

DOCTORAL (PH.D.) THESIS

**INVESTIGATIONS ON PLATINUM-CATALYSED
HYDROFORMYLATION REACTIONS**

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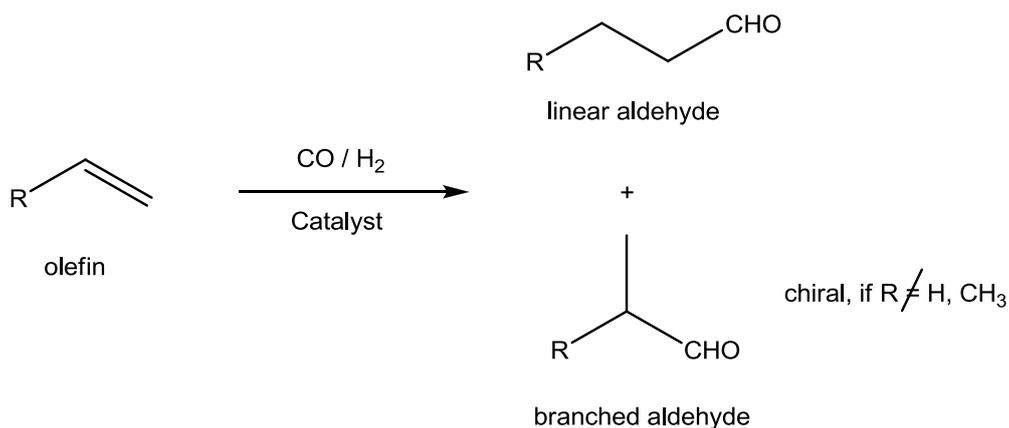
I. Introduction

It has been recognised in the first decades of the 19th century that certain materials can increase the rate of a chemical reaction and they are not consumed by the reaction, *i.e.*, they can be recovered. This phenomenon is called catalysis. Nowadays *ca.* 95% of the industrial products are synthesised by catalytic reactions.

Two types of catalysts can be distinguished, depending on whether a catalyst exists in the same phase as the substrate or not. Heterogeneous catalysts act in a different phase, and homogenous catalysts can be found in the same phase as the reactants. Both types of catalysts have their own advantage. While heterogeneous catalysts can easily be separated from the reaction media, retrieval of the homogenous catalysts is much more complicated. Furthermore, the catalytically active sites (number of the active metal centres) of a heterogeneous catalyst is significantly fewer compared to a homogenous one, namely, in the latter case all of the dissolved metal atoms can act as an active centre. The homogenous transition metal catalysts have the advantage that the ligands situated in their coordination sphere can be varied. The structural modification of these ligands can cause changes in the catalytic behaviour of the complexes and allows fine tuning of the catalysts. It is also an important feature that homogenous catalysts and catalytically active intermediates can be characterized with numerous conventional spectroscopic methods (NMR, IR, UV-vis).

It is widely accepted that the homogenous catalytic processes are environmentally more acceptable, and some of them have become a catalyst with important industrial application. These processes have several beneficial properties (applicable in alternative solvents, small amount of by-products, higher atom efficiency, high selectivity) and can be considered as environmentally benign processes in green chemistry or in sustainable chemistry.

Hydroformylation, investigated in this work, is the addition of synthesis gas (mixture of CO and H₂) to olefins in the presence of a catalyst under the formation of aldehydes. Formally, a hydrogen (H) and a formyl group (HCO) are added to C=C double bond in an atom-economical manner. The reaction leads to a mixture of isomeric products, n-aldehyde (linear regioisomer) and iso-aldehyde (branched regioisomer). As a side-reaction, hydrogenation of the alkene resulting in the formation of alkane takes also place (Scheme 1.).



Scheme 1. The hydroformylation reaction

The proportion of the products (chemo-, regio- and enantioselectivity) is highly influenced by the reaction conditions (temperature, partial pressures), as well as the properties of the catalyst. *P*-Ligands applied in hydroformylation are of crucial importance, since their structural variation modifies the steric and electronic properties of the ligand and the transition metal complexes alike. The systematic variation of these ligands allows us to get deeper insight into the structure-activity and structure-selectivity correlations. Beyond that, the proper selection of the ligands and substrates and the inspection of their behaviour in the hydroformylation possibly allows us to get an insight into reaction mechanism. Its deeper understanding is a key to practical applications.

II. Aims of the study

The basic objective of my PhD study is to investigate novel *P*-ligands in the platinum-catalysed hydroformylation reaction. I have focused my attention especially on the following details:

- 1) Synthesis of platinum complexes containing a wide variety of monodentate achiral ligands (2-diphenylphosphinobenzaldehyde derivatives, phospholene, phospholane derivatives) and polydentate (*P,N*- and *P,N,P*-type) ligands, as well as their structural characterisation and catalytic testing in hydroformylation reaction (structure-activity, structure-selectivity correlations).
- 2) Investigation of asymmetric hydroformylation reactions of *para*-substituted styrenes in order to find out further mechanistic details.

III. Methods

Standard inert Schlenk-technique and high-pressure autoclave method was used. The experiments involving high pressure were performed with high purity syn-gas in a 100 cm³ stainless steel autoclave.

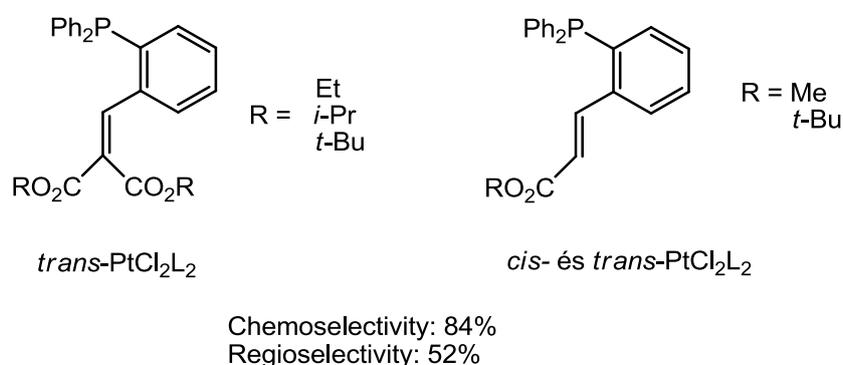
The conversion and the product distribution of the catalytic experiments were determined by using GC/MS. The ¹H-, ¹³C- and ³¹P-NMR spectra were recorded on Varian Inova 400 spectrometer.

IV. Results

In the course of my PhD work, platinum complexes of novel-type ligands were synthesised, characterised and tested in hydroformylation reaction. The numerous experimental results allow us to draw important conclusions regarding structure–activity and structure–selectivity correlations. Furthermore, investigating the details of asymmetric hydroformylation reaction, a correlation between *para*-substituents of styrene and catalytic selectivity was determined.

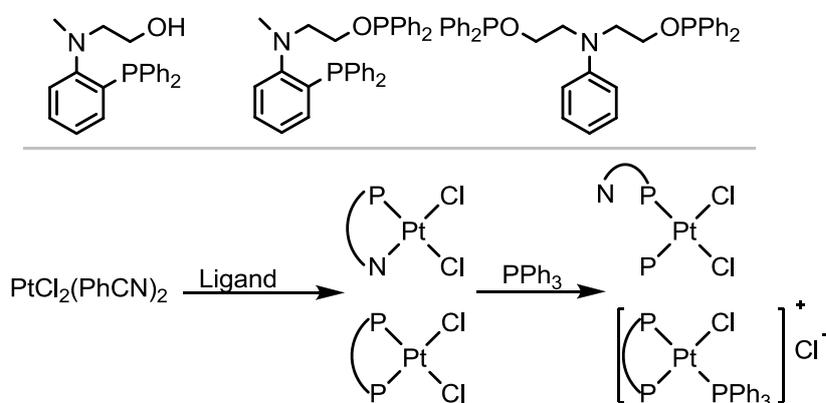
My results and observations are summarised as follows:

1. 2-Diphenylphosphinobenzaldehyde derivatives form platinum(II) complexes with *trans* geometry due to steric hindrance. A mixture of *cis/trans* geometrical isomers was formed when ligands with one ester functionality were used. ^{31}P NMR studies revealed that coupling constants of *cis*-monoester complexes are significantly smaller than that observed in the corresponding *cis*-PtCl₂(PPh₃), presumably due to the effect of the *ortho*-substituents. This effect is minimal when the phosphine ligands are in *trans* arrangement on the metal centre.
2. Moderate hydroformylation activity but low regioselectivity towards branched aldehyde was observed using the above complexes as catalysts. There is no significant difference in selectivity obtained with *trans*-type diester complexes and *cis* and *trans* complexes containing monoester ligands. This phenomenon can be explained by the structural similarity of the catalytically active intermediates formed *in situ*. It is either due to *cis-trans* isomerisation or *P*-ligand dissociation.



Scheme 2. 2-diphenylphosphinobenzaldehyde derivatives

3. Platinum complexes of *P,N*- and *P,N,P*-type ligands show a variety of coordination modes. In the case of the *P,N* ligand the monodentate-*P* and the heterobidentate-*P,N* coordination was observed, while in the case of the *P,N,P* ligands the *P,P*-bidentate coordination mode was preferred. The stability of the complexes was investigated by *in situ* NMR spectroscopy. By the addition of PPh_3 the coordinating *N*-donor atom was substituted and *cis*- $\text{PtCl}_2\text{P}(\text{PPh}_3)$ complex was formed. In contrary, in the case of *P,P*-type complexes the ionic $[\text{PtP}_3\text{Cl}]^+$ complexes were formed by the dissociation of one of the two chloro ligands.

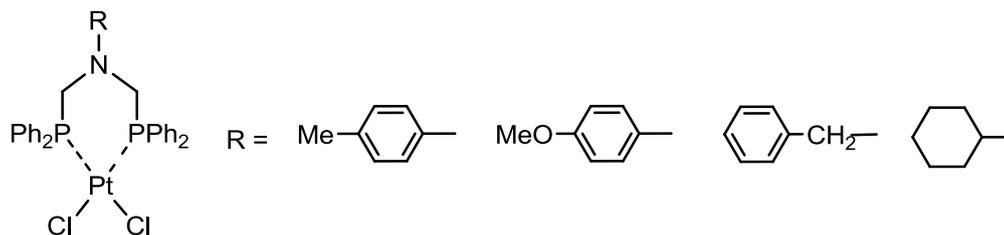


Scheme 3. Platinum complexes of *P,N*- and *P,N,P*-type ligands

The above platinum complexes proved to be precursors to catalysts of low activity and moderate chemo- and regioselectivity for the hydroformylation of styrene. Remarkable increase in regioselectivity was observed in the presence of *para*-toluenesulfonic acid additive in the case of heterobidentate-*P,N*-complexes.

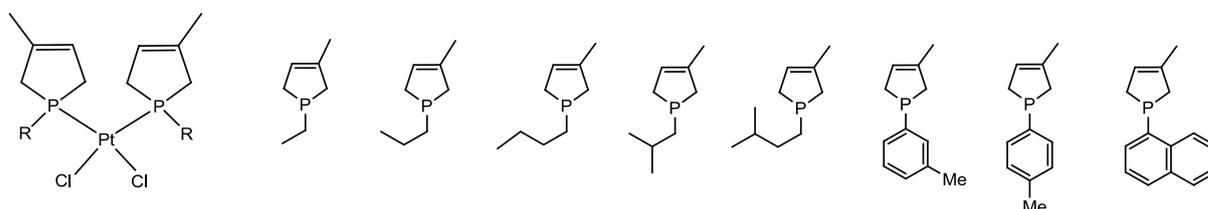
4. Platinum complexes of bis-phosphine *P,N,P*-type ligands (Scheme 4) were tested as catalyst precursors in the hydroformylation of styrene. The formation of both aldehyde regioisomers was observed in all cases while the formation of branched aldehyde is highly preferred over the linear one (regioselectivity ~80%). Regioselectivity is only slightly influenced by the temperature. Interestingly, the amount of the SnCl_2 co-catalyst has no effect on selectivity but influences the activity of the catalyst. We have found that the precursors are active even at low $\text{Pt}:\text{SnCl}_2$ ratios. However, the activity

of the complexes was decreased at low temperatures (60 °C) when SnCl₂ was used in excess.



Scheme 4. Bis-phosphine *P,N,P*-type ligands

5. Racemic and optically active 1-alkyl and 1-aryl phospholane ligands were tested in platinum-catalysed hydroformylation reaction. The *cis*-platinum complexes proved to be moderately active and highly regioselective catalysts. The enantioselectivity remained below 25% and cannot be raised significantly by lowering the reaction temperature. The steric properties of the *P*-alkyl substituents have no effect either on activity or on selectivity. It can be concluded that the change of alkyl groups to aryl substituents brought in most cases an increase in the catalytic activity while the chemo- and regio-selectivities remained unchanged.



Scheme 5. 1-alkyl and 1-aryl phospholene ligands

6. To determine whether the electronic properties of the substrate have any influence on the selectivity of the hydroformylation reaction, hydroformylations catalysed by PtCl(SnCl₃)[(*S,S*)-BDPP] and tin(II)-chloride were conducted. The following effects of electron-donor or electron-acceptor properties of the *para*-substituents of styrene on the hydroformylation were observed and discussed.
- The *para*-substituents have no effect on the catalytic activity at high (100 °C) temperatures.

- b. The chemoselectivity is significantly lower using styrene possessing *para*-substituents characterized by a positive Hammett-constant.
- c. Lower and higher preference for the branched aldehyde regioisomer was shown with styrenes containing *para*-substituents with electron-acceptor and electron-donor character, respectively. It can be concluded that the regioselectivity is dominantly governed by the used catalytic system.
- d. It has been observed with all styrene derivative that the formation of (*S*)- and (*R*)-2-arylpropanal is favoured at low and high temperature, respectively, when (*S,S*)-BDPP was used as optically active ligand. The electron-donor or electron-acceptor properties of the *para*-substituents of styrene show correlation with the changes in enantioselectivity, especially with the reversal temperature of the enantioselectivity. The reversibility of the formation of the Pt-branched alkyl intermediates, leading to the corresponding (*R*)- and (*S*)-enantiomers of 2-arylpropanals, depends on the Hammett constants.

V. Publications

1. **P. Pongrácz**, L. Kollár, A. Kerényi, V. Kovács, V. Ujj, G. Keglevich:
Hydroformylation of styrene in the presence of platinum(II) complex catalysts incorporating cyclic phosphines and phosphonous diesters as P-ligands
J. Organomet. Chem. **696** (2011) 2234-2237. IF: 2.384
2. **P. Pongrácz**, G. Petőcz, M. Shaw, D. B. G. Williams, L. Kollár:
Platinum complexes of 2-diphenylphosphinobenzaldehyde-derived P-alkene ligands and their application in the hydroformylation of styrene
J. Organomet. Chem. **695** (2010) 2381-2384. IF: 2.205
3. G. Keglevich, P. Bagi, Á. Szöllősy, T. Körtvélyesi, **P. Pongrácz**, L. Kollár, L. Drahos:
Platinum(II) complexes incorporating racemic and optically active 1-alkyl-3-phospholenes and 1-propyl-phospholane P-ligands: Synthesis, stereostructure, NMR properties and catalytic activity
J. Organomet. Chem. **696** (2011) 3557-3563. IF: 2.384
4. E. Bálint, E. Fazekas, **P. Pongrácz**, L. Kollár, L. Drahos, T. Holczbauer, M. Czugler, G. Keglevich:
N-benzyl and N-aryl bis(phospha-Mannich adducts): Synthesis, and catalytic activity of the related bidentate chelate platinum complexes in hydroformylation
J. Organomet. Chem. **717** (2012) 75-82. IF: 2.384
5. K. M. Pietrusiewicz, A. Flis, V. Ujj, T. Körtvélyesi, L. Drahos, **P. Pongrácz**, L. Kollár, G. Keglevich:
Synthesis and use of borane and platinum(II) complexes of 3-diphenylphosphino-1-phenylphospholane (LuPhos)
Heteroatom Chem. **22** (2011) 730-736. IF: 1.243
6. **P. Pongrácz**, I. D. Kostas, L. Kollár:
Platinum complexes of P,N- and P,N,P-ligands and their application in the hydroformylation of styrene
J. Organomet. Chem. **723** (2013) 149-153. IF: 2.384
7. P. Bagi, T. Kovács, T. Szilvási, **P. Pongrácz**, L. Kollár, L. Drahos, E. Fogassy, G. Keglevich:
Platinum(II) complexes incorporating racemic and optically active 1-alkyl-3-phospholene P-ligands: Synthesis, stereostructure, NMR properties and catalytic activity
J. Organomet. Chem. **751** (2014) 306-313. IF: 2.384
8. **P. Pongrácz**, T. Papp, L. Kollár, T. Kégl:
Influence of the 4-Substituents on the Reversal of Enantioselectivity in the Asymmetric Hydroformylation of 4-Substituted Styrenes with PtCl(SnCl₃)[(2S,4S)-BDPP]
Organometallics **33** (2014) 1389-1396. IF: 3.963

9. P. Bagi, T. Szilvási, **P. Pongrácz**, L. Kollár, L. Drahos, G. Keglevich
Platinum (II) Complexes Incorporating Racemic and Optically Active 1-Aryl-3-
phospholene P-Ligands as Potential Catalysts in Hydroformylation
Current Organic Chemistry **19** (2014) 1 IF: 3,222

VI. Presentations

1. **P. Pongrácz**, G. Petőcz, M. Shaw, D. B. G. Williams, L. Kollár:
Hydroformylation of styrene in the presence of platinum-P-alkene-ligands tin(II)-
chloride catalytic systems
8th European Workshop on Phosphorous Chemistry
Münster (Germany), 28-29 March, 2011.
2. P. Bagi, **P. Pongrácz**, L. Kollár, G. Keglevich:
Platinum complexes incorporating chiral phospholene P-ligands, synthesis and
catalytic activity
10th European Workshop on phosphorous Chemistry
Regensburg (Germany), 18-20 March, 2013.
3. **P. Pongrácz**, T. Papp, L. Kollár, T. Kégl:
Influence of 4-substituents on the reversal of the enantioselectivity in the
hydroformylation of styrenes
11th European Workshop on Phosphorous Chemistry
Sofia (Bulgaria), 24-26 March, 2014.
4. **P. Pongrácz**, T. Papp, L. Kollár, T. Kégl:
A *para*-szubsztituensek hatása az enantioszelektivitásra sztirol hidroformilezésének
reakciójában
III. Interdiszciplináris Doktorandusz Konferencia
Pécs (Hungary), 15-17 April, 2014.