Author's review of him research

(annex 2b)

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2016

1.1 Names and Surname: Arkadiusz Feliks Kłys

1.2 Experience and professional degrees:

- 1991-1996 - Faculty of Mathematic Physics and Chemistry University of Lodz
- 1996 – Master's Degree in Chemistry, University of Lodz
- 2001- PhD in Chemistry, University of Lodz
- 2002-2009 - Faculty of Pharmacy, Medicinal University of Lodz
- 2009- Master's Degree in Pharmacy, Medicinal University of Lodz

1.3 Professional experience

- 1996 - Master' Degree in Chemistry, Faculty of Mathematic, Physics and Chemistry, Master's Degree, University of Lodz
- 1996-2001 - employed a full-time assistant in Department of Organic Chemistry, Faculty of Chemistry, University of Lodz
- 2001- PhD in Chemistry, Faculty of Physics and Chemistry, University of Lodz, specialisation: Chemistry
- 2001-2009 - employed a full-time lecturer in in Department of Organic Chemistry, Faculty of Chemistry, University of Lodz
- 2001 -2005 Postdoctoral fellowship in McMaster University Hamilton Canada (total 18 month)
- 2009-2014 - employed a full-time lecturer and exercise a function of Head of Laboratory of Molecular Spectroscopy, Faculty of Chemistry, University of Lodz
- 2014 - 2016 - employed a full-time assistant and exercise a function of Head of Laboratory of Molecular Spectroscopy, Faculty of Chemistry, University of Lodz
- 09.2016 - employed a full-time senior chemist (scientific and technical) in Department of Organic Chemistry, Faculty of Chemistry, University of Lodz

1.4 Achievements of Scientific Research

Results of my scientific research are collection of publications included on Institute for Scientific Information (ISI) Master Journal List, conference presentations and other scientific activities. These achievements which are a summary of my research are summarized below (according to Scopus base and Web of Science, data of 01.09.2016):

- complete publications list: - **28**, including:
- before received PhD degree - **5** publications (all included on ISI Master Journal List)

- after received PhD degree **23** publications (only one is not included on ISI Master Journal List)
- total Impact Factor of all publications: **57,042** (2,113 per one publication)
- total sum of the pointss for publication included in the Ministry of Science and Higher Education (MSHE) list: **700** (25,0 per one publication)
- total Impact Factor from all publications which are included in the base for applying for doctoral Hab. Degree: **15,167** (2,17 per one publication)
- total sum of the pointss from the MSHE which are included in the base for applying for doctoral Hab. Degree: **190** (27,1 per one publication)
- total Impact Factor of paper published before received PhD degree: **12,616** (2,52 per one publication)
- total sum of the pointss for publication included in the MSHE list obtained before received PhD Degree: **145** (29 per one publication)
- total Impact Factor of paper obtained after received PhD Degree: **42,318** (2,015 per one publication)
- total sum of the pointss for publications included in the MSHE list obtained after received PhD Degree: **530** (35,3 per one publication)
- number of citations: **165** (Scopus); **146** (Web of Science); without auto-citations: **120** (Scopus); **124** (Web of Science)
- Hirsch Index: **8** (according to Scopus i Web of Science)
- international and national conference presentations:25
- scientific grant: as project manager – **1**, as a project contractor - **5**

1 – habilitation grant MSHE **204 331837** Synthesis and properties of 1,1'-diphosphaferrocen as a potential material for non-linear optics. 37-th edition of project (01.02.2009 – project manager)

2. Achievements of scientific researches defined in art. 16 paragraph 2 of the Act of 14-st, March 2003 on academic degrees and academic title and degrees and title in art (Journal of Laws, No. 65, item 690, as amended)

2.1 The title of scientific achievements:

„Heterometallocenes derivatives: optics activity and coordination complexes"

2.2 Publication included in scientific achievement

H1. **Kłys, A**., Zakrzewski, J., Jerzykiewicz, L.

Resolution and determination of the absolute configuration of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene-2-carboxaldehyde.

Tetrahedron Asymmetry, 2003, Vol. 14, Issue 21, pp. 3343-3346
IF (2015) = 2,108, IF_5(2015) = 1,973, MSHE pointss – 25 pointss
Number of citations (without auto-citations): 6 (4)
I was involved in planned and performed the synthesis and developed methodology of separation of obtained series of diastereisomers, discussion during working on the manuscript, writing an experimental section and analysis of obtained NMR and IR spectra. My contribution: 85%

H2. **Kłys, A**., Małecka, M., Zakrzewski, J.

Synthesis and structure determination of stereoisomeric 2,2'-dibenzoyl-3,3',4,4'-tetramethyl-1,1'- diphosphaferrocenes.

J. Arkivoc Vol. 2007, Issue 6, pp. 172-178
IF (2015) = 1,165, IF_5(2015)= 1.181 MSHE pointss – 20 pointss
Number of citations (without auto-citations): 0 (0)
I was involved in planned and performed the synthesis, developed methodology of separation of obtained compounds, co-editing manuscript, results discussion, writing an experimental section and analysis of NMR spectra. My contribution:75%

H3. Mucha, B., **Kłys, A.,** Rybarczyk-Pirek, A., Zakrzewski, J.

Diastereospecific addition of Grignard reagents to 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene-2-carbox aldehyde.

Tetrahedron Asymmetry, 2007, Vol. 18, Issue 15, ppp 1766-1768
IF (2015) = 2,108, IF_5(2015)= 1,973 MSHE pointss – 25 pointss
Number of citations (without auto-citations): 5 (4)
I was involved in performed part of synthesis, planed conducted experiments, developed methodology of separation of obtained compounds, co-editing manuscript, results

discussion, writing an experimental section with analysis of obtained NMR spectra. My contribution: 60%

H4. **Kłys, A**., Rybarczyk-Pirek, A., Zakrzewski, J.

Reaction of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene with [Re2(CO)8(CH3CN)2]: Novel coordination modes of the 1,1′-diphosphaferrocene ligand.

Journal of Organometallic Chemistry, 2008, 693 (7), pp. 1166-1170
IF (2015) = 2,336, IF_5(2015)=2,090 MSHE pointss – 30 pointss
Number of citations (without auto-citations): 4 (4)
I was involved in planed the synthesis, developed methodology of separation of obtained compounds, co-editing manuscript, results discussion, writing an experimental section with analysis of obtained NMR and IR spectra. My contribution: 75%

H5. Mucha, B., **Kłys, A**., Zakrzewski, J., Makal, A., Woźniak, K.

Unusual diastereoselective reduction of 2-propionyl-3,3′,4,4′- tetramethyl-1,1′-diphosphaferrocene to the corresponding alcohol by BH3·Me2S. X-Ray diffraction and DFT study.
New Journal of Chemistry, 2009, 33 (4) , pp. 807-812

IF (2015) = 3,006, IF_5(2015)= 2,940 MSHE pointss – 30 pointss
Number of citations (without auto-citations): 3 (3)
I was involved in planed and performed the synthesis, carried out all theoretical calculations, co-editing manuscript, results discussion, writing an experimental and theoretical calculation section, analysis of obtained NMR and MS spectra. My contribution: 55%

H6. **Kłys, A.***

Resolution and determination of the absolute configuration 2,2′-diacetyl-3,3′, 4,4′-tetramethyl-1,1′- diphosphaferrocenes.

Journal of Organometallic Chemistry,7 00, pp. 1-3
* corresponding author
IF (2015) = 2,336, IF_5(2015)= 2,090 MSHE pointss – 25 pointss
Number of citations (without auto-citations): 0 (0)

I was involved in planed and performed the synthesis, developed methodology of separation of obtained enantiomers, editing manuscript, results discussion, analysis of obtained NMR, CD spectra. And X-ray data. My contribution: 60%

H7. **Kłys, A.*, Makal, A, Zdzienicka, A.**

Properties and separation method of enantiomers of the monoandbis-substituted derivatives of 3,30,4,40-tetramethyl-1,10diphosphaferrocene: structural analysis using X-ray diffraction and circular dichroism

Tetrahedron Asymmetry, DOI information: 10.1016/j.tetasy.2016.11.003

*corresponding author
IF (2015) = 2,108, IF_5(2015)= 1,973 MSHE pointss – 30 pointss
Number of citations (without auto-citations): 0
I was involved in planed all work, developed methodology of separation of obtained enantiomers, carried out all theoretical calculations included in paper, editing manuscript, analysis of X-ray data. My contribution: 75%

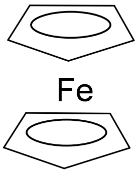
2.3 Discussion of the scientific purpose and scientific achievements

Introduction

The scientific purpose of presented researches were:
- developed an efficient synthesis method allow to obtain enantiomeric pure and chiral derivative of 1,1'-diheterometallocen,
- determined the absolute configuration of obtained compounds,
- analysis of the ability to form another stereogenic centre in nucleophilic addiction reaction
-attempted to determine CD spectra and estimate rules allow to determine the absolute configuration of obtained compounds,
- show the possibility of obtained coordinated complex compounds of such derivatives,
- developed efficient synthesis method of compound known earlier that I was used in my research,
-carried out a simulation of chiraloptics properties based on theoretical calculations in this type of compounds.

1,1'-diheterometallocens

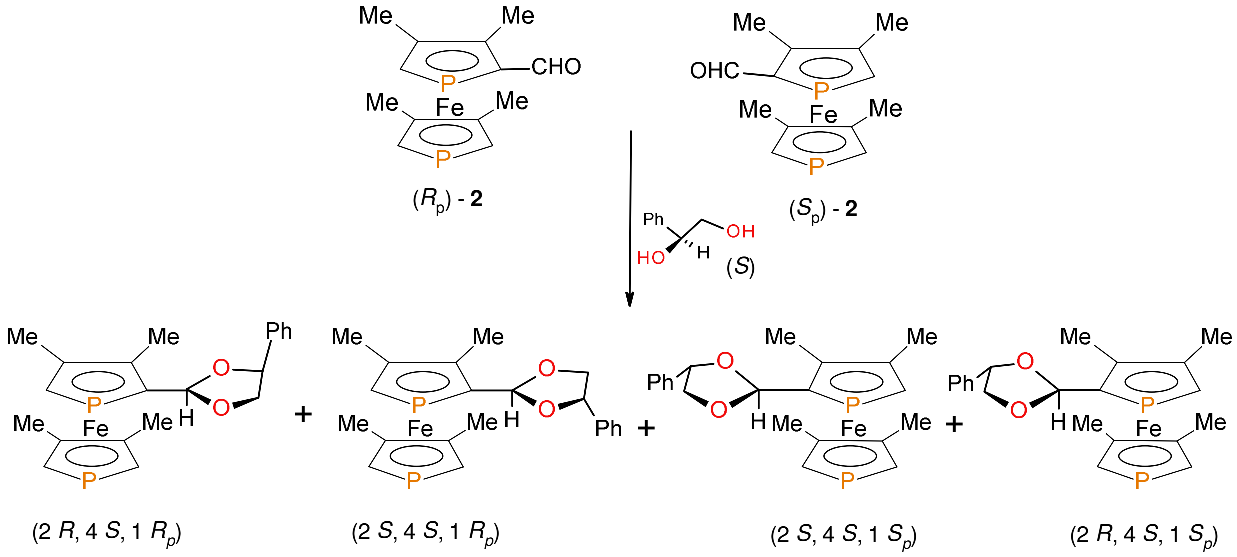
In 1951, Pauson and Kealy[1] described ferrocene which was the first metalorganic compound having a unique and previously unknown "sandwich" structure.



Despite the discovery of the aforementioned researchers should mentioned about paper of Miller and co-workers[2] published in 1952 but sent to the editor befor Pauson and Kealy paper. This discovery was the beginning of new branch of chemistry - "Metalorganics Chemistry" and new inspirations for further research and analysis including metallocenes. The first heterometallocen (azaferrocene) has been described by Pauson[3] and King[4] in 1964, two independent research groups. The first report on the phosphaferrocen appeared in the same year on *Organo-phosphorus compound* conference which Joshi has presented its synthesis. This synthesis methods has been described in paper published in 1971[5] in which the authors shown synthesis of the expected product although presence of absorption band in IR spectra suggesting the existence of coordinated carbon oxide. This authors retreated from its discovery in 1973. The first documented and confirmed synthesis of phosphaferrocene has been shown in 1977[6], by Mathey and co-workers. In 1979 the 1-azaferrocene has been descreined.[7] Next hetero-compound belong to sibaferrocene analogue has been presented by Ashe in 1987. The first report for 1,1'-diheretoferrocene was shown by Seela group in 1968[8] in which the author shown that obtained 1,1'diazaferrocene was very unstable. Fast developed of chemistry of 1,1'-dihteroferrocene 15 groups began in the late seventies, when Mathey and co-workers described 1,1'-diarsaferrocene.[7] In 1980 this authors show synthesis method and properties of 3,3',4,4'-tetramethyl-1,1'diphosphaferrocene.[9] In the same year Ashe et al presented synthesis method of 2,2',5,5'-tetramethyl-1,1'-distibaferrocenue.[10] Eight years later Khun shown much stable 1,1',2,2',3,3',4,4'-octamethyl-1,1'-diazaferrocene[11] which is the heaviest of 1,1'diheteroferrocene. 1,1'-dibismaferrocene has been described by Ashe and co-workers in 1992.[12] A small number of literature on phospha- and diphosphaferrocene derivatives prompted me to undertake research on this branch of chemistry.

Result discussion:

Until 2001, described only three chiral and pure enantiomeric derivatives of 1,1'-diphosphaferrocene for which absolute configuration has been established. They were the only known chiral diheteroferrocene derivatives. The first separation of enantiomers was shown by G. Fu in 1988.[13] The author described methodology of enantiomers separation using derivatives of 2,2'-siphenyl-3,3'4,4'-tetramethyl-1,1'-diphosphaferrocene with C_2 symmetry using High performance liquid chromatography (on a chiral stationary phase). Subsequent publications relate to enantiomeric separation compound with C_1 symmetry i.e. (S)-(α)-methylobenzyl amide with 2-carboxy-3,3',4,4'-tetramethyl1,1'-diphosphaferrocene acid[14], and 2-carobxy-3,3',4,4'-tetramethyl-1,1'-diphosphaaferrocene[15], which the enantiomers were obtained by crystallization with chiral compound-brucine. The separation methodology of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene-2-kcarobxyaldehye **1** has been reported. [16] This approach characterized by low efficiency and difficulties in separation diastereomeric pair of imine. In this paper the absolute configuration of obtained enantiomers has not been established. During my research, I decided to develop a new, efficient method for the last-mentioned compounds, which can be used to receive pure enantiomers in large amount (grams). The important element was an elimination of disadvantages of previously methods and established absolute configuration of separated enantiomers. These achievements were described in paper **H1**. In propose method a chiral compound, (*S*)-(+)-1-phenylo-1,2-ethanodiol has been used. Reaction of 3,3',4,4'-tetramethyl-1,1'-difphosphaferroceno-2-carboaldehyde **1** with (*S*)-(+)-1-phenylo-1,2-ethanodiol leads to receive four diastereomeric acetals what was presented in Scheme 1.



Scheme 1: Synthesis of diastereomeric acetals of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene-2-carboaldehyde.

Obtained acetals in ratio 1:1:1:1 were separated using column chromatography on silica gel. The fourth eluted acetal occur in crystalline form, the last three occur as oil. For crystalline acetal a X-ray analysis has been performed and established an absolute configuration (2” *R*, 4”*S*, 1*R*). The obtained molecular structure of this compound based on X-ray analysis was presented in Figure 2.

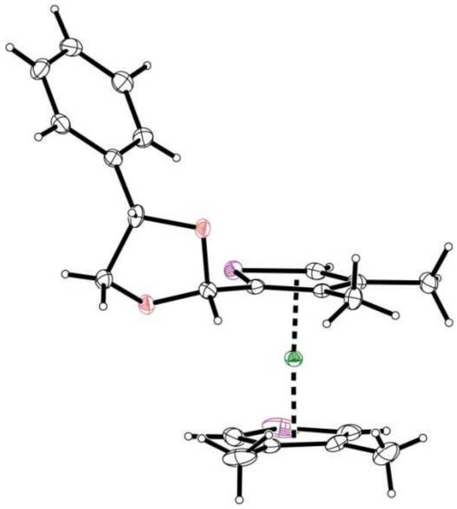
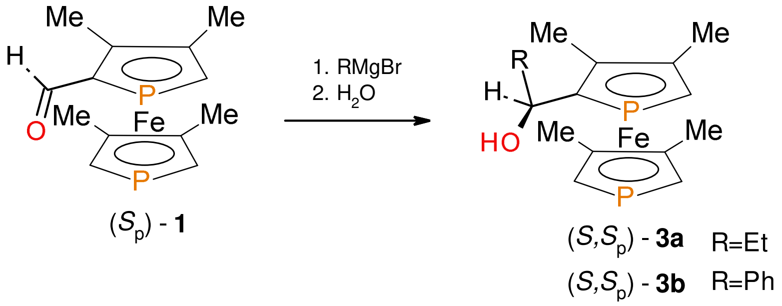


Figure 2. Structure (2”*R*, 4”*S*, 1*R*) of acetal of 3,3’,4,4’-tetramethyl-1,1’-diphosphaferrocene-2-carboxyaldehyde with 1-phenylo-1,2-ethanodiol

In obtain structure the distance between phosphorus atoms was 3,646 Å and is lower than sum of Van der Waals rays (1,9 Å). This results may indicate the existence of interaction „back-bonding” between phosphorus atoms what was suggested by Strzyzewska et al.[17] This interaction has been also noticed by Asche in the case of 1,1’-diheterometallocene which contain heavier atoms such as arsenic, antimony or bismuth.[18] The research performed by Asche were based only on analysis of distance between heteroatoms compared with Van der Waals rays and unfortunately do not contain any experimental data (inter alia electronic density) and the theoretical calculations were conducted at relatively low level. In the obtained structure, a dihedral angle between planes going through phosphorus atom, the centre of the ring and iron atom is 48.4 (2) ° and a J-coupling between phosphorus atoms is $J_{P-P'}$=14,1 Hz based on ^{1}H NMR (in $CDCl_3$ solution).

Obtained diastereomeric acetals were hydrolysed to receive enantiomers of 3,3’,4,4’-tetramethyl1,1’-diphosphaferrocene-2-carboxyaldehyde. Established reliable configurations were performed using analysis of ^{1}H NMR spectra in presence of chiral compound (tris[3-(trifluoromethylohydroxsymethylene-d-camphor]-(+)-Europium^{III} complex) and also obtained molecular structure of acetal. It was found that fractions 1 and 4 contain (*S_p*)- configured compound and the fractions 2 and 3 contain (*R_p*)- configured species. The purity of obtained enantiomers were above 99%, what was confirmed using ^{31}P NMR spectra in presence of above mentioned Europium complex. The received data were collected in paper **H1**. Having a suitable method allows to obtain enantiomeric pure aldehyde **1** I decide to check influence of planar chirality element on nucleophilic addition to carbonyl group reaction in the case of metallocene. Although, the diastereomeric reaction may be analysed using racemic compound, I decided to expand my research on studies of CD (circular dichroism) spectra what need to used pure diastereomeric pair. The nucleophilic addition to carbonyl group reaction in the case of mtalloorganic compounds has been previously widely described. The example of using this reaction for complexes: 2-disubstituted ferrocene-[19], (η^4-dien) tricarbonyl iron-[20], (η^3-allylo)tricarbonyllactoniron-[20], (trimethylenomethane)tricarbonyl iron[20]- or phosphaferroceno-[21] aldehyde and ketone with metalorganic reagents have been shown.

For my research, I chose ethylo- and phenylo- magnesium bromide. Reaction of above mentioned reagents with (S_p)-**1** suitable alcohol (S,S_p)-**3a** and (S,S_p)-**3b** have been obtained. This reaction is resented in Scheme 2.



Scheme 2. Reaction for obtaining (S,S_p)-**3a** and (S,S_p)-**3b** compounds.

The ^{1}H and ^{31}P NMR spectra confirmed that this reaction lead to receive only one diastereomeric, which at the same time proves that it is steroselective reaction. To confirm this assumption the similar reaction with (R_p)- **1** enantiomer has been performed. This reaction also lead to obtain disatereomers with the opposite configurations, (R,R_p)-**3a** and (R,R_p)-**3b**. According to the expectation in the reaction mixture the product with mixed configuration (R,S_p) or (S,R_p) has not been noticed. On ^{1}H and ^{31}P NMR spectra duplication of suitable signals were not observed. The last conformation was X-ray analysis for crystalline derivatives of product **3b** with bis-$W(CO)_5$. The received molecular structure is presented in Figure 3.

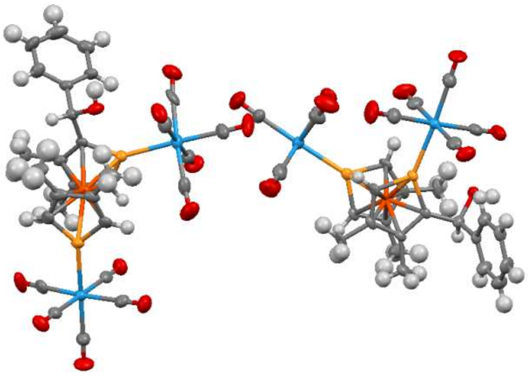


Figure 3. Structure of two crystallography independent molecules (*S*, S_p) – **3b** as a complex with two part of $W(CO)_5$

In the case of this structure, where the unit cell contains two independent molecules the distance between two phosphorus atoms (in the same molecules) is 3,971 Å and 4,247 Å, respectively. The established dihedral angle is -81,87° and -114,23°, respectively. This distances are much bigger than previously described probably due to huge steric hindrance of $W(CO)_5$ group.

Obtained results allow to conclude that, configuration of new, established during addition Grignarda reagents to carbonyl group, stereogenic centre is complies with model of *exo* nucleophile attack on carbonyl group in *s-cis* conformation. This configuration of carbonyl group, in the case of **1**, confirm NOE interaction between methyl group of phospholic ring and proton of aldehyde group obtained from ^{1}H NMR spectra. Moreover, important data proving this conclusion is X-ray analysis for 3,4-dimethyl-1-phosphaferroceneo-2-carobysladehyde[22] available in literature. Additionally, CD spectra obtained for both pair of enantiomers show full symmetry for both derivatives in visible range as well as UV range, what confirm received only one enantiomer. The observed Cotton effect occur in similar case and characterized by similar efficiency. Both stereogenic centre have opposite configurations. It could be expected that strong Cotton effect in range of 220-250 nm are a result of π-π^*transition in phenyl species, in turn Cotton effect in range of 300-600 nm are a result of d-d transition in metallocene moiety. This results were described in paper **H2**. The CD spectra for obtained pair of diastereomers were presented in Figure 3.

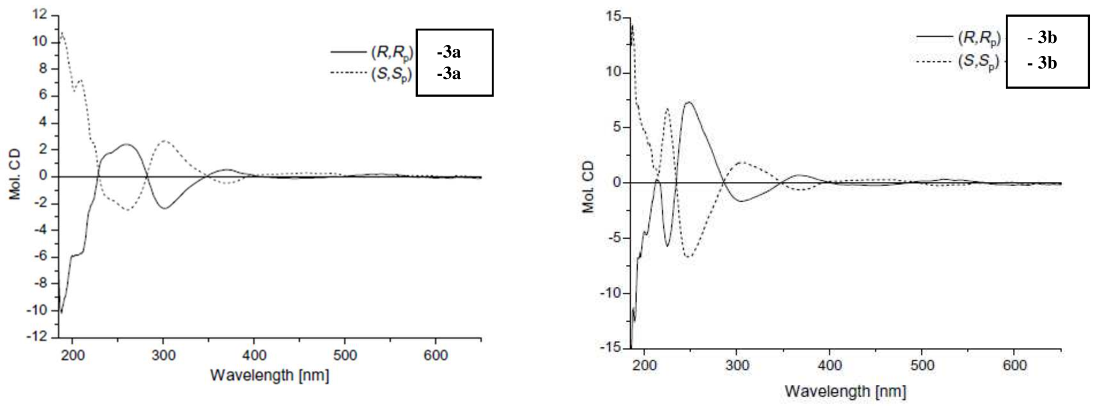


Figure 3. The CD spectra a pair of **3a** and **3b**

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In contrast to above data, much less information is available about nucleophilic addition to carbonyl group in metalorganic compounds specially in the case of metalorganic chiral ketones. Mathey and co-workers[9] shown that reduction of 2-acetylo-3,3',4,4'-tetramethyl-1,1'-diphosphafaferrocene using sodium borohydride lead to obtain a diastereoisomeric mixture of alcohol in ratio 2:1, but they do not established absolute configuration of more important product. Moreover, Roberts et al[23] shown that reduction of 2-acetylo-3,4-dimethylophosphaferrocene lead to receive mixture of equimolar diastereomeric alcohols. Due to this fact that only *exo* attack is possible, during reaction two reactive conformers of these *cis* and *trans*-ketones were present. These results prompted me to answer to the question if the reduction of 2-propionyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene **4** using $BH_3 \cdot Me_2S$ (BMS) complex will lead to stereoselective product. For this purpose, the compound **4** has been used due. If this reaction is stereoselective only earlier suitable alcohols described in paper **H2** can be obtained. Literature reports and previously received results which show that reduction of acetylene derivatives is not stereoselective, prompted me to perform theoretical calculation of energy of suitable conformers **4**. These calculations have been performed using density functional theory with B3LYP potential and 6-31G* base. In contrast to the case **1** to the obtained data shows that *s-trans* configuration is thermodynamically preferred. The energy difference between suitable conformers **4** is 4,0 kcal·mol^{-1} and according to the Boltzmann distribution provide to obtain both conformers in relation 99,9% to 0,1%. Additionally, the energy of transition state between *s-cis* and *s-trans* configuration is over 10 kcal·mol^{-1}. The reliable confirmation of this assumptions was crystallographic structure (Figure 4) of compound **4** in which configuration of carbonyl motifs is in *trans* position.

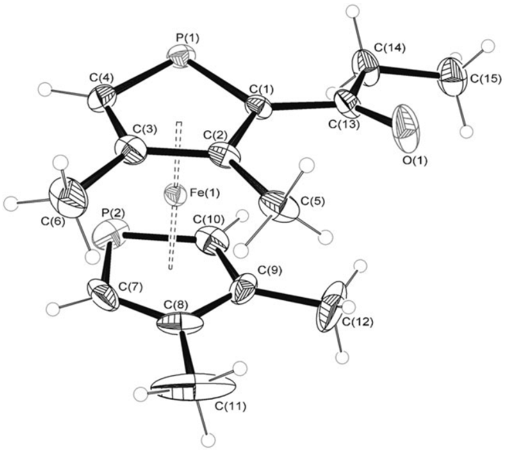


Figure 4. Structure of 2-propionyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene

Received structure lead to assumption that calculated structure could be incorrect because in preferred conformation the carbonyl atom of oxygen is below phospholic ring plane but in the structure, obtain form calculation this atom is under phospholic ring plane, closer to iron atom.

The analysis of the crystal packing show interaction (2,423(3) Å) between oxygen atom and hydrogen atom of methyl C5H group with neighbouring molecule. The particles connected via this interaction form a chain in (101) direction and this effect is responsible for a position of carbonyl group. It wort to mention that in received structure the distance between phosphorus atoms and dihedral angle P1-Cg1-Cg2-P2 are 3,610 Å and 42,86° respectively.

During reduction of **4** using BMS complex the product **5** has been obtained which were compared to the product of reaction compound **1** with EtMgBr. Based on obtained results it was found that both reactions lead to receive the same product. The configuration of this product cannot be established using NMR spectra and additionally this compound was an oil phase. Because of that I decided to transform this product to crystalline derivatives using reaction with labile complex of $W(CO)_5THF$. Obtained structure is presented in Figure 5.

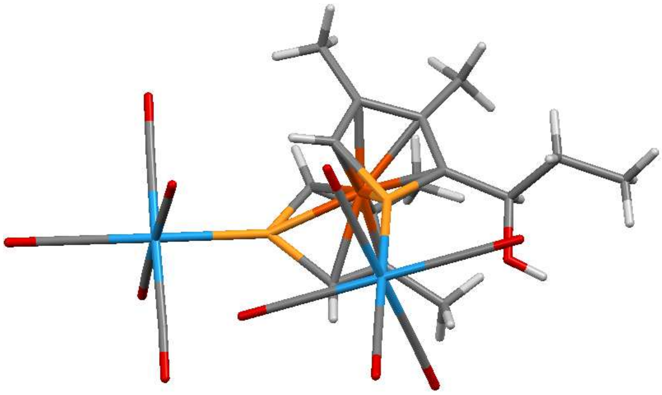
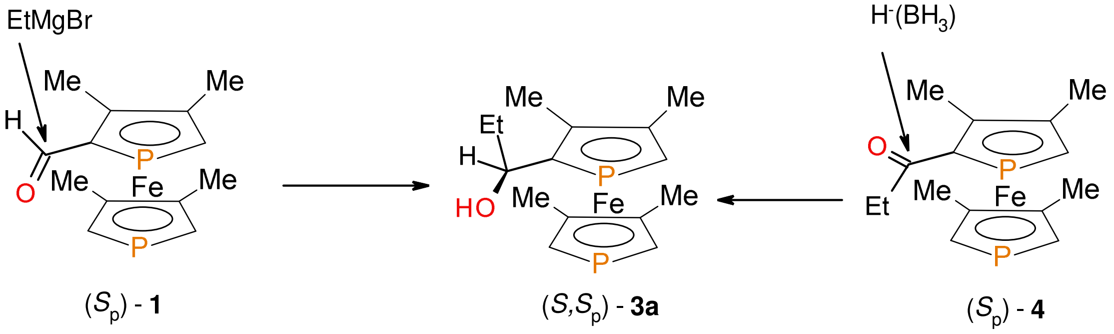


Figure 5. Structure of complex **5** with two $W(CO)_5$ species.

This structure is very similar to obtain earlier structure of phenyl derivative **3b**. Presented data shows that stereoselective reduction of propionyl derivatives of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene using BMS is possible to perform. The reduction reaction is different in the case of acetylene derivatives,[9,24] in which probably a both conformers of substrate in solution are present. These data show little differentiation of methyl group and carbonyl atom of oxygen whereby the rotation around C-C=O bond cannot be inhibited in both analysed nucleophilic addition (paper H2 and H5).

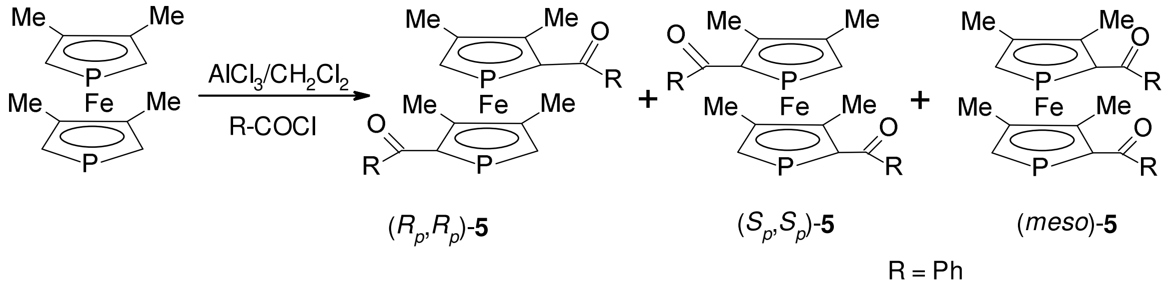
Nucleophile attack take place form *exo* site what in the case of inhibited or absence of rotation lead to the same product with determined configuration. This examples also show that planar chirality in these types of compounds can control absolute configuration the next stereogenic centre.[3] The directions of possible attack are presented in Scheme 3.



Scheme 3. Comparison of stereochemistry of nucleic addition reaction

The next element shown in this report is synthesis and enantiomeric separation disubstituted of 1,1'-diphosphaferrocene derivatives with C_2 symmetry. Such derivatives synthesis was described in literature by Mathey et al,[9,13,25–27] who obtained 2,2'diacetyl derivatives which have not been separated on enantiomers. Moreover, the authors did not show which of obtained fraction is *meso* or *rac* mixture. The first separation on enantiomers of 2,2'-bisphenyl-3,3',4,4,'-tetrematethyl-1,1'-diphosphaferrocene has been described by Fu and co-workers[13] in 1998 using preparative High performance column chromatography on column with chiral phase (DiacelChiracel OD). Next method allows to obtain chiral depravities of 1,1'-diphosphaferrocene with C_2 symmetry has been shown by Carmichel et al where the authors achieved (*S*)-(+)-2,2'-bis (tert-buthylodimethylsilyl) -1,1'-diphosphaferrocene enantiomer using synthesis of diastereomeric complexes with palled.[26]

In the first step of my research I have developed a synthesis method of 2,2'-dibenzoil-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene – paper **H2**. The expected derivatives were obtained using Friedel-Crafts reaction. This reaction leads to receive enantiomeric mixture of (S_p,S_p) and (R_p,R_p) and also *meso* form. This conclusion was presented in Scheme 4.



Scheme 4. Synthesis of 2,2'-dibenzoil-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene

In this paper **[H2]** I was shown a separation of obtained compounds on *rac* pair and *meso* compound using column chromatography. Unfortunately, I filed to receive pure enantiomers at this stage. On the ^{1}H NMR spectrum a signal of H5 proton has "unnatural" pattern, which was shown in Figure 6.

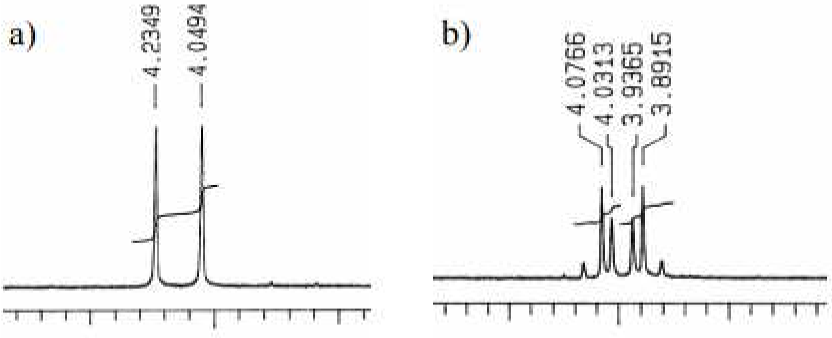


Figure 6 ^{1}H NMR spectrum, signal of H5 proton of 2,2'-dibenzoil-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene a) *rac* b) *meso*

This problem has been previously noticed by Mathey et al in 1992 in the case of 2,2'-(diphenylphosphine) derivatives but the details were not presented.[25] Moreover, the spectra was also not submitted. The reliable description of this effect resulting from magnetic non-equivalence of ^{31}P atoms were collected in paper **H7**. Moreover, the paper **H2**, contain X-ray structure *meso* form as derivatives in which phosphorus atoms were coordinated to $W(CO)_5$ groups.

Based on obtained data, it was showed that *meso* form characterized by less polarity as well as that *rac* form is more polarity taking to a count separation on chromatographic column. This discovery allows to obtain a compound configuration based on NMR spectra. For this purpose, i.e. identification of *rac*/*meso* form in these types of derivatices, the ^{1}H NMR spectrum of phospholic proton H5 has been used.

During my research, I was shown that High performance liquid chromatography can be employed in received chiral 1,1'-diphosphaferrocene derivatives, mono- with C_1 symmetry as well as bis- substituted with C_2 symmetry. There results were described in papers **H6** and **H7**. In paper **H6** I was presented that we can obtain a pure enantiomer of 2,2'-diacetylo-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene **6** using column with chiral Lux Cellulose-2 (Sophadex company) which is a modified cellulose by tri(3-chloro-4-methylpahenylocarbamate).

This separation can be performed using hundreds of milligrams in short time. In the case of using modern HPLC the closed-circuit solvent to minimalized the costs can be applied. This process can be also automatized. The structure of one of enantiomers of ((S_p,S_p)-**6**) was determined employed X-ray analysis and showed in Figure 7.

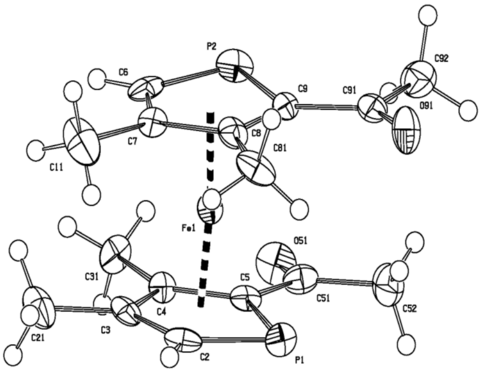


Figure 7. X-ray structure of (S_p,S_p)-2,2'-diacetylo-3,3',4,4'-tetramethyl-1,1'-diphosphafaferrocene

In this structure the distance between phosphorus atoms and dihedral angle P1-Cg1-Cg2-P2 are 4,238Å and 101.3 (5) ° respectively. For separated enantiomer pair **6** the CD spectra were also performed (Figure 8).

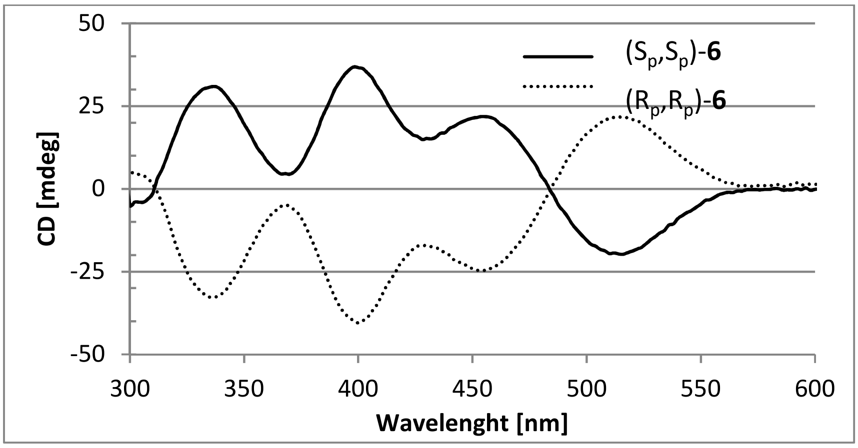


Figure 8. CD spectra for (S_p,S_p)- i (R_p,R_p)- 2,2'-diacetylo-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene

I was also found that this spectrum has characterized patter, therefore in the next step I proposed to using CD spectra for identification of absolute configuration of these types of compounds. This approach was supported by experimental and theoretical data collected in another paper, H7, where increased the number of analysed CD spectra and also presented theoretical calculation in order to verify the predictability of the CD spectra in these types of compounds.

In the next step of my research I decided to using above mentioned approach to receive other enantiomers. For this purpose, the earlier synthetized and described by me derivatives have been chosen i.e. 2-propionyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene **4**, 2,2'-bispropionyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene **6** and 2,2'-bisbenzoyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene **5**. These compounds were obtained using Friedel -Crafts reaction. A very big facilitation was the ability to use normal phase and reversed-phased column chromatography.

Obtaining a good separation in the case of normal phase for propionyl derivatives were not possible. The separation conditions of enantiomers are collected in table 1.

rac-derivative	Mixture of solvents	Ratio	Retention time and configuration of eluted fraction
4	Methanol: H_2O	9:1	(S_p) 15.9 : 17.6 (R_p)
6	Hexane : IPA	20:1	(R_p)[a] 5.7 : 6.8 (S_p)[a]
7	Methanol : H_2O	9:1	(S_p,S_p)[a] 10.7 : 13.2 (R_p,R_p)[a]
5	Hexane : IPA	40:1	(R_p,R_p)[a] 6.1 : 7.1 (S_p,S_p)[a]

Table 1 Separation conditions of enantiomers [a]-absolute configuration determined by X-ray structure.

The absolute configuration of three derivatives has been determined using X-ray crystallography and in the case of **4** derivatives for this purpose the CD spectrum have been used. Due to the use CD spectra for estimation of absolute configuration I decide to expand studies of this issue. I also decided to analyse the impact of substituent configuration in **2**c position and transition configuration in the case of mono-derivatives on CD spectra. Moreover, I intended to answer the question if the absolute configuration of mono and di-substituted can be obtain using CD spectra. These theoretical calculations were performed using advanced approach. First of all the geometry optimisation employed DFT B3LYP[28] method and 6-31G(d) base have been performed and then CD spectra were simulated using TDDFT B3LYP approach and different base TZVP[29] or aug-cc-VTZ[30,31]. Moreover, model IEFPCM has been applied to determine influence of solvent. These theoretical calculation lead to answer to the basic question: which method TDDFT provides the best reliable pattern of CD spectra and what is an impact of substituent configuration in **2** position (in the case of mono and di-substituted) on these CD spectra. According to the literature report[32,33] it was found that simulated CD spectra characterized by some position band errors about 0.31 eV but shape, number or and sign of Cotton effect correspond to experimental spectra. It was also found that better agreement theoretical data with experimental results can be obtain using in simulation the solvent effect. There was not also a significant effect of substituent configuration in **2** position on CD spectrum in diagnostic range. The theoretical and experimental data were collected in Figure 9-14.

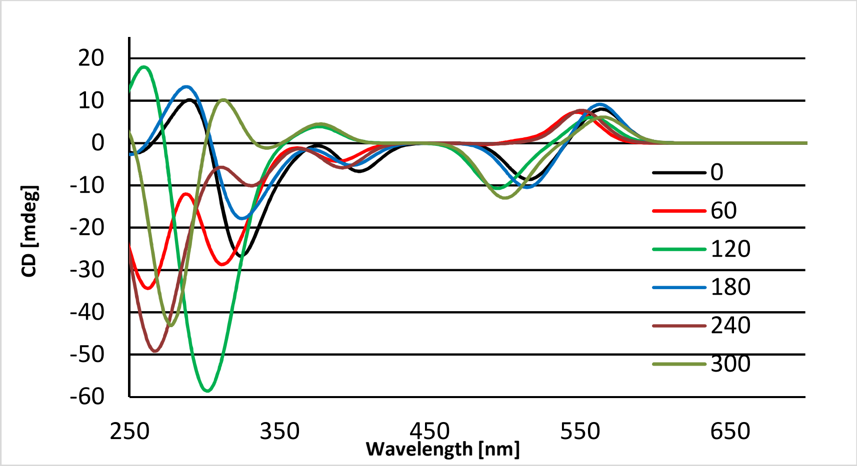


Figure 12. The graph of the theoretical CD spectrum depending on the torsion angle P1-C2-C7-O1 dla (*R*$_p$)-**4**

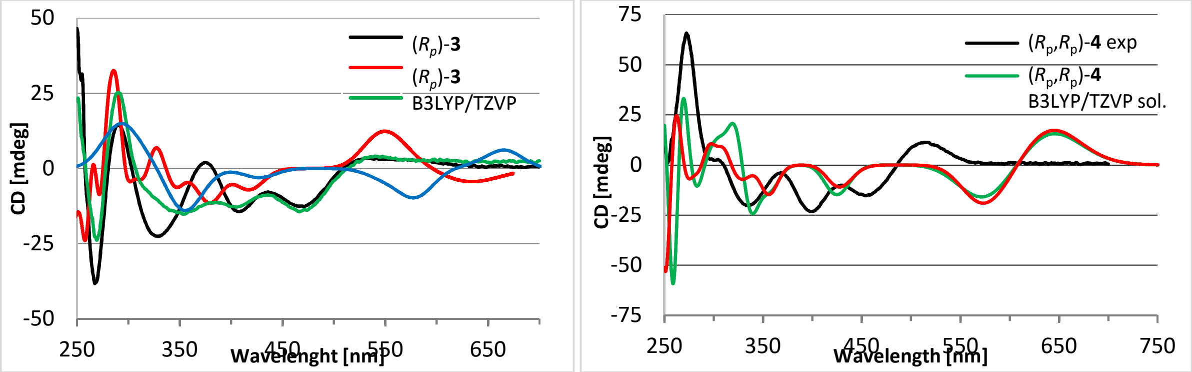


Figure 13 and 14. Comparison of theoretical and experimental spectra for (*R*$_p$,*R*$_p$)-**56** (*R*$_p$)-**7**, (*R*$_p$,*R*$_p$)-**5**,

Based on the obtained information I found that in the case of 1,1-difosfaferrocenu derivatives:

-in order to determine the absolute configuration would be the best region in the range of 350-600 nm which are present mainly band related to d-d transitions and/or "charge transfer" of the metallocene systems;

I suggested the following rules to determine the absolute configuration:

> -analyzing the CD spectrum from the lower energy for (*S*$_p$) or (*S*$_p$,*S*$_p$) derivative the Cotton effect occurs with a minus sign and then two to three effects Cotton with a plus sign;
>
> -analyzing the CD spectrum from the lower energy for (*R*$_p$) or (*R*$_p$,*R*$_p$) derivative the Cotton effect occurs with a plus sign and then two to three effects Cotton with a minus sign;

In the paper **H7** a large number of X-ray data have been reported where the structure of analyzed compound can be obtain without transformation in W(CO)5 derivatives. The derivatives of 7 characterized by a large distance between phosphorus atoms and dihedral angle P1-Ct1-Ct2-P2 which is ±155°. In the case of (R_p,R_p)-**5** these dihedral angle is only -29,6°. Additionally, in (S_p,S_p)-**7** compound a three independent molecules in unit cell two of which are very similar and show dihedral angle P1-Ct1-Ct2-P2 19,2° and 17,7° have been observed. Moreover, the third molecule is characterized by unusual value of dihedral angle (P1-Ct1-Ct2-P2 116,4°) and large P1-P1' distance. Similar effect was obtained from theoretical calculation in solution which were carried out to simulate CD spectra. The unexpected observations which were observed in paper **H2** and developed in the **H6** i **H7** was magnetic nonequivalence of phosphorus atoms. This result is noticed on ^{1}H NMR spectra which in some cases the proton signal of phospholyl H5 represents AA′XX′ (Figure 6) spin system and in many other show presents doublet or doublet of doublets. Carmichael[24] et all show established such description but he has not made a detailed study of this issue. The firs reliable specification of NMR spectra for 2,2' disubstituted derivatives has been shown in paper H7 where I have shown that the ^{31}P NMR spectrum (without proton decoupling) represent AA′XX′ spin system and additionally enables appointsment of J-coupling $^2J_{P\text{-}P'}$ which is typical over 20Hz. Moreover, the ^{13}C NMR spectra should be properly characterized as a AA′X or ABX spin systems. According to the description proposed for inter alia complexes with two phosphine[32], diphosphine[32,33] or dimers phosphol[34]. In order to make a full description ^{13}C NMR spectra for second order spin systems the theoretical simulations have been performed because the determination of J-coupling is not possible to obtain directly from experimental spectra. Figure 15 show a comparison of part of experimental and theoretical spectrum.

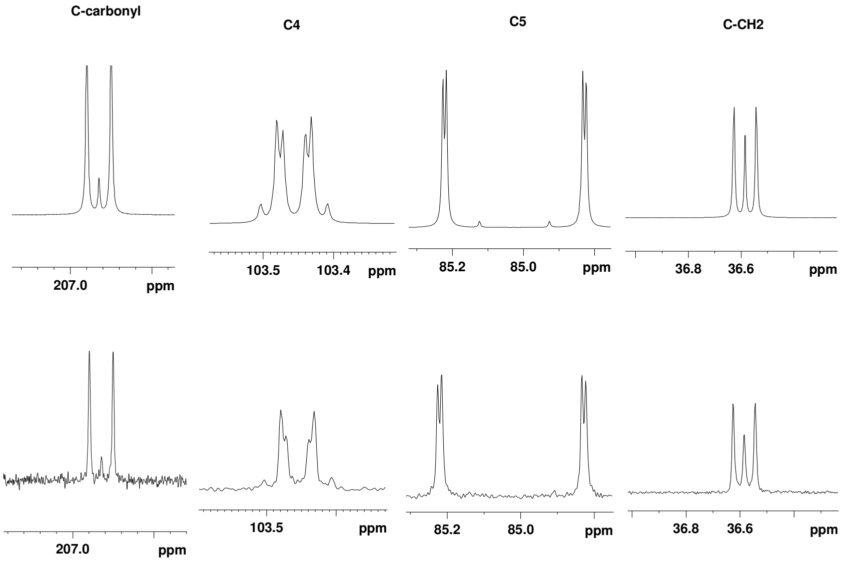


Figure 15. Comparison of simulate (top) and experimental (bottom) $^{13}C\{^{1}H\}$ NMR spectra for *rac* **5.**

In the **H7** paper I was shown that J-coupling $^{2}J_{P\text{-}P'}$ can be observed also in the case of *meso* compounds in where I found that the inequivalence of atoms is characteristic only for *racemic* compounds. Based on theoretical calculations of geometry respective compounds and crystallographic data I confirm that the J-coupling and also its value is dependent of dihedral angle P1-Ct1-Ct2-P2 which could be described by Karplus equation.[35,36]

In paper **H2**, **H3**, **H5** I was used the possibility of coordination of phosphorus atoms to metallic centre in $W(CO)_5$ complex. The ability to coordination of phosphorus atoms to metallic centre have been already widely described earlier.[37] However, the possibility of coordination of 1,1'-diphosphaferrocene to metallic centre in metallic cluster have not been described.

The studies showing this issue I presented in paper **H4** where the possibility to obtain a complex in which both phosphorus atoms are coordinated to both metals in bimetallic complex. To this research the $Re_2(CO)_{10}$ complex has been chosen due to fact that in the case of $Mn_2(CO)_{10}$ compound the linear complexes with only one connection between phosphorus atom (in 1,1'- diphosphaferrocene) and metal have been received. This result may be due to too little Mn-Mn bond length where in the case of Re-Re bond this value is much longer.

In the papers **H2**, **H3**, **H5** the ability of phosphorus atoms coordination to metallic centre in $W(CO)_5$ complex has been used. This property has been previously reported.[39] Moreover, the possibility of coordination 1,1'-diphosphaferrocene to metallic centres in metalloclusters has not been presented. This studies may be import, inter alia, in the case of employed chiral

1,1'diphosphaferrocene derivatives on C_2 symmetry in asymmetric catalysis or studies of interactions of in these compounds with surface.

Obtained research results were collected in paper **H4** in which I showed the possibility of received a complex in which both phosphorus atoms are coordinated to two metals in bimetallic complex. In these research I chosen $Re_2(CO)_{10}$ complex because in the case of $Mn_2(CO)_{10}$ the linear complexes have been obtained[39] in which only one metal is connected to phosphorus atom in 1,1'-diphosphaferrocene.

Probably, it is a result of too small a Mn-Mn bond length, in the case of rhenium a bond length is longer which allow to receive expected product.

As starting material was used labile complex such $[Re_2(CO)_8(CH_3CN)_2]$. Which easy form predicted complexes with 3,3',4,4'-tetramethyl-1,1'-diphosphaferrcene. It was characterised using inter alia X-ray crystallography and obtained structure was presented in Figure 16.

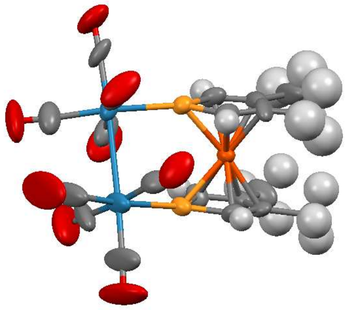


Figure 16. Structure of 3,3',4,4'-tetremathyl-1,1'-diphosphaferrocenem complex with $Re_2(CO)_8$

In this structure the Re-Re bond length is 3,095 Å and it is bigger than $Re_2(CO)_{10}$ – 3,041 A but is similar to bond length in classic bisphosphonic complexes i.e. (Z)-$Ph_2PCH=CHPPh_2$. The distance between phosphorus atoms and dihedral angle P1-Cg1-CG2-P1'were 3.279 Å and 17,0°, respectively.

The presented research shows that:

- I developed enantiomers separation method of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene-2-carobxyaldehyde;
- I established its absolute configuration;
- I demonstrated that in these cases of compounds the planar chirality has impact on absolute configuration new chiral centre sp^3 in nucleophilic addition reactions;

-I showed that high resolution column chromatography approach with chiral column can be used to obtain pure enantiomers of mono and bis-derivatives of 1,1'-diphosphaferrocene;
-I showed that circular dichroism spectroscopy lead to obtain absolute configuration of these types of compounds and also I proposed suitable rules;
- I carried out reliable description of ^{1}H, ^{13}C, i ^{31}P spectra with unusually pattern in the cases of bis-derivatives of 1,1'-diphosphaferrocene;
-I showed that 1,1'-diphosphaferrocene derivatives have ability to performed coordination complexes with metal clusters and have configurations in which both phosphorus atoms are linearly arranged close to each other;

In future, I plan to focus on:
- application of chiral optics method to determine absolute configuration of metallocene and heterometallocene.
-applications of bis –derivatives of 1,1'-diphosphaferrocene in asymmetric catalysis;
-application of DNMR approach in studies of dynamics and the possibility of rotation substituents in 2 positions or in above mentioned derivative;
- Studies of interaction in1,1'-diphosphaferrocene derivatives with surface;
-develop my interests of application of nuclear magnetic resonance in studies of natural compounds.

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