

From electronic effects to conformational model  
– Novel concepts in design of the Hoveyda-Grubbs-type  
complexes



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Summary of professional accomplishments submitted for the habilitation procedure

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Warsaw, June 2015

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1. Name and surname: **Michał Barbasiewicz**

2. Scientific diploma and degrees:

**Ph. D. degree in chemistry**, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland, **04<sup>th</sup> of November 2005**, supervisor: Professor Mieczysław Mąkosza, title of the Ph. D. thesis: „*Studies of intermolecular reactions of  $\gamma$ - and  $\delta$ -halocarbanions*”

**M. Sc. degree in chemistry**, Warsaw University of Technology, Faculty of Chemistry, Warsaw, Poland, **05<sup>th</sup> of July 2001**, supervisor: Professor Michał Fedoryński, D. Sc., title of the master thesis: „*Effect of concentration of potassium hydroxide solution on the reaction course in catalytic two-phase system*”

3. History of employment

**adjunct**, University of Warsaw, Faculty of Chemistry, 15<sup>th</sup> of February 2009 – presently

Humboldt Research Fellowship for **Postdoctoral Researchers**, Friedrich Alexander Universität Erlangen-Nürnberg, Erlangen, Germany, 01<sup>st</sup> of November 2006 – 31<sup>st</sup> of August 2008

**assistant**, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland, 01<sup>st</sup> of December 2005 – 31<sup>st</sup> of October 2006

4. Indication of achievement resulting from Article 16 Section 2 of the Act on University Degrees and the University Title and on University Degrees and the University Title in the Field of Fine Arts of March 14, 2003 (Journal of Laws No. 65, item 595, with later amendments):

a) Title of scientific achievement,

**From electronic effects to conformational model – Novel concepts in design of the Hoveyda-Grubbs-type complexes**

b) List of publications constituting the scientific achievement; the scientometric data taken from Web of Science at 19<sup>th</sup> of May 2015

**H1**. M. Barbasiewicz,\* *Novel concepts in catalyst design—a case study of development of Hoveyda-type complexes*; chapter in *Olefin Metathesis - Theory and Practice*, First Edition. Edited by K. Grela, John Wiley & Sons, Inc. **2014**; pp. 475-481 (a review).

Number of citations = 0.

The article was prepared exclusively by myself. I estimate my contribution to be equal to **100%**.

**H2.** M. Barbasiewicz,\* K. Grudzień, M. Malińska, *A Missing Relative: A Hoveyda–Grubbs Metathesis Catalyst Bearing a Peri-Substituted Naphthalene Framework*; *Organometallics* **2012**, *31*, 3171-3177.

IF<sub>2012/2013</sub> = 4.145 / 4.253; number of citations = 9.

My contribution to this work consisted of planning of the research and the experiments, synthesis of ligand and *peri*-substituted ruthenium complex, NMR measurements, calculations, data processing, preparing of the Supporting Information file, as well as writing and publishing of the manuscript. I estimate my contribution to be equal to **85%**.

**H3.** K. Grudzień, M. Malińska, M. Barbasiewicz,\* *Synthesis and Properties of Bimetallic Hoveyda–Grubbs Metathesis Catalysts*; *Organometallics* **2012**, *31*, 3636-3646.

IF<sub>2012/2013</sub> = 4.145 / 4.253; number of citations = 12.

My contribution to this work consisted of planning of the research and the experiments, synthesis of ruthenium complexes, NMR measurements, data processing, preparing of the Supporting Information file, as well as writing and publishing of the manuscript. I estimate my contribution to be equal to **70%**.

**H4.** K. Grudzień, M. Barbasiewicz,\* *Studies on synthesis of quinonylidene Hoveyda-type complexes*; *Appl. Organometal. Chem.* **2015**, *29*, 322-327.

IF<sub>2015/2013</sub> = - / 2.017; number of citations = 0.

My contribution to this work consisted of planning of the research and the experiments, synthesis of ruthenium complexes, NMR measurements, data processing, preparing of the Supporting Information file, as well as writing and publishing of the manuscript. I estimate my contribution to be equal to **70%**.

**H5.** M. Barbasiewicz,\* M. Michalak, K. Grela,\* *A New Family of Halogen-Chelated Hoveyda–Grubbs–Type Metathesis Catalysts*; *Chem. Eur. J.* **2012**, *18*, 14237-14241.

IF<sub>2012/2013</sub> = 5.831 / 5.696; number of citations = 12.

My contribution to this work consisted of partial planning of the research and the experiments, synthesis of ligand and ruthenium complex **5e**, selected NMR measurements, data processing,

preparing of the Supporting Information file, as well as writing of a draft version of the manuscript, and responses for reviewers. I estimate my contribution to be equal to **45%**.

**H6.** M. Barbasiewicz,\* K. Błocki, M. Malinska, R. Pawłowski, *Intriguing substituent effect in modified Hoveyda–Grubbs metathesis catalysts incorporating a chelating iodo-benzylidene ligand*; *Dalton Trans.* **2013**, 42, 355-358.

IF<sub>2013/2013</sub> = 4.097 / 4.097; number of citations = 7.

My contribution to this work consisted of planning of the research and the experiments, synthesis of ruthenium complexes, NMR measurements, data processing, preparing of the Supporting Information file, as well as writing and publishing of the manuscript. I estimate my contribution to be equal to **70%**.

**H7.** M. Barbasiewicz,\* M. Malińska, K. Błocki, *Latent Metathesis Catalyst Stabilized with NO<sub>2</sub>···I Interaction*; *J. Organomet. Chem.* **2013**, 745-746, 8-11.

IF<sub>2013/2013</sub> = 2.302 / 2.302; number of citations = 5.

My contribution to this work consisted of planning of the research and the experiments, synthesis of ruthenium complex, NMR measurements, data processing, preparing of the Supporting Information file, as well as writing and publishing of the manuscript. I estimate my contribution to be equal to **70%**.

**H8.** K. Grudzień, K. Żukowska, M. Malińska, K. Woźniak, M. Barbasiewicz,\* *Mechanistic Studies of Hoveyda-Grubbs Metathesis Catalysts Bearing S-, Br-, I-, and N-coordinating Naphthalene Ligands*; *Chem. Eur. J.* **2014**, 20, 2819-2828.

IF<sub>2014/2013</sub> = - / 5.696; number of citations = 3.

My contribution to this work consisted of planning of the research and the experiments, synthesis of selected ruthenium complexes, NMR measurements, data processing, preparing of the Supporting Information file, as well as writing and publishing of the manuscript. I estimate my contribution to be equal to **65%**.

**H9.** B. Bieszczad, M. Barbasiewicz,\* *The Key Role of the Nonchelating Conformation of the Benzylidene Ligand on the Formation and Initiation of Hoveyda-Grubbs Metathesis Catalysts*; *Chem. Eur. J.* **2015**, DOI: 10.1002/chem.201501959.

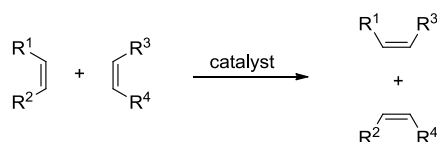
IF<sub>2015/2013</sub> = - / 5.696; number of citations = 0.

My contribution to this work consisted of planning of the research and the experiments, synthesis of ruthenium complexes and selected ligands, NMR measurements, data processing, preparing of the

Supporting Information file, as well as writing and publishing of the manuscript. I estimate my contribution to be equal to **90%**.

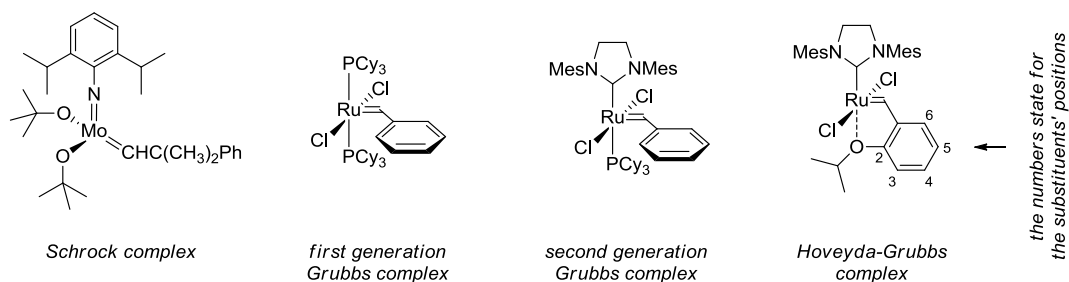
c) Brief description of the scientific goal and the results described in the publications constituting scientific achievement

Catalytic olefin metathesis reaction was observed for the first time in late fifties of the XX century, and is currently a powerful tool of organic synthesis used for the formation of carbon-carbon double bonds. Over a number of years the methodology was gradually developed from high-temperature heterogenic systems, to homogenous catalysts, active under ambient temperature; and crowning of the remarkable progress was the Nobel Prize in chemistry awarded for Grubbs, Schrock, and Chauvin in 2005.<sup>1</sup>



general scheme of the olefin metathesis reaction

First important homogenous catalysts were well-defined complexes of molybdenum and ruthenium, described by Schrock and Grubbs, respectively. However, only the latter were developed in a number of studies, focused on mechanistic details, and revealing structure-activity relationships of the complexes. One can say that presently the ruthenium Grubbs and Hoveyda-Grubbs complexes are one of the best known catalytic systems described in scientific literature (Cy - cyclohexyl; Mes - 2,4,6-trimethylphenyl).

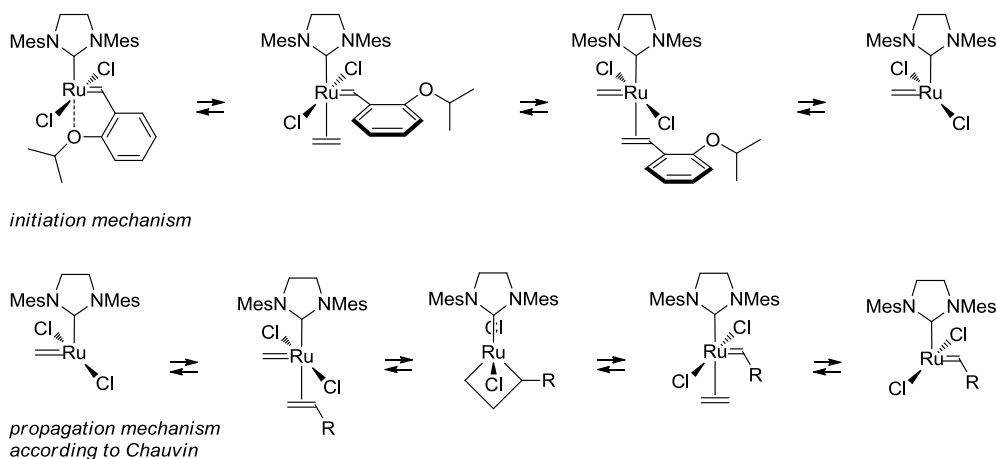


Numerous structural modifications at the ruthenium coordination sphere, as application of N-heterocyclic carbenes (NHC) in second generation catalysts, and chelating ligands in the Hoveyda-Grubbs complexes, enabled considerable stabilization of the structures with simultaneous *increase* of the catalytic activity. The changes were *milestones* of development of the systems, and every modification took advantage of optimized elements, and knowledge, concerning their mechanism of

<sup>1</sup> [http://www.nobelprize.org/nobel\\_prizes/chemistry/laureates/2005/](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/) (access at 18th of May, 2015)

action. In the end, over 100 derivatives of the Hoveyda-Grubbs complex were published, without counting further analogs of the system.

By analyzing a classical mechanism of action of the complexes, consisting of stages of initiation, propagation and termination of the catalytic cycle, one can notice that the chelating ligand undergoes dissociation and exchange at the initiation step, whereas auxiliary ligands remain in the coordination sphere of the ruthenium, controlling every of the stages. At the same time the *initiation* process limits the rate of the catalyzed reaction, by release of the 14-electrons propagating species, which undergo consecutive propagation cycles, according to the Chauvin model.<sup>2,3</sup>



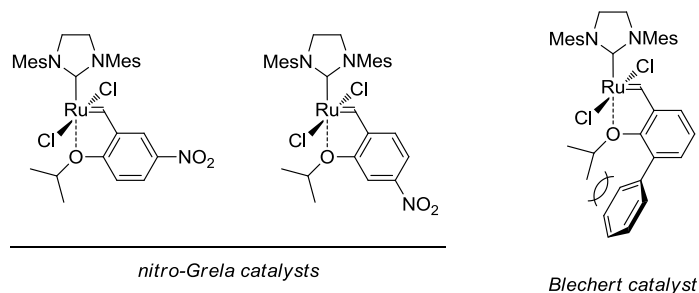
At early stages of development of the Hoveyda-Grubbs complexes two alternative strategies concerning increase of the catalytic activity were proposed. First was an electronic activation suggested by Grela,<sup>4</sup> and another a steric activation described by Blechert.<sup>5</sup> The first approach concerned introduction of electron-withdrawing substituents in positions 4 and 5 of the benzylidene ring, which decreased the electron density on the oxygen atom, and thus weakened the Ru···O bond. A similar effect of weakening of the bond was achieved by introduction of phenyl group in position 3 of the benzylidene ring, which caused out-of-plane distortion of the coordinating OiPr group. A more detailed description of evolution of the structures was described in a review article.[H1]

<sup>2</sup> X. Solans-Monfort, R. Pleixats, M. Sodupe, *Chem. Eur. J.* **2010**, *16*, 7331-7343

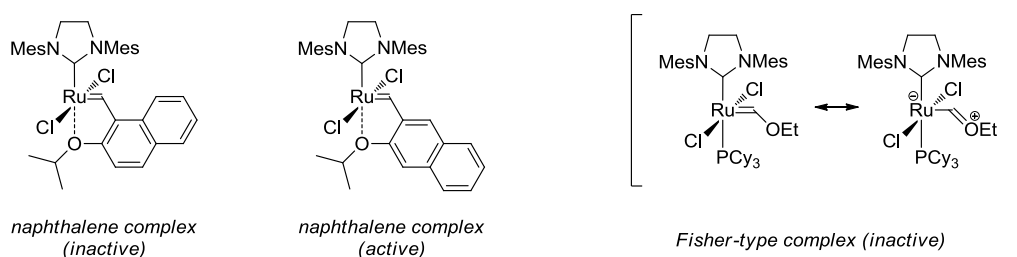
<sup>3</sup> T. Vorfalt, K.-J. Wannowius, H. Plenio, *Angew. Chem. Int. Ed.* **2010**, *49*, 5533-5536

<sup>4</sup> A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos, K. Grela, *J. Am. Chem. Soc.* **2004**, *126*, 9318-9325

<sup>5</sup> H. Wakamatsu, S. Blechert, *Angew. Chem. Int. Ed.* **2002**, *41*, 2403-2405

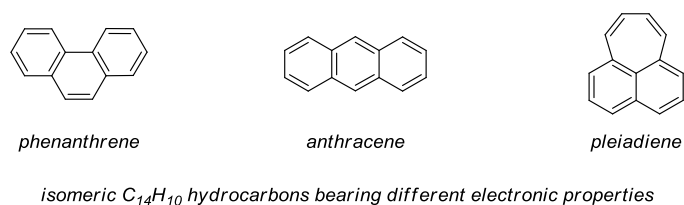


An interesting observation, which may contribute to new effects controlling the catalytic activity, was extraordinary difference between naphthalene analogs of the Hoveyda-Grubbs complex.<sup>6</sup> As an explanation of the retarded initiation of angular (phenanthrene-like) isomer we postulated steric effect of distant aromatic ring adjacent to the Ru=C bond, and electronic effect related to the  $\pi$ -electron delocalization from the oxygen atom, through the ligand structure, to the ruthenium center.



Due to the alternation of lengths and order of bonds in the naphthalene framework, electron delocalization within the chelate ring was expectedly facilitated in the angular isomer, in which the fragment linking the coordinating sites has a double bond character. According to the literature data increase of the electron density on the ruthenium center substantially reduces the catalytic activity of co-called *Fisher-type complexes*, which possess a donor substituent on the carbene carbon atom.<sup>7</sup>

At this stage of knowledge I commenced *an independent research* to verify factors, which control catalytic activity of the metathesis catalysts. Considering influence of the electronic effects I decided to apply structural analogies between naphthalene complexes and polycyclic aromatic hydrocarbons (PAHs). As in phenanthrene the external aromatic rings display an increased electron delocalization (aromaticity), in anthracene the effect is limited, whereas in isomeric pleiadene the diene fragment has an electronically isolated character, and undergoes addition reactions, typical for olefins. **[H2]**

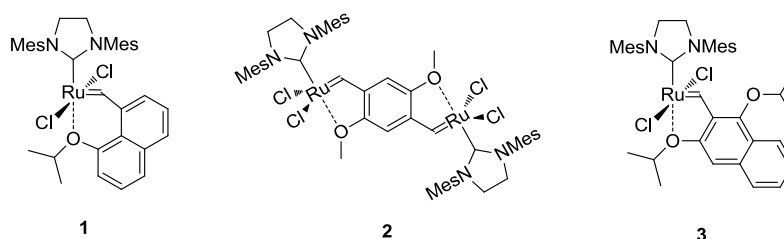


<sup>6</sup> M. Barbasiewicz, A. Szadkowska, A. Makal, K. Jarzemska, K. Woźniak, K. Grela, *Chem. Eur. J.* **2008**, *14*, 9330-9337

<sup>7</sup> J. Louie, R. H. Grubbs, *Organometallics* **2002**, *21*, 2153-2164

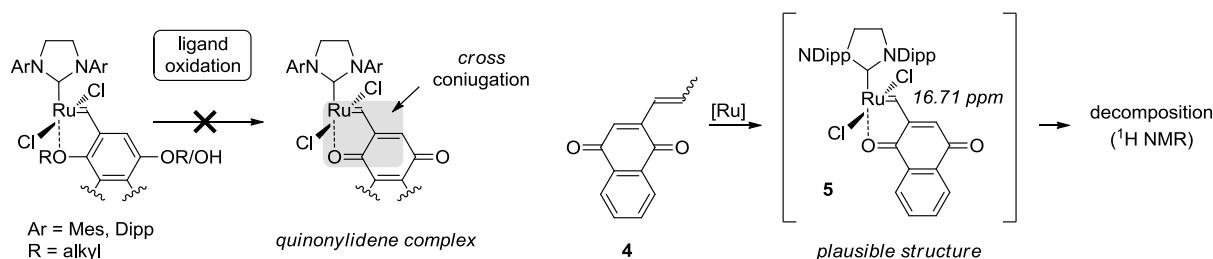


I assumed that ruthenium complexes assembled on *peri*-substituted naphthalene framework (**1**) could display a reduced electron delocalization within the chelate, and thus *increased* activity, as compared with the parent Hoveyda-Grubbs complex. In consistency with the expectations the synthesized catalyst appear to be an exceptionally fast initiator (faster even than the nitro-Grela catalyst), but of reduced stability. However, unambiguous interpretation of the results was complicated by the fact that chelate ring in **1** is six-membered (in contrast to five-membered structures of other isomers of the naphthalene complexes), that caused structural distortions of the ruthenium coordination sphere, and possibly accelerated the initiation process. Therefore, a definite recognition between structural (steric) and electronic effects operating in the systems required further studies.



An interesting opportunity to observe the  $\pi$ -electronic effects was synthesis of bimetallic catalysts bearing two chelate rings assembled on the benzene core. [**H3**] In this case the systems also were able to form angular (phenanthrene-like) or linear (anthracene-like) structures, depending on the arrangement of the coordinating sites of the ligand. Of particular importance was the fact that such structures should initiate stepwise, by a release of two propagating species, and rates of the individual processes can differ from each other, and depend on subtle electronic effects. Although angular bimetallic systems were expected to display increased electronic stabilization, their synthesis witnessed pronounced problems concerning selectivity and stability of the products. However, we succeeded in preparation of linear bimetallic complex **2**, which displayed activity similar to related monometallic catalysts. This meant that in the isomer the catalytic centers initiate roughly independently, and thus no cooperativity of the initiation process is observed. A limited stabilization effect was also supported by synthesis of naphthalene complex bearing two coordination sites (**3**). The isolated product possessed a linear rings junction, while its angular isomer (of expected higher stability) was not detected.

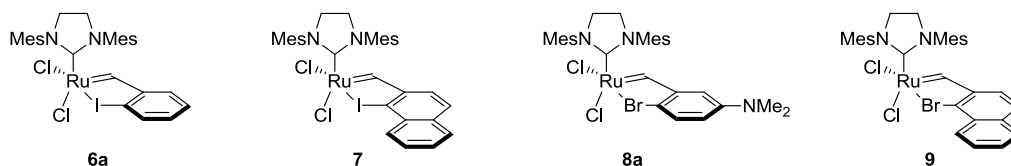
A quest of new catalysts with reduced electron delocalization within the chelate ring *inspired* attempts at synthesis of quinonylidene complexes – unprecedented analogs of the Hoveyda-Grubbs system with oxidized form of the chelating ligand (in the sense of quinone – hydroquinone redox pair; Dipp - 2,6-diisopropylphenyl). [**H4**]



In such structures the coordinating sites would be linked by a so-called *cross* conjugation, which substantially reduces the electron delocalization.<sup>8</sup> Additional features were the opportunity to control the catalytic activity by ligand redox process, and the release of quinone on the course of the initiation process, which may inhibit undesired isomerization processes.<sup>9</sup> Unfortunately, despite of numerous attempts at oxidation of alkoxy- and hydroxy-substituted Hoveyda-Grubbs complexes we failed to isolate the desired products. However, for the complexes we observed interesting structure-activity correlations from the spectrum of steric activation, as described by Blechert. However, using <sup>1</sup>H NMR spectroscopy we demonstrated formation of complex **5** in a ligand exchange reaction with vinylquinone **4** (oxidized form of ligand). The product displayed a resonance peak characteristic for carbene proton expected for quinonylidene complex. Unfortunately, the structure was unstable, and easily decomposed to undefined by-products, making its isolation and characterization virtually impossible.

Analogs of the Hoveyda-Grubbs complex varied by a type of coordinating heteroatom in the chelating benzylidene ligand are represented in literature by derivatives of nitrogen, phosphorus, sulfur and selenium. All of them feature with an increased stability of the Ru···heteroatom bond that limits rate of the initiation, and, due to so-called *trans effect* of the NHC ligand, changes geometry of the ruthenium coordination sphere (in this case a *cis*-Cl<sub>2</sub> geometry is preferred, in contrast to *trans*-Cl<sub>2</sub> structure of the parent Hoveyda-Grubbs complex). Catalysts of this type are called *latent*, and are applicable in e.g. Ring Opening Metathesis Polymerizations (ROMP), in which a mixture of monomer and catalyst reacts only after heating.

An interesting variant of the above-mentioned heteroanalogs of ruthenium complexes were derivatives of covalently bonded halogen atoms. It is worth to stress, that simple organic halides (e.g. haloarenes) are useful substrates in transition metal catalyzed reactions, whereas their coordination compounds (in which the halogen atoms act as  $\sigma$ -donors) are rare and only moderately stable.<sup>10</sup> Our studies begun from attempts at ligand exchange of ruthenium precursor with 2-halostyrenes.[H5] Surprisingly, under these conditions 2-iodopropenylbenzene formed stable ruthenium complex **6a** with high yield, whereas synthesis of corresponding bromocomplexes required additional stabilization by the presence of donating dimethylamino group (**8a**), or naphthalene ligand (**9**). It was a hint that  $\pi$ -electronic effects may indeed control the stability of the systems, although quantitatively the effect was comparable to the donor effect of the nitrogen atom. The new class of catalysts appeared to be active in numerous metathesis reactions, while their simplicity of preparation, and stability toward oxygen and moisture allowed a patent pending and commercialization of the invention.[P3]

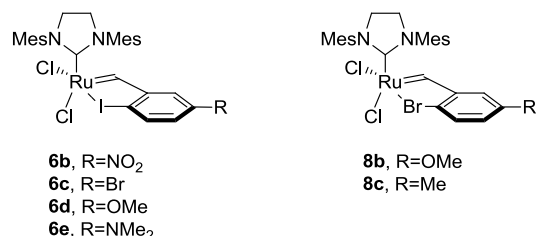


<sup>8</sup> N. F. Phelan, M. Orchin, *J. Chem. Educ.* **1968**, *45*, 633-637

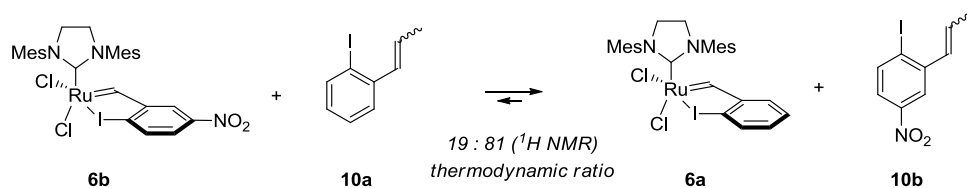
<sup>9</sup> S. H. Hong, D. P. Sanders, C.W. Lee, R. H. Grubbs, *J. Am. Chem. Soc.* **2005**, *127*, 17160-17161

<sup>10</sup> R. J. Kulawiec, R. H. Crabtree, *Coord. Chem. Rev.* **1990**, *99*, 89-115

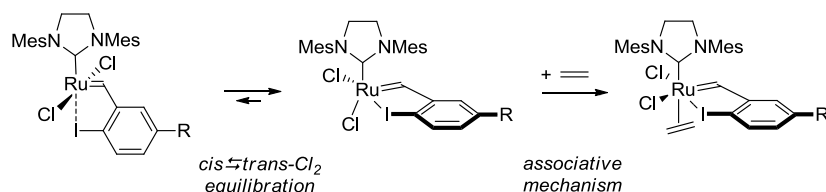
Mechanistic studies of the new class of catalysts resulted in unexpected observations. At the beginning we tested the influence of substituents present in a position 5 of the benzylidene ring.[H6] As known from the literature, in the parent Hoveyda-Grubbs complex presence of the nitro group at this position substantially increases the catalytic activity,<sup>4</sup> whereas electron donors display an opposite effect. Altogether, we prepared four substituted iodocomplexes **6b-e**, bearing acceptor (NO<sub>2</sub>, and Br) and donor substituents (NMe<sub>2</sub>, and OMe), and two bromocomplexes **8b-c** (see the *Supporting Information* for details).



Activity profiles of the catalysts indicated that introduction of the nitro group substantially *decreases* the catalytic performance, however donors also *decrease* the activity, but to a lesser extent. Looking for the explanation of the intriguing observation we carried out a ligand equilibration experiment (**6b** + **10a** ⇌ **6a** + **10b**), in which a thermodynamic composition of the mixture suggested a stronger binding of the unsubstituted ligand **10a**. It was consistent with the expectations, as the acceptor nitro group should decrease stability of the Ru···I-Ar bond.

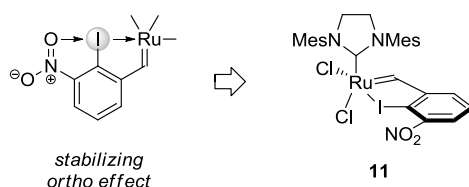


The apparent contradiction between thermodynamic stabilization of unsubstituted complex **6b**, and its faster initiation (as compared with **6b**) suggested that the Ru···I-Ar bond is not broken in the rate-determining step of the reaction. As an alternative explanation we proposed two mechanisms of the initiation process with the initial *cis* ⇌ *trans*-Cl<sub>2</sub> equilibration (and without breaking of the Ru···I-Ar bond), or associative process with transient six-coordinated structure. In the light of further research the two proposals seemed to be exceptionally accurate.

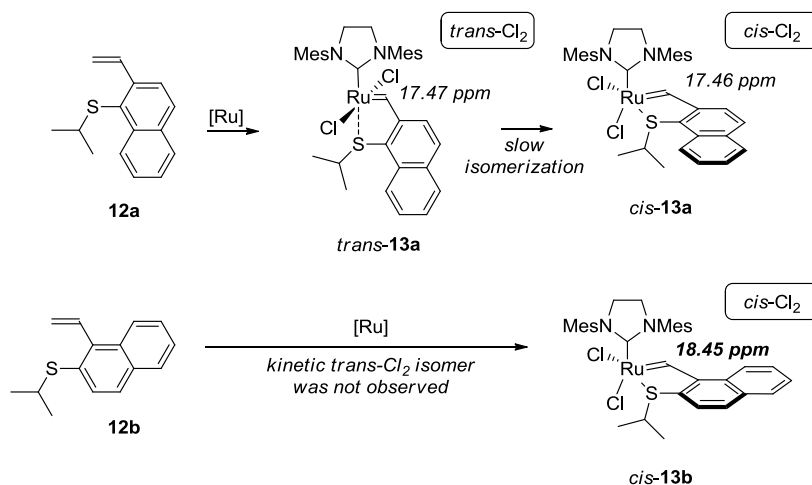


Unexpected effect was displayed also by the nitro group present in position 3 of the benzylidene ring of iodocomplex **11**. [H7] In this case the *deactivating* effect was even stronger than for 5-isomer (**6b**), and so-formed catalyst displayed essentially no activity at 25 °C. So, again the halogen complexes possessed disparate properties as compared with ether-chelated congeners, for which substituents in position 3 increase the rate of initiation.<sup>5</sup> However, instead of out-of-plane distortion of the coordinating site (according to the Blechert concept), the coordinating halogen atom was rather polarized in a structurally congested NO<sub>2</sub>→I→Ru fragment, and thus resulted in

stabilization of the Ru...I-Ar bond confirmed with ligand equilibration experiments. The influence of the nitro group was observed also with  $^{13}\text{C}$  NMR spectroscopy for carbon atoms bonded with iodine (the peaks were detected in a characteristic range of the spectrum at 90-110 ppm, due to a so-called *heavy atom effect*). Both, in a free ligand and its complexed form the nitro group present in a 5 position of the benzylidene ring caused deshielding, whereas at position 3 shielding of the *ipso* carbon atom, as compared with the unsubstituted system. The shielding expectedly correlated with an increased electron density at that site, and was consistent with trends of thermodynamic stabilization of the chelates (**6b** < **6a** < **11**).



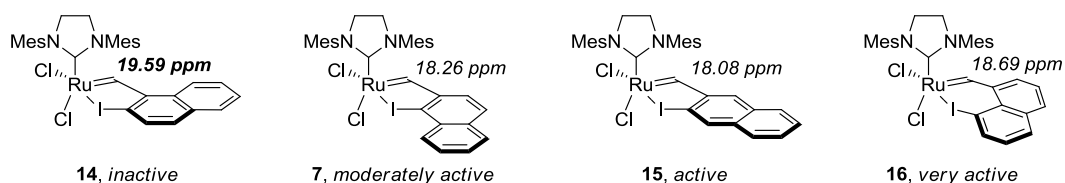
Mechanistic studies focused on explanation of the *naphthalene* effect of benzylidene ligands in heteroanalogs of the Hoveyda-Grubbs complex, led to further interesting observations. [H8]



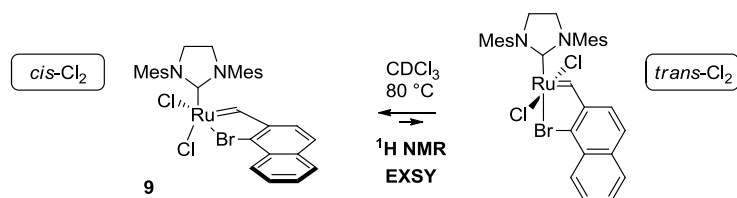
For sulfur analogs two isomeric naphthalene ligands (derivatives of 1,2-disubstituted naphthalene) reacted with the ruthenium precursor in different manner. While ligand **12a** reacted in a way similar to the benzene ligand, giving a kinetic *trans*-Cl<sub>2</sub> complex; **12b**, in which second aromatic ring was adjacent with the vinyl substituent, led directly the thermodynamic product *cis*-**13b**. The data suggested that isomeric naphthalene complexes **13a** and **13b** are formed by different mechanisms despite both of them have angular phenanthrene-like structures, and thus similar electronic effects are expected. So the key role was played by the second aromatic ring of the ligand present in a position adjacent to the vinyl substituent, and its steric effect.

Similar correlations were observed for a series of isomeric naphthalene iodo complexes. Catalyst **14** was inactive in model metathesis reaction, and its synthesis required particularly harsh reaction conditions (111 °C). In turn complex **7** differed only slightly from **6a** and **15**. Interestingly, in the same way as for ether-chelated complexes a *peri*-substituted isomer **16** displayed an exceptionally high catalytic activity in the series.

In the same article [H8] the reader may find an explanation of differences of chemical shifts of benzyldiene protons observed for the complexes.

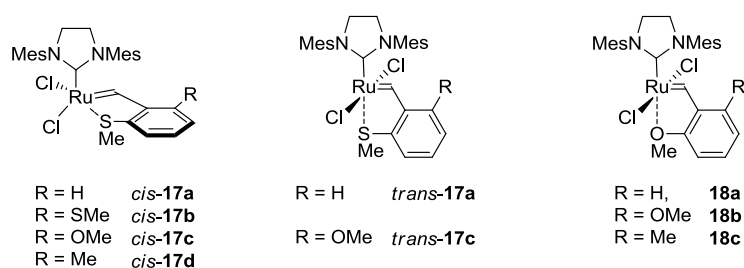


Initiation mechanism of the prepared bromo- and iodo complexes was studied using *spin-exchange spectroscopy* technique (EXSY  $^1\text{H}$  NMR). Although  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and X-ray studies of the systems supported a predominant *cis*- $\text{Cl}_2$  form, at elevated temperature we detected also presence of minor symmetrical equilibrium form *trans*- $\text{Cl}_2$ . This form, due to the *trans* effect of the NHC ligand, was expected to easily open the chelate ring, and thus initiate faster in the catalytic cycle.



By correlation between contents of the minor *trans*- $\text{Cl}_2$  form, present in equilibrium, and catalytic activities of the complexes, we assumed that first decisive step of the initiation mechanism consists of *cis*  $\rightleftharpoons$  *trans*- $\text{Cl}_2$  isomerization (under these conditions distinguishing between effect of the equilibrium contents, and rates of how fast they are established was difficult). Unfortunately numerous exceptions complicated the mechanistic picture, and suggested the presence of at least *one more factor* controlling the observed catalytic activity.

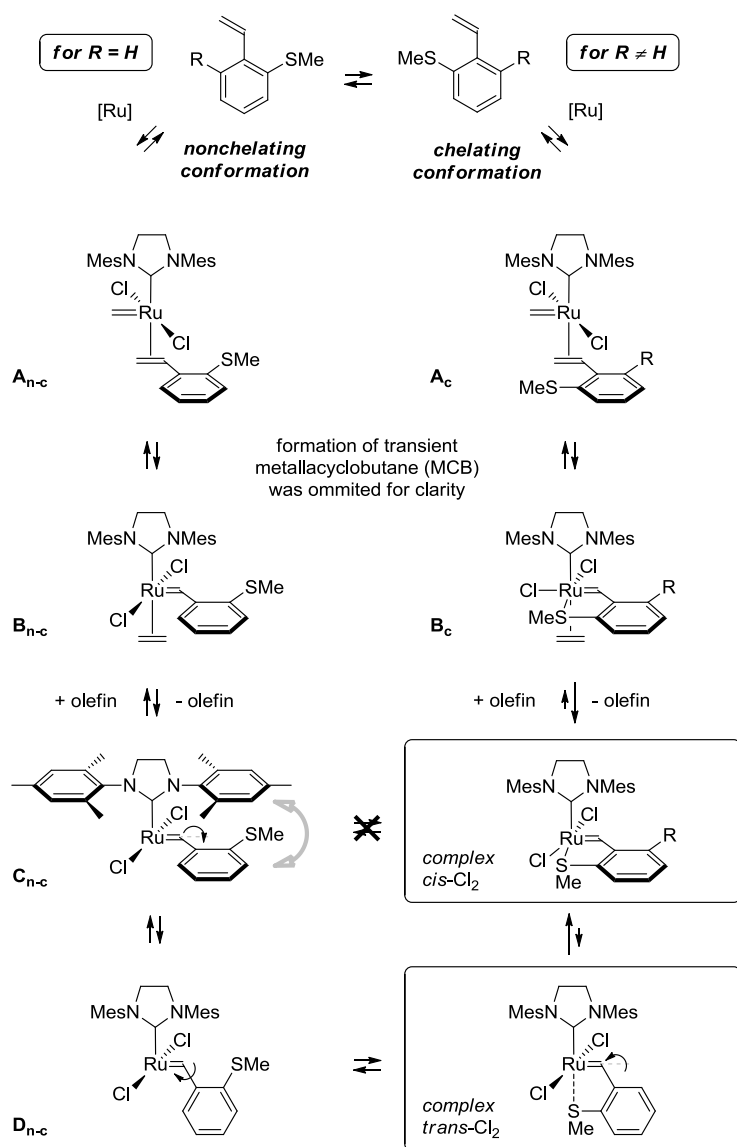
At the end we decided to study an effect of substitution at the 6 position of the benzyldiene ring on properties of *S*- and *O*-chelated Hoveyda-Grubbs-type complexes (catalysts **17**-**18**). [H9]



On the basis of mechanism of initiation of the ether-chelated complexes (see page 7), and course of the formation of the ruthenium complexes **13a** and **13b** with sulfur-derived naphthalene ligands we reckoned that substitution at the position adjacent to the vinyl group may influence equilibrium of conformers of the chelating ligands (forms, which differ by the torsion angle around the  $=\text{C}-\text{C}_{\text{arom}}$  bond). Ligand unsubstituted at the 6 position ( $\text{R}=\text{H}$ ) in the course of the exchange process may achieve a nonchelating conformation (n-c), and thus behave as a simple styrene or other olefin participating in the reaction. Then, after the cycle of metathesis structure  $\text{C}_{\text{n-c}}$  is formed, but a steric hindrance between the aromatic rings (shown as a grey arrow) prevents a direct cyclization of the

chelate ring. Not until the conformation  $D_{n-c}$  is achieved the cyclization leads to the kinetic *trans*-Cl<sub>2</sub> isomer. In turn, when the substituent is present in 6 position of the benzylidene ring ( $R \neq H$ ) chelating conformation (c) is forced *in the exchange process*. In such a case both coordinating sites of the ligand (the vinyl group and the heteroatom) interact with the ruthenium center, and in effect the *cis*-Cl<sub>2</sub> structure is formed directly. The same mechanism can be applied for the analysis of the reverse process of the catalysts initiation. Unsubstituted catalysts initiate by nonchelating conformation, but when it is unachievable an alternative (high-energy) associative mechanism operates (by structure  $B_c$ ).

Most likely the same scenario remains valid for inactive isomer of the naphthalene complexes, for which a distant aromatic ring adjacent to the carbene carbon atom plays the same role as other substituents at the 6 position of the benzylidene ring.



The presented results describe an *evolution* of concept of the design of new Hoveyda-Grubbs-type complexes, and their mechanism of action. It is worth to stress, that research studies of the catalysts are carried out by numerous groups all over the world, and number of papers, new concepts, and mechanistic details is continuously growing. Although a fraction of the effects is currently well-understood, more detailed ideas lead to polemics and discussions, demonstrating how complexed the systems are. As an example we can mention a so-called *boomerang mechanism* of release-return of the benzyldiene ligand postulated Barrett,<sup>11</sup> excluded by Plenio,<sup>12</sup> and again supported by Fogg,<sup>13</sup> depending on the model under study, detection technique, and interpretation of the data. Following the same, in my research experimental details described in a previous communication concerning the naphthalene complexes<sup>6</sup> initially hid the interplay between electronic and conformational effects of the naphthalene ligands. However, in the end the data inspired valuable studies - apart of mechanistic issues presented in the dissertation, syntheses of new ligands were objectives for studies of cooperating students, and some of the catalysts were tested in polymerization studies and commercialized.

Main achievements of the dissertation are:

- synthesis of *peri*-substituted naphthalene complex **1** of exceptionally fast initiation,[**H2**]
- synthesis of bimetallic complex **2**,[**H3**]
- synthesis of new class of ruthenium complexes, bearing covalently bonded halogen atoms **6-9** and **11** (Br, I).[**H5-H7**] The accomplishment has consequences not only for catalysis, but for metalloorganic chemistry as well, demonstrating formation of unprecedented stable complexes. Moreover the metathesis catalysts were patented and are now commercially available.<sup>14</sup>
- observation of *cis*↔*trans*-Cl<sub>2</sub> equilibrium for halogen-chelated complexes, and correlation of contents of the minor *trans*-Cl<sub>2</sub> forms with the catalytic activities,[**H8**]
- formulation of mechanism of the exchange process of benzyldiene ligand substituted in a 6 position of the benzyldiene ring, supported by the formation of sulfur complexes, and initiation of ether-chelated systems.[**H9**] In a future the postulated high-energy mechanism of initiation of the catalysts can be applied for design of new catalysts active at elevated temperatures.

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<sup>11</sup> M. Ahmed, A. G. M. Barrett, D. C. Braddock, S. M. Cramp, P. A. Procopiou, *Tetrahedron Lett.* **1999**, *40*, 8657-8662

<sup>12</sup> T. Vorfalt, K. J. Wannowius, V. Thiel, H. Plenio, *Chem. Eur. J.* **2010**, *16*, 12312-12315

<sup>13</sup> J. M. Bates, J. A. M. Lummiss, G. A. Bailey, D. E. Fogg, *ACS Catalysis* **2014**, *4*, 2387-2394

<sup>14</sup> [http://chemistry.unicore.com/Products/#tax\\_reactiontype\\_ms=Metathesis](http://chemistry.unicore.com/Products/#tax_reactiontype_ms=Metathesis) (M91-93; access at 19<sup>th</sup> of May 2015)

## 5. Other scientific publications and achievements

Within the research projects to date I explored various areas of organic synthesis. As an undergraduate student I carried out internships at the Institute of Organic Chemistry PAS (group of Professor Mieczysław Mąkosza) studying synthesis of alkyl nitrites (**A1**), and nitroindoles (**A2**), whereas my Master thesis at the Warsaw University of Technology (group of Professor Michał Fedoryński) concerned alkylation reactions, and generation and addition of difluorocarbene in a catalytic two-phase system (**A6**). My Ph. D. thesis, and following one year employment at the IOC PAS (group of Professor Mieczysław Mąkosza) was focused on intermolecular reactions of  $\gamma$ - and  $\delta$ -halocarbanions, and their analogs, which react by the Darzens mechanism (**A3**, **A4**, **A5**, **A8**, **A11**, **A14**, **A16**, **A21**). At the same time at IOC I informally cooperated with Professor Karol Grela in projects concerning the olefin metathesis (**A7**, **A9**, **A10**, **A13**). Post-doctoral research stay as a Humboldt fellow took place at the group of Professor John Gladysz at Friedrich-Alexander Universität Erlangen-Nürnberg in Germany, and consisted of synthesis and conformational analysis of cage diphosphines, and their complexes with platinum and borane (**A12**, **A15**, **A18**, **A22**). Next I was employed at the University of Warsaw, Faculty of Chemistry, where during my habilitation project I explored synthesis of new Hoveyda-Grubbs complexes. Apart from the mechanistic studies described in the dissertation (**H1-H9**) the complexes found practical applications in Ring Opening Metathesis Polymerization (**A19**, **A23**), and as patented, commercially available olefin metathesis catalysts (**P3**). Currently, under SONATA BIS grant of the National Science Center (2014-2019) I began studies concerning new, completely different project concerning applications of sulfur and selenium compounds in organic synthesis.

**Up-to-date informations concerning list of papers, conference talks, research funding, and professional curriculum vitae are available under:**

**[www.aromaticity.pl](http://www.aromaticity.pl)**

### a) list of publications

**A1.** M. Mąkosza,\* M. Barbasiewicz, K. Wojciechowski, *Can Nitroalkanes be Obtained Directly from Alcohols and Sodium Nitrite in Acetic Acid – Hydrochloric Acid Mixture?*; *Synlett* **2001**, 1121-1122.

IF<sub>2001/2013</sub> = 2.465 / 2.463; number of citations = 2.

**A2.** N. Moskalev, M. Barbasiewicz, M. Mąkosza,\* *Synthesis of 4- and 6-substituted nitroindoles*; *Tetrahedron* **2004**, 60, 347-358.

IF<sub>2004/2013</sub> = 2.643 / 2.817; number of citations = 22.



**A3.** M. Barbasiewicz, M. Judka, M. Mąkosza,\* *New reactions of  $\gamma$ -halocarbanions – underestimated active intermediates in organic synthesis; Russ. Chem. Bull., Int. Ed.* **2004**, 53, 1846-1858 (przeгляд).

IF<sub>2004/2013</sub> = 0.529 / 0.509; number of citations = 7.

**A4.** M. Mąkosza,\* M. Barbasiewicz, D. Krajewski, *Diastereoselective Synthesis of Tetrahydrofurans via Reaction of  $\gamma,\delta$ -Epoxy-carbanions with Aldehydes; Org. Lett.* **2005**, 7, 2945-2948.

IF<sub>2005/2013</sub> = 4.368 / 6.324; number of citations = 10.

**A5.** M. Barbasiewicz, M. Mąkosza,\* *Simple Synthesis of Tetrahydrofurans via Reaction of Enolates of  $\gamma$ -Chloro-ketones with Aldehydes; Synthesis* **2006**, 1190-1194.

IF<sub>2006/2013</sub> = 2.333 / 2.443; number of citations = 13.

**A6.** M. Barbasiewicz, K. Marciniak, M. Fedoryński,\* *Phase transfer alkylation of arylcetonitriles revisited; Tetrahedron Lett.* **2006**, 47, 3871-3874.

IF<sub>2006/2013</sub> = 2.509 / 2.391; number of citations = 11.

**A7.** M. Barbasiewicz,\* A. Szadkowska, R. Bujok, K. Grela,\* *Structure and Activity Peculiarities of Ruthenium Quinoline and Quinoxaline Complexes: Novel Metathesis Catalysts; Organometallics* **2006**, 25, 3599-3604.

IF<sub>2006/2013</sub> = 3.632 / 4.253; number of citations = 69.

**A8.** M. Barbasiewicz, M. Mąkosza,\* *Intermolecular Reactions of Chlorohydrine Anions: Acetalization of Carbonyl Compounds under Basic Conditions; Org. Lett.* **2006**, 8, 3745-3748.

IF<sub>2006/2013</sub> = 4.659 / 6.324; number of citations = 26.

**A9.** M. Barbasiewicz,\* M. Bieniek, A. Michrowska, A. Szadkowska, A. Makal, K. Woźniak,\* K. Grela,\* *Probing of the Ligand Anatomy: Effects of the Chelating Alkoxy Ligand Modifications on the Structure and Catalytic Activity of Ruthenium Carbene Complexes; Adv. Synth. Catal.* **2007**, 349, 193-203.

IF<sub>2007/2013</sub> = 4.977 / 5.542; number of citations = 39.

**A10.** X. Gstrein, D. Burtscher, A. Szadkowska, M. Barbasiewicz, F. Stelzer, K. Grela, Ch. Slugovc,\* *Ruthenium Quinoline and Quinoxaline Complexes: Thermally Triggered Initiators for Ring Opening Metathesis Polymerization*; *J. Polym. Sci. A* **2007**, *45*, 3494-3500.

IF<sub>2007/2013</sub> = 3.529 / 3.245; number of citations = 49.

**A11.** M. Barbasiewicz, A. Brud, M. Mąkosza,\* *Synthesis of Substituted Tetrahydropyrans via Intermolecular Reactions of  $\delta$ -Halocarbanions with Aldehydes*; *Synthesis* **2007**, 1209-1213.

IF<sub>2007/2013</sub> = 2.257 / 2.443; number of citations = 2.

**A12.** K. Skopek, M. Barbasiewicz, F. Hampel, J. A. Gladysz,\* *Three-Fold Intramolecular Ring-Closing Metatheses Involving cis Adducts of Phosphorus Donor Ligands: Syntheses, Structures, and Properties of Parachute-Like Complexes*; *Inorg. Chem.* **2008**, *47*, 3474-3476.

IF<sub>2008/2013</sub> = 4.147 / 4.794; number of citations = 26.

**A13.** M. Barbasiewicz,\* A. Szadkowska, A. Makal, K. Woźniak, K. Grela,\* *Is the Hoveyda-Grubbs Metathesis Catalyst a Vinylogous Fischer-type Carbene? Aromaticity-Controlled Activity of Ruthenium Complexes*; *Chem. Eur. J.* **2008**, *14*, 9330-9337.

IF<sub>2008/2013</sub> = 5.454 / 5.696; number of citations = 31.

**A14.** A. Wojtasiewicz, M. Barbasiewicz, M. Mąkosza, *Intramolecular Addition of  $\gamma$ -Chlorocarbanions to Electrophilic Groups – Synthesis of Tricyclic Tetrahydrofurans, Pyrrolidines and Cyclopentanes*; *Eur. J. Org. Chem.* **2010**, 1885-1894.

IF<sub>2010/2013</sub> = 3.206 / 3.154; number of citations = 3.

**A15.** A. J. Nawara-Hultsch, K. Skopek, T. Shima, M. Barbasiewicz, G. D. Hess, D. Skaper, J. A. Gladysz,\* *Syntheses and Palladium, Platinum, and Borane Adducts of Symmetrical Trialkylphosphines with Three Terminal Vinyl Groups*, *Z. Naturforsch. B* **2010**, *65b*, 414-424.

IF<sub>2010/2013</sub> = 0.816 / 0.772; number of citations = 4.

**A16.** Z. Komsta, M. Barbasiewicz, M. Mąkosza,\* *Diastereoselective synthesis of tetrahydrofurans from aryl 3-chloropropylsulfonides and aldehydes*; *J. Org. Chem.* **2010**, *75*, 3251-3259.

IF<sub>2010/2013</sub> = 4.002 / 4.638; number of citations = 2.

**A17.** A. Poater, F. Ragone, A. Correa, A. Szadkowska, M. Barbasiewicz, K. Grela, L. Cavallo, *Mechanistic Insights on the Cis-Trans Isomerization of Ruthenium Complexes Relevant to Olefin Metathesis Catalysts*; *Chem. Eur. J.* **2010**, *16*, 14354-14364.

IF<sub>2010/2013</sub> = 5.476 / 5.696; number of citations = 42.

**A18.** M. Stollenz, M. Barbasiewicz, A. J. Nawara-Hultsch, T. Fiedler, R. M. Laddusaw, N. Bhuvanesh, J. A. Gladysz, *Dibridgehead Diphosphines that Turn Themselves Inside Out*; *Angew. Chem. Int. Ed.* **2011**, *50*, 6647-6651.

IF<sub>2011/2013</sub> = 13.455 / 11.336; number of citations = 16.

**A19.** A. Leitgeb, A. Szadkowska, M. Michalak, M. Barbasiewicz, K. Grela, C. Slugovc, *Unequal siblings: Adverse characteristics of naphthalene-based hoveyda-type second generation initiators in ring opening metathesis polymerization*; *J. Polym. Sci. A: Polym. Chem.* **2011**, *49*, 3448-3454.

IF<sub>2011/2013</sub> = 3.919 / 3.245; number of citations = 15.

**A20.** P. Knapkiewicz, K. Skowerski, D. E. Jaskólska, M. Barbasiewicz, T. K. Olszewski, *Nitration Under Continuous Flow Conditions: Convenient Synthesis of 2-Isopropoxy-5-nitrobenzaldehyde, an Important Building Block in the Preparation of Nitro-Substituted Hoveyda-Grubbs Metathesis Catalyst*; *Org. Process Res. Dev.* **2012**, *16*, 1430-1435.

IF<sub>2012/2013</sub> = 2.739 / 2.549; number of citations = 5.

**A21.** M. Barbasiewicz, M. Mąkosza, *Intermolecular Reactions of  $\gamma$ -Halocarbanions—Stepwise Analogs of 1,3-Dipolar Cycloaddition*; *Helv. Chim. Acta* **2012**, *95*, 1871-1890 (przeгляд).

IF<sub>2012/2013</sub> = 1.383 / 1.394; number of citations = 0.

**A22.** A. J. Nawara-Hultsch, M. Stollenz, M. Barbasiewicz, S. Szafert, T. Lis, F. Hampel, N. Bhuvanesh, J. A. Gladysz, *Gyroscope-Like Molecules Consisting of PdX<sub>2</sub>/PtX<sub>2</sub> Rotators within Three-Spoke Dibridgehead Diphosphine Stators: Syntheses, Substitution Reactions, Structures, and Dynamic Properties*; *Chem. Eur. J.* **2014**, *20*, 4617-4637.

IF<sub>2014/2013</sub> = - / 5.696; number of citations = 4.

**A23.** J. Wappel, K. Grudzień, M. Michalak, M. Barbasiewicz K. Grela, C. Slugovc; *Initiation efficacy of halo-chelated cis-dichloro configured ruthenium based second generation benzylidene complexes in Ring-opening Metathesis Polymerization*, *Monatsh. Chem.* **2015**, DOI: 10.1007/s00706-015-1494-8.

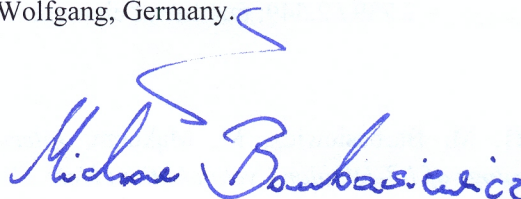
IF<sub>2015/2013</sub> = - / 1.347; number of citations = 0.

b) list of patents

**P1.** K. Grela, M. Barbasiewicz, A. Szadkowska, *Complex of ruthenium and osmium, method of production thereof and use thereof as (pre)catalysts of the metathesis reaction*; international patent WO 2007140954 A1 (published also, as EP2029278A1, EP2029278B1, US8318965, US8658796, US20100174068, US20130079515), the Intellectual Property was purchased by UMICORE AG & Co. KG, Hanau-Wolfgang, Germany.

**P2.** R. Kadyrov, A. Szadkowska, K. Grela, M. Barbasiewicz, *Schwefelhaltige Metathesekatalysatoren*; german patent DE 102007020694 A1 (published also, as CN101298462A, CN101298462B, EP1990348A2, EP1990348A3, US8183382, US20080275247); the Intellectual Property was purchased by Evonik Degussa GmbH, Germany.

**P3.** K. Grela, M. Michalak, M. Barbasiewicz, *Nowe kompleksy rutenu, sposób ich wytwarzania oraz zastosowanie w reakcji metatezy olefin (New complexes of ruthenium, method for their preparation, and their application in olefin metathesis reactions)*; polish patent PL 216649 (published also, as WO2012168183 A1, CN103648644A, EP2718016A1, US20140171607); the Intellectual Property was purchased by UMICORE AG & Co. KG, Hanau-Wolfgang, Germany.



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