

The elementary reactions of platinum-alkyl complexes and their application in hydroformylations

PhD Thesis

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1. Introduction

Homogeneous catalytic reactions, those transforming unsaturated hydrocarbons with carbon monoxide and hydrogen toward aldehydes in the presence of transition metal complexes as catalysts, have been known for more than 70 years. In this way, the formal addition of formaldehyde to carbon-carbon double bond resulted in aldehydes. The hydroformylation is of high industrial importance, since it provides intermediates for plastic industry. The aldol-type condensation of n-butanal, formed in the hydroformylation of propene, and a consequent hydrogenation yields in C₈ alcohols (mainly 2-ethyl-hexanol, 'isooctylalcohol'). The latter compounds are the alcohol components of phthalic esters known as plasticisers. Cobalt-carbonyl complexes as catalytic precursors were used in the beginning, then rhodium-complexes gained more attention due to their high regioselectivity under mild reaction conditions.

The investigation of the catalytic features of platinum-phosphine-tin(II)chloride systems have gained more attention since the late seventies. Although their catalytic activity falls behind the activity of the rhodium-based ones, their application in asymmetric hydroformylations, especially with styrene and other vinaromatics as substrates, resulted in high optical yields.

The novel methodologies towards the synthesis of optically active compounds are in the forefront of modern chemistry not only because of their fundamental interest, but also of their high practical importance. The synthesis of enantiomerically pure chiral compounds is of special importance in medicine and pharmacology. The absolute configuration of a given compound is closely related to its biological activity. In order to control the asymmetric synthesis, the deep knowledge of the structure of catalysts, as well as that of the elementary steps of homogeneous catalytic reactions, are necessary.

The insertion reaction is one of the general elementary key-reactions of the homogeneous catalytic reactions [1]. On one hand, the insertion of small molecules (alkenes, isonitriles, carbon monoxide) into metal-carbon bond was already investigated. For example, the transition metal-acyl complexes, obtained by the insertion of carbon monoxide into metal-alkyl/aryl bonds, are intermediates of utmost importance in hydroformylation. Platinum-acyl complexes possessing chiral diphosphines are key intermediates in enantioselective hydroformylations [2,3].

On the other hand, insertion of carbene-type compounds into metal-carbon bond might also take place. A carbene $:CR^1R^2$ ($R^1=H$, $R^2=COOEt$), formed 'in situ' from ethyl diazoacetate, inserts into platinum-methyl or platinum-halide bond and a novel stereogenic centre is formed in the α -position of the alkyl chain. Diastereoselective insertion takes place in the presence of an optically active ligand situated in the coordination sphere of the transition metal [4-6].

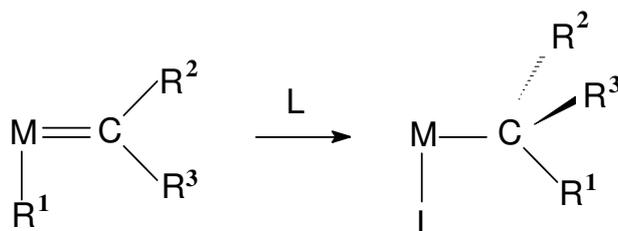


Figure 1. The formation of an asymmetric centre via the insertion of a carbene

Sporadic information is available on the possible influence of the chiral ligand on the formation of a stereogenic centre in the target molecule. It is supposed that the stereochemistry of the alkene insertion is influenced by the conformation of the platinum-chelate ring. However, even less are known on the effect of the platinum-chelate ring conformations with various diphosphines on the formation of stereogenic centre(s) [7].

The high importance of the insertion reactions described above encouraged us to carry out research in this field in order to shed some light into the fine mechanistic details. Obviously, the structural characterization of the starting complexes and products, as well as their investigations related reactivity were also planned.

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- [1] J.P. Collman, L.S. Hegedüs, J.R. Norton, R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mill Valley, California, 1987, pp. 621-630.
 [2] S. Gladiali, J.C. Bayón, C. Claver, *Tetrahedron Asymmetry* **6** (1996) 1453.
 [3] F. Agbossou, J-F. Carpentier, A. Mortreux, *Chem. Rev.* **95** (1995) 2485.
 [4] P. Bergamini, E. Costa, S. Sostero, A.G. Orpen, P.G. Pringle, *Organometallics*, **10** (1991) 2989.
 [5] P. Bergamini, E. Costa, S. Sostero, A.G. Orpen, P.G. Pringle, *Organometallics*, **11** (1992) 3880.
 [6] P. Bergamini, E. Costa, P. Cramer, J. Hogg, A.G. Orpen, P.G. Pringle, *Organometallics*, **13** (1994) 1059.
 [7] L. Kollár, J. Bakos, I. Tóth, B. Heil, *J. Organomet. Chem.* **370** (1989) 257.

2. Aims of the planned research

- Synthesis of basic platinum-alkyl, platinum-aryl and platinum-halogeno-alkyl/aryl complexes.
- The investigation of the above complexes by simple reactions, as well as their solution and solid structural characterization by ^1H , ^{13}C , ^{31}P NMR and x-ray crystallography.
- The investigation of the insertion reactions of a carbene, formed *in situ* from ethyl diazoacetate, into platinum-halide and platinum-carbon bond.
- The investigation of the insertion of carbon monoxide into platinum-aryl bond by HP NMR.
- The application of organoplatinum compounds as novel tin(II)halide-free catalytic systems in hydroformylation reaction.

3. Methods

Synthetic laboratory methods: standard inert Schlenk-techniques, high-pressure autoclave techniques.

Analytical methods: ^1H , ^{13}C and ^{31}P NMR, IR, GC-MS, x-ray crystallography.

4. Results

The major achievements of my PhD research are as follows.

1. $\text{Pt}(\text{PP})(\text{alkyl/aryl})_2$ and $\text{Pt}(\text{PP})(\text{X})(\text{alkyl/aryl})$ complexes were synthesised and characterised by various analytical methods both in solution and solid state.

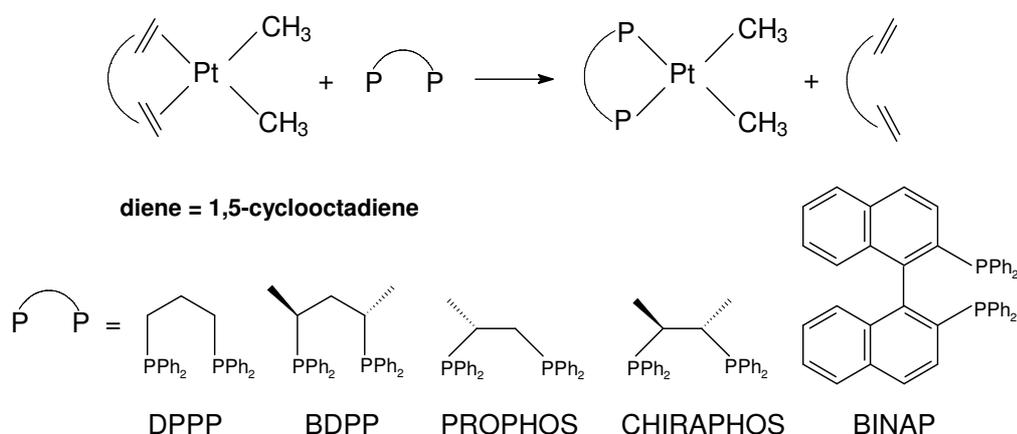


Figure 2. The ligand-exchange reaction of platinum-dimethyl-COD-complex and the diphosphine ligands used

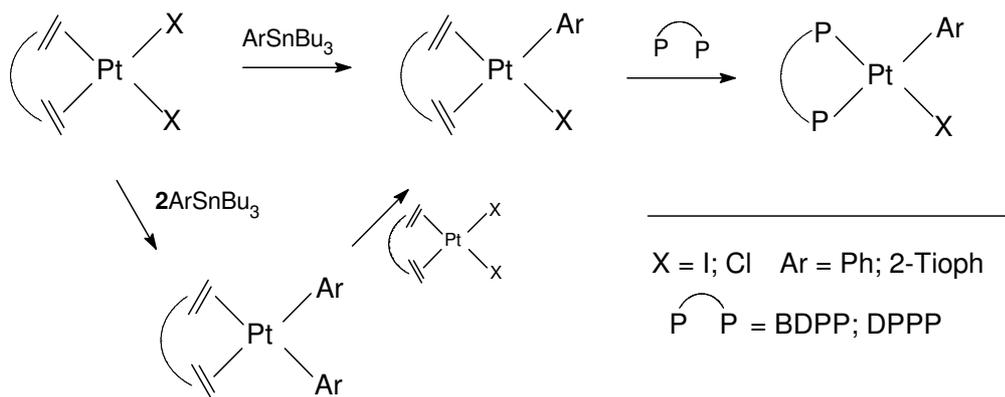


Figure 3. The synthesis of $Pt(PP)(X)(\text{alkyl/aryl})$ complexes

2. Novel $Pt\{(S,S)\text{-BDPP}(I)(R)\}$ ($R = \text{Me, Ph, 2-Tioph, Bn}$) complexes were synthesised in ligand-exchange reactions.

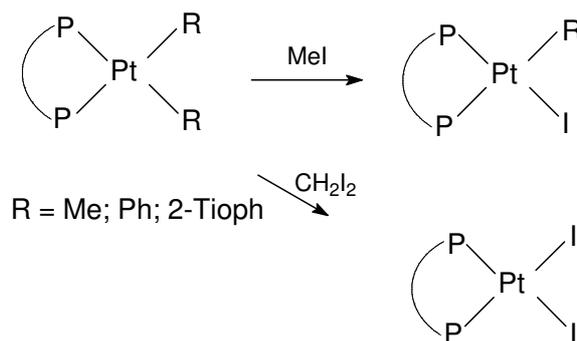


Figure 4. The synthesis of $Pt\{(S,S)\text{-BDPP}(I)(R)\}$ ($R = \text{Me, Ph, 2-Tioph}$) complexes

3. $Pt\{(S,S)\text{-BDPP}\}(I)(\text{Me})$, $Pt\{(S,S)\text{-BDPP}\}I_2$ and $Pt\{(S,S)\text{-BDPP}\}(I)(\text{Ph})$ complexes were investigated by x-ray crystallography. It was found that the Pt-BDPP chelate ring could form different conformations. Four conformations such as twist-boat, skew, chair and envelope were determined for the above three complexes. The bond angles around the central platinum depend on the chelate conformations.

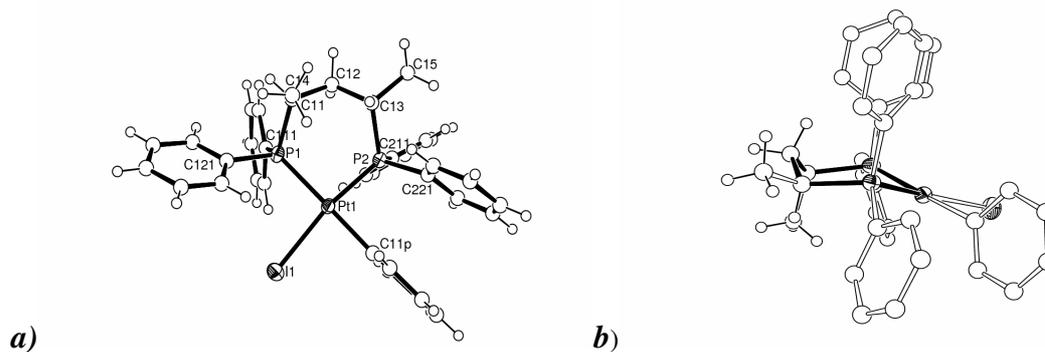


Figure 5. The ORTEP diagram of the Pt{(2S,4S)-BDPP}(Ph)I complex (a) the square-planar arrangement of the ligands around platinum can be seen on the top-view., (b) the chair conformation can be seen from the side-view

5. The insertion of a carbene, formed *in situ* from ethyl diazoacetate, was investigated. It was found that no reaction takes place by using Pt(PP)(alkyl/aryl)₂ complexes. In case of Pt(PP)X(aryl) complexes a chemoselective insertion into Pt-C bond occurred. A simple insertion of the carbene was observed only, *i.e.* monoinserted complexes with one stereogenic centre in the side-chain were obtained exclusively. Furthermore, the insertion reactions are more pronounced in the presence of highly polarizable iodo ligands.

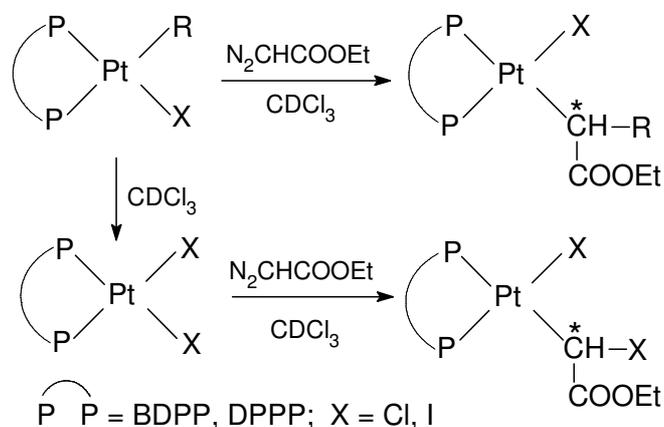


Figure 6. The insertion of carbene into platinum-aryl and platinum-halide bonds by using Pt(P-P)(X)(R) complexes (R = Ph, 2-Tioph).

5. The diastereoselectivity of the carben insertion was investigated by using ((S,S)-BDPP) as optically active diphosphine. Upon its influence, higher diastereoselectivities were obtained with chloro than with iodo ligand.
6. Platinum-acyl complexes were formed by the insertion of carbon monoxide into the platinum-aryl bond. It has to be noted that no insertion into the Pt-X bond takes place.

The yield of the insertion is thoroughly influenced by the type of the aryl and halide ligands. The phenyl and iodo derivatives proved to be the most active ones in insertion reaction. It was determined by HP NMR that the extent of the insertion can be increased by higher carbon monoxide pressure.

- Upon reacting $\text{Pt}\{(S,S)\text{-BDPP}\}(\text{R})_2$ type complexes with Lewis acids such as $\text{B}(\text{C}_6\text{F}_5)_3$, BPh_3 and BF_3 , the formation of a vacant coordination site and in parallel, that of the corresponding borate anion was observed. In the presence of carbon monoxide or PPh_3 , the formation of a complex cation $[\text{Pt}\{(S,S)\text{-BDPP}\}\text{R}(\text{L})]^+$ was detected by NMR ($\text{L} = \text{PPh}_3, \text{CO}$).

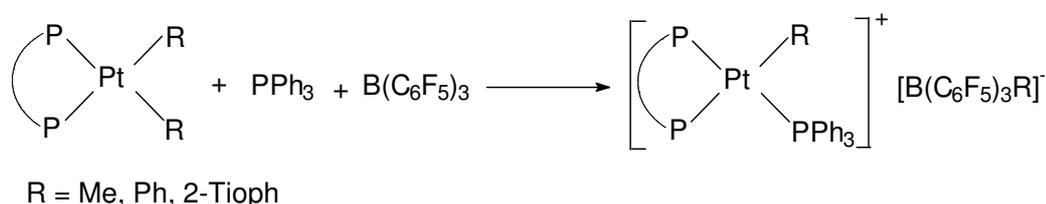


Figure 7. The formation of $[\text{Pt}(\text{BDPP})(\text{PPh}_3)(\text{alkyl/aryl})]^+$ complexes

- Enantioselective hydroformylation of styrene was carried out by using the above catalytic systems containing boron additives. The activity and enantioselectivity of the system formed 'in situ' from $\text{Pt}\{(S,S)\text{-BDPP}\}(\text{R})_2$, $\text{B}(\text{C}_6\text{F}_5)_3$, or BF_3 was analysed. The enantioselectivity of the reaction depended strongly on the structure of the catalyst precursor, and especially on the type of the aryl ligand.

5. Papers, conference lectures

A) Papers served as a basis of the PhD Thesis

L. Jánosi, L. Kollár, P. Macchi, A. Sironi:

Synthesis of platinum-iodo-alkyl/aryl complexes in ligand-exchange reactions: Determination of the structure of $\text{Pt}\{(S,S)\text{-bdpp}\}(\text{X})\text{I}$ complexes ($\text{X} = \text{Me}, \text{I}$) by X-ray crystallography.

J. Organomet. Chem. 691 (2006) 2846-2852. IF.: 2.232

L. Jánosi, L. Kollár, P. Macchi, A. Sironi:

Insertion of ethyl diazoacetate into the platinum-carbon bond of $\text{Pt}(\text{diphosphine})(\text{halide})(\text{aryl})$ complexes. X-ray structure of the $\text{Pt}\{(2S,4S)\text{-bdpp}\}\text{I}(\text{Ph})$ complex.

Trans. Met. Chem. 32 (2007) 746-752. IF.: 0.918

L. János, L. Kollár:

The formation of Pt(P-P)(X)(COAr) (X=Cl, I; Ar=Ph, 2-Thioph) complexes via insertion of carbon monoxide.

Trans. Met. Chem. 33 (2008) 317-321. IF.: 0.918

L. János, T. Kégl, L. Kollár:

Platinum-alkyl-B(C₆F₅)₃ (or BF₃) 'in situ' systems as tin(II) halide-free enantioselective hydroformylation catalysts.

J. Organomet. Chem. 693 (2008) 1127-1135. IF.: 2.232

B) Further scientific papers

G. Petőcz, **L. János**, W. Weissensteiner, Zs. Csók, Z. Berente, L. Kollár (2000):

Synthesis and NMR investigation of Pt(CN)₂(diphosphine) and [Pt(CN)(triphosphine)]Cl complexes.

Inorg. Chim. Acta 303 (2000) 300-305. IF: 1.200

D. Fernandez, P. Sevilano, M. I. García-Seijo, A. Castiñeiras, **L. János**, Z. Berente, L. Kollár, M.E. García-Fernández:

Influence on reactivity of chloro ligand substitution in mononuclear cationic palladium (II) and platinum (II) triphos complexes. X-ray structure of the nitrate derivatives.

Inorg. Chim. Acta 312 (2001) 40-52. IF.:1,394

M.I. García-Seijo, P. Sevilano, A. Castiñeiras, **L. János**, Z. Berente, L. Kollár, M.E. García-Fernández :

Mononuclear cationic palladium(II) and platinum(II)-triphos complexes: The formation of polynuclear platinum-triphos ionic and covalent complexes.

Polyhedron 20 (2001) 855-868. IF.: 1.200

L. János, T. Kégl, L. Hajba, Z. Berente, L. Kollár:

Platinum complexes of (*R*)-N,N-bis(2-(diphenylphosphino)ethyl)-1-phenyl-ethylamine (PNP): their synthesis and characterisation.

Inorg. Chim. Acta 316 (2001) 135-139. IF.:1,394

Kuik, R. Skoda-Földes, **L. János**, L. Kollár:

Facile synthesis of unsymmetrical 1,n'-disubstituted ferrocenoyl amino acid derivatives via palladium-catalyzed aminocarbonylation.

Synthesis 10 (2007) 1456-1458. IF.: 2,333

C) Conference lectures served as a basis of the PhD Thesis

L. Kollár, **L. János**, A. Sironi:

Synthesis of platinum-iodo-alkyl/aryl complexes in ligand-exchange reactions. X-ray structural determination of Pt{(S,S)-BDPP}(X)I complexes. (OP-15, 39)

VIth Int. Conf. Inorg. Chem.

Funchal (Portugal), 31.03 -02. 04. 2005.

Rangits G., **János L.**, Petőcz Gy., Kollár L.:

Platina-komplexek koordinációs kémiai vizsgálata szerves oldószerekben és ionfolyadékokban Szervetlen és Fémorganikus Kémiai Munkabizottság Mikroszimpoziuma

Pécs, 2003. április 10-11.

L. Jánosi, A. Sironi, L. Kollár:

The characterization of novel platinum-phosphine-iodo complexes by means of x-ray crystallography and ^{31}P NMR.

8th Symposium on Instrumental Analysis. (P29)

Graz, 25-28. 09. 2005.

L. Jánosi, P. Macchi, A. Sironi, L. Kollár:

Insertion of ethyl diazoacetate into Pt-aryl and Pt-halogen bonds.

37th International Conference on Coordination Chemistry (ICCC-37),

Cape Town, 13-18 August, 2006 (P-551)

L. Kollár, **L. János**i, T. Kégl:

NMR investigations of the platinum-alkyl/aryl – $\text{B}(\text{C}_6\text{F}_5)_3$ in situ systems as catalysts.

9th Int. Symp. on Instrumental Analysis

Pécs, June 29-July 2, 2008 (p. L-06)

D) Further conference lectures

G. Petőcz, **L. János**i, Z. Berente, L. Kollár:

Synthesis and NMR investigation of $\text{Pt}(\text{CN})_2(\text{diphosphine})$ and $[\text{Pt}(\text{CN})(\text{triphosphine})]\text{Cl}$ complexes.

5th Symposium on Instrumental Analysis,

Pécs, oktober 24-27, 1999 pp. 44.(P-26)

L. Jánosi, L. Kollár:

Többfogú ligandumok platinakomplexei.

Magyar Tudomány Napja,

Pécs, 2000. november 9.

L. Jánosi, Z. Berente, L. Kollár:

Mononuclear cationic and polynuclear ionic and neutral complexes of platinum(II): NMR study of Pt-PPP and Pt-PNP type complexes.

6th Symposium on Instrumental Analysis,

Graz, june 24-27, 2001, , pp.28. (L-17)

Jánosi László:

Többfogú ligandumok platinakomplexei.

XXV. Kémiai Előadói Napok.

Szeged, 2002. október 28-30.

G. Petőcz, **L. János**i, Z. Berente, P. Sevillano, E. Garcia-Fernandez, L. Kollár:

Synthesis and Characterization of Platinum(II) Complexes Containing Polydentate Ligands.

2nd Singapore International Chemical Conference (SICC-2) (Frontiers in Chemical Design and Synthesis)

Singapore, 18-20. 12. 2001.