Third EuCheMS Inorganic Chemistry Conference
"Chemistry over the horizon"

EuCheMS
European Chemical Sciences
Division of Inorganic Chemistry

Book of Abstracts

Wrocław 2015

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Dear Collegues,

We have the great pleasure to welcome you to Wrocław, for the Third EuCheMS Inorganic Chemistry Conference EICC-3 *"Chemistry over the horizon"*. The first two Inorganic Chemistry Conferences were held in Manchester (2011) and Jerusalem (2013). This time we meet in Wrocław to broaden our scientific interests in the most *"trendy"* fields of inorganic chemistry: supramolecular and coordination chemistry, organometallics and catalysis, nanoparticles and nanocatalysis, energy and photochemistry, bioinorganics and metalloenzymes, materials, reaction mechanisms and theory and other.

The meeting is organized by the Faculty of Chemistry, University of Wrocław. We have invited lecturers who are outstanding scientists from renowned European scientific centers.

Do not forget to keep extra time to visit Wrocław, the city with very interesting history. The conference site will be located close to the heart of Wrocław's historic Ostrów Tumski and within walking distance from other historic attractions such as the City Hall and Market Place. Arts and entertainment places such as the National Museum, Opera, Panorama Racławicka and several theatres are also nearby.

We wish you scientific satisfaction and enjoyable stay in Wrocław!

The Organizing Committee of the

Third EuCheMS Inorganic Chemistry Conference
EICC-3 *"Chemistry over the horizon"*.

28th June - 1st July 2015
Wrocław, Poland

PROGRAMME

Each presentation Has been given a unique code. The code indicates the theme within which the presentation falls, the abstract number, and type of presentation. E.g. BM_01 or BM_P01 (P denotes a poster presentation)

PL	Plenary speaker
BM	Bioinorganic and Metalloenzymes
OC	Organometallic and Catalysis
M	Materials
SC	Supramolecular and Coordination chemistry
EP	energy and Photochemistry
MT	Reaction mechanism and Theory

This numbering system is used throughout the abstract book.

Sunday, June 28, 2015

Registration

9:00- 14:00 the Faculty of Law

Plenary& Keynote

15:00- 15:45
Pl_01 Redox Active Metallodrugs: Benefits and Concerns
Zeev Gross
Israel Institute of Technology, Israel

15:45- 16:15
K_01 Metal ions in biomimetic cavities
Olivia Reinaud
Paris Descartes Univ., France

16:15- 16:45
K_02 Fenton Like Reactions Proceed Via a Variety of Mechanisms
Ariela Burg[1], Haya Kornweitz[2], Dan Meyerstein[2,3]
[1]SCE – Shamoon College of Engineering, [2]Beer-Sheva , Ariel Univ., Ariel, Ben-Gurion [3]Univ. of the Negev, Beer-Sheva.

16:45- 17:15 Coffee break

Session 1: *Bioinorganic and Metalloenzymes*

17:15-17:35
BM_01 Biomimetic Redox Reactions of the Cu^{II} Thiolate Complex
Erica C.M. Ording-Wenker, Elisabeth Bouwman
Leiden University, Netherlands

17:35- 17:55
BM_02 Exploring mystery of the first theoretically designed biocatalysts
Andrzej Sokalski, Wiktor Beker, Edyta Dyguda-Kazimierowicz
University of Technology, Poland

17:55- 18:15
BM_03 Nuclear spin catalysis in bioinorganic chemistry of metalloenzymes
Vitaly Koltover
Russian Academy of Sciences, Russia

18:15-18:35
BM_04 Learning on nonnatural bioinorganics: Molecular Modeling of Artificial Metalloenzymes
Jean-Didier Maréchal
The Autonomous University of Barcelona, Spain

18:35-18:55
BM_05 Chemistry of the Nitrogenase P-Cluster and FeMo-co
Kazuyuki Tatsumi
Nagoya Univ., Japan

Session 2: *Organometallics and catalysis*

17:15-17:35
OC_01 Entrapment of the complex Cu(2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane) in sol-gel electrodes for electrocatalysis
Ariela Burg[1], Inbar Elias[2],Dror Shamir[3], Dan Meyerstein[2,4]
[1] SCE – Shamoon College of Engineering, Beer-Sheva, Israel, [2] Ben-Gurion Univ. of the Negev, Israel, [3] Nuclear Research Centre, Israel, [4] Ariel University, Israel

17:35- 17:55
OC_02 C-H Activation Reactions in Zr and Y Complexes Anchored by Disubstituted Cyclam Ligands
Ana M. Martins, Luis G. Alves, Filipe Madeira, Luis F. Veiros
Lisbon Univ., Portugal

17:55- 18:15

OC_03 Selective oxidation of alkanes with m-chloroperbenzoic acid catalyzed by a heterometallic Co/Fe complex
Dmytro S. Nesterov[1],Armando J. L. Pombeiro[1]
Lisbon Univ., Portugal

18:15-18:35
OC_04 Molecular metal hydride carbonyl clusters
Iacopo Ciabatti, Cristina Femoni, Mohammad Hayatifar, Maria Carmela Iapalucci
Stefano Zacchini
University of Bologna, Italy

18:35-18:55
OC_05 H Atom Abstraction versus Chelate Complex Formation – Reactivity Patterns of side-on coordinated S,N-substituted Alkynes
Wolfram W. Seidel, Julia Rüger, Kai Helmdach
Univ. of Rostock, Germany

Session 3: *Materials*

17:15-17:35
M_01 Characterization of Cu(II) and Ag(I) compounds with N,O donor ligands and application for metalorganic layer deposition
Magdalena Barwiołek, Robert Szczęsny, Edward Szłyk
Nicolaus Copernicus Univ., Poland

17:35- 17:55
M_02 Zwitterionic derivatives of closo-borates as polar materials for LCD applications
Piotr Kaszyński[1]
Univ. of Łódź, Poland

17:55- 18:15
M_03 $R_2T_{3-x}Si_x$, new pseudo-binary phases and prospective magnetocaloric materials (R = Ce, Pr, Nd, Gd, Tb, Dy; T = Co, Ni).
Tadhg Mahon, Sophie Tencé, Bernard Chevalier, Etienne Gaudin
Univ. Bordeaux, France

18:15-18:35
M_04 Phase relationships and complex crystal structures of ternary and quaternary selenides
Frank Heinke[1], Philipp Urban[1], Jordana Schiller[1], Christina Fraunhofer[2], Gerald Wagner[1], Oliver Oeckler[1]
[1] Leipzig Univ., Germany, [2] LMU Munich, Germany

18:35-18:55
M_05 Alginate/chitosan core-shell materials with bioactive functionalities
Anna Regiel-Futyra[1], Aleksandra Mazgała[1], Justyna Michna[1],Małgorzata Kus-

Liśkiewicz[2], Silvia Irusta[3,4], Manuel Arruebo[3,4], Agnieszka Kyzioł[1]
[1]Jagiellonian Univ.,Poland, [2]Univ. of Rzeszow, Poland, [3]Univ. of Zaragoza, Spain
[4]Networking Research Center on Bioengineering, Biomaterials and Nanomedicine, Spain

19:00- 22:00 Welcome Reception

Monday, June 29, 2015

Plenary& Keynote

8:45- 9:30
PL_02 Organometallic Nanoparticles. Surface chemistry, magnetic heating and catalysis
Bruno Chaudret
National Institute of Applied Sciences, France

9:30- 10:00
K_03 Transition Metal Superatoms - the Frontier Between Inorganic Chemistry and Catalysis
Valentine P. Ananikov
Russian Academy of Sciences, Russia

10:00- 10:30
K_04 New ruthenium complexes with chelating ligands for olefin metathesis and beyond
Karol Grela
Univ. of Warsaw, Poland

10:30-11:00
K_05 eNHChanting new chemistry with Cu and Zn
Michael K. Whittlesey
University of Bath, , UK

11:00- 11:30 Coffee break

Session 4: *Bioinorganic and Metalloenzymes*

11:30-11:50
BM_06 X-ray Spectroelectrochemistry – A useful use of sample?
Joey Yeo, M. Tauhid Islam, Christopher Chantler, Stephen Best
Univ. of Melbourne, Australia

11:50-12 :10
BM_07 Coordination Complexes with Aminophenol-based Redox-Active Ligands.
Bioinorganic and Inorganic Perspectives
Rabindranath Mukherjee
Indian Institute of Technology and Indian Institute of Science Education and Research, India

12:10-12:30
BM_08 Copper(II) binding to Angiogenin: new insights in the role of metal ionsin angiogenesis
Diego La Mendola[1], Fabio Arnesano[2], Orjan Hansson[3], Chiara Giacomelli[1], Vincenzo Mangini[2], Maria Letizia Trincavelli[1], Cristina Satriano[4], Antonio Magrì[5], Claudia Martini[1], Giovanni Natile[2], Enrico Rizzarelli[5]
[1]Univ.of Pisa, Italy, [2]Univ. of Bari, Italy; [3]Univ. of Gothenburg, Sweden; [4] Univ. of Catania, Italy, [5]National Council of Research (CNR), Italy.

12:30-12:50
BM_09 Functionalization of polypirydyl ruthenium complexes for biomedical applications
Małgorzata Brindell[1], Olga Mazuryk[1]
[1]Jagiellonian Univ., Poland

Session 5: *Organometallics and catalysis*

11:30-11:50
OC_06 Metalloporphyrins as active N-heterocyclic carbene (NHC) transfer reagents
Bryan Hogan, Martin Albrecht[*]
Univ. College Dublin, Ireland

11:50-12:10
OC_07 An Electrochemical Flow-Reactor for the Synthesis of Metal-NHC Catalysts
Charlotte E. Willans, B. N. Nguyen, Michael R. Chapman
Univ. of Leeds, UK

12:10-12:30
OC_08 Synthesis of nucleophilic carbene complexes and borenium species from a $P^{(V)}$-stabilized geminal dianion
Lafage Mathieu[1], Heuclin Hadrien[2], Mézailles Nicolas[1]
[1] Paul Sabatier Univ., France, [2]Ecole Polytechnique, France

12 :30- 12 :50
Partner`s presentation

Session 6: *Materials*

11:30-11:50
M_06 Building Block Replacement in Metal-Organic Frameworks

Wojciech Bury[1,2], Olga Karagiaridi,[2] Pravas Deria,[2]Joseph E. Mondloch, [2]David Fairen-Jimenez,[3] Omar K. Farha,[2,4] and Joseph T. Hupp[2]
[1]Warsaw Univ. of Technology, Poland; [2]Northwestern Univ.,United States; [3], Univ. of Cambridge, UK; [4] King Abdulaziz University, Saudi Arabia

11:50-12:10
M_07 Conjugated Poly-ynes and Poly(metalla-yne)s for New Materials Applications
Raya A. Al-Balushi[1], Muhammad S. Khan[1]
[1]Sultan Qaboos University, Oman.

12:10-12 :30
M_08 New hydrides $RTXH_{1.5}$ (R = Rare-earth; T = Sc,Ti; X = Si,Ge)
Sophie Tencé[1], Tadhg Mahon[1], Etienne Gaudin[1],Bernard Chevalier[1]
[1]Univ. Bordeaux, France

12 :30- 12 :50
Partner`s presentation

12 :50- 14 :30 Lunch

Plenary& Keynote

14:30-15:15
PL_03Carbaporphyrinoids – AQuestfor Macrocyclic Surroundings in Organometallic Chemistry
Lechosław Latos-Grażyński
Univ. of Wrocław, Poland

15:15-15:45
K_06 Oxidative transformation of poly- and perfluorinated aromatics catalyzed by phthalocyanine and porphyrin μ-nitridodiiron complexes
Cédric Colomban[1],Evgeny E. Kudrik,[1,2] Pavel Afanasiev,[1]Alexander B. Sorokin[1]
[1] Institute of Researches on Catalysis and Environment France, [2]State Univ. of Chemistry and Technology, Russia

Session 7: *Bioinorganic and Metalloenzymes/ Nanoparticles and nanocatalysis*

15:55-16:15
BM_10 Gallium(III) complexes of macrocyclic bis(phosphonate)-containing ligands for imaging of bone metastases
Marian Meckel,[1] Vojtěch Kubíček,[2] Frank Rösch,[1]Petr Hermann[2]
[1]Johannes Gutenberg Univ., Germany; [2]Charles Univ. in Prague, Czech Republic

16:15-16:35
NN_01 Catalytic Bimetallic Nanoparticles For Green Chemistry
Jessica Stanley, Paul Benndorf, Falk Heinroth, Tony Masters and Thomas Maschmeyer
Univ. of Sydney, Australia

16:35-16:55
NN_02 Real-time imaging of atom migration and nanocrystallisation on
multi-doped graphenic surfaces
Anaïs Pitto-Barry, Richard Beanland, Peter J. Sadler, Nicolas P. E. Barry
Univ. of Warwick, U.K.

Session 8: *Organometallics and catalysis*

15:55-16:15
OC_09 Redox Transformations of Molecular MNR_x Species in the Context of Nitrogen Fixation and
Amine Activation
Sven Schneider
University of Göttingen, Germany

16:15-16:35
OC_10 Formation of a ZwitterionicBoronium Species from the Reaction of a Stable Carbenoid with
Borane: CO_2 Reduction
Samuel Y.-F. Ho[1,2], Cheuk-Wai So[2], Nathalie Saffon-Merceron[1], Nicolas Mézailles[1]
[1]Paul Sabatier Univ., France, [2] Technological University, Singapore

16 :35-16 :55
OC_11Polyhedral boron hydrides as Lewis acids
Igor B. Sivaev, Vladimir I. Bregadze
Russian Academy of Sciences, Russia

16:55-17:15
OC_12Indium Trihydride Complexes and the First Indium Subhydride
Alasdair I. McKay[1], Anthony R. Leverett[1]and Marcus L. Cole[1]
[1]Univ.of New South Wales, Australia

Session 9: *Supramolecular and Coordination chemistry*

15:55-16:15
SC_01Dinuclear Metallacycles with Single Anion Bridges: Unusual Magnetic and NMR Properties
Daniel L. Reger[1], Andrea E. Pascui[1], Mark D. Smith[1], Julia Jezierska[2], Andrew Ozarowski
[1]Univ.University of South Carolina, USA, [2]Univ.of Wrocław, Poland, [3]Florida State Univ.,
USA.

16:15-16:35
SC_02 Metallacryptates or Metallacoronates– Influence of Coordination number and Templates on
Product Formation
Chien Thang Pham[1], Hung Huy Nguyen[2], Ulrich Abram[1]
[1]Free Univ. of Berlin, Germany, [2]Hanoi Univ. of Science, Vietnam

16:35-16:55
SC_03 Metal azo-complexes based on heterocyclic derivatives of pyrazolones
Olga Kovalchukova[1,2], Nguyen Van[1], MikhaelRyabov[1], RusulAlabada[3], Oleg Volyansky[2]
[1]Peoples' Friendship Univ. of Russia, Russia, [2]Moscow State Univ. of Design and Technology, Russia, [3]Al Muthanna Univ., Iraq

16:55-17:15
SC_04Tuning triphyrins(n.1.1) properties with coordination
Miłosz Pawlicki
Univ. of Wrocław, Poland

17:15-19:30 Poster session

Tuesday, June 30, 2015

Plenary & Keynote

8:45-9:30
PL_04 Transmission electron microscopy as an important technique for structural characterization of inorganic materials
Wei Wan, Sven Hovmöller, Xiaodong Zou
Stockholm Univ., Sweden

9:30-10:00
K_07 Homogeneous catalysed H_2 generation using C1 entities and H_2O as H_2 source
Leo E. Heim[1], Nils E. Schlörer, Jong-Hoo Choi, Martin H. G. Prechtl[1]
[1]Univ. of Cologne, Germany

10:00-10:30
K_08 Chemistry based on non-precious metal PNP and PCP pincer complexes
Karl Kirchner
Vienna Univ. of Technology, Austria

10:30-11:00
K_09 Organolanthanides for catalytic olefin hydrophosphination
Trifonov A.A., Basalov I.V., Kissel A.A., Yurova O.S.
Russian Academy of Sciences

11:00-11:30 Coffee break

Session 10: Nanoparticles and nanocatalysis

11:30-11:50
NN_03 Specific interactions between noble metal nanoparticles and inorganic mixed-metal oxide supports in efficient electrocatalytic oxidations of organic fuels

Iwona A. Rutkowska*, Anna Wadas, Ewelina Marks, Weronika Ozimek, Jakub Sek, Aleksandra Rogalinska, Pawel J. Kulesza
Univ. of Warsaw, Poland

11:50- 12:10
NN_04 Synthesis, Characterization, Crystal structure of Cadmium-isonicotinate Metal Organic frameworks and its adsorptive removal of Methyl orangefrom Aqueous Solution
Adedibu C. Tella[1],[*]Margaret D. Olawale[1,2], Markus Neuburger[3], Joshua A. Obaleye[1]
[1]Univ. of Ilorin, Nigeria, [2]Elizade Univ., Ondo State Nigeria, [3]Univ. of Basel, Switzerland

12:10-12:30
NN_05 Dependence of defect species and morphology on composition and dopant type of $Ce_{1-x}RE_xO_{2-y}$
Oksana Mendiuk[1], Leszek Kepinski[1]
[1]Institute of Low Temperature and Structure Research, PAS, Poland

12:30-12:50
NN_06 A nano-capacitor based on doped graphene layers composed with boron nitride–graphene as an insulator
Majid Monajjemi, Farand Farzi, Nahid Moradiyeh
Islamic Azad Univ., Iran

Session 11: Organometallics and catalysis

11:30-11:50
OC_13 Catalysis of Thiocyanate Formation
Sigridur G. Suman,(1,2) Johanna M. Gretarsdottir,(1) Paul E. Penwell,(3) Snædís Björgvinsdóttir,(1) Jon Petur Gunnarsson,(1) Sindri Frostason,(1) Egill Skulason,(1) and Anna Garden(1,3)
[1]Univ. of Iceland, Iceland,, [2]Chemical Science and Technology Laboratory, USA,
[3]Univ. of Otago, New Zealand

11:50- 12:10
OC_14 Radical organometallic reactions: TEMPO and dialkylzincs
Krzysztof Budny-Godlewski[1], Dominik Kubicki[1], Iwona Justyniak[2], Janusz Lewiński[1,2]
[1]Warsaw Univ. of Technology, Poland, [2]Institute of Physical Chemistry, Poland

12:10-12:30
OC_15 Odd Electron Reactivity at Late Transition Metals Mediated by Redox-Active Ligand-to-Subtrate Single Electron Transfer
Jarl Ivar van der Vlugt[1]
[1]Univ. of Amsterdam, the Netherlands

12:30-12:50
OC_16 Ruthenium(IV) catalysts with phosphinous acid ligands for the selective hydration of nitriles to amides in water under mild conditions
Eder Tomás-Mendivil, Rebeca González-Fernández, Pedro J. González-Liste, Pascale Crochet, Victorio Cadierno

Univer. de Oviedo, Spain

Session 12: Supramolecular and coordination chemistry

11:30-11:50
SC_05 Multicopper(II) Cores and Metal–organic Networks: from Aqueous Medium Self-assembly to Applications
Alexander M. Kirillov
Univer. of Lisbon, Portugal

11:50- 12:10
SC_06 High-Field EPR Spectroscopy of Trinuclear Copper(II) Complexes
Andrzej Ozarowski
Florida State Univ., USA

12:10-12:30
SC_07 Alkynyl-phosphine Au^I and Au^I-Cu^I complexes based on phosphine template: some features of the photophysical properties
Grachova E.V.[1], Shakirova Yu.R.[1], Strelnik I.D.[2]Koshevoy I.O.[3], Tunik S.P.[1]
[1]St. Petersburg State Univ., Russia, [2]Russian Academy of Sciences, Russia, [3]Univ. of Joensuu, Finland

12:30-12:50
SC_08 A series of novel copper(I) hydrotrispyrazolylborate complexes for ethene detection
Tom van Dijkman[1], Maxime Siegler[2] and Elisabeth Bouwman[1]
[1]Leiden Univ., The Netherlands, [2]John Hopkins Univ.,USA

12:50-14:30 Lunch

Plenary & Keynote

14:30 -15:15 Chair:
PL_05 Twinning, Incommensurabilities and General Bad Behaviour- how new methods, sources and detectors allow the study of Nature's dirty little secrets
Sven Lidin
Lund Univ., Sweden

Session 13: Reaction mechanisms and theory

15:25-15:45
MT_01 Direct Oxygenation of Aliphatic C-H Groups with H_2O_2 Mediated by Mn-Aminopyridine Synthetic Enzyme Models
Roman V. Ottenbacher[1], Evgenii P. Talsi [1], Konstantin P. Bryliakov [1]
[1]Novosibirsk State Univ. and Boreskov Institute of Catalysis, Russia

15:45-16:05
MT_02 Splitting of hydrogen by activation at a single non-metallic center
Sławomir J. Grabowski [1,2]
[1]Univ. of the Basque Country and Donostia International Physics Center (DIPC), Spain

16:05- 16:25
MT_03 Computational Study on the Hydrolysis of PCl andSiClbonds.
László Nyulászi, Dénes Szieberth, László Könczöl, Gergő Szabó, János Károly Pánczél, Zsófia Sólyom, Gábor Turczel
Budapest Univ. of Technology and Economics, Hungary

16:25-16:45
MT_04 Probing the role of π interactions in the reactivity of oxygen species
Łukasz Mąkolski[1], Karolina Zelga[1], Rafał Petrus[2], Dominik Kubicki[1,3], Piotr Zarzycki[3], Piotr Sobota[2], Janusz Lewiński[1,3]
[1]Warsaw Univ. of Technology, Poland, [2]Univ. of Wrocław, Poland, [3]Polish Academy of Sciences, Poland

16:45-17:05
MT_05 Fascinating Boron-Nitrogen-Containing Heteroaromatic Compounds.Electronic Structure Analysis.
Chrostowska Anna[1], Darrigan Clovis[1], Dargelos Alain[1], Graciaa Alain[1]
[1,]Univ. de Pau et des Pays de l'Adour, France

Session 14: Organometallics and catalysis

15:25-15:45
OC_17 Ru(II) arene complexes immobilized on mesoporous silicas as catalyst precursors for the oxidative cleavage of alkenes
Hendrik Kotze and Selwyn F. Mapolie
Stellenbosch University, South Africa

15:45-16:05
OC_18 Cyclometallation, Steric and Electronic Tendencies In a Series of Pd(II) Complex Pre-catalysts Bearing Imidazole-phenol Ligands and Effects on Suzuki-Miyaura Catalytic Efficiencies
Abiodun O. Eseola[1,2], Helmar Gorls[2], Joseph A. O. Woods[3], Winfried Plass[2]
[1]Redeemer's University, Nigeria.
[2]Friedrich-Schiller-Universität Jena, Germany.
[3]University of Ibadan, Ibadan – Nigeria.

16:05- 16:25
OC_19 Synthesis of Heteroleptic Tin N,O–β–Heteroarylalketonate Complexes,
Their Properties and Reactivity
Ján Podhorský[1], Corinna Hegemann[2], Lisa Czympiel[2], Zdenek Moravec[1], Jiri Pinkas[1] and Sanjay Mathur[2]
[1]Masaryk University, Czech Republic
[2]University of Cologne, Germany

16:25-16:45
OC_20 Spectroscopic studies of paramagnetic Group 5 organometallic complexes with an emphasis on Vanadium
Joshua Telser[1], Peter L. Damon[2], Trevor W. Hayton[2], Andrew Ozarowski[3], J. Krzystek[3], Eva M. Zolnhofer[4], Karsten Meyer[4], Gayan Wijeratne[5], Timothy A. Jackson[5], Daniel J. Mindiola[6]
[1]Roosevelt Univ., USA, [2]Univ. of California, USA, [3]Florida State Univ., USA
[4]Friedrich-Alexander-Univ., Germany, [5]Univ. of Kansas, USA, [6]Univ. of Pennsylvania, USA

16:45-17:05
OC_21 Functional Schiff Base Complexes on The Peripheral Position of Co(II)Phthalocyanine as Oxidation Catalysts in Bleaching System

Pınar Şen[a], Salih Zeki Yıldız[a]
[a]Sakarya Univ., Turkey

Session 15: Supramolecular and coordination chemistry

15:25-15:45
SC_09 Fe^{II}, Zn^{II} and Cu^{II}bis(pyrazolyl)methane complexes for polymerisation catalysis
Ulrich Herber[1], Alexander Hoffmann[1],Sonja Herres-Pawlis*[1]
[1] RWTH Aachen Univ., Germany

15:45-16:05
SC_10 Coordination Chemistry of Thioether Ligands on CuX Salts: From Molecules to Luminescent Materials and MOFs
Michael Knorr[1], Fabrice Guyon[1], Marek M. Kubicki[2]
[1]Univ. de Franche-Comté –France, [2]Univ.de Bourgogne –France

16:05- 16:25
SC_11 Can a non-porous Cu^{II} coordination polymer be as good catalyst as porous Cu^{II} MOFs?
Edurne S. Larrea[1], Marta Iglesias[2], María I. Arriortua[1,3]
[1]Univ. del País Vasco, [2]Instituto de Ciencia de Materiales-CSIC, Spain, [3]Basque Centre for Materials, Spain

16:25-16:45
SC_12 Copper(I) and Silver(I) Bisphosphine Complexes: from Synthesis to Electroluminescent Properties
Béatrice Delavaux-Nicot[1], Adrien Kaeser[1,2], Omar Moudam[1,2],
Jean-François Nierengarten[2], [1]Paul Sabatier Univ., France, [2]Univ. de Strasbour, France.

16:45-17:05
SC_13 Coordination mode of the 1, 3-bis [5-(2-pyrimidinyl)-1, 2, 4-triazol-3-yl] propane
Eziz Bayjyyev[1], Vladimir V. Pankov[1], Wolfgang Linert[2]
[1]Belarusian State Univ., Republic of Belarus., [2]Vienna Univ. of Technology, Chemistry, Austria

17:05-19:00 Poster Session

19:30- 22:00 Conference Dinner

Wednesday, July 1, 2015

Keynote & Invited Lecture

8:30-9:00
K_10 X-ray photoelectron spectroscopy of binary and ternary fluorides
Miroslav Boča
Slovak Academy of Sciences, Slovakia

9:00-9:30
K_11 Reactivity of Substrate Radicals
Bas de Bruin
Univ. of Amsterdam, The Netherlands

9:30-9:50
IL_01 Metal–assisted activation of small molecules for biomedical control
Maria Oszajca[1], Przemysław Łabuz[1], Alicja Franke[2], Wojciech Macyk[1], Rudi van Eldik[1], Grażyna Stochel[1]
[1]Jagiellonian Univ., Poland [2]University of Erlangen-Nuremberg, Germany

9:50-10:10
IL_02 Iron-Nitrosyl Models for Class III Dioxygenases
Ferman A. Chavez[1], Jia Li[1], Atanu Banerjee[1], Piotr L. Pawlak[1], William W. Brennessel[2]
[1]Oakland Univ., Univ. of Rochester

10:10-10:30
IL_03 Inorganic and bioinorganic mechanistic studies. Rewarding high-lights and cover-pages
Rudi van Eldik[1,2]
[1]Univ. of Erlangen-Nuremberg, Germany, [2]Jagiellonian Univ.

10:30-10:50
IL_04 Nanostructured Hybrid Inorganic Systems for Efficient Photoelectrochemical Solar Systems and Electrocatalytic Reduction of Carbon Dioxide
Paweł J. Kulesza
Univ. of Warsaw

11:00-11:30 Coffee break

Session 16: *Reaction mechanisms and theory*

11:30-11:50
MT_06 Sodium phosphaethynolate as a building block
Benkő Zoltán[1,2], Heift Dominikus[2,3], Grützmacher Hansjörg[2]
[1]Budapest Univ. of Technology and Economics, Hungary, [2]ETH Zürich, Switzerland [3] Institut National des Sciences Appliquées, France
11:50-12:10
MT_07 Electron Transfer Reaction within Polyoxometalate Clusters of Redox Active Supports
QiZheng, De-Liang Long, Lee Cronin
Univ. of Glasgow, UK

12:10-12:30
MT_08 Synergy of Co and Ti sites in electrochemicalwatersplitting
Bartłomiej M. Szyja[1], Rutger A. van Santen[2]
[1]Univ. of Münster, Germany, [2]Eindhoven Univ. of Technology, The Netherlands

12:30-12:50
MT_09 Si···H···Si and H···Si···H interactions: structure and dynamics
Sergei F. Vyboishchikov[1], Georgii I. Nikonov[2], and Yevhen Horbatenko[1]
[1]Univ.de Girona, Spain, [2]Brock Univ., Canada

Session 17: *Organometallics and catalysis/Energy and photochemistry*

11:30-11:50
OC_22 Organometallic Chemistry of Macrocycles and Cages
Guo-Xin Jin
Fudan Univ., China

11:50-12:10
EP_01 Theory in investigations of the thermodynamics and kinetics of the thermal dissociation of simple inorganic solids
Beata Zadykowicz, Piotr Storoniak, Jerzy Błażejowski
Univ. of Gdańsk, Poland

12:10-12:30
EP_02 Energy Transfer and a Role of Lewis Base Ligands and Silver Plasmons in Optical Behaviour of New Type of Lanthanide Phosphors
V.Amirkhanov[1], P.Gawryszewska[2], D.Kulesza[2], J.Legendziewicz[2] ,V.Thrush[1]
[1]Kyiv National Taras Shevchenko Univ., Ukraine , [2]Univ. of Wroclaw, Poland

12:30-12:50
EP_03 Homo- and hetero-aryl Lewis acidic boranes: H2 activation by an electrochemical-frustrated Lewis pair approach
Robin J. Blagg, Gregory G. Wildgoose
Univ.of East Anglia, U.K.

12:50-13:10
EP_04 Novel Copper (III) Tetra-Phenyl-Porphyrin-Fullerene dyads
Magal Saphier[1,2]**,** Tova Yifrah[3], Israel Zilbermann[1,3]**,** Oshra Saphier[2]**,** Dan Meyerstein[3,4]and Dirk M. Guldi[5]
[1]Nuclear Research Centre Negev, Israel, [2]Sami Shamoon College of Engineering, Israel
[3]Ben-Gurion Univ.of the Negev, Israel, [4]Ariel Univ. Center of Samaria, Israel
[5]Friedrich-Alexander-Univ. Erlangen-Nuernberg, Germany

Session 18: *Supramolecular and coordination chemistry*

11:30-11:50
SC_14 Shaping of iron-triazole polymers into spin crossover nanocomposites
Carole Aimé, Thibaud Coradin, Cécile Roux,Hugo Voisin
UPMC Univ. Paris 06, France

11:50-12:10
SC_15 Lantern-Type Rhodium(II) Dinuclear Complexes with Formamidinato and

CarboxylatoBridging Ligands
Makoto Handa[1], Takahisa Ikeue[1], Yusuke Kataoka[1], Daisuke Yoshioka[2], and Masahiro Mikuriya[2]
[1]Shimane Univ., Japan [2]Kwansei Gakuin Univ., Japan

12:10-12:30
SC_16 Silver N-Heterocyclic Carbene Complexes as Anticancer Agents
Heba Abdelgawad[1], Prof. Roger M. Phillips[2],Dr. Charlotte E. Willans[1]
[1]Univ. of Leeds, UK, [2]Univ. of Huddersfield, UK

12:30-12:50
SC_17 Single ion magnet (SIM) behavior in new Schiff-base lanthanide coordinating systems
Adam Gorczyński[1], Dawid Pakulski[1], Marta Fik[1], Damian Marcinkowski[1], Maciej Kubicki[1], Maria Korabik[2], Violetta Patroniak[1]
[1]Adam Mickiewicz Univ., Poland , [2]Univ. of Wroclaw, Poland

13:10-14:30 Lunch

Invited Lecture

14:30-14:50
IL_05 Chiral Complexes of Bis(N-confused Porphyrin)
Piotr J. Chmielewski
Univ. of Wroclaw

Session 19: *Materials*

14:50-15:10
M_10 Half-sandwich Iridium- and Rhodium-based Organometallic Architectures
Ying-Feng Han
Fudan Univ., China

15:10-15:30
M_11 Integrated platforms for the discovery of inorganic nanosized clusters
Victor S. Sangorrin[1], Lee Cronin[2]
[1]Univ. of Nottingham, UK, [2]Univ. of Glasgow, UK

15:30-15:50
M_12 Synthesis, characterization, antimicrobial studies and corrosion inhibition potential of 1,8-dimethyl-1,3,6,8,10,13- hexaazacyclotetradecane
Henry U. Nwankwo, David A. Isabirye, Eno E. Ebenso
North West Univ., South Africa

Session 20: ***Energy and photochemistry/Supramolecular and coordination chemistry***

14:50-15:10

EP_05 The water oxidation mechanism on anatase TiO_2 photoanodes – a transient photo-induced absorption study of this model system
Andreas Kafizas[1], Steph Pendlebury,[1]Yimeng Ma, [1] Camilo Mesa-Zamora,[1] Florian Le Formal,[1]Nuruzzaman Noor,[2] Claire J. Carmalt,[2] Ivan P. Parkin,[2] James R. Durrant[1]
[1]Imperial College London, UK ,[2]Univ.College London, UK

15:10-15:30

SC_22 Bimetallic Phosphorus-Based Complex as Building Block for One- and Two Dimentional Organometallic-Organic Hybrid Material.
Bianca Attenberger[1], Stefan Welsch[1], Mehdi Elsayed Moussa[1], Manfred Scheer[1]
[1]Univ. of Regensburg, Germany

15:30-15:50

SC_23 Stable Silanetriols – Building Blocks for Surfactants, Micelles and Cages
N. Hurkes, S. Spirk, R. Pietschnig
Univ. of Kassel, Germany

15:50-16:10

SC_24 Novel heterocyclic amide- and phosphinoxide-bearing ligands: synthesis, extraction, and photoluminescent properties
[1]Leonid A. Korotkov, [1]Alexey V.Ivanov, [1]Tsagana B. Sumyanova, [1]Anastasiya V. Kharcheva, [2]Alena Paulenova, [1]Marina D. Reshetova,[1]Stepan N. Kalmykov, [1]Nataliya E. Borisova,
[1]Lomonosov Moscow State Univ., Russia [2]Oregon State Univ., USA

Session 21: ***Supramolecular and coordination chemistry***

14:50-15:10

SC_18 New Trimetallic Group Six Cluster Sulfides for Photophysical Applications
Eva M. Guillamón, Emma Domingo, David Recatalá, Rosa Llusar, Francisco Galindo
Univ. of Jaume I, Spain

15:10-15:30

SC_19 Cyanido-bridged Hetero Metal ComplexesBased on Dinuclear Ruthenium Carboxylate
Masahiro Mikuriya[1], Makoto Handa[2]
[1]Kwansei Gakuin Univ., Japan, [2]Shimane Univ., Japan

15:30-15:50

SC_20 A novel bi-functionalized system based on the $[Mo_6O_{19}]^{2-}$polyanion
Patricio Hermosilla-Ibáñez[1,2], Andrés Vega[2,3], Verónica Paredes-Garcia[2,3],Evgenia Spodine[2,4], Diego Venegas-Yazigi[1,2]
[1]Univ. Santiago, Chile, [2]CEDENNA, Chile, [3]Univ. of Andrés Bello, Chile, [4]Univ. Chile, Chile

15:50-16:10

SC_21 Coordination Chemistry of Linear Oligopyrroles Formed upon Degradation of Porphyrin Derivatives

Jacek Wojaczyński

University of Wroclaw

Lectures

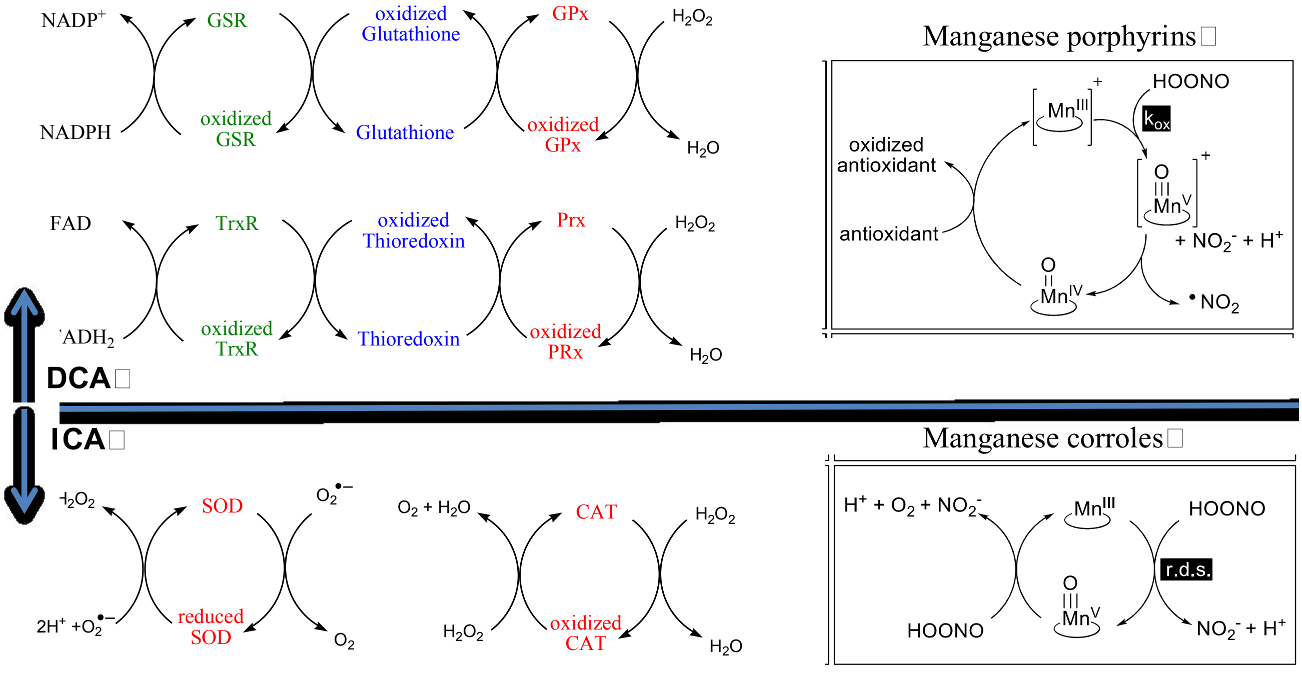
PL_01
Redox Active Metallodrugs: Benefits and Concerns

Zeev Gross

Schulich Faculty of Chemistry, Technion – Israel Institute of Technology,
chr10zg@tx.technion.ac.il

Introduction: Classical *antioxidant therapy* deals with stoichiometric antioxidants whose role is sacrificial, i.e., they are consumed on a one-to-one basis by being oxidized instead of vital biomolecules. On the other hand, *catalytic antioxidants* detoxify reactive oxygen and nitrogen species (ROS and RNS, respectively) without being permanently oxidized, and one molecule may hence disarm numerous toxins. The benefits of catalytic antioxidants in cellular and animal models of many diseases are quite established and have been summarized in many reviews.

Critical Issues: The main aim of this presentation is to provide a perspective on the utility of ROS/RNS decomposition catalysts, with focus on porphyrin and corrole metal complexes, for disease prevention or treatment. Particular emphasis is on the often-ignored fact that redox-based therapy is potentially harmful because it may actually induce rather than decrease oxidative stress. Also emphasized are the significant differences between catalytic antioxidants that act dependent and independent on other cofactors, termed **DCA** and **ICA**, respectively (Scheme 1).



Outlook: Investigations aimed at identifying the factors that increase the antioxidant versus pro-oxidant potency of synthetic metal complexes are ongoing, since they are crucial for the optimal design of redox-based drug candidates for combating the numerous diseases that are affected by oxidative stress. Most recent research on the effects of catalytic antioxidants on ageing will be presented as well.

Literature:

[1] Haber, A.; Gross, Z. *Chem. Commun.* **2015**, *51*, 5812-5827 (*Perspective Article*)

PL_02

Organometallic Nanoparticles

Surface chemistry, magnetic heating and catalysis

Bruno Chaudret

Laboratoire de Physique et Chimie des Nano-Objets

Institut National des Sciences Appliquées, 135 avenue de Rangueil
31077 Toulouse (France) - chaudret@insa-toulouse.fr

Organometallic nanoparticles are prepared by decomposition in mild conditions of organometallic precursors in solution. The decomposition is preferably achieved under dihydrogen which results in the formation of a clean surface, covered with hydrides and able at performing further chemistry or growth processes. Addition of various ligands may modify both the physical and the chemical properties of the particles as well as the growth process allowing the formation of particles of defined sizes and shapes. In this respect, nanospheres, nanorods, nanocubes, nanowires of iron and cobalt or nano-arrows, nanocubes and dendritic particles of platinum can be obtained. Some of these nano-objects organize into super-lattices.

The surface characterization may be achieved by standard techniques of material science (XPS, WAXS, HRTEM) as well as by the use of NMR (solid state, solution and gas phase). In particular, static solid state ^{2}D NMR and MAS ^{13}C NMR are particularly efficient to locate and study the dynamics of surface ligands as well as to study the reactivity of the particles, for example towards H/D exchange in complex organic molecules, hydrogenation and oxidation reactions. In addition, one objective of the group is to couple the physical and chemical properties of the nanoparticles.

The lecture will present first the synthesis of ruthenium nanoparticles stabilized by common ligands (e.g. N-heterocyclic carbenes), and their reactivity, in particular towards C-H activation. In addition, the lecture will discuss the growth of new iron and iron carbide nanoparticles, and their use to achieve reactions typical of heterogeneous catalysis, such as Fischer-Tropsch Syntheses, induced by magnetic heating.

Some recent publications:

* A simple chemical route toward monodisperse iron carbide nanoparticles displaying tunable magnetic and unprecedented hyperthermia properties A Meffre, B Mehdaoui, V Kelsen, P-F Fazzini, J Carrey, S Lachaize, M Respaud, B Chaudret NanoLetters **2012**, *12*, 4722.
* Complex nano-objects displaying both magnetic and catalytic properties: A proof of concept for magnetically induced heterogeneous catalysis A Meffre, B Mehdaoui, V Connord, J Carrey, P-F Fazzini, M Respaud, B Chaudret NanoLetter **2015**, in press
* Heterocyclic Carbene-Stabilized Ruthenium Nanoparticles: a Case Study on Ligands Location and their Influence on Reactivity P Lara, O Rivada-Wheelaghan, S Conejero, R Poteau, K Philippot, B Chaudret Angew Chem Int Ed Engl, **2011**, *50*, 12080.

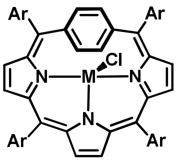
PL_03

Carbaporphyrinoids – A Quest for Macrocyclic Surroundings in Organometallic Chemistry

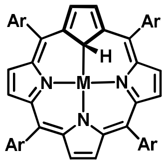
Lechosław Latos-Grażyński

Department of Chemistry, University of Wrocław, 14 F. Joliot-Curie St., Wrocław 50 383, POLAND,
e-mail: lechoslaw.latos-grazynski@chem.uni.wroc.pl

Reconstruction of the porphyrin core involving the introduction of CH unit(s) in place of one of the pyrrolic nitrogen atoms created a new class of macrocycles - carbaporphyrinoids, which reveal fascinating properties in terms of their electronic structure, aromaticity and their potential ability to bind metal ions. Carbaporphyrinoids realize the specific concept of macrocyclic ligand construction by fusing the structural frame of porphyrin and carbon donor(s) introduced by appropriately chosen moieties (carbo- or heterocycles, dienes or alkynes). The entrapment of metal ions in a coordination core of carbaporphyrinoids creates a very efficient protection of the metal-carbon bond. These macrocycles enforce the specific intramolecular reactivity, rearrangements and peculiar coordination architecture as illustrated by representative examples **1** - **6**.[1-4]



1



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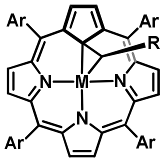

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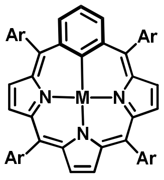

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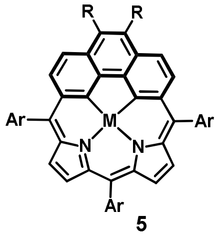

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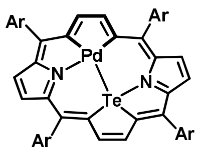


6

A replacement of a single pyrrole of *meso*-tetraarylporphyrin by cyclopentadiene moiety seen in **2** and **3** seems to be a notion of the very first choice for the creation of "true" 21-carbaporphyrins which ideally conserve the fundamental frame of porphyrin, seen also in 21-heteroporphyrins and in the first metallaporphyrin (21-pallada-23-tellura-porphyrin) **6**.[2] It remains a challenge to create 5,10,15,20-tetraaryl-21-carbaporphyrins that are potentially amenable to diverse structural modifications. Noticeably the contraction of *m*-phenylene or *p*-phenylene – embedded in *m*- or *p*-benziporphyrin **1** and **4** – to cyclopentadiene, mediated by transition metal cations, produced complexes of 21-carbaporphyrins **2** or **3**.[1;3] The coordination surrounding of rhodium(III) in **3** facilitates the stabilization of peculiar structural motif which is related to rhodacyclopropane. The unique reversible methyl-methylene-hydride transformation encountered at the Rh(III) 21-carbaporphyrin cavity of **3** can be considered as the stimulating example of selective and reversible C-H bond activation.

In due course one can expect that 21-carbaporphyrins can prompt developments in carbaporphyrinoid and organometallic chemistry building on specific reactivity of cyclopentadienyl moiety.

Literature

[1] B. Szyszko, L. Latos-Grażyński, L. Szterenberg, *Angew .Chem. Int. Ed.* **2011**, *50,* 6587.
[2] E. Pacholska-Dudziak, M. Szczepaniak, A. Książek, L. Latos-Grażyński, *Angew. Chem. Int. Ed.* **2013**, *52,* 8898.
[3] B. Szyszko, K. Kupietz, L. Szterenberg, L. Latos-Grażyński, *Chem. Eur. J.* **2014**, *20,* 1376.
[4] B. Szyszko, L. Szterenberg, A. Białońska, L. Latos-Grażyński, *Angew. Chem. Int. Ed.* **2015,** *54, DOI:* 10.1002/anie.201500732 .

PL_04

Transmission electron microscopy as an important technique for structural characterization of inorganic materials

Wei Wan, Sven Hovmöller and Xiaodong Zou

Berzelii Center EXSELENT on Porous Materials and Inorganic and Structural Chemistry, Department of Materials and Environmental Chemistry, Stockholm University, 106 91 Stockholm, Sweden

Transmission electron microscopy is an important technique for structur a characterization of inorganic materials[1]. Crystals millions times smaller than what is needed for X-ray diffraction can be studied, and the crystallographic structure factor phases, which ar lost in diffraction, can be obtained from high resolution transmission electron microscopy images. Recently two methods, automated 3D electron diffraction (ED) data collection [2,3 and through-focus structure projection reconstruction [4] were developed. The data collectio is automatic and controlled by software. More than 1000 ED frames can be collected from an arbitrarily oriented crystal in less than an hour (Fig. 1) [3]. The unit cell, possible space group and ED intensities can be obtained. The 3D ED methods have shown to be very powerful and efficient for phase identification and structure determination including multiphasic samples an disordered crystals. Now a unknown structure can be solved in less than 8 hours, from the data collection to structure solution. Here I will present the new TEM techniques and the i applications for solving the structures from a wide range of inorganic crystals, including zeolites, metal-organic frameworks, metal oxides and intermetallic compounds. [5,6]

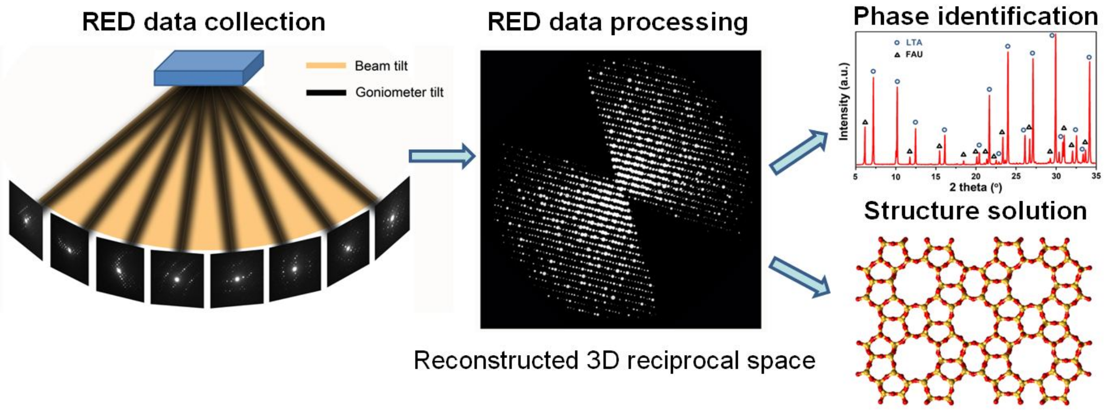


Fig. 1. Illustration of a complete structure solution from Rotation Electron Diffraction (RED) data.

Literature:

[1] Zou, X.D.; Hovmöller S.; Oleynikov, P., *Electron Crystallography*, IUCr texts on crystallography, Oxfor University Press, **2011**.

[2] Kolb, U.; Gorelik, T.; Kübel, C.; Otten, M. T.; Hubert, D. Towards automated diffraction tomography: Part I—Data acquisition. *Ultramicroscopy* **2007**, 107, 507–513.

[3] Wan, W.; Sun, J.L.; Su, J.; Hovmoller, S.; Zou, X. D., Three-dimensional rotation electron diffraction: software RED for automated data collection and data processing. *J. Appl. Cryst.* **2013**, 46, 1863–1873.

[4] Wan, W.; Hovmoller, S.; Zou, X.D., Structure projection reconstruction from through -focus series of high-resolution transmission electron microscopy images. *Ultramicroscopy* **2012**, 115**,** 50–60.

[5] Willhammar, T.; Yun, Y.F. and Zou, X.D., Structure determination of porous materials by electron crystallography. *Adv. Funct. Mater.* **2014**, 24, 182–199.

[6] Yun, Y.F.; Wan, W.; Hovmöller, S.; Zou, X.D. Three-dimensional electron diffraction as a complementary technique to powder X-ray diffraction for phase identification and structure solution o powders, *IUCrJ* **2015**, 2, 267–282.

PL_05

Twinning, Incommensurabilities and General Bad Behaviour- how new methods, sources and detectors allow the study of Nature's dirty little secrets

Sven Lidin

Lund University

The fiction of the perfect crystal has been a successtory that has taught us so much about what we know about the solid state. And yet it is precisely that, a fiction. Real crystals are finite, full of defects often not single even in terms of the number of phases contained. Thanks to modern crystallography we now have the means of studying not only perfection but also the imperfections and this gives us valuable insight into local behaviour of more or less ordered systems.

Twinning was one of the first "bad behaviour" problems encountered in crystallography and it remains one of the most serious, but today we can also successfully study multiphasic "single" crystals and even ordered aperiodic materials. In this lecture I will give a very brief outline of the history and importance of crystallography, the challenges it has faced and the issues it has settled. I will discuss twinning, polyphasic crystals and incommensurability in one, two or more dimensions and how we can treat such systems today. I will also touch upon the remaining technological challenges that faces crystallography as it enters into its second century as the prime method of structural elucidation in areas from materials science to structural biology.

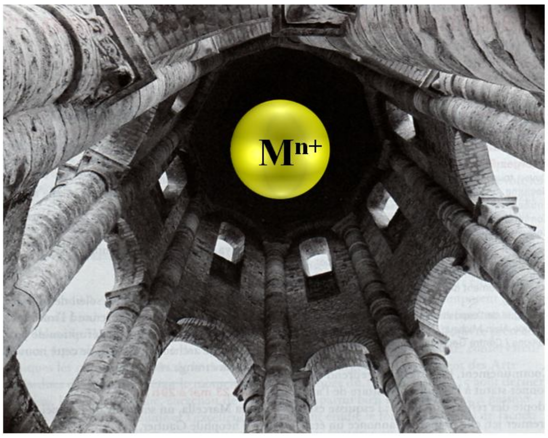
K_01

Metal ions in biomimetic cavities

Reinaud Olivia

Laboratoire de Chimie et Biochimie Toxicologiques et Pharmacologiques, CNRS UMR 8601,
Université Paris Descartes, Sorbonne Paris Cité, 45 rue des Saints Pères, 75006 Paris.
Olivia.Reinaud@parisdescartes.fr

The aim of our work is to design supramolecular systems that will mimic both the coordination core and the hydrophobic pocket of a metallo-enzyme active site. Our strategy relies on the synthesis of cavity-based ligands that allow the control of the coordination spheres of the metal ion (1rst, 2nd and 3rd), together with the approach and the binding of an exogenou molecule. Since many years, we have been developing systems based on the calix[6]arene scaffold, giving rise to the so-called "funnel complexes".[1] Various aspects such as dioxygen activation at a mononuclear Cu(I) center, [2] supramolecular control of hetero-multinuclear binding of metal ions,[3] guest covalent capture by a host, [4] and water-soluble receptors have been developed.[5]



Quite recently, we started to explore metal complexes based on the resorcin[4]arene scaffold, which provides a supramolecular environment different in shape, rigidity and binding properties, so-called "Bowl-complexes".[6]

Hence, various aspects of these cavity-complexes will be presented and the Bowl vs. Funnel supramolecular concepts for biomimetic metal complexes will be discussed.

Literature:

[1] a) D. Coquière, S. Le Gac, U. Darbost, O. Sénèque, I. Jabin, O. Reinaud, *Org. Biomol. Chem.*, **2009**, *7*, 2485-2500; b) J.-N. Rebilly, O. Reinaud, *Supramol. Chem.* **2014**, 454-479; c) J.-N. Rebilly, B. Colasson, O. Bistri, D. Over, O. Reinaud, *Chem. Soc. Rev.* **2015**, *44*, 467-489; d) O. Bistri and O. Reinaud, *Org. Biomol. Chem.*, **2015**, *13*, 2849–2865.

[2] G. Thiabaud, G. Guillemot, I. Schmitz-Afonso, B. Colasson, O. Reinaud, *Angew. Chem. Int. Ed.* **2009**, *48*, 7383-7386.

[3] a) B. Colasson, N. Le Poul, Y. Le Mest, O. Reinaud, *J. Am. Chem. Soc.* **2010**, *132*, 4393–4398; b) N. Bernier, N. Menard, B. Colasson, J.-N. Rebilly, O. Reinaud, *Inorg. Chem.* **2013**, *52*, 4683–4691.

[4] a) B. Colasson, O. Reinaud, *J. Am. Chem. Soc.* **2008**, *130*, 15226-15227; b) N. Menard, O. Reinaud, B. Colasson, *Chem., Eur. J.,* **2013**, *19*, 642–653.

[5] a) O. Bistri, B. Colasson, O. Reinaud, *Chem. Sci.*, **2012**, *3*, 811–818; b) A. Brugnara, F. Topić, K. Rissanen, A. de la Lande, B. Colasson, O. Reinaud, *Chem. Sci.* **2014**, 3897 – 3904.

[6] a) J. Gout, S. Rat, O. Bistri, O. Reinaud, *Eur. J. I. C.*, **2014**, 2819-2828; b) J. Gout, A. Višnjevac, S. Rat, A. Parrot, A. Hessani, O. Bistri, N. Le Poul, Y. Le Mest, O. Reinaud, *Inorg Chem* **2014,** *53*, 6224–6234.

K_02

Fenton Like Reactions Proceed Via a Variety of Mechanisms.

Ariela Burg[1], Haya Kornweitz[2], Dan Meyerstein[2,3]

1. Chemical Engineering Dept., SCE – Shamoon College of Engineering, Beer-Sheva.
2. Biological Chemistry Dept., Ariel University, Ariel.
3. Chemistry Dept., Ben-Gurion University of the Negev, Beer-Sheva.

The Fenton like reactions are of key importance in advanced oxidation processes, AOPs, and in biology. Their mechanism was in debate for many years: the question being whether the active intermediates formed are hydroxyl radicals or $L_{m-1}M^{n+2}=O$ complexes. It is now accepted that usually the mechanism involves two steps:

(1) $M^nL_m + H_2O_2 \overset{-L,\ -H^+}{<===>} L_{m-1}M^n(O_2H)/L_{m-1}M^n(H_2O_2)$

$\overset{L}{--->} M^{n+1}L_m + \cdot OH + OH^-$

(2) $L_{m-1}M^n(H_2O_2) ---> L_{m-1}M^{n+2}=O + H_2O$

$\overset{RH}{--->} M^{n+1}L_m + R\cdot + H_2O + OH^-$

It was also shown that at least for M = Fe, in the presence of excess H_2O_2, the following reaction is of major importance:

(3) $(H_2O)_5Fe(OOH)^{2+} + Fe(H_2O)_6^{2+} \overset{2H^+}{--->} ((H_2O)_5Fe^{IV}=O + Fe(H_2O)_6^{3+})/(2Fe(H_2O)_6^{3+} + \cdot OH)$

Recent results point out that the reactions:

(4) $(H_2O)_{6-l-1}M^n(OOH)_l(H_2O_2) ---> (H_2O)_{6-l-1}M^n(\cdot OOH)(OOH)_{l-1}(OH) + \cdot OH$

(5) $(H_2O)_{6-l-1}M^n(OOH)_l(H_2O_2) ---> (H_2O)_{6-l-1}M^{n+1}(\cdot OOH)(OOH)_{l-1}(OH) + OH^-$

are the source of the ROS when reaction (2) is endothermic. Furthermore in the presence of HCO_3^-/CO_3^{2-}, which is present in AOPs and in biology, the reactions:

(6) $LM^n(CO_3)(H_2O)_n + H_2O_2 <==> LM^n(CO_3)(H_2O)_{n-1}(OOH)$

(7) $LM^n(CO_3)(H_2O)_{n-1}(OOH) ---> LM^n(CO_4)(H_2O)_{n-1}$

(8) $LM^n(CO_4)(H_2O)_{n-1} ---> LM^{n+1}(OH)(H_2O)_n + CO_3^{\cdot -}$

(9) $LM^n(CO_4)(H_2O)_{n-1} + H_2O_2 <==> LM^n(CO_4)(H_2O)_{n-2}(OOH) + H^+$

(10) $LM^n(CO_4)(H_2O)_{n-2}(OOH) ---> LM^n(OH^-)_2(^{\cdot}OOH)(H_2O)_{n-2} + CO_3^{\cdot -}$

have to be considered. This means that in these systems carbonate anion radicals are the major reactive species.

K_03

Transition Metal Superatoms - the Frontier Between Inorganic Chemistry and Catalysis

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Mechanistic studies have shown that a variety of metal species are generated during well-known catalytic reactions.[1-4] Mononuclear species, metal clusters and nanoparticles are easily accessible on catalyst activation stage or during the course of the catalytic reaction. Formation of "cocktail" of metal species in solution is not uncommon starting with wide variety of different metal precursors (pre-catalysts).[3] Recent studies provided important evidence on unusual reactivity of small metal clusters, especially the properties connected with "superatomic" structural units.[2]

Using metal clusters as "superatomc" building blocks provides fascinating opportunity to reveal novel chemical transformations and to create new generation of highly efficient catalysts. Application of metal clusters and polynuclear complexes for catalysis of organic reactions and possible involvement of "superatomic" cores in catalysis will be presented and discussed.

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K_04

New ruthenium complexes with chelating ligands for olefin metathesis and beyond

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Ruthenium-catalyzed olefin metathesis reactions represent an attractive and powerful transformation for the formation of new carbon-carbon double bonds [1]. This area is now quite familiar to most chemists as numerous catalysts are available that enable a plethora of olefin metathesis reactions [1]. However, formation of substituted and crowded double bonds, decreasing the amount of metal, using metathesis in medicinal chemistry, in aqueous media, etc. still remain a challenge, making industrial applications of this methodology difficult [2].

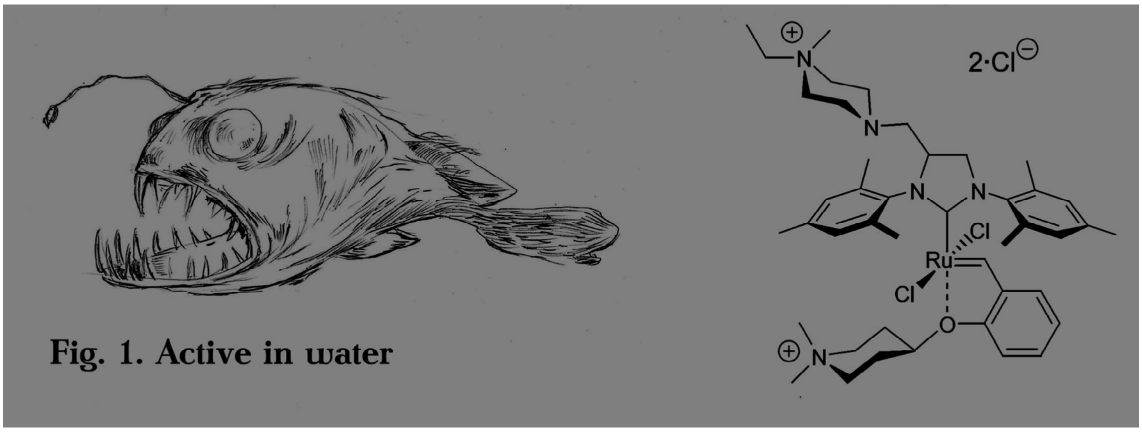

Fig. 1. Active in water

These limitations can be solved by designing new, more active and stable catalysts and catalysts that can be easier removed/recycled [3].

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K_05

eNHChanting new chemistry with Cu and Zn

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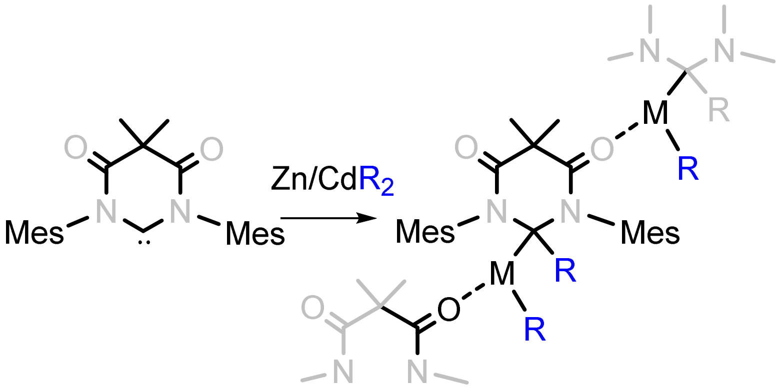
N-heterocyclic carbene (NHC) ligands have changed the face of organometallic chemistry in the last 10-20 years. Although five-membered Arduengo-type ligands continue to be the NHCs of choice for most applications, there have been many efforts to prepare derivatives with different stereoelectronic properties. NHCs based on six- and seven-membered ring structures (so-called ring-expanded carbenes) offer a wider variation of both σ-donor/π-acceptor properties and steric bulk, thereby allowing even more 'tuneability' of the coordination sphere of a metal centre. This talk will discuss how recent results on Ni [1] has led onto studies with Cu [2] and subsequently Zn (Figure below) [3] that have illustrated some very unexpected properties of metal-coordinated large ring carbenes.



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K_06

Oxidative transformation of poly- and perfluorinated aromatics catalyzed by phthalocyanine and porphyrin μ-nitrido diiron complexes

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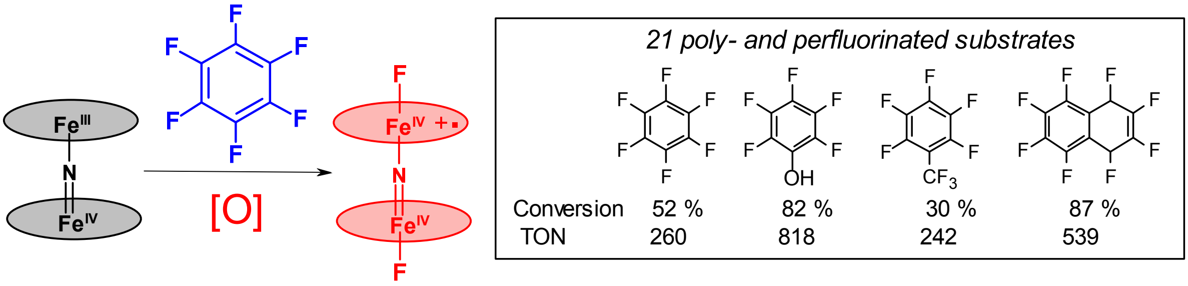
Carbon – fluorine bonds are the strongest single bonds in organic chemistry which activation and cleavage usually associated with organometallic and reductive approaches are particularly difficult. Unprecedented cleavage of C-F bonds of poly- and perfluorinated aromatics under oxidative conditions was evidenced in the presence of μ-nitrido diiron phthalocyanine complex (PcFe^{III}(μ-N)Fe^{IV}Pc) [1]. The reaction proceeds via the formation of a high-valent diiron phthalocyanine cation-radical complex with fluoride axial ligands, [(Pc)(F)Fe^{IV}(μ-N)Fe^{IV}(F)(Pc$^{+\cdot}$)], which was isolated and characterized by UV-vis, EPR, ^{19}F NMR, ESI-MS, Fe K edge EXAFS, XANES and Kβ X-ray emission spectroscopy.



A wide range of fluorinated aromatics including C_6F_6, $C_6F_5CF_3$, C_6F_5CN, $C_6F_5NO_2$ were efficiently converted in mild conditions using H_2O_2 as the oxidant. The PcFe^{III}(μ-N)Fe^{IV}Pc immobilized onto carbon support showed increased catalytic activity in heterogeneous defluorination in water providing up to 4825 C-F cleavages per catalyst molecule.

A current challenge in bio-inspired catalysis is the development of efficient catalysts readily accessible on a large scale. In this context, (Pc)Fe^{III}(μ-N)Fe^{IV}(Pc) complexes seem to be promising candidates combining availability and high reactivity in many reactions [2]. *N*-Bridged diiron macrocyclic complexes show a new unexpected reactivity and provide a novel promising approach to challenging catalytic transformations under mild and clean conditions [3]. Mechanistic issues of this unusual reactivity are discussed and tentative mechanism of defluorination under oxidative conditions is proposed.

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K_07

Homogeneous catalysed H_2 generation using C1 entities and H_2O as H_2 source

Leo E. Heim[1], Nils E. Schlörer, Jong-Hoo Choi, Martin H. G. Prechtl[1*]

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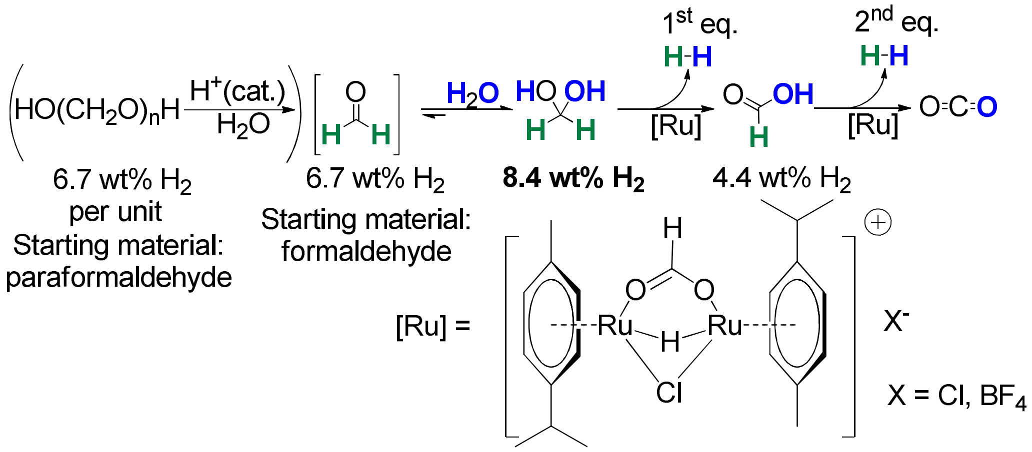
For findings towards new energy storage systems, an intensively studied fuel molecule is H_2 owing its high energy content, and the possibility to store it in form of hydridic and protic hydrogen.[1,2] Recently, we showed that water in presence of C1-entities like (para)formaldehyde (FA) is suitable for molecular hydrogen-storage as these molecules can be easily and selectively dehydrogenated forming pure H_2 and CO_2.[3] The reaction runs on air using a novel water-stable molecular catalyst under base-free conditions. Both molecules, H_2O and H_2CO, act equally as source of H_2. Isotope-labelling experiments (^2H, ^{13}C and ^{18}O) confirm that the H_2 released originates from both, H_2O ($H_2{}^{18}O$ or D_2O) and H_2CO (^2H and ^{13}C-labelled). Isotope-labelled complexes and gaseous products could be assigned by means of NMR, ESI-MS and continuous gas-phase MS. A theoretical efficiency of 8.4 wt% of H_2 considering 1 eq. H_2O and H_2CO is possible. This is higher than for formic acid (4.4 wt%), even when technical aq. H_2CO is used, the solution has a min. efficiency of 5.0 wt%. This catalytic decomposition of H_2CO can be envisioned as novel approach for simultaneous H_2 production and decontamination treatment of wastewater with formaldehyde impurities a waste to value approach. Currently, we perform experimental and theoretical mechanistic studies, and develop further catalysts towards room-temperature H_2 generation from water and C1-units in general.[4]



Scheme: Exemplary hydrogen generation from formaldehyde and water.

Acknowledgement: MIWF-NRW is acknowledged for the Scientist Returnee Award 2009 and we are grateful for the Ernst-Haage Foundation Prize 2014 of the Max-Planck-Institute for Chemical Energy Conversion.

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K_08

CHEMISTRY BASED ON NON-PRECIOUS METAL PNP AND PCP PINCER COMPLEXES

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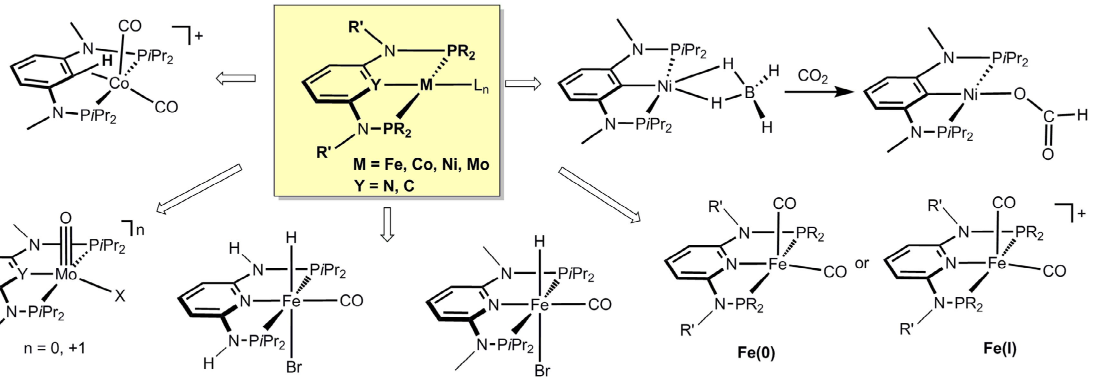
One of the ways of modifying and controlling the properties of transition metal complexes is the use of so-called “pincer” ligands. This class of tridentate ligands has found numerous applications in various areas of chemistry, including catalysis, due to their combination of stability, activity and variability. We are currently focusing on the synthesis and reactivity of non-precious metal complexes containing PNP and PCP pincer ligands based on the 2,6-diaminopyridine and 1,3-diaminobenzene scaffolds where the aromatic ring and the phosphine moieties are connected via NH, N-alkyl, or N-aryl linkers. The advantage of these ligands is that both substituents of the phosphine and amine sites can be systematically varied in a modular fashion which has a decisive effect on the outcome of reactions.



hydrogenation of aldehydes, ketones, CO_2

chemoselective hydrogenation of aldehydes (TON > 10^4)

This has resulted in the preparation of a range of new pincer complexes which exhibit unusual properties [1-5]. The use of such complexes as catalysts in different reactions has also been investigated. This lecture presents an overview of recent research in the field of aminophosphine-based pincer complexes with emphasis on the non-precious metals iron, molybdenum, cobalt, and nickel.

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K_09

Organolanthanides for catalytic olefin hydrophosphination

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Institute of organometallic chemistry of Russian Academy of Sciences

Lanthanide complexes proved to be efficient catalysts for a wide range of transformations of unsaturated substrates (polymerization, hydroamination, hydrosilylation, hydroboration etc).

The synthesis and characterization of heteroleptic alkyl, hydrido, amido rare-earth (+2 and +3) and alkaline-earth complexes supported by various N,N-, N,N,N,N-, N,N,O-, N_2,O_4-, N,N,P(O)-ligands as well as their catalytic activity in intermolecular olefin hydrophosphination and hydroamination will be reported. The new complexes afford highly active, chemoselective and, in the case of monoadditions, 100% *anti*-Markovnikov regiospecific catalysts (down to 0.04 mol-% loading) for the hydrophosphination of styrene with $PhPH_2$ under mild conditions. The highest TOF 330 h^{-1} at 60 °C was observed for Yb(II) amido complex. These complexes also turned out to be efficient precatalysts for the intermolecular hydroamination of styrene and pyrrolidine.

K_10

X-ray photoelectron spectroscopy of binary and ternary fluorides

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Abstract Molten salt method that is frequently used method for preparation of different materials or pure compound at high temperatures, suffers with one unfavorable but principal complication. When particular phases are mixed and melted some reaction usually takes place and consequent cooling provides product of these chemical or physical processes. The reaction product, however, usually contains impurities that arise either from i) starting components or ii) competitive reactions. Both major and minor phases are either known and fully structurally characterized, or their stoichiometry is believed to be known based on only XRD. The following complications may arise: i) phase characterized by only XRD may happen to be shown as incorrect ii) the unknown phase is present and its composition could be estimated based on isostructural properties, iii) the amount of the phase is below detection limit of XRD and remains unrevealed.

X-ray photoelectron spectroscopy could reveal the presence of low concentration phases, as unreacted reactants or product of competitive reactions because the detection limit of this spectroscopy is much lower. Moreover, some important information about the structural properties can be retrieved from surface of studied samples.

X-ray photoelectron spectroscopy was applied for identification of differently bonded fluorine atoms in series of compounds NaF, K_2TaF_7, K_3TaF_8, K_2ZrF_6, $Na_7Zr_6F_{31}$ and K_3ZrF_7. Three different types of fluorine atoms were described qualitatively and quantitatively. Uncoordinated fluorine atoms (F^-) provide signals at lowest binding energies, followed by signals from terminally coordinated fluorine atoms (M—F) and then bridging fluorine atoms (M—F—M) at highest energy. Based on XPS signals assigned to fluorine atoms in compounds with correctly determined structure it was suggested that fluorine atoms in K_3ZrF_7 have partially bridging character.

In the second example, the series of the phases $KTaF_6$, K_2TaF_7, K_3TaF_8 vs $KNbF_6$, K_2NbF_7 and K_3NbF_8, correlation of XPS data was performed.

Keywords X-ray photoelectron spectroscopy, binary and ternary fluorides, molten salts

K_11

Reactivity of Substrate Radicals

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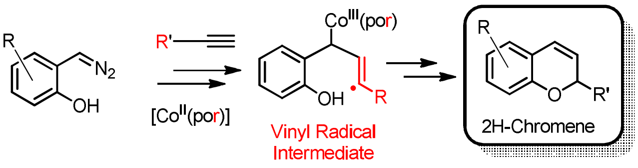
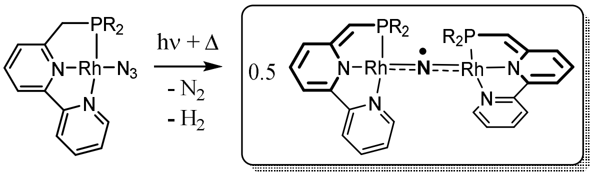
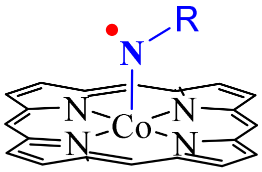
Organometallic compounds of Co, Rh, Ir metals are abundantly used as catalysts for a variety of important transformations in industry and academic research laboratories. Our current understanding of the organometallic reactivity of these metals is however mainly based on studies of diamagnetic complexes, while much less is known about the structure, reactivity and properties of their paramagnetic analogs.
This presentation focusses on the open-shell 'metallo-radical reactivity' of these metals, in which the involvement of 'substrate radicals' was shown to be important.







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IL_01

Metal–assisted activation of small molecules for biomedical control.

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Understanding the mechanism of activation of small moleculesin natural and biomimetic systems at the molecular level has stood at the center of interest for many years, both from fundamental and applied perspectives. Reactive oxygen, nitrogen, sulphur and chlorine species mediate many processes in biology, environment and medicine. Complex regulatory networks secure their homeostasis in natural processes and make a challenge in systems design by man.

Depending on the expected activities various modes of small molecules activation are possible. In many of them metal ions and compounds play a crucial role. They can serve as adsorption, coordination, electron or energy transfer centers in homogenous or heterogenous systems for both thermal and photochemical activation processes [1-3].

Selected examples of metal assisted activation of O_2 and H_2O_2 molecules will be presented and discussed both from mechanistic and biomedical control perspectives [4-6].

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Acknowledgements:
The support from the National Science Centre (grant no. DEC-2012/05/B/ST5/00389) is gratefully acknowledged.

IL_02

Iron-Nitrosyl Models for Class III Dioxygenases

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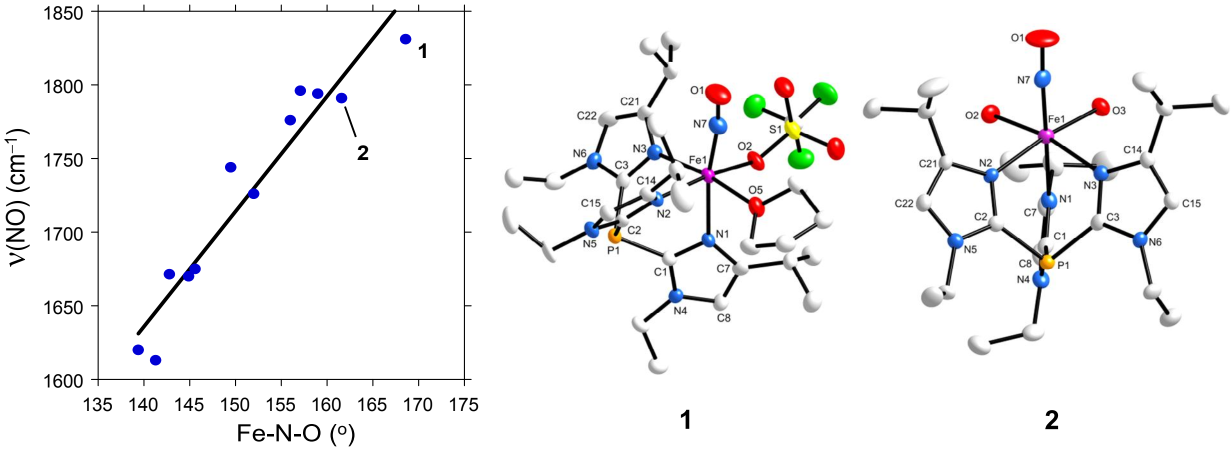
Class III dioxygenases, contains His$_3$ iron (II) binding sites in contrast to Class I and II sites possessing 2His-1-Carboxylate metal binding sites. The lack of a carboxylate group renders the iron site more Lewis acidic altering the mechanism for dioxygenase reactivity. Enzymes containing His$_3$ metal binding sites include gentisate 1,2-dioxygenases (GDO), salicylate 1,2-dioxygenase (SDO), 3-hydroxyanthranilate 3,4-dioxygenases (HAD), 1-hydroxy-2-naphthoate dioxygenase (HNDO), and cysteine dioxygenase (CDO) [1]. These enzymes belong to the cupin superfamily characterized by two highly conservative sequence motifs of $G(X)_5HXH(X)_{3,4}E(X)_6G$ and $G(X)_5PXG(X)_2H(X)_3N$ [2]. Nitric oxide has been used to study ferrous active sites since they are spectroscopically silent and do not exhibit low energy absorption bands. Although many nonheme enzymes form stable Fe-NO complexes, a number of them are known to react reversibly with formation of paramagnetic nitrosyl-iron centers which according to the Enemark and Feltham notation are of the $\{FeNO\}^7$ type [3]. In our efforts to synthesize models that reproduce the reversibility of iron-nitrosyl formation, we have synthesized $[Fe(T1Et4iPrIP)(OTf)_2]$ (T1Et4iPrIP = tris(1-ethyl-4-isopropyl-imidazolyl) phosphine) which reversibly binds nitric oxide to afford [Fe(T1Et4iPrIP)(NO)(THF)-(OTf)](OTf) (**1**), the first example of a 6-coordinate $\{FeNO\}^7$ $S = 3/2$ complex containing a linear Fe–N–O group and exhibiting the highest ν(NO) for compounds in this class (1831 cm^{-1}). DFT studies reveal an enhanced degree of β electron transfer from the π*(NO) to the iron d orbitals accounting for the large stretching frequency. Reaction of **1** with 2 equiv water affords $[Fe(T1Et4iPrIP)(NO)(H_2O)](OTf)_2$ (**2**) which is more electron rich and has a lower ν(NO) (1791 cm^{-1}).



1 **2**

Fig. 1 Plot of Fe-nitrosyl Fe-N-O bond angle vs ν(NO) [1].

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IL_03

Inorganic and bioinorganic mechanistic studies. Rewarding high-lights and cover-pages

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In this contribution I would like to demonstrate how mechanistic studies in inorganic and bioinorganic chemistry can be very challenging and also rewarding. Clarification of reaction mechanisms based on the application of all available experimental and computational methods, enabled us to reveal the intimate details of the underlying mechanisms. This can be a real high-light in a researcher’s career, even more when the accepted publication is accompanied by an invitation for a cover-page design. Then the artistic talents of the researcher and his team are challenged to present the mechanistic information in a pictorial form. Can we be artists? Can we ‘sing our song’ through a cover-page picture?

Several examples selected from our own work will be presented to show how the mechanistic question was resolved and how it was presented in the form of a cover page. I have been involved in mechanistic studies for approx. 45 years and it has been a lot of fun all the way, filled with many high-lights and 25 cover pages [1-7].

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IL_04

Nanostructured Hybrid Inorganic Systems for Efficient Photoelectrochemical Solar Systems and Electrocatalytic Reduction of Carbon Dioxide

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Significant progress has recently been made in the development of n-type metal oxide semiconductors able to act as sunlight-driven photoanodes for oxygen generation (photoelectrochemical water splitting to oxygen and hydrogen). Among important issue for the semiconducting oxides characterized by indirect optical transition are the long absorption depths in visible part of the solar spectrum. We demonstrate here utility of gold nanoparticles (modified or stabilized with Keggin-type polyoxometallates, $PMo_{12}O_{40}^{3-}$, as capping agents) to enhance photocurrents generated by mesoporous tungsten trioxide, WO_3, photoanodes irradiated with visible light in aqueous solutions. To demonstrate generation of localized surface plasmons, we have performed measurements using scanning near-field optical microscope (SNOM). The mechanism for the interaction between the gold plasmons and the semiconductor is complex but sound.

We will also show that nano-electrocatalytic systems are of importance to the development of the effectively operating iodine-based charge relays in dye sensitized solar cells and in molecular electronic (charge storage) devices. The ability of platinum to induce splitting of I-I bond in the iodine (triiodide) molecule is explored here to enhance electron transfers in iodine/iodide redox couple. Following incorporation of Pt nanoparticles, charge transport has been accelerated within the triiodide/iodide-containing 1,3-dialkylimidazolium room-temperature ionic liquid. When both Pt nanoparticles and multi-walled carbon nanotubes have been introduced to ionic liquid system, a solid-type (non-fluid) electrolyte has been obtained. The dye-sensitized solar cell with this electrolyte has yielded reasonably high power conversion efficiencies (up to 7.9% under standard reporting conditions).

By utilizing combination of metal oxide semiconductors, we have also been able to drive effectively photoelectrochemical reduction of carbon dioxide. The combination of titanium (IV) oxide (TiO_2) and copper (I) oxide (Cu_2O) has been explored toward the reduction of carbon (IV) oxide (CO_2) before and after sunlight illumination. Application of the hybrid system composed of both above-mentioned oxides resulted in high current densities originating from photoelectrochemical reduction of carbon dioxide mostly to methanol (CH_3OH) as demonstrated upon identification of final products. The role of TiO_2 is not only stabilizing: the oxide is also expected to prevent the recombination of charge carriers.

Our research interests also concern development of electrocatalytic systems for reduction of carbon dioxide. For example, instead of conventional Pd nanoparticles, nano-sized Pd immobilized within tridentate Schiff-base ligands of the supramolecular complex, $[Pd(C_{14}H_{12}N_2O_3)Cl_2]_2 \cdot MeOH$, have been considered. Reduction of carbon dioxide begins now at less negative potentials and is accompanied by significant enhancement of the CO_2-reduction current densities. Among important issues are specific interactions between nitrogen coordinating centers and metallic palladium sites at the electrocatalytic interface.

IL_05
Chiral Complexes of Bis(N-confused Porphyrin)

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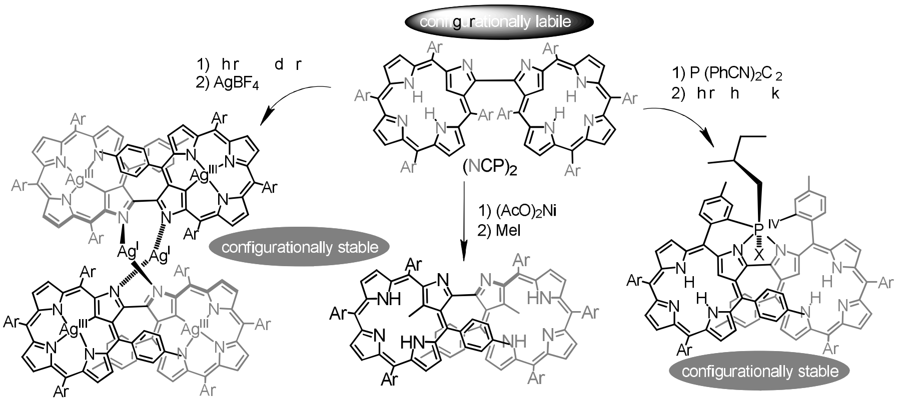
Owing to their optical and redox properties which can be relatively easily modified, the systems comprising porphyrinoids can be applied in the light harvesting, catalysis, biomimetics, phototherapy, and many other areas of theory and practice. Chirality can be introduced into these aromatic macrocycles by substituents attached on various parts of the macrocycle or can be an intrinsic property of the porphyrin ring. For the porphyrins of C_s point symmetry, dimerization converts prochiral monomers into axially chiral bis(porphyrin)s, though in most cases rotation around the bridging bond causes configurational instability preventing separation of the enantiomers [1].



$(NCP)_2$ that consists of two directly linked subunits of N-confused porphyrin, is unique among the bis(porphyrinoid)s owing to coordination sites localized inside the macrocyclic cores and on the perimeter of each subunit. Consequently, $(NCP)_2$ can bind up to three metal ions and, in the protonated form, up to four anions. Rotational freedom of the subunits allows point-to-axial chiral information transfer and subsequent enantiomerization upon chiral anion binding. The resulting ee can be fixed by metalation or transmetalation [2]. Coordination of platinum(II) to both external nitrogens accompanied by double orthometalation of adjacent *meso*-aryls causes restriction in the $(NCP)_2$ dynamics, though thermally stimulated racemization or chiral induction upon oxidative addition of enantiopure alkyl can be observed for this apparently rigid helical system [3]. Again, metalation of the interior of both subunits prevents racemization, thus making the system configurationally stable. Dynamics of $(NCP)_2$ framework, ability of the dimer to interact with variety of cationic and anionic agent, as well as its optical and redox properties can be employed in molecular sensing and enantioselective catalysis.

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ORAL PRESENTATION

BM_01

Biomimetic Redox Reactions of the Cu^{II} Thiolate Complex

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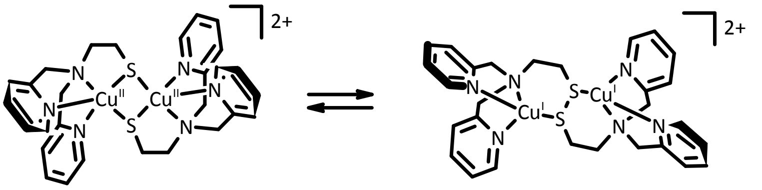
The ability of copper to cycle between Cu^{II} and Cu^{I} oxidation states is essential for its role in many biological processes. It has been reported that minor changes in a ligand structure result in a drastic change in the type of copper compound formed [1];either a Cu^{II} μ-thiolate compound bearing similarity to the biological Cu$_A$ site, or a Cu^{I}disulfide complex is formed. We have investigated this redox equilibrium to find out when the biologically-relevant Cu^{II} μ-thiolate species forms and whether we can tune this equilibrium in a controllable fashion.



With the use of two novel asymmetric ligands we found that the equilibrium between the Cu^{I} and Cu^{II} species depends on both solvent and temperature; the Cu^{II}μ-thiolate complex forms under kinetic control, whereas the Cu^{I}disulfide complex is the most stable species. The energies involved in this equilibrium have been quantified, both experimentally (VT-NMR) as well as theoretically (DFT). The DFT calculations and the experimental findings give a consistent view that is further supported by X-ray crystal structures [2].

The Cu^{II}μ-thiolate/Cu^{I} disulfide equilibrium has also been reported to be controlled by the presence of protons. Isolation of a complex containing both Cu^{II} thiolate moieties and dissociated Cu^{I} ions directed us to consider the possibility that the proton-induced conversion of a Cu^{II} thiolate compound to a Cu^{I} disulfide species might actually result in dissociation of the ligand. From our experimental data it was not immediatedly clear what happens after addition of two H^{+} per dinuclear complex. Thus, the protonation of these complexes was studied computationally with DFT; the calculations showed that indeed the pyridyl-nitrogen is protonated, but in addition revealed that ligand dissociation is favored by more than 100 kJ mol^{-1} over conversion to a protonated Cu^{I} disulfide complex [3].

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BM_02

Exploring mystery of the first theoretically designed biocatalysts

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Limited catalytic activity of the first theoretically designed biocatalysts [1-2] can be considerably enhanced by directed evolution, but the role of corresponding aminoacid substitutions has not been fully explained yet [3-4]. Results for mutated Kemp eliminases and adenosine deaminases obtained within our Differential Transition State Stabilization approach [5-6] allow to explain catalytic role of aminoacid substitutions, in contrast to conventional methods based on transition state stabilization hypothesis introduced by L. Pauling [7]. Possible applications of catalytic fields technique [5-6] in catalyst design for systems with dominant electrostatic will be discussed too.

Acknowledgements: This work was supported by Wrocław Research Centre under the project BIOMED "Biotechnologies and advanced medical technologies" (POIG 01.01.02-02-003/08) financed from European Regional Development fund Operational Programme Innovative Economy 1.1.2

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BM_03

Nuclear spin catalysis in bioinorganic chemistry of metalloenzymes

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All chemical reactions obey the law of conservation of spin angular momentum (‘spin’): any reaction is only allowed when the total spin of reactants is identical to the total spin of products. Correspondingly, some reactions can be accelerated by changing in the electron spin of the reactants via magnetic fields of magnetic nuclei, the so-called “magnetic isotope effect”. In chemistry, magnetic isotope effects have long been known for a number of magnetic isotopes, among them – ^{13}C, ^{29}Si, ^{199,201}Hg, etc [1]. Recently, magnetic isotope effects have been discovered in living cells [2]. Among three stable isotopes of Mg, ^{24}Mg, ^{25}Mg and ^{26}Mg with natural abundance about 79, 10 and 11 %, only ^{25}Mg has the nuclear spin ($I = 5/2$) and, hence, the nuclear magnetic field. Two other nuclei have no spin ($I = 0$) and no magnetic field. It was revealed that the rate constant of post-radiation recovery of yeast cells is twice higher for the cells enriched with magnetic ^{25}Mg when compared to the cells with nonmagnetic ^{24}Mg. In the experiments with another commonly accepted cell model, bacteria *E. coli*, it was revealed that, upon transferring into novel growth media, the cells passed the adaptation period essentially faster if the growth medium was enriched with ^{25}Mg in comparison with the media enriched with nonmagnetic ^{24}Mg or ^{26}Mg [2]. Furthermore, the nuclear spin catalysis has been documented in the reaction driven by one of the most important metalloenzymes of cell bioenergetics, myosin. The effects of different isotopes of magnesium on ATP hydrolysis driven by the catalytic fragment (subfragment-1) of myosin isolated from myometrium were studied [3]. The enzyme activity has turned out to be 2–2.5 times higher in the reaction media enriched with ^{25}Mg as compared to the activity of the same enzyme in the reaction media enriched with the spinless ^{24}Mg or ^{26}Mg. The catalytic effect of the nuclear spin of ^{25}Mg was observed at physiological concentration, 5 mM, of ^{25}MgCl$_2$. At that, no magnetic isotope effect has been detected in the non-enzymatic ATP hydrolysis. Obviously, the nuclear spin of ^{25}Mg accelerates the chemo-mechanical cycle of myosin, thus setting the enzyme macromolecule for acceptance and hydrolysis of next ATP molecules [3]. Factual evidence of MIE, on its own, unambiguously indicates that there is a “bottle-neck” in the reaction under study, i.e. – a spin-selective intermediate, such as an ion-radical pair or the conformational excitation of the macromolecule into a low-level triplet state or ortho/para isomerization of water protons, that limits the rate of the reaction and may be accelerated by the magnetic field of the isotope’s nuclear spin. Although detailed physicochemical mechanisms require further investigations, the nuclear spin catalysis opens novel, based on the stable magnetic isotopes, ways of control over efficiency and reliability of bioinorganic nanoreactors. [Supported by RFBR, project no. 14-04-00593a].

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BM_04

Learning on nonnatural bioinorganics: Molecular Modeling of Artificial Metalloenzymes

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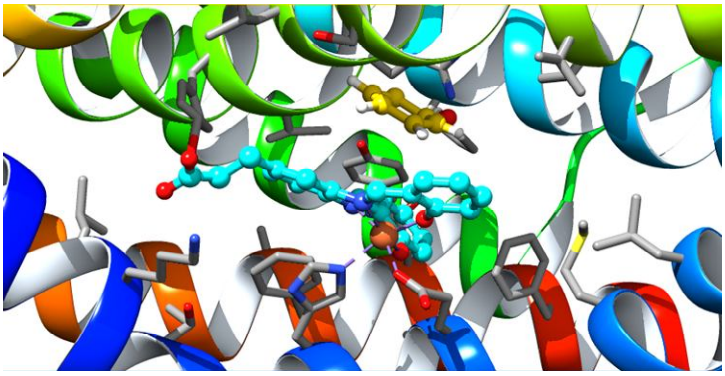
Merging synthetic compounds with biological entities is a concept increasingly explored to expand the scope of enzymatic reactions. One of the most proficient strategies consists in the integration of organometallic scaffolds into biological frameworks (i.e., protein, DNA or peptides).

Despite the major successes of several groups in developing efficient biometallic hybrids, the prediction and analysis of their molecular behavior still represents a complex exercise. The lack of evolutionary pressure generally leads to a first generation of molecules with relatively low stability and difficult structural characterization. Moreover, the identification of the best complementarities among biological receptor, organometallic cofactors and substrates implies a major combinatorial space that challenges biochemical and chemical intuitions.

Virtually, molecular modeling could be of the best allies in this field since computational methodologies can deal with processes related to molecular recognition andcatalytic mechanisms. However, the modeling of artificial metaloenzymes stands out of the scope of standard approaches and novel methodologies are needed.

In the recent years, our group designed, tested and applied a series of computational strategies in the field of artificial bioinorganics. From protein-ligand dockings to multi-scale approaches, our work allowed to better understand the molecular mechanism of artificial metaloenzymes, provided information on how they mechanistically diverge from natural ones and gave some hints on how we could computationally guide the design of new candidates. In this talk, I will briefly present the underpinning concepts of our strategies and the most important results obtained so far both from pure computational works and in collaboration with experimentalists.



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Muñoz Robles, V.;Durrenberger, M.;Heinisch, R.;Lledós, A.;Schirmer, R.; Ward T. R.; Maréchal, J.-D. J. Am. Chem. Soc. 2014, 136, 15676-15683

BM_05

Chemistry of the Nitrogenase P-Cluster and FeMo-co

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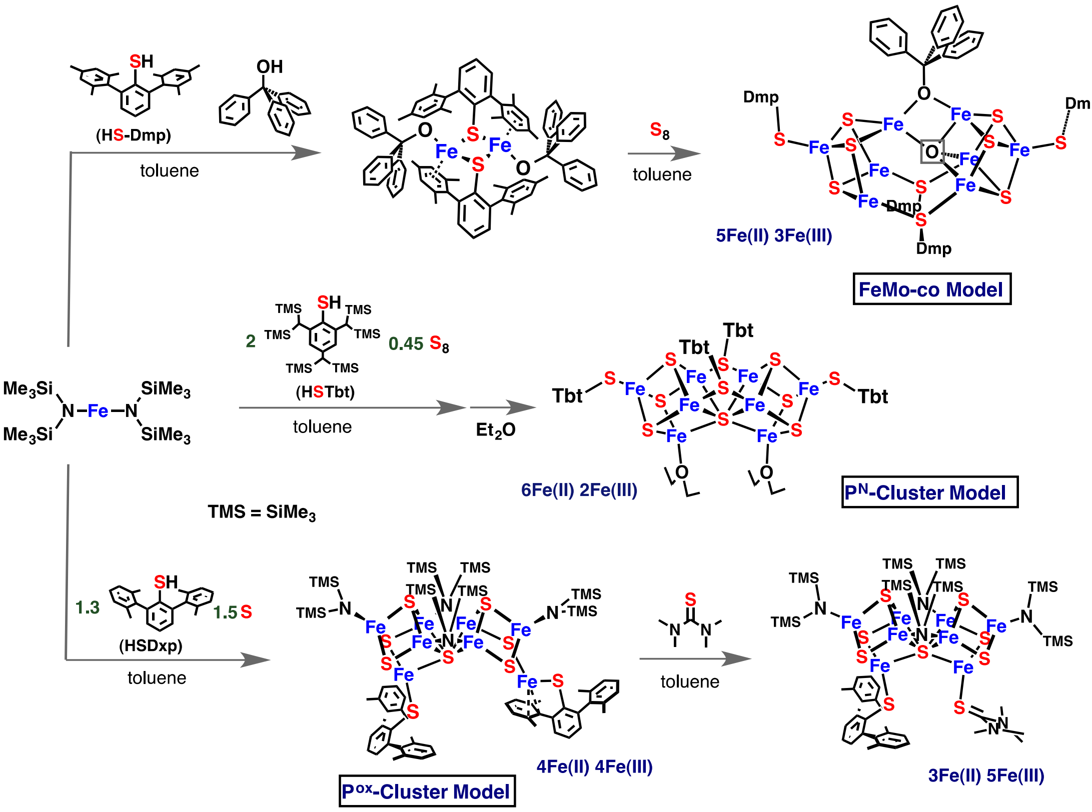
The active centers of metalloenzymes regulate highly efficient and selective chemical transformations under mild conditions, and an important and pressing mission of chemists has been to synthesize model active centers in vitro and to elucidate the mechanisms of the biological functions. We have developed a new synthetic route to meta stable Fe/S clusters in non-polar solvents using $Fe\{N(TMS)_2\}_2$ (TMS = $SiMe_3$) as the precursor, resulting in isolation of unprecedented clusters with structural diversity, showing a realm of possibility in chemical synthesis of Fe/S and Fe/Mo/S clusters. This presentation shows our study on the chemical synthesis of metal sulfide clusters, which are relevant to the P-cluster and FeMo-co of nitrogenase. Their spectroscopic and chemical properties characteristic of these clusters are discussed with the emphasis on flexibility of the cluster geometries and the oxidation states.



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BM_06

X-ray Spectroelectrochemistry – A useful use of sample?

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Chemical/biochemical/electrical energy interconversions commonly require transition-metal-based redox catalysis for their progress at useful rates. The changes in composition, structure and reactivity that accompany a change of redox state are critical to the functioning of the catalyst and present greatest challenges to study. The combination of electrochemistry and spectroscopy can allow in situ measurement of reactive species and clarify aspects of the chemistry. We have shown that for diiron compounds related to the [FeFe]-hydrogenase H-cluster the combination of IR spectroscopy, theory and EXAFS can allow identification of the reduction products allowing insight into the reaction path [1, 2]. However the extension of those studies is frequently restricted by sampling requirements and limitations on the reliability of the conclusions drawn from the analysis.

The paper will focus on the application of X-ray spectroscopy (XAS) of biomimetic complexes and the extension of those investigations to proteins where the redox state of the system is controlled electrochemically. We have shown that in situ XAS measurements can be conducted on sample volumes of 200 μL [3]. The electrogenerated sample can be freeze-quenched in the reticulated vitreous carbon working electrode (Fig.1) thereby allowing low-temperature fluorescence XAS measurements. has a 10×2×2 mm compartment that acts both as the cell and working electrode (WE) chamber where the sample is freeze-quenched prior to transfer to the beamline cryostat. Issues related to data quality and analysis of XAS/EXAFS measurements in terms of stereochemical information will also be discussed [4].

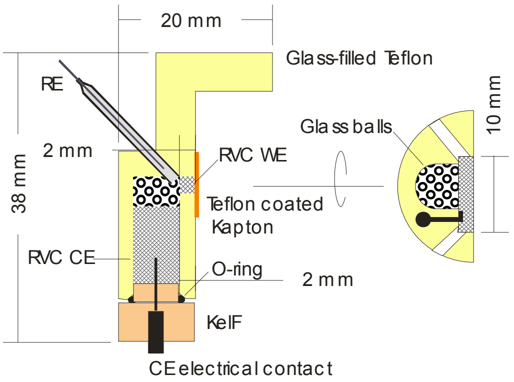

Figure 1 Schematic of the in-situ spectroelectrochemical cell for XAS measurements. Once electrosynthesis is complete the cell is frozen in liquid nitrogen and the reference electrode (RE) and electrical connections and flow tubes are removed and the cell can be loaded into the beamline cryostat for fluorescence XAS measurements.

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BM_07

Coordination Complexes with Aminophenol-based Redox-Active Ligands. Bioinorganic and Inorganic Perspectives

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In recent years synthesis and properties of metal-coordinated radicals have gained momentum due to their importance in biology. The determination of molecular structure, investigating the magnetic, spectral and redox properties, and correct assignment of electronic structure of metal complexes of 2-anilino-4,6-di-*tert*-butylphenol-derived ligands in their deprotonated forms have drawn the attention of inorganic chemists due to redox-active nature of such ligands [1]. As a part of our continuing efforts to understand the properties of metal-coordinated ligand radical species from the standpoint of modeling Galactose Oxidase activity [2,3], we have directed our attention to designing new ligands of 2-anilino-4,6-di-*tert*-butylphenol appended with benzylthioether, ethylthioether, thioalkylpyridines and azo functionality [4,5], to investigate their coordination behavior towards transition metal ions, and to investigate radical coupling-driven reactions.

In this presentation, an account of detailed molecular (X-ray), spectroscopic and magnetic and reactivity (redox) aspects of a number of ligand radical-coordinated metal complexes involving a group of redox-active ligands to correctly assign the spin-state of the metal and oxidation level of the coordinated ligands will be discussed. Our designed chelating ligands provide bis-phenolate(2−) and phenoxyl(1−) radical, *o*-amidophenolate(2−), *o*-iminobenzosemiquinonate(1−) radical and *o*-benzoquinone forms of the coordinating ligands. The electronic structure of the complexes is then rationalized by the Density Functional Theory (DFT) calculations, which can successfully account for the observed properties of the complexes. Radical-driven reactivity aspects (N–N and –O–C–O– bond formation) will be discussed.

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BM_08

Copper(II) binding to Angiogenin: new insights in the role of metal ionsin angiogenesis

Diego La Mendola[1], Fabio Arnesano[2], Orjan Hansson[3], Chiara Giacomelli[1], Vincenzo Mangini[2], Maria Letizia Trincavelli[1], Cristina Satriano[4], Antonio Magrì[5], Claudia Martini[1], Giovanni Natile[2], Enrico Rizzarelli[5]

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Angiogenin(Ang), a member of the ribonuclease family, is a normal constituent of the human plasma but strongly overexpressed in patients affected by different types of cancers. Indeed, Ang is a potent angiogenesis stimulator and interacts with endothelial cells inducing a wide range of responses, such as angiogenesis, cell proliferation, cell migration, and pro-survival effects[1]. The biological role of Angisnot limited to induction of angiogenesis, recent findings demonstrate that Ang is down-regulated in mouse models of Parkinson's and Alzheimer's diseases, and is emerging as one of the key factorsin amyotrophic lateral sclerosis (ALS), where Angacts as a motoneuronsneuroprotective agent. Copper(II) is well known to play an essential role in neurodegenerative diseases and it has also been demonstrated to bean essential cofactor duringangiogenesis*in vivo*. Moreover, serum copper levels are raised in a wide variety of human cancers and correlate with the tumor malignancy. During angiogenesis, cellular coppertranslocatesextracellularly,therefore the metal binding to extracellular proteins involved in angiogenesis, includingAng, is a possible pathway through which copper takes part to the signalling process. The activity of Ang is strongly influenced by the presence of copper(II) ions [2], even though previous reports indicate that copper and Ang stimulate angiogenesis by different mechanisms and pathways. It is to emphasize that the data reported till now have been obtained by using the recombinant form of Ang (r-Ang). Such a recombinant form contains a methionine as first residue, at variance withthe wild-type isoform (wt-Ang), which has a glutamic residue, with amino group spontaneously cyclizing in the pyro-glutamate form.

In the present report, we address the copper(II) binding to wt-Ang and rAng proteins by means of a multitechnique approach, including spectroscopic and spectrometricmethods such as NMR, EPR, UV-vis, CD, ESI-MS, and biochemical RNAase activity assays. We show that the two protein isoforms bind copper ions differently and that the metal binding affects both the intracellular localization of Angand the protein-induced angiogenesis. These results highlight the tight relationship between copper and Ang, pointing out the biological relevance of theAng-copper complex in the regulation of endothelial cell function, and revealing a possible new mechanism at the basis of vascular pathologies.

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BM_09

Functionalization of polypirydyl ruthenium complexes for biomedical applications

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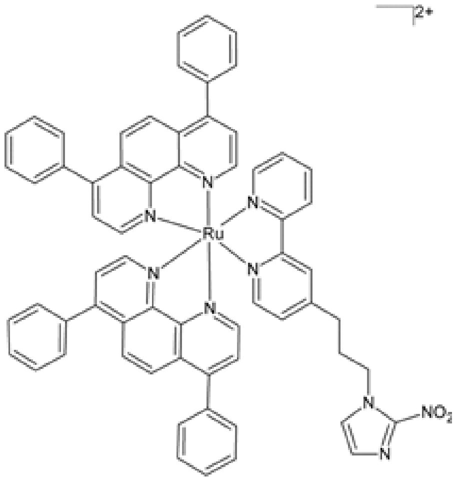
During the last decade growing interest in applications of Ru polypyridyl complexes as luminescent dyes for optical imaging or as cytotoxic agents for the treatment of various types of cancer has been observed.The unique optical features (intense and long lifetime of luminescence strongly dependingon the molecular oxygen concentration, emission close tonear-infrared) together with favorable biological properties (ability topass cellular membrane, reasonable solubility in aqueous media) giverise to their application in optical imaging. However, one of the most interesting research aspects is a dual imaging and therapeutic application of such compounds. The combining of diagnostic andtherapeutic properties in one compound is so called theranosticsand recently has attracted the attention of researchers. In this context an appropriate modification of polypyridyl ligands through the introduction of different substituents can tune not only their luminescent properties but alsotheir cytotoxicity. The aim of ourstudywas to modify polypyridyl ruthenium complexes to increase cellularaccumulation, to obtain better selectivity toward hypoxic tissues aswell as to combine cytotoxic activity with imaging properties.Very recently we have designed a new Ru polypyridyl complexcomprising nitroimidazole unit (Scheme 1) for cancer treatment and its visualization directed towards hypoxic cells [1].The photophysical properties in the context of the biological activity of this complex will be discussed [1,2] In additionwe showed the multifaceted relationship between lipophilicity, protein interaction and luminescence properties of ruthenium(II) complexes affecting cell imaging and cytotoxic properties [3]. Our results pointed out that both the imaging and cytotoxic properties ofthe studied ruthenium complexes are strongly influence bythe level of internalization and protein interaction. Moreover they are not only cytotoxic but are also potentially invasive andanti-metastatic agents.



Scheme 1. $[Ru(dip)_2(bpy\text{-}2\text{-}nitroIm)]^{2+}$

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BM_10

Gallium(III) complexes of macrocyclic bis(phosphonate)-containing ligands for imaging of bone metastases

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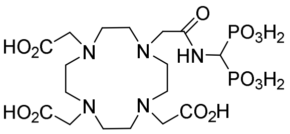
Methylene-bis(phosphonate) group has a high affinity for tissues with high efflux of Ca^{2+} as e.g. bone metastases, and is used as a targeting group to image/treat the lesions. Among radioisotopes suitable for PET, the generator-produced ^{68}Ga ($\tau_{1/2}$ 67.7 min, 89 % β^+, 0.83 MeV) is increasingly used as an alternative to ^{18}F. Metal radioisotopes used in nuclear medicine must be firmly complexed and macrocycle-based ligands form the most stable complexes. Good ligands for Ga^{3+} should be based on NOTA or DOTA. Conjugation of the macrocycles and bis(phosphonate) (BP) group creates ligands targeting calcified tissue which can be also used for a theranostic^{68}Ga-^{177}Lu pair.

Solution chemistry of the Ga^{3+}-DOTA [1] and Ga^{3+}-NOTA [2] systems was revised and the knowledge was used to prepare DOTA-BP conjugates **1** and **2**which were labelled with ^{68}Ga.[3] The radiotracer has been used successfully in patients to image bone metastases. As NOTA skeleton is generally better than DOTA one for Ga^{3+}, NOTA-BP conjugate **3** was prepared[4] and it was shown to perform much better in patients. Complexation of Ga^{3+} among the ligands is different and will be discussed. Aqueous solution studies of Ga^{3+} are still not routine and some problems concerning the work will be pointed out.



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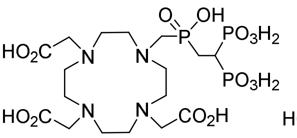

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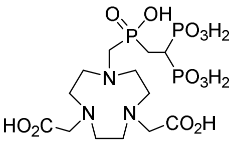

3

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OC_01

Entrapment of the complex Cu(2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane) in sol-gel electrodes for electrocatalysis

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Heterogeneous catalysis offers a number of advantages, including the possibility of recycling the catalyst. Heterogeneous catalysis can be applied through the sol-gel process. Cu^{II}(2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane) complex was entrapped in sol-gel matrix electrodes and the activity of the copper complex as an electro-catalyst was studied.

Copper complexes, and Cu(I) complexes in particular, are known as catalysts of a variety of homogeneous processes. However, little is known about the mechanism of their activity in heterogeneous systems. The electro-catalytic activity of the Cu(2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane) complex, was studied in the de-chlorination reaction of tri-chloro-acetic acid (TCA).The effects of pH and substrate concentration were studied using cyclic voltammetry at different scan rates and product analysis.

The results points out that:

1. The (CuL_1) complex is an electro-catalyst for the reduction of TCA both in homogenous and heterogeneous systems.
2. The pH of the solution in the heterogeneous electrochemical process does not affect the electro-catalytic properties of the complex in the electrodes. Plausibly the pH of the solution does not change the structure of the complex when it is entrapped in the electrode.
3. The catalyst can be recycled and used in a large number of recycles, even after changes in the substrate concentration and the pH.
4. The nature of the sol-gel matrix, as determined by using different precursors, affects dramatically the rate of the electro-catalytic process.

Based on the nature of the final products a tentative mechanism of the electro-catalytic process is proposed.

OC_02

C-H Activation Reactions in Zr and Y Complexes Anchored by Disubstituted Cyclam Ligands

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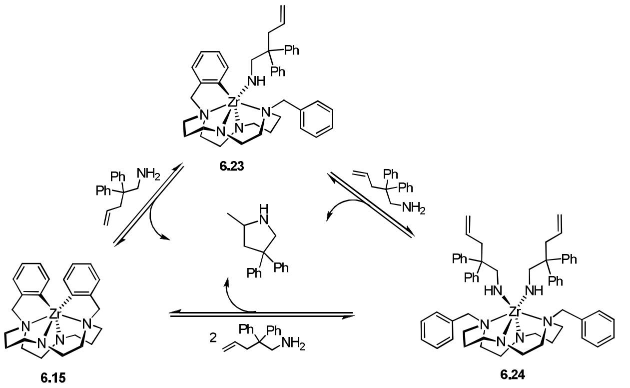
The reactivity of *trans*-disubstututedcyclam-based diamido diamine zirconium complexes revealed particular features that are intimately related to the nature of the tetraazamacrocyclic frame. Despite being isoelectronic with the bis-cyclopentadienyl and unsaturated tetrazamacrocycle donor sets (porphirins, annulenes, etc.) we have shown that the properties of the Zr-N bonds within the saturated macrocycle are very distinct, originating reactivity patterns that differ considerably from other systems.

Our study of (R$_2$-Cyclam)ZrX$_2$complexes, where R stands for benzyl, substituted benzyl or allyl pending groups,involved an extensive work on synthesis and structural characterization as well as reactivity studies and catalytic applications in ROP of cyclic esters and metal-mediated cyclam functionalization.[1]

In this communication we will discuss intramolecular C-H activation reactions of Zr and Y complexes that lead to new types of cyclam-based metal complexes and discuss the reactivity of those compounds as catalysts ofthe intramolecular hydroamination of aminoalkenes.[2] NMR and DFT studies of the reaction mechanism disclosed a cooperative metal-ligand mechanism that involves the C-H activation bonds of the benzyl or allyl pending arms.



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OC_03

Selective oxidation of alkanes with *m*-chloroperbenzoic acid catalyzed bya heterometallic Co/Fe complex

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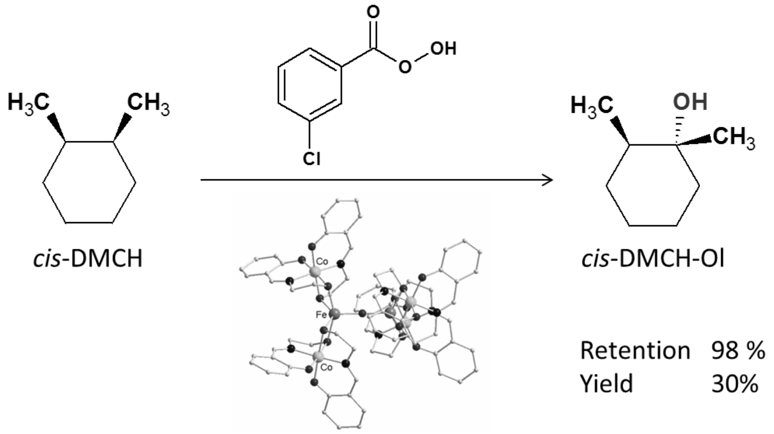
Selective oxidation of inert alkanes remains a challenge in modern chemistry. A few catalysts (mainly of iron) based on N-donor ligands are effective for the stereospecific oxidation of alkanes with H_2O_2.[1]Further, it has been known that some oxidation agents, such as *m*-chloroperbenzoic acid (mCPBA), reveal enhanced selectivity (including stereoselectivity) in the oxidation of organic substrates catalyzed by metal complexes or salts.[2]However,most ofthe reported catalytic systemson the oxidation of alkanes with mCPBAdisplay either negligible yields based on substrate or very low TONs (turnover numbers; molsof product per mol of catalyst), making their practical applications limited.

We have found that the heterometallic Schiff base complex$[Co_4Fe_2O(L)_8]\cdot 4DMF\cdot H_2O$[3] revealshigh 3°/ 2° selectivity (up to 15) in the oxidation of methylcyclohexane and high stereospecificity in the oxidation of 1,2-dimethylcyclohexane (retention of *cis* or *trans* configurations up to 98%), supported by high yields based on substrate (up to 30%) and oxidant, mCPBA, (up to 60%), as well as high TONs (up to 4×10^4). The parameters and behaviour of this novel catalytic system have been extensively studied by means of kinetic methods, spectroscopy and ^{18}O isotopic labelling.Details of these studies will be discussed.

This work has been supported by the Foundation for Science and Technology (FCT), Portugal (project UID/QUI/00100/2013; fellowships SFRH/BPD/42000/2007 and SFRH/BPD/99533/2014).



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OC_04

Molecular metal hydride carbonyl clusters

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Metal hydrides are of fundamental importance in chemistry, both as solid-state materials and molecular compounds.[1] They are key intermediates in various catalytic reactions and have promising applications for hydrogen storage.[2] Metal clusters and nanoparticles are intermediate species between mononuclear complexes and bulky materials.[3] Hydride atoms in molecular clusters may display several coordination modes, since they can be coordinated to the surface of the cluster as terminal, edge or face bridging ligands, as well as located in semi-interstitial, or fully interstitial positions.

Herein we will present a few recent cases of molecular metal hydride carbonyl clusters. We will describe the first example of a low-valent transition metal cluster containing an interstitial hydride enclosed within a tetrahedral cavity, *i.e.*, $HFe_4(CO)_{12}(AuPPh_3)_3$.[4] This species originates from the addition of a $[AuPPh_3]^+$ fragment to $[HFe_4(CO)_{12}(AuPPh_3)_2]^-$ with concomitant migration of the unique hydride from a triangular face of the Fe_4-cage to its interstitial tetrahedral cavity. Hydride migration from the surface to the inside of the cluster may be related to the high fluxionality observed in solution for these species and, more in general, to hydrogen diffusion in metal clusters, nanoparticles and bulk materials.

As a further example, we will report on the $[H_{3-n}Co_{15}Pd_9C_3(CO)_{38}]^{n-}$ (n = 0-3) tri-carbide poly-hydride clusters.[5] These species are easily interconverted by simple protonation-deprotonation reactions. More interestingly, their inner Pd_9 core is reversibly transformed from octahedral to trigonal prismatic upon removal/addition of hydride ligands. This indicates that hydride ligands may have fundamental stereochemical effects on the structure of large metal cages. The role of hydride ligands in larger clusters as well as the problems of their identification and location will be discussed.[6]

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OC_05

H Atom Abstraction versus Chelate Complex Formation – Reactivity Patterns of *side-on* coordinated *S*,*N*-substituted Alkynes

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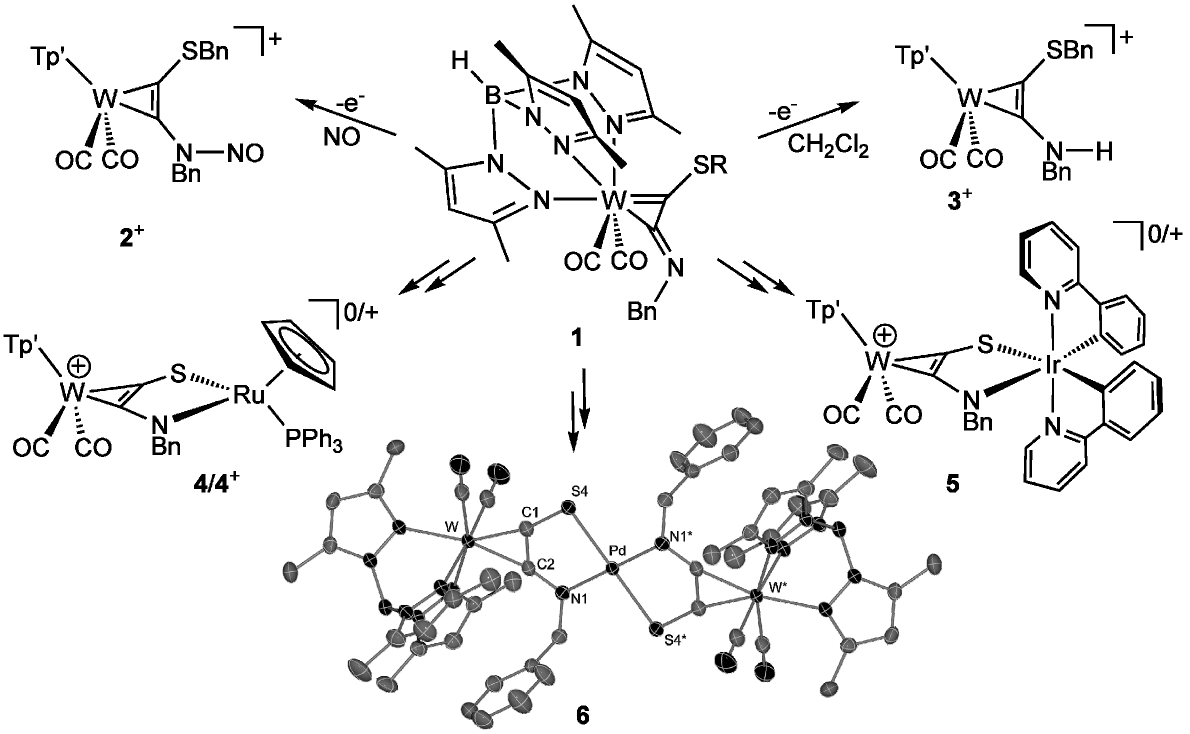
Alkynes with proximate donor substitution are electronically flexible linkers with a high conjugation potential. Thus, acetylene diolate, $[O–C{\equiv}C–O]^{2-}$, allowed the formation of dinuclear complexes displaying the μ- κ^1- κ^1-coordination mode[1] In contrast, *side-on* coordination at the triple bond renders the sulfur congener acetylene dithiolate, $[S–C{\equiv}C–S]^{2-}$, acdt^{2-}, a *S*,*S'*-chelate ligand leading to a μ-η^2-*C*,*C'*-κ^2-*S*,*S'* complex topology.[2]



The reactivity and coordination behavior of a mixed *S*,*N*-system with a terminal thiolate and an amide substituent will be presented.Oxidation of the imine **1** led to aS=1/2 complex, which shows predominant spin density at W according to EPR spectroscopy. However, radical reactivity like addition of NO or H atom abstraction is observed at the N center. Removal of the protective group at S (R = $C_2H_4SiMe_3$) and subsequent reaction with complex precursors led to polynuclear complexes **4** to**6**. Spectroscopic investigations on the intermetallic coupling in the redox-active complexes **4**/**4**$^+$ and **5**/**5**$^+$ will be discussed.

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OC_06

Metalloporphyrins as active N-heterocyclic carbene (NHC) transfer reagents

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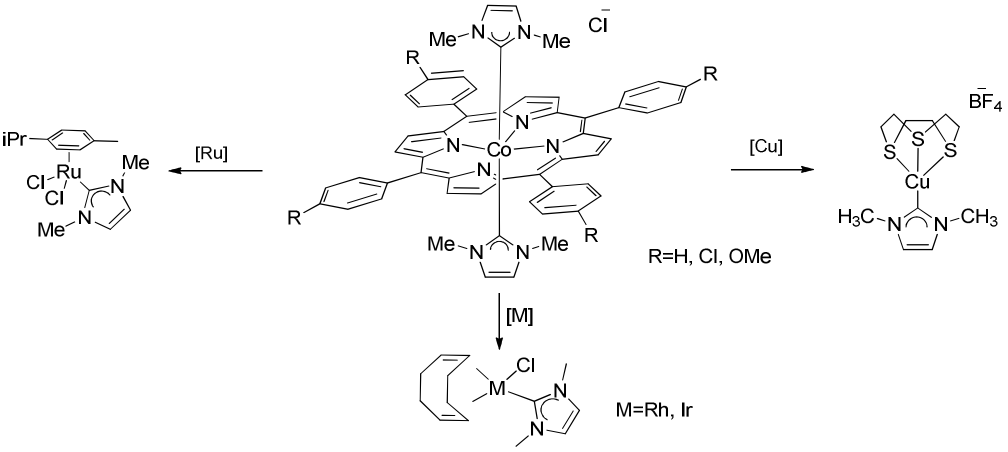
With the growing relevance of NHCs as ligands in transition metal catalysis,the development of new synthetic methods forNHC complex formation has become increasingly important in recent years.[1]An often-used method involves transmetallation of Ag-NHC complexes or related precursors.[2] However, these carbene transfer methods lack for tunability of the carbene transfer reagent.

We have discovered porphyrin Co(III) complexes which contain a labile NHC ligand and which therefore show activity as carbene transfer agents. Modification of the porphyrin ligand and the NHC substituents provides a methodology for custom-tailoring the transfer ability of these porphyrin NHC hybrid systems. This understanding has allowed us to develop optimised conditions and an efficient method of selectiveNHCtransfer, as well as to exploit the unique *trans* effect of these ligands.



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OC_07

An Electrochemical Flow-Reactor for the Synthesis of Metal-NHC Catalysts

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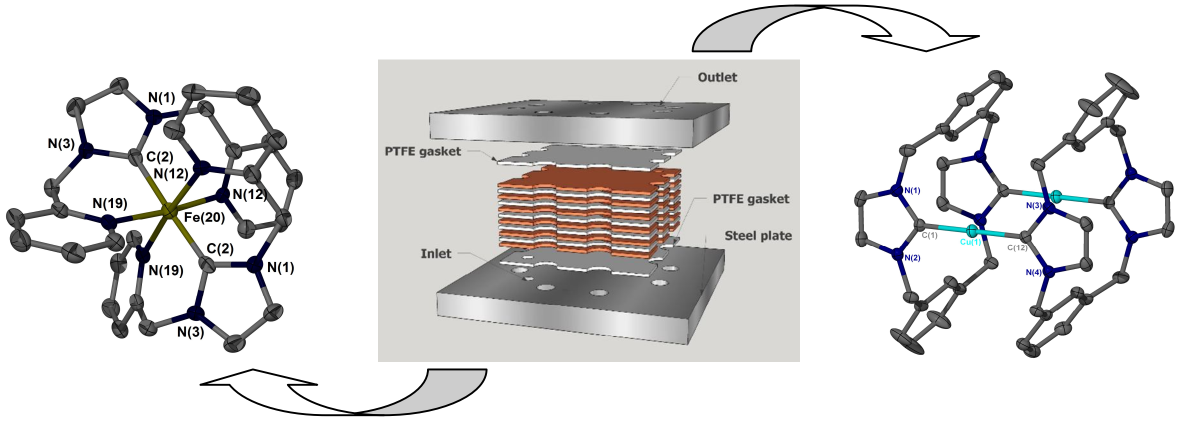
Institute of Process Research and Development (iPRD), School of Chemistry, University of Leeds

Developed by Arduengo over two decades ago, the notion of employing *N*-heterocyclic carbenes (NHCs) as ancillary ligands for transition metal-based catalysts has been refined such that they now present all required attributes for broad application – typically offering high return over their phosphine rivals (*e.g.* enhanced thermal stability and greater tunability).[1]

Despite these advances, a number of drawbacks currently exist with traditional methods of metal-NHC preparation, notably when considering such complexes for industrial use. The pre-requisite for strongly basic/strictly inert conditions within current syntheses largely limits the scope of suitable substrate for metal-NHC complexation.[2] Complementary routes include transmetallation of a carbenic moiety from a basic metal oxide (*e.g.* Ag_2O),[3] leading to the accumulation of metal salt byproducts.

In light of these challenges, the design, construction and optimisation of an innovative electrochemical flow-reactor has been developed which circumvents such issues. The electrochemical approach, which has been published in *Chemical Communications*,[4, 5] provides a clean and atom economical route to metal-NHCs as a result of: (i) no external reagents are required, (ii) a simple evaporative work-up and (iii) hydrogen gas is the only byproduct.



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OC_08

Synthesis of nucleophilic carbene complexes and borenium species from a $P^{(V)}$-stabilized geminal dianion

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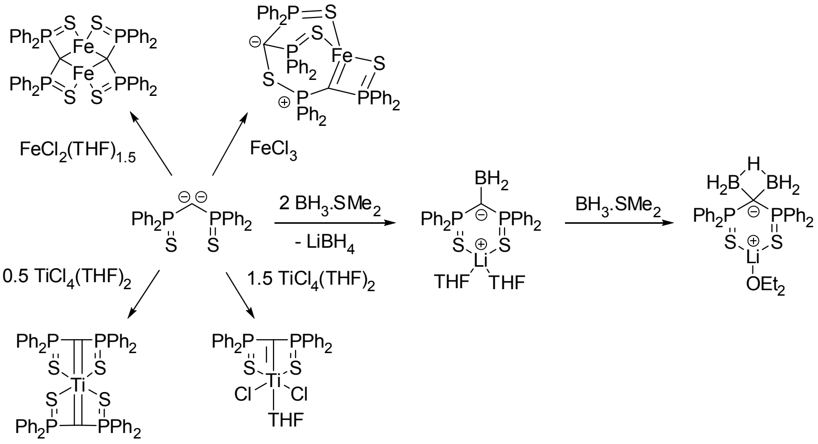
The chemistry of phosphorus-stabilized geminal dianions has been developed to a large extent in the past decade. They proved to be universal precursors for the synthesis of carbene complexes of d- and f-block metals, as they provide all four electrons needed for the creation of the C=M double interaction. In parallel to our studies on the coordination chemistry of these dianions, [1] we have also obtained the related room-temperature stable carbenoids and proved their strong electrophilic character (insertion into a BH bond of BH_3) [2].

In the present communication, we discuss the coordination of the bis(thiophosphinoyl)-stabilised geminal dianion to $Ti^{(IV)}$ [3], $Fe^{(II)}$ and $Fe^{(III)}$. We highlight the very peculiar nucleophilic reactivity of the titanium monocarbene complex towards carbodiimides, which was rationalized by DFT calculations.

We also present the coordination of the same dianion to borane BH_3, which leads to a very rare borenium species, which features a C-B double bond character. This species is then capable of coordinating a second borane molecule to yield a diborane-like species. The electronic situation, also probed by DFT, will be presented.



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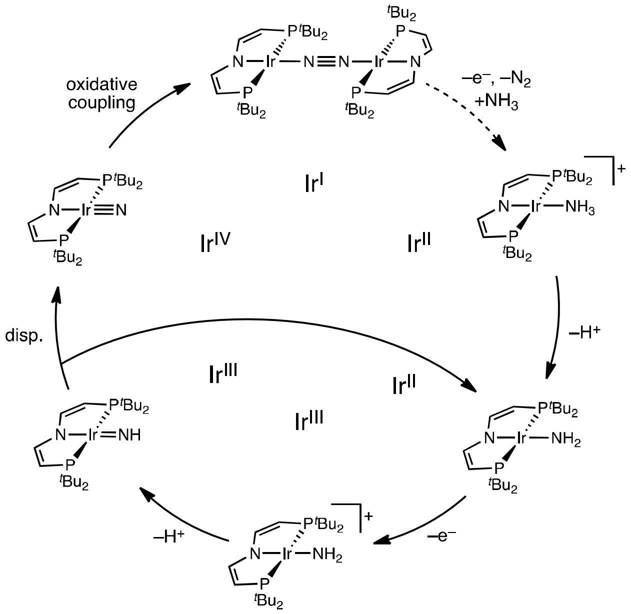
OC_09

Redox Transformations of Molecular MNR_x Species in the Context of Nitrogen Fixation and Amine Activation

Sven Schneider

Georg-August-Universität Göttingen

Synthetic nitrogen fixation at ambient condition remains as one of the most challenging problems in homogeneous catalysis. In reverse, catalytic amine oxidation is of interest for transformations related to ammonia based chemical energy storage or NR-group transfer reactions.In this contribution, the use of transition metal pincer platforms for redox transformations of NR_x ligands will be presented. Elementary steps relevant to these reactions, such as N_2 splitting and coupling,[1] hydrogen atom transfer reactions (Figure),[2] or oxidative coupling of NR_x ligands will be discussed with particular emphasis on experimental thermochemical parameters, such as MNR_x–H bond dissociation energies, and on electronic structure / reactivity relationships of key intermediates.



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OC_10

Formation of a ZwitterionicBoronium Species from the Reaction of a Stable Carbenoid with Borane: CO_2 Reduction

Samuel Y.-F. Ho[1,2], Cheuk-Wai So[2], Nathalie Saffon-Merceron[1], Nicolas Mézailles[1]

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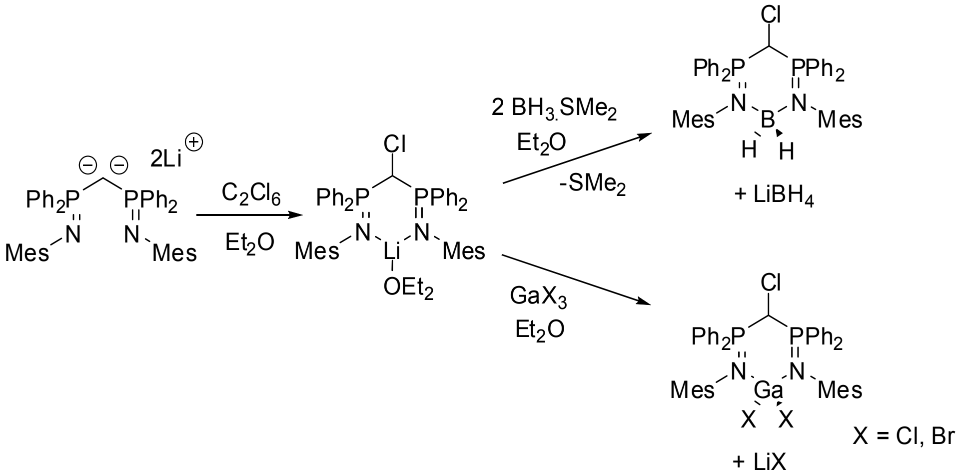
In recent years, there have been important advancements in the search of stable Li-Cl carbenoid species. [1] In 2007, our group reported the mild oxidation of a stable geminal dianion as a novel route to form these compounds. [2] These carbenoids, like carbenes, possess both nucleophilic and electrophilic character. However, due to the presence of the strong accepting P(V) moieties at the central carbon atom, these carbenoids have a more pronounced electrophilic character.

Our group studied the reactivity of the bis-thiophosphinoylcarbenoid in particular with BH_3. It is shown that the carbenoid is able to insert into one B-H bond of BH_3. [3] Hence, we postulate that with a more nucleophilic iminophosphorane moiety, it would change the carbenoid's reactivity. In this presentation, we will report the synthesis of a stable bis-iminophosphorane carbenoid and its reaction with BH_3 to form a novel zwitterionicboronium species. The carbenoid and the boronium species were found to be one of the best catalyst for the CO_2 reduction with BH_3 to form methanol derivatives. [4]



The reactivity of the Li-Cl carbenoid towards GaX_3 (X = Cl, Br) has allowed us to understand the mechanistic formation of the GaX_2-Cl carbenoids. These results will also be presented.

Literature:

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[3] Heuclin, H.; Ho, S. Y. F.; Le Goff, X. F.; So, C. W.; Mézailles, N., Facile B–H Bond Activation of Borane by Stable Carbenoid Species.*J. Am. Chem. Soc.***2013**, 135 (24), 8774-8777.
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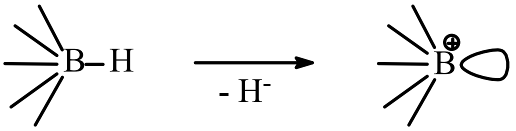
OC_11

Polyhedral boron hydrides as Lewis acids

Igor B. Sivaev, Vladimir I. Bregadze

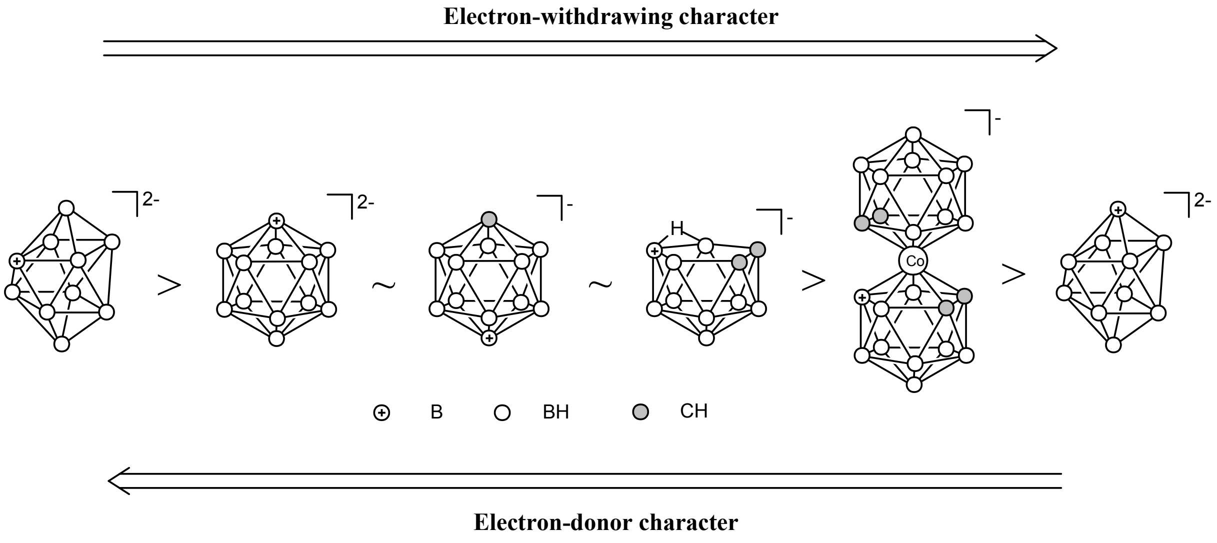
A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences

A formal abstraction of one hydride atom from polyhedral boron hydrides results in generation of quasi-borinium cation being very strong and very reactive Lewis acid [1]. The Lewis acidity strength depends on the type of boron hydride and a place of hydride removal.



Quasi-borinium cation
Lewis acid

A reliable scale of electron-withdrawal/electron-donating character of Lewis acids derived from anionic polyhedral boron hydrides was established on the base of analysis of ^{1}H NMR spectra of five series of borane derivatives bearing different substituents (-OBu, -O$^+$(CH$_2$CH$_2$)$_2$O, -NH$^+$=CHPh, -NH$_2$$^+CH_2$Ph, -S$^+Me_2$). The relative electron-withdrawal properties were found to increase in the order $[2\text{-}B_{10}H_9]^{2-}$ > $[B_{12}H_{11}]^{2-}$ ~ $[12\text{-}CB_{11}H_{11}]^-$ ~ [10-*nido*-7,8-$C_2B_9H_{10}]^-$ > [8-3,3'-Co(1,2-$C_2B_9H_{10}$)(1,2-$C_2B_9H_{11}$)]$^-$ > $[1\text{-}B_{10}H_9]^{2-}$ [2].



Some analogies in electron-withdrawal/electron-donating character of quasi-borinium cations and known metal-based Lewis acids will be discussed.

This work was supported in part by the Russian Foundation for Basic Researches (15-03-05822).

Literature:

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OC_12

Indium Trihydride Complexes and the First Indium Subhydride

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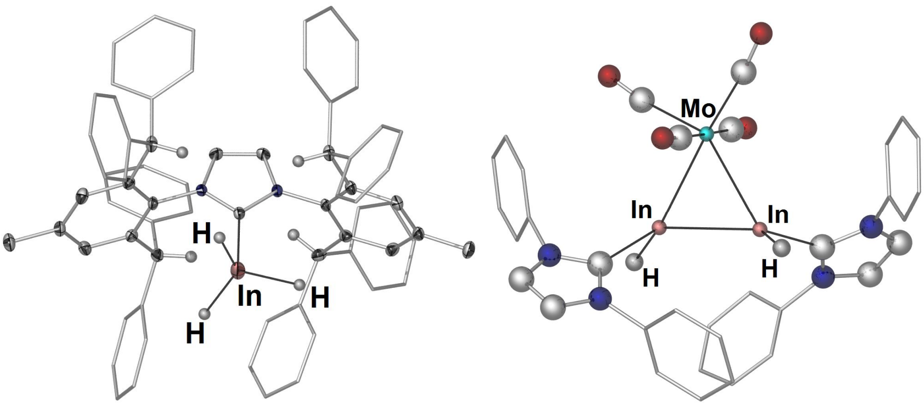
The hydride chemistries of the heaviest group 13 metals, indium and thallium, are notoriously challenging.[1] Groundbreaking inert gas matrix isolations and theoretical work have provided valuable reconnaissance,[2] leading to the first isolations of indium trihydride complexes.[3] There are no widely recognised syntheses of thallium hydrides, nor have lower oxidation state indium hydrides been isolated.



One of our objectives is to develop the synthetic and materials chemistry of indium trihydride and routes to thallium hydrides. This contribution details the synthesis of several ambient temperature and even air stable indium trihydride complexes (image, left), the comprehensive study of InH_3 complex decomposition pathways,[4] the first σ-complexes of In-H bonds, and the synthesis of the first indium(I) hydride; [(NHC)HIn-InH(NHC){μ-Mo(CO)$_4$}] (image, right). Our preliminary forays into thallium hydride chemistry will also be discussed.[5]

Literature:

[1] *The Group 13 Metals: Al, Ga, In and Tl. Chemical Patterns and Peculiarities*, Aldridge, S.; Downs, A.J., Eds. Publisher: Wiley-Blackwell, Chichester, **2011**.

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OC_13

Catalysis of Thiocyanate Formation

Sigridur G. Suman,[1,2] Johanna M. Gretarsdottir,[1] Paul E. Penwell,[3] Snædís Björgvinsdóttir,[1]
Jon Petur Gunnarsson,[1] Sindri Frostason,[1] Egill Skulason,[1] and Anna Garden[1,3]

[1]*Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland,*
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[3]*Department of Chemistry, University of Otago, Union Place West, Dunedin 9016, New Zealand*

The catalysis of the reaction of cyanide and thiosulfate is of great importance in the context of cyanide removal from aqueous solutions. The reaction itself is spontaneous and has been shown to be a second order reaction.[1]The reaction proceeds rather slowly, and is industrially inefficient.[2] This transformation may be accomplished using a molybdenum sulfur catalyst. A suitable catalyst is able to increase the rate of this transformation more than tenfold, even at neutral pH in water. DFT calculations were used in parallel with experimental data to explore the mechanism of the catalysis and the complexity of otherwise apparently simple reaction. A complex crystallized post-reaction in a precipitation experiment, and revealed the catalyst had exchanged its ligands for cyanide, and dimerized. This is undoubtedly a potential deactivation route in the process.[3]

We present study of the catalysis of the thiocyanate formation, and it's pH dependance. The results from the DFT studies will be presented and the reaction chemistry of the catalysts.

Literature:

[1] Singleton, D.R.; Smith, D.W., Improved Assay for Rhodanese in Thiobacillus spp. *App. Environm. Microbiology*, **1988**, *nov*, 2866-2867.
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OC_14

Radical organometallic reactions: TEMPO and dialkylzincs

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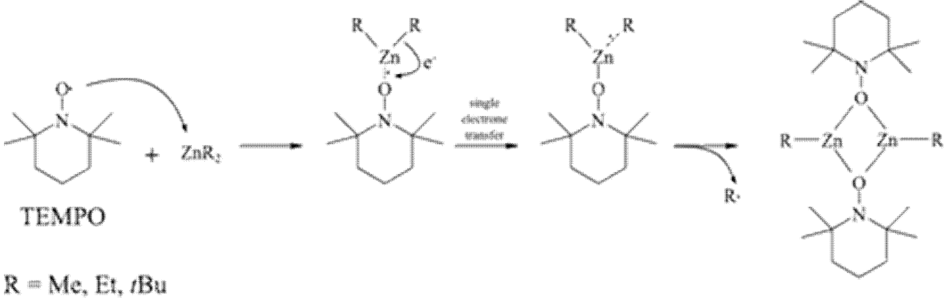
(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) is a stable free radical receiving anincreasing attention due to its catalytic and oxidative role in various reactions, including industrial oxidation of primary alcohols.[1] It is also commonly used as a radical scavenger probing chemical and biological systems. TEMPO's coordination chemistry is a topic of a significant interest as its bonding and reactivity carry mechanistic implications for the processes mentioned above.[2] Surprisingly, until now reports on its reactivity towards dialkylzinc (ZnR_2) species remained contradictory and vague. For example, Grirrane et al. noted that $ZnEt_2$ does not react with TEMPO unless $Zn(Cp^*)_2$ is also present in the reaction,[3a] whereas Bertrand et al. evidenced that TEMPO EPR signal instantaneously disappears upon addition of diethylzinc.[3b]

Herein some of the uncertainties surrounding this topic will be cleared out.[4] A report on our studies on the nature of reactions of TEMPO with ZnR_2 (Scheme 1) will be presented.



Scheme 1. Reaction of TEMPO with ZnR_2.

Literature:

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OC_15

Odd Electron Reactivity at Late Transition Metals Mediated by Redox-Active Ligand-to-Subtrate Single Electron Transfer

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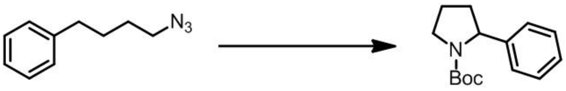
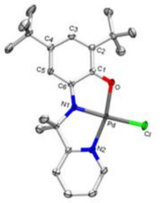
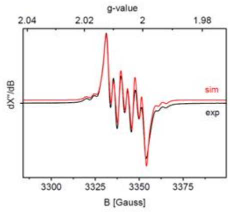
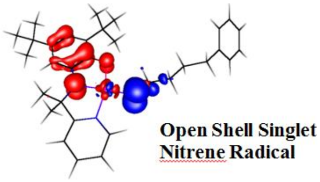
Redox-active ligands can induce noble metal reactivity upon base metals by acting as an electron reservoir.[1,2] However, establishing 'base metal-like' odd-electron reactivity with closed-shell noble metals using redox-active ligands is very rare. We introduced novel redox-active tridentate ligand designs, with NNO and PNO donor sets, that show fascinating reactivity in the coordination sphere of palladium(II). A paramagnetic palladium complex has been isolated (S = ½) that can undergo reversible ligand-based one-electron oxidation and reduction. Interestingly, the unpaired electron can be transferred to a bound organic substrate, effectively generating a single-electron reduced substrate in the coordination sphere of Pd^{II}. This activated intermediate can subsequently react in an intramolecular fashion following an odd-electron pathway. This exciting feature has been exploited to convert alkyl azides into pyrrolidines for the first time using Pd^{II}.[3] Following the same protocol, homolytic bond scission of disulfides gives rise to unique ligand mixed-valent dinuclear species.[4] The magnetic properties of related mono-ligated bridged complexes have also been investigated.[5] This presentation will discuss the concepts and potential of this chemistry.









Research funded by the European Research Council (ERC Starting Grant, *EuReCat* to JIvdV).

Literature:

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OC_16

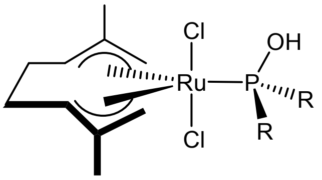
Ruthenium(IV) catalysts with phosphinous acid ligands for the selective hydration of nitriles to amides in water under mild conditions

Eder Tomás-Mendivil, Rebeca González-Fernández, Pedro J. González-Liste, Pascale Crochet, Victorio Cadierno*

Laboratorio de Compuestos Organometálicos y Catálisis (Unidad Asociada al CSIC), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, 33006 Oviedo, Spain. E-mail: vcm@uniovi.es

Amide bond forming reactions are among the most important and widely studied transformations in organic chemistry, but they also present a contemporary challenge because of the industrial need for cleaner and more atom-economical protocols. Nitrile hydration ideally represents the simplest method for the sustainable preparation of primary amides. However, strong acids and bases combined with harsh reaction conditions have been traditionally employed to promote the process, lowering its selectivity and applicability. In this context, significant efforts have been devoted in recent years to the search of homogeneous catalysts able to promote the selective conversion of nitriles to amides employing directly water as solvent under neutral conditions [1].

Ruthenium complexes are particularly effective nitrile hydration catalysts, and promising results in water have been described with the help of hydrophilic phosphine ligands [2]. However, high temperature regimes (≥ 100 ºC) and metal loadings (5 mol%) are typically needed to achieve good conversions. As a significant improvement [3], herein we present the synthesis and characterization of a new series of Ru(IV) complexes (see figure) able to catalyze the selective hydration of organonitriles in water under remarkably milder conditions (60 ºC), and featuring a high activity at a low metal loading (1 mol%).



R = alkyl or aryl group

Literature:

[1] García-Álvarez, R.; Crochet, P.; Cadierno, V., Metal-catalyzed amide bond forming reactions in an environmentally friendly aqueous medium: Nitrile hydrations and beyond. *Green Chem.* **2013**, *15*, 46-66.

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OC_17

Ru(II) arene complexes immobilized on mesoporous silicas as catalyst precursors for the oxidative cleavage of alkenes

Hendrik Kotze and Selwyn F. Mapolie

Department of Chemistry and Polymer Science,Stellenbosch University, South Africa

Oxidative cleavage of alkenes is often employed as a convenient way to produce valuable oxygenates which are often important feedstocks for the fine chemical industry. These types of reactions have traditionally been carried out using stoichiometric amounts of oxidants such as ozone or permanganate solutions but it can also be performed catalytically using a transition metal catalyst in conjunction with an oxidant such as IO_4^- or H_2O_2. Groups6-8 metals have typically been found to be effective catalysts for this process [1]. It has previously been reported that ruthenium complexes with N-donor ligands in the presence of $IO(OH)_5$ as oxidant are capable of selectively oxidizing both terminal and internal alkenes to carboxylic acids. Thus for example 1-octene was found to be selectively converted into heptanoic acid under relatively mild reaction conditions [2].

In this paper we present some preliminary results on the use of silica-immobilized ruthenium arene complexes with auxiliary N,N' chelating ligands as catalyst precursors for the oxidative cleavage of alkenes. Immobilization of ruthenium (II) arene complexes onto mesoporous silica supports (MCM-41 and SBA-15) was achieved by reacting siloxane functionalized p-cymene complexes with native MCM-41 and SBA-15 respectively. An example of such an immobilized catalyst system is shown in Figure 1.

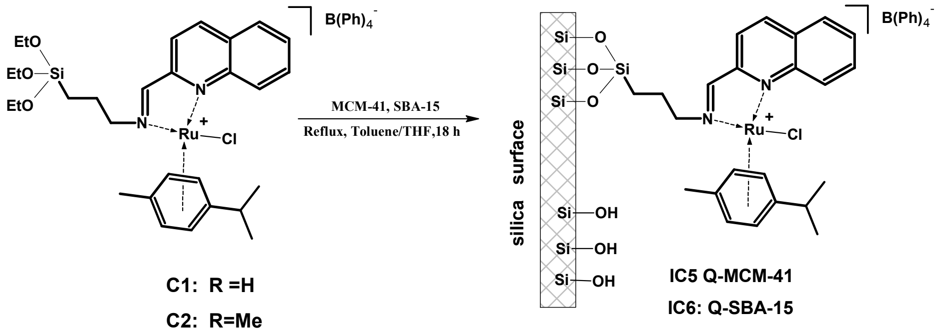

Figure 1: Example of a Ru-arene complex immobilized on mesoporous silica

The "heterogenized" homogeneous catalysts were tested in the oxidative cleavage of linear alkenes as well as activated alkenes. The performance of the immobilized catalysts were evaluated against model homogeneous catalysts and it was found that immobilized catalysts showed enhanced overall activity and displayed a different selectivity profile than the model complexes.

Literature:

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[2] Shoair A.G.F.;. Mohamed R.H.; Improved Procedure for Ruthenium-Catalyzed Oxidative Cleavage of Alkenes With $IO(OH)_5$,*Synthetic Communications*, **2006**, 36, 59-64.

OC_18

Cyclometallation, Steric and Electronic Tendencies In a Series of Pd(II) Complex Pre-catalysts Bearing Imidazole-phenol Ligands and Effects on Suzuki-Miyaura Catalytic Efficiencies

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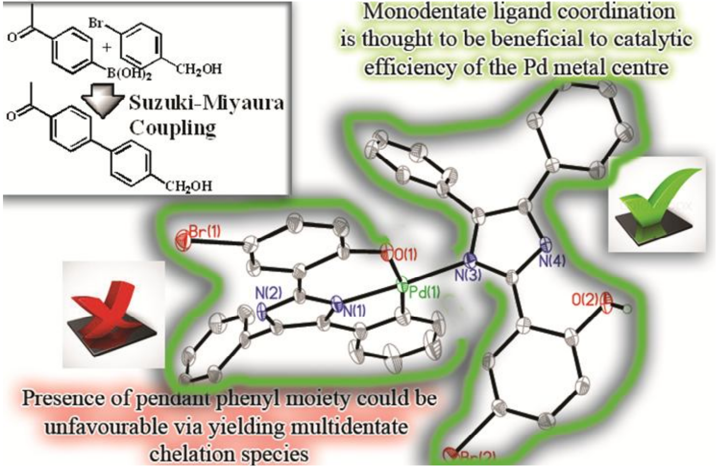
A series of new structurally and electronically diversified palladium complexes have been prepared and characterized. While single crystals grown from precipitated products of complexation reactions confirmed the bis-ligand **Pd(N^O)$_2$** coordination, few crystals obtained from reaction filtrates involving the 2-(4,5-diphenyl-1H-imidazol-2-yl)phenols provided evidence for formation of N^O^C chelation species achieved by cyclometallation. Results from structural analyses and catalytic outcomes generally indicate that desirable variables on the ligand frameworks for obtaining superior catalyst activities either provides hemilabile or sterically strained chelation characters, which would both favour generation of monodentate coordination species at the catalysis temperature. In particular, correlation was observed between tendency for cyclometallation in the palladium complexes and poor Suzuki-Miyaura catalytic prospects. Based on hopeful activity obtained for the complex bearing 4-bromo-2-(4,5-dimethyl-1H-imidazol-2-yl)phenol, it was also concluded that sterically bulky ligand is not a necessity for high coupling efficiency, while presence of potentially cyclometallating substituent moieties in the vicinity of the palladium centre may in fact destroy catalytic prospects.



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OC_19

Synthesis of Heteroleptic Tin N,O–β–Heteroarylalketonate Complexes, Their Properties and Reactivity

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In our work, we synthetized two novel heteroleptic alkoxidic compounds, containing tin (IV) coordinated with N,O–β–heteroarylalkenolatoligands, $Sn(4,5\text{–}Me\text{–}OxCHCOCF_3)_2(O^tBu)_2$ and $Sn(2\text{–}PyCHCOCF_3)_2(O^tBu)_2$:

Those compounds were fully structurally characterized and their properties and reactivity towards water and fluorination agents were investigated. Obtained results were compared with homoleptic tin (II) N,O–β–heteroarylalkenolato complexes already published in literature,$Sn(4,5\text{–}Me\text{–}OxCHCOCF_3)_2$[1] and $Sn(2\text{–}PyCHCOCF_3)_2$[2].

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OC_20

Spectroscopic studies of paramagnetic Group 5 organometallic complexes with an emphasis on Vanadium

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Complexes of vanadium are of interest for their relevance towards occurrences of vanadium in Nature [1], such as in the active site cofactor of the vanadium-containing nitrogenase found in the bacterial genus *Azotobacter* [2] and in marine organisms, such as ascidians (sea squirts) [3, 4]. Vanadium complexes are also of medicinal interest as insulin mimics [3, 5-7]. Vanadium is of fundamental interest as the earliest transition metal with significant redox activity (oxidation states ranging from −1 ($3d^6$, as in $[V(CO)_6]^-$) to +5 ($3d^0$).

Our interest is in vanadium in its paramagnetic oxidation states, namely V^{II} ($3d^3$, $S = 3/2$), V^{III} ($3d^2$, $S = 1$), and V^{IV} ($3d^1$, $S = 1/2$). The electronic structure of these states can be fruitfully investigated by electron paramagnetic resonance (EPR), particularly at high-frequency and -field (HFEPR), and magnetic circular dichroism (MCD) spectroscopies, as well as by magnetometry. We will describe case studies on representative members of each of these oxidation states, with an emphasis on organometallic complexes, as these have been less studied than more traditional coordination complexes. These include for V^{II}: vanadocene (Cp_2V) and $[(nacnac)V^{II}(OAr)]$; for V^{III}: $[(nacnac)V(N_3)(N(4\text{-}MeC_6H_4)_2)]$, nacnac = $[ArNC(CH_3)]_2CH–$, Ar = 2,6-$(CHMe_2)_2C_6H_3$; and for V^{IV} (as well as Nb^{IV} and Ta^{IV}), a series of ketimide [8] complexes: $[(V, Nb, Ta)^{IV}(N{=}C(^tBu)_2]$. Computational studies will also be described to complement the spectroscopic results.

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OC_21

Functional Schiff Base Complexes on The Peripheral Position of Co(II)Phthalocyanine as Oxidation Catalysts in Bleaching System

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Oxidation reactions are of great importance in the chemical industry. Molecular oxygen, hydrogen peroxide, sodium hypochlorite, ozone and organic peroxides are used as oxidants frequently in textile industry[1].

In particular, development of oxidants as bleaching agents in bleaching processes play a major role for the pulp and paper production, waste water treatment and industrial and domestic laundry for stain removing[2]. The main bleaching systems in oxidative bleach is based on destroy unwanted stains on the fabric in order to achieve the desired cleaning effect. In further studies, chemists have been trying to improve laundry bleaching as low as at 20 ^{o}C by using of catalyst due to decreasing of activation energy. The first introduced bleach catalyst was Mn-1,4,7-trimethyl-1,4,7-triazacyclononane (Mn-TMTACN) allowing to substitute 5% bleach activator (TAED: tetra acetyl ethylene diamine) usage by only 0.05 % of the catalyst in 1994[3].

To incorporate hydrogen peroxide/catalyst combination into detergent formulation is expected to reduce the amount of chemicals and the costs[4]. So far, several novel coordination compounds of salen, saltren, terpyridine-type ligands and triazole derivatives have been synthesized and tested, possessing significant potential in activating hydrogen peroxide in bleach process[5]. Several transition metal complexes were also reported for the mentioned intention.

In this study,we have developed a novel phthalocyanine derivative transition-metal catalyst for laundry cleaning applications. A series of phthalocyanine complexes in which two Schiff base Mn(III) and Co(III) complexes substituted are directly linked through oxygen bridges to the cobalt-phthalocyanine core were synthesized and characterized. We measured the oxidative bleach performance at room temperature in presence of H_2O_2 by online spectrophotometric method [6].

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OC_22

Organometallic Chemistry of Macrocycles and Cages

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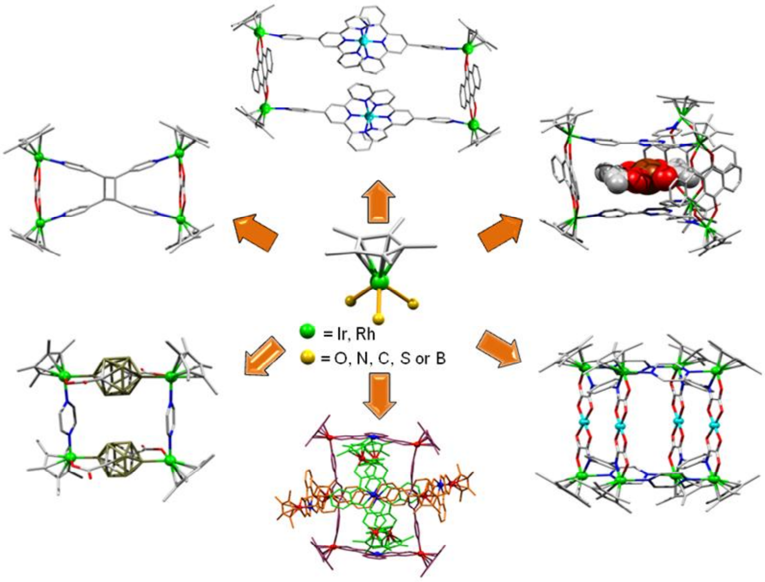
The construction of new inorganic and organometallic macrocycles and cages with interesting structural features and technologically useful functions have been topics of intense study with considerable potential.[1] One of the chief motivating factors to growth in this field is the development of new, functional and tunable donor building blocks that can bridge transition metals. Ideal building blocks should be easily accessible, exhibit high affinities toward transition metals, and possess facial coordination sites can undergo exchange reactions with various ligands.



Motivated by interest in supramolecular chemistry with organometallic half-sandwich complexes, we have initiated a new approach for preparing organometallic macrocycles via C-H and B-H activations with Terephthalate and dicarboxylate carborane.[2] We report herein an efficient method for synthesizing molecular macrocycles of half-sandwich iridium and rhodium complexes via C-H and B-H activation directed muticomponent self-assembly under mild condition.[3]

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M_01

CHARACTERIZATION OF Cu(II) AND Ag(I) COMPOUNDS WITH N,O DONOR LIGANDS AND APPLICATION FOR METALORGANIC LAYER DEPOSITION

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Study of copper(II) and silver(I) complexes of Schiff-base ligands has become a point of interest, due to their structural features and potential applications in various fields of technology and science. Compounds of copper(II) and silver(I) are known to display biological activity or luminescence and have been used in OLED devices.[1]

Isolated new ligands and Ag(I) complexes were characterized by ^{1}H, ^{13}C, ^{15}N NMR, IR, Uv-Vis absorption spectroscopy and the structure of ligands and complex solved by X-ray crystallography. Additionally, the fluorescence properties of the new compounds were measured in the Uv-Vis range. The new group of hybrid layers precursors based on Cu(II) and Ag(I) Schiff-base complexes were prepared.

Obtained complexes were mixed with ZnO nanoparticles and used for thin layers deposition by spin coating and dip coating methods on silicon. The new layers of complex/Si, complex/ZnO/Si and, ZnO/Si have been prepared and characterized by spectral (IR) and microscopic methods(SEM, AFM) powder X-ray diffraction. The fluorescence properties of new layers were studied in UV-Vis range.

Deposition processes parameters such as: time of coating and deposition speed was varied to get layers with the optimal different thickness and morphology. Thin layers of the silver(I) complexes were deposited on Si(111) by a spin- and dip-coating method and characterized with scanning electron microscopy SEM/EDS, atomic force microscopy (AFM) and fluorescence spectroscopy. Uniform layers were obtained optimal

Acknowledgements
Authors would like to acknowledge the financial support from National Science Centre (grant **2013/09/B/ST5/03509**).

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M_02

Zwitterionic derivatives of *closo*-borates as polar materials for LCD applications

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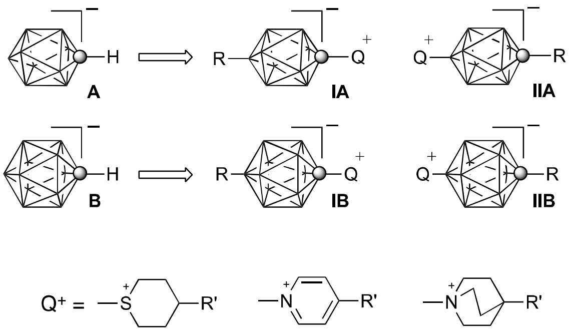
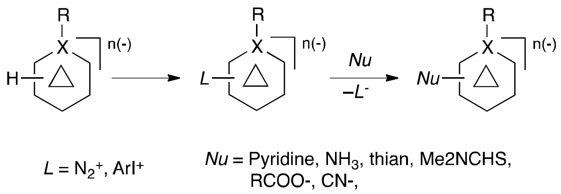
Zwitterionic derivatives of [*closo*-1-CB$_9$H$_{10}$]$^-$(**A**) and [*closo*-1-CB$_{11}$H$_{12}$]$^-$(**B**) of general structure **I** and **II** have substantial longitudinal dipole moment between 8–16 D and are of interest as high dielectric anisotropy ($\Delta\varepsilon$) additives to nematic liquid crystals for LCD applications [1].During the past several years, we have developed general synthetic methods, which include replacement of the dinitrogen (L = N$_2^+$) [2] and aryliodonium (L = ArI$^+$) [3] with nucleophiles, for the preparation of these zwitterionic derivatives containing pyridinium [4], sulfonium [1], and quinuclidinium fragments.The methods will be briefly discussed and examples of liquid crystalsand their properties will be presented.





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M_03

$R_2T_{3-x}Si_x$, new pseudo-binary phases and prospective magnetocaloric materials (R = Ce, Pr, Nd, Gd, Tb, Dy; T = Co, Ni).

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In the search for new magnetocaloric materials we investigate ternary intermetallic systems containing magnetic elements such as rare earth and transition metals. During these investigations, we have discovered a new solid solution: $Gd_2Co_{3-x}Si_x$, with $0.29 < x < 0.5$ which crystalizes in the orthorhombic *Cmce* space group with the La_2Ni_3-type structure [1]. The structure consists of a three-dimensional network of Gd-atoms forming channels running along the *a*-axis, and puckered two-dimensional layers of Co/Si-atoms with a Kagome-like structure stacked along the *c*-axis (*see Figure*). Interestingly, these ferrimagnetic phases have a tuneable Curie Temperature (T_C) between 280 and 338 K depending on the concentration of Co. We have extended the studyof this solid solution to other rare earths. In each case, the R_2T_3 pure binaries do not exist (x = 0), the phases being stabilised only by a partial substitution of Si for Co. The light rare earths such as Ce, Pr and Nd, have been shown to form the phase with Co and only after an annealing at low temperatures of around 500°C. Their compositions were studied by electron microprobe analysis and their magnetic properties were measured.

The same kinds of systems have been studied with nickel as the transition metal and new phases are only formed with the heavy rare earths Gd, Tb or Dy. We focused on the Gd compounds due to the high magnetic moment of gadolinium. By varying the starting composition we were able to obtain a $Gd_2Ni_{3-x}Si_x$ solid solution that undergoes a ferromagnetic transition around 96 K which barely changes with the composition (contrary to what was observed with the homologous solid solution with Co). Besides this, these materials have an appreciable magnetocaloric effect of 5 $J.K^{-1}.kg^{-1}$ at the Curie temperature for an applied field of 2 Tesla.

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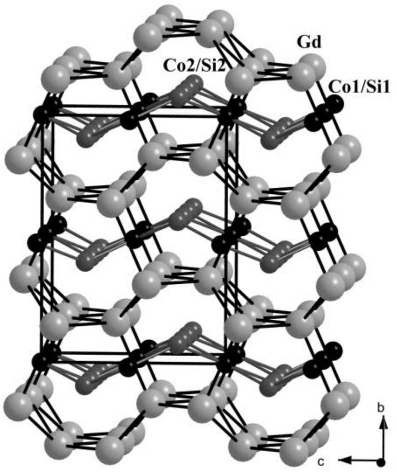

Figure. Crystal structure of $Gd_2Co_{3-x}Si_x$.

M_04

Phase relationships and complex crystal structures of ternary and quaternary selenides

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Although there has been worldwide competition in the search for improved thermoelectric materials, there is still huge demand concerning strategies for increasing the efficiency of thermoelectric generators. Solid-state synthesis often aims at the reduction of the phononic part of the thermal conductivity by hierarchical architecturing with a focus on the nanoscale. Newer approaches try to independently optimize the charge carrier concentration and mobility, aiming at the enhancement of the power factor ($S^2\sigma$; S = Seebeck coefficient, σ = electrical conductivity) by an independent increase of S.[1,2] To this end, band structures with multiple populated extrema are favorable. These often occur in materials with complex crystal structures.

Unusual and complex chemical compositions and complicated disordered crystal structures are often found in sulfide minerals like lillianite or boulangerite.[3,4] However, sulfides often lack sufficient electrical conductivity. The exchange of sulfur by selenium is a promising way towards new complex chalcogenides with reasonbable conductivities.[5]

Several new compounds were synthesized in the system Ag/Pb/Bi/Se. Their structures can be derived from the lillianite structure type. They differ with respect to the size of the distorted NaCl-type slabs which form herringbone-like arrangements characterized by chemical twinning. Single-crystal data of $Ag_2Pb_3Bi_4Se_{10}$, $Ag_5Pb_{14}Bi_{13}Se_{36}$ and $Ag_3Pb_2Bi_7Se_{14}$ (all of which crystallize in the space group *Cmcm*) are characterized by mixed site occupancies and positional disorder of atoms around mirror planes. Syntheses often yield mixtures of closely related compounds. Due to theis similarity, it is reasonable to use such mixtures for an initial thermoelectric characterization.

In the related system Cu/Pb/Bi/Se, homogeneity ranges in solid solutions series formally result from the replacement of $2Pb^{2+}$ by Cu^+ and Bi^{3+}. Both $Cu_2Pb_8Bi_{10}Se_{24}$ and $Cu_3Pb_6Bi_{11}Se_{24}$ crystallize in the lillianite structure type (space group *Cmcm*). Resonant X-ray scattering experiments with synchrotron radiation can reveal the Pb-Bi distribution on the cation sites. . Intriguing results for $Cu_{2-x}Se$,[6] which exhibits a high thermoelectric figure of merit due to pronounced dynamical disorder of copper atoms, inspired high-temperature synchrotron studies of $Cu_2Pb_8Bi_{10}Se_{24}$ single crystals.

The system Sn/Bi/Se is characterized by structures with varying dimensionality. Rock-salt-type phases and layered structured may coexist. In addition, there are ribbon-like struc-tures in new compounds like $(SnSe)_{\sim 2}Bi_2Se_3$, $(SnSe)_{\sim 1.5}Bi_2Se_3$ and $(SnSe)_{\sim 0.9}Bi_2Se_3$ whose structures correspond to members of the lillianite series, which proves the chemical variability of this structure type. The presence of multiply mixed atom positions in $(SnSe)_{\sim 2}Bi_2Se_3$ requires the combination of various methods to yield the cation and vacancy distribution .

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M_05

Alginate/chitosan core-shell materials with bioactive functionalities

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Since bacteria resistance depends on their aggregation in multicellular community of polysaccharides, proteins, metabolites, DNA *etc.* (biofilm) [1], there is an urgent need to develop innovative therapies that can disrupt the complex structure of the biofilm.The complexity of the biofilm makes difficult to overcome infection by the host defense system and/or reduce the efficacy of the antibiotics treatment. Proposed potential therapy includes applicationof hydrolytic enzymes, that can dissolve the polymeric matrix of the biofilm, and subsequently a well-known bacteria-sensitive antibiotic [2, 3].Polymeric core-shell materials constructed of alginate and chitosan are proposed as a new effectivebiomaterialsto fight down resistantpathogenic microorganismsproducingbiofilm.Alginate core was loaded with antibiotic, while enzyme increasing biofilm susceptibility to antimicrobial agentswas immobilized on chitosan shell.

Detailed studies on alginate/chitosan materialsconstructed of alginate core loaded with antibiotic (*i.e.* ciprofloxacin) and chitosan shell with immobilized lytic enzyme are presented: (*i*) size and zeta potential were studied by dynamic light scattering technique (DLS)andnanoparticle tracking analysis (NTA), (*ii*) particles shape and morphology were investigated with scanning electron microscopy (SEM), (*iii*) drug loading efficiency and cumulative drug release profiles were evaluated with UV-Vis spectrophotometry, (*iv*) enzymatic activity was measured for free and immobilized enzyme, (*v*) biological activity on human lung adenocarcinoma epithelial (A549cell line) and mouse fibroblast (NIT3T3 cell line)*in vitro* was determined by MTT assay, (*vi*) antibacterial activity was evaluated against two Gram-negative biofilm forming bacterial strains: *Pseudomonas aeruginosa* and *Escherichia coli*.

Acknowledgements: This work was supported by Polish Foundation of Science within POMOST project “Alginate/chitosan core-shell beads with bioactive functionalities” (POMOST/2013-7/7).

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M_06
Building Block Replacement in Metal-Organic Frameworks

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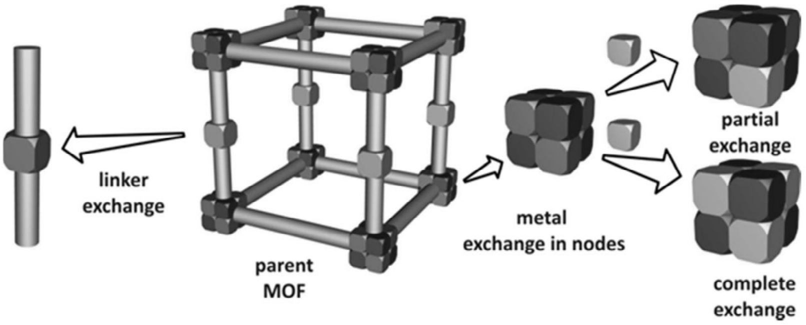
Metal-organic frameworks (MOFs) are a class of hybrid solid materials constructed of multitopic organic linkers and metal-ion-containing nodes/secondary building units (SBUs). It has been demonstrated recently that MOFs are not inert materials and might undergo the exchange of their building units. *Building block replacement* (BBR) is a methodology that relies on a non-destructive exchange of structural components of the MOF.[1]This methodology opens up a very broad strategy for the synthesis of isostructural MOFs and enables the introduction of various functionalities into MOFs. These post-synthesis exchange reactions involve: solvent assisted linker exchange (SALE), non-bridging ligand replacement, and transmetalation. In this presentation some selected examples of BBR approach will be presented.[2-4]



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[1] Deria, P.; Mondloch, J.E.; Karagiaridi, O.; Bury, W.; Hupp, J.T.; Farha, O.K., Beyond post-synthesis modification: evolutionof metal–organic frameworks via buildingblock replacement.*Chem. Soc. Rev.***2014**, 43 (16), 5896-5912.

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M_07

Conjugated Poly-ynes and Poly(metalla-yne)s for New Materials Applications

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Conjugated poly-ynes and poly(metalla-ynes) constitute an important class of fascinating materials in view of their potential applications in opto-electronic (O-E) devices such as photo cells, field-effect transistors, photo switches, light emitting diodes, liquid crystal displays and non-linear optics [1]. In poly(metalla-ynes) the photo-physical properties of transition metal fragments are coupled to those of the organic poly-ynes. For example,the incorporation of heavy metal fragment like bis(trialkylphpsohine)Pt(II) along the polymer backbone introduces large spin-orbit coupling to allow light emission from the triplet exited state. In this context, Pt(II) poly-ynes incorporating a wide variety of spacer groups have been widely investigated in our laboratory. Pt-poly-ynes are excellent triplet emitters. The triplet states in Pt-poly-yne can be investigated through, by direct optical excitation. Consequently, the Pt-poly-yne can serve as model compounds to study the basic photo-physical properties of conjugated hydrocarbons poly-ynes. The conjugated spacer is important in tuning the O-E properties of the Pt(II) poly-ynes. Azobenzene is a well-known photo-responsive chromophore that undergoes photo- and thermal induced geometric isomerizations [2]. Carbazoles generally act as electron donors and are widely used as blue light emitting materials [3].

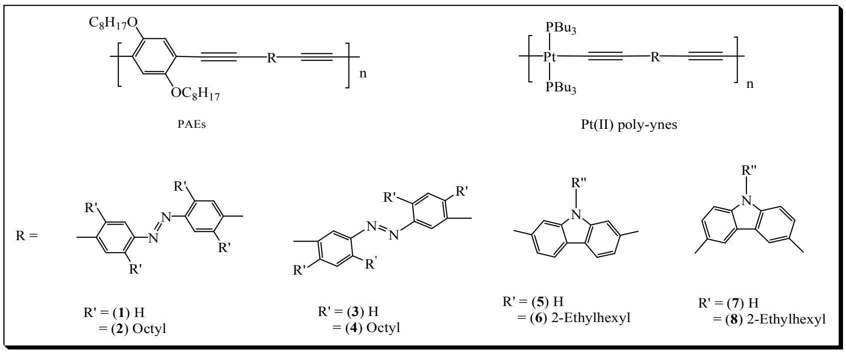

Chart 1. Organic poly-ynes and Pt(II) poly-ynes.

Herein, we present the synthesis, spectroscopic and structural characterization of some new poly(arylenethynylene)s (PAEs) and Pt(II) poly-ynes incorporating azobenzene and carbazole spacers (**Chart 1**). We also present the photo-physical properties of these new materials and explore their potential for application in O-E devices.

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M_08

New hydrides $RTXH_{1.5}$ (R = Rare-earth; T = Sc,Ti; X = Si,Ge)

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Among the *RTX* (*R* = rare-earth, *T* = transition metal, and *X* = Si, Ge) intermetallics some of them crystallize with the tetragonal CeFeSi-type structure or with the CeScSi-type one which is a derivative of the former one. In both structural types, layers of empty [Ce_4] tetrahedra are observed but the [FeSi] or [ScSi] layers are different. This layer is made of edge-shared [Si_4] tetrahedra filled by Fe in the CeFeSi-type and of [Si_4] square planes with Sc in the center in the CeScSi-type. It is noteworthy that some *RTX* ternaries such as *R*TiGe (*R* = Gd, Tb) present both structural types corresponding to the low- and the high-temperature forms.

It was shown in the past that, in the case of the CeFeSi-type structure, the [Ce_4] tetrahedra can be filled by hydrogenleading to CeFeSiH-type hydrides. This induces very interesting modulation of the physical properties [1]. More recently, it was also shown that it is possible to stabilize hydrides upon hydrogenation of the CeScSi-type intermetallics such as CeTiGe, CeScSi, NdScSiorTbTiGe. It also yields drastic modulation of the magnetic properties of the pristine compounds by reducing or destroying the magnetic ordering (see figure for the example of GdScGe)[2, 3]. For the first time the crystallographic positions of hydrogen (or deuterium) atoms have been determined from neutron diffraction data on $NdScSiD_{1.5}$ and $CeTiGeH_{1.5}$. The case of $NdScSiD_{1.5}$will be presented in details since the deuteration process was precisely studied by*in-situ* neutron diffractionexperiments.The role played by hydrogen in the chemical bonding is analyzed by band structure calculation.

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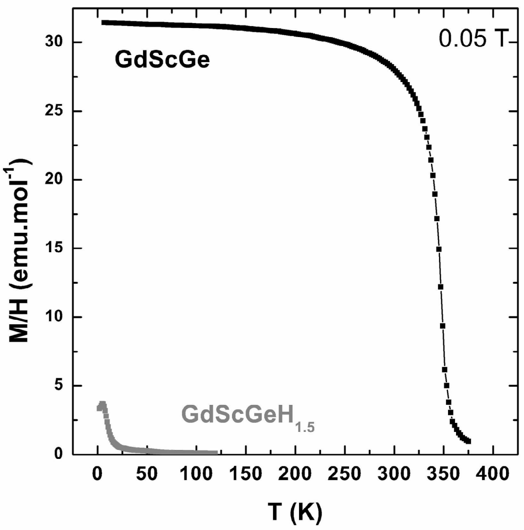

*Figur*e. Temperature dependence of the magnetization of GdScGe and $GdScGeH_{1.5}$.

M_09

Half-sandwich Iridium- and Rhodium-based Organometallic Architectures

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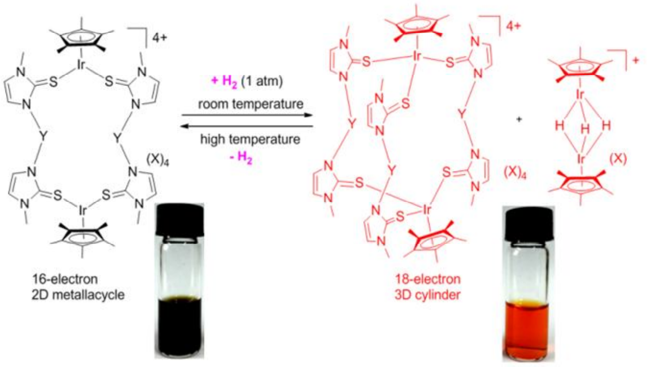
Over the last two decades, researchers have focused on the design and synthesis of discrete functional structures with particular shapes and sizes.Synthetic methodologies for the construction of discrete self-assemblies have also been extensively developed. We entered this area with a desire to design specific assemblies by using half-sandwich metal complexes as building blocks. The fragments of iridium and rhodium with organic Cp*π-ligands have also become a key component of our molecular design [1-3].



Recently, we have found that H_2 can initiate unusual transformations between organometallic assemblies. If the Cp* group acts as a monodentate ligand, then the reversible constitutional switching between the two distinct complexes is accompanied by reversible changes in the coordination mode of the metal center from triangular to tetrahedral coordination geometries. The present system reversibly provides a foundation on which to develop organometallic switching systems that can be triggered by hydrogen.

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M_10

Integrated platforms for the discovery of inorganic nanosized clusters

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The discovery of new molecules, materials and reactions is essential to the scientific progress and to develop new applications from fundamental research. Despite this, research methods are generally manual, slow and cumbersome, thus limiting the discovery to application pathway. Here, a set of integrated and modular platforms designed for the discovery inorganic nanosized clusters and nanomaterials will be presented [1-3]. The incorporation of in-line analytics enables real-time characterization and self-optimization of the reaction conditions,[4] increasing the experimental throughput, thus reducing the number of experiments required to discover new compounds. The application to discover polyoxometalates based on tungsten and molybdenum oxide will be presented, being the first compounds discovered in fully automated synthetic platforms.

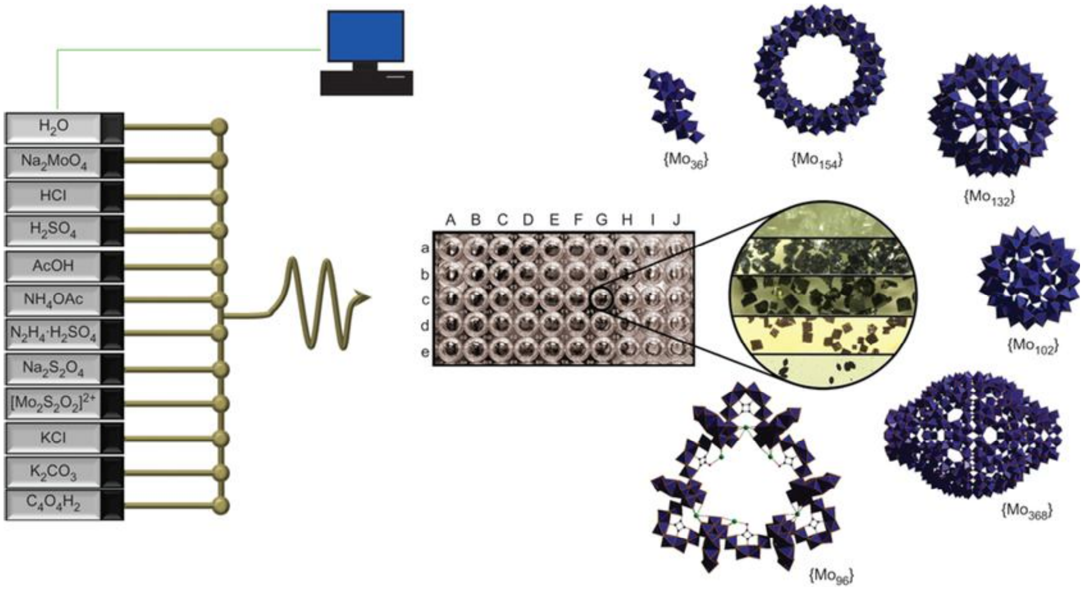

Figure 1. Schematic representation of a continuous-flow synthetic platform designed for th exploration of complex reaction parameter spaces and for the discovery of new compound (from ref. 2)

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M_11

Synthesis, characterization, antimicrobial studies and corrosion inhibition potential of 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane

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Macrocyclic complexes belonging to transition group metal ions have received tremendous attention for many years due to their characteristic unique potential to act as antifungal, antitumor [1], antibacterial [2], antiviral, antifertile, anticarcinogenic and anticancer [3] agents. Study on corrosion inhibition potential and antibacterial activity of 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane ligand is uncommon.

The synthesis of 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane ligand was carried out by the demetallation of the prepared 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecanenickel(II) complex.

The characterization of the ligand and the nickel(II) complex was carried out using the UV-Vis, FT-IR, EDX, MS, NMR and TGA techniques. The structure was confirmed by the methods used and the TGA showed the mode of thermal stability and decomposition. The ligand displayed three steps losses upon dynamic heating at 1200 °C.

The biological activity of the ligand against two bacterial strains namely *Staphylococcus aureus* and *Enterococcus* species was also studied. The result shows the ligand to be potentially active towards the bacterial strains.

The corrosion inhibition potential of the ligand was studied using Potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The PDP and EIS showed that the %IE increases as the concentration increased. The CV provided insight into the kinetics and the effect of scan rate on peak currents.

The ligand was found to be a mixed-type inhibitor. The phenomenon of chemisorption mechanism was proposed from the thermodynamic parameters obtained. The experimental result fits the Langmuir adsorption isotherm.

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NN_01

Catalytic Bimetallic Nanoparticles For Green Chemistry

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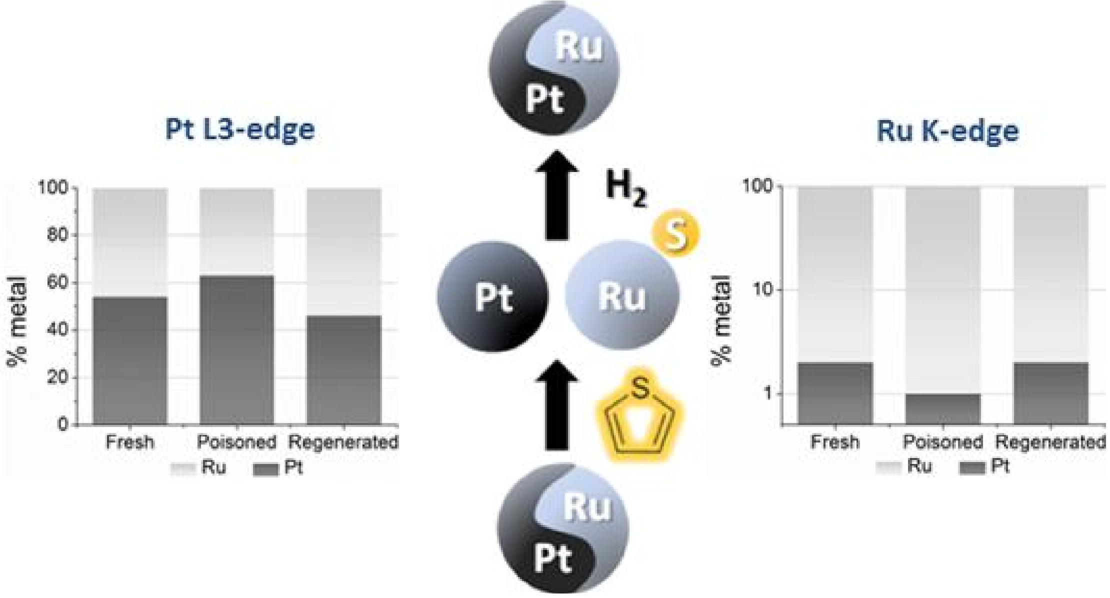
We report studies on the application of bimetallic nanoparticles for biomass conversion and hydrogen storage. In the first application, supported bimetallic Pt-Ru alloyed nanoparticulate catalysts, which show improved sulfur tolerance for a model aqueous phase reforming reaction, were investigated using X-ray absorption spectroscopy (XANES and EXAFS) at the Pt L_{III} and the Ru K-edges, before and after poisoning with a sulfur-containing species (as thiophene). Preliminary EXAFS investigations confirmed the alloyed character of the bimetallic catalysts, and further experiments clearly showed changes to the Pt/Ru bonding environments induced by sulfur poisoning, *i.e.* that the metal partially dealloyed. However, after regenerating the poisoned catalysts under pure H_2 at 300 °C, the Pt-Ru alloy appeared to be reformed. These results are consistent with catalytic and XRD investigations, and with a sulfur and hydrogen spillover *in-situ* self regeneration mechanism.

In a second application, aimed at facilitating the drive towards ever lower energy processing, robust bimetallic aluminosilicate-supported Pt-Ru catalysts that can operate under atmospheric conditions have been developed for the rapid room temperature hydrogenation of aromatics (toluene and tetralin) at 1 atm H_2. The toluene/methylcyclohexane couple has the added interest of being a promising cyclic hydrocarbon combination for the storage of hydrogen.

The easily handled air-stable catalysts were prepared using the incipient wetness method and characterised by ICP-AES, XRD, TEM as well as nitrogen sorption measurements. Compared to their monometallic counterparts, the bimetallic catalysts displayed significantly higher turn-over-frequencies (TOFs), consistent with a synergistic relationship between platinum and ruthenium



EXAFS of alloying/dealloying of bimetallic nanoparticle catalysts during desulfurization.

NN_02

Real-time imaging of atom migration and nanocrystallisation on multi-doped graphenic surfaces

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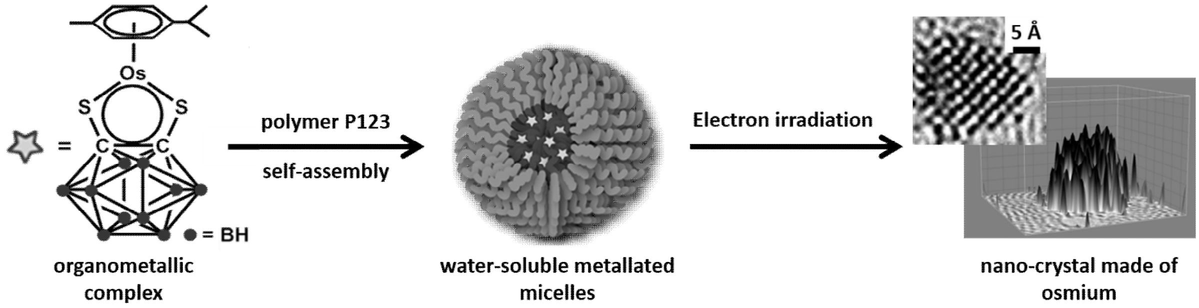
Nanoscopic objects are more and more tailored for use as materials of the future, for example in medicine, industrial manufacturing, construction, and space exploration[1,2]. The dynamics of formation of such objects are still to be fully understood,and the formation of nanoscopic crystals and their growth-control at the level of individual atoms remains a challenge [3].

We discuss a new general method for the fabrication of multi-heteroatom-doped-graphenic matrices decorated with very small and defined Ångstrom-sized, 3D-metal crystals using aberration-corrected transmission electron microscopy[4]. This technology allows experimental observation of crystal assembly from single metal atoms and captures the dynamics of metal cluster formation in real space with atomic precision. This technology not only allows the production of Ångstrom-sized homo- and hetero-crystals, highly novel materials with potentially useful and unusual properties, but also provides new insight into the dynamics of nanocrystals and pathways for their assembly from single atoms.



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NN_03

Specific Interactions between Noble Metal Nanoparticles and Inorganic Mixed-Metal Oxide Supports in Efficient Electrocatalytic Oxidations of Organic Fuels

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Recently, there has been growing interest in development of electrochemical energy conversion systems utilizing small organic molecules as alternative technologies to hydrogen based fuel cells. Such organic molecules as formic acid, methanol, dimethyl ether or ethanol can be ideally oxidized to carbon dioxide. But realistically the reactions are rather slow at ambient conditions. Obviously, there is a need to develop novel electrocatalytic materials.

Platinum has been recognized as the most active catalytic metal towards oxidation of ethanol at low and moderate temperatures. But Pt anodes are readily poisoned by the strongly adsorbed intermediates, namely by CO-type species, requiring fairly high overpotentials for their removal. To enhance activity of Pt catalysts towards methanol and ethanol oxidation, additional metals including ruthenium, tin, molybdenum, tungsten or rhodium are usually introduced as the alloying component. More recently it has been demonstrated that catalytic activity of platinum-based nanoparticles towards electrooxidation of ethanol has been significantly enhanced through interfacial modification with ultra-thin monolayer-type films of metal oxo species of tungsten, titanium or zirconium. Also gold in combination with platinum has been demonstrated to produce novel high performance bimetallic catalysts.

We pursue a concept of utilization of mixed metal (e.g. zirconium/tungsten or titanium/tungsten) oxide matrices for supporting and activating noble metal nanoparticles (e.g. Pt, Pt-Ru) during electrooxidation of methanol, ethanol, formic acid and dimethyl ether. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account possibility of specific interactions of noble metals with transition metal oxide species as well as existence of active hydroxyl groups in the vicinity of catalytic noble metal sites.Among useful characteristics of metal oxides and related systems are the following: they can generate –OH groups at low potentials that induce oxidation of passivating CO adsorbates (e.g. on Pt); they can potentially break C-H bonds (e.g. by hydrogen tungsten oxide bronzes); and they can possibly weaken C-C bonds during ethanol oxidation (e.g. through changes of the electronic properties of Pt). There have been numerous reports in this area, but further research is still necessary to elucidate exact enhancement mechanisms that are operative.

NN_04

Synthesis, Characterization, Crystal structure of Cadmium-isonicotinate Metal Organic frameworks and its adsorptive removal of Methyl orangefrom Aqueous Solution

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The new cadmium(II) isonicotinate metal organic framework $[CdC_{12}H_{10}N_2O_5].C_4H_7O$ was synthesized by reaction of cadmium acetate with isonicotinic acidunder reflux in a 1: 1 molar ratio. The compound was characterized by elemental analysis, Infra-red and UV-Visible spectroscopies, SEM and Single crystal X-ray diffraction.

The crystal is orthorhombic, space group p b c a, a= 12.2494(10) Å, b = 15.4646 (13) Å, c= 18.8445 (17) Å, V = 3569.8 (3) Å^3, Z = 8. The coordination about the cadmium is pentagonal bipyramidal,(7-coordinate geometry) involving four carboxylate oxygen atoms from two isonicotinate groups and two pyridine nitrogen atoms from two isonicotinate groups and a water molecule in the axial position.

The MOF (Cadmium-isonicotinate $[Cd(INA)_2]$.ISB (ISB =Isobutanol) was studied for the adsorptive removal of methyl orange (MO) from Aqueous solution. The effect of operating parameters such as constant time, initial solution pH, initial dye concentration and temperature on the adsorption of MO were also studied [1,]. The experimental data can be best described by the Langmuir isotherm model [2,3] and revealed the ability of $[Cd(INA)_2]$.ISB to adsorb 166 mg of methyl orange per gram of adsorbent at 25^{0}C , pH 7.0 with adsorbent dosage of 0.130 g L^{-1} . The kinetic of methyl orange adsorption followed a pseudo-second-order kinetic model, indicating the co-existence of physisorption and Chemisorption, with intraparticle diffusion being the rate controlling step.

These results suggested that $[Cd(INA)_2]$ can be used as an adsorbent for removal of MO from aqueous solution.

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NN_05

Dependence of defect species and morphology on composition and dopant type of $Ce_{1-x}RE_xO_{2-y}$

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Many investigations are focused on ceria based materials because of their crystal structure (fluorite type) which easily tolerates large reversible oxygen extraction from the lattice [**1, 2**]. Doping ceria with lanthanide or transition metal ions can be used to tune or enhance its specific properties. It also improves thermal stability of nanocrystalline ceria against sintering [3, 4]. In this work shape-controlled $Ce_{1-x}RE_xO_{2-y}$ (RE=Er, Gd, Tb, Pr) were produced by microwave assisted hydrothermal treatment. The effect of the different rare earth dopants and its content on the morphology, phase composition and defect species of the resulting material was studied by XRD, SEM-EDS-EBSD, TEM and Raman spectroscopy.

The lattice parameters of the rare earth doped ceria were different from that of pure CeO2 already for low doping level(x=0.01). The change of lattice parameters resulted from the substitution of cerium by rare-earth cations, which may have different ionic radius and/or different oxidation state. Raman spectroscopy showed that oxidation state of Tb and Pr in $Ce_{1-x}RE_xO_{2-y}$ depends on their doping level: for x<0.1 are mainly Tb^{3+}/Pr^{3+} with small portion of Tb^{3+}/Pr^{3+} cations were present, and vise-versa for x>0.1. The oxidation states of Gd^{3+}(0.105nm) and Er^{3+}(0.1004) were different than that of Ce^{4+}(0.097 nm) but also they have larger ionic radius which means two defect sites were observed for all doping levels .

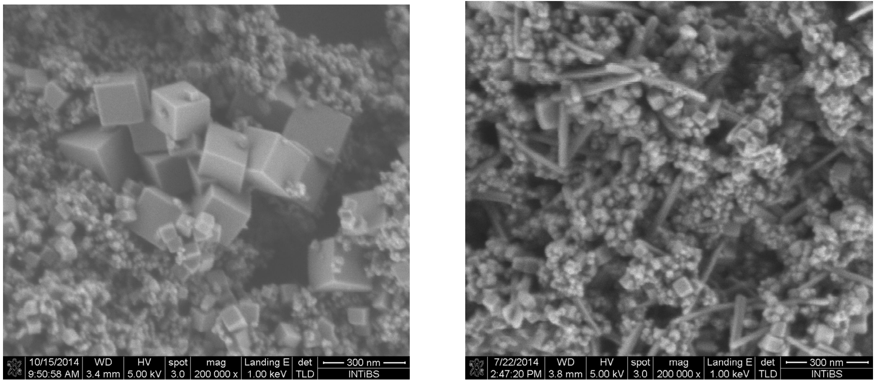

Fig.1. Morphology of $Ce_{1-x}Tb_xO_{2-y}$ (a)x=0.05,(b) x=0.5

Furthermore morphological differences were observed for different doping levels: nanocubes of the mixed Ce-RE oxide with fluorite structure and bimodal size distribution were formed when the level was low (Fig.1 (a)). At higher levels (x > 0.3) rod-like particles of RE hydroxide were also detected (Fig.1 (b)). The latter is in agreement with XRD results where second phase of RE hydroxide appeared. Mean size of the particles was strongly depends on the rare-earth dopant and concentration.

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NN_06

A nano-capacitor based on doped graphene layers composed with boron nitride–graphene as an insulator

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Graphene can be used in the field of electronics, capacitors, superconductors, in batteries and diodes. In this study, we have shown the model of a nanoscale dielectric capacitor composed of a few graphene layers separated by an insulating medium containing a few h-BN layers. It has been exhibitedthe dopants in the graphene plates increase the capacitance of capacitors and they are suitable for hetero-structures of the dopant-G/hBN/dopant-G capacitor. we have specifically studied the dielectric properties of different h-BN/graphene of G/**h-BN**/G (GBN) including hetero-structures, BG/h-BN/BG (BGBN), AlG/h-BN/AlG (AlGBN), MgG/h-BN/MgG (MgGBN) , and BeG/ h-BN/BeG (BeGBN) stacks for the monolayer of dielectrics. Moreover, we studied the multi dielectric properties of different $(\text{h-BN})_n$/graphene hetero-structures of BG/ $(\text{h-BN})_n$/BG [BG $(\text{BN})_n$].

SC_01

Dinuclear Metallacycles with Single Anion Bridges: Unusual Magnetic and NMR Properties

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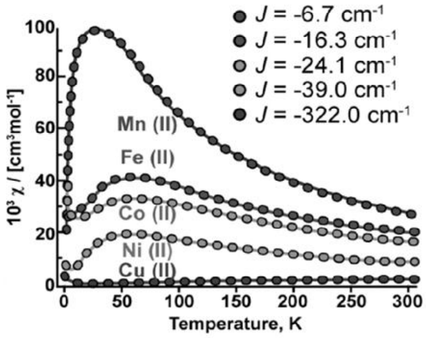
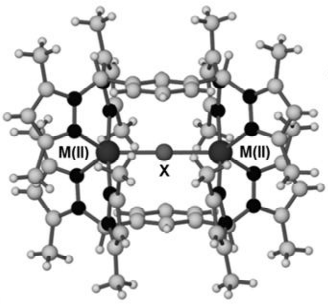
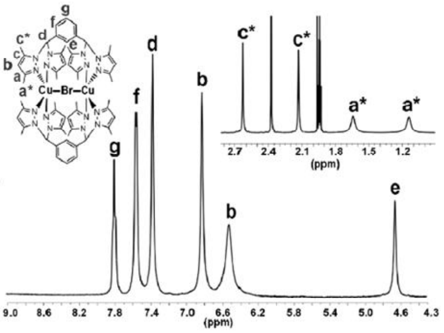
[2]Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland
[3]National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA.

We have synthesized a series of dinuclear metallacycles supported by the m-bis[bis(1-pyrazolyl)methyl]benzene, $\mathbf{L}_m$, or*m*-bis[bis(3,5-dimethyl-1-pyrazolyl)methyl]benzene, $\mathbf{L}_m^*$, ligands of the type $[M_2(\mu\text{-}X)(\mu\text{-}\mathbf{L}_m)_2](ClO_4)_3$ (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) (X = CN^-, F^-, Cl^-, OH^-, Br^-),where the metal centers are in a distorted trigonal bipyramidal geometry [1, 2, 3]. These complexes represent the first extensive series of dinuclear complexes with a linear or nearly linear M(II)–X–M(II) bridging arrangement. They show strong antiferromagnetic magnetic properties and provide a unique opportunity to determine the impact of systematic chemical and structural changes on these properties, both in the solid state (SQUID) and solution (NMR), while holding the overall structure constant. We have shown that the complexes retain the solid state structure in solution, but that $[Zn_2(\mu\text{-}OH)(\mu\text{-}\mathbf{L}_m)_2](ClO_4)_3$is dynamic, undergoing an unusual rearrangement process.







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[1] Reger, D. L.; Pascui, E. A.; Smith, M. D.; Jezierska, J.; Ozarowski, A.“Syntheses, Structural, Magnetic and EPR Studies of Monobridged Cyanide and Azide Dinuclear Copper(II) Complexes: Antiferromagnetic Superexchange Interactions,”*Inorg. Chem.* **2015**, *54*, pp 1487-1500.

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SC_02

Metallacryptates or Metallacoronates– Influence of Coordination number and Templates onProduct Formation

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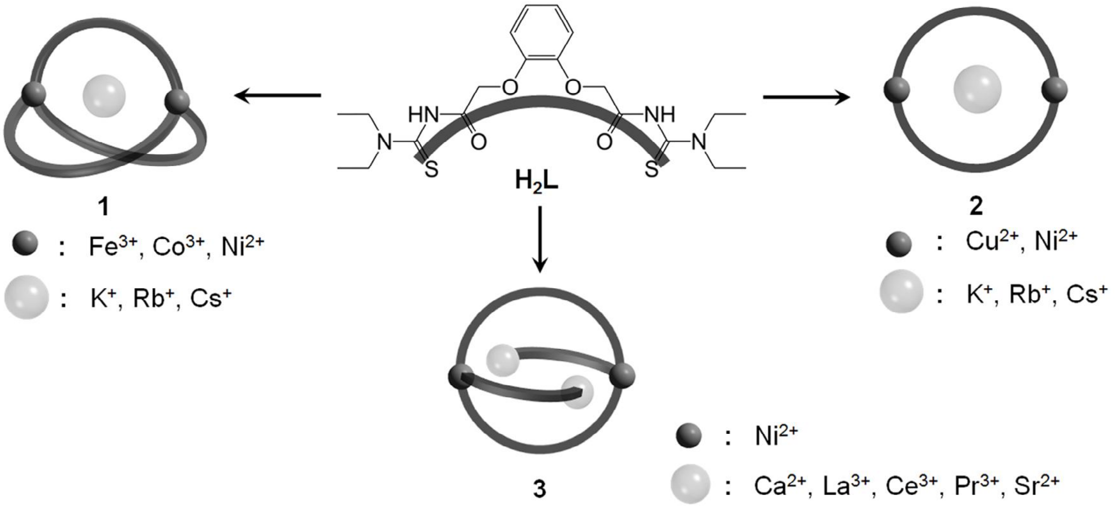
The formation of discrete supramolecular assemblies based on coordinative metal-ligand bonds is an area of great interestin supramolecular chemistry. A wide variety of aesthetic structures with predetermined shapes, sizes and functionalities have been designed through self-assembly guided by chemical information being encoded in the subunits [1-3].
Here, we report the controlled formation of two-membered metal cryptates**1**, and coronates**2**,**3**from one-pot reactions ofnovel catechol-spaceredaroylbis(thioureas) **H_2L**with various metal ions.



Scheme 1.*Different metallatopomersfrom the versatileligand**H_2L***

Reactions of the potentially bis(bidentate) ligand with hexacoordinate metal ions such as Fe^{3+} orCo^{3+}in the presence of alkali metal ions generate{2}-metallacryptates(**1**)of the composition$[M^{I}\subset(M^{III}_{2}L_{3})](PF_{6})$ ($M^{I} = K^{+}, Rb^{+}, Cs^{+}$; $M^{III} = Fe^{3+}, Co^{3+}$). On the other hand, the {2}-metallacoronates$[M^{I}\subset(Cu^{II}_{2}L_{2})](PF_{6})$ (**2**) result from the combination of the H_2L with thetetracoordinateCu^{2+} ion.Both types of metallatopomers $M^{I}[M^{I}\subset(Ni^{II}_{2}L_{3})]$ (**1**) and$[M^{I}\subset(Ni^{II}_{2}L_{2})](PF_{6})$ (**2**) can be isolated with Ni^{2+} ions depending on the reaction conditions applied.Interestingly, the decrease of the size of the guest ionin the Ni^{2+} metallacoronates inducesthe formation of compounds**3** with a lariat ether-typestructure. They provide more donor atoms and a largercavity to encapsulate two guest ions.
The novel compounds show interesting magnetic, optical and redox properties.

Literature:

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SC_03

Metal azo-complexes based on heterocyclic derivatives of pyrazolones

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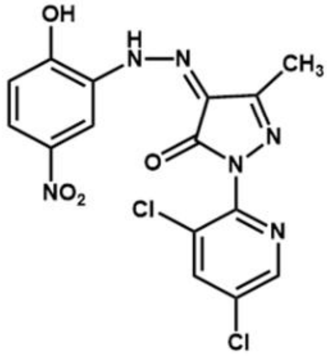
[1]Peoples' Friendship University of Russia, Moscow, Russia
[2]Moscow State University of Design and Technology, Moscow, Russia
[3]Al Muthanna University,Samawah, Al Mutanna, Iraq

Novel ligands based on heterocyclic derivatives of azopyrazolone and more than 50 their metal complexes were synthesized and studied with a set of methods: elemental analysis, IR, UV-VIS, ^{1}H NMR spectroscopy, ESR, X Ray analysis, quantum chemical modeling (DFT B3LYP):



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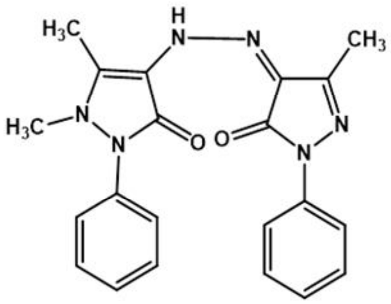

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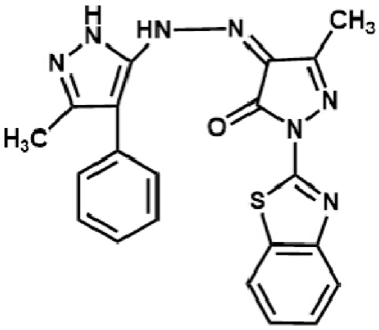

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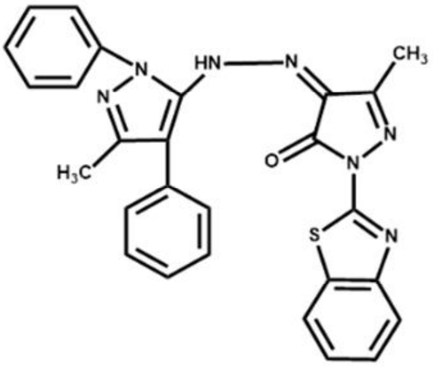

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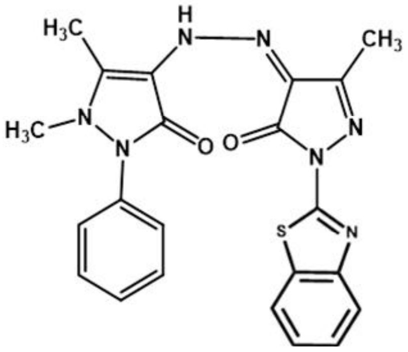

5

Crystal and molecular structures of the ligands and their metal complexes are described by the X-Ray analysis and quantum chemical modeling methods. The problems of tautomeric equilibria and competing coordination are described.

The equilibria in ethanol aqueous solutions at ionization of the ligands and complex formation were studied by the spectrophotometric titration; the ionization constants of the ligands and the formation constants of the complexes were calculated. The correlations of the stability constants values *vs* the physical characteristics of the metal ions were described.

The organic molecules and their metal complexes were tested as colorants for wool and polyamide fibers. The fungicide activity of copper complexes was also detected.

SC_04

Tuning triphyrins(*n*.1.1) properties with coordination

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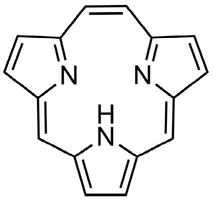
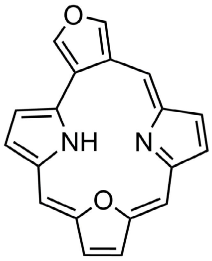
Triphyrins(***n***.1.1) (n = 1-6, see below) present a new aspect of porphyrinoid chemistry explored toward coordination abilities[1] or electronic properties.[2] A significantly modified shape, and in consequence also the π-conjugation (electron distribution) results in several possibilities creating new paths for exploration. The number of available structures presents a variety of motifs creating new coordination environments or opening several paths for the research – i.e. chiral agent.[3] On the other hand the aromatic delocalization of triphyrins(*n*.1.1) was not yet explored and the research concentrates on unmodified electron circuit (14π or 18π) focusing on the linear and nonlinear optical properties.

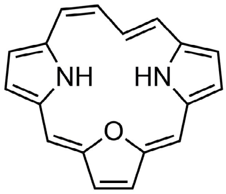
1. triphyrin(1.1.1)



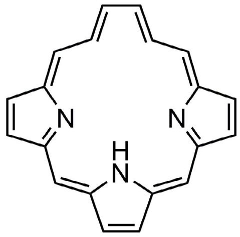
2. triphyrin(2.1.1)



3. triphyrin(3.1.1)



4. triphyrin(4.1.1)



6. triphyrin(6.1.1)

The **2.1.1** structural motif (i.e. **2**) is, along with the boron(III) triphyrin(1.1.1) (**1**) the most explored construction that opens outstanding opportunities for exploring the mentioned properties, nevertheless the number of synthetic paths leading to those intriguing macrocycles is still rather limited. The synthetic aspects for the formation of heterotriphyrins(***n***.1.1) will be presented. The rational and general approach for formation of 2.1.1 structures,[4] along with the coordination induced the electronic properties modifications of final skeletons[4,5] including aromaticity switching and controlling the fluorescence behaviour will be discussed.

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SC_05

Multicopper(II) Cores and Metal–organic Networks: from Aqueous Medium Self-assembly to Applications

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Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Portugal.
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The present contribution will summarize our recent research on the application of aqueous medium self-assembly methods towards the design and synthesis of a wide variety of mixed-ligand multicopper(II) coordination compounds derived from different aminoalcohols and aromatic carboxylic acids as building blocks [1, 2]. The obtained products vary from the discrete 0D multicopper(II) complexes of diverse nuclearity to different 1D and 2D coordination polymers or 3D metal-organic frameworks. The presentation will focus on the following main topics.

(1) Synthetic aspects, structural, supramolecular and topological features of the self-assembled aminoalcoholate multicopper(II) compounds.
(2) Host-guest and magnetic properties.
(3) Application of the obtained multicopper(II) cores as bio-inspired catalysts or catalyst precursors for (i) the mild oxidation of alkanes (typically cyclohexane as a model substrate with industrial relevance) by hydrogen peroxide into alcohols and ketones, (ii) the hydrocarboxylation of gaseous and liquid C_n alkanes, by carbon monoxide, water and potassium peroxodisulfate, into the corresponding C_{n+1} carboxylic acids, and (iii) the selective oxidation of various alcohols by air or peroxides to the corresponding carbonyl compounds.

Acknowledgment. This work was supported by the Foundation for Science and Technology (project PTDC/QUI-QUI/121526/2010), Portugal.

Literature:

[1] Dias, S.S.P.; André, V.; Kłak, J.; Duarte, M.T.; Kirillov, A.M. Topological diversity of supramolecular networks constructed from copper(II) aminoalcohol blocks and 2,6-naphthalenedicarboxylate linkers: self-assembly synthesis, structural features, and magnetic properties. *Cryst. Growth Des.* **2014**, *14*, 3398-3407.

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SC_06

High-Field EPR Spectroscopy of Trinuclear Copper(II) Complexes

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Compared to the dinuclear copper complexes, the trinuclear systems present a much more complicated picture of the metal-metal interactions which sometimes result in interesting phenomena like the “spin frustration” in the antiferromagnetic triangular arrangements [1]. On the other hand, the linear compounds [2, 3], particularly when ferromagnetic [3], are especially well suited for the high-field EPR spectroscopy, as they exhibit large zero-field splitting of the ground quartet state (S=3/2).

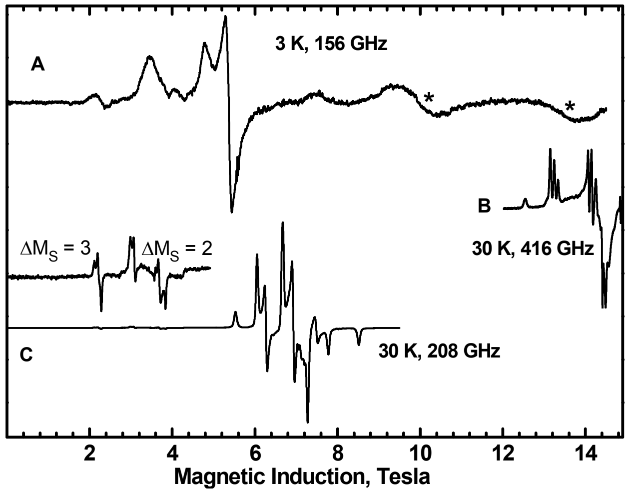

Fig. 1. HF EPR spectra of a frustrated system (A) [1]; an antiferromagnetic linear complex (B) [2] and a ferromagnetic linear complex (C) [3].

In this work, anomalous g values ($g < 1$) were observed in the ground $S = 1/2$ state of some spin-frustrated systems (signals marked with * in plot A, Fig 1) [1]. Spectra due to a ground $S=1/2$ state as well as to the excited $S=1/2$ and $S=3/2$ states were seen in a linear antiferromagnetic trimer (plot B in Fig 1) [2]. Several ferromagnetic centrosymmetric complexes of a general formula $[Cu_3(RCOO)_4(tea)_2]$ (tea = triethanolamine) were prepared and investigated by HF EPR and magnetic methods.

For a full interpretation of the EPR spectra and magnetic susceptibility data of the latter compounds, the spin Hamiltonian had to be used in a form

$$\hat{H} = J_{12}(\hat{\mathbf{S}}_1 \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2 \hat{\mathbf{S}}_3) + J_{13}\hat{\mathbf{S}}_1 \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_1\{\mathbf{D}_{12}\} \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2\{\mathbf{D}_{12}\} \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_1\{\mathbf{D}_{13}\} \hat{\mathbf{S}}_3 +$$

$$\mu_B B\{\mathbf{g}_1\} \hat{\mathbf{S}}_1 + \mu_B B\{\mathbf{g}_2\} \hat{\mathbf{S}}_2 + \mu_B B\{\mathbf{g}_1\} \hat{\mathbf{S}}_3$$

where $\{\mathbf{D}_{ij}\}$ are the zero-field splitting tensors for respective pairs.

The g matrices of interacting ions as well as the zero-field splitting tensors were determined. The EPR-derived parameters were used in the interpretation of the magnetic susceptibility data and helped to prove the absence of intermolecular interactions.

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[1] Vasylevskyy, S. I.; Senchyk, G. A.; Lysenko, A. B.; Rusanov, E. B.; Chernega, A. N.; Jezierska, J.; Krautscheid, A.; Domasevitch, K. V.; Ozarowski, A., 1,2,4-Triazolyl-Carboxylate-Based MOFs Incorporating Triangular Cu(II)-Hydroxo Clusters: Topological Metamorphosis and Magnetism. *Inorg. Chem.* **2014,** 53, 3642-3654.

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[3] Paper in preparation, **2015**.

SC_07

Alkynyl-phosphine Au^I and Au^I-Cu^I complexes based on phosphine template: some features of the photophysical properties.

Grachova E.V.[1], Shakirova Yu.R.[1], Strelnik I.D.[2]Koshevoy I.O.[3], Tunik S.P.[1]

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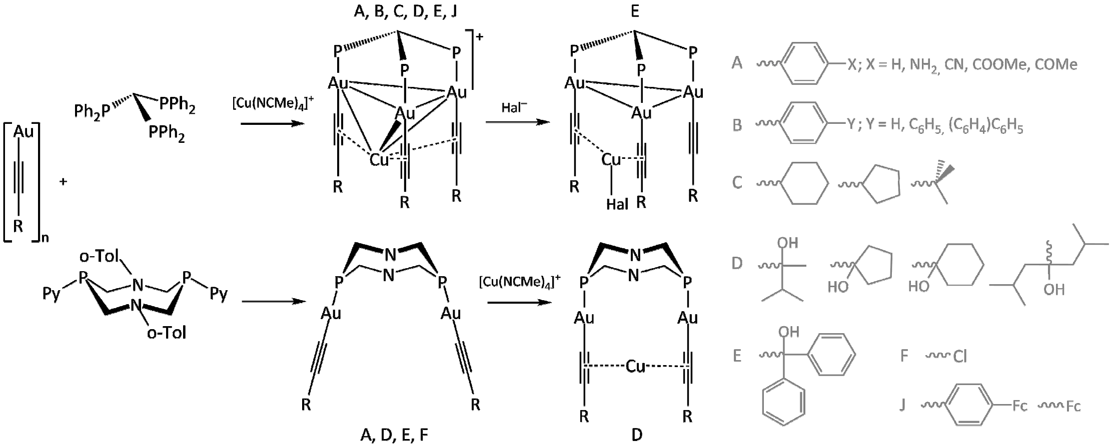
[2]*A.E. Arbuzov Institute of Organic and Physical Chemisty of Kazan Scientific Center of Russian Academy of Sciences, Kazan, Russia*
[3]*Department of Chemistry, University of Joensuu, 80101, Joensuu, Finland*

Several series of the Au^I-Cu^{I}alkynyl-phosphine complexes stabilized by two different phosphine templates were obtained [1−4]. All complexes show luminescence in solution and/or in the solid state and them photophysical properties have been systematically investigated. It has been found that the luminescence of all complexes depend dramatically on alkyne ligands nature.



The main point of the story is the fact that several complexes presented demonstrate distinct luminescence vapochromic response to volatile organic compounds (VOC). For the same cases a huge emission band shifting from deep red to green range of spectra has been found. The phenomenon observed can be possible explained by solid state recrystallization of the complex after VOC molecule absorption. This hypothesis is supported by the single crystal X-Ray analysis where different packing and relative position of solvent and complex molecules were observed.

The authors greatly appreciate financial support of SPbSU research grant 0.37.169.2014; RFBR grant 14-03-32077. The work was carried out using equipment of the Centers for Magnetic Resonance, for X-ray Diffraction Studies, for Chemical Analysis and Materials Research, for Optical and Laser Materials Research of SPbSU.

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[3] Shakirova J. R.; Grachova E. V. et al., Luminescent heterometallic gold-copper alkynyl complexes stabilized by tridentate phosphine. *Dalton Trans.***2012**, 41, 2941-2949.
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SC_08

A series of novel copper(I) hydrotrispyrazolylborate complexes for ethene detection

Tom van Dijkman[1], Maxime Siegler[2] and Elisabeth Bouwman[1]
[1]Leiden institute of chemistry, Leiden University, Metals in Catalysis, Biomimetics and Inorganic materials, The Netherlands. email: tomvandijkman@chem.leidenuniv.nl
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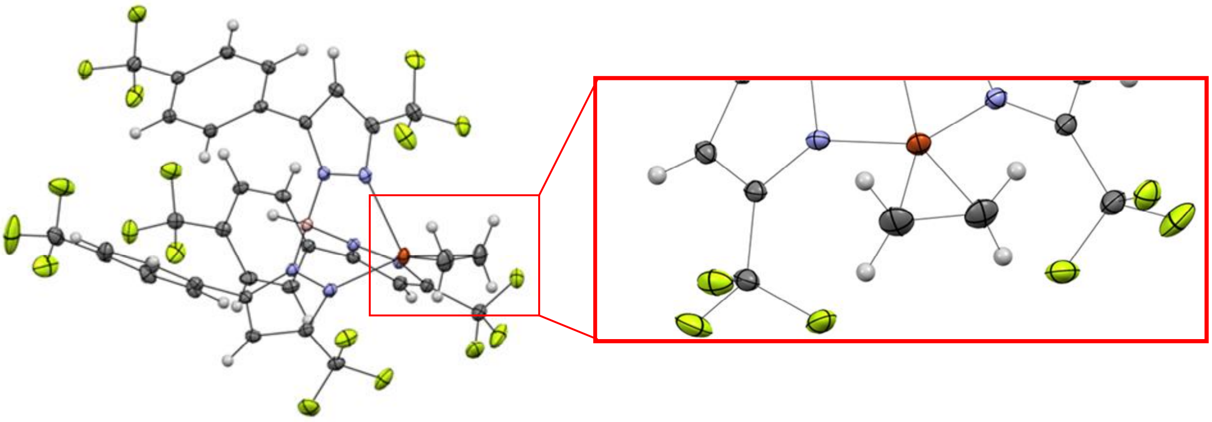
Ethene is everywhere; it's used industrially to produce many useful products like polyethylene and ethylene glycol; it's also emitted by motor vehicles due to incomplete combustion of hydrocarbons and it's present naturally in the atmosphere as a plant hormone. Ethene causes susceptible plants to undergo various changes such as the ripening of fruit; flower petals falling off; the formation of brown spots and the alteration of shadow-avoiding behavior.[1] Quantitative analysis of ethylene levels in transport of fruits, vegetables and flowers is at present not economically viable because current state-of-the-art sensors require too much space and electricity and are too costly to be shipped with the produce.

The aim of my project is to develop sensitizing compounds to be integrated into small, affordable sensors. These sensitizers are copper scorpionate complexes that can reversibly react with low concentrations of ethene to temporarily form ethene complexes. These complexes mimic the copper-containing proteins that bind ethylene in natural systems such as the ETR-1 (Ethylene Response 1) protein found in Arabidopsis thaliana. The reaction of the copper(I) scorpionate complexes with ethene can be monitored by measuring the change they can induce in the conductance of carbon materials like single walled carbon nanotubes to determine the concentration of atmospheric ethene.[2]

I will present various new scorpionate ligands and their copper complexes which can be used for the detection of ethene gas. I will address the synthesis, characterizations and chemistry of the ligands and the complexes.



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SC_09

Fe^{II}, Zn^{II} and Cu^{II}bis(pyrazolyl)methane complexes for polymerisation catalysis

Ulrich Herber[1], Alexander Hoffmann[1],Sonja Herres-Pawlis*[1]

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One of the major requirements for catalytical activity is the presence of free coordination sites. Tridentate *N*,*N*,*N*-bis(pyrazolyl)methane ligands with pyrazolyls functionalizedin 3-position tend to form bisfacial, coordinatively saturated complexes in combination with transition metals (Fe/Zn/Cu^{II}). The reasons herefore lie in the low sterical demand of the ligands, as well as in the partlyoccuringisomerisationof pyrazolyle substituentsand the associateddecreaseof repulsive interactions.[1-3]

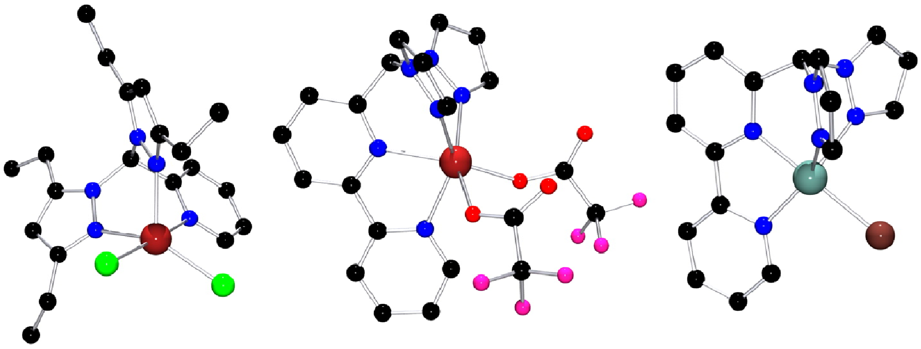

Figure1.Molecular structure of [(L2)$FeCl_2$] (K1), [(L3)$Fe(CF_3CO_2)_2$] (K2) and [(L1)CuBr]$^+$ (K3).

Toenforce the monofacial coordination mode two new ligandsHC(3,5-PhPz)$_2$(Py)**L1**andHC(3,5-EtPz)$_2$(Py) **L2**, that are functionalised in 3- and in 5-position equally,were synthesised. The reactionof**L1**with several Fe/Zn/Cu^{II}saltsleads to a wide varietyof new, but bisfacialcomplexes. In contrast, the reactionof**L2**and $FeCl_2$affords the monofacial complex [(**L2**)$FeCl_2$] **K1**. Another different approachto inhibitbisfacial coordination is the implementation ofa fourth donor moiety. Hereby,the ligands HC(Pz)$_2$(BiPy) **L3**, HC(3,5-MePz)$_2$(BiPy) **L4**andHC(3-*t*BuPz)(BiPy) **L5**could be synthesised for the first time. The conversionwith selected Fe/Zn/Cu^{II}saltsresults in complexeswhose metal centersare coordinated by all four *N*-donors as shown in Figure 1 with [(**L3**)$Fe(CF_3CO_2)_2$] **K2**and [(**L1**)CuBr]Br **K3**. In a next step**K2**was tested as a single-site catalyst in ring opening polymerisation of*rac*-lactide. First studies have shown promising results regarding molecular mass distribution and reaction control.

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SC_10

Coordination Chemistry of Thioether Ligands on CuX Salts: From Molecules to Luminescent Materials and MOFs

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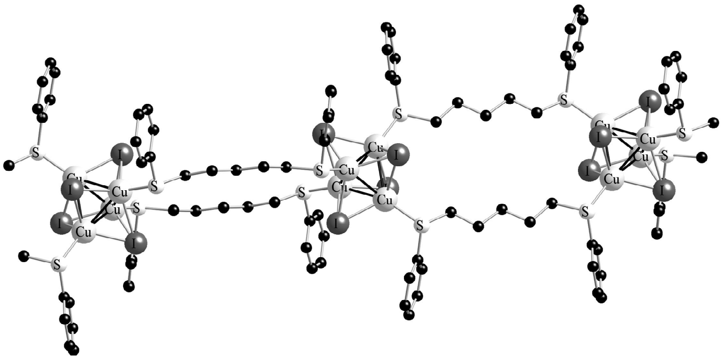
In the context of our work on the organic and organometallic chemistry of sulfur-rich organic ligands, we have designed a rich panel of π-conjugated ligands such as 2-azabutadienes[$Ar_2C=N-C(H)=C(SR)_2$, and vinylferrocenes*Z*-[(RS)(H)C=C(SR)-Fc]bearing thioether groups and investigated their coordination chemistry. We have also usedsimple RSR alkyl sulfides and dithioetherligands to self-assemble coordination polymers (CPs) and Metal-Organic Frameworks (MOFs) of varying dimensionality incorporating softCu(I) ions.We demonstrate that the reaction of aromatic and aliphatic dithioethers of type $RS-(CH_2)_n-SR$ (n = 1-8), $RS-CH_2CH=CHCH_2-SR$ and $RS-CH_2C\equiv CCH_2-SR$ with CuX gives rise to CPs, in which dinuclear $Cu(\mu_2-X)_2Cu$ rhomboids, tetranuclear Cu_4I_4 cubane units,hexanuclear Cu_6I_6 clusters or octanuclear Cu_8I_8 clusters are present. These polymetallic secondary building units (SBUs) act as connecting nodes, which are spanned by the dithioether ligands. We are currently investigating the different parameters (metal-to-ligand ratio, solvent, lengths and rigidity of the spacer, substitution pattern of -SR), which are controlling the topologies and dimensionalities of the resulting networks. In order to correlate the temperature-dependent emissions of these strongly luminescent materials with the Cu···Cu distances within the SBUs, some X-ray diffraction studies were performed at variable temperature. The emission properties are also rationalized by means of DFT and TD-DFT calculations.



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SC_11

Can a non-porous Cu^{II} coordination polymer be as good catalyst as porous Cu^{II} MOFs?

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Porous coordination polymers or MOFs have experienced a rapid emerge in the last two decades because of the properties that they may present,[1] standing out, among others, the interesting activity as heterogeneous catalysts shown by this type of materials.[2] In this sense, incompletely coordinated metal cations, also known as unsaturated metal centres (UMC) can be used as Lewis acid sites in catalytic reactions, important for organic synthesis. The use of metalloligands as linkers for the construction of MOFs is a promising approach to obtain unsaturated metal sites. This way, using a second metal as framework node, mixed metal-organic frameworks (M'MOFs) can be obtained in a 'two-step self-assembly' synthesis.

[NaCu(2,4-HPdc)(2,4-Pdc)] (2,4-H_2Pdc = pyridine-2,4-dicarboxylic acid) has been obtained by hydrothermal reaction of [Cu(2,4-HPdc)$_2$(H_2O)$_2$] metalloligand, NaOH and a transition metal salt. [NaCu(2,4-HPdc)(2,4-Pdc)] is isoestructural to [CuMn(2,4-Pdc)$_2$] [3] and crystallizes in the triclinic space group *P-1*. The 3D structure is built up from [Cu(2,4-HPdc)$_2$(H_2O)$_2$] metalloligands and [NaO_6] octahedra. The structure is not porous, however, the unsaturated Cu(II) centres at the surface can act as heterogeneous Lewis acid catalytic centres. In fact, this compound is an active heterogeneous catalyst for the cyanosilylation of different aldehydes and Knoevenagel condensations and can be reused at least for five times with no activity loss along the successive cycles. The activity showed by this compound is comparable with the activity of other Cu^{II} MOFs with structural pores.

Acknowledgements: This work has been financially supported by the "Ministerio de Economia y Competitividad" (MAT2013-42092-R), the "Gobierno Vasco" (Basque University Research System Group, IT-630-13) and UPV/EHU (UFI 11/15) which we gratefully acknowledge. The authors thank the technicians of SGIker (UPV/EHU) for their technical support. Edurne S. Larrea thanks the Gobierno Vasco for her contract.

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SC_12

Copper(I) and Silver(I) Bisphosphine Complexes: from Synthesis to Electroluminescent Properties

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Electroluminescent properties of group 11 elements have attracted attention only in recent years. The discovery of strongly luminescent copper(I) complexes incorporating bisphosphine ligands in their coordination sphere has been the starting point of this research. In particular, McMillin et al. have reported heteroleptic Cu(I) complexes prepared from 1,10-phenanthroline derivatives and bis[2(diphenylphosphino)phenyl]ether (POP),[1] characterized by remarkably high emission quantum yields from their long lived metal-to-ligand charge-transfer (MLCT) excited states. Following this key finding, numerous examples of related heterolepticCu(I) complexes have been prepared from bisphosphine and aromatic diimine ligands[2].Eventually, copper(I) compounds prepared exclusively from bisphosphine ligands were also reported[3].Some of these compounds exhibit excellent emission properties exploited to fabricate efficient electroluminescent devices; therefore, inexpensive and earth-abundant copper(I) is an attractive alternative to noble metal ions for such applications[3b 4].In recent years, investigations have been also extended to analogous silver (I) and gold(I) derivatives[3b 5].Our latest results in this field of research will be presented.

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SC_13

Coordination mode of the 1, 3-bis [5-(2-pyrimidinyl)-1, 2, 4-triazol-3-yl] propane

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The coordination chemistry of flexible ditopic ligands has attracted recent attention due to their demonstrated versatility forming new attractive coordination structures and topologies and, associate with this, their potential applications [1]. The flexible ditopic ligand 1,3-bis[5-(2-pyrimidinyl)-1,2,4-triazol-3-yl]propane H_2L displays remarkable versatility in the coordination mode depending on the counter anion. The structure of 1,3-bis[5-(2pyri-midinyl)-1,2,4-triazol-3-yl]propane is established from the NMR and IR spectra.With copper(II)nitrate H_2L acts as a tetradentate chelate forming a mononuclear complex. The reaction with copper(II) perchlorate gives a centrosymmetric dinuclear complex coordinating the deprotonated form of the ligand. Reaction with copper(II) chloride leads to a pentanuclear complex in which binuclear species are bridged by a $CuCl_2$ fragment. All complexes were crystallographically characterized. Additionally, magnetic properties of bi- and pentanuclear complexes were studied.The bispyrazolyl ligand H_2L was synthes-ized by the reaction of 2-CN-pyrimidine and glutaric acid’s hydrazide. The product is obtained in good yield and is easily purified.Target complexes were obtained by the reaction of H_2L with equimolar amount of a $Cu(NO_3)_2{\cdot}3H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$ and $CuCl_2{\cdot}2H_2O$ in water–methanol solution, namely $[Cu(H_2L)NO_3]NO_3$(1), $[Cu_2(HL)_2](ClO_4)_2{\cdot}3H_2O$ (2) and$[\mu\text{-}CuCl_2\}\{(\mu\text{-}Cl)Cu(HL)(H_2O)Cl_2\}_2]{\cdot}H_2O$ (3).These three complexes were prepared in same conditions but have remarkable different structures as result ofdifferent coordination mode of ligands. Molecular structures are shown in Fig.1, 2 and 3. Magnetic studies for 2 and 3 show that all the complexes are predominantly antiferromagnetic in nature. Magnetic studies for 2 and3 show that all the complexes are predominantly antiferromagnetic in nature. The strength of the antiferromagnetic coupling of triazole bridged complexes depends strongly on the trigonal distortion parameter s and thus the orientation of the magnetic orbitals.

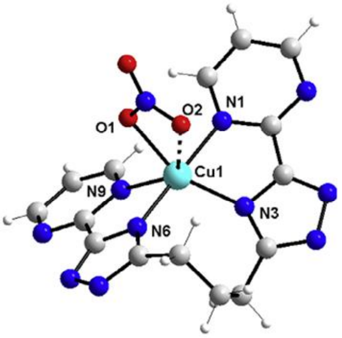

Fig.1 Structure of complex 1

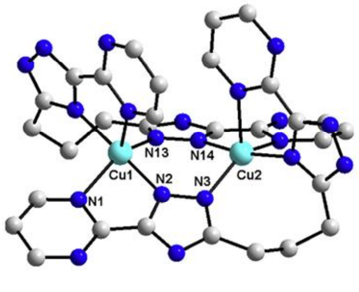

Fig.2 Structure of complex 2

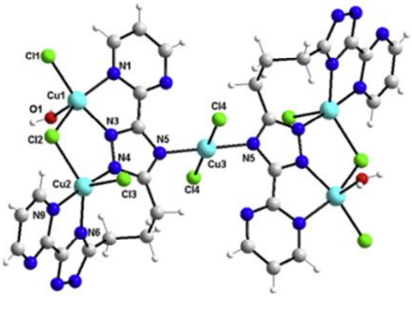

Fig.3 Structure of complex 3

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SC_14

Shaping of iron-triazole polymers into spin crossover nanocomposites

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Due to their capacity to switch between states with different properties, spin crossover materials have been considered as promising tools for display and memory storage devices. This is especially true for the iron-triazole group of spin crossover compounds, made of iron (II) sites linked together by triazole ligands into polymeric chains, which have been extensively studied in the solid state because of their sharp transition profile and their wide hysteresis[1].

In this context, the objective of this work is to prepare nanocomposites in the gel state by combining iron-triazole polymer both as spin crossover specie and as building block with silica nanoparticles. The objective is to transfer the abrupt transition and hysteresis typical of a solid state iron-triazole polymer to a soft matter state such as a gel. This was achieved by combining$[Fe(Atrz)_3]SO_4$where Atrz is 4-amino-1,2,4 triazole, which is known to present the desired transition properties[2], and sulfonate functionalized nanoparticles.By adjusting the polymer synthesis conditions, we obtained a stable semi crystalline suspension in a polyol medium. When the nanoparticles were added duringsample preparation a purple gel presenting an abrupt spin transition and hysteresis (fig 1) assessed by SQUID magnetometry measurements was obtained. The morphological features of the system were assessed with various electron microscopy techniques.

Further shaping of the gels allowed us to obtain an easy to handle material containing up to 40% in mass of spin crossover specie (fig 2). This is to our knowledge the most concentrated spin crossover composite described in the literature, and opens the way for the design of a new type of hybrid spin crossover materials.

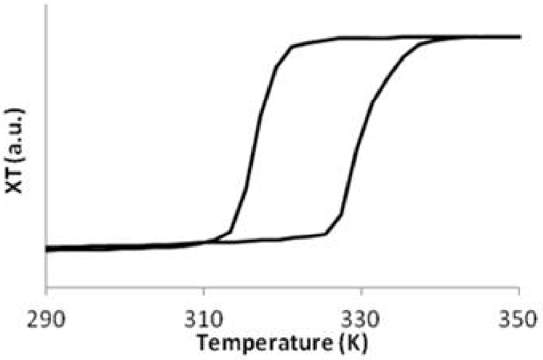

Fig 1

Fig 2

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SC_15

Lantern-Type Rhodium(II) Dinuclear Complexes with Formamidinato and CarboxylatoBridging Ligands

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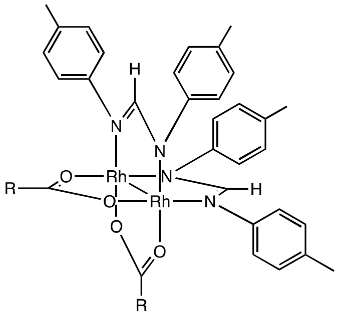
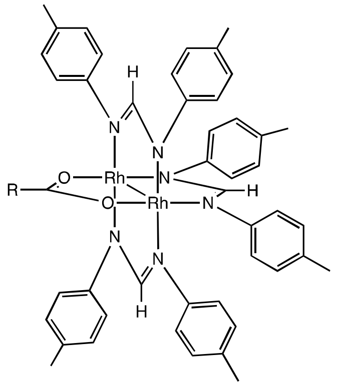
Much interest has been devoted to the lantern-type dinuclear complexes due to their unique dinuclear structure themselves and interesting properties based on the metal-metal interaction[1]. Formamidinate ions are known to work as the intra-dimer bridging ligands, although carboxylato ions have been more widely used as the ligands [1-3]. Formamidinate ions have stronger donating nature compared with carboxylate ions. The structures and properties will be tunably changed if the combination of formamidinato and carboxylato bridges is systematically changed in the dinuclear core.In this study, the mixed-ligand rhodium(II) dinuclear complexes having formamidnato and carboxylate bridges with *cis*-(2:2) and (3:1) arrangements, *cis*-$[Rh_2(4\text{-Me-pf})_2(O_2CR)_2]$ and $[Rh_2(4\text{-Me-pf})_3(O_2CR)]$ (4-Me-pf$^-$ = bis(4-methylphenyl)formamidinate ion; R = CF_3, CH_3, $C(CH_3)_3$, C_6H_5, C_6F_5)were synthesized and characterized. The molecular structures of the *cis*-(2:2) and (3:1) complexes are schematically shown below; the structureshave been confirmed by X-ray crystal analysis. It was found that the redox behaviors were affected by the numbers of formaminato and/or carboxylato bridge more than introduced substituents groups on the carboxylate ligands. Dimer-of-Dimers type tetranuclear complexes with bis(carboxylato) linker ligands such as terephthalate ion will be also discussed in the presentation.



***cis*-(2:2) complex**



(3:1) complex

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SC_16

Silver N-Heterocyclic Carbene Complexes as Anticancer Agents

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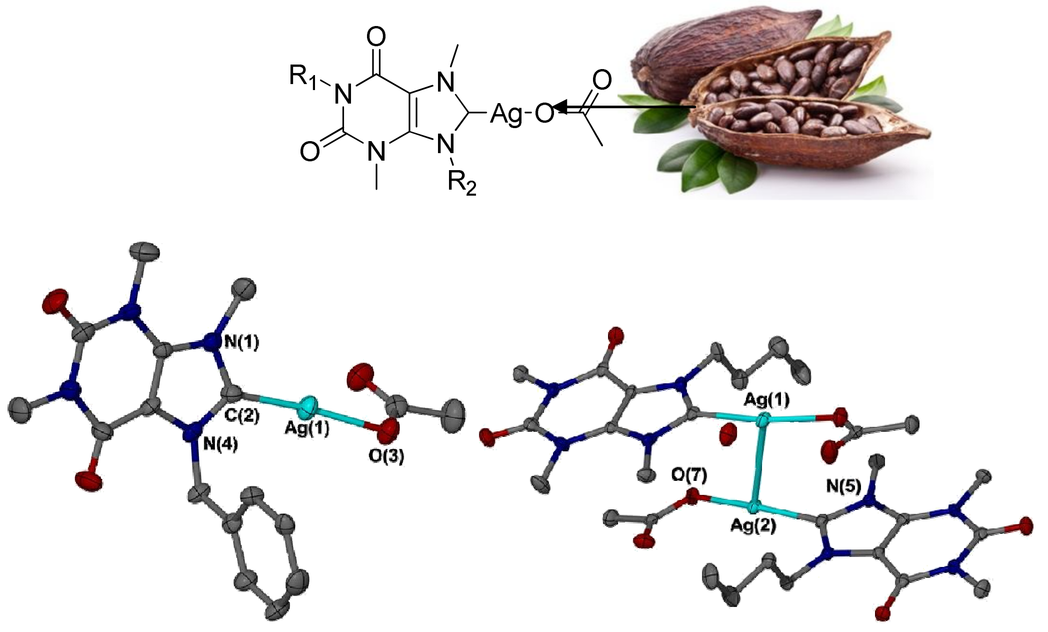
The discovery of the platinum-containing compound cisplatin as a chemotherapeutic compound opened a new area of research in organometallic chemistry for the treatment of cancer.[1]Reports have shown that silver-N-heterocyclic carbene (NHC) complexes demonstrate significant promise as chemotherapeutic agents.[2-4]

This work describes the synthesis of novel silver-NHC complexes derived from xanthine precursors such as theophylline, theobromine and caffeine, which are natural products found in, for example, cocoa beans.These complexes were assessed for their cytotoxicity against eight cancerous cell lines and results were compared to those obtained for cisplatin. Hydrophobicity studies and structure activity relationships indicate that both stability and ligand sterics play important roles in the activity of these complexes as anticancer agents.



R_1 = Me, R_2 = Benzyl

R_1 = Me, R_2 = ^{n}Bu

Figure 1: Novel caffeine-based silver(I)-NHC complexes.

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SC_17

Single ion magnet (SIM) behavior in newSchiff-base lanthanide coordinating systems

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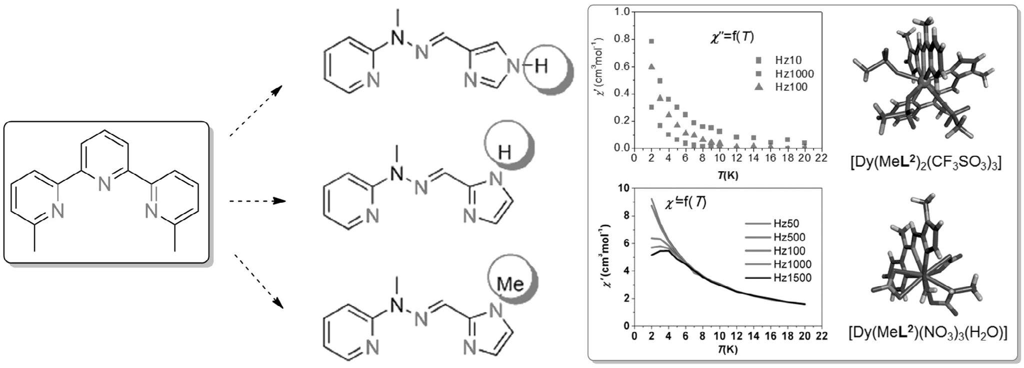
Supramolecular chemistry of *N*-heterocyclic complexes has been given particular attention and has attracted interest of researchers from variety of different domains, those include material chemistry, catalysis and biology to name a few.

We have previously shown interesting magnetic and biological properties of transition metal complexes with 6,6''-dimethyl-2,2':6',2''-terpyridine ligand. [1-3] Since such N_3-tridentate meridional binding pocket was found to efficiently coordinate variety of metal centers in accordance to their electronic properties, we have decided to synthesize a series of easily accessible Schiff-base ligands and evaluate their propensity towards lanthanide ions. Successful syntheses followed detailed investigation of their structure/property rationale in terms of single ion magnet (SIM) behaviour.[4]



Acknowledgements:

This research was carried out as a part of the Polish Ministry of Science and Higher Education project (Grant No. 0111/DIA/2012/41) in the frame of “Diamond Grant” programme.

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SC_18

New Trimetallic Group Six Cluster Sulfides for Photophysical Applications

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Recent works have demonstrated the eligibility of molybdenum or tungsten sulfides to design new photoactive materials [1]. In this context, transition metal clusters containing $[M_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3]^{4+}$ and $[M_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3]^{4+}$ (M = Mo, W) triangular units, represented in the figure, are very attractive precursors for these materials. Indeed, over the last years our research group has reported a wide family of M_3S_7 and M_3S_4 clusters showing very different properties by functionalization of their outer positions with ligands of different nature. In fact, to conveniently functionalize these chalcogenide-bridge trinuclear clusters, the appropriate choice of the outer substituents plays a crucial role.

$M_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ $M_3(\mu_3\text{-}S)(\mu\text{-}S)_3$

Figure 1. Representative scheme of the M_3S_7 and M_3S_4 cluster cores, respectively.

Due to the non-innocent redox character of diimines and bipyridine derivatives, such ligands are good candidates to induce photoredox or photoluminescence properties to the M_3S_7 and M_3S_4 trinuclear units [2, 3]. However, the search of suitable starting materials remains a challenge when neutral ligands are used. Recently, thiourea cluster derivatives have emerged as the preferred precursors due to their high substitutional lability of this neutral ligand [3].

In this work, we prove the reactivity of these M_3S_7 and M_3S_4 thiourea precursors *vs* photoactive organic diimine or bipyridine derivatives. The photophysical properties of the new materials are also discussed.

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SC_19

Cyanido-bridged Hetero Metal ComplexesBased on Dinuclear Ruthenium Carboxylate

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It is known that dinuclear ruthenium carboxylate has a paddle-wheel or lantern type core made-up by *sym-sym*-bridging of four carboxylatoligands [1]. We have been interested in the ruthenium(II)-ruthenium(III) mixed-valence state, because this unit gives paramagnetc$S$ = 3/2 spin state as building block to assemble the metal-metal bonding units(Fig. 1) [2].In order to introduce an systematic study, we synthesized a series of chlorido-bridged chain compounds of dinuclear ruthenium(II,III) 3,4,5-trialkoxybenzoates, $[Ru_2\{3,4,5\text{-}(n\text{-}C_mH_{2m+1}O)_3C_6H_2CO_2\}_4Cl]_n$ (m = 2—18) and found that the antiferromagnetic interaction becomes stronger for the longer alkyl chain compounds. We called this phenomenon as a molecular fastener effect in magnetic interaction [3].We synthesizedone-dimensional chain complexes of dinuclear ruthenium carboxylates with the linking ligands such as *N,N'*-didentate ligand, *p*-quinones, and organic and inorganic cyano groups as the extended systems [4,5].In most cases, the magnetic interaction between the dinuclear units is antiferromagneticand the nature of the magnetic interaction depends on the linking group [2-5]. In few cases, ferromagnetic or ferrimagnetic behavior was found in some metal-assembled systems [4]. We will discuss on the magnetic properties based on the crystal structures.

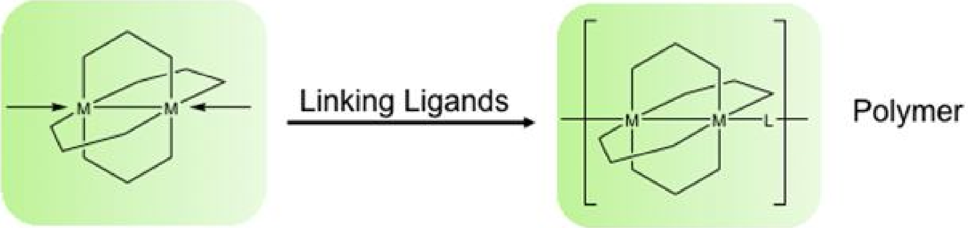

Fig. 1. Dinuclear ruthenium carboxylate and linking ligands.

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SC_20

A novel bi-functionalized system based on the $[Mo_6O_{19}]^{2-}$polyanion

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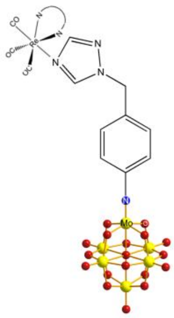
Polyoxometalates (POMs) can be used as building blocks to obtain new hybrid materials derived from the functionalization with organic molecules and/or metal ion complexes, thus increasing their electronic and structural versatility [1]. In the particular case of the $[Mo_6O_{19}]^{2-}$polyanion, the terminal oxygen atoms are sufficiently reactive to becovalently substituted with the organoimido ligand. In addition, the incorporation of an organometallic fragment to the organic-inorganic hybrid system allows obtaining a material with different physical properties to that ofthe precursor [2].

In this work, we present the synthesis and electronic study based on the bi-functionalization of the $[Mo_6O_{19}]^{2-}$polyoxometalate, first with an aromatic amine (mono-functionalized) and then with a Re(I) complex (bi-functionalized), as shown in scheme 1. Figure 1 shows the UV-vis absorption spectra of the tetrabutylammonium salt of $[Mo_6O_{19}]^{2-}$, mono and bi-functionalized. The electronic transition at 325 nm was assigned to an O-Mo charge-transfer transition in $[Mo_6O_{19}]^{2-}$. The shift to 345 nm gives evidence that the Mo-N bond is formed in theorganoimidocompound [3]. The broad absorption band c.a. 365 nm permits to assess that the bi-functionalization with the organometallic complex was successful.



Scheme 1

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SC_21

Coordination Chemistry of Linear Oligopyrroles Formed upon Degradation of Porphyrin Derivatives

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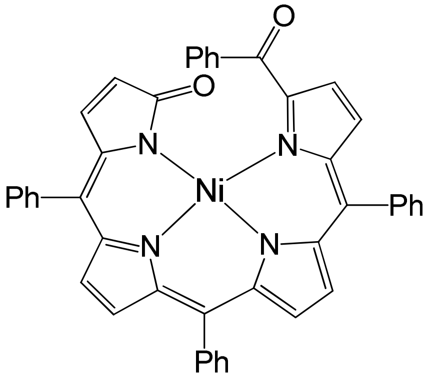
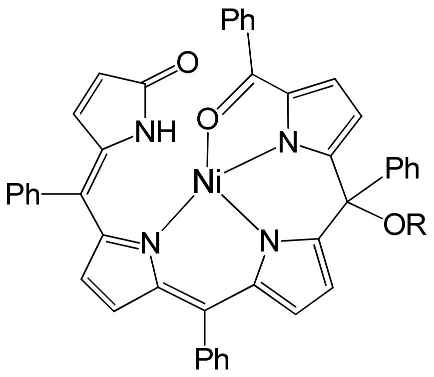
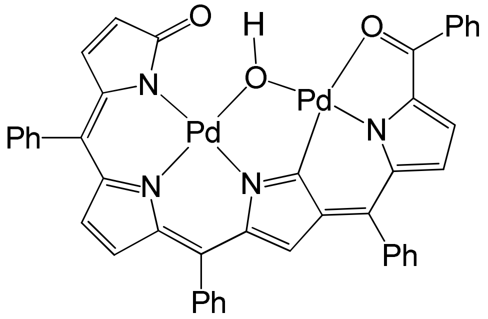
Degradation of tetrapyrrolic macrocycles is used by living organisms as a method of removal of unwanted heme or chlorophyll and as a way of synthesis of linear systems (bilins) which fulfill important physiological functions [1]. Most model studies on the oxidative decomposition of cyclic tetrapyrroles were directed toward understanding of the mechanisms of the processes observed *in vivo*. On the other hand, isolated reaction products, such as biliverdin and its analogues, were recognized as compounds exhibiting interesting chemical properties and biological activities distinct from their parent macrocycles. In particular, a conformational flexibility and diverse, sometimes unpredictable coordination modes attracted a particular attention [2]. The contribution focuses on the use of linear oligopyrroles produced in the course of photooxidation of porphyrin derivatives as ligands for various metal ions.







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SC_22

Bimetallic Phosphorus-Based Complex as Building Block for One- and Two-dimentionalOrganometallic-Organic Hybrid Material.

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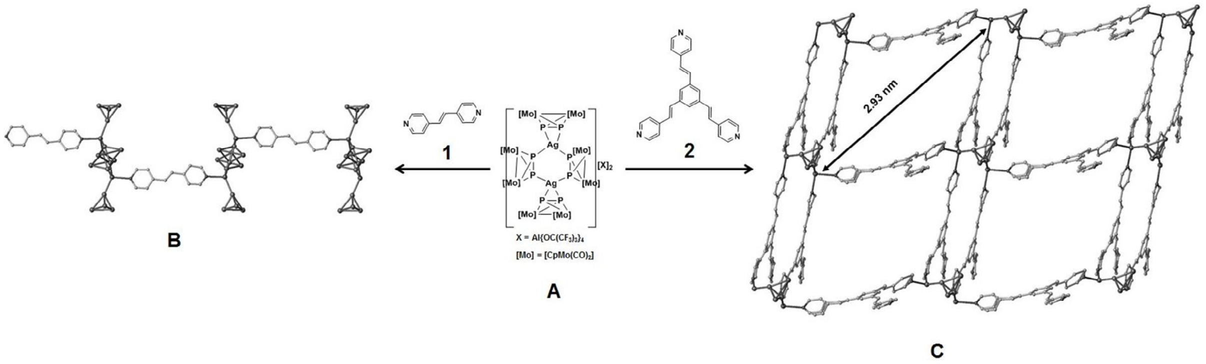
Our group explore extensively the potential of organometallic complexes based on polyphosphorus ligands as bridging units between metal centers[1]. These complexes shows a versatile coordination behavior and allow the formation of one- and two-dimentional coordination polymers[2] as well as giant spherical molecules[3].In one approach the dimeric compound **A** was synthesized from the reaction of the tetrahedrane complex $[Cp_2Mo_2(CO)_4(\eta^2\text{-}P_2)]$ with the silver salt of the weakly coordinating anion$[Al\{OC(CF_3)_3\}_4]^-$ [4].The reaction of **A** with the ditopic ligand **1** leads to the formation of a one dimentional organometallic-organic hybrid polymer**B**[5].This polymer consists of $[Ag_2(\mathbf{A})_4]$ units, which are linked to polycationic chains by the connector **1**.

More recently a variety of multitopic ligands were synthesized and reacted with complex **A**. The reaction of **A** with the tritopic ligand **2** leads to the formation of a two dimentional network**C** with cavities in the nanometer range.This novel synthetic route will probably allow us to synthesize other networks with controlled porosity by changing the multitopic ligands involved. In addition it opens up new opportunities to incorporate defined functionalities in solid-state architectures of phosphorus ligand complexes. Recent progresses along this approach will be presented.



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SC_23

Stable Silanetriols – Building Blocks for Surfactants, Micelles and Cages

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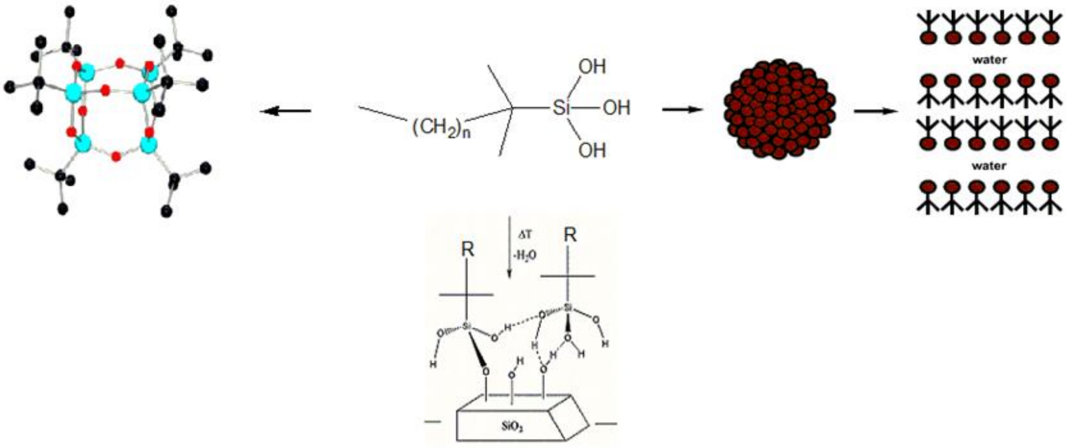
In neutral silanetriols the maximum number of polar silanol groups is attached to the same silicon atom besides an organic substituent. Since the first preparation[1] and structural characterization[2] the main research focus for this type of compounds has been mainly devoted to their synthesis, solid state structures and conversion to metallasiloxanes.[3,4]

The combination of highly polar silanol units with an unpolar organic moiety gives rise to a pronounced amphiphilic character of such compounds.[5] We are interested to extend the scope of this unusual class of compounds to the liquid state and especially to solutions where aggregation and micelle formation can be observed.[6]

Besides their surfactant properties silanetriols are also ideal precursors for controlled surface modifications.[7] Moreover, silanetriols can be converted to complex molecules and cages using controlled condensation reactions.[8,9]

Given sufficient steric protection, the good solubility and stability also allow applications in biological systems. We found inhibition of hydrolytic enzymes like *AChE* well below the toxicity level even for structurally simple silanetriols.[10]



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SC_24

Novel heterocyclic amide- and phosphinoxide-bearing ligands: synthesis, extraction, and photoluminescent properties

[1]Leonid A. Korotkov, [1]Alexey V.Ivanov, [1]Tsagana B. Sumyanova, [1]Anastasiya V. Kharcheva, [2]Alena Paulenova, [1]Marina D. Reshetova,[1]Stepan N. Kalmykov, [1]Nataliya E. Borisova,

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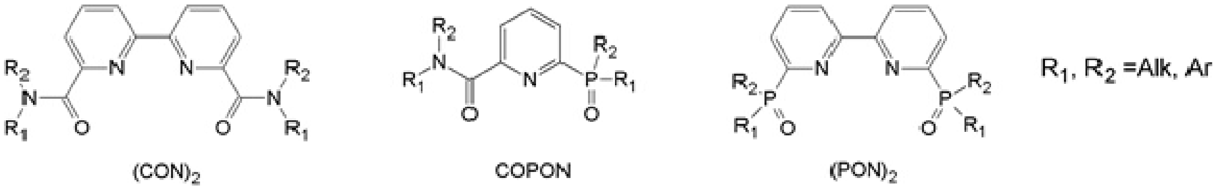
In spent nuclear waste treatment processes there is a necessity for improved ligands for the separation ofactinides and lanthanides. Although the chemical properties of An^{3+} and Ln^{3+} aresimilar,it has been shown [1]that ligands containing soft N-donor atoms are capable of separating the two groups ofelements.

Figure 1.



Inthisworkwesynthesizedandcharacterizedanovelpolydentateligands (Figure 1)consistingof aN-heterocyclicelectron-deficientframeworkbearingamideorphosphinoxide moieties as well as series of their complexes with trivalent 4f-element ions.ThechemicalstoichiometryofLn^{3+}complexeswithtetradentateligands (**(CON)$_2$** and **(PON)$_2$**)isdeterminedtobe1:1 using X-ray crystallography, mass-spectrometry, and UV-Vis titration. Tridentate ligands form complexes ML, ML_2 and ML_3. Thestabilityconstantsofsome actinide and lanthanide complexes of ligands are estimated in acetonitrile by UV-Vis spectrometry(lg$\beta_1$varyfrom 4.5 to 8). UO_2^{2+}-cation demonstrates best affinity to investigated ligands.

Extraction experiments were performed for Am^{3+}/Eu^{3+} pair in nitric acid solution (1-5M).Diamides**(CON)$_2$** exhibit excellent extraction ability (distribution ratios run up to 50) and high selectivity toward americium over europium in highly acidic solution.0.01M solution of tridentate **COPON**in nitrobenzeneshows quantitative extraction of f-elements from any nitric acid concentration. No selectivity was observed for this kind of extractant.

The ligands **(CON)$_2$** form highly luminescent complexes with Eu^{3+}, $Tb^{3+}$and Sm^{3+}.The luminescence lifetime of all Eu-complexes at 293K and 77K is about 1 and 1.5 ms respectively.

This work was supported by Ministry of Science and Education of RF (№14.604.21.0082 RFMEFIBBB14X0211).

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EP_01

Theory in investigations of the thermodynamics and kinetics of the thermal dissociation of simple inorganic solids

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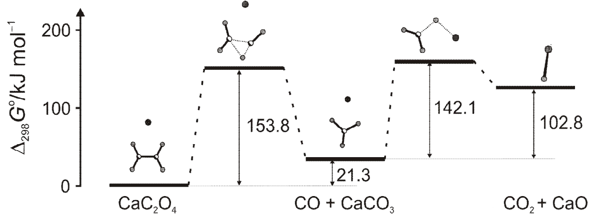
Two main types of processes occur in the world around us. One consists of photochemical processes naturally forced by the absorption of solar radiation – this is photosynthesis. The other involves thermal processes taking place in living matter and implemented by humans to satisfy their needs. Every thermal process, i.e. the conversion of substrates to products, occurs within a certain temperature range characteristic of the system in question. Within this range the process continues until equilibrium is reached, when both types of reactants co-exist; beyond it, either substrates or products predominate. The thermal behaviour of chemical systems is readily understood and described on the basis of reversible and irreversible thermodynamics, i.e. reaction thermodynamics and kinetics. The limited experimental possibilities of acquiring information about the thermodynamics and kinetics of thermal processes encourage the use of computational methods. With theoretical methods one can predict the structure and thermodynamic and kinetic characteristics of gaseous systems. But the possibilities of extending such methods to solid systems are limited.

This presentation demonstrates the application of quantum chemistry methods to examine chemical processes going on in simple inorganic systems involving solids. To begin with, it will discuss the results of computational studies of the thermal dissociation of calcium oxalate monohydrate [1]. This compound dissociates stepwise with increasing temperature – this is shown in the scheme below. The decomposition is first considered for a stoichiometric unit of the compound and then for gaseous molecular clusters. The results indicate that both the thermodynamic and the kinetic characteristics of the individual decomposition steps depend on the presence of other molecules in the vicinity of the reacting centre. The predicted thermodynamic and kinetic characteristics are then used to reproduce the pattern of thermal analysis data. Comparison of the experimental and theoretically predicted thermoanalytical characteristics shows that inclusion of the molecular environment generally enhances the predictive ability of theory with respect to a compound's thermal decomposition.



Further insight into the thermodynamics and kinetics of the thermal dissociation of solids can be gained by combining the results of quantum chemistry and crystal lattice energy calculations. This will be demonstrated for the thermal decomposition of calcium oxalate monohydrate, and also N,N,N-trimethylmethanaminium and 1-methylpyridinium halides, which were investigated some time ago.

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This work wafinanced by the State Funds for Scientific Research (Grant DS/530-8220-D493-14).

EP_02

Energy Transfer and a Role of Lewis Base Ligands and Silver Plasmons in Optical Behaviour of New Type of Lanthanide Phosphors

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Keywords: energy transfer,Tb(III), Eu(III) , chelates, luminescence, silver plasmons

The studies of lanthanide chelates and their derivatives had been greatly intensified due to their potential use in photonic devices such as OLED's, optical markers, luminescence sensors, laser materials and fluorescent lighting.Moreover, because of unique luminescence the Eu(III) and Tb(III) complexes with heterobiaryl ligands are known as excellent light-conversion molecular devices (LCMD). The luminescence of lanthanide ion in those type of chelates is sensitised by efficient ligand –to- metal energy transfer(ET). Apart from the donor-acceptor properties, the location of ligand singlet and triplet ststes as well as the charge transfer (CT) states affect the energy transfer process and emission quantum yield. Thus from application point of view the investigation of the same type of Ln(III) chelates, but with different second Lewis base ligand are very important.

The goal of this work is focused on the new lanthanide compounds appropriate for OLED's and solar energy conversion.

The new type of Ln(III) chelates; Ln(SP)$_4$, and Ln(SP)$_3$L (where SP= $C_6H_5S(O)_2NP(O)(OCH_3)_2$ and L=2,2' dipyridine(1) and 1,10phenanthroline(2)) was obtained and characterised by the high-resolution absorption and photoluminescence spectroscopy at 293, 77, and 4K as well as by the decay times measurements. Both type of compounds show a very strong emission after excitation in the UV range of ligand bands. The dynamic of the excited state will be discused. The energy levels diagrams of the ligands and M(III) electronic states were prepared. The paths of the energy transfer are analysed and mechanism of this process will be proposed. Undoubtedly, important spectral characteristics of those compounds are controlled by donor-acceptor properties of the ligands and the energy location, electron –phonon coupling, ET efficiency and the quantum yield.

EP_03

Homo- and hetero-aryl Lewis acidic boranes: H_2 activation by an electrochemical-frustrated Lewis pair approach

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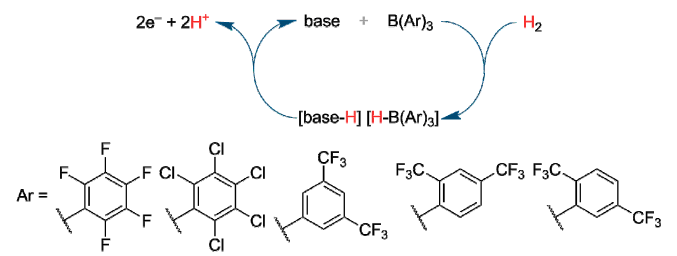
The cleavage of $H_2$by frustrated Lewis pairs (FLPs) with an electron-deficient borane as the Lewis acid is now well established, with $B(C_6F_5)_3$ as the archetypal example [1]. By combining this classical FLP chemistry with electrochemical oxidation of the resultant borohydride;we have demonstrated significant reductions in the voltage, compared to that of H_2, required for the net liberation of two protons and two electrons, and hence a decrease of the required energetic driving force [2-3].

We are developing a range of tri-aryl boranes incorporating between one and three unique aryl rings, with varying steric and electronic contributions [4]. This allows us to fine-tune both the reactivity of the neutral borane for classical FLP H_2 activation, and the electrochemical properties for the two-electron oxidation and proton liberation of the borohydride.



Scheme electrochemical-frustrated Lewis pair (eFLP) concept

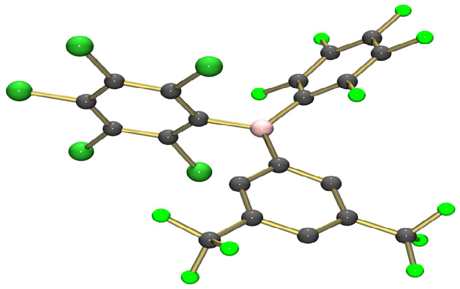


Figure $B(C_6Cl_5)(C_6F_5)\{C_6H_3 3,5\text{-}(CF_3)_2\}$

These studies provide further insight into the combination of electrochemical and FLP reactions;with the novel species having potential applications beyond hydrogenation, including for electro-synthesis and within various devices [5].

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EP_04

Novel Copper (III) Tetra-Phenyl-Porphyrin-Fullerene dyads

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[3] *Chemistry Dept., Ben-Gurion University of the Negev, Beer-Sheva, Israel*

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Recently the chemistry of Copper(III) tetra-phenyl-porphyrin was revised [1], the study included UV-Vis absorption; emission spectra, E.S.R measurements, X-ray Photoelectron Spectroscopy(XPS) and Cyclic Voltammogram results.

Surprisingly the Copper(III) tetraphenylporphyrin results from the disproportionation of Cu^{II} in dry organic solvents in the presence of the free base tetra-phenyl-porphyrin.

$$2Cu^{II} + H_2TPP \rightleftharpoons \mathbf{Cu^{III}(TPP)}^{+} + Cu^{I} + 2H^{+}$$

The new, Cu^{III}(porphyrin is EPR silent and exhibits different UV-vis absorption, fluorescence patterns different than the well known Cu^{II}(TPP), $Cu^{II}(TPP^{\cdot +})$ and Cu^{II} $(TPP^{\cdot +2})$.

The new, Cu^{III}(porphyrin) exhibits closed-shell, diamagnetic properties. Photoinduced electron-transfer processes have been measured using a new fullerene-based $Copper^{III}$- tetra-phenyl-porphyrin (TPP) dyad. The nanosecond experiments show photoinduced charge separation with a life-time of more than 1000ns. Detailed results will be presented.

Literature:

[1] Magal Saphier, Tova Yifrah, Israel Zilbermann, Oshra Saphier, Dan Meyerstein and Dirk M. Guldi; J. Porphyrins Phthalocyanines 2012; 16: 1124-1131

EP_05

The water oxidation mechanism on anatase TiO_2 photoanodes – a transient photo-induced absorption study of this model system

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The amount of solar energy reaching the surface of earth in one hour is nearly twice the total energy currently generated in a year [1]. To fully utilise this resource, significant technological advances are required. Existing solar conversion technologies have focused on the conversion of solar energy to electricity or heat. However these technologies have two limitations: (i) the lack of a viable, scalable energy storage strategy that addresses the intermittency of sunlight and (ii) the lack of a viable mechanism to convert sunlight into a transportable fuel (≈ $^1/_3$ of global energy demand). Plant photosynthesis demonstrates the direct conversion of sunlight to chemical fuels, where "bio-inspired" strategies have emerged and are attracting extensive interest particularly for the solar generation of H_2 fuel from splitting water [2].

Solar driven water splting first received significant attention in the 1970's due to the pioneering report of Fujishima and Honda using TiO_2 [3]. The development of improved photocatalysts for solar water splitting has largely been an empirical process, with few studies of the underlying mechanisms. Findings thusfar point to the essential requirement of long-lived photo-generated holes (*i.e.* a few seconds) for efficient water oxidation to be observe [4]. As water oxidation is the '*bottle-neck*' in the overall water splitting reaction, gaining a true insight into the reaction kinetics is needed if better photocatalysts are to be designed.

A new technique for probing the accumulation and reaction of photo-generated charges is presented – transient photo-induced absorption spectroscopy. Demonstrating for a model system, anatase TiO_2, we show how the reaction order and kinetics for water oxidation, with respect to the accumulated surface hole density, changes with light intensity. A transition to higher reaction order is observed above a surface hole concentration threshold, which is associated with a change in the water oxidation mechanism (Figure 1).

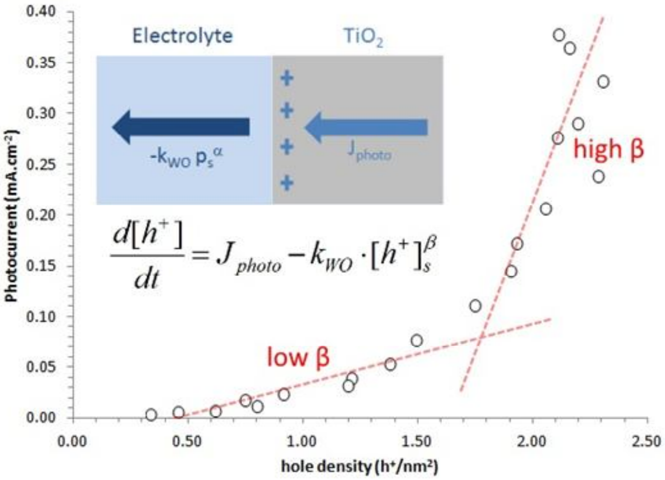

Figure 1: The relationship between photo-current (mA.cm^{-2}) and accumulated surface hole density on an anatase TiO_2 photoanode.

Literature:

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MT_01

Direct Oxygenation of Aliphatic C-H Groups with H_2O_2 Mediated by Mn-Aminopyridine Synthetic Enzyme Models

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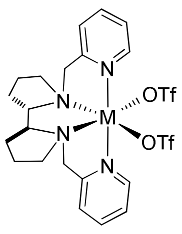
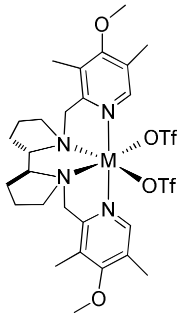
Design of bioinspired transition metal complexes capable of mediating direct C-H oxygenation with high efficiency and selectivity under mild conditions has been one of the major challenges of contemporary synthetic chemistry [1]. The milestone work of Chen and White [2] laid the foundation for designing predictably selective catalytic C-H oxygenation, conducted by non-heme bioinspired Fe complexes. In this contribution, we present a series of structurally related Mn complexes, capable of catalyzing selective C-H oxygenations with H_2O_2 as the environmentally benign oxidant, and report a detailed investigation of the reaction mechanism.

Structures of some Mn(II) pre-catalysts, along with some oxidation examples are presented below. It was found that Mn catalysts perform with a much higher efficiency (up to 970 turnovers), regioselectivity and stereospecificity than their iron(II) prototypes, converting organic substrates with aliphatic C-H groups to the corresponding alcohols and ketones [3].



1



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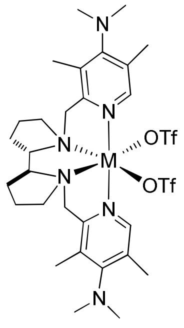

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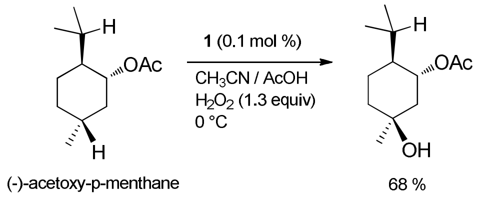

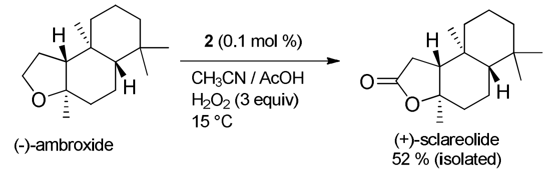

Mechanistic investigations reveal that the catalysts operate via mechanism similar to the classical rebound mechanism originally proposed for cytochrome P450, with oxomanganese(V) complex being the most likely active oxygen transferring species [4]. Further studies will be aimed at direct observation of the elusive high-valent Mn intermediate.

This work was supported by the Russian Foundation for Basic Research, grant 14-03-00102.

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MT_02

Splitting of hydrogen by activation at a single non-metallic center

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Reactions of the dihydrogen with transition metal complexes are often investigated commonly with related aspects of the hydrogenation catalysis [1]. The special attention is paid recently on the molecular hydrogen activation by frustrated Lewis pairs [2]. The studies on one-center or non-metallic activation sites which may be utilized in processes of the splitting of dihydrogen are rather rare [3]. For example, H_2 may be activated if it acts as the Lewis base in the A-H...σ interactions [4]. Other non-metallic centers and structures of corresponding species are analyzed theoretically here. The $PF(CH_3)_2...H_2$ complex (Fig. 1) linked through the $P...H_2$ interaction is the preliminary stage of the dihydrogen cleavage process. Mechanisms of the latter reaction are discussed for S and P centers interacting with H_2 molecule; the reactions in the gas phase and in different solvents are analyzed [5].

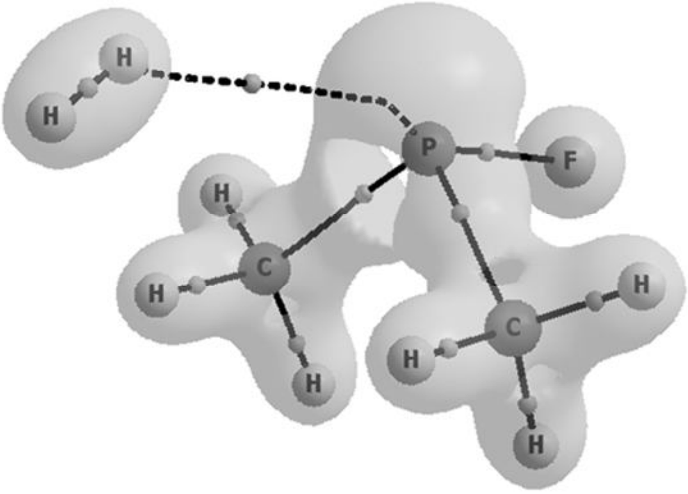

Fig. 1 The molecular graph of $PF(CH_3)_2...H_2$, lines correspond to bond paths with bond critical points (small circles), the reactive surface ($\nabla^2\rho(r)=0$) is presented.

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MT_03

Computational Study on the Hydrolysis of PCl andSiClbonds.

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Zsófia Sólyom, Gábor Turczel

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Phosphorus trichloride is a key intermediate in the phosphorus industry, its P-Cl bond making it highly susceptible against hydrolysis. The hydrolysis was significantly slowed down in certain ionic liquids (IL) [1] and it has been contemplated that reduction of the clustering of water molecules in the IL shall affect the hydrolytic activity. Recently we noticed that the hydrolytic behaviour of carbenes is indeed strongly affected by the number of the reacting water molecules [2] changing completely the reaction channel by the increasing number of water molecules. In the present work we report about a computational mechanistic investigation including density functional and ab initio calculations on the possible reaction pathways of different phosphorus and silicon chlorides with water clusters consisting of different number of water molecules. Also ab initio molecular dynamics studies will be presented to describe the reactivity of PCl_{bond} in water as a solvent to account properly for the Gibbs free energy in case of the large systems, and large number of interacting water molecules – to simulate properly a solution phase reaction. Apart from the results presented on phosphorus chlorides the hydrolytic behavior will be compared to that of chlorosilanes. The results show that the gas phase reaction between a single water molecule and phosphorus trichloride is prohibited by a significant (ca 30 kcal/mol) energy barrier, which depends somewhat on the substituents at phosphorus. Similarly, chlorosilanes exhibit a substantial barrier in the hydrolysis reaction with a single water molecule[3]. These barriers remained similarly large at different computational levels, and were also unaffected – as expected - by using a continuum model for the solvent water. With the increasing number of the clustering water molecules the reaction barrier is reduced. Substituents affect somewhat the barrier, and the details of the mechanism, furthermore, the ability for solvatation of the resulting chloride ion is of great importance. The molecular dynamics studies reveal a small activation Gibbs free energy in aquous solution in agreement with the generally accepted hydrolytic behaviour of the phosphorus halogen and silicon halogen bonds.

Acknowledgements

COST Action CM1302 SIPS and OTKA K 105417 is gratefully acknowledged for support.

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MT_04

Probing the role of π interactions in the reactivity of oxygen species

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Understanding the mechanisms by which O_2 molecule can be activated is of interest due to its biological and technological relevance.[1] Astonishingly, roles played by direct π interactions with O_2 on the structure and reactivity of metal-O_2 complexes as well as the oxygenation reactions course has been barely reported in the literature.[2] Very recently, we revealed that low-coordinate alkylzinc centers have a strong propensity to form a noncovalently-bonded adducts in which the association of molecues is attained through intermolecular Zn…π interactions.[3] So, we anticipated that properly designed organozinc entities featuring intramolecular Zn…π-aromatic interactions offer an exceptional possibility to study role of π interactions in the O_2 activation process.

Herein, we report the synthesis and structural characterizationof a series of ethylzincaryloxides with different dispositionsof aromatic rings toward the metal center and comparetheir reactions with O_2. We are interested in gaining deeper insightinto the various structural features of ethylzincaryloxideframeworks and the dependence of their reactivity on differentaryloxide scaffolds. To provide a more complete basis for a discussionof the relative importance of intramolecularπ-aromaticinteractions with reactive oxygen species, an ab initio studyinto a possible initial intermediate was carried out.[4]

Literature:

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MT_05

Fascinating Boron-Nitrogen-Containing Heteroaromatic Compounds.Electronic Structure Analysis.

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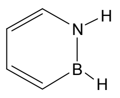
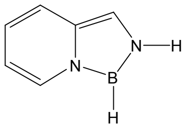
[2]Université de Pau et des Pays de l'Adour, Laboratoire des Fluides Complexes et leurs Réservoirs, UMR CNRS TOTAL 5150; Av. de l'Université, 64 000 Pau, France.

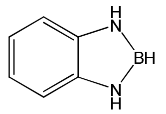
Ultraviolet photoelectron spectroscopy (UV-PES) is a well-established technique to provide ionization energies of molecules in gas phase. These experimental data supported by quantum calculations for the consistency of the assignments of PE spectra provide fundamental information about electronic structure and bonding that is obtained by no other technique. Representative examples to illustrate the advantages and wide applicability will be exclusively chosen from our research in the field of Boron(B)-nitrogen(N)-containing heteroaromatic compounds which are a family of heterocycles that are isoelectronic and isostructural to the family of classical organic counterparts as benzene, or mono-nitrogen containing heterocycles such as pyrrole, indole, iso-indole or anthracene.Their development significantly expands the structural diversity and potential utility of aromatic compounds, but the properties and reactivity of such BN-aromatic heterocycles have not been fully explored due to the lack of available synthetic methods for their preparation. In this presentation, we provide a comprehensive analysis of the electronic structure of BN-heterocycles such as 1,2-dihydro-1,2-azaborine[1], two BN indoles[2,3], 1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridine[4] and two BN-anthracenes[5], in comparison with their carbonaceous derivatives.



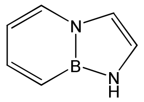
1,2-dihydroazaborine



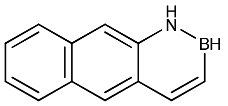
“fused” BN indole



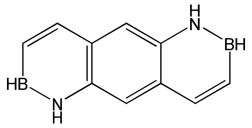
“external” BN indole



BN iso-indole



BN anthracene



bis-BN anthracene

Literature:

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MT_06

Sodium phosphaethynolate as a building block

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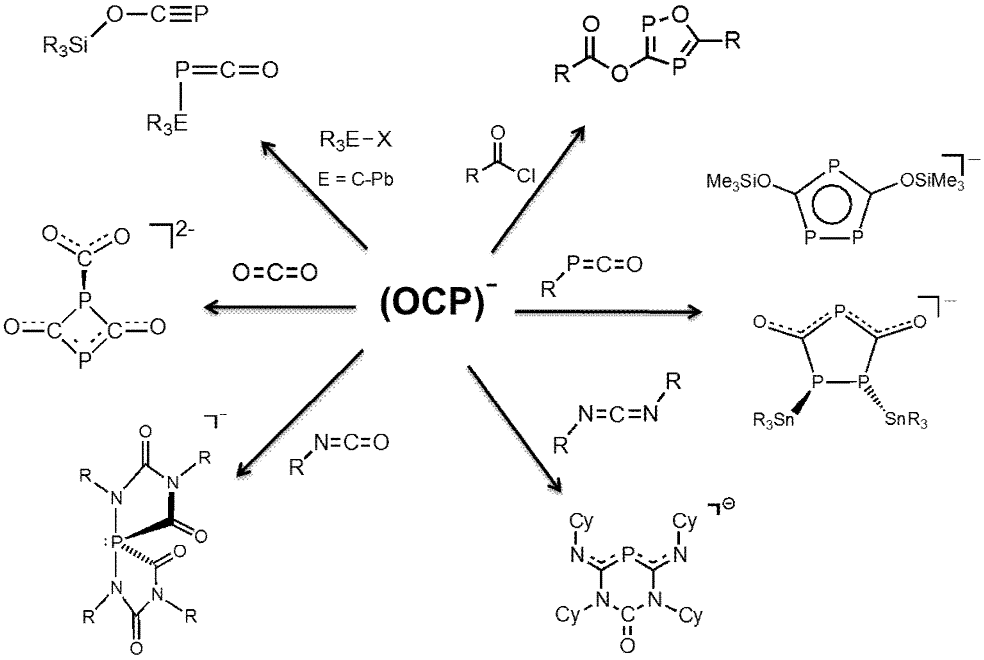
The phosphaethynolate anion (PCO^-) is a sparsely investigated representative of chemical species having carbon-phosphorus multiple bonds. In contrast to its lighter analogue, the cyanate ion, the phosphaethynolate anion can take part in (see also figure below):

a) cycloadditions,[1]
b) nucleophilic substitutions,[2]
c) P− transfer reactions, either with or without the release of carbon monoxide.[3]



Herein the versatile reactivity of the phosphaethynolate anion as a simple building block will be presented. To elucidate the reaction mechanisms leading to these remarkably different products, low temperature NMR investigations and high level computations have been carried out, which will also be discussed.

Literature:

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MT_07

Electron Transfer Reaction within Polyoxometalate Clusters of Redox Active Supports

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Compared with polyoxometalates (POMs)constructed from conventional templates (PO_4^{3-}, SO_4^{2-}, SiO_4^{2-}, etc.), POMs based on redox-active templates,e.g. SeO_3^{2-}, TeO_3^{2-}, are of greaterinterest since they have more diverse structural types and redox activities, enabling them to have extraordinary potential in further applications[1]. The ability to store and transfer electrons within POM clusters has shed light on how to engineer single molecule-based electronic devices[2].In the last decade, we have been pioneering in this area and have discovered the first number of POM clusters supported byredox-active templates,SO_3^{2-}, TeO_6^{6-}, IO_3^{-} and IO_6^{5-}[2-4]. We have investigated the electronic properties of the structure types $\{W_{18}O_{54}(XO_3)_2\}$(X = S and Se) and $\{W_{18}O_{56}(XO_6)\}$ (X = W, I and Te)[5] and attempted the design and manipulationof these clusters as molecular electronics [2]. In this contribution, we present the assembly of a new family of POM clusters supported by an unusual trigonal pyramidal anion template HPO_3^{2-}.Herewith,the intramolecular reaction mechanism of the electron transfer reaction between the template hetero-atom $P^{III}$and cluster cage W^{VI} centers ($P^{III} + 2W^{VI} \rightarrow P^{V} + 2W^{V}$) is investigated using mass spectrometry,^{31}P and ^{1}H NMR and EPR spectroscopy. Comparison with theelectronic properties ofanalogue systems possessingtrigonal pyramidal SO_3^{2-} and SeO_3^{2-} templates is performed. Possible formation of intermediate valence species of X-X bonding,P^{IV}-P^{IV}*vs* S^{V}-S^{V} and Se^{V}-Se^{V}, within the cluster type $\{W_{18}O_{54}(XO_3)_2\}$ (X = P, S and Se)is discussed.

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MT_08

Synergy of Co and Ti sites in electrochemical water splitting

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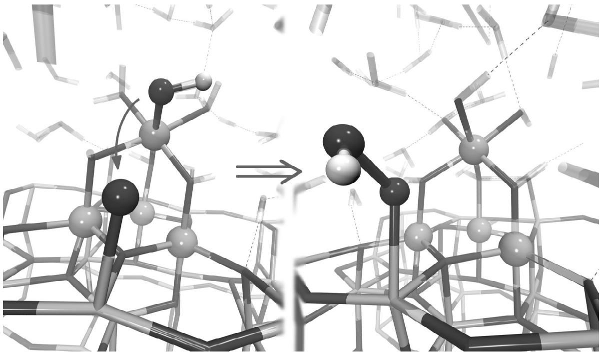
One of the most frequently investigated processes in the field of solar energy conversion is the water splitting reaction, which is an important option to store electricity generated by renewable primary energy either directly (in form of the light) or converted to the electricity by the photovoltaic cells. Both the electrocatalytic and photochemical processes require the use catalysts in order to provide the satisfactory reaction rates, however, the optimum system for the combined reaction has not yet been identified.

We report a computational study of the cooperative effect of small four atom cobalt oxide cluster and the (100) anatase TiO_2 support in the electrochemical splitting reaction of water. The results have been obtained explicitly including solvent water molecules using Car-Parrinello MD simulations. The solvent effect starts with the protonation of the top oxygen atom in the Co_4O_4 cluster, with the hydroxyl group being attached to the Co atom. The same effect occurs also in the oxygen atoms forming the bridges between the Co atoms in the cluster, whereas the hydroxyls bind to the TiO_2 surface. As a result, the Co_4O_4 cluster gains positive formal charge (+3) and the surface – negative charge (-3).
The Red-Ox reaction steps in the catalytic cycle involve TiO_2 hydroxyl groups as well as elementary reaction steps on the Co cluster and are consistent with the electrochemical water decomposition as proposed by Nørskov group [1]. There are two crucial steps of the reaction: first being the formation of the lone oxygen atom on the Ti site of the anatase as a result of the deprotonation of the surface hydroxyl group; the second is the O-O bond formation at the interphase of Co_4O_4 particle and TiO_2 support. Essential observation is the peroxide species is formed out of the hydroxyl group from the Co_4O_4 cluser and lone oxygen present on the anatase surface. This is shown in Figure 1. Interestingly, the peroxide formation step does not increase the energy of the system, and as such it is not a rate controlling step. Instead, the overpotential required to overcome the formation of the hydroxyl on the Ti site is the highest and amounts to 0.32 V.



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MT_09

Si···H···Si and H···Si···H interactions: structure and dynamics

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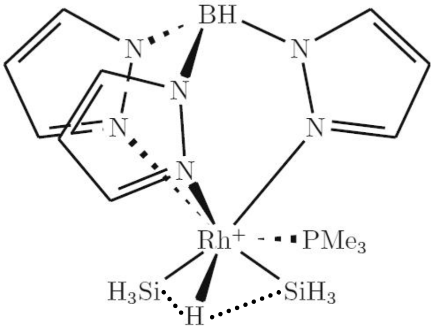
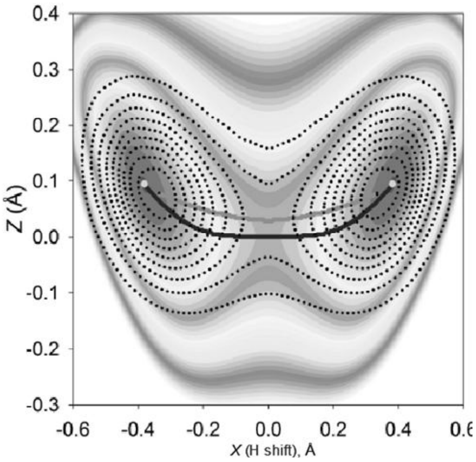
The silyl···hydride interactions of various kinds in transition-metal complexes are well known [1], but in certain cases the hydride can be linked to *two* silyl ligands simultaneously, as indicated by *J*(Si–H) spin-spin coupling constants and Mayer bond indices. For instance, the iron complexes $Cp(CO)Fe(SiMe_nCl_{3-n})_2H$ (Cp = cyclopentadienyl) exhibit a double Si···H···Si interaction, which can be interpreted as a disilylhydride ligand $(R_3Si{-}H{-}SiR_3)^-$, while related complexes $Cp(CO)Fe(SiMe_nCl_{3-n})H(Me)$ are usual η^2-Si–H silane σ-complexes. The "dihydride" complexes $Cp(CO)Fe(SiMe_nCl_{3-n})H_2$ can be either usual dihydrogen complexes, e.g. $Cp(CO)Fe(SiMe_2Cl)(\eta^2\text{-}H_2)$, or have double H···Si···H interactions, e.g. $Cp(CO)Fe(H)_2(SiMe_3)$ [2]. In the rhodium complexes $Cp(L)Rh(SiX_3)_2(H)$ and $Tp(L)Rh(SiX_3)_2(H)$ (Tp = trispyrazolylborate), the hydride ligand interacts at least with one of the silyls, and in many cases with both, but is located asymmetrically with regard to them [3]. This gives rise to a double-well potential of the hydrogen transfer, with a barrier $\Delta^{\ddagger}E$ varying from ~0.1 to 3 kcal/mol.

To understand the dynamics of the hydrogen in these complexes, the vibrational Schrödinger equation was solved in three dimensions. The analysis of the resulting vibrational wavefunction reveals various patterns of hydrogen dynamic behavior depending on the barrier [4]. If the barrier is small ($TpRh(SiH_3)_2(SiMe_3)(H)$, $\Delta^{\ddagger}E<0.1$ kcal/mol, or $CpRh(SiMe_3)_2(SiF_3)(H)$, $\Delta^{\ddagger}E = 0.6$ kcal/mol), the hydrogen is *delocalized* between two silicons, but in the case of a larger barrier ($TpRh(SiH_3)_2(PMe_3)(H)^+$, $\Delta^{\ddagger}E = 1.1$ kcal/mol) it is localized around the energy minima, and the hydrogen transfer occurs classically. The complex $TpRh(SiF_3)_2(PMe_3)(H)^+$ is an intermediate case with two distinct minima and a substantial *tunneling*.



$\Delta^{\ddagger}E = 1.1$ kcal/mol



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POSTER
PRESENTATIONS

BM_P01

Metal complexes of bioactive chalcones

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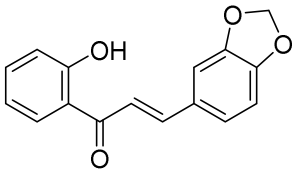
Chalcones constitute a group of C3-C6-C3 compounds which present a broad spectrum of biological activities [1]. Although several metal complexes derived from chalcones have been reported [2], this remains a field unexplored. In this communication, we will present the preparation, characterization and antiproliferative activity of a series of metal complexes (Cu, Co, Ru, Mn) derived from two synthetic chalcones (**1** and **2**)



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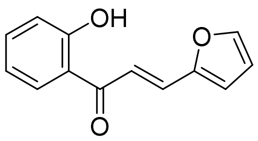

2

Upon complexation with the metals the yellow colour of the ethanolic solution of the compounds **1** and **2** change to brown or black. The stoichiometry of the reaction is 2:1 (chalcone:metal) and the general formula of the complexes obtained is $(Chalcone)_2M$. Some crystal structures were obtained as for example the one shown in Fig. 1

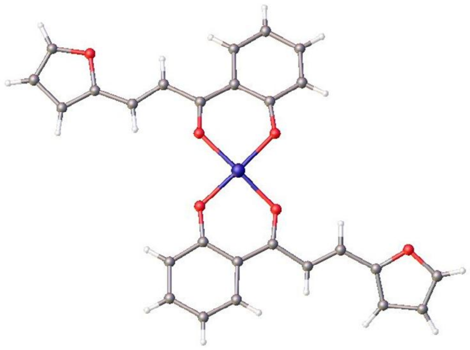

Fig 1: Structure of $(CH_2)_2Cu$

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BM_P02

IN SILICO STUDIES OF CARBOPLATIN BIOTRANSFORMATION HYDROLITIC AND ELECTRON TRANSFER PATHWAYS

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The mechanism of biological activity of carboplatin is still unclear and its explanation constitutes a very challenging task. In continuation of our study on mechanistic aspects of pharmacological action of platinum-based drugs [1], we present computational simulations of reaction paths that might unravel how the introduced carboplatin is turned into the shape of active drug able to interact effectively with target biomolecules.

The object of the study was the series of reaction paths initiated by the impact of species present in biological milieu and able to trigger off the nucleophilic substitution (H_2O) or dissociative electron attachment (electron donors, free electrons, aquated electrons).

Consequently, calculations of structural and energetical parameters of following reaction courses were carried out:

(1) two stage carboplatin hydrolysis;
the reactants were $\{([Pt(\mathbf{N}H_3)_2(\mathbf{O}OC\text{-}C_4H_6\text{-}CO\mathbf{O})] + H_2O) + H_2O\ \}$;
(2) two stage electron impact on carboplatin;
the reactants were $\{([Pt(\mathbf{N}H_3)_2(\mathbf{O}OC\text{-}C_4H_6\text{-}CO\mathbf{O})] + e^-) + e^-\ \}$;
(3) electron and water gradual impact on carboplatin;
the reactants were $\{([Pt^{II}(\mathbf{N}H_3)_2(\mathbf{O}OC\text{-}C_4H_6\text{-}CO\mathbf{O})] + e^-) + H_2O\} + H_2O$.
(4) water and electron gradual impact on carboplatin;
the reactants were $\{([Pt(\mathbf{N}H_3)_2(\mathbf{O}OC\text{-}C_4H_6\text{-}CO\mathbf{O})] + H_2O) + e^-\ \}$;

Conclusions:

- The computational simulations of two alternative pathways, and their combinations, were investigated as hypothetical courses of carboplatin biotransformation.
- The comparison of calculated parameters allow to state that the carboplatin biotransformation is not restricted to hydrolytic pathway as was commonly accepted.
- The most concurrent pathway represents the sequence of reactions initiated by electron attachment.

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BM_P03

Copper(II) complexes of alloferon mutants containing two histidyl binding side inside peptide chain Structure Stability and Biological Activity

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Alloferon 1 is a linear tridecapeptide with the following amino acid sequence: H-His^{1}-Gly-Val-Ser-Gly-His^{6}-Gly-Gln-His^{9}-Gly-Val-His^{12}-Gly-OH, while alloferon 2 is composed of 12 amino acids with the following sequence: H-Gly-Val-Ser-Gly-His^{5}-Gly-Gln-His^{8}-Gly-Val-His^{11}-Gly-OH. These peptides were discovered by Chenrych in 2002 in the blood of the insect *Calliphora vicina* (Diptera) previously infected by bacteria gram-negative *Escherichia coli* and gram positive *Micrococcus luteus*.[1,2] *In vivo* experiments reveal that alloferon induces interferon (IFN) synthesis in mice.[1] A further study has shown that alloferon stimulate the synthesis of INF through NF-kB activation.[3] Alloferons' physiological role in the host organisms is not yet known however it is noticeable that cytotoxic hemocytes functionally similar to mammalian NK cells represent a significant portion of the maggot blood cells. Experimental data demonstrate a strong stimulatory effect of alloferon on the un vivo cytotoxic activity of human peripheral blood lymphocytes directed to the lysis of tumor cells.[2] Importantly, preclinical studies have shown that alloferon has no toxicity to normal cells and does not effect the growth of normal cells.[4]

In this study the copper(II) complexes of the H1A/H9A, H1A/H12A and H1A/H6A mutants of alloferon 1 were performed by the combined application of potentiometric equilibrium, spectroscopic (UV-Visible, CD, EPR) and MS methods in solution. At physiological pH 7.4 the $CuH_{-1}L$ complex dominates with $4N\{NH_2,N^-,2N_{Im}\}$ binding sites. The logK^* value for the $CuH_{-1}L$ complex of the H1A/H12A (-16.87) is about one log unit higher in comparison to that of the H1A/H6A peptide (-17.73). For the Cu(II)-H1A/H12A system the copper(II) ions in the $CuH_{-1}L$ complex are coordinated to the His^{6} and His^{9} residues, while for the Cu(II)-H1A/H6A system to the His^{9} and His^{12} residues. It may suggest that the size of the chelate rings as well as the structure organization of the side chains of the peptides in the complexes formed may have an impact on the complex stability.

The induction of apoptosis in vivo in insect cells of *T. molitor* by the ligands and their copper(II) complexes at pH 7.4 and the degree of caspase activation on hemocytes of *T. molitor* were determined. Moreover, the effects of the alloferon mutants H1A/H12A, H1A/H9A and H1A/H6A) and their copper(II) complexes on the phenyloxidase enzyme activity in *T. molitor* were studied.

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BM_P04

Synthesis and Cytotoxic Activity of Ruthenium Complexes with Ethacrynic Acid Derived Ligands

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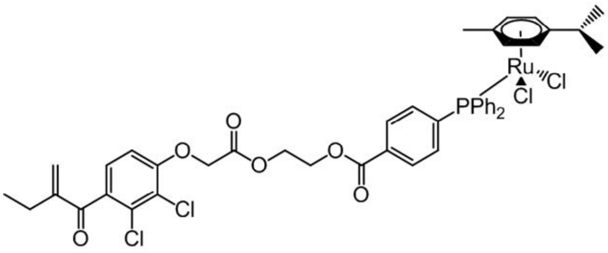
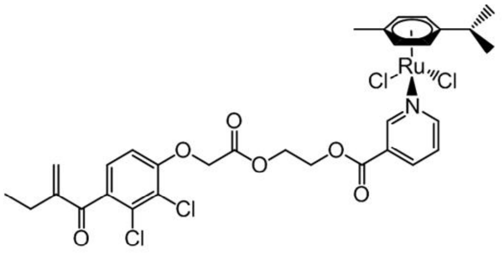
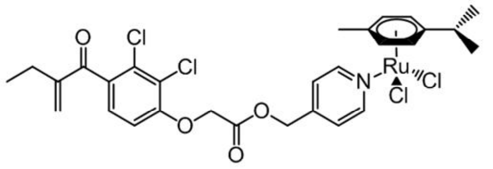
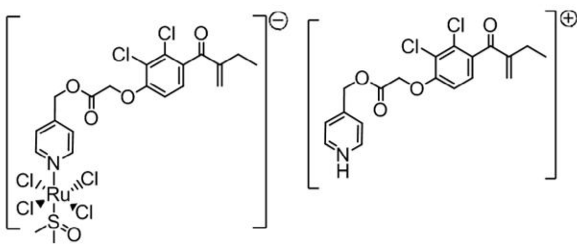
There is currently high interest in the design of organic motifs containing biologically-active fragments to be incorporated within suitable metal complexes, in order to confer them enhanced anticancer activity. One of the possible approaches regards the inclusion of the skeleton of ethacrynic acid, which is an effective inhibitor of glutathione transferases (GST), *i.e.* a family of cytosolic detoxification enzymes associated with drug resistance in primary and metastatic tumours [1]. Triphenylphosphine and pyridine-based molecules functionalized with the ethacrynic acid skeleton were synthesized and incorporated as ligands within Ru(II) arene and Ru(III) NAMI-A type complexes, respectively (see Scheme) [2]. All of the new compounds were characterized by analytical and spectroscopic methods, and by single-crystal X-ray diffractometry in one case. Preliminary cytotoxic studies will be presented.









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BM_P05

Structural Investigation of DinuclearIron(III) Complexes Relevant to Renal Injuries and Carcinogenesis

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Oxidative renal tubular injuries and carcinogenesis were reported to be caused to rodent kidneys by injection of a solution containing iron(III) ion and a chelating ligand (chalator), nitrilotriacetate [$(\mathrm{nta})^{3-}$] or iminodiacetate [$(\mathrm{ida})^{2-}$] (Fig. 1) [1]. On the other hand, however, no injury was observed when *N*-(2-pyridylmethyl)iminodiacetate [$(\mathrm{pac})^{2-}$] was used as the chelating ligand. From the spectroscopic studies, the iron(III) ions were suggested to exist as *μ*-oxo-diiron(III) complexes in solution [2]; however, detailed structures have not been clarified. Therefore, in this study, we investigated the dinuclear iron(III) structures, $[\mathrm{Fe_2}(\mu\text{-}\mathrm{O})(\mathrm{nta})_2(\mathrm{H_2O})_2]^{2-}$ (**1**), $[\mathrm{Fe_2}(\mu\text{-}\mathrm{O})(\mathrm{edda})_2(\mathrm{H_2O})_2]$ (**2**), $[\mathrm{Fe_2}(\mu\text{-}\mathrm{O})(\mathrm{ida})_2(\mathrm{H_2O})_4]$ (**3**), and $[\mathrm{Fe_2}(\mu\text{-}\mathrm{O})(\mathrm{pac})_2(\mathrm{H_2O})_2]$ (**4**), based on the DFT computations, where ethylenediamine-*N*,*N*'-diacetate [$(\mathrm{edda})^{2-}$] is the chelating ligand.

DFT computations were performed using GAMESS program on FUJITSU PRIMERGY CX400 (TATARA computer)at Kyushu University.Structural optimizationswere performed with LC-BOP/6-31G. Molecular structures were drawn using Winmostar software.

In this study, the most stable isomers were found for four dinuclear iron(III) complexes **1**-**4**on the basis of DFT method, considering all the possible isomers. For example, in the case of nta complex **1**, four isomers were finally obtained, and the most stable isomer is shown in Fig. 2. Since the renal injuries were suggested be caused with respect to hydrogen peroxide, the structures of $\mathrm{H_2O_2}$-adducts were examined for **1**-**4**.As a result, carcinogenic **1** and **3** were found to interact with hydrogen peroxide easily, forming $\mathrm{H_2O_2}$-adductswith a μ-$\mathrm{H_2O_2}$-1*κO*,2*κO'* bridge, while such an interaction was found to be impossible for non-carcinogenic **4**. In the case of **2**, the interaction seemed to be impossible; however, after a deformation, a$\mathrm{H_2O_2}$-adduct was obtained. This seems to be consistent with the low carcinogenicity of **2**.

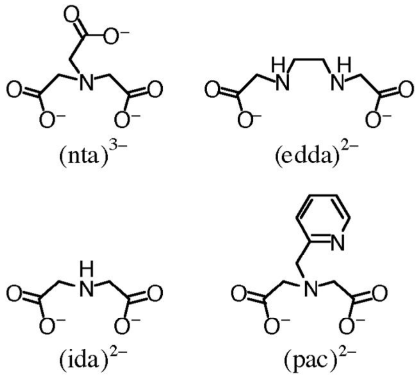
$(\mathrm{nta})^{3-}$ $(\mathrm{edda})^{2-}$ $(\mathrm{ida})^{2-}$ $(\mathrm{pac})^{2-}$

Fig. 1. Chemical structures of chelating ligands (chelators).

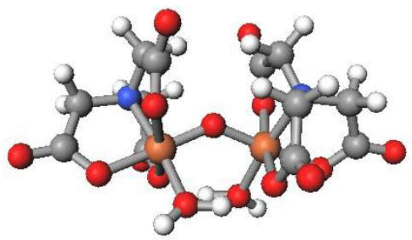

Fig. 2. Optimized structure for $[\mathrm{Fe_2O}(\mathrm{nta})_2(\mathrm{H_2O})_2]^{2-}$.

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BM_P06

ElectronicStructures of One-ElectronOxidized Nickel(III)-PhenolateComplexes

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Oxidation chemistry of redoxa ctive transition metal complexes with pro-radical ligands and their detailed electronic structures have been actively pursued in recent years. Many efforts for determination of the experimental oxidation number have been close to the goal of the “truth oxidation state” in various oxidized metal complexes with non-innocent ligands. Depending on the relative energies of the redox-active orbitals, metal complexes with non-innocent ligands exist in two limiting descriptions, either a metal-ligand radical (M^{n+}(L$^{\bullet}$)) or a high valent metal (M$^{(n+1)+}$(L^{-})) complex [1]. Oxidized Ni^{II}-salen-type complexes are known to exist in either form, and the factors that control the locus of oxidation in these complexes are being pursued currently [2];One-electron oxidation of Ni-salen-type complexes forms the Ni^{II}–phenoxyl radical species, while addition of exogeneous ligands to the Ni^{II}–phenoxyl radical solution gives the metal-centered oxidation, Ni^{III}–phenolate species.

In order to understand high eroxidation state of the oxidized Ni^{II}-salen-type complexes, we have characterized detailed electronic structures of the one-electron oxidized Ni^{III} complexes, [Ni(**salcn**)(py)$_2$]$^{2+}$ and [Ni(**salpn**)(py)$_2$]$^{2+}$[3]. These two Ni^{III} complexes have same donor groups, while the chelate ring size of the dinitrogen backbone is different. The Ni^{III} complexes exhibited different oxidation potential at 0.79 V for [Ni(**salcn**)(py)$_2$]$^{+}$ and 0.41 V for [Ni(**salpn**)(py)$_2$]$^{+}$. Addition of the 1 equiv. of [Ru(bpy)$_3$](PF$_6$)$_3$ to the solution of the Ni^{III} complex gave the one-electron oxidized forms, which were EPR silent at 4 K. XANES of these Ni^{III} complexes and [Ni(**salcn**)(py)$_2$]$^{2+}$exhibited the same pre-edgeat 8334.2 eV, while the pre-edge of [Ni(**salpn**)(py)$_2$]$^{2+}$ was shifted ca. 0.5 eV lower than Ni^{III} complex, [Ni(**salpn**)(py)$_2$]$^{+}$. From these results, the valence state of the oxidized complexes [Ni(**salcn**)(py)$_2$]$^{2+}$ and [Ni(**salpn**)(py)$_2$]$^{2+}$can be assigned to a Ni^{III}–phenoxyl radical and Ni^{II}-bis(phenoxylradical), respectively.

Literature:

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BM_P07

Bioinorganic Chemistry of the Complexes of Cadmium(II), Iron(II) and Zinc(II) with Hydroxyproline in Solution

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The stability constants of Cd^{2+}, Fe^{2+} and Zn^{2+} complexes with hydroxyproline were determined by Paper Electrophoretic Technique (PET). This method is based on the movement of a spot of metal ion in an electric field at various pH of background electrolyte [12]. A graph of pH against mobility gives information about the formation of binary complexes and permit to calculate their stability constants. The stability constant of the ML (first) and ML^2 (second) complexes of cadmium(II) – hydroxyproline, iron(II) – hydroproline and zinc(II) – hydroproline have been found to be (4.41 ± 0.01; 2.95 ± 0.06), (4.11 ± 0.01; 2.81 ± 0.11) and (4.83 ± 0.02; 3.28 ± 0.07) (logarithm stability constant values), respectively at ionic strength 0.1 mol L^{-1} (perchloric acid as background electrolyte) and a temperature of 35 ºC. The first and second stability constants of metal complexes follow the order Zn(II) > Cd(II) > Fe(II).

Keywords: Paper electrophoretic technique, cadmium(II) complexes, iron(II) complexes, zinc(II) complexes, stability constants.

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BM_P08

Iron(III) complexes with a testosterone arm for artificial enzymes

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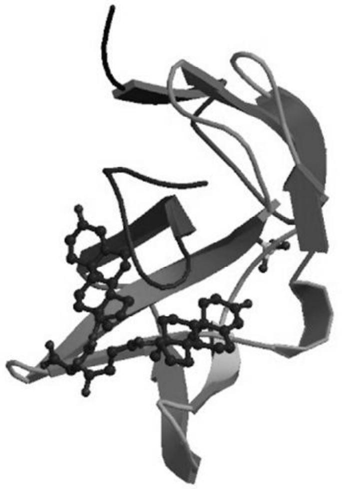
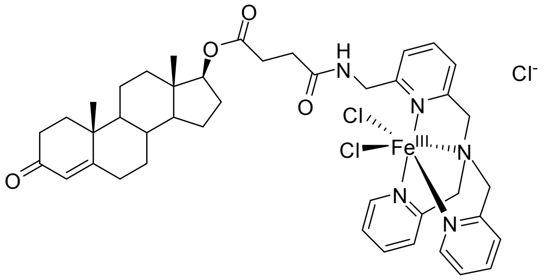
Enzymes are naturally occurring catalysts capable of carrying out chemical reactions with high selectivity and in mild conditions.Many strategies are applied by chemists to obtain enzyme mimics [1], in order to improve the efficiency of organic reactions.Among them, we are interested in the assembly of bio-hybrids composed of a protein in interaction with an iron-based catalyst, for oxygen activation.

In this communication, we will present the synthesis of a new iron(III) complex (**1**) with a tripod ligand bound to a testosterone arm, allowing recognition by neocarzinostatin(NCS) 3.24[2].The complex was characterized by UV-Vis absorption spectroscopy, electrochemistry and HR-MS.The bio-hybrid was prepared and characterized by UV-Vis and fluorescence quenching.

We have investigated the reactivity of both complex **1** and the biohybrid, in the presence of 3,5-di-*t*-butylcatechol and protocatechuic acid. Preliminary results in these catechol dioxygenase reactions suggest a solvent-dependent reactivity.We will disclose our latest results.





Complex **1**

Literature:

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OC_P01

Aminocarbonylation of arylhalides using palladium compounds containing phosphorus-nitrogen ligands

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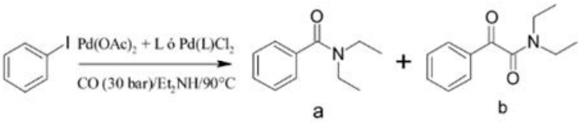
From an industrial and pharmaceutical point, the aminocarbonylation of arylhalides is an interesting reaction because several products can be obtained through this process, like steroidal derivatives, among others [1,2]. These reactions can be catalyzed by Pd(II) complexes [1,2], and Pd(II) complexes containing P^N type ligands have been studied before in the alkoxycarbonylation of styrene, showing good activities and selectivities [3]. This work shows the results of the study of Pd(II) complexes containing new P^N ligands, derivated from aminoquinoline, used as catalysts in the aminocarbonylation of iodobenzene. This reaction was carried out in a high-pressure, temperature-controlled reactor, and can be carried out using a Pd(II) complex containing P^N ligands, or a Pd(II)Cl_2 precursor and the ligand added in situ to the medium. Substrates (Et_2NH and iodobenzene), solvent (DMF) and catalyst were mixed in a Schlenk tube under N_2 atmosphere, and then charged in the reactor. CO (30bar) was charged thereafter and the reactor was set up at 90°C. Samples were collected every 1 hour and analyzed in a gas cromatograph equipped with a FID.



Entry	Compound	Time (h)	Conversion (%)	Selectivity a	Selectivity b
1	2-APQ[a]	3	99	14	86
2	8-APQ[a]	3	99	16	84
3	1-APiQ[a]	3	93	14	86
4	8-OPQ[a]	3	96	25	74
5	Pd(2APQ)Cl_2[b]	3	98	34	66
6	Pd(8APQ)Cl_2[b]	3	99	40	60
7	Pd(1APiQ)Cl_2[b]	3	98	14	86
8	Pd(8OPQ)Cl_2[b]	3	99	34	66

The reaction studied *in situ*(1-4) with all ligands shows similar selectivity towards the ketocarboxamide (b) product (86%), achieving conversions between 93%-99%. When the catalytic reaction was carried using Pd(P^N)Cl_2, the selectivity changed mildly. These results suggest that the intermediate species in the catalytic reaction are Pd(II) compounds containing P^N ligands and these ligands stabilize the Pd(II) compounds under CO pressure.

Acknowledgments
We want to thanks CONICYT for the financial support given by Fondecyt-Chile programs 1120149 and 1120685.

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OC_P02

Unusual reactivity of azuliporphyrins with ruthenium

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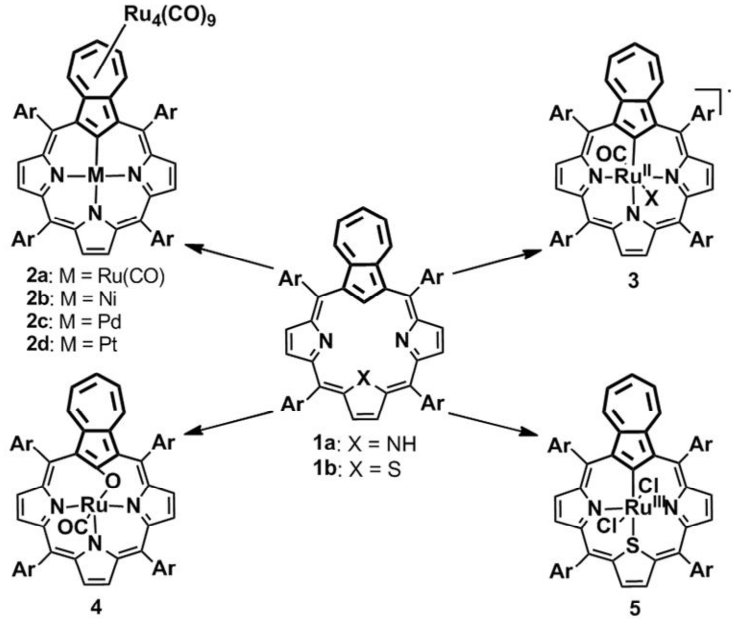
Insertion of a metal ion into a carbaporphyrinoid coordination cavity provides a unique surroundings for investigation of metal-carbon interactions. Thus, catalytically active ruthenium has been reacted with azuliporphyrin **1**. Reaction of triruthenium(0) dodecacarbonyl with tetraarylazuliporphyrin **1a** activates the azulene fragment as a separate coordination platform within macrocyclic limits giving, besides generation of regular complex [Ru(TArAP)(CO)], a series of [M(TArAP){$Ru_4(CO)_9$}] **2a**-**d**polymetalic species[1].

[Ru(TArAP)(CO)] undergoes either one-electron oxidation or oxygenation with insertion of an oxygen atom into the Ru-C bond [2]. One-electron oxidation afforded $[Ru(TArAP)(CO)]^{+\bullet}$ **3** recognized as the first ever observed π-cation radical of metallocarbaporphyrinoids. The radical **3** reveals ^1H NMR features of the $d_{xy}^2 d_{xz}^2 d_{yz}^2 a_{2u}^1$ electronic ground state of ruthenium porphyrins characterized by unprecedented spin density distribution localized on the azulene unit. The spin density distribution determined by DFT confirmed the π-cation radical electronic structure reproducing the diagnostic spectroscopic features including π-delocalization. Oxygenation of [Ru(TArAP)(CO)] yields ruthenium(II) 21-hydroxyazuliporphyrin **4** prone to form the cyclic head-to-tail dimer $[Ru(TArAP)(CO)]_2$. The dimer adopts a cyclic head-to-tail structure with the azulenolate groups forming bridges from one macrocycle to the ruthenium(II) in the adjacent unit.

Insertion of ruthenium into 23-thiazauliporphyrin affords **5** characterized by alternative to **3** the $d_{xy}^2(d_{xz}d_{yz})^3$ ground state. It is consistent with coordination of ruthenium(III) as reflected by specific pattern of spin density distributiondetermined by ^1H NMR.The present results are of relevance to “paramagnetic” organometallic chemistry explored in the macrocyclic environment providing the peculiarplatform for catalytically active metals.



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OC_P03

CARBON-REIFORCED POLYMER COMPOSITES FOR TRIBOLOGICAL APPLICATIONS

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1 Baikov Institute of Metallurgy and Material Sciences Russian Academy of Sciences, Moscow, Russia

Carbon composites based on thermosetting polymers are frictional meterials which combine high structural strength, shock resistance, dimensional stability comparable with that of metal alloys, and ability to run in water lubricants. Carbon fabrics, unlike all the fillers used in antifrictional polymer composites, have high strength, elasticity and heat conductivity, they do not expand in water, and the products of carbon fabrics frictional dispersion act as a solid lubricant (graphite).

Tribotechlical properties exhibited by different types of carbon composites during friction in water were found to vary within 1-2 orders of magnitude; friction coefficient and durability were found to be highly dependent on the structure of carbon fibers, chemical composition and structure of the polymer matrix, additives, and process conditions.

Tribotechnical properties of composites can also be enhanced without changing the original molecular and supramolecular structure, by means of inclusion of additional structural elements of different physical, chemical nature and morphology. Such elements, however, must have prominent effect on the conditions of the «tribopolymer» film formation and its properties.

Fluoropolymers (PTFE and its modifications) are prospective additives for enhancement of frictional carbon-reinforced polymer composites. However, PTFE is chemically inert and weakly binds with the matrix and fibers; also, its direct incorporation into a composite is technologically difficult.

Herein we suggest a technology for modification of carbon fabrics by means of fluoropolymer addition and provide results of tribological tests of the sample produced.

Carbon fabric surface modification was carried out by means of aerosol deposition of tetrafluoroethylene telomer solutions in acetone with consequent thermally induced polymerisation of the tetrfluoroethylene telomer.

Acetone evaporation results in a white fluoropolymer precipitate on the surface of the carbon fabric. According to IR, NMR, XRD, and AFM studies of the product indicate that the molucular structure of the polymer is close to that of the inductrial high molecular weight polytetrafluoroethylene F-4.

The carbon composite was tested for its durability, and the results were compared with the data for the unmodified material UGET-URAL-T15R-ECHO.

The obesrved results can be due to the following physical and chemical processes. Durability of carbon-reinforced composites exhibits nonmonotonic dependence on the counterface firmness (whereas standard antifrictional materials exhibit higher wear when a more firm counterface is used). Weak adhesion of the fiber to the matrix (which is the case of the material studied) promotes this process. Also, steel SH15 (bearing steel) is not corrosionpro of (unlike steel 20X13), and oxidation processes can have a prominent effect on friction in an aqueous medium.

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OC_P04

Solid state radical reactions of TEMPO and organozincs

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

Although phenomenon of electrostatic properties of amber were known since ancient Greeks, its nature became extensively studiedduring last five decades. The forming work of Urbański that noticed formation of radicals on the surface of grinded amber was forgotten for many years.[1] Then, in 2013 Grzybowski explained how mechanoradicals stabilize static charges on the surface of rubbed polymers.[2]Nowadays mechanochemistry – the way of breaking and forming new chemical bonds with mechanical force – is a growing new discipline of chemistry. The lack of solvent not only opens new pathways of green chemistry, but also allows for formation of products not yet accessed by conventional chemistry.

Many recent works of organometallic mechanochemistry show synthetic strategies competitive to those with classic „wet-approach”.[3] Strikingly, few of them are reported with clear evidence for its mechanism.

Herein we present a new solid-state synthesis of *tert*-butyl and phenylzinc complexes stabilized by TEMPO-anion with clear evidence for radical mechanism of the process.[4]

$$R_2Zn_{(s)} + TEMPO_{(s)} \longrightarrow [RZn(TEMPO)]_{2(s)}$$

$$+$$

$$R = tBu\text{: } TEMPOR$$

$$R = Ph\text{: } Ph_2$$

Scheme 1. Reactions of TEMPO with R_2Zn (R = *t*Bu, Ph).

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OC_P05

Hydrogen-Free Cobalt-Rhodium Heterobimetallic Nanoparticle-Catalyzed Reductive Amination of Aldehydes and Ketones with Amines in the Presence of Carbon Monoxide and Water

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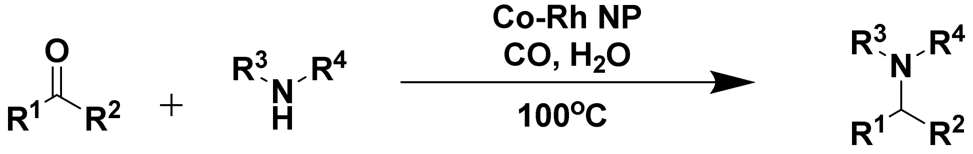
Homogeneous metal complexes-catalyzed direct reductive amination procedures are well documented.[1]Two types of reducing agents are employed for direct reductive amination of aldehyde with amines:[2] based on metal-catalyzed hydrogenation and hydride reducing agents.[3] However, the use of hydrogen is not recommendable in an industrial application, considering the risk of explosion. Reducing agents limit many substrates having reducible functionalities and some reducing agents could generate toxic byproducts. Recently, alternatives to the use of hydrogen or hydride have been reported.[4]

We recently found that cobalt-rhodium heterobimetallic nanoparticle-catalyzed reductive amination of aldehydes and ketones with amines in the presence of carbon monoxide without an external hydrogen source gave amines in high yields. Scope of the reaction will be presented.



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OC_P06

Palladium(II) complexes with phosphino-oxime ligand: Application to catalytic rearrangement and dehydration of aldoximes

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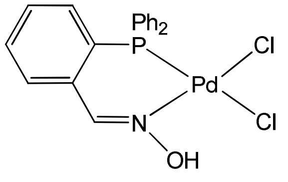
Coordination of heteroditopic ligands featuring mixed *P,N*-donor sets, such as phosphines with amino, imino, pyridyl, iminophosphorane or oxazoline groups, has been extensively studied and their resulting complexes have found application in a wide range of catalytic synthetic processes [1]. In contrast, bidentate phosphine ligands containing an oxime functionality still remain uncommon in the literature [2].

In the present communication, we report the synthesis of the first phosphino-oxime palladium(II) complexes (**1** and **2** in Scheme) easily obtained from the $[PdCl_2(\eta^4\text{-cod})]$ precursor. These derivatives, and especially complex **1**, turned out to be active in the catalytic transformation of oximes, the outcome of the reaction being dependant of the solvent used. Thus, catalytic experiments performed in water gave rise to the rearrangement of the oxime, providing the selective formation of the corresponding amide [3]. In contrast, the reactions made in MeC≡N conduced to high yields of the organonitriles, through dehydration processes (see Scheme).



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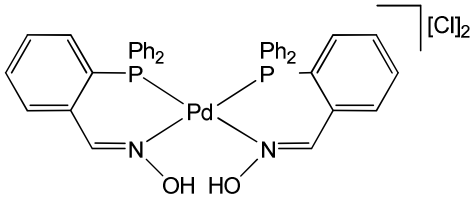

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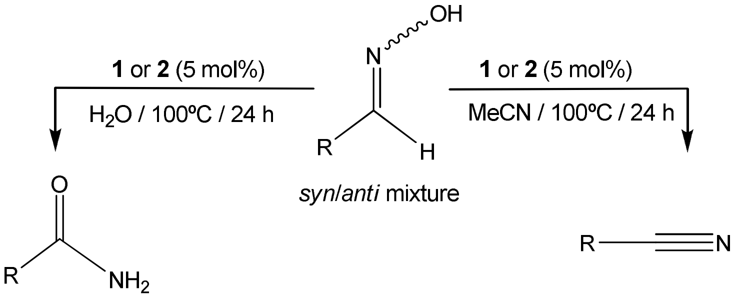

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OC_P07

Non-metathesistransformations of acetylenesmediated by second generationruthenium alkylidenecomplexes

Izabela Czeluśniak[1], Anna M. Trzeciak[1], Jarosław Handzlik[2], Maciej Gierada[2]

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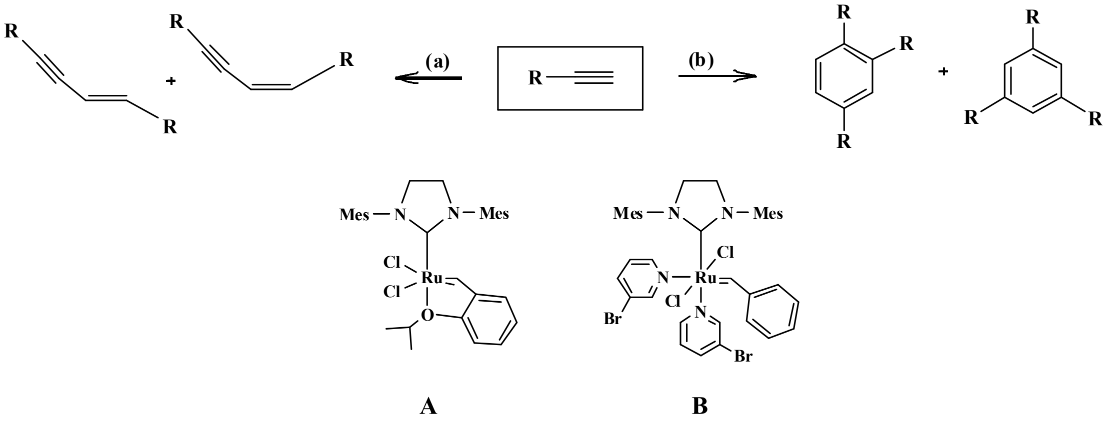
[2] *Faculty of Chemical Engineering and Technology, Cracow University of Technology,*
Warszawska 24,31-155 Cracow, Poland

Alkynes are able to take part in a large number of reactions with transformation of the triple bond. The catalytic conversion of alkynes yields polyacetylenes,enynes, enol-esters,arene derivatives,and so on. Two examples of the non-metathesis transformation of the terminal alkyne, cyclotrimerization (*a*) and dimerization (*b*) (Scheme 1), are particularly important since their products can be used as precursors for the synthesis of complex compounds, including natural products[1]. A number of homogeneous catalysts based on Ru, Co, Ni, Pd, Mo etc. have been designed for those transformations [2-4]. Among them, ruthenium catalysts play an important role due to their functional group tolerance.



Scheme 1

Here, we report the catalytic properties of second-generation phosphine-free ruthenium alkylidene catalysts: Hoveyda–Grubbs complex (**A**) and the second-generation Grubbs catalyst modified by 3-bromopyridine (**B**), with regard to the non-metathesis transformation of monosubstitutedacetylenes, e.g. cyclotrimerization and dimerization (Scheme 1). Because the selectivity of the reactions depends on the intermediates formed by the substrate and the transition metal species, some mechanistic aspects of initiation were also elucidated with quantum mechanical calculations.

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OC_P08

Template synthesis of triphosphinemacrocyles

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Phosphines have enjoyed spectacular success as supporting ligands for many transition metal complexes; their highly tuneablestereoelectronic properties coupled with favourable bonding characteristics ensure their continued widespread use in many homogeneous catalytic systems. This poster discusses our recent progress towards the synthesis of 1,4,7-triphosphacyclononanes and other macrocyclictriphosphinearchitectures*via* the ring closure of an oligomerictriphosphine compound.

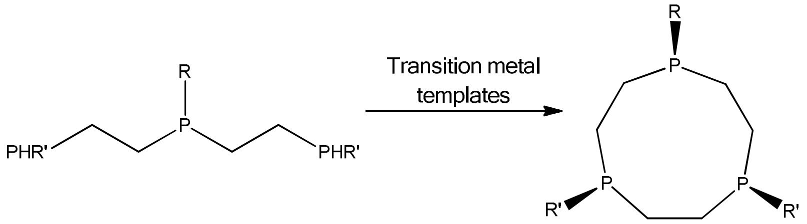

Figure 1: Proposed route to macrocyclic triphosphine ligands

Previous work within our group has identified Fe-piano stool complexes as efficient templates for the stereospecific formation of 9-12 membered macrocyclic rings[1]. Herein, we report a practical, large scale synthesis of *tert*-butyl*bis*(2-phenylphosphinoethyl)phosphine and examine its reactivity with a number of potential transition metal templates [2].Accordingly, photolysis of $[Fe(C_5R_5)(CO)_2(NCMe)]^+$ (R = H, Me) in the presence of thetriphosphineyields the piano stool templates analogous to the previously studied systems. Treatment of these with an excess of butyl lithium results in deprotonation of only a single secondary phosphine to yield an unusual mixed phosphide/phosphine complex. Alkylation of these species has been studied with a view towards formation of the target macrocyclic ligands.

Furthermore, we have surveyed the coordination chemistry of thetriphosphine with other first row transition metals in order to identify potential new transition metal templates. In particular, reaction with $CrCl_3(thf)_3$ yields *fac*-$CrCl_3$(triphosphine); an unusual coordination mode ideally suited to macrocycle formation (Figure 2).

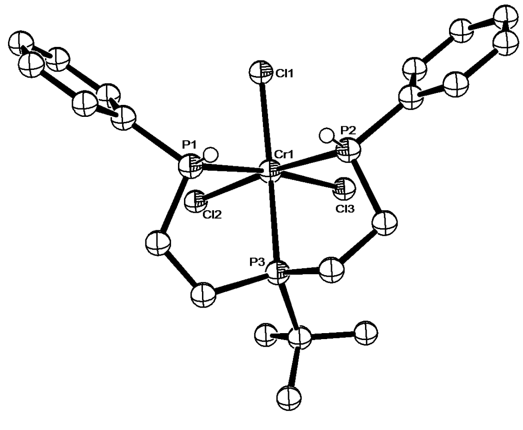

Figure 2: ORTEP representation of Cr(III) complex

Literature:

[1] Edwards, P.; Haigh, R.; Li, D.; Newman, P., Template Synthesis of 1,4,7-Triphosphacyclononanes. *J. Am. Chem. Soc.*2005, 128 (11), 3818-3830.
[2] Driver, M; Edwards, P.; Newman, P.; Straube, A., Manuscriptin preparation.

OC_P09

Understanding Product Selectivity in Rhodium-Catalysed Oxidative Coupling

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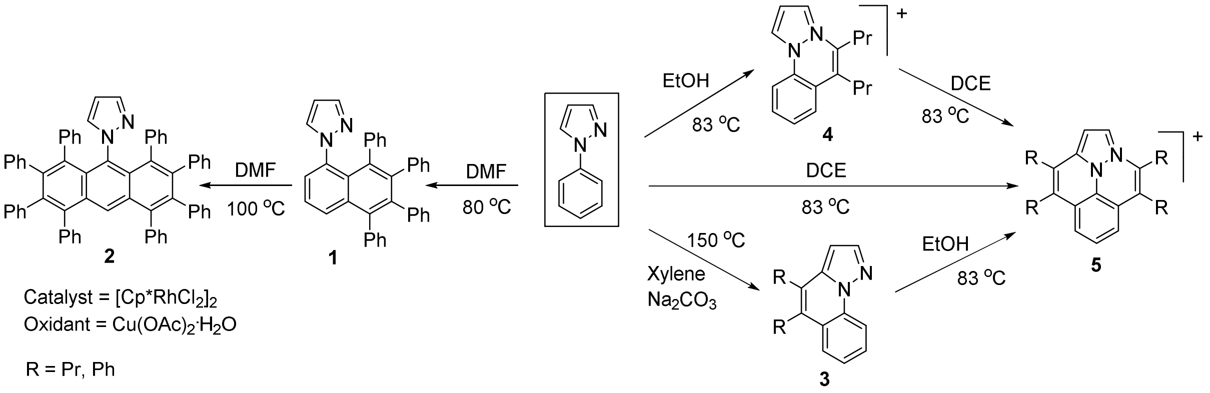
Directed C-H functionalisationcatalysed by [Cp*RhCl$_2$]$_2$ and related derivatives has recently attracted a large amount of interest as a convenient, atom economical route to new C-Y bonds (Y = C, N, O).[1,2] For example, 1-phenylpyrazole is a versatile substrate for oxidative coupling with internal alkynes forming carbocycles (**1**, **2**) or heterocycles (**3**) via C,C coupling (**Scheme 1**).[3]



Scheme 1: Product scope of 1-phenypyrazole in oxidative coupling with internal alkynes.

Herein, we demonstrate that C,N coupling to form (**4**, **5**)is also facile. Furthermore, we show that combined experimental and computational studies can help identifythe key steps within the catalytic cycle which control product selectivity. Our results suggest that product selectivity is dependent on anion coordination and the reductive elimination step, enabling rational control over product selectivity by altering the nature of the alkyne and reaction conditions.

Literature:

[1] Song, G.; Wang, F.; Li, X., C-C, C-O and C-N Bond Formation via Rhodium(III)-CatalysedOxidative C-H Activation. *Chem. Soc. Rev.***2012,**41 (9), 3651-3678.
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[3] Umeda, N.; Hirano, K.; Shibata, N.; Sato, H.; Miura, M., Rhodium-Catalysed 1:1, 1:2, and 1:4 Coupling Reactions of Phenylazoles with Internal Alkynes through the RegioselectiveCleavages of Multiple C-H Bonds. *J. Org. Chem.***2011,** 76 (1), 13-24.

OC_P10

Synthesis, Computational and Application Studies of Group VI and VII Multimetal Carbene Complexes

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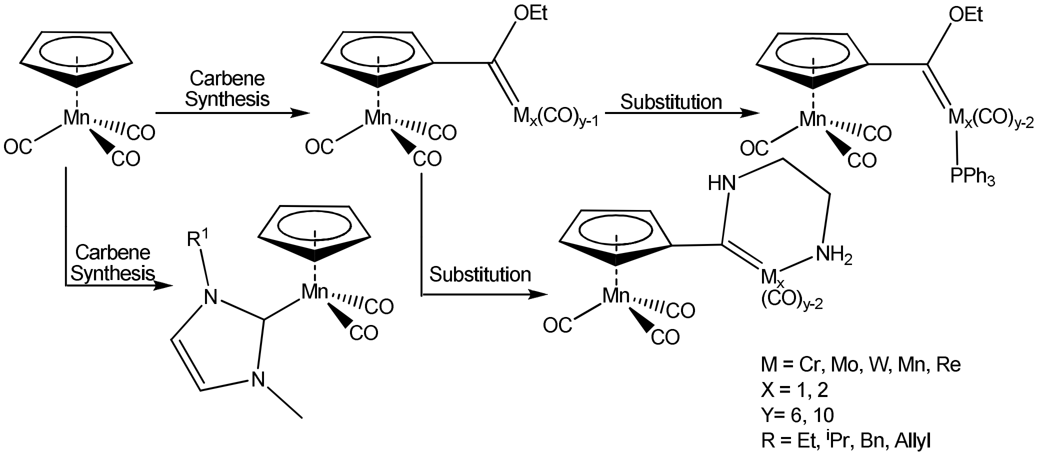
The activation of simple organic molecules by employing mutlimetallic transition metals establishes an area of research continuously growing in significance [1]. Fischer carbene complexes have found vast applications in metal mediated reactions, olefin metathesis and cycloaddition reaction [2, 3] and received attention for the applicability as organic building blocks [4]. These systems are, however, mostly limited to single transition metal carbene complexes and very few studies have been published on multimetal or cluster carbene complexes. NHC (N-heterocyclic carbene) complexes of group VII transition metals, containing carbonyl ligands, have also been limited to only a few complexes and hybrid multicarbene complexes nonexistent in literature.

Fischer carbene complexes of group VI and VII transition metals (Cr, Mo, W, Mn, Re) bearing at least two or three transition metals, entirely in electronic interaction have been synthesized in our research laboratory. The multimetal Fischer carbene complexes have been further modified by the substitution of carbonyl ligands for phosphine and amine moieties. Fischer carbene complexes will also be synthesized from a NHC-bearing metal synthon.All complexes have been fully characterized and current DFT studies are in progress to predict potential HOMO and LUMO regions. Electronic potential maps were generated to provide an indication as to the electronic environments and density of electron rich and poor regions. The application potential of theFischer, NHC and hybrid complexes, in conjunction with the DFT studies, will be discussed.



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[2] Barluenga, J. *Pure Appl. Chem.,* 1996, **68**, 543.

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OC_P11
ansa-Titanocene complexes for the investigation of fundamental steps of overall watersplitting

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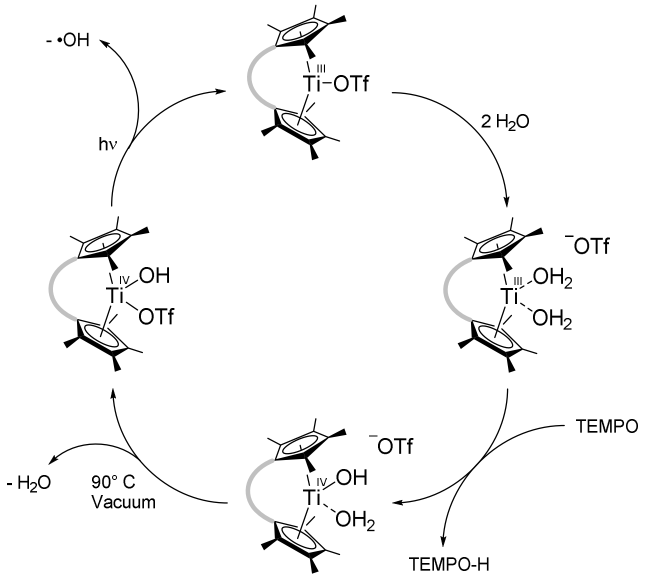
Artificial photosynthesis has attracted much interest in the last decade. The relatively simple reaction - at first glance - of splitting water into its corresponding elements has gained much attraction. However, while a plethora of papers are dealing with different approaches for water splitting,[1,2] only few research is done regarding the fundamental steps.



Scheme 1:Fundamental steps for postulated water splitting mechanism.

In our group we have investigated the potential of titanocene complexes for the investigation of elementary steps of overall water splitting.[3] In this contribution we show that formal reduction of water at a Ti centre is possible using TEMPO, while oxidation can be done by light irradiation due to OH radical abstraction. Thus, a formal cycle of water splitting could be modelled.

Literature:

[1] M. Klahn, T. Beweries,*Rev. Inorg. Chem.***2014**, *34*, 177; and references cited therein.
[2] M. D. Kärkäs, O. Verho, E. V. Johnston, B. Åkermark,*Chem. Rev.***2014**, *114*, 11863.
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OC_P12

Oxidation of [CpMo(CO)$_3$R] Complexes with *tert*-Butylhydroperoxide

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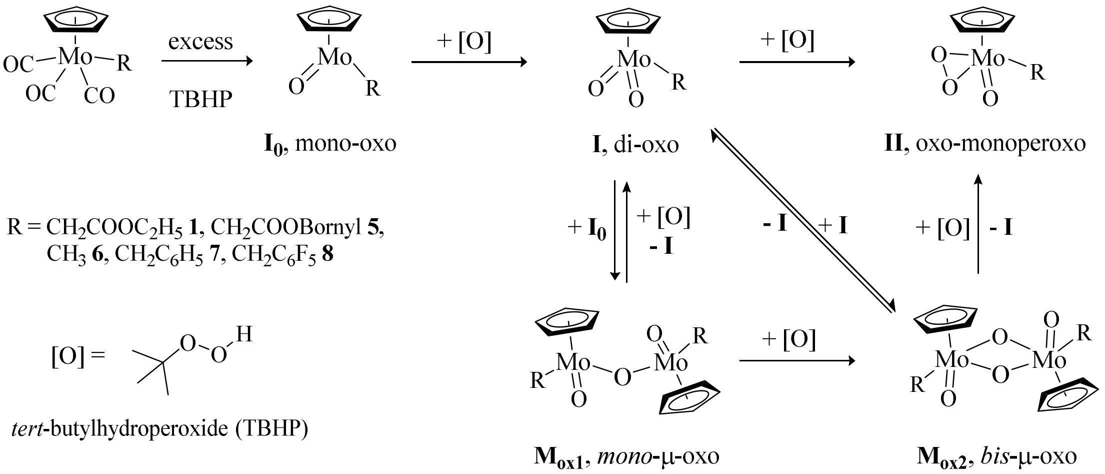
Oxidative decarbonylation of complexes of the type[CpMo(CO)$_3$R] (Cp = C_5H_5, R = alkyl, halide, NHC, alkylester, etc.) during the epoxidation reaction of unfunctionalized alkenes with *tert*-butylhydroperoxide (TBHP) oxidant results in formation ofcatalytically active Mo(VI) oxo complexes[CpMoO$_2$R] and [CpMo(O)(O$_2$)R][1]. As yet, the mechanism of this crucial process and of subsequent epoxidation is poorly understood. Indisputably, an understanding of the fate of catalytic species is important in the interest of rational catalyst design and process development. Therefore we investigated the oxidation of several such complexes(having different R) by NMR, *in situ* IR techniques and DFT calculations.



^{1}H and ^{13}C NMR study for complexes R = $CH_2COOC_2H_5$**1**, CH$_2$COOBornyl**5**, CH_3**6**, $CH_2C_6(H/F)_5$**7**, **8** in $CDCl_3$shows the formation of complexes **I**, **II** and transient species assigned as **A** and **B**. ν(Mo-O-Mo) at 678 and 655 cm^{-1}can be identified during oxidation of **5** monitored by *in situ* IR. DFT calculations for R = CH_2COOCH_3 indicate that the involvement of [CpMo^{IV}(O)R], **I$_0$** and [(CpMo^{V}(O)R)$_2$(μ-O)$_{1,2}$], **M$_{ox1,2}$** species in various oxidative transformations is energetically feasible. Oxidative decarbonylation of **5** at different reaction temperatures and oxidant and precatalyst concentrations has also been studied. IR and mass spectroscopic analysis of the precipitate obtained from oxidation of **5** suggests that it is an oxomolybdenum species without ligand R. Furthermore, ^{1}H and ^{13}C NMR study of catalytic epoxidation of *cis*-cyclooctene using **1**[2] and **5**[2,3] illustrates the inhibitory effect of the substrate on various oxidative transformations of the precatalyst.

Literature:

[1] Grover N.; Kühn F.E., Catalytic Olefin Epoxidation with η^5-Cyclopentadienyl Molybdenum Complexes. *Curr. Org. Chem.***2011**, 16(1), 16-32.
[2] Grover N.; Drees M.; Kühn F.E., Oxidation of [CpMo(CO)$_3$R] Olefin Epoxidation Precatalysts with *tert*-Butylhydroperoxide. *J. Catal.***2015**, Submitted.
[3] Grover N.; Pöthig A; Kühn F.E., Cyclopentadienyl molybdenum alkylester complexes as catalyst precursors for olefin epoxidation. *Catal. Sci. Technol.***2014**, 4, 4219-4231.

OC_P13

Organometallic Complexes of N-Heterocyclic Carbene Ligands Bearing Carboranes for Catalytic Applications

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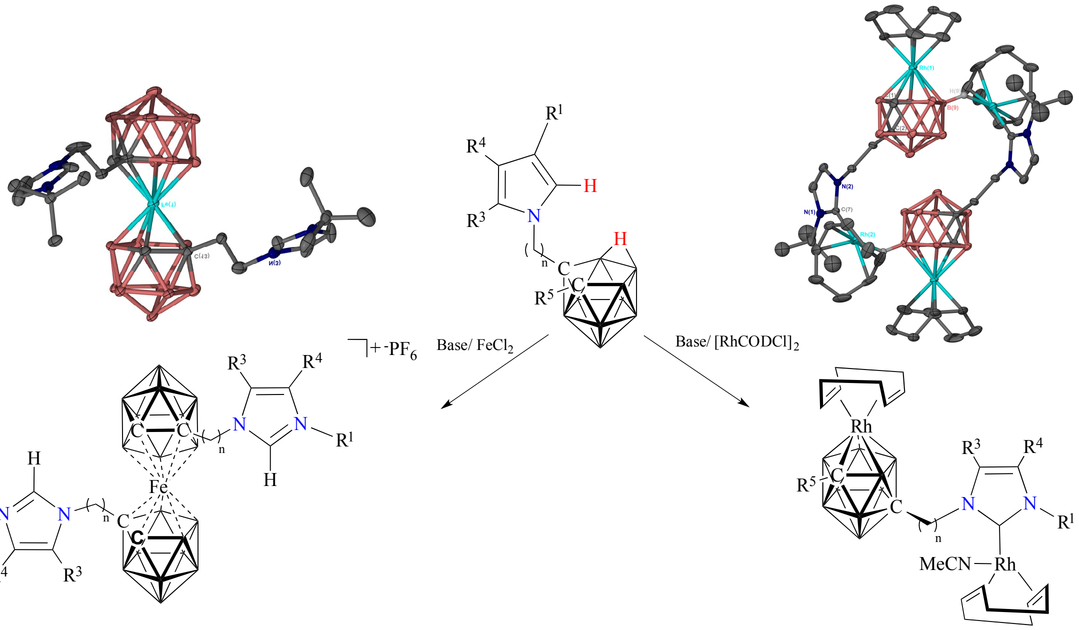
School of Chemistry, University of Leeds, UK

The development of new catalysts and catalytic processes is essential for a sustainable future. Ligand design is central to these developments as they control the activity and reactivity of a metal centre. The past two decades has seen an explosion of research into N-heterocyclic carbenes (NHCs) as ligands for catalysts. NHCs owe their success to their stability and synthetic versatility allowing for fine-tuning of steric and electronic effects through alteration of the N-substituents and backbone substituents (Figure 1. R^1-R^4). As a result, metal-NHCs have been used widely in a plethora of catalytic applications.[1]

Carboranes, which are polyhedral clusters of boron, carbon and hydrogen are another important class of ligand and have very different properties to NHCs. They can coordinate to a metal through either a boronor a carbon atom, or through the open face of a nido-carborane to form a metallacarborane, in analogy to the widely used cyclopentadienyl ligand.[2,3]The fusion of these two very different families of compounds will lead to unusual chemical behaviour and to the development of a new generation of ligands for catalysis.



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[2]Grimes, R. N.*Coord. Chem. Rev*. **2000**, 200-202, 773.
[3]Hawthorne, M. F.; Young, D.C.; Wegner, P. A. *J. Amer. Chem. Soc.***1965**, 87, 1818.

OC_P14

Contraction of rhodium(III) *meta*-benziporphyrin

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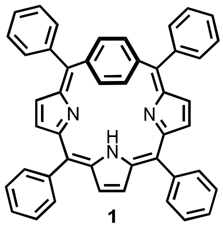
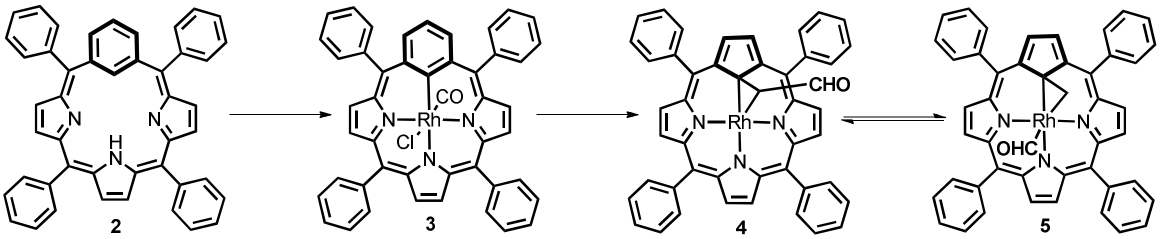


Macrocyclic environment allows for exploration of coordination variants less possible for monodendate or princer ligands. Porphyrins, by many treated as quintessential macrocyclic ligands have already demonstrated their coordination abilities, binding several transition metals,showing different coordination modes.Carbaporphyrins, belonging to this group, show a potential of being a suitable chemical background for observing unique features of a M-C bond reactivity.For instance palladium(II) or gold(III) complexes of *p*-benziporphyrin (**1**) gave a contraction of *p*-phenylene to cyclopentadienyl unit.[1,2]

The presented studies have been focused on *meta*-benziporphyrin (**2**) isomeric to**1**,[3] where one of the pyrrole rings of regular porphyrin has been replaced by *meta*-phenylene. *meta*-Benziporphyrin has been be applied as a fundamental platform to explore an impact of inner rhodium-carbon bond on overall structural and reactivity properties of rhodium*meta*-benziporphyrins once related to regularrhodium porphyrins.



Rhodium(III) *m*-benziporphyrin**3**provided the unique environment to activate*m*-phenylene unit. Taking advantage of the additional stabilization due to geometrical constraints of the porphyrin macrocycle a cascade of intramolecular rearrangements has been efficiently promoted. Accordingly the remarkable, facile rhodium(III) stimulated contraction of *m*-phenylene to cyclopentadiene has been identified affording subsequently the rhodium(III) 21-carbaporphyrin **4**incorporating the rhodacyclopropane moiety**.**The unique**4**–**5**conversion can be considered as an intriguing example of selective and reversible C-C bond activation.

Literature:

[1]Szyszko, B.; Latos-Grażyński, L.; Szterenberg, L.,*Angew. Chem. Int. Ed.***2011**, *50*, 6587.
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OC_P15

Well-suited ancillary ligand for the synthesis of single-site zinc initiator for ROP of cyclic esters.

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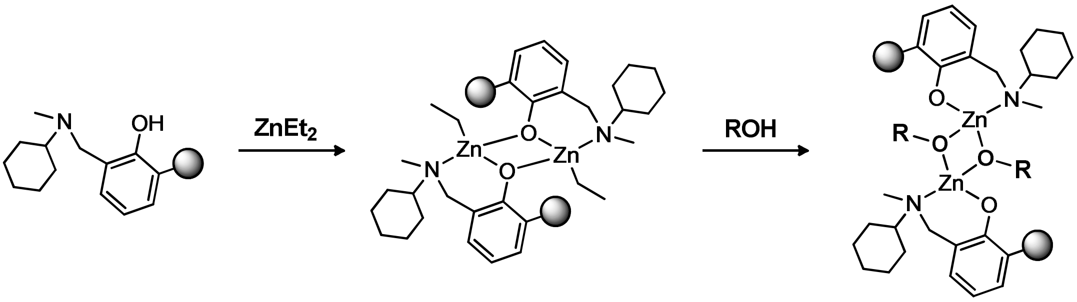
The coordination chemistry of zinc compounds, with functionalized aminophenolate ligands has been intensively studied over recent years, due to the fact that they form excellent initiators for ring opening polymerization (ROP) of cyclic esters.Most of them are generated *in situ* in a direct reaction between heteroleptic complexes of the general formula L-Zn-R and alcohols to give “single-site”L-M-OR compounds. The structural motive (L-Zn-R)$_2$ is the most wanted and expected pre-initiator for ROP, proposed by other research groups working with ancillary ligands containing N,O-donor atoms. On the other hand,an alternate catalyst system containing undesirably formed L$_2$Zn and an external alcohol also can promote ROP with high efficiency. [1,2]

The new aminophenolate ligand design strategy focuses on modelling accessibility to zinc centre for stable heteroleptic dimer formation. However modification is always proposed on nitrogen substituents with unchanged di-tert-butylphenol core. We present that subtle perturbation in proximity of hydroxyl group may be more interesting for designing of ancillary ligand (**Scheme**).The influence of N-methylcyclohexylamine derived aminophenolate ligand architecture on the heteroleptic complexes formation has been investigated by spectroscopic methods, X-ray analysis and DFT calculations.



Scheme. Synthesis of single-site zinc initiators from *ortho*functionalized aminophenols.

Literature:

[1] Wojtaszak, J.; Mierzwicki, K.; Szafert, S.; Gulia, N.; Ejfler, J.,Homoleptic aminophenolates of Zn, Mg and Ca. Synthesis, structure, DFT studies and polymerization activity in ROP of lactides. *Dalton Trans.***2014**, 43, 2424-2436.

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OC_P16

Application of palladium complexes bearing acyclic(hydrazido)(amino)-carbene ligands as efficient catalysts for copper-free sonogashira coupling

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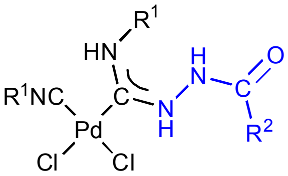
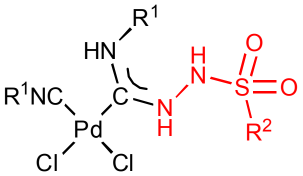
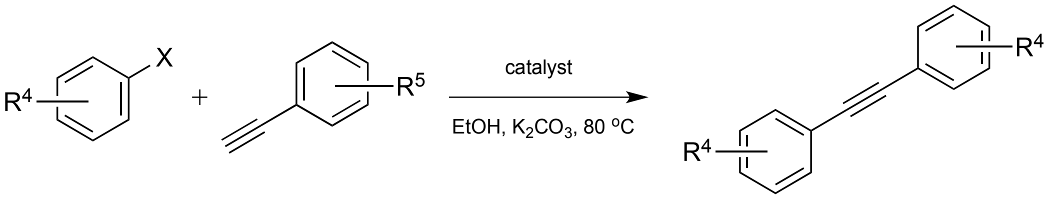
Complexes with acyclic diaminoarbene ligands (ACDs) have gained prominence as efficient and available alternative to the widely used catalysts based on *N*-heterocyclic carbenes (NHCs). In this study, we prepared a series of palladium-ACDs via the metal-mediated coupling between *cis*-$[PdCl_2(CNR^1)_2]$ [R^1 = cyclohexyl (Cy), *t*-Bu , 2,6-$Me_2C_6H_3$ (Xyl), 2-Cl-6-MeC_6H_3] andvarious carbohydrazides $R^2CONHNH_2$ [R^2 = Ph, 4-ClC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 4-$CH_3C_6H_4$, 3,4-$(MeO)_2C_6H_3$, naphth-1-yl, fur-2-yl, 4-$NO_2C_6H_4CH_2$, Cy, 1-(4-fluorophenyl)-5-oxopyrrolidine-3-yl , (pyrrolidin-1-yl)C(O), 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propane-1-yl, EtNHC(O)] or sulfohydrazides $R^3SO_2NHNH_2$ [R^3 = Ph, 4-MeC_6H_4].





Complexes exhibited high activity [yield of product up to 75–96%, and TONs up to 10^4] in Sonogashira coupling of various aryl iodides with a range of substituted aromatic alkynes without the need of copper co-catalyst. The catalytic procedure runs at 80 °C for 1 h in EtOH using K_2CO_3 as a base. No formation of homocoupling or acetylene decomposition products was detected.



This work has been partially supported by the Saint Petersburg State University (research grant from Laboratory of Cluster Catalysis), RAS Presidium Subprogram coordinated by acad. N. T. Kuznetsov, and Russian Fund for Basic Research (grants14-03-01005, 14-03-31204 мол_а, 12.50.2525.2013and 12.15.341.2014). SAT is grateful to Saint Petersburg State University for the postdoctoral fellowship. Authors thank the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research of Saint Petersburg State University, and Portuguese NMR (IST-UTL Center) and mass-spectrometry (IST Node) networks.

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[2] E.A. Valishina, M.F.C. Guedes da Silva, M.A. Kinzhalov, S.A. Timofeeva, T.M. Buslaeva, M. Haukka, A.J.L. Pombeiro, V.P. Boyarskiy, V.Yu. Kukushkin, K.V. Luzyanin. *J. Mol. Catal. A.*, 2014, *in press*.

OC_P17

From *p*-Benziporphyrin to Rhodium(III) 21-Carbaporphyrins. Imprinting Rh···η^2-CC , Rh···η^2-CO and Rh···η^2-CH Coordination Motifs

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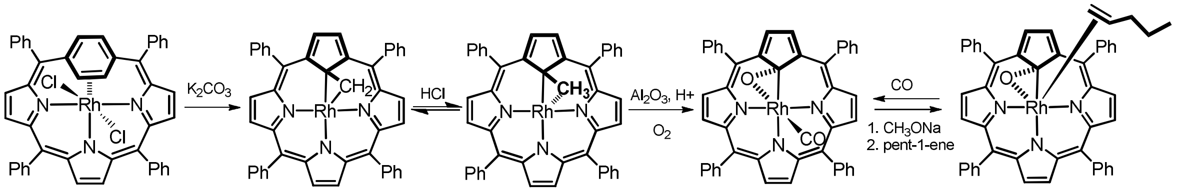
[1] *University of Wroclaw Department of Chemistry,F. Joliot-Curie 14, Wroclaw (Poland).*

Carbaporphyrinoids including *p*-benziporphyrin [1], provide an intriguing surrounding for the advanced investigation of organometallic chemistry confined to an unique macrocyclic environment. The close proximity of CH or CC bonds to the metal ion enforces an unusual coordination geometry and eventually unique reactivity. For instance palladium(II) or gold(III) altered the fundamental frame of *p*-benziporphyrin, allowing facile contraction of *p*-phenylene to cyclopentadiene.[2,3]

Our objective is to study the rhodium(III)-triggered reactivity at the carbaporfirynoids surrounding. The choice of a metal cation is strongly motivated by the extensive interest in reactions catalyzed by rhodium porphyrins or rhodium pincer ligand complexes and in particular by their capability to contribute in processes in which the activation of the single bond is of the critical importance in synthetic and catalytic conditions.



1-Rh **2**-Rh **4**-Rh **3**-Rh-CO **3**-Rh-pent-1-ene

The rhodium(III)*p*-benziporphyrin(**1**-Rh)evidently cast a suitable platform to explore fundamental factors that determine the unique transformation of the *p*-phenylene unit, prompted by equatorial η^2-CC interaction, to form the unique rhodium(III) 21-carbaporphyrin (**2**-Rh)which the CNNN macrocyclic coordination cavity assists the creation of peculiar Rh···η^2-CC, Rh···η^2-CO or Rh···η^2-CH coordination motifs. When **2**-Rh dissolved in dichloromethane saturated with gaseous HCl is placed on basic alumina it converts to Rh(III) 21-hydroxy-21-carbaporphyrin where an apical position is occupied by carbonyl (**3**-Rh-CO). **2**-Rh also reacts rapidly with HCl to yield a resultant C(21)-methylated species **4**-Rh. The Rh(III) 21-hydroxy-21-carbaporphyrin reacts with sodium methoxide, followed by addition of pent-1-ene enforced the formation of **3**-Rh-(pent-1-ene).

The specific coordination surrounding facilitates the stabilization of peculiar structural motifs related to the rhodacyclopropane and – after oxygenation-oxarhodacyclopropane architectures. The peculiar reversible methyl-methylene-hydride transformation encountered at the 21-carbaporphyrin cavity can be considered as the stimulating example of selective and reversible C-H bond elimination, providing snapshots of active species and encouraging a further exploration.

Literature:

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OC_P18

Tungsten(0)-Catalyzed Construction of Pyran Ring in Reaction of Alkynol and Secondary Amine

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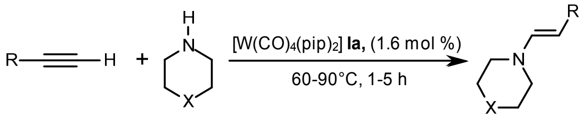
Alkynes are widely available reagents and the catalytic addition of the N−H bond of amines to the triple bond of alkynes, RC≡CH, is of great significance in the synthesis of enamines and the other nitrogen containing compounds.This atom-economical process is mostly catalyzed by complexes based on such metals as Rh, Ru, Pd, Au, Ag, lanthanides or actinides [1-3].

Recently, we found the highly selective and efficient hydroamination of alkynes with cyclic secondary amines in the presence of a tungsten(0) piperidine complex *cis*-[W(CO)$_4$(pip)$_2$](**Ia**) (Scheme 1)[4]. However, we observed that in similar reaction conditions, a reactivity of alkynols is somewhat different.

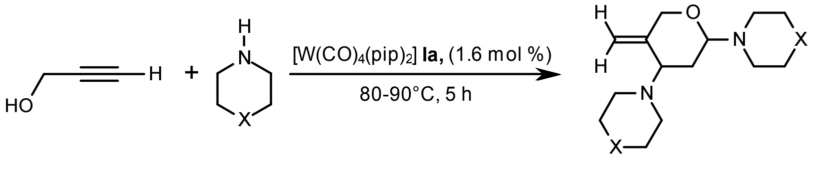


1 **2** **3**

R = Ph **1a**, C_6H_4-4-Me **1b**, C_6H_4-4-F **1c**, n-C_4H_9 **1d**, CH_2OMe **1e**, CH_2OH **1f**, CH(OH)Me **1g**, CH_2CH_2OH **1h**, C(OH)Me_2 **1i**
X = CH_2 **2a**, - **2b**, O **2c**, NMe **2d**, NH **2e**, CHMe **2f**, CH_2-3-Me **2g**

Scheme1

As an extension of our continuous study on hydroamination of triple C≡C bond, we have now found that in the presence of tungsten(0) catalyst the hydroamination of prop-2-yn-1-ol (**1f**) was accompanied by the hydroalkoxylation/cyclization and elimination of water molecule processes, leading to the construction of pyran ring (Scheme 2).



1f **2** **4**

X = CH_2 **2a**, - **2b**, O **2c**, NMe **2d**, CHMe **2f**, CH_2-3,5-Me_2 **2h**

Scheme2

Allcompounds containing the pyran ring (**4**) were identified by GC-MS and isolated with high yield.Their molecular structureswere revealed in solution by one and two-dimensional ^{1}H and ^{13}C NMR spectroscopy.

Acknowledgements:
This research was supported by a grant from the National Science Centre, Poland (No. 2013/09/N/ST5/00402).

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OC_P19

The Use of $Sc(OTf)_3$ as the Catalyst for the Synthesis of Thioether-FunctionalizedOrganosiliconCompounds

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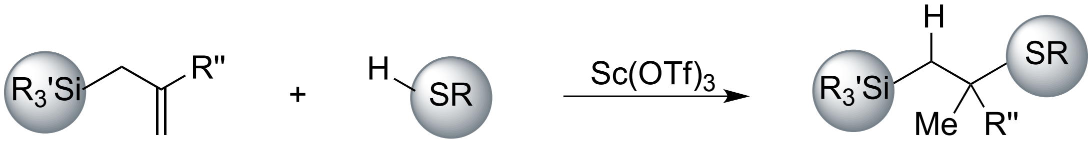
Hydrothiolation reactions allow the introduction of thioether functionality into unsaturated systems [1]. Sulfur-containing organosilicon compounds are highly important as building blocks in complex organic structures such as polymers and dendrimers [2]. They have been also used in the functionalization of superparamagnetic materials [3].

To our knowledge, all earlier research on the addition of thiols to allylsilaneshave been based on free-radical reactions. The radical-type addition of thiols dominantly leads to the expected anti-Markovnikov compounds [4].

In the communication we report the first use of a Lewis acid catalyst in the addition reaction of both aromatic and aliphatic thiols to unsaturated organosilicon compounds. Scandium(III) triflate demonstrates high catalytic activity in this process under very mild conditions (25°C, 1-10h). The number of thioether-functionalized organosilicon species were obtained with appreciable selectivity. It is the first example of allylsilaneshydrothiolation that gives the Markovnikovregioisomer as the main product. Ethynylsilanes are also successfully used in the hydrothiolation in the presence of $Sc(OTf)_3$. The application of ethynylsilanes led to the formation of double-addition products – mostly *β*-dithioacetals [5].



R = alkyl, aryl R' = alkyl, aryl, siloxyl R'' = H or Me

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OC_P20

Synthesis and characterization of Zn(II), Co(II) and Cu(II) complexes bearing *N*-methyl-*N*-((pyridin-2-yl)methyl)cyclohexanamineligand

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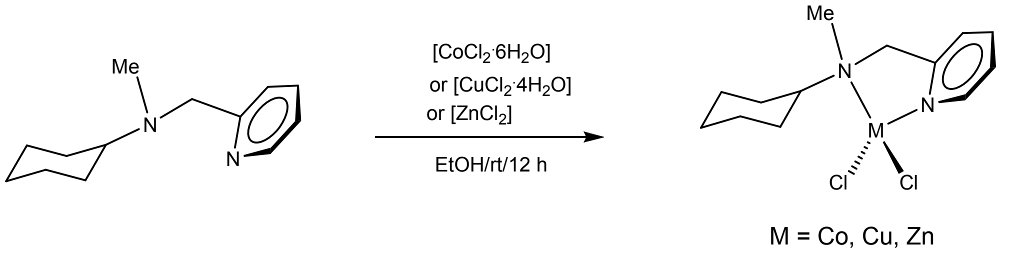
The New complexes **[(nmpc)MCl$_2$]** (M = Co, Cu, Zn) were synthesized by the reaction of the corresponding metal starting materials, anhydrous **[ZnCl$_2$], [CoCl$_2$·6H$_2$O]** and**[CuCl$_2$·2H$_2$O]** with *N,N'*-bidentate*N*-methyl-*N*-((pyridin-2-yl)methyl)cyclohexanamine (**nmpc**), respectively. The X-ray crystalstructure of **[(nmpc)ZnCl$_2$]** and **[(nmpc)CoCl$_2$]** were best described as a distorted tetrahedral geometry resulting in the formation of an four-membered metallocyclic ring.**[(nmpc)CoCl$_2$]**showed the highest catalytic activity for the polymerization of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) with an activity of 7.45×10^4g PMMA/molCo·h at 60°C among the others compared to the reference complex **[CoCl$_2$]** (4.03×10^4g PMMA/molCo·h) or **[CoCl$_2$·6H$_2$O]** (4.73×10^4g PMMA/molCo·h) or **[CoCl$_2$·6H$_2$O]** (4.73×10^4g PMMA/molCo·h).



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OC_P21

Direct syntheses of novel Ni(II) and Ru(II) NHC complexes

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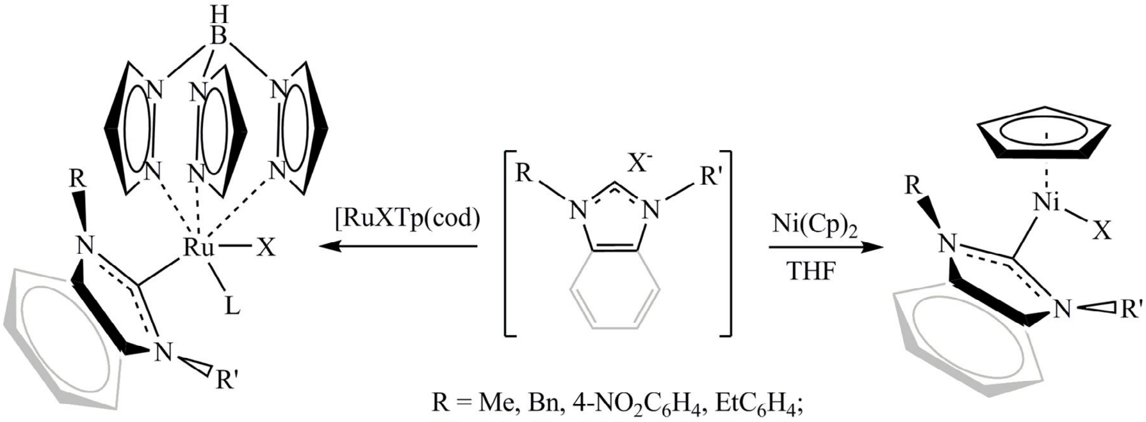
In recent years, *N*-heterocyclic carbenes have radically developed to being employed as efficient synthetic precursors, biologically active compounds, and highly active organocatalysts for unique transformations [1, 2]. These NHC complexes exhibit sought after properties including stability through strong metal-carbene binding, ease of handling, and compatibility with a wide range of low and high oxidation state metals [2].

We are currently investigating novel direct synthetic routes to new group 8 and 10 transition metal NHC complexes which exhibit stability in solution, with high catalytic activity. A range of symmetric and asymmetric aliphatic-arene NHC ligands has been synthesised and reacted in the known one-step reaction with $NiCp_2$ to give rise to novel NiBr(Cp)(NHC) complexes in high yield (> 72%, Figure 1) [3]. The hydrotris-(pyrazolyl)borate (Tp) ligand has also been extensively employed as an alternative ligand to the comparable ligand of C_5R_5 since they exhibit similar electronic properties, and therefore gives rise to 'half-sandwich' metal complexes for which, especially RuCp and RuTp complexes, a vast range of synthetic routes and applications in organocatalysis exist [4]. An investigation into direct routes to a range of neutral RuXTp(L)(NHC) and related complexes from the readily available polymer $[RuCl_2(1,5\text{-cod})]_x$ are currently underway, which will also be discussed. Reaction and chemical properties of the novel Ni(II)- and Ru(II)-NHC complexes synthesised will be presented.



$R = Me, Bn, 4\text{-}NO_2C_6H_4, EtC_6H_4$;
$R' = Me, Bn, 4\text{-}NO_2C_6H_4, EtC_6H_4$;
$X = Br, I; L = CH_3CN$

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OC_P22

Diversity of structures of alkyl zinc alkoxides

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Alkylalkoxy zinc derivatives have many applications in modern material chemistry, which are either already used on common basis in organometallic synthesis, or are still in development. Knowing the impact of the ligand structure on the aggregation of the obtained complexes allows to design new functional materials in a more rational way. In the literature many different types of aggregation of organometallic complexes were described (Figure 1). For alkylzinc derivatives the dimeric (type I)[1] and tetrameric (type II)[2,3] structures are the most common. Trimeric form of alkylzinc derivatives has been mentioned only once up to date[4].

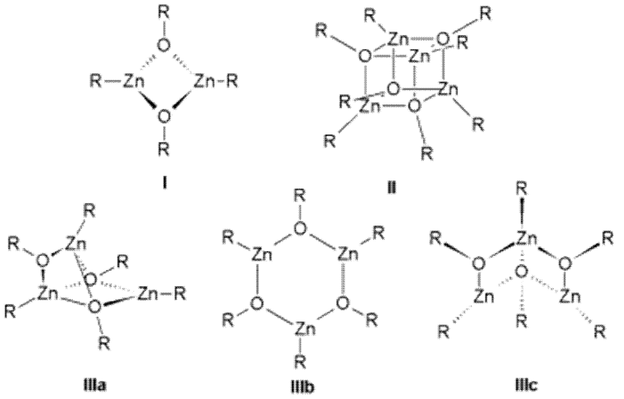

Figure 1.

During the research di-*tert*-butylzinc and three alcohols with different electron and steric structures were used. Three new model alkoxyzinc derivatives with different types of aggregation were characterized and particularly interesting results were obtained in a reaction with diphenylmethanol. This complex crystallized in a very rare and uncommon way as a trinuclear block. So far, in the literature there was only one trimeric complex of zinc mentioned and it was of the IIIa type.[4] The [$\{Ph_2HCOZntBu\}_3$] obtained the roof conformation (IIIc type) that has never been known before for this kind of aklylzinc complexes supported by monodentate alcohols.

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OC_P23

Complexes of Ni(II) Containing PN and PNP Ligands as Catalysts in Hydrogen Transfer Reaction.

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Catalytic hydrogenation plays a very important role for generating fine chemical products [1]. Conventional hydrogenation reactions use molecular hydrogen as a reagent. However, it is possible that in the presence of a metal complex, a donor molecule transfer hydrogen to an unsaturated substrate (e.g. an amine) which acts as an acceptor. Donor molecules commonly used are formic acid or 2-propanol, the latter simultaneously playing the role of solvent.

In this study, catalysts of nickel (II) with ligands of the type PNP and PN [2] were used. New compounds $[NiBr(PNP)]Br$ **(1)** and $[NiPPh_3(PNP)](CF_3SO_3)_2$ **(2)** after being appropriately characterized by spectroscopic methods (IR, NMR and others) and X-ray diffraction were used as catalysts in the hydrogen transfer reaction towards the N-benzylideneaniline substrate. Isopropanol or formic acid was used in the catalytic systems as hydrogen donor source. Both systems were tested under basic condition using potassium tert–butoxide or triethylamine in different ratio (substrate/catalysts: 200/1).

In table 1, it can be seen that both Ni (II) complexes show catalytic activity in short reaction times. With both complexes a gradual increase in conversions was observed when the base in the process was reduced. This allow to increase the yield up to 100% of conversion with **(1)** and 93% with **(2)** in the total absence of a base, when formic acid was used as source of hydrogen.

% Conversión

	$[NiBr(PNP)]Br$			**$[Ni(Ph_2P\text{-}NH\text{-}py)_2](CF_3SO_3)_3$**		
Hours (h)	iPrOH/t-BuOK	$HCOOH/Et_3N$	HCOOH	iPrOH/t-BuOK	$HCOOH/Et_3N$	HCOOH
0	9	75	53	6	63	75
1	10	90	86	12	75	90
2	11	93	100	9	75	93
3	11	91	100	8	76	93
4	18	87	100	4	80	93
5	2	87	100	4	85	93

Table 1. **Results of the catalytic activities of (1) and complex (2), for the hydrogen transfer reaction of the N-benzylideneaniline.**

The new complexes of Ni (II) containing ligands of PN and PNP type show an excellent activity in the hydrogenation reaction of N-benzylidenaniline. In this reaction, various metals have been used, such Ru and Pd, but nickel compounds have not been reported as catalysts for this reaction. The results obtained in our study represent an alternative to those metals already studied, due to the lower cost of nickel and considering that 100% of yield is obtained.

Acknowledgements: We thanks to Fondecyt-Chile (Projects 1120865 and 1120685).

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OC_P24

Synthesis, structural characterization and photophysical study of cyclometalated arylplatinum(II) complexes containing bis(diphenylphosphino)acetylene as bridging ligand

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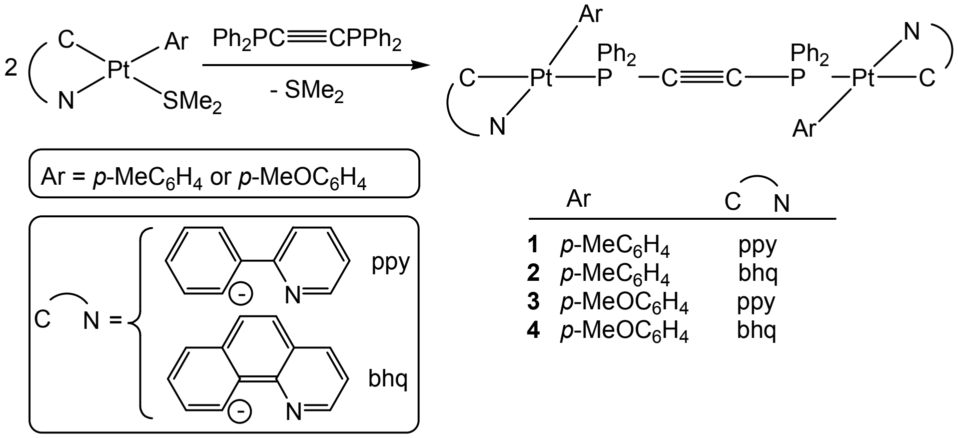
Cyclometalated square-planar platinum(II) complexes are currently attracting widespread interest due to their potential in the development of optoelectronic devices, photocatalysts and sensors [1-3]. In this area, square-planar mononuclear platinum(II) complexes containing a single cyclometalating ligand and a large range of noncyclometalating ancillary ligands have been widely studied both in solution and in the solid state due to their rich photophysical properties [4]. Despite these, the related photophysical investigations with diplatinum complexes are scarce [5].

The cyclometalated complexes [PtAr(C^N)(SMe_2)] (C^N = 2-phenylpyridinate or benzo[h]quinolinate, and Ar = *p*–MeC_6H_4 or *p*–$MeOC_6H_4$, react with 1,1'–bis(diphenylphosphino)acetylene, dppac, in a 2:1 ratio very easily in acetone at room temperature to give the symmetrical binuclear cycloplatinated(II) complexes [Pt_2Ar_2(C^N)$_2$(μ–dppac)], **1–4**, (C^N = ppy or bhq) in which the dppac ligand is bridging bidentate (see Scheme). The electronic structures of the complexes **1-4** have been calculated with the density functional theory (DFT). Additional information about the geometries and electronic spectra of these cyclometalated platinum(II) complexes has been investigated.



	Ar	C N
1	*p*-MeC_6H_4	ppy
2	*p*-MeC_6H_4	bhq
3	*p*-$MeOC_6H_4$	ppy
4	*p*-$MeOC_6H_4$	bhq

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OC_P25

Synthesis of primary and secondary amines catalyzed by well-defined diamino and diimino Mo_3S_4 clusters

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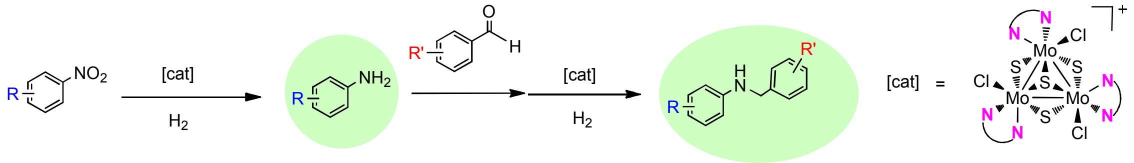
Aromatic amines are important intermediates in the manufacture of dyes, pigments, agrochemicals, pharmaceuticals and polymers. The direct hydrogenation of nitroarenes is the most environmentally benign and cost-effective methodology for the preparation of primary amines[1]. For the synthesis of secondary amines, several methodologies have been reported, but the tandem reductive amination using nitroarenes as starting materials is a clean and atom-economical alternative[2]. In this context, heterogeneous catalysts are preferred on the bulk industrial scale, but their chemoselectivity limitations make the use of selective homogeneous catalysts the most convenient approach.



Scheme 1. Synthesis of primary and secondary amines catalyzed by Mo_3S_4 clusters.

Recently, we have reported the transfer hydrogenation of nitroarenes mediated by a Mo_3S_4 cluster functionalized with outer diphosphane ligands[3]. On the other hand, we have investigated the reduction of nitroarenes under hydrosilylation conditions using a novel diamino Mo_3S_4 cluster as catalyst[4]. Here, we present the use of well-defined diamino and diimino clusters in the chemoselective hydrogenation of nitroarenes bearing other sensitive reducible moieties to provide a wide range of primary amines. Preliminary results are presented on the tandem reductive amination between nitroarenes and aldehydes catalyzed by a diamino complex using hydrogen as reductant.

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OC_P26

Synthesis of long 1-iodopolyynes and their use as a substrates for palladium(II)-end capped polyynes

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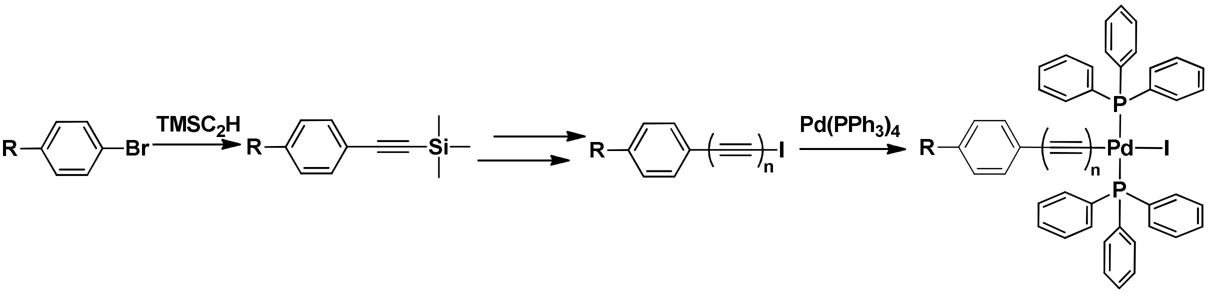
Organic, organometallic, and metal-containing polyynes have been attracting a constant interest of the scientific community for more than fifty years.[1] Such species may be regarded as a model compounds of hypothetical linear allotropic form carbon – carbyne. Carbyne still remains elusive but polyynes have a significant application potential, for example as precursors of conducting polymers, in nanoelectronics as molecular wires and switches or as materials with nonlinear optical response.[2] Organometallic compounds are important group of polyynes and to date the most intensive studies concern rhenium, ruthenium and especially platinum complexes.[3] However, palladium end-capped polyynes are very rare and nearly unexplored.

Here we present the synthesis of the longest known palladium end-capped polyynes.[4] First, the synthesis of long 1-iodopolyynes with carbon chain up to decapentayne was carried out. The iterative strategy with Cadiot-Chodkiewicz cross-coupling as a key step was applied (see Scheme 1.). Next the reaction of 1-iodopolyynes with Pd(PPh$_3$)$_4$ was performed. As a result series of palladium complexes was obtained. Decapentayne reported here is the longest known palladium end-capped polyyne.



Scheme 1. Synthesis of 1-iodopolyynes and palladium end-capped polyynes.

All palladium end-capped polyynes and 1-iodopolyynes were fully characterized with the use of ^{1}H, ^{13}C and ^{31}P NMR, IR, UV-Vis, HRMS(ESI) and TGA-DTA methods. Moreover X-ray single crystal analysis was performed for few compounds.

The authors would like to thank the National Science Centre (UMO-2012/05/N/ST5/00665) for support of this research.

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OC_P27

Cross-coupling reactions between organosilanes and olefins catalyzed by palladium(II) complexes

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Palladium-catalyzed cross-coupling reaction is a powerful tools for synthesis of arylated olefins. Arylated olefins are ubiquitous structural motifs in natural products, pharmaceutical intermediates, cosmetology and organic materials[1]. Of the many organometalloids known to undergo coupling reactions, organosilicon reagents are the most intriguing since they are inexpensive, non-toxic, readily prepared and environmentally friendly.

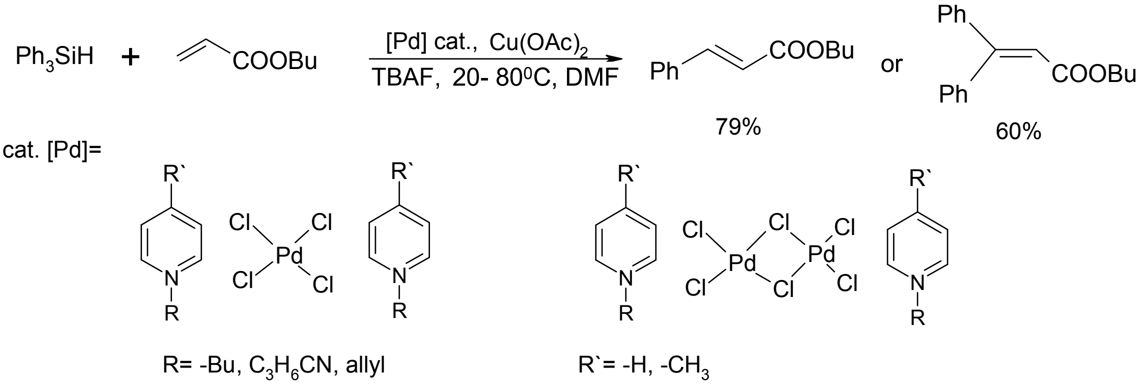

Figure 1 Arylation of olefins catalyzed by anionic palladium(II) complexes

In this work we present a new way leading to arylated olefins, based on a cross-couplin triphenylsilane or aryl trialkoxysilanes with acrylates catalyzed by anionic palladium(II complexes[2] (Fig.1). The reaction was studied with variation of parameters such a different oxidants (e.g. copper salts, oxygen, AgF), salts, time and solvents. Studie shown a positive effect of the presence of pyridinium cations on the catalytic activity o palladium complex. Also effect of the temperatures on the selectivity of the reactio have been observed. As a alternative for traditional oil bath a microwave reactor ha been used.

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OC_P28

Palladium-catalyzed Heck arylations of allylic alcohols

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Palladium-catalyzed Heck reaction with allylic alcohols as substrates is interesting because it generates variety of arylatedketones or aldehydes as products. The regioselectivity of the insertion for terminal alkenols is mainly controlled by steric factors and the addition of the aryl moiety usually occurs on the unsubstituted carbon of the double bond [1].

β-Aryl ketones, products ofthis type Heck reaction can be usedfor the synthesis of medicinal products, for example 4-phenyl-2-butanones (enzymatic inhibitors) [2]. Main product (A) from the reaction shown on Fig. 1, 3-phenylpropionaldehyde,might synergize with the major compound trans-cinnamaldehyde in Cinnamomumosmophloeum extract for their antibacterial and anti-inammatory effects on H. pylori infection [3].

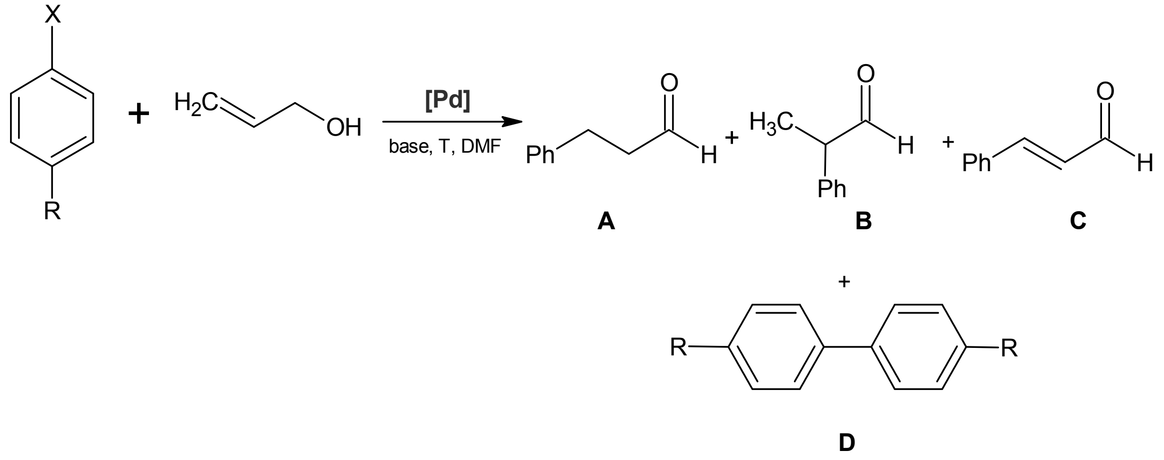

Figure 1. Heck arylation of allyl alcohol catalyzed by palladium catalyst

In this work we would like to present our result of synthesis of arylated ketones, involving different aryl halides and catalysed by $Pd(OAc)_2$, $PdCl_2COD$ or Pd(0) nanoparticles. The reaction was studied with variation of parameters such as different temperature (85^oC - 130^oC), time (1.5h –24h) and addition of molten salts (TBAB). In this reaction we used weak bases- $NaHCO_3$, NaOAc, Et_3N. We have been observing effect of the time on the selectivity of this reaction and base influence on the yield.

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OC_P29

Effect of the chiral ionic liquids containing a (-)-menthyl group on the palladium-catalyzed Heck arylation of homoallylic alcohols

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Palladium-catalyzed Heck reaction has been well known as one of the most important methods for the formation of new C-C bonds in organic chemistry.[1] Using as its substrates allylic alcohols is an interesting because it is easy way to obtain carbonyl compounds.[2]
Reaction products: the arylated allylic alcohols undergo isomerization to carbonyl compound compounds which are useful intermediates for the synthesis of pharmaceuticals, fragrances or natural product for example 4-arylo-2-butanones.[3,4]

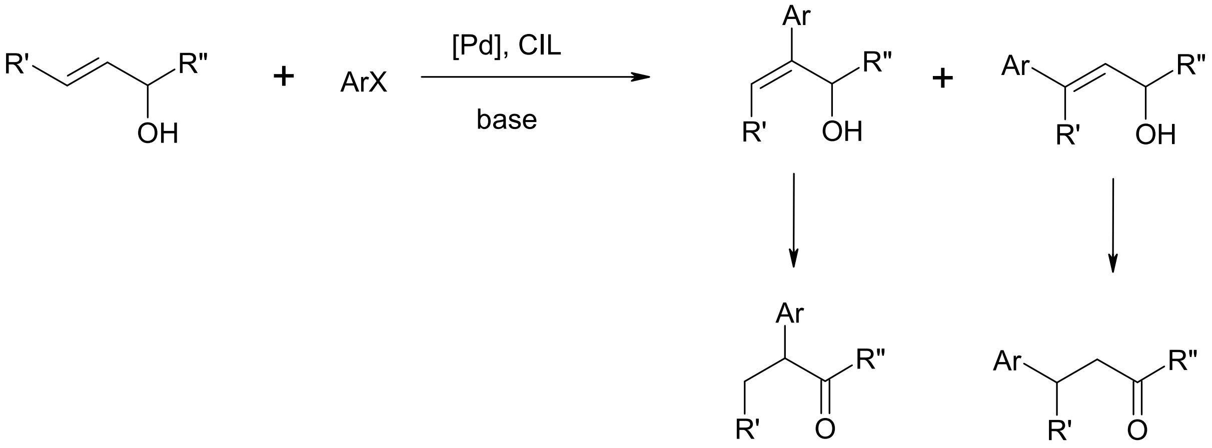

Figure 1.Heck arylation of homoallylicalcohols.

The aim of the work is to find new method of synthesis of arylated ketones, involving a cross-coupling between homoallylic alcohols and aryl halides(Fig.1). We used $PdCl_2(COD)$ as a catalyst and chiral ionic liquids containing (-)-menthyl group as co-catalyst. The reaction was carried out at 80°C and 24h in the presence of weak base – $NaHCO_3$. As a model C-C coupling reaction we used Heck arylation 3-buten-2-ol with different aryl iodide.
Studies shown that cation of ionic liquid has a positive effect on the selectivity and yields of products.

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OC_P30

The carbonylative Suzuki cross-coupling reaction catalyzed by H – spirophosphorane palladium complexes

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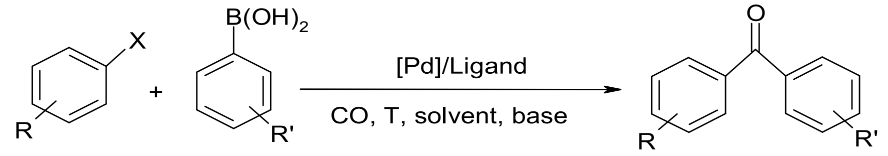
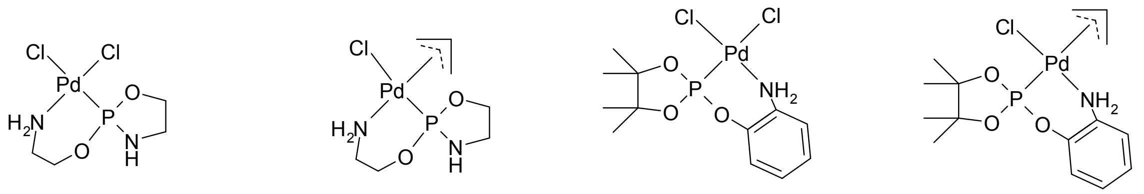
In the last decades the carbonylative cross-coupling reactions of arylboronic acid with aryl halides are significant interest in academia and fine chemical industry (scheme 1). Products of these reactions – diarylketones constitute an interesting structural motif which is frequently present in non-steroidal anti-inflammatory drugs (Nepafenac, Fenofibrate), occurs in UV screens (Sulisobenzone, Oxybenzone) and natural products (Papaveraldine).



X = Cl, Br, I
R, R' = alkil, aryl, halide

Scheme 1. The carbonylative Suzuki cross-coupling reaction.

Until now, catalytic activity of palladium complexes incorporating hydrospirophosphorane ligands in carbonylative Suzuki reactions of arylboronic acid with aryl halides have been never studied. In this work the coordination properties of $HP(OCH_2CH_2NH)_2$ and $HP(OC_6H_4NH)(OCMe_2CMe_2O)$ ligands towards $[PdCl_2(cod)]$ and $[Pd(\mu\text{-}Cl)(C_3H_5)]_2$ precursors has been performed. Four catalysts: $[PdCl(C_3H_5)\{P(OCMe_2CMe_2O)OC_6H_4NH_2]$, $[PdCl_2\{P(OCH_2CH_2NH)OCH_2CH_2NH_2\}]$ $[PdCl_2\{P(OCMe_2CMe_2O)OC_6H_4NH_2]$, $[PdCl(C_3H_5)\{P(OCH_2CH_2NH)OCH_2CH_2NH_2\}]$ with hydrospirophosphorane ligand connected to palladium atom in bidente mode have been obtained (scheme 2) and characterized by spectroscopic methods. The catalytic activity of these catalysts was tested in carbonylative Suzuki reaction of phenylboronic acid with 4-iodoanisole. The results show that under mild reaction conditions (2h, CO (balloon pressure), 100 ^{0}C) these complexes are relatively high-yielding and selective catalysts for Suzuki carbonylative cross-coupling reaction. Analysis of post-catalytic solution by Transmission Electron Microscopy showed a presence of palladium nanoparticles which are generated *in situ* during reaction. Mercury test showed that they are one of the active form of palladium catalyst.



$[PdCl_2\{P(OCH_2CH_2NH)OCH_2CH_2NH_2\}]$ $[PdCl(C_3H_5)\{P(OCH_2CH_2NH)OCH_2CH_2NH_2\}]$ $[PdCl_2\{P(OCMe_2CMe_2O)OC_6H_4NH_2\}]$ $[PdCl(C_3H_5)\{P(OCMe_2CMe_2O)OC_6H_4NH_2\}]$

Scheme 2. H-spirophosphorane palladium catalysts

OC_P31

AlkylzincPhosphates: Synthesis, Structural Diversity and Materials Chemistry

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The impact of organophosphorus chemistry on modern chemistry is difficult to quantify, but it can be assume that the study of this element has influenced all areas of chemical science.The number of known phosphorus compounds is greater than 10^6, but phosphate estersare probably still the most underestimated organophosphorus compounds in organometallic and coordination chemistry. What's more? In excess of many inorganic zinc phosphate found in the CCDC database, only 5 are alkylzinc derivatives, of which only 4 adopt a conventional $RZn(O_2POR)$ arrangement. Therefore, gain experience from coordination chemistry of organophosphorus and utilize this approach in the construction of new organometallic precursors of functional ZnO-based nanomaterials is in the particular significance.

In the reported work, we focused on the synthesis and structure characterization of novel alkylzinc complexes derived from selected phosphates.We obtained a great diversity of molecular structures: from simple tetramers to unprecedented heptadecanuclearalkylzinc phosphatecomplexes. Moreover, we present the largest multinuclear zinc aggregate to date, which features several interesting structural motifs. All of studied complexes appear to be very promising precursors toward ZnO nanocrystals (NCs) of controlled size and shape under mild conditions using a bottom-up approach from organometallic precursor. The obtained nanometer size NCs are highly monodispersed. Furthermore, the obtained ZnO NPs exhibit green or yellow photoluminescence and relatively high quantum yield. Systematic studies on optical, physical and chemical properties of resulting ZnO NPs were investigatedand confirmed by many analytical techniques.

OC_P32

Palladium supported on aminopropylene functionalized silicone polymernanospheres. Simple and effective catalyst for Suzuki-Miyaura C-C coupling.

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Over the last few decades, palladium-catalyzed coupling reactions have gained particular attention for their role in the synthesis of fine chemicals and pharmaceutical ingredients. Using palladium catalyzed coupling reactions in the pharmaceutical industry offers some advantages however, while soluble Pd complexes are commonly used as catalysts, their efficient separation after reaction for subsequent recycling remains a challenge and has economic and environmental implications[1].This is a significant problem for the pharmaceutical industries because strict guidelines are followed to limit the levels of heavy metals in products for human consumption[2].

Our recent studies shows, that NH_2modified silicone polymers[3, 4]are really good candidate as support for palladium based fine chemicals catalyst.

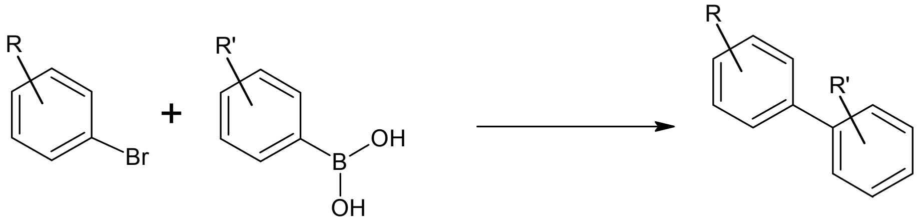

fig.1. Suzuki-Miyaura C-C coupling reaction scheme.

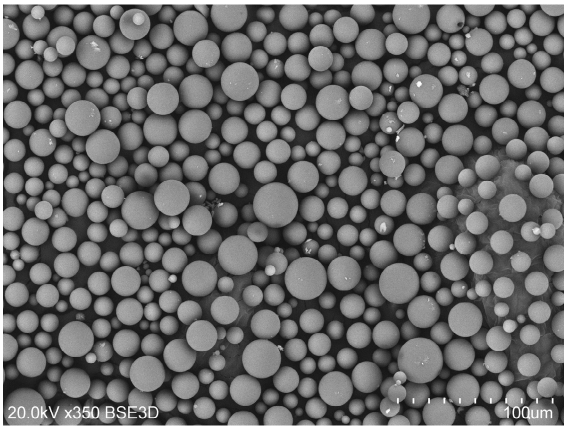

fig.2. SEM of supported palladium.

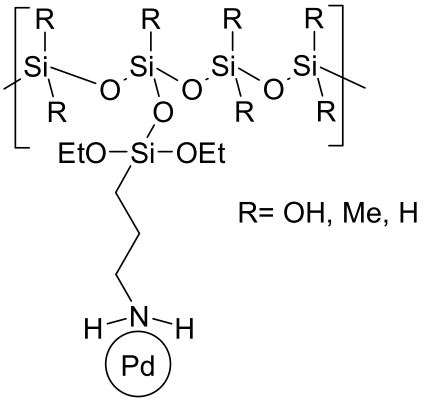

fig.3. Representation of catalyst structure

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OC_P33

The characterization and application of the new polymer supported palladium catalysts prepared under supercritical conditions.

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Due to the ever increasing need for new, heterogeneous catalyst, our attention has been directed to the synthesis of the new polymer supports for metal complex catalysts based on epoxy resin cured with multifunctional polythiourethanes. The immobilization of homogeneous palladium catalyst $PdCl_2(PhCN)_2$ carried out under supercritical conditions enable a more accurate and better distribution of the metal complex in a polymer matrix.

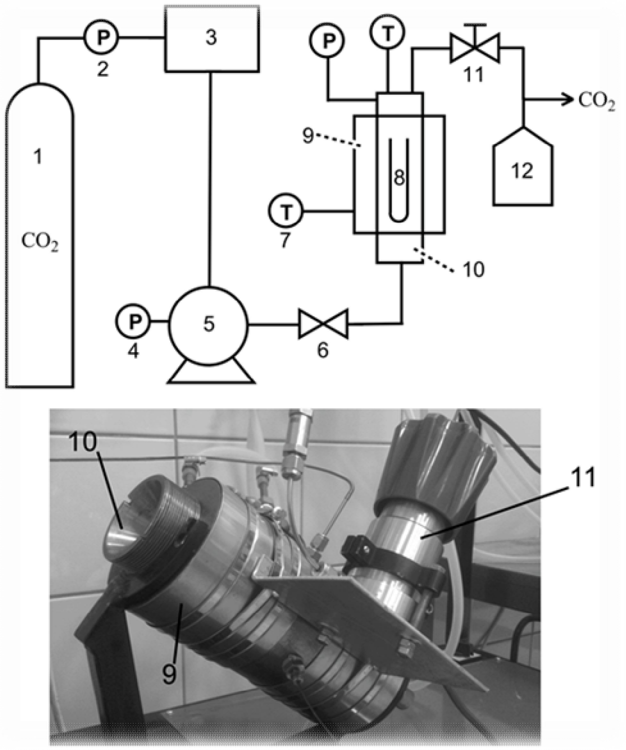

Figure 1. Scheme of supercritical immobilization equipment; the photograph of autoclave with thermostated bath: (1) CO2 bottle; (2, 4) pressure gauge; (3) cooling bath cryostat; (5) liquid pump; (6) needle valve; (7) temperature sensor; (8) glass tube; (9) thermostated bath; (10) autoclave; (11) pressure reduction valve; (12) solvent trap.

The morphology, chemical structure of the polymeric supports, the types of binding groups presented in the polymer and condition of immobilization influence on the selectivity of catalytic reactions. The use of these materials provides to obtain low cost, able to simple separation from the reaction medium and chemically resistant supports which can be used in many areas of chemical technology.

M_P01

Effect of heat treatment on the morphology and product yield of porous ZrB_2 nanofiber

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Abstract

One of the most potential strategic ultra-high temperature ceramics, zirconium diboride (ZrB_2) nanofibers with the diameter of 297±103 nm were fabricated by electrospinning technique and subsequent heat treatment. Upon pyrolyzing under carefully three step process, high-purity and crystalline ZrB_2 nanofibers retaining the morphological features of the as-spun nanofibers were obtained. The resulting material is characterized by TG–DSC, XRD, FE-SEM, EDX, and BET. The EDX analysis confirms that the products obtained at 1350 °C are containing only zirconium, and boron with no oxygen. It was found that the crystallite sizes of nanofibres were about 59 nm.

Keywords: Zirconium diboride; Nanofiber, Electrospinning; Heat treatment; Carbon source.

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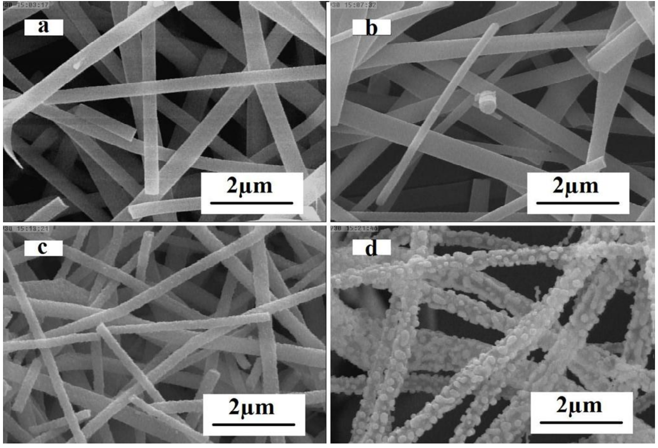

Fig.FSE-SEM images of the stabilized 8 wt% PVP/Zr(OPr)4 nanofiber at 150 ˚C/24 h anda) pre-oxidized at 350 ˚C/4h and b) followed by carbonization at 1350 ˚C/4 h, with theheating rate of 2 ˚C/min for both of them, c) pre-oxidized at 350 ˚C/4h with the heating rateof 20 ˚C/min and d) followed by carbonization at 1350 ˚C/4 h with the heating rate of 2˚C/min in graphite crucible.

M_P02

SiCwhiskers /Carbon Nanofibers Composite for High-Temperature Li-Ion Battery Anode

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Lithium-ion battery is widely used in military and civilian small appliances. But, it is still with limited at high charge and discharge rate, because of the heat generation behavior during the charging and discharging and degradation by long-time storage [1]. To overcome this deficiency of lithium-ion batteries and improve safety and reliability of the battery, the electrospun SiO_2/polyacrylonitrile (PAN) nanofibers were calcinated at 1400 °C under an inert gas to form Silicon carbide(SiC) whiskers /carbon nanofiber (CNF) composites and used as new anode material of Lithium-ion battery. SiC is ceramic semiconductor material which has high chemical stability, high hardness, high thermal conductivity and low thermal expansion coefficient[2] to improve the stability of battery during the high discharge rate. The electrospun CNF has special three-dimensional nanofiber network structure allows easy access of electrolytes. In addition, the shorter pores path of nanoscale diameter of nanofiber can reduce the distributed resistance and enhances the rate handling ability [3].

Measurements of discharge capacity are done by assembling SiC/carbon nanofibers composite as anode material on a coin cell. The capacity of pure CNF and C/Si=3.43 composite are 165 and 103 mAh/gat 0.1C discharge rate and room temperature. When discharge rate increaed to 10C, the capacity remained 17.5% which is better than that of pure CNF (47.5% capacity reduction). It indicates that SiC/CNF composites can quickly discharge at high current density. For high temperature testing(60 °C),the capacity of C/Si=3.43 composite did not change significantly comparing with operation at room temperature. When discharge rate increaed to 10C, the capacity remained 50% (pure CNF was fail at this condiction). At 0.1C discharge rate and 60 °C, the capacity still remained90% (pure CNF was only 33%) when the discharge rate return from 10C. As results shown, SiC whiskers growth on CNF as anode of Lithium-ion battery for high current discharge and temperature has the significant effect upon the functional features the batteries.

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M_P03

The effect of humidity on the resistive gas sensor response in chlorine

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Chlorine is a very reactive gas characterized by unpleasant, suffocating smell and is a strong poison for humans and animals [1]. Currently, it is widely used as an agent for water treatment and as one of the main substrates of many chemical reactions carried out under industrial conditions. The harmfulness of this compound in conjunction with its wide range of applications causes that there is a need to detect and control this gas concentration in the environment. On the market there are available only electrochemical chlorine sensors which can operate only within a certain range of humidity. However, unsatisfactory in industrial conditions. The devices that will be able to solve this problem may be resistive gas sensors.

The subject of this study was to develop a resistive chlorine sensor with active layer in the form of zinc oxide microrods. The growth of ZnO structures was carried out in water solution of zinc nitrate (V) and hexamethylenetetramine using the chemical bath deposition method in the presence of electric field. The structure and morphology of obtained sensitive layer was characterized by electron scanning microscope (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). To determine the gas-sensitive properties Temperature-Stimulated Conductance method (TSH) was used. During the measurements sensor was tested in an atmosphere containing a precisely defined concentration of chlorine and humidity. Obtained results showed that developed sensor allow to detect chlorine (Fig. 1). It was also found that the humidity have a significant influence on the sensor response.

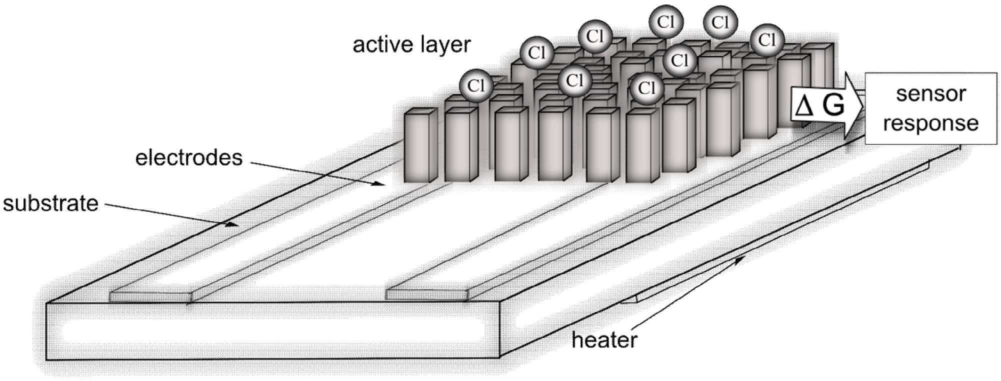

Fig. 1. Schematic view on the construction of resistive chlorine sensor.

Acknowledgement

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HUMAN CAPITAL
NATIONAL COHESION STRATEGY

EUROPEAN UNION
EUROPEAN
SOCIAL FUND

Literature:

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M_P04

ELIMINATION OF POLLUTANTS BY SYNTHETIC ZEOLITE

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Summary

The use of heavy metals is essential in many branches and applications of industry. This practice poses a problem because of their sometimes high toxicity it human being and the animals, of the extremely strict limits must be observed for the concentration of heavy metals in polluted water, an experimental study was undertaken for the elimination of heavy metals Cadmium and Zinc snuffs separately and mixes some for synthetic solutions by a crystalline aluminosilicate (NaX zeolite synthesized at the pure laboratory starting from the products by the method of direct synthesis and which shows a rate of crystallization 92,64%).The experiment is carried out in discontinuous and continuous system for various masses of zeolite, a temperature of 25°C and 30°C, a follow-up of the evolution of pH before and after elimination.

Keywords :zéolite, elimination, metals,waste waters.

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M_P05
Influence of Aging and Crystallization on Zeolite 4A Synthesis

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Zeolites are crystalline, microporous, aluminosilicate materials with basic crystalline skeletons composed of SiO_4 and AlO_4 tetrahedrons, used as catalysts, ion exchangers, molecular sieves and adsorbents in various industries. Almost all physico-chemical parameters such as alkalinity and chemical composition of the gel, mixing order of reactants, temperature, aging/crystallization time have a profound effect on the transformation of hydrogel into zeolite crystals [1,2]. In the present work, zeolite 4A was prepared by hydrothermal synthesis under room-temperature conditions. The influence of important synthesis parameters such as aging temperature, crystallization temperature and time on the particle size, crystallinity, dehydration and silicone conversion were performed.

Sodium silicate and aluminium hydroxide ($Al(OH)_3$) were used respectively as silicone and aluminium source in zeolite synthesis. Zeolite 4A was synthesized by hydrothermal method with a gel composition of $3,29Na_2O:Al_2O_3:1,64SiO_2:131,8H_2O$. Sodium aluminate and sodium silicate solutions were mixed under vigorous stirring at 20°C, with a SiO_2/Al_2O_3molar ratio of 1.7 in a glass temperature controlled reactor. After synthesis, the precipitates were filtered and washed until the pH reached around 10. Chemical analysis, X-ray diffraction analysis (XRD), particle size distribution measurements and thermal gravimetric analysis (TGA) were used through characterization.Synthesis conditions and final product characterization analyses are listed in Table 1.

Table 1. Synthesis conditions and zeolite characterization results.

	Z1	**Z2**	**Z3**	**Z4**	**Z5**	**Z6**	**Z7**	**Z8**	**Z9**	**Z10**	**Z11**	**Z12**	**Z13**
Aging time (hour)	2	2	2	2	2	2	2	2	2	2	2	2	2
Aging temp. (°C)	20	20	20	20	20	20	20	20	20	20	30	40	50
Crystallization temp. (°C)	60	80	90	100	120	140	100	100	100	100	100	100	100
Crystallization time (hour)	4	4	4	4	4	4	3	5	6	17	4	4	4
TGA weight loss(900°C; %)	-	-	21.2	21.6	20.3	20.1	20.7	20.3	21.6	20.3	20.7	20.1	20.3
Particle size (d (0,5); µm)	-	19.9	3.8	5.9	4.8	11.3	17.6	6.4	5.2	4.5	5.0	5.4	4.8
Relative crystallinity (%)	*	49.6	85.8	95.9	90	83.6	33.6	92.8	92	91	94	91.3	91.7
Si conversion (%)	-	-	94	92.6	95.9	97.3	-	94.4	96.1	93.1	92.1	91.1	90.6

*Amorphous phase was observed.

From the results, the maximum degree of crystallinity was observed at the and of 4 hours of crystallization at 100°C. There was no significant change in the crystallinity by increased temperature.The particle size was decreased by increasing crystallization time.Gel aging temperature rising caused a slight decrease in crystallization rate and particle size because of the extended induction period. Si conversion efficiency and water content wereindependent of the crsytallization and aging periods.

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M_P06

Effect of Nd substitution on structural, magnetic and dielectric properties of $SrFe_{12}O_{19}$ hexaferrite

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Ewa Markiewicz[2], Adam Pietraszko[1]

[1]*Institute of Low Temperature and Structure Research, PAS, Wrocław, Poland*
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Hexaferrites are known as the remarkable magnetic materials that make them suitable for wide variety of applications such as permanent magnets in microwave, data storage, recording and magnetooptical devices [1]. Among hexaferrities family, M-type hexaferrites ($SrFe_{12}O_{19}$, denoted as SrM), with a magnetoplumbite structure type have been extensively studied for several decades because of high coercive force, large magnetocrystalline anisotropy, high saturation magnetization (64 emu·g^{-1}), as well as excellent chemical stability and high Curie temperature (743 K).

Many papers recently focused on the influence of rare earth substitution on magnetic and microwave absorption properties of ferrite materials [4]. Using rare earth as dopants has been reported as a propitious method in an increase of the O–Fe–O interaction, which would result in changed magnetic properties of the doped SrM materials [2].

In the present study, hexaferrite $Sr_{1-x}Nd_xFe_{12}O_{19}$ series with different substitution ratios (x = 0.03, 0.05, 0.07, 0.09) were prepared by means of the precipitation method. The X-ray diffraction (with CuK$_\alpha$ radiation) was used for phase identification and determination of the crystallites size by applying the Scherrer formula. The morphology of the samples was analyzed using Scanning Electron Microscopy (Fei Nova NanoSEM 230). Magnetic (PPMS fitted with VSM probe) and dielectric response (pellets, Alpha-A Novocontrol with Quatro Cryosystem) were measured and results will be presented.

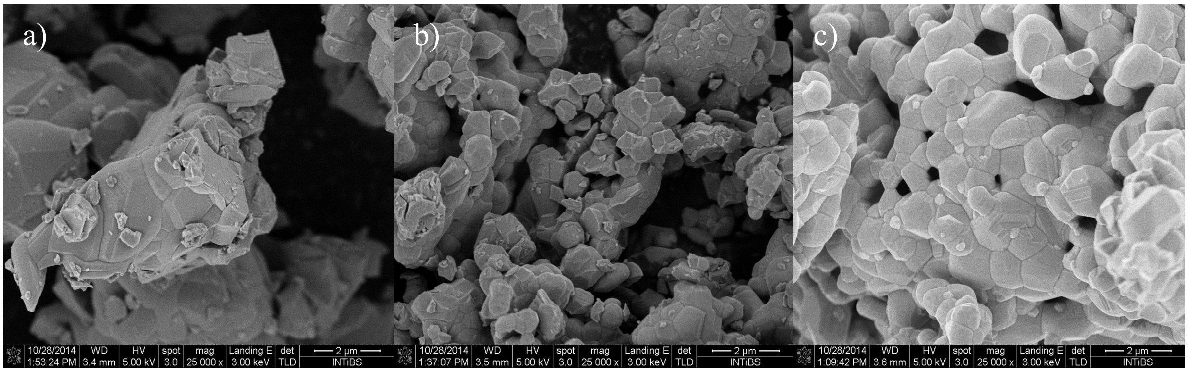

Fig. 1. SEM micrograph of $Sr_{1-x}Nd_xFe_{12}O_{19}$ phase with different substitution ratios: a) $x = 0.03$; b) $x = 0.05$; c) $x = 0.09$.

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M_P07

Assessment of biocompatible chitosan-silver materials for antibacterial therapy

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Due to the long-term overuse of antibiotic the Multidrug-Resistance (MRD) of bacterial strains is rather a rule than an exception. Nowadays, additional efforts are needed to develop effective antibacterial materials and therapies. Herein, the preparation of polymer-metal nanoparticlebionanocompositeand its biological activity is presented [1]. In this work, the strong exertion was made to obtain materials with required properties such as biocompatibility, biodegradability and non-toxicity.

Chitosan (CS), biocompatible polymer, was used as reducing and stabilizing agent for silver nanoparticles (AgNPs) synthesis. In order to optimize the biological activity of AgNPs different variables were analyzed *e.g.* the chitosan average molecular weight, deacetylation degree, silver concentration, and the addition of ascorbic acid. Moreover, the dependence between the chitosan properties and the obtained AgNPs features was evaluated. Physicochemical characterization of nanoparticles and nanocompositeswas conducted with several techniques:UV-Vis and IR spectroscopy, TG, TEM, XPS, ICP-MS, *etc*.

Chitosan with the medium molecular weight and the highest deacetylation degree appeared to be the optimum in silver nanoparticles synthesis. A fast reduction of silver ions was favored which consequently leads to smaller size-nanoparticle formation compared to the other formulations, homogenouslydispersed across the membrane. The addition of ascorbic acid enhanced the fast reduction of silver ions and consequently NPs with the smallest average diameter were formed. A complete bactericidal effect towards Gram-negative (*Pseudomonas aeruginosa, Eschierichia coli*)and Gram-positive (*Staphylococcus aureus*) bacterial strainswas determined. Moreover, low cytotoxic effects towards human keratinocytes and mouse fibroblasts were obtained *in vitro* for materials without ascorbic acid.

Acknowledgements: This work was supported by the National Science Centre through the PRELUDIUM (2012/07/N/ST5/00157) project.

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M_P08

Unexpected formation of $[Ru(\eta^5\text{-}C_5H_5)(PH\{CH_2N(CH_2CH_2)_2O\}_2)(PPh_3)_2]BF_4$ - the first „piano-stool” ruthenium complex bearing secondary aminomethylphosphane ligand

Michał Płotek[1,2], Radosław Starosta[3], Urszula K. Komarnicka[3], Agnieszka Skórska-Stania[1],
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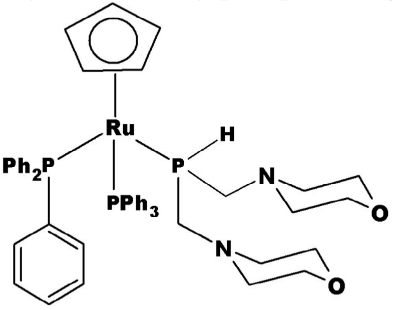
Reactions of phosphanes with ruthenium(III) chloride in methanolic solution generally lead to reduction of ruthenium from III to II oxidation state, giving the diamagnetic $[RuCl_2(\text{phosphane})_3]$ or $[RuCl_2(\text{phosphane})_4]$ coordination compounds. However, Higham*et al.*[1, 2] showed that in reaction of $RuCl_3$ with hydroxymethylphosphanes ($P(CH_2OH)_3$ or $P(CH_2OH)_2Ph$) apart from ruthenium reduction and phosphanes binding, a simultaneous cleavage of P-C bond took place. It finally led to complexes of Ru(II) with two molecules of tertiary phosphane and two molecules of the secondary one: $[Ru\{PPh(CH_2OH)_2\}_2\{PPh(CH_2OH)H\}_2Cl_2]$ and $[Ru\{P(CH_2OH)_3\}_2\{P(CH_2OH)_2H\}_2Cl_2]$.

The similar process takes place when we useda half-sandwich $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$ as a starting compound.The reaction of [Ru(η^5we used -$C_5H_5)Cl(PPh_3)_2$] with $P\{CH_2N(CH_2CH_2)_2O\}_3$ in the presence of $NaBF_4$, do not lead to a straightforward substitution of the Cl^- ion, but involves a simultaneous P-C bond cleavage in $P\{CH_2N(CH_2CH_2)_2O\}_3$, resulting in formation of the secondary phosphane - $PH(CH_2\text{-morph})_2$, which gives the $[Ru(\eta^5\text{-}C_5H_5)PH\{CH_2N(CH_2CH_2)_2O\}_2(PPh_3)_2]BF_4$ complex - the first “piano-stool” ruthenium complex with secondary aminomethylphosphane ligand [3].



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M_P09

The fight against pollution of heavy metals

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We live in a time and in a world heavily polluted. In the list of the great dangers awaiting the man can be placed on top of the list pollution by heavy metals: lead, mercury, cadmium, etc. Fatigue, Depression, Thyroid disorder, Alzheimer's, Parkinson's, Cancer, are some of the health problems caused by heavy metal pollution. The environmental protection has long since become a major political and economic issue. Among the priorities include safeguarding water resources. All countries of the world are concerned either because they lack water or because they pollute [1]. There are several ways to remove these heavy metals, ion exchange by zeolites is one of these means and the latter based on our work [2].

Zeolites were among the main clean up materials either by adsorption [3-4], ion exchange [5] and catalysis [6]. Lead and cadmium, heavy metals, is one of the main dangers fulminate the flora and fauna of our small planet [7], so many resources are deployed to remedy them. The elimination of lead and cadmium by ion exchange has been extensively studied [8]. However, exchange capacity of more and larger formed a major challenge for researchers and industry.

The objective is to find more efficient zeolitic materials as zeolites themselves to the elimination of lead and cadmium. Thus, we present the preparation of composite materials zeolite-zeolite based on a core-shell model. Zeolites high exchange capacity of zeolites core are covered surface with high adsorption capacity. A nanocrystal of zeolite A (zeolite surface) grow on the surface of large crystals of zeolite X (zeolites core).

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M_P10

Synthesis Studyand Possible Areas of Application of Materials BasedonPolyacrylonitrile Derivatives andHeterometallic d-Elements(Cu, Fe) Complexes

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Thegeneral principle of the synthesis of fibrous inorganic ion-exchanging composites containing the combination of polymer analogous conversion reactions of the fibres and cycles of ion-molecular layeringisused[1-3].

The synthesis of thin nanomolecular layers of**Cu(II)** and **Fe(III)** hexacyanoferrates **(II)** was performed by the method of the chemosorption layering on a matrix which represented the derivatives of polyacrylonitrile fibres containing$\mathbf{HO{-}N{=}\dot{C}{-}NH_2}$groups with the degree of substitution of**CN**-groups about 50%. The synthesized materials were studied by using methods for chemical and X-ray analyses electronic-microscopy IR-spectroscopy and sorption investigations. The compositionsof the synthesized pellicular hexacyanoferrates are describedaccording to the data from X-ray studying by the formulas:

$$\mathbf{K_xCu_{(2-x)}[Fe(CN)_6] \cdot 4H_2O} \text{ and } \mathbf{K_xFe_{(4-x)}[Fe(CN)_6]_3}$$

(compounds I and II respectively).

The formation of heteroatomic cycles by polyacrylonitrile derivatives (with participation of strong **H**-bonds) was shown by the method of IR-spectroscopy.The cycles were able to disintegrate under the effect of the ions of **d**-metals. It is suggested that strong adhesion of the layers with the matrix is caused by formation of linkage between$\mathbf{[Fe(CN)_6]^{4-}}$-ions and the ions in chelates composition through **CN**-bridges.

The $\mathbf{K^+}$-ions in these compositescan be exchanged for other ions mainly $\mathbf{Cs^+}$.The testingof ion-exchange property of the synthesized compositions on the basis of the **Cu(II)**and **Fe(III)** ferrocyanides was carried out by sorption from water solutions of the stable and radioactive caesiumisotopeions.The equilibrium ion-exchange capacity of the $\mathbf{Cs^+}$-ionsgreatlydepends on the layer thickness which isdetermined by the number of layering cycles**(n)** and reach maximum1,0 $\text{mmol} \cdot \text{g}^{-1}$when**n = 8**.It was shown that process of ion-exchange proceeded in two stages (sorption on the surface and diffusion of the ions into the layer). Ion-exchange equilibrium on synthesized ionites is reached approximately 30 times faster than on corresponding powdery crystalline ferrocyanides. Distribution coefficients of $\mathbf{^{137}Cs^+}$-ions for **Cu(II)** and **Fe(III)** hexacyanoferrates are $1.70 \cdot 10^4$ and $1.20 \cdot 10^4$ respectively.

This indicates the future of their practical use inion-exchange technologiesfor examplein water preparation in deactivation and purification of waste waters and also in radiationresearches during the measurement of low-level specific radioactivity by the method of pre-concentrating.

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M_P11

Synthesis and Photoluminescence Properties of $Al_2Si_2O_7$ doped with Eu^{3+}

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$(Al_{1.90}Eu_{0.10})Si_2O_7$ was synthesized at 700 °C and 1100 °C for 12 h in air using the solid state method. All starting materials Al_2O_3(A.R.), SiO_2 (99.8%), and Eu_2O_3 (99.99%) were weighed and mixed homogeneously in an agate mortar. Thermal behaviour of starting materials were investigated using Thermogravimetry (TG) and differential thermal analysis (DTA). The crystal structure of $(Al_{1.90}Eu_{0.10})Si_2O_7$ was searched X-ray diffraction (XRD). The luminescence spectrum of $(Al_{1.90}Eu_{0.10})Si_2O_7$ was recorded using photoluminescence spectrophotometer. The excitation and emission spectra of phosphor are shown in Fig. 1. $(Al_{1.90}Eu_{0.10})Si_2O_7$ has five excitation peaks, 298 nm, 362 nm, 383 nm, 395 nm and 466 nm, belongs to Eu^{3+} ions. The emission peaks, 588 nm, 609 nm, 645 nm and 678 nm-697 nm correspond to $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+}, respectively. Emission spectra of Eu^{3+} usually consist of sharp lines from 550 to 750 nm corresponding to the f-f transitions [1-2].

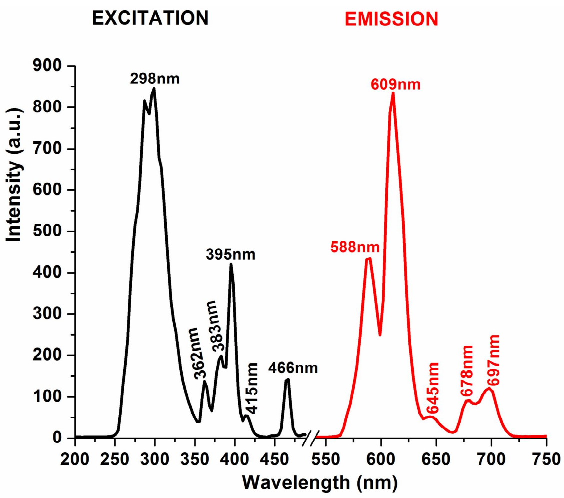

Figure 1. The excitation and emission spectra of $(Al_{1.90}Eu_{0.10})Si_2O_7$.

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M_P12

A New Route for the Preparation of Bimetallic $M'_{0.2}Mn_{0.8}PS_3$ Phases ($M' = Cu^{II}, Ni^{II}, Co^{II}$)

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The study of lamellar composites and their intercalation compounds has received great attention for many years and many layered compounds are being studiedto date [1,2]. Many bimetallic phases, $M'_XM_{1-X}PS_3$, have been synthesized mainly by the ceramic method [3], achieving different compositions. In the present work, a new route for the preparation of bimetallic phases is presented, achieving a common stoichiometry, $M'_{0.2}Mn_{0.8}PS_3$. In addition the spectroscopic properties of these bimetallic phases will be discussed.

New bimetallic phases were obtained in a two-step reaction. The first step, insertion of potassium ions in the interlamellar space of the $MnPS_3$phase permits to obtain $K_{0.4}Mn_{0.8}PS_3$[2,3].This precursor is useful because the interlamellarcations are easily removed by other guests ions. Due to the similar radii of the inserted 3d ions with that of the radius of manganese(II) ions, these do not remain in the interlamellar space but fill the vacancies of the lamellae, forming bimetallic phases. This process has been confirmed by FTIR and powder X-ray diffraction. Pristine $MnPS_3$shows one vibration of the PS_3 group at 575 cm^{-1}, while $K_{0.4}Mn_{0.8}PS_3$ has two at557 and 608 cm^{-1}. The obtainedbimetallic phases have only one band at 575 cm^{-1}, similar to the pure phase. In addition, the powder X-ray diffractograms of the bimetallic phases have the 001 peak at an angle similar to that of $MnPS_3$. This fact indicates that the interlamelar distance is similar to that of the pure phase (6.5Å), proving that the potassium ions are no longer in the interlamellar space.

The energy GAP of these phases were obtained by diffuse reflectance spectroscopy, and the obtained values are: $MnPS_3$, 2.50 eV; $K_{0.4}Mn_{0.8}PS_3$, 2.65 eV; $Cu_{0.2}Mn_{0.8}PS_3$, 2.44 eV; $Ni_{0.2}Mn_{0.8}PS_3$, 1.64 eV; $Co_{0.2}Mn_{0.8}PS_3$, 1.58 eV. The shift in the absorption edge of these bimetallic phases is in agreement with data described in literature for the pristine phases.

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M_P13
LUMINESCENT 1,3,2-BENZODIAZABOROLES

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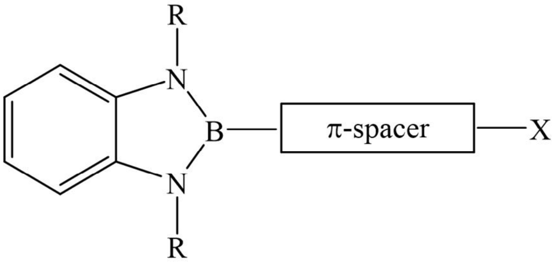
The interest in species **I** containing 1,3,2-benzodiazaborole building blocks has recently increased because of their potential use as emitting materials in optoelectronic devices.



I R = C_2H_5, C_6H_5; X = π -acceptors

In the vast majority, these heterocycles behave as π-donors towards accepting groups X, when linked by a π-conducting spacer. With R = C_2H_5or C_6H_5prominent acceptors are aryl, thienyl, dimesitylboryl or *ortho*-carboranyl functions. The introduction of perfluoroaryl groups as substituents at the N atoms, however, imposes acceptor qualities on the benzodiazaborolyl unit, which are comparable to that of the familiar $BMes_2$group. The luminescence of the title compounds is highly solvent dependent featuring Stokes shifts up to 20000 cm^{-1}.

The relationship between the molecular structures and some photophysical properties of the here presented compounds is discussed.

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M_P14

Functional Schiff Base Complexes of Mn(III) and Co(III) as Oxidation Catalysts for Laundry Bleaching System

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The most important interest of the chemical industry related with the oxidation reactions are the bleaching processes [1]. Because of the traditional chlorine-based bleaching agent's damage to the environment with chlorinated by-products, hydrogen peroxide is employed as a powerful oxidant and environmentally friendly since the by-products from its decomposition are water and oxygen being non-toxic. Although hydrogen peroxide is favorable bleaching agent due to this features, in order to provide sufficient bleaching of chromophores is needed long reaction times and high temperatures ($T \approx 95$ °C) [2]. However, their activity is kinetically low under many experimental conditions.

In further studies, design and development transition metal complexes have been great attention due to effectively catalyze substrate oxidation by hydrogen peroxide or molecular oxygen [3]. Hydrogen peroxide based bleach catalyst play a major role for the pulp and paper production, waste water treatment and laundry for industrial and domestic applications [4].

So far, several novel transition metal complexes of salen, saltren, terpyridine-type ligands and triazole derivatives have been synthesized and tested, possessing significant potential in activation of hydrogen peroxide [5].

These results prompted us to investigate the Schiffs base metal complexes as bleach catalysts for oxidation reactions with hydrogen peroxide for laundry cleaning applications. In this study, we have developed a novel Mn(III) and Co(III)-salen derivatives for laundry cleaning applications. We measured the oxidative bleach performance in three technique such as at 25 °C with alone and as in polymer dopped in presence of H_2O_2 by online spectrophotometric method and as real washing conditions [6].

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M_P15

Preparation of Metal Containing Epoxy Polymers and Investigation of Their Properties as Fluorescent Probe

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Schiff base ligands are very effective in constructing supramolecular architectures such as coordination polymers, double helical and triple helical complexes [2]. In addition, Schiff base derivatives incorporating a fluorescent moiety are appealing tools for optical sensing of metal ions [3]. Metal containing polymers (MCPs) are well-known systems in which the combinations of local parameters are possible by means of fluorometric techniques. Generally, without incorporation of the fluorescent groups with polymers is unspecific, and it is not useful to analyze their fluorescent properties. Therefore, it is necessary to prepare a new type epoxy polymers with fluorescent groups in terms of metal sensing prop and the other photochemical applications [4].

Schiff base complexes were prepared as di-hydroxyl functional monomers by the template reaction of salicyl hydrazon with OH- substituted aromatic aldehydes in the presence of metal salts such as Cu(II), Ni(II), Cd(II), La(III), Sm(III) and Gd(III). The prepared Schiff base metal chelate complexes were polymerized with the di functional monomer diglycidyl ether Bisphenol-A (DGEBA) to obtain metal containing epoxy polymers.The preparations of epoxy polymers have been carried out at 150 and 185 °C.The synthesized complexes and polymers were characterized by FTIR, UV-VIS and mass spectroscopies. The solid phase UV-Vis and fluorescence spectra were recorded for the prepared polymer composites to characterize the photophysical properties(Fig 1).

The prepared polymers have some interesting photo physical properties, and they might have availability potential for the above mentioned technology fields.

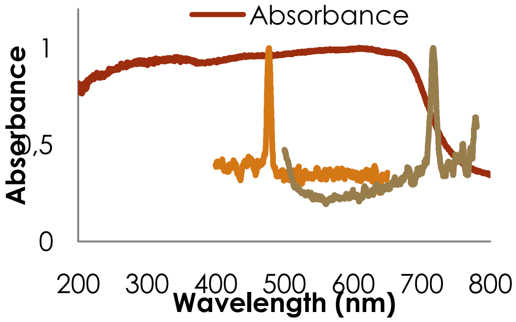

Fig.1. UV-VIS and Fluorescence Spectrum of metal containing epoxy polymer in solid phase.

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NN_P01

Synthesis of rhodium nanoparticles using water as reducing agent

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Transition metal colloids have been synthesized, according to the literature, in five general synthetic methods: (1) chemical reduction of transition metal salts, (2) ligand reduction and displacement from organometallics, (3) thermal, photochemical, or sonochemical decomposition, (4) electrochemical reduction, and (5) metal vapor synthesis. The most widely used method of nanoparticles preparation is reduction of transition metal salts in the presence of stabilizing agents, such as polymers or surfactants. A wide range of reducing agents have been used in nanoparticles synthesis: gas, such as hydrogen or carbon monoxide, hydrides or salts such as sodium borohydride or sodium citrate, or even oxidable solvents such as alcohols. [1-3]

We discovered novel green methodology for the synthesis rhodium nanoparticles from $Rh(acac)(CO)_2$, $Rh_2(OAc)_4$ and $RhCl_3.3H_2O$ as precursors, using water as reducing agent at 25 - 80 ^oC. Rhodium nanoparticles were obtained in the absence and in the presence of polymers, such as polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVOH) as the stabilizing agents. Rh(0) nanoparticles have been characterized by means of transmission electron microscopy (TEM) and Infrared spectroscopy (IR), Catalytic activity of the synthesized Rh/PVP was successfully tested in the hydrogenation of benzene and the hydroformylation of 1-hexene in a water medium. In both cases excellent results were obtained.

$$\mathrm{Rh(acac)(CO)}_2 \xrightarrow[80^0\mathrm{C}]{\mathrm{H_2O}} \mathrm{Rh\ NPs\ (2\ nm)}$$

$$\mathrm{Rh(acac)(CO)}_2 \xrightarrow[80^0\mathrm{C}]{\mathrm{PVP,\ H_2O}} \mathrm{Rh\ NPs\ (2\ nm)}$$

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NN_P02

Synthesis and characterization of Ni-based catalysts supported on calcium hydroxyapatite for application in glycerol steam reforming

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Nowadays, energy is mainly produced from non-renewable energy sources (f. e. petroleum, coal, natural gas), what causesthe emission of air pollutants. In this context, search for alternative energy sources seems necessary. One of the alternative energy sources is hydrogen, which is defined as energy carrier for the future.It is characterized by high energy content per unit of weight (about 120 kJ/g) [1]. More and more often, the hydrogen production via steam reforming of glycerol ($C_3H_8O_3 + H_2O \rightarrow 7H_2 + 3CO_2$) are considered. This process allows to obtain a high hydrogen yield. Theoretically, 7 mol of hydrogen can be received from 1 mol of glycerol.

Catalysts for steam reforming of glycerol can be divided into two groups: noble metal catalysts and base metal catalysts. However, the most studies are conducted on catalytic system based on nickel, due to its high activity in glycerol steam reforming. Mainly, catalysts are deposited on oxide support such as: CeO_2, TiO_2, MgO, ZrO_2 orAl_2O_3. [2]. Some studies also suggest that calcium hydroxyapatite($Ca_{10}(PO_4)_6(OH)_2$)can be used as a catalysts support for glycerol steam reforming [3].

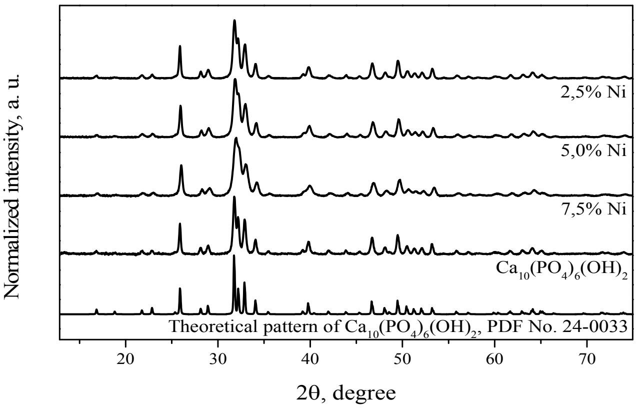

Figure 1: XRD pattern of hydrothermal prepared hydroxyapatites.

The objective of the presented study was to comparethephysicochemical properties of hydroxyapatite promoted with nickel ions. The hydroxyapatite catalysts were prepared through microwave-assisted hydrothermal and incipient wetness impregnation method with variable nickel loadings.Catalysts were characterized by XRD,FT-IR, Raman spectroscopy, TEM SEM, BET, and TPR – H_2.

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NN_P03

Ni or Co Promoted MoS_2 Nanoparticles as Catalysts in Light Driven Water Reduction

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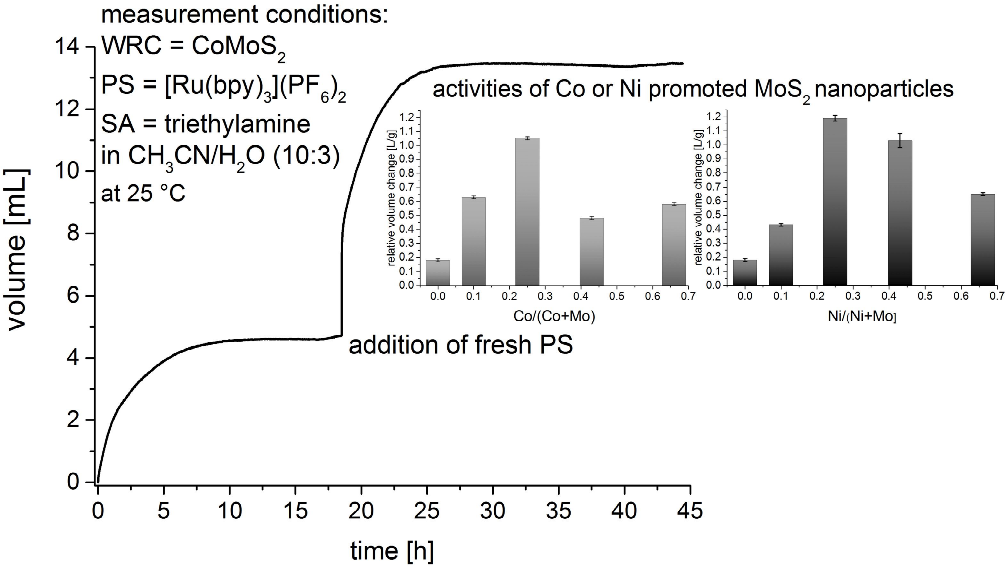
Besides being established catalysts in hydrodesulphurisation (HDS), MoS_2 nanoparticles gained attention as water reduction catalysts (WRC) for photo- or electrocatalyticH^+ reduction, thus indicating mechanistic analogies.[1] So since promoting MoS_2 nanoparticles with transition metals was found to enhance catalyst activity for HDS,this may be expected for light driven H^+ reduction with multicomponent catalyst systems, too.

The results presented were obtained from multicomponent catalyst systems containing $[Ru(bpy)_3](PF_6)_2$ as photosensitiser (PS) andtriethylamine as sacrificial agent. The WRCs were MoS_2 nanoparticles promoted with Ni- or Co-amounts between 0 and 0.4 based on overall amount of metal. The H_2 evolution curves of all multicomponent catalyst systems were measured at isobaric conditions and showed activityduring irradiation, which ceased within 16-20 h. This deactivation was assigned todegradation of PS asdescribed previously.[3] Fresh PS reactivated the multicomponent catalyst systems. All transition metal promoted MoS_2 nanoparticles showed enhanced activity as WRC. In analogy to findings in HDS[2] for Ni as well as Co the optimal amount of promotor was found to be around 0.25.



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NN_P04

Influence of electron – beam irradiation on properties of magnetic iron nanoparticles prepared from iron (II) chloride

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Iron oxides have a few structures called hematite (α- Fe_2O_3) maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4), where the latter is very promising material to medical applications due to its biocompability [1]. In this work, influence of electron – beam, (EB), irradiation on properties of magnetite (Fe_3O_4) has been studied. Magnetite was synthesized by co-precipitation method in acidic media form $FeCl_2$ in presence of oxygen [2].

Obtained black precipitate was irradiated by EB from linear accelerator Elektronika ELU-6e (20 Hz, 4µs, 160 cm), in argon atmosphere, in the range of doses 25 - 300 kGy. Properties of obtained particles were investigated by Raman spectroscopy, XRD and DLS analysis.

Analysis of XRD diffractograms showed, that synthesized black precipitate contained Fe_3O_4 phase. The size of crystallites estimated according to Scherer's equation was in the range of 24 - 34 nm.

DLS data showed, that distribution of hydrodynamic radiuses of particles suspended in aqueous solution has depended on the dose of irradiation. The smallest values of hydrodynamic radii (50 – 90 nm) were observed for non-irradiated particles, whereas the biggest hydrodynamic radii (800 - 1000 nm) were recorded in samples irradiated with dose of 25 kGy. These differences may be due to aggregation of iron oxide particles in water and presence of "water shell" around them [3].

In Raman spectra of non-irradiated samples the bands at 665 cm^{-1} and 310 cm^{-1} assigned to magnetite phase [4] have been recorded. After EB irradiation, the intensity of magnetite bands gradually decreased and new bands attributed to hematite (at 219, 280 cm^{-1} and 400 cm^{-1}) and maghemite (at 704 cm^{-1}) have been observed. These results might suggest, that EB irradiation induce transformation of magnetite into maghemite and hematite.

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NN_P05

Metal complex confined in nanochannels:Enhancement of selectivity

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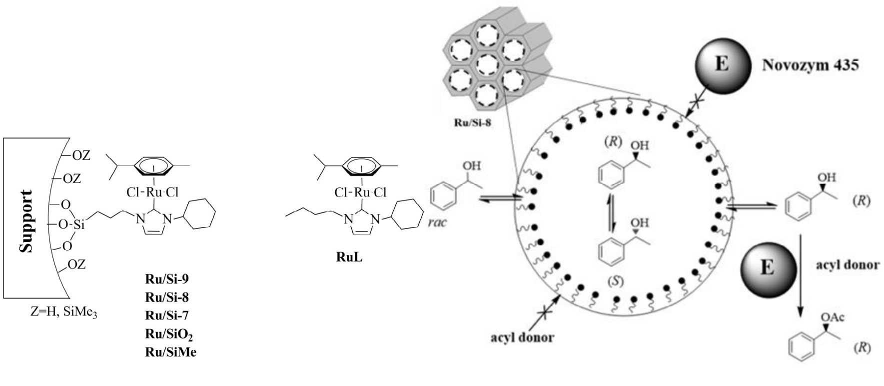
To enhance the selectivity of metal catalysts, the most common way is to tune the steric and electronic properties of metal complexes through ligand modification.However, there are very few examples which involve the control of selectivity in tandem reactions through adjusting space size and surface properties.In this study, we demonstrated that the selectivity for the tandem reaction was remarkably enhanced through confining metal catalyst core in the nanocage. Dichloro(η^6-*p*-cymene) (1-butyl-3-cyclohexyl-imidazolin-2-ylidene) ruthenium(II) (**RuL**) was synthesized and confirmed. Five heterogeneous catalysts with similar ruthenium cores were prepared by chemical immobilization method using various silica-based supports, including mesoporous silica SBA-15 of different pore sizes (**Ru/Si-9**, **Ru/Si-8** and **Ru/Si-7**), non-porous silica particles (**Ru/SiO$_2$**) and surface trimethylsilylated SBA-15 (**Ru/SiMe**). The dynamic kinetic resolution of 1-phenylethanol, which includes metal-enzyme bicatalytic racemization in tandem with stereoselectiveacylation, gave product in 99% yield and 0% ee with homogeneous catalyst RuL; whereas the heterogeneous **Ru/Si-8**exhibited high catalytic activity and enantioselectivity (up to 96% yield and 99% ee). The racemization and acylation abilities of different catalysts were analyzed. The influences of pore size and surface properties for heterogeneous catalysts were investigated, and nanocage effect was found to be the key factor in stereoselectivity.



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NN_P06

High-Yield Synthesis of Amido-Functionalized Polyoctahedral Oligomeric Silsesquioxanes

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Polyoctahedral oligomeric silsesquioxanes (POSS) constitute a group of organosilicon compounds with the basic structure of general formula $(RSiO_{3/2})_8$ [1]. Their attractiveness derives from the fact that they can contain numerous functional groups as side-chains, spawning various possibilities to attach organic fragments. These groups – the so-called organic shell – can be varied. Thus, such molecules can fundamentally be regarded as truly inorganic core/shell structures that are able to bind organic moieties, polymers, and natural biomaterials. Moreover, the presence of the three Si–O bonds imparts superior thermal, mechanical, and chemical stability, which makes these compounds extremely interesting from an industrial point of view [2].

Here we present a new synthetic approach that allows a high-yield synthesis of POSS from alkoxy silanes as a precursors. We have also been able to obtain nanoparticles of amido-functionalized POSS species containing various organic substituents to be bound to the siloxane cage-like core (Figure 1) which were synthesized in high yield and purity while avoiding the formation of other ($n \neq 8$) silsesquioxanes or polymeric/oligomeric compounds. We demonstrated that by using the wide range of organic substituents, it is possible to prepare functionalized nanoparticles that are difficult to obtain by using pure organic molecules without their attachment to the siloxane core. Notably, the spherical-shaped particles do not form agglomerates and are nicely separated. Such organic-inorganic nanohybrids open up a wide field of applications, for instance as a column fillers for advanced organic and inorganic synthesis or efficient drug delivery systems. These kinds of material can effectively replace functionalized silica, and add unique characteristics including superior thermal, mechanical, and chemical properties [3].

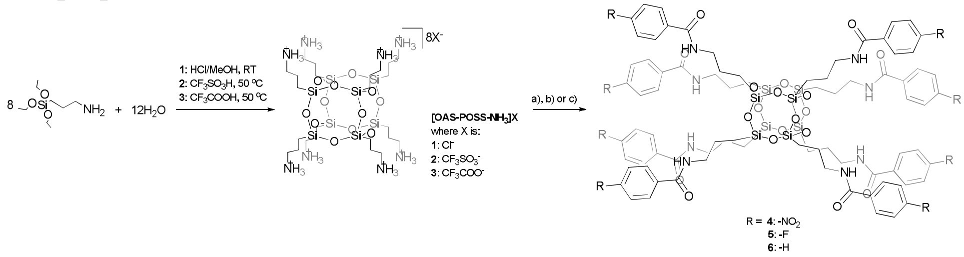

Figure 1. Synthesis of $[OAS\text{-}POSS\text{-}NH_3]X$. a) **4**: 4-nitrobenzoyl chloride, NEt_3, DMF, 0˚C; b) **5**: 4-fluorobenzoyl chloride, NEt_3, DMF, 0˚C; c) **6**: benzoyl chloride, NEt_3, DMF, 0˚C.

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NN_P07

Thin multiwall carbonnanotubes as a model for nano-cylindrical capacitors

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Carbon nanotubes are narrow seamless graphitic cylinders, which show an unusual combination of a nanometer-size diameter and millimeter-size length. Controlling and designing of a nanotube diameter are needed for developing nanotube growth methods and nano-cylindrical capacitors. Nanotubes with a diameter of less than 10 angstrom provide the ideal nano space in one-dimension. We have modeled our system with three parts including a two-layer cylindrical capacitor and one part of the X doped (X=Be and Li) as an impurity among the atoms of the outer nanotube layers. The total energy including three terms of the band structure energy, the inner and outer tubes and the electrostatic energy of the layers have been calculated.

We have simulated our capacitor model in viewpoint of various band gap energies considering the SWCNT as an inner tube and the SWCNT as an outer tube with different diameters and chiralities in the ranges of ($5.0 < d < 9.0$Å) and ($12.0 < d < 18.0$Å) for inner and outer tubes, respectively. Our model capacitors are based on m; n @m'; n' chiralities including the 4; 4@10; 5, 4; 4@9; 50; 4; 4@8; 0, and m'; n' @m'; n' chiralities including the 7; 3@ 10; 3, 7; 4@10; 4, 7; 5@10; 5, 7; 6@10; 6, and m; n @ m; n chiralities including the 4; 4@**8; 8**, 5; 5@**9; 9**, 6;6@**10; 10**, and4; 4@**10; 10** where the X-doped (X= Be, Li)tubes are in boldface. The productive capacitances have been yielded for armchair chiralities.

NN_P08

Static and dynamic calculations of formic acid dimer inside single-walled carbon nanotube

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Carbon nanotubes (CNT) play a very important role in materials chemistry and are the subject of many experimental and theoretical studies [1]. Open-ended single-walled carbon nanotubes (SWCNT) are considered in many studies as a model system in nanoconfined chemistry. Due to their special structure (tubular morphology) CNTs might be considered as "nanoreactors" for chemical reactions [2].

The cyclic formic acid dimer (FAD) is one of the simplest hydrogen bonded system. The possible double proton transfer, also important from the biological point of view, is the reason of widespread interest of experimental and theoretical studies.

Analysis of non-covalent interaction between formic acid dimer and pyrene (as a simple model of the carbon nanotube wall) was carried out with both Density Functional (with dispersion correction) and Wave Function Methods to estimate the energy of such interactions. Some novel approaches as Spin-Component Scaled and F12 variants of second-order Møller–Plesset Perturbation Theory were applied. Results shows a very good agreement of DFT energies with those obtained using more sophisticated methods [3].

Preliminary investigation of double proton transfer inside SWCNT was carried with Car-Parrinello Molecular Dynamics. It shows influence of SWCNT on FAD by reducing barrier height. The reaction was observed in 300K and with relatively short simulation time.

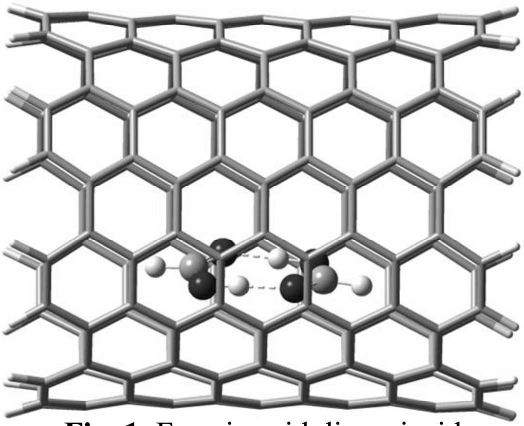

Fig. 1. Formic acid dimer inside (8,8) SWCNT 15Å.

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NN_P09

Controlled Hyaluronic acid cellular uptake by means of silica nanoparticles

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The use of nanotechnology in medicine is settled to spread rapidly. The controlled delivery of active biomolecules to cells draws more and more interest, due to the challenging need of enhanced drug bioavailability, efficiency of release and triggered cytotoxicity. In the present study we addressed the cellular uptake of hyaluronic acid (HyA) and its fluorescent derivatives (HyAF) by means of core-shell silica nanoparticles (NPs).

HyA is a disaccharide glucuronic acid/N-acetylglucosamine polymer, which offers high potentiality of conjugation with prodrugs, drugs, proteins, lipids and other biomolecules via the carboxylate group on the glucuronic acid residue, the primary hydroxyl on the N-acetylglucosamine moiety, or via reductive amination chemistry through the reducing end of HyA. The tailoring of HyA hydrogel physico-chemical properties (chemistry, surface charge, hydrophilicity, viscoelastic character) as well as those of the silica nanocarriers (including the nanoparticle surface decoration with PEG, carboxy and amino-groups, and the functionalization in the core with dye molecules) was scrutinized to drive the controlled uptake of HyA and HyAF compounds in HeLa and SH-SY5Y neuroblastoma cells.

Different techniques have been used to characterize physicochemical properties of the hybrid bio-organic/inorganic multifunctional nanoassemblies of HyA/NPs and HyAF/NPs: the hydrodynamic size and surface charge determination was measured by means of dynamic light scattering and zeta potential measurements; the topography and nanomechanical analyses through atomic force microscopy; the electron- and energy-transfer processes by UV-visible and fluorescence spectroscopy.

The effects on HeLacelllines to the treatment by the differently functionalized hyaluronic acid/silica nanoparticle systems were scrutinized by viability assays and live cell imaging confocal microscopy. Results showed the high potentiality of the used strategy to finely control the biomolecule-cell interaction.

SC_P01

Synthesis and theoretical study of trinuclear Mo_3S_4 clusters bearing chiral aminophosphine ligands

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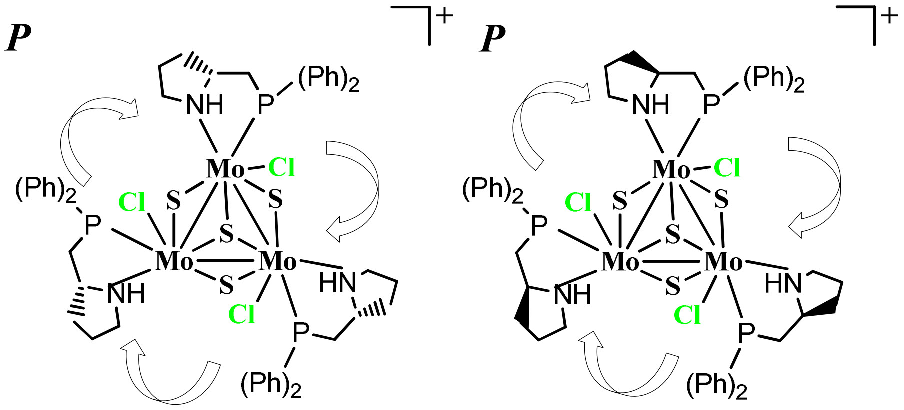
During the past years, our research group has preparedseveral enantiomerically pure molybdenum and tungsten clusters bearing chiral diphosphines, by reacting polymeric $\{M_3S_7X_4\}_n$ phases with optically pure ligands. *P*-M_3S_4 complexes are obtained starting from (*R,R*)-diphosphines, while their enantiomers *M*-M_3S_4 are isolated in the presence of (*S,S*)-diphosphines[1,2]. *P* and *M* symbols refer to the rotation of the halogen atoms in $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3X_3(\text{diphosphine})_3]^+$around the C_3 axis, with the capping sulphur atom pointing towards the viewer.

Recently, aminophosphines have emerged as versatile ligands, since they combine the *π*-acceptor properties of the phosphorus atom with the *σ*-donor character of the nitrogen atom [3]. Chiral aminophosphines such as (*R*) and (*S*)-2-[(Diphenylphosphino)-methyl]pyrrolidine have been used in order to synthesize new optically pure Mo_3S_4 clusters. Surprisingly, while the (*R*)-aminophosphine led us to the *P*-complex, the (*S*)-aminophosphine did not yield the corresponding *M*-complex as found in the diphosphinetrinuclear complexes. As observed in the figure, two different *P* optically pure complexes were obtained, preserving the chirality of the ligand. These results were confirmed by X-ray diffraction and circular dicroism:



In order to study this unexpected result, DFT calculations were performed. The geometric structures of the four possible diastereosiomers (two *P* and two *M*)were optimized, and energetic considerationsagree withthe formation of the P isomers in both cases, as observed experimentally.

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SC_P02

Spectroscopic and Magnetic studies of different of mixed valence states of Keggin phosphomolybdate

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The Polyoxometalates (POMs) belong to an extensive family of inorganic polyanions, formed by the condensation of polyhedral metal-oxygen units. Keggin, in 1933 [1] informed the first study of a 12-phosphotungstic acid structure. Nowadays, all the 12-phospho-tungstic and -molybdic acid structures are known as Keggin POMs. In the present work, we studied the electronic and spectroscopic properties of the molybdenum Keggin. The different mixed valence states were obtained by electrosynthesis. In Figure 1A is shown the cyclic voltammetry (CV) of 1mM of $[PMo_{12}O_{40}]^{3-}$ where the three reversible redox couples are observed.[2] The UV spectra of the studied POM show a Ligand-Metal Charge Transfer absorption for the oxidized and reduced states (Fig. 1B). The reduced state (dashed line) shows a Inter-Valence Charge Transfer between 450 and 1200 nm. The EPR spectrum of the reduced POM at 130 K shows a narrow line (*g* factor 1.945) and its hyperfine structure has been detected at temperatures below 64 K [3].

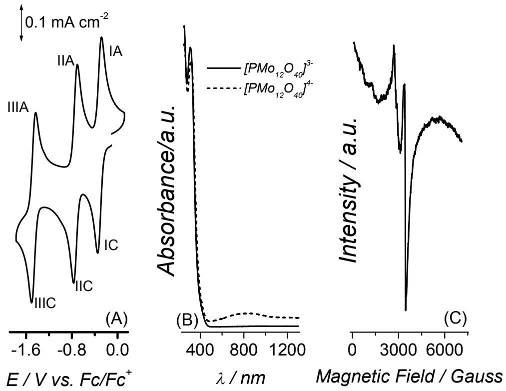

Figure 1. (A) CV of 1mM of $[PMo_{12}O_{40}]^{3-}$ in MeCN, (B) UV-Vis spectra of $[PMo_{12}O_{40}]^{3-}$ (solid line) and $[PMo_{12}O_{40}]^{4-}$ (dashed line) and (C) EPR spectrum of $[PMo_{12}O_{40}]^{4-}$ at 130 K.

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SC_P03

Coordination Chemistry of Transition Metal Complexes Bearing Imidazol(in)ium-2-dithiocarboxylate Ligands

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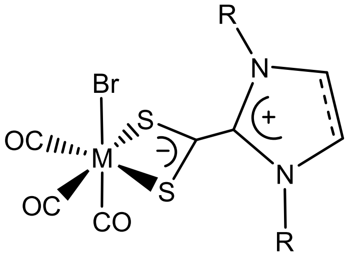
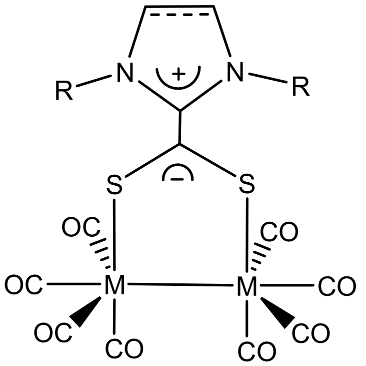
Over the past fifty years, N-heterocyclic carbenes (NHCs) have turned into powerful organocatalysts and ubiquitous ligands for organometallic chemistry and homogeneous catalysis [1]. However, much of their potential to generate other ligand systems remains unexplored [2]. In 2009, our group reported that imidazol(in)ium salts could be readily converted into the corresponding 2-dithiocarboxylate betaines, which showed a higher robustness when compared to the well-known phosphane-carbon disulphide adducts. The resulting zwitterions reacted with the [RuCl$_2$(*p*-cymene)]$_2$ dimer in the presence of KPF$_6$ to afford cationic complexes with the generic formula [RuCl(*p*-cymene)(S$_2$C•NHC)]PF$_6$, in which the dithiocarboxylate group acted as a κ^2-*S,S′* chelating ligand [3]. Moreover, imidazol(in)ium-2-dithiocarboxylate adducts could also be employed as bridging ligands to bind two metal-ligand fragments together in unprecedented homoleptic digold complexes of the type [Au$_2$(S$_2$C•NHC)$_2$](PF$_6$)$_2$ [4].

The potential of NHC•CS$_2$ zwitterions to generate homo- and heterobimetallic systems prompted us to investigate the preparation of a large family of mono- and binuclear complexes based on groups 6 to 8 transition metals bearing these ligands. In this work, we shall disclose the synthesis of new mononuclear carbonyl complexes used as building blocks for the assembly of higher nuclearity materials and their characterization on the basis of X-ray diffraction analysis and spectroscopic techniques.





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SC_P04

Trinuclear lanthanides(III) complexes of achiral macrocyclic ligand

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The 3+3 macrocycles based on diformylphenols and 1,2-diaminocyclohexane form interesting trinuclear complexes[1-6]. Here we present lanthanide(III) complex of a similar enantiopure macrocyclic amine derived from R, R-1,2-diphenylethylenediamine and 2,6-diformyl-4-tert-buthylphenol (Fig.1).

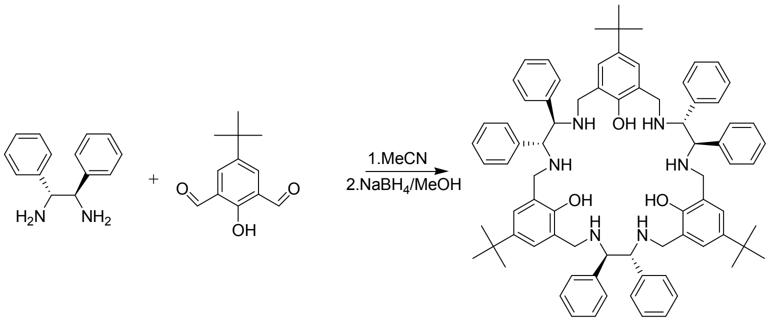

Fig. 1 Synthesis of the macrocyclic ligand 3 + 3

The resulting ligand was reacted with lanthanide(III) and yttrium(III)ions.These complexeswere characterized by ESI MS and NMR spectroscopy. X-ray crystal structures show that the large macrocycle is able to bind three Ln(III) ions, which are additionally connected by hydroxo bridges. In the case of Dy(III) complex the trinuclear macrocyclic units are additionally connected via chloride bridges forming a hexanuclear complex(Fig.2).

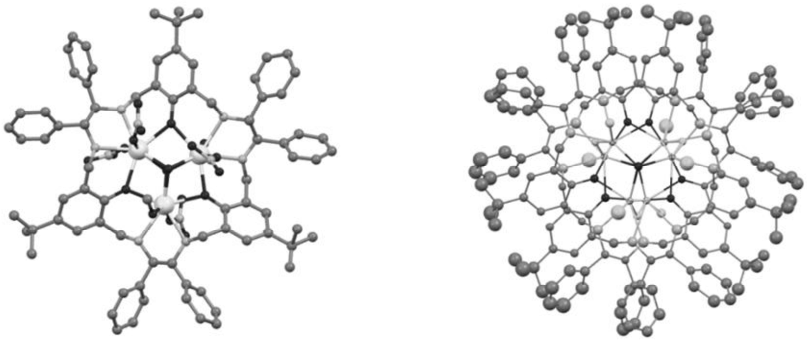

Fig. 2 Trinuclearyttrium(left) and dysprosium(right) complex of a macrocyclic ligand type3+3

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SC_P05

Tricarbonyl Complexes of Rhenium and Technetium with Tridentate Schiff Bases

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The *fac*-$[M(CO)_3X_3]^{2-}$ anions (M = Re, X = Br; M = ^{99}Tc, X = Cl) are facile starting materials for the synthesis of novel rhenium(I) and technetium(I) tricarbonyl complexes [1,2]. They readily react with potentially bidentate ligands under replacement of two halido ligands. Such products, however, are less inert against ongoing ligand exchange. More robust complexes are formed with tripodal ligands, and the resulting chelates are suitable for bioconjugation, which makes them candidates for applications in nuclearmedical diagnostics (^{99m}Tc) and therapy ($^{186,\,188}$Re). Potentially tridentate Schiff bases with *P,N,O* (HL^1 and HL^2) or *P,N,P* donor sets (L^3) have been prepared by condensation of salicylaldehyde or (2-formylphenyl)diphenylphosphine with the corresponding amines and reacted with *fac*-$[M(CO)_3X_3]^{2-}$ complexes.

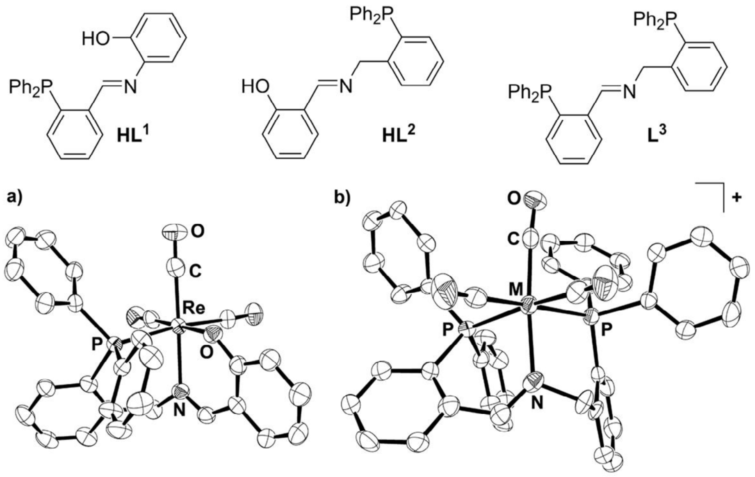

Fig. 1: Potentially tridentate Schiff bases and molecular structures of their Re and Tc complexes: a) $[Re(CO)_3(L^2)]$ and b) $[M(CO)_3(L^3)]^+$ (M = Re, Tc).

Fig. 1shows the tridentate coordination of the representative ligandsHL^2 and L^3 to rhenium and ^{99}Tc (^{99}Tc: weak ß$^-$ emitter, half-life $2.11 \cdot 10^5$ a) giving neutral and cationic complexes. The formation of the$[Re(CO)_3(L^3)]^+$cationrequires the removal of the Br$^-$ ligands of$[Re(CO)_3Br_3]^{2-}$ by AgPF$_6$prior the reaction with L^3. Otherwise, the neutral complex$[Re(CO)_3Br(L^3)]$ is formed. Corresponding reactions with $[^{99m}Tc(OH_2)_3(CO)_3]^+$(^{99m}Tc: pure γemitter, half-life 6 h) were done at nanomolar concentration level and studied by HPLC.

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SC_P06

Thermally and light induced spin crossover in 2D coordination polymer $[Fe(hbtz)_2(C_3H_5CN)_2](ClO_4)_2$

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Metal ions with electronic configurations $3d^4$-$3d^7$ usually form stable octahedral high spin (HS) or low spin (LS) complexes. Nevertheless, if the difference $|\Delta - \bar{P}|$ (Δ - energy gap between t_{2g} and e_g levels; $\bar{P}$ - interelectronic repulsion energy) is comparable with thermal energy (k_BT), a HS⇆LS conversion (SCO) can be triggered by the change of temperature, application of pressure or by light irradiation [1]. 1- and 2-substituted tetrazoles as well as 1-substituted-1,2,3-triazoles belong to the group of ligands which can form complexes with iron(II) which exhibit SCO phenomenon. Due to monodentate coordination fashion, mentioned above azoles are utilized to preparation of bis(azolyl)alkane-type ligands suitable to construction of iron(II) SCO polymeric materials. In this case, a perturbation produced by SCO can trigger conformational alterations of flexible bridging ligand molecules. Moreover, our investigations revealed an ability of tetrazol-2-yl and 1,2,3-triazol-1-yl based ligands to formation of heteroleptic complexes containing $[Fe(azolyl)_4(RCN)_2]$-type cores [2]. What is important, this type of complexes exhibit SCO phenomenon, too.

$[Fe(hbtz)_2(C_3H_5CN)_2](ClO_4)_2$ can be prepared in the reaction of hbtz (1,6-di(tetrazol-2-yl)hexane) with iron(II) perchlorate in the presence of allyl cyanide. In this complex basal plane of coordination octahedron is formed by tetrazol-2-yl rings, whereas axial positions are occupied by nitrile molecules. Each iron(II) ion is connected by hbtz molecules to four other ones. This bridging mode leads to formation of 2D network. The complex exhibit thermally induced SCO. HS→LS transition is accompanied by shortening of Fe-N bond lengths at about 8 %. Single crystal X-ray diffraction studies revealed that HS→LS transition is accompanied by conformational alterations of allyl cyanide molecules and by formation of superstructure in the LS phase. In the novel phase disordering of allyl cyanide disappears and bridged iron(II) ions no longer occupy the common plane.

We have found that the change of the spin state can also be induced optically. LS→HS switching was carried out at 10 K by application of laser light irradiation of 520 nm wavelength (LIESST). The spin state switching undergoes completely, however an obtained HS phase is metastable and after turning off the laser light immediately starts HS→LS relaxation. Taking into account successfully realized optically induced SCO (monitored by SQUID) we have decided to determine crystal structure of metastable HS phase. In the optically produced phase the Fe-N distances are characteristic for the HS form, however the motif of superstructure (observed for LS phase) is preserved. Thus, light induced LS→HS switching leads to formation of novel HS phase structurally different from the starting one.

This work was funded by the Polish National Science Centre Grant No. DEC-2011/01/B/ST5/06311

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SC_P07

Self-assembly process leading to formation of compounds based on different types of polyoxoanions from one reaction mixture

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Polyoxometalates (POMs) are attracting attention as catalysts in both homogeneous and heterogeneous processes. Lately a lot of research efforts have been focused on their functionalization by transition metal complexes. Substitution of six-valent metal centers, for example W(VI) and Mo(VI), with metal atoms of lower valency, such as V(V), is an effective method of obtaining polyoxoanions with increased charge density. This approach is a perspective way of extending the ability of such building blocks to coordinate greater number of cations, leading to sophisticated structural types.

New complexes have been successfully obtained by means of one-step reaction in mild conditions using commonly available reagents. The interaction in the mixtures was studied:

$$Cu^0 – en – (NH_4)_2HPO_4 – V_2O_5 – (NH_4)_6Mo_7O_{24}/(NH_4)_{10}H_2W_{12}O_{42} – H_2O.$$

The Mo-containing system yields three compounds based on mixed-metal tri-capped Keggin $[PMo_{12-x}V_xO_{40}(VO)_3]^{m-}$, regular Keggin $[PMo_{12□x}V_xO_{40}]^{m-}$ and monometal Strandberg $[P_2Mo_5O_{23}]^{6-}$ anions (Fig. 1). While there are only two analogous compounds were isolated from W-containing system. The absence of the complex with $[P_2W_5O_{23}]^{6–}$ anion in the latter system could be explained by its instability in comparison with the Mo-containing one. To the best of our knowledge, the compound $(NH_4)_y[Cu(en)(H_2O)]\{[Cu(en)_2]_5[Cu(en)(H_2O)]_2[PMo_{12-x}V_xO_{40}(VO)_3]\}\cdot nH_2O$ is the first example of complex with tri-capped molybdovanadophosphate Keggin-type anion.

EPR spectra of polycrystalline compounds with capped anions exhibit only one signal from Cu(II), however, this fact is not indicating the absence of reduced Mo or V atoms. This is a commonly occurred situation which could indicate that the electrons are delocalized over all the atoms of the POM skeleton [1].

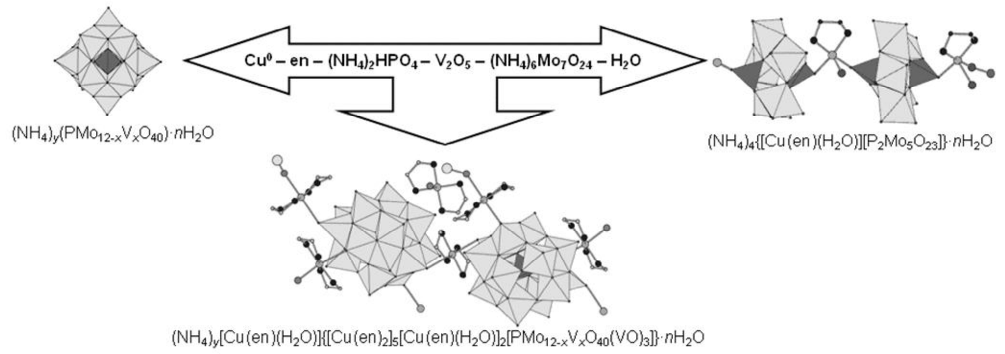

Fig. 1: Structure of compounds originating from the Mo-containing system

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SC_P08

Investigations of oxydiacetate complexes of VO(IV), Co(II) and Ni(II) in DMSO-H_2O binary mixtures

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Recently, it has been found that the oxydiacetate complexes of VO(IV), Co(II) and Ni(II) (Fig.) can protect effectively the mouse hippocampal neuronal cell line (HT22) as well as Human Dermal Fibroblasts adult (HDFa) cell line against an oxidative damage induced by H_2O_2 [1, 2]. To get a better insight into physicochemical and biological properties of the complexes their stability in the dimethylsulfoxide (DMSO) – water (H_2O) binary systems (0-50 %v/v DMSO-H_2O) was investigated by using the potentiometric and conductometric titration methods.

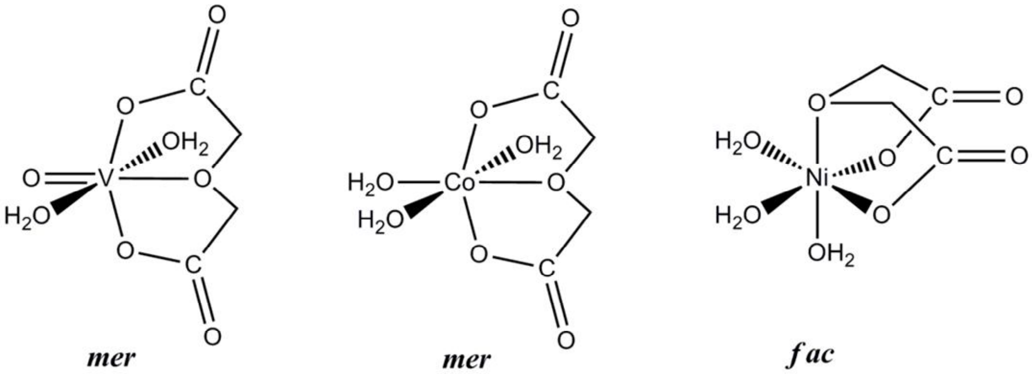

Figure. Coordination modes of oxydiacetate to VO(IV), Co(II) and Ni(II).

The stability constant values for the complexes studied increase in the sequence Co(ODA) ≈ Ni(ODA) < VO(ODA) (ODA denotes oxydiacetate anion). This finding is in a good agreement with the classification of the donor – acceptor atoms based on the HSAB theory. A softer character of Co(II) and Ni(II) with respect to VO(IV) results in the formation of less stable complexes with the ligands containing hard donor atoms. On the other hand, the cobalt(II) and nickel(II) complexes, in contrary to VO(ODA), are stable in a much broader pH range. Furthermore, conductometric measurements reveal that the stability of the complexes increases in proportion to the amount of DMSO in the system. Thus, in media with low dielectric constants the complexes behave as weak electrolytes.

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SC_P09

Iridium (III) cyclometalated complexes with bisphosphine ligands

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In the last few years, many examples of sky-blue and deep-blue emitting cyclometalated iridium (III) complexes bearing biimidazole, 2-pyridyl triazolate,bis-imidazolium carbene-type, picolinic acid N-oxide, have been explored, but challenges still remain regarding the efficiencies and stabilities of such emitters in devices. Perhaps surprising, given their common use as ligands, phosphorous-based ligands have been little investigated in cyclometalated iridium (III) systems; the few examples include benzyl diphenylphosphine [1], a phosphonite [2] and several bent phosphine chelators [3, 4].

We have sought to systematically explore bisphosphine compounds as potential new ancillary ligands in cyclometalated iridium (III) complexes. Six different common bisphosphines have been evaluated, initially in the simple iridium bis(phenylpyridinato) complex (Fig. left). We have also looked to improve both the photophysical properties and solubility of these complexes by exploring the effect of replacing the simple phenylpyridinato ligands with two different extended ligands (Fig. right)

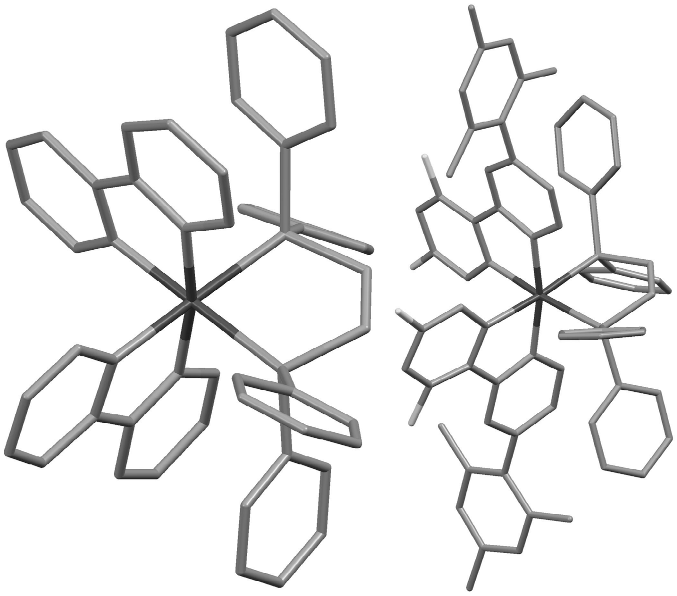

Figure. Views of the structures of two of the cationic bisphosphine complexes, with bis(phenylpyridinato) ligands (left), and extended ligands (right). Solvent, anions and hydrogen atoms omitted.

Literature:

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SC_P10

Synthesis, crystal structure and characterization of new Ag (I) coordination compounds with bitopic ligands

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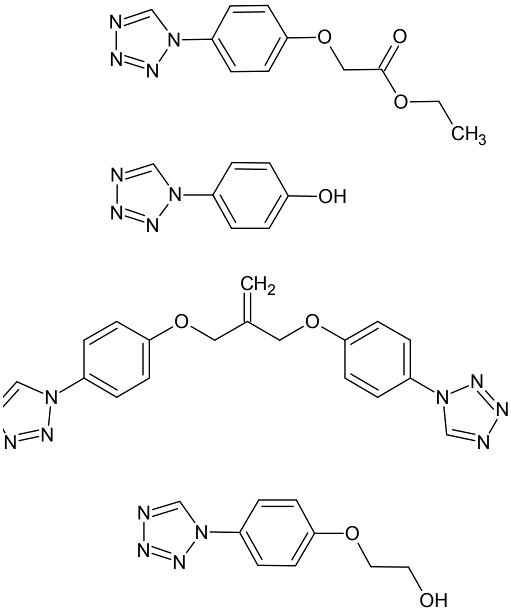
Different physical and chemical properties of solids can be predicted by applying crystal engineering principles to the construction of coordination polymers[1-2]. Design and synthesis of novel polymeric metal-organic frameworks has been extensively studied over the last two decades.This interest is mainly related with their potential applicability in diverse technological and industrial areas, such a gas absorption, catalysis or magnetic materials. Various physical and chemical properties of solids can be predicted by applying crystal engineering principles to the construction of coordination polymers (CPs). This approach seems interesting in the study of self-assembly of suitable metal ions and structural characterization of organic building blocks. Besides these aspects, metal-organic systems are held together by non-covalent interactions such as hydrogen bonding, including the CH···π interactions.



monomer

[Ag(ethyl [4-(1*H*-tetrazol-1-yl)phenoxy]acetate]NO$_3$]

1D

[Ag(μ_2-4-(1*H*-tetrazol-1-yl)phenol)]NO$_3$]

2D

[Ag(1-{4-[(2-{[4-(1H-tetrazol-1-yl)phenoxy]methyl}prop-2-en-1-yl)oxy]phenyl}-1*H*-tetrazole)]NO3]

3D

[Ag(2-[4-(1*H*-tetrazol-1-yl)phenoxy]etanol)]NO$_3$]

Figure. 1

In this communication we will presented synthesis, structure and properties of four new silver(I) coordination compounds:

Literature:

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SC_P11

A Luminescent Dinuclear Cu(I) Helical Complex Prepared from 2-Diphenylphosphino-6-Methylpyridine, and its Copper Derivatives

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Concerning Cu(I) complexes, the coordination chemistry of P,N-ligands is often complicated and mixtures of complexes in equilibrium are sometimes obtained in solution. It is likely that these considerations may have hampered interest in projects directed towards the preparation of luminescent Cu(I) complexes from P,N-ligands. A few recent reports revealed spectacular emission quantum yields for coordination compounds based on P,N-ligands [1].

As part of this research, we became interested in exploring the coordination chemistry of 2-diphenylphosphino-6-methylpyridine (dpPyMe) with Cu(I) cations. Thus, a stable dinuclear Cu(I) complex $[Cu_2(\mu\text{-dpPyMe})_3(CH_3CN)](BF_4)_2$has been successfully obtained. Its axial CH_3CN ligand can be suitably exchanged with other nitrile ligands to yield new dinuclear copper compounds. Their electrochemical and photophysical properties have been systematically investigated. It is noteworthy that the Cu(II)/Cu(I) redox potentials are very sensitive to steric effects and redox-induced changes of the coordination sphere around the copper centre. Correlations of the electrochemical data with DFT calculations and RX structures have been highlighted. The $[Cu_2(\mu\text{-dpPyMe})_3(L)](BF_4)_2$derivatives are weak emitters in solution but remarkable emission quantum yields have been found in rigid matrices at room temperature [2].

Literature:

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[2] a) Cid, J.-J.; Mohanraj, J.; Mohankumar, M.; Holler, M.; Accorsi, G.; Brelot, L.; Nierengarten, I.; Moudam O.; Kaeser, A.; Delavaux-Nicot, B.; Armaroli, N.; Nierengarten, J.-F. *Chem. Commun.*__2013__, 49(9), 859-861; b) Cid, J.-J.; Mohanraj, J.; Mohankumar, M.; Holler, M.; Monti, F.; Accorsi, G., Karmazin-Brelot, L. Nierengarten, I.; Malicka, J. M.; Cocchi, M.; Delavaux-Nicot, B.; Armaroli, N.; Nierengarten, J.-F. *Polyhedron*__2014__, 82, 158-172.

SC_P12

Synthesis and characterization of new Mo_3S_7 clusters

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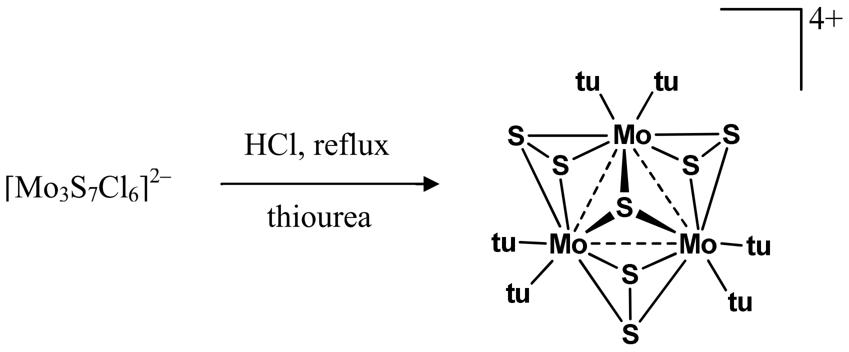
Over the last four decades, the chemistry of clusters containing $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3]^{4+}$ core has been extensively developed. The robustness and the easy modification of the coordination environments in M_3Q_7 units make these transition metal cluster chalcogenides very versatile systems [1]. An appropriate choice of ligands allows the preparation of molecular cluster systems with potential applications as new optical limiting material or as molecular conductors or magnets [2].

In this work, we report the synthesis of a new Mo_3S_7 cluster of formula $[Mo_3S_7(tu)_6]^{4+}$ (tu = thiourea). The synthetic route of this trimetallic cation starts from the $[Mo_3S_7Cl_6]^{2-}$anion and takes place through a simple ligand substitution reaction, represented in the next scheme [3].



Slow evaporation of the HCl solution of the complex affords crystals of the $[Mo_3S_7(tu)_6]Cl_4$ complex which has been characterized by X-ray structural analysis. This thiourea derivative constitutes a very promising starting material to develop new Mo_3S_7-based complexes. The potential of this $[Mo_3S_7(tu)_6]^{4+}$cluster as precursor will be presented.

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SC_P13

Copper(II) Metal-organic and Supramolecular Networks Self-assembled from Aminoalcohols and Pyromellitic Acid

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As a part of our general research line on the self-assembly synthesis of copper(II) metal-organic and supramolecular networks [1], the present contribution will describe a new series of coordination compounds generated from a reaction system composed of copper(II) nitrate as a metal source, various aminoalcohols as main building blocks, pyromellitic (1,2,4,5-benzenetetracarboxylic) acid as a linker, and alkali metal hydroxides (optional) as pH-regulators. Depending on the type of an aminoalcohol building block [e.g., triethanolamine, diethanolamine, *N*-methyldiethanolamine, *N*-ethyldiethanolamine, *N*,*N*-dimethylethanolamine] and the reaction conditions (stoichiometry, solvent, temperature, solution pH and kind of pH regulator), diverse copper(II) crystalline products have been self-assembled, ranging from discrete complexes to coordination polymers.

The characterisation of the obtained products by IR spectroscopy, ESI(±)-MS, elemental analysis and single crystal X-ray diffraction will be discussed, and the main structural, hydrogen bonding and topological features will be highlighted. The application of selected compounds as bio-inspired pre-catalysts for the mild oxidation of cyclohexane to cyclohexanol and cyclohexanone, by aqueous hydrogen peroxide in acidic MeCN/H_2O medium, will be reported.

Acknowledgment. This work was supported by the FCT (projects PTDC/QUI-QUI/121526/2010, RECI/QEQ-QIN/0189/2012, PEst-OE/QUI/UI0100/2013, IF/01395/2013 and SFRH/BPD/78854/2011), Portugal.

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SC_P14

Chiral potassium and sodium azacryptates

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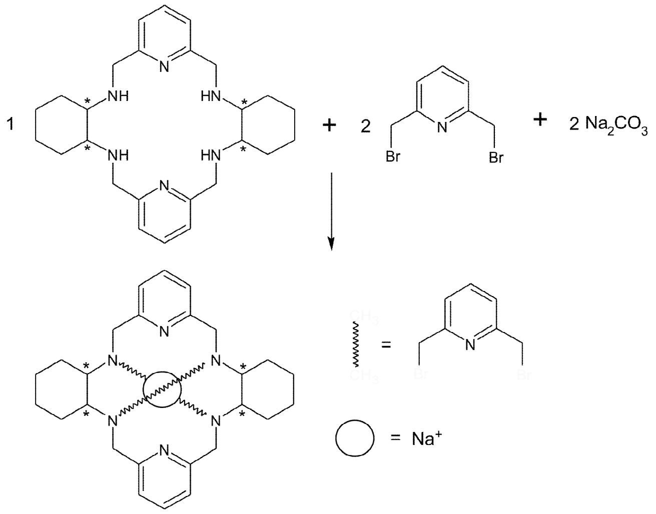
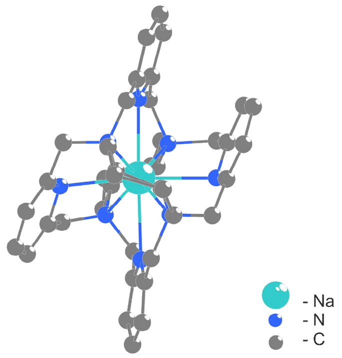
Macrocyclic chiral ligand L forms enantiopure Ln(III) complexes, which can undergo helicity inversion [1, 2]. We are interested in further modification of this ligand by N-alkylation of four amine groups. In particular reaction of L with 2,6-bis(bromomethyl)pyridine results in formation of chiral cryptand L2. Similarly as other cryptatands, for instance Lehn's cryptate [5, 6], the alkylation reaction leads to isolation of alkali metal cryptates $[Na^+ \subset L2]Br$ or $[K^+ \subset L2]Br$ using sodium carbonate or potassium carbonate, respectively, as bases. The preliminary X-ray crystal structures of $[Na^+ \subset L2]Br$ and $[K^+ \subset L2]Br$ show helical conformation of cryptand L2 and two types of pyridine rings. The NOESY data are in accord with the crystal data indicating characteristic close contacts of the compact structure of L2.

L2 exhibits high affinity for alkali metal cations, particularly for sodium. This can be exemplified by the reaction protonated L2 with cesium hydroxide run in glass vials – in this case $[Na^+ \subset L2]$ was obtained with the sodium cations originating from glass. Competition NMR and ESI MS experiments indicate stronger binding of sodium cation in comparison with potassium cation.





This work is supported by NCN Grant 2013/11/N/ST5/01373.

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SC_P15

Solvolysis of the dimeric [Re(CO)$_3$(N∩O$^-$)]$_2$complexes.

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The *fac*-Re(CO)$_3^+$ions forms neutral dimeric complexes with anionic bidentate N∩O$^-$ ligand. These neutral dimers, with a general formula Re$_2$(CO)$_6$(N∩O$^-$)$_2$, undergo in strongly coordinating media dissociative solvolysis yielding monomeric species Re(CO)$_3$(N∩O$^-$)(*solv*), where *solv* =a solvent molecule. Occurring solvolysis processes can be straightforwardly monitored due to distinct changes in UV-VIS spectra of the solvolysed dimers that allows determination their solvolysis rate k_{solv}. Already reported kinetic studies [1-5] have established that dissociative solvolysis is a first orderreaction with respect to both Re$_2$(CO)$_6$(N∩O$^-$)$_2$ and *solv* reactant.

$$\mathrm{Re_2(CO)_6(N{\cap}O^-)_2} + 2\,solv \xrightarrow{k_{\text{solv}}} 2\,\mathrm{Re(CO)_3(N{\cap}O^-)}(solv)$$

with $[\mathrm{Re(CO)_3(N{\cap}O^-)}(solv)] = 2[\mathrm{Re_2(CO)_6(N{\cap}O^-)_2}]_0(1 - \exp(-k_{\text{solv}}[solv]t))$

Dependingon the N∩O$^-$ ligand nature the dimeric species Re$_2$(CO)$_6$(N∩O$^-$)$_2$can be relatively labile (*e.g.*, complex with 8-hydroxyquinolinatoanion [1]) or quite stable (*e.g.*, complex with 2-(1-methyl-1*H*-benzoimidazol-2-yl)-phenolato anion [2]) with differences in the solvolysis rate as high as four orders of magnitude (with k_{solv} rates being equal to 6.4×10^{-3}and5.5×10^{-7} M^{-1}s^{-1}, respectively. Noteworthy, still more stable Re$_2$(CO)$_6$(N∩S$^-$)$_2$ complex with 8-thiohydroxyquinolinato anion requires prolongedtreatment with boiling pyridine for quantitative conversion of Re$_2$(CO)$_6$(N∩S$^-$)$_2$ into Re(CO)$_3$(N∩S$^-$)(*pyr*) [6]. It has been also found that the observed solvolysis rate depends strongly on properties of the reaction medium [1-5]. Moreover, in view of the already reported kinetic data the observed overall solvolysis rate increase roughly with basicity of the reaction medium expressed in terms of the donor number DN characterizing the given solvent.

Despite evident differencesin stability of Re$_2$(CO)$_6$(N∩O$^-$)$_2$ species,scarcityof the already reported experimental data do not allow discussrole of the coordinating ligand nature in more details. The same is true for differences in k_{solv} values for the given Re$_2$(CO)$_6$(N∩O$^-$)$_2$ complex that are distinctly dependent on the solvolysis medium. The aim of the presented investigations was to explain the already reported observation in more quantitative way with attempt to clarifythe role of N∩O$^-$ ligand attached to *fac*-Re(CO)$_3^+$ core.

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SC_P16

Synthesis, spectral and geometrical of a cadmium bromide complex with a multi-*N*-donor oxazolidine ligand

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In this research, the ligand, 2-(2-(pyridin-2-yl)oxazolidin-3-yl)-*N*-(pyridin-2-ylmethylene) ethanamine, POPME, was prepared *via* microwave-supported Schiff base and oxazolidination reactions. The cadmium bromide complex [Cd(POPME)Br_2] was prepared and identified by elemental analysis, IR, Raman and ^1H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction. In the crystal structure of [Cd(POPME)Br_2], the cadmium atom has a distorted octahedral CdN_4Br_2 environment. However the crystals contain a racemic mixture of R,R and S,S isomers. In the crystal network, there are intermolecular C–H…Br and N–H…Br hydrogen bonds. The bromide atoms act as proton acceptors whereas the carbon and nitrogen atoms participate in hydrogen bonding as proton donors.

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SC_P17

Isotropic and Anisotropic Spin-Spin Interactions in Metallacycles with Single M-X-M Bridges

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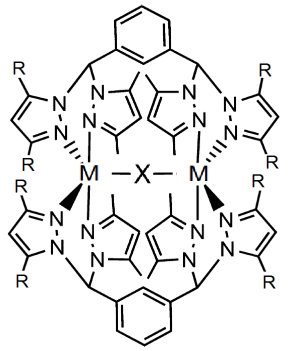

Schematic presentation of of cationic complexes
$[\mathbf{M}_2(\mu\text{-}\mathbf{X})(\mu\text{-}\mathbf{L_m})_2]^{3+}$, **R=H**
$[\mathbf{M}_2(\mu\text{-}\mathbf{X})(\mu\text{-}\mathbf{L_m}^*)_2]^{3+}$,**R=CH$_3$**

Two ligands composed of two bis(pyrazolyl)methane units linked by a *m*-substituted arene spacer; bis[bis(1-pyrazolyl) methyl]benzene,(**L_m** with **R=H**) and *m*-bis[bis(3,5-dimethyl-1-pyrazolyl)-ethyl]benzene, (**L_m*** with **R=CH$_3$**), have become a basis for the syntheses [1-4] of cationic binuclear metallacycles (see Scheme) in which two metal(II) ions (**M**) are held in close proximity by single **M-X-M** bridges. It was shown by X-ray crystal studies that the bulky **L_m^*** ligand rigorously enforces the linearity of the bridging group, while **L_m** allows formation of bent bridges.

In this presentation we intend to overview the magnetic and EPR properties of 3d transitionmetalcomplexes shown in the Scheme bytaking into account the effects provided by:

a) the bridges **X=F^-**, **Cl^-**, **Br^-**, **OH^-**, **CN^-**in the complexes with **M=Cu(II)**and **L_m***
b) metal ions **M= Mn(II)**, **Fe(II)**, **Co(II)**, **Ni(II)**, **Cu(II)** in the complexes with **X=F^-** and **L_m***
c) ligands **L_m**and **L_m***in the complexes with **M=** **Cu(II)** and **X=OH^-**

The complexes magnetic properties are analyzed in terms of the isotropic spin-spin magnetic interactions ($H = -\mathbf{J}S_1S_2$), which are reflected in the temperature dependence of magnetic moments. The anisotropic spin-spin interactions ($H = S_1\mathbf{D}S_2$), causing splitting of S>1/2 spin states in zero magnetic field are reflected in **D** values measured by EPR at microwave frequencies 9 - 420 GHz and at various temperatures.

DFT calculations allowed the prediction of the efficiency and pathways of the isotropic spin-spin interactions ("broken symmetry") and the understanding of the nature of the metal ion ground state in the distorted trigonal bipyramidal coordination.

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SC_P18

Reactions in Ru(III) pyridinecarboxylate–L-ascorbic acid systems. Kinetic and mechanistic studies

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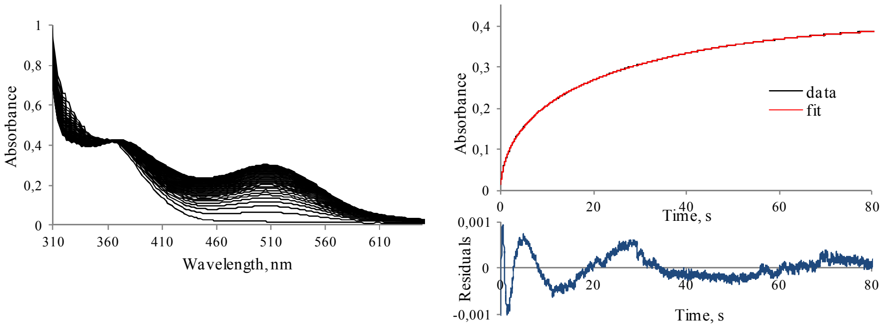
In recent years we have been engaged in mechanistic studies of the reduction of ruthenium(III) complexes with *N*,*O*-donor chelating pyridinecarboxylate ligands by L-ascorbic acid. L-ascorbic acid, one of the main physiological antioxidants, undergoes two consecutive, one electron oxidations to form ascorbate radical ($Asc^{\bullet -}$) and dehydroascorbate. The thermodynamic driving force for the overall oxidation process is the second reaction step. On the other hand, the $Asc^{\bullet -}$ radical has a redox potential high enough to be an efficient oxidant, especially at pH < 8.

Recently, we have examined the kinetics of the reduction of *cis*-$[RuCl_2(pic)_2]^-$ (**1**) and *trans*-$[RuCl_2(dpicOEt)_2]^-$ (**2**) complexes (where pic and dpicOEt = picolinato and monoesterified dipicolinato ligands, respectively) that were identified by single crystal X-ray diffraction. The reactions were followed spectrophotometrically using a stopped-flow technique under pseudo-first order conditions as a function of reductant and oxidant concentrations and pH. A triphasic absorbance increase within the visible range accompanying formation of the Ru(II) product in both systems, can apparently be reproduced by a triple exponential function (see Figures). This may indicate that a mixture of three Ru(III) species of different reactivity undergoes parallel pseudo-first order reduction reactions. However, all attempts to purify or to separate these species either by recrystallization, or on silica gel and ion exchangers, failed. It is noteworthy that, in contrast with this finding, formation of the Ru(II) in the *mer*-$[Ru(pic)_3]$–L-ascorbic acid system studied previously [1] is nicely described by a single exponential. It seems that the difference in the kinetic behavior of the three complexes could be related to their different redox properties; the redox potential of *mer*-$[Ru(pic)_3]$ is much higher than those of **1** and **2**, viz. 0.330, 0.0342 and 0.0622 V, respectively, and the $Asc^{\bullet -}$ radical is able to re-oxidize the Ru(II) generated in the latter two systems.



Spectral changes and kinetic trace for the reaction of the *cis*-$[RuCl_2(pic)_2]^-$-ascorbic acid system fitted to three exponentials; $[Ru(III)] = 1\cdot10^{-4}$ M, $[AscH_2]_T = 1\cdot10^{-3}$ M, pH = 7.90, 298 K, 506 nm.

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SC_P19

Redox-Induced Linkage Isomerism in $[Ru(NH_3)_5(NVF)](PF_6)_2$

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A new ruthenium (II) complex, of formula $[Ru(NH_3)_5(NVF)](PF_6)_2$, (**1**) (with NVF = *N*-vinylformamide), was synthesized following synthetic methods developed by Meyer *et. al.* [1] and characterized by spectroscopic and electrochemical techniques.

The presence of two coordination sites in NVF can lead to a redox-dependent linkage isomerization process, such as previously described in $[Ru(NH_3)_5(AM)](PF_6)_2$ (with AM = acrylamide) [2].

Cyclic voltammetry and UV-visible spectroelectrochemical measurements at room temperature indicate that upon oxidation of the metallic center in (**1**) , a rapid linkage isomerization takes place from a vinyl-coordinated Ru(II) to an amide-coordinated Ru(III), both in acetonitrile and in dimethylformamide.

This is another example of “molecular hysteresis” that can be applied in the design of molecular memory devices.

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SC_P20

New iridium isocyanide complexes

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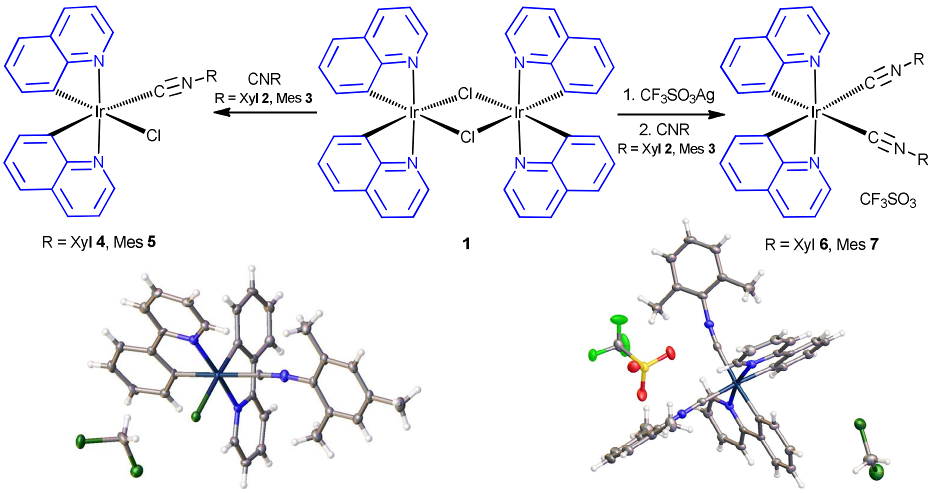
Among platinum group metals, palladium and platinum isocyanide complexes are well recognized[1]. In this context, iridium-isocyanides attracted much less attention.

In the course of our studies on chemistry of metal-isocyanide derivatives, we have synthesized several new iridium(III) isocyanide complexes of the general formulae $[(ppy)_2IrCl(\underline{C}NR)]$ and $[(ppy)_2Ir(\underline{C}NR)_2](CF_3SO_3)$ (ppy = 2-phenylpyridine-*C*^{2},*N*′). Indeed, the complexes $[(ppy)_2IrCl(CNR)]$ (R = Xyl, Mes; isolatedyields 82–87%), were prepared starting from the binuclear complex $[(ppy)_2Ir(\mu\text{-}Cl)]_2$ upon reaction with one equiv of appropriate CNRinrefluxingCH_2Cl_2. The corresponding *bis*(isocyanide)species $[(ppy)_2Ir(CNR)_2](CF_3SO_3)$ (R = Xyl, Mes; isolatedyields76–79%) were generated from $[(ppy)_2Ir(\mu\text{-}Cl)]_2$uponchloride abstraction with CF_3SO_3Agin a CH_2Cl_2/MeOH (4:1) mixture and followed by addition of two equivs of CNR(R = Xyl, Mes) in CH_2Cl_2[2].



All obtained compounds were fully characterized by ^1H, and $^{13}C\{^1H\}$ NMR and IR spectroscopies, ESI$^+$ MS and elemental analyses (CHN), and also by X-ray diffraction.

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SC_P21

METAL COMPLEXES WITH NEW LINEAR DIAMINOBISPHENOLATE LIGANDS.

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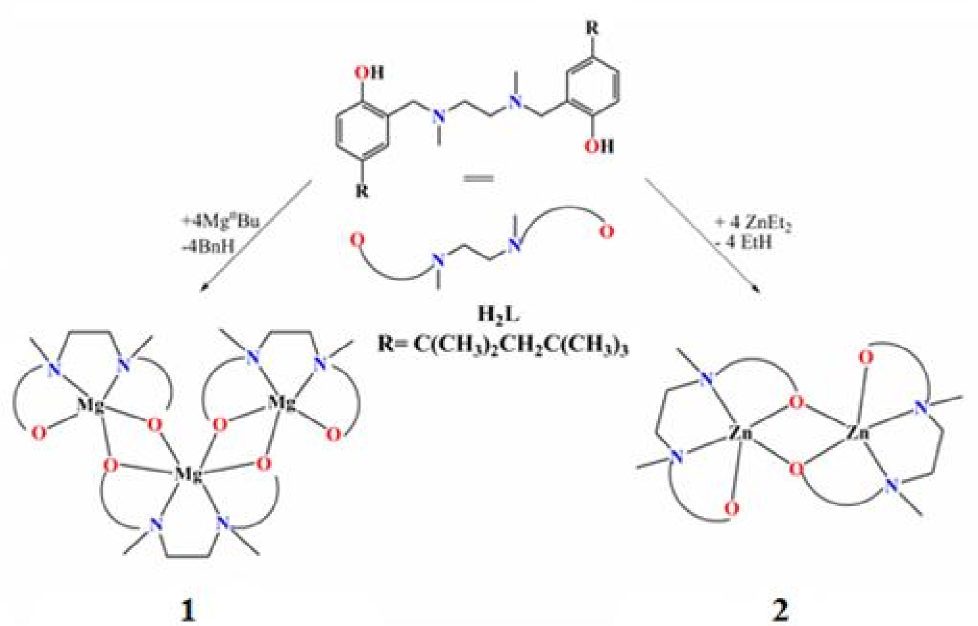
Polydentate diaminebis(aryloxido) (ONNO) ligands have been used extensively in both transition and main group metal coordination chemistry in catalyst development, metalloenzyme mimicry and cytotoxicity against particular cells as well as magnetic studies[1]. Such broad application range arises from the great modification possibilities either on the phenyl group or amine one leading to the convenient variation of steric factors and donor ability of those class ligands. A particularly convenient method for the synthesis of metal complexes supported by diaminebis(aryloxido) ligands is through a metathesis route involving various metal precursors and protonated ligands (Scheme)[2].

Synthetic strategy and structural study of Mg and Zn complexes will be presented in details.



Scheme. Synthetic strategy of[$Mg_3(\mu\text{-}L\text{-}\kappa^4O,N,N,O)_3$] (**1**) and [$Zn_2(\mu\text{-}L\text{-}\kappa^4O,N,N,O)_2$](**2**).

The authors would like to thank the National Science Centre (Poland) (Grant Nr 2012/05/N/ST5/00697) for the financial support.

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SC_P22

Electronic structures and coordination abilities of Ar(R)C=N-CH=C(X)$_2$ 2-azabuta-1,3-dienes (R = Ph, CN; X = Cl, SR').

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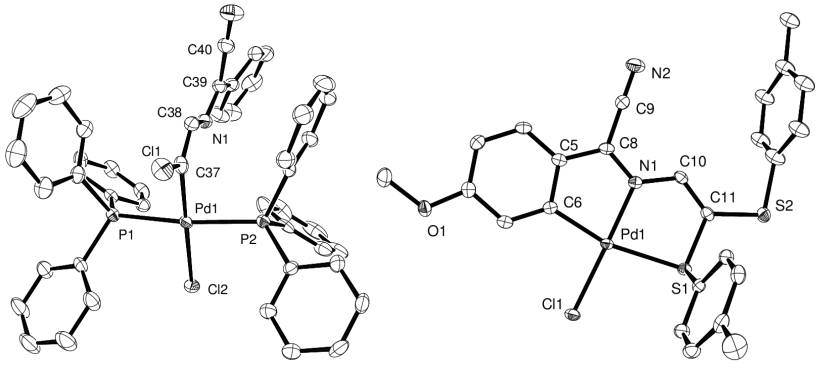
Azabuta-1,3-dienes are the class of polyvalent reagents that are easily functionalized. are interested in coordination ability of this class of Ar(R)C=N-CH=CX_2 (R = Ph, CN; X = SR') potential ligands. We synthetized the precursor molecule (Ar=Ph, R=Ph, X=Cl; **1Ph,C** 1999 [1]. It has been shown that it may undergo an insertion of metallic fragment (Pd, Pt) i one or two C-Cl bonds [2]. Once functionalized with $^{-}$SR nucleophiles the resulting (**2Ph,S** ligandslead to chelated and ortho-metallated complexes [3]. As expected, the central four ato chain is conjugated and the conjugation extends on the aryl ring.

In order to improve the conjugation (planarity) we introduced recently the elect withdrawing CN group in place of the phenyl. The goal of this substitution is to get the materi exhibiting enhanced photophysical properties, despite the expected overall stabilization of molecules in CN-series (**1CN,Cl**) and (**2CN,SR'**) and so their hindered reactivity.

The comparative electronic structures of some ligands in both R=Ph and R=CN series h been studied with DFT. The derived energetics, electrophilicity indexes, atomic charges (N AIM), Fukui functions, hardness/softness over main molecular chain agree with experime reactivity and electronic spectroscopies. The challenge for improved emission properties confirmed by the quantum yields, which are 3-4 times higher in the CN series than in the series of the 2-aza-1,3-butadiene ligands.

Like with (**1Ph,Cl**) the activation of the first and of the second vinylic C-Cl bond observed through the insertions of Pd and Pt fragments therein in (**1CN,Cl**) (Figure left). T *ortho*-metallation reactions involving Pt and Pd and some molecules from (**2CN,SR')** fam with chelation occurring through N and S atoms are also observed (Figure right), despite lower energies of N and S lone pairs.

Search for new systems with enhanced luminescent properties, new coordination mo and theoretical and spectroscopic studiesin CN series are currently in progress.



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SC_P23

Porphyrin-decorated polypyridines for dye sensitized solar cells

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The presented work focuses on the synthesis of new organic ligands and their metal complexes for application as sensitizers in dye-sensitized solar cells (DSCs). Although a wide range of such complexes exists, a major problem still has to be overcome: the inefficient absorption in the range covered by sunlight. Most dyes can only partially absorb the visible light, depending on their structure. In general they mostly absorb in the UV region with high extinction coefficients and absorb less effectively in the visible range. Aromatic rings, unsaturated substituents and conjugated structures provide ligand centred transitions in the UV, while complexation to a metal ion adds, for example, a metal-to-ligand charge transfer band (MLCT), typically in the visible.

Our group focuses on the application of copper(I) polypyridine complexes as dyes. My research fits in this context as I am developing porphyrin-based polypyridine dyes. With the aim of expanding the porphyrin absorption over the largest energy range possible, derivatives of the commercially available tetraphenylporphyrin (TPP) were synthesized. The well-known light-harvesting ability of TPP has been coupled with the MLCT of transition metal ions to which it complexes and with the UV absorption arising from the polypyridine domain.

The spectroelectrochemical characterization of **L**(**L** = [ZnTPP-phtpy]), (phtpy = 4'-phenyl-2,2':6',2''-terpyridine), [Zn**L**$_2$]$^{2+}$ and [Fe**L**$_2$]$^{2+}$ was performed. TPP and ZnTPP were used as model compounds to investigate how the presence of an octahedral metal domain influences the absorption spectrum upon oxidative/reductive cycle. The simple ligand **L** shows features which are characteristic of a ZnTPP derivative. Examining the [Zn**L**$_2$]$^{2+}$ complex, it displays very similar spectral features with respect to the ligand. It is reasonable since the zinc(II) centre cannot exist in more than one oxidation state, and so does not display an MLCT band upon complexation. Considering the [Fe**L**$_2$]$^{2+}$ complex, the presence of an oxidizable metal centre allows an MLCT band to appear in the same spectral region of the porphyrin Q band. The MLCT band is reversible upon oxidative cycle as it would be expected for a redox couple as Fe^{II}/Fe^{III}.

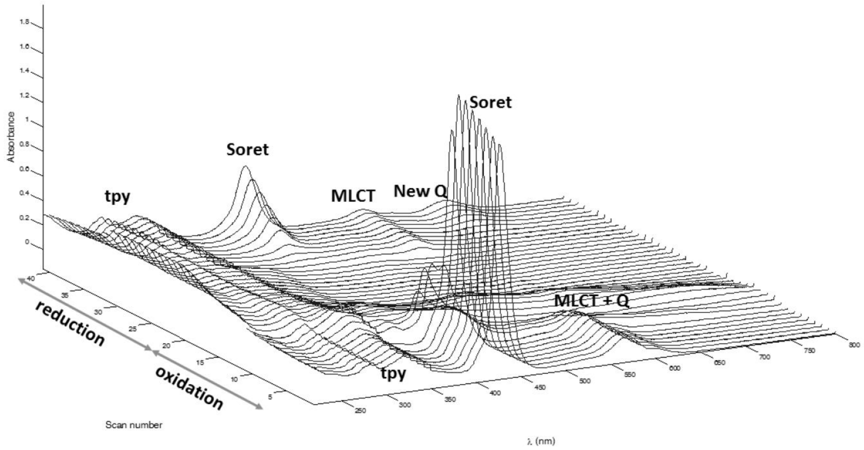

Figure: oxidative spectroelectrochemistry of the [Fe**L**$_2$]$^{2+}$ complex.

SC_P24

Stereochemical aspect of influence of [Cu(*diethylenetriamine*)(H_2O)]SO_4·H_2O chelate compound onto combustibility decrease of epoxy-amine composite materials

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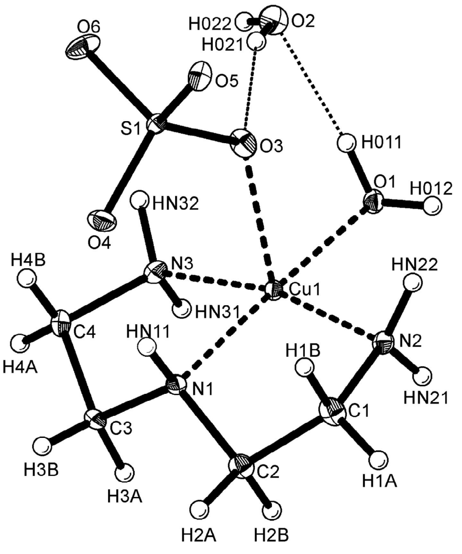
It is known that copper(II) salts can be used for effective suppression of the inflammation of amines and nitriles [1]. In this flame retardant process, the decisive role belongs the chemical interaction (Cu–N donor-acceptor bonding), which causes the formation of practically incombustible copper(II) complex. It opens up new vistas of using the transition metals salts in production of self-extinguishing epoxy-amine composites. Recently there has been a tendency to use, as a hardener of epoxy resins, the chemically bonded amines with salts of transition metals instead of the pure amines. Therefore, we undertook an attempt to study interaction of *diethylenetriamine* (hardener) with copper(II) sulfate whose anhydrous salt in solid state has been employed as retarder in the prototype of epoxy-amine polymeric materials with the depressed combustibility. The chelate complex of [Cu(*diethylenetriamine*)(H_2O)]SO_4·H_2O (see Figure) have been synthesized and its crystal structure has been determined by X-ray diffraction methods (Sp.gr. $P\bar{1}$, a = 7.2819(4), b = 8.4669(4), c = 8.7020(3) Å, α = 83.590(3), β = 89.620(4), γ = 84.946(4)°, V = 531.09(4) Å^3, Z = 2). The crystals of this chelate consist of discrete [Cu(*diethylenetriamine*)H_2O]$^{2+}$ complex cations and hydrated [H_2O·SO_4]$^{2-}$ anions. The environment of the Cu(II) atom is elongated square pyramid which consists of three N atoms of the *diethylenetriamine* and O atom of the water molecule in the basal plane of the square pyramid. The apical position of the coordination polyhedron is occupied by complementary O atom of the sulfate anion. The average lengths of the in-plane Cu–N and Cu–O bonds are 2.00 Å whereas the length of the axial Cu–O bond is 2.421(1) Å. The crystal packing is governed by strong hydrogen bonds of O–H···O and N–H···O types. Thus, the strong coordination bonds that arise between metal atoms of incombustible $CuSO_4$ and nitrogen atoms of the amine hardener are responsible for the flammability suppression of the epoxy-amine compositions. The high stability of this compound in solid state is a determining factor at producing of the self-extinguishing epoxy-amine composites modified by $CuSO_4$.



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SC_P25

New herringbone array in the Cu^{II}-PDC system: thermal analysis and crystallochemical correlations

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Porous Solid Coordination Frameworks, also known as Metal Organic Frameworks (MOFs), have been focused the attention of many researches because of their potential applications in fields like gas storage, gas separation, drug delivery, sensors, heterogeneous catalysis,...[1,2] Among the wide variety of ligands to create these frameworks, our work is based on the combination of polycarboxylate and bipyridine ligands.[3] In fact, we have been using 2,5-pyridinedicarboxylate (PDC) as main ligand, since PDC has been showed up to twenty four different coordination modes and it exhibits five potential donor atoms. In this sense, this work is based on the combination of Cu^{II} with PDC and 4’4-bipyridine (4’4-bipy) ligands, giving rise to compound $[Cu_2(PDC)_2(4'4\text{-bipy})(H_2O)_2]\cdot MeOH$. The synthesis has been carried out at 140 ºC for 72h under solvothermal conditions, using a mixture of H_2O and MeOH as solvents. The crystal structure for the compound consists of 2D herringbone-type layers. Molecules of methanol are located in between as crystallization moieties. This way, the layer are interconnected via hydrogen bonds by means of the crystallization molecules. The 3D supramolecular framework exhibits channels along the [010] direction. Thermogravimetric and thermodiffractometric analysis have been carried out in order to characterize the thermal stability of the compound. Finally, we have correlated the structural features of the compound with other herringbone-arrays found in literature.[3]

Acknowledgments: This work has been financially supported by “Ministerio de Economía y Competitividad” (MAT2013-42092-R), “Gobierno Vasco” (Basque University System Research Group, IT-630-13) and UPV/EHU (UFI 11/15) which we gratefully acknowledge. SGIker (UPV/EHU) technical support (MEC, GV/EJ, and European Social Fund) is gratefully acknowledged. F. Llano-Tomé thanks “Ministerio de Ciencia e Innovación” for his fellowship (BES-2011-045781).

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SC_P26

NEW, CHIRAL MACROCYCLIC Zn^{II}, Cu^{II} AND Ni^{II} COMPLEXES

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The chiral nonaazamacrocyclic amine L (Fig.1) is an interesting ligand for the formation of enantiopure complexes.[1,2] It forms a trinuclear Cu(II) complex [2] similarly as does an analogous triphenolic macrocyclic [3]. We have obtained new series of Ni(II), Cu(II) and Zn(II) chloride complexes of L. All compounds were characterized using ESI MS, CD, NMR and elemental analysis. X-ray crystal structures of trinuclear complexes indicate that the six-coordinate Ni^{2+} or five-coordinate Cu^{2+} ions are bridged by one Cl^- ion lying in the middle of the molecule. In the case of zinc complex, only two zinc ions are coordinated inside the macrocyclic ligand which is accompanied by considerable macrocycle ruffling in comparison with the Cu(II) and Ni(II) trinuclear derivatives. The coordination of only two Zn(II) was confirmed also by NMR titration. The magnetic measurements in the 1.8 – 300 K of the new trinuclear Cu(II) derivative indicate antiferromagnetic interactions, in contrast to the previously reported Cu(II) complex which exhibit ferromagnetic interactions [2].

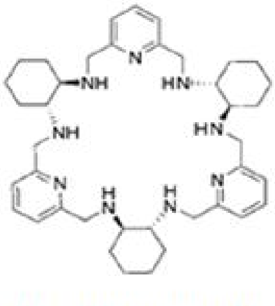
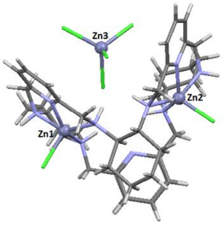
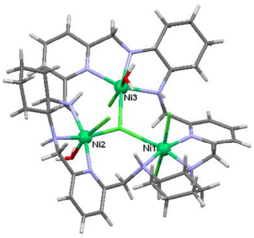
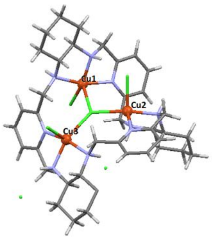


Fig.1. Structure of L_1







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SC_P27

Formation/DissociationKinetic Study of Cu(II) Complexes of *Cyclen*-like Macrocyclic Ligands with Pendant Thiol Group

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Copper(II) complexes of macrocyclic ligands are employed in medicine for diagnostics and/or for cancer treatment ($^{60\text{-}62,\ 64/67}$Cu) [1]. These metal complexes should exhibit a high thermodynamic stability as well as kinetic inertness under physiological conditions and therefore the knowledge of their thermodynamic andkinetic properties is important in order to evaluate their usefulness in this field.

As part of our ongoing research work in the field of copper(II) complexes of biological interest [1], new *cyclen* derivatives bearing a 2-ethanethiol pendant arm *2-[1,4,7,10-tetraazacyclododecane-1-yl]-ethanethiol,* **L1 = cyclen-SH**, and*10-(2-sulfanylethyl)-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid*, **L2 = H_4DO3A-SH)**were synthesized and characterized [2,3]. As extension of this research project, herein we report the study dealing with formation and dissociation of copper(II) complexes of both macrocyclic ligands. Comparing their kinetic properties[4], this study showed that both ligandsare suitable for further conjugation with biomolecules, aiming their use in medicinal chemistry.

This study was supported by the Grant Agency of the Czech Republic (No 13-08336S) and EU (CEITEC CZ.1.05/1.1.0/02.0068). PL thanks the GRICES for a travel grant.

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SC_P28

New organically templated metal sulfates with 4-aminopyridinium

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4-Aminopyridine forms a series of inorganic-organic hybrids with different halogen salts which exhibit ferroelectric, ferroelastic and interesting magnetic properties [1-3]. The only representative of double 4-aminopyridinium metal sulfate was nickel analog described by T. Sahbani [4]. During the course of our investigations on sulfate materials, a series of new metal (Cu^{II}, Co^{II}, Mg^{II}, Mn^{II}, Zn^{II}, Cd^{II}, Fe^{III}) sulfates templated by 4-aminopyridinium has been prepared and structurally characterized by vibrational spectroscopy (IR and Raman) and single crystal X-ray diffraction. Additionally, Hirshfeld surface analysis have been used to compare the intermolecular interactions in the crystal structures of new compounds. The results of optical and magnetic properties for these compounds will be presented and discussed.

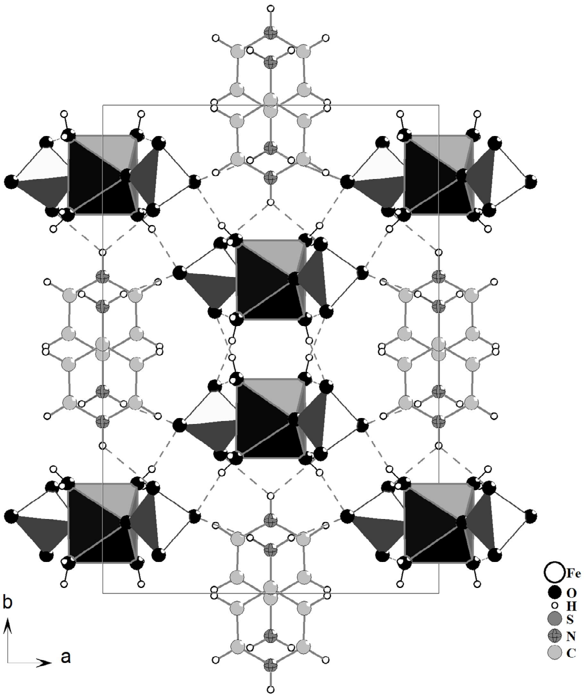

Fig. 1. Crystal structure projection for compound ($(C_5H_7N_2)[Fe^{III}(H_2O)_4(SO_4)_2]$). Dashed lines indicate the hydrogen bonds.

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SC_29

Cyclen Based Ligand for Complexation of PET Metals

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Molecular imaging has became the technique of choice for the management of patients with cancer and other diseases. It is also a valuable investigative tool for the study of drug action and the development of new therapeutic approaches. A number of techniques based upon fundamentally different physical principles give rise to 3D images with diagnostic value and are now well established in clinical applications and in drug discovery research. Our interest focuses in particular upon Positron Emission Tomography (PET) and Single-Photon Emission Computed Tomography (SPECT) which may be used to give information on functional process as well as structure. In certain disease conditions, these techniques provide diagnostic support for clinicians for which other methods are not well suited and they are becoming of increasing importance in obtaining 3D images of patients *in vivo*,.[1]

The basis of PET relies upon administering a radiopharmaceutical agent that contains a positron emitting radioisotope. Non-metallic radionuclides such as ^{15}O, ^{11}C and ^{18}F are currently most widely used in PET imaging, but their short half-lives limits their application.[2]

Metallic radionuclides such as ^{64}Cu, ^{86}Y, ^{89}Zr, ^{68}Ga, present longer half-lives and deliver the opportunity to form imaging probes that better match the biological half-lives of several important classes of biological molecules such as poly-peptides or antibodies.[3]

Clearly, the successful design of a PET imaging probe (as with other applications of metal-based imaging agents), requires that the metal is bound to a suitable ligand system (or set of ligands) that will form complexes that remain robust under physiological conditions. Most studies to date rely upon ligand systems that have been shown to be effective for some metal, predominantly applied to applications in MRI, but have not been optimized for binding Y and Zr PET isotopes. One of the most widely used approaches is to apply ligands based upon the cyclen core structure; examples include DOTA, DO3a, DO2a, etc. [4]

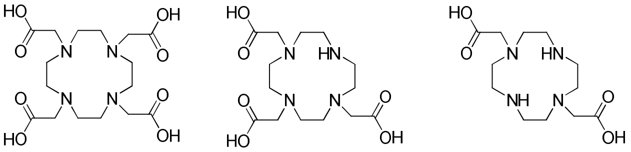

Fig 1: DOTA, DO3a and DO2a

The aim of this research is to develop macrocyclic ligands suitable for chelating Y and Zr radionuclides and to compare these ligands to the 'industry standard' chelator desferrioxamine (DFO).[5]

An example of our approach that we will discuss includes extending the functionality of this ligand system by incorporation of an alcohol group, thus enabling the attachment of biological targeting entitites.

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SC_30

Synthesis and properties of novel Cu and Cu/Mn complexes with N-*tert*-butyldiethanolamineand trimethylacetic acid

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A number of coordination compounds with sophisticated crystal structures have been obtained by spontaneous self-assemblyusing simple flexible diethanolamine ligands.[1] Following our interest in the preparation of mono- and polynuclear complexes with N,O-donor ligands[2] we have explored the synthetic systems containing N-*tert*-butyldiethanolamine (H_2tBuDea) and pivalic (trimethylacetic) acid (HPiv). One can expect that the presence of an aliphatic bulky substituent (the *tert*-butyl fragment) in these ligands facilitates the formation of polynuclear compounds.

The interactions of zerovalent metal and/or metal salt with H_2tBuDea and HPiv in non-aqueous solutions lead to the formation of the novel complexes $\{[Cu_2(Piv)_4(H_3t\text{BuDea})](Piv)\}_n$(**1**) [3]and $[Cu_2(Ht\text{BuDea})_2(OAc)_2]$ (**2**), as well as the heterometallic compound $[Cu_3Mn_2(OAc)_2(Piv)_4(t\text{BuDea})_2(Ht\text{BuDea})_2]\cdot CH_3CN$ (**3**). The complex **1** features a 1D polymeric structure where the diethanolamine showsthequite rare non-chelating bridging coordination mode, while complex **2**showsa binuclear molecular structure.Compound **3** has a pentanuclear cage structure in the formation of which take part all the ligands used in the initial synthetic system (Fig. 1). Theantiferromagnetic exchange coupling within the dicopper unit in **1** was found to be of exceptionally high magnitude resulting in a diamagnetic behaviour of **1**. The magnetic and catalytic properties of **2** and **3** are under investigation.

This work has been supported by the Foundation for Science and Technology (FCT), Portugal (project UID/QUI/00100/2013; fellowship SFRH/BPD/63710/2009).

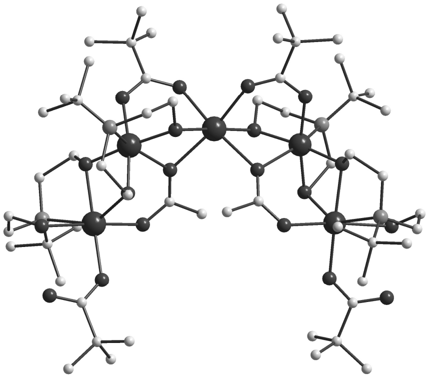

Fig. 1. Molecular structure of $[Cu_3Mn_2(OAc)_2(Piv)_4(t\text{BuDea})_2(Ht\text{BuDea})_2]\cdot CH_3CN$ (**3**).

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SC_31

Regiospecifity of Reactions of the Second Substituent Introduction in Monosubstituted Derivatives of Cluster $[B_{12}H_{12}]^{2–}$ Boron Anion

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Reactions of the following monosubstituted derivatives of dodecahydro-*closo*-dodecaborate (2–) anion were studied:

– reaction of $[B_{12}H_{11}\mathbf{Y}]^{2–}$, **Y** = I, OH, OC(O)$CH_3$ and SCN with acetic acid in the presence of oxygen and atmospheric moisture. The single-stage procedure of the hydroxy group introduction into monosubstituted $[B_{12}H_{12}]^{2–}$ anion derivatives without the formation of acetoxo derivatives was developed;

– reaction of $[B_{12}H_{11}\mathbf{Y}]^{2–}$, **Y** = I, OH, OC(O)$CH_3$ and SCN with formic acid in an inert atmosphere (Fig. 1**a**);

– reaction of $[B_{12}H_{11}\mathbf{Y}]^{2–}$, **Y** = I, OH, OC(O)$CH_3$ and SCN with dimethyl sulfoxide in the presence of acetic anhydride in an inert atmosphere (Fig. 1**b**);

– reaction of $[B_{12}H_{11}\mathbf{Y}]^{2–}$, **Y** = I, OH and OC(O)CH_3 with $(SCN)_2$ solution in dichloromethane in an inert atmosphere (Fig. 1**c**, 1**d**).

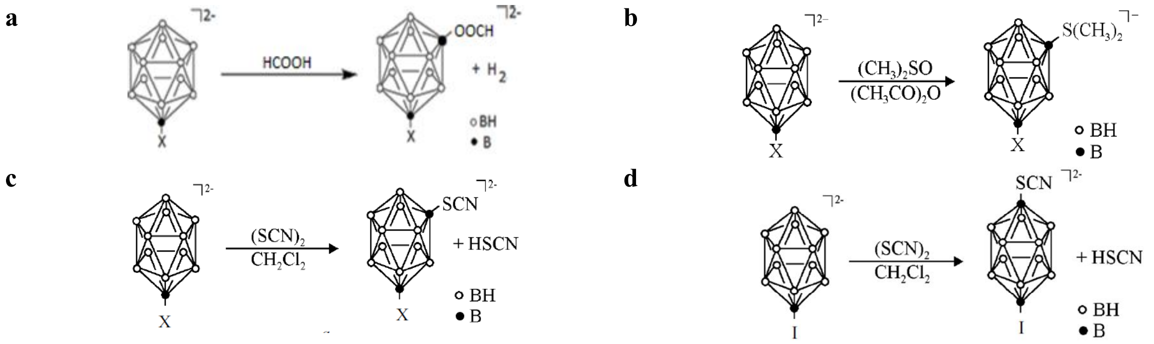

Figure 1 – Reactions of the second substituent introduction in monosubstituted derivatives of $[B_{12}H_{12}]^{2–}$ anion

It was found for the reactions under consideration that substituents have the electron-seeking effect and decrease the reactivity of monosubstituted anions as compared to that of $[B_{12}H_{12}]^{2–}$.

The reactions under consideration were shown to have the regioselective character. The I, OH, OC(O)CH_3 and SCN substituents are *meta*-orientants with respect to the introduced OH, OC(O)H and $S(CH_3)_2$ groups and the OH, OC(O)CH_3 substituents are *meta*-orientants with respect to the introduced SCN group. In the case of the reaction of thiocyanogenation of $[B_{12}H_{11}I]^{2–}$ anion, the 1,12-$[B_{12}H_{10}I(SCN)]^{2–}$*para*-isomer is formed.

It was found that the introduction of OH group into monosubstituted derivatives of $[B_{12}H_{12}]^{2–}$ increases substantially their water solubility as compared to that of non-substituted anion.

Data on the synthesis of disubstituted derivatives of cluster $[B_{12}H_{12}]^{2–}$ boron anion and on the orientation effect of substituents can be used in developing BNCT preparations in the case of two biologically active substituents introduced into the boron skeleton of molecule.

SC_P32

The Thermal Decomposition of Lanthanide-Thiocyanate Based Ionic Liquids

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New lanthanide containing ionic liquids (ILs) based on Thiocyanate complexes of the type $[BMIM]_x[Ln(NCS)_{x+3}]$ (BMIM= 1-Butyl-3-Methylimidazolium; x=3,4,5) have been reported in recent studies[1-4]. These complexes are highly efficient in dissolving lanthanide complexes within ILs.

The present work includes thermal decomposition study of the ionic liquids of this type with Ln=SmorEu. The thermal decomposition of [BMIM][NCS], $[BMIM]_3[Ln(NCS)_6]$, $[BMIM]_4[Ln(NCS)_7]$ and $[BMIM]_5[Ln(NCS)_8]$ were measured using thermo-gravimetric analysis (TGA), and temperature programmed desorption analysis (TPD) coupled with mass spectrometer (MS) for analysis of the gaseous residues.

The decomposition temperature of the lanthanide containing IL were found to be higher than that measured for [BMIM][NCS], suggesting stabilization of the ionic liquid by complexation to the lanthanide. Moreover $[BMIM]_3[Ln(NCS)_6]$, was more stable than $[BMIM]_4[Ln(NCS)_7]$ and $[BMIM]_5[Ln(NCS)_8]$, due to stronger bond with less thiocyanate ligands in the inner sphere.

It was found that all $[BMIM]_x[Ln(NCS)_{x+3}]$ decomposed to $Ln(NCS)_3$ in a stepwise fashion via $[BMIM]_3[Ln(NCS)_6]$ intermediate. Both [BMIM][NCS] and $[BMIM]_x[Ln(NCS)_{x+3}]$ are assumed to decompose by nucleophilic attack mechanism to give the gaseous products: Methyl-thiocyanate and Butyl-imidazole majorly, or Butyl-thiocyanate and methyl-imidazole minorly. The products distribution is dictated by steric hindrance when thiocyanate attacks the methyl group, rather than the butyl group.

Interestingly, with elevating decomposition temperatures, more Butyl-thiocyanate and Methyl-imidazole were measured in the products, presumably because the higher temperature provides sufficient energy to make the less favorable decomposition route more probable.

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SC_P33

Syntheses of Zn spiro-complexes

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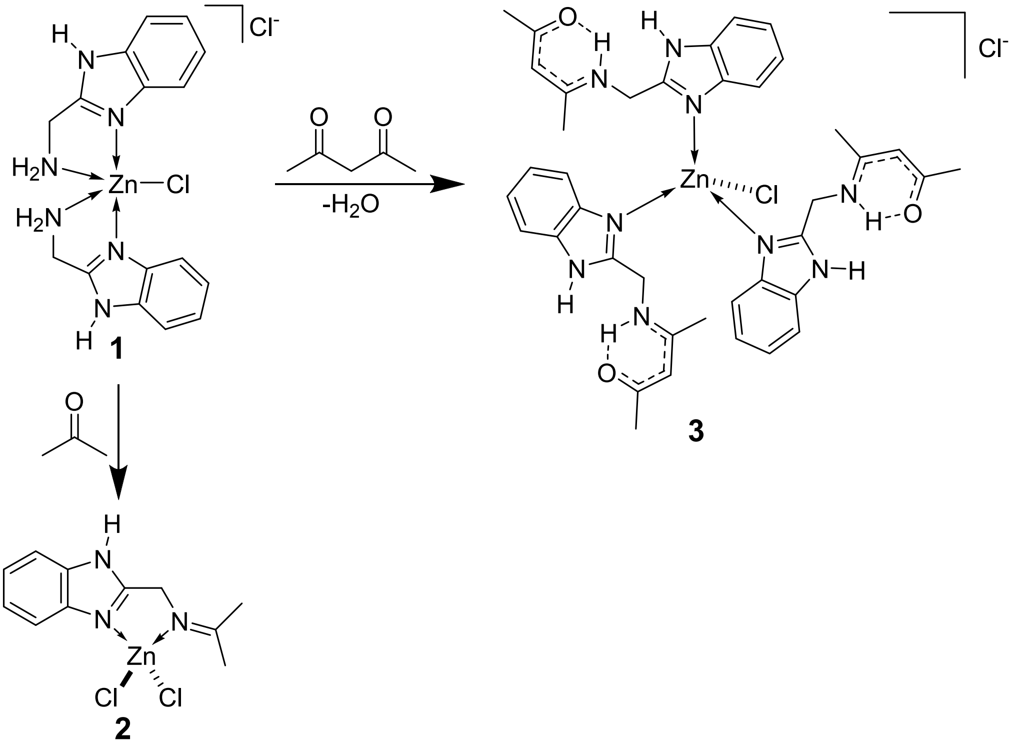
The interaction of Zn(II) with the active site of Zn metalloenzimes has a significant effect on the catalytic activity of these macromolecules.Zn(II)is principally bonded to histidineand cysteine residues [1]. But, the presence of histidine in the active site is especially significant because the Zn(II) geometry is dependent on the acid-base properties of imidazolic group. Moreover, it is known that theZn(II) geometry affects the aza-additions of amines and imidazolic groups [2]. Thus, the addition of nitrogen ligands toward aldehydes and ketones could be promoted by the presence of N→Zn(II) bonds.

We chose to study the aza-addition reactions of Zn-complexes derived from 2-(aminomethyl)benzimidazole**1** toward ketone and 2,4-pentadione. We found that Zn promotes the aza-addition of amine group. The reaction yields the imine compound **2**in presence of simple ketones. However, the helical Zn-complex **3**was obtained when 2,4-pentadione was used. The crystallography studies of **3** showed the presence of delocalized systems O-C-C-C-N. These arrangements have a pseudocyclic structure due to presence of N-H•••O hydrogen bond interactions and they are in concordance with the Hückel rules for aromaticity. The molecular structure **3**is stabilized by the presence of π-π interactions between pseudocyclic and benzimidazole systems [3].



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[3] This work was supported by SEP-CONACyT 169010.

SC_P34

Transition Metal Complexes of Tris(aminomethyl)phosphine Oxide – X-ray Structures and Thermodynamic Studies

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α-Aminoalkylphosphine oxides are well-known electroneutraltripodal ligands. Theyform coordination compounds with transition metal ions such as Co(II/III), Cu(II), Ni(II), Zn(II), often with a high selectivity. For example,tris(2-aminoethylphosphine oxide) (TEAPO), *P*-(*N*,*N*-dimethylaminomethyl)-*P*,*P*-diphenylphospine oxide, *P*-aminoethyl-*P*,*P*-dimethylphosphinecan be mentioned.[1,2]Moreover, transition metalion complexes of these ligands have been usedin homogenous catalysis or as potential template precursors in synthesis of a range of macrocyclic compounds such as polyazamacrocycles, crown ethers, cryptands, clathrochelates, etc.[3]

Tris(aminomethyl)phosphine oxide (TAMPO) as the simplest ligand of this family was synthesized.[4]Itsprotonization constants and stability constants of its complexes with selected transition metal ions were studied in solutions by potentiometric titrations. The ligand is less basic than TAME (1,1,1-tris(2-aminomethyl)ethane), an analogous ligand without phosphorus atom, pointing out electron-withdrawing character of the phosphoryl group.Complexes of TAMPO are less stable than those of TAME. The crystal structures of TAMPO·3HCl, [Ni(TAMPO)]Cl_2, [Cu(TAMPO)]Cl_2 and [Co(TAMPO)]Cl_3 (Figure 1) were determinedby X-ray single-crystal diffraction analysis. The complexes are octahedral coordinated by only nitrogen atoms and the copper(II) complex exhibits distinct Jahn-Teller distorsion of coordination polyhedron.

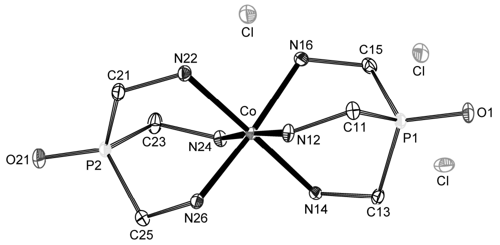

Figure 1: Structure of [Co(TAMPO)]Cl_3

This work was supported by the Grant Agency of the Czech Republic P207/11/1437.

Literature:

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SC_P35

Synthesis, structure and photophysical properties of Ln^{3+} complexes with derivatives of amidophosphates

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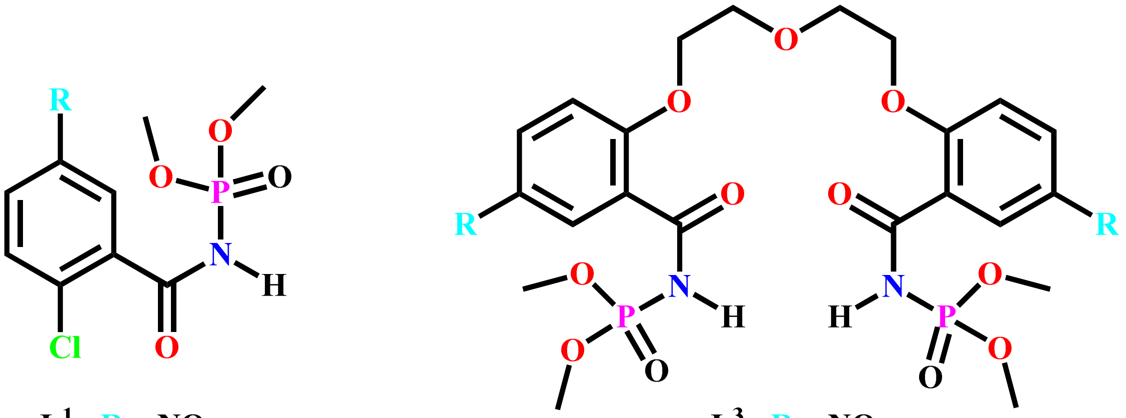
Increased interest in the emission properties of lanthanide complexes containing ultraviolet and visible sensitizers is being driven by the desire to produce efficient and selective luminescent probes. Of special interest are chelating ligands that efficiently encapsulate the lanthanide ions and due to their structure reduce multiphonon quenching of lanthanide emission.

The Ln^{3+} complexes (where Ln = Eu, Tb, Yb, Lu) with amidophosphate derivative ligands (**L**[1], **L**[2], **L**[3], **L**[4] – Fig. 1) have been synthesized. They are promising as new sensitizers of visible and near-infrared luminescence. This work describes the synthesis of the ligands and complexes, their X-ray structures and spectroscopic properties of complexes in the temperature range 77 – 295 K. The photophysical properties are discussed basing on emission and excitation spectra, decay times and quantum yields. The correlation between the structural and spectroscopic properties will be derived from these investigations and the influence of NO_2 group on Yb^{3+} emission will be presented. The effect of the charge transfer state in Yb and Eu complexes on efficiency of the ligand to metal energy transfer will be shown.



L^1 : R = NO_2
L^2 : R = NH_2

L^3 : R = NO_2
L^4 : R = NH_2

Figure 1. Structures of **L**[1], **L**[2], **L**[3], **L**[4] ligands.

SC_P36

Structural and physico-chemical characteristics of 2,2'-bipyridyl(iminodiacetato)oxovanadium(IV) dihydrate

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In recent years the oxovanadium(VI) complexes are of interest for many researchers. Vanadium plays an important role in many biological processes, for example in the cellular regulation [1]. Moreover, the oxovanadium(IV) complexes are used as insulin-mimetics [2]. Furthermore, the oxovanadium(IV) complex with the ODA ligand shows the protective activity against oxidative damage [3-5].

The crystal structure of $[VO(IDA)bipy]\cdot 2H_2O$ has been determined by the X-ray diffraction method (IDA= iminodiacetic anion; bipy= 2,2'-bipyridine). The stability of title compound in aqueous solutions was investigated by using the potentiometric titration method. Moreover, the kinetics of substitution reactions of VOIDA with 2,2'-bipyridine was investigated in aqueous solutions by using the UV-Vis stopped-flow method in the 293 – 308 K temperature range, at different concentrations in range 0.1 – 0.5 mM of VOIDA and at the constant concentration of bipy (0.05 mmol/L). Furthermore, the antioxidant properties of the title complex against superoxide radicals were studied by using the nitrobluetetrazolium (NBT) method and cyclic voltammetry (CV). In addition, the reactivity of the complex studied towards organic radicals namely,1,1-diphenyl-2-picrylhydrazyl radical (DPPH·) and 2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) radical ($ABTS^{\cdot+}$) was investigated by using the UV-Vis technique. The results of antioxidant tests show that VO(IDA)bipy scavenge superoxide free radicals as well as organic radicals ($ABTS^{\cdot+}$ and $DPPH^{\cdot}$).

Acknowledgements

This research was supported by the National Science Centre (grant 2012/07/B/ST5/00753).

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SC_P37

Optical Properties of Heteroleptic Diimine Molybdenum(IV) Clusters

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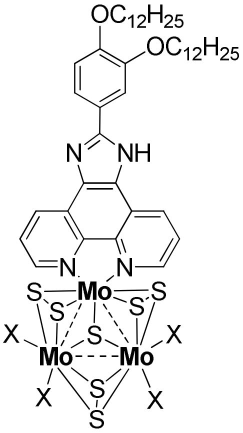
Transition metal cluster chalcogenides can be conveniently functionalized with different ligands with the view to the preparation of molecular materials with diverse applications. The appropriate choice of outer ligands in $M_3(\mu_3\text{-}Q)(\mu\text{-}Q_2)_3$ units (M = Mo, W; Q = S, Se) has resulted in molybdenum or tungsten clusters exhibiting interesting properties, such asphotocatalysis,[1] non-linear optics[2] or magnetic conductity.[3]

Now our interest has been focused on the preparation of heteroleptic diimine complexes by starting from $[Mo_3S_7X_6]^{2-}$ units (X = Cl, Br), and most importantly on the coordination of a novel emissive imidazo[4,5-f]-1,10-phenanthroline ligand with long alkoxy chains. The species prepared by coordination of this imidazo-phenanthroline ligand represent to the best of our knowledge, the first examples of trinuclear molybdenum cluster chalcogenides that exhibit luminescence properties.



X = Cl, or Br

Literature:

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SC_P38

Inorganic polyphosphate as a scaffold for self-assembly of cationic porphyrins

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The polymers with alternating phosphate groups in the chain are widespread in the living organisms and in the all biological systems. Inorganic polyphospate (PPS) represents a linear chain of orthophosphate residues each carrying a monovalent negative charge, therefore it can serve as polyanionic scaffold to assemble cationic macromolecules [1]. The rotational flexibility of the P-O-P bonds allows the conformational adjustment of PPS chains to the π-π stacks of cationic organic dyes. Cationic *meso*-porphyrins are well-known macrocyclic compounds possessing by unique photophysical properties and high photosensitizing ability, which can form ordered aggregates on polyanionic scaffolds that makes them promising agents for applications in nanomedicine and nanotechnology including design of new photonic materials and devices etc. Comprehensive spectroscopic study of polyphosphate (PPS) induced aggregation of tetra-cationic *meso*-porphyrin TMPyP4 [2] and its tricationic derivative, $TMPyP^{3+}$ (Fig.1) [3], was performed in aqueous solutions in a wide range of molar phosphate-to-dye ratios using different spectroscopic techniques and DFT calculation method. It was established that both porphyrin dyes form the stable π-π stacking-aggregates onto PPS chains: *H*-type in the case of TMPyP4, and mixture of *J*- and *H*-aggregates in the case of $TMPyP^{3+}$. Molecular modeling shows that the flexibility of PPS strand allows a realization of spiral or "face-to-face" one-dimensional structures formed by $TMPyP^{3+}$ porphyrin molecules. The peculiarity of PPS structure allows a formation of two porphyrin stacks on opposite sides of polymer strands that result in appearance of higher order aggregates. Their size estimated from light scattering data is about several hundred nanometers. Whereas in the case of TMPyP4–PPS system only columnar H-aggregates are formed being approximately 14 nm in length. The aggregates of tricationic porphyrin is substantially more stable in comparison with tetracationic ones, they do not disintegrate even at *P/D* > 1000.

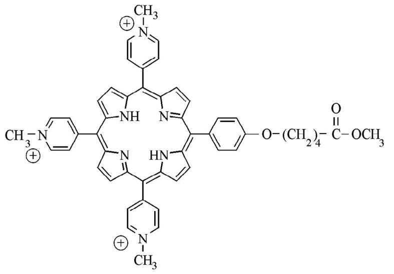

Fig. 1. Molecular structures of $TMPyP^{3+}$ porphyrin.

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SC_P39

Chiral pentacoordinate H-spirophosphoranes – ligands of choice for new palladium complexes

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The stability and reactivity of metal complexes are function of both the position of the metal in the periodic table and the nature of the ligands. While the former provides for diverse chemical reactivity, the structure of ligands allow the reactivity of a given metal to be fine tuned.Thus, thedesign and construction of new chiral H-spirophosphoranes(HSP) – promising ligands in palladium coordination chemistry, has become for us a subject of interests, especially as the number of palladium complexes with spirophosphoranesis still limited. Moreover, during the course of our studies we have demonstrated that, even small changes within the structure of non-chiral HSP ligands may dramatically affect the chemical and catalytic properties of complexes.[1,2]

Herein we report the synthesis and structural properties of new chiral phosphorus ligandsderived from (1S,2R)-(+)-2-amino-1,2-diphenylethanol, L-phenylalaninol and L-valinol

(Chart 1.), and their reactivity towards palladium precursors.

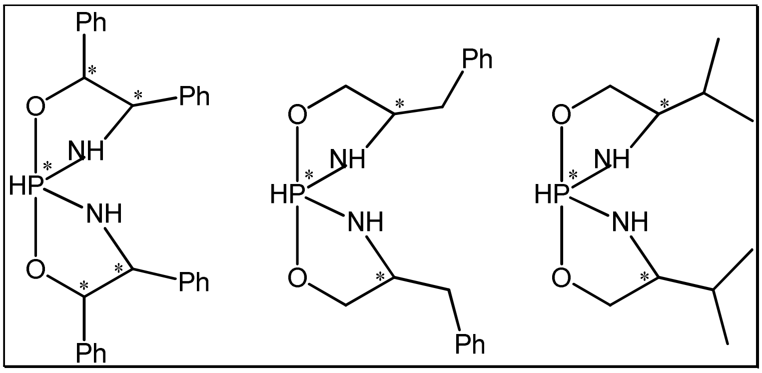

Chart 1.

The molecular structures of HSP ligands and palladium complexes were determined based on IR, multinuclear NMR data as well as single crystal X-ray diffreaction data. In order to establish the absolute configurations of some of enantiomers, their solid-state CD spectra were measured.

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SC_P40

New water-soluble copper(I/II) coordination compounds with 1,3,5-triaza-7-phosphaadamantane (PTA) and 1,3,5-triaza-7-phosphaadamantane-7-oxide (PTA=O)

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One of the most common approaches to obtaining water-soluble transition metal complexes is the use of ligands with hydrophilic properties. Among water-soluble phosphines, like cage-like tertiary aminophosphine 1,3,5-triaza-7-phosphaadamantane (PTA) and its derivatives, (*e.g.* PTA=O) [1]. This is mainly conditioned by interesting physicochemical properties of the ligand and good solubility of coordination compounds with these ligands in polar solvents. Water solubility is one of the most important properties to enable the use of coordination compounds in medicinal chemistry [2], as water-soluble anticancer agents (Cu, Ag, Au, Ru), catalysts (Ru, Rh, Pd) or as luminescent materials (Au, Cu, Ag) [3].

In this contribution we report synthesis, as well as structural and spectroscopic characterization and magnetic properties of some new copper(II) and copper(I/II) discrete complexes or coordination polymers: [μ-Cu_2(acetate)$_4$(MeOH)$_2$][PTA=O] **(1)**, [μ-{Cu_2(acetate)$_4$}$_3$(μ-*N,N,O*-PTA=O)]$_n$ **(2)**, [μ-Cu(II)$_2$(acetate)$_4$(μ-*N,P*-PTA)-μ-Cu(I)(acetate)(*P*-PTA)$_3$]$_n$ **(3)** and [Cu_2(formate)$_4$(*N*-PTA=O)$_2$] **(4)**. The obtained compounds have been isolated as air- stable crystalline solids, which have been characterized by infrared spectroscopy, elemental and single crystal X-ray diffraction analyses. The synthesized compounds show interesting magnetic properties. Additionally, compound **(4)** has been successfully examined as an antibacterial and antifungal agent in aqua media.

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SC_P41

Structure and antioxidant properties of new complex salt of aqua-(2-methylnitrilotriacetato-N,O,O',O")-oxidovanadium(IV) with 4-aminoquinaldinium cation

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The glycine derivatives, namely nitrilotriacetate (NTA^{3-}) and 2-methylnitrilotriacetate ($DCAla^{3-}$) are strong-binding ligands. They act as tetradentate agents and form 1:1 metal-ligand complexes with majority of ions [1, 2]. Oxygen atoms of three carboxylic groups and a central nitrogen atom participate in the metal binding. Metal ion complexes with the these type of ligands are widely used in the immobilized metal (ion) affinity chromatography (IMAC) for a separation of histidine-rich proteins from other protein material [3]. Moreover, they are used in biotechnology and biochemical studies, among others, for the crystallization of proteins on monolayers and in the temporary immobilization of proteins (particularly those possessing an engineered polyhistidine tag) on surfaces [4].

The subject of our continuous interest are polycarboxylate metal complexes since it has been found that some polycarboxylate VO(IV) complexes can protect effectively the mouse hippocampal neuronal cell line (HT22) against an oxidative damage [5, 6]. Thus, the investigations of new oxidovanadium(IV) complexes support both cognitive aspects as well as practical arguments.

In this report, the crystal structure as well as antioxidant properties of new oxidovanadium(IV) complex, namely (4-aminoquinaldinium) $[VO(DCAla)(H_2O)]\cdot 2H_2O$ towards superoxide radical anion ($O_2^{\bullet -}$), organic radical cation $ABTS^{\bullet +}$ and a stable free-radical molecule, 2,2-diphenyl-1-picrylhydrazyl (abbreviation DPPH), are presented.

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SC_P42

Coordination Properties of Dipyrrin-Bridged Inverted Porphyrin Dimer

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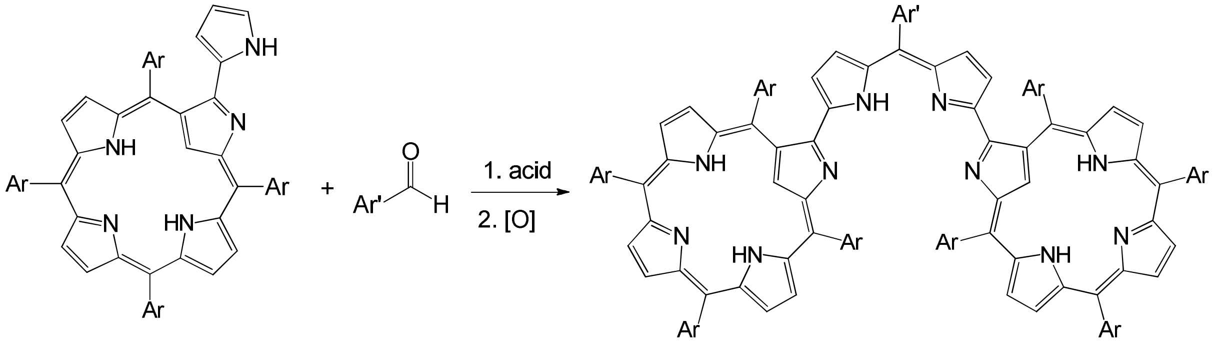
An inverted porphyrin with a pendant pyrrole (2-aza-3-(2-pyrrolyl)-5,10,15,20-tetraaryl-21-carbaporphyrin **1**) was first identified among the products of a Rothemund condensation of pyrrole and aryl aldehyde [1]. This compound, being an isomer of a pentapyrrolic macrocycle sapphyrin, can be also prepared *via* the reaction of 2-aza-21-carbaporphyrin with pyrrole. In this contribution, the application of **1** to the synthesis of 3,3'-(5-aryldipyrrin)-bridged inverted porphyrin dimer **2** are described.



1 **2**

The presence of the two macrocyclic crevices together with dipyrrin bridging unit make compound **2** an attractive ligand for the multiple coordination of both anions and cations, including various metals as well as boron (leading to BODIPY derivatives [2]).

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SC_P43

EPR and DFT Insight into Interaction between o-Semiquinone Radicals and Metal Ions

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Organic radicals play increasingly important roles in modern biochemistry and material science. Semiquinones are organic radical anions being the intermediate form in the redox equilibrium between quinones and hydroquinones. These radicals are present in all life forms as they act as electron-transfer agents in the mitochondrial respiratory chain and in the reaction centres of bacterial and plant photosynthesis [1].

o-Semiquinones are known to possess chelating ability towards metal ions [2], which is particularly important for the activation of electron transfer through interaction with cations acting as Lewis acids [2a, 2b]. In this work EPR spectroscopy and density functional theory (DFT) were used to elucidate the interaction between o-semiquinone radicals and various diamagnetic metal ions: Mg^{2+}, Ca^{2+}, Hg^{2+} and Pb^{2+} [3]. The effect of complexation on the molecular and electronic structures of the radicals were established and correlated with the g tensor. The relative stability of the complexes were also investigated.

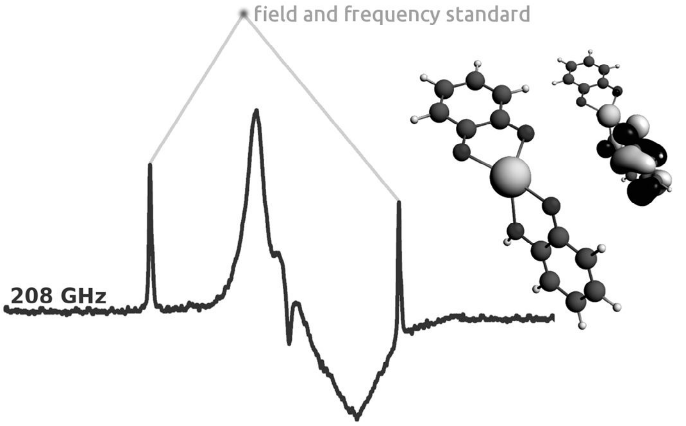

Figure: EPR spectrum, DFT-predicted molecular structure and the singly occupied molecular orbital of the semiquinone – Hg(II) complex

Literature:

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SC_P44

Thermodynamics of oxydiacetate and thiodiacetate complexation with Co^{2+} and Ni^{2+} ions

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The oxydiacetate (ODA) and thiodiacetate (TDA) anions (Fig.) can serve as flexible, bridging organic ligands capable to form one-, two- or three-dimensional networks. Physicochemical features of these ligands permit the synthesis of new compounds (including heterometallic systems) of potential relevance for solid state technologies and as models for magnetic studies. For these reasons much attention has recently been focused on structural and magnetic characteristics of ODA and TDA coordination compounds [1, 2]. However, to the best of our knowledge, there are few reports on stabilities of these complexes in solutions. Consequently, it was the reason that prompted us to embark on these studies.

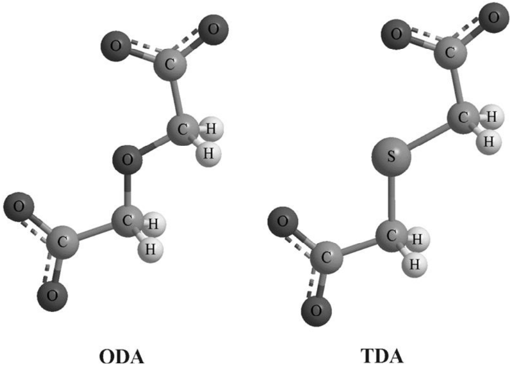

Figure. Oxydiacetate (ODA) and thiodiacetate (TDA) ligands.

The isothermal titration calorimetry technique supported by potentiometric titration data was used to determine thermodynamic parameters for the complexation of the cobalt(II) and nickel(II) ions with the ODA and TDA ligands. The substitution of the ethereal donor atom in the ODA ligand by the sulphur donor atom (the TDA ligand) results in the decrease of the enthalpy of the complex formation.

A more covalent character of the M-$S_{(\text{thioether})}$ bond in comparison to the M-$O_{(\text{ethereal})}$ bond is probably the most important factor responsible for the release of a larger amount of energy during the formation of M-TDA ($\Delta_{\text{MODA}}H > \Delta_{\text{MTDA}}H$) albeit the M-$S_{(\text{thioether})}$ bond is longer than the M-$O_{(\text{ethereal})}$ bond.

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SC_P45
New isocyanide complexes of iridium

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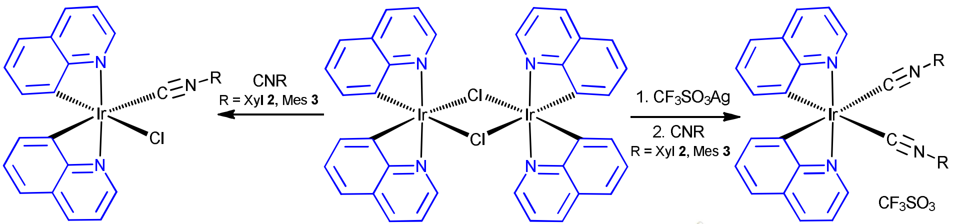
Among platinum group metals,palladium and platinum isocyanidecomplexesarewell recognized[1].In this context, iridium-isocyanides attracted much less attention.

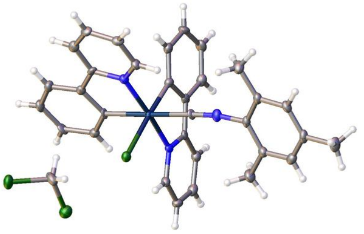
In the course of our studies on chemistry of metal-isocyanide derivatives, we have synthesized several new isocyanide complexes of iridium(III)of the general formulae $[(ppy)_2IrCl(\underline{C}NR)]$ and $[(ppy)_2Ir(\underline{C}NR)_2](CF_3SO_3)$ (ppy = 2-phenylpyridine-C^2,N').Indeed, complexes $[(ppy)_2IrCl(CNR)]$ (R = Xyl, Mes; isolatedyields 82–87%), were prepared starting from the binuclear complex $[(ppy)_2Ir(\mu\text{-}Cl)]_2$upon reaction with one equiv of appropriate isocyanideinrefluxingCH_2Cl_2. Corresponding *bis*(isocyanide)complexes $[(ppy)_2Ir(CNR)_2](CF_3SO_3)$ (R = Xyl, Mes; isolatedyields76–79%), were generated from $[(ppy)_2Ir(\mu\text{-}Cl)]_2$uponremoval of chlorides with CF_3SO_3Agin mixture CH_2Cl_2/MeOH (4:1)and further action of two equivsof respective isocyanide(R = Xyl, Mes)in CH_2Cl_2[2].

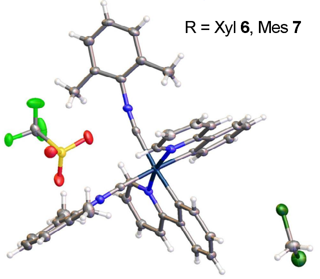


R = Xyl **4**, Mes **5**

1

R = Xyl **6**, Mes **7**





All obtained compounds were fullycharacterized by ^1H, and $^{13}C\{^1H\}$ NMR and IR spectroscopies, ESI$^+$ MS and elemental analyzes (CHN), and by X-ray diffraction.

Acknowledgements. The authors thank Saint Petersburg State University (НИР 12.38.225.2014) and Russian Foundation for Basic Research (grant 14-03-31204 мол_а).The authors are grateful to the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research of Saint Petersburg State University.

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EP_P01

Co_9polioxometalateprocessability into plastic organic thin films for catalytic water oxidation

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Finding a solution to the ever-increasing energy demand worldwide is, arguably, the biggest challenge that scientists are facing in the present decade [1]. The harvesting of solar energy, and its transformation into fuels, would lead to abundant energy and represents the only sensible major alternative to fossil fuels. A straightforward approach to face this problem is the development of an artificial photosynthesis device. One of the bottlenecks in this field is the lack of a good enough catalyst for the production of oxygen. That is the reason why the research for a robust, fast and inexpensive water oxidation catalyst (WOC) is currently a hot topic [2].

Polyoxometalates (POMs) have been proposed as potential candidates for water oxidation catalysis [3] since they combine the chemical features of metal oxides and the easy processing and high activity of the homogeneous species. Here it will be presented the use of the nonanuclear cobalt-containing polyoxometalate cluster $\{Co_9(H_2O)_6(OH)_3(HPO_4)_2(PW_9O_{34})_3\}^{16-}$ (Co_9) as a good catalyst in the oxygen evolving reaction (OER). $Co_9$is a robust water oxidation catalyst, which has demonstrated to work efficiently and remain active in the solid state [4]. Here we will show different strategies to optimize its electrocatalytic performance by processing Co_9 into large surface area electrode. The incorporation of this catalytic species into plastic organic anodes will be presented as a suitable approach to obtain good processability, activity, durability and adaptability to different conducting surfaces. Moreover, a complete characterization of the cobalt species will be performed to prove that Co_9 is a true catalyst.

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EP_P02

The symmetrical octatetraynes with *p*-substituted phenyl end-groups: synthesis, characterization and NLO properties

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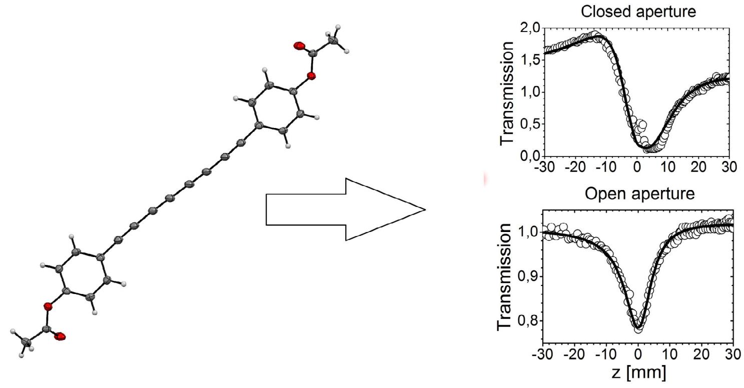
Carbon-rich compounds have been extensively explored during the last few decades. One class of such species are polyynes - compounds with a linear carbon chain consisting of alternating triple and single bonds between carbon atoms [1], which are considered as a model for still unknown carbyne $(-C\equiv C-)_n$, a linear sp-hybridized allotrope of carbon [2]. Oligoynes and polyynes are foreseen to be of interest for numerous applications, for instance as components for wires or switches in optoelectronic devices [3] or as ingredients of co-crystals with conducting polymers [4].

The work presents the synthesis of three new octatetraynes with ester-substituted phenyl end-groups and their full characterization. We also report the results of spectrally-resolved investigation of nonlinear optical properties (NLO) for these compounds, performed using the femtosecond *f*-scan technique at various wavelengths in the visible and near-infrared range (540-1600 nm). The synthesized phenyl end-capped octatetraynes, exhibit strong nonlinear absorption and nonlinear refraction properties, which can be attributed to the presence of unsaturated carbon's chains and electron-withdrawing functional groups.



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EP_P03

Bio-inspired Photoredox Catalysis With Molybdenum Complexes

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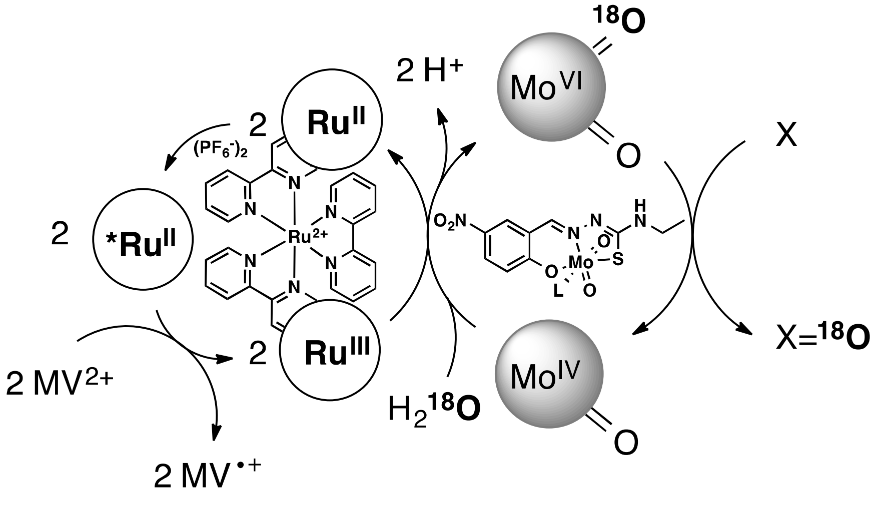
Photo-driven redox reactions with clean reagents, such as water, have received great attention for both environmental and economic interests.Nature has chosen molybdenum to play a key role in biological oxidation reactions [1], especially in oxygen transferases, such as sulfite oxidase, xanthine oxidase and DMSO reductase. This transition metal has the ability to switch between oxidation states (VI) and (IV), and therefore it has been studied for bio-inspired redox catalysis since the 1980's. We recently studied the electronic fine-tuning of thiosemicarbazone molybdenum complexes toward oxygen transfer reaction from DMSO to triphenylphosphine[2] and we determined that electron-withdrawing groups in *para*-position of the O- donor accelerate the reaction which is consistent with the generallyaccepted mechanism of nucleophilic attack on the molybdenum oxo ligand. Although DMSO is commonly used as the sacrificial oxidant in biomimetic catalytic cycles, water would be a more sustainable alternative asoxygen source.We have studied a two-component system consisting ofthiosemicarbazone molybdenum complex as catalyst and$[Ru(bpy)_3]^{2+}$ as photosensitizer in presence of methylviologen as sacrificial oxidising agent. Photo-driven oxygen transfer from water to triphenylphosphine (TON 4) has been proven by an ^{18}O labelling experiment and by^{31}P NMR spectroscopy. A *nitro*-substituted thiosemicarbazone molybdenum complex has been immobilised on polystyrene and it has shown activity in heterogeneous catalysis.Furthermore, a new single component dyad, where catalyst and photosensitizer are covalently linked, has been synthetized to improve stability and electron transfer efficiency.



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EP_P04

High Power-Density WO_{3-x}–Grafted andCorannulene-Modified Graphene Nanostructures for Micro-Supercapacitors

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Supercapacitors are novel nanoengineered devices bridging the gap between traditional electronic capacitors and conventional batteries. Supercapacitorsutilizethehigh electrochemical double-layer capacitance of carbon nanostructures, augmenting it with high storage capability of pseudocapacitance nanomaterials. They offer exceptionally fast charging/discharging, high specific capacitance, enhanced safety, and low leakage currents opening up new applications in automotive, energy, military, and other industries. The unique qualities of supercapacitors are related to structural designs of various carbon-supported supercapacitor systems. In this work, we have employed grafting of WO_{3-x} nuclei onto thegraphene oxide (GO) defect sites by electrochemical processing and nanoparticle growth, followed by the reduction of unprotected oxidation sites of GO to form a highly-conductive reduced graphene oxide (rGO) support. In order to further limit the stacking interactions between the rGOnanosheets, we have modified graphene sheets with corannulene which is a $C_{20}H_{10}$polyaromatic hydrocarbon (PAH) compound forming a nanocup (or: Bucky bowl) structure and can separate the rGOnanosheets in more hydrophobic locations of rGO where WO_{3-x}nanoforms are missing.The chemical structure, morphology, and electrochemical properties of this material were characterized by Raman spectroscopy (RS) and other methods, followed by electrochemical testing using the electrochemical quartz crystal nanogravimetry (EQCN), cyclic voltammetry (CV), as well as potential-pulse and current-pulse charging/discharging characteristics. The proposed WO_{3-x}–grafted and corannulene-modified graphene nanostructures offer high volumetric power-density and show a promising perspective for potential applications asmicro-supercapacitorsin emergingtechnologies.

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EP_P05

Spectroscopy and structure of Ln^{3+} complexes with naphthylsulfonylamidophosphates as new light converting molecular devices

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This work presents a detailed study of lanthanide complexes with dimethyl 2-naphthylsulfonylamidophosphate $Na[Ln(\mathbf{L^1})_4]$ (**1Ln**) and *bis*(4-methylphenyl) 2-naphthylsulfonylamidophosphate $Na[Ln(\mathbf{L^2})_4]$ (**2Ln**) (where Ln = Eu^{3+}, Gd^{3+}, Tb^{3+} and Yb^{3+}) in wide range of temperatures from 4 to 295 K with the aim to probe the specific energetic and structural characteristics that influence ligand-to-metal energy transfer and luminescence efficiency. The work focuses also on the role of the LMCT state on the ligand-to-metal energy transfer. Spectroscopic results of **1Ln** where $[\mathbf{L^1}]^-=[(C_{10}H_7S(O)_2NP(O)(OCH_3)_2)]^-$ and **2Ln** complexes where $[\mathbf{L^2}]^-=[(C_6H_5S(O)_2NP(O)(C_6H_4\text{-}p\text{-}CH_3)_2)]^-$ will be compared with those obtained for the earlier investigated compounds - $Na[Ln(\mathbf{L^3})_4]$ where $[\mathbf{L^3}]^-=[(p\text{-}CH_3)C_6H_4S(O)_2NP(O)(OCH_3)_2]^-$.

In these ligands, that are P, N, S – hetero-substituted analogs of *β*-diketones, the number of C=O vibrations (~1600 cm^{-1}), present in *β*- diketones, have been eliminated. They have been replaced with the low energetic vibrations P=O (~1250 cm^{-1}) and S=O (~1350 cm^{-1}). Replacing of the carbon atom at the same time, which is in *β*-diketones, with the nitrogen atom eliminates high-power vibrations of C-H from six-membered chelate ring, which is created as a result of coordination with the lanthanide ion. This reduces the multiphonon quenching of lanthanide emission. Photophysical properties in combination with the thermodynamic stability of the complexes, their resistance to UV radiation, and even on synchrotron radiation, create potential possibilities for constructing of light converting molecular devices.

EP_P06

Photophysical and theoretical studies of structure and spectroscopic properties of axially substituted Yb(III) mono-phthalocyanines in different media.

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Keywords: ytterbium, monophthalocyanine, DFT and H-F methods, spectroscopic behaviour, sol-gel systems, polymers codoped by Yb-complexes, and silver particles.

Abstract.The lanthanide complexes with phthalocyanines and porphyrins belong to the group of most investigated compounds because of their unique luminescence properties and variety of applications. The special interest is directed to medical application mainly in photodynamic therapy. This paper is devoted to photophysical studies of the chloro-ytterbium monophthalocyanine complexes in solutions,solid state, silica matrices and PMMA polymer which can design their applicability. The DFT and Hartree-Fock (HF) methods were used to generate structures , theoretical IR and Raman spectra which were correlated with experimental data. The mechanism of the affect of conformation changes, steric obstacles, extra-coordination of solvent molecules and molecule immobilization in polymer and inorganic matrices on lanthanide and phthalocyanine optical behaviour are discussed. The attention is paid for radiative and non-radiative processes, the intramolecular energy transfer and the role of the charge-transfer state in this process, electron-phonon coupling, multiion cooperative interactions, non-linear proceses and dynamics in excited states. Moreover, the role of the solvent molecule exchange dynamic on the biological interactions of the systems under study will be also analysed.

EP_P07
Thermochromic carborane-containing osmium complexes

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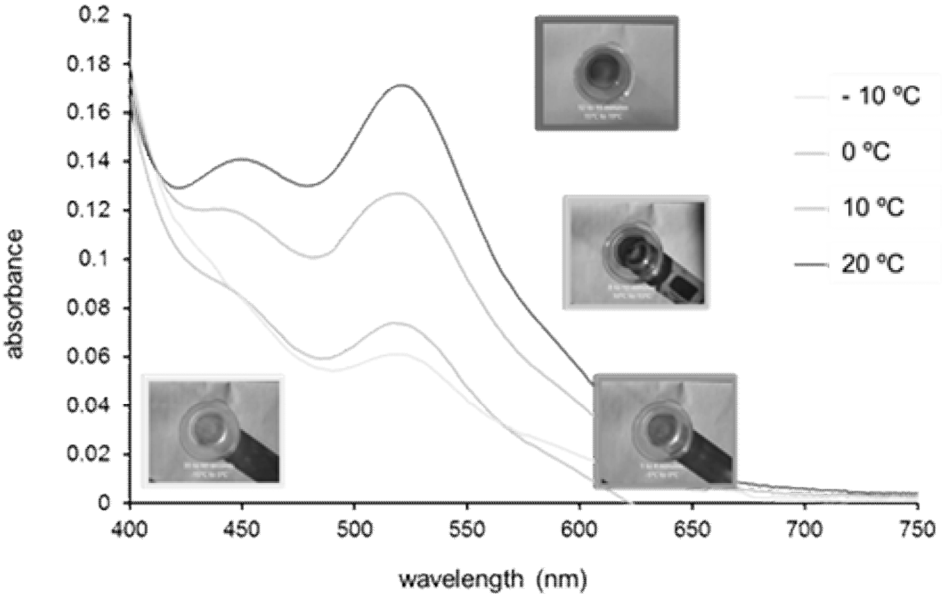
Arene osmium complexes are a versatile class of organometallic compounds. Their accessibility, robustness, air-stability are examples of the unique properties that allow their applications in various fields of chemistry (*e.g.* catalysis), and as anticancer drug candidates [1]. Carboranes possess unusual properties, including high symmetry and remarkable stability and their combination with half-sandwich complexes of osmium is leading to the development of a new class of compounds with applications in chemical and biological areas [2].



UV-visible monitoring of the thermochromism of a carborane osmium complex in dichloromethane.

Here, we study the interaction of a 16-electron carborane-containing arene osmium complex with a series of pyridine derivatives. The compounds exhibit dramaticthermochromic properties [3]. The effects of the temperature, solvent, and metal-to-ligand stoichiometry are reported and rationalised.

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EP_P08

Unusual superhalogen anions

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Superhalogens are extraordinary inorganic compounds exhibit enormously large electron affinities exceeding the electron affinity of chlorine atom (3.62 eV). Their existence was predicted in 1981 by Gutsev and Boldyrev [1] who proposed a simple formula describing one class of these compounds, MX_{k+1}(where M corresponds to a metal atom of maximal formal valence k, surrounded by k + 1 halogen ligands X).

The purpose of exploring novel superhalogen species is to provide reliable predictions of their physical chemical properties, considering the possible use of such compounds as electron acceptors (oxidizing agents) in various chemical processes. Our previous contribution to these studies covers the explanation of the ability of selected, moderately reactive molecules to form stable systems containing superhalogens. As we have demonstrated, even the molecules possessing high ionization potentials (such as SiO_2, NH_3, $CHCl_3$, CCl_2F_2) should form stable and strongly bound ionic compounds, whenever they are combined with appropriately selected superhalogen systems (acting as oxidizing agents)[4]. In addition, we showed that the competition between the electron binding energy of the superhalogen system and the ionization potential of the molecule combined the superhalogen is a key factor for predicting the stability of certain species [5][6].

According to recent findings, the presence of halogen atoms in superhalogen species is not obligatory since the alternative ligands might be applied instead [7]. Hence, in present contribution it was demonstrated that halogen ligands (F, Cl, Br, I) might be replaced with alternative ligands and the electronic stabilities of the resulting anions may even exceed those obtained with the VII main group elements.

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Aknowledges

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EP_P09

SiCwhiskers /Carbon Nanofibers Compositefor High-Temperature Li-Ion Battery Anode

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Lithium-ion battery is widely used in military and civilian small appliances. But, it is still with limited at high charge and discharge rate, because of the heat generation behavior during the charging and discharging and degradation by long-time storage [1]. To overcome this deficiency of lithium-ion batteries and improve safety and reliability of the battery, the electrospun SiO_2/polyacrylonitrile (PAN) nanofibers were calcinated at 1400 °C under an inert gas to form Silicon carbide(SiC) whiskers /carbon nanofiber (CNF) composites and used as new anode material of Lithium-ion battery.SiC is ceramic semiconductor material which has high chemical stability, high hardness, high thermal conductivity and low thermal expansion coefficient[2]to improve the stability of battery during the high discharge rate.The electrospun CNF has special three-dimensional nanofiber network structure allows easy access of electrolytes. In addition, the shorter pores path of nanoscale diameter of nanofiber can reduce the distributed resistance and enhances the rate handling ability[3].

Measurements of discharge capacity are done by assembling SiC/carbon nanofibers composite as anode material on a coin cell.The capacity of pure CNF and C/Si=3.43 composite are 165 and 103 mAh/gat 0.1C discharge rate and room temperature. When discharge rate increaed to 10C, the capacityremained17.5% which is better than that of pure CNF(47.5% capacity reduction). It indicates that SiC/CNF composites can quickly discharge at high current density. For high tempreature testing(60 °C),the capacity of C/Si=3.43 composite did not change significantlycomparingwithoperation at room temperature.When discharge rate increaed to 10C,the capacityremained 50% (pure CNF was fail at this condiction). At 0.1C discharge rateand 60 °C, the capacity still remained90% (pure CNF was only 33%) whenthe discharge rate return from 10C. As results shown, SiC whiskersgrowth on CNF as anode of Lithium-ion battery for high current discharge and temperature has the significant effect upon the functional features the batteries.

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MT_P01

A DFT Mechanistic Study on Cooperative Rh-Cu catalysis. The Oxidative Cross-Coupling between Benzoic Acid and Alkynes

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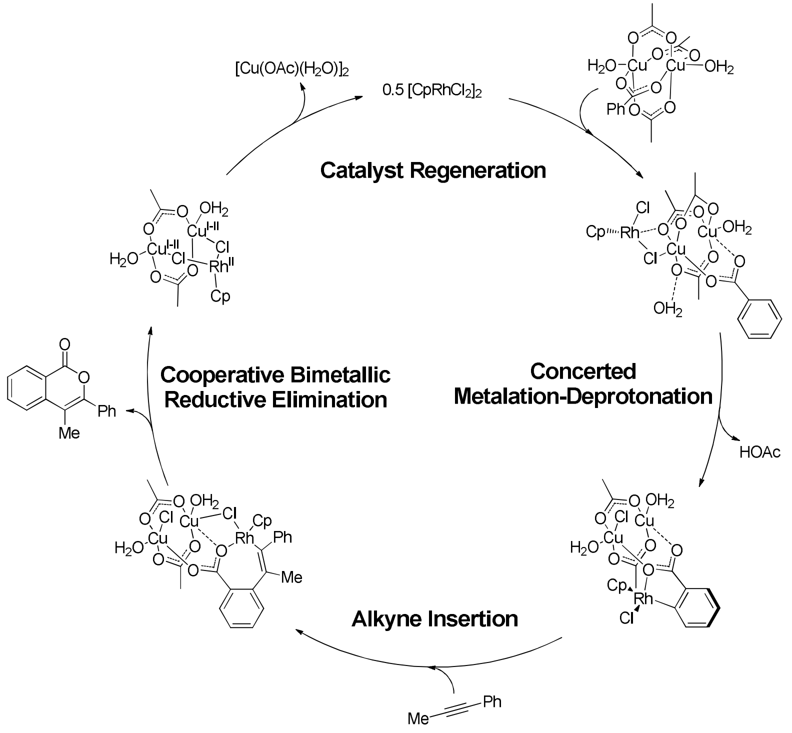
Oxidative coupling reactions have been developed in the last years as a clean and efficient alternative to the classic cross-coupling procedures due to their atom economy, easily C-H bond functionalizations and, in the ideal case, the possibility of using molecular oxygen as final oxidant, producing only water as waste product. Although many reactions have been discovered in the recent years, the mechanistic understanding of these reactions is still a challenge, and should help for the design of new reactions in a rational way.

Herein, we present a theoretical study (DFT methodology) on the mechanism of the coupling between alkynes and benzoic acids [1,2], with a special focus on the key role of copper acetate in the chemoselectivity of the reaction, favoring the formation of the isocoumarin derivative. We discovered a cooperative effect between metals, rhodium and copper, in the catalytic cycle.



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MT_P02

A DFT study of cooperative effects in oxidative addition reaction of a dimeric Pt(II) complex with MeI

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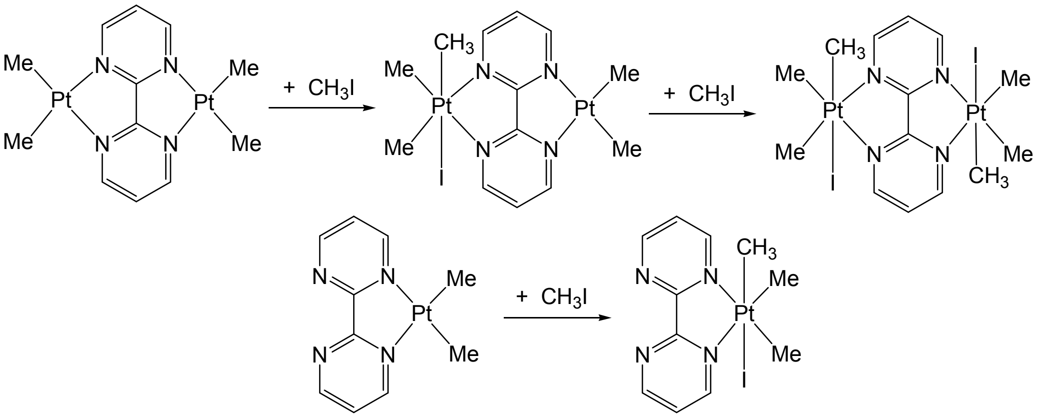
One of the great interest in contemporary chemistry is the synthesis of multimetallic transition-metal complexes in which two or more metal atoms are held at particular distances from each other [1-2]. Bimetallic systems, through cooperative steric or electronic effects between the two adjacent metal centers, might give rise to distinct and different reactivity patterns which are not available to the mononuclear analogues. It is shown that cooperative effects between two metal centers can enhance the reactivity of bimetallic complexes [3], but in some cases, increased steric hindrance in bimetallic systems decreases the reactivity of binuclear system [4].

The density functional theory calculations were used to study the cooperative effects between two adjacent platinum centers on the oxidative addition of methyl iodide to dimeric complex [$Me_2Pt(\mu$–bipym)$PtMe_2$], in which bipym = 2,2'-bipyrimidine (see Scheme). A double MeI oxidative addition was considered and the classical S_N2 mechanism was suggested for both steps, and the involved transition states and intermediates were proposed. Consistent with the suggested mechanism, large negative $\Delta S^{\ddagger}$ values were found in each step. The calculated energy barrier was smaller in the second step as compared to the first step because of the electronic effects transmitted through the 2,2'-bipyrimidine ligand and the steric effects. In a comparative study, the monomeric complex [$PtMe_2$(bipym)], was used in the MeI oxidative reaction as a “calibration reaction” to evaluate the effect of bipym ligand on the rate of the reaction of MeI with dimeric complex, [$Me_2Pt(\mu$–bipym)$PtMe_2$].



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MT_P03

Kinetics and mechanism of the substitution reactions between some Pd(II) complexes and unsaturated N-heterocycles

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Over the past few decades anti-tumor activity of some Pd(II)complexes has been demonstrated and the interest in understanding their mechanism of interaction with biologically relevant molecules increase [1-2]. The main target for antitumor active palladium complexes is DNA and behavior of such complexes toward different purine and pyrimidine derivatives were studied in details [3,4]. Beside, a lot of the other biomoleculs, which contain unsaturated N-heterocycles, such as pyrazole, imidazole or pyrazine derivatives, could be potential targets for transition metal complexes.

The part of our interest was to investigate substitution reactions of some monofuntional and bifunctional Pd(II) complexes with N-donor heterocyclesfor the better explanation of structure-reactivity relationship of such compounds. On the other side, N-heterocycles, used as entering ligands (pyrazole and its derivatives, imidazole, 1,2,4-triazole, pyrazine, pyrimidine, pyridazine) are very common in different fields of medicine and pharmacy. Namely, they are building blocks of some biomoleculs as well as constituents of different drugs (analgetics, anti-bacterial, anti-viral, anti-inflammatory, anti-glycemia, anti-parasitic) which can be injected together with anti-tumor agents [4].

The reactions were studied by stopped-flow spectrophtometry and ^{1}H NMR spectroscopy at constant ionic stranght in addition of extra chloride to suppres the sponatnious hydrolysys of complexes. The reactions of monofunctional complexes ($[Pd(terpy)Cl]^+$ (terpy = 2,2';6',2"-terpyridine), $[Pd(bpma)Cl]^+$ (bpma = bis(2-pyridylmethyl)amine), $[Pd(dien)Cl]^+$ (dien = diethylentriamine or 1,5-diamino-3-azapentane), $[Pd(Me_4dien)Cl]^+$ (Me$_4$dien = 1,1,7,7-tetramethyldiethylenetriamine) and $[Pd(Et_4dien)Cl]^+$ (Et$_4$dien = 1,1,7,7-tetraethyldiethylenetriamine) undergodirect nucleophilic attackin a reversible manner while the substitution of bifunctional complexes ($[Pd(cbdca)Cl_2]$ (cbdca = 1,1-cyclobutandicarboxilato), ($[Pd(mal)Cl_2]$(mal = malonato)($[Pd(ox)Cl_2]$(ox = oxalato)occursin two reversible steps. According to the observed negative value for entropy of activation, an associative mode of substitution is confirmed for all reactions.

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MT_P04

Theoretical study of the hydrolysis of chlorosilane

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Silyl-halides, especially silyl-chlorides are widely used materials in the industry. The main principle of their application is the high reactivity of silicon-chloride bond. Most importantly chlorosilanes are used to produce silicone polymers, chromatography stationary phases by hydrolysis and condensation reactions. However, this high reactivity of silicon-chloride bond in hydrolytic reactions can be a serious drawback in some cases. Thus, the handling of chlorosilanes is difficult, restricting their applicability.

Hydrolyis of silyl-chlorides is a bimolecular nucleophilic substitution reaction (S_N2), which proceeds with inversion of configuration in neutral conditions [1]. Gas phase studies are rare, most of them being quantum chemical studies including some contradictory results. For instance, only retention pathway was calculated in these investigations, so they cannot explain the stereochemistry of the reaction in solution.

In our previous quantum chemical study [2] we investigated the reaction between the prototype molecule of H_3SiCl and water clusters consisting of different number of water molecules (from one to five). We revealed that the reactivity of SiCl bond with water strongly depends on the size of reactant water cluster. The increasing number of water molecules decreases the activation barrier of hydrolysis. With one water molecule the activation energy is non-negligible (ca. 25 kcal/mol), even with two water molecules the energy of transition state is significantly reduced, making the hydrolyis more feasible. Ab initio molecular dynamics simulation with 58 water molecules in the unit cell resulted ca. 2 kcal/mol barrier. These results indicate that the high susceptibility of SiCl bond in hydrolysis should be attributed to reaction with water clusters.

The effect of additional water molecules to the reaction mechanism was also studied. Retention and inversion pathways was located and energetically compared for certain investigated systems. With small water clusters the retention pathway is more favorable, although the activation barrier converges to ca. 15 kcal/mol with the increasing size of water cluster. From four water molecules hydrolysis with inversion of configuration is preferred. These results are in a good agreement with experiments, explaining the stereochemistry of the hydrolysis in solution.

The stationary points of reactions were calculated at different levels of theory, including DFT functionals (B3LYP, B97D and M062-x with 6-31+G* and aug-cc-pVTZ basis sets) and MP2 method (6-31+G*,cc-pVDZ and aug-cc-pVDZ basis sets). Single points energies were calculated at MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels of theory. The results of different methods slightly differ from one another, but showing the same trends.

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MT_P05

Cyclic and Acyclic Fructose Conformers in the Gas Phase: A Large-Scale Second-Order Perturbation Theory Study

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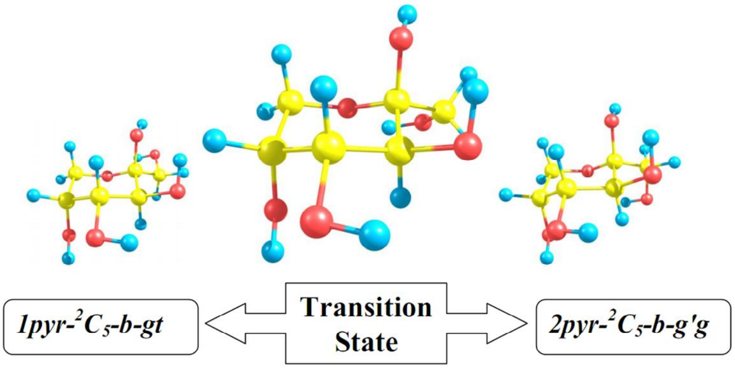
We performed large-scale second-order perturbation theorygas-phase calculations to study about five hundred structures of D-fructose.The two lowest energy fructose structures identified are β-pyranoses possessing $^2C_5$ chair, with ΔG(298K) of 6 kJ/mol, differing in orientation of the equatorially positionedhydroxymethyl group,*gt* and *g'g*, where the *gt*rotamer is the global minimum, consistent with the recent microwave spectroscopy study. We have found that interconversionsfrom the fructose global minimum to the second and third most stable β-pyranose rotamers involve the energy barriers of *ca.* 30 kJ/mol. Among numerousfructofuranose conformers discovered (about 250), a pair of the ($^3T_2$) α- and (E_3) β-anomersare energetically most preferred and lie at least 12 kJ/mol above the global minimum. We also found that the fructose open-chain structures lie significantly higher in energy than the most stable cyclic species. The commonly used M06-2X density functionalperforms well compared to MP2 and G4 theory at identifying the low-energy fructose minima, including the global one, and at reproducing their intramolecularH-bond geometric parameters.The lowest-energy gas-phase pyranose and furanose structures of fructose benefit from the stabilization due to the cooperative or quasi-linear H-bondingand both *endo* and *exo*anomeric effects.



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MT_P06

Oxygen Atom Transfer Reaction From Oxyhalogenated Anions To Carbon Monoxide

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The selective oxidation of organic and inorganic substrates has gained much importance in recent years, for example in the preparation of high value-added organics or in the field of the environmental remediation. Oxygen atom transfer (OAT) reactions are an important class of oxidation reactions that are widely applied and technologically relevant. A reaction of particular importance is the oxidation of harmful carbon monoxide to the more benign carbon dioxide in the presence of heterogeneous catalysts, a process that is relevant for example in the abatement of environmental pollution or in case of the poisoning of fuel cell, where the absorbed CO molecules, generated as reaction intermediates, block active sites of the catalyst hindering further reactions.

OAT to carbon monoxide has been mainly accomplished by metal-dioxo, metal peroxo and metal-oxo species, that offer pathways for the selective oxidation of this compound. Gas phase studies have been especially useful in elucidating the intrinsic behaviour of such species, that can be investigated with rigorous exclusion of many complicating parameters such as solvent and aggregation effects, counterions, ligands, etc. [1-4].

In contrast, little is known about the reactivity of non-metal oxides, and it is worth investigating these reactions in the gaseous isolated state to gain a better understanding of the mechanism of oxidation of CO.

As a continuation of our interests in the activation of small molecules by metal-free ionic species [5], here we report on the activation of carbon monoxide by oxyhalogenated anions, (XO^-, X = Cl, Br, I). The reaction has been studied in the gas phase at room temperature by mass spectrometry in the high pressure regime characteristic of ion trap experiments (ITMS). The gas-phase XO^- anions, prepared by electrospray ionization (ESI) of aqueous saline solutions of either $NaXO_2$, $NaXO_3$, or $NaXO_4$, were reacted with CO under the overall pressure of approximately 3 mTorr, which was maintained using a helium gas buffer. The rate constant and the efficiency of the reactions have been measured.

Acknowledgments. This work is supported by the MIUR FIRB 2010 project.

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MT_P07

Catalytic oxidation of $(CH_3)_2SO$ by N_2O promoted by BH_4^- in aqueous solutions

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Dan Meyerstein[2,3]

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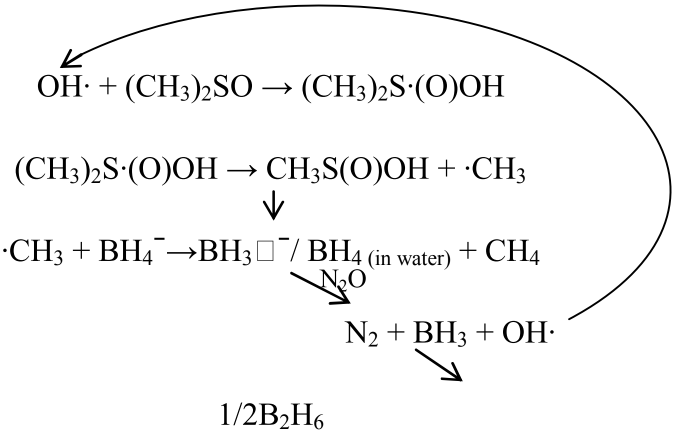
The radiolysis of $(CH_3)_2SO$ in N_2O saturated aqueous solutions yields CH_4 and C_2H_6 via the following reactions:

(1) $(CH_3)_2SO + OH\cdot \rightarrow (CH_3)_2S\cdot(O)OH \rightarrow \cdot CH_3 + CH_3S(O)OH$
(2) $\cdot CH_3 + (CH_3)_2SO \rightarrow CH_4 + \cdot CH_2(CH_3)SO$
(3) $2\cdot CH_3 \rightarrow C_2H_6$

with a yield of $G(CH_4) + 2G(C_2H_6) = 6.0$.

Surprisingly when $NaBH_4$ is added to the solution $G(CH_4) + 2G(C_2H_6) > 100$ is obtained, indicating that a chain reaction occurs. This result indicates that under these conditions the following catalytic process occurs:



$$OH\cdot + (CH_3)_2SO \rightarrow (CH_3)_2S\cdot(O)OH$$

$$(CH_3)_2S\cdot(O)OH \rightarrow CH_3S(O)OH + \cdot CH_3$$

$$\cdot CH_3 + BH_4^- \rightarrow BH_3□^- / BH_{4\,\text{(in water)}} + CH_4$$

$$\xrightarrow{N_2O} N_2 + BH_3 + OH\cdot$$

$$1/2B_2H_6$$

The reaction: $BH_4 + N_2O \rightarrow N_2 + BH_3 + OH\cdot$ was previously reported [1].

(4) $OH + BH_4^- \rightarrow BH_4 + OH^-$

The effect of $[(CH_3)_2SO]$ and of the dose rate were studied. The results point out that N_2O saturated solutions in the presence of BH_4^- can be used to catalytically hydroxylate various organic compounds.

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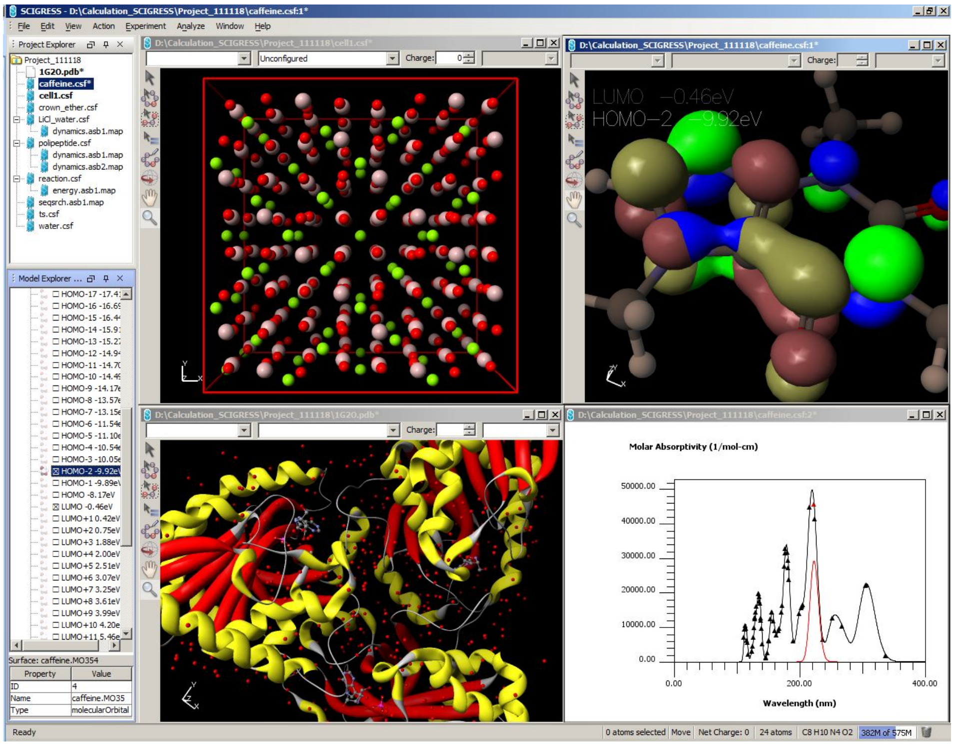
SCIGRESS

SCIGRESS is a leading computer-aided chemistry modeling package designed for computational chemists as well as experimental chemists conducting research in life sciences, materials and chemicals and undergraduate and graduate educators. Designed by chemists for use by chemists, SCIGRESS incorporates a wide range of modeling and analysis techniques, including many developed and validated by experts in computational chemistry.

Chemists who need answers about realistic molecular systems can use SCIGRESS effectively without becoming experts in the details of computational techniques. SCIGRESS facilitates access to its methods by easy-to-use graphical interface which intuitively guides users through varying calculation methods and offers alternatives to balance accuracy and computational requirements.

SCIGRESS can apply a wide range of computational models, from molecular mechanics through rigorous quantum electronic structure techniques, to all types of molecular systems, from organic molecules, to inorganics, polymers, materials systems (metals, oxides, ceramics, semiconductors), and whole proteins.



SCIGRESS Features

- Determination of total energy (DFT), heat of formation (semi-empirical methods) or strain energy (MM).
- Reaction mechanism determination via transition state searching and evaluation and visualization of intrinsic reaction coordinates.
- Determination of low energy conformations.
- Vibrational analysis including visualization of IR spectra and normal modes of vibration.
- Interactions with radiation including visualization of UV-visible spectra, and identification of molecular orbitals responsible for orbitals electronic transitions.
- 3D-visualization of electronic surfaces including orbitals, electron densities, and electrostatic surfaces.
- Molecular dynamics study and analysis of phase transitions, expansion, defects, compressibility, tensile strength, adsorption, absorption, and thermal conductivity.
- QSAR/QSPR analysis.
- Protein-ligand docking.
- Quantum chemistry of full proteins.

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