Short thesis for the degree of doctor of philosophy (PhD)

Activity of Ir(I)-NHC complexes in hydrogenation – dehydrogenation – catalytic hydrogen storage in organic compounds

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List of abbreviations

1-butyl-3-methylimidazolium chloride	
1-benzyl-3-methylimidazolium chloride	
1,5-cyclooctadiene	
1-ethyl-3-methylimidazolium chloride	
electrospray ionization mass spectrometry	
1-hexyl-3-methylimidazolium chloride	
1,1'-methylene-bis(3-benzyl-imidazolium)dichloride	
1,1'-methylene-bis(3-(2,4,6-trimethylbenzyl)	
imidazolium)dichloride	
Liquid Organic Hydrogen Carriers	
1,3-dimethylimidazolium chloride	
sodium salt of monosulfonated triphenylphosphine	
sodium salt of trisulfonated triphenylphosphine	
N-heterocyclic carbene	
Nuclear Magnetic Resonance	
1-octyl-3-methylimidazolium chloride	
triphenylphosphine	
Turnover Frequency: (mol reacted substrate) / (mol	
catalyst × time), h^{-1}	

[2,4,6-triMeBnmimH]Cl: 2,4,6-trimethylbenzyl-3-methyl-imidazolium chloride

I. Introduction and objectives

One of the main problems of today is the energy crisis, which was caused by the imbalance between energy demand and energy production. Our energy and transport systems are mainly based on fossil fuels. The limited availability of these energy carriers, their high price volatility, their contribution to global warming and their negative impact on human health have contributed significantly to the search for alternative energy sources. One of the ideal alternative fuels is hydrogen, which is an excellent fuel, outstanding calorific value, furthermore its combustion provides only pure water. The safety transport and storage of hydrogen has not yet been solved. The energy stored in hydrogen can be released by burning it in fuel cells. Energy storage in hydrogen could be a solution to meet its energy demand, so my goal was to investigate a liquid organic hydrogen storage system (LOHCs) based on secondary alcohol dehydrogenation and ketone hydrogenation.

For this purpose, I carried out a detailed study of both sub-processes by using as catalysts not only Ir(I) complexes containing *N*-heterocyclic carbene (Ir-NHC) but also those that coordinated both NHC and phosphine (Ir-NHC-phosphine).

One of the sub-processes, the reduction of ketones, is important in its own right, as it produces one of the industrial organic feedstocks, alcohols. Their production (instead of the hydrogen gas operation) can be more safely achieved by transfer hydrogenation, where the hydrogen is supplied by some other hydrogen source, such as solvent (2-PrOH, HCOOH). My objectives were to study the catalytic activity of Ir-NHC and Ir-NHC-phosphine complexes not only in the hydrogenation of ketones, but also in hydrogen transfer reactions.

II. Experimental methods

The Ir-carbene and Ir-NHC-phosphine complexes are sensitive to air, so all reactions were performed under oxygen-free conditions using standard Schlenk techniques.

The ligands, Ir(I)-NHC and Ir(I)-NHC-phosphine complexes were fully characterized by various spectroscopic methods (¹H-NMR, ¹³C-NMR, IR, ESI-MS) and single X-ray diffraction.

¹H, ¹³C and ³¹P NMR spectra were recorded on Bruker 360 MHz NMR spectrometer at room temperature. The spectra were evaluated using the WIN-NMR software by Bruker.

Infrared spectra were recorded on a PerkinElmer, Spectrum Two FT-IR Spectrometer in ATR mode.

ESI-MS measurements were collected by Cynthia Nagy (University of Debrecen, Department of Inorganic and Analytical Chemistry) on a Bruker maXis II MicroTOF-Q type Qq-TOF-MS instrument in positive ion mode. The spectra were evaluated using Compass Data Analysis 4.4 software from Bruker.

X-ray diffraction data for [IrCl(cod)(mmim)], 1; [IrCl(cod)(emim)], 2; [IrCl(cod)(Bnmim)], [IrCl(cod)(2,4,6-triMeBnmim)], 6: 7: [Ir(cod)(emim)(*m*tppms)], [Ir(cod)(mmim)(*m*tppms)], **1b**: **2b**: [Ir(cod)(hexmim)(*m*tppms)], [IrCl(cod)(Bnmim)(PPh₃)], 4b; **6a**: $[{\rm IrCl(cod)}_2(\mu^2-L1)],$ [Ir(cod)(Bnmim)(*m*tppms)], 6b; 8 and [{IrCl(cod)}₂(μ^2 -L2)], 9 were collected by Dr. Attila Bényei (University of

Debrecen, Department of Physical Chemistry) on a Bruker D8 Venture system. The molecular structures were determined by Dr. Antal Udvardy (University of Debrecen, Department of Physical Chemistry).

The transfer hydrogenation reactions were run using Schlenk tube while hydrogenation reactions were carried out in medium pressure glass reactor. The reaction mixtures were analysed by gas chromatography (Hewlett Packard 5890 Series II) with using flame ionization detector. The column was Cyclodex B (30 m \times 0.320 mm \times 0.25 µm) and SUPELCOWAX (30 mm \times 0.320 mm \times 0.25 µm).

The dehydrogenation reactions were carried out under argon atmosphere in Schlenk vessel with a cooler. The analytical method used was gas chromatography.

The dehydrogenation – hydrogenation catalytic cycle was carried out in a special flask. The cooler and a balloon filled with hydrogen gas were connected to the flask. The yield of product was determined by gas chromatography.

III. New scientific results

1. Several types of Ir(I)-*N*-heterocyclic carbene and mixed-ligand Ir(I)-NHC-phosphine complexes were synthetized and characterized.

During my PhD work I have synthetized several new complexes containing *N*-heterocyclic carbene [IrCl(cod)(NHC)] and [Ir(cod)(NHC)(P)] (P = PPh₃ and its water-soluble variants, i.e., *m*tppms-Na, *m*tppts-Na₃) (*Figure 1*.).

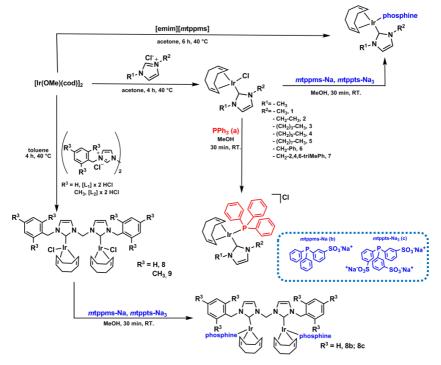


Figure 1. Synthesis of Ir(I)-NHC, Ir(I)-NHC-phosphine and Ir(I)-diNHC, Ir(I)-diNHC-phosphine complexes

In the synthesis of the [IrCl(cod)(NHC)] (1-7) catalysts, in each case, I attached a methyl group to one nitrogen of the carbene, and $-(CH_2)_n$ -CH₃ (n = 0-5) substituents of increasing length or benzyl ring to the other. The complexes were fully characterized by various spectroscopic methods (¹H-NMR, ¹³C-NMR, IR, ESI-MS) and I studied the activity of the synthesized compounds in different homogeneous catalytic reactions.

2. Single crystal X-ray diffraction was used to verify the molecular structure of 9 of the prepared Ir(I)-NHC and Ir(I)-NHC-phosphine catalysts.

The structure of [Ir(cod)(mmim)X] (1, 1b), [Ir(cod)(emim)X] (2, 2b), [Ir(cod)(Bnmim)X] (6, 6b), (X = Cl, mtppms), $[IrCl(cod)(Bnmim)(PPh_3)]$ (6a), [Ir(cod)(hexmim)(mtppms)] (4b), [IrCl(cod)(2,4,6-triMeBnmim)] (7) complexes were determined by single-crystal X-ray diffraction.

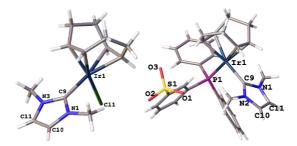


Figure 2. Molecular structures of the [IrCl(cod)(mmim)] (1) and [Ir(cod)(mmim)(*m*tppms)] (1b) complexes (CHCl₃ molecules are omitted for clarity.)

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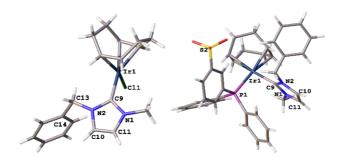


Figure 3. Molecular structures of the [IrCl(cod)(Bnmim)] (6) and [Ir(cod)(Bnmim)(*m*tppms)] (6b) complexes

I confirmed that the structures of the different space-filled complexes are very similar, as confirmed by the Ir-C bond distances. This finding may explain why I found no significant difference in their catalytic activity when examining the effect of increased carbon chain on catalyst activity modification.

3. Four, new dinuclear complexes of the type $Ir(I)-(\mu^2-diNHC)$ and their water-soluble phosphine analogues were synthetized and characterized, furthermore the structure of two complexes were determined by single-crystal X-ray diffraction.

I have prepared two new Ir-diNHC complexes, namely $[{IrCl(cod)}_2(\mu^2-L1)]$ -t (8) and $[{IrCl(cod)}_2(\mu^2-L2)]$ -t (9), and I got the $[{Ir(cod)(mtppms)}_2(\mu^2-L1)]$ (8b) and Na₄[{Ir(cod)(mtppts)}_2(\mu^2-L1)] (8c) complexes when I reacted catalyst (8) with sulfonated phosphine (*mtppms*-Na or *mtppts*-Na₃) (*Figure 1*.). These compounds were characterized by

multinuclear NMR and IR spectroscopy, ESI-MS. Additionally the molecular structure of $[{\rm IrCl(cod)}_2(\mu^2-L1)]$ (8) and $[{\rm IrCl(cod)}_2(\mu^2-L2)]$ (9) were confirmed by single-crystal X-ray diffraction (*Figure 4.*).

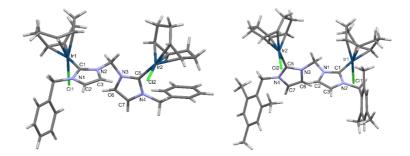


Figure 4. Capped sticks presentation of the structures of $[{IrCl(cod)}_2(\mu^2-L1)]$ (8) and $[{IrCl(cod)}_2(\mu^2-L2)]$ (9)

(In 9, benzene molecules are omitted for clarity.)

I found that the structural and catalytic properties of the dinuclear complexes are similar to those of their analogues prepared with single-stranded NHC ligands.

4. I have demonstrated that both Ir-carbene and Ir-carbene-phosphine complexes were active catalyst for the transfer hydrogenation of ketones under specific reaction conditions.

4.1. My studies showed that the prepared complexes are suitable for catalysing the industrially important process of transfer hydrogenation of ketones.

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The catalytic activities of the various catalysts were compared in the transfer hydrogenation of acetophenone in basic 2-propanol (*Figure 5.*).



Figure 5. Catalytic transfer hydrogenation of acetophenone in basic 2propanol

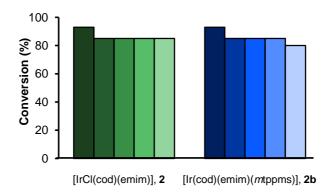
Turnover frequencies in the 280-670 h^{-1} range were determined. The highest catalytic activity (TOF = 670 h^{-1}) in transfer hydrogenation of acetophenone showed [IrCl(cod)(Bnmim)] (6) complex. The coordination of water-soluble phosphine (*m*tppms-Na, *m*tppts-Na₃) led to pronounced loss of the catalytic activity in hydrogen transfer reaction (2c, 3b, 4b, 6b vs. 2, 3, 4, 6).

4.2. Optimum reaction conditions were established in catalytic transfer hydrogenation of acetophenone.

To find the optimal reaction conditions, in addition to determining the appropriate [S]/[Ir] ratio, which was 5/1, I was studied the effect of different bases (*t*-BuOK, KOH, NaOH, Cs_2CO_3 , $CsHCO_3$, HCOOCs and HCOONa) on the reaction. I found that *t*-BuOK proved to be the most efficient base for reactions carried out with the catalyst [Ir(cod)(emim)(*m*tppms)] (**2b**), and therefore I used this base in further experiments.

4.3. I confirmed the stability of [IrCl(cod)(emim)] (2) and [Ir(cod)(emim)(*m*tppms)] (2b) complexes in the transfer hydrogenation reaction of acetophenone from 2-propanol.

From a practical point of view, the stability and reusability of catalysts is important, which can be achieved by recycling the reaction mixture. I have demonstrated that the reaction was carried out in the same reaction mixture during repeated addition of the substrate, and the catalysts retained their activity and stability even after cycle 5 (*Figure 6.*).



Cycles: 1 (**a**), 2 (**a**), 3. (**b**), 4 (**b**), 5 (**b**). Cycles: 1 (**b**), 2 (**b**), 3. (**b**), 4 (**b**), 5 (**c**).

Figure 6. Catalytic activities of 2 and 2b upon repeated additions of

acetophenone

n (cat. 2, 2b) = 0.01 mmol, n (acetophenone) = 0.5 mmol/cycle, n (t-BuOK) = 0.05 mmol, T = 80 °C, t = 1 h, V (2-PrOH) = 1.0 mL 4.4. I found that the rate of transfer hydrogenation of acetophenone varied in the extreme depending on the amount of water added to 2-propanol when the reactions were catalyzed by complexes containing water-soluble phosphine.

I have studied of transfer hydrogenation of acetophenone in 2propanol-water mixtures over a wide concentration range (18-100 v/v% 2-PrOH) with a number of Ir(I)-NHC-phosphine (**2b**, **2c**, **3c**, **6c**) and Ir(I)diNHC-phosphine (**8b**, **8c**) complexes. I have made an interesting observation on the rate of transfer hydrogenations in 2-propanol-water mixtures, which differed from the usual effects during solvent concentration changes. The reduction rate in water/2-propanol mixtures showed a significant increase with increasing water concentration.

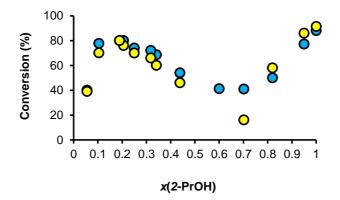


Figure 7. The conversion of acetophenone as a function of solvent composition in transfer hydrogenation from 2-PrOH catalysed by **2b** and **2c**

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[Ir(cod)(emim)(mtppms)], 2b (\bullet), Na<sub>2</sub>[Ir(cod)(emim)(mtppts)], 2c (\bullet)

n (cat. 2b, 2c) = 0.01 mmol, n (acetophenone) = 1 mmol, n (t-BuOK) = 0.05 mmol,

T = 80 °C, t = 1 h, V (total) = 1.0 mL, [S]/[C]/[B] = 100/1/5
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I interpreted this phenomenon by specific solvation of catalytically active complexes. It is probable that the structure of the 2-PrOH-water system changes as a function of composition and that this in some way affects the catalytic activity of highly hydratable, sulfonated phosphinecontaining complexes, however, this phenomenon is still remain elusive.

The catalysts $[{Ir(cod)(mtppms)}_2(\mu^2-L1)]$ (**8b**) and Na₄[{Ir(cod)(mtppts)}_2(\mu^2-L1)] (**8c**) showed similar behavior than mononuclear Ir(I)-NHC-sulfonated phosphine complexes. I have demonstrated that the structural and catalytic properties of the dinuclear complexes were similar with their mononuclear NHC ligands analogues.

5. I have proved that the synthesized Ir(I)-carbene and Ir(I)-carbenephosphine complexes are active catalysts in the reduction of ketones with H_2 gas.

Ketones can be reduced not only hydrogen transfer but also by molecular H_2 . The general scheme of this process is shown in *Figure 8.* – similar to transfer hydrogenation – the use of the base is also essential for hydrogenation reactions, as it deprotonate and participate in the formation of catalytically active species.

$$R_1 \xrightarrow{O} R_2 + H_2 \xrightarrow{cat./base} R_1 \xrightarrow{OH} R_2$$

Figure 8. Hydrogenation reaction of ketones

5.1. I have found that, among the Ir(I)-NHC complexes, the [IrCl(cod)(mmim)] (1) catalyst was the most efficient in the hydrogenation of acetophenone.

I have compared the activity of the prepared carbene and carbenephosphine complexes in the hydrogenation reaction of acetophenone. The results obtained are presented in Table 1.

Entry	Catalyst	Conv. (%)	TOF (h ⁻¹)
1.	[IrCl(cod)(mmim)], 1	98	490
2.	[Ir(cod)(mmim)(<i>m</i> tppms)], 1b	43	215
3.	[IrCl(cod)(emim)], 2	78	390
4.	[Ir(cod)(emim)(<i>m</i> tppms)], 2b	39	195
5.	[IrCl(cod)(bmim)], 3	50	250
6.	[Ir(cod)(bmim)(<i>m</i> tppms)], 3b	63	315
7.	[IrCl(cod)(hexmim)], 4	93	465
8.	[Ir(cod)(hexmim)(<i>m</i> tppms)], 4b	65	325
9.	[Ir(cod)(omim)(<i>m</i> tppms)], 5b	48	240
10.	[IrCl(cod)(Bnmim)], 6	89	445
11.	[Ir(cod)(Bnmim)(<i>m</i> tppms)], 6b	51	255

Table 1. Hydrogenation of acetophenone with various complexes

n (cat.) = 0.01 mmol, n (acetophenone) = 2.5 mmol, n (t-BuOK) = 0.5 mmol, T = 95 °C, t = 30 min, V (toluene) = 1.0 mL, p(H₂) = 10 bar

The coordination of *m*tppms remarkably decreased the catalytic activity; this statement was true in every case except **3**, **3b** complexes. Among the complexes containing phosphine the [Ir(cod)(hexmim)(mtppms)], **4b** catalyst was found to be the most efficient in the hydrogenation of acetophenone. Since the highest conversion among the catalysts used was

obtained with [IrCl(cod)(mmim)], **1** complex, thus I used this catalyst in further reactions.

5.2. I have shown that changes in parameters such as temperature and pressure affect the hydrogenation reaction.

When examining the temperature dependence, I found that the conversion of acetophenone was almost complete (96%) at 80 °C under given conditions. When varying the pressure, I found that 10 bar H_2 pressure favoured the reaction, but the hydrogenation reaction was already taking place at atmospheric pressure.

6. I have demonstrated that the Ir(I)-NHC and Ir(I)-NHC-phosphine complexes catalyse not only the hydrogenation reactions of ketones, but also the dehydrogenation of the secondary alcohols formed.

The dehydrogenation of secondary alcohols formed ketones and hydrogen gas (*Figure 9.*). I chose 1-phenylethanol as a model compound for the dehydrogenation of secondary alcohols and I used the prepared complexes as catalyst.



Figure 9. Catalytic dehydrogenation of secondary alcohols

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6.1. It was demonstrated, that changing the parameters, such as the concentration of 1-phenylethanol, the quality and quantity of the base, affects the degree of transformation.

In the dehydrogenation reactions with different bases (*t*-BuOK, KOH, NaOH, etc.), *t*-BuOK proved to be the most efficient in this case as well, so I used *t*-BuOK in my further measurements.

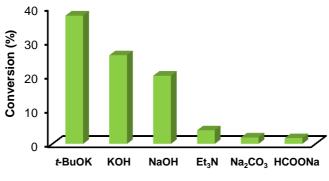


Figure 10. Effect of various bases on the dehydrogenation of 1-phenylethanol

n ([Ir(cod)(emim)(*m*tppms)], **2b**) = 0.01 mmol, n (1-phenylethanol) = 0.25 mmol, n (base) = 0.05 mmol, V (toluene) = 1.0 mL, T = 95 °C, t = 2 h, closed system

7. It was achieved a 1-phenylethanol/acetophenone hydrogen storage catalytic cycle at atmospheric pressure. I found that the ratedetermining step in the reaction is the formation of hydrogen, so I controlled the cycle by the controlled addition of H_2 gas.

After demonstrating that the complexes under investigation are active catalysts for the hydrogenation of ketones with H_2 gas and the dehydrogenation of the secondary alcohols formed, I combined the two processes in one apparatus and implemented the hydrogen storage cycle with the same complex (1).

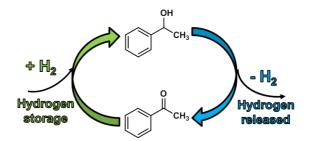


Figure 11. 1-phenylethanol – acetophenone hydrogen storage system

The dehydrogenation of 1-phenylethanol produces acetophenone and hydrogen gas, while the hydrogenation process converts acetophenone to 1phenylethanol at atmospheric pressure. The rate of hydrogen evolution is the rate determining step in the reaction rate. The two processes can be controlled by the controlled addition of hydrogen.

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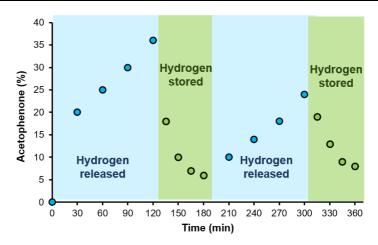


Figure 12. Secondary alcohol – ketone based hydrogen storage cycle dehydrogenation (●) hydrogenation (●)

n ([IrCl(cod)(mmim)], 1) = 0.04 mmol, n (1-phenylethanol) = 2.0 mmol, n (*t*-BuOK) = 2.0 mmol, V (toluene) = 4.0 mL, T = 95 °C, P(H₂) = 1 bar, open system

IV. Possible applications of the results

The research presented in my thesis is basic research in the field of homogeneous catalysis and catalytic hydrogen storage, in addition to catalyst development. My results demonstrate that *N*-heterocyclic carbenes and various phosphine ligands form stable complexes with iridium. The complexes prepared are active catalysts in hydrogenation of ketones and in transfer hydrogenation and dehydrogenation of secondary alcohols. The 1-phenylethanol/acetophenone hydrogenation catalytic cycle was realized at atmospheric pressure without the use of high pressure. The two processes were controlled by the controlled addition of H₂ gas.

The practical application of the results is expected to be mainly in the field of energy storage in hydrogen. The hydrogenation of ketones is also important because the reaction products are alcohols, which are the building blocks of pharmaceuticals, flavours, fragrances and pesticides.

V. List of publications

Publications related to the dissertation

English articles in international journals:

- <u>Krisztina Orosz</u>, Gábor Papp, Ágnes Kathó, Ferenc Joó, Henrietta Horváth; Strong Solvent Effects on Catalytic Transfer Hydrogenation of Ketones with [Ir(cod)(NHC)(PR₃)] Catalysts in 2-Propanol-Water Mixtures, *Catalysts*, 2020, *10* (1), 17. (IF: 3.444)
- <u>Krisztina Orosz</u>, Csilla Enikő Czégéni, Antal Udvardy, Gábor Papp, Natália Marozsán, Ágnes Kathó, Ferenc Joó, Horváth Henrietta; Synthesis and catalytic application of new [{IrCl(cod)}₂(µ²diNHC)] and [{Ir(cod)(sulfonated-phosphine)}₂(µ²-diNHC)] complexes, Phosphorus, Sulfur, and Silicon and the Related Elements, 2022, 4, 1-4. (IF: 1.082)

List of other publications

English articles in international journals:

 Henrietta Kovács, <u>Krisztina Orosz</u>, Gábor Papp, Ferenc Joó, Henrietta Horváth; **Immobilization of an Iridium(I)-NHC-Phosphine** Catalyst for Hydrogenation Reactions under Batch and Flow Conditions, *Catalysts*, 2021, 11 (6), 656. (IF: 3.520)



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Registry number: Subject: DEENK/146/2023.PL PhD Publication List

Candidate: Krisztina Andrea Orosz Doctoral School: Doctoral School of Chemistry MTMT ID: 10066114

List of publications related to the dissertation

Foreign language scientific articles in international journals (2)

- Orosz, K. A., Czégéni, C. E., Udvardy, A., Papp, G., Marozsán, N., Kathó, Á., Joó, F., Horváth, H.: Synthesis and catalytic application of new [{IrCl(cod)}(2)(mu(2)-diNHC)] and [{Ir(cod)(sulfonated phosphine)}(2)(mu(2)-diNHC)] complexes. *Phosphorus Sulfur Silicon Relat. Elem.* 197 (5-6), 583-586, 2022. ISSN: 1042-6507. DOI: http://dx.doi.org/10.1080/10426507.2021.2024829 IF: 1.052 (2021)
- Orosz, K. A., Papp, G., Kathó, Á., Joó, F., Horváth, H.: Strong Solvent Effects on Catalytic Transfer Hydrogenation of Ketones with [Ir(cod)(NHC)(PR3)] Catalysts in 2-Propanol-Water Mixtures.

Catalysts. 10 (1), 17-18, 2020. EISSN: 2073-4344. DOI: http://dx.doi.org/10.3390/catal10010017 IF: 4.146



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List of other publications

Foreign language scientific articles in international journals (1)

 Kovács, H., Orosz, K. A., Papp, G., Joó, F., Horváth, H.: Immobilization of an Iridium(I)-NHC-Phosphine Catalyst for Hydrogenation Reactions under Batch and Flow Conditions. *Catalysts.* 11 (6), 1-11, 2021. EISSN: 2073-4344.
 DOI: http://dx.doi.org/10.3390/catal11060656
 IF: 4.501

Total IF of journals (all publications): 9,699 Total IF of journals (publications related to the dissertation): 5,198

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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