

## Final report FK-128333

Starting from  $[\text{Ir}(\text{MeO})(\text{cod})]_2$ , which is a convenient source of Ir(I) for synthesis of *N*-heterocyclic carbene complexes, several Ir(I)-carbene complexes were obtained by using various carbene ligands in acetone. The  $[\text{Ir}(\text{MeO})(\text{cod})]_2$  dimer reacted with omimHCl (1-methyl-3-octyl imidazolium chloride), bnmimHCl (1-benzyl-3-methyl imidazolium chloride) and mesCH<sub>2</sub>imHCl (1-methyl-3-(2,4,6-trimethyl-benzyl) imidazolium chloride) yielding  $[\text{IrCl}(\text{cod})(\text{omim})]$ ,  $[\text{IrCl}(\text{bnmim})(\text{cod})]$ ,  $[\text{IrCl}(\text{cod})(1\text{-methyl-3-(2,4,6-trimethyl-benzyl)-imidazol-2-yl}]$  mononuclear complexes. Furthermore an analogue containing methyl groups on both nitrogens of imidazole was prepared (IrCl(cod)(mmim), mmim: 1-methyl-3-methyl imidazolium) respectively. Their structures were determined by spectroscopic methods and were found similar to analogous  $[\text{M}(\text{I})(\text{cod})(\text{NHC})]^+$  complexes (Figure 1).

Besides of these mononuclear complexes we prepared dinuclear complexes using not only Ir(I) as transition metal but Rh(I), as well. For this purpose firstly we prepared the ligands. For synthesis of 1,1'-dibenzyl-3,3'-methylene diimidazolium dichloride (L1) and 1,1'-di(2,4,6-trimethyl-benzyl)-3,3'-methylene diimidazolium dichloride (L2), bis-imidazolyl-methane reacted with benzyl chloride (1. case) and 2,4,6-trimethyl-benzyl-chloride (2. case) in acetonitrile. Both products were obtained in a pure solid form. 1,1'-dibenzyl-3,3'-butylene diimidazolium dichloride (L3) and 1,1'-di(2,4,6-trimethyl-benzyl)-3,3'-butylene diimidazolium dichloride (L4) were prepared by the same methods using the corresponding imidazols (1,4-bis(imidazol-2-yl)-butane) and benzyl chloride and 2,4,6-trimethyl-benzyl-chloride. We also synthesized some dinuclear complexes  $[\text{Ir}(\text{I})-(\mu^2\text{di-N-heterocyclic carbene})]$  ( $\mu^2\text{di-NHC}$ : 1,1'-dibenzyl-3,3'-methylene diimidazolium dichloride; 1,1'-di(2,4,6-trimethyl-benzyl)-3,3'-methylene diimidazolium dichloride (Figure 1).

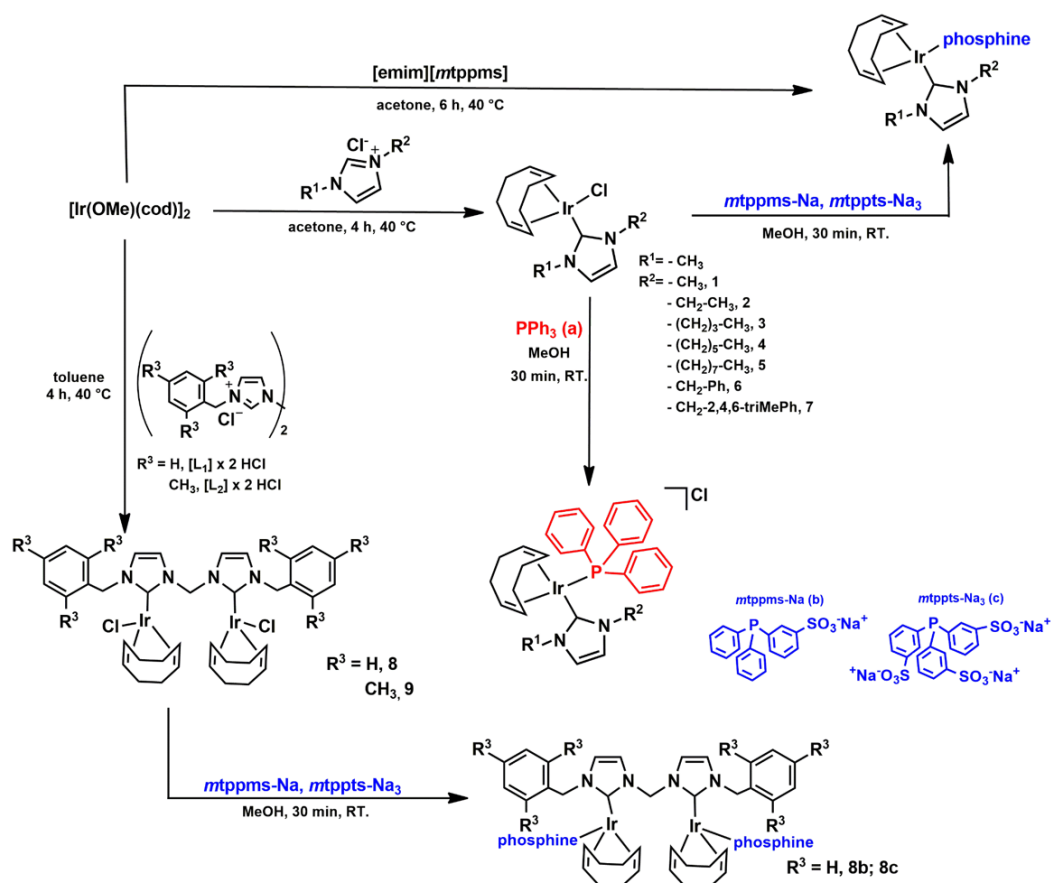


Figure 1. Synthesis of Ir(I)-NHC and Ir(I)-NHC-phosphine and Ir(I)-diNHC, Ir(I)-diNHC-phosphine complexes

Several  $[\text{RhCl}(\text{cod})]_2(\mu\text{-di-NHC})$  complexes were prepared by the classical solvents method. In addition to all of this an environment-friendly, convenient, fast and solvent-free mechanochemical synthesis has been carried out for several diimidazolium salts and the bridging dinuclear rhodium-NHC carbene complexes. A systematic study of both the mechanochemical and solvent synthesis has been implemented to determine the effects of various factors influencing the reactions. We established that using mechanochemical methods (ball mill) had several advantages against the solvent method, such as the simplicity of the procedure, zero-solvent condition, possible multipurpose application, etc.

Starting from  $[\text{IrCl}(\text{cod})]_2$  new Ir(I)-carbene complexes were obtained by using the known analytical reagent, Nitron ligand in THF for catalytic purposes. The structures were determined by spectroscopic methods and were found similar to analogous  $[\text{Ir}(\text{I})(\text{cod})(\text{Nitron})]^+$  complexes. In the presence of the water-soluble phosphines *mtp*pm and *mtp*pts, new water-soluble Ir(I)-Nitron-phosphines mixed ligands complexes could be obtained.

Besides of the general synthetic procedure the  $[\text{IrCl}(\text{cod})(\text{Nitron})]$  and Ir(I)-Nitron-phosphines complexes was synthesized using the solvent free mechanochemical (ball mill) technique, as well. We proved that the structure of the prepared complexes were agree with the structure of complexes obtained in the classical solvent. Formation of  $[\text{IrCl}(\text{cod})(\text{Nitron})(\text{PPh}_3)]$ ,  $[\text{Ir}(\text{cod})(\text{Nitron})(\text{mtp}pm)] and  $\text{Na}_2[\text{Ir}(\text{cod})(\text{Nitron})(\text{mtp}pts)] could also be followed by uv-vis spectrophotometry. In methanolic solutions, titration of  $[\text{IrCl}(\text{cod})(\text{Nitron})]$  with  $\text{PPh}_3$ , *mtp*pm and *mtp*pts resulted in very large spectral changes in the 350-600 nm range. Molar ratio curves constructed for various wavelengths showed the exclusive formation of a stable 1:1 complex which was identified by NMR spectroscopy, as well. In the case of  $\text{Na}_2[\text{Ir}(\text{cod})(\text{Nitron})(\text{mtp}pts)] the stability of the particles was investigated at different pH values and the changing was followed by  $^{31}\text{P}\{^1\text{H}\}$  NMR. The results show that the intensity of the signals belonging to the complex and the hydride particle was the highest at pH 6.5, so the most stable complex and hydride can be assigned to the catalytic activity in the neutral medium. However, in the alkaline range, the intensity of the signals decreased, it is likely that the complex and hydride particles decomposed. In the NMR spectra recorded at different pH values, the value of the chemical shift of the signal at 17.87 ppm did not change, proving that no protolytic processes took place.$$$

The catalytic properties of the new Ir-Nitron-phosphine complexes were investigated in two model reactions: hydrogenation of water-soluble carboxylic acids in a homogeneous aqueous solution and hydrogenation of alkynes in an aqueous-organic two-phase system.

Several water-soluble palladium(II) complexes were also prepared by using sulfonated salan-type ligand (HSS: *N,N'*-bis(2-hydroxy-5-sulfonatobenzyl)-1,4-diaminoethane; PrHSS: *N,N'*-bis(2-hydroxy-5-sulfonatobenzyl)-1,4-diaminopropane; BuHSS: *N,N'*-bis(2-hydroxy-5-sulfonatobenzyl)-1,4-diaminobutane). The protonation constants of the ligands and the stability constants of their metal complexes ( $[\text{Pd}(\text{HSS})]$ ,  $[\text{Ni}(\text{HSS})]$ ) were determined using pH-potentiometry. The catalytic activity of these complexes in the hydrogenation and redox isomerization of oct-1-en-3-ol were investigated in detail. Based on the comparison of the pH-dependence of the catalytic activity and the species distribution determined by pH photometry, we concluded that  $[\text{PdL}]^{2-}$  possesses the highest catalytic activity in this reaction. The catalytic activities of palladium complexes containing salan-type ligands were tested in formate dehydrogenation/bicarbonate reduction and formic acid decomposition/ $\text{CO}_2$  reduction catalytic cycles, but the studied complexes did not show significant activity.

Rhodium(I) dinuclear complexes prepared with the new carbene ligands (L1, L2, L3, L4) were used in PA (phenylacetylene) polymerization reaction. The resulting polymers are very valuable compounds having phenyl substituents with a conjugated polyene backbone. However, using the dinuclear Rh(I)-complexes containing methylene and butylene bridge in the carbene we could not obtain monodisperse products (with narrow molecular weight distribution), although the polymerization was complete.

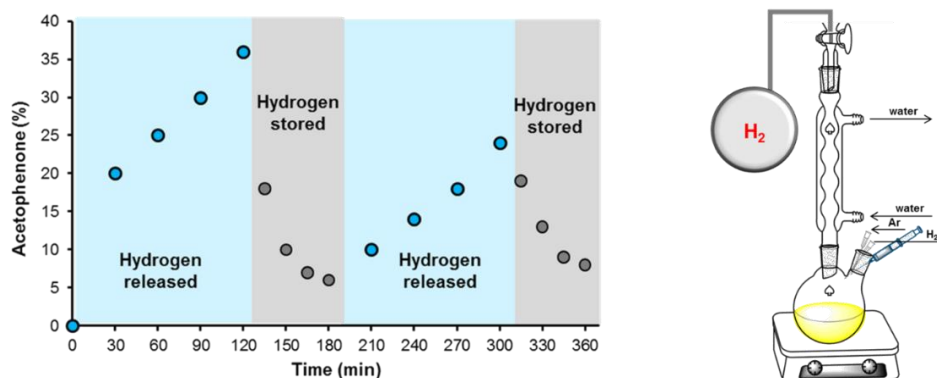
The synthesized novel  $[\{\text{IrCl}(\text{cod})\}_2(\text{di-NHC})]$  dinuclear complexes and their water soluble phosphine derivatives was used in the hydrogenation reactions. The water soluble Ir(I)-diNHC-phosphine type complexes showed high activity in transfer hydrogenation from 2-PrOH of different ketones and hydrogenation of various alkynes. The change of pH in aqueous solution of Ir-diNHC-*mtp*pts exhibited low differences in the conversion of the products.

The mechanism of formate-bicarbonate dehydrogenation/hydrogenation cycle using  $[\text{Na}_2[\text{Ir}(\text{emim})(\text{mtppts})]]$  complex as catalyst was described by DFT calculations. Calculations indicated a surprising result: a rare intramolecular CH activation occurs in the complex containing one phosphine and a hydride intermediate with a cyclometallic structure was formed by interaction between the central Ir and the ethyl group of emim ligand. This observation was proved by NMR measurements, as well.  $[\text{Na}_2[\text{Ir}(\text{cod})(\text{mtppts})]]$  was immobilized on eight different kinds of anion exchange resins. One of the heterogenized complexes, which anchored onto Lewatit MonoPlus, was used as catalyst in the hydrogenation of phenylacetylene in an H-Cube continuous flow reactor. Conditions were optimized by investigating of dependence on reaction temperature, pressure and flow rate. It has also been found that the catalytic activity of the heterogenized complex is practically constant after several cycles. We extended our measurements to hydrogenation of other unsaturated compounds besides phenylacetylene such as bulky diphenylacetylene and benzylidene acetone containing not only C=C unsaturated bond but C=O bond, as well. We determined similar catalytic activity and stability in case of both substrates. For benzylidene acetone, selective hydrogenation was observed for the C=C bond. The activity of  $[\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]]$  in the *hydrogenation of levulinic acid to  $\gamma$ -valerolactone* was also assessed. We also studied the hydrogenation of cesium bicarbonate and dehydrogenation of cesium formate not only in batch system but in microfluidic hydrogenation H-Cube reactor using  $[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})] + 2 \text{mtppts}$  system as catalyst. The continuous flow hydrogenation reactor has many advantages compare to the batch reactor. We investigated both reactions at various temperatures, pressures and flow rates using solutions of various substrate concentrations. It has been experimentally demonstrated that the production of hydrogen can be well controlled by controlling the temperature. Such a possibility provided by flow systems may have high importance in the case of mobile devices where hydrogen supply must be dynamically adjusted to the feed requirements.

The used complexes proved to be catalytically active in both reactions under mild reaction conditions. In the same way as normal carbenes, the  $[\text{Na}_2[\text{Ir}(\text{cod})(\text{Nitron})(\text{mtppts})]]$  was successfully immobilized on a Lewatite MonoPlus ion exchange resin, and then the catalytic activity of the immobilized catalyst was studied in various hydrogenation reactions (phenylacetylene, diphenylacetylene, 1-hexene, benzylidene acetone) and the formate decomposition.

Hydrogen storage in inorganic salts (such as formates) is not the only way to store. Organic liquid compounds (for example alcohols, quinoline derivatives) with higher amounts of hydrogen density are in the focus of interest, as well, their dehydrogenation can be released relatively larger quantities  $\text{H}_2$  and the starting material can be recovered by hydrogenation of formed compound. We conducted intensive studies in this research area. During our earlier investigation, we have recognized that Ir-NHC-phosphine complexes had catalytic activity in the racemisation of optically pure alcohols, which reaction consists of the alcohol dehydrogenation and ketone hydrogenation steps. We have established that the series of our new Ir-NHC and Ir-NHC-phosphine complexes catalyze both the solvent-free dehydrogenation of secondary alcohols and the additive-free reversible hydrogenation of various carbonyl compounds. We were pleased to observe, that the same catalysts were also active in the dehydrogenation of 1-phenylethanol to acetophenone upon lowering the hydrogen pressure and with no change in the temperature.

Hydrogenations were carried out in toluene solution at 95 °C, with a substrate:catalyst ratio 50:1 in the presence of t-BuOK under 10 bar  $\text{H}_2$  pressure. Dehydrogenation of 1-phenylethanol was carried out under the same conditions except that the reaction flask was continuously purged with argon at ambient pressure. Despite the mild reaction conditions, with  $[\text{IrCl}(\text{cod})(\text{mmim})]$  (Figure 2) as the catalyst, a TOF = 490  $\text{h}^{-1}$  was achieved in hydrogenation, and TOF = 11  $\text{h}^{-1}$  in dehydrogenation. We successfully combined the two sub-processes into a cycle. Based on these findings, a hydrogen battery was designed, in which both the hydrogenation and dehydrogenation were carried out under the above reaction conditions but at 1 bar  $\text{H}_2$  pressure in both directions.



**Figure 2.** Reversible hydrogenation-dehydrogenation of acetophenone and 2-phenylethanol, respectively.

$n$  ( $[\text{IrCl}(\text{cod})(\text{mmim})]$ ) = 0.04 mmol,  $n$  (1-phenylethanol) = 2 mmol,  $n$  ( $t$ -BuOK) = 2 mmol,  $V$  (toluene) = 4 mL,  $T$  = 95 °C;  $[\text{S}]/[\text{C}]/[\text{B}]$  = 50/1/50, open system, 1 bar H<sub>2</sub> gas.

In our previous work the water-soluble *cis-mer*- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$  was employed as a catalyst for the selective decomposition of formic acid to H<sub>2</sub> + CO<sub>2</sub> in an aqueous solution. The easily synthesized compound showed high catalytic activity (TOF up to 298 000 h<sup>-1</sup>) and stability. We have investigated the effect of halide on the reaction in an aqueous solution.

The inhibition effect of chloride, bromide and iodide ions is due to the lower activity of the corresponding halide complexes. In contrast the effect of fluoride ions is exactly the opposite because the rates of gas evolution are much higher. It was caused by the formation of HF, which was confirmed by DFT calculations.

The hydrogenation of bicarbonate (it means the back step in aqueous formate/bicarbonate hydrogen storage system) with this Ir-dihydride takes place at a relatively low rate, the primary reason for which may be the alkaline pH of the solution. The much higher catalytic activities were measured when we also use CO<sub>2</sub> in the gas phase in the hydrogenation of hydrogen carbonate solutions. This is due to the acidification of HCO<sub>3</sub><sup>-</sup> solutions, the pH of the solutions is shifted to 4-5 by CO<sub>2</sub>.

We confirmed that this finding is also true for the reactions studied by the Ir-carbon complexes, i.e. that the hydrogenation of bicarbonate occurs with higher activity in the presence of CO<sub>2</sub>.

Further studies were performed, that the water-soluble *cis,mer*- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$  was an excellent catalyst for reduction of terminal alkynes by hydrogen transfer from aqueous HCOOH/HCOONa mixtures, as well. The conversions strongly depended on the pH of the reaction mixtures, and the highest rate of phenylacetylene transfer hydrogenation was observed at pH 3. The same dihydrido-Ir(III) complex actively catalyzed also the hydrogenation of terminal alkynes under mild conditions. It was also found, that an excess of the *mtppps* ligand inhibited the reaction. This was rationalized by the formation of *cis*- $[\text{IrH}_2(\text{mtppps})_4]^+$ . The mechanism of hydrogenation and transfer hydrogenation of phenylacetylene was also studied by DFT calculations, which revealed several possibilities for protonation of a vinyl intermediate as the crucial step in the formation of the styrene product.

*In conclusion: Novel water-soluble transition metal (Ir-, Ru-, Rh- and Pd-) complexes were prepared for catalytic purposes. The complexes have been used as catalysts, mainly in HCOO<sup>-</sup>/HCO<sup>3-</sup> cycles in aqueous solutions and in acetophenone/1-phenylethanol cycles in organic media, which are suitable for hydrogen storage in liquid organic hydrogen storage (LOHC) systems. Both cycles have been studied in detail and their uniqueness and practical applicability has been demonstrated. In addition to hydrogen storage, our complexes have been used as catalysts in other hydrogenation, hydrogen transfer reactions in both homogeneous and heterogeneous phases.*

The submitted book chapter can be seen as a kind of summary of our results: Henrietta Horváth, Gábor Papp, Ágnes Kathó, and Ferenc Joó *Catalysis for a Sustainable Environment* (A.J.L. Pombeiro, M. Sutrathar, E.C.B.A. Alegria, Editors), 2022, Chapter 39, prepared for publication (Hydrogen storage and recovery with the use of chemical batteries)

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**Conference participation (supported by the National Research, Development and Innovation Office NKFI-FK128333)**

H. Kovács, G. Papp, M. Purgel, Á. Kathó, F. Joó, H. Horváth: Reversible chemical hydrogen storage with iridium complexes. XXIV. Nemzetközi Vegyészkonferencia, 24-27.10.2018. Szovátafürdő, Romania-oral lecture (hungarian)

H. Kovács, G. Papp, F. Joó, H. Horváth: Investigation of the catalytic activity of immobilized  $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$  in a flow reactor. International Symposium on Metal Complexes (ISMEC2019), 11-14. 06. 2019. Hajdúszoboszló – Debrecen, Hungary-poster presentation

H. Horváth, G. Papp, H. Kovács, K. Orosz, Á. Kathó, F. Joó: Preparation and application of water soluble Ir(I)-NHC-Phosphine complexes in homogeneous catalytic hydrogenation and hydrogen storage. 53. Komplexkémiai Kollokvium, 21-23.05.2019., Velence, Hungary-oral lecture (hungarian)

Cs. E. Czégéni, A. Udvardy, S. De, Á. Kathó, F. Joó: Synthesis and structural investigation of transition metal complexes using chelating and bridging N-heterocyclic carbene ligand precursors. XXIV. Nemzetközi Vegyészkonferencia 24-27.10.2018., Szovátafürdő, Romania-poster presentation

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F. Joó, G. Papp, G. Ölveti, H. Horváth: Hydrogenation of Carbon Dioxide to Formic Acid in Neutral or Acidic Aqueous Solutions. EUCOMC-XXIII, 23rd Conference on Organometallic Chemistry, 16-20.06.2019, Helsinki, Finland-oral lecture

F. Joó, N. Lihi, Sz. Bunda, A. Udvardy: Coordination Chemistry and Catalytic Applications of Transition Metal-Sulfosalen Complexes in Aqueous Media, 7th Simposio Latinoamericano de Química de Coordinación y Organometalica SILQOM7, 27-30.08.2019. Cartagena de Indias, Colombia, -oral lecture

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