THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (PhD)

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

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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$_2$(η$^6$-C$_{10}$H$_{14}$)(pta)], (abbreviated as RAPTA-C), exhibits promising antitumor properties. It has been reported in the literature that the [RuCl$_2$(η$^6$-C$_{10}$H$_{14}$)(pta-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 \textit{in situ} catalysts formed in reaction of various water soluble Ru(II)-precursors ([{RuCl$_2$(η$^6$-C$_{10}$H$_{14}$)}]$_2$, RuCl$_3$·H$_2$O, [RuCl$_2$(dmso)$_4$]) and phosphines (pta, (pta-Bn)Cl).

Several [RuCl$_2$(η$^6$-\textit{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$_2$(η$^6$-C$_{10}$H$_{14}$)(pta)] and [RuCl$_2$(η$^6$-C$_{10}$H$_{14}$)(pta-Bn)]Cl in this reaction in more detail and to clarify the role of the base. The [RuCl$_2$(η$^6$-C$_{10}$H$_{14}$)(mtppms-Na)] containing monosulfonated triphenylphosphine (mtppms-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$_2$(η$^6$-C$_{10}$H$_{14}$)(pta)] and [RuCl$_2$(η$^6$-
C_{10}H_{14})(pta-Bn)Cl in the reduction of oxo-compounds b) to work out a base-free method.

The [RuCl_2(\eta^6-C_{10}H_{14})(mtpms-Na)] containing monosulfonated triphenylphosphine (mtpms-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(\eta^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<sub>10</sub>H<sub>14</sub>:** 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

**(mtppms-Na):** sodium salt of monosulfonated triphenylphosphine

**NMR:** Nuclear Magnetic Resonance

**PPh<sub>3</sub>:** triphenylphosphine

**pta:** 1,3,5-triaza-7-phosphaadamantane; 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]<sub>3.7</sub>decane

**pta-Bn:** benzyl-pta

**pta-Me:** methyl-pta

**t:** reaction time

**T:** temperature

**TOF:** turnover frequency, \((\text{mol reacted substrate})\times(\text{mol catalyst}\times\text{time})^{-1}\)

**UV-vis:** Ultraviolet–visible spectroscopy

Water-soluble phosphines used in this study:

![pta](image)

**pta:** R = –

**pta-Me:** R = CH<sub>3</sub>

**pta-Bn-X:** X = H, tBu, CH<sub>3</sub>, NO<sub>2</sub>, Cl
IV. NEW SCIENTIFIC ACHIEVEMENTS

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

1.1. It was proved that the aqueous solution of RuCl₃·3H₂O in the presence of 5 equivalents of pta catalyzes the hydration of benzonitrile however, its activity does not reach the trans-[RuCl₂(pta)₄] known in the literature. Mer-trans-[RuCl₂(OH₂)(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 [{RuCl₂(η⁶-C₁₀H₁₄)}₂] in the presence of 6 equivalents of (pta-Bn)Cl can catalyse the hydration of nitriles more efficiently than the [RuCl₂(η⁶-C₁₀H₁₄)(pta-Bn)]Cl described in the literature (Figure 1).

\[
\text{Figure 1: Hydration of benzonitrile to benzamide}
\]

The activity of [RuCl₂(η⁶-C₁₀H₁₄)(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 [RuCl₂(dmso)₄] does not catalyze the hydration of benzonitrile even in the presence of 3 equivalents of mttpms-Na. But an active catalyst is formed when the aromatic phosphine is replaced by L=pta, (pta-Me)CF₃SO₃, (pta-Bn)Cl ligands. The (pta-Bn)Cl promotes most effectively this process and the observed efficiency is greater than the cis-cis-trans-[RuCl₂(dmso)₂(pta-Bn)₂]Cl₂.

1.4. It was proved that a) the aqueous solutions of [RuCl₂(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 [{RuCl₂(η⁶-C₁₀H₁₄)}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 = tBu-, CH₃-, NO₂-, Cl groups of p-substituted benzyl chloride (Figure 2).
Two of them are new compounds (R = CH₃, Cl) and their molecular structure was determined by X-ray diffraction.

1.6. The scope of the hydration was also explored using in situ catalysts formed in the reactions of [RuCl₂(dmso)₄] (or [{RuCl₂(η⁶-C₅H₁₀)}₂]) and 3 equivalents of (pta-Bn)Cl. It was found that most of the studied nitriles (except 2-pyridinecarboxylate 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>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Ru=[RuCl₂(dmso)₄]</th>
<th>Ru=[{RuCl₂(η⁶-C₅H₁₀)}₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzonitrile</td>
<td>99 (90) {42}</td>
<td>99 (80) {18}</td>
</tr>
<tr>
<td>2</td>
<td>4-Tolunitrile</td>
<td>99 (65) {64}</td>
<td>98 (91) {49}</td>
</tr>
<tr>
<td>3</td>
<td>4-Chlorophenyl-acetonitrile</td>
<td>98 (56)</td>
<td>96 (51)</td>
</tr>
<tr>
<td>4</td>
<td>4-Chlorobenzonitrile</td>
<td>98 (86) {59}</td>
<td>98 (68) {60}</td>
</tr>
<tr>
<td>5</td>
<td>4-(Trifluoromethyl)benzonitrile</td>
<td>95 (72) {47}</td>
<td>90 (47) {43}</td>
</tr>
<tr>
<td>6</td>
<td>3-Phenylpropionitrile</td>
<td>97 (90) {16}</td>
<td>98 (93) {27}</td>
</tr>
<tr>
<td>7</td>
<td>1,3-Dicyanobenzene</td>
<td>99 (91)</td>
<td>99 (99)</td>
</tr>
<tr>
<td>8</td>
<td>1,4-Dicyanobenzene</td>
<td>99 (99)</td>
<td>99 (99)</td>
</tr>
<tr>
<td>9</td>
<td>4-Nitrobenzonitrile</td>
<td>98 (77)</td>
<td>98 (49)</td>
</tr>
<tr>
<td>10</td>
<td>3-Pyridinecarbonitrile</td>
<td>99</td>
<td>95 (86)</td>
</tr>
<tr>
<td>11</td>
<td>4-Pyridinecarbonitrile</td>
<td>99</td>
<td>97 (66)</td>
</tr>
<tr>
<td>12</td>
<td>2-Pyridinecarbonitrile</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>13</td>
<td>Propionitrile</td>
<td>95</td>
<td>85</td>
</tr>
<tr>
<td>14</td>
<td>Butyronitrile</td>
<td>92 (32)</td>
<td>82 (25)</td>
</tr>
<tr>
<td>15</td>
<td>i-Butyronitrile</td>
<td>97 (47)</td>
<td>92 (89)</td>
</tr>
<tr>
<td>16</td>
<td>Acetonitrile</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Reaction conditions: n_Ru = 5×10⁻² mol, ([pta-Bn]Cl):[Ru]=3, n_subst. = 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 [RuCl₂(dmsos)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 [RuCl₂(dmsos)₄] + 3 (pta-Bn)Cl catalyst](image)

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 [{RuCl₂(η⁶-C₁₀H₁₄)}₂] containing the modified resin (Figure 5).

![Figure 5: Supported [RuCl₂(η⁶-C₁₀H₁₄)(pta-Bn)]⁺ half-sandwich complex design Merrifield resin](image)

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) [RuCl₂(η⁶-C₁₀H₁₄)(pta)] and [RuCl₂(η⁶-C₁₀H₁₄)(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).
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 [RuCl₂(η⁶-C₁₀H₁₄)(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 [RuCl₂(η⁶-C₁₀H₁₄)(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 [RuCl₂(η⁶-C₁₀H₁₄)(pta)] for [RuCl₂(η⁶-C₁₀H₁₄)(pta-Bn)]Cl the conversion decreases per cycle and there is no conversion in cycle 5 (Table 2).

![Redox isomerization of oct-1-en-3-ol](image)

**Figure 6: Redox isomerization of oct-1-en-3-ol**

**Table 2: Redox isomerization of oct-1-en-3-ol with homogenous and solid-supported [RuCl₂(η⁶-C₁₀H₁₄)(pta-Bn)]⁺ catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>octan-3-one (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl₂(η⁶-C₁₀H₁₄)(pta-Bn)]Cl</td>
<td>-</td>
<td>97 59 25 2 0</td>
</tr>
<tr>
<td>Supported Ru(II)-complex</td>
<td>Merrifield resin</td>
<td>60 82 92 90 90</td>
</tr>
</tbody>
</table>

*Conditions: t=1h, t=2h, t=3h; [sub]:[Na₂CO₃]:[Ru]=100:2:1; n_Ru=210⁻⁵ mol (homogenous); [sub]:[Na₂CO₃]:[Ru]=66:1:3:1; n_Ru=310⁻⁵ 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 [RuCl₂(η⁶-C₁₀H₁₄)(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 [RuCl₂(η⁶-C₁₀H₁₄)(pta)] gradually turned lemon yellow on the effect of 2 equivalents of Na₂CO₃. A well as a new signal appears on the effect of Na₂CO₃ at δ = -33.2 ppm instead of the [RuCl₂(η⁶-C₁₀H₁₄)(pta)] ³¹P NMR signal (δ = -35.5 ppm) in the ³¹P NMR spectra. These phenomena were rationalized assuming ligand exchange leading to formation of [Ru(η²-O₂CO)(η⁶-C₁₀H₁₄)(pta)] (Figure 7). The new complex was characterized by different spectroscopic methods (¹H, ¹³C, ³¹P-NMR, UV-Vis) and its composition was confirmed by elemental analysis.
[Ru(η²-O₂CO)(η⁶-C₁₀H₁₄)(pta)]²H₂O 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(η²-O₂CO)(η⁶-C₁₀H₁₄)(pta)]) is more active in the redox isomerization of allyl alcohols than the in situ [RuCl₂(η⁶-C₁₀H₁₄)(pta)] and 2 equivalents of Na₂CO₃. The role of the carbonate ligand is shown by the suggested mechanism (Figure 8):

This complex is significantly more active than the hitherto known in situ [RuCl₂(P)(η⁶-arene)]+base catalysts. Aqueous solutions of [Ru(η²-O₂CO)(pta)(η⁶-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(η²-O₂CO)(η⁶-C₁₀H₁₄)(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).
Synthesis, heterogenization and catalytic applications of water-soluble Ru(II)-complexes

**Table 3:** Isomerization of allylic alcohols with [Ru($\eta^2$-O$_2$CO)($\eta^6$-C$_{10}$H$_{14}$)(pta)] catalyst in water

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Conversion (%)</th>
<th>TOF (h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>prop-1-en-3-ol*</td>
<td>24</td>
<td>96</td>
</tr>
<tr>
<td>but-1-en-3-ol*</td>
<td>27</td>
<td>108</td>
</tr>
<tr>
<td>pent-1-en-3-ol</td>
<td>97</td>
<td>388</td>
</tr>
<tr>
<td>hex-1-en-3-ol</td>
<td>93</td>
<td>372</td>
</tr>
<tr>
<td>hept-1-en-3-ol</td>
<td>97</td>
<td>388</td>
</tr>
<tr>
<td>okt-1-en-3-ol</td>
<td>99</td>
<td>396</td>
</tr>
</tbody>
</table>

*Conversion determined by $^1$H NMR spectroscopy.*

Conditions: $n_{Ru}=10^{-7}$ mol; $n_{subs.}=2 \times 10^{-3}$ mol; $V_{H_2O}=3$ ml; $T=75^\circ$C.
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 [RuCl₂(η⁶-C₁₀H₁₄)(pta)]-t, [RuCl₂(η⁶-C₁₀H₁₄)(pta-Bn)]Cl or Merrifield resin supported Ru(II)-complex instead of [RuCl₂(η⁶-C₁₀H₁₄)(mtppms-Na)] (Table 4).

![Figure 9: Reduction of cyclohexanone](image)

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

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>KOH</th>
<th>2 eq. Na₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Sz]:[K]=500:1</td>
<td>[Sz]:[K]=100:1</td>
</tr>
<tr>
<td>[RuCl₂(η⁶-C₁₀H₁₄)(mtppms-Na)]</td>
<td>99*</td>
<td>99</td>
</tr>
<tr>
<td>[RuCl₂(η⁶-C₁₀H₁₄)(Bn-pta)]Cl</td>
<td>10</td>
<td>94</td>
</tr>
<tr>
<td>[RuCl₂(η⁶-C₁₀H₁₄)(pta)]</td>
<td>31</td>
<td>98</td>
</tr>
<tr>
<td>RuCl₂(η⁶-C₁₀H₁₄)(pta-Bn)]⁺-Merrifield</td>
<td></td>
<td>67**</td>
</tr>
</tbody>
</table>

Conditions: *literature data; n₉₀₀=1·10⁻⁵ mol, V₂-propanol=9,25 ml, t=1h, T=82°C **t= 3h; n₉₀₀=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 Na₂CO₃, it can also be reduced by [RuCl₂(η⁶-C₁₀H₁₄)P] (P=pta, (pta-Bn)Cl, mtppms-Na) complexes. Of these bases, Na₂CO₃ is the most effective if [base]:[Ru] = 2.

![Figure 10: Reduction of benzaldehyde in hydrogen transfer reactions from 2-propanol](image)

4.3. In the hydrogen transfer reaction of benzaldehyde catalyzed by [RuCl₂(η⁶-C₁₀H₁₄)(pta)] from 2-propanol if the ratio of [Na₂CO₃]:[Ru] is more than 3, salting out occurs and as a result, conversion is reduced.

4.4. Similar to the preparation of [Ru(η²-O₂CO)(η⁶-C₁₀H₁₄)(pta)] (see point 3.5.), the [Ru(η²-O₂CO)(η⁶-C₁₀H₁₄)(mtppms-Na)] was also isolated in solid form. It was proved that the activity of in situ [RuCl₂(η⁶-C₁₀H₁₄)(P)] + 2 Na₂CO₃ catalysts is higher than that of the [Ru(η²-O₂CO)(η⁶-C₁₀H₁₄)(P)] complexes (P = pta, mtppms-Na) however, the use of [Ru(η²-O₂CO)(η⁶-C₁₀H₁₄)(P)] is advantegous/preferable in neutral aqueous solutions in case of base-sensitive substrates.
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]:[RuCl₂(η⁶-C₁₀H₁₄)(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 [RuCl₂(η⁶-C₁₀H₁₄)(pta)] + 2 Na₂CO₃ catalyst

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzaldehyde</td>
<td>80</td>
</tr>
<tr>
<td>4-fluorobenzaldehyde</td>
<td>30</td>
</tr>
<tr>
<td>2-fluorobenzaldehyde</td>
<td>19</td>
</tr>
<tr>
<td>4-ethoxybenzaldehyde</td>
<td>79</td>
</tr>
<tr>
<td>3-methylbenzaldehyde</td>
<td>87</td>
</tr>
<tr>
<td>2-hydroxybenzaldehyde</td>
<td>26</td>
</tr>
<tr>
<td>cinnamon aldehyde</td>
<td>11 (just C=O)</td>
</tr>
<tr>
<td>hexanal</td>
<td>59</td>
</tr>
</tbody>
</table>

Conditions: n_Ru=1·10⁻⁵ mol, [Sub]:[Na₂CO₃]:[Ru]=100:2:1, V₂-propanol=9.25 ml, t=1 h, 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 [RuCl₂(η⁶-C₁₀H₁₄)(pta)] + 2 Na₂CO₃ catalyst

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexanone</td>
<td>86</td>
</tr>
<tr>
<td>acetofenone</td>
<td>67</td>
</tr>
<tr>
<td>m-methylacetophenone</td>
<td>68</td>
</tr>
<tr>
<td>p-methylacetophenone</td>
<td>80</td>
</tr>
<tr>
<td>octan-3-one</td>
<td>30</td>
</tr>
</tbody>
</table>

Conditions: n_Ru=1·10⁻⁵ mol, [Sub]:[Na₂CO₃]:[Ru]=100:2:1, V₂-propanol=9.25 ml, t=1 h, 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

2. Anup Kumar Misra, Éva Bokor, Sándor Kun, Evelin Bolyog-Nagy, Ágnes Kathó, Ferenc Joó, László Somsák
   Chemoselective hydration of glycosyl cyanides to C-glycosyl formamides using ruthenium complexes in aqueous media

3. Evelin Bolyog-Nagy, Antal Udvardy, Ágnes Barczáné-Bertók, Ferenc Joó, Ágnes Kathó
   Facile synthesis of [Ru(η²-O₂CO)(pta)(η⁶-p-cymene)], an outstandingly active Ru(II) half-sandwich complex for redox isomerization of allylic alcohols
   Inorganica Chimica Acta 455 (2017) 514-520

   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
   Inorganica Chimica Acta 470 (2018) 82-92

Az értekezés témakörében tartott előadások/ Lectures related to the dissertation


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


6. E. Bolyog-Nagy, 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


List of publications related to the dissertation

Foreign language scientific articles in international journals (4)

   DOI: http://dx.doi.org/10.1016/j.ica.2017.04.054
   IF: 2.433

   DOI: http://dx.doi.org/10.1016/j.ica.2016.06.041
   IF: 2.264

   DOI: http://dx.doi.org/10.1016/j.tetlet.2015.09.040
   IF: 2.347
DOI: http://dx.doi.org/10.1002/ chin.201448044
IF: 2.379

Total IF of journals (all publications): 9,423
Total IF of journals (publications related to the dissertation): 9,423

The Candidate's publication data submitted to the IDEa Tudóstér have been validated by DEENK on the basis of the Journal Citation Report (Impact Factor) database.

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