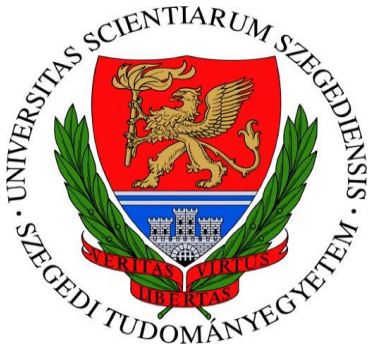
SELECTIVE HYDROGENATIONS ON ANCHORED METAL COMPLEXES

SUSHEN UNDRALA

PhD. Dissertation



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I. INTRODUCTION

Catalysis is the key to the efficiency of chemical conversions. Nowadays, in the age of the green chemistry, it is needed more and more [1]. Most of the chemical reactions in industry are catalytic, and many chemists work to understand the molecular details of the working catalysts [2].

Selectivity of the catalytic processes has became an issue of increasing importance, because the production of the least amount of side products is very important for the industry, from both environmental and economical points of view.

The academic research in organometallic chemistry has grown in the last decades and has provided much of the understanding for homogeneous catalysis [3,4]. Due to this intensive research work, the steps of the homogeneous catalytic processes are well known even at a molecular level. Chemical engineers charged with applying this knowledge in the technology. In addition to, the homogeneous catalysts have identical catalytic sites and therefore usually have high selectivity.

However, the most widely used industrial catalysts are solid materials, especially metals, metal oxides and metal sulfides, sometimes used in combination with each other, like the metals supported on metal oxides. These heterogeneous catalysts are preferred for industrial processes because they can be easily separated and reused in a subsequent cycle. Unfortunately, the surfaces of the heterogeneous catalysts are complex, and may have regions with different compositions and structures. These structures are difficult to characterize, especially under the conditions of the catalytic reactions. Because of this surface complexity, the heterogeneous catalysts have lower selectivity and the surface catalysis is only poorly understood in comparison with homogeneous catalysis.

Consequently, heterogenizing homogeneous complexes by immobilization is a trend toward the development of the chemically homogeneous but physically heterogeneous catalysts, which can successfully combine the high selectivity of homogeneous catalysts with the easy separation and recycling of the heterogeneous ones [5,6].

The basic goal of my PhD work was to develop selective heterogeneous catalysts and to study the application of them. For this purposes I have prepared several metal complexes

and their heterogenized analogues. The heterogenized complexes were characterized by spectroscopic methods and were applied in the selective hydrogenation of different starting materials.

II. LITERATURE OUTLINE

II.1. Heterogenized metal complexes

The preparation and application of heterogenized metal complexes, which can successfully combine the excellent performance of homogenous catalysts with the easy separation and recycling of the heterogeneous ones, is a relatively new field of the catalytic research. In this introductory chapter I try to summarize the different ways of preparation of heterogenized metal complexes on inorganic matrices and show some applications of such catalysts in synthetic organic chemistry.

In general, immobilized catalysts can be classified according to the nature of either the support material or the linkage between the support and the complex. The nature of the support material is often more important than the anchoring mode. Organic polymers [7-15] and inorganic supports are the most widely used support materials.

Immobilization of metal complexes on inorganic matrices has several important potential advantages over the use of organic polymer supports. Inorganic solids, unlike polymers, prevent the intermolecular aggregations of the active surface species due to their rigid structures. Besides, inorganic supports have superior thermal stability and their mechanical stability is often excellent, since swelling can largely be avoided. The preparation of highly dispersed inorganic materials is now an easy technology and crystalline and noncrystalline materials with controlled particle dimension and pore diameters are available.

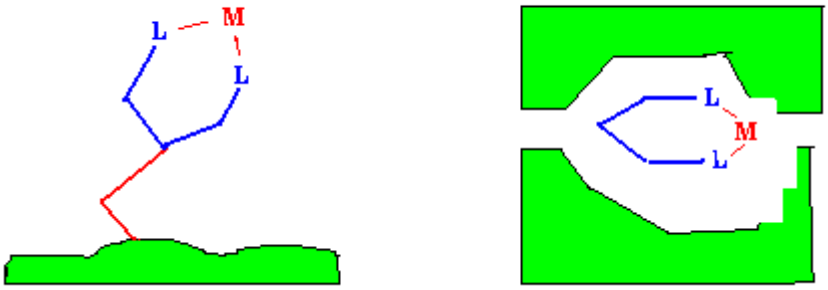
The inorganic supports have generally inert porous structures with high specific surface area. Amorphous oxides, in particular silica, alumina and zirconia are the most widely used inorganic supports.

Other applied supports with a more defined structure are clay materials, pillared clays and layered double hydroxides. Pillared clays contain stable metal oxide clusters which separate the layers that build the clay. LDHs often denoted as hydrotalcite-like compounds belong to the class of synthetic anionic clays. They possess a positively charged layered structure with compensating anions between the sheets [16].

Other popular supports include zeolites. These crystalline materials, mostly alumino-silicates, have well-defined pores and channels in the micropore range. Zeolite Y can be transformed into a mesoporous structure, the so-called USY zeolite, through steaming [17]. This change in porosity can be beneficial to prevent hindered mass transport and enable reactivity towards more bulky molecules. Most of the zeolites have three-dimensional pore system with different shape-selective properties.

II.2. Immobilization methods of metal complexes

The immobilization of metal complexes can be performed in two different ways. The first is the building of the metal complex inside a porous support (encapsulation), while the second is the direct attachment of the metal complex to the surface of a support by a linkage group (covalent grafting).



Grafted complex Encapsulated complex

Grafting the metal complexes to a surface by covalent bonds is an obvious method but has often lead to unsatisfactory results, because the weak bonds can cause the leaching of the complexes, while the too strong bonds make the complexes to be rigid and it is often lead to the decrease of the selectivity.

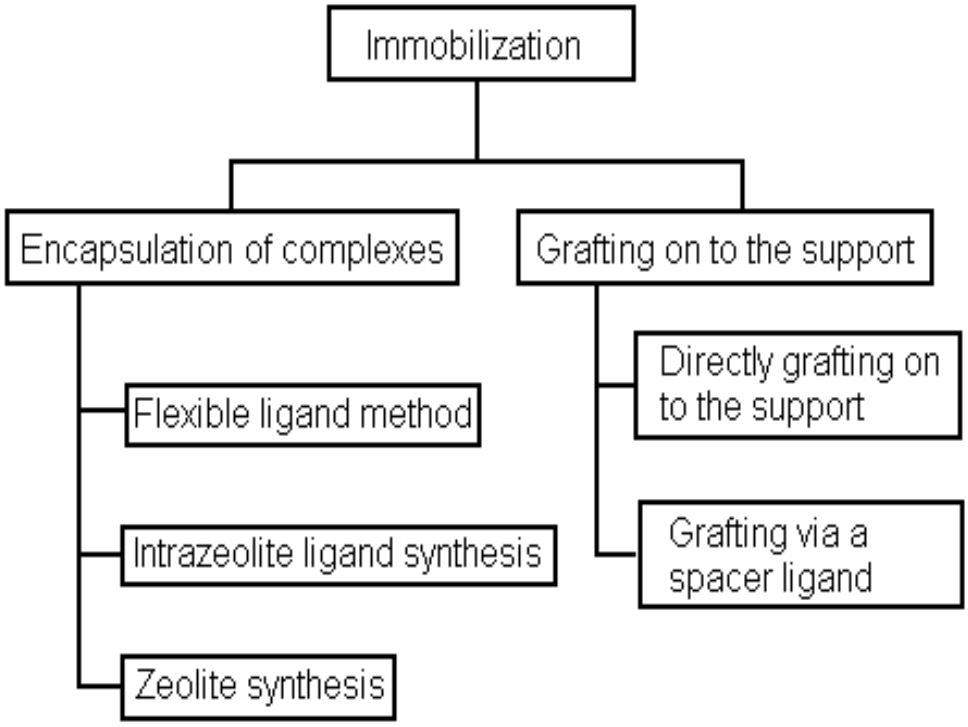
Encapsulation of the metal complexes are free from the above mentioned problems, because in the metal macrocycles are trapped in the cages of the porous materials topologically rather than chemically. The term *ship-in-a-bottle complex* [18] is widely used for these encapsulated catalysts.

Among the porous materials, zeolites with three dimensional structure seems to be the best for building the complex inside the support. The three dimensional channel system includes supercages, where the metal complex can be built. Since the diameter of the channels

is much smaller than the supercage, the complex after its formation can not diffuse out even if it is not bound chemically to the zeolites.

These complexes may retain their solution-like activity, while the zeolite is also expected to impart shape selectivity to the catalyst. The zeolite should also provide a stabilizing effect by blocking bimolecular deactivation pathways (*site isolation effect*).

Both the encapsulated and the grafted complexes can be synthesized by different preparation methods (Scheme 1).

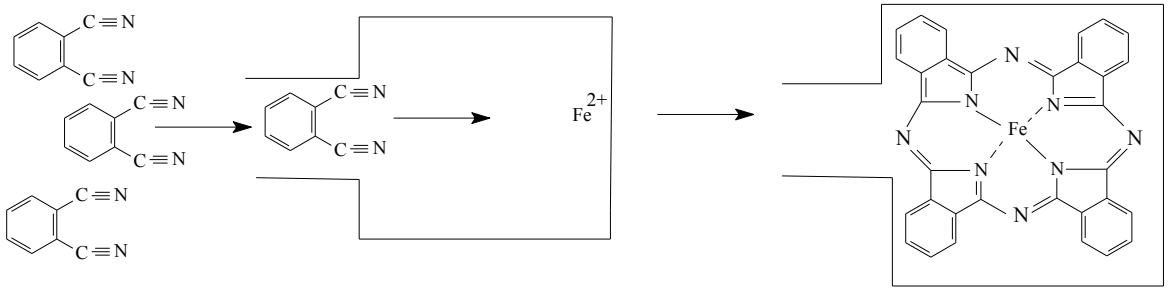


Scheme 1. Preparation methods of immobilized catalysts

II.3. Encapsulation of metal complexes

Metal macrocycles encapsulated in zeolites can be synthesized in different ways [19-26]. *The flexible ligand method* (or intrazeolite complexation) involves the diffusion of a ligand into the pores of a metal-exchanged zeolite, where upon complexation with the metal ion, it becomes too large to exit. The method is limited to prepare encapsulated complexes, having relatively small and flexible ligands. The salen molecules, substituted by not too large groups, are flexible enough, thus this procedure is very suitable for the preparation of metal-salen complexes.

The *intrazeolite ligand synthesis* (or template synthesis) method involves the diffusion of ligand precursors into the zeolite pores where they assemble around an intrazeolite metal ion that acts as a template (Scheme 2).



Scheme 2. Preparation of encapsulated iron phthalocyanine by the intrazeolite ligand synthesis method

In addition to the metallophthalocyanines only the intrazeolite ligand synthesis method is useful for the preparation of larger salen-type complexes. In this case the ion-exchanged zeolite is impregnated by the substituted salicylaldehyde and the substituted diamine in methanol is added slowly to this mixture [27].

The basis of the *zeolite synthesis* method [20] is "building the bottle around the ship" by crystallization of the zeolite around a metal complex which serves as a template for zeolite synthesis. This affords the advantage of encapsulating a well-defined intrazeolite complex without contamination from free ligand as well as uncomplexed metal ions. The high degree of metal complexation is very important for high selectivity because the unchelated metal ions can catalyze side reactions. The possibility of these contaminations is the major disadvantage of the intrazeolite synthesis method. Unfortunately, the zeolite synthesis method is restricted to metal complexes, e.g. metallophthalocyanines, that are stable enough under the relatively harsh conditions of the zeolite synthesis.

II.4. Metal complexes grafted to the supports

Direct attachment of a metal complex to the surface of a support by simple adsorption or ion-pair formation are the simplest routes to produce physically heterogeneous catalysts with active sites identical to homogeneous systems [28-31]. However, according to the weak interactions between the metal complex and the surface, the leaching is characteristic to these type of immobilized catalysts.

In principle grafting of the metal complexes to the surfaces of inorganic solids by covalent bonds can produce stable catalysts free from leaching problems [32-52]. It is achieved, however, only rarely. Too weak bonds usually lead to leaching of the metal. However, if the bond is too strong, the anchoring process often induces modification of the coordination sphere and the oxidation state of the metal. It means that in many cases the supported catalysts have different chemical structures than the homogeneous catalyst and these structural changes can cause severe reduction of the catalyst selectivity. Covalent attachment of the metal complexes to the support surface via a spacer ligand can solve the problems mentioned above. It was found that a spacer ligand with three methylene groups can usually produce immobilized complexes with enough flexibility and solution-like selectivity.

II.5. Metal complexes grafted via heteropoly acids

An important drawback of the heterogenization method via covalent bonds between the metal complex and the surface of the support is the fact that the ligands have to be functionalized, which very often requires significant preparative efforts. Augustine and coworkers have introduced, however, a new immobilization procedure which can heterogenize the commercially available metal complexes without any additional structural changes [53-60].

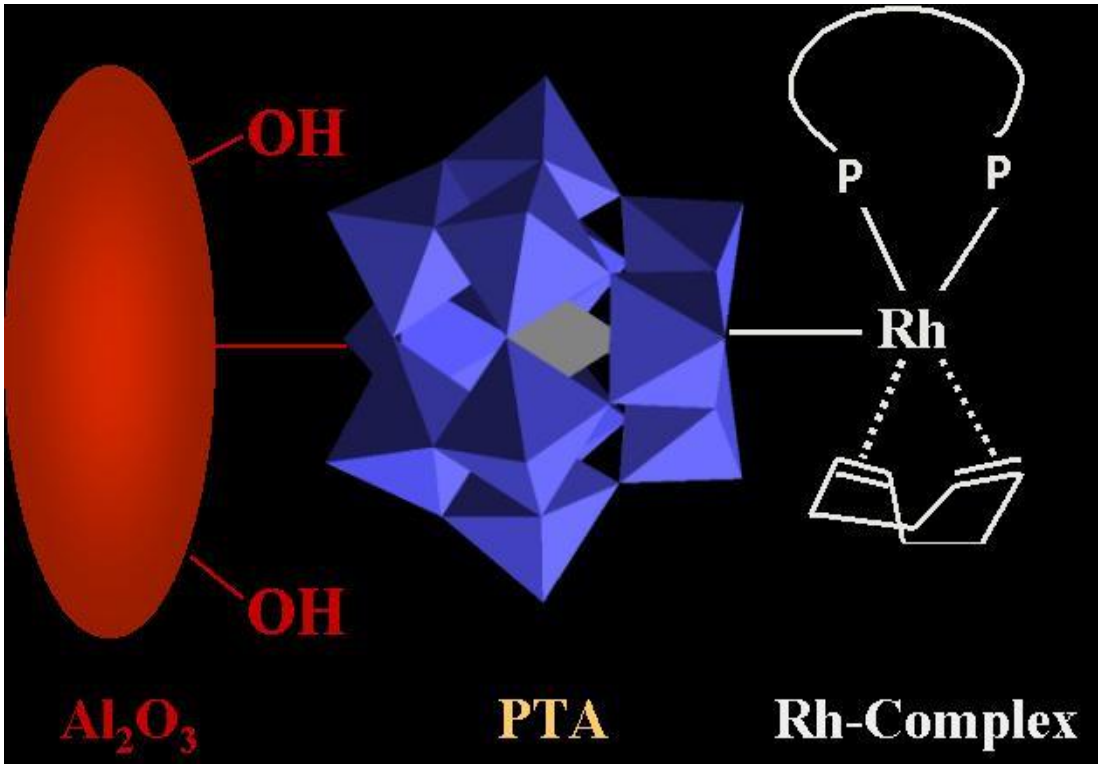


Figure 1. Schematic representation of the structure of alumina-heteropoly acid-metal complex system

The method involves the attachment of a metal complex to a solid support using a heteropoly acid as anchoring agent. The concept is claimed to be generally applicable for a variety of systems: montmorillonite, carbon, alumina and lanthana were used as supports, while different heteropoly acids were applied as anchoring agents. Basic alumina was found to be the best support and tungstophosporic acid (frequently abbreviated as PTA, phosphotungstic acid) was the best anchoring material. The structure of the support-heteropoly acid-metal complex system is illustrated on Figure 1.

The heteropoly acids are attached to the support by interaction of the acidic protons of the acids with the basic sites of the supports. Either ion pairing or covalent bond between surface oxygen atoms and the metal centers of the complexes have been proposed to account for the immobilization of the metal complexes onto the heteropoly acids [61].

Augustine et al. originally assumed the ion pair with the metal cation and the oxygen anion of the HPA, but later they accepted the existence of the covalent bond. The direct bonding between the metal atom and an oxygen on the surface of the HPA was based on the crystallographic structures of the complexes formed by the interaction of Rh(COD) and Ir(COD) and an HPA [62]. Other evidence in support of this arrangement has also been presented [63,64]. UV absorption data have also presented some evidence supporting the covalent attachment of the complex to the HPA. It was shown that Rh(DiPamp) complexes having various counterions gave significantly different UV spectra depending on whether the complex contained a Rh^+ or a Rh-X covalent bond. The Rh^+ species with different counterions had spectra distinguished by absorption doublets at 340 and 460 nm. The Rh–Cl complex had a single absorption band at 280 nm while the Rh-OAc species had a single band at 285 nm. When each of these complexes was treated with PTA, washed thoroughly and then dissolved they all showed only a single absorption band at 285 nm. This similarity with the Rh-OAc spectrum suggests the presence of a Rh-O bond between the complex and the PTA but does not support the presence of a Rh^+ species.

It was also considered that if these anchored species were ion pairs, then one should be able to remove them by treatment with an excess of another anion. To test this, a sample of [Rh(dppb)] anchored onto PTA/Al_2O_3 was stirred for 30 h with a large excess of $LiBF_4$ in ethanol under an inert atmosphere. Analysis of the reaction liquid showed that, at most, 2–3 % of the Rh present on the catalyst was lost. However, tungsten was also detected with a Rh : W ratio of 1:12. Since there are 12 tungsten atoms in a PTA molecule, these data indicate that this procedure apparently did not remove only the Rh complex from the PTA but, instead, somehow removed the Rh/PTA from the alumina.

The preparation of these type of heterogeneous catalysts simply involves mixing of the support with the heteropoly acid prior to adding a solution of a cationic or a neutral transition metal complex. This technique has been found to be particularly amenable to enantioselective catalysis by immobilized rhodium complexes with chiral diphosphine ligands such as Di-Pamp, MeDuphos, Prophos or Binap. No decay in both activity and enantioselectivity was observed even after 15 consecutive runs, but in some cases both the activity and the enantioselectivity improved dramatically in the first reuse and remained constant during the further experiments.

II.6. The application of heterogenized metal complexes

The heterogenization of metal complexes has about a 30 year history. Numerous heterogeneous systems have been developed, based on catalytic reactions applied in homogeneous conditions. The most widely studied areas are the oxidation and the hydrogenation reactions. Several examples have been reported on other reactions such as C–C coupling, hydroformylation and metathesis. The field has rapidly expanded over the past few years and the results are summarized in excellent reviews [65-70].

Immobilization of metal complexes generates heterogeneous catalysts, which are generally more complicated than their homogeneous analogs. It is, therefore, not surprising that the effect of heterogenization is still very often unpredictable. Some of the heterogenized analogs of homogeneous complexes are less active and lose part of their activity in the recycling step. However, there are cases when activities, chemo- or enantioselectivities of the heterogenized sample are superior to the corresponding homogeneous catalyst [49, 71-86]. Several different theories have appeared in the literature explaining the improved activities of the heterogeneous systems.

The earliest theory explaining the enhanced activity of heterogenized complexes refers to the encapsulated complexes. It states that the molecular sieve can impose an unusual, high energy geometry at a metal site that enhances its catalytic properties. In bioinorganic chemistry this is referred to as the entactic state and it is generally believed to play a major role in determining the activity of metalloenzymes.

Thomas et al. [87] state that the improved activity of the heterogeneous catalyst, as compared to the homogeneous analog, can be explained by the „confinement concept” in which the key point is the favorable interaction of the substrate with both the pore wall and the chiral directing group (Figure 2).

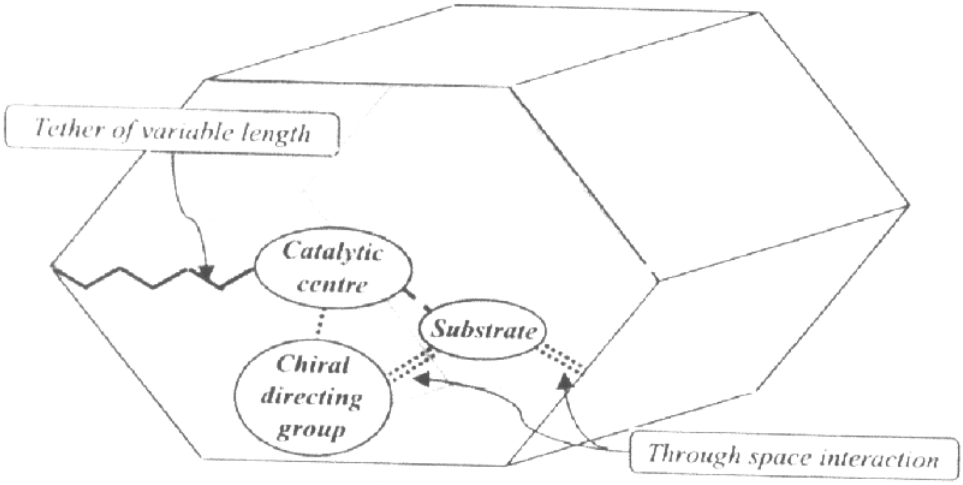


Figure 2. Schematic representation of the confinement concept

Compared to the situation in solution, this confinement of the substrate in small pores leads to a larger influence of the chiral directing group on the orientation of the substrate relative to the reactive catalytic center. The MCM-type materials seem to be very interesting from this respect, due to their regular structure and variable pore diameter. However, the tight caging of the immobilized catalysts can cause sometimes lower enantioselectivities and activities. The lower activity can be due to the reduced mass transport in the small pores [88]. The reduced enantioselectivity can result from either a too strong physisorption of the complex on the wall of the support, or a restricted environment that prevents the chiral metal complex to take the suitable conformation, necessary to induce chiral recognition.

Corma et al. [89, 90] suggest a role of the steric constraints present while using a supported complex. They hypothesize that interaction of the ligands with the pendant hydroxyl groups present on all of the supports used may lead to an increased rigidity of the overall catalytic structure. This, in turn, would restrict rotation of the transition state and favor formation of nearly pure stereoisomers.

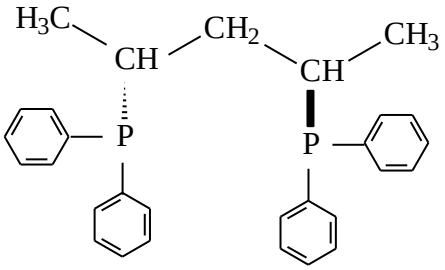
Another concept explaining the better performance of the heterogenized system is the „*site isolation*", i.e. attaching the catalyst to the support in such a way that the catalytic sites can no longer interact with each other. The effective site isolation was realized by matching three factors: a tight attachment of the ligand to the support, a low concentration of the surface ligands, and selecting an appropriate catalyst precursor. Under homogeneous conditions

some metal complexes form less active multinuclear complexes. Upon immobilization, however, the formation of such complexes can be prevented.

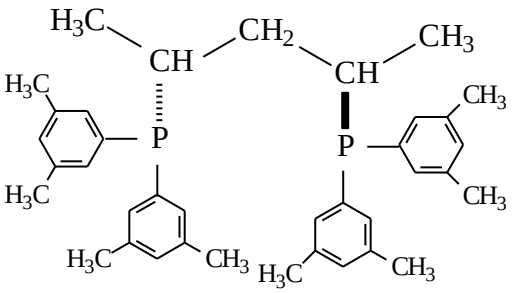
III. EXPERIMENTAL

III.1. Materials used

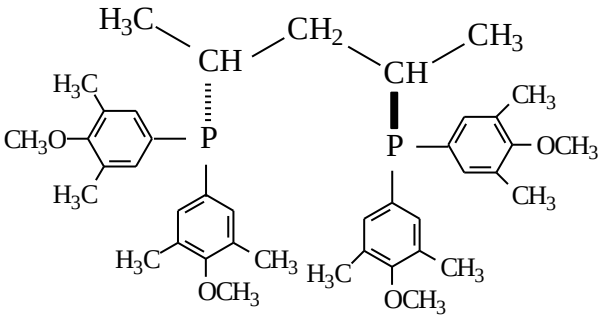
During the experiments (2*S*,4*S*)-(-)-2,4-bis(diphenylphosphino)pentane [(*S*,*S*)-bdpp], (2*S*,4*S*)-(-)-2,4-bis[bis(3,5-dimethylphenyl)phosphino)]pentane [(*S*,*S*)-Me_2bdpp], (2*S*,4*S*)-(-)-2,4-bis[bis(4-methoxy-3,5-dimethylphenyl)phosphino)]pentane [(*S*,*S*)-Me_2-MeObdpp] and (1*R*,3*R*)-1,3-diphenyl-1,3-bis(diphenylphosphino)propane [(*R*,*R*)-Ph_2bdppr] were used as chiral ligands.



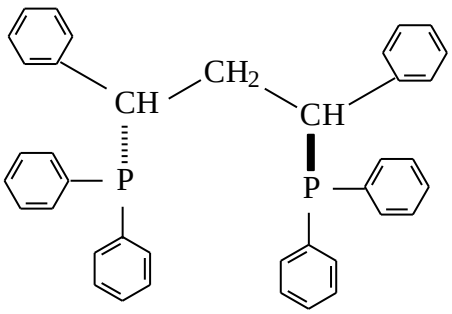
(*S*,*S*)-bdpp



(*S*,*S*)-Me_2bdpp



(*S*,*S*)-Me_2-MeObdpp



(*R*,*R*)-Ph_2bdppr

Scheme 3. Chiral ligands for the preparation of chiral Rh-complexes

The chiral ligands above were prepared in the Department of Organic Chemistry, University of Pannonia, Veszprém, according to published procedures [91,92]. The preformed chiral complexes listed below were also prepared at the same Department.

[Rh(nbd)(*S*,*S*)-bdpp]PF_6

[Rh(nbd)(*S*,*S*)-Me_2bdpp]PF_6

[Rh(nbd)(*S*,*S*)-Me_2-MeObdpp]PF_6

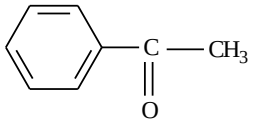
Scheme 4. Preformed crystalline chiral Rh-complexes used in this work

For the *in situ* method the $[Rh(nbd)Cl]_2$, that is the [di-μ-chlorobis(norbornadiene)dirhodium(I)], and the ruthenium(III)chloride for the preparation of the carbene complexes were purchased from Alfa Aesar. For the carbene synthesis the 1-butyl-3-methylimidazolium chloride was purchased from Fluka, while *alpha*-terpinene was an Aldrich product.

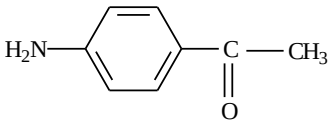
During the immobilization experiments basic aluminium oxide (CAMAG 5016-A-I) was used from Aldrich.

Tungstophosphoric acid was used as heteropoly acid (HPA) for the anchoring process and the tungstophosphoric acid hydrate was a Merck product.

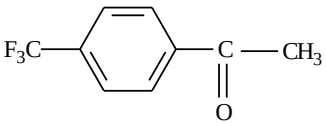
(*Z*)-α-acetamidocinnamic acid was purchased from Aldrich and the methyl ester of this compound was prepared by a standard process [93]. Propanal, *trans*-cinnamaldehyde, allyl alcohol, acetone, acetophenone and its substituted derivatives [methyl-(4-trifluoromethylphenyl)-ketone and (4-aminophenyl)-methyl-ketone] (Scheme 5) were purchased from Aldrich and used as received. Methanol and ethanol from Aldrich were used as solvents.



Acetophenone



(4-aminophenyl)-methyl-ketone

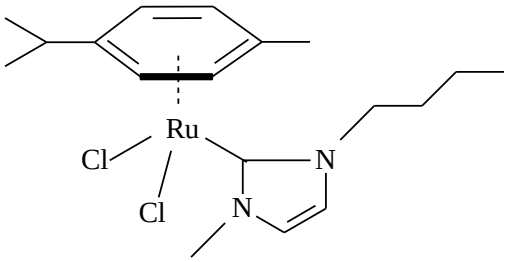


methyl-(4-trifluoromethylphenyl)-ketone

Scheme 5. Acetophenone and its substituted derivatives

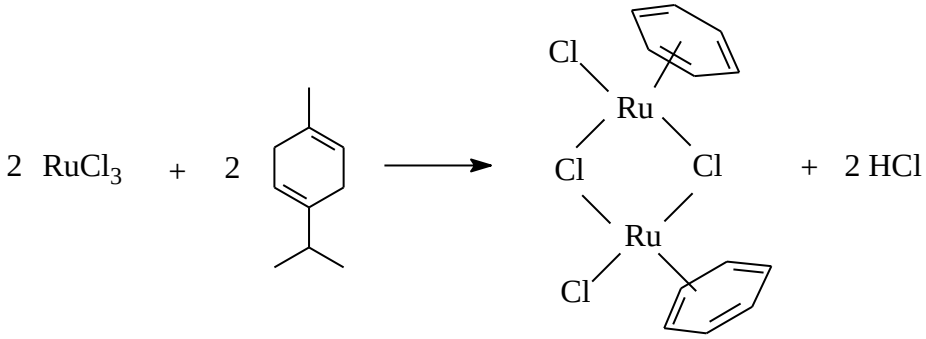
III.2. Preparation of the Ru(II)-NHC complex

A water-soluble Ru(II)-*N*-heterocyclic carbene complex, the $[RuCl_2L(C_{10}H_{14})]$, where L is the 1-butyl-3-methylimidazol-2-ylidene and $C_{10}H_{14}$ is the *p*-cymene, can be synthesized easily [94].



Scheme 6. The structure of the $[RuCl_2L(C_{10}H_{14})]$ complex.
L = 1-butyl-3-methylimidazol-2-ylidene
$C_{10}H_{14}$ = *p*-cymene

$[RuCl_2(C_{10}H_{14})]_2$. This molecule was synthesized from $RuCl_3$ and *alpha*-terpinene according to a literature process [95].

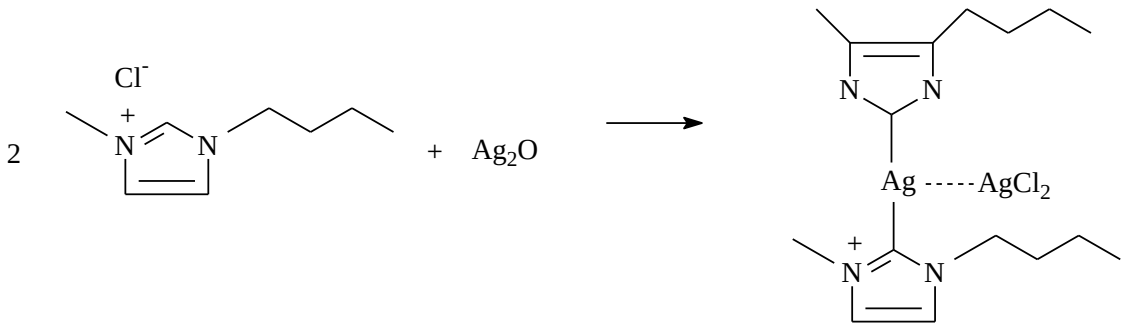


All manipulations were carried out using standard Schlenk techniques. 0.9 g $RuCl_3$ was added into a three necked round bottomed flask. The flask was evacuated and filled Ar with three times. 50 ml water free ethyl alcohol and 7.6 ml *alpha*-terpinene were placed into the flask. The mixture was stirred at 90 °C for 4 hours. The reaction mixture was put in a freezer for one night to crystallize and the crystals were filtered.

[Ag(1-butyl-3-methylimidazolin-2-ylidene)$_2$]-[$AgCl_2$]. This compound can be obtained in the reaction of 1-butyl-3-methylimidazolium chloride and Ag_2O in CH_2Cl_2.

1.72 mmol 1-butyl-3-methylimidazolium chloride was dissolved in 25 ml of dichloromethane and transferred into a Schlenk vessel. 1.03 mmol Ag_2O was added, and the mixture

was stirred for 3 h at 50 °C under an Ar atmosphere. The unreacted Ag_2O was filtered off under Ar, and the solution was directly applied for the further synthetic step.



Scheme 7. Preparation of the [Ag(1-butyl-3-methylimidazolin-2-ylidene)$_2$]-[$AgCl_2$] complex

[$RuCl_2L(C_{10}H_{14})$]. 0.44 mmol [$RuCl_2(C_{10}H_{14})]_2$ was taken up in 5 ml of dichloromethane and added to the solution of [Ag(1-butyl-3-methylimidazolin-2-ylidene)$_2$] [$AgCl_2$]. During this process AgCl formed as a white precipitate and the mixture was stirred for 2 h at 40 °C. After filtration in air, the solvent was removed in vacuo to give a brown waxy substance. The Schlenk vessel containing the raw material was immersed into liquid nitrogen, and 5 ml of diethyl ether was added. The raw material was treated with ether for a couple of minutes, and the ether was removed by a pipet. This treatment was repeated five times, when a pale orange powder was obtained.

III.3. Preparation of the HPA/Al_2O_3 system

Figure 3 shows the experimental setup for the preparation of the anchored complexes. The first step of the anchoring process of the metal complexes developed by Augustine is the adsorption of the heteropoly acid on alumina. The right side of the Figure 3 shows the experimental setup of this process. Basic alumina was the best support and tungstophosphoric acid (HPA) was the best anchoring agent.

For the preparation of the HPA/Al_2O_3 1.5 g of basic Al_2O_3 was suspended in 30 mL of methanol in a round bottomed flask. 288 mg (0.1 mmol) of tungstophosphoric acid hydrate was dissolved in 25 mL of methanol and this solution was added dropwise into the alumina suspension with efficient stirring. The stirring was continued for two days at room temperature, under an Ar atmosphere. The solution was removed from the solid material and the solid residue was suspended in 30 mL of methanol.

Figure 3. The experimental setup for the preparation of anchored complexes

III.4. Anchoring the preformed complexes

Originally we used for the immobilization procedure the preformed crystalline complexes prepared at the Department of Organic Chemistry, University of Pannonia, Veszprém. In this case it was assumed that the cationic complex is anchored to the oxygen of the heteropoly acid by an ionic bond.

$$HPA—O^{-}\ ^{+}[Rh(nbd)(S,S\text{-bdpp})]$$

During this anchoring process 0.1 mmol of [Rh(nbd)(*S*,*S*)-bdpp]PF_6, or [Rh(nbd)(*S*,*S*)-Me_2bdpp]PF_6 or [Rh(nbd)(*S*,*S*)-4-Me_2-MeObdpp]PF_6 complexes were dissolved in 40 mL of deoxygenated methanol and this solution was dropped slowly with stirring to the suspension of the 1.5 g HPA/Al_2O_3.

The stirring was continued for another two days. The solution was removed and the solid residue was washed with methanol, until a colorless solution was obtained. The light yellow solid material was dried at 30 ºC for two hours in vacuum and for one day under argon.

III.5. Anchoring by the *in situ* method

Because an ionic bond was assumed between the metal of the complex and the oxygen of the heteropoly acid, originally only cationic complexes were used for the anchoring process. Later it was found, however, the bond between the metal of the complex and the oxygen of the heteropoly acid has a covalent character and neutral complexes were also anchored successfully.

At the same time at the Department of Organic Chemistry, University of Pannonia, Veszprém, a method was developed for the *in situ* preparation of the homogeneous complexes in the reaction vessel just before the catalytic reaction. This method was faster and cheaper than the original one, nevertheless gave the same catalytic results.

On the basis of these findings a similar *in situ* method was decided to use in the immobilization process, too. According to this the original procedure was modified, and the crystalline metal complexes were not prepared in the separate steps, instead *in situ* prepared complexes were used for the anchoring process.

During this modified procedure the methanolic suspension of the heteropoly acid adsorbed on alumina was prepared first according to the procedure described in Section III.3. in the round bottomed flask can be found on the right side of Figure 3.

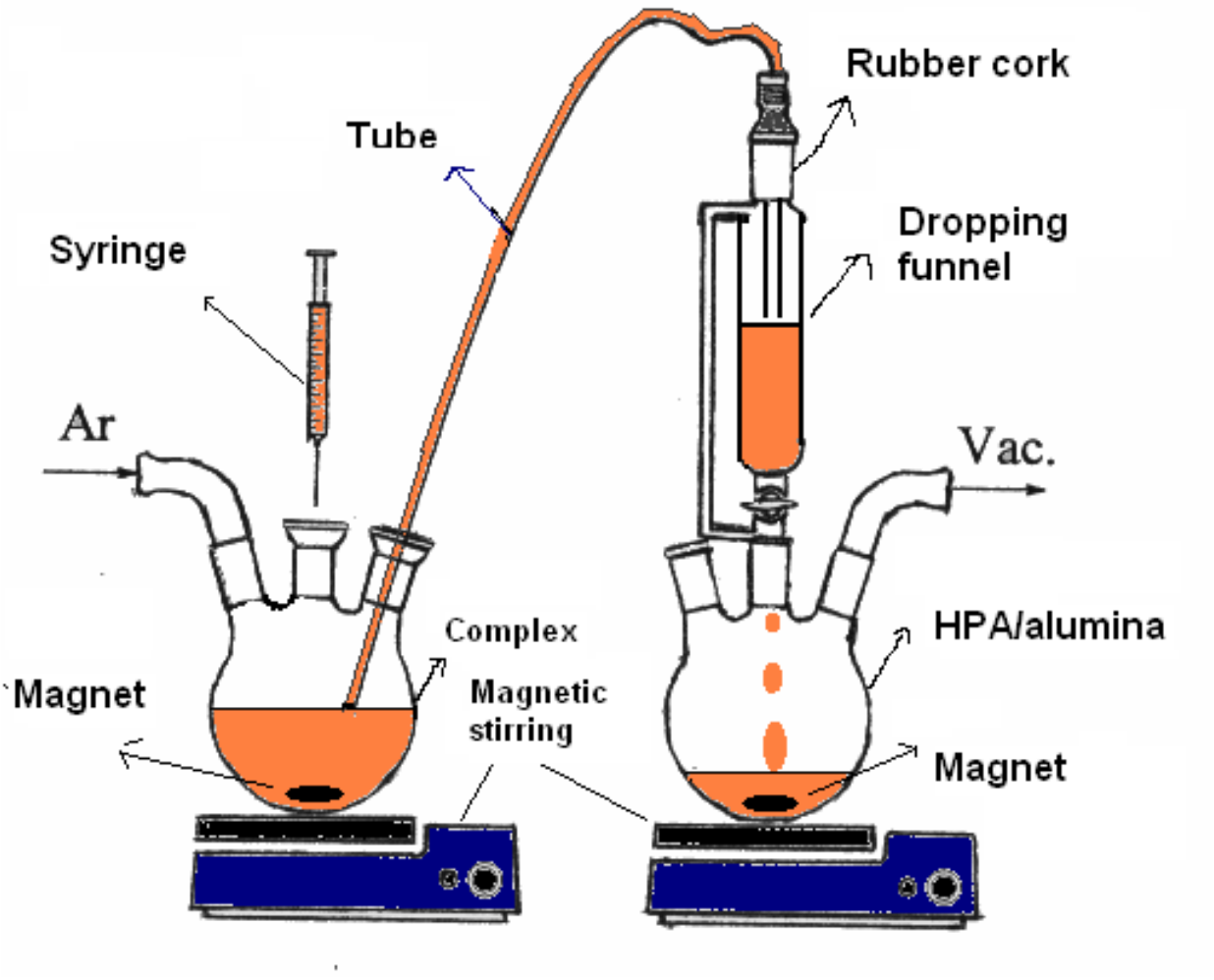


Figure 4. Schematic representation of the transformation of the *in situ* prepared complexes to the HPA/Al_2O_3

The second step is the *in situ* preparation of the metal complex. For this purpose 48.4 mg (100 μmol) $[Rh(nbd)Cl]_2$ and 110.9 mg (250 μmol) solid (*S*,*S*)-bdpp or 118.4 mg (250 μmol) (*S*,*S*)-Me_2bdpp or 126.15 mg (250 μmol) (*S*,*S*)-Me_2-MeObdpp was measured in a separate flask (the left side of Figure 3) and purged with Ar.

The solid materials were dissolved in 40 ml of methanol with stirring and the appearance of the dark orange color shows the formation of the complex. During this process the solution of the [RhCl(nbd)L] complexes were formed, where L are (*S*,*S*)-bdpp, (*S*,*S*)-Me_2bdpp or (*S*,*S*)-Me_2-MeObdpp. These complexes formed *in situ* in the above steps were transferred into the methanolic suspension of HPA/Al_2O_3 stirred under argon and the stirring was continued for two days.

The transfer of the *in situ* prepared complexes from the flask to the other round bottomed flask containing the HPA/Al_2O_3 suspension needs air-free conditions. Figure 4 shows a simple experimental setup which meets this requirement, because the complex solution is transferred by argon pressure from the left flask to the right one through a narrow tube connecting to the dropping funnel through a rubber cork.

After two days the liquid was removed from the round bottomed flask and the solid material was washed with methanol until the colorless extract was obtained. The light yellow solid material was dried at 30 ºC for two hours in vacuum and for one day under argon.

III.6. Catalyst characterization

Metal content. The metal content of the anchored catalysts was determined using a JOBIN YVON 24 type ICP-AES instrument; samples were dissolved in cc. HNO_3. Table 1. summarizes the metal content data of the different immobilized catalysts.

Table 1. Metal content of the different heterogenized catalysts

Catalyst precursor	μmol metal/g catalyst
[Rh(nbd)(*S*,*S*)-bdpp]PF_6	12.0
[Rh(nbd)(*S*,*S*)-Me_2bdpp]PF_6	11.7
[Rh(nbd)(*S*,*S*)-4-Me_2-MeObdpp]PF_6	12.0
[Rh(nbd)(*S*,*S*)-bdpp]	45.2
[Rh(nbd)(*S*,*S*)-Me_2bdpp]	48.0
[Rh(nbd)(*S*,*S*)-Ph_2bdppr]	68.0
[$RuCl_2L(C_{10}H_{14})$]	73.6

FT-IR spectra. The FT-IR spectra of the support, the Rh complexes and the heterogenized samples were recorded on a Bio-Rad FTS–65 A spectrophotometer, in the range of 400 – 4000 cm^{-1}, in KBr pellets.

Figure 5 shows the FT-IR spectra of the [Rh(nbd)(*S*,*S*)-Me_2-MeObdpp]PF_6 complex and its heterogenized version. The comparison of these spectra shows that the homogeneous complexes and the heterogenized samples have several similar bands (1380,1410 and 1480 cm^{-1}), indicating the anchoring of the same complex.

Similar observation was found in the case of the two other preformed complexes {[Rh(nbd)(*S*,*S*)-Me_2bdpp]PF_6 and [Rh(nbd)(*S*,*S*)-bdpp]PF_6 } and their heterogenized analogs. Taking the spectra of the *in situ* complexes and the heterogenized samples similar conclusions can be drawn.

In the case of the Ru(II)-*N*-heterocyclic carbene complexes the FT-IR spectra of the support, the spectra of the [$RuCl_2L(C_{10}H_{14})$] complex (Figure 6) and the heterogenized sample showed the bands at 1380 cm^{-1}, and 1470 cm^{-1}, characteristic for the [$RuCl_2L(C_{10}H_{14})$] complex, which suggests that the unchanged complex was anchored during the heterogenization process.

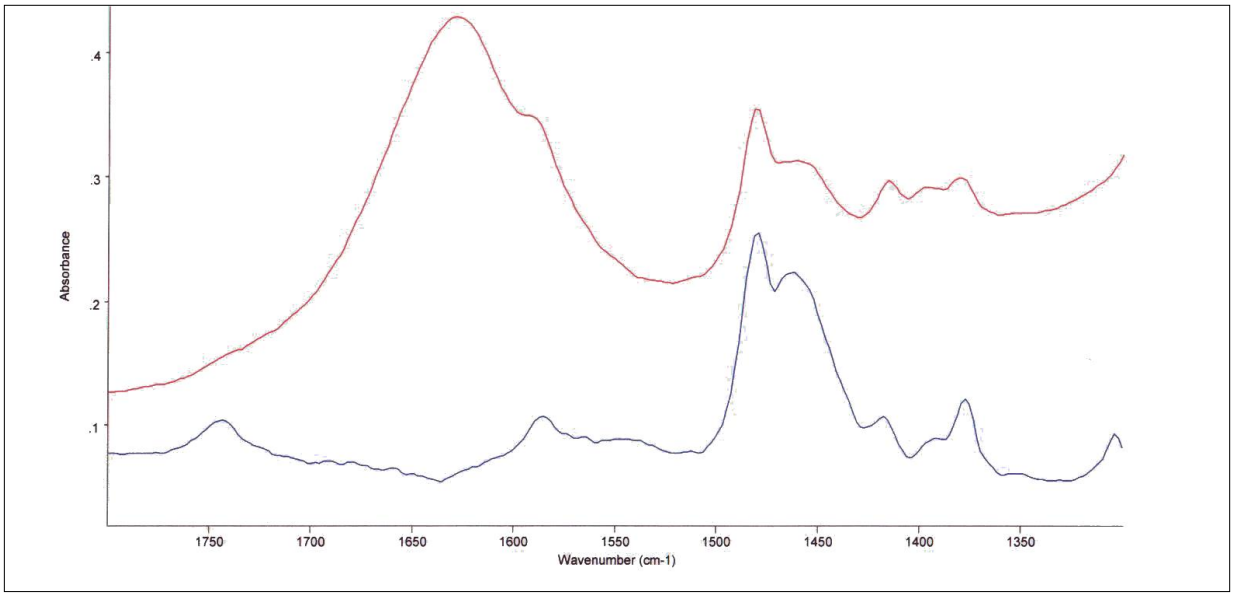


Figure 5. FT-IR spectra of homogeneous and heterogenized [Rh(nbd)(*S*,*S*)-Me_2-MeObdpp] PF_6 complex.

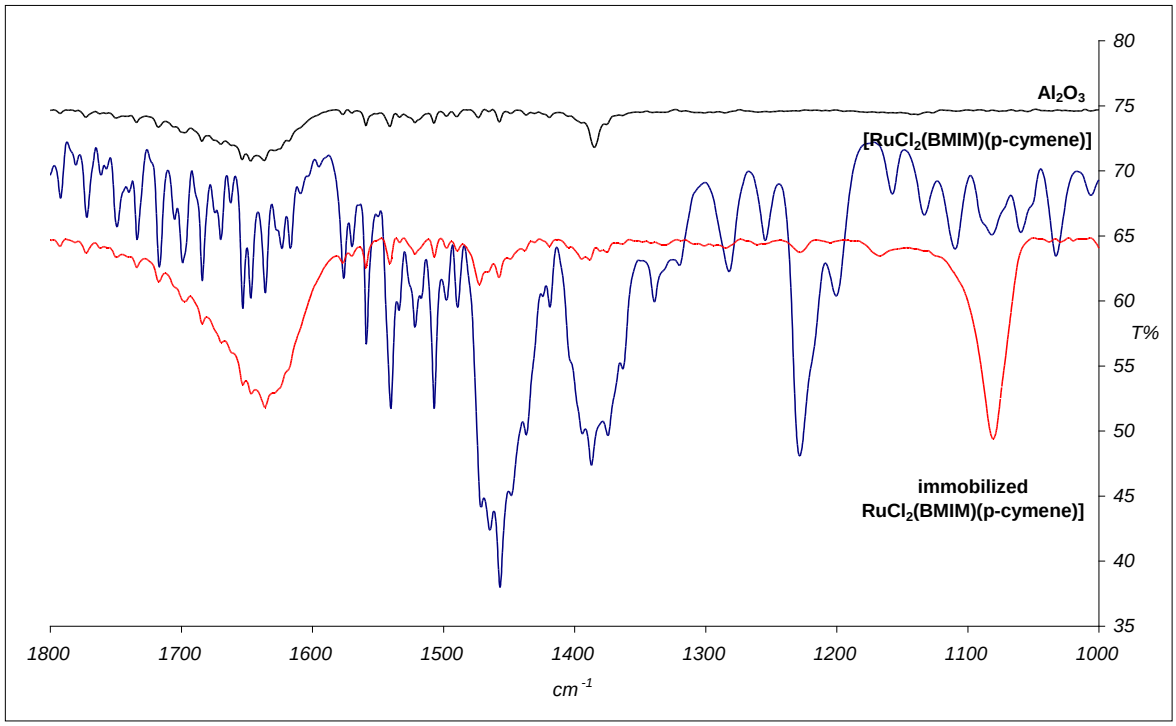


Figure 6. FT-IR spectra of the support, the homogeneous and the heterogenized $[RuCl_2L(C_{10}H_{14})]$ complex.

NMR spectra. The NMR spectra were recorded at room temperature using a Bruker Avance spectrometer operating at 11.7 Tesla magnetic field (^{31}P: 202.46 MHz).

Solid state ^{31}P NMR spectra of the heterogenized sample show similar resonances like the complexes in liquid phase. That is the data obtained from the solid state ^{31}P NMR spectroscopy has also supported our assumption, that the anchored complexes on the surface are very similar to the original complexes in the liquid phase. The resonances between 33-40 ppm are broader than in liquid phase (30 ppm) which can be a sign of the attachment to the support.

III.7. Hydrogenation experiments

Hydrogenation experiments were done in a batch reactor of 30 mL capacity, at different temperatures and different hydrogen pressures (Figure 7). The reactor can be evacuated and pressurized by argon or hydrogen and it is equipped with a septum for the injection of starting materials and to take samples. The reactor was shaken in a vortex manner.

Hydrogenation of cinnamic acid derivatives on chiral Rh-complexes.

(*Z*)-methyl(2-acetamidocinnamate) or (*Z*)-2-acetamidocinnamic acid were hydrogenated at 25 ºC and 0.2 MPa hydrogen pressure. 5 μmol [Rh(nbd)(*S*,*S*)-bdpp]PF_6, or [Rh(nbd)-(*S*,*S*)-Me_2bdpp]PF_6 or [Rh(nbd)(*S*,*S*)-Me_2-MeObdpp]PF_6 homogeneous complex or 100 mg of the adequate heterogenized catalyst were prehydrogenated in 5 ml of methanol for 10 minutes at 0.5 MPa hydrogen pressure. Then 51.75 mg (250 μmol) of (*Z*)-methyl(2-acetamidocinnamate) or 51.25 mg (250 μmol) (*Z*)-2-acetamidocinnamic acid, dissolved in 5 mL of methanol was injected, the reactor was pressurized with H_2 and then the reaction was started with stirring.

Samples were taken every 10 minutes from the reaction mixture, and the products were analyzed by capillary gas chromatography.

The enantiomeric excess was determined on Permabond®-CHIRASIL-L-VAL column [25 m, internal diameter 0.25 mm, film thickness 0.25 μm, carrier gas: He, F.I.D. detector; the retention times of the enantiomers are 40.7 min (*R*), 40.9 min (*S*), temperature program 100-170 ºC (2 ºC/min.)].

The heterogenized catalysts were used in several subsequent runs. After the reactions the reaction mixture was removed from the catalyst, it was dried under vacuum and Ar, then reused.

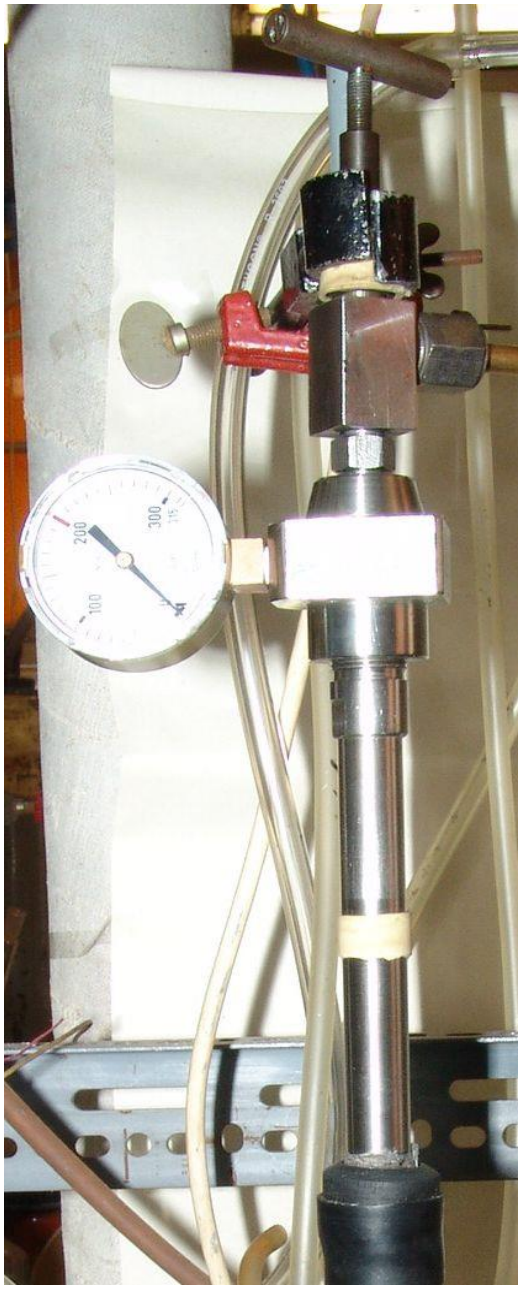


Figure 7. Batch reactor for the hydrogenation experiments

Hydrogenation of C=O bond over [$RuCl_2L(C_{10}H_{14})$] complexes.

Allyl alcohol, propanal, cinnamaldehyde, acetophenone or acetone were hydrogenated in a batch reactor under 0.4 MPa hydrogen pressure. Approximately the same conditions were applied in alcoholic and in aqueous media. In ethanol: 4.7 mg (10.42 μmol) soluble or 150 mg (9.99 μmol Ru) heterogenized catalysts were dissolved or suspended in 3 mL of anhydrous ethanol. 3 μL $(C_2H_5)_3N$ and 0.4 mmol of the substrate were added and the reactor was pressurized with H_2. The reactions were initiated by starting the stirring at 65 ºC. In water: 6.3 mg (14 μmol) homogeneous or 200 mg (14.72 μmol Ru) heterogenized catalysts were added into 3 mL of water. After adding 3 mL of phosphate buffer, 1.0 mmol of substrate was injected, the reactor was pressurized with H_2 and the reaction was initiated by starting the stirring at 80 ºC. Samples were taken every hour from the reaction mixture and the products were analyzed by capillary gas chromatography (Hewlett Packard 5890 Series II) using a HP-FFAP (nitroterephtalic acid modified PEG) column at 70 ºC.

The heterogenized catalysts were used in several subsequent runs. At the end of the reactions the liquid was removed by a Pasteur pipette, the solid catalyst was washed with ethanol and dried in vacuum under Ar, then reused.

Hydrogenation of C=O bond over chiral Rh-complexes.

Acetophenone and it's substituted derivatives, methyl-(4-trifluoromethylphenyl)-ketone and (4-aminophenyl)-methyl-ketone were hydrogenated in a batch reactor at 50 ºC and 2.5 MPa hydrogen pressure.

5 μmol [Rh(nbd)(*S*,*S*)-bdpp], [Rh(nbd)(*S*,*S*)-Me_2bdpp] or [Rh(nbd)(*S*,*S*)-Me_2-MeO-bdpp] homogeneous or 250 mg of the adequate heterogenized complexes were prehydrogenated in 5 mL of methanol for 10 minutes at 1.0 MPa hydrogen pressure at room temperature. Then 250 μmol starting material [30.0 mg of acetophenone, 47.0 mg methyl-(4-trifluoromethylphenyl)-ketone or 33.8 mg (4-aminophenyl)-methyl-ketone] was dissolved in 5 mL of methanol and was injected into the reactor. The reactor was pressurized with H_2 and then the reaction was started with stirring. Every reaction was run for 6 hours and the products were analyzed by capillary gas chromatography. The enantiomeric excess was determined on a Cyclodex-β column, using He as a carrier gas: F.I.D. detector; at isotherm temperature 120 ºC.

The heterogenized catalysts were used in several subsequent runs. After the reactions the reaction mixture was removed from the catalyst, which was dried under vacuum and Ar, then reused.

IV. RESULTS and DISCUSSION

IV.1. Enantioselective hydrogenation of C=C bond on Rh-complexes anchored by different methods

At the beginning of our research work we have anchored the preformed [Rh(nbd)(*S*,*S*)-bdpp]$^+$ PF_6^-, or [Rh(nbd)(*S*,*S*)-Me_2bdpp]$^+$ PF_6^- or the [Rh(nbd)(*S*,*S*)-Me_2-MeObdpp]$^+$ PF_6^- complexes using heteropoly acids as anchoring agents with the method developed by Augustine et al. and described in III. 4. The heterogenized catalysts were applied in the hydrogenation of (*Z*)-2-acetamidocinnamic acid and its methyl ester.

According to the original anchoring process the heterogenization takes place in two steps: the synthesis of the preformed [Rh(nbd)L]$^+$ PF_6^- type crystalline metal complex in a separate step, followed by the anchoring of this complex from alcoholic solution. Later we introduced a modified process (III.5.) which is much faster and economical.

The FT-IR characterization has shown that the two processes gave the same heterogenized catalysts.

To check the validity our statement on the basis of the spectroscopic characterization about the similar structure of the catalysts immobilized by the two heterogenization methods we have studied the hydrogenation of (*Z*)-methyl-(2-acetamidocinnamate) on catalysts immobilized by both methods. It was found that our heterogenized samples were active in this reaction. The heterogenized samples produced via two different ways gave the similar catalytic results, supporting the conclusion what we had. Namely, we have prepared the same heterogenized catalyst in both ways.

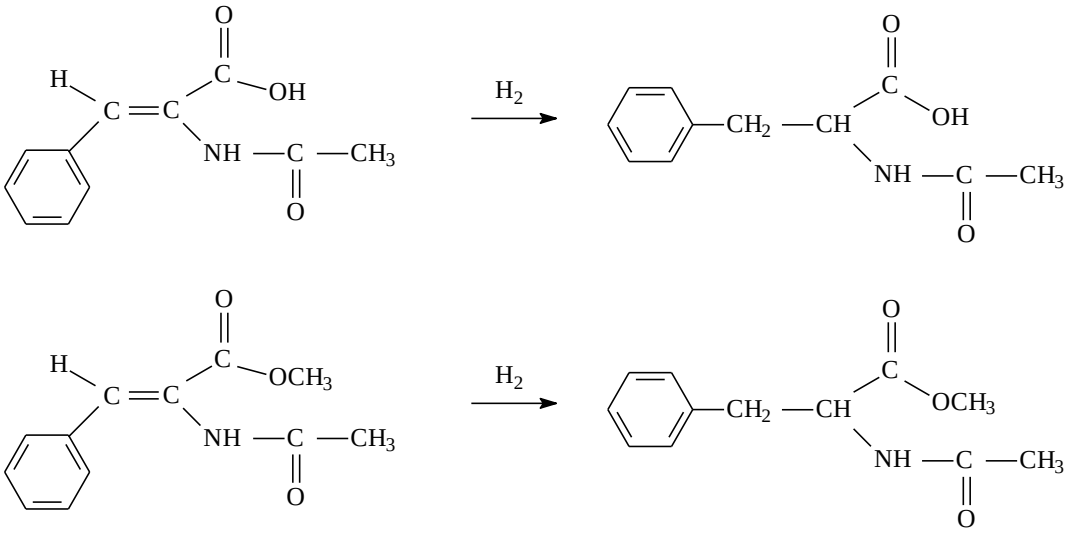
IV.2. Substituent effect in the enantioselective hydrogenation of C=C bond on anchored chiral Rh-complexes

Recently differently substituted [Rh(nbd)(*S*,*S*)-bdpp]PF_6 complexes, with different basicity were prepared and applied in the hydrogenation of (*Z*)-methyl(2-acetamidocinnamate) and dimethyl itaconate [91]. The basicity was varied by using *p*-CH_3O-, *p*-CH_3, *p*-H, *p*-CF_3-, 3,5-$(CH_3)_2$- and 3,5-$(CF_3)_2$- substituents on the diphenyl-phosphine moieties of the molecule. The results of the hydrogenation experiments showed an increase in enantioselectivity and activity with increasing basicity. So, the electronic tuning of the ligand gave a chance to improve the selectivity and activity.

The aim of our work was to study the substituent effect of the similar immobilized complexes. We were curious, whether the same tuning effect can be observed in heterogeneous condition or not.

The *in situ* preparation method produced catalysts similar to the ones produced by using the preformed complexes. Since the *in situ* method is much faster and cheaper, we used this modified method for the preparation of immobilized catalysts during the further research work.

To producing highly enantioselective, reusable catalysts we have anchored the [RhCl(nbd)(*S*,*S*)-bdpp], the [RhCl(nbd)(*S*,*S*)-3,5-Me_2bdpp] and the [RhCl(nbd)(*S*,*S*)-3,5-Me_2-4-MeObdpp] complexes as it was described in Section III.5. The heterogenized catalysts were applied in the hydrogenation of (*Z*)-2-acetamidocinnamic acid and its methyl ester.



Scheme 8. Hydrogenation of (*Z*)-2-acetamidocinnamic acid and its methyl ester

Table 2 and Table 3 show the results observed in the two hydrogenation reactions. In order to evaluate the performance of our heterogenized catalysts we have studied the hydrogenation on both heterogeneous and homogeneous catalysts, as well. For the fair comparison we have used the same protocol in all cases except the amount of catalyst.

Table 2 shows the results about the activity and the enantioselectivity of the hydrogenation of (*Z*)-2-acetamidocinnamic acid on differently substituted Rh-bdpp complexes.

Table 2. Activity and enantioselectivity of the hydrogenation of (*Z*)-2-acetamidocinnamic acid on differently substituted [Rh(nbd)(*S*,*S*)-bdpp] complexes

Catalysts	**TOF** (h^{-1})	***ee*** (%)
[RhCl(nbd)(*S*,*S*)-bdpp]	180	93
[RhCl(nbd)(*S*,*S*)-bdpp]/HPA/Al_2O_3	1370	95
[RhCl(nbd)(*S*,*S*)-Me_2bdpp]	390	94
[RhCl(nbd)(*S*,*S*)-Me_2bdpp] /HPA/Al_2O_3	1800	96
[RhCl(nbd)(*S*,*S*)-Me_2-MeObdpp]	450	96
[RhCl(nbd)(*S*,*S*)-Me_2-MeObdpp]/HPA/Al_2O_3	3000	98.5

Reaction conditions: 5 μmol homogeneous complex or 100 mg heterogenized sample, 250 μmol substrate, 25 °C, 0.2 Mpa H_2, reaction time: 5 min.

As Table 2 clearly shows all of the heterogenized catalysts were active in the hydrogenation of (*Z*)-2-acetamidocinnamic acid. The specific activity of the immobilized samples were higher then the same activity of the homogoneous analogs. These findings are in a good correlation with our former [96,97] and some other author's findings [68,95] namely the heterogenized catalysts exhibit a higher activity than the homogeneous analogs. A possible explanation is the „site isolation" of the complex [71,98] which can be easily done by the anchoring.

On the differently susbstituted Rh complexes a definite increase could be observed both in activity and in enantioselectivity with increasing basicity. The increase in activity can be seen on Figure 8, while in enantioselectivity on Figure 9.

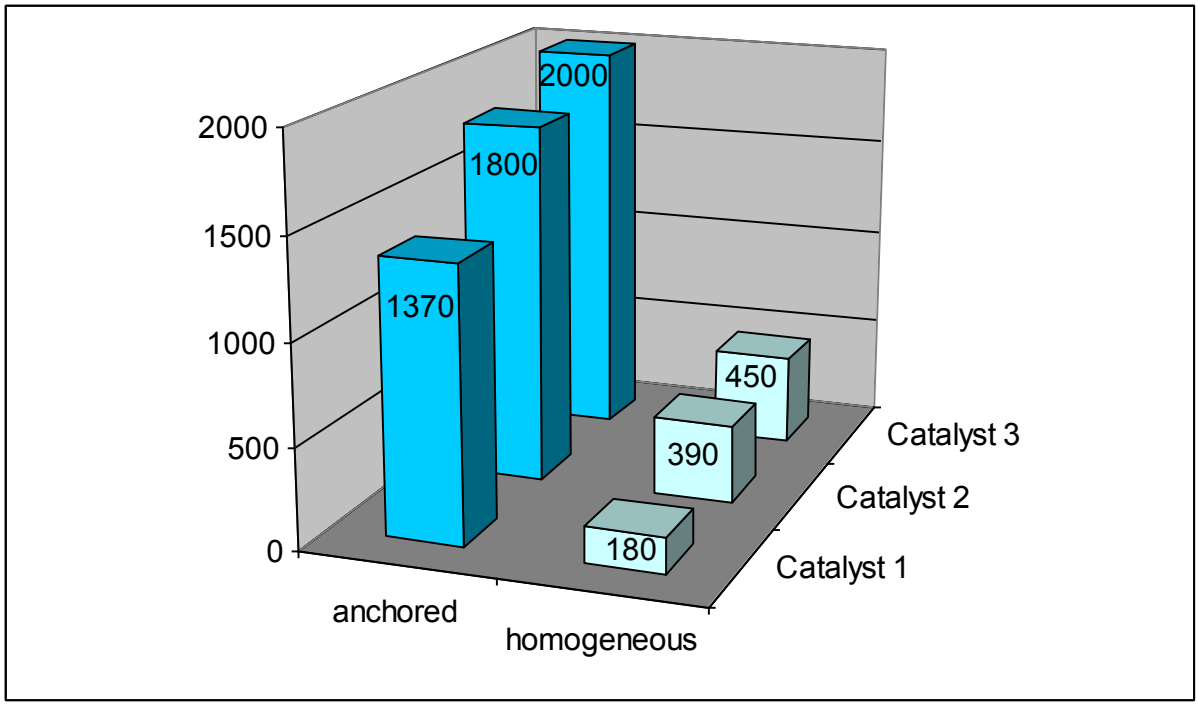


Figure 8. The change of activity with increasing basicity in the hydrogenation of (*Z*)-2-acetamidocinnamic acid on different anchored and homogeneous [Rh(nbd)(bdpp)] complexes.

catalyst 1	catalyst 2	catalyst 3
[Rh(nbd)(*S*,*S*)-bdpp]	[Rh(nbd)(*S*,*S*)-Me_2bdpp]	[Rh(nbd)(*S*,*S*)-Me_2-MeObdpp]

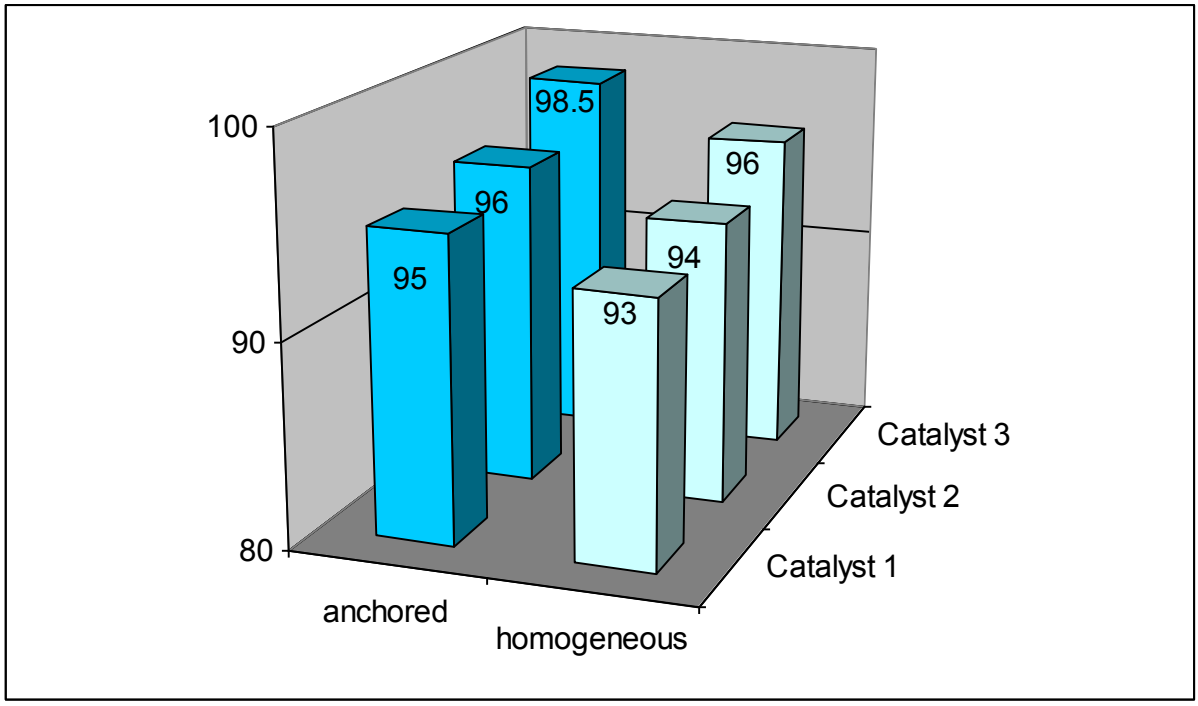


Figure 9. The change of enatioselectivity with increasing basicity in the hydrogenation of (*Z*)-2-acetamidocinnamic acid on different anchored and homogeneous [Rh(nbd)(bdpp)] complexes.

catalyst 1	catalyst 2	catalyst 3
[Rh(nbd)(*S*,*S*)-bdpp]	[Rh(nbd)(*S*,*S*)-Me_2bdpp]	[Rh(nbd)(*S*,*S*)-Me_2-MeObdpp]

The hydrogenation of (*Z*)-methyl(2-acetamidocinnamate) was also studied on differently substituted Rh complexes (Table 3).

Table 3. Activity and enantioselectivity of the hydrogenation of (*Z*)-methyl(2-acetamidocinnamate) on differently substituted [Rh(nbd)(*S*,*S*)-bdpp] complexes.

Catalysts	**TOF** (h^{-1})	***ee*** (%)
[RhCl(nbd)(*S*,*S*)-bdpp]	51	90
[RhCl(nbd)(*S*,*S*)-bdpp]/HPA/Al_2O_3	249	89
[RhCl(nbd)(*S*,*S*)-Me_2bdpp]	96	91
[RhCl(nbd)(*S*,*S*)-Me_2bdpp] /HPA/Al_2O_3	450	94
[RhCl(nbd)(*S*,*S*)-Me_2-MeObdpp]	120	98
[RhCl(nbd)(*S*,*S*)-Me_2-MeObdpp]/HPA/Al_2O_3	562	99

Reaction conditions: 5 μmol homogeneous complex or 100 mg heterogenized sample, 250 μmol substrate, 25 °C, 0.2 Mpa H_2, reaction time: 10 min.

From the results obtained in the hydrogenation of (*Z*)-methyl(2-acetamidocinnamate) on different Rh-complexes we can draw similar conclusions as in the case of (*Z*)-2-acet-amidocinnamic acid. All the immobilized catalysts were active in the reaction, as a matter of fact they had a higher specific activity than the homogeneous analogs.

The hydrogenation of the ester was a little bit slower than the hydrogenation of acid, as it was expected from the earlier results. Comparing the differently substituted catalysts a definite increase can be found both in activity (Figure 10) and in enantioselectivity (Figure 11) with increasing basicity.

As Table 3 and Figure 10 and 11 show not just all the immobilized catalysts were active in the hydrogenation reactions, but they had higher activity and enantioselectivity as their homogeneous counterpart.

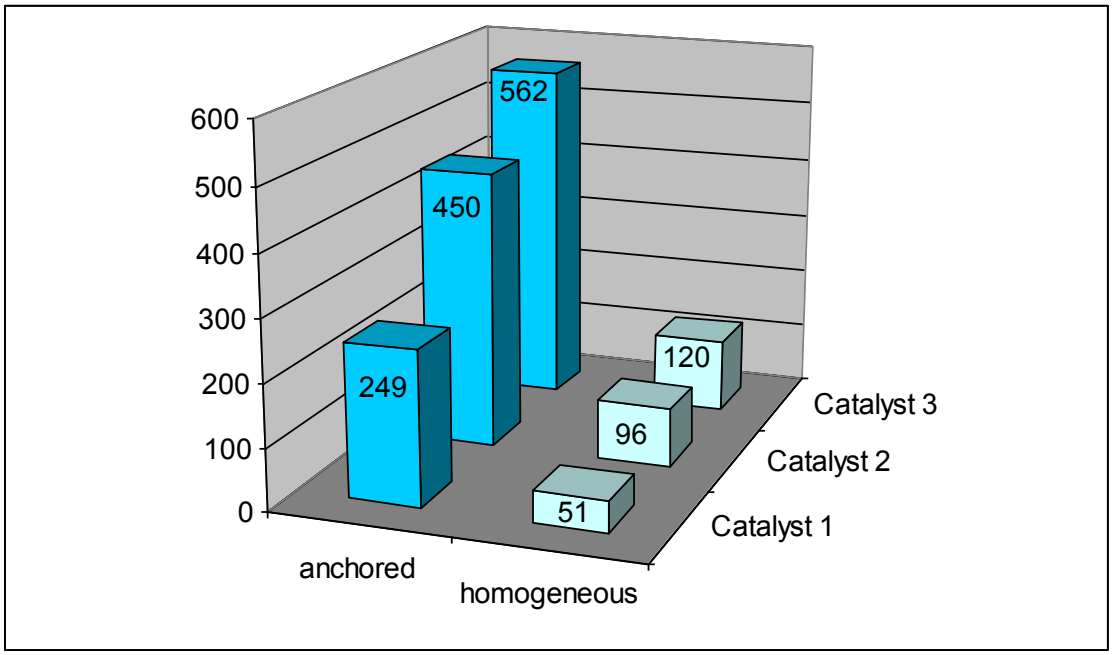


Figure 10. The change of activity with increasing basicity in the hydrogenation of (*Z*)-methyl(2-acetamidocinnamate) on different anchored and homogeneous [Rh(nbd)(*S*,*S*)-bdpp] complexes.

catalyst 1 [Rh(nbd)(*S*,*S*)-bdpp] catalyst 2 [Rh(nbd)(*S*,*S*)-Me_2bdpp] catalyst 3 [Rh(nbd)(*S*,*S*)-Me_2-MeObdpp]

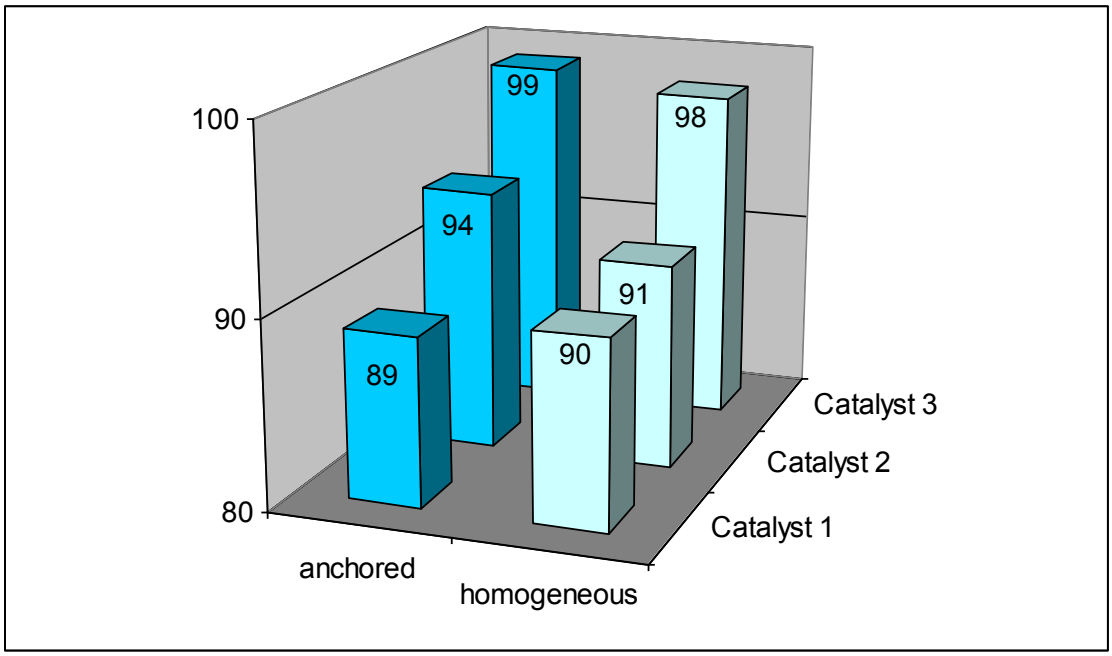


Figure 11. The change of enatioselectivity with increasing basicity in the hydrogenation of (*Z*)-methyl(2-acetamidocinnamate) on different anchored and homogeneous [Rh(nbd)(*S*,*S*)-bdpp] complexes.

catalyst 1 [Rh(nbd)(*S*,*S*)-bdpp] catalyst 2 [Rh(nbd)(*S*,*S*)-Me_2bdpp] catalyst 3 [Rh(nbd)(*S*,*S*)-Me_2-MeObdpp]

Figure 12 convincingly shows that the heterogenized catalysts can be reused in several subsequent runs without any significant loss of catalytic performance. The activity remained basically unchanged in three subsequent runs. The same is true for the enantioselectivity, too.

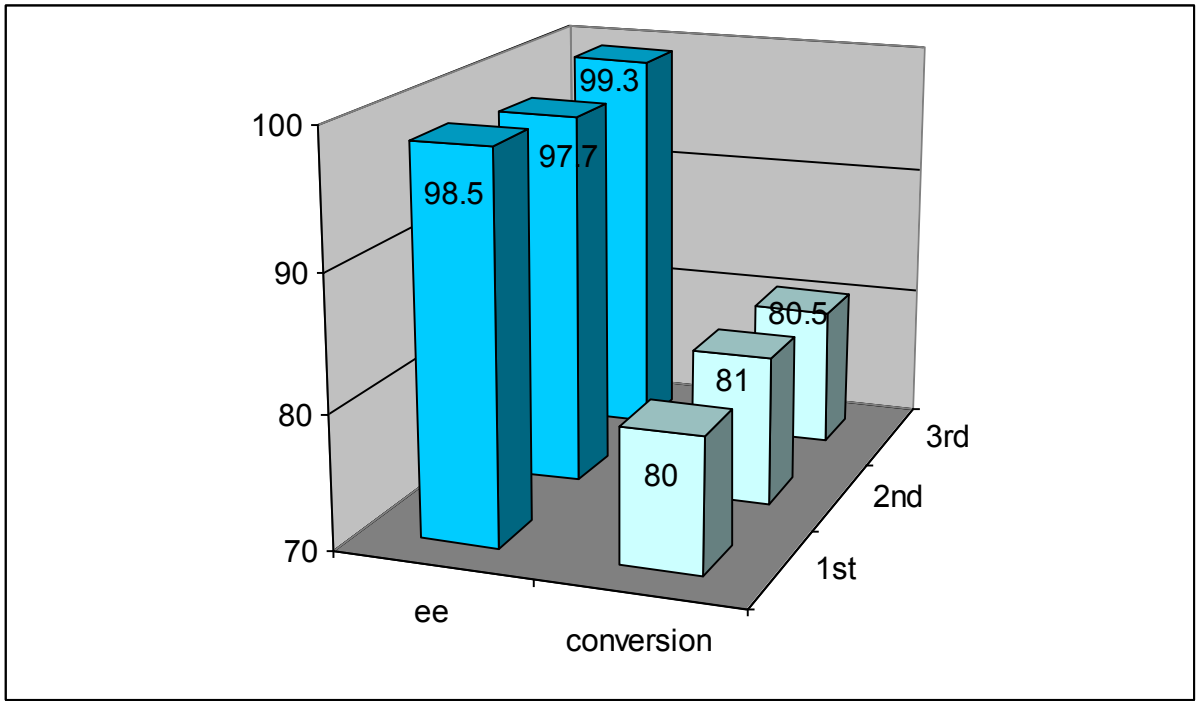


Figure 12. The conversion and enantioselectivity values of the hydrogenation of (*Z*)-2-acetamidocinnamic acid on [Rh (nbd)(*S*,*S*)-Me_2-MeObdpp] / HPA/-Al_2O_3 catalysts in three subsequent experiments

As a summary the differently substituted [RhCl(*S*,*S*)-bdpp] complexes were successfully heterogenized using the modified *in situ* version of the anchoring method developed originally by Augustine. The original and the modified methods produce similar heterogenized catalysts with similar catalytic performances, but the *in situ* method is much easier and cheaper.

The immobilized catalysts show enantioselectivity similar to the homogeneous complexes, showing that the heterogenized complexes protect their solution like structures. The specific activities of the heterogenized catalysts were even higher than the homogeneous complexes. The effect of the ligands was the same in the case of the heterogenized catalysts as in the homogeneous counterparts.

IV.3. Enantioselective hydrogenation of C=O bond on anchored Rh complexes

The asymmetric reduction of the C=O group for the production of enantiomerically pure secondary alcohols has a fundamental importance in modern synthetic chemistry [99]. The Noyori's catalyst, [Ru(binap)] opened the way to the efficient asymmetric hydrogenation of C=O group of functionalized ketones, which are capable to coordinate via two points to the reactive metal centre.

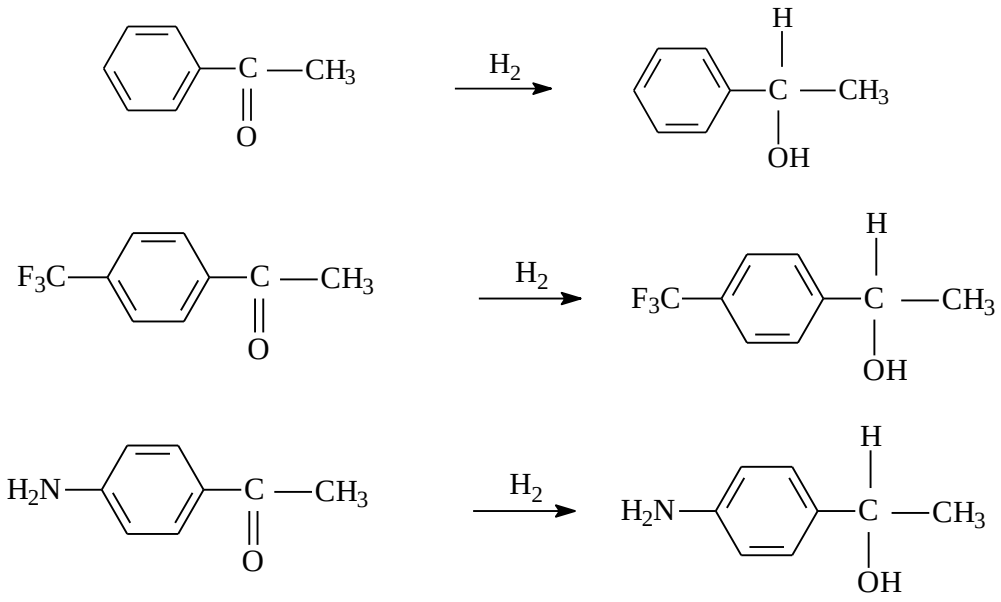
The „second generation" of Noyori's catalyst, in which there is a ruthenium metal centre having a chiral diphosphine and a chiral diamine ligand made possible the asymmetric hydrogenation of unfunctionalised ketones, too [100]. Aromatic, heteroaromatic and unsaturated ketones could be reduced with excellent productivity and enantioselectivity; however, aliphatic ketones were reduced only with moderate enantioselectivity.

At the Department of Organic Chemistry, University of Pannonia, Veszprém, the hydrogenation of C=O bond was studied on different homogeneous chiral Rh-complexes and worked out the best circumstances for the C=O hydrogenation on these complexes.

Recently the effect of substituents has been reported of the different Rh complexes on the hydrogenation of (*Z*)-methyl(2-acetamidocinnamate). The ligand basicity was varied by using *p*-CH_3O-, 3,5-$(CH_3)_2$ and *p*-CH_3O-3,5-$(CH_3)_2$- substituents on the phenyl rings of the diphenylphosphine moieties of the molecule. The results of the hydrogenation experiments showed an increase in enantioselectivity and activity with increasing basicity. So, the electronic tuning of the ligand gave a chance to improve the selectivity and activity.

Our aim was the to apply the conditions worked out at the University of Pannonia for the hydrogenation of C=O bond to the hydrogenation on anchored chiral Rh-complexes, prepared by the *in situ* anchoring method. At the same time we wanted to study how the substitution of the ligands can influence the C=O bond hydrogenation. We also wanted to compare the substituent effects in the hydrogenation of C=O and C=C bonds.

In this experiment we have prepared the [RhCl(nbd)(*S*,*S*)-bdpp]**,** the [RhCl(nbd)(*S*,*S*)-Me_2bdpp] and the [RhCl(nbd)(*R*,*R*)Ph_2bdpr)] complexes by the *in situ* immobilization method and used these heterogenized catalysts for the hydrogenation of C=O bond of acetophenone and it's substituted derivatives [methyl-(4-trifluorophenyl)-ketone and (4-aminophenyl)-methyl-ketone].



Scheme 9. Hydrogenation of acetophenone and its derivatives

To compare the performances of the anchored and the homogeneous catalysts we prepared the appropriate homogeneous complexes by also the *in situ* complex preparation method and hydrogenated the substances. To have the fair comparison we have used the same reaction condition for all of the studied starting materials.

Table 4. Enantioselective hydrogenation of methyl-(4-trifluorophenyl)-ketone to (*S*)-1-(4-trifluorophenyl)etan-1-ol on three homogeneous and heterogenized Rh complexes.

Catalysts	**Conversion** (%)	***e.e.*** (%)	**TOF** (h^{-1})
[RhCl(nbd)(*S*,*S*)-bdpp]	62.1	75.0	5.2
[RhCl(nbd)(*S*,*S*)-bdpp]/HPA/Al_2O_3	39.0	51.0	1.4
[RhCl(nbd)(*S*,*S*)-Me_2bdpp]	93.8	60.0	7.8
[RhCl(nbd)(*S*,*S*)-Me_2bdpp]/HPA/Al_2O_3	48.1	58.1	1.67
[RhCl(nbd)(*R*,*R*)-Ph_2bdpr)]	97.8	80.0	8.15
[RhCl(nbd)(*R*,*R*)-Ph_2bdpr)]/HPA/Al_2O_3	34.0	60.0	0.83

Reaction conditions: 5 μmol homogeneous catalyst or 250 mg anchored complex; 10 mL EtOH, 6 μL Et_3N, 250 μmol methyl-(4-trifluorophenyl)-ketone, 2.5 MPa H_2 pressure, 50 °C; reaction time: 6 h.

The investigation was started with the hydrogenation of methyl-(4-trifluorophenyl)-ketone and the results are compiled in Table 4.

Data in Table 4 show that all the catalysts were active in the hydrogenation of methyl-(4-trifluorophenyl)-ketone with slightly different activity and enantioselectivity. [RhCl(nbd)-(*S*,*S*)-Me_2bdpp] and [RhCl(nbd)(*R*,*R*)-Ph_2bdpr)] complexes had about the same activity, meanwhile [RhCl(nbd)(*S*,*S*)-bdpp] was a little bit less active. The [RhCl(nbd)(*S*,*S*)-Me_2bdpp] catalyst showes less enatioselectivity than the other two.

Comparing the homogeneous and heterogeneous systems an interesting observation can be found. The heterogenized complexes were slightly less reactive than the homogeneous ones. This observation is in contrast to our earlier results, since so far we usually had higher activity on the heterogenized samples.

To check the effect of substituents on the hydrogenation of acetophenone derivatives we have studied the hydrogenation of unsubstituted (Table 5) and NH_2-substituted (Table 6) aceto-phenone derivatives, as well. The obtained results are compiled in the adequate Tables.

Table 5. Enantioselective hydrogenation of acetophenone on three homogeneous and heterogenized Rh complexes

Catalysts	**Conversion** (%)	***e.e.*** (%)	**TOF** (h^{-1})
[RhCl(nbd)(*S*,*S*)-bdpp]	50.9	75.0 (*S*)	4.25
[RhCl(nbd)(*S*,*S*)-bdpp]/HPA/Al_2O_3	36.6	73.3 (*S*)	1.23
[RhCl(nbd)(*S*,*S*)-Me_2bdpp]	71.2	68.2 (*S*)	5.9
[RhCl(nbd)(*S*,*S*)-Me_2bdpp]/HPA/Al_2O_3	47.8	67.1 (*S*)	1.67
[RhCl(nbd)(*R*,*R*)-Ph_2bdpr)]	75.1	88.0 (*S*)	6.25
[RhCl(nbd)(*R*,*R*)-Ph_2bdpr)]/HPA/Al_2O_3	45.8	64.0 (*S*)	1.16

Reaction conditions: 5 μmol homogeneous catalyst or 250 mg anchored complex; 10 mL EtOH, 6 μL Et_3N, 250 μmol acetophenone, 2.5 MPa H_2 pressure, 50 °C; reaction time: 6 h.

Table 6. Enantioselective hydrogenation of (4-aminophenyl)-methyl-ketone on three homogeneous and heterogenized Rh complexes

Catalysts	**Conversion** (%)	***e.e.*** (%)	**TOF** (h^{-1})
[RhCl(nbd)(*S*,*S*)-bdpp]	1.5	75.0 (*S*)	0.13
[RhCl(nbd)(*S*,*S*)-bdpp]/HPA/Al_2O_3	0.9	75.6 (*S*)	0.03
[RhCl(nbd)(*S*,*S*)-Me_2bdpp]	1.8	88.0 (*S*)	0.15
[RhCl(nbd)(*S*,*S*)-Me_2bdpp]/HPA/Al_2O_3	0.6	78.2 (*S*)	0.016
[RhCl(nbd)(*R*,*R*)-Ph_2bdpr)]	5.2	72.0 (*S*)	0.42
[RhCl(nbd)(*R*,*R*)-Ph_2bdpr)]/HPA/Al_2O_3	3.1	80.0 (*S*)	0.08

Reaction conditions: 5 μmol homogeneous catalyst or 250 mg anchored complex; 10 mL EtOH, 6 μL Et_3N, 250 μmol (4-aminophenyl)-methyl-ketone, 2.5 MPa H_2 pressure, 50 °C; reaction time: 6 h.

Experimental data in Table 5 and Table 6 show that all of our Rh complexes were active in the hydrogenation of the two other acetophenones derivatives. Comparing the different complexes they had more or less similar activity and enantioselectivity in each of the starting material, respectively. The same is holds for the comparison of the homogeneous and the heterogeneous samples.

Considering the differently substituted acetophenone derivatives the data show a definite substituent effect regarding the hydrogenation activities. As it is well known the two applied substituents, CF_3 and NH_2, have the opposite electronic effect. In other words we expect a higher reaction rate for the CF_3-substituted derivative, while the NH_2-substituted one, expected to have a lower reaction rate. The obtained data for the hydrogenation of these derivatives on homogeneous catalysts are in a good correlation with this tendency, which can be seen on Figure 13.

The slowest reaction rates were observed in the case of (4-aminophenyl)-methyl-ketone, which can be rationalized by the strong electron donating capability of the NH_2-group. Consequently, the highest activity and enantioselectivity was observed in the hydrogenation

of methyl-(4-trifluorophenyl)-ketone. Using the heterogeneous catalysts the effect of the substituents is similar, but not so explicit than in the case of soluble complexes (Figure 14).

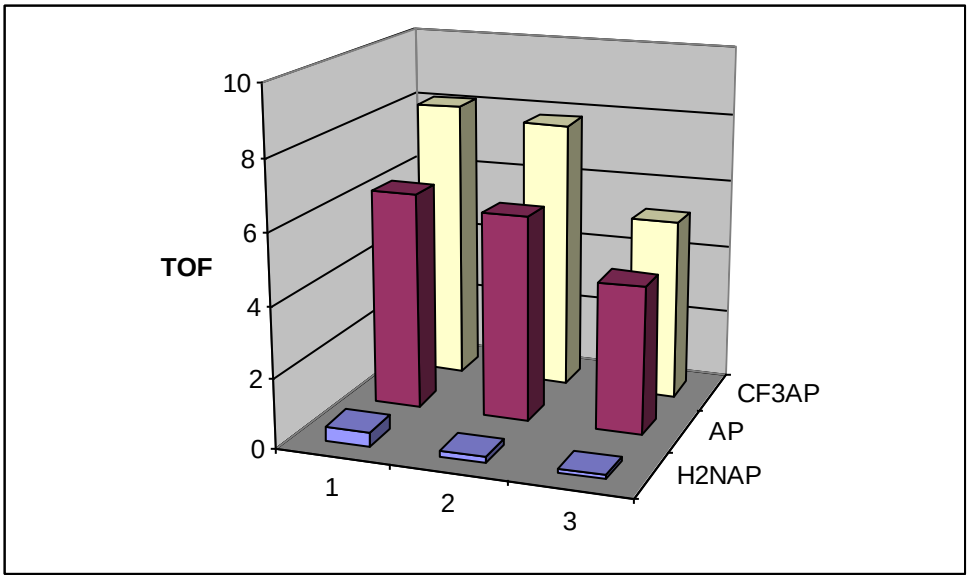


Figure 13. The effect of substituents on the rates in the hydrogenation of acetophenone derivatives on different homogeneous Rh-complexes.

Substrates	Catalysts
CF3AP **:** methyl-(4-trifluorophenyl)-ketone	1: [Rh(nbd)(*R*,*R*)-Ph_2bdpr)]
AP: acetophenone	2: [Rh(nbd)(*S*,*S*)-Me_2bdpp]
H2NAP: (4-aminophenyl)-methyl-ketone	3: [Rh(nbd)(*S*,*S*)-bdpp]

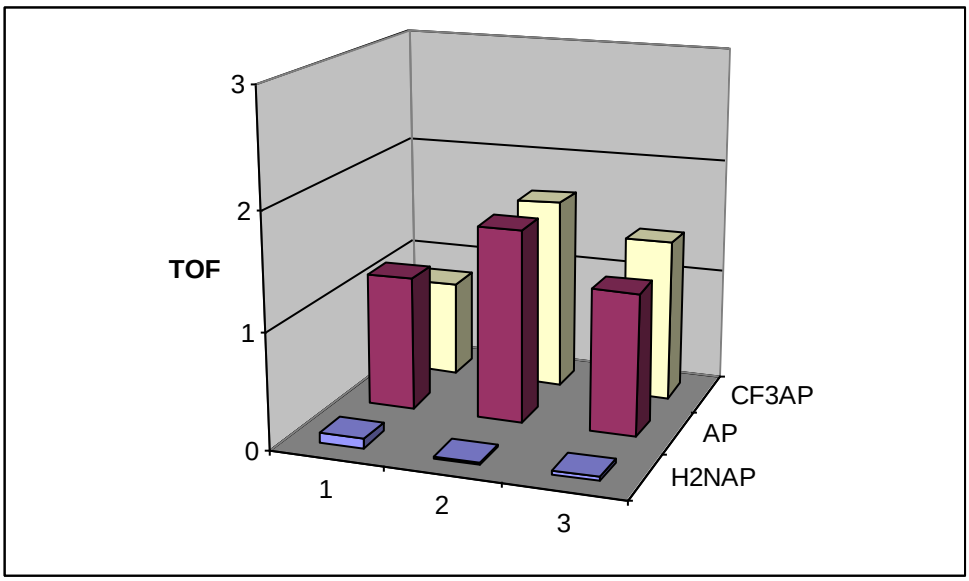


Figure 14. The effect of substituents on the rates in the hydrogenation of acetophenone derivatives on different heterogenized Rh-complexes.

Substrates	Catalysts
CF3AP**:** methyl-(4-trifluorophenyl)-ketone	1: [Rh (nbd)(*R*,*R*)-Ph_2bdpr)]/ HPA/Al_2O_3
AP: acetophenone	2: [Rh(nbd)(*S*,*S*)-Me_2bdpp]/ HPA/Al_2O_3
H2NAP: (4-aminophenyl)-methyl-ketone	3: [Rh(nbd)(*S*,*S*)-bdpp]/HPA/Al_2O_3

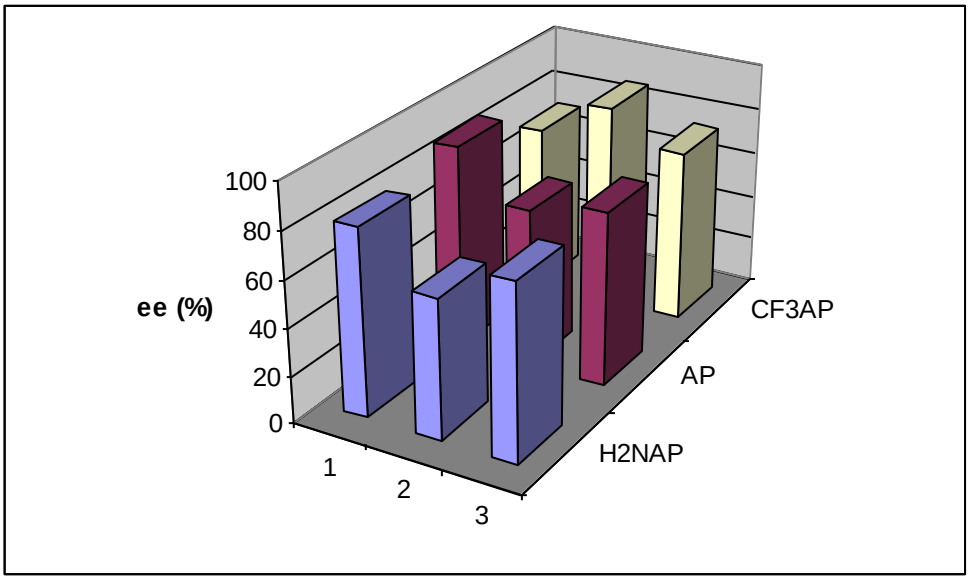


Figure 15. The effect of substituents on the enantioselectivity in the hydrogenation of acetophenone derivatives on different homogeneous Rh-complexes

Substrates	Catalysts
CF3AP **:** methyl-(4-trifluorophenyl)-ketone	1: [Rh(nbd)(*R*,*R*)-Ph_2bdpr)]
AP: acetophenone	2: [Rh(nbd)(*S*,*S*)-Me_2bdpp]
H2NAP: (4-aminophenyl)-methyl-ketone	3: [Rh(nbd)(*S*,*S*)-bdpp]

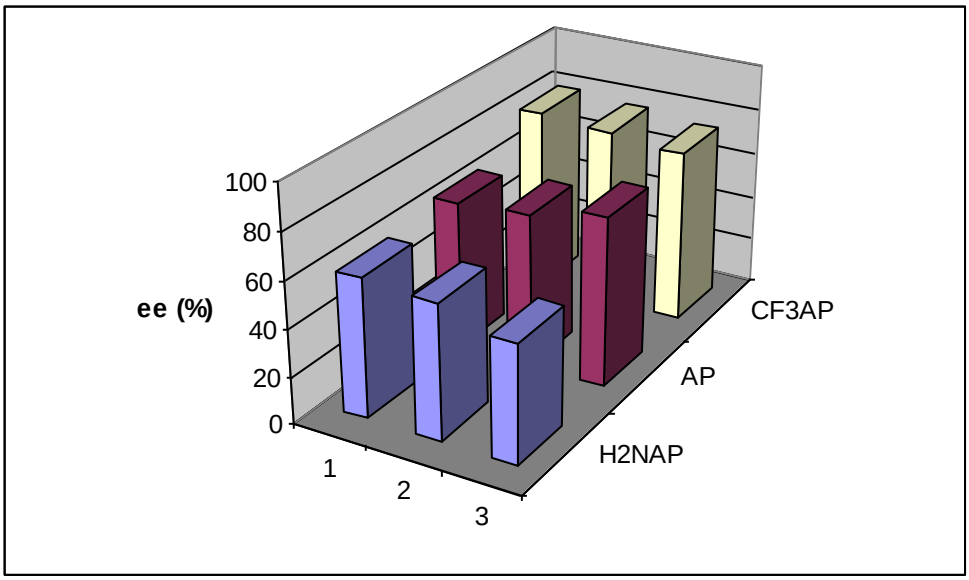


Figure 16. The effect of substituents on the enantioselectivity in the hydrogenation of acetophenone derivatives on different heterogenized Rh-complexes

Substrates	Catalysts
CF3AP**:** methyl-(4-trifluorophenyl)-ketone	1: [Rh(nbd)(*R*,*R*)-Ph_2bdpr)]/ HPA/Al_2O_3
AP: acetophenone	2: [Rh(nbd)(*S*,*S*)-Me_2bdpp]/ HPA/Al_2O_3
H2NAP: (4-aminophenyl)-methyl-ketone	3: [Rh(nbd)(*S*,*S*)-bdpp]/HPA/Al_2O_3

Comparing the different complexes a slightly increasing activity was observed in the following order of complexes: [Rh(nbd)(*S*,*S*)-bdpp] < [Rh(nbd)(*S*,*S*)-Me_2bdpp] < [Rh(nbd)-(Ph_2bdpr)]. This is similar to the activity order observed in the case of the C=C bond hydrogenation. Using the different starting materials the observed activity order is similar, only the extent are different.

Regarding the enantioselectivities, the comparison can be seen on Figure 15 and 16. The trend is not so significant as it was in the case of C=C hydrogenation. In that case we observed an increasing enantioselectivity with increasing activity in the order of phosphine basicity. As Figure 15 and 16 shows that in the case of C=O hydrogenation we are not able to establish a real tendency in the enantioselectivities.

The major advantage of the immobilization is the possibility to recycle the catalysts. We have applied all of our heterogenized catalysts in three subsequent runs and one example can be seen on Figure 17.

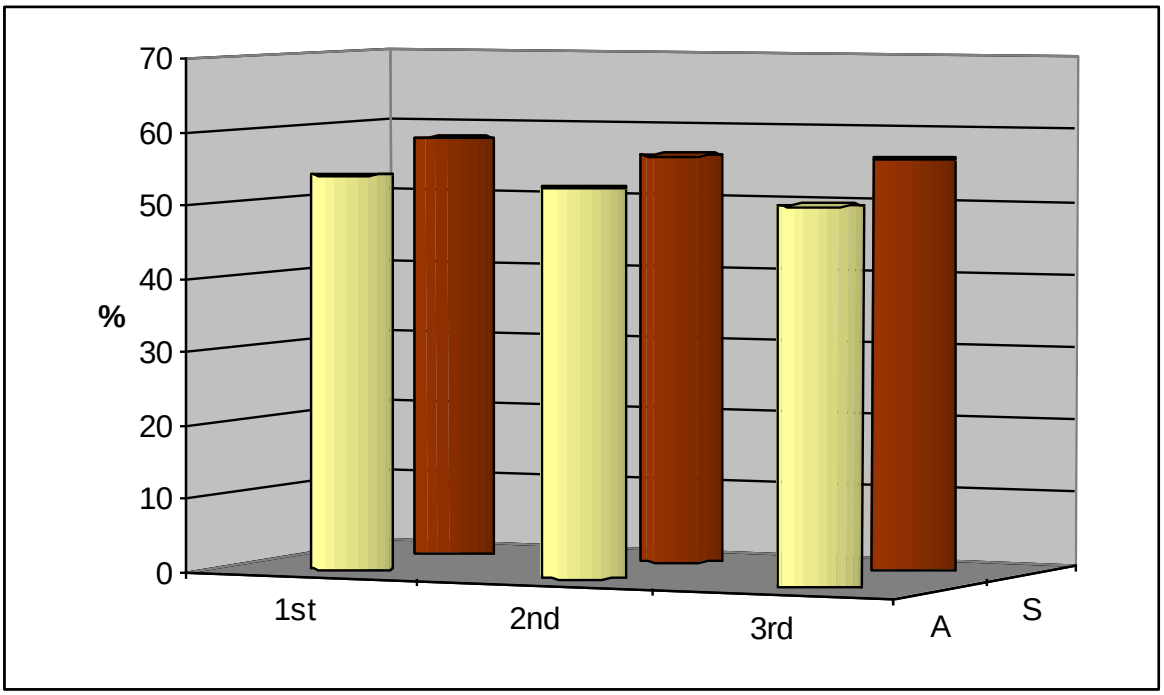


Figure 17. The activity and enantioselectivity in three subsequent runs in the hydrogenation of methyl-(4-trifluorophenyl)-ketone on the heterogenized [Rh(nbd)(*S*,*S*)-Me_2bdpp]/ HPA/Al_2O_3 catalyst.

A: activity

S: enantioselectivity

The activity and the enantioselectivity have not change significantly in three subsequent runs, as it can be seen on Figure 17. In other words our immobilized complexes behave like heterogeneous catalysts, meanwhile their activities and enantioselectivities are very close to the homogeneous analogs.

Checking the possible leaching of our heterogenized samples, we applied the so called Sheldon test [101]. Stopping the reaction the catalysts were removed from the reaction mixture and the former reaction conditions was settled for the remaining reaction mixture. A sample was taken after 6 hours and was analyzed by GC. No further transformation was observed without catalyst, which means that the Sheldon test confirmed the absence of the leaching which was concluded formerly from the unchanged activity of the recycling experiments.

IV.4. New application of an anchored Ru(II)-*N*-heterocyclic carbene complex

In the past few years the catalytic application of transition metal complexes containing *N*-heterocyclic carbene (NHC) ligands has received increased attention [94, 102-105]. Important examples include – among others – the hydrogenation and hydrogen transfer reactions [106-111]. Organometallic catalysis in water is a mature field of catalysis and serves as the basis of industrial processes [112-114]. Despite their extremely strong basicity, *N*-heterocyclic carbenes are able to form complexes stable to water [115,116]. Although the possibility of using water soluble transition metal – NHC complexes has been recognized, this was not followed by the systematic investigation of the catalytic properties of these complexes.

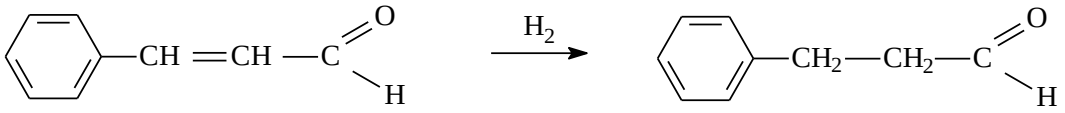
A new water soluble Ru(II)-NHC complex was readily available by the reaction of the [{$RuCl_2$(*p*-cymene)}$_2$] and [AgL_2] [$AgCl_2$], obtained in the reaction of 1-butyl-3-methylimidazolium chloride and Ag_2O in CH_2Cl_2 [94]. The complex is soluble in CH_2Cl_2 and was isolated upon precipitation with diethyl ether as a pale orange powder.

This complex dissolves well also in water, and during this process one or two chloride ligands were replaced by water.

$$[RuCl_2L(C_{10}H_{14})] \underset{}{\overset{H_2O}{\rightleftharpoons}} [RuCl(H_2O)L(C_{10}H_{14})]^{+} + [Ru(H_2O)L(C_{10}H_{14})]^{2+}$$

Aqueous solutions of the $[RuCl_2L(C_{10}H_{14})]$ complex react with hydrogen with a color change from orange to deep red, and the resulting solutions show considerable catalytic activity in the hydrogenation of various unsaturated substrates, like acetone and acetophenone. This is a remarkable observation considering that the C=O bonds of these compounds are usually difficult to hydrogenate

In the case of cinnamaldehyde, where both C=C and C=O bonds can be hydrogenated, the C=C double bond reacted preferentially.



Scheme 10. C=C bond hydrogenation of cinnamaldehyde

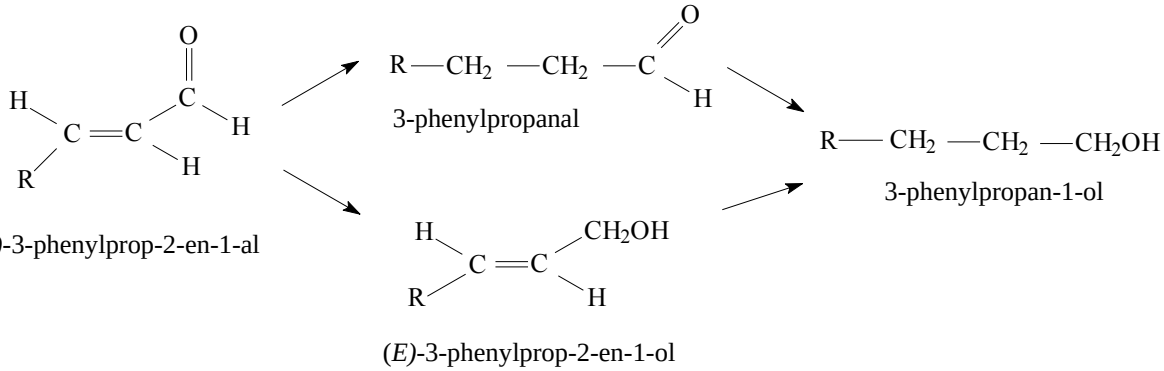
In the hydrogenation of allyl alcohol propan-1-ol and propanal were produced in an approximately 1 to 1 ratio. This was the first example of a redox isomerization catalyzed by a water-soluble transition-metal-NHC complex catalyst.

The readily available water soluble [$RuCl_2L(C_{10}H_{14})$] complex described above is stable toward decomposition or aggregation in aqueous systems in a wide pH range and up to relatively high temperatures (80 ^oC) and it is active and selective catalysts for the hydrogenation of different starting materials. With the final aim to have a good and selective heterogeneous catalyst we have prepared the heterogenized version of this new *N*-heterocyclic carbene complex, on Al_2O_3 support, using tungstophosphoric acid as anchoring agent.

The catalysts were applied in the hydrogenation of various substrates including aldehydes, ketones and unsaturated alcohols because our goal was the extension of the application of the heterogenized complexes.

The substrates were hydrogenated in two different solvents both in alcoholic and aqueous media, checking the applicability of the heterogenized complex in water, with special regard to the use of heteropoly acid as anchoring agent. To our knowledge this was the first example of applying a heterogenized *N*-heterocyclic carbene complex catalyst in aqueous medium.

Hydrogenations in alcohol. In aqueous solution on [$RuCl_2L(C_{10}H_{14})$] the C=C double bond of cinnamaldehyde reacted preferentially [94], producing 3-phenylpropanal.



Scheme 11. Products of the hydrogenation of (*E*)-3-phenylprop-2-en-1-al (*trans*-cinnamaldehyde) (R = Ph)

However, the unsaturated alcohol, the (*E*)-3-phenylprop-2-en-1-ol, producing by the hydrogenation of the C=O bond, is the most valuable product in this system. The selective hydrogenation of the C=O bond in the presence of the C=C bonds is, however, not a simple challenge.

Fortunately, we have prepared earlier the heterogenized [{$RuCl_2$(*m*tppms)$_2$}$_2$] complex and applied it in the hydrogenation of α,β-unsaturated aldehydes [96]. This catalyst was able to hydrogenate selectively the C=C or C=O double bonds depending on the basicity of the solvent. In alcoholic media the basicity was varied by adding different amounts of $(C_2H_5)_3N$. Under such conditions, [{$RuCl_2$(*m*tppms)$_2$}$_2$] catalyzed the hydrogenation of *trans*-cinnamaldehyde exclusively at its C=O bond both in homogeneous and in heterogenized forms.

Table 7. Hydrogenation of various substrates on soluble and heterogenized [$RuCl_2L(C_{10}H_{14})$] in ethanol (L=1-butyl-3-methylimidazol-2-ylidene).

Substrate	**Catalyst**	**Conversion** (%)	**TOF** (h^{-1})
propanal	[$RuCl_2L(C_{10}H_{14})$]	92.8	35.3
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	98.0	17.5
trans-cinnamaldehyde	[$RuCl_2L(C_{10}H_{14})$]	52.2*	19.8
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	28.0$^{\#}$	5.0
allyl alcohol	[$RuCl_2L(C_{10}H_{14})$]	100	38.0
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	25.4	4.5
acetophenone	[$RuCl_2L(C_{10}H_{14})$]	25.1	9.5
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	16.0	2.8
acetone	[$RuCl_2L(C_{10}H_{14})$]	24.2	9.2
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	16.9	3.0

Reaction condition: 10.42 μmol [$RuCl_2L(C_{10}H_{14})$] or 11.08 μmol Ru complex heterogenized catalyst, 42.7 μmol $(C_2H_5)_3N$, 396.0 μmol of substrate, 65 °C, 0.4 Mpa H_2, t = 1 h for homogeneous, 2 h for heterogenized catalyst, 3 mL ethanol.

Product distribution for *trans*-cinnamaldehyde (mol%):

	*	#
3-phenylpropionaldehyde:	40.6	41.8
3-phenylprop-2-en-1-ol:	49.0	51.8

3-phenylpropanol: 10.3 6.4

In the present study, we applied the soluble and heterogenized *N*-heterocyclic carbene complexes in alcoholic medium in the presence of $(C_2H_5)_3N$, which is the suitable condition for the hydrogenation of the C=O bond. Allyl alcohol, propanal, *trans*-cinnamaldehyde, acetone and acetophenone were hydrogenated using this condition and the results are shown in Table 7.

As Table 7 clearly shows both the homogeneous and the heterogenized complexes were active in the hydrogenation of the substrates possessing C=C or/and C=O functions. Hydrogenation of the C=O bond occurred with relatively good conversions, even in the case of acetone and acetophenone. This is a remarkable observation considering that both substrates have no activated C=O bonds, usually difficult to hydrogenate.

During the hydrogenation of *trans*-cinnamaldehyde both the C=C and C=O bonds were hydrogenated almost to equal extent. A small amount of the completely hydrogenated product, 3-phenylpropan-1-ol, was also formed.

Table 8. Hydrogenation of various substrates on soluble and heterogenized $[RuCl_2L(C_{10}H_{14})]$ in ethanol in the presence of PPh_3 (L=1-butyl-3-methylimidazol-2-ylidene)

Substrate	**Catalyst**	**Conversion** (%)	**TOF** (h^{-1})
propanal	$[RuCl_2L(C_{10}H_{14})]$	99.8	28.2
	$[RuCl_2L(C_{10}H_{14})]/Al_2O_3$	97.8	17.5
trans-cinnamaldehyde	$[RuCl_2L(C_{10}H_{14})]$	90.3*	25.5
	$[RuCl_2L(C_{10}H_{14})]/Al_2O_3$	58.4#	10.4
allyl alcohol	$[RuCl_2L(C_{10}H_{14})]$	98.2	27.7
	$[RuCl_2L(C_{10}H_{14})]/Al_2O_3$	24.0	4.3

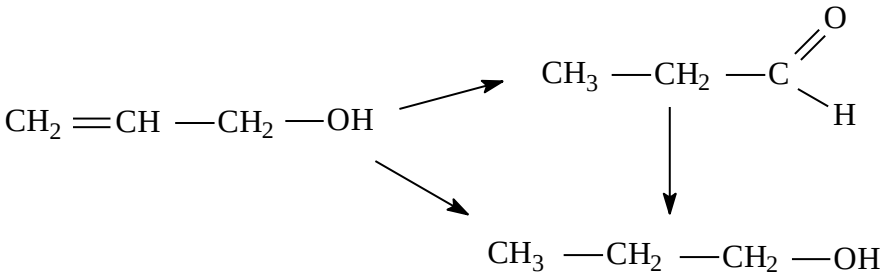
Reaction condition: 10.42 μmol $[RuCl_2L(C_{10}H_{14})]$or 11.08 μmol heterogenized Ru complex, 85.4 μmol Et_3N, 51 μmol PPh_3, 396 μmol of substrate, 65 °C, 0.4 Mpa H_2, t = 1 h for homogeneous, 2 h for heterogenized complex, 3 mL EtOH

Product distribution for *trans*-cinnamaldehyde (mol%):

	*	#
3-phenylpropanal:	2.4	7.5
3-phenylprop-2-en-1-ol:	87.9	90.5
3-phenylpropan-1-ol:	9.7	1.9

We have also studied the hydrogenation of the same substrates with the [$RuCl_2L$-($C_{10}H_{14}$)] catalyst in the presence of triphenylphosphine. Interestingly, under such conditions neither acetone nor acetophenone could be hydrogenated, although both substrates reacted with reasonable conversions in the absence of PPh_3. Conversely, propanal, *trans*-cinnamaldehyde and allyl alcohol were hydrogenated with good conversions (Table 8).

In the case of *trans*-cinnamaldehyde, selective C=O hydrogenation occurred, but some C=C hydrogenation was also detected (52.9 % and 4.4 %). This circumstances seems to be good for the selective hydrogenation of C=O bond but a more detailed study is required to find the best reaction conditions and for the clarification of the role of PPh_3 in these hydrogenations. It seems likely that PPh_3 replaces one of the Cl^- ligands in [$RuCl_2L(C_{10}H_{14})$], resulting in the formation of a new catalytic species.



Scheme 12. Hydrogenation and isomerization of allyl alcohol

In the case of allyl alcohol a fast C=C hydrogenation occurred, and propan-1-ol was produced. No isomerization to propanal was observed, in contrast to the same reaction performed in homogeneous aqueous solution [96], which was the first example of a redox isomerization catalyzed by a water-soluble transition metal – NHC complex catalyst.

With all substrates, except propanal, the specific activities of the heterogenized complexes were lower than those of the homogeneous ones. This is an interesting observation, especially in the light of our former experiences with heterogenized catalysts in other systems [23] when substantially higher specific activities were determined for the heterogenized catalysts then for their homogeneous counterparts. The possible explanation for this phenomenon may concern the availability of the metal complex catalysts on the surface of the support. It is likely that the *N*-heterocyclic carbene complex, [$RuCl_2L(C_{10}H_{14})$], is strongly bound to the

alumina surface by the basic nitrogenes of the NHC ligand. This strong bond could result in a worse availability and smaller activity of the complex.

Table 9. Hydrogenation of various substrates on soluble and heterogenized [$RuCl_2L(C_{10}H_{14})$] in water (L=1-butyl-3-methylimidazol-2-ylidene)

substrate	**catalyst**	**Conversion** (%)	**TOF** (h^{-1})
propanal	[$RuCl_2L(C_{10}H_{14})$]	100	74.3
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	73.5	26.0
trans-cinnamaldehyde	[$RuCl_2L(C_{10}H_{14})$]	97.7 *	72.6
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	70.7 #	25.0
allyl alcohol	[$RuCl_2L(C_{10}H_{14})$]	100	74.3
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	35.0	12.4
acetophenone	[$RuCl_2L(C_{10}H_{14})$]	50.8	37.8
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	41.7	14.7
acetone	[$RuCl_2L(C_{10}H_{14})$]	83.9	62.3
	[$RuCl_2L(C_{10}H_{14})$]/Al_2O_3	22.3	7.9

Reaction condition: 14 μmol $RuCl_2L(C_{10}H_{14})$ or 14.7 μmol heterogenized Ru complex, 3 mL of phosphate buffer (0.1 M, pH = 6.90), 1040 μmol of substrate, 80 °C, 0.4 MPa H_2, t = 1 h for homogeneous, 2 h for heterogenized complex.

Product distribution for *trans*-cinnamaldehyde (mol%):

	*	#
3-phenylpropanal:	91.2	56.8
3-phenylprop-2-en-1-ol:	3.21	30.3
3-phenylpropan-1-ol:	3.21	30.3

Hydrogenation in water. Water is an environmentally friendly solvent used more and more frequently in biphasic catalysis [112, 113]. Based on the results obtained in ethanol as solvent it seemed interesting to extend our studies into the use of aqueous media. To this end, the same substrates as before were hydrogenated in aqueous phosphate buffer (0.1 M, pH = 6.90). The results are shown in Table 9.

To our knowledge, this is the first systematic examination of the performance of the same *N*-heterocyclic carbene complex catalyst, soluble and heterogenized, in the same reactions both in aqueous and organic solvents.

As Table 9 clearly shows, both the homogeneous and the heterogenized complexes were active in hydrogenation of C=C and C=O double bonds in aqueous media.

For both the soluble and the heterogenized catalysts the specific activities were found considerably higher in aqueous systems than in ethanol as solvent. Another remarkable observation is that the heterogenized complex produced similar conversions both in aqueous and in ethanolic solutions, that is no substantial drop was observed in the activity. However, the specific activity of the heterogenized complex was about the half of those obtained in homogeneous systems. Nevertheless, it can be concluded, that the heterogenized catalysts, prepared by the method of Augustine, are suitable for use in aqueous reaction media, too.

Catalyst recycling. One of the major advantages of using heterogenized complexes is the possibility to recycle the catalyst. We have studied the recovery and reuse of the heterogenized Ru-NHC complex in the hydrogenation of several substrates, in three subsequent runs; the results can be seen on Figure 19.

It is clearly seen on Figure 19 that the heterogenized Ru-NHC complex catalyzed the hydrogenations in three subsequent runs in alcohol without any significant change in activity. In other words our heterogenized complex is recyclable retaining its original catalytic properties. Similar recycling experiments were done also in water, and the results can be seen on Figure 19. Similar to the case of the ethanolic systems, the results shown on Figure 18., allow the conclusion, that the heterogenized Ru-NHC complexes retain their catalytic activity in several cycles in aqueous solvents, too.

As a summary **a** new heterogenized Ru(II)-*N*-heterocyclic carbene complex catalyst was synthesized, characterized by spectroscopic methods and applied in the hydrogenation of various C=C and C=O unsaturated substrates. The anchored catalyst hydrogenated both the C=C and the C=O double bonds with reasonable activity – similar to the homogeneous catalyst – both in alcoholic and in aqueous media. Additionally, the prepared catalyst showed the advantages of the heterogeneous system, i.e. easy separation and efficient recycling.

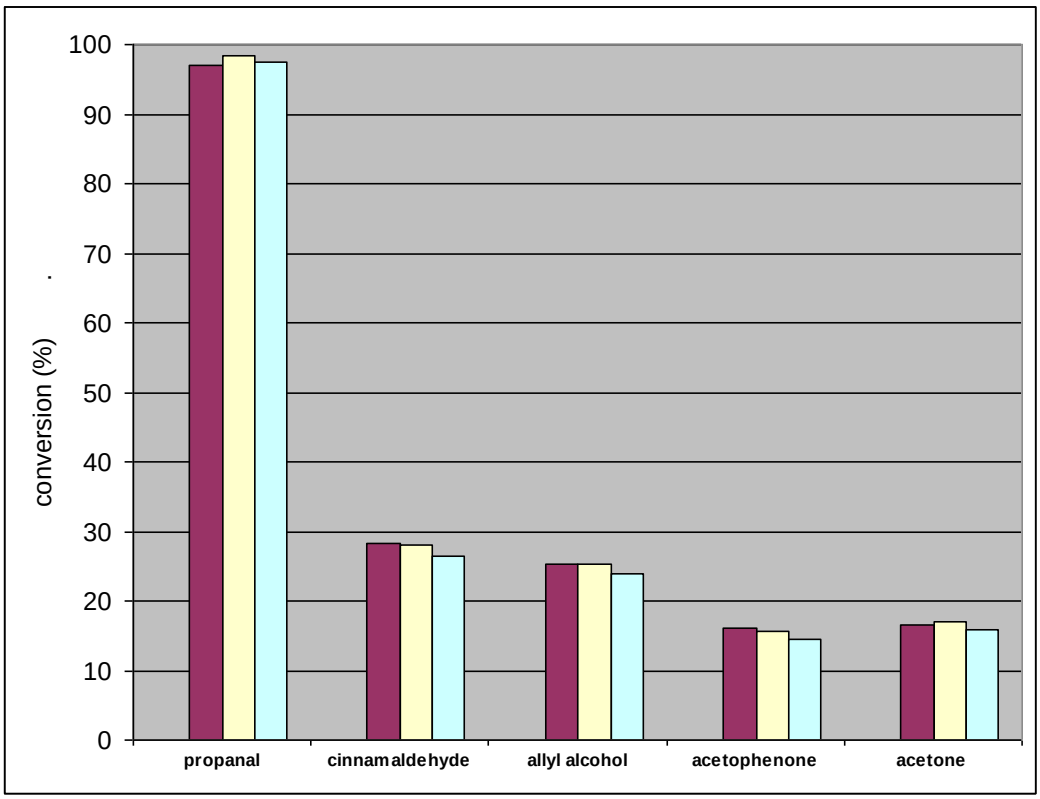


Figure 18. The activity of the heterogenized catalyst in the hydrogenation of various substrates in three subsequent runs in ethanol

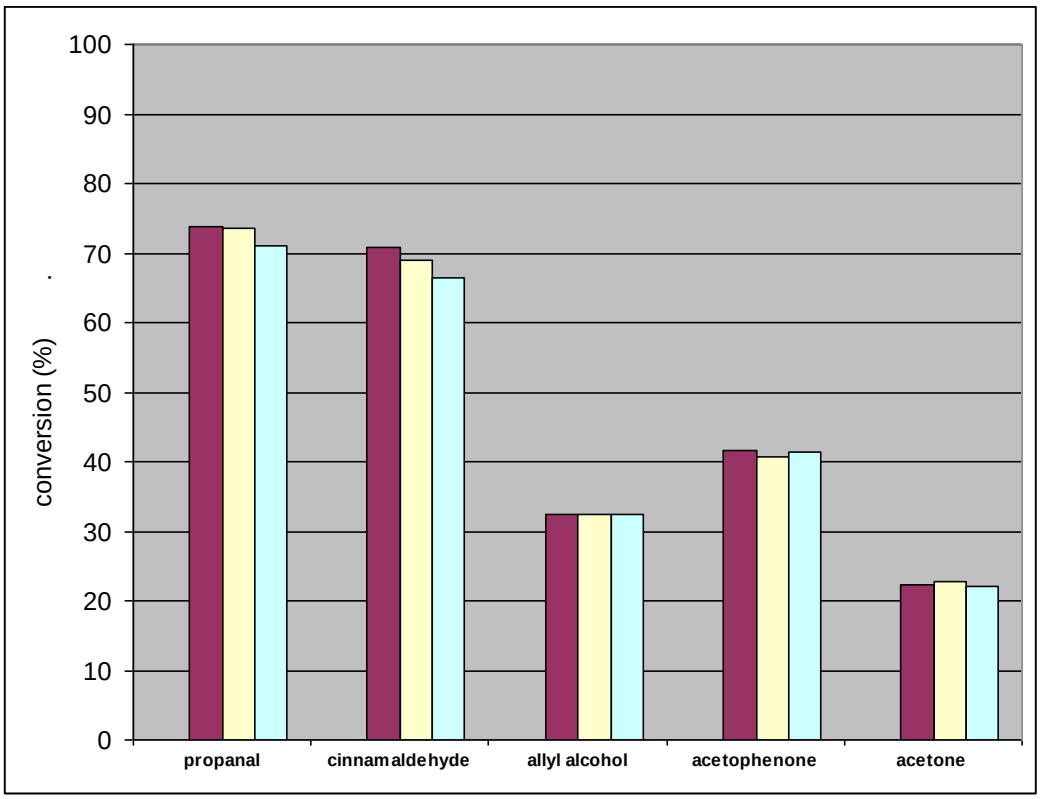


Figure 19. The activity of the heterogenized catalyst in the hydrogenation of various substrates in three subsequent runs in water

V. SUMMARY

1. Preformed crystalline [Rh(*S*,*S*)-bdpp]PF_6 type complexes were immobilized on Al_2O_3 support, via an anchoring method using heteropoly acid as anchoring agent developed by Augustine. Spectroscopic data showed that the homogeneous and the heterogenized complexes have similar structures and, consequently similar catalytic properties.

2. The original method was modified using *in situ* prepared complexes instead of the preformed ones. According to the spectrospcopic data and the catalytic measurements both methods produced the same heterogenized catalysts, but the *in situ* method is much faster and cheaper. The immobilized catalysts produced via the *in situ* method can also be reused in several subsequent experiments without any significant loss of catalytic properties.

3. The *in situ* prepared heterogenized catalysts were successfully applied in the hydrogenation of (Z)-2-acetamidocinnamic acid. The specific activity of the immobilized samples were higher than the activity of the homogeneous analogs, in a good correlation with our former findings.

4. The differently substituted immobilized [Rh(*S*,*S*)-bdpp] complexes showed electronic tuning similar to the homogeneous complexes, namely the activity increased with increasing ligand basicity. The same was true for the enantioselectivity, too, but the extent of the effect was much lower.

5. The enantioselective hydrogenation of (Z)-acetamidocinnamic acid and (*Z*)-methyl-(2-acetamidocinnamate) were hydrogenate on the differently substituted [Rh(*S*,*S*)-bdpp] complexes. The hydrogenation rate of the ester was lower than that of the acid, but otherwise both hydrogenations were similar.

6. The *in situ* prepared anchored Rh complexes were also used for the enantioselective hydrogenation of the C=O bonds of acetophenone derivatives. Using the conditions developed for the homogeneous complexes to hydrogenate the C=O bond, the anchored catalysts were also able to hydrogenate the C=O bonds with reasonable activity and enantioselectivity.

7. The heterogenized complexes were slightly less reactive than the homogeneous ones. This observation is in contrast to our earlier results, since so far we usually had higher activity on the heterogenized samples.

8. Considering the differently substituted acetophenone derivatives the heterogenized catalysts show the similar substituent effect as the homogeneous complexes but this effect was not so explicit than in the case of soluble complexes.

9. The leaching of the anchored complex was also checked by applying the Sheldon test, which confirmed the absence of the leaching.

10. New water soluble Ru(NHC) complex was prepared and immobilized by the *in situ* anchoring method. The selective hydrogenation of different starting materials were studied on these catalysts in organic solvents and in aqueous solution, as well.

11. The specific activities of the heterogenized complexes were usually lower than those of the homogeneous ones. It was possible to filter out the anchored catalysts from the reaction mixture and to recycle in several subsequent runs without any significant loss of catalytic properties.

12. During the hydrogenation of *trans*-cinnamaldehyde the chemoselectivity was shifted from the preferential C=C hydrogenation to the hydrogenation of both groups and the C=C and C=O bonds were hydrogenated almost to equal extent.

13. In the presence of triphenylphosphine neither acetone nor acetophenone could be hydrogenated, meanwhile propanal, *trans*-cinnamaldehyde and allyl alcohol were hydrogenated with good conversions. Using triphenylphosphine in the case of *trans*-cinnamaldehyde, selective C=O hydrogenation occurred. It seems likely that PPh_3 replaces one of the Cl^- ligands in $[RuCl_2L(C_{10}H_{14})]$, resulting in the formation of a new catalytic species.

14. In the case of allyl alcohol a fast C=C hydrogenation occurred, and propan-1-ol was produced, while no redox isomerization to propanal was observed.

15. One of our goal was to check the applicability of the anchored complexes in water, with special regard to the use of heteropoly acid as anchoring agent. To our knowledge this was the first example of applying a heterogenized *N*-heterocyclic carbene complex catalyst in aqueous medium.

16. It can be concluded, that the heterogenized catalysts, prepared by the method of Augustine, are suitable for the use in aqueous reaction media, too. Furthermore specific activities were found considerably higher in aqueous systems than in ethanol as solvent.

VI. Összefoglalás

1. A kristályos [Rh(*S*,*S*)-bdpp]PF_6 típusú komplexeket alumínium-oxid hordozóhoz kötöttük heteropolisavak segítségével az Augustine-féle eljárás segítségével. A felvett spektrumok azt mutatták, hogy a heterogenizált komplexek a homogén komplexekhez hasonló szerkezetűek voltak, és katalitikus szempontból is hasonlóan viselkedtek.

2. Az eredeti módszer módosítottuk, és a kikristályosított komplexek helyett magában az elegyben állítottuk elő a heterogenizálandó komplexeket. Mind a spektrumok, mind pedig a katalitikus vizsgálatok azt mutatták, hogy a két módszer hasonló tulajdonságú heterogenizált katalizátorokat eredményezett, ugyanakkor az *in situ* módszer sokkal gyorsabb és olcsóbb volt. Az *in situ* módon előállított katalizátorokat is alkalmaztuk egymás után következő mérésekben a katalitikus tulajdonságok észrevehető változása nélkül.

3. Az *in situ* módszerrel heterogenizált komplexekkel sikeresen hidrogéneztük a (Z)-2-acetamidofahéjsavat. A heterogenizált komplexek fajlagos katalitikus aktivitása nagyobb volt, mint a homogén komplexeké, ami jól egyezik a korábbi tapasztalatainkkal.

4. A különbözőképpen szubsztituált homogén [Rh(*S*,*S*)-bdpp] komplexek katalitikus aktivitása nőt a ligandumok bázikusságának függvényében és ugyanez volt megfigyelhető a heterogenizált komplexek esetében is. Hasonló effektus volt megfigyelhető az enantioszelektivitás esetében is, de itt a hatás jóval kisebb volt.

5. A (*Z*)-metil-(2-acetamidocinnamát) hidrogénezési sebessége kisebb volt, mint a savé, más vonatkozásban azonban az észter a savhoz hasonlóan viselkedett.

6. Az *in situ* módszerrel heterogenizált Rh-komplexeket alkalmaztuk az acetofenon-származékok C=O kötésének enantioszelektív hidrogénezésére is Azokat a körülményeket alkalmazva, amelyek között a homogén komplexek alkalmasak voltak a C=O kötés hidrogénezésére, a heterogenizált komplexek is megfelelő aktivitást és enantioszelektivitást mutattak.

7. A fenti reakcióban a heterogenizált komplexek valamivel kisebb katalitikus aktivitást mutattak, mint a homogének, ami ellentétes azon korábbi megfigyeléseinkkel, hogy a heterogenizált komplexek általában nagyobb katalitikus aktivitást mutatnak.

8. A szubsztituált acetofenon származékok esetében a heterogenizált komplexek hasonló szubsztituenshatást mutattak, mint a homogén komplexek, de ez a hatás az oldható komplexek esetében kifejezettebb volt.

9. A heterogenizált komplexek leoldódása a Sheldon-teszttel is vizsgáltuk, és azt találtuk, hogy a leoldódás nem megy végbe.

10. Egy új heterogenizált Ru(NHC)-komplexet állítottunk elő az *in situ* heterogenizálási módszerrel. A heterogenizált komplex megfelelő aktivitással hidrogénezte a C=C és a C=O kötéseket, etanolban és vízben is.

11. A fenti katalizátorok fajlagos katalitikus aktivitása kisebb volt, mint a homogén komplexeké. A heterogenizált katalizátort kiszűrés után ismételten fel tudtuk használni több kísérletben is az aktivitás jelentősebb csökkenése nélkül.

12. A *trans*z-fahéjsav hidrogénezésénél a szelektív C=C hidrogénezéstől a C=C és a C=O közel azonos átalakulásáig tolódik el a szelektivitás.

13. Trifenilfoszfin jelenlétében sem az aceton, sem az acetofenon sem hidrogéneződik. Ezzel szemben a propanal, a *transz*-fahéjaldehid és az allil-alkohol jó termeléssel hidrogéneződött. Trifenilfoszfin jelenlétében a *transz*-fahéjaldehid esetében szelektív C=O hidrogénezés történt. Valószínű, hogy a PPh_3 helyettesíti a Cl^- ligandumot a $[RuCl_2L(C_{10}H_{14})]$ komplexben, és ezzel egy új katalitikusan aktív forma jöhet létre.

14. Az allil-alkohol esetében a C=C kötés hidrogéneződésével propán-1-ol képződött, és végbement az izomerizáció is propanallá.

15. Egyik célunk az volt, hogy megvizsgáljuk heterogenizált katalizátoraink alkalmazhatóságát vizes közegben, különös tekintettel arra, hogy heteropolisavakat használtunk a komplexek rögzítésére. Tudomásunk szerint első ízben alkalmaztunk heterogenizált *N*-heterociklusos karbén-komplexet vizes közegben.

16. Azt találtuk, hogy az Augustine-féle módszerrel előállított heterogenizált katalizátorok használhatók vizes közegben is, sőt a fajlagos aktivitás jóval nagyobb volt vízben, mint etanolban.

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