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UNIVERSITÄT LEIPZIG



From Molecules to Functionalised Materials

**Intensive Lecture Course
at the**

„Babeş Bolyai“ University

**Cluj-Napoca
13th – 17th October 2010**



Stabilitätspakt für Südosteuropa
Gefördert durch Deutschland
Stability Pact for South Eastern Europe
Sponsored by Germany

Scientific Programme

Wednesday, October 13

arrival of participants in Cluj-Napoca

Thursday, October 14

Location: *Universitas Hotel, Conference Hall, Pandurilor 7*

8:30-9:00 Opening session

9:00-10:30 Prof. dr. Robert Bruce King
The Metallurgist's Periodic Table

10:30-11:00 Coffee break

11:00-12:30 Assoc. Prof. dr. Igor Kuzmanovski
Prediction of Toxicity and Data Exploratory Analysis of Estrogen-Active Endocrine Disruptors Using Counter-Propagation Artificial Neural Networks

12:30-14:00 Lunch

14:00-16:00 Poster session

16:00-18:00 Visit of Babes-Bolyai Institutes for research

19:00 *Get-together party*

Friday, October 15

Location: *Faculty of Chemistry and Chemical Engineering, Arany János Street 11, room 147*

9:00-10:30 Prof. dr. Evamarie Hey-Hawkins,
Application of Metal-organic Frameworks in Catalysis

10:30-11:00 Coffee break

11:00-12:00 Assoc. Prof. dr. Radu Silaghi-Dumitrescu
Blood Substitutes I

12:00-13:00 PhD public defence, *Coordination Polymers of Polycarboxylates: Design, Synthesis and Structures*, Ioana Grosu (scientific supervisors: Prof. dr. Luminita Silaghi-Dumitrescu, Prof. dr. Evamarie Hey-Hawkins)

13:00-14:30 Lunch

14:30-15:30 Assoc. Prof. dr. Radu Silaghi-Dumitrescu
Blood Substitutes II

15:30-16:00 Coffee Break

16:00-20:00 Assoc. Prof. dr. Radu Silaghi-Dumitrescu, *Blood Substitute*, lab work

Saturday, October 16

Location: *Faculty of Chemistry and Chemical Engineering, Arany János Street 11, room 97*

9:00 -10:30 Assoc. Prof. dr. Jane Bogdanov
Magnetic Properties of Organic Compounds

10:30-11:00 Coffee break

11:00-12:00 Lect. Dr. Luiza Gaina, *Materials for Food Industry*

12:00-14:30 Lunch

14:30-16:30 Lect. Dr. Luiza Gaina, *Materials for Food Industry*, lab work

Sunday, October 17

departure of participants





Workshop “From Molecules to Functionalised Materials“



Book of Abstracts



UNIVERSITÄT LEIPZIG

*Cluj-Napoca, Romania,
13-17 October 2010*

Lectures

THE METALLURGICAL PERIODIC TABLE

Robert Bruce King

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The metallurgist's Periodic Table proposed by H. E. N. Stone in 1979 on the basis of alloy systematics and valence hyperbolas has the four divides listed below. In this connection a divide is placed in such a position in the Periodic Table that any element near to and on one side of the divide will form a compound or compounds with a counterpart element on the other side of that divide:

(1) *The ionic divide at the noble gases (Group 18)*: Elements on the immediate right of the ionic divide (e.g., the alkali and alkaline earth metals) form cations whereas elements on the immediate left of the ionic divide (e.g., the halogens and chalcogens) form anions.

(2) *The covalent divide (Group 14: C, Si, Ge, Sn, Pb)*: Elements on the immediate right of the covalent divide (i.e., hyperelectronic elements) form molecules with lone electron pairs and are *n*-dopants in semiconductors. Elements on the immediate left of the covalent divide (i.e., hypoelectronic elements) form molecules with multicenter bonding and are *p*-dopants in semiconductors.

(3) *The composite divide (Group 12: Zn, Cd, Hg)*: These elements, particularly mercury, function as pseudo-noble gases. Thus mercury is by far the most volatile of the metals and forms a monoatomic vapor. Furthermore, the cation Tl^+ and the anion Au^- with the mercury electronic configuration are relatively stable species.

(4) *The transition metal divide (Group 6: Cr, Mo, W)*: The Group 6 metals have a lower superconducting critical temperature than the metals immediately surrounding them in the Periodic Table. From the chemical point of view the Group 6 metals can exhibit the maximum possible bond order of 6 in the diatomic molecules M_2 . Furthermore, their binary octahedral metal carbonyls $M(CO)_6$ exhibit some properties suggestive of "molecular noble gases."

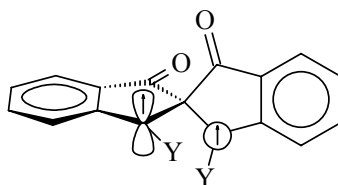
The post-transition metals located between the composite and covalent divides in the Periodic Table exhibit some chemical and electrical properties which are atypical for elements traditionally regarded as metals. This suggested to Klemm a refinement of the traditional dichotomy of metals and non-metals into a tetrachotomy of metals, metametals, semimetals, and non-metals. Zintl first showed by potentiometric titrations with alkali metals in liquid ammonia that some of the metametals and semimetals form cluster anions. The Zintl-Klemm concept was elaborated about a half century ago to account for the stoichiometry and structures of such anionic metal units in intermetallics. In modern times these classical ideas have been partially supplanted by the Wade-Mingos rules relating to three-dimensional aromaticity, such as that found in the polyhedral boranes. The jellium model, originally developed by physicists, is also relevant in explaining the special stability of bare clusters with 20 total valence electrons such as P_4^- as well as those with 40 total valence electrons such as Al_{13}^- .

MAGNETIC PROPERTIES OF ORGANIC COMPOUNDS

Jane Bogdanov

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Recently, there has been a lot of interest in designing "electronic," "optical," and "magnetic" *molecular* devices (switches, relays, diodes, etc) based on molecular building blocks. The design of molecular devices and new materials depends on the preparation of molecules with predictable and tunable electrical, optical and magnetic properties. For organic compound to have magnetic properties it must possess unpaired electron(s). Most organic molecules are diamagnetic, but there are some that exist as triplets in the ground state. The crucial step towards the design of organic molecular ferromagnets is thorough understanding of the spin-spin interactions in the basic building block i.e understanding the factors that influence the singlet-triplet energy gap (ΔE_{ST}) in diradicals. There are very few systems with an option of singlet-triplet tunability and a potential to be used as a high-spin building block for organic magnetic materials. An overview of the most promising organic high-spin building blocks is given with special emphases on the utilization of the phenomenon of spiroconjugation for design of such building blocks.



References:

1. Underhill, A. E.; Day, P. *Metal-Organic and Organic Molecular Magnets*; Royal Society of Chemistry: Cambridge, 2000.
2. Bogdanov, J. *Ph. D. Thesis, The Pennsylvania State University*, 2005.
3. Borden, W. T. *Diradicals*; Wiley: New York, 1982.
4. Maslak, P. *Adv. Mater.* **6** (1994) 405.

PREDICTION OF TOXICITY AND DATA EXPLORATORY ANALYSIS OF ESTROGEN-ACTIVE ENDOCRINE DISRUPTORS USING COUNTER-PROPAGATION ARTIFICIAL NEURAL NETWORKS

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A novel algorithm for optimization of counter-propagation artificial neural networks has been used for development of quantitative structure-activity relationships model for prediction of the estrogenic activity of endocrine-disrupting chemicals. The search for the best model was performed using genetic algorithms. Genetic algorithms were used not only for selection of the most suitable descriptors for modeling, but also for automatic adjustment of their relative importance ¹. Using our recently developed algorithm for automatic adjustment of the relative importance of the input variables, we are able developed simpler models with very good generalization performances by using only few interpretable descriptors ^{1,2}. One of the developed models is in details discussed in this article. The simplicity of the chosen descriptors and their relative importance for this model helped us in performing a detailed data exploratory analysis which gave us an insight in the structural features required for the activity of the estrogenic endocrine-disrupting chemicals ³.

References:

1. I. Kuzmanovski, M. Novič, M. Trpkovska, *Anal. Chim. Acta*, **642** (2009) 142.
2. G. Stojković, M. Novič, I. Kuzmanovski, *Chemometr. Intell. Lab. Syst.*, **102** (2010) 123.
3. N. Stojić, S. Erić, I. Kuzmanovski, *J. Mol. Graph. Model.*, (2010) **in press**.



Workshop "From Molecules to Functionalised Materials" – Cluj-Napoca, October 2010

APPLICATION OF METAL-ORGANIC FRAMEWORKS IN CATALYSIS

Evamarie Hey-Hawkins

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Metal-organic frameworks (MOFs) are a class of inorganic–organic hybrid materials in which metal ions or inorganic clusters (so-called secondary building units (SBUs), often formed in situ) are bridged by multidentate ligands to form polymeric coordination networks.¹ This relatively new class of porous polymers are promising materials for technical applications in separation, storage and heterogeneous catalysis, and the growing number of publications and patents focussed on metal-organic frameworks reflects the worldwide current interest in this research area.^{1,2}

The diversity of ligands as possible linkers and of metal ions and metal clusters as building units (nodes) is the basis for the variety of structural topologies with corresponding special properties.^{1,3} MOFs are valuable supplements to the already known zeolite materials and mesoporous molecular sieves. An essential advantage of MOFs compared with mesoporous materials is their crystalline structure. This results in uniform, strictly regular pore and cavity sizes and the possibility of detailed structural investigation by X-ray analysis. Compared to zeolites, the presence of linkers in MOFs allows tailoring of a wide variety of pore sizes (from 2 to 100 nm).

These porous coordination polymers are formed in organic solvents by self-assembly on reacting metal salts or complexes with the corresponding linkers. A promising field of application for porous coordination networks is heterogeneous catalysis, where MOFs can offer completely new possibilities and perspectives for employment as catalysts or for the synthesis of improved anchored catalysts. This area is still largely unexplored³ and will be the main focus of this lecture.

References:

1. (a) S. Kaskel, *Handbook of Porous Solids*, Vol. 2, Wiley-VCH, 1190, 2002; (b) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **43** (2004) 2334.
2. K. Sanderson, *Nature* **2007**, 448, 746.
3. *Chem. Soc. Rev.* **38** (2009), Special Issue on "Metal-Organic Frameworks".



Workshop "From Molecules to Functionalised Materials" – Cluj-Napoca, October 2010

ARTIFICIAL OXYGEN CARRIERS BASED ON PROTEINS

Radu Silaghi-Dumitrescu¹, Eva Fischer-Fodor,² Augustin Mot,¹ Florina Deac,¹
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Bianca Iacob,¹ Grigore Damian⁴

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The possibility of producing artificial oxygen carriers ("blood substitutes") in laboratory using proteins will be discussed. Hemoglobin purification and derivatization with several types of reagents will be presented. An alternative to hemoglobin-based oxygen carriers will also be presented, employing the marine worm oxygen-carrying protein, hemerythrin, which is accessible via recombinant DNA techniques for overexpression in *E. coli*. A battery of tests for hemoglobin and hemerythrin-based blood substitutes is presented, ranging from dioxygen affinity measurements, free-radical generation and quantitation, to millisecond kinetics, cell culture tests, and small animal testing. The presentation will point out recent results from our group, and students will be given hands-on experience on several of the methods mentioned above.



Workshop "From Molecules to Functionalised Materials" – Cluj-Napoca, October 2010

MATERIALS FOR FOOD INDUSTRY

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Packaging of food is a dynamic field. It is driven largely by consumer demands for fresher, safer, more nutritious, and convenient produce. The exponential growth in the semi-processing of fresh produce requires specialized active and intelligent packaging that maintains the quality and nutrition of its contents. Definitions for *intelligent* and *active* packaging are evolving as these two fields evolve. Most seem to agree that active packaging connotes a package that "responds" to a suboptimal physiological or environmental condition in the package and improves it. Intelligent packaging, on the other hand, involves a package sensing conditions in a package and communicating this information to a human or an appliance.

References:

1. Gordon L. Roberstson, *Food Packaging, Principles and Practice*, CRC Press, 2006.
2. C. L. Wilson, *Intelligent and Active Packaging for Fruits and Vegetables*, CRC Press, 2007.

Poster presentations

Workshop "From Molecules to Functionalised Materials" – Cluj-Napoca, October 2010

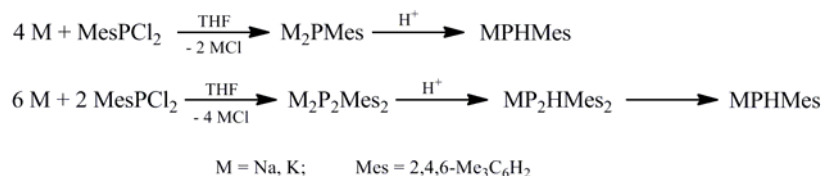
MESITYL-SUBSTITUTED PHOSPHANIDES OF THE HEAVIER ALKALI METALS

Ivana Jevtovikj, Peter Lönnecke, Evamarie Hey-Hawkins

Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany, e-mail: ivana.jevtovikj@chemie.uni-leipzig.de; hey@uni-leipzig.de

Alkali metal phosphanides with the general formula MPR_2 or MPHR are key starting materials in the synthesis of main group, transition metal and f-element phosphanide and phosphinidene complexes. In addition, these compounds can exhibit a variety of molecular structures depending on the substituent on phosphorus and the type of solvent or donor ligand employed. A commonly used strategy for the preparation of alkali metal phosphanides involves deprotonation of primary or secondary phosphines with an organometallic base.¹

In this contribution, we present two new mesityl-substituted alkali metal phosphanides which were isolated as the only product in the attempt to synthesise mesitylphosphanediide $\text{M}_2(\text{PMes})$ and 1,2-dimesityldiphosphane-1,2-diide $\text{M}_2(\text{P}_2\text{Mes}_2)$.



In ethereal solvents, quantitative protonation/disproportionation, caused by the strongly basic alkali metal mono- or diphosphanediides, leads to formation of MPHMe as the final product. After addition of TMEDA (*N,N,N',N'*-tetramethylethylenediamine) (for the Na salt) or PMDETA (*N,N,N',N'',N''*-pentamethyldiethylenetriamine) (for the K salt) the products $\{\text{Na}(\text{TMEDA})\text{PHMe}\}_\infty$ (**1**) and $\{\text{K}(\text{PMDETA})\text{PHMe}\}_2$ (**2**) were obtained. Compounds **1** and **2** were structurally and spectroscopically characterised.

References:

1. K. Izod, *Adv. Inorg. Chem.*, **50** (2000) 33.

SWITCHABLE FERROCENYL PHOSPHINES AS PRECURSORS FOR IMMOBILISED CATALYSTS

Martyna Madalska, Evamarie Hey-Hawkins

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The class of ferrocenyl phosphines has grown over the last decade, because many of these compounds were found to be excellent ligands for transition metals in homogeneous catalysis.¹ We have already developed high-yield syntheses for enantiopure chiral ferrocenyl phosphines and shown that the Fe²⁺ center is selectively and reversibly oxidizable.² Recently, a new type of phosphines has been synthesized, namely, potentially switchable phosphines in which one group is UV/Vis-, pH-, or redox-active, which seem suitable for modifying the catalytic properties of the corresponding transition metal phosphine complexes in situ, that is, changing their activity and selectivity. Using 1,1',2-substituted ferrocenyl derivatives will allow introduction of planar chirality besides C- or P-chiral centers as well as an anchor group R' (R' = -CH=CH₂, -Si(OMe)₃) on the second cyclopentadienyl ring, which can be used for grafting the ligands onto surfaces.³

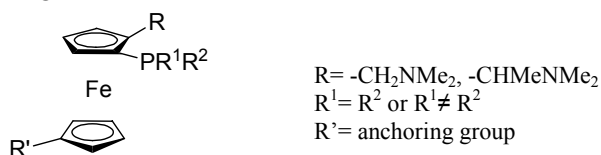


Figure 1

The R'-substituted phosphines and complexes thereof with transition metals (Rh, Ru, Pd) will be prepared and grafted onto suitable surfaces (carbon, polymers, silica etc.), and their catalytic reactions (asymmetric hydrogenation, asymmetric hydroformylation and C-C coupling) will be studied.

The immobilised switchable catalysts may offer a new approach to this field. Therefore, these chiral multicentered catalysts are already highly interesting in their own right.

References:

1. T.J. Colacot, *Chem. Rev.* **103** (2003) 3101.
2. S. Tschirschwitz, P. Lönnecke, E. Hey-Hawkins, *Organometallics* **26** (2007) 4715; R. Kalio, P. Lönnecke, E. Hey-Hawkins, *J. Organomet. Chem.* **693** (2008) 590.
3. P. Štěpnička, *Ferrocenes. Ligands, Materials and Biomolecules*, Wiley (2008).

PHOSPHORUS-RICH TRANSITION METAL COMPLEXES AS PRECURSORS FOR METAL PHOSPHIDES M_xP_y

Aslihan Kircali, Sebastian Bauer, and Evamarie Hey-Hawkins

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The chemistry of polyphosphorus compounds has developed impressively over the last four decades. While the synthesis, reactivity and properties of organic cyclooligophosphanes have already been intensively studied, the number of metal complexes of these species described in the literature is still small. However, the few known examples have shown that cyclic and catenated oligophosphanide anions exhibit a rich coordination chemistry (due to the possibility that each P atom may be involved in coordination through its free electron pair).¹

Additionally, metal complexes with anionic polyphosphorus ligands may be an alternative for the development of rational syntheses of binary metal phosphides (M_xP_y with $y > x$), which are a fascinating class of compounds with interesting structures and properties for materials science. Thus, metal phosphides may behave as metallic or semimetallic conductors or (in most cases) as semiconductors. In addition, rare earth metal phosphides have been extensively investigated due to their interesting magnetic properties.² Up to now, metal phosphides have mainly been obtained by solid-state synthetic techniques, under extreme conditions with long reaction times, or via the molecular phase to enable their use in the preparation of new materials.

Herein, we report the synthesis and characterisation of the first iron(II) complex with ten phosphorus atoms, $[Fe\{cyclo-(P_5tBu_4)\}_2]$, which can be used as a precursor for the synthesis of binary metal phosphides (M_xP_y with $y > x$).

References:

1. R. Wolf, A. Schisler, P. Lönnecke, C. Jones, E. Hey-Hawkins, *Eur. J. Inorg. Chem.* (2004), 3277; R. Wolf, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* (2006), 632 and *Angew. Chem. Int. Ed.* **44**, (2005), 6241; S. Gómez-Ruiz, A. Schisler, P. Lönnecke, E. Hey-Hawkins, *Chem. Eur. J.* **13**, (2007), 7974; S. Gómez-Ruiz, R. Wolf, S. Bauer, H. Bittig, A. Schisler, P. Lönnecke, E. Hey-Hawkins, *Chem. Eur. J.* **14**, (2008), 4511.
2. H.-G. von Schnering, W. Hönle, *Chem. Rev.* **88**, (1988), 243; S. L. Brook, S. C. Perera, K. L. Stamm, *Chem. Eur. J.* **10**, (2004), 3364.

GLYCOSYLATED CARBABORANYLPHOSPHONATES FOR POTENTIAL USE AS BNCT AGENTS IN TUMOUR THERAPY

Johannes Kunig, Evamarie Hey-Hawkins

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Since the introduction of boron neutron capture theory (BNCT) by *Locher* in 1936, several investigations toward synthesizing useful compounds, including derivatives of amino acids, porphyrins, liposomes, monoclonal antibodies, and epidermal growth factors, were carried out and reviewed.¹ Until now, only BPA (*L*-*para*-boronophenylalanine), its fructose complex, and BSH (sodium mercapto-*closo*-dodecaborate) made it into clinical trials on high-grade gliomas and melanomas.² Nevertheless, their complete pharmacokinetic behaviour and biodistribution are uncertain and need to be further investigated.

We focus on conjugates of glycosides and carbaboranyl bis-phosphonites, which combine the boron-bearing part with a hydrophilic, less toxic and tumour-selective moiety. Previously, we reported novel 6'-galactosyl-substituted carbaboranyl phosphonates and phosphonothioates as disodium salts,³ which exhibit high water solubility and low cytotoxicity, but failed to show sufficiently high accumulation rates in *in vivo* studies on BALB/c mice bearing CRL tumour lines.

Further investigations now include different glycosidic moieties, such as glucose, mannofuranose and mannopyranose, as well as galactose attached via the anomeric centre.

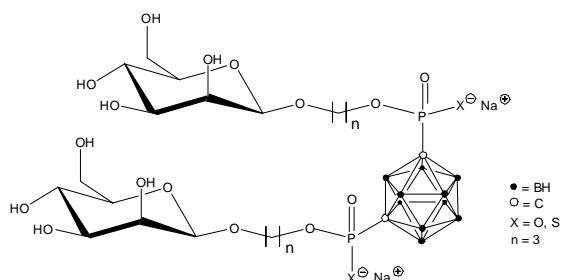


Figure 1. Deprotected *meta*-carbaboranyl conjugate of β -mannopyranose

References:

1. V. I. Bregadze, *Anti-Cancer Agents in Med. Chem.* **6** (2006), 75; J. F. Vaillant, *Coord. Chem. Rev.* **232** (2002), 172; A. H. Soloway, *Chem. Rev.* **98** (1998), 1515.
2. R. F. Barth, *Clin. Cancer Res.* **11** (2005), 3987-4002; Y. Nakagawa, *J. Neuro-Oncol.* **62**, (2003), 87.
3. S. Stadlbauer, P. Lönnecke, P. Welzel, E. Hey-Hawkins, *Eur. J. Org. Chem.* (2009), 6301.

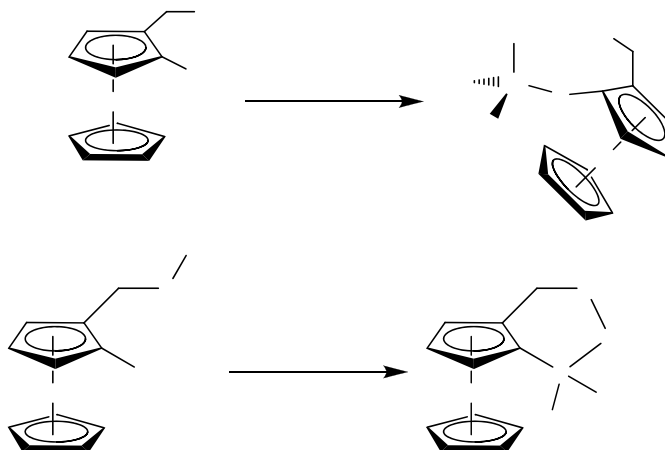
NOVEL FERROCENYL PHOSPHINE PRECURSORS FOR THE SYNTHESIS OF NEW HYBRID MATERIALS

Julian R. F. Pritzwald-Stegmann, Peter Lönnecke and Evamarie Hey-Hawkins

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Recent advances in technology demand extraordinary properties from materials which traditional materials, such as polymers and ceramics, cannot provide. This has spurred the development of advanced hybrid materials which combine the best attributes of different worlds into one system. As part of a continuing investigation into the development of new smart molecules for use as building blocks for hybrid materials, a series of ferrocenyl phosphine compounds have been synthesised as precursors.

The copper(I) complex [(*N,N*-dimethylaminomethyl)phosphanylferrocene]iodobis(triphenylphosphine)copper(I) (**1**) was synthesised from a combination of copper(I) iodide, triphenylphosphine and (*N,N*-dimethylaminomethyl)phosphanylferrocene under mild conditions. The treatment of (*N,N*-dimethylaminomethyl)phosphanylferrocene with one mole of trimethylgallium results in the formation of an adduct which upon the addition of a second mole of trimethylgallium forms **2** via the elimination of methane. Both **1** and **2** will be used for the formation of well-defined, *in situ* functionalised, inorganic/organometallic building blocks which can be used for the preparation of novel hybrid materials through the bottom-up approach. The strategies currently under investigation to form other precursors will also be discussed.



STUDYING THE ION TRANSFERS ACROSS LIQUID/LIQUID INTERFACE IN THE PRESENCE OF SACCHARIN BY MEANS OF SQUARE-WAVE VOLTAMMETRY

Katerina Stankoska, Valentin Mirčeski

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The objective of the study are the thermodynamic and kinetic parameters of the ion transfer processes across water/nitrobenzene interface measured by means of square-wave voltammetry at thin-film electrodes. The electrode system consists of edge plane pyrolytic graphite electrode (EPGE) covered with a thin-film of an organic solvent nitrobenzene (NB), that contains a lipophilic neutral redox probe, lutetium bis(tetra-*tert*-butylphthalocyaninato), LBPC. This surface-modified electrode is immersed in an aqueous electrolyte solution (AQ) wherewith a three-phase electrode is obtained. LBPC undergoes one electron electrochemical reversible redox reactions in oxidation and reduction mode. An oxidation and reduction process of LBPC is accompanied with simultaneous transfer of the appropriate ions across the AQ/NB interface in order to maintain the electroneutrality of the organic phase.

In a set of experiments, the transfer processes of the strongly hydrophilic cations Li^+ , Na^+ and K^+ is analyzed in detail, in the presence of saccharin in the aqueous phase. From the collected data it has been concluded that saccharin facilitates and accelerates the cations transfer across the liquid/liquid interface. In addition, the transfer of the saccharinate anion has been also studied in a separate experiment and the standard Gibbs energy of that transfer across the interface has been determined.

STUDING THE REDOX CHEMISTRY OF A HEME-LIKE COMPLEX USING THIN-FILM THREE PHASE ELECTRODES

Natalija Atanasovska, Hristina Zdravkovska, Birhan Sefer, Valentin Mirčeski

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The redox chemistry of a heme-like complex 5,10,15,20-tetraphenylporphyriniron(III) chloride (Fe(III)-TPP-Cl) is studied using thin-film three phase electrode methodology by means of voltammetric techniques. The electrode ensemble comprises a thin-film of water immiscible organic solvent (e.g. nitrobenzene or n-octanol) contain the redox active heme-like complex and suitable organic salt imposed on a surface of edge plane pyrolytic graphite electrode (EPPGE). The EPPG electrode is immersed into an aqueous electrolyte and used in a conventional three-electrode cell. Schematic presentation of the working electrode is shown at Figure 1, which is known as a three phase electrode.

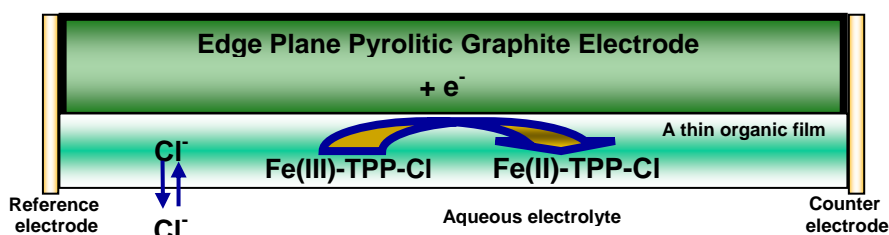


Figure 1 Schematic presentation of the working electrode

The overall electrochemical process proceeds as coupled electron-ion transfer reaction and the redox chemistry of Fe(III)-TPP-Cl involves two quasireversible redox transformations typical for Fe(III)/Fe(II) couple. Both processes are coupled with chemical reactions inside the thin organic film and ion transfer reactions across the thin-film / aqueous electrolyte interface involving chloride expulsion from the organic film and cation ingress from the aqueous phase.

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GAMMA SPECTROMETRY AS AN ANALYTICAL METHOD FOR INVESTIGATION OF RADIOACTIVITY IN SOILS

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Natural radionuclides in the soil are the main external source of irradiation of the population. Natural environmental radioactivity and associated external exposure due to gamma-radiation depends primarily on the geological and geographical conditions, and appears at different levels of radionuclides in the soil of each region in the world ¹. Concerning the Republic of Macedonia, there are reports by Dimovska ^{2,3}, presenting results on the specific activity from the natural radionuclides in the soils of cities Veles and Kavadarci. Complete study of the soils in Macedonia has also been performed ⁴.

The external exposure on the human being from terrestrial radiation is directly connected with the concentration of ²²⁶Ra, ²³²Th and ⁴⁰K in the soil. Some of the previously obtained results on determination of the specific activity of soil samples on ²²⁶Ra, ²³²Th and ⁴⁰K employing gamma spectrometry measurements will be presented. According to the results, gamma spectrometry can successfully be used for analysis of natural radionuclides in soil samples and monitoring of the radiation in the environment.

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PRINCIPLES AND APPLICATION OF VOLTAMMETRIC TECHNIQUES

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A short presentation of the basic principles and characteristic of voltammetric techniques is given, in particular addressing the conventional cyclic voltammetry, as well as advanced pulsed voltammetric techniques such as square-wave and differential pulse voltammetry. An overview of the electrochemical methods for determination of organic, inorganic compounds and biomolecules is shortly presented, which include fundamental studies of oxidation and reduction processes in various media, adsorption processes on electrode surfaces, electron transfer and reaction mechanisms, kinetics of electron transfer processes, transport, speciation, and thermodynamic properties of solvated species. The basic features of the current-potential curves (voltammograms) are briefly discussed, which are the main output from the voltammetric experiment, providing information for the mechanistic, energetic and kinetic aspects of the studied electrode processes.

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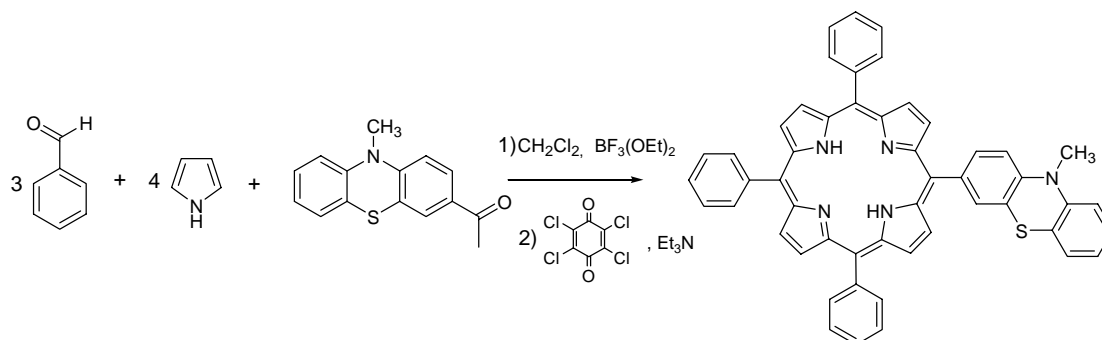
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SYNTHESIS AND CHARACTERIZATION OF SOME NEW PORPHYRINS WITH PHENOTHIAZINE UNITS

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The design and synthesis of basic porphyrin building blocks for the construction of highly ordered systems often require incorporation of different peripheral substituents. Most of the reported methods generally adopted acid-catalyzed condensation of aldehydes with pyrrole^{1,2}. The synthesis of tetraphenylporphyrin developed by Adler³ involves the addition of benzaldehyde and pyrrole to an open bath of refluxing propionic acid. J. S. Lindsey⁴ developed an alternative procedure complementary to that Adler, pyrrole and the desired benzaldehyde (10^{-2} M) are allowed to react at room temperature in dry CH_2Cl_2 under N_2 with trace acid catalysis (10^{-3} M BF_3 or 10^{-2} M trifluoroacetic acid). Porphyrins with 10-methylphenothiazine in β position were obtained according to Lindsey procedure and the products were characterized by NMR, MS (APCI) and UV-Vis methods.



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NEW OCTAKIS-(TRIMETHYLSILYL) AND OCTAKIS-(N-PROPYL-TRIMETOXISILAN) LOWER RIM SUBSTITUTED CALIX[8]ARENES

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New lower rim silyl substituted calix[8]arenes have been synthesized by reaction of the parent *p*-tert-butylcalix[8]arene with *n*-BuLi at low temperature followed by addition of trimethylchlorosilane/(3-chloropropyl)-trimethoxysilane when octakis-(trimethylsilyl)calix[8]arene /octakis-(*n*-propyl-trimethoxysilan)calix[8]arene is obtained. New calixarene derivatives have been characterized by NMR and IR spectroscopy.

A PM3 energy profile calculation with Spartan06 for a monosubstituted calixarene[8]arene (Figure 1) shows a barrier for the inversion of the methylene group accompanied by a corresponding rotation of the arene ring of less than 15 kcal/mol, comparable with the experimentally determined barriers of interconversions of various calix[4,8]arenes¹.

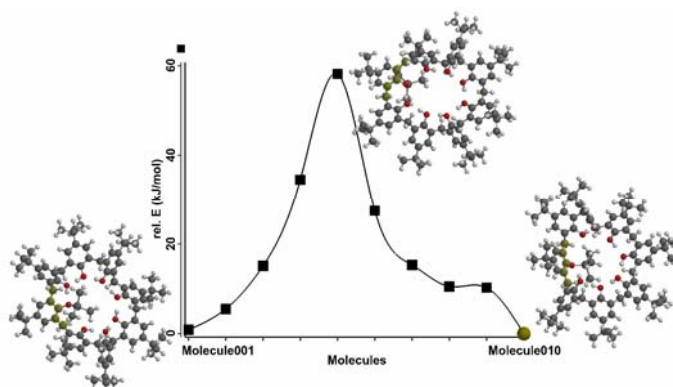


Figure 1. PM3 energy profile for a monosubstituted calixarene[8]arenes

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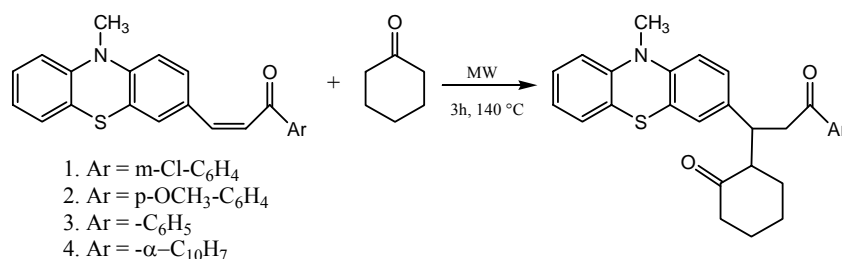
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MICROWAVE ASSISTED MICHAEL ADDITION OF CYCLOHEXANONE TO 1,3-(HETERO)ARYL-PROPENONES

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An increasing number of published papers, several books^{1, 2} and review articles show that almost all conventionally heated reactions, including synthesis and functionalization of heterocyclic compounds, were performed using microwave assisted technique³⁻⁵. We applied this technique for the Michael addition reaction, one of the most useful methods for the mild formation of C-C bonds. Michael addition consists of an addition of nucleophile to an α,β -unsaturated carbonyl substrate. The most common carbon nucleophiles are nitromethane, cyclohexanone, diethyl malonate etc.⁶ This work presents the Michael addition of cyclohexanone nucleophile to phenothiazinyl chalcones (Scheme 1) under microwave assisted conditions.



Scheme 1

Advantages of the MAOS were related to shorter reaction times and good yields. The structures of the addition products were confirmed by mass spectrometry.

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SYNTHESIS AND CHARACTERIZATION OF NOVEL TRÖGER'S BASES WITH PHENOTHIAZINE UNITS

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Tröger's bases are a group of substances that have recently reemerged in research because of their unique properties as chiral agents, receptors or catalyst. This work shows the synthesis and characterization of novel Tröger's bases with phenothiazine units starting from chloro-phenothiazines with an amino-phenothiazine intermediate. The reaction conditions and synthesis of one such Tröger's base (6H, 2H-tetrahydro-10' Me, 10'' Me-2,3-phenothiazinyl-[1,5]diazocine) are discussed and characterization of the molecule is done with $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, UV-Vis and fluorescence spectroscopy. We undertook a series of reaction conditions to reveal the best synthetic route. Physical characterization methods reveal properties that could be valuable in further research.

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DERIVATIZATION OF HEMOGLOBIN WITH PERIODATE-GENERATED RETICULATION AGENT: EVALUATION OF OXIDATIVE REACTIVITY FOR POTENTIAL BLOOD SUBSTITUTES

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Periodate modification of hydroxyl groups in sugars and in derivatives thereof, including adenosine triphosphate (ATP), has previously been employed in order to prepare dialdehyde-type reagents, which were then utilized in crosslinking reactions on hemoglobin, yielding polymerized material with useful dioxygen-binding properties and hence proposed as possible artificial oxygen carriers ("blood substitutes"). Here, the periodate protocol is shown to be applicable to a wider range of oxygen-containing compounds, illustrated by starch and polyethyleneglycol. Derivatization protocols are described for hemoglobin with such periodate-treated crosslinking agents, and the dioxygen-binding properties and redox reactivities are investigated for the derivatized hemoglobins, with emphasis on pro-oxidative properties. There is a general tendency of the derivatization to result in higher autooxidation rates. The reactivity towards peroxide (seen as representative for oxidative stress) is also affected by derivatization, as witnessed, among others, by varying yields of ferryl (Fe(IV)-oxo) and free radical generated. In cell culture tests (human umbilical vein epithelial cells, HUVEC), the derivatization protocols show no toxic effect.

REDUCTIVE CHEMISTRY WITH CHROMIUM AND IRON-SUBSTITUTED DAWSON POLYOXOMETALATES

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Chemical reduction of an iron(III) substituted Dawson 5-molybdo-12-tungsto-2-phosphate $K_7[Fe(H_2O)P_2Mo_5W_{12}O_{61}] \cdot 17H_2O$ complex, with dithionite in aqueous solution is reported alongside with similar data for the monolacunary Dawson molybdo-tungsto-diphosphates $[P_2Mo_5W_{12}O_{61}]^{10-}$. UV-vis absorption and low-temperature EPR (electron paramagnetic resonance) spectra indicate several distinct species and an unprecedented change of spin state at the ferric center, induced indirectly by reduction of the polyoxometalate framework.