72) {47}	90 (47) {43}
6	3-Phenylpropionitrile	97 (90) {16}	98 (93) {27}
7	1,3-Dicyanobenzene	99 (91)	99 (99)
8	1,4-Dicyanobenzene	99 (99)	99 (99)
9	4-Nitrobenzonitrile	98 {77}	98 {49}
10	3-Pyridinecarbonitrile	99	95{86}
11	4-Pyridinecarbonitrile	99	97{66}
12	2-Pyridinecarbonitrile	10	20
13	Propionitrile	95	85
14	Butyronitrile	92{32}	82{25}
15	*i*-Butironitrile	97{47}	92{89}
16	Acetonitrile	0	0

Reaction conditions: n$_{Ru}$ = 5·10^{-5} mol, [(pta-Bn)Cl]:[Ru]=3, n$_{subs.}$ = 1·10^{-3}mol, V$_{H2O}$=3 ml, T=100°C (reflux)

In collaboration with the University of Debrecen of Department of Organic Chemistry, it was found that the aqueous solution of [RuCl$_2$(dmso)$_4$] and 3 equivalents of (pta-Bn)Cl was suitable for the hydration of glycosyl cyanides. For example *β-D*-galactopyranosyl cyanide protected with acetyl groups can be transformed to the corresponding *C*-galactosylformamide with 85 % yield (*Figure 4*).
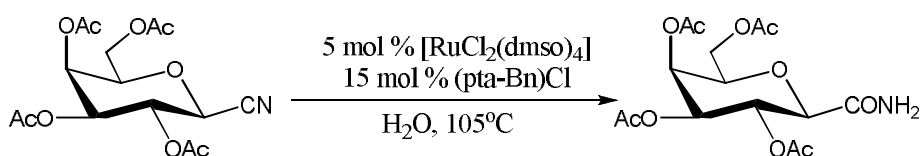

Figure 4: Transformation of *β-D*-galactopyranosyl cyanide to *C*-galactosylformamide with *in situ* [RuCl$_2$(dmso)$_4$] + 3 (pta-Bn)Cl catalyst

2. The 1,3,5-triaza-7-phosphaadamantane (pta) supporting on Merrifield resin and its use for the formation of heterogeneous half-sandwich Ru(II)-complex

Pta was reacted with chloromethylphenyl groups (~1 mmol/g) of Merrifield resin. The presence of covalently bonded phosphine was confirmed by IR spectroscopy and the average 0.926 mmol pta/1 g resin value was calculated from the nitrogen content determined by elemental analysis. Heterogenized half-sandwich Ru(II)-complex was obtained by refluxing of methanolic solution of [{RuCl$_2$(η^6-C$_{10}$H$_{14}$)}$_2$] containing the modified resin (*Figure 5*).

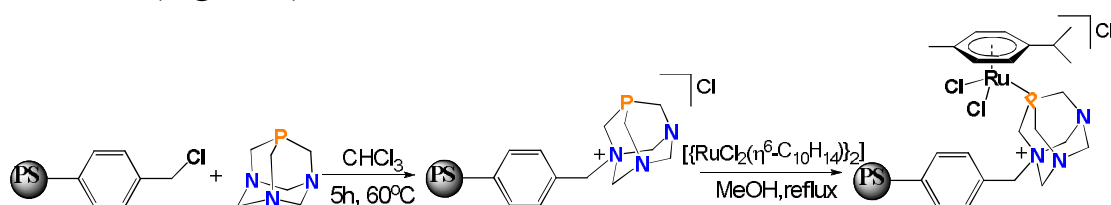**Figure 5:** Supported [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta-Bn)]$^+$ half-sandwich complex design Merrifield resin

According to the P and Ru content (determined by ICP-OES), one gram of resin contains 0.55 mmol of complex.

3. Conversion of allylic alcohols with homogeneous and solid supported Ru(II)-phosphaurotropin complexes

3.1. It was found that in strongly basic solutions (pH=11-12, 0.2 M phosphate buffer) [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta)] and [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta-Bn)]Cl were effective and selective catalysts for redox isomerization of oct-1-en-3-ol, full conversion of the substrate was achieved in 1 h at 80°C with octan-3-one as the sole product. However, the reactions were very slow in pH=4-10 solutions (*Figure 6*).
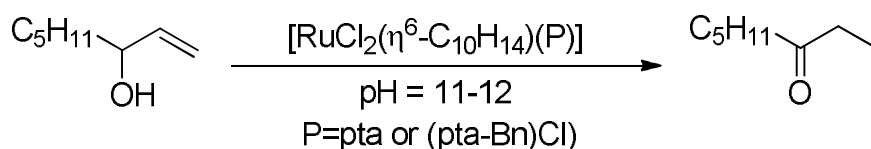
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Figure 6: Redox isomerization of oct-1-en-3-ol

3.2. It was shown that with the *in situ* catalyst obtained by stirring with aqueous solution of 0.02 mmol sodium carbonate and 0.01 mmol $[RuCl_2(\eta^6-C_{10}H_{14})(pta)]$ for 15 minutes, 1 mmol oct-1-en-3-ol can be completely converted to octan-3-one at 75°C in one hour. However, the conversion is halved at 70°C and barely any isomerization at T≤60°C (similar conclusions using $[RuCl_2(\eta^6-C_{10}H_{14})(pta-Bn)]Cl$ as catalyst).

3.3. It was established that: a/ the aqueous solution of the *in situ* catalyst described in point *3.2.* is reusable and does not lose significantly the activity for five cycles; b/ replacing $[RuCl_2(\eta^6-C_{10}H_{14})(pta)]$ for $[RuCl_2(\eta^6-C_{10}H_{14})(pta-Bn)]Cl$ the conversion decreases per cycle and there is no conversion in cycle 5 (*Table 2*).

Table 2: Redox isomerization of oct-1-en-3-ol with homogenous and solid-supported $[RuCl_2(\eta^6-C_{10}H_{14})(pta-Bn)]^+$ catalysts

Catalyst	Support	octan-3-one (%)				
		1. cycle	2. cycle	3. cycle	4. cycle	5. cycle
$[RuCl_2(\eta^6-C_{10}H_{14})(pta-Bn)]Cl$	-	97	59	25	2	0
Supported Ru(II)-complex	Merrifield resin	60 82 92	92	92	90	90

Conditions: t=1h, t=2h, t=3h; [sub]:[Na$_2$CO$_3$]:[Ru]=100:2:1; n_{Ru}=2·10^{-5} mol (homogenous); [sub]:[Na$_2$CO$_3$]:[Ru]=66:1,3:1; n_{Ru}=3·10^{-5} mol (supported); V_{H2O}=4,6 ml; T=75°C

3.4. It was shown that the activity of the Merrifield resin-supported Ru(II)-complex is less than the $[RuCl_2(\eta^6-C_{10}H_{14})(pta-Bn)]Cl$ described in *3.3.*, but its efficacy is barely reduced even in cycle 5 (*Table 2*).

3.5. It was observed that the initial orange color of aqueous solution of $[RuCl_2(\eta^6-C_{10}H_{14})(pta)]$ gradually turned lemon yellow on the effect of 2 equivalents of Na_2CO_3. A well as a new signal appears on the effect of Na_2CO_3 at δ= -33.2 ppm instead of the $[RuCl_2(\eta^6-C_{10}H_{14})(pta)]$ ^{31}P NMR signal (δ = -35,5 ppm) in the ^{31}P NMR spectra. These phenomena were rationalized assuming ligand exchange leading to formation of $[Ru(\eta^2-O_2CO)(\eta^6-C_{10}H_{14})(pta)]$ (*Figure 7*). The new complex was characterized by different spectroscopic methods (^{1}H, ^{13}C, ^{31}P-NMR, UV-Vis) and its composition was confirmed by elemental analysis.
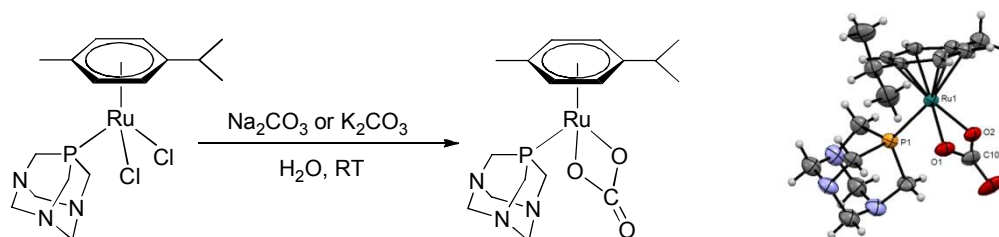
Figure 7: Preparation and molecular structure of [Ru(η^2-O$_2$CO)(η^6-C$_{10}$H$_{14}$)(pta)]

[Ru(η^2-O$_2$CO)(η^6-C$_{10}$H$_{14}$)(pta)]·2H$_2$O was isolated as a single crystal and its molecular structure was determined by X-ray diffraction. It was found that the carbonate ion coordinates to the Ru(II)-ion as a bidentate ligand.

3.6. It was proved that the [Ru(η^2-O$_2$CO)(η^6-C$_{10}$H$_{14}$)(pta)] is more active in the redox isomerization of allyl alcohols than the *in situ* [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta)] and 2 equialents of Na$_2$CO$_3$. The role of the carbonate ligand is shown by the suggested mechanism (*Figure 8*):
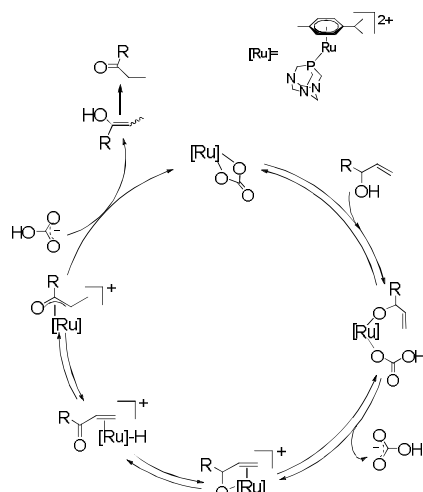

Figure 8: Suggested mechanism of redox isomerization of allyl alcohols catalyzed by [Ru(η^2-O$_2$CO)(η^6-C$_{10}$H$_{14}$)(pta)]

This complex is significantly more active than the hitherto known *in situ* [RuCl$_2$(P)(η^6-arene)]+base catalysts. Aqueous solutions of [Ru(η^2-O$_2$CO)(pta)(η^6-*p*-cymene)] are close to neutral (pH=7.24) so this catalyst can be applied in case of base-sensitive substrates, too.

3.7. During the isomerization of allylic alcohols of different chain lengths catalyzed by [Ru(η^2-O$_2$CO)(η^6-C$_{10}$H$_{14}$)(pta)], it was observed that the conversion of prop-1-en-3-ol and but-1-en-3-ol showed modest reactivities in contrast to the water-insoluble 1-en-3-ols which were fast converted to the corresponding ketones (*Table 3*).

Table 3: Isomerization of allylic alcohols with $[Ru(\eta^2\text{-}O_2CO)(\eta^6\text{-}C_{10}H_{14})(pta)]$ catalyst in water

Substrate	Conversion (%)	TOF (h^{-1})
prop-1-en-3-ol*	24	96
but-1-en-3-ol*	27	108
pent-1-en-3-ol	97	388
hex-1-en-3-ol	93	372
hept-1-en-3-ol	97	388
okt-1-en-3-ol	99	396

Conditions: $n_{Ru}=1\cdot10^{-5}$ mol; $n_{subs.} = 2\cdot10^{-3}$ mol; $V_{H2O}=3$ ml; T=75°C. * Conversion determined by ^1H NMR spectroscopy.

4. Reduction of oxo compounds in a hydrogen transfer reaction from 2-propanol

4.1. It was pointed that the reduction of cyclohexanone (*Figure 9*) described in the literature can also be performed using [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta)]-t, [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta-Bn)]Cl or Merrifield resin supported Ru(II)-complex instead of [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(*m*tppms-Na)] (*Table 4*).
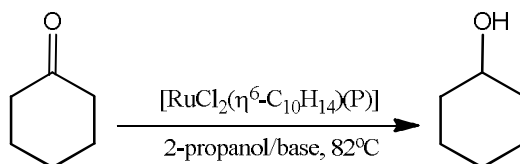

Figure 9: Reduction of cyclohexanone

Table 4: Reduction of cyclohexanone with various Ru(II)-phosphaurotropin complexes

Catalysts	KOH		2 eq. Na$_2$CO$_3$
	[Sz]:[K]=500:1		[Sz]:[K]=100:1
	15 min	1h	1h
[RuCl$_2$(η^6-C$_{10}$H$_{14}$)(*m*tppms-Na)]	99*	99	98
[RuCl$_2$(η^6-C$_{10}$H$_{14}$)(Bn-pta)]Cl	10	94	90
[RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta)]	31	98	86
RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta-Bn)]$^+$-Merrifield			67**

Conditions: *literature data; n_{Ru}=1·10^{-5} mol, V$_{2\text{-propanol}}$=9,25 ml, t=1h, T=82°C **t= 3h; n_{Ru}=2·10^{-5} mol

4.2. It was confirmed that benzaldehyde was not reduced in 2-propanol without a base, but in the presence of KOH, HCOONa or Na$_2$CO$_3$, it can also be reduced by [RuCl$_2$(η^6-C$_{10}$H$_{14}$)P] (P=pta, (pta-Bn)Cl, *m*tppms-Na) complexes. Of these bases, Na$_2$CO$_3$ is the most effective if [base]:[Ru] = 2.
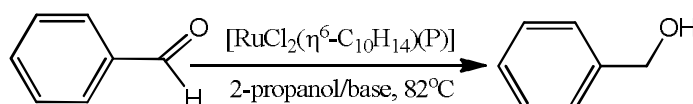

Figure 10: Reduction of benzaldehyde in hydrogen transfer reactions from 2-propanol

4.3. In the hydrogen transfer reaction of benzaldehyde catalyzed by [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta)] from 2-propanol if the ratio of [Na$_2$CO$_3$]:[Ru] is more than 3, salting out occurs and as a result, conversion is reduced.

4.4. Similar to the preparation of [Ru(η^2-O$_2$CO)(η^6-C$_{10}$H$_{14}$)(pta)] (see point *3.5.*), the [Ru(η^2-O$_2$CO)(η^6-C$_{10}$H$_{14}$)(*m*tppms-Na)] was also isolated in solid form. It was proved that the activity of *in situ* [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(P)] + 2 Na$_2$CO$_3$ catalysts is higher than that of the [Ru(η^2-O$_2$CO)(η^6-C$_{10}$H$_{14}$)(P)] complexes (P = pta, *m*tppms-Na) however, the use of [Ru(η^2-O$_2$CO)(η^6-C$_{10}$H$_{14}$)(P)] is advantegous/preferable in neutral aqueous solutions in case of base-sensitive substrates.

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4.5. It was found that the optimum temperature for the reduction is the boiling point of 2-propanol, 82°C. At lower temperatures, conversion is greatly reduced and there is hardly any conversion below 60°C.

4.6. Conversions decreased at [benzaldehyde]:[RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta)]>100. This self-inhibition phenomenon occurs with cyclohexanone at [subs.]:[Ru]>300.

4.7. Examining several oxo compounds, I have found that the fluorobenzaldehyde derivatives containing the electron withdrawing substituent are less transformed than the benzaldehyde, whereas the conversion of ethoxy- or methyl- substituted derivatives having electron donating substituent is greater. Cinnamon aldehyde is selectively formed into cinnamon alcohol (*Table 7*).

Table 7: Reduction of aldehydes with *in situ* [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta)] + 2 Na$_2$CO$_3$ catalyst

Substrate	Conversion (%)
benzaldehyde	80
4-fluorobenzaldehyde	30
2-fluorobenzaldehyde	19
4-ethoxybenzaldehyde	79
3-methylbenzaldehyde	87
2-hydroxybenzaldehyde	26
cinnamon aldehyde	11 (just C=O)
hexanal	59

Conditions: n$_{Ru}$=1·10^{-5} mol, [Sub]:[Na$_2$CO$_3$]:[Ru]=100:2:1, V$_{2\text{-propanol}}$=9,25 ml, t=1h, T=82°C

Among the ketones the conversion of acetophenone and its derivatives is less than cyclohexanone (86 %), but significantly exceeds the conversion of octan-3-one (30 %) (*Table 8*).

Table 8: Reduction of ketones with *in situ* [RuCl$_2$(η^6-C$_{10}$H$_{14}$)(pta)] + 2 Na$_2$CO$_3$ catalyst

Substrate	Conversion (%)
cyclohexanone	86
acetofenone	67
m-methylacetophenone	68
p-methylacetophenone	80
octan-3-one	30

Conditions: n$_{Ru}$=1·10^{-5} mol, [Sub]:[Na$_2$CO$_3$]:[Ru]=100:2:1, V$_{2\text{-propanol}}$=9,25 ml, t=1h, T=82°C

V. POSSIBLE APPLICATIONS OF THE RESULTS

This dissertation is focused on the development of environmentally friendly, catalytic processes. To achieve this, I tried to reduce the amount of organic solvents or avoid using them by the use of water-soluble catalysts. The *in situ* catalysts I have developed are based on commercially available Ru(II)-sources and ligands but preparation of them is also easy. In almost all cases, the catalyst can be reused after filtration/separation of the desired product.

Beyond recycling, one of the catalysts can be applied in case of acid- or base-sensitive substrates too because pH of it is close to neutral. During the catalytic experiments three model reactions were studied. Among them, the amides obtained by hydration of nitriles are industrially important raw materials.

VI. TUDOMÁNYOS PUBLIKÁCIÓK/LIST OF PUBLICATIONS

Az értekezés témájához kapcsolódó közlemények/ Publications related to the dissertation

Angol nyelvű közlemények nemzetközi folyóiratban/English articles in international journals:

1. Evelin Bolyog-Nagy, Antal Udvardy, Ferenc Joó, Ágnes Kathó
Efficient and selective hydration of nitriles to amides in aqueous systems with Ru(II)-phosphaurotropine catalysts
Tetrahedron Letters 55 (2014) 3615-3617

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1. Bolyog-Nagy E., Udvardy A., Joó F., Kathó Á.: *Nitrilek szelektív hidratálása amidokká foszfaurotropint tartalmazó Ru(II)-komplexekkel vizes közegben* **48. Komplexkémiai Kollokvium 2014. 05. 28-30. Siófok, Magyarország**
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4. Bolyog-Nagy E., Udvardy A., Barczáné-Bertók Á., Joó F., Kathó Á.: *Allil-alkoholok redukciója és redox izomerizációja Ru(II)-komplexszekkel* **XXI. Nemzetközi Vegyészkonferencia 2015. 09. 23-27. Csíksomlyó, Románia**

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6. <u>Bolyog-Nagy E.</u>, Udvardy A., Barczáné Bertók Á., Joó F., Kathó Á.: *Allil-alkoholok redox izomerizációja foszfa-urotropint tartalmazó félszendvics Ru(II)-katalizátorokkal* **50. Komplexkémiai Kollokvium 2016. 05. 30.-06. 01. Balatonvilágos, Magyarország**

Az értekezés témakörében bemutatott poszterek/ Poster presentations related to the dissertation

1. Udvardy A., <u>Nagy E.</u>, Joó F., Kathó Á.: *Homogén és heterogenizált N-alkil-1,3,5-triaza-7-foszfaadamantánt tartalmazó Ru(II)-katalizátorok* **XVIII. Nemzetközi Vegyészkonferencia 2012. 11. 22-25. Félixfürdő, Románia**

2. Udvardy A., <u>Nagy E.</u>, Joó F., Kathó Á.: *Homogén és heterogenizált N-alkil-1,3,5-triaza-7-foszfaadamantánt tartalmazó Ru(II)-katalizátorok* **XXXV. Kémiai Előadói Napok, 2012. 10. 29-31. Szeged, Magyarország**

3. A. Udvardy, <u>E. Bolyog-Nagy</u>, Á. Kathó: *Ru(II)-complexes of N-alkyl-1,3,5-triaza-7-phosphaadamantane as homogeneous and heterogenized catalysts* **18th International Symposium on Homogeneous Catalysis 2012. 07. 09-13. Toulouse, Franciaország**

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6. <u>E. Bolyog-Nagy</u>, A. Udvardy, F. Joó, Á. Kathó: *Efficient and selective hydration of nitriles to amides in aqueous systems with Ru(II)-phosphatriazaadamantane catalysts* **Workshop "Metal, water and Sun 2015" 2015. 05. 21-22 Almeria, Spanyolország**

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8. A. Udvardy, <u>E. Bolyog-Nagy</u>, Á. Barczáné-Bertók, F. Joó, Á. Kathó: *Redox isomerization of allylic alcohols catalyzed by water soluble half-sandwich Ru(II)-phosphaurotropin complexes* **8th Green Solvents conference, 2016. 10. 16-19. Kiel, Németország**

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Candidate: Evelin Bolyog-Nagy
Neptun ID: D7R3M4
Doctoral School: Doctoral School of Chemistry
MTMT ID: 10044912

List of publications related to the dissertation

Foreign language scientific articles in international journals (4)

1. Udvardy, A., Serrano-Ruiz, M., Passarelli, V., **Bolyog-Nagy, E.**, Joó, F., Kathó, Á., Romerosa, A.: Synthesis and catalytic activity of new, water-soluble mono- and dinuclear ruthenium(II) complexes containing 1,3,5-triaza-7-phosphaadamantane: Study of the effect of the visible light.
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2. **Bolyog-Nagy, E.**, Udvardy, A., Barczáné-Bertók, Á., Joó, F., Kathó, Á.: Facile synthesis of [Ru(η2-O2CO)(pta)(η6-p-cymene)], an outstandingly active Ru(II) half-sandwich complex for redox isomerization of allylic alcohols.
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3. Misra, A. K., Bokor, É., Kun, S., **Bolyog-Nagy, E.**, Kathó, Á., Joó, F., Somsák, L.: Chemoselective hydration of glycosyl cyanides to C-glycosyl formamides using ruthenium complexes in aqueous media.
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