Annex No. 3

SELF-PRESENTATION

1. Names and surname

Zygmunt Grzegorz Flisak

2. Scientific degrees

2003 – Doctor of chemical sciences degree conferred by the resolution of the Faculty of Mathematics, Physics and Chemistry, University of Opole, dated December 11, 2013. Ph.D. dissertation entitled *Study of the coordinative ethylene polymerization over Ti, V, Zr, Hf complexes using computer molecular modeling.* Supervisor: D.Sc. Krzysztof Szczegot, assoc. prof. Ph.D. dissertation with honors.

1997 – Master of Science, Engineer diploma. Major: chemical technology, specialty: chemistry and technology of polymers. Faculty of Chemistry, Wroclaw University of Science and Technology.

3. Information on current and previous employment at the research institutions

2004 – to present: Assistant Professor, Faculty of Chemistry (before September 30, 2008 Faculty of Mathematics, Physics and Chemistry), University of Opole

1998 – 2004: Research and Teaching Assistant, Faculty of Mathematics, Physics and Chemistry, University of Opole

4. Scientific achievement according to the article 16 paragraph 2 of the Act on Academic Degrees and Academic Title as well as Degrees and Title in Art, dated March 14, 2003 (Dz. U. 2016 item 882 with changes by Dz. U. 2016 item 1311)

Scientific achievement is a series of monothematic publications.

a) Title of scientific achievement

DETERMINING THE ROLE OF SELECTED LIGANDS AND COCATALYSTS IN THE COORDINATIVE OLEFIN POLYMERIZATION PROCESS USING THE METHODS OF COMPUTATIONAL CHEMISTRY

b) List of publications constituting scientific achievement according to the article 16 paragraph 2 of the Act

The scientific achievement consists of a series of 11 original papers and one review. The references to these papers are denoted with the **H** prefix. The total *Impact Factor* (IF) calculated according to the publication date (unless otherwise indicated) by using the *Journal Citation Reports* database is equal 54.195 for this series. The citation number according to the *Web of Science* database is denoted by the CN symbol. The total citation number for the series of publications constituting scientific achievement is equal 165 without autocitations (as of May 8, 2018). Three papers have a single author and the students were the coauthors of another two papers. The corresponding author's name is indicated with the envelope sign (✉).

H1 Z. Flisak, T. Ziegler ✉, DFT Study of Ethylene and Propylene Copolymerization over a Heterogeneous Catalyst with a Coordinating Lewis Base, *Macromolecules* **2005**, *38*, 9865–9872, IF=4.024; CN=32.

I participated in the research design and carried out DFT calaculations related the the energetic profiles of propagation and termination reactions. I also developed the method of stochastic simulation and carried out relevant calculations using the custom-made software. Participated in the interpretation of the results. Took part in manuscript preparation and its editing after the reviews. I estimate my contribution at 70%.

H2 Z. Flisak ✉, Multidentate Tetrahydrofurfuryloxide Ligand in a Ziegler-Natta Catalyst Studied by Molecular Modeling, *Macromolecules* **2008**, *41*, 6920–6924, IF=4.407; CN=14.

Unassisted work. My contribution is 100%.

H3 R. A. Stapleton, J. Chai, A. Nuanthanom, Z. Flisak, M. Nele, T. Ziegler, P. L. Rinaldi, J. B. P. Soares, S. Collins ✉, Synthesis of Low Density Poly(ethylene) Using Nickel Iminophosphonamide Complexes, *Macromolecules* **2007**, *40*, 2993–3004, IF=4.411; CN=26.

I developed the method of stochastic simulation, carried out appropriate calculations using the custom-made software and employing the results of DFT calculations that I received. Participated in discussions with experimentalists, interpretation of the results and writing the part of the manuscript relevant to the stochastic simulation. My contribution is ca. 30%.

H4 Z. Flisak, T. Ziegler ✉, 'Dormant' secondary metal-alkyl complexes are not omnipresent, *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15338–15342, IF=9.643; CN=11.

I participated in the design of research. Carried out the DFT calculations related to the separation of the counter ion, monomer uptake and its insertion into the carbon–carbon bond in the presence of the counter ion. participated in the analysis of the results, manuscript writing and its editing after the reviews. I estimate my contribution at 70%.

H5 Z. Flisak ✉, Theoretical study of isomerism in phenoxyimine-based precursors of coordinative olefin polymerization catalysts, *J. Mol. Catal. A* **2010**, *316*, 83–89, IF=2.872; CN=9.

Unassisted work. My contribution is 100%.

H6 Z. Flisak ✉, P. Suchorska, Structural Flexibility of Bis(phenoxyimine) Titanium Complexes in the Early Stages of Olefin Polymerization Process: A DFT Study, *Organometallics* **2010**, *29*, 6196–6200, IF=3.888; CN=6.

I designed the subject and scope of research. As the advisor, supervised the calculations carried out by the student within her master's thesis. Carried out the remaining DFT calculations, performed the interpretation of results, wrote the manuscript and edited it after reviews. I reckon my contribution at 80%.

H7 Z. Flisak ✉, A. Shiga, Counter anion binding in the phenoxyimine, salan and metallocene olefin polymerization catalysts activated with perfluorophenylborate, *J. Organomet. Chem.* **2012**, *718*, 124–130, IF=2.000; CN=3.

I designed the scope of research. Carried out calculations related to the geometry optimization and energy decomposition. Participated in the interpretation of data and manuscript preparation. Edited manuscript after reviews. I reckon my contribution at 70%.

H8 Z. Flisak ✉, Thermodynamics of Titanium and Vanadium Reduction in Non-Aqueous Environment Calculated at Various Levels of Theory, *J. Phys. Chem. A* **2012**, *116*, 1464–1468, IF=2.771; CN=2.

Unassisted work. My contribution is 100%.

H9 Z. Flisak ✉, G. P. Spaleniak, M. Bremmek, Impact of Organoaluminum Compounds on Phenoxyimine Ligands in Coordinative Olefin Polymerization. A Theoretical Study, *Organometallics* **2013**, *32*, 3870–3876, IF=4.253; CN=6.

I designed the subject and scope of research. As the advisor, supervised the calculations carried out by the student within her master's thesis. Directed the interpretation of data and participated in it. Developed the manuscript and edited it after reviews. I reckon my contribution at 70%.

H10 Z. Flisak, W.-H. Sun ✉, Progression of Diiminopyridines: from Single Application to Catalytic Versatility, *ACS Catal.* **2015**, *5*, 4713–4724, IF=9.307; CN=49.

I designed the scope of the review. Performed the critical analysis of the literature, emphasizing current achievements in experimental and theoretical research on the complexes bearing bis(imino)pyridine complexes, their application in the areas beyond the coordinative olefin polymerization and outlined the perspectives of future research. I wrote the manuscript and participated in its revision. I estimate my contribution at 80%.

H11 J. Ba, S. Du, E. Yue, X. Hu, Z. Flisak, W.-H. Sun ✉, Constrained formation of 2-(1-(arylimino)ethyl)-7- arylimino-6,6-dimethylcyclopentapyridines and their cobalt(II) chloride complexes: synthesis, characterization and ethylene polymerization, *RSC Adv.* **2015**, *5*, 32720–32729, IF=3.289; CN=24.

I took part in the research design. Carried out DFT calculations and performed the interpretation of the results of these calculations. Correlated the results of experimental and theoretical research. Particiapted in manuscript writing and its revision after the reviews. My contribution is estimated at 40%.

H12 H. Suo, Y. Zhang, Z. Ma, W. Yang ✉, Z. Flisak ✉, X. Hao, X. Hu ✉, W.-H. Sun ✉, 2-Chloro/phenyl-7-arylimino-6,6-dimethylcyclopenta/*b*/pyridylnickel chlorides: Synthesis, characterization and ethylene oligomerization, *Catal. Commun.* **2017**, *102*, 26–30, IF(2016)=3.330; CN=0.

I participated research design, analyzed experimental and theoretical results searching for the interplay between them and took part in manuscript writing. My contribution is ca. 30%.

c) Report on the objective and the results of the research together with the discussion on potential applications

i. Introduction

The polyolefins make up the most widely applied group of commodity plastics. Although the low-pressure polymerization of olefins was discovered 65 years ago and the scientists dispute whether the coordinative polymerization can be referred to as the exploited field of science, many research centers still conduct extensive research in this area. Based on the results of these efforts, it may be concluded that – apart from the enzymatic catalysis – the process of

coordinative olefin polymerization is the most advanced example of selective chemical synthesis [1].

The knowledge related to the coordinative olefin polymerization is usually gained as a result of laborious empirical study, where serendipity is the essential prerequisite of success. Despite the enormous amount of data collected, the consecutive decades still bring around breakthroughs. The development of aluminoxanes as cocatalysts in the 1980s can be considered as one of them, giving rise to the so-called metallocene revolution and the revived interest in coordinative olefin polymerization. This surge led to the postmetallocene catalytic systems at the end of the 1990s; simultaneously the previously unknown possibility of promoting the process by the complexes of group 8–10 metals was discovered. The steeply growing library of available ligands, central atoms, cocatalysts and their possible mutual combinations imposed the introduction of high throughput screening into the laboratory praxis. Understanding the mechanism of the process at the molecular level by the experiments carried out *in silico* became indispensable.

The coordinative polymerization starts with the reversible uptake of the olefin molecule to the active site, leading to the formation of a π-complex. Then the reaction proceeds through the four-membered transition state and the product features a free coordination site, which enables subsequent uptake of another olefin molecule. To the best of my knowledge, the first paper describing the ethylene insertion into the metal–carbon bond according to this mechanism investigated by means of computational chemistry was published 40 years ago [2] and employed a simplified model of the active site. The advent of the density functional theory as a method of choice applied to the description of organometallic compounds [3] together with the simultaneous increase in the available computational power facilitated the exploration of more complex models that include the ligands within the metallic center coordination sphere, the cocatalyst, the solvent and reflect the weak interactions between the components of the catalytic system. Since the DFT methods do not reach the so-called chemical accuracy (the error of the order of 1 kcal/mol), achievieng merely the qualitative agreement of the thermodynamic and kinetic calculations with the results of experimental research has been sufficient thus far. However, the tendency to develop the computational protocols based on carefully selected combinations of density functionals and basis sets has become evident in the recent years [4–6], at least with respect to the computation of relative values.

It is expected that the efforts put into understanding the coordinative polymerization by means of theoretical methods will culminate in the possibility of designing new catalytic systems of the properties defined in advance.

d) Scientific objective, results and discussion

Coordinative olefin polymerization has been the object of my study throughout my career at the University of Opole. I noticed the growing number of scientific papers devoted to the application of theoretical methods to investigate this process long time ago; yet many aspects still remain unresolved, especially the widely understood roles of the ligand and the cocatalyst, and – first of all – the mutual interactions of these components. This fact prompted me to undertake the investigations within this area aiming at emphasizing the importance of theoretical study for the prospective catalyst design and the industrial applications.

Classical heterogeneous systems. The inspiration to carry out this research was the fact that the classical Ziegler–Natta systems supported on $MgCl_2$ and modified with the Lewis base have long been the object of experimental study at the Faculty of Chemistry, University of Opole [7, 8]. In this setting, the possibility of understanding the factors that govern the ethylene and propylene copolymerization promoted with such a catalytic system within the project executed

in prof. Tom Ziegler's group at the University of Calgary (Canada) in the cooperation with the industrial partner, Eastman Chemical Co. with the headquarters in Longview, TX (USA) turned out to be especially attractive. The University of Calgary was the academic center with one of the best records of achievements in theoretical investigation of olefin polymerization at that time. Within the [**H1**] paper, I carried a series of calculations related to the barriers of ethylene and propylene insertion over different active sites containing tetrahydrofuran (THF) as a Lewis base coordinated to the titanium atom at the oxidation state of three and adsorbed on the $MgCl_2$ surface. The active sites were constructed according to the previous works of the group [9–11]. My calculations yielded the three-dimensional matrix of insertion rate constants based on the Arrhenius-Eyring equation:

$$r_{a,b,c} = \frac{kT}{h} \exp(\frac{-\Delta G^{\#}_{a,b,c}}{RT})[C_n H_{2n}][M], \tag{1}$$

where the a, b and c indices define the separate transition states characterized by three possible alkyl groups attached to the metal atom and corresponding to the model of the growing polymer chain (n-propyl, 2-butyl, *iso*-butyl), five monomer orientations with respect to the metal–carbon bond (one for ethylene and four for propylene, i.e. 1,2-*re*; 1,2-*si*; 2,1-*re*; 2,1-*si*) and three tetrahydrofuran orientations with respect to the support (representing three isomeric active sites), respectively. $\Delta G^{\#}_{a,b,c}$ denotes the insertion Gibbs free energy (in reality, only the energy values were available) and $[C_nH_{2n}]$ and [M] stand for the olefin and active site concentrations, respectively. Based on the results of DFT calculations I was also able to build the matrix of termination rates containing the $r_{T,a,b,c}$ elements. Two matrices containing 45 elements each turned out to be practically imposible to analyze due to their size; therefore stochastic simulation generating the polymer chains based on the results of DFT calculations was developed. For a selected active site (fixed value of c) and arbitrarily chosen initial value of a, the probability π of an event (insertion or termination) may be determined as relative rate calculated with respect to the sum of all insertion and termination rates for a given active site:

$$\pi_b = \frac{r_b}{\sum_{b=1}^{5}(r_b + r_{T,b})}. \tag{2}$$

Additionally, the probabilities are normalized:

$$\sum_{b=1}^{5}(\pi_b + \pi_{T,b}) = 1. \tag{3}$$

The simulation involves generation of a random number. If this number corresponds to one of the insertion processes, the applicable mer (ethylene or propylene) is added to the polymer molecule. Then the a value is modified correspondingly and the simulation is repeated until the termination is encountered. It must be mentioned that such an approach was applied in the pioneering work [12] for the analysis of the polymer microstructure. The stochastic simulation (and especially its results) may be considered as important achievement of my research, since it provides the bridge between the physicochemical data obtained from theoretical calculations (e.g. insertion and termination barriers), usually difficult for the interpretation by the experimentalists, and the macroscopic properties of the polymer, such as molecular weight and its distribution, which can be directly observed in a laboratory. These two quantities determine the processability of the polymer and therefore are of great importance to the industrial applications. It must be stressed that the curves of molecular weight distribution obtained in my stochastic simulation are similar to the experimental curves registered using the gel permeation

chromatography (GPC). The results of DFT calculations and the stochastic simulation brought me to the conclusion that the ethylene reactivity ratio (ranging from 4.58 to 8.49, depending on the kind of the active site) is by 1–2 orders of magnitude greater than the propylene reactivity ratio (ranging from 0.001 to 0.07). Although this finding may be considered trivial from the experimentalist's point of view [13], earlier theoretical study related to the copolymerization over the catalyst without the Lewis base concluded with the result, which was contradictory to the experimental findings and indicated higher reactivity of the olefin containing three carbon atoms [10].

The subsequent generations of Ziegler-Natta catalysts were modified with multidonor ligands [14]. One of such ligands is the tetrahydrofurfuryl alcohol and the anion derived from it. The experimental study, partially conducted at my home university [7], suggest that its application as an internal Lewis base yields the catalytic system that reaches higher activity in ethylene polymerization comparing with the system modified with tetrahydrofuran. These reports inspired me to determine the Ti–O bond strength in the compounds containing tetrahydrofurfurol by means of computational chemistry within the study pursued before obtaining the Ph.D. degree [15]. The experience gained in prof. Tom Ziegler's group motivated me to continue this research and to make an atempt to explain the influence of this ligand on the selectivity of the catalyst in propylene polymerization [**H2**]. I advocate the statement that the scientific research and teaching activities are inseparable; therefore I came up with the idea of using the Bailar method [16], which is appreciated in teaching coordination chemistry, to delimit the possible structures of the active sites. As a result of this approach, I was able to indicate two feasible models of the active sites and make an essential observation leading to the statement that due to geometric constraints, the number of the active sites for the system under investigation is smaller than this corresponding to the system modified with a monodentate ligand [**H1**]. Therefore I was able to postulate that the stereoregulating properties of the ligand do not only stem from the changes in steric hindrance around the central atom, but also from the elimination of potentially non-selective active sites. Similar conclusions were drawn by Cavallo and coworkers [17]; however, their conclusions were based on the observation of the ligand–support interactions, rather than the ligand–metal interplay, like in Refs. **H1, H2**.

I am convinced that the exprimental and theoretical study of the clasical Ziegler–Natta systems will never stop producing intriguing results: just five years ago it turned out that apparently inactive THF ligand undergoes the ring-opening reaction promoted by the transition metal atom contained in the active site [18].

Metallocene and post-metallocene systems. In the 20$^{\text{th}}$ century, researchers' efforts concentrated on the management of the polyolefin molecular structure and morphology. The discovery of the single-site catalysts was instrumental in this approach, as it was found that the properties of the product depend strictly on the structure of the pracatalyst – the transition metal complex [19]. In some of these systems, the active site can travel along the growing polymer chain according to the mechanism called the *chain walking* [20], which makes it possible to obtain the polyolefins of a varying degree of branching in homopolymerization of only one monomer – ethylene. Such behavior is usually displayed by the catalysts based on the compounds of group 8–10 metals, including the Keim catalysts obtained from the nickel complexes with the iminophosphonamide ligands [**H3**]. The number and the length of branches are determined by the ratio of the *chain walking* probability to the monomer insertion probability. Assuming this is equal to the ratio of the corresponding reaction rates, we can write as follows:

$$\frac{\pi_{cw}}{\pi_{ins}} = \frac{k_{cw}[\beta_0]}{k_{ins}[\pi_0]} = \frac{k_{cw}}{k_{ins}K_{eq} \cdot P}, \tag{4}$$

where π_{cw} i π_{ins} denote the probabilities of *chain walking* and insertion, respectively; k_{cw} oraz k_{ins} are the corresponding reaction rate constants; β_0 stands for the metal alkyl in equilibrium with the corresponding π-complex (π_0) under ethylene pressure of P as defined by the equilibrium constant K_{eq}. The process is amenable by the stochastic simulation, which proceeds along the three channels: primary (1), secondary (2) and higher secondary (3) alkyls. There are three competitive processes in each channel, namely *chain walking* forward leading to the elongation of a branch, *chain walking* backward shortening a branch and insertion. These processes are selected based on a random number and the energetic barriers calculated by menas of DFT, as in Ref. **H1**. The stochastic simulation carried out by me yielded good agreement in the contents of short branches ($\leq C_5$) in the polymer. However, it failed in predicting the relatively high number of branches containing six carbon atoms. This result may suggest that the formation of long branches proceeds *via* the alternative process, which has not been recognized so far – or it may result from adopted simplifications. It is widely known that the structure of the ligand bound to the selected metal atom in the precursor strongly affects the set of *chain walking* and termination barriers [21]; therefore even slight modifications of this structure will severely impact the simulation run and the contents of particular branches in the final material. The mechanism of branching formation, as a subject of great academic and industrial importance, still attracts unabated attention [22].

Early theoretical calculations on the single-site homogeneous catalysts assumed that the model of the active site can be represented the positively charged species containing the alkyl group attached to the transition metal cation and surrounded by the ligands that modify the electronic and steric properties of these species. Adopting such a model leads to the results indicating negligible olefin insertion energetic barriers for the majority of cases. For example, the barriers calculated for the four metallocene and constrained-geometry (CGC) catalysts of different structure do not exceed 10 kcal/mol; moreover, the rudimentary $TiCl_2CH_3^+$ model displays no insertion barrier as calculated by numerous methods and basis sets [5]. This alarming results would suggest that the majority of catalysts should be highly active, which is contradictory to the empirical knowledge. However, it is known that the cationic active site derived from the precursor is always assisted by the counter anion generated from the cocatalyst [23]. Furthermore, the separation of a catalytic ion pair followed by the monomer molecule uptake requires significant amount of energy [24]. Therefore the activity of the catalytic system depends not only on the insertion barrier, but also the energy of the ion pair separation (or olefin uptake barrier if the uptake takes place concomitantly with the counter ion separation).

Having such knowledge at my disposal, I encountered intriguing discrepancy in the literature data. The intuitive phenomenon of drop in activity after the regioerror [25], caused by the formation of the so-called *dormant* active sites, was challenged [26]. This situation motivated me to carry out the theoretical study in this area [**H4**]. As a result, I demonstrated that the slight change in polarity of the solvent determines the rate-limiting step (insertion vs. separation). Furthermore, it turned out that the selected catalytic systems display diferent sensitivity toward the polarity of the polymerization medium. This enabled me to state that the *dormant* active sites, although ubiquitous, are not the universally occurring phenomenon. Not only did these findings contribute to the argument on the *dormant* active sites, but also inspired my other works on the counter anions in the olefin polymerization process.

The reports on single-site catalysts based on complexes of group-4 metals with the phenoxyimine ligands (FI, from Japanese *FenokishiImin*) [27] – see Fig. 1 – can be considered as a milestone in the history of olefin polymerization. I found these systems intriguing because they were the most active homogeneous olefin polymerization catalysts at the time [28]. The complexes exhibit octahedral geometry with two chloride ligands and two bidentate monoanionic phenoxyimine ligands around the transition metal atom. Such geometry induces the existence of five geometrical isomers, of which three possess corresponding enantiomers. There are lit-

erature reports on several dozen of phenoxyimine-based precursors; for the vast majority of them only one isomer of the C_2 symetry, depictively denoted as N,N-*cis*-O,O-*trans*, has been isolated. Together with the accompanying enantiomer, it is shown schematically in the fourth column of Fig. 2. My pursuit of explanation the reason for the occasional deviations from this rule was the origin of the **H5** paper. The Bailar method was applied again [16], together with its implementation [29] supplemented with the custom-made graphical interface beased on the POV-Ray package [30] – see Fig. 2. On the basis of DFT calculations, I succeeded in demonstrating that the single factor determining the isomeric preferences for this group of compounds is the steric hindrance of the substituents attached to the imine nitrogen atom and the deviations mentioned above are related to its extreme values.

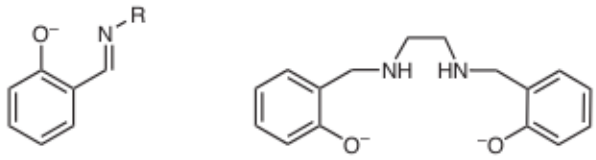

Figure 1: The FI ligand (on the left-hand side) and the salan (on the right). Two FI ligands, in which R = CH_3 and R = C_6H_5 were selected for calculations.

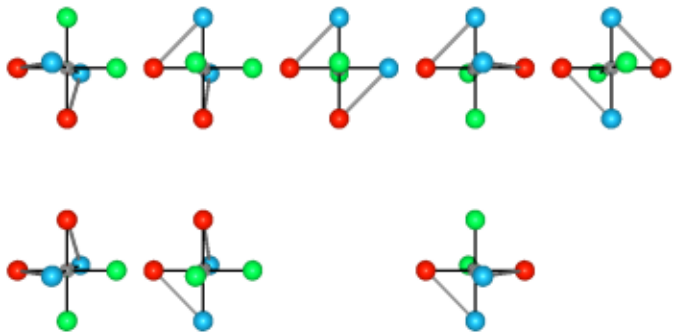

Figure 2: Eight isomers of the phenoxyimine precursor. From the catalysis point of view, only three structures with the chlorine atoms in the *cis* position with respect to each other are important. Each of these three structures has an enantiomer. The titanium atom is located in the middle of the octahedron; the chlorine atoms are green, oxygen – red and nitrogen – blue.

Understanding this relationship was necessary in order to proceed to the next stage of the research on the catalysts with the phenoxyimine ligands. As mentioned before, the dissociation of the catalytic ion pair may constitute the rate-limiting step in the polymerization process. The literature data indicate that considerable energy may be required to separate the counter anion in many cases [24]. This energy may exceed the value of insertion barrier; therefore neglecting the separation process in the theoretical analysis may often lead to erroneous conclusions. Within the **H6** paper, I assigned myself the task of comparing the magnitude of energetic barriers corresponding to the transfer of the counter ion from the first to the second coordination sphere in the titanium catalysts with the phenoxyimine as well as salen [31] ligands and the counter ion derived from perfluorophenyl borate, i.e. transforming the *Inner Sphere Ion Pair* (ISIP) into the *Outer Sphere Ion Pair* (OSIP). The structure of the appropriate ligands is shown in Fig. 1. The analysis of the dependence of the energy on the distance between the titanium atom and the methyl group belonging to the counter anion, compiled for the calculations in the gas phase and shown in Fig. 3 leads to the conclusion that the electronic properties of the ligand considerably influence the magnitude of the barrier corresponding to the counter anion transfer

to the second coordination sphere. This finding, known for a long time [24] is also reiterated in relatively new papers [32]. However, it is astonishing that the counter anion in one of the ion pairs (FI, R = C_6H_5) is very weakly bound and its transfer to the second coordination sphere is practically barrierless. Furthermore, the energy of the ion pair dissociation leading to the separation of the anion and the cation to the infinite distance (Table 1) correlates with the energy of counter anion transfer to the second coordination sphere. Also, the dissociation energies calculated by me are markedly lower than the values published so far for the metallocene systems [24]. The insertion barriers calculated for the FI catalyst (R = C_6H_5) are also very low (4.4 kcal/mol for the isolated cationic active site and 6.9 kcal/mol in the presence of counter ion, respectively). These two facts: weak cation–anion interactions and low insertion barrier – rationalize high activity of the phenoxyimine-based catalysts. It must be mentioned that the **H6** paper is coauthored by the student, who started her research at the third year of study. For me, collaboration with gifted students is the source of inspiration and considerable satisfaction and I am extremely grateful to them.

Table 1: Barriers of counter ion separation to the second coordination sphere and to the infinity

Catalytic system	Separation barrier, kcal/mol	
	to the second coordination sphere	to infinity
Salan	15	66
FI (R = CH_3)	8	50
FI (R = C_6H_5)	≈0	–

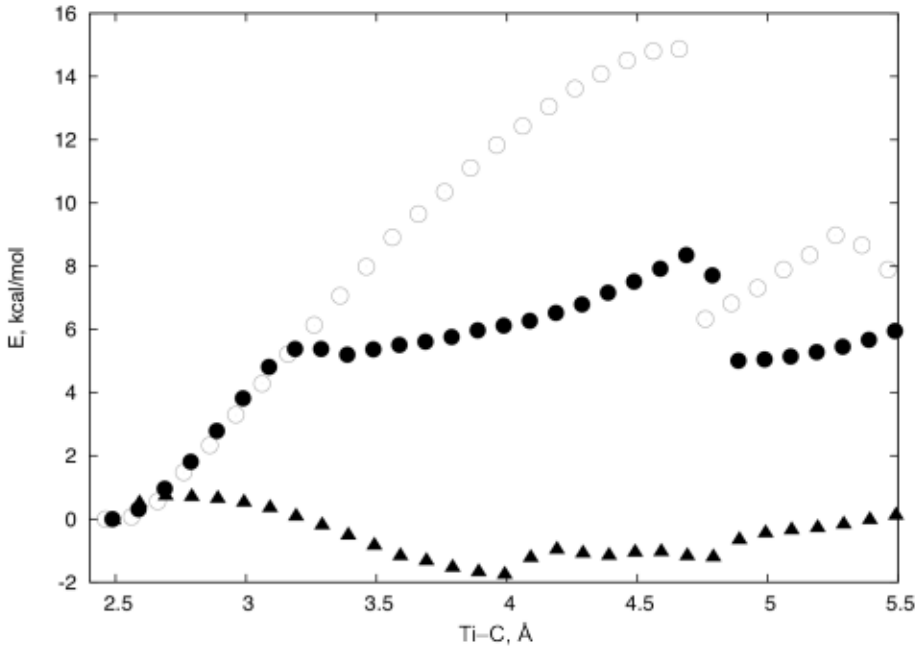

Figure 3: Transfer of the counter ion to the second coordination sphere. Circles denote the salen catalyst, discs – the phenoxyimine catalyst with the methyl group at the nitrogen atom and triangles – the phenoxyimine catalyst with the phenyl group at the nitrogen atom. The energy for individual ion pairs was calculated with respect to the corresponding equilibrium structures.

The discovery of unexpectedly weak interactions in the FI-based catalytic ion pairs prompted

me to widen the research on this subject using additional tools. I demonstrated that among the selected metallocene and post-metallocene systems, the phenoxyimine precursor bears the most negative charge [**H7**]. The nature of the interactions in the catalytic ion pair was investigated by means of Energy Decomposition Analysis (EDA) [33], successfully utilized in the description of organometallic compounds that are important for olefin polymerization [34]. The method allows to decompose the total energy of interaction between two fragments into four contributions:

$$\Delta E_{total} = \Delta E_{dist} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}, \tag{5}$$

where ΔE_{dist} corresponds to the energy related to deformation of fragments from their equilibrium geometry to the adduct geometry, ΔE_{elstat} constitutes the energy of electrostatic interaction, ΔE_{Pauli} is the element describing repulsion and the ΔE_{orb} expression denotes the energy related to the bond formation. My calculations concluded with a statement that the electrostatic interactions correspond to ca. 70% of the total energy of attractive interactions in the ion pairs. Within the post-metallocene systems under investigation, this quantity is almost independent on the ligand and the variations in the cation–anion interaction energies are caused by orbital interactions of different strength.

Ligands active in the oxidation–reduction processes. The most recent area of my scientific interests include intended and unintended oxidation–reduction reactions that occur during the activation of transition metal complexes (precursors) with the aluminum and boron compounds (cocatalysts). It is assumed that the main role of the cocatalyst is the alkylation of the transition metal compound (i.e. the formation of the metal–carbon bond) and the abstraction of one of the ligands (usually chlorine atom or a methyl group), which leads to the formation of the free coordination site [35]. It is also believed that highly reactive cocatalyst scavenges trace impurities from the polymerization medium; these impurities could potentially poison the generated catalytic system. Since widely used cocatalysts, e.g. triethylaluminum and aluminoxanes (which contain unreacted alkyl aluminum derivatives), are strong reducing agents, they can react with the transition metal cation; moreover they can also modify the nature of ligands contained within the precursor.

My research in this area was inspired by the reports from the Fujita group, stating that the action of trialkylaluminum on the zirconium precursor bearing phenoxyimine ligands may lead to the reduction of the imine group [28]. Therefore it is expected that the catalytic system activated with a strong reducing agent will behave in a differrent way comparing with the system, in which the cocatalyst has no reductive properties. Undertaking the study on the mechanism of redox reactiuns in the organometallic compounds, I was aware of the fact that in certain situations it is impossible to univocally determine the oxidation state of the metal in the coordination compound due to the competitive reduction of ligands. Such ligands are referred to as *non-innocent* [36]. Therefore it was legitimate to examine the halides of selected transition metals reduced with organoaluminum compounds before embarking on the analysis of the process involving the ligand itself.

Beyond any doubt, the titanium oxidation state in the classical Ziegler–Natta catalysts is equal +3, whereas the catalytic precursors contain the titanium at the oxidation state of four [37]. It is assumed that the reduction of the transition metal atom is a two-stage process, taking place according to the following reaction equations [38]:

$$\mathrm{MCl_4 + Al(CH_3)_3 \rightarrow Cl_2M(\mu_2Cl_2)Al(CH_3)_2 + \frac{1}{2}C_2H_6} \tag{6}$$

$$\mathrm{Cl_2M(\mu_2Cl_2)Al(CH_3)_2 \rightarrow MCl_3 + Al(CH_3)_2Cl} \tag{7}$$

The results of experimantal study carried out at the Faculty of Chemistry, University of Opole, suggesting that vanadium is more easily reduced than titanium [39], are consistent with the standard electrode potentials in water [40]. This fact motivated me to compare the susceptibility of vanadium and titanium chlorides toward the reduction process. I managed to demonstrate that elemental hydrogen is not potent enough to transform the metal in both titanium(IV) chloride and vanadium(IV) chloride to the lower oxidation states from the thermodynamics point of view. Gradual reduction toward lower oxidation states becomes thermodynamically more and more unfavorable [**H8**]. Assuming that the energy of the reduction process can be approximated by the electron affinity of the reduced substance (which – in turn – corresponds to the LUMO orbital energy), I was able to correlate these two quantities for the titanium and vanadium chlorides, where the metals occur at different oxidation states. In the final part of the paper, I demonstrated that – according to expectations – the energy of vanadium(IV) chloride reduction with trimethylaluminum according to Eq. 6 is less than zero and almost twice more negative than the corresponding value for titanium(IV) chloride. This finding was independent on the computational method (including coupled clusters).

The investigation on the possibility of the imine group reduction was continued based on the conclusions mentioned above. The free FI ligand displays the intermolecular hydrogen bond and exists as a pair of tautomeric forms: phenol-imine (O–H$\cdots$N) and keto-amine (O$\cdots$H–N). The former is ususally more stable [41] – see Fig. 4. Nomura and coworkers demonstrated that the direct reaction of the phenoxyimine with trimethylaluminum leads to methane liberation and the formation of the cyclic coordination compound [42]. It must be stressed that the imine double bond is preserved in this compound, therefore the reduction process does not occur at this stage (Fig. 4). According to my calculations presented in Ref. **H9**, the reaction of the FI ligand with trimethylaluminum leading to the formation of the cyclic coordination compound encounters significantly lower barrier comparing with the competitive process of imine reduction. In addition to that, the cyclic coordination compound is more thermodynamically stable than the product of reduction. It does not mean, however that the reduction of the imine group is impossible. My calculations indicate that if two moles of aluminum hydride are applied, the hypothetical reduction product shown in Fig. 4 can be formed and the reaction is hindered by an insignificant barrier [**H9**]. The analogous reduction of the cyclic coordination compound with trimethylaluminum is thermodynamically and kinetically less favorable. However, it is known that the trialkylaluminum formulations contain small amounts of aluminum hydride; therefore my theoretical calculations prove that the thesis put forward in Ref. [28] is correct.

Bearing in mind that it is more difficult to reduce titanium than vanadium, I also demonstrated that the ligand within the bis(phenoxyimine) titanium(IV) complex can also be reduced [**H9**]. For the calculations, the most stable isomer was selected – *vide supra* [**H5**]. There are two stages to the reduction process: first, one Ti–N bond is broken (the barrier is equal only 5.5 kcal/mol) and then the attack of trimethylaluminum (or better: aluminum hydride) on the C=N bond is possible in a way similar to the free ligand.

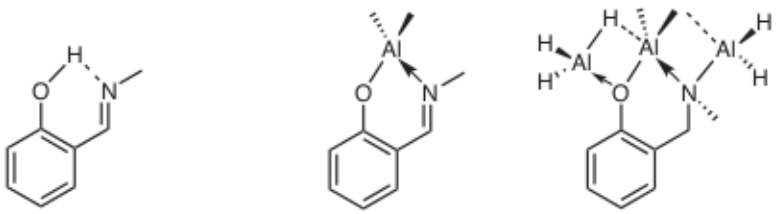

Figure 4: The fenol-imine form of the FI ligand, the aluminum cyclic coordination compound with the FI ligand and the hypothetical product of its reduction with aluminum hydride.

In the recent years, my scientific interests have approached the bis(imino)pyridine iron(II)

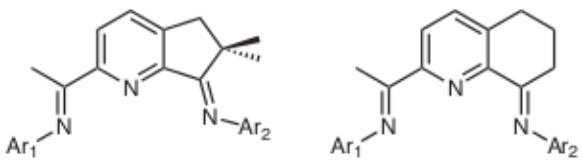

Figure 5: Bis(imino)pyridine ligands containing fused cycloalyl rings. The size of the cycloalkyl ring affects the mutual position of the three donor nitrogen atoms.

complexes. Initially, these compounds had been considered some kind of a curiosity and the object of basic research [43] against a background trend toward the study of multidonor ligand complexes and their properties of that time. Only independent works of Brookhart and Gibson groups [44, 45] revealed the potential of these compounds and their importance in the low-pressure olefin polymerization. Nowadays, it can be stated that they constitute universal precursors of catalysts that promote numerous processes in organic synthesis [**H10**], making it possible to replace expensive light platinum-group metals with much more abundant iron and nickel. Prof. Wen-Hua Sun of the Chinese Academy of Sciences in Beijing has impressive scientific output on the subject [46]. Therefore, in order to broaden my knowledge, I initiated the collaboration with his group in 2013. This collaboration continues up to the present day.

The redox processes involving the bis(imono)pyridine complexes are challenging to the computational chemistry due to the fact that the ligands incorporated within them can be referred to as *non-innocent*. The complexes exposed to the action of reducing agents undergo the multielectron process: first, the ligand is attacked [47]; it was shown that only deep reduction can efficiently change the oxidation state of the transition metal atom [48]. Intricate electronic properties of the ligand together with the nature of the late-transition-metal ion often preclude the correct description of such systems by DFT methods [**H10**] and the application of multireference methods becomes necessary [49]. On the other hand, it is worth mentioning that the cmplexes of titanium with the bis(imino)pyridine ligand do not pose such problems [50].

The electronic properties of the late-transition-metal complexes with the bis(imino)pyridine ligands can also be modified by the changes in spatial orientation of the donor nitrogen atoms. Small changes to the position of one imine nitrogen atom resulting from different sizes of cycloalkyl rings and their conformations (see Fig. 5) influence the energy of the metal–nitrogen bond and significantly change the activity of the catalytic system generated from the precursor modified in such a way [**H11**]. Furthermore, the nature of substituents attached to the cycloalkyl ring within the nickel complexes with iminopyridine derivatives influences the metal–carbon bond length. Since this bond participates in the insertion process it can be tentatively postulated that the processes of ethylene polymerization and oligomerization as well as the composition of their products can be controlled by careful selection of such substituents [**H12**].

Outlook. Preparation of the review paper **H10** during my stay in Beijing gave strong direction to my current research interests. There is relatively small number of theoretical papers devoted to the olefin polymerization catalyzed by the complexes of late-transition metals with the redox-active ligands in the world literature. Without any doubt, this is due to the difficulties in description by means of DFT methods described above. Comprehensive study of the polymerization promoted with such catalytic systems would significantly contribute to understanding this economically important process. To conduct such study, the scientific tools must be supplemented not only with the familiar computational methods (e.g. CASPT2, perhaps molecular dynamics) available in the commercial software packages, but also implementations of custom automation and simulation procedures using the Python language. These actions would aim at establishing the virtual designer dedicated to the new catalytic systems, which

integrates particular methods and utilizes the rules of *high throughput calculations*. With the current state of information and computational technology, the successful accomplishment of such a task seems to be feasible.

Understanding the mechanism of catalytic processes at the theoretical level is impossible without close colaboration with the experimental groups. Such collaboration will be intensified and broadened with a view to sign bilateral agreements and create the international multidisciplinary research group. I also intend that these actions will reflect in the curriculum of my home university and the mobility of students as well as Ph.D. students in all institutions participating in the project.

e) Discussion of other scientific achievements

The cooperation with Prof. Wen-Hua Sun of the Chinese Academy of Sciences resulted in a series of papers related to the catalysts obtained from the complexes of group 8–10 metals with the nitrogen-based bi- and tridentate ligands. It is known that these catalysts display significant activity in ethylene polymerization, yet undergo the deactivation process at elevated temperatures (starting from 50 °C), which seriously limits their industrial applications. It is assumed that the deactivation process may possibly be caused by the rotation of phenyl groups attached to the imine nitrogen atoms, which leads to the intramolecular C–H bond activation [51]. It was demonstrated that increasing the steric hindrance exerted by the substituents located at the *ortho*- position of the phenyl groups markedly improves the stability of the catalytic system at elevated temperatures and the bezhydryl (diphenylmethyl) group is especially beneficial [46]. I participated in the research demonstrating its efficiency in the catalysts based on the iron(II) complexes with the bis(imino)pyridine derivatives [52] as well as diimine [53] and iminopyridine [54] nickel(II) complexes. I also studied the influence of the size of the cycloalkyl ring fused with the pyridine ring which bears the imine group (*vide supra*) in the bis(imino)pyridine-based complexes on the activity of the catalytic system and the properties of the resultant polyethylene [55, 56]. I also have certain contribution to the experimental study of ethylene oligomerization catalysts based on nickel compounds [57] as well as neodymium-based catalyst of isoprene polymerization [58].

Additional area of my scientific activity is the study on the double metal cyanide (DMC) catalysts and the mechanism of oxirane polymerization promoted by these systems. The catalysts can be described by the following formula:

$$\mathrm{M^{I}_{x}[M^{III}(CN)_6]_y \cdot L^{1}_{a1} \cdots L^{n}_{an}}, \tag{8}$$

where $\mathrm{M^{II}}$ and $\mathrm{M^{III}}$ denote the metals at the oxidation state of two and three, respectively (these are usually zinc and cobalt); $\mathrm{L^1 \cdots L^n}$ are the ligands (commonly alcohols and ethers), while $\mathrm{x, y, a1 \cdots an}$ denote stoichiometric coefficients. It is assumed that that the active site is located at the zinc atom and the entire catalytic system is a Lewis acid. Therefore Lewis bases may modulate the properties of the catalyst (or even poison it); thus they are essential to the oxirane polymerization process. The polymer obtained with the DMC catalysts contains smaller amount of side-products and is more homogeneous (characterized by lower molecular weight distribution) comparing with the polieterols obtained with the classical process carried out with strong bases [59].

An episode in my scientific career was the attempt to characterize the conjugated polyenes as pigments in the red and pink coral coming from the waters surrounding Taiwan [60]. The results of this study indicate that the Raman intensities strongly depend on the number of carbon–carbon double bonds within the polyene molecule. This fact, together with the experimental spectra, may suggest that only two to three polyenes differing slightly in the number of C=C bonds may be responsible for the colour.

It is worth mentioning that the research on DMC catalysts and corals was performed at the Faculty of Chemistry, University of Opole.

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