

## A STUDY OF RUTHENIUM-BASED CATALYSTS USED IN HOMOGENEOUS TRANSFER HYDROGENATION OF ACETOPHENONE

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A detailed comparison of catalytic properties of two different ruthenium-based catalysts in the reaction of homogeneous hydrogenation of acetophenone was performed. Additionally, methods of synthesis of both catalysts were tested and optimized in order to achieve the best possible quality and purity of the final catalysts.

NMR analysis was used to analyze and identify the composition of ruthenium compounds and gas chromatography was used to analyze the conversion rate of hydrogenation reactions.

It was determined that  $\text{RuCl}_2(\text{PPh}_3)_3$  obtained with a modified method described by Shaw's group (Shaw et al., 2007) had the best catalytic properties in the reaction performed under conditions described in Liang Wang's publication (Wang et al., 2014). It was also determined that for concentration ratio of substrate to  $\text{RuCl}_2(\text{PPh}_3)_3$  amounting to 250:1 the conversion rate was much higher than that of the reaction performed with a double dose of the catalyst. Results of experiments also show that samples of the post-reaction solution should be analyzed right after the reaction, because even if they are stored in low temperature the amount of product can change up to 3–5% compared to the base sample and this change is not predictable.

These findings have significant implications for further research of the reaction of homogeneous transfer hydrogenation of ketones. With the right catalysts and methods of their synthesis other parameters of this reaction can be optimized. The most important one is a change of solvent from isopropyl alcohol to a less toxic substance like water. This may increase the value of the reaction in green chemistry and chemical industry.

**Keywords:** ruthenium-based catalysts, transfer hydrogenation, ketones, catalysis,  $\text{RuCl}_2(\text{PPh}_3)_3$

### 1. INTRODUCTION

The reaction of hydrogenation of multiple bonds with gaseous hydrogen in presence of homogeneous metallic catalysts has been known in organic chemistry since 1938, when it was observed for the first time by Otto Roelen. Since then it has been determined that performing this type of reaction has some significant advantages over these, where heterogeneous catalysts are used. Homogeneous catalysts are very effective and selective even when the reaction is performed under mild conditions. It also allows scientists to study the mechanism and kinetics of the reaction. Its use is also beneficial for the industry –

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it does not require a high hydrogen pressure and hazardous reducing reagents. Thanks to these features, the interest of this reaction type has been steadily growing, which resulted in a great number of decisive publications, like invention of optically active homogeneous catalysts in 1968 by William Knowles and Leopold Horner. Simultaneously to the studies of the reaction based on gaseous hydrogen a new approach was taken. In 1952 it was suggested that it might be possible to perform a reaction of catalytic hydrogen transfer from an organic molecule to various organic acceptors under mild conditions. It could be conducted in photochemical or biological processes, heterogeneous, homogeneous and photochemical catalysis.

The reaction of hydrogenation was one of several possible hydrogen transfer processes, which were classified by Braude and Linstead as follows (Brieger and Nestruck., 1974):

- hydrogen migrations, which take place within one molecule,
- hydrogen disproportionation, that takes place between two identical molecules, where one accepts the role of a donor and the other one acts as an acceptor,
- reaction of transfer hydrogenation-dehydrogenation, which occurs between two different molecules that act as a pair of donor and acceptor.

Many different hydrogen donors are used, but primary and secondary alcohols are usually a preferred choice. During hydrogenation they are oxidized to the corresponding ketone or aldehyde but depending on the choice of the catalyst and the conditions of the reactions, formation of various amounts of unconventional products can be observed.

The choice of the right catalyst is also very important. In industrial heterogeneous reaction of hydrogenation usually compounds of metals like iron, nickel and chromium are used due to their low cost and decent catalytic properties. They are also often used in their metallic form (Grzywa and Molenda, 2000). In homogeneous reaction, organic transition metal complexes are usually used as catalysts. In these compounds not only the type of the central atom is important, but also the type of ligands is extremely significant. Usually derivatives of aliphatic compounds are used, because derivatives of aromatic compounds may lead to too aggressive oxidation and removal of oxygen molecule from the oxidized compound. They also may lead to unwanted side reactions of saturation of the aromatic ring or hydrogenolysis. The type of ligand also determines the solubility of the catalyst in the reaction environment. Groups like CO, CN and PPh<sub>3</sub> are very effective in an organic environment, while ligands like amino sulfonamides are soluble in inorganic solvents. Some groups, like TPPTS (3,3',3''-phosphanetriyltris(benzenesulfonic acid) trisodium salt), are soluble in both types of solvents. In order to maximize the effectiveness of the reaction transition metals like ruthenium (Ryandler, 1979), nickel (Hurd and Perletz, 1946) and platinum (Ryandler, 1979) are often used as a central atom due to their good catalytic properties. Sometimes other metals are also used because they have some special properties even though they are worse catalysts in general. For example, osmium minimizes the probability of side reactions occurring and iridium, which is a mediocre catalyst in this type of reactions, is extremely efficient in the reaction of hydrogenation of hexane-2,5-dione to 2,5-dimethyltetrahydrofuran (Ryandler, 1979).

Hydrogenation is a reaction between molecular hydrogen and another compound or element. The general mechanism of this reaction can be summarized with a simplified equation (A is a substrate, B is a product of the reaction):



The exact mechanism of the reaction highly depends on the type of the catalyst and type of the substrate. Due to the large amount of energy needed for breaking a chemical bond in particles of the substrate usually a catalyst is used in a reaction. The reaction can be carried out without it, but then it requires very high temperature and pressure (Vougioukalakis and Grubbs, 2010). Generally, when heterogeneous catalysts are used the mechanism of the reaction can be summarized in a few steps:

- adsorption of reagents on surface of the catalyst,
- dissociation of the particle of gaseous H<sub>2</sub>,
- creation of a bond between one of the carbon atoms of ketone and dissociated hydrogen atom,
- creation of a bond between the second carbon atom of ketone and dissociated hydrogen atom,
- product of the reaction leaves surface of the catalyst.

In case of homogenous catalysts, the reaction mechanisms are different for different types of transition metal complex compounds. All of these mechanisms assume that a reaction starts with a direct interaction between the complex compound and hydrogen molecules. This triggers a cycle of reactions that lead to the transformation of a complex compound and reagents. The reaction terminates when the reaction product is generated and the catalyst particles are regenerated.

The mechanism of the reaction is also dependent on the type of hydrogen donor. If the source of hydrogen molecules is different than gaseous hydrogen, the reaction is called transfer hydrogenation. In the case of homogeneous hydrogenation of acetophenone studied in this research isopropyl alcohol was used as a donor of hydrogen. This reaction can be summarized as follows:

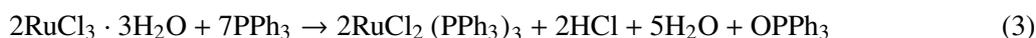


As stated before this type of reaction requires a large amount of energy, which means that an optimization of the reaction conditions is crucial for its profitability. If homogeneous catalysts are used, the temperature of the reaction should not exceed the decomposition temperature of the catalyst. In this case catalysts have to be activated with potassium hydroxide and a choice of temperature.

Most of the current research was based on optimal parameters stated in other publications. Therefore, the aim of this research was to find the effect of change of crucial reaction parameters on the amount of the product. Two different catalysts were compared, and also additional parameters of the reaction were studied.

## 2. METHODS

Firstly, both catalysts were synthesized in the laboratory. For RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, instructions from Michigan University (Gatsis, 1972) were used. It is a multistep reaction summarized by an equation:



For this reaction 300 mg RuCl<sub>3</sub>·H<sub>2</sub>O, 1800 mg PPh<sub>3</sub> and 50 ml of pure, degassed and anhydrous methanol were used. They were mixed in a distillation flask and set to boil under argon atmosphere. After an hour the reaction mixture was filtered. The collected precipitate was washed three times with 10 ml of non-stabilized diethyl ether. Then it was dried with a rotary evaporator and a vacuum pump and analyzed with NMR.

The second sample was synthesized with instructions from the other publication (Shaw et al., 2007). It was very similar to the first method. The only differences between them were the amount of methanol (65 ml instead of 50 ml) and duration of the reaction (2.5 hours instead of 1 hour). All other steps were identical to those of the first method.

The reaction was performed in the atmosphere of an inert gas, which reduced the probability of a reaction between ruthenium compounds and oxygen (Ugo, 1970). <sup>31</sup>P spectra in D<sub>2</sub>O in NMR of catalysts produced in both reactions were obtained.

RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> obtained during synthesis with the first method was contaminated with unreacted substrates. The yield of produced catalyst was not very high, which is shown in Fig. 1 (first peak from the left).

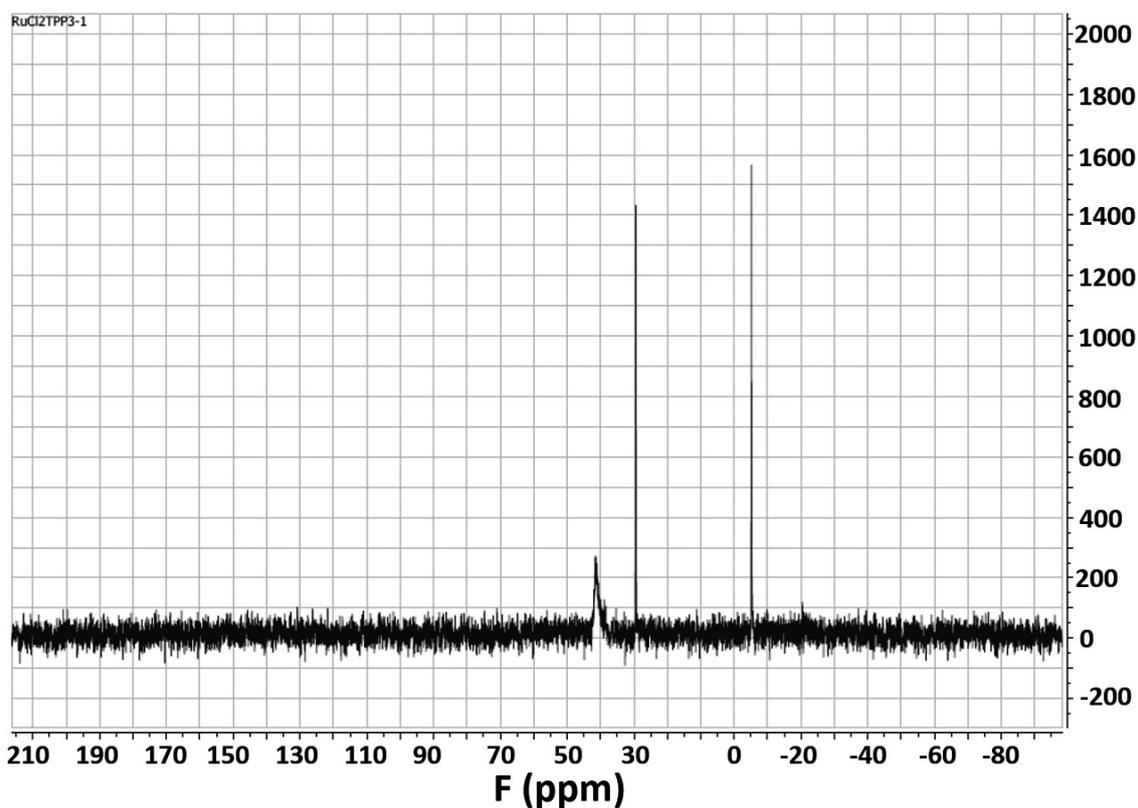


Fig. 1.  $^{31}\text{P}$  spectrum of  $\text{RuCl}_2(\text{PPh}_3)_3$  sample produced in the first reaction

Results for the catalyst obtained during the second reaction were significantly better, as shown in Fig. 2. For this reason, the first sample was not used during the reaction of hydrogenation. Instead, the reaction was carried out with the second sample. The reaction was also carried out without the synthesized catalyst

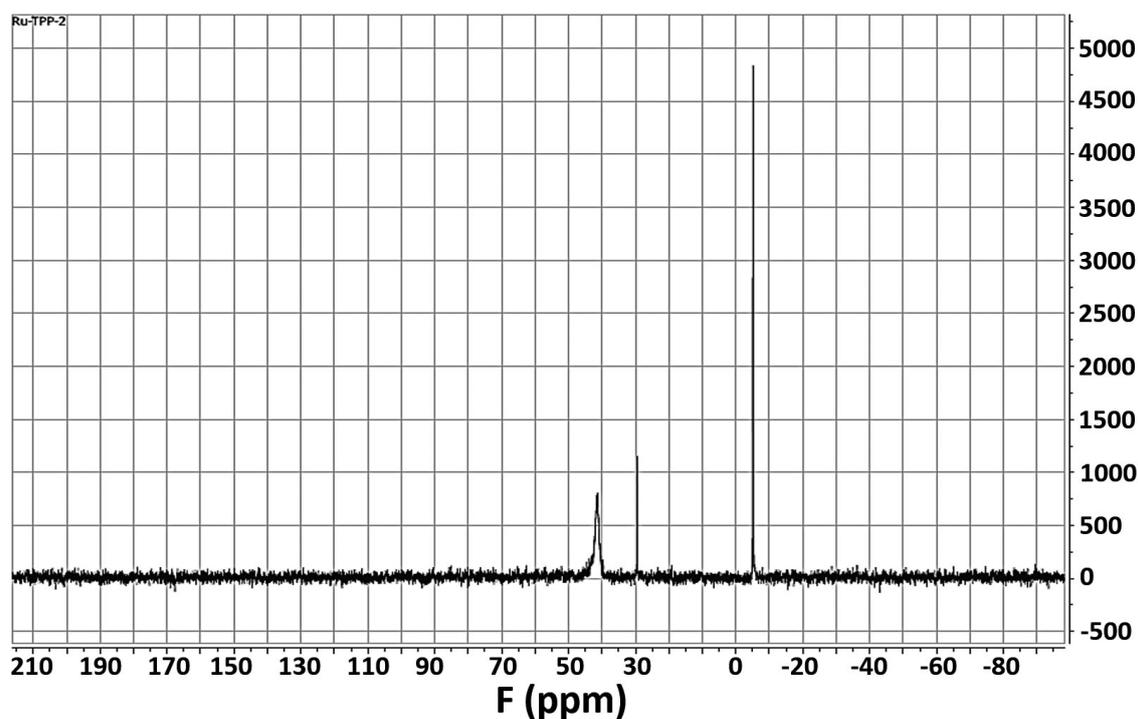


Fig. 2.  $^{31}\text{P}$  spectrum of  $\text{RuCl}_2(\text{PPh}_3)_3$  sample produced in the second reaction

– instead,  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{PPh}_3$  were added to check if synthesizing the catalyst before the reaction of hydrogenation would improve the rate of the reaction.

The second catalyst,  $\text{RuCl}_2(\text{TPPTS})_2 \cdot 6\text{H}_2\text{O}$ , was synthesized with the procedure given by Herrmann (Herrmann and Brauer, 2000). It assumed that the molar ratio of reagents was as follows:  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O} : \text{TPPTS} = 1 : 5$ . Firstly, 0.355 g of TPPTS was dissolved in 15 ml of water. Then 0.0325 g of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was added. They were mixed and heated up to 50 °C. After 24 hours the mixture was dried with a rotary evaporator and a vacuum drier. Then the solid product of the reaction was collected and closed in a container filled up with argon. The second sample was prepared in the same way, but the proportion of TPPTS and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was reduced to  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O} : \text{TPPTS} = 1 : 2.5$ . This time 206 mg of TPPTS and 38 mg of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  were used, the amount of other reagents remained the same. Both samples were analyzed with NMR and their  $^{31}\text{P}$  spectra in  $\text{D}_2\text{O}$  were obtained.

The reaction of hydrogenation was performed in the same way for every catalyst. Firstly, 3 g of acetophenone, 30 cm<sup>3</sup> isopropyl alcohol and 0.0784g KOH were mixed in a distillation flask. Then the amount of a chosen catalyst shown in Table 1 was added to the flask. The mixture was mixed and heated up to 60 °C in an argon atmosphere. After 6 hours the reaction was stopped. The reaction mixture was poured into smaller containers and left for 5 minutes in order to let the precipitate fall to the bottom of a container. Then samples were analyzed with gas chromatography in order to determine the composition of a post-reaction mixture (Wang et al., 2014). The amount of used catalysts was calculated in a way that ensured that the same amount of ruthenium was present in every sample. Results of these calculations are presented in Table 1.

Table 1. Mass of catalysts used in the reaction of hydrogenation

Catalyst	Comments	Mass of substances [g]
$\text{RuCl}_2(\text{PPh}_3)_3$	Reaction performed without the synthesized catalyst	$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ : 0.0261 $\text{PPh}_3$ : 0.1567
$\text{RuCl}_2(\text{PPh}_3)_3$	Synthesized in an argon atmosphere	0.1739
$\text{RuCl}_2(\text{TPPTS})_2 \cdot 6\text{H}_2\text{O}$	First sample	0.1699
$\text{RuCl}_2(\text{TPPTS})_2 \cdot 6\text{H}_2\text{O}$	Second sample	0.3118

### 3. RESULTS

For  $\text{RuCl}_2(\text{TPPTS})_2 \cdot 6\text{H}_2\text{O}$ , the amount of the obtained catalyst for both samples was similar, but the first sample (synthesized with higher excess of reagents) was more contaminated.

As shown in Fig. 3, the post-reaction mixture contains not only  $\text{RuCl}_2(\text{TPPTS})_2$  (57 ppm), but also TPPTS that have not reacted (ca. 4.8 ppm) and some contaminations (34.2 ppm). According to the literature (Bhanage et al., 2000), it is probably OTTPTS.

The reaction of hydrogenation was carried out with catalysts listed in Table 1 twice for each catalyst while the results of the reaction are given in Table 2. Additional tests were carried out in order to examine the impact of other reaction parameters on the amount of produced 1-phenylethanol. For  $\text{RuCl}_2(\text{PPh}_3)_3$ , two reactions were accomplished with a double amount of catalyst and for the other two the reaction duration was extended from six to ten hours. The results of these tests are presented in Table 3.

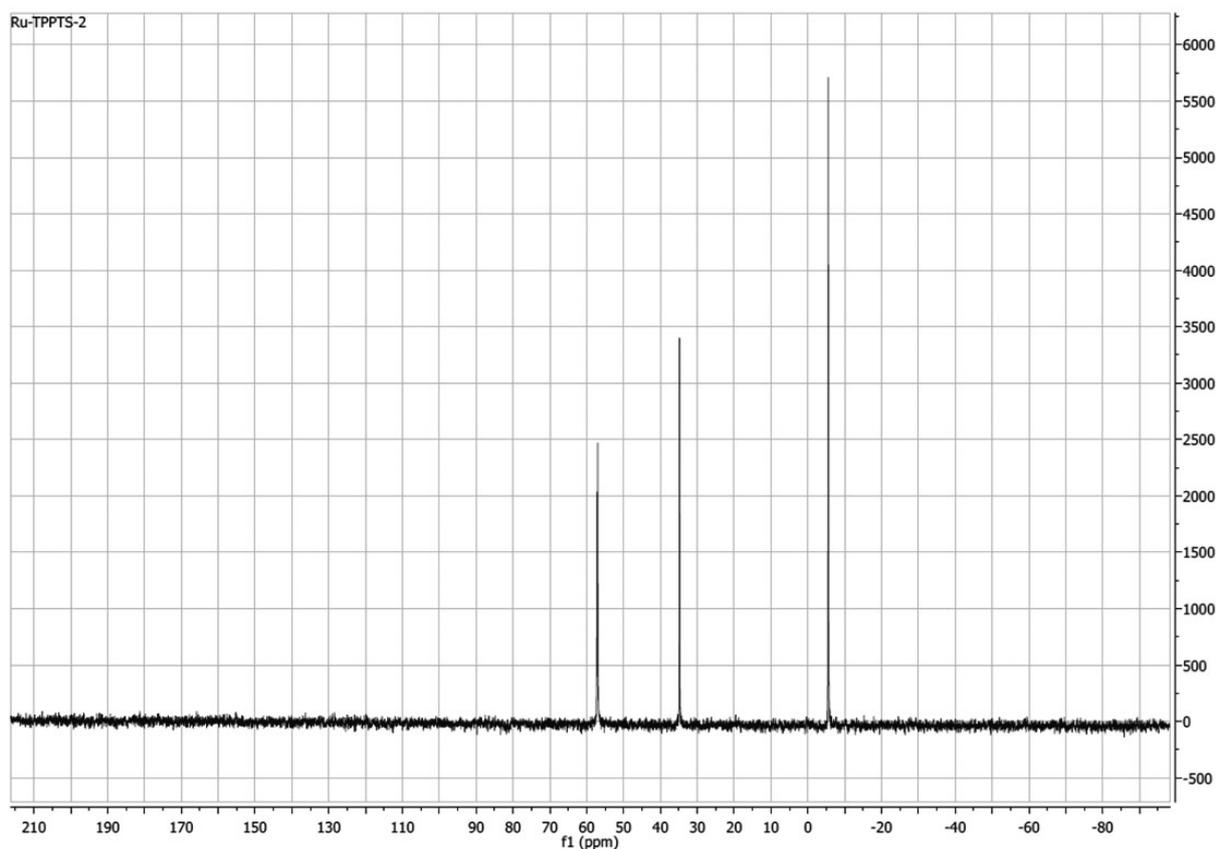


Fig. 3.  $^{31}\text{P}$  spectrum of  $\text{RuCl}_2(\text{TPPTS})_2$  sample produced in the first reaction

Table 2. Amounts of reagents in post reaction mixture for standard parameters of the reaction

Catalyst	Comments	$m_{\text{acetophenone}}$ [g]	$m_{1\text{-phenylethanol}}$ [g]	$n_{\text{acetophenone}}$ [mol]	$n_{1\text{-phenylethanol}}$ [mol]
$\text{RuCl}_2(\text{PPh}_3)_3$	Reaction performed without the synthesis of the catalyst	2.944	0.056	$2.450 \times 10^{-2}$	$4.590 \times 10^{-4}$
		2.944	0.056	$2.450 \times 10^{-2}$	$4.590 \times 10^{-4}$
		2.944	0.056	$2.450 \times 10^{-2}$	$4.590 \times 10^{-4}$
$\text{RuCl}_2(\text{PPh}_3)_3$	Reaction performed without the synthesis the catalyst	2.946	0.054	$2.452 \times 10^{-2}$	$4.399 \times 10^{-4}$
		2.946	0.054	$2.452 \times 10^{-2}$	$4.399 \times 10^{-4}$
		2.946	0.054	$2.452 \times 10^{-2}$	$4.399 \times 10^{-4}$
$\text{RuCl}_2(\text{PPh}_3)_3$	Second sample	2.422	0.578	$2.016 \times 10^{-2}$	$4.727 \times 10^{-3}$
$\text{RuCl}_2(\text{PPh}_3)_3$	Second sample	2.427	0.573	$2.020 \times 10^{-2}$	$4.687 \times 10^{-3}$
$\text{RuCl}_2(\text{TPPTS})_2$	First sample	2.905	0.095	$2.417 \times 10^{-2}$	$7.808 \times 10^{-4}$
$\text{RuCl}_2(\text{TPPTS})_2$	First sample	2.904	0.096	$2.417 \times 10^{-2}$	$7.865 \times 10^{-4}$
$\text{RuCl}_2(\text{TPPTS})_2$	Second sample	2.899	0.101	$2.413 \times 10^{-2}$	$8.231 \times 10^{-4}$
$\text{RuCl}_2(\text{TPPTS})_2$	Second sample	2.899	0.101	$2.413 \times 10^{-2}$	$8.249 \times 10^{-4}$

The conversion rate of acetophenone for each reaction was calculated based on the obtained data. Results are shown in Table 4.

Table 3. Amounts of reagents in post reaction mixture for modified parameters of the reaction

Catalyst	Comments	$m_{\text{acetophenone}}$ [g]	$m_{1\text{-phenylethanol}}$ [g]	$n_{\text{acetophenone}}$ [mol]	$n_{1\text{-phenylethanol}}$ [mol]
$\text{RuCl}_2(\text{PPh}_3)_3$	Increased amount of the catalyst	2.570	0.430	$2.139 \times 10^{-2}$	$3.524 \times 10^{-3}$
$\text{RuCl}_2(\text{PPh}_3)_3$	Increased amount of the catalyst	2.570	0.430	$2.139 \times 10^{-2}$	$3.524 \times 10^{-3}$
$\text{RuCl}_2(\text{PPh}_3)_3$	Extended reaction time	2.133	0.867	$1.775 \times 10^{-2}$	$7.095 \times 10^{-3}$
$\text{RuCl}_2(\text{PPh}_3)_3$	Extended reaction time	2.139	0.861	$1.780 \times 10^{-2}$	$7.045 \times 10^{-3}$

Table 4. Conversion rate of acetophenone

Catalyst	Comments	Reaction parameters	Conversion rate of acetophenone [%]
$\text{RuCl}_2(\text{PPh}_3)_3$	Reaction performed without the synthesis of the catalyst	6 hours	1.869
$\text{RuCl}_2(\text{PPh}_3)_3$	Reaction performed without the synthesis of the catalyst	6 hours	1.791
$\text{RuCl}_2(\text{PPh}_3)_3$	Second sample	6 hours	19.251
$\text{RuCl}_2(\text{PPh}_3)_3$	Second sample	6 hours	19.085
$\text{RuCl}_2(\text{TPPTS})_2$	First sample	6 hours	3.179
$\text{RuCl}_2(\text{TPPTS})_2$	First sample	6 hours	3.203
$\text{RuCl}_2(\text{TPPTS})_2$	Second sample	6 hours	3.352
$\text{RuCl}_2(\text{TPPTS})_2$	Second sample	6 hours	3.357
$\text{RuCl}_2(\text{PPh}_3)_3$	Synthesized in an argon atmosphere	6 hours, increased amount of catalyst	14.348
$\text{RuCl}_2(\text{PPh}_3)_3$	Synthesized in an argon atmosphere	6 hours, increased amount of catalyst	14.344
$\text{RuCl}_2(\text{PPh}_3)_3$	Synthesized in an argon atmosphere	10 hours	28.893
$\text{RuCl}_2(\text{PPh}_3)_3$	Synthesized in an argon atmosphere	10 hours	28.689

In order to examine the impact of storing conditions of the samples of post reaction mixture on the quality of the measurements it was decided that an additional experiment should be performed. Four samples (without the precipitate) were collected from post reaction mixture obtained in the reaction catalyzed by  $\text{RuCl}_2(\text{TPPTS})_2$  (second sample, with smaller amounts of reagents). Two of them were stored in a freezer

in constant temperature of  $-15\text{ }^{\circ}\text{C}$  for 19 hours, the others were stored in  $20\text{ }^{\circ}\text{C}$  for the same time. Results are shown in Table 5.

Table 5. Conversion rate of acetophenone after 19 hours

Catalyst	Storage conditions	Conversion rate of acetophenone [%]	Change in relation to base sample [%]
$\text{RuCl}_2(\text{TPPTS})_2$	$20\text{ }^{\circ}\text{C}$	3.656	+9.062
$\text{RuCl}_2(\text{TPPTS})_2$	$20\text{ }^{\circ}\text{C}$	3.596	+7.130
$\text{RuCl}_2(\text{TPPTS})_2$	$-15\text{ }^{\circ}\text{C}$	3.478	+3.766
$\text{RuCl}_2(\text{TPPTS})_2$	$-15\text{ }^{\circ}\text{C}$	3.535	+5.307

#### 4. DISCUSSION

Carrying out the reaction of hydrogenation with  $\text{RuCl}_2(\text{PPh}_3)_3$  without prior synthesis of the catalyst is highly ineffective and leads to minimal production of 1-phenylethanol. Time saved by skipping the reaction of synthesis does not compensate the negligible conversion rate of acetophenone. It may be an effect of low concentration of the catalyst in the solution and possible side reactions of ruthenium compounds. Due to the low conversion rates further research of this type of reaction was suspended.

The results obtained during the reaction with  $\text{RuCl}_2(\text{TPPTS})_2$  were disappointing. Obtained conversion rates were significantly lower than those obtained in other publications (Wang et al., 2014). It may be a result of high contamination of this catalyst which is shown in Fig. 3. The amount of unwanted substances was noticeable, but their identification was not possible with the available methods of analysis.  $\text{RuCl}_2(\text{TPPTS})_2$  is usually recommended for two-phase systems (Wang et al., 2014). In order to increase the rate of reaction in future research an addition of water to reaction environment is planned. It is also worth adding that decreasing the amount of TPPTS during catalyst synthesis had a positive effect on the catalytic properties of the final product, but the conversion rate increase was negligible. It was still a desirable effect, because using smaller increase of TPPTS resulted in a much smaller cost of the final catalyst. It was also determined that TPPTS was not an inhibitor of the reaction of hydrogenation of ketones.

$\text{RuCl}_2(\text{PPh}_3)_3$  was a very good catalyst for this type of reaction. The obtained conversion rates were high, but in the synthesis of the catalyst a large amount of side products (as shown in Figs. 1 and 2.), like e.g. oxidized compounds of ruthenium, were observed. It is planned to develop new methods of purification of  $\text{RuCl}_2(\text{PPh}_3)_3$  and optimize the reaction parameters before starting a new research (Cho et al., 2001). Increasing the amount of the catalyst in this reaction resulted in lower conversion rates. Usually, this should increase the rate of the reaction due to enhanced possibilities of collision between the molecule of the substrate and the catalyst. When the concentration of the catalyst is already high enough, the reaction rate should remain more or less the same. In the case of  $\text{RuCl}_2(\text{PPh}_3)_3$  this is a bit different due to the presence of particles of  $\text{PPh}_3$ . They inhibit the reaction of formation of coordinatively unsaturated molecules and they also react with the free coordination sites in the central atom of the complex. This prevents the coordination of ketone and the whole reaction of hydrogenation (Houghton, 1985). It could also change the reaction route. Increasing the time of reaction from 6 to 10 hours resulted in almost 50% increase of the conversion rate.

Results from Table 5 indicate that the analysis of the post-reaction mixture should be made as fast as possible, because the reaction does not stop even at low temperature. Furthermore, the increase of the product was noticeably different even in the case of samples stored under the same conditions.

The results of this research are very promising. The research can be further developed by changing the donor of hydrogen to a more environmentally friendly substance like ethanol to check if this reaction can be used in green chemistry. Due to the homogeneous nature of the reaction, methods of recovering the catalyst have to be invented. In addition, other parameters of the reaction also have to be optimized in order to increase the feasibility of practical application of this process in industry.

## 5. CONCLUSIONS

In the homogeneous reaction of hydrogenation of acetophenone in organic environment,  $\text{RuCl}_2(\text{PPh}_3)_3$  was much more effective as a catalyst than  $\text{RuCl}_2(\text{TPPTS})_2$ . The reaction of hydrogenation and synthesis of both catalysts should be carried out in the atmosphere of an inert gas in order to minimize the amount of undesired side products. Increasing the amount of TPPTS during synthesis of  $\text{RuCl}_2(\text{TPPTS})_2$  above a certain value is not recommended as it results in only a slight increase of the amount of the produced catalyst. An increase of the time of reaction results in higher conversion rate of reagents while an increase of  $\text{RuCl}_2(\text{PPh}_3)_3$  amount above some value may result in a decrease of the conversion rate of acetophenone. Samples of the reaction product should be analyzed immediately after experiments in order to obtain reliable results.

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