



Mechanistic investigation of water soluble Rh(I)- and Ru(II)-phosphine catalysts

PhD thesis

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1. Introduction and objectives

Hydrogenation reactions proceeding in aqueous solutions catalyzed by organometallic complexes present an area of homogenous catalysis of great importance. Aqueous phase catalysis does not only provide special reaction conditions concerning the distinct properties of water as contrasted with non-polar organic solvents, but offers the possibility for avoiding the problem of catalyst separation by the application of two-phase (aqueous-organic) systems. In addition, water is often cited as an ideal solvent, since it is cheap, readily available, non-toxic and totally compatible with the environment.

Hydrogenation reactions catalyzed by water soluble phosphine complexes of rhodium and ruthenium have been examined thoroughly in our research group for the last few decades. The main goal of my work was to explore unknown parts of the mechanistic behaviour of these catalysts. This was carried by investigating two reactions and for this purpose modern experimental techniques (high pressure NMR-spectroscopy) and quantum chemical methods were applied.

Many complexes of platinum group metals prepared with water soluble phosphines are known. A well-described and thoroughly investigated group of these ligands are the sulfonated aromatic phosphines, which are very stable, can be synthesized easily and are soluble in water in a wide pH-range. Mainly the complexes of *mtpmps* = sodium salt of meta-sulfonatophenyl-diphenyl-phosphine and *mtppts* = *tris*-(meta-sulfonatophenyl)-phosphine ligands have been investigated. In addition, the behaviour of complexes prepared with aliphatic phosphines has been also examined in our research group. An interesting representative is *pta* = 1,3,5-triaza-7-phosphaadamantane (the structures are shown in Figure 1).

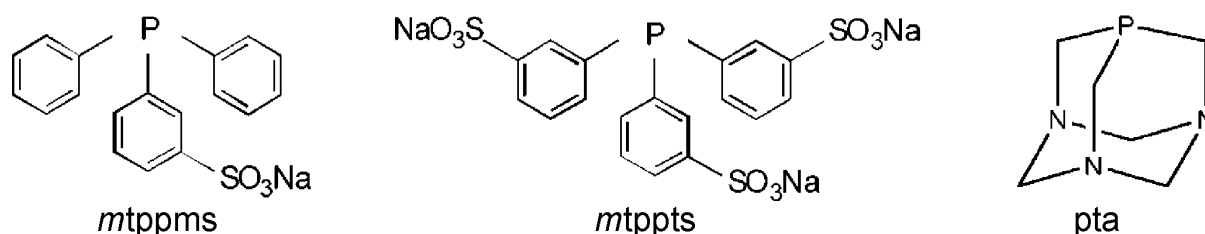


Figure 1 The applied phosphine ligands.

In several cases it was observed that during catalytic hydrogenation reactions carried out with the rhodium and ruthenium complexes of the above phosphines, different quantities

of deuterium and hydrogen were incorporated into the product. The ratio of the different isotopomers was determined by the catalyst, substrate, the applied gas/solvent pair (e.g. H₂O/D₂ or D₂O/H₂) and the pH of the reaction mixture. One main goal of my PhD work was to investigate how different complexes catalyze the H/D direct isotope exchange between the gas phase and the solvent (Eqs. 1-2) and to explore the possible mechanism of this process. For this purpose, NMR-spectroscopy and theoretical methods were applied.



Homogeneous catalytic hydrogenation of carbon dioxide belongs to the most thoroughly investigated reactions aiming at utilizing CO₂ as a C1 building block for organic syntheses. Moreover, the excessive emission of CO₂ is the main reason for the dangerously increasing greenhouse-effect, thus utilization of CO₂ is a question of importance concerning environmental protection.

The hydrogenation of CO₂ in aqueous solutions has been investigated thoroughly for the last few years in our research group. The experiments, which were mostly carried out with [$\{\text{RuCl}_2(\text{mtppps})_2\}_2$] showed that the reactions were very slow when unbuffered solutions of CO₂ were to react. Nevertheless, high catalytic activity was found in slightly basic solutions (at pH = 8), which suggests that HCO₃⁻, present as the major species at this pH, is likely a more reactive form than CO₂ in aqueous reaction media. The hydrogenation of bicarbonate results in the formation of formate (Eq. 3).



Since spectroscopic and kinetic results did not provide further information about the reaction intermediates, theoretical mechanistic calculations were thought to be important to reveal the mechanistic steps of HCO₃⁻ reduction in aqueous solutions (Eq. 4).

2. Applied experimental and theoretical methods

NMR-spectroscopy was applied for the experimental investigation of the H/D isotope exchange. In a typical experiment the solution of the catalyst was charged into a high pressure sapphire NMR tube (Figure 2) and was pressurized with hydrogen up to 20 bar. The tube was shaken in a thermostated chamber at 300 rpm, and the reaction was followed by *in situ* ^1H and ^2H -NMR measurements.

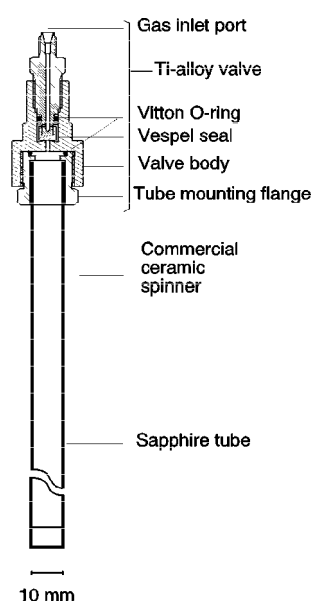


Figure 2 High pressure sapphire NMR-tube

Density functional theory has been applied for the calculations. In most cases the aromatic phosphine ligands were simplified by PMe_3 model ligands.

Most of the calculations have been performed at the B3LYP/SDDP level of density functional theory using the Gaussian 98 and Gaussian03 programs, where B3LYP is the applied hybrid functional and SDDP refers to a basis set including the Stuttgart-Dresden relativistic small core ECP basis set for rhodium and the Dunning/Huzinaga DZ + polarization all electron basis set for the lighter atoms. In one case calculations were carried out with the ADF 2004.01 program package by applying the BLYP density functional along with the ZORA triple- ξ polarization Slater-type orbital basis set.

Solvent molecules were modelled by small water clusters, and the effect of the bulk aqueous medium was estimated by the application of the polarizable continuum model (PCM) as implemented in Gaussian.

3. New scientific results

I: It was shown that all the investigated complexes were active in the catalysis of the H/D exchange process.

It was shown by high pressure NMR-spectroscopic measurements that all the investigated complexes catalyze the H/D isotope exchange between H₂ and D₂O (Table 1), whereas one catalyst [RhCl(*mtpms*)₃] was shown to behave the same way in the D₂/H₂O system.

Catalyst	pH	T (°C)	TOF _{max} (h ⁻¹)
[RuCl ₂ (<i>pta</i>) ₄]	5.5	25	8.5
[RuCl ₂ (<i>pta</i>) ₄]	5.5	70	338
[RhCl(<i>pta</i>) ₃]	5.2	70	908
[{RuCl ₂ (<i>mtpms</i>) ₂ } ₂]	2.5	25	1250
[RhCl(<i>mtpms</i>) ₃]	2.5	25	800
[RhCl(<i>mtppts</i>) ₃]	6.5	25	989

Table 1 Specific rate of H/D exchange catalyzed by water soluble Ru(II)- and Rh(I) phosphine complexes in D₂O-H₂ system

It was also found that the complexes containing sulfonated aromatic phosphines (*mtpms* and *mtppts*) had much higher activity in the isotope exchange, than complexes of the aliphatic *pta* ligand.

II. It was also shown that pH had a considerable effect on the reaction rate of the H/D exchange in the case of all the catalysts

With all the complexes the catalytic activity declined in alkaline solutions, thus the key role of hydroxonium ions in the reaction was supposed (Fig. 3). Drop in the activity in acidic solutions was found for *pta* complexes, which was explained by the possible protonation of this ligand.

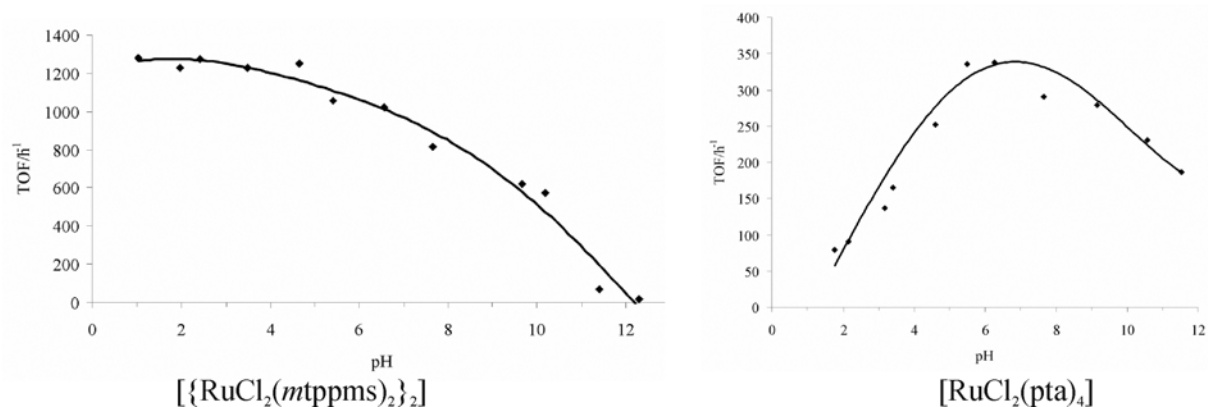


Figure 3 The rate of H/D exchange catalyzed by different Ru-phosphine complexes

III. On the basis of experimental results, a reaction mechanism was proposed

On the basis of the fact that the catalytic activity declined in basic solutions, in the case of all the catalysts, the proposed mechanism involves the protonation of the catalytically active hydride species (with D₃O⁺) and formation of a η²-HD-complex. Since this intermediate was not detected by spectroscopic methods, theoretical methods were applied to confirm the suggested mechanism.

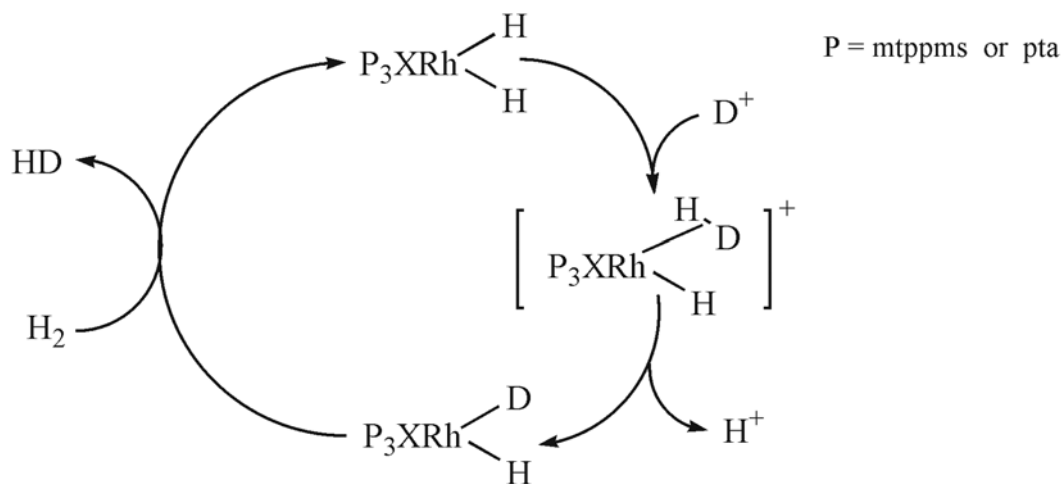


Figure 4 Suggested mechanism of the H/D exchange catalyzed by [RhXP₃] complexes

IV. Density functional theory was applied to provide a theoretical background for the proposed reaction mechanism of the H/D exchange catalyzed by water soluble rhodium(I)-hydrides

IV/1. It was shown by model calculations (PMe_3 model phosphine) that the η^2 -dihydrogen complex formed by the protonation of the hydride is a stable compound.

The protonation of the most stable isomer of $[\text{RhH}_2\text{Cl}(\text{PMe}_3)_3]$, which is *cis-mer*- $[\text{RhH}_2\text{Cl}(\text{PMe}_3)_3]$ (**1**) (Fig. 5), has been investigated. Calculations showed that the most favourable process was the protonation of the hydride ligand, which is in trans position to a phosphine. This process leads to the formation of the cationic $[\text{RhH}(\text{H}_2)\text{Cl}(\text{PMe}_3)_3]^+$ (**2**) complex (Fig. 5).

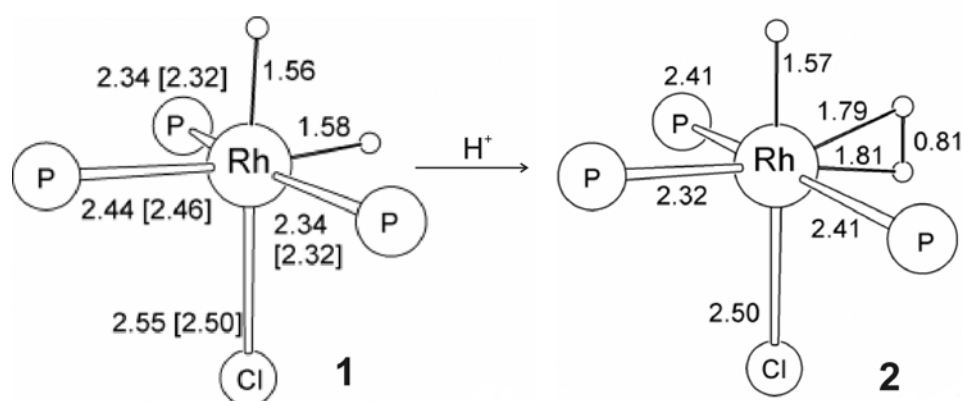


Figure 5 Optimized structures of *cis-mer*- $[\text{RhH}_2\text{Cl}(\text{PMe}_3)_3]$ (**1**) and $[\text{RhH}(\text{H}_2)\text{Cl}(\text{PMe}_3)_3]^+$ (**2**)

IV/2. The protonation process was modelled by the application of small water clusters ($[(\text{H}_3\text{O})(\text{H}_2\text{O})_n]^+$, where $n=2$ or 4)

The protonation process in acidic aqueous medium was modelled by the application of $[(\text{H}_3\text{O})(\text{H}_2\text{O})_2]^+$, since H_3O^+ is too acidic to represent the real protonating agent. By using these models, it was shown, that both the protonation and deprotonation processes, that is, the RhH_2 (**3**) \rightarrow $\text{RhH}(\text{H}_2)^+$ (**4**) or the reverse reaction is thermodynamically feasible and can occur via small energy barriers (TS_{3-4}), which is consistent with the high catalytic activities shown under mild conditions (Fig. 6).

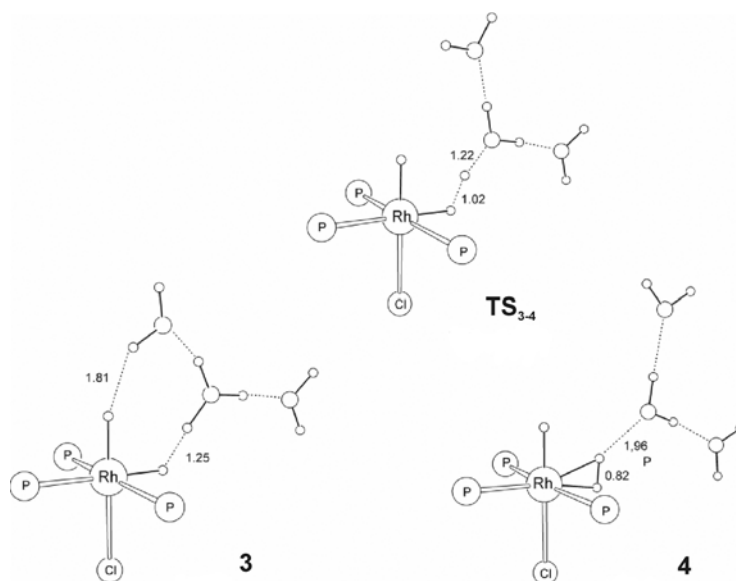


Figure 6 Structures representing the interaction between *cis-mer*-[RhH₂Cl(PMe₃)₃] and [(H₃O)(H₂O)₂]⁺

The calculations also showed that systematic extension of the model, that is the application of [(H₃O)(H₂O)₄]⁺ clusters did not significantly change the energetics of the protonation reaction.

IV/3. Two possible mechanisms emerging from the present work were proposed.

The first mechanism involves protonation of the dihydride by D₃O⁺ via a dihydrogen bonded complex resulting in the RhH(HD)⁺ intermediate. The η²-HD ligand may then undergo fast internal rearrangement so as the H atom of Rh-H becomes the leaving proton and it is transferred back to the D⁺ donating D₂O molecule (Fig. 7). An alternative mechanism can be suggested from our results, in which the leaving proton of the intermediate is not transferred back to the same water molecule (D₂O(a)) but it shifts to another adjacent water molecule (D₂O(b)) (Fig. 8).

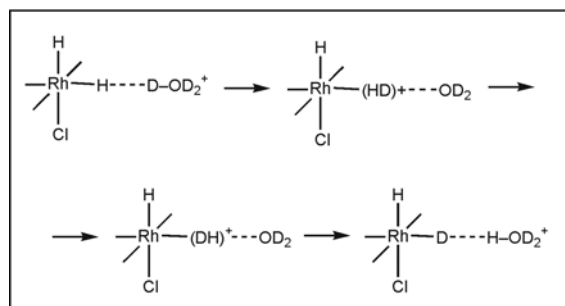


Figure 7 Mechanism of the H/D exchange I.

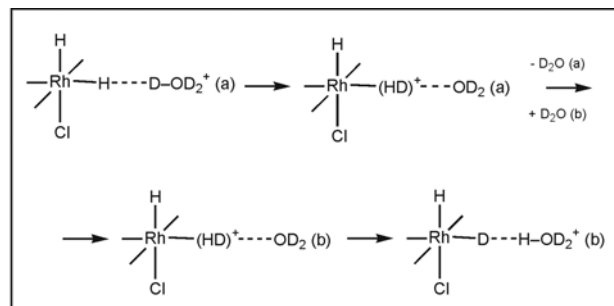


Figure 8 Mechanism of the H/D exchange II.

V. Density functional theory was applied to provide a mechanistic background for the aqueous phase reduction of HCO_3^- catalyzed by $[\{\text{RuCl}_2(\text{mtppps})_2\}_2]$

V/1. Calculations suggested that $\text{cis-}[\text{RuH}_2(\text{mtppps})_4]$, which is formed from $[\{\text{RuCl}_2(\text{mtppps})_2\}_2]$ under H_2 at the pH of bicarbonate solutions, was not likely to be the catalytically active species.

Calculations show that $\text{cis-}[\text{RuH}_2(\text{mtppps})_4]$ is not likely the active catalyst. This conclusion arises from the steric hindrance of hydride ligands, shown by calculations using $\text{cis-}[\text{RuH}_2(\text{PPh}_3)_4]$ model complex, and the very high energy barrier, which was found for the direct reaction of $\text{cis-}[\text{RuH}_2(\text{PMe}_3)_4]$ and HCO_3^- . Based on these results, the dissociation of a phosphine ligand was assumed, and $\text{cis-}[\text{RuH}_2(\text{PMe}_3)_3]$ was considered as the model for the catalytically active hydride species.

V/2. It was shown that coordination and subsequent protonation of HCO_3^- led to the formation of a CO_2 -complex and this CO_2 can be inserted into the Ru-H bond. The mechanism found for the catalyst regeneration from the formate-complex formed is different from those proposed in the case of CO_2 reduction in organic solvents.

The steps of the reaction mechanism are the following. Coordination of bicarbonate ion to the initial complex is followed by a proton assisted OH^- elimination step and formation of a complex involving a weakly bound CO_2 (Figure 9). The proton-transfer reaction (protonation of the coordinated bicarbonate) was described by the application of trimeric water clusters tested in the H/D exchange reaction.

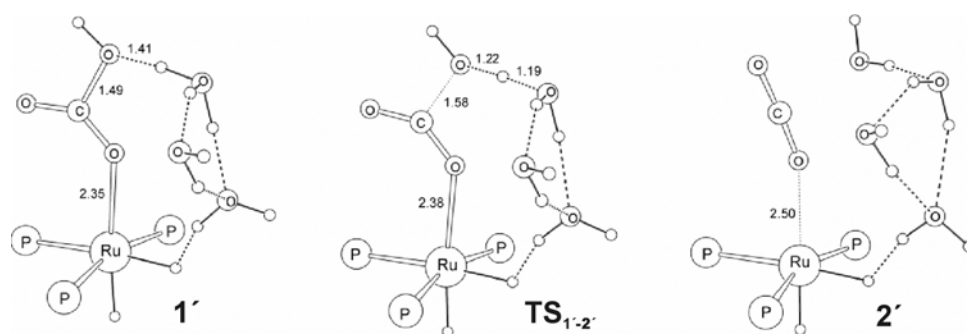


Figure 9 Structures representing the OH^- elimination from the coordinated HCO_3^-

The weakly bound CO₂ rearranges to $\eta^2_{\text{C,O}}$ coordination mode, then CO₂ is inserted into the Ru-H bond. The complex formed rearranges and [RuH(PMe₃)₃(HCO₂)] η^1 -formate complex is formed, which has a vacant coordination site in *trans* position to the remaining hydride ligand. It was also shown that the regeneration of the catalyst can occur via steps, which are different from those proposed in the case of CO₂-reduction taking place in organic solvents. In organic solvents metathesis of a coordinated H₂ and formate leads to formic acid, which dissociates to regenerate the catalyst. The proposed reaction path in aqueous solution involves coordination of a water molecule and dissociation of formate, which leads to the formation of a RuH⁺ type monohydride species. The coordination of a H₂ to this complex, subsequent deprotonation by the surrounding water molecules and dissociation of the coordinated water leads to the regeneration of the active RuH₂P₃ species.

V/3. All steps of the reaction mechanism have been described and the energy profile for the reaction has been determined.

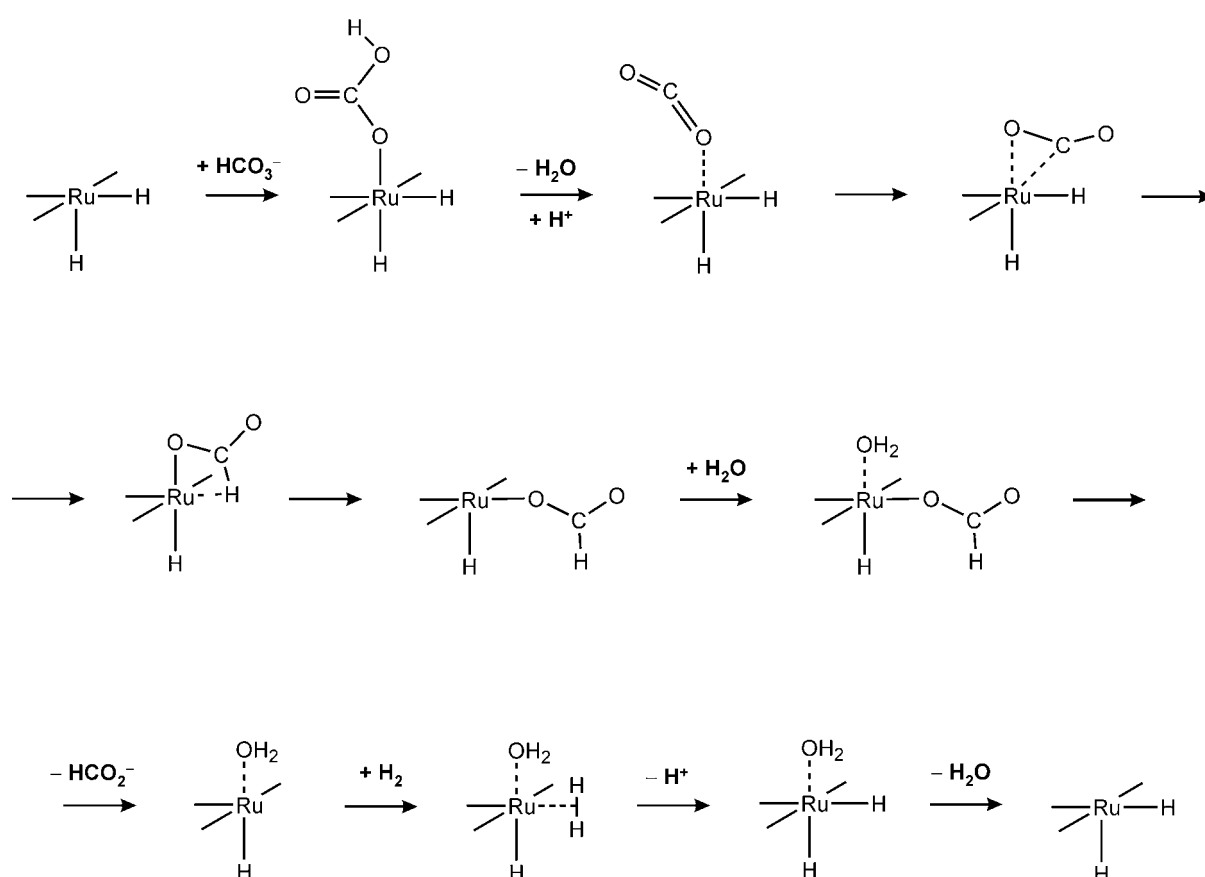


Figure 10 Scheme of the aqueous phase reduction of HCO₃⁻

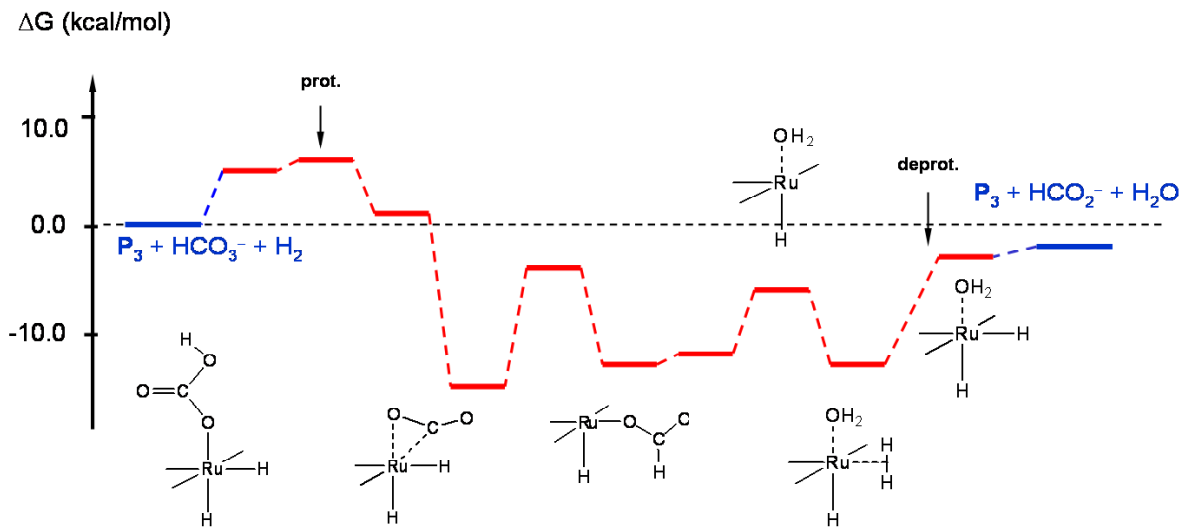


Figure 11 Energy profile of the aqueous phase reduction of HCO_3^-

4. List of Publications

Papers related to the dissertation

1. **Kovács, G.**; Nádasdi, L.; Joó, F.; Laurenczy, G.: H/D exchange between H₂-D₂O and D₂-H₂O catalyzed by water soluble tertiary phosphine complexes of ruthenium(II) and rhodium (I), *Compt. Rend. French. Acad. Sci., Series IIC Chemistry* **2000**, *3*, 601.
2. **Kovács, G.**; Nádasdi, L.; Laurenczy, G.; Joó, F.: Aqueous organometallic catalysis. Isotope exchange reactions in H₂-D₂O and D₂-H₂O systems catalyzed by water-soluble Rh- and Ru-phosphine complexes, *Green Chemistry* **2003**, *5*, 213.
3. **Kovács, G.**; Schubert, G.; Joó, F.; Pápai, I.: Theoretical Mechanistic Study of Rhodium(I) Phosphine-Catalyzed H/D Exchange Processes in Aqueous Solutions, *Organometallics* **2005**, *24*, 3059.
4. **Kovács, G.**; Schubert, G.; Joó, F.; Pápai, I.: Theoretical investigation of catalytic HCO₃⁻ hydrogenation in aqueous solutions, *Catalysis Today*; közlésre elfogadva

Other papers

5. **Kovács, G.**; Pápai, I.: Hydride Donor Abilities of Cationic Transition Metal Hydrides from DFT-PCM Calculations, *Organometallics*; közlésre beküldve
6. **Kovács, G.**; Ujaque, G.; Lledós, A.; Joó, F.: Theoretical investigation of the selective of C=C vs. C=O hydrogenation in acidic media catalyzed by [$\{\text{RuCl}_2(\text{mtpms})_2\}_2$], *Organometallics*; közlésre beküldve
7. Rossin, A.; **Kovács, G.**; Ujaque, G.; Lledós, A.; Joó, F.: Regioselective C=O hydrogenation of trans-cinnamaldehyde to cinnamyl alcohol with the water-soluble complexes [RuH₂(mtpms)_x] (x=3,4; mtpms=(meta-sulphonatophenyl)diphenylphosphine). A theoretical study of the reaction mechanism and selectivity; előkészületben

Lectures and posters presented at conferences and meetings

Lectures

1. **Kovács, G.**; Joó, F.; Nádasdi, L.; G. Laurency, G.: Hydrogen/deuterium exchange between the gas and the aqueous solution phase catalyzed by water soluble phosphine complexes of rhodium and ruthenium, 4th Annual Meeting of the COST D10/0001 Working Group, 24-27 May, **2001**, Debrecen, Hungary
2. **Kovács, G.**; Nádasdi, L.; Joó, F.; Laurency, G.: A H/D csere katalízise ródium(I) és ruténium(II) vízoldható foszfin komplexeivel, IX. Nemzetközi Vegyészkonferencia, Kolozsvár, Románia, **2003**. november 14-16.
3. **Kovács, G.**: Mechanistic studies on catalytic hydrogenation in water, Working Group Meeting COST action D30-WG0001, 7-9 October, **2005**, Debrecen, Hungary

Posters

1. **Kovács, G.**; Nádasdi, L.; Joó, F.; Laurency, G.: H/D exchange in aqueous catalytic systems-an important side reaction of catalytic hydrogenation, "*Clean Processes and Environment: the Catalytic Solution*" 12th Jacques Cartier Meeting, Lyon, France, 6-8 December **1999**
2. Laurency, G.; **Kovács, G.**; Nádasdi, L.; Joó, F.: H/D exchange in aqueous catalytic systems - an important side reaction of catalytic hydrogenation, *COST mid Term Evaluation Meeting*, Brussels, Belgium, 4-5 December **1999**
3. **Kovács, G.**; Nádasdi, L.; Joó, F.; Laurency, G.: H/D isotope exchange in aqueous solutions catalyzed by water soluble phosphine-complexes, *Hungarian COST Chemistry Day*, Budapest, Hungary, 20 October **2000**
4. **Kovács, G.**; Nádasdi, L.; Joó, F.; Laurency, G.: H/D exchange between H₂-D₂O and D₂-H₂O in aqueous solution – catalytic effect of the soluble phosphine complexes of ruthenium (II) and rhodium (I), *Workshop of COST Action D10 Final Evaluation Meeting*, Kraków, Poland, 6-9 June **2002**
5. **Kovács, G.**; Schubert, G.; Pápai, I.; Joó, F.: Theoretical investigation of the H/D exchange in aqueous solutions catalyzed by rhodium(I) phosphine complexes, *14th International Symposium on Homogeneous Catalysis*, Munich, Germany, 5-9 July **2004**

6. **Kovács, G.**; Schubert, G.; Pápai, I.; Joó, F.: Theoretical investigation of the H/D exchange in aqueous solutions catalyzed by rhodium(I) phosphine complexes, *Euroconference on New Theoretical and Spectroscopical Approaches to Inorganic Problems*, San Feliu de Guixols, Spain, 4-9 September **2004**

7. **Kovács, G.**; Ujaque, G.; Rossin, A.; Lledós, A.; Joó, F.: Theoretical investigation of the selectivity in the hydrogenation of unsaturated aldehydes catalyzed by $\{[\text{RuCl}_2(\text{tppms})_2]_2\}$, *XVI. FECHM Conference on Organometallic Chemistry*, Budapest, Hungary, 3-8 September **2005**

8. **Kovács, G.**; Schubert, G.; Pápai, I.; Joó, F.: Theoretical Mechanistic Study of Rhodium(I) Phosphine Catalyzed H/D Exchange Processes in Aqueous Solutions, *Frontiers in Catalysis*, Visegrád, Hungary, 8-10 September **2005**