PhD Theses

Selective hydrogenation of α,β-unsaturated oxocompounds with water-soluble Ru- and Rh-phosphane complexes

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Explanation of the abbreviations and trivial names in the theses

cinnamaldehyde	(2E)-3-phenylprop-2-en-1-one
cinnamyl-alcohol	(2E)-3-phenylprop-2-en-1-ol
celloszolv	2-etoxyethanol
citral	3,7-dimethyl-octa-2,6-dien-1-al
***i*PrOH**	propan-2-ol
PPh$_3$	triphenylphosphane
***m*tppms; P**	3-diphenylphosphinobenzenesulphonic acid Na-salt
***m*tppts**	3,3',3''-phosphinotriilbenzenesulphonic acid Na-salt
[P]	concentration of the 3-diphenylphosphinobenzenesulphonic acid Na-salt
[Cat.]	concentration of the catalyst
[S]	concentration of the substrate
NMR	Nuclear Magnetic Resonance spectroscopy
TOF	Turnover Frequency (h^{-1})

1. Introduction and objectives

Catalysts used in the chemical industry have not only to be active and highly selective, but also have to be easily separable from the products and can be reused in the following processes. The first two properties are the common features of homogeneous catalysts, while the last two are the attributes of heterogeneous catalysts. Many research groups have been working on the unification of these favorable properties.

In the well-known aqueous-organic biphasic systems the catalyst is solved in the aqueous phase, which is immiscible with the organic phase, containing the substrate. The reaction is carried out by intensively stirring the reaction mixture. After that, the two phases can be easily separated through decantation. In ideal cases, the organic phase contains the product(s), while the catalyst-containing aqueous phase can be reused in a new catalytic process. The foundations of the aqueous-organic biphasic catalysis were made by the Department of Physical Chemistry at University of Debrecen. It was demonstrated that unsaturated carboxylic acids can be hydrogenated in aqueous media in the presence of the water-soluble analogs of $[RhCl(PPh_3)_3]$ and $[RuCl_2(PPh_3)_3]$. The catalysts were made water-soluble by applying the monosulphonated version of PPh_3 (*m*tppms) as the ligand.

It was demonstrated that these complexes can catalyze not only the two-phase hydrogenation of cinnamaldehyde, but they are also active in hydrogen transfer reactions using $HCOO^-$ as hydrogen source. The catalyst, $[\{RuCl_2(mtppms)_2\}_2]$ was solved in aqueous HCOONa solution, while the substrate was solved in chlorobenzene. After intensive stirring of the two phases, cinnamyl-alcohol was selectively produced, which could be easily separated from the aqueous phase containing the hydrogen source and the catalyst. It was also demonstrated that using $[RhCl(mtppms)_3]$ instead of $[\{RuCl_2(mtppms)_2\}_2]$, the selective reduction of the C=C bond takes place in the case of cinnamaldehyde. Because of the difference in the selectivity between the Ru(II)- and Rh(I)-compunds, *my aim was to investigate the reactions catalyzed by the [RhCl(mtppms)₃] in more details, including the hydrogenation of other aldehydes.*

I also aimed to determine the advantages of the monophasic system over the biphasic system. In this case the reduction is carried out in a phase that can fully solve the three components (the substrate, HCOONa and the water-soluble catalyst), followed by an induced phase separation to extract the product.

More detailed knowledge of the interactions between the HCOO⁻ and the catalysts can be very useful to understand the reaction-mechanisms. *I decided to determine the compositions and the structures of the hydrido-complexes formed in the catalytic reactions via multi-nuclear NMR-methods.*

HCO_3^- is a byproduct of hydrogen transfer reactions from HCOO⁻. The reduction of HCO_3^- to HCOO⁻ catalyzed by the [{RuCl₂(*m*tppms)₂}₂] is well-known, so an idea presented itself to produce catalytic amounts of HCOO⁻ from HCO_3^- for the reduction of aldehydes (**Figure 1.**).
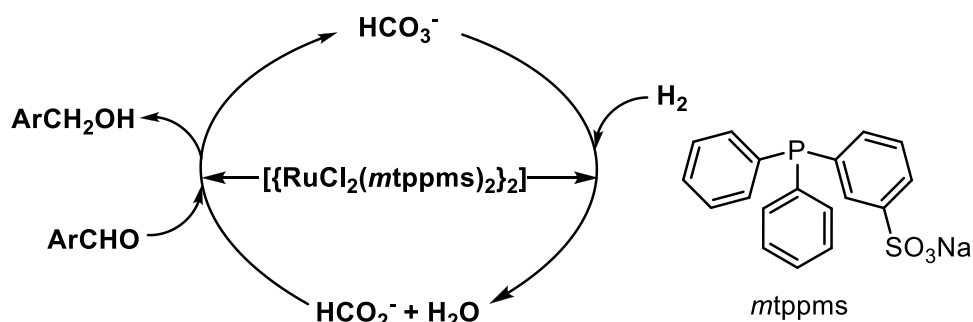

Figure 1.: Selective reduction of aldehydes in the presence of catalytic amount of HCO_3^-

To verify the hypothetical cycle shown in **Figure 1.**, *I studied the conversions of cinnamaldehyde in the presence and absence of HCO_3^- in various H_2-pressures.*

2. Applied experimental techniques

Schlenk-technique was used in the preparation of the ligand and the catalysts applied in the experiments. Hydrogen transfer reactions were carried out under inert atmosphere. Reactions under 2-10 bar hydrogen pressures were carried out in high pressure glass reactors made in the Department of Physical Chemistry.

Distilled water or 0.2 M phosphate buffers were used in the reactions. The buffer solutions were made from reagent grade NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. The pH of the solutions was determined by calibrated pH-meters.

A HEWLETT-PACKARD 5890 Series II gas chromatograph with CARBOWAX 30M capillary column and an Agilent 7890A gas chromatograph with Chrompack WCOT Fused Silica 30 m×32 μm CP WAX52CB capillary column, both equipped with flame ionization detectors (FID), were applied in the measurements of organic products of the catalytic reactions.

The structures of the hydrido-complexes were determined using ^{31}P-, ^{13}C- and ^{1}H-NMR techniques, using a BRUKER DRX 360 instrument.

3. New scientific results

3.1 It was demonstrated that cinnamaldehyde is selectively reduced from HCOONa to
a) cinnamyl-alcohol in the presence of [{RuCl₂(*m*tppms)₂}₂] and b) 3-phenylpropanal in the presence of [RhCl(*m*tppms)₃] in mixtures of water/*i*PrOH

1.a) Cinnamaldehyde was fully converted to cinnamyl-alcohol in mixtures of water and water-soluble organic solvents (volume ratio 2:1) in the presence of HCOONa and [{RuCl₂(*m*tppms)₂}₂], at a temperature of $T = 30°C$ after 2 hours. Among the organic solvents examined, *i*PrOH was found the most useful. I also demonstrated that *i*PrOH functions as a solvent and not as a hydrogen source.
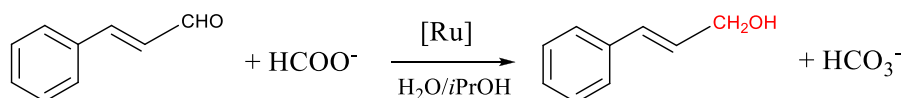
Varying the water/*i*PrOH volume ratio, the ideal mixture was found to contain 4.0 mL of water and 3.5 mL of *i*PrOH: the conversion reached 88.5% after 1 hour, a 45-fold increase compared to the 2% conversion reached in aqueous-organic biphasic system at the same conditions.

1.b) 3-phenylpropanal was the only product in the presence of [RhCl(*m*tppms)₃]. In the mixture of 4.0 mL water and 3.5 mL *i*PrOH, the conversion was measured to 41% ($T = 30°C$), which remained the same in the range of 20-80% *i*PrOH volume ratio. Conversions of cinnamaldehyde were measured between 40-50% using other water-miscible organic solvents. I found that *i*PrOH was only functioned as a solvent as it was the case with the Ru(II)-catalyst.
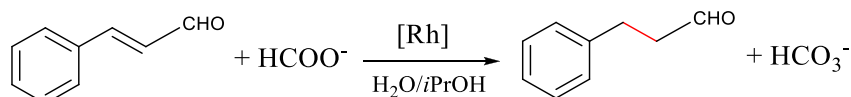
2./ The reaction rate went through a maximum as a function of HCOONa. The highest conversion was reached at [HCOO⁻]/[S] = 10:1 ratio both in the cases of [{RuCl₂(*m*tppms)₂}₂] and [RhCl(*m*tppms)₃]. Further increasing the amount of HCOO⁻, two phases were formed through salting out, which resulted in a decrease of the conversions.

3./ Using HCOOH/HCOONa mixtures as hydrogen source in various ratios, it was found that *i*./ no reaction occurred when only HCOOH was used; *ii*./ with the increasing amount of HCOONa, the conversion increased equally, thus only the latter functions as a hydrogen source.

4./ It was demonstrated that the reaction rate reach a maximum at [S]/[Cat.] = 50:1 ratio as a function of substrate concentration. Further increasing the substrate concentration, the conversion was dropped significantly in the case of [{RuCl$_2$(*m*tppms)$_2$}$_2$], and decreased moderately in the presence of [RhCl(*m*tppms)$_3$] because of the inhibitor effect of the substrate.

5./ It was found that the conversion increased until [P]/[Ru] = 6:1 ratio in the case of [{RuCl$_2$(*m*tppms)$_2$}$_2$] and [P]/[Rh] = 5:1 ratio in the case of [RhCl(*m*tppms)$_3$] as a function of *m*tppms concentration. The conversion remained constant when the concentration of *m*tppms was further increased.

6./ The effect of temperature was also studied. The virtual activation energies was determined, which resulted at 88 kJ/mol in the case of [{RuCl$_2$(*m*tppms)$_2$}$_2$] (**Figure 2.**) and 91 kJ/mol in the presence of [RhCl(*m*tppms)$_3$] (**Figure 3.**).
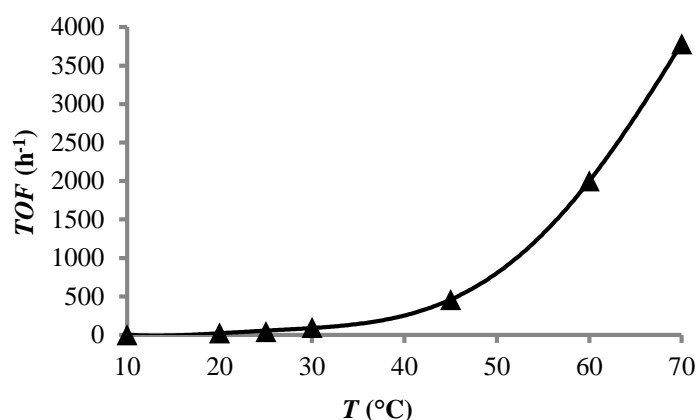

Figure 2.: Effect of the temperature on the formation of the cinnamyl-alcohol

1.0 mmol cinnamaldehyde; 0.0025 mmol [{RuCl$_2$(*m*tppms)$_2$}$_2$]; 0.04 mmol *m*tppms; 4.0 mmol HCOONa; V_{water} = 4.0 mL; V_{iPrOH} = 3.5 mL
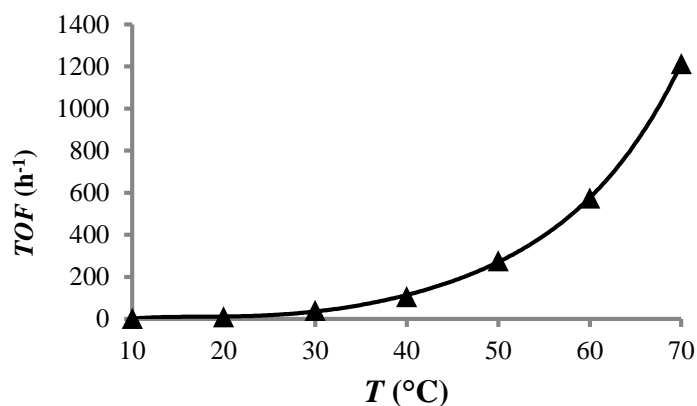
Figure 3.: Effect of the temperature on the formation of the 3-phenylpropanal

1.0 mmol cinnamaldehyde; 0.01 mmol [RhCl(*m*tppms)$_3$]; 0.07 mmol *m*tppms; 6.0 mmol HCOONa

V_{water} = 4.0 mL; V_{iPrOH} = 3.5 mL

7.a) Reactions between [{RuCl$_2$(*m*tppms)$_2$}$_2$], *m*tppms and HCOONa in the absence of cinnamaldehyde were also studied, applying ^{1}H-, ^{13}C and ^{31}P-NMR techniques. Formations of *trans,mer*-[H$_2$RuX(*m*tppms)$_3$] (X = H$_2$O, HCOO$^-$) complexes were observed (**Figure 4.**).

δ[H$_{1-2}$] = -17.7 ppm (td)
J[H$_{1-2}$-P] = 23 Hz

δ[P$_a$] = 43.7ppm
δ[P$_b$] = 77.3 ppm

δ[H$_{1-2}$] = -19.2 ppm (td)
J[H$_{1-2}$-P] = 25 Hz

δ[P$_a$] = 44.0 ppm
δ[P$_b$] = 79.2 ppm

δ[C] = 174.0 ppm (br)
J[C-H] = 195 Hz
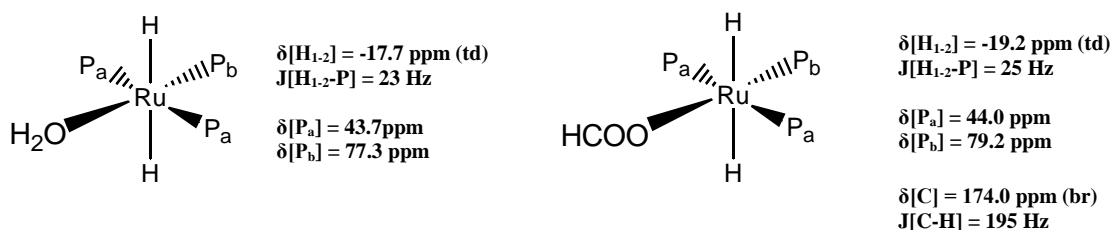
Figure 4.: ^{1}H-, ^{13}C- and ^{31}P NMR properties of the Ru-dihydrides

7.b) *Cis,mer*-[H$_2$RhX(*m*tppms)$_3$] (X = H$_2$O, HCOO$^-$) complexes (**Figure 5.**) were identified as products of the reactions between [RhCl(*m*tppms)$_3$], *m*tppms and HCOONa, using the same techniques as described in the case of the Ru(II)-complexes.

^{1}H-NMR = -8.63 ppm (d)
-18.5 ppm (s)

^{31}P-NMR = 40.72 ppm (dd)
22.66 ppm (dt)

J[H-P$_b$] ~ can not be determined
J[P$_a$-Rh] ~ 114 Hz
J[P$_b$-Rh] ~ 57 Hz
J[P$_a$-Rh] ~ 19 Hz

^{1}H-NMR = -8.35 ppm (d)
-18.3 ppm (s)

^{31}P-NMR = 42.25 ppm (dd)
24.16 ppm (dt)

^{13}C-NMR = 173.84 ppm (d)

J[C-P$_{a-b}$] ~ 4 Hz
J[C-H] ~ 195 Hz
J[H-P$_b$] ~ 156 Hz
J[P$_a$-Rh] ~ 114 Hz
J[P$_b$-Rh] ~ 86 Hz
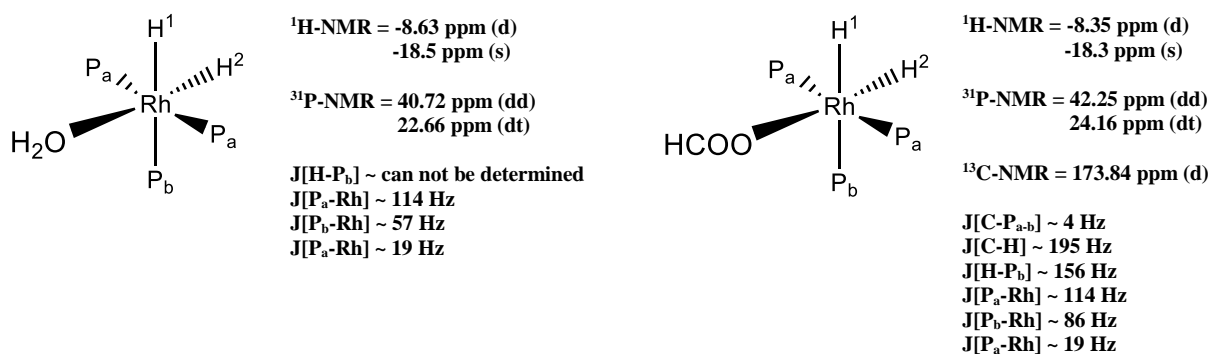J[P$_a$-Rh] ~ 19 Hz

Fiure 5.: ^{1}H-, ^{13}C- and ^{31}P NMR properties of the Rh-dihydrides

8./ Based on the results of the catalytic reactions and the NMR measurements, the following reaction mechanisms were suggested:

a) The substrate is coordinated to the place of the H_2O ligand in *trans,mer*-[$H_2Ru(H_2O)(m$tppms$)_3$]. Internal hydride migration to the coordinated aldehyde would result the corresponding alkoxyde from which the corresponding alcohol would release by protonation of water while the coordination of $HCOO^-$ would occur. The *trans,mer*-[$RuH_2(H_2O)(m$tppms$)_3$] would reform by the decomposition of $HCOO^-$ to HCO_3^- within the coordination sphere of Ru(II) (**Figure 6.**).

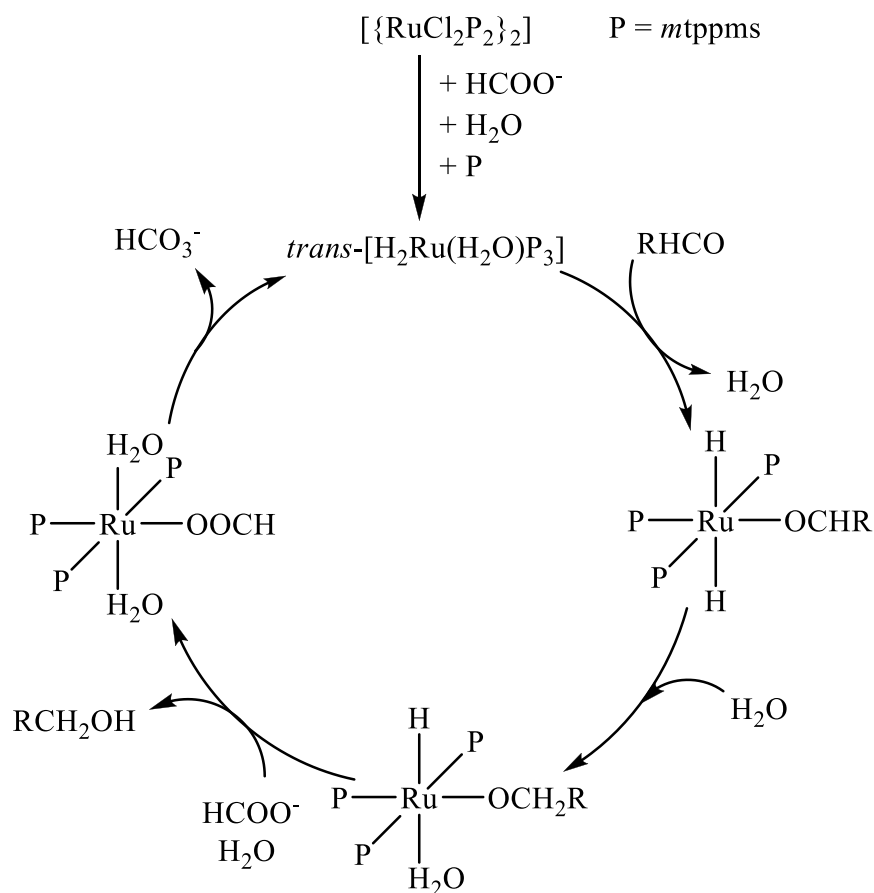**Figure 6.:** Suggested reaction mechanism for the aldehyde's hydrogen transfer reductions from aqueous $HCOO^-$ catalysed by [{$RuCl_2(m$tppms$)_2$}$_2$] + n $m$tppms

b) Cinnamaldehyde would coordinate through the C=C bond to replace the H_2O ligand in *cis,mer*-[$H_2Rh(H_2O)(m$tppms$)_3$]$^+$. Followed by the reductive elimination of 3-phenylpropanal and coordination of $HCOO^-$, [$Rh(HCOO)(m$tppms$)_3$] would form from which *cis-mer*-[$H_2Rh(H_2O)(m$tppms$)_3$]$^+$ would reform through internal redox reactions (**Figure 7.**).

[RhClP₃]   P = *m*tppms

| + HCOONa
| + H₂O
| + P
↓

HCO₃⁻   *cis-mer*-[H₂Rh(H₂O)P₃]   Ph—CH=CH—CHO

H₂O

[Rh(HCOO)P₃]   [H₂Rh(Ph-CH=CH-CHO)P₃]

Ph—CH₂CH₂—CHO   HCOO⁻

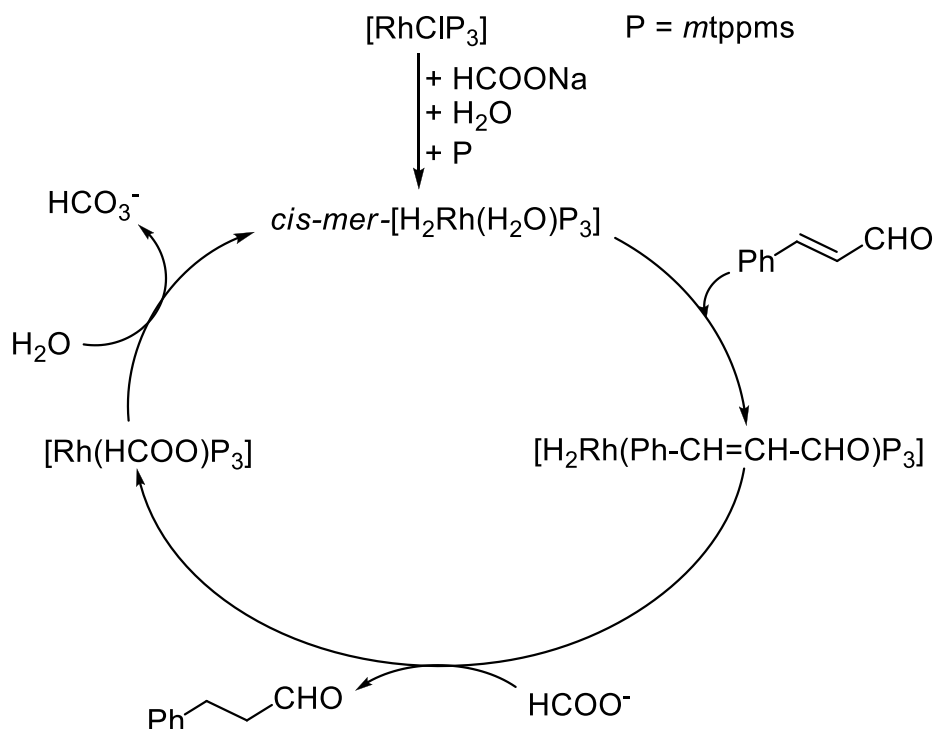**Figure 7.:** Suggested reaction mechanism for the cinnamaldehyde's hydrogen transfer reductions from aqueous HCOO⁻ catalysed by [RhCl(*m*tppms)₃] + n *m*tppms

9./ Various aldehydes were reduced to the corresponding alcohols using [{RuCl₂(*m*tppms)₂}₂] (**Table 1.**), except pyridine-3-aldehyde and 2-aminobenzaldehyde, both were supposedly coordinated to Ru(II) through their N-atoms. Only the C=O bond was reduced, when C=C bonds were also present. It was found that the conversions were smaller when the substrate contained electrophile groups. Ketones were not reduced at the same conditions. Utilizing higher temperature and longer reaction time ($T = 50°C$; $t = 4$ h), the corresponding alcohols were formed at 2% in the case of acetophenone, and 3% in the case of isophorone, respectively.

Table 1.: Hydrogen transfer reduction of various aldehydes in water/iPrOH mixtures

Aldehyde	Conversion (%)	
	t = 0.5 hours	t = 1 hour
cinnamaldehyde	33	65
3-phenylpropanale	44	79
benzaldehyde	36	82
citronellal	37	81
4-bromobenzaldehyde	100	100
4-ethoxybenzaldehyde	100	100
citral	32	65
ciklohexanecarboxaldehyde	40	61
2-fluorobenzaldehyde	no data	39
3-fluorobenzaldehyde	no data	24
4-fluorobenzaldehyde	no data	48
4-trifluoromethylbenzaldehyde	no data	40
3-methylbenzaldehyde	no data	19
pyridine-3-aldehyde	0	0
2-aminobenzaldehyde	0	0

1.0 mmol substrate; 0.0025 mmol [{RuCl$_2$($m$tppms)$_2$}$_2$]; 0.04 mmol $m$tppms; 6.0 mmol HCOONa; V_{water} = 4.0 mL; V_{iPrOH} = 3.5 mL; T = 30°C

10./ It was demonstrated that using [RhCl($m$tppms)$_3$] in the catalytic reduction of citral, both the reduction of the C=C and C=O would take place. Product ratio was depended on the temperature: the conversion reached 22.4%, of which 17.0% were citronellal and 5.4% were unsaturated alcohol (geraniol + nerol) at T = 30°C, while at T = 40°C citronellol was also produced. It was found that the selectivity decreased significantly as the function of temperature (**Figure 8.**).
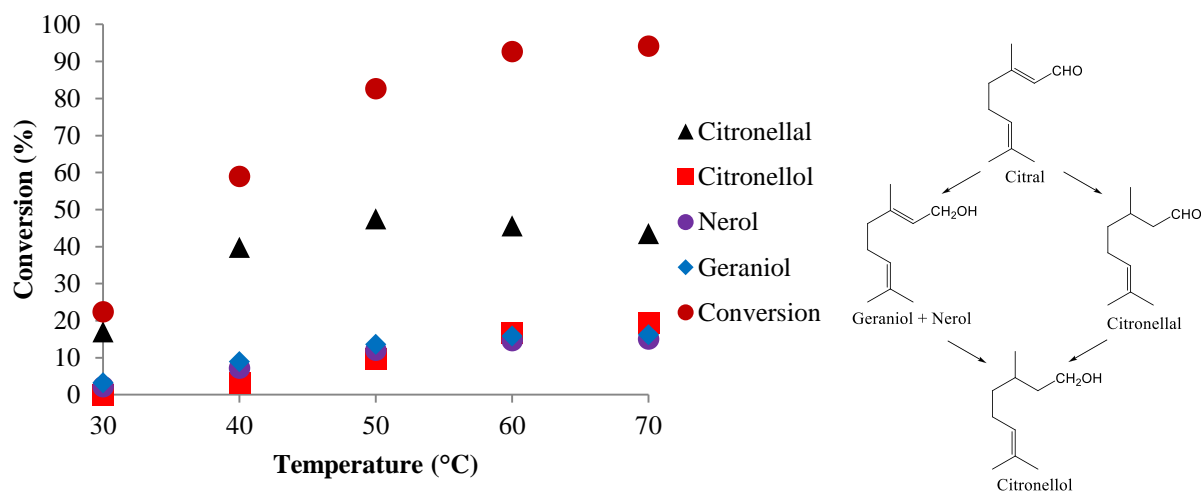
Figure 8.: Hydrogen transfer reduction of citral in water/*i*PrOH mixture using [RhCl(*m*tppms)$_3$] catalyst

1.0 mmol citral; 0.01 mmol [RhCl(*m*tppms)$_3$]; 0.07 mmol *m*tppms; 6.0 mmol HCOONa;

V_{water} = 4.0 mL; V_{iPrOH} = 3.5 mL; t = 1 hour

11./ Various saturated aldehydes were used to compare the monophasic system to the aqueous-organic biphasic system at the same conditions. It was observed that the formation of the corresponding alcohols was more effective in the monophasic system with the sole exception of the 2-fluorobenzaldehyde (**Table 2.**). However, the difference between the two systems in terms of conversion was significantly smaller than it was observed in the reactions of cinnamaldehyde catalyzed by [{RuCl$_2$(*m*tppms)$_2$}$_2$].

Table 2.: Hydrogen transfer reduction of saturated aldehydes in mono- and biphasic systems

Aldehyde	Conversion (%)	
	water/*i*PrOH	water
benzaldehyde	60	57
3-tolualdehyde	87	57
4-bromobenzaldehyde	2	0
4-trifluoromethylbenzaldehyde	80	67
2-fluorobenzaldehyde	76	77
3-fluorobenzaldehyde	78	66
4-fluorobenzaldehyde	84	49
3-phenylpropionaldehyde	12	0
ciklohexane-carboxaldehyde	14	0
pyridine-3-aldehyde	0	0

1.0 mmol substrate; 0.01 mmol [RhCl(*m*tppms)$_3$]; 0.07 mmol *m*tppms; 6.0 mmol HCOONa;

T = 50°C; t = 1 hour;

Solvent: [a]V_{water} = 4.0 mL + V_{iPrOH} = 3.5 mL, or [b]V_{water} = 7.5 mL

3.2 It was demonstrated that in the presence of catalytic amounts of HCO_3^-, the selective hydrogenation of cinnamaldehyde - catalyzed by [{RuCl₂(*m*tppms)₂}₂] - takes place significantly faster

1./ It was observed that in aqueous-organic biphasic system, hydrogenation of cinnamaldehyde was more effective in the presence of NaHCO₃ compared to the 0.2 M phosphate buffer solution at the same conditions.

Both conversion and selectivity were significantly decreased, when monophasic water/*i*PrOH mixtures were used as reaction media.

2./ The effect of HCO_3^- was also studied. Maximum conversion was reached in the presence of $n = 0.2$ mmol NaHCO₃ at $p(H_2) = 1$ bar (**Figure 9.**). It was found that the conversions were increased significantly, when the catalyst was reacted with H_2 for 10 minutes before the addition of the substrate.
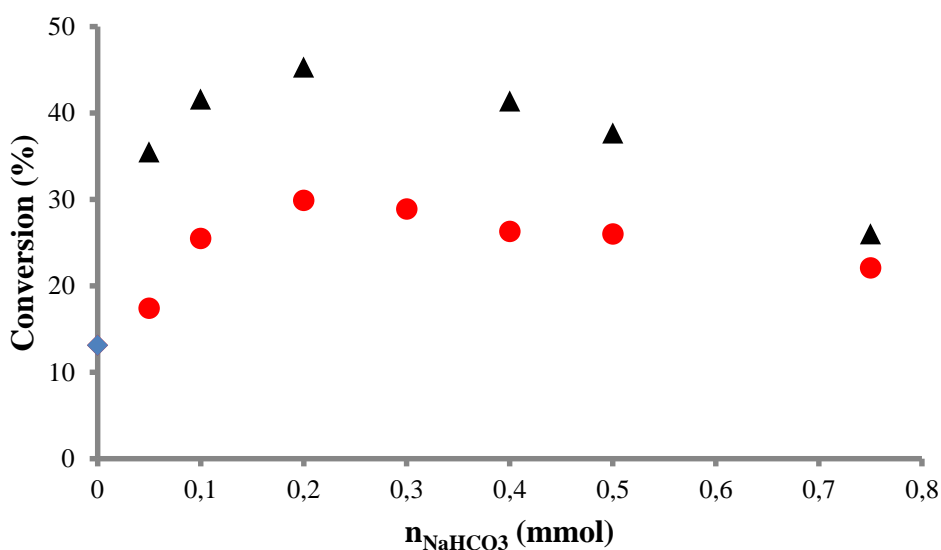

Figure 9.: Effect of the amount of the NaHCO₃ in the reduction of cinnamaldehyde

0.4 mmol cinnamaldehyde; 0.005 mmol [{RuCl₂(*m*tppms)₂}₂]; 0.08 mmol *m*tppms;

$V_{water} = 7.5$ mL; $p(H_2) = 1$ bar; $T = 50°C$; $t = 1$ hour

Symbols: ● without pre-hydrogenation; ▲ 10 minutes long pre-hydrogenation of NaHCO₃;

♦ in the absence of NaHCO₃ the reaction was carried out in 7.5 mL 0.2 M phosphate buffer, pH = 8.3

Cinnamyl-alcohol was the only product applying $p(H_2) = 10$ bar after 20 minutes of reaction. The highest conversion was reached in the presence of $n = 0.2$ mmol NaHCO₃.

3./ It was demonstrated that the conversions were increased as the function of the ligand/catalyst ratio ($p(H_2) = 10$ bar; $T = 50°C$). Cinnamyl-alcohol is the only product, except in absence of added $m$tppms ('5.4% cinnamyl-alcohol + 3.1% 3-phenylpropanal).

4./ It was demonstrated that in the transfer hydrogenation reaction of cinnamaldehyde carried out in the $T = 30\text{-}70°C$ temperature range under $p(H_2) = 1$ bar, cinnamyl-alcohol was the main product, but trace amounts of 3-phenylpropanal and 3-phenylpropanol were also observed. Using 0.2 M phosphate buffer solutions, the conversions were significantly smaller at the same conditions (cinnamyl-alcohol was the only product in the $T = 30\text{-}60°C$ temperature range, but at $T = 70°C$ trace amounts of 3-phenylpropanal and 3-phenylpropanol were detected).

The conversions were increased lineal either in the presence of 0.20 mmol NaHCO$_3$ or in 0.2 M phosphate buffer (pH = 8.3) at $p(H_2) = 10$ bar. It was found that the sole product was cinnamyl-alcohol, which was formed significantly faster in the presence of NaHCO$_3$ (**Figure 10.**).
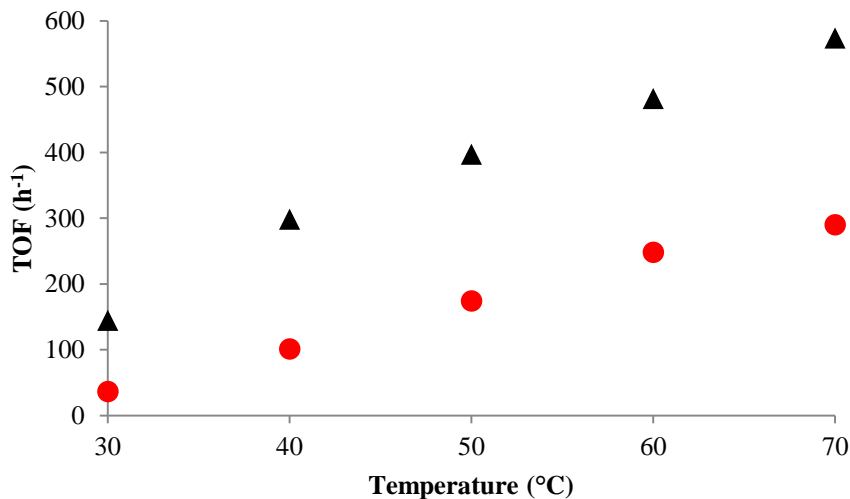

Figure 10.: Effect of HCO_3^- vs. the temperature in the reduction of cinnamaldehyde at $p(H_2) = 10$ bar

1.0 mmol cinnamaldehyde; 0.0025 mmol [{RuCl$_2$($m$tppms)$_2$}$_2$]; 0.04 mmol $m$tppms;

$t = 1$ hour

Symbols: ● 7.5 mL 0.2 M phosphate buffer solution; ▲ V$_{water}$ = 7.5 mL + 0.2 mmol NaHCO$_3$

5./ The effect of H$_2$-pressure was also studied. The conversions were increased significantly faster as the function of H$_2$-pressure in the presence of 0.1 mmol of NaHCO$_3$ than in 0.2 M phosphate buffer (pH = 8.3) at $T = 50°C$ (**Figure 11.**).
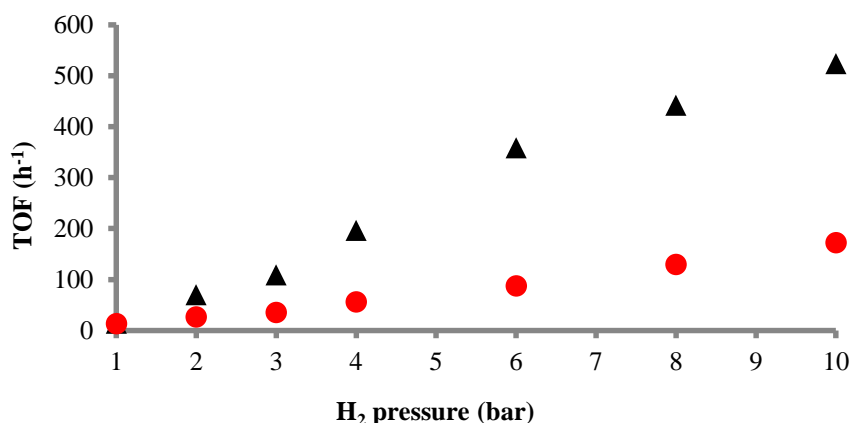
Figure 11.: The effect of the H_2-pressure in the formation of cinnamyl-alcohol in the presence as well as the absence of $NaHCO_3$

1.0 mmol cinnamaldehyde; 0.0025 mmol [{RuCl$_2$(*m*tppms)$_2$}$_2$]; 0.04 mmol *m*tppms;

$V_{aqueous\ phase}$ = 7.5 mL; T = 50°C; t = 1 hour

Symbols: ● 0.2 M phosphate buffer, pH = 8.30; ▲ 13.3 mM $NaHCO_3$ solution

6./ The reaction between [{RuCl$_2$(*m*tppms)$_2$}$_2$], *m*tppms and $NaHCO_3$ at $p(H_2)$ = 1 bar was also investigated, using ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. *Cis*-[H$_2$Ru(H$_2$O)(*m*tppms)$_3$] was formed in the absence of HCO_3^-, while *trans,mer*-[H$_2$Ru(H$_2$O)(*m*tppms)$_3$] was the product in the presence of HCO_3^-. Between the two hydrido-complexes, the latter one is a more active catalyst in the selective reduction of aldehydes. The rate increasing effect of the HCO_3^- can be interpreted with the aforementioned difference in the catalytic activity between the two complexes.

7./ Based on the results of the catalytic reactions and the multinuclear NMR measurements, the following reaction mechanism was suggested:

[Ru(H$_2$O)$_2$(HCO$_3$)$_2$(*m*tppms)$_2$] is formed from the reaction between [{RuCl$_2$(*m*tppms)$_2$}$_2$] and HCO_3^- under argon atmosphere, which is transformed into *trans*-[Ru(H)$_2$(H$_2$O)(*m*tppms)$_3$] in the presence of H_2. When cinnamaldehyde is added, *trans*-[Ru(H)$_2$(RCHO)(*m*tppms)$_3$] would form, from which the catalytically active *trans*-[Ru(H)$_2$(H$_2$O)(*m*tppms)$_3$] would reform, while cinnamyl-alcohol would release (**Figure 12.**).

[{RuCl$_2$(*m*tppms)$_2$}$_2$]
+
*m*tppms

HCO$_3^-$

H$_2$O
(HCO$_3$)⟍ | ⟋*m*tppms
Ru
(HCO$_3$)⟋ | ⟍*m*tppms
H$_2$O

HCO$_2^-$ H$_2$

RCHO

H
H$_2$O⟍ | ⟋*m*tppms
Ru
*m*tppms⟋ | ⟍*m*tppms
H

H
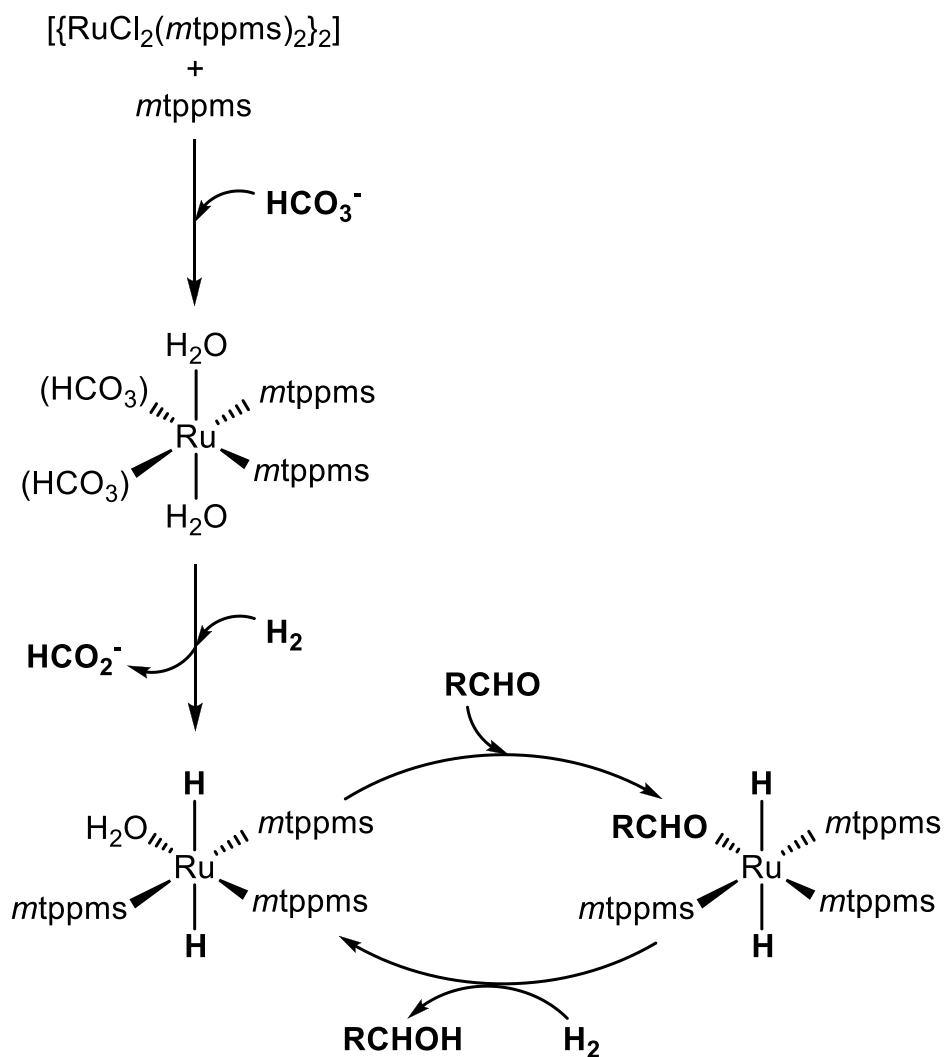RCHO⟍ | ⟋*m*tppms
Ru
*m*tppms⟋ | ⟍*m*tppms
H

RCHOH   H$_2$

Figure 12.: Suggested reaction mechanism for the hydrogenation reaction of cinnamaldehyde in aqueous organic biphasic system, in the presence of [{RuCl$_2$(*m*tppms)$_2$}$_2$] + *m*tppms and catalytic amount of NaHCO$_3$.

4. Possible future applications

The increasing industrial production and the need for new materials and substances are causing serious environmental damages worldwide, while the continuous increase for necessaries require the increasing of industrial production and the development of new materials. However, this quasi contradiction can be solved by applying the principles of green chemistry.

A few examples for those principles can be mentioned, like low energy consumption, environment-friendly solvents or the application of fast and selective catalysts.

Numerous compounds of α,β-unsaturated aldehydes are widely used as substrates in the flavour, cosmetic, food or pharmaceutical industries. I studied the hydrogen transfer reactions of cinnamaldehyde as a model compound, using $[\{RuCl_2(m\text{tppms})_2\}_2]$ and $[RhCl(m\text{tppms})_3]$ catalysts, utilizing the previously mentioned principles of green chemistry.

The selective conversion of various industrially important α,β-unsaturated aldehydes can be achieved with the records of this thesis, while the environmental impact can be significantly decreased. Furthermore, the method can be used in the conversion of heat-sensitive substrates or reactions where heat-sensitive products are formed, because of the application of low temperatures here.

5. Tudományos publikációk/ List of publications

Az értekezés témájához kapcsolódó közlemények/ Publications related to the dissertation

1. <u>Imre Szatmári</u>, Gábor Papp, Ferenc Joó, Ágnes Kathó: **Promoter effect of bicarbonate in hydrogenation of cinnamaldehyde catalyzed by a water-soluble Ru(II)-phosphine complex**
   Inorganica Chimica Acta 472 (2018) 302–306 (IF (2017): 2,264)

2. Ágnes Kathó, <u>Imre Szatmári</u>, Gábor Papp, Ferenc Joó: **Effect of 2-Propanol on the Transfer Hydrogenation of Aldehydes by Aqueous Sodium Formate using a Rhodium(I)-sulfonated Triphenylphosphine Catalyst**
   Chimia 69 (2015) 339-344 (IF: 1)

3. <u>Imre Szatmári</u>, Gábor Papp, Ferenc Joó, Ágnes Kathó: **Reductions Unexpectedly fast catalytic transfer hydrogenation of aldehydes by formate in 2-propanol-water mixtures under mild conditions**
   Catalysis Today 247 (2015) 14-19 (IF: 4,312)

4. Gábor Papp, Henrietta Horváth, Gábor Laurenczy, <u>Imre Szatmári</u>, Ágnes Kathó, Ferenc Joó: **Classical and non-classical phosphine-Ru(II)-hydrides in aqueous solution: Many, various, and useful**
   Dalton Transactions 42 (2013) 521-529 (IF: 4,097)

Az értekezés témakörében tartott előadások/ Lectures related to the dissertation

1. Kathó Ágnes, <u>Szatmári Imre</u>, Papp Gábor, Joó Ferenc:**Fahéjaldehid szelektív redukciója vízoldható ruténium(II)-foszfinkomplexekkel**
   MTA Szervetlen és Fémorganikus Kémiai Munkabizottság ülése
   Zsórifürdő, 2009. május 08.

2. Szatmári Imre, Kathó Ágnes: **Fahéjaldehid szelektív redukciója *i*-propanol-víz elegyben vízoldható Ru(II)-foszfán komplexekkel**

43. Komplexkémiai Kollokvium

Siófok, 2009. május 27-29.

3. Kathó Ágnes, Bertók Ágnes, Udvardy Antal, Szatmári Imre, Papp Gábor, Torma Krisztián, Susmit Basu, Voronova Krisztina, Horváth H. Henrietta, Ambroz Almássy, Czégéni Csilla Enikő, Ősz Katalin, Horváth Henrietta, Csajbók Éva, Joó Ferenc: **Klórozott szénhidrogének reduktív dehalogénezése**

MKE 1. Nemzeti Konferencia

Sopron, 2011. május 22-25.

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

1. Szatmári Imre, Papp Gábor, Prof. Dr. Joó Ferenc, Dr. Kathó Ágnes: **Fahéjaldehid szelektív redukciója propán-2-ol/víz elegyben vízoldható Ru(II)-foszfán katalizátorral**

XV. Nemzetközi Vegyészkonferencia

Marosvásárhely, 2009. november 12-15.

2. Imre Szatmári, Gábor Papp, Ferenc Joó, Ágnes Kathó: **Selective reduction of cinnamaldehyde in propan-2-ol/water mixture with water-soluble Ru(II)-phosphane catalyst**

17th International Symposium on Homogeneous Catalysis (ISHC-17)

Poznan, Lengyelország, 2010. július 4-8

3. Szatmári Imre, Papp Gábor, Kathó Ágnes: **Fahéjaldehid redukciója víz-propanol elegyekben vízoldható Rh-foszfán katalizátorral**

MKE 1. Nemzeti Konferencia

Sopron, 2011. május 22-25.

4. <u>Imre Szatmári</u>, Gábor Papp, Ferenc Joó,Ágnes Kathó: **Bicarbonate catalysis in the hydrogenation of cinnamaldehyde**

11th International Conference on Carbon Dioxide Utilization

Université de Bourgogne, Dijon, Franciaország, 2011. június 27-30.

5. <u>Imre Szatmári</u>, Gábor Papp and Ágnes Kathó: **Reductions of aldehydes in izopropanol-water mixtures catalyzed by water-soluble Rh-phosphane complex**

18th International Symposium on Homogeneous Catalysis

Toulouse, Franciaország, 2012. július 9-13.

4. <u>Imre Szatmári</u>, Gábor Papp, Ferenc Joó,Ágnes Kathó: **Bicarbonate catalysis in the hydrogenation of cinnamaldehyde**

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Registry number: DEENK/283/2018.PL
Subject: PhD Publikációs Lista

Candidate: Imre Szatmári
Neptun ID: AEQG83
Doctoral School: Doctoral School of Chemistry
MTMT ID: 10050643

List of publications related to the dissertation

Foreign language scientific articles in international journals (4)

1. **Szatmári, I.**, Papp, G., Joó, F., Kathó, Á.: Promoter effect of bicarbonate in hydrogenation of cinnamaldehyde catalyzed by a water-soluble Ru(II)-phosphine complex.
   Inorg. Chim. Acta. 472, 302-306, 2018. ISSN: 0020-1693.
   DOI: http://dx.doi.org/10.1016/j.ica.2017.06.061
   IF: 2.264 (2017)

2. Kathó, Á., **Szatmári, I.**, Papp, G., Joó, F.: Effect of 2-Propanol on the Transfer Hydrogenation of Aldehydes by Aqueous Sodium Formate using a Rhodium(I)-sulfonated Triphenylphosphine Catalyst.
   Chimia. 69 (6), 339-344, 2015. ISSN: 0009-4293.
   DOI: http://dx.doi.org/10.2533/chimia.2015.339
   IF: 1

3. **Szatmári, I.**, Papp, G., Joó, F., Kathó, Á.: Unexpectedly fast catalytic transfer hydrogenation of aldehydes by formate in 2-propanol-water mixtures under mild conditions.
   Catal. Today. 247, 14-19, 2015. ISSN: 0920-5861.
   DOI: http://dx.doi.org/10.1016/j.cattod.2014.06.023
   IF: 4.312

4. Papp, G., Horváth, H. H., Laurenczy, G., **Szatmári, I.**, Kathó, Á., Joó, F.: Classical and non-classical phosphine-Ru(II)-hydrides in aqueous solutions: many, various, and useful.
   Dalton Trans. 42 (2), 521-529, 2013. ISSN: 1477-9226.
   DOI: http://dx.doi.org/10.1039/C2DT31793A
   IF: 4.097

List of other publications

<u>Hungarian abstracts</u> (1)

5. Kathó, Á., Bertók, Á., Udvardy, A., **Szatmári, I.**, Papp, G., Torma, K. G., Basu, S., Voronova, K., Horváth, H. H., Almási, A., Czégéni, C. E., Ősz, K., Horváth, H., Csajbók, É., Joó, F.:
Klórozott szénhidrogének reduktív dehalogénezése.
In: MKE 1. Nemzeti Konferencia : 2012. május 22-25., Sopron. Szerk.: Magyar Kémikusok Egyesülete, MKE, [Budapest], 1, 2012.

Total IF of journals (all publications): 11,673
Total IF of journals (publications related to the dissertation): 11,673

The Candidate's publication data submitted to the iDEa Tudóstér have been validated by DEENK on the basis of Web of Science, Scopus and Journal Citation Report (Impact Factor) databases.

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