XI\textsuperscript{th} International Seminar for Ph. D. Students on Organometallic and Coordination Chemistry

April 06\textsuperscript{th} – 10\textsuperscript{th} 2008

Youth Hostel „Mortelgrund“
Sayda
Germany

Organizing Institutions

H. Lang
Technische Universität
Chemnitz

W. Kläui
Heinrich-Heine-Universität
Düsseldorf
Welcome Address

A very warm welcome is expressed to all participants of the XIth International Seminar for Ph. D. Students on Organometallic and Coordination Chemistry in Sayda. The topic of the seminar covers all modern aspects in organometallic and metal-organic chemistry including main-group elements.

We are very pleased to announce two plenary, seven invited, and fifty-four short lectures, summarizing the most actual knowledge in different areas of transition metal and main-group element chemistry in all kinds of systems, including both, theoretical and experimental aspects. We hope that this platform will lead to fruitful and manifold discussions and bring the different experts together in a warm and relaxed way. An open exchange of ideas should be encouraged by all who attend this symposium. The size of this meeting with ca. 90 attending scientists should allow to interact between different disciplines, to promote creative collaborative studies, and of course to stimulate further research topics in new areas in a interdisciplinary way.

We wish all participants of this meeting a very nice and pleasant stay in Sayda, in the heart of the Erzgebirge.

Heinrich Lang                Wolfgang Kläui
Organizing Committee

Organizing Institutions:

- TU Chemnitz
  Faculty of Natural Science
  Institute of Chemistry
  Inorganic Chemistry
  Strasse der Nationen 62
  09111 Chemnitz
  Germany

- HHU Düsseldorf
  Department of Inorganic Chemistry
  Universitätsstrasse 1
  40225 Düsseldorf
  Germany

Local Organizing Committee:

- Prof. Dr. H. Lang
  Tel. 0049 371 53121210
  Heinrich.Lang@chemie.tu-chemnitz.de

- Prof. Dr. W. Kläui
  Tel. 0049 211 8112286
  Klaeui@uni-duesseldorf.de

- J. Ruder
  Tel. 0049 371 53121210
  Jutta.Ruder@chemie.tu-chemnitz.de

- N. Rüffer
  Tel. 0049 371 53131836
  Natalia.Rueffer@chemie.tu-chemnitz.de

- U. Stöß
  Tel. 0049 371 53131330
  Ute.Stoess@chemie.tu-chemnitz.de

- S. Tripke
  Tel. 0049 371 53135818
  Sascha.Tripke@chemie.tu-chemnitz.de
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for the generous support of the XIth International Seminar for Ph. D. Students
on Organometallic and Coordination Chemistry.
Previous Meetings

1st Regional Seminar of Ph. D. Students in Organometallic Chemistry;
Merseburg, Germany, December 3, 1993;
organized by Prof. Dr. K.-H. Thiele

2nd Regional Seminar of Ph. D. Students in Organometallic Chemistry;
Prague, Czech Republic, December 1 – 3, 1994;
organized by Dr. K Mach

3rd Regional Seminar of Ph. D. Students in Organometallic and Organophosphorus Chemistry;
Heiligenstadt, Germany, April 15 – 19, 1996;
organized by Prof. Dr. P. Binger and Prof. Dr. U. Zenneck

4th Regional Seminar of Ph. D. Students in Organometallic and Organophosphorus Chemistry;
Polanica-Zdrój, Poland, October 5 – 9, 1997;
organized by Prof. Dr. P. Sobota and Prof. Dr. A. Pietrzykowski

5th Regional Seminar of Ph. D. Students in Organometallic and Organophosphorus Chemistry;
Seč, Czech Republic, April 26 – 29, 1999;
organized by Prof. Dr. J. Holeček

6th Regional Seminar of Ph. D. Students in Organometallic and Organophosphorus Chemistry;
Karpacz, Poland, April 9 – 13, 2000;
organized by Prof. Dr. P. Sobota and Prof. Dr. A. Pietrzykowski

7th Regional Seminar of Ph. D. Students in Organometallic and Coordination Chemistry;
Bad Kösen, Germany, March 3 - 7, 2002;
organized by Prof. Dr. D. Steinborn and Dr. H. Schmidt

8th Regional Seminar of Ph. D. Students in Organometallic Chemistry;
Hrubá Skalá, Czech Republic, September 29 – October 3, 2003;
organized by Dr. K. Mach

9th Regional Seminar of Ph. D. Students in Organometallic and Organophosphorus Chemistry;
Szklarska Poreba, Poland, April 10 – 14, 2005;
organized by Prof. Dr. P. Sobota and Prof. Dr. A. Pietrzykowski

10th Regional Seminar of Ph. D. Students in Organometallic and Coordination Chemistry;
Medlov, Czech Republic, September 17 – 22, 2006;
organized by Prof. Dr. J. Holeček and Dr. A. Růžička
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Alphabetical List of Lecturers

Addresses of Lecturers

During the conference, e-mail messages can be received under the addresses or numbers given below:

   sascha.tripke@chemie.tu-chemnitz.de

   website www.tu-chemnitz.de/chemie/anorg/ispsoc/

   and faxes: 0049-371-531 21219
Programme

Sunday, April 06 2008

until 18:00  Welcome

18:15 - 19:15 Dinner

19:30 - 19:45 Opening Remarks
Vice-President for Research, Prof. Dr. Dr. Dietrich R. T. Zahn
Dean, Faculty of Natural Sciences, Prof. Dr. Karl Heinz Hoffmann
Prof. Dr. Heinrich Lang

Chair: H. Lang

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10:55 - 11:10  Coffee Break

Chair: W. Kläui

11:10 – 11:55  J. Zakrzewski  
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11:55 – 12:00  W. Kläui
Düsseldorf
Closing Remarks

12:00 – 13:00  Lunch

13:00  Departure
KEYNOTE LECTURES
Modern approaches to the study of “mixed-valence” compounds

Paul J. Low

Department of Chemistry, Durham University, South Rd, Durham, DH1 3LE, UK.

Metal complexes of general form \([\{M\}\{\mu\text{-bridge}\}\{M\}]^+\) with open shell electronic structures are the subject of a considerable degree of historical and contemporary interest. In the case of systems where the unpaired electron can be attributed to a metal centre, the concepts of mixed valency can be invoked, and analysis of the associated Intervalance Charge Transfer transition in terms of the coupling between the metal centres using methods developed by Noel Hush (and others) is appropriate.

However, as the metal, ancillary ligand and/or bridging ligand orbitals mix, the concept and applicability of “metal centred valency” becomes increasingly inappropriate and new treatments and descriptions of the underlying electronic structure are necessary. Equally, in cases where redox-active or “non-innocent” ligands are present, electrochemical and spectroscopic data must be carefully analysed to ensure accurate descriptions and analyses are employed.

In this presentation the use of spectroscopic and computational methods in the characterisation of radical cations \([\{\text{Cp}^*(dppe)\text{Ru}\}\{\mu\text{-bridge}\}\{\text{Ru(dppe)Cp}\}]^+\) will be described. Through variation in the nature of the bridging moiety it is possible construct systems that behave as pseudo-classical mixed valence systems (illustrated below for a diethynyl carboranyl bridged system), offer highly delocalised electronic structures or bridging-ligand centred radical character.
Half-sandwich metallocarbonyl $\eta^1$-N-imidato complexes in bioorganometallic chemistry

Janusz Zakrzewski,
Department of Chemistry, University of Lodz, 90-136 Lodz, Narutowicza 68, Poland
janzak@uni.lodz.pl

The aim of the lecture is to present synthesis of CpM(CO)$_n$ ($\eta^1$-N-imidato) complexes (M = Fe, Mo, W; n = 2 or 3), their electronic structure and reactivity toward various biomolecules. These complexes have been used as IR-detectable labeling reagents for proteins. To increase the sensitivity of the detection, metallocarbonyl dendrimers have been synthesized and coupled e.g. with anti-analyte antibodies. Some of the title complexes display enzyme-inhibiting activity (e.g. toward GST, papain).

Results presented in the lecture have been obtained, in large part, in collaboration with the Prof. Jaouen’s team (ENSCP, Paris).
INVITED LECTURES
Metal complexes and organometallic compounds as precursors for electronic and ceramic materials. Old ligands, new tricks.

Piotr Sobota

Faculty of Chemistry, Wrocław University, 14, F. Joliot-Curie, 50-383 Wrocław, Poland

For the last two decades, there has been a growing interest in the development of the chemistry of mixed-metal bi- and polynuclear o xo, alkoxo and alkoxo-organometallic complexes. Such interest derives from their fascinating structural chemistry, interesting catalytic properties, and high potential for industrial applications. High applicability of such compounds is an effect of a cooperation of two different metals in a single molecule which gives rise to properties that are not a simple sum of the properties of the individual metals and is often crucial for a system to achieve a desired activity. The classical example would be the cooperation of titanium and aluminum in an olefin polymerization catalyst. Instead, well-defined group 2 heterobimetallic alkoxo complexes are known as very efficient single-source precursors (SSP) for the fabrication of highly pure oxide-ceramic materials. These are crucial for today’s technology and are utilized for the production of superconductors, microelectronic circuits, sensors, and ferroelectric materials. In our research group we have synthesized several structurally interesting heterobimetallic alkoxo-organometallic complexes containing main group and transition metals. The lecture will highlight the synthesis of a mixed-metal alkoxo-organometallic complexes, an excellent single-source precursors for oxide materials.

Hydroxycarbenes in Catalysis – Platina-β-diketones as Model Complexes

Dirk Steinborn, Michael Werner, Sebastian Schwieger

Institut für Chemie – Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg
Kurt-Mothes-Straße 2, 06120 Halle, Germany

Beginning with an overview on hydroxycarbenes–metal complexes as intermediates in homogeneously catalyzed processes, the electronically unsaturated (16 ve) platina-β-diketones 1, hydroxycarbone complexes that are stabilized by intramolecular O–H···O hydrogen bonds to neighbored acetyl ligands (Scheme 1), will be presented. Analogously, organic β-diketones 2 are considered as enols stabilized by intramolecular O–H···O hydrogen bonds to keto groups. The strengths of the hydrogen bonds in type 1 complexes have been calculated to be up to twice as strong as those in acetylacetone.

Due to the electronic unsaturation, the platina-β-diketones 1 were found to readily undergo oxidative addition reactions with a wide variety of mono- and bidentate N, O, S and P donors \( L_2/L \) yielding diacetylhydridoplatinum(IV) complexes 3 (Scheme 2). Depending on the type of ligand \( L_2/L \) and the reaction conditions, these complexes can react in a C–H or H–X reductive elimination reaction yielding acetyl platinum(II) complexes 4a and 4b, respectively. Finally, the usage of platina-β-diketones 1 as precatalysts in hydrosilylation of olefins and acetylenes will be discussed.

It seems that the stabilization of platina-β-diketones by O–H···O bridges to acyl ligands is perfectly balanced: On the one hand, they are stable enough to be handled without difficulties but, on the other hand, they are reactive enough to undergo a manifold of interesting, unexpected and entirely new reactions. Thus, further insight is achieved into elementary steps where hydroxycarbenes are involved which is of interest both for organometallic chemistry and for homogeneous catalysis.

Selected References
Bioinspired oxidation reactions with highly preorganized dicopper complexes

Franc Meyer

Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany

Numerous enzymes take advantage of the cooperative action of two proximate metal ions within their active site, in particular for multielectron redox transformations (e.g., for the activation of O₂ at dicopper sites and subsequent oxygenation and oxidation chemistry). These natural systems represent a guiding line for novel bioinspired catalysts.[1] We have prepared a series of highly preorganized bimetallic complexes based on compartmental pyrazolate ligands, in which molecular parameters such as the metal-metal separation can be tuned by appropriate modifications of the ligand scaffold.[2] These systems allow to study structure/activity correlations in cooperative two-center reactivity.[3] Selected examples of copper-mediated oxidation reactions as well as insight into structural and electronic details of O₂-activation at the multicopper sites will be presented.

This work is supported by the DFG (International Research Training Group GRK 1422; www.biometals.eu)

Inorganometallics and catalysis

Bogdan Marciniec

Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Numerous reactions of organic compounds catalyzed by TM complexes developed in the last half century occur via active intermediates involving metal-carbon bonds i.e. organometallics. Per analogy, organic derivatives of a heteroatom such as silicon, boron, germanium and other p-block elements (E) in the presence of TM complexes undergo transformations via respective intermediates containing metal-heteroatom (TM–E) bond called inorganometallics [1, 2]. In these transformations these complexes are actual catalysts and E does not play role of ancillary ligands but undergoes transformation to get products (E–C, E–E, E–E’, where E = Si, Ge, B, Sn..).

The aim of the lecture is to present exemplary reactions occurring in the presence of TM (M=Ru, Rh, Ir, Pd) complexes containing or generating TM–H or TM–E bonds, such as hydrometallations and bismetallations and particularly trans-metallations. The latter reactions based on catalytic activation of sp² and sp-carbon-hydrogen bonds as well as O–H bond of alcohols and silanols with vinylmetaloids (CH₂=CH–E) can be summarized as follows [3]:

\[ \text{ER}_n^+ + \text{E}^+ \cdot \cdot \cdot \text{H} \rightarrow \text{[TM]} \rightarrow \text{H} + \text{[TM]} \rightarrow \text{E} \rightarrow \text{R}_n \text{E} \rightarrow \text{E}' + \]

\[ E = \text{Si, B, Ge}; \quad \text{E} \rightarrow \text{H} = \equiv \text{C} \cdot \text{H}, \equiv \text{C} \cdot \text{H}, \equiv \text{C} \cdot \text{OH}, \equiv \text{Si} \cdot \text{OH} \]

A notable peculiarity of these processes is that they open as a new universal route for synthesis of well-defined molecular and macromolecular compounds with E–E’ functionality.

References:
Coordination Chemistry of Divalent Carbon(0) Compounds – Theoretical Results and Experimental Challenge

Gernot Frenking

Fachbereich Chemie, Philipps-Universität, Hans-Meerwein-Strasse, D-35043 Marburg, Germany

The topic of the lecture are theoretical studies of coordination compounds with divalent carbon(0) ligands which have the general formula CL₂ where L is a σ electron donor. The chemical bond between the ligand L and carbon is a L→C donor-acceptor bond which means that the carbon atom in CL₂ carries two electron lone pairs. This makes divalent carbon(0) compounds exceptionally strong donors. Experimentally known examples for CL₂ are carbodiphosphoranes C(PR₃)₂ which have already been synthesized in 1963. A theoretically predicted new class of divalent carbon(0) compounds are carbodicarbenes C(NHC)₂ (1) where NHC = N-heterocyclic carbene. The latter compounds are related to tetraaminoallenes 2 (R = NX₂). The calculations predict that divalent carbon(0) compounds serve as strong Lewis bases which yield main-group and transition metal complexes that possess promising chemical properties which should be investigated with experimental methods.

\[ \text{CDP} \]

\[ \text{1} \]

\[ \text{2} \]

\[ R_3P! \rightarrow C \rightarrow PR_3 \]

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The Design of Mixed-donor Ferrocene Ligands for Enantionselective Allylic Alkylation

Petr Štěpnička

Charles University in Prague, Faculty of Science, Department of Inorganic Chemistry
Hlavova 2030, 128 40 Prague, Czech Republic; E-mail: stepnic@natur.cuni.cz

Enantioselective allylic substitution [1] has become a widely accepted testing tool used for assessing the catalytic performance of chiral ligands. It also represents a powerful synthetic method that allows stereoselective construction of new C–C bonds in functionalised molecules.

A number of chiral ferrocene donors have been studied in this reaction with varying success [2]. This contribution will deal with the preparation of two classes of novel chiral ferrocene donors combining different coordination sites – chiral phosphinoalkenes [3] and chiral phosphinoamides [4], and their utilisation in palladium-catalysed allylic alkylation. Particular attention will be paid to investigations aimed at understanding the mechanism of chiral information transfer from the ligand to the formed product.


Organoantimony and organobismuth pincer compounds

Libor Dostál*

Department of General and Inorganic Chemistry, Faculty of Chemical Technology,
University of Pardubice, nám. Čs. Legií, 532 10, Pardubice, Czech Republic,
*libor.dostal@upce.cz

Y,C,Y chelating, well known as pincer, ligands represent an extremely useful platform for coordination chemistry of both transition and main group elements. These ligands can be quite easily tuned at specific positions of their skeletons and it has usually pronounced influence on chemical behavior of synthesized complexes especially central metals.

Pincer type complexes of heavier pnictogens (Sb, Bi) have become targets of scientific interest only recently. The latest results concerning this field of hypervalent antimony and bismuth compounds containing O,C,O and N,C,N ligands will be shown and discussed.

\[
\begin{align*}
\text{OR} & \quad \text{OR} \\
\text{M} & \quad \text{M} \\
\text{N} & \\
\text{N} & \\
M &= \text{Sb, Bi}
\end{align*}
\]
SHORT LECTURES
Structural Relationships
in Polynuclear Bismuth Oxo Clusters

Dirk Mansfeld, Tobias Rüffer, Heinrich Lang, Markus Schürmann, Michael Mehring*

Technische Universität Chemnitz, Institut für Chemie, 09107 Chemnitz, Germany
a) Technische Universität Dortmund, Anorganische Chemie II, 44221 Dortmund, Germany
b) X-ray crystallography

The selective synthesis of metal oxide based materials with defined particle size is of current interest within application-orientated research projects. Special focus is given to the synthesis of nanoparticles. An important step on the way to prepare materials based on nanoparticular metal oxides is the control of the nucleation process. Polynuclear metal oxo clusters may serve as model compounds for a better understanding of this process. In contrast to transition metal oxo clusters few examples of structurally characterized, main group metal oxo clusters of high nuclearity, are known.

In line with our research on bismuth oxo compounds several intermediates in the course of hydrolysis of monomeric precursors, for example bismuth silanolates, were isolated and structurally characterized. The metal oxo clusters \([\text{Bi}_9\text{O}_7\text{(OSiMe}_3\text{)}_{13}], [\text{Bi}_{18}\text{O}_{18}\text{(OSiMe}_3\text{)}_{18}]\) and \([\text{Bi}_{22}\text{O}_{26}\text{(OSiMe}_2\text{Bu})_{14}]\) are representatives among these compounds [1-4]. The characterization of structurally related compounds contributes to the fundamental understanding of the formation process and the assembly principles of bismuth oxido particles. Here we present structural relationships between several bismuth oxo clusters.

Fig. 1 The formation of \([\text{Bi}_{18}\text{O}_{18}\text{(OSiMe}_3\text{)}_{18}]\) by partial hydrolysis of \([\text{Bi}(\text{OSiMe}_3\text{)}_3]_3\).

Water-soluble Platinum Clusters: Syntheses and Catalytic Activity

Mareike Meyer, Wolfgang Kläui

*Heinrich-Heine-Universität, Universitätsstr. 1, 40225 Düsseldorf, Germany

Metal clusters of only a few nanometers in diameter can be considered to fill the gap from binuclear metal complexes to the metallic state. Therefore they are of major interest in catalytic research.

We succeeded in synthesizing water soluble platinum clusters of 2 – 4 nm in size by reduction of an aqueous solution of K₂PtCl₄ with hydrogen gas in the presence of the stabilizing ligand 2-diphenylphosphanoethylbisodiumphosphonate [1]. Furthermore, we are able to define dimensions and size distribution of the emerging clusters by varying the conditions during synthesis.

Scheme 1: Synthesis of water-soluble platinum clusters

The obtained clusters are stable when exposed to air and can be stored in solution over months without coagulation. All clusters are efficient catalysts in the hydrogenation of olefins. The catalytic activity is size-dependent; decreasing the main diameter increases the activity. Due to their excellent water-solubility our platinum clusters are most promising catalysts especially in “Green Chemistry”.

Arene Iron And Arene Ruthenium Complexes And Their Use For MOCVD Applications

Ilona Jipa\textsuperscript{a}, Katia Michkova\textsuperscript{b}, Nadejda Popovska\textsuperscript{b}, and Ulrich Zenneck\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a} Department für Chemie und Pharmazie, Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-91058 Erlangen, Germany

\textsuperscript{b} Lehrstuhl für Chemische Reaktionstechnik, Universität Erlangen-Nürnberg, Egerlandstrasse 3, D-91058 Erlangen, Germany

Ruthenium thin films are of significant interest as promising candidates for microelectronic applications like microelectrodes or microelectric contacts and thin films or nanoparticles of iron at oxidic surfaces are of specific interest as catalysts for carbon nanotube (CNT) formation. We investigate \{\text{[arene](diene)M}]\ derivatives systematically with M = Ru and Fe as MOCVD (Metal Organic Chemical Vapor Deposition) precursors, which combine a good vapor pressure with thermal decomposition temperatures below 200 °C and a well controllable follow-up chemistry of the released ligands after the MOCVD process.[1]

\text{[\text{Benzene}(1,3\text{-cyclohexadiene})Ru]} was investigated as a designed MOCVD precursor where the inherent structural and chemical features of the ligands help the formation of pure ruthenium films.[2] Main focus was spent to evaluate such process parameters, which grant the purity of the deposited ruthenium films without the help of a reactive gas component.

\text{[(1,3-Butadiene)(toluene)Fe]} and a fluidized bed reactor were identified as an ideal combination for the MOCVD of Fe nanoparticles (Fe-NP) or Fe thin films on oxidic powders of different kind.[3] Several Fe coated powders were used successfully as heterogeneous metal catalysts for a diameter controlled CNT preparation.


Element Organic Frameworks with high Permanent Porosity

Marcus Rose, a Winfried Böhlmann, b Stefan Kaske*a

aDepartment of Inorganic Chemistry, Dresden University of Technology, Mommsenstr. 6, 01062 Dresden, Germany

bFaculty of Physics and Earth Science, University of Leipzig, Linnéstr. 5,04103 Leipzig, Germany

Porous materials such as metal-organic frameworks (MOFs, [1]) have high potential for applications in adsorption, separation, gas storage and heterogeneous catalysis. Their modular concept was used to develop a new class of highly microporous materials (d < 2 nm) that combine properties like high hydrophobicity, high stability against water and good thermal stability. In the following, we report the integration of elements such as silicon and their use as connectors. At the same time, organic linkers are used to tailor the pore size, resulting in porous, highly hydrophobic and thermally stable element organic frameworks (EOFs) via an organometallic route. The primary building block Tetrakis(4-bromophenyl)silane [2] was lithiated fourfold by reaction with n-butyllithium under inert conditions. Subsequent reaction with tetraethylorthosilicate (TEOS) at 263 K resulted in the formation of the porous network poly(1,4-phenylene)silane (EOF-1). A biphenylene linker was used to obtain larger pores in poly(4,4’-biphenylene)silane (EOF-2) on a one-step reaction. EOF-1 and EOF-2 are X-ray amorphous. They show no decomposition in air, moisture or aqueous solutions and have good thermal stability in air up to 673 K. Both compounds are highly porous with specific BET surface areas of 780 m²g⁻¹ (EOF-1) and 882 m²g⁻¹ (EOF-2) as determined from the nitrogen physisorption isotherms measured at 77 K. Water adsorption isotherms at 298 K show a high hydrophobicity for both materials. Summarizing, we have presented a new approach for the design of hydrophobic microporous frameworks with accessible pore systems using organo-element chemistry. In our view, an extension of the concept in terms of elements used as nodes and organic linkers as connectors will lead to valuable adsorbents and catalyst supports with well defined porosity and functionality.

Design and Characterization of Novel Chiral Building Blocks for the Construction of Functional Porous Materials

T. Kaczorowski, a J. Lewiński, a W. Bury, a M. Dranka, a W. Śliwiński, a I. Justyniak, b J. Lipkowski b

a Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
b Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

In the last decade, there has been tremendous interest in designing and synthesis of functional solids based on metal-organic coordination networks. One of the most difficult challenges in materials chemistry is to master synthesis of crystal networks with desired topology and properties by appropriate choice of organic ligand (or organometallic metalloligand) and metal precursor. The employment of various multitopic, conformationally rigid and flexible ligands with different binding modes and strengths is very fruitful in the construction of well-defined solid-state structures with expected physical and chemical properties.

This report is focused on the construction of achiral and homochiral coordination polymers combining homoleptic zinc alkyls, $R_2Zn$, as connectors and different bipyridine-type compounds as linkers. Various combinations of these subunits lead to zig-zag chains (I), helices (II) and fabrics (III) with or without porous architecture.[1] The successful construction of porous homochiral architectures was achieved by the employment of alkylaluminum derivatives of cinchonine as metalloligands. The selected porous materials demonstrated highly desirable properties of enantioseparation of racemic organic compounds and gas sorption.

From supramolecular structures to intelligent surfaces

Schirrmacher, C., Bruhn, C., Siemelung, U., Käfer, D., Witte, G.

aUniversität Kassel, Heinrich-Plett-Str. 40, 34132, Kassel, Germany

bRuhr-Universität Bochum, Universitätsstr. 150, 44780, Bochum, Germany

Surfaces that can react on external stimuli in a reversible manner (so called smart surfaces) are of big research interest. For this purpose we developed a modular synthetic concept, using the spontaneous self assembly of functional adhesive molecules which form self assembled monolayers on Au(111) and HOPG. The adsorbing molecules are designed in a modular way. The binding unit contains disc like thioether functionalized phthalocyanines and porphyrines. The metall centre serves as “docking station for rod like assembly groups containing spacer and terminal functional units. By this concept the functional units are lateral separated and are able to fulfill their function without any disturbance by neighbour molecules. A similar strategy was already successfully used for tripodal binding groups. Planned and already established functions are redoxactivity, photoisomerisation, complexation of catalytic active metals and immobilisation of oncogenic proteins.


Selfassembled monolayers based on thiol functionalized transition metal complexes

Katrin Döring, Michael Zharnikov, Andrey Shaporenko, Tobias Weidner, Rudolf Holze, and Heinrich Lang*
a
Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl für Anorganische Chemie, Straße der Nationen 62, 09111 Chemnitz, Germany.
b Universität Heidelberg, Institut für Angewandte Physikalische Chemie, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany.
c Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Professur für Physikalische Chemie / Elektrochemie, Straße der Nationen 62, 09111 Chemnitz, Germany.

Different synthesis methodologies to prepare thiols of type \( R\text{–C\equiv-C\text{–C}_6\text{H}_4\text{–C}_6\text{H}_4\text{–SR} \) and \( \text{L}_n\text{M}\text{–C\equiv-C\text{–C}_6\text{H}_4\text{–C}_6\text{H}_4\text{–SR} \) (e.g., type A molecule: \( \text{L}_n\text{M} = (\eta^5\text{-C}_5\text{H}_5)\text{–(C\text{–C}_5\text{H}_4)}\text{Fe, (C–C\text{–C}_6\text{H}_4)}\text{Ru; R = H, COMe} \) will be reported [1]. The chemisorption of these molecules from solution onto gold surfaces gave Self-Assembled Monolayers (SAMs), which have been characterized by photoelectron spectroscopy, impedance, NEXAFS (near edge X-ray absorption fine structure spectroscopy), and SERS (surface enhanced raman spectroscopy) [2, 3].

![Molecule A](image)

(M = Fe, Ru)

Spectroscopic and thermal properties of lanthanides (III) complexes with 2,2’-biphenyldicarboxylic acid

Justyna Sienkiewicz*, Zofia Rzączyńska, Alina Kula

Department of General and Coordination Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Poland

The complexes of Y(III) and lanthanides(III) from La to Lu with 2,2’-biphenyldicarboxylic acid were obtained as hydrated precipitates with the metal:ligand ratio of 2:3 and the general formula of \( \text{Ln}_2(\text{C}_12\text{H}_8(\text{COO})_2 \cdot n \text{H}_2\text{O}) \), where \( n=3 \) for the first isostructural series from La to Er and \( n=6 \) for the second series of Tm, Yb and Lu(III) complexes.

The complexes were characterized by FTIR and Raman spectroscopy. The characteristic of carboxyl vibrations in the free diphenic acid are found at 1685 cm\(^{-1}\) as strong vibrations of the protonated carboxylic group COOH and also strong bands at 1412 and 1578 cm\(^{-1}\) assigned to the symmetric and asymmetric \( \text{C}=\text{O} \) stretching vibrations of the other deprotonated carboxylic group of acid. During coordination of metal ions the bands of 1685 cm\(^{-1}\) disappear in the spectra of complexes and symmetric and asymmetric bands of the \( \text{COO}^\cdot \) groups appear. In the spectra of Y and La to Er the asymmetric vibration bands of \( \text{COO}^\cdot \) groups are present at 1532-1521 cm\(^{-1}\) and symmetric vibration bands of \( \text{COO}^\cdot \) groups are at 1412-1402 cm\(^{-1}\). The \( \Delta \nu(\text{COO}^\cdot) \) values for each complex of La-Er(III) group are smaller than those of Tm-Lu complexes and suggest that carboxylic group in those complexes posses different coordination modes. In a high energy region in the IR spectra there are the bands in range 3700-3100 cm\(^{-1}\), which indicates absorption peaks due to \( \text{O}-\text{H} \) bonds of water molecules. These bands are associated with hydrogen bonds formation and change their positions with changing the hydrogen bond energy.

The curve of TG/DTG and DTA thermal analysis show that hydrated complexes of lanthanides from La-Lu heated in air lose all water molecules in one step. Temperature of dehydration process for trihydrated complexes is about 150\(^\circ\)C, but for heksahydrated complexes is lower down 100\(^\circ\)C. The anhydrous compounds are stable up to about 350\(^\circ\)C in air atmosphere and decompose on heating directly to the oxides; \( \text{Ln}_2\text{O}_3 \), \( \text{Tb}_2\text{O}_{10} \) and \( \text{Pr}_6\text{O}_{11} \). The temperature of oxide formation is in the range of 600-750\(^\circ\)C, excepting 400\(^\circ\)C (for Ce complex).

The gas product analysis which is connected with decomposition process was carried out for gadolinium(III) complex as the representative complex for all isostructural compounds of Y and La-Er group complexes. These spectra confirm, that not deamination takes place.
Immobilized Ru complexes on mesoporous molecular sieves as catalysts for olefin metathesis

David Bek, Hynek Balcar, Jan Sedláček, Jiří Čejka

J. Heyrovský Institute of Physical Chemistry AS CR, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic

Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Albertov 2030, CZ-128 40, Prague 2, Czech Republic

Mesoporous molecular sieves with unique properties such as large surface area, large void volume and narrow pore size distribution represent modern supports for designing advanced catalysts including catalysts for olefin metathesis [1]. New heterogeneous catalyst for ring opening metathesis polymerization (ROMP) has been prepared by immobilization of [RuCl₂(p-cymene)]₂ on siliceous mesoporous molecular sieve SBA-15 (S_{BET} = 915 m²/g, V = 1.10 cm³/g, d = 6.3 nm). The catalyst of 1% weight content of Ru, was prepared by stirring of dried SBA-15 with [RuCl₂(p-cymene)]₂ in CH₂Cl₂ at room temperature for 5 hours. Activity of the catalyst was tested in ROMP of 2-norbornene in toluene (1).

After catalyst activation with trimethylsilyldiazomethane before reaction, high molecular weight polynorbornene of M_w = (2.8–7.4)×10^5 in the yields up to 77% were obtained (1 h, 60°C). The structure of polymer was proved by IR spectroscopy. Leaching of the immobilized catalyst was not observed. Catalyst can be easily separated from reaction mixture in contrast to the corresponding homogeneous system [2] and, therefore, polymeric product without catalyst residues can be obtained.

Perfluoroalkylation by Cross-metathesis of Alkenes

Barbara Eignerová, a,b  Martin Kotora⁎, a,b

a Department of Organic and Nuclear Chemistry, Faculty of Science, Charles University, Hlavova 2030, 12843 Prague 2, Czech Republic
b Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

A number of compounds with attached perfluoroalkylated chains exhibit interesting biological properties. Therefore, it is of general synthetic interest to develop new methodology that would enable to introduce perfluoroalkyl groups into various molecules under mild reaction conditions. Recently, it was shown that one such option is ruthenium catalysed cross-metathesis with perfluoroalkylated ethenes [1].

Currently, we are working on a related methodology that would allow the synthesis of arenes, ferrocenes, saccharides and steroids, bearing perfluoroalkyl substituents. Our procedure is based on the cross-metathesis of easily available 3-perfluoroalkylpropenes with compounds having the terminal double bond. Effect of the substrate structure on cross-metathesis selectivity and reactivity and other mechanistic features will be presented.

\[ \text{R}^1\text{C} = \text{R}^2 \xrightarrow{\text{Ru-cat}} \text{R}^1\text{C} = \text{R}^2 \]

\[ \text{R}^1 = \text{C}_6\text{F}_{13}, \text{C}_3\text{F}_7, \text{i-C}_3\text{F}_7 \]

\[ \text{R}^2 = \begin{array}{c}
\text{arenes} \\
\text{ferrocenes} \\
\text{saccharides} \\
\text{steroids}
\end{array} \]

Non-hydrolytic route to synthesis methylalumoxanes in reaction of aliphatic dicarboxylic acids with trimethylaluminium, activity and applications.

M. Marczewski,^a^ A. Boczkowska,b M. Siekierski,a A. Pietrzykowski*,a
Warsaw University of Technology, ^a^Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw; ^b^Faculty of Materials Science and Engineering, Woloska 141, 02-507 Warsaw, Poland

Methylalumoxanes (MAO) are one of the most studied classes of organoaluminium compounds. This is due to their important role in catalytic systems used in olefin polymerization.

Here we report the non-hydrolytic method of synthesis of methylalumoxane. The reactions between aliphatic dicarboxylic acids (malonic, adipinic, succinic, itaconic) and trimethylaluminium at various molar ratios were studied. According to a method developed in our group new methylalumoxanes containing eight aluminium atoms per molecule have been recently synthesized [1]. The activity of synthesized compounds was tested towards styrene polymerization and compared to activity of commercially available methylalumoxane.

Methylalumoxanes obtained from itaconic and succinic acids have been used as components improving properties of polyurethanes and in synthesis of polymer electrolytes. The mechanical properties of prepared polyurethanes and properties of polymer electrolytes will be discussed on the presentation.

Catalyst development for hydroformylation of long-chain olefins in sc CO₂

Cezar Ionescu, Olaf Walter, Stephan Pitter, Eckhard Dinjus

ITC-CPV, Forschungszentrum Karlsruhe, D-76201 Karlsruhe, Germany.

The hydroformylation is one of the most important industrial applications of homogeneous catalysis including for short chains olefins an effective catalyst recycling as shown in the Rhone-Poulenc-Ruhr-Chemie process. For long chain olefins however still some development for an effective catalyst recycling is needed.

One possibility offers the application of sc CO₂ (low Tₐ and pₐ) as the solvent in catalysis. Two different approaches for catalyst recycling are presented here (Scheme 1):

A) The application of the sc CO₂ as solvent under homogeneous reaction conditions with following separation of the catalyst by simple changing of p, T [1, 2].

B) The application of sc CO₂ as solvent and mobile in supported ionic liquid phase (SILP) and supported catalysis.

Scheme 1. Possible separation approach

The results of these different approaches will be presented including the physical chemical background for the phase separation technology (A) as well as an evaluation of their feasibility.

Catalytic activity of Pd(II) complexes with triphenylphosphito ligands in Sonogashira reaction in ionic liquids media

Izabela Błaszczzyk, Anna M. Trzeciak, Józef J. Ziółkowski
Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

Orthopalladation reaction is an activation of the ortho-C-H bond in phenyl ring leading to the formation of new Pd-C bond. Complexes of that type have reactive C-Pd bond and are additionally stabilized by coordination of the triarylphosphite ligands (Pd-P bond) to palladium, what can present interesting reactivity in C-C bond forming processes. As a result of the organometallation reaction two new palladacycle complexes with substituted triarylphosphite ligands P(OR)3 (R = m-MeC6H4, o-MeC6H4) have been prepared. The reactivity of the obtained complexes as well as their non-orthometallated analogues, PdCl2[P(OR)3]2, has been tested in copper-free Sonogashira reaction.

\[
\begin{align*}
\text{PhI} + \text{PhC} = \text{CH} & \xrightarrow{[\text{Pd}] \text{NET}_3, \text{IL}} \text{PhCH} = \text{Ph} \\
\end{align*}
\]

Reaction conditions: [Pd] 1 mol%; [PhI] 1 mmol; [PhC=CH] 1 mmol; [NEt3] 1.9 mmol; [IL] 1.5 ml; 80°C; t= 1 or 4 h

All reactions were carried out using iodobenzene and phenylacetylene as substrates, NEt3 as a base and reducing agent and imidazolium ionic liquids as solvents. The [bmim][PF6] and [emim][SO4C2H5] ionic liquids has been chosen. The application of ionic liquids as reaction media instead of organic solvents makes it possible to construct recyclable catalytic system what also has been tested. The obtained palladium complexes show high activity in both ionic liquids. The yield of diphenylacetylene depends on the kind of catalyst precursor and ranged from 31 to 98%. The best results were obtained for PdCl2[P(O-m-MeC6H4)3]2 (84%) and for orthopalladated dimer with the same phosphite (98%) in [bmim][PF6].

Allenylidene Complexes of Palladium.
Synthesis and Catalytic Properties

Florian Kessler, Helmut Fischer*
University of Konstanz, Universitätsstraße 10, 78457, Konstanz, Germany

Chromium complexes containing a \(\pi\)-donor substituted allenylidene ligand are readily available in an easy to perform one-pot fashion. Reaction of (CO)\(_5\)Cr[THF] with appropriate deprotonated alkynes as the cumulenyldiene precursor, followed by alkylation of the resulting alkynylchromate with R\(_3\)O[B\(_4\)] yields the corresponding allenylidene complexes in high yields. The allenylidene ligands may be transferred from chromium to tungsten [1].

However, a transfer of the allenylidene ligands to catalytically active late transition metals like palladium could not be realized. We now report on a direct straightforward route to palladium allenylidene complexes starting from commercially available N,N-dimethylpropiolamide as the C\(_3\)-source, e.g.

\[
\begin{align*}
H-C=C-C\text{O} & \quad \text{1.) NBS, AgNO}_3 \\
NMe_2 & \quad \text{2.) } \text{Pd(PPh}_3\text{)}_4 \\
& \quad \text{3.) MeOTf} \\
\end{align*}
\]

The new palladium allenylidene complexes are active pre-catalysts in Mizoroki-Heck C-C-coupling reactions. The dependence of the activity of the allenylidene complexes on the co-ligands will be discussed.

New 1’-(Diphenylphosphanyl)ferrocenecarboxamides Bearing 2-Hydroxyethyl Groups at the Amide Nitrogen

Jiří Schulz, Ivana Císařová, Petr Štěpnička

Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 12840 Prague, Czech Republic; E-mail: stepnic@natur.cuni.cz

While studying the coordination and catalytic chemistry of ferrocene phosphinocarboxylic ligands [1], we turned also to the corresponding phosphinoamide derivatives [2]. As a continuation of our work, we decided to prepare two new phosphinoferrocenyl amides bearing 2-hydroxyethyl chains at the amide nitrogen and to study their coordination and catalytic properties.

Carboxamides 1 and 2 have been synthesized by amidation of 1’-(diphenylphosphino)-ferrocenecarboxylic acid (Hdpf) [1,3]. Due to polar nature of 1 and 2 and the possibility of forming hydrogen bonds, these ligands may exert good solubilities in polar reaction media and also serve as useful synths for supramolecular coordination chemistry. Hence, palladium complexes [PdCl₂L₂] (3, L = 1; 4, L = 2) were also synthesized. As revealed by X-Ray diffraction studies, the ligands and their complexes associate in the solid state by means of hydrogen bonds, forming supramolecular arrays the complexity of which ranges from one-dimensional chains to complicated three-dimensional networks. The palladium complexes 3 and 4 were successfully tested in Pd-catalyzed Suzuki reaction in polar solvents.

Palladium complexes with NHC ligands used as catalysts of Suzuki – Miyaura reaction in green solvents.

M. S. Szulmanowicz A. M. Trzeciak

Faculty of Chemistry, University of Wroclaw, 14 F. Joliot-Curie, 50-383 Wroclaw, Poland

Suzuki - Miyaura reaction is a very important way of biaryl compounds synthesis used as non-steroidal anti-inflammatory drugs, anti-pain drugs and pesticides. Palladium complexes with N – heterocyclic carbene (NHC) ligands have found many applications in C-C cross-coupling reactions. Three new carbene complexes of palladium Pd(moktim-y)2Cl2, Pd(miop-y)2Cl2 and Pd(bmim-y)2Br2 were obtained and used as catalyst precursors in the model Suzuki- Miyaura reaction of 2–bromotoluene and phenylboronic acid. The reaction product, 2-methylbiphenyl, may be used in the food industry.

![Fig. 1](image1.png)

Fig. 1 [Pd]=

![Fig. 2](image2.png)

Fig. 2

2 - bromotoluene + phenylboronic acid → [Pd] NaHCO3 110°C 2 - methylbiphenyl

The aim of our research was to check the activity of palladium complexes in the Suzuki reaction in ecological solvent like water or ethylene glycol. We found that carbene complexes Pd(bmim-y)2Br2, Pd(moktim-y)2Cl2, Pd(miop-y)2Cl2 are good catalyst precursors of the Suzuki- Miyaura reaction. We received 50% yield of product in water and 90% - 97% yield in ethylene glycol. During the reaction Pd(0) nanoparticles were formed in situ and isolated from the reaction mixture after immobilization on Al2O3. It was found that Pd(0) is catalytically active and the reaction yield depends on the size of nanoparticles.

Phosphinoferrocene Amides Derived from Glycine – Synthesis, Coordination Properties, and Catalytic Utilization

Jiří Tauchman, Ivana Císařová, Petr Štěpnička*
Charles University in Prague, Faculty of Science, Department of Inorganic Chemistry, Hlavova 2030, 128 40, Prague, Czech Republic; E-mail: stepnic@natur.cuni.cz

For quite a long time, our group has focused on the chemistry of ferrocene-based phosphanylcarboxylic acids and their derivatives [1]. In recent years we have studied mainly phosphinoferrocene amides that combine central and planar chirality (e.g., 1–3) [2,3]. Donors of this type are not only versatile ligands but also proved to be useful catalyst components for both enantioselective and achiral metal-mediated organic transformations.

With this contribution, we report on the preparation of the first ‘conjugates’ of a carboxyphosphinoferrocene unit with an amino acid, viz. compounds 4. Coordination ability of these new ligands has been probed in Pd(II) complexes and their catalytic properties were tested in Suzuki-Miyaura cross-coupling reaction.

![Chemical Structures]

A biopolymer as stabilizing agent of gold nanoparticles

Irene Domínguez, Avelino Corma, Patricia Concepción, Vicente Fornés and María J. Sabater*
Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia,
Avenida de los Naranjos s/n, 46022 Valencia, Spain

Gold nanoparticles are already being used in a range of applications [1] and it is particularly exciting its use in catalysis. During 1980s, Haruta [2] found that small gold particles supported on different oxides can be used to oxidize CO at less than 0 °C. From then on, the synthesis of gold nanoparticles has received a lot of attention, different supports, stabilizing and reducing agents have been used for this purpose [3].

We have carried out the formation of gold nanoparticles using a biopolymer, chitosan, as stabilizer of gold nanoparticles with not additional reducer. The chitosan was deposited on silica in order to improve the weak mechanical properties and poor diffusion of the biopolymer. Two materials with different chitosan/SiO2 ratio were synthesized. Before and after gold incorporation the solids were characterized by different techniques what led us to study the metal-support interactions. This interaction, between gold and NH and OH groups of chitosan, could allow good dispersion of nanocrystals on the biopolymer what could contribute to the benefits found in chitosan with respect to others supports [4].

Determination of metal particle sizes by TEM showed an average particle size of 4-6 nm and 2-4 nm for the material with lower and higher chitosan/SiO2 ratio respectively, what showed the important stabilizer power of this biopolymer.

New Polymer-Metalloidrug Conjugates for Cancer Diagnostics

Nadine E. Brückmann, a Peter C. Kunz,* a

aHeinrich-Heine-Universität Düsseldorf, Universitätsstr. 1, 40225, Düsseldorf, Germany

In order to improve current cancer pharmaceuticals, new transport systems are developed that deliver drugs directly to tumors, where the drug can subsequently be released. This delivery is made possible by the fact that macromolecules accumulate in tumors due to the EPR-Effect [1]. Although polymers are now widely used in therapeutic approaches, only a few examples of diagnostically used polymer-conjugates exist [2]. The use of technetium as a radiotracer is of particular interest to cancer diagnostics and its chemistry is best resembled by its heavier congener rhenium. Therefore, macromolecules carrying ligands that are able to bind M(CO)₃ (M = Tc, Re) are interesting for diagnostic as well as therapeutic (in the case of ¹⁸⁸Re) approaches.

We developed the polymerizable ligand bis(2-pyridylmethyl)-4-vinylbenzylamine (L), a chelating ligand suitable for the coordination of M(CO)₃-fragments. Copolymerization of the ligand with N-(2-hydroxypropyl)methacrylamide (HPMA) results in a biocompatible copolymer-backbone capable of carrying the medically interesting technetium and rhenium cores directly into the tumor tissue.

Synthesis of ferrocenyl conjugates of thioanalogos of steroids and nucleosides via the Mitsunobu reaction using \(N\)-(ethoxycarbonyl)ferrocenecarbothioamide as the pronucleophile

Anna Wrona, Janusz Zakrzewski*

Department of Organic Chemistry, University of Lodz, Narutowicza 68, 90-136 Lodz, Poland

The introduction of redox-active ferrocenyl groups into biomolecules is one of the hot topics in bioorganometallic chemistry [1]. In this communication we report on the use of \(N\)-(ethoxycarbonyl)ferrocenecarbothioamide 1 [2] in synthesis of ferrocenyl conjugates of the thioanals of some hydroxyl-containing biomolecules. We have found that 1 undergoes the Mitsunobu reaction with alcohols and PPh₃/DEAD to afford thioimidates 2.

\[ \begin{align*}
1 & \quad \begin{array}{c}
\text{Fe} \\
\text{N} \\
\text{S} \\
\text{COOEt}
\end{array} \\
\text{H} \end{align*} \]

\[ \begin{align*}
2 & \quad \begin{array}{c}
\text{Fe} \\
\text{N} \\
\text{S} \\
\text{COOEt}
\end{array} \\
\text{R}
\end{align*} \]

Using this reaction we have synthesized e.g. ferrocenyl conjugates of thiocholesterol 3, protected 5’-thioadenosine 4 and 2’-deoxy-5’-thioadenosine 5.


Imidazolylphosphanes for Medicinal Bioorganometallic Chemistry

Wilhelm Huber,*a Peter C. Kunz,*a

*aHeinrich-Heine-Universität Düsseldorf, Universitätsstr. 1, 40225, Düsseldorf, Germany

Tris(imidazolyl)phosphines (TIP) show versatile coordination chemistry. We developed the novel imidazol-4(5)-ylphosphane class of ligands (4-TIP) besides the long known imidazol-2-yl-phosphanes (2-TIP) [1]. The 4-TIP ligands are more stable to hydrolysis and show different hydrophilicity/hydrophobicity (e.g. water solubility) depending on the substitution pattern of these compounds.

Here we present several complexes of these ligands related to medicinal bioorganometallic chemistry. With 4-tris(2-isopropyl-imidazolyl)phosphine oxide (4-TIPOiPr) the complex I was synthesized. Half-sandwich Ruthenium(II) complexes of the type [Ru(η⁶-arene)(L)Cl]⁺ are known as anti-tumor agents and even show cytotoxicity in cis-platin resistant cells lines. Analogues to cis-platin they bind to DNA oligonucleotides forming monofunctional adducts. [4]. Inert binding of TIP to the M(CO)₃⁺ fragment (M = Mn, Tc, Re) leads to interesting moieties (II) for diagnosis (⁹⁹mTc, t₁/₂ = 6 h, Eγ = 140 keV) and therapy (¹⁸⁸Re, t₁/₂ = 19,6 h, Eγ = 2,1 MeV, ¹⁸⁶Re, t₁/₂ = 88,9 h, Eγ = 1,09 MeV; Mn(CO)₃ as CORM). Especially the use of metal complexes as CO-releasing molecules (CORM) is a rising field [3].

Ferrocene Diphosphanes with Planar Chirality – Ligands for Enantioselective Catalysis

Martin Lamač, Ivana Císařová, Petr Štěpnička*
Charles University in Prague, Faculty of Science, Department of Inorganic Chemistry
Hlavova 2030, 128 40 Prague, Czech Republic; E-mail: stepnic@natur.cuni.cz

We have recently reported utilisation of several (phosphanyl)ferrocenecarboxylic acids, and related amides combining planar and central chirality as ligands in enantioselective palladium-catalysed allylic alkylation reaction [1,2]. As a next step in investigating the role of individual chirality elements and the different donor atoms available in the ligands, we have turned to compounds derived from well known 1,1'-bis(diphenylphosphanyl)ferrocene, dppf [3]. Thus, acid 1 has been prepared in a racemic form from 1,1'-dibromoferrocene, and subsequently resolved into the enantiomers via the corresponding ester 2 with a chiral sugar derivative – diacetone-D-glucose. Our current research is aimed at exploiting the coordination behaviour of both racemic and optically pure ligands and, particularly, at catalytic testing of chiral compounds in enantioselective allylic alkylation.

VANADIIUM COMPLEXES OF THE ONNO - TYPE LIGAND.
SYNTHESIS, CHARACTERIZATION AND REACTIVITY

Tomasz Nerkowski, Zofia Janas and Piotr Sobota

Faculty of Chemistry, University of Wroclaw, 14 F. Joliot - Curie
50-383 Wroclaw, Poland

It is well known that vanadium complexes occurs in many biological systems in which its coordination environment is created by O, S, N donor ligands.[1] The studies of sulphur-rich ligation of vanadium has been an increased interest due to the effort of understanding of vanadium nitrogenase, enzyme that catalyses the reduction of dinitrogen to ammonia and converting of acetylene into ethene and ethane. In these both aspects vanadium complexes containing 2,2'-oxydiehanethiolate (SOS)²⁻ and 2,2'-thiobis{4-(1,1,3,3-tetramethyl-buthyl)phenolate} (OSO)²⁻ ligands have been studied in our laboratory. It was shown that the vanadium centre ligated with the (SOS)²⁻ ligand are adept at binding coligands such as hydrazine, hydrazido(2-), nitrido, relevant to the nitrogenase.[2] Furthermore, this ligand as well as (OSO)²⁻ ligand create highly active single-site vanadium catalysts for ethene polymerization.[3] As a part of our ongoing study on these both aspects we were interested in preparation, structural study and reactivity of new vanadium complexes with the N,N-dimethylethylenediamino-bis(2-methylene-1,1,3,3-tetramethyl-buthylphenolate) (ONNO)²⁻ ligand (Scheme).

Metal Complexes with Aryloxo, Aminobisaryloxo and Aryloxoimine Ligands - Synthesis and Catalytic Activity

Katarzyna Krauzy - Dziedzic, Sławomir Szafert, Jolanta Ejfler, Piotr Sobota*

Faculty of Chemistry, Wroclaw University, 14, F. Joliot-Curie, 50-383 Wroclaw, Poland

Transition and main group metal aryloxides is a fast growing family of complexes that find application in numerous areas of chemical industry. The very early interest in such compounds as lubricants is now driven out by their use in synthetic organic chemistry - especially in enantioselective synthesis and catalysis [1]. They also find increasing application as initiators and catalysts in different polymerization processes [2].

Simple homoleptic metal aryloxides, although well known, are not very common. We have lately prepared an interesting titanium 7-benzofuranoxide by direct reaction of Ti(O\text{Pr})_4 or TiCl_4 with commercially available 2,3-dihydro-2,2-dimethyl-7-benzofuranol (1). This simple, monomeric in solution complex has proven to be an excellent initiator for ROP of cyclic esters and good catalyst in the addition of terminal acetylenes to aryl aldehydes [3].

Based on this result we have prepared a series of Ti, Zr and Mg complexes with different aminobisaryloxo (2) and aryloxoimine (3) ligands that were obtained in Mannich type reaction from 3,5-disubsituted phenols, formaldehyde and primary amines. The complex preparation and initial results of their catalytic activities will be presented.


Heteromultimetallic Transition Metal Complexes

C. Schreiner, R. Packheiser, B. Walfort and H. Lang*  
Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl für Anorganische Chemie, Straße der Nationen 62, 09111 Chemnitz, Germany.  
E-mail: heinrich.lang@chemie.tu-chemnitz.de

The study of heteromultinuclear transition metal complexes in which different metal atoms are connected by π-conjugated organic and/or inorganic carbon-rich bridging units is an intriguing area of research, since such species may offer the possibility to study electronic communication between the redox-active termini, exhibit non-linear optical properties or provide, for example, cooperative effects in homogeneous catalysis.[1] We report on the synthesis of novel heteromultimetallic complexes of structural type A – C.

![Structural formulas A, B, C](image)

The structural and electrochemical properties of the resulted heterotri- to hetero-pentametallic complexes is discussed.

1) Heinrich Lang, Rico Packheiser and Bernhard Walfort Organometallics 2006, 25, 1836.
Unexpected Titanocene Cyclopentadienide/Alkoxo Group Exchange

Anna Drag, Józef Utko, Łukasz John, Lucjan B. Jerzykiewicz, and Piotr Sobota*
Faculty of Chemistry, Wrocław University, 14, F. Joliot-Curie, 50-383 Wrocław, Poland

The chemistry of metal sandwich group 4 metallocenes has attracted considerable attention due to their applications in stoichiometric and catalytic reactions [1]. This rich chemistry is dominated by their applications in olefin polymerization and is also promoted by noteworthy transformations, involving reduction to Cp₂Ti(III) and Cp₂Ti(II) species, loss of ring to give TiCl₃Cp compound, and replacement of halogen by other unidate ligands. As a part of our ongoing study we were interested in the preparation of mixed-metal alkoxo-organometallic single-source precursors (SSP) for highly pure oxide-ceramics possess perovskite structure. This has prompted us to study the behavior of titanocene TiCl₂Cp₂ towards exchange chlorine atoms with metal alkoxo species. The successful route to substitution of titanium ligands in TiCl₂Cp₂ by 2-methoxyethanol is shown in Scheme. Direct reaction of TiCl₂Cp₂ with metallic Sr, Ca and Mn in 2-methoxyethanol gave unexpected cyclopentadienyl-free colorless heterometallic 1-3 complex.

These results open an attractive opportunities for preparation of new highly reactive compounds, which have not been prepared yet by other routs. Such complexes exemplifies an attractive starting materials for a wide range of syntheses.

Synthesis, Structures and Reactions of Chiral Titanocene and Zirconocene Complexes

Marcus Klahn, Perdita Arndt, Barbara Heller, Wolfgang Baumann, Anke Spannenberg, and Uwe Rosenthal*

Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock, Germany

Organometallic complexes containing chiral ligands are important as catalytic or stoichiometric mediators of enantioselective reactions [1]. So there was the approach to synthesise group 4 metallocenes with chiral substituted cyclopentadienyl ligands. A good example for this is the (-)-menthylcyclopentadienyl ligand [2]. Starting from the metallocene dichlorides (1, 2) the alkyne complexes (3, 4) and the difluorides (5, 6) are formed. It was possible to synthesise the so far unknown bis(8-phenylmenthylcyclopentadienyl)-dichlorozirconium(IV) (7), which possibly provide a greater influence in stereoselective reactions. This feasible influence is due to the phenyl-groups which tend to form π-stacking complexes [3]. Further reactions of these complexes, e.g. hydrosilylation of imines and the formation of metallacycles, are under investigation.

Unprecedented Si-C and C-H Activation Steps in the Formation of Hafnocene Alkyne Complexes

Stephan Peitz, Torsten Beweries, Vladimir V. Burlakov, Marc A. Bach, Perdita Arndt, Wolfgang Baumann, Anke Spannenberg, Uwe Rosenthal*

Leibniz-Institut für Katalyse e. V. an der Universität Rostock
Albert-Einstein-Str. 29a, D-18059 Rostock, Germany

The chemistry of titanocene and zirconocene alkyne complexes \( \text{Cp}'_2 \text{M}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3) \) has been the subject of several reviews. These complexes play an important role in many stoichiometric and catalytic reactions by generating the corresponding metallocenes “\( \text{Cp}'_2 \text{Ti} \)” and “\( \text{Cp}'_2 \text{Zr} \)” under mild conditions [1].

![Figure 1. Interactions of \( \text{Me}_3\text{SiC}_2\text{SiMe}_3 \) with Decamethylhafnocene.](image)

Recently we reported on the synthesis of the first hafnocene alkyne complexes with an intact starting alkyne, the compounds \( \text{Cp}^*_2 \text{Hf}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3) \) (1) and \( \text{Cp}_2 \text{Hf}(\text{PMe}_3)(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3) \) [2]. By simultaneous Si-C and C-H activation steps during the synthesis of 1 two by-products 2 and 3 are formed, showing some unexpected structural motifs [3].

Divergent Coordination Modes of Zinc Alkyls Based on Various Pyrrolyl Ligands

Izabela Kraszewska, Maciej Dranka, Iwona Justyniak, Janusz Lewiński*

Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

The chemistry of organozinc compounds has a long history, in which many application for metal alkyls have been found in both organic and organometallic chemistry. Over recent years the exploitation of zinc complexes supported by $\beta$-diketiminato ligand systems has provided a number of spectacular results.[1]

As part of ongoing structure and reactivity studies involving the RZn(X,Y) chelate complexes, we have initiated to examine the solid state and solution structure of alkylzinc N,N'-chelate and N,O-chelate complexes based on pyrrolyl ligands. We turned our attention to bi- and trifunctional pyrrolyl ligands, anticipating that a combination of pyrrole and Schiff base type ligands or carbonyl group may provide spectacular results.

Series of zinc alkyl complexes supported by pyrrolyl ligands have been synthesized and structurally characterized. Our studies demonstrate that pyrrolyl ligands are electronically very flexible ligand system. For example, we have found that pyrrolylaldiminate type ligand in zinc complexes shows $\sigma$-N or the dihapto $\eta^2$-$\pi$-donor type of coordination of pyrrolyl ligand. The most diverse of coordination modes we have observed for zinc complexes stabilized by 2,2’-dipirryl-diketone: the $\sigma$-N and the dihapto $\eta^2$-$\pi$-donor type for the pyrrolyl unit and a double coordination of the carbonyl group.

The identification and characterization of weak intermolecular interactions as well as their influence on the supramolecular structure of the studied complexes will be discussed.

Complexation of Sodium and Potassium Salts by Ditopic Hosts Based on Organotin-substituted Crown Ethers

Alain Charly Tagne Kuate, a Gregor Reeske, a Markus Schürmann, a Klaus Jurkschat *a

aTechnische Universität Dortmund, Lehrstuhl für Anorganische Chemie II, D-44221 Dortmund, Germany.

The central role played by cations and anions in physiology has provided the inspiration for the design of abiotic receptors that bind selectively and simultaneously both ions. [1]. We have synthesized receptors 1 - 4 and investigated their complexation properties. NMR studies reveal the high potential of Ph2ClSn-CH2-16-crown-5[2], 1, and Ph2ClSn-CH2-19-crown-6, 2, to complex NaSCN and KSCN, respectively, while in addition to NMR studies, X-ray diffraction analyses showed that the robust receptors {Ph2(I)Sn-CH2-Sn(Ph)(I)-CH2-16-crown-5}[3], 3, and {Ph2(I)Sn-CH2-Sn(Ph)(I)-CH2-19-crown-6, 4, overcome the lattice energy of NaF in CD3CN and of KF in CDCl3 and bind these salts as separated ions to give the ditopic complexes 3·NaF and 4·KF, respectively. Most recently, receptor 5 has been synthesized and its complexation properties are currently investigated.

C,N-chelated Organotin(IV) Fluorides

Petr Švec, Zdeňka Padělková, Aleš Růžička

Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, nám. Čs. legií 565, CZ-532 10, Pardubice, Czech Republic. E-mail: gty@post.cz

Generally organotin(IV) fluorides tend to form oligo- or polymeric species with 2D and 3D structures connected via fluorine bridges and thus to saturate their tin coordination vicinity/number up to seven. These species often with changeable composition, structure and properties are not useful in synthetic or catalytic applications.

To prevent the formation of polymeric species, we decided to saturate the tin coordination sphere by adjacent donor atom. For such a duty we have selected the 2-(N,N-dimethylaminomethyl)phenyl group as a C,N-chelating ligand (L\textsubscript{CN}) which was frequently studied in the literature [1].

The structure, reactivity and use of some C,N-chelated organotin(IV) fluorides will be discussed.

![Fig. 1: The molecular structure of two isomers of [L\textsuperscript{CN}(n-Bu)SnF\textsubscript{2}]{n}}](image-url)

Intramolecularly coordinated heteroleptic stannylenes:

Syntheses and Structures

Vajk Deáky\textsuperscript{a}, Markus Henn\textsuperscript{a}, Markus Schürmann\textsuperscript{a}, Bernhard Mahieu\textsuperscript{b} und Klaus Jurkschat\textsuperscript{*a},

\textsuperscript{a}Lehrstuhl für Anorganische Chemie II, Technische Universität Dortmund, D-44221, Dortmund, Germany

\textsuperscript{b}Laboratoire de Chimie Physique Moléculaire et de Cristallographie (CPMC)
B-1348 Louvain-la-Neuve, Belgium

In course of our systematic studies on heavy carbene-analogues [1] and related compounds [2], we herein present results concerning (i) configurational stability of the intramolecularly coordinated heteroleptic stannylenes 1-4, (ii) reaction of 1-4 with chalcogenes providing the four-membered rings 5-12, (iii) synthesis, structure and reactivity of the stannylene transition metal complexes 13-16, and (iv) the first heteroleptic stannylene ruthenium complex 17.


Structure and reactivity of transition metal complexes containing the heteroleptic organostannylene 2,6-(Me₂NCH₂)₂C₆H₃SnCl

J. Martincová, R. Jambor, M. Schürmann, K. Jurkschat

a Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, nám. Čs. legií 565, CZ-532 10, Pardubice, Czech Republic.
b Lehrstuhl für Anorganische Chemie II der Technischen Universität Dortmund, D-44227 Dortmund, Germany.

In course of a systematic study on the reactivity of heteroleptic organostannylenes [1, 2] reactions of the heteroleptic stannylene 2,6-(Me₂NCH₂)₂C₆H₃SnCl (R₂SnCl) [3] with selected transition metal derivatives (TM) are reported. These reactions provided a variety of novel complexes R(Cl)Sn-TM (Fig.1). In the latter complexes the stannylene is a two-electron-donor ligand.

The preparation, structure and reactivity of these complexes will be discussed.

1,1’-Diphosphaferrocenyl conjugates of aminoacid esters

Bartosz Mucha, Janusz Zakrzewski

Department of Organic Chemistry University of Lodz 90-136 Lodz, Narutowicza 68

There has been considerable interest in the introduction of redox-active ferrocenyl groups into natural aminoacids, peptides or proteins [1]. One of the most important methods of synthesis of ferrocenyl conjugates of aminoacids is the reaction of ferrocenecarboxaldehyde (FcCHO) with aminoacid esters, giving corresponding imines, reduced in situ to FcCH₂NHCH(R)COOR’. Recently we became interested in the application of this approach for synthesis of 1,1’-diphosphaferrocenyl conjugates of aminoacids from aldehyde 1. However, this aldehyde is planary chiral and the use of the racemic compound would lead to mixtures of diastereomers. Fortunately, we earlier described an efficient method of resolution of this compound [2] and herein we report on synthesis of stereoisomers 2 and 3 from glycine, L-alanine and L-phenylalanine methyl esters. We have also found that 2a reacts with one eq. of W(CO)₅(THF) to give mixtures of complexes 4-6, which were separated by column chromatography and their structures were confirmed by spectroscopic data.

Synthesis of bimetallic complexes with nickelafuorenyl ring

Elżbieta Kamińska, Piotr Buchalski, Antoni Pietrzykowski*

Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland

The aim of this work was to optimize synthesis of nickelafuorenyllithium and to study reactions of this compound with iron and cobalt acetylacetonates. The first part of the work was to synthesize nickelafuorenyllithium in various solvents. Reactions carried out in two of the applied solvents (diethyl ether and tetrahydrofurane) gave satisfactory results. The reaction carried out in diethyl ether was more effective. The yield of the product was higher and less reaction steps were needed to get the final compound.

In the second part of this work the reactions of nickelafuorenyllithium with iron(II) acetylacetonate and pentamethylyclopentadienylcobalt(II) acetylacetonate were studied. In the first reaction bimetallic complex (nickel – iron) was not formed.

In the second reaction the new bimetallic complex, with both cobalt and nickel atoms, was formed. The EI mass spectrum of the complex 1 showed its molecular ion at m/e 469 with an isotopic pattern characteristic for one nickel atom in a molecule. The molecular structure of the complex 1 was determined by X-ray diffraction analysis.
REACTION OF NICKELOCENE WITH METHYLLITHIUM IN THE PRESENCE OF OLEFINS

Beata Herbaczynska, Antoni Pietrzykowski*, Lucjan B. Jerzykiewicz

aWarsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw, Poland
aUniversity of Wroclaw, Faculty of Chemistry, Joliot-Curie 14, 50-353 Wroclaw, Poland

Nickelocene reacts with organolithium and –magnesium compounds (LiR, RMgX) forming in the first step an unstable 16 VE species {CpNiR}. This species undergoes further reactions: hydrogenation, coupling, elimination etc., forming a wide range of cyclopentadienyl-nickel clusters. The main product of the reaction of nickelocene with methyllithium is ethylidyne-tri(cyclopentadienynickel) cluster (NiCp)₃(μ₃-CCH₃). The other products isolated at lower yield were: π-allyl complex (NiCp)(η³-C₅H₇), di(cyclopentadienynickel) complex (NiCp)₂(μ-C₅H₆), and clusters (NiCp)₃(μ₃-CH), (NiCp)₃(μ-CCH₃), (NiCp)₅, (NiCp)₆C, (NiCp)₆C₂. The reaction of nickelocene with methyllithium carried out in the presence of olefins allowed for isolation of the π-complex CpNi(Me)(η²-alkene). This complex, stable below 0 ºC, undergoes slow thermal decomposition at room temperature, forming the same products as in the previous reaction. The main product was also the cluster (NiCp)₃(μ₃-CCH₃).[1,2,3]

However, the main product of the reaction of methyllithium with nickelocene derivative, bearing alkenyl substituents in the cyclopentadienyl rings, was the dinickel compound of the structure shown below:

Intramolecular stabilization of the dinickel compound by the formation of olefinic complex with nickel, appeared to be strong enough to prevent the formation of higher clusters in consequent reactions.

Group IV and V metal complexes of the (NOSON)- and (ONNO)- type ligands; synthesis, structure and catalytic activity

Izabela Jaźyna, Piotr Sobota, Zofia Janas*

Faculty of Chemistry, University of Wrocław, 14, F. Joliot-Curie, 50-383 Wrocław, Poland.

One of the most significant application of group IV metal complexes is the catalytic polymerization of α-olefins. In recent years there is a growing recognition that nonmetallocene complexes hold great promise as olefin polymerization catalysts [1]. Most successful developments in terms of catalysis have appeared using chelating, polydentate bis(aryloxide) ligands having an additional coordinating heteroatom (N, O, S).

Recently we have described the family of titanium complexes based on the 2,2’-thiobis{4-(1,1,3,3-tetramethylbutyl)phenolato} (OSO) ligand, which led after activation with aluminum alkyls to highly active, well-defined, single-site catalysts to ethene polymerization process [2]. As a part of our ongoing study on this area we were interested in modification of the (OSO) ligand with additional heteroatom like nitrogen to achieve new ligands of the (NOSON)- and (ONNO)- type (Scheme) and their application to generation of group IV and V metal complexes that might serve as catalysts for olefin polymerization process. Synthesis of two new ligands and their Ti, Ta, Nb complexes will be presented in details.

\[ (\text{OSO})_2 + 2 \text{NH}_2\text{tBu} + 2 \text{HCHO} \rightarrow (\text{NOSON})_4 \]

\[ (\text{OSO})_2 \quad (\text{NOSON})_4 \quad (\text{ONNO})_2 \]

**1,1,2,2,3,3,4-Hepta-<sup>1</sup>butyl-4-magnesio-chloro-tetrastanna-cyclobutane: synthesis and reactions**

M. Lechner, a K.Decker, a R.Fischer, a F.Uhlig* a

*Institute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 16, A-8010, Graz, Austria

Magnesio- tin compounds are reactive intermediates for the synthesis of cyclic organo- tin products that are inaccessible by other synthetic pathways. [1]

1,1,2,2,3,3,4-Hepta-<sup>1</sup>butyl-4-magnesio-chloro-tetrastanna-cyclobutane (1) can be synthesised starting either from di-tert-butyldichlorostannane or from octa-tert-butyldichlorotetrastannane in a Grignard type reaction. This product is fully characterised by multinuclear NMR spectroscopy (\(^{119}\text{Sn}, \(^{1}\text{H} \text{and } ^{13}\text{C}\)) Due to its nucleophilicity 1 is an interesting starting point for further derivatisation reactions.

![Image of the molecule](image_url)

Among the resulting products synthesised are \(^{1}\text{Bu}_{7}\text{Sn}_4\text{Me}, \(^{1}\text{Bu}_{7}\text{Sn}_4\text{Pr} \text{ and } ^{1}\text{Bu}_{7}\text{Sn}_4\text{Br}. \(^{1}\text{Bu}_{7}\text{Sn}_4\text{Me} \text{ could be characterized by X-ray crystal structure analysis.}

This presentation deals with a description and comparison of the two different ways to obtain 1,1,2,2,3,3,4-hepta-tertbutyl-4-magnesio-chloro-tetrastanna-cyclobutan. Furthermore some reaction of compound 1 will be discussed as well.

Investigating the catalytic hydrogenation with rhenium(I) nitrosyl complexes

B. Dudle\textsuperscript{a}, H. Berke\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}Institut of inorganic chemistry, university of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

Catalytic hydrogenations belong to the standard tools of synthetic organic chemistry. Nevertheless there are only rare examples of non noble metal based catalysts for such reactions. Our research interest is therefore focused on the development of new rhenium based catalysts for hydrogenation. Recently the rhenium-nitrosyl complexes [ReH\textsubscript{2}(\eta\textsuperscript{2}-C\textsubscript{2}H\textsubscript{4})(NO)(PR\textsubscript{3})] and [ReH(\eta\textsuperscript{2}-BH\textsubscript{4})(NO)(PR\textsubscript{3})] (R=\textit{isopropyl, cyclohexyl}) have successfully been used as hydrogenation and hydrosilylation catalysts\cite{1},\cite{2}. It was anticipated that these catalyst precursors lose initially the weakly bound ligand (C\textsubscript{2}H\textsubscript{4} or BH\textsubscript{3}) and the catalytic cycle then follows than a typical Wilkinson-type mechanism:

Challenged by these results we investigated other, similar complexes and found, that also [ReH\textsubscript{2}(NO)(PPh\textsubscript{3})\textsubscript{3}], [ReHCl(NO)(PPh\textsubscript{3})\textsubscript{3}] and [ReHCl(C\textsubscript{2}H\textsubscript{4})(NO)(PPh\textsubscript{3})\textsubscript{2}] complexes catalyse the hydrogenation of the model substrates ethylene, 1-hexene and cyclohexene. Therefore we study these reactions in greater detail to obtain experimental data to confirm the proposed mechanism and also to get further information on the optimization of the catalyst.

\textsuperscript{1} A. Chualeb, H.W. Schmalle, H. Berke to be published
\textsuperscript{2} Y. Jiang, H. Berke, \textit{chem. Comm.} \textbf{2007}, 37, 3571-3573
High-Selective Dehydrogenative Silylation Catalyzed by Rhenium Complexes: Reaction Development and Mechanistic Studies

Yanfeng Jiang, Christian M. Frech, Olivier Blacque, Fox Thomas, Heinz Berke*
Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstr.190, CH-8057 Zürich, Switzerland.

Dehydrogenative silylation reaction, which permits the direct production of unsaturated silyl compounds from olefins and silanes, has drawn increasing attention during the last two decades. However, a major drawback of this reaction is the formation of hydrosilylated by-products. Thus, highly chemoselective processes are desired. So far, catalysts for selective dehydrogenative silylation are mainly limited to late transition metal complexes, such as [M₃(CO)₁₂] (M = Fe, Ru, Os),² cationic [Rh(COD)₂]BF₄/PPh₃,³ [RuH₂(H₂)₂(PCy₃)₂]⁴ and cationic Pd(II) complexes ⁵.

We would like to report rhenium(I) complexes [Re(Br)₂(NO)(PR₃)₂(L)] (L = H₂, CH₃CN and ethylene; R = 'Pr a and Cy b)⁶ catalyzed highly selective dehydrogenative silylation of substituted styrenes with silanes. Mechanistic studies were carried out, which shed a light into the initial reaction path and the catalytic cycle. Extension of these studies concern obtaining more active rhenium complexes applying ligand tuning.

Silylative coupling of terminal alkynes with vinylsilicon compounds catalyzed by ruthenium complexes

Beata Dudziec, Bogdan Marciniec

Adam Mickiewicz University, Faculty of Chemistry, Department of Organometallic Chemistry, Grunwaldzka 6, 60-780 Poznań, Poland

Substituted alkynylsilanes are an important group of reagents commonly used in many fields of chemistry, e.g. as alkynylation agents in synthesis of organic, organosilicon and natural products as well as precursors of optoelectronic materials[1]. Alkynylsilanes can be prepared by classical stoichiometric routes or by metal complex – catalyzed reactions[2].

Herein, we present a new catalytic silylative coupling reaction of terminal alkynes with vinyl-substituted organosilicon compounds proceeding in the presence of ruthenium complexes. It is an efficient and direct way for the synthesis of substituted alkynylsilanes[3].

\[ \text{R} \equiv \text{SiR'}_3 + \text{[Ru]} \text{ (1-2 mol\%)} \xrightarrow{\text{toluene}} \text{R} \equiv \text{SiR'}_3 \]

\[ \text{R} = \text{alkyl, silyl, germyl} \]

\[ \text{R'} = \text{alkyl, aryl, alkoxyl} \]

This process can be employed for modification of multivinylsubstituted silicon compounds since monoalkynyl-substituted products are obtained selectively. The mechanism of this particular (sp)C-H activation based on the stoichiometric reactions of catalyst with substrates and DFT calculation methods has been discussed.


New catalytic route to boryl- and borylsilyl substituted buta-1,3-dienes

Jędrzej Walkowiak, Magdalena Jankowska-Wajda, Bogdan Marciniec*
Department of Organometallic Chemistry, Faculty of Chemistry, A.Mickiewicz University,
Grunwaldzka 6, 60-780 Poznań, Poland, e-mail: marcinb@amu.edu.pl

Dienylboronates and dienylsilylboronates constitute a class of functionalized building blocks commonly used in organic and natural products synthesis, since the boronate moiety, as well as silyl group, can be easily converted into other functional groups [1,2]. Borylsubstituted buta-1,3-dienes can be prepared by classical stoichiometric routes using organometallic reagents or more recently by catalytic methods.

In the communication we report a new convenient method for selective synthesis of 1-boryl and 1-boryl-4-silyl substituted buta-1,3-dienes via one step coupling of terminal alkynes (also silylacetylenes) with vinylboronates catalyzed by complexes containing [Ru]-H bond, occurring according to the following equitation:

\[
\begin{align*}
\text{B} & \text{O} - \text{O} - \text{B} + \text{R} & \text{[Ru-H]} & \text{R} \rightarrow \text{B} & \text{O} - \text{O} - \text{B} + \text{B} & \text{O} - \text{O} - \text{B} + \text{R}
\end{align*}
\]

The stoichiometric reactions were carried out to prove the mechanism of this new process, in which insertion of terminal acetylene to [Ru]-H bond is the preliminary step followed by insertion of vinylboronate to Ru-C= bonds and elimination of boryl dienes. It is in contrast to previously recognized reactions of acetylenes with vinylsilanes and vinylgermanes, which occur via preliminary insertion of vinylmetalloid into M-H bond to give M-E bond (and ethylene) followed by insertion of acetylene into M-E bond and elimination of silyl and germyl functionalized ethynes [3,4].

Oligonuclear Ethenyl Bridged Styryl Complexes of Ruthenium: Synthesis, Electrochemical and Spectroelectrochemical Investigation

Michael A. Linseis, Rainer F. Winter*
Institut für Anorganische Chemie der Universität Regensburg, Universitätsstraße 31, 93053, Regensburg, Germany
J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, Prague, Czech Republic

The Ru-vinyl entity exhibits strong delocalization of the redox orbitals over the metal as well as the organic bridging ligand [1]. Although “non-innocent” behaviour is well known for inorganic coordination compounds, there are only few examples of organometallic systems with direct metal-carbon bonds. Recently the electrochemical behaviour of mononuclear ruthenium-vinyl-complexes has been studied in a systematic way to link the metal vs. ligand contribution to experimentally accessible values like half-wave potentials, oxidation induced CO band shifts and ESR-parameters [2]. We have now extended our studies to di- and tetranuclear stilbene and tetrphenylethene derived complexes [{RuCl(CO)(PR³)2L}2{µ₂-bis(styryl)ethene}] and [{RuCl(CO)(PR³)2L}4{µ₄-tetrakis(p-styryl)ethene}] (R³ = Ph, 'Pr, Et; L = none or ethyl isonicotinate). The complexes were investigated by electrochemistry, IR- and UV/Vis/NIR-spectroelectrochemistry and ESR-spectroscopy in order to probe for the degree of electron delocalization in their various oxidized forms and the relative metal and ligand contributions to the respective redox orbitals. These studies also revealed strong electrochromism, particularly of the tetranuclear complexes. Our experimental results are backed by quantum chemistry.

Styryl complexes of Ruthenium and Osmium as Probes for Electron Transfer Across Multiple Hydrogen Bridges

Markus Pichlmaier, a Stanislav Záliš b and Rainer F. Winter*, a

a) Institut für Anorganische Chemie, Universitätsstraße 31, 93040, Regensburg, Germany
b) J. Heyrovský Institute of Physical Chemistry v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

Electron transfer is one of the most fundamental processes in chemistry and biology. The spatial organization of electron donor and acceptor sites in enzymes and artificial supramolecular systems often depends on strong hydrogen bridges. A quadruply hydrogen bonding, symmetrical DDAA motif based on ureapyrimidones has recently been shown to efficiently mediate electron transfer between two ferrocenyl substituents [1]. We here discuss the synthesis, structures, solution behaviour and the electron transfer properties of ureapyrimidone dimers 2a,b and 3a (see Chart) having redox active ruthenium and osmium styryl substituents in their backbones. This general structure ensues a high charge and spin density at the styryl group in the oxidized state(s) [2], while the carbonyl ligand of complexes 2a,b and 3 provides an indicative, charge-sensitive spectroscopic label. Both these attributes are missing in the ferrocenyl substituted counterpart.

The issue of the presence and strength of electronic interactions between the two identical styryl units is addressed by in situ IR and UV/Vis/NIR spectroelectrochemistry. The results on the ureapyrimidone-bridged dimers are compared to those for the phenylurea substituted styryl ruthenium complex 5, which is monomeric in solution. Quantum chemical calculations performed on simplified model complexes aid in the interpretation of our experimental results.

Synthesis, characterization and properties investigation of tungsten and molybdenum hydrides.

A. Dybov, O. Blacque, T. Fox, C. Frech, H. Berke*

Anorganisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

The hydrogenation of C=O double bonds of ketones and aldehydes play an important role in the agricultural, pharmaceutical and other chemical industries. Up to now, most of the homogeneous catalysts promoting this reaction are based on precious metals, such as ruthenium and rhodium. Tungsten and molybdenum hydride complexes were shown to provide hydride transfers to ketones that is the first step in a hypothetical catalytic cycle of the hydrogenation reaction [1,2]. The ligand trans to the hydrogen atom has a crucial influence on its activity.

We report the synthesis of 1,2 – bis(diisopropylphosphino)ethane molybdenum and tungsten hydride complexes with NO:

\[
\text{MNO} \quad P \quad P \quad P \quad P \\
\text{M} = \text{W, Mo}
\]

In addition, we discuss reactions which show the chemical properties of the corresponding hydrides. The temperature dependent $^2$H T$_1$ experiments have been done, that allowed to calculate of T$_{1\text{min}}$ and estimate the ionicity of M – D bond.

Catalytic hydrogenation experiments are on going and respective results will be reported.


New macrocyclic complexes of copper and nickel –
on the network and charge density topologies

Radosław Kamiński, Paweł Śledź, Sławomir Domagała
Bohdan Korybut-Daszkiewicz, Krzysztof Woźniak

aDepartment of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
bDepartment of Chemistry, Warsaw University, Pasteura 1, 09-093 Warsaw, Poland
cInstitute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Macrocyclic complexes of copper and nickel are very interesting and vigorously studied building blocks for new molecular machines precursors design and synthesis. So far these moieties have been applied in i.e. preparation of electrochemically controlled molecular shuttle [1], and further studies on them are currently under way.

Here we report the structural and experimental charge density analyses of new model macrocyclic and bis-macrocyclic [2] copper and nickel complexes, which may be potentially applied in synthesis of molecular machines and crystal engineering.

Organometallic Complexes Supported by Bis(imidazolin-2-imino)pyridine Pincer Ligand and by Chiral Ligand

Sabina Filimon, Dejan Petrovic, Tarun K. Panda, Matthias Tamm*

Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina zu Braunschweig, Hagenring 30, 38106, Braunschweig, Germany

Since Brookhart’s and Gibson’s concurrent discovery in the 1990s that late transition metal complexes of the Schiff base 2,6-bis(imino)pyridine ligands are exceptionally active olefin polymerization catalysts [1,2], these pincer-type ligands have attracted a lot of attention [3]. Recently, we have introduced the tridentate bis(imidazolin-2-imino)pyridine ligand (TLBu) and its application in copper coordination chemistry [4]. The TLBu ligand can be best described by the two limiting resonance structures A and B (Scheme 1) and can be considered as a potentially more basic analogue of Schiff base 2,6-bis(imino)pyridine ligands [3]. Due to the highly basic nature of the ligand, it can stabilize a number of Lewis acidic metal ions.

![Scheme 1](image.png)

The interesting results reported for dioxygen activation with related guanidine copper complexes encouraged a reactivity study of the cationic copper(I) complex towards dioxygen or other oxygenating agents. Important discoveries have also been made in the field of lanthanide (III) coordination chemistry with multidentate ligands. To gain insight into the ligand behavior towards lanthanides, the reaction of TLBu with LnCl₃ was studied, and the synthesis of cationic lanthanide alkyl complexes was attempted.


Norbert Grzegorzek, Miłosz Pawlicki, Lechosław Latos-Grażyński*

Department of Chemistry, University of Wrocław, 14 F. Joliot-Curie St, Wrocław 50-383, Poland

Carbaporphyrinoids are porphyrin analogues containing a CH fragment instead of one of the pyrrolic nitrogens. This so called “internal carbon” is often found susceptible to substitution reactions. Examples reported to date include alkylations, halogenations, nitration, internal fusion, acetoxylation, cyanation, oxygen insertion, regioselective pyridination, and formation of a ketal. Recently reported carbaporpholactone 1 provides a suitable environment to stabilize the rare oxidation states (copper(III) or silver(III)) of coordinated metal ions due the formation of σ-metal-carbon bond. Regioselective reaction of silver(III) carbaporpholactone with potassium diphenylophosphide in THF yields 21-(diphenylphosphino)-carbaporpholactone 2 as the single substitution product which in oxidative reaction conditions transforms quantitatively into 21-(diphenylphosphoryl)-carbaporpholactone 3 as confirmed by detailed NMR studies. A mechanism involving a high-valent silver complex is proposed for the phosphination reaction.

The structure of copper(II) of 21-(diphenylphosphoryl)-carbaporpholactone 3-Cu has been determined at 173 K by X-ray diffraction: 3-Cu presents unique features related to the hybrid nature of 3. The copper(II) is five-coordinate with bonds to three pyrrolic nitrogens, the oxygen atom of phosphoryl moiety, and to the pyrrole C(21) carbon. Further aspects of the reactivity of carbaporpholactone complexes are currently explored in our laboratory.
Helical Porphyrinoids: Incorporation of Ferrocene Subunits into Macrocyclic Structures

Irena Simkowa, Marcin Stępień, Lechosław Latos-Grażyński
Department of Chemistry University of Wrocław, 14 F. Joliot-Curie St., 50-383 Wrocław, Poland

Ferrocene-containing porphyrinoids have been synthesized, in which ferrocene-1,1'-diyl units are linked to a dipyrrin 2a and 2b, dicarba[2b] and thiatripyrrin 5 to form macrocyclic structures.

\[
\begin{align*}
&1. \text{ArCHO, BF}_3\cdot\text{Et}_2\text{O} \\
&2. \text{DDQ (1 equiv)}
\end{align*}
\]

Fe
HN
HN
Ar
Ar
H
S
Tol
Tol

\[
\begin{align*}
2a \text{ Ar} &= \text{Ph (8%)} \\
2b \text{ Ar} &= \text{C}_6\text{F}_5 (34%)
\end{align*}
\]

\[
\begin{align*}
&1. \text{CH}_2\text{Cl}_2, \text{BF}_3\cdot\text{Et}_2\text{O} \\
&2. \text{Et}_3\text{N} \\
&3. \text{DDQ (2 equiv)}
\end{align*}
\]

Fe
HN
HN
Ar
Ar

\[
\begin{align*}
3b \text{ Ar} &= \text{C}_6\text{F}_5 (1%)
\end{align*}
\]

NMR spectroscopic evidence shows that these new systems, adopt helical conformations, which undergo an inversion process in solution. The helical conformation of 2 was confirmed by X-ray diffraction. Moreover, small amounts of unexpected scrambling products have been isolated and characterized, namely a dipyrrin-bisferrocenophane and two expanded bisferrocene macrocycles. Formation of these systems, which contain macrocyclic rings of different sizes, is a consequence of the structural flexibility of the ferrocene unit. Cyclic voltammetry demonstrates that ferrocene oxidation is reversible in all systems reported here, and that it is finely tuned by the properties of the macrocyclic system.
A New Class of Imidazole based N,N,O Ligands:
Synthesis, Structure and Reactivity

Nina Fischer, a Liv Peters, a Nicolai Burzlaff*, a

Inorganic Chemistry, Department of Chemistry and Pharmacy,
University of Erlangen-Nürnberg, Egerlandstraße 1, D-91058, Erlangen, Germany

Tripodal ligands such as bis(pyrazol-1-yl)acetic acid (Hbpza) and its derivatives (e.g. Hbdmpza, Hbd/tbpza) have shown to be versatile structural mimics for the facial 2-His-1-carboxylate triad of non-heme iron oxygenases and for the 2-His-1-carboxylate motif of gluzincines [1]. Recently, the work of our group and others has focused on the synthesis of imidazole based tripodal ligands such as the bis(N-methylimidazol-2-yl)propionic acid (Hb mip) [2,3]. Here, we report on the synthesis of bis(N-methylimidazol-2-ylmethyl)acetic acid (Hbmima) as a first example of a new class of tridentate N,N,O ligands. Complexes bearing this and related ligands as well as coordination polymers thereof will be presented.

Mononuclear Lanthanide and Titanium Imido Complexes

Alexandra Trambitas, Tarun K. Panda, Sören Randoll, Thomas Bannenberg, Matthias Tamm*
Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina, Hagenring 30, D-38106, Braunschweig, Germany

In the last two decades transition metal imido complexes have attracted considerable interest since they proved to be active catalysts in different catalytic transformations like metathesis, cycloaddition, C-H activation, polymerisation and hydroamination reactions [1]. In stark contrast to the rich chemistry of imido complexes containing d-block elements, lanthanide imido complexes are largely unexplored, and reports on well-defined imido complexes containing 4f-elements are scarce [2].

As a terminal ligand, the formally dianionic imido ligand (NR)$_2^-$ coordinates with a metal-nitrogen multiple bond consisting of one $\sigma$ and either one or two $\pi$ interactions [3]. This resembles the bonding in transition metal complexes containing monoanionic imidazolin-2-iminato ligands of type I, which can be described by the two limiting resonance structures IA and IB (Scheme 1), indicating that the ability of the imidazolium ring to stabilize a positive charge leads to highly basic ligands with a strong electron donating capacity towards early transition metals [3]. Therefore, lanthanide complexes with terminal imidazolin-2-iminato ligands, [4] which will be presented here, can serve as accurate models for elusive mononuclear lanthanide imido complexes, and their structural investigation could lead to a better understanding of lanthanide-nitrogen multiple bonding [2]. Novel Ti imido complexes have been also synthesised and their reactivity towards cyclooctatetraene studied.

Synthesis and Structure of Tetrameric Gallium (I) Amides

Annekathrin Seifert, Gerald Linti

University of Heidelberg, Institute of Inorganic Chemistry, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Gallium amides, with gallium in the low oxidation state +1, might be well-defined starting materials for the synthesis of novel organo gallium compounds and metalloid gallium clusters [1]. The cluster chemistry of gallium has made vast progress during the last years. In most cases bulky organyl or silyl substituents have been used.

The amino substituted gallatetrahedranes Ga₄[N(SiMe₃)dipp]₄ (dipp = 2,6 diisopropylphenyl), 1, and Ga₄tmp₄ (tmp = 2,2,6,6-tetramethylpiperidino), 2, are the first oligomeric gallium(I)amides. Their synthesis [2], structure, bonding and some reactions of these compounds will be discussed.

\[
4 \text{Gal}^+ + 4 \text{LiNRR}^' \xrightarrow{\text{toluene/thf, -78°C, -LiI}} [\text{GaNRR}']_4
\]

\[
\text{NRR}' = \begin{array}{c}
\text{N(SiMe}_3\text{)} \\
\text{iPr} \\
\text{iPr}
\end{array} = \text{N(SiMe}_3\text{)dipp}
\]

\[
\begin{array}{c}
\text{N} \\
\text{2}
\end{array} = \text{tmp}
\]


Synthesis and structure of alkylaluminium and alkylgallium derivatives of phthalic and phthalamic acid

Daniel Prochowicz,a Wojciech Bury,a Janusz Lewiński a and Iwona Justyniak,b

aFaculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw
bInstitute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warsaw, Poland

The chemistry of organoaluminum carboxylates and carboxylate alumoxanes has been under investigation in the last few decades due to their wide potential applications in materials science as precursors for alumina fibers or aluminum oxides. Nevertheless, the knowledge about the structure and reactivity of organogallium carboxylates is rather scant. Recently, we have reported the synthesis and structure characterization of the first examples of alkylaluminum derivatives of mono- and dicarboxylic acids [1]. We have also provided an efficient route to tetramethylalumoxane moieties and carboxylate-substituted alumoxanes [2].

Here we present the synthesis and structural characterization of a series of clusters derived from Me3Ga and phthalic acid by using various molar ratios. Moreover, we have extended the former studies to phthalamic acid (Scheme 1). Addition of 2 equiv. of Me3Al to phthalamic acid resulted in the formation of the new tetranuclear adduct I. In contrast, the similar reaction with Me3Ga at different molar ratios afforded the dinuclear gallium compound II and a novel carboxylate galoxane III was obtained. The reactivity of novel aluminum and gallium derivatives of phthalic and phthalamic acid will also be discussed.

Scheme 1

Cyclopentadienyl Iron - Bismuth Compounds
Synthesis, Structure and Reactivity

Katarzyna Wójcik, Petra Ecorchard, Heinrich Lang, Michael Mehring *
Technische Universität Chemnitz, Institut für Chemie, 09107 Chemnitz, Germany.

Over the last years there has been considerable interest in bismuth compounds because of their wide spectrum of applications in many aspects of our live. For example for more than two centuries bismuth compounds have been used in medicine and still can be found in medical formulations [1]. Recently, bismuth containing heterometallic oxides, thin films, nanoparticles and nanofibers have received considerable interest for their potential applications as oxidation catalysts, next generation memory devices, high Tc superconductors, high temperature electrolytes, nonlinear optical materials and “green” lubricant [2, 3].

In our work we focus on heterometallic bismuth transition metal compounds [4, 5], which are of interest as a new class of potential starting materials for more sophisticated molecular precursors for heterometallic bismuth–containing compounds [5]. In this context the reactivity of cyclopentadienyldicarbonyl iron derivatives with bismuth halides (Cl, Br), bismuth siloxides and alkoxides have been studied. The synthesis, structure and reactivity of \([\text{Cpy(CO)}_2\text{Fe-BiX}_2]\) (\(\text{Cpy} - \text{C}_5\text{H}_5, \text{tBu}_2\text{C}_5\text{H}_3, \text{C}_5\text{Me}_5, \text{X}- \text{Cl, Br}\)) will be discussed.

![Fig1. The solid state structure of \([(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe-BiBr}_2]\)](image)

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Addresses
David Bek  
Research Group Prof. Dr. Jiří Čejka  
J. Heyrovský Institute of Physical Chemistry  
AS CR, v.v.i,  
Dolejškova 3  
182 23 Prague 8, Czech Republic  
dbek@atlas.cz

Dr. Libor Dostál  
Department of General and Inorganic Chemistry  
Faculty of Chemical Technology  
University of Pardubice  
nám. Čs. Legií  
532 10 Pardubice, Czech Republic  
libor.dostal@upce.cz

Izabela Błaszczyk  
Research Group Prof. Dr. Anna Trzeciak  
Faculty of Chemistry  
University of Wrocław  
14 F. Joliot-Curie  
50-383 Wrocław, Poland  
izabl@eto.wchuwr.pl

Anna Drag  
Research Group Prof. Dr. Piotr Sobota  
Faculty of Chemistry  
Wrocław University  
14, F. Joliot-Curie  
50-383 Wrocław, Poland  
annad@eto.wchuwr.pl

Nadine E. Brückmann  
Research Group Prof. Dr. Wolfgang Kläui  
Heinrich-Heine-Universität Düsseldorf  
Universitätsstr. 1  
40225 Düsseldorf, Germany  
brueckmn@uni-duesseldorf.de

Balz Dudle  
Research Group Prof. Dr. Heinz Berke  
Institut of inorganic chemistry  
University of Zürich  
Winterthurerstrasse 190  
8057 Zürich, Switzerland  
balz@aci.unizh.ch

Vajk Deáky  
Research Group Prof. Dr. Klaus Jurkschat  
Lehrstuhl für Anorganische Chemie II  
Technische Universität Dortmund  
D-44221 Dortmund, Germany  
vdeaky@gmx.de

Beata Dudziec  
Research Group Prof. Dr. Bogdan Marciniec  
Adam Mickiewicz University  
Faculty of Chemistry  
Department of Organometallic Chemistry  
Grunwaldzka 6  
60-780 Poznań, Poland  
beta62@o2.pl

Katrin Döring  
Research Group Prof. Dr. Heinrich Lang  
Technische Universität Chemnitz  
Fakultät für Naturwissenschaften  
Institut für Chemie  
Lehrstuhl für Anorganische Chemie  
Straße der Nationen 62  
09111 Chemnitz, Germany  
katrin.doering@chemie.tu-chemnitz.de

Alexander Dybov  
Research Group Prof. Dr. Heinz Berke  
Institut of inorganic chemistry  
University of Zürich  
Winterthurerstrasse 190  
8057 Zürich, Switzerland  
adybov@aci.uzh.ch

Irene Domínguez  
Research Group Prof. Dr. Jiří Čejka  
J. Heyrovský Institute of Physical Chemistry  
AS CR, v.v.i,  
Dolejškova 3  
182 23 Prague 8, Czech Republic  
irene.dominguez@jh-inst.cas.cz

Barbara Eignerová  
Research Group Prof. Dr. Martin Kotora  
Department of Organic and Nuclear Chemistry  
Faculty of Science  
Charles University  
Hlavova 2030  
12843 Prague 2, Czech Republic  
eignerova@uochb.cas.cz
Anna Wrona
Research Group Prof. Dr. Janusz Zakrzewski
Department of Organic Chemistry
University of Łódź
Narutowicza 68
90-136 Łódź, Poland
anna_wrona@interia.pl

Prof. Dr. Janusz Zakrzewski
Department of Organic Chemistry
University of Łódź
Narutowicza 68
90-136 Łódź, Poland
janzak@uni.lodz.pl
<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>7:00 - 8:00</td>
<td>Breakfast</td>
<td>IL1</td>
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<tr>
<td>8:30 - 9:05</td>
<td>Sobota</td>
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<tr>
<td>9:05 - 9:20</td>
<td>Mansfeld</td>
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<td>9:20 - 9:35</td>
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<tr>
<td>9:35 - 10:05</td>
<td>Kaczorowski</td>
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<td>10:05 - 10:25</td>
<td>Jipa</td>
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<td>10:25 - 10:40</td>
<td>Przechowicz</td>
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<td>10:40 - 10:55</td>
<td>Schirrmacher</td>
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<td>10:55 - 11:10</td>
<td>Wójcik</td>
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<td>11:10 - 11:25</td>
<td>Martincová</td>
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<td>Kamińska</td>
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<td>11:40 - 13:00</td>
<td>Lunch</td>
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<td>13:00 - 13:35</td>
<td>Excursion to Freiberg</td>
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<td>Štěpniška</td>
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<td>Jiang</td>
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<td>Freiberger Dom</td>
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<td>Fishgold</td>
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<td>14:35 - 14:55</td>
<td>Coffee Break</td>
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<td>14:55 - 15:10</td>
<td>Linweis</td>
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<td>Pichlmaier</td>
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<td>Domínguez</td>
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<td>15:50 - 16:10</td>
<td>Tauchman</td>
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<td>Huber</td>
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<td>18:05 - 18:15</td>
<td>Dinner</td>
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<td>18:15 - 19:15</td>
<td>Opening Remarks</td>
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<td>19:00 - 20:30</td>
<td>Conference Banquet, Castle of Augustusburg</td>
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