10th International School of Organometallic Chemistry

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Camerino, Italy
05-09 September 2015
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Organometallic Chemistry at the Forefront of Societal Challenges

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INTRODUCTION

Organometallic Chemistry at the Forefront of Societal Challenges

The ISOC series is the most important school on organometallic chemistry at the European level, organized under the auspices of EuCheMS (the European Association for Chemical and Molecular Sciences) and the Interdivisional Group of Organometallic chemistry of the Italian Chemical Society. The aim is to encourage the presence of young researchers and Ph.D students both from University and Industry, including those not directly involved in organometallic research projects, in order to bring together young researchers and distinguished European scientists as a contribution to the important goal of increasing the transfer of knowledge at a high level between different European countries and different generation of scientists. The 10th edition of ISOC will focus on the role of organometallic chemistry in finding solutions to many of the major societal challenges in the 21st century: from the development of sustainable energy solutions to the mitigation of climate change, from the synthesis of effective therapeutics to the production of new materials ranging from novel polymers to nanomaterials, from the generation of industrial feedstocks to the remediation of the environment. The scientific community is increasingly being stimulated to tackle problems of practical interest and the society will undoubtedly rely on advances made in the field of organometallic chemistry.

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TIMETABLE

5th sept	6th sept	7th sept	8th sept	9th sept
9.00-13.00 **Registration**	**9.00-10.30** **Olivia Reinaud** *Coordination chemistry in biomimetic cavities* **10.30-11.00** **Coffee break** **11.00-12.30** **Jieping Zhu** *Palladium-catalyzed domino processes for the synthesis of heterocycles* **12.30** **Lunch**	**9.00-10.30** **Jose Luis Mascareñas** *New advances in metal catalyzed cycloadditions* **10.30-11.00** **Coffee break** **11.00-12.30** **Nuno Maulide** *Molecular gymnastics: organic synthesis with rearrangements* **12.30** **Lunch**	**8.30-10.00** **Jacques Maddaluno** *Organolithium chemistry: an analytical resurrection* **10.00-11.30** **Axel Jacobi von Wangelin** *The significance of reductive chemical processes: Examples from industry, research, and future societies* **11.30-11.45** **Coffee Break** **11.45-13.15** **F. Matthias Bickelhaupt** *Theoretical organometallic chemistry: new concepts and design principles* **13.15** **Lunch**	**8.30-10.00** **Greta R. Patzke** *Transition metal oxocluster catalysts: from structure-activity relationships to artificial photosynthesis* **10.30-12.00** **Tobin Jay Marks** *Interface science of unconventional photovoltaic devices*
15.00-15.30 **Opening session** **15.30-17.00** **Pierre Braunstein** *Metal-Ligand Interplay for the design of the first and second coordination spheres: fundamental aspects and applications* **17.00-17.30** **Coffee break** **17.30-19.00** **Enzo Alessio** *The battle against cancer with metal compounds* **20.30** **Welcome Dinner**	**14.30-16.00** **Gianluca Farinola** *Organometallic approaches to conjugated molecules and polymers for optoelectronics* **16.00-16.30** **Coffee Break** **16.30-18.00** **Gerhard Erker** *Frustrated Lewis pair chemistry - principles and recent developments* **18.00-19.00** **Flash Presentation** **19.00-20.00** **Poster session** **20.30** **Dinner**	**14.30-16.00** **Bas de Bruin** *New catalytic developments involving carbene reactivity* **16.00-16.30** **Coffee Break** **16.30-18.00** **Flash Presentation** **18.00-20.00** **Poster session** **20.30** **Dinner**	**15.00** **Social Tour** **20.30** **SOCIAL Dinner**	

TIMETABLE

Saturday, 5 September:

15.00: Opening Session
15.30: Prof. Pierre Braunstein **"*Metal-Ligand Interplay for the design of the first and second coordination spheres: fundamental aspects and applications*"**
17.00: Coffee break
17.30: Prof. Enzo Alessio **"*The battle against cancer with metal compounds*"**
20.30: Welcome Dinner

Sunday, 6 September:

09.00: Prof. Olivia Reinaud **"*Coordination chemistry in biomimetic cavities*"**
10.30: Coffee break
11.00: Prof. Jieping Zhu **"*Palladium-catalyzed domino processes for the synthesis of heterocycles*"**
12.30: Lunch
14.30: Prof. Gianluca Farinola **"*Organometallic approaches to conjugated molecules and polymers for optoelectronics*"**
16.00: Coffee break
16.30: Prof. Gerhard Erker **"*Frustrated Lewis pair chemistry - principles and recent developments*"**
18.00: Flash Presentation
19.00: Poster session
20.30: Dinner

Monday, 7 September:

09.00: Prof. Jose Luis Mascareñas **"*New advances in metal catalyzed cycloadditions*"**
10,30: Coffee break
11,00: Prof. Nuno Maulide **"*Molecular gymnastics: organic synthesis with rearrangements*"**
12,30: Lunch
14,30: Prof. Bas de Bruin **"*New catalytic developments involving carbene reactivity*"**
16.00: Coffee break
16.30: Flash Presentation
18.00: Poster session
20.30: Dinner

Tuesday, 8 September:

08.30: Prof. Jacques Maddaluno **" *Organolithium chemistry: an analytical resurrection*"**
10.00: Prof Axel Jacobi von Wangelin **"*The significance of reductive chemical processes: Examples from industry, research, and future societies*"**
11,30: Coffee break
11.45: Prof. F. Matthias Bickelhaupt **"*Theoretical organometallic chemistry: new concepts and design principles*"**
13.15: Lunch
15,00: Social Tour
20,30: Social dinner

Wednesday, 9 September:

08.30: Prof Greta R. Patzke **"*Transition metal oxocluster catalysts: from structure-activity relationships to artificial photosynthesis*"**
10.30: Prof. Tobin Jay Marks **"*Interface science of unconventional photovoltaic devices*"**
12.00: Prizes and Closing Ceremony

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Prof. Enrico Marcantoni

SPEAKERS

Prof. Pierre Braunstein **France, CNRS-Université de Strasbourg**

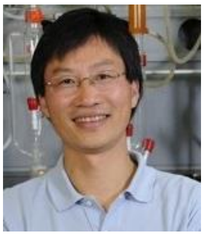
Metal-Ligand Interplay for the design of the first and second coordination spheres: fundamental aspects and applications

Prof. Enzo Alessio **Italy, University of Trieste**

The battle against cancer with metal compounds

Prof. Olivia Reinaud **France, University of Paris Decartes**

Coordination chemistry in biomimetic cavities



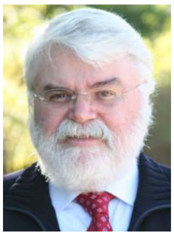
Prof. Jieping Zhu **Switzerland, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne**

Palladium-catalyzed domino processes for the synthesis of heterocycles

Prof. Gianluca Farinola **Italy, University of Bari**

Organometallic approaches to conjugated molecules and polymers for optoelectronics

SPEAKERS



Prof. Gerhard Erker **Germany, University of Münster**

Frustrated Lewis pair chemistry - principles and recent developments

Prof. Jose Luis Mascareñas **Spain, CIQUS University of Santiago de Compostela**

New advances in metal catalyzed cycloadditions

Prof. Nuno Maulide **Austria, University of Vienna**

Molecular gymnastics: organic synthesis with rearrangements

Prof. Bas de Bruin **Netherlands, University of Amsterdam**

New catalytic developments involving carbene reactivity

Prof. Jacques Maddaluno **France, CNRS-University of Rouen**

Organolithium chemistry: an analytical resurrection

SPEAKERS

Prof. Axel Jacobi von Wangelin **Germany, University of Regensburg**

The significance of reductive chemical processes: Examples from industry, research, and future societies

Prof. F. Matthias Bickelhaupt **Netherlands, VU University Amsterdam and Radboud University Nijmegen**

Theoretical organometallic chemistry: new concepts and design principles

Prof. Greta R. Patzke **Switzerland, University of Zurich**

Transition metal oxocluster catalysts: from structure-activity relationships to artificial photosynthesis

Prof. Tobin Jay Marks **USA, Northwestern University**

Interface science of unconventional photovoltaic devices

Metal-Ligand Interplay for the Design of the First and Second Coordination Spheres: Fundamental Aspects and Applications

Prof. Pierre Braunstein

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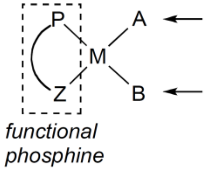
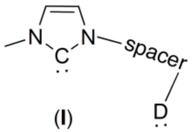
Global energy needs In addition to the stronger metal-ligand interactions of the covalent- or dative-type that characterize the first coordination sphere of a metal centre, weaker interactions, such as H-bonding and metallophilic interactions, can occur that can often be viewed as shaping the second coordination sphere of the metal. Although the energies involved in the latter case are smaller, the influence of these weaker interactions on the chemical and/or physical properties of a metal complex has long been recognized.

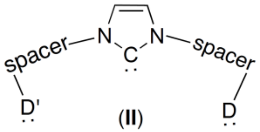
We shall focus on the properties of transition metal complexes that are directly associated with the presence of functional ligands able to chelate a metal centre through at least two chemically-different donors. This has direct implications on the reactivity of the other ligands, see *e.g*. positions A and B)



Based on the 'phosphine mimicry' of N-heterocyclic carbenes (NHCs), a number of functional NHCs have been investigated and their rich chemistry is attracting increasing attention (see **I**). Chelating or bridging modes can be envisaged, depending on the spacer used. NHC-based « pincer-type » ligands also fall into this category (see **II**) (for simplicity, all the donor groups in **I** and **II** have been taken as neutral, 2 e donors, but this does not have to be the case).



(**I**)



(**II**)

We will examine specific features associated with different donor functions connected to the NHC core. These will include oxygen-, sulfur,- imine,- and phosphine-based functionalities.

Some of these ligands can be tailored to behave as short-bite ligands and this will give us the opportunity to discuss unique features associated with the presence of an additional functionality in short-bite diphosphine ligands.

The Battle Against Cancer and Other Diseases with Metal Compounds

Prof. Enzo Alessio

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The general aim of the lecture is that of showing the huge potentialities that coordination and organometallic compounds have in the field of medicinal inorganic chemistry. Given the time limit, the lecture will be restricted to therapeutic applications of metal compounds (real or potential), excluding radioactive metals for radiotherapy, and will not deal with diagnostic applications, i.e. the use of metal compounds as imaging agents.

After a general introduction, the first part of the lecture will focus on the most successful inorganic drugs so far, i.e. on Pt anticancer compounds. Their serendipitous discovery, development and, above all, their chemical features and mechanism of action will be treated. The problems and limitations of Pt anticancer drugs will lead to introduce anticancer compounds based on other metals and, in particular, on ruthenium, both coordination complexes (e.g. KP1019 and NAMI-A) and organometallic species (e.g. piano-stool compounds). At the end of this part of the lecture, a general classification of metal based drugs depending on their mode of action will be proposed.

From this point onward the lecture will focus on organometallic species exclusively, and the distinctive features of organometallic compounds that make them particularly appealing for being investigated in medicinal inorganic chemistry will be highlighted. Different approaches to the development of organometallic drugs – not limited to the anticancer field – will be shown, in particular the bio-isosteric replacement of phenyl rings with metallocene fragments in bioactive molecules (such as in the antimalarial drug *ferroquine* and in the anticancer compounds named *ferrocifens*). In addition to potential anticancer species, examples of organometallic compounds investigated as selective enzyme inhibitors and as antibacterial drugs will be shown.

In the final part of the lecture, the use of light for the activation of metal compounds in biological systems (i.e. photo-dissociation of ligands, caged complexes) will be addressed.

For each argument treated, the lecture will provide updated references.

Coordination Chemistry in biomimetic cavities

Prof. Olivia Reinaud

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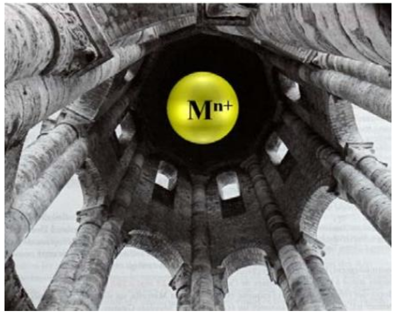
Supramolecular chemistry concerns the reversible assembly of discrete entities through the establishment of multiple weak interactions between the different components. As these phenomena are fundamental in the biological world, Nature has been a major source of inspiration for chemists involved in the supramolecular field. Biomimetic inorganic chemistry is mainly focused on mimicking the first sphere coordination environment of the metal ion. Little information is available concerning the influence, or even the control, that the microenvironment provided by a protein can have on the reactivity of the metal. Exploration of this aspect through the construction of cavity-based complexes will be presented and discussed.[1] Hence, the concepts of "funnel" complex and "bowl" complex will be illustrated by selected examples that gave rise to:

- The elaboration of receptors that are highly selective for neutral molecules[2] and efficient even in the highly competitive medium, which is water,[3]
- A new proposed mechanism for copper mono-oxygenases,[4]
- The design of systems allowing the control of hetero-multinuclear binding of metal ions,[5]
- A biomimetic strategy for the selective functionalization of a cavity: Guest Covalent
- Capture by a Host.[6]



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Palladium-catalyzed Domino Processes for the Synthesis of Heterocycles: Case of Indoles and Indole Alkaloids

Prof. Jieping Zhu

Laboratory of Synthesis and Natural Products, Institute of Chemical Sciences and Engineering,
Ecole Polytechnique Fédérale de Lausanne, EPFL–SB–ISIC–LSPN, CH–1015 Lausanne, Switzerland.
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The indole nucleus is a ubiquitous heterocycle found in many bioactive natural products, pharmaceuticals and agrochemicals. The synthesis and functionalization of indoles have attracted chemists for over a century and remain an active research area.[1] This presentation will be divided into two parts. The first part will focus on the Pd(II)-catalyzed bis-*nucleophilic* addition across a triple bond. The concept led to the development of efficient synthesis of indoloisoquinolinones, 3-alkynylindoles and cyclizative cross-coupling reactions under aerobic conditions.[2] Detailed mechanistic and kinetic studies allowed us to propose subsequently a robust and low-catalyst loading process for the access to this important class of heterocycles. The second part will discuss the development of a Pd-catalyzed decarboxylative cross coupling of aliphatic carboxylic acids with vinyltriflates for the synthesis of 1-aryl-1-vinyl-alkanes and the application of this methodology in the total synthesis of monoterpene indole alkaloids.[3]

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Organometallic Approaches to Conjugated Molecules and Polymers for Optoelectronics

Prof. Gianluca M. Farinola

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Progress of organic optoelectronics is largely based on the possibility to optimize the performances of molecular and polymeric organic semiconductors. Not only optical and electronic properties, but also processability and stability can be finely tuned and enhanced by molecular design. On the other hand, industrial production of plastic solar cells,[1] organic light emitting diodes[2] and other organic electronics devices[3] requires synthetic methods scalable up to thousands of kilograms, keeping in consideration costs and environmental impact.

Synthetic protocols of molecular and polymeric semiconductors are commonly based on organometallic reactions which are efficient, versatile and highly selective.[4]

The lecture will discuss the most important organometallic approaches to conjugated oligomers and polymers for applications in organic photonics and electronics. Classical Pd-catalyzed cross-coupling processes (*e.g.* Stille, Cassar-Heck-Sonogashira, Suzuki-Miyaura reactions) as well as more recent methods (*e.g.* direct arylation by C-H bond activation) will be presented for the synthesis of several classes of conjugated polymers and small molecules for optoelectronics.

Besides discussing scope and limitations of the organometallic methods, the lecture will introduce the issue of industrial scalability of the synthetic processes,[1] an important aspect that has been often neglected in the literature, showing possible approaches to quantify the synthetic accessibility[5] as a key parameter in the evaluation of the real practical significance of the organometallic protocols.

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Frustrated Lewis Pair Chemistry - Principles and Recent Developments

Prof. Gerhard Erker

Organisch-Chemisches Institut, Universität Münster, Germany Corrensstr. 40, Münster.
Email: erker@uni-muenster.de

Lewis acids and bases usually undergo a neutralizing adduct formation when brought together. However, Lewis acids and bases that feature very bulky substituents at their central atoms can evade this neutralization reaction. This may lead to situations of combinations of active Lewis acids and bases in solution. Such "frustrated Lewis pairs" (FLPs) offer the chance to observe cooperative reactions with added substrates. This has indeed been observed. A variety of phosphane/borane or amine/borane FLPs were shown to undergo unusual reactions with added small molecules. Several examples will be presented including heterolytic dihydrogen cleavage and metal-free catalytic hydrogenation, but also a number of new reactions such as CO reduction by [B]-H boranes or the development of a phospha-Stork chemistry. Eventually some developments toward active metal containing FLPs will be presented and discussed. These use Group 4 metallocenes as Lewis acids, but there are also systems made up by combinations of Group 4 metallocenes and boranes. The utilization of such systems in catalysis will be discussed.

References

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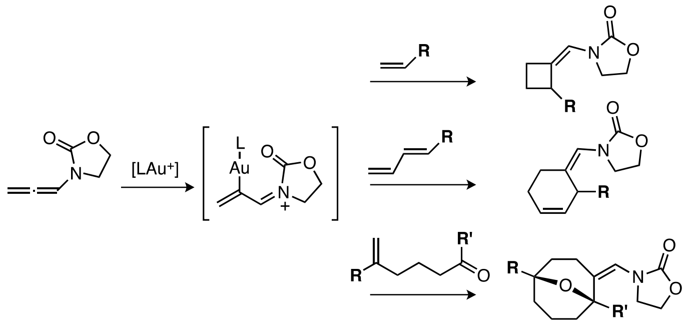
New Advances in Metal Catalyzed Cycloadditions

Prof. José Luis Mascareñas

Departmento de Química Orgánica and Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) C/Jenaro de la Fuente s/n. Campus Vida Universidade de Santiago 15782 Santiago de Compostela, Spain.
Email: joseluis.mascarenas@usc.es

Cycloaddition reactions allow the direct assembly of cyclic skeletons from acyclic precursors, and therefore represent invaluable tools to streamline the synthesis of complex polycyclic products. While classical cycloadditions are somewhat restricted to specific, electronically complementary reactants, the potential of cycloaddition chemistry can be enormously expanded by taking advantage of the coordination and activation capabilities of metal complexes.[1] In recent years we have unveiled several new cycloaddition modes of alkylidenecyclopropanes by using palladium or nickel catalysts.[2] We have also developed several platinum or gold-catalyzed reactions of allenes consisting of formal (4 + 3) and (4 + 2) cycloadditions.[3] The intermolecular version of these reactions could be better accomplished by using allenamides as cycloaddition partners. These substrates work as efficient two carbon components in a variety of gold-catalyzed cycloadditions with different types of alkenyl derivatives (see scheme).[4] Most recently, our work in cycloaddition chemistry is moving towards the discovery of "anomalous" annulations involving C-H activation processes.[5]



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Molecular Gymnastics: C-C Bond Formation with Rearrangements

Prof. Nuno Maulide

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Email: nuno.maulide@univie.ac.at

The turn of the century brought about a pressing need for new, efficient and clean strategies for the chemical synthesis of biorelevant compounds. Our group has studied the use of various molecular rearrangements and atom-economical transformations as particularly appealing means towards the streamlined synthesis of complex small molecule targets.[1,2,3]

In this lecture, we will present an overview of our research in these areas and how they provide efficient solutions for total synthesis as well as platforms for the discovery of unusual reactivity.

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New Catalytic Developments Involving Carbene Reactivity

Prof. Bas de Bruin

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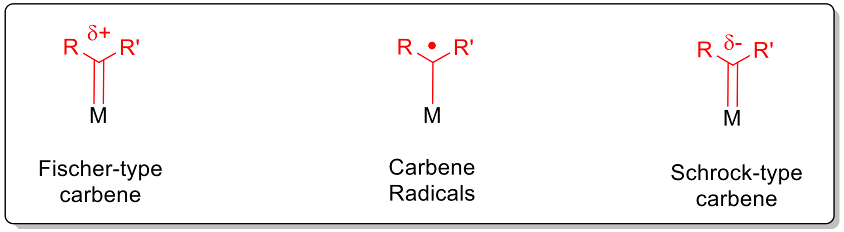
This presentation starts with an overview of catalytic reactions involving Fischer- and Schrock-type carbenes. These reactions play an important role in several processes ranging from synthesis of fine chemicals to polymeric materials.



The second part of this presentation focusses on new developments in our own group using both Fischer-type carbenes and a new carbene type: carbene radicals. These new reactions give access to novel reaction patterns that are not only interesting from a fundamental perspective, but also give access to completely new synthetic protocols to synthesize pharmaceuticals and polymers.

Organolithium Chemistry: an Analytical Resurrection

Prof. Jacques Maddaluno

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Organolithium reagents are now commonplace in modern organic synthesis. In fact, their popularity has progressively pushed these reagents in the far back of the “routine tools” drawer, to a point where they are barely considered worthy of an active contemporary research in organometallic chemistry.

We wish to show in this lecture that indeed the synthetic applications of organolithium, in particular as deprotonating agents, has been largely explored and mastered in the last 25 years. But we also want to emphasize that relatively little is known about the structure of these reagents in solution while this parameter is likely to exert a significant influence on their reactivity. Since modern analytical and theoretical tools have opened refined accesses to the intimate organization of these species in solution and to some aspects of their reactivity, we are convinced it is now time for an analytical resurrection of this class of compounds.

In the first part of this lecture, we will remind the participants with the fundamentals of this type of chemistry, in terms of stability and reaction conditions. We will then examine in relative details the main families of deprotonation reactions by organolithium bases (and the factors influencing the chemoselectivity, the ortho-lithiation, lateral lithiation) and their mechanisms. We will next consider another important class of reactions: the halogen-lithium exchange and its main characteristics.

In the second part of the lecture, we will spend the remaining time on more exploratory aspects of the chemistry of organolithium reagents, based on our own researches. In particular, we will give a rapid overview on the carbolithiation of alkynes and the use of chiral mixed aggregates for the enantioselective addition of organolithium reagents on carbonyl compounds. These results make an extensive use of modern analytical tools, in particular NMR ones, as well as of theoretical (DFT) computations to provide with a wide description of this domain of organometallic chemistry.

The Significance of Reductive Chemical Processes: Examples from Industry, Research & Future Societies

Prof. Axel Jacobi von Wangelin

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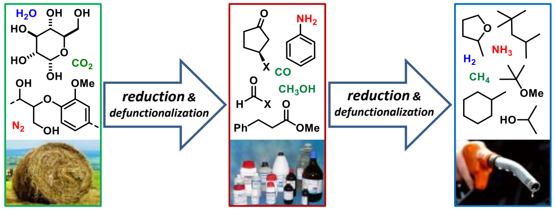
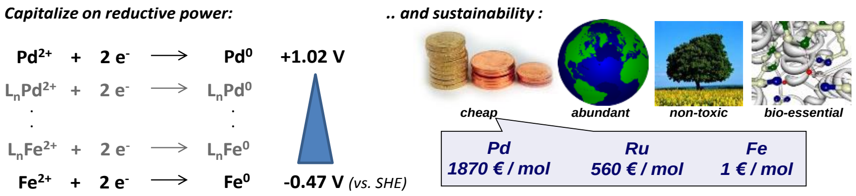
The aerobic conditions on our planet have enabled the accumulation of oxidized matter whereas reduced chemicals constitute most valuable energy carriers. The future shortages of energy-rich resources make efficient reductive conversions of available raw materials into valuable chemicals and fuels one of the greatest challenges of modern societies.



Over the past decades, **metal-catalyzed reductions and related reductive processes** have emerged as key synthetic methods for the preparation of diverse building blocks, fine chemicals, pharmaceuticals, agrochemicals and materials. Such reactions are mostly operated with noble or toxic catalyst metals (Pd, Ni, Cu, Co, Rh, Pt etc.) - which is only partially due to their good catalytic activity. The relatively high stability of noble metals in lower oxidation states has allowed facile catalyst syntheses, implementations of structural variations, and spectroscopic and mechanistic studies that led to a deeper understanding of the underlying elemental steps and consequently to a steady progress in the development of more effective catalyst systems and reaction parameters. However, the commonly employed catalysts exhibit detrimental effects on the environment and generate high operational costs. **Iron catalysts** are a promising yet under-utilized alternative for reductive transformations. From an abstract thermodynamic perspective it is obvious that base metals (e.g. Fe) exhibit a much stronger reductive power in low oxidation states than commonly employed noble metals.



Capitalize on reductive power:

Pd^{2+} + 2 e^- ⟶ Pd^0 +1.02 V

L_nPd^{2+} + 2 e^- ⟶ L_nPd^0

L_nFe^{2+} + 2 e^- ⟶ L_nFe^0

Fe^{2+} + 2 e^- ⟶ Fe^0 -0.47 V *(vs. SHE)*

.. and sustainability :

Pd	Ru	Fe
1870 € / mol	560 € / mol	1 € / mol

Fe accounts for 5% of the earth's crust, it's the 10th most abundant element of the universe and has no critical hazard profile. The Fe-catalyzed N_2 fixation (Haber-Bosch) and CO reduction (Fischer-Tropsch) are the two largest technical reductions. But only very recently, other efficient Fe-catalyzed reductions, hydrogenations, and reductive coupling reactions have been developed.

Theoretical Organometallic Chemistry: New Concepts and Design Principles

Prof. F. M. Bickelhaupt

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The aim of this work is to understand[1] the factors that determine the activity and selectivity of transition-metal catalysts in oxidative-addition steps that occur in bond activation and cross-coupling reactions. We studied the effect of varying the metal M along the d^{10} metals of groups 9, 10 and 11, in combination with varying the number as well as the type of ligands, using relativistic density functional theory (DFT)[2] and the activation strain model (ASM).[1]

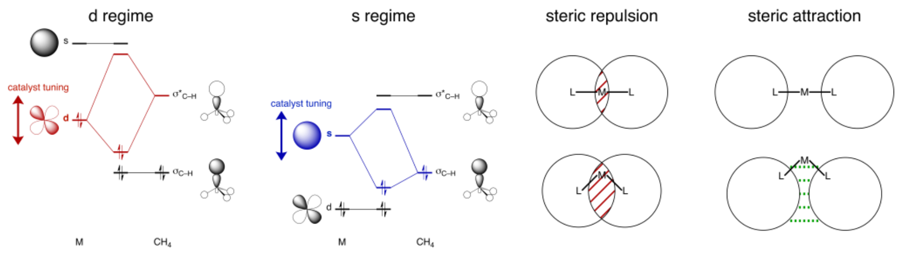

Figure 1. Schematic illustration of concepts presented in this lecture.

Three concepts for tuning a catalyst's activity emerge: (i) d-regime catalysts; (ii) s-regime catalysts; and (iii) bite-angle flexibility (see Figure 1, left). These concepts explain why the effect of one and the same ligand on a catalyst's activity can be completely different, even opposite, for catalysts from different electronic regimes. Furthermore, I will point out why not the bite angle itself, but its flexibility is decisive for the catalyst's activity. Finally, I show how the latter is influenced not only by steric repulsion but also by what we designate "steric attraction" (see Figure 1, right).

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Transition Metal Oxocluster Catalysts: From Structure-Activity Relationships to Artificial Photosynthesis

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Inspired ***Scope:*** Artificial photosynthesis has emerged as a promising and elegant strategy to convert solar energy resources into clean and sustainable fuels.[1] After decades of research into the mechanisms of water splitting processes, water oxidation still remains a challenging bottleneck towards technological implementations. This renders the design of robust, economic and efficient water oxidation catalysts a highly relevant current research target.

Background: The introduction is followed by an overview of recent progress in artificial photosynthesis setups. The pros and cons of heterogeneous and molecular catalysts for water splitting are briefly compared. Next, up-to-date concepts for the construction and application of molecular water oxidation and reduction catalysts (WOCs and WRCs) are discussed. The oxygen-evolving complex (OEC) of photosystem II is introduced as a leading design paradigm for the construction of bio-inspired WOCs.[2]

Polyoxometalates as WOCs and WRCs: This section sets out with a brief introduction to the structural and analytical chemistry of polyoxometalates (POMs) as a key family of multi-functional oxoclusters which attract increasing interest for catalytic applications.[3] Next, latest developments on POM-based WOCs are summarized and their interplay between hetero- and homogeneous catalysis is discussed. Two case studies[4] on the structure-activity relationships (SAR) of POM catalysts round this section off and shed light on the challenging interaction of POMs with standard photosensitizers, along with the key influence of subtle factors, such as crystallographic disorder, on the water oxidation performance. Furthermore, the upcoming use of POMs as WRCs is highlighted, followed by a systematic investigation of structural features of small polyoxotungstates and their effects on the photocatalytic water reduction activity.

Molecular cubanes as bio-inspired WOCs: The final part summarizes the present efforts to translate the structural features of the OEC into molecular cubanes as platforms to investigate the parameters and mechanisms of bio-related artificial photosynthesis. Given that the construction of active WOCs based on direct OEC replicas remains a major challenge, considerable current activities are directed on $\{Co_4O_4\}$-based cubane WOCs. Latest results on the SAR of $\{Co(III)_4O_4\}$-WOCs and their stability under operational conditions are discussed. Moreover, the catalytic performance of a new $\{Co(II)_4O_4\}$-WOC with a flexible OEC-inspired ligand architecture is introduced in more detail as a model system for translating bio-mimetic features into stable WOCs. Solution stability tests, activity parameters, and ligand exchange as well as flash photolysis studies provide an insight into the mechanisms associated with Co-cubane WOCs. Future trends for molecular oxocluster WOC design are presented in the outlook.

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Interface Science of Soft Matter Photovoltaics

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The ability to fabricate molecularly tailored interfaces with nanoscale precision offers means to selectively modulate charge transport, molecular assembly, and exciton dynamics at hard matter-soft matter and soft-soft matter interfaces. Such interfaces can facilitate transport of the “correct charges” while blocking transport of the “incorrect charges” at the electrode-active layer interfaces of organic photovoltaic cells. This interfacial tailoring can also suppress carrier-trapping defect densities at interfaces and stabilize them with respect to physical/thermal de-cohesion. For soft matter-soft matter interfaces, interfacial tailoring can also facilitate exciton scission and photocurrent generation in such cells. In this lecture, challenges and opportunities in organic photovoltaic interface science are illustrated for four specific and interrelated areas of research: 1) controlling charge transport across hard matter(electrode)-soft matter interfaces in organic photovoltaic cells, 2) controlling charge transport by specific active layer nano/microstructural organization in the bulk active material and at the electrodes, 3) controlling exciton dynamics and carrier generation at donor-acceptor interfaces in the active layer, 4) designing transparent conducting oxide electrodes with improved properties. It will be seen that such rational interface engineering along with improved bulk-heterojunction polymer structures guided by theoretical/computational analysis affords exceptional fill factors, solar power conversion efficiencies greater than 10%, and enhanced cell durability.

POSTERS

Poster 1

Green Valorization of Glycerol by Metal Catalysts

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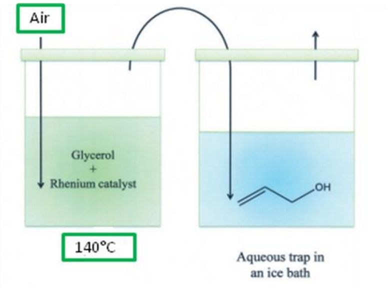
The increasing of biodiesel production leads to a growing supply of the by-product, glycerol. This prompts researchers to investigate for selective chemical transformations of glycerol, aiming to obtain derivatives with high added value and wide-ranging uses as new fuels, polymers and fine chemicals.[1]

Several catalytic pathways were proposed to achieve efficient, cheap and "green" deoxygenation, such as selective thermal processing, hydrogenolysis, acid-catalyzed dehydration and bio-mediated reactions.

However a very competitive methodology, namely, deoxydehydration reaction (DODH) has been only marginally investigated. DODH can remove two adjacent hydroxyl groups from vicinal diols to afford the corresponding unsaturated derivatives which, in the case of glycerol, is the allyl alcohol, a useful building block commonly employed for many applications.

In the present study we describe a green conversion of glycerol in allyl alcohol using several rhenium-based catalysts: $ReCl_5$, ReI_3, $[(C_6H_5)_3P]_2ReO_2I$.

Recovery of the reaction products was achieved using an ice-cooled water trap collecting the gas flow coming from the reaction vessel, where air was continuously bubbled (Figure 1). [2]



Scheme 1. Schematic representation of the reactor employed for rhenium catalyzed DODH of glycerol.

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Poster 2

The Palladium-Catalyzed Heck arylation of Homoallylic Substrates in the Presence of Ionic Liquids Containing (-)-Menthyl Group

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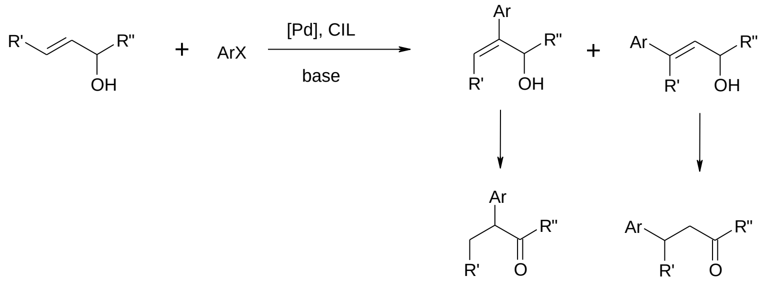
Palladium-catalyzed Heck reaction has been well known as one of the most important methods for the formation of new C-C bonds.[1] It is interesting to use allylic alcohols as substrates in Heck reaction, because it is an easy way to obtain carbonyl compounds which are useful intermediates for the synthesis of pharmaceuticals, fragrances or natural products.[2]

The first Heck reaction products, arylated allylic alcohols, can undergo isomerization to carbonyl compounds, for example to 4-aryl-2-butanones.[3,4]



In this paper we present new method of synthesis of saturated 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^{o}C and 24h in the presence of weak base – $NaHCO_3$. We tested a lot of variation of parameters such as solvents or time in order to obtain high yield of desired product.

For comparison, an alternative pathway leading to saturated carbonyl compound under the same conditions was studied. Using unsaturated ketones instead of homoallylic alcohols it was possible to obtain unsaturated ketones which were next hydrogenated in the same catalytic system. In both reactions we observed positive effect of the presence of ionic liquids.

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Poster 3

Divalent Lanthanides and Alkaline-Earth Metal Complexes in Intermolecular Hydrophosphination Reactions of Olefins

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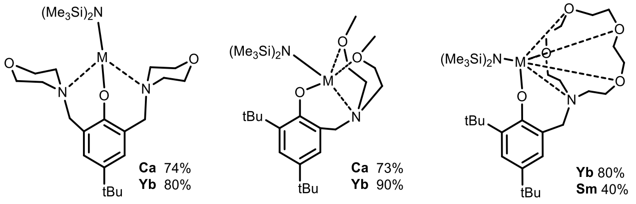
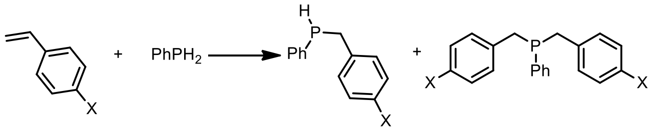
Hydrophosphination reactions it is an addition of the P-H bond of the phosphorous compounds to C-C unsaturated bond, which is a convenient synthetic method of forming a C-P bond. Such phosphorus-organic compounds find a wide range of applications, from ligands in metal complexes to building blocks in medical chemistry and catalysts of organic synthesis.

Were obtained and structurally characterized a series of stable heteroleptic amide complexes of divalent ytterbium, samarium, and calcium containing aminoethyl-phenolate ligand systems.



The resulting compounds exhibit high catalytic activity, productivity and selectivity in the intermolecular hydrophosphination reaction between styrene and phenylphosphine with high TON and TOF, up to 0.04% catalyst loading.



X = H, Me, tBu, Cl, F, OMe

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Poster 4

Complexes of Yttrium Supported by Bulky Amido-Imino and en-Diamido Ligands. Synthesis, Structure, Reactivity and Catalytic Activity in Intermolecular Hydrophosphination and Hydroamination Reactions of Olefins

Alexander A. Kissel,[a]* Tatyana V. Mahrova,[a] Dmitry M. Lyubov,[a] Anton V. Cherkasov,[a] Georgy K. Fukin,[a] Alexander A. Trifonov,[a] Iker Del Rosal,[b] Laurent Maron[b]

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Due to the high biological and industrial importance of nitrogen-containing and phosphorus-containing molecules, of great interest to the scientific and industrial research had development of effective methods for the synthesis of these molecules. Hydroelementation reactions, that is the addition of E–H (E = N, P) functionalities across C–C multiple bonds, are atom-economic processes for the synthesis of valuable compounds that may be one of the prospective application fields of organo-rare-earth complexes.

The compounds containing bond Ln-C and Ln-H are of interest, both in terms of basic research and the use of these complexes in the conversion reaction of unsaturated substrates, due to the high reactivity of these derivatives of lanthanides.

A monoanionic amido-imino and dianionic en-diamido ligand systems were successfully employed for the synthesis of alkyl $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC(Me)}]_2\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2$ (**1**), $\{[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NC(Me)=C(Me)N-C}_6\text{H}_3\text{-}i\text{Pr}_2\text{-}2,6]\text{Y}(\text{CH}_2\text{SiMe}_3)_2\}^-\{\text{Li(THF)}_4\}^+$ (**2**), $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N=C(Me)-C(CH}_2)\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]\text{Y}(\text{CH}_2\text{SiMe}_3)_2$ (THF) (**4**) and hydride $\{[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC(Me)}]_2\text{YH(THF)}\}_2$(THF) (**3**) complexes (Figure 1).

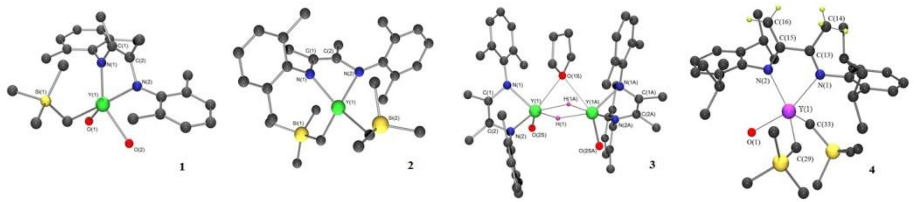

Figure 1.

Alkyl and hydrido complexes **1**, **2**, **3** and **4** proved to be an efficient catalysts of hydroelementation reactions. They enable hydrophosphination of para-substituted styrenes and 4-vinylpyridine with $PhPH_2$ and Ph_2PH under mild conditions with formation of the anti-Markovnikov product. Furthermore these complexes initiate hydroamination of para-substituted styrenes with pyrrolidine.

Acknowledgements – This work was supported by the Russian Foundation for Basic Research (Grant no. 12-03-93109-НЦНИЛ).DML thanks for a Grant of President of Russian Federation for young scientists (grant no. MK-5702.2015.3).

Poster 5

Metal Complexes with Di(N-Heterocyclic Carbene) Ligands Bearing an *Ortho*-, *Meta*- or *Para*-Phenylene Bridge

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Di(N-heterocyclic carbene) ligands (diNHC) are one of the most interesting classes of compounds studied for the syntheses of transition metal complexes with a wide range of applications, spanning from photophysics, catalysis and medicine.[1] Generally the employed diNHCs have a flexible alkyl chain as bridging group between the carbene moieties. In this work, we present our recent results on diNHC ligands with rigid *ortho*-, *meta*- and *para*-phenylene bridging group, which could be interesting because the different geometry of functionalization of the aromatic ring should influence the bridging vs. chelating coordination of the dicarbene.[2,3] Furthermore, a limited number of examples are present in the literature with these ligands and in most cases they involve the *meta*-phenylene bridge, which can act also as *CCC*-pincer ligand as a consequence of the metalation of the phenylene bridge in the C2 position (with Ru(II), Ir(III) or Pt(II) centers).[3] We have synthesized the dinuclear bridging diNHC silver(I) complexes and studied their ability to transfer the diNHC ligands to other metal centers (like Ru(II), Ir(III), Cu(I) and Au(I)). As expected, Ag(I), Au(I) and Cu(I) complexes present the classical linear coordination; the diNHC transmetalation to the Ir(III) and Ru(II) centers is successfully only with the *ortho*-phenylene ligand and affords the chelate complexes (Figure 1). Finally, the solid state structures and the luminescence properties of the Ag(I) and Au(I) complexes will be discussed and compared.

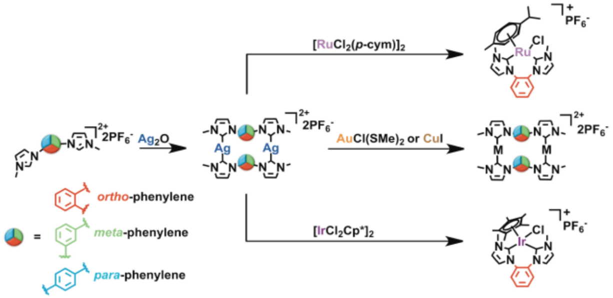

Figure 1.

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Poster 6

Mn(III) Complexes Containing Hydrophilic Chiral Ligands

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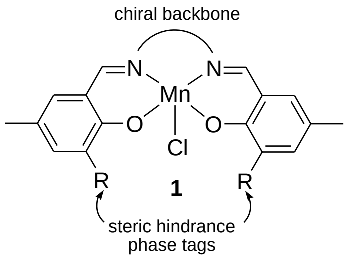
Complexes of Mn (III) containing chiral derivatives of salicylethylenediamine (salen) have remarkable stereo-orienting properties in enantioselective catalysis, for example in the asymmetric epoxidation of unsaturated substrates.[1]

The environmental impact of these transformations can be reduced by using a well tolerated reaction solvent, such as water, which offers numerous advantages for its cost and safety. On these grounds, the present study aims to prepare a library of Mn(III) complexes (**1**) containing the structural motifs useful for the extension of these enantioselective processes in aqueous environments.[3] More precisely, the tetradentate ligand will be based on the chiral frame resulting from *trans*-1,2-cyclohexanediamine or stilbendiamine.



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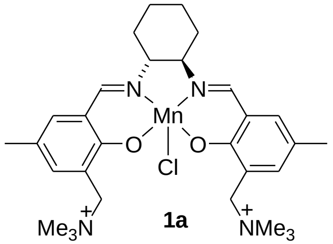

1a

Hydrophilic substituents R will be introduced in the key positions 3 and 3’, for prompting both enantioselectivity[1] and water solubility (an example is **1a**).

The compounds will then be evaluated in the asymmetric epoxidation reaction of styrenes in water.

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Poster 7

Biomimetic Association of a Copper Ion and Organic Redox Units Using Calix[6]Arene Based Ligands

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Calix[6]arenes are interesting platforms that can be functionalized in order to design ligands that mimic the active site of metallo-enzymes.[1] Previously, a calix[6]arene covalently linked to a TMPA unit was used to model the active site of mono-copper oxygenases.[2] This work aims to develop models of copper oxidases such as galactose oxidase and amine oxidase that associate an organic redox co-factor next to the copper center (a tyrosine residue and a topaquinone, respectively). The strategy presented relies on the synthesis of calix[6]TMPA derivatives that incorporate phenol or quinone units in the hosting cone (Figure 1).

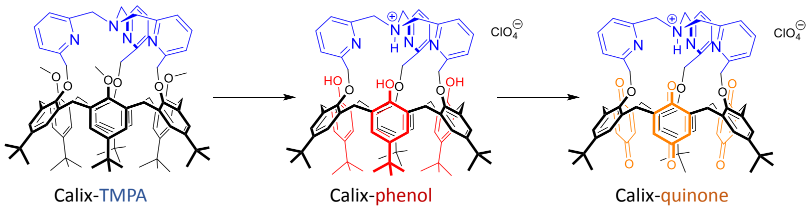

Figure 1

First insights into calix-phenol reactivity highlight the formation of a radical species (Figure 2). The synthesis of the ligands, the host-guest and redox properties of the corresponding copper complexes will be presented.

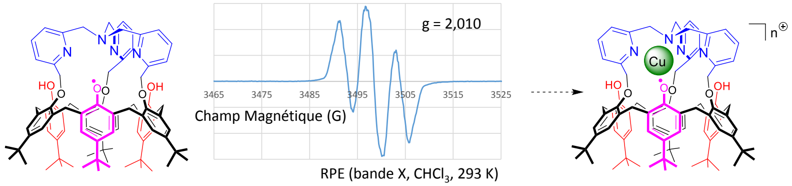

Figure 2

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Poster 8

Luminescent Metal Tetrazolate Complexes: From Design To Applications

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In homogeneous The preparation and the study of the physical and chemical properties of coordination compounds containing 5-aryl tetrazolate [R-CN_4^-] ligands is the focus of our research program. In particular we have demonstrated how these synthetically versatile nitrogen-rich ligands can actually rule the luminescent output of the corresponding Ru(II), Ir(III), Re(I) and Pt(II) – based complexes.[1,2] The synthetic versatility of tetrazolate derivatives combined with the peculiar sensitivity to electrophiles that is displayed by tetrazolate complexes constitute the basis for the further development of their coordination chemistry and their applicative scenarios. Following a similar approach, we have prepared a new family of anionic Ir(III) tetrazolate complexes and new Re(I)-based species containing ditopic tetrazolate ligands. (Figure 1) The photophysical properties of the new molecules will be presented herein, and particular attention will be dedicated to their use as components for soft salts and to the study of their chemosensing abilities.

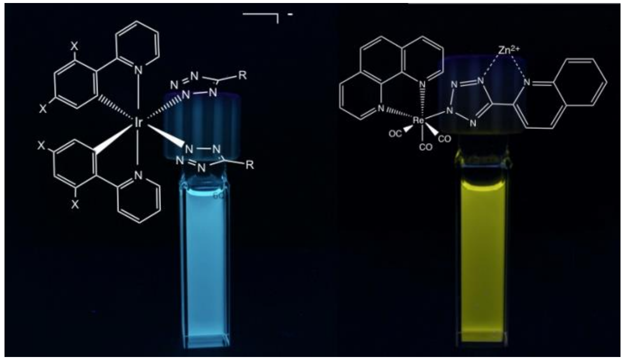

Figure 1

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Poster 9

Electro-Synthesis Towards High Energy Intermediates

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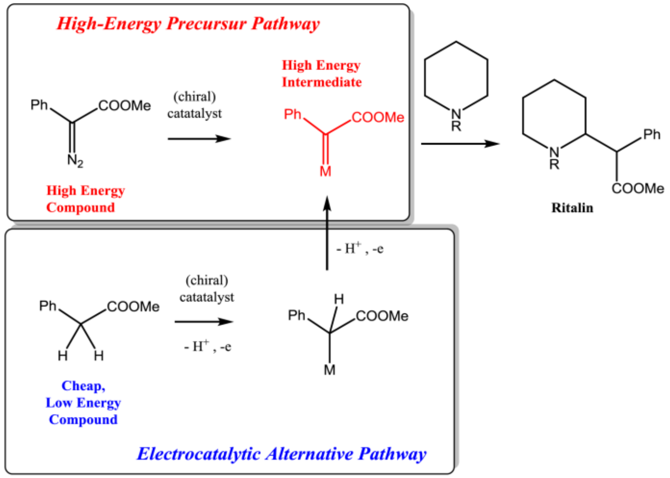

Figure 1.

Many (multistep) reactions involve the synthesis of high energy intermediates. This puts a high demand on the environment through energy consumption and waste formation. A possible solution is the use of electro-synthesis. In this case the energy isn't stored in molecules but in electrons. The exact amount of energy can be applied. One possible application can be found in the synthesis of Ritalin. The high energy intermediate shown in Figure 1 can be reached through double deprotonation and oxidation.

Poster 10

New Luminescent Ir(III) Complexes with 1,2,3-Triazolylidenes as NHC-Type Ligand

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Triazolylidene derivatives have found a wide range of application, especially in organometallic chemistry and catalysis, due principally to the relatively high covalent contribution to the M–NHC bond and to their strong donating abilities. The success of this class of ligand can be also attributed to easily preparation of the triazole precursor via the readily accessible Cu(I) catalysed 'click' cycloaddition of an alkyne and azide (CuAAC).[1] Subsequent alkylation of the triazole with a suitable alkylating agent is generally selective and yields the 1,3,4-substituted triazolium salt. Metal complexation is ready available too via direct metallation with Ag_2O and subsequent transmetallation with a wide range of metal precursors, giving a whole library of metal-triazolylidene complexes.[2]

Only few examples of triazolylidene metal complexes that show photochemical properties have been reported.[3]

Here we report the first examples of luminescent Ir(III) complexes bearing two triazolylidene ligands.

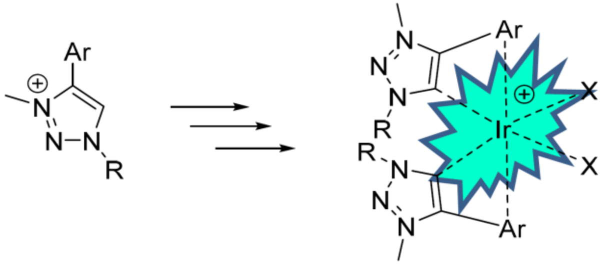

Figure 1.

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Poster 11

Functionalization of Ferrite Nanoparticles by Phenanthroline/Palladium Complexes and Their Use as Catalysts in Pharmaceutical Syntheses

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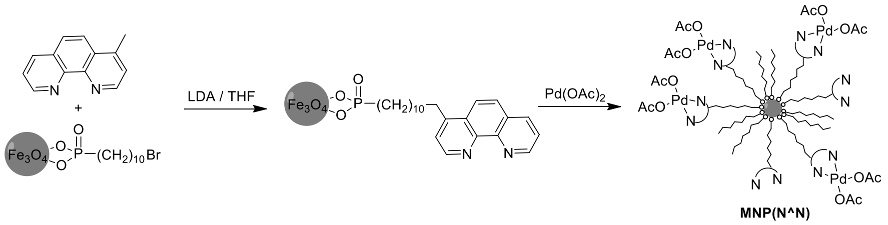
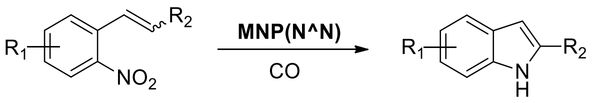
We In the last decade magnetic nanoparticles (MNP) have been widely used as a support for the immobilization of homogeneous catalysts. The small size of these particles allows their thorough dispersion in the reaction media thus nearing the homogeneous environment of soluble catalysts. At the same time, their magnetic properties allow to easily recover the catalyst at the end of the reaction. In our group, we developed a method with high reproducibility for the synthesis of ferrite MNP functionalized with a phosphonic acid bearing a halogen in the ω position to allow further modification. Owing to our interest in carbonylation and reductive cyclization reaction of nitro compounds, catalyzed by palladium/phenanthroline complexes,[1-3] we functionalized the protecting layer with a phenanthroline ligand.



$Pd(OAc)_2$ was then immobilized on the **MNP(N^N)** and the catalyst tested in the cyclization of nitrostyrenes to indoles using CO as a reductant.[4] The indole skeleton is present in several molecules of pharmaceutical interesting, one example is fluvastatin.



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Poster 12

Metal Bound *Cis* Olefin of Olive Oil Fatty Acid in $[PtI_2(Me_2phen)(\eta^2\text{-alkene})]$ Complexes: a Potential Platinum Delivery to Hydrophobic Targets

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It is known that distorted square planar complex of formula $[PtX_2(Me_2phen)]$ (Me_2phen, 2,9-dimethyl-1,10-phenanthroline, X = Cl, Br, or I) can react reversibly with olefins giving the corresponding very stable pentacoordinate species of the type $[PtX_2(Me_2phen)(\eta^2\text{-olefin})]$.[1] This kind of complexes has a trigonal bipyramidal geometry, with the two halogens in axial positions, and the neocuproine and the olefin bound to platinum in the trigonal plane[2] (Figure 1a). The reactivity of the square planar species towards olefin is strongly favoured by halogen sterical hindrance which determines distortion of the coordination geometry, increasing in the order Cl < Br < I.[1,3] We studied the reaction between the very sterically hindered square planar species, $[PtI_2(Me_2phen)]$, and unsaturated moieties of esterified fatty acid chains naturally occurring in olive oils. We performed experiments directly with extra virgin olive oils (EVOOs) and different standards of methyl esters of fatty acids, as *cis*-Δ^9 methyl oleate and *cis, cis*-Δ^9, Δ^{12} methyl linoleate.

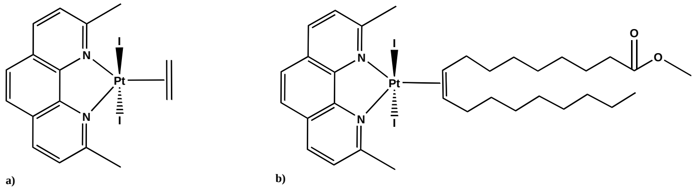

Figure 1. (a) Structure of general pentacoordinate complexes; b) structure of synthesized $[PtI_2(Me_2phen)(\eta^2\text{-Methyloleate})]$

The pentacoordinated Pt(II) species (Figure 1b) obtained by the coordination of the $[PtI_2(Me_2phen)]$ complex with the *cis* olefin groups of the esterified fatty acid moieties were characterized by 1D and 2D NMR spectroscopy. ^1H, ^{13}C, ^{195}Pt chemical shifts signals were analysed and discussed, suggesting the formation of mono and bis-adducts. Moreover, Diffusion Ordered Spectroscopy (DOSY) NMR experiments were performed to discriminate the different species obtained. Being the potential pharmacological activity of water-soluble pentacoordinate complexes already demonstrated[4], this preliminary study could suggest a possible use of these pentacoordinate species as prodrugs also on hydrophobic targets.

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Poster 13

Pd Mediated Cross Coupling Reactions for the Synthesis of New MOF Linkers

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MOFs (Metal Organic Frameworks) are a large class of ultraporous crystalline polymers, generated from the self-assembly of metallic ions or clusters and bridging organic linkers. The wide choice both in organic ligands and metallic nodes leads to an extraordinary modulation of the final structural proprieties. For these reasons, the design of the organic linkers has a key role in obtaining the desired topology of the MOF network. Pd-catalyzed cross coupling reactions are certainly a powerful tool for the ligand synthesis and provide several advantages over conventional organic synthesis, such as functional group tolerance, one step procedures and, consequently, reduction of wastes. Buchwald and coworkers proposed an easy synthetic pathway for the metal-catalyzed aminations of aryl halides,[1,2] process that proved to be quite difficult in other reaction conditions. Exploiting this procedure is also possible to form C-N bonds by using very poor nucleofiles, such as amides, combined with aryl chlorides with excellent yields.[3] In this communication we report on the successful application of the Buchwald protocol for the construction of novel organic linkers useful for the fabrication of new MOFs. A scheme summarizing the isolated ligands is reported in Figure 1. A series of ditopic or tritopic ligands characterized by different degrees of flexibility, linearity and denticity were isolated and fully characterized. Their use as organic linkers for the fabrication of new MOFs frameworks is currently under investigation in our laboratory.

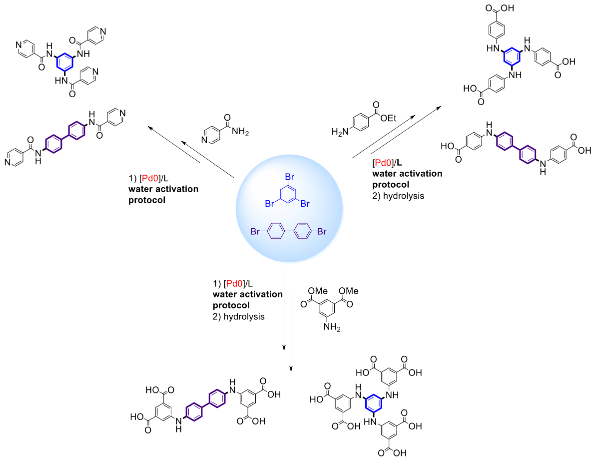

Figure 1.

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Poster 14

Manipulating Radicals: Using Cobalt to Steer Radical Reactions

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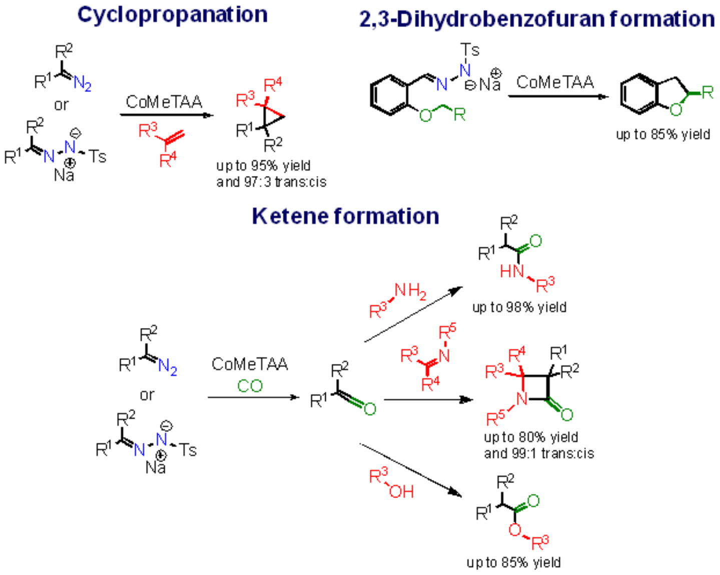
Cobalt(II) Schiff base complexes have proven to be effective catalysts for radical-type transformations, such as cyclopropanation or aziridination.[1,2] This work focuses on finding suitable catalysts for the activation of diazo compounds, which can subsequently lead to formation of β-lactams, 2,3-dihydrobenzofuranes, amides, cyclopropanes, etc. This research shows that cobalt(II) catalysts based on ligands such as tetraazaannulenes or salens proved very active towards the activation of diazo-compounds, in some cases outclassing their porphyrin equivalents.[3]



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Poster 15

DFT Investigation on [FeFe]-Hydrogenases and Biomimetic Models: Implications on the Activation of H_2

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[FeFe]-hydrogenases are enzymes that catalyze the reversible oxidation of H_2 with extremely high turnovers.[1] The chance of carrying out the same transformation in a controlled and productive way, has attracted a broad scientific community, since H_2 is a clean and high density fuel. The enzyme active site consists of a di-iron cluster, bound to a Fe_4S_4 cubane. Several biomimetic catalysts have been synthesized, but their activity is much lower than that of the natural system, particularly in the oxidation direction. Remarkably, it was recently showed that the presence of a metallic redox-active ligand has important implications in catalysis, since H_2 activation can be driven by partial spin delocalization among the metallic centers.[2] Here we present a DFT study on H_2 activation, in both natural and biomimetic systems, in order to highlight the effect of ligands nature on catalysis.

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Poster 16

Aminocarbonylation in Aqueous Medium Catalyzed by Palladium(II) Complexes with Ar,Ar′-BIAN Ligand (Ar,Ar′-BIAN = Bis(aryl)acenaphthenequinonediimine)

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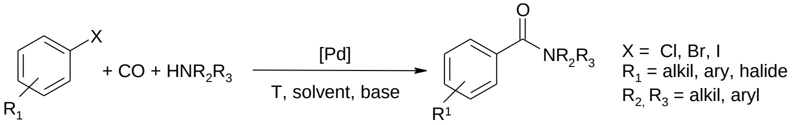
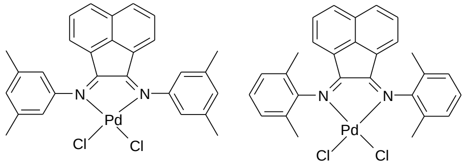
In the last decades the aminocarbonylation of primary and secondary amines with aryl halides is of significant interest in academia and fine chemical industry (Scheme 1). Products of these reactions – amides – constitute an interesting structural motif which is frequently present in pharmaceuticals (atorvastatin, mosapride),[1] in biologically active compounds having antagonistic action to many hormones[2,3] and in components for the manufacture of synthetic fibers (nylon, perlon).



Scheme 1. The aminocarbonylation reaction.

Up to now, catalytic activity of palladium complexes incorporating Ar,Ar’-BIAN ligand in aminocarbonylation of aniline with aryl iodides have been never studied. In this work the study of the coordination properties of (3,5-$(CH_3)_2C_6H_3)_2$-BIAN and (2,6-$(CH_3)_2C_6H_3)_2$-BIAN ligands towards [$PdCl_2$(cod)] precursor has been performed. Two complexes: [((3,5-$(CH_3)_2C_6H_3)_2$-BIAN)$PdCl_2$] and [((2,6-$(CH_3)_2C_6H_3)_2$-BIAN)$PdCl_2$] with Ar,Ar′-BIAN ligand connected to palladium atom in a bidentate mode have been obtained (Scheme 2) and characterized by spectroscopic methods. The catalytic activity of these complexes was tested in aminocarbonylation reaction of aniline with iodobenzene. The results show that, under mild reaction conditions (CO (balloon pressure), 4h, 90 ^{0}C) and in green solvent (water), these complexes generate relatively high-yielding and selective catalysts for aminocarbonylation reaction. Analysis of post-catalytic solution by Transmission Electron Microscopy showed the presence of palladium nanoparticles which are generated *in situ* during reaction.



[((3,5-$(CH_3)_2C_6H_3)_2$-BIAN)$PdCl_2$] [((2,6-$(CH_3)_2C_6H_3)_2$-BIAN)$PdCl_2$]

Scheme 2. Palladium catalyst with Ar,Ar'-BIAN ligand.

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Poster 17

The Tethered Aminohydroxylation of Glycals Allows a Stereodirected Access to 2- and 3-Aminosugars

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The aminohydroxylation reaction is an extremely useful method for the oxidation of alkenes to form 1,2-aminoalcohols. This moiety is present in important synthetic pharmaceutical targets like aminosugars, key constituents of a wide variety of natural substances.[1] In 2001, Donohoe and co-workers introduced an innovative method to obtain vicinal aminoalcohols through an intramolecular aminohydroxylation of olefins, called "tethered aminohydroxylation".[2] This method is an adaptation of the Os-mediated Sharpless aminohydroxylation, but it guarantees a full regiocontrol by tethering the nitrogen source to the allylic alcohol. We describe herein the results of the application of this method on d-glucal and d-galctal and on their derivatives, in order to obtain 2-amino and 3-aminosugars with different configurations at the stereogenic carbon atoms depending on the starting glycals. Glucals and galactals showed complementary reactivity in dependence of the stage at which the reaction was performed, i.e., directly or after double-bond shift consequent to a Ferrier rearrangement. This method allows access to both classes of 2-amino (compound **1**-**2**) and 3-amino (compound **3**) sugar derivatives (Figure 1). The oxazolidinone moiety of the compound **3** was easily removed with a basic treatment to obtain the free 3-aminosugar with excellent yield.

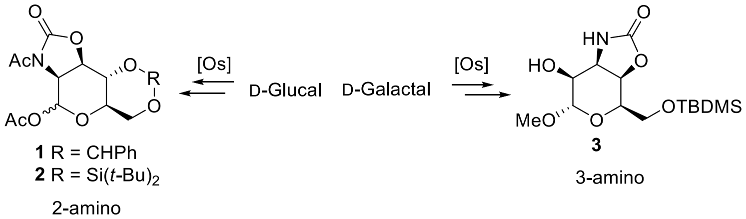

Figure 1.

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Poster 18

Copper(II)-Catalyzed Cyclizations of Alkynes as an Efficient Tool for the Synthesis of Haloalkylidene-Substituted Heterocycles

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Nitrogen- and oxygen-containing heterocycles are important motifs in many biologically active compounds. Intramolecular transition metal-catalyzed aminations and alkoxylations of carbon-carbon multiple bonds represent one of the most effective approaches for their synthesis.[1] Among the metals, copper is challenging because of the low cost and the tolerance toward many reactive functional groups, not requiring rigorously anaerobic and anhydrous conditions.[2] As a part of our ongoing interest toward intramolecular transition metal-catalyzed reactions involving C-H and heteroatom-H functionalization,[3] here we describe domino copper(II)-catalyzed alkoxyhalogenation and aminohalogenation processes of alkynylureas, secondary amides and carbamates to afford a range of haloalkyliden-substituted heterocycles in good yields (Figure 1).

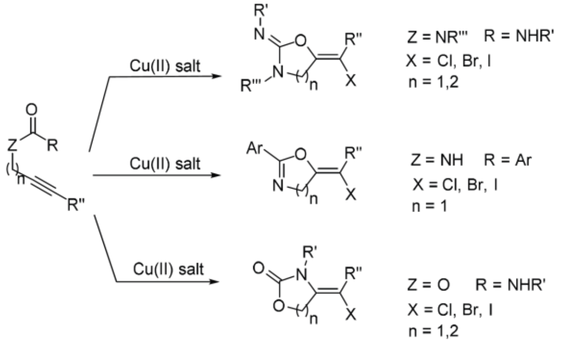

Figure 1.

Although the selected substrates contain a CONH group which can provide either C-N or C-O bonds, totally selective pathways were observed, depending solely on the type of substrates. The target were achieved working with stoichiometric or catalytic copper(II)-salts, in the latter case combined with N-halosuccinimide.

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Poster 19

Synthesis and Characterization of New Ruthenium(II) Arene Acylpyrazolone Complexes

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Arene ruthenium(II) complexes have been widely studied in the recent years, and their chemistry has been extensively studied for arenes such as benzene and para-cymene. They have found applications in catalysis, supramolecular assemblies, molecular devices.[1] Moreover, they have shown antiviral, antibiotic and anticancer activities.[2]

Recently, mononuclear Ru-acylpyrazolone complexes have been shown to exhibit interesting *in vitro* activity in some cancer cells.[3]

On the basis of the our previous work,[4] we extend our investigation to the interaction of several acylpyrazolones ligands with (arene)ruthenium(II)dichloride acceptors and PTA (1,3,5-triaza-7-phosphaadamantane)(Figure 1). Their structures have been confirmed by analytical and spectral data. X-ray diffraction studies and their biological activity are under investigation.

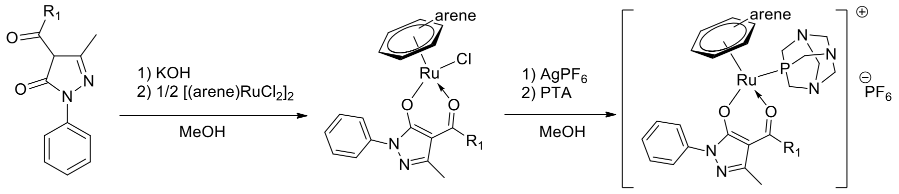

Figure 1.

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Poster 20

The Influence of Structure of Dialkylindium Alkoxides and Aryloxides on its Reactivity Towards N-Heterocyclic Carbenes (NHC).

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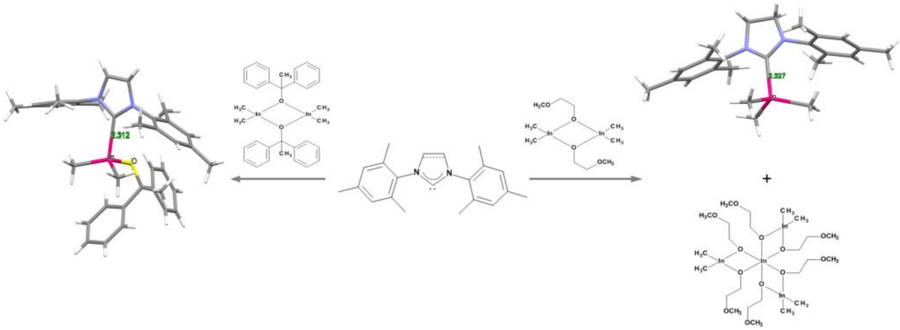
Despite the fact that transition-metal complexes with N-heterocyclic carbenes (NHC) have been widely used as catalysts in many different areas of chemistry, there are much fewer reports on main-group-metal complexes with NHC[1,2]. As a part of our research, we have demonstrated that monomeric complexes $Me_2Ga(NHC)(OR)$ - a products of reactions of $[Me_2GaOR]_2$ with NHC, are formed by breaking the Ga_2O_2 bridges followed by formation of strong Ga-C_{NHC} bond. Such compounds are able to polymerize racemic lactide (*rac*-LA) in controlled and stereoselective manner leading to isotactic polylactide (PLA)[3,4]. Therefore, we have been interested in synthesis, structure and catalytic activity of indium analogues. We have shown that there is a significant difference in reactivity of $[Me_2InOR]_2$ towards NHC, which can result in either disproportionation reaction leading to $Me_3In(NHC)$ and $Me_6In_4(OR)_6$, or the formation of $Me_2In(NHC)(OR)$ complexes (Scheme 1). On the basis of the X-ray structures and NMR spectra I am going to focus on the influence of alkoxide and aryloxide groups on the bridging In_2O_2 bonds and relate it to the reactivity of $[Me_2InOR]_2$ towards NHC.



Scheme 1.

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Poster 21

Sensitising NMR: Developing Magnetisation Transfer Catalysis

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Novel bidentate iridium carbene complexes have been synthesised, characterised and shown to be effective catalyst precursors for the hyperpolarisation of heterocycles. Hyperpolarisation is the method that changes insensitive NMR into a highly sensitive technique.[1] The Signal Amplification By Reversible Exchange (SABRE)[2] process involves the catalytic transfer of magnetisation from *para*hydrogen (p-H_2) to a substrate at low magnetic field. The best performing catalysts to date are charged species that consequently fail to deliver good activity in non-polar solvents.

This research set out to address this, by synthesising novel neutral iridium complexes, **1** and **2**, and analysing their subsequent reactions with p-H_2 and substrate (**Errore. L'origine riferimento non è stata trovata.**). Both species efficiently enhance the NMR signals of tested substrates, in non-polar and polar solvents. Intermediate alkene dihydride complexes were observed at low temperature and the mechanism of exchange has been extensively studied.[3] The active catalytic species, **3**, was found to be solvent dependent, with the Ir-O bond being stable in DCM but cleaved in methanol. For **4** this was not the case.[3] Both active complexes undergo substrate and H_2 exchange thus enabling them to act as SABRE catalysts. This study provides insight into the design of effective homogeneous catalysts for magnetisation transfer.

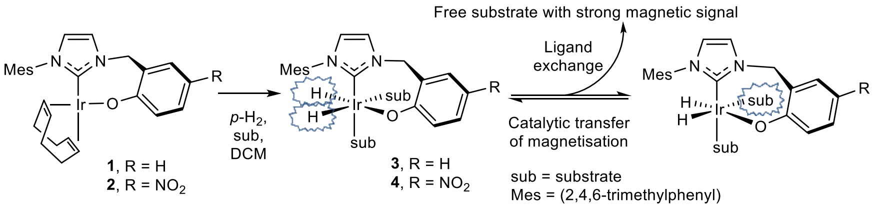

Figure 1.

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Poster 22

Easy-to-Synthesise, Robust, Organo-Osmium Asymmetric Transfer Hydrogenation Catalysts

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Asymmetric transfer hydrogenation (ATH) is an important process in organic synthesis for which the Noyori-type Ru^{II} catalysts [(arene)Ru(Tsdiamine)] are well established and widely used.[1] We demonstrate for the first time the catalytic activity of the osmium analogues.[2] X-ray crystal structures of the 16 electron Os^{II} catalysts are almost identical to those of Ru^{II}.[3] The Os^{II} catalysts are readily synthesised and exhibit excellent enantioselectivity in ATH reactions (Figure 1).[1] The complexes exhibit moderate antiproliferative activity in cancer cells, which can be further enhanced by the co-administration of sodium formate.

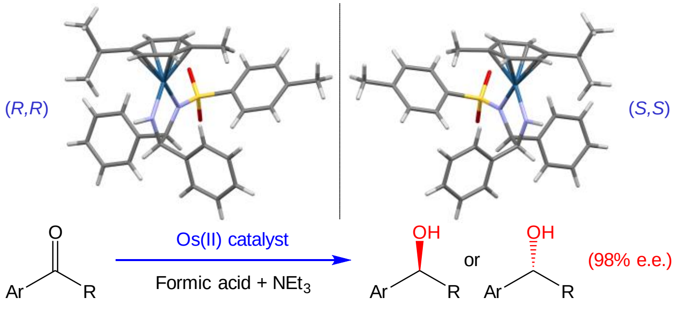

Figure 1.

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Poster 23

Poly(4-Vinylpyridine) Wrapped Carbon Nanotubes: an Efficient Supporting System for the Heterogenization of Methyltrioxorhenium

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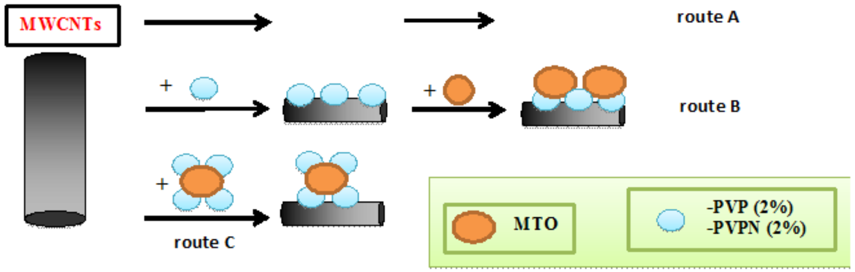
Carbon nanotubes (CNTs) are well explored quasi one-dimensional nanostructured materials that are characterized by unique electronic, mechanical and structural properties. Thus far, CNTs have been proven to have great potential, among other, in material sciences and medicinal chemistry. In addition, CNTs are chemically stable in many media, present a high surface area and can undergo chemical functionalizations thus rendering them potentially very useful for catalytic ends.[1]

Taking into account these aspects and following our ongoing interest in developing new reliable, inexpensive and easily preparable supports for the heterogenization of methyltrioxorhenium (MTO),[2] we decide to study, as an example, the behavior of new supporting systems obtained by simple grinding of pristine CNTs and polymers as poly(4-vinylpyridine)[3] (PVP) and poly(4-vinylpyridine) *N*-oxide (PVPN) (Scheme, route B). Different strategies based on direct loading of MTO or of preformed MTO/PVP or MTO/PVPN adducts on pristine CNTs, have been also explored (Scheme, routes A and C).

Herein, the preliminary results we have obtained in the use of these new heterogeneous catalysts for the selective oxidation of organic substrates, in the presence of H_2O_2 as main oxidant, will be showed.



Scheme 1.

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Poster 24

Encapsulated rhodium catalysts for asymmetric hydroformylation

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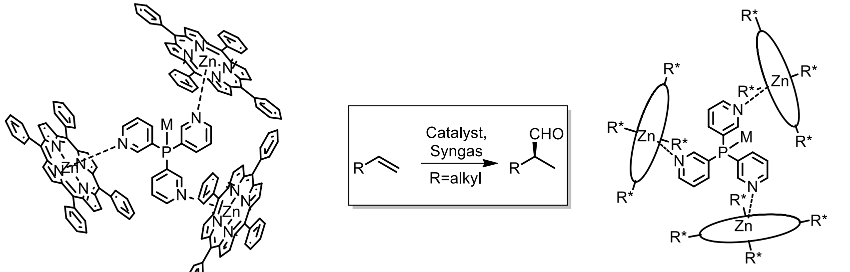
Hydroformylation is one of the largest homogeneously catalyzed processes.[1] Because many side products can be formed under catalytic conditions, controlling selectivity is of key importance. The hydroformylation of unfunctionalized alkenes traditionally leads to the selective formation of the linear product. Previous research in our group led to the discovery of a supramolecular assembly capable of 1-octene hydroformylation with the branched product as the major product[2] (**[1]**), even at elevated temperatures.[3,4] The selectively formed branched product in these reactions contains a stereogenic carbon atom, allowing for enantioselective hydroformylation, generating high value chiral aldehydes form cheap starting material. An efficient and widely applicable method for the asymmetric hydroformylation of unfunctionalized alkenes has not been found.



[1]

target complex

The goal of this research is to create a chiral supramolecular assembly for the asymmetric hydroformylation of unfunctionalized alkenes. In this work we explored chiral analogues of our previous successful supramolecular assembly by applying chiral porphyrin building blocks. Characterization and catalytic studies of the chiral supramolecular assemblies will be discussed

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Poster 25

Dioxidomolybdenum(VI) Complexes of α-Amino Acids

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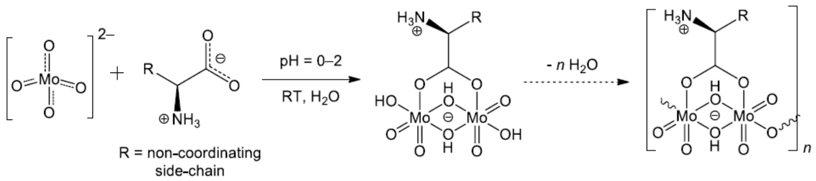
The Molybdenum(VI)/α-amino acid system has aroused interest for the implications associated with the biochemical roles of its components as well as for the possibility to obtain potential catalysts for environmentally friendly stereoselective reactions.[1]

Studies on the interaction between molybdates and α-amino acids in water have been mostly devoted to α- amino acids with a polar or ionisable side-chain and only in few cases a well-defined product has been isolated in the solid state.[2]

On the other hand, the interaction between Mo(VI) and α-amino acids with a non-polar side chain has been much less investigated in solution, although solid products have been isolated from highly acidic media (pH = 0-2).[3,4] The exploration of this piece of chemistry holds an important drawback: in general, the products are insoluble materials whose crystallographic characterization still remains a hard, not achieved task. As a matter of fact, only limited and often controversial spectroscopic data have been reported so far, therefore the Mo-oxido scaffold and the amino acid coordination mode have not been clearly elucidated.

In the light of this preface, we investigated the reactions of $Na_2MoO_4 \cdot 2H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ with a selection of α-amino acids in acidic aqueous solution and carried out a detailed solid state characterization of the isolated Mo(VI) complexes.[4] The combination of IR and NMR data and DFT calculations has allowed the unprecedented structural identification of the dinuclear core and of the κ(O,O′) bidentate bridging coordination mode of the α-ammonium acidate ligand. The formation of coordination polymers presumably occurs by condensation reactions.



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Poster 26

Photophysical Properties of Zn-Porphyrin Complexes Decorated with an Easily Accessible Anchoring Ligand

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Since their discovery, porphyrins have played an important role in the organic and organo-metallic chemistry. They have been studied as dyes in energy production devices, like dye sensitized solar cells (DSSC),[1] or as organic ligands for metallo-complexes in photosynthetic systems, inspired by natural light harvesting complexes.[2] Carboxylic groups are usually used for anchoring dyes on to semiconductor surface.[3] Here we present the results of the photophysical studies for two different Zn-porphyrin complexes synthetized starting from a new, versatile porphyrin ligand. (Fig 1)

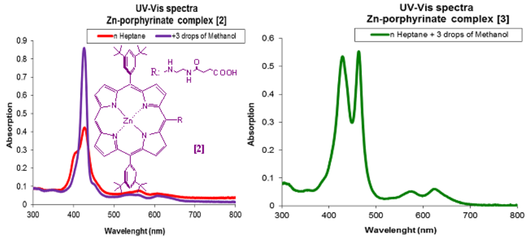

Figure 1. UV-Vis spectra for the two Zn-complexes [2] and [3].

Zn-porphyrinate complex [2] shows self-assembly in non-coordinating solvents like *n*-heptane and can be easily functionalized exploiting the porphyrin free *meso* position and the carboxylic group at the end of the linear chain. These aspects make it a potential and versatile building block for supramolecular architectures.

Zn-porphyrinate complex [3] presents a wider wavelength range for light absorption than Zn-complex [2]. Furthermore its generation occurs in very soft experimental conditions and doesn’t require metallic catalysts [like Ag (I)] usually employed to promote the *meso-meso* coupling reaction between metallo-porphyrins.[4]

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Poster 27

Cage Controlled Catalysis through Co-Encapsulation of Catalyst and Substrate

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Nature arrives at high selectivities and activities in enzymatic transformations by confining the active site in a bulky protein structure. Due to the complexity of proteins, simpler, synthetically more accessible cage analogues have been studied to ultimately achieve higher activity and selectivity in known catalytic transformations. Our group has previously concluded that the co-encapsulation of substrate and catalyst within synthetic cages or the template-ligand approach are two of the potential strategies for nature-inspired catalysis in confined spaces (see figure below).[1] In this study we explore the co-encapsulation of various guests and catalysts within synthetic cages, to evaluate the potential of this approach using this specific type of cage compounds. We evaluate the concept of co-encapsulation within synthetic M_4L_6 capsules designed by the group of Nitschke.[2-4] Larger porphyrin-edged capsules designed by the same group are currently also being explored.[5]

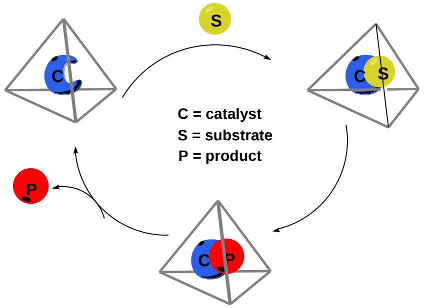

Figure 1.

This poster will present the recent results of the co-encapsulation of different transition metal complexes, ligands and substrates within cationic tetrahedral capsules constructed of bis-bidentate pyridyl-imine based ligands coordinated to iron(II) vertices. Spectroscopic data confirming the encapsulation of various guests within the synthetic cages will be demonstrated. Preliminary results on the activity of encapsulated species in catalytic transformations will be discussed as well.

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Poster 28

Synthesis and Functionalization via Direct Lithiation of α-Aryl-substituted Tetrahydropyrans

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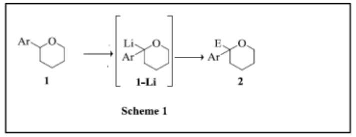
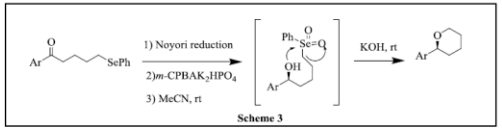
Many biologically active and widely distributed natural products contain a tetrahydropyran moiety. The tetrahydropyran core is, indeed, a useful "building block" not only in organic chemistry, but also in biological and medicinal chemistry.[1] Building on our recent successful -lithiation-electrofilic interception protocols applied to phenyloxetane[2] and phenyltetrahydrofuran[3] derivatives, we have now extended the result of such an investigation to the preparation of 2,2-disubstituted tetrahydrofurans **2** starting from the parent - arylated precursors **1** (Scheme 1). The synthesis of racemic **3**, starting α-aryl-substituted tetrahydropyrans has been accomplished exploiting a one-pot strategy, under microwave conditions, which involves a preliminary Heck cross-coupling reaction followed by an hydrogenation procedure (Scheme 2). On the other hand, the preparation of the corresponding optically active substrates was based on a selenium–mediated cyclization starting from δ-phenylseleno ketones (Scheme 3).[2] In this communication, the influence of the solvent and the temperature, and the nature of the organolithium employed, on the effectiveness of such a direct -functionalization of these oxygenated heterocycles will be discussed as well as the chemical and configurational stability of the putative anion **1-Li** (Scheme 2).

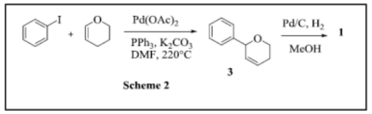


1 1-Li 2

Scheme 1



Scheme 3



3

Scheme 2

Acknowledgements: This work was finantially supported by the Interuniversities Consortium C.I.N.M.P.I.S, and by the University of Bary.

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Poster 29

Aminoethyl Glycine Peptide Nucleic Acids (*aeg*-PNA): the Study of their Interaction with DNA by Means of Stopped Flow Technique

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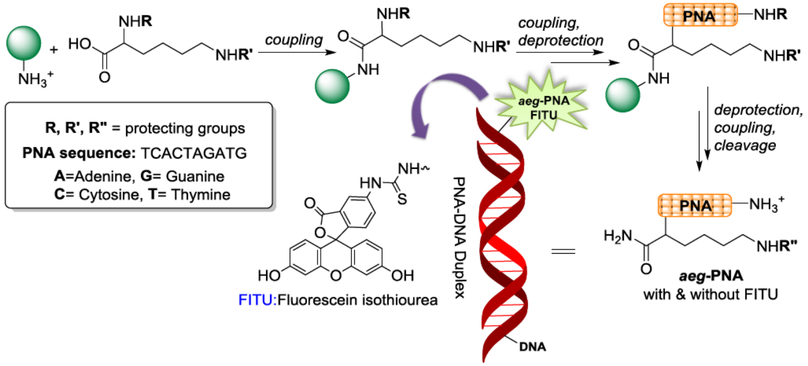
Stopped-flow technique is useful for studying fast reactions that have half-lives as short as a few milliseconds.[1] This technique has never been used to study the interaction between Peptide Nucleic Acids (PNA) and DNA strands in the formation of hybrids. PNAs are mimics of DNA, in which the entire sugar-phosphate backbone has been replaced by a peptide amide bond backbone composed of *N*-(2-aminoethyl) glycine subunits. PNAs show unique properties that set them apart from other traditional DNA analogues.[2] Normally the affinity of PNA for DNA is detected by using melting temperature[3] but sometimes this technique is not appropriate, especially if PNA contain some thermal sensitive functional groups. So, we have started an innovative study of PNA-DNA interaction by using stopped-flow technique and for this we have synthesised the PNA sequences reported in Scheme 1.



Scheme 1. Synthesis of *aeg*PNA decamers.

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Poster 30

Epoxidation Reactions in a Self-Assembled Molecular Cage

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Both in industry and academia obtaining high activity and selectivity is required for applied catalysts. Although many highly active and selective catalysts have been reported to date, many reactions still suffer from low activity, selectivity or even both. As in nature's catalysts, enzymes, applying a second coordination sphere could supply the solution for these challenging reactions.[1] In our research we investigated the use of a self-assembled molecular cage to improve the catalytic performance of various catalysts.

The cubic M_8L_6 cage depicted in figure 1 has been shown to be suitable for the encapsulation of pyridine functionalized porphyrins.[2] The Zn-porphyrin planes of this cubic cage can be used to selectively coordinate catalysts containing a pyridine moiety. Recently we reported the possibility to perform size-selective catalysis within the confinement of this molecular cage with encapsulated cobalt porphyrins.[3]

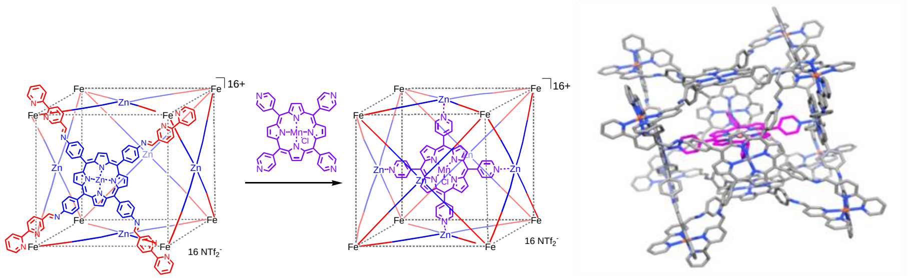

Figure 1.

The main degradation pathways for manganese porphyrin catalysts in oxidation reactions are bimetallic. Therefore we envisioned that encapsulation of a manganese catalyst would improve the lifetime and therefore the activity of the catalyst. In this poster we will disclose the results of our research towards improving the catalytic activity of a manganese porphyrin by encapsulation in a molecular cage. Secondly a cage induced substrate selectivity will be discussed.

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Poster 31

Microwave-Assisted Transesterification and Hydroformylation of Natural Oils: a Sustainable Approach for Transformation of *Calophyllum inophyllum* into Value-Added Products

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The use of renewable resources in the manufacturing of value-added products is one of the great challenges for the chemical researchers of this decade.[1] The direct use of vegetable oils and animal fats as combustible fuels is not a suitable alternative to fossil fuel oils due to their high viscosity and low volatility. However the transesterification reaction of natural oils allows the reduction of these drawbacks and therefore it has been commonly used for the production of biodiesel, including the use of catalysts based on renewable sources.[2] Furthermore, the transition metal catalyzed hydroformylation reaction constitute an efficient process to promote the reduction of high olefin content in an one-step transformation of natural unsaturated fatty esters into the corresponding aldehydes, or derivatives, thereby increasing their economic value. Recently, the use of microwave (MW) irradiation to promote transesterification reactions of natural oils has attracted the attention of several researchers due to the demands for the development of more energetically friendly processes.[2,3] In this work we describe an eco-friendly approach for the transesterification of *Calophyllum inophyllum* seeds oil, based in the use of heterogeneous catalysts obtained from renewable sources under microwave irradiation, followed by hydroformylation of the resultant long chain methyl esters.

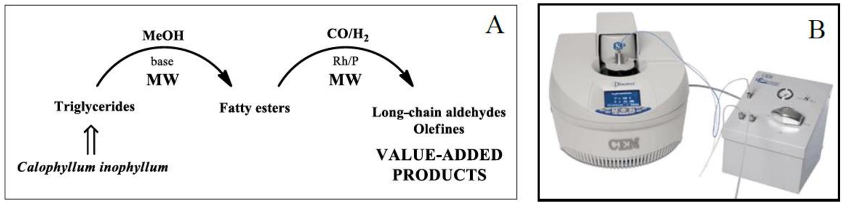

Figure 1. (A) Microwave assisted reactions of natural oils; (B) CEM Discover® SP microwave synthesizer connected to a syngas addition system.

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Poster 32

Role of Electron Transfer Processes in the *N*-demethylation of *N,N* dimethylanilines and *S*-Oxidation of Aromatic Sulfides Promoted by the Nonheme Iron Complex [Fe^{II}(N4Py)](OTf)$_2$

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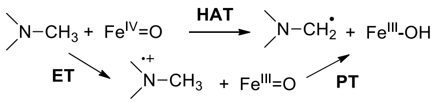
The role of electron transfer processes has been investigated in two of the most important reactions promoted by nonheme iron(II) complexes, namely the *N*-demethylation of *N,N*-dimethylanilines and *S*-Oxidation of Aromatic Sulfides. In the oxidative *N*-demethylation of *N,N*-dimethylanilines promoted by nonheme iron(IV)-oxo species, a mechanistic dichotomy between a direct hydrogen atom transfer and a sequential electron transfer/proton transfer mechanism (ET/PT) can be envisaged (Scheme 1).[1,2]



Scheme 1.

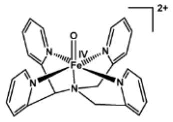
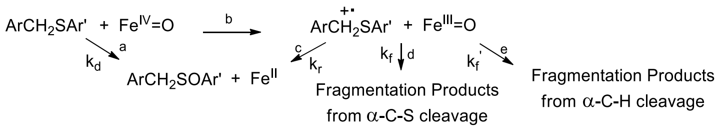


Figure 1

We have investigated the kinetic isotope effects profiles in the *N*-demethylation of a series of 4-X-*N,N*-dimethylanilines promoted by [Fe^{IV}(O)(N4Py)]$^{2+}$(Figure 1). The results obtained are in agreement with the ET/PT mechanism in which the deprotonation of the anilinium radical cation represents the rate determining step. The bell shaped KDIE$_{intra}$ *vs.* p*K*a anilinium radical cation profile observed, allowed us to estimate the p*K*a value of [Fe^{III}(OH)(N4Py)]$^{2+}$. In the oxidation of aromatic sulfides to sulfoxides catalyzed by nonheme iron(IV) oxo complex, two mechanisms are possible: direct oxygen atom transfer (Scheme 2, path a) and a sequential electron transfer/oxygen transfer mechanism (Scheme 2, path b-c).[3] Using aryl diphenylmethyl sulfides whose radical cations are characterized by high fragmentation rate constants, we found that the formation of the sulfoxide is accompanied by products deriving from the α-C-S and α-C-H bond cleavage in the radical cation (Scheme 2, path d,e) thus supporting the occurrence of the ET-oxygen rebound mechanism.



Scheme 2.

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Poster 33

Synthesis of Arylated 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.

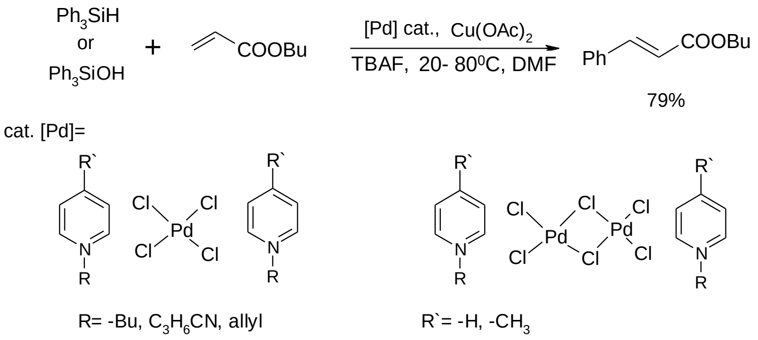

Figure 1. Reaction of organosilanes with olefins catalyzed by anionic palladium complexes.

In this work we present a new way leading to arylated olefins, based on a cross-coupling triphenylsilane and triphenylsilanol with different olefins catalyzed by anionic palladium(II) complexes (Fig.1).[2] The reaction was studied with variation of parameters such as different oxidants (e.g. copper salts, oxygen, AgF), salts, time and solvents. Studies shown a positive effect of the presence of pyridinium cations on the catalytic activity of palladium complex. Also effect of the temperatures on the selectivity of the reaction have been observed.

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Poster 34

Development of simple and mild hydroamination reaction catalyzed by NHC-gold complexes

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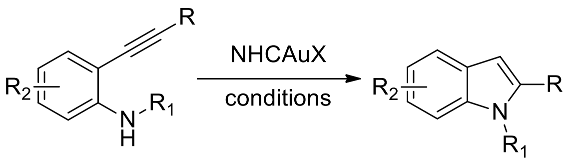
An hydroamination reaction of 2-alkynylanilines as substrates is potentially an important transformation. It can give rise to indole derivatives amenable to further interesting synthetic manipulations en route to natural products and some analogues.[1-2]

However, there are only few reports describing the hydroamination which have been published to date.[3-5] Various sources of catalysts, including palladium, platinum, as well as copper were used in heterocyclizations, and relatively drastic conditions were systematically employed.[6-8] Thus, the development of an efficient and general catalytic approach for these reactions is highly desirable.

The project is devoted to the development of the simple and mild method for synthesis of indoles. Preliminary results establishing the feasibility of the approach will be presented. (**Scheme 1**)



Scheme 1.

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Poster 35

Switching Selectivity of Gold Catalysts by Encapsulation in a Self-Assembled Cage

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Supramolecular catalysis is inspired by enzymes, which show very high activities and selectivities by using a confined space around their active center. This principle can be mimicked by encapsulation of transition metal complexes in a synthetic capsule.[1] In this research project, a self-assembled hexameric resorcin[4]arene cage is employed (Figure 1), which can encapsulate the gold carbene complex IPr-Au-OTf.[2]

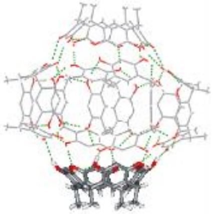

Figure 1. A self-assembled hexameric resorcin[4]arene cage.[2]

In the current contribution we use encapsulation as a way to completely switch the selectivity of dinuclear gold catalysts[3]. Outside the capsule, the complex exists as a dimer that is able to catalyze dimerization of the substrate[4] (Figure 2). However, the dinuclear complex is too large to be encapsulated, so inside the cage it exists as a monomeric species. As the monomeric and dimeric complexes have a completely different selectivity, the product distribution of the reaction reverses upon encapsulation.

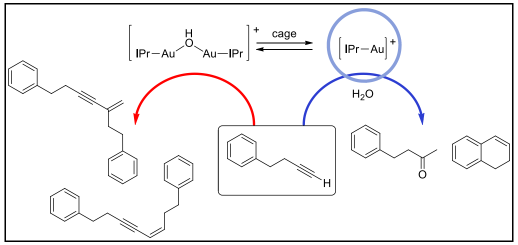

Figure 2. The cage completely changes the selectivity of the gold catalyst.

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Poster 36

Mono- and Multinuclear Organometallic Rhodium and Ferrocenyl Quinolines as Potential Antiparasitic Agents

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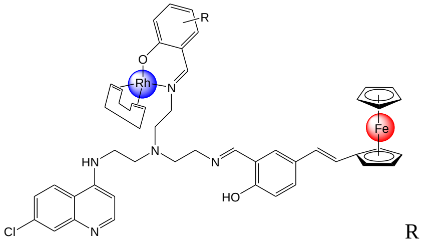
One of the most frequent occurring infectious diseases worldwide is malaria. The World Health Organization (WHO) reported approximately 198 million cases of malaria in 2013.[1] One of the most successful antimalarial drugs, chloroquine (CQ), has been rendered almost useless due to the occurrence of drug resistance.[2] Currently, artemisinin-based combination therapy is the main treatment for malaria, but resistance in some parts of the world has recently been documented.[3] Ferroquine (FQ), a ferrocene-containing derivative of CQ, shows better activity than its parent compound, CQ.[4] Based on the success of this metal-based drug, interest has been generated towards using metal complexes for the treatment of parasitic diseases. This prompted investigation of the antiparasitic activity of mononuclear and dinuclear organometallic complexes of chloroquine (Figure 1). It is believed that increasing the number of active moieties positively influences biological activity.[5] This study investigated the effect of incorporating polyamine scaffolds, multinuclearity as well as lipophilicity on antiparasitic activity.



R = 5-Cl, 3-OMe, H

Figure 1.

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Poster 37

Multi-Component Assemblies of tris(2-pyridylmethyl)amine Ligands, Metals and Amino Acids for Chiroptical Sensing

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Stereodynamic optical probes own generally a molecular fragment present in two enantiomeric forms which in presence of an analite give rise to a preferential diasteroisomer able to furnish an optical readout.[1] Recently we reported about a new molecular probe used for the reliable determination of the enantiomeric excess of free amino acids.[2] Herein we report the use of new metals and the measurement of the induced circular dichroism of the resulting multicomponent assembly. The study highlight the complex equilibria present in solution for the formation of the assembly and the specie responsible of the CD signal(Figure 1).

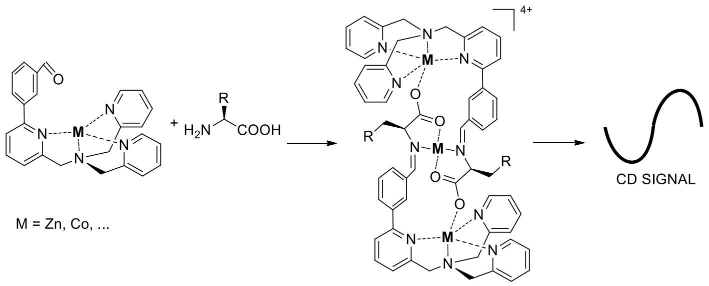

Figure 1.

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Poster 38

Cooperative Coordination and Ionic Interactions Assisted *E*/*Z* Isomerization of Arylhydrazone of Ethyl 2-Cyanoacetate in Complexation with Copper(II)

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The *E*/*Z* isomerization around the double bond in organic molecules recently attracted considerable attention, mainly in view of their use as catalysts, sensors, gels, liquid crystals, molecular switches, etc.[1-3] For instance, controllable *E*/*Z* isomerisation around the C=N double bond in hydrazones, what makes them good candidates for the construction of molecular switches, electronics, rotors and similar nanomachines.[1,2] All reported *E*/*Z* isomerizations in hydrazones are regulated by pH, coordination-coupled proton transfer, resonance-assisted hydrogen bonding [X···H−Y ↔ Y···H−X (X, Y = N, O, S, etc.), RAHB] or its cooperation with ionic interactions, auxiliary ligand or solvation.[1-4] Here we report a new cooperative coordination and ionic interactions assisted *E*,*Z* → *E* or *E*,*Z* → *Z* isomerization of (*E*/*Z*)-4-(2-(1-cyano-2-ethoxy-2-oxoethylidene)hydrazinyl)-3-hydroxybenzoic acid (**H_3L**), which occurs upon interaction with Cu^{II} in different reaction conditions (Scheme). Aquasoluble [$Cu_2(X)_2(\mu\text{-}HL)_2$], X = CH_3OH (**1**), $(CH_3)_2NCHO$ (**2**) and [$Cu(en)_2HL$]·CH_3OH·H_2O (**3**) Cu^{II} complexes were isolated by reaction of Cu^{II} nitrate hydrate with the H_3L, in the presence (for **3**) or absence (for **1** and **2**) of ethylenediamine (en), and were characterized by elemental analysis, IR spectroscopy and X-ray single crystal diffraction.

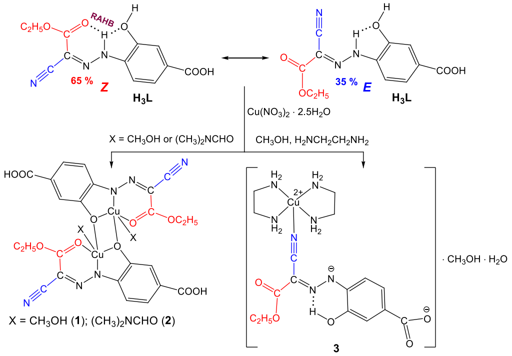

Figure 1. *E*/*Z* isomerization of H_3L in the synthesis of **1**–**3**.

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Poster 39

Synthesis and Biological Evaluations of Novel Arene Ru(II) Complexes of 4-acyl-5-pyrazolone-based Hydrazone Ligands

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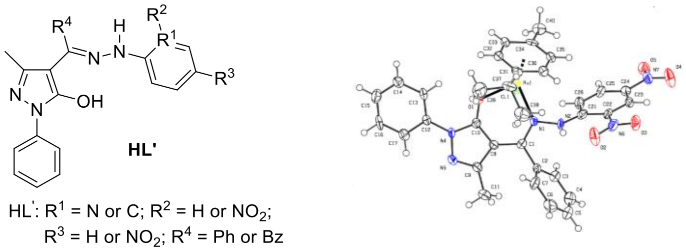
We Hydrazone compounds, bearing –CH=N–NH–C(O)– functional groups, are a special kind of Schiff bases which have extensive biological properties. In fact their chemistry is particularly intriguing due to their capability to easily furnish valuable chemotherapeutics such as anticancer, antibacterial, antifungal and antiprotozoal agents[1] as well as enzyme inhibitors.[2]

As an extension of our research on acylpyrazolone chemistry[3] and relative Ru-arene compounds[4] the present work has the aim to design, synthesize and study the biological properties of new half-sandwich η^6-arene-ruthenium(II) complexes with different 4-acyl-5-pyrazolone-based hydrazone scaffolds with general structure HL' (Figure 1). Preliminary results on DNA *vs* BSA protein binding and on the effect as anti-*Trypanosoma brucei* parasite agents[5] will be reported.



HL': R^1 = N or C; R^2 = H or NO_2;
R^3 = H or NO_2; R^4 = Ph or Bz

Figure 1.

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Poster 40

The bimca-ligand: Synthesis and Application of its Rhodium and Iridium Complexes

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Introduced by Shaw in 1976, pincer-type ligands have become an important ligand class in organometallic chemistry during the last decades.[1] Nearly 15 years ago, they were combined with NHCs either as backbone or side donor moieties. Nowadays a broad range of tridentate mono- or biscarbene ligands are increasingly used in the synthesis of highly active homogenous catalysts.[2] In 2007 we reported the monoanionic bis(imidazolinylidene)carbazolide (bimca) ligand **2a** as anionic pincerligand with two carbene moieties.[3] Since then we established a simplified synthetic access to its precursor **2** and prepared a decent-sized ligand library **2a-g**.[4] The stable lithium and potassium carbene complexes **3,4ag** where synthesized by deprotonation with an appropriate basic precursor and could be characterized by NMR spectroscopy. Further reaction with Rh(I) or Ir(I) carbonyl precursors led to the formation of M(bimca)(CO) complexes (M = Rh, Ir) **5,6a-g,** while after the reaction with precursors such as Vaska's complex or Rh(m-Cl)(cod)]$_2$ also MIII(bimca) complexes were observed.[5,7]

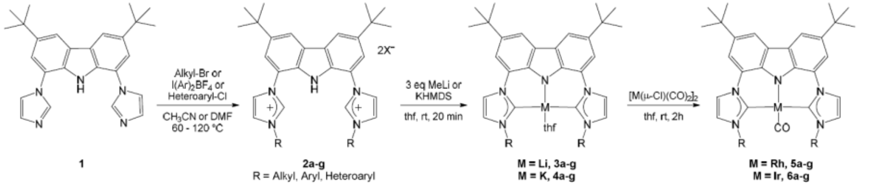

Figure 1.

The Rh(I) and Ir(I) carbonyl complexes **5,6a-g** show a highly nucleophilic reactivity caused by the strong s-donor and weak p-acceptor character of the NHC moieties in addition to the monoanionic carbazolide donor.[3-6] Their nucleophilic character could be applied in different catalytic and stoichiometric reactions. Both complexes show an interesting reactivity towards allyl halides leading to the h1-allyl complexes.[3,5] The Rh(I) complex **3a** shows a high catalytic activity in the *Meinwald* rearrangement of epoxides.[6]

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Poster 41

Borate Carbene Complexes: Synthesis, Reactivity and Biological Evaluation

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Boron containing carbene complexes have never been investigated till now for their possible applications as anticancer drugs.[1] Our research group reported the synthesis of coinage metal-NHC complexes obtained from the precursors {[HB(RImH)$_3$]Br$_2$} (R = Benzyl, Mesityl and t-Butyl)[2] and {[H$_2$B(BnTzH)$_2$]Br}.[3]

Here we present the synthesis of the new ligand {[H$_2$B(*p*NO$_2$BnTzH)$_2$]Br}[3] and the related coinage carbene complexes. The synthesis of this ligand led to the isolation of the byproduct: {[HTz(*p*NO$_2$Bn)$_2$]Br}.[4] This new ligand was also prepared by direct synthesis and used as carbene precursor for the formation of the related Cu(I), Ag(I), and Au(I) mono carbene complexes. Their citotoxicity was evaluated over a panel of human cancerous cell lines and the results are here reported.

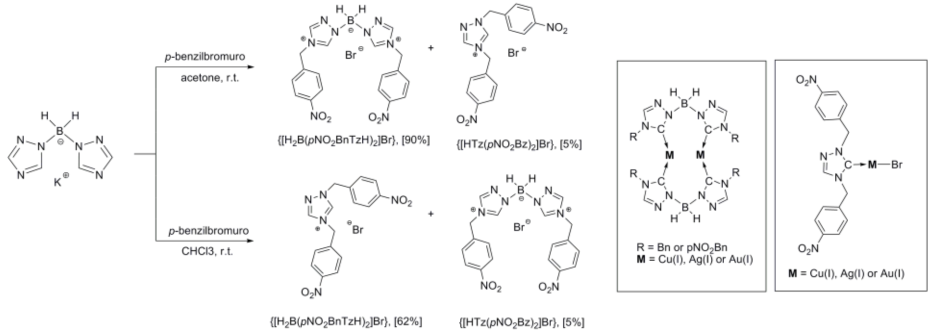

Figure 1.

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Poster 42

Ru(II) and Cu(I) Complexes with Unsymmetrical N-Heterocyclic Carbenes Bearing N-Phenylpyrrole / N-Phenylindole Moiety

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Exceptionally wide range of applications of n-heterocyclic carbenes (Figure 1) as organocatalysts and neutral ligands for transition metals comes from their easily tunable electronic and steric properties.[1] Our group specializes in olefin metathesis catalyzed by Ru(II) complexes with various ligands, including self-designed NHC's.[2] Recently we developed class of ruthenium catalysts with new, unsymmetricaly substituted (R1, R2 = aryl, benzyl) NHC ligands (figure 2).[3,4] Poster presentation will concern synthesis of their analogues bearing N-phenylpyrrole and N-phenylindole moieties, which were used in preparation of ruthenium(II) and copper(I) complexes.

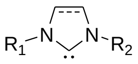
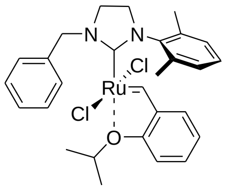


Figure 1.



Ablialimov et. al., 2014

Figure 2.

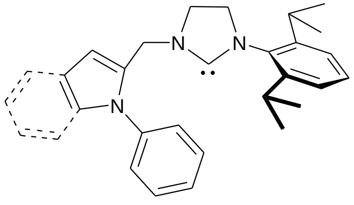


Figure 3.

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Poster 43

Ruthenium(II)-arene RAPTA Type Complexes Bearing Dibenzoylmethane: Organometallic Chemistry and Biological Activity

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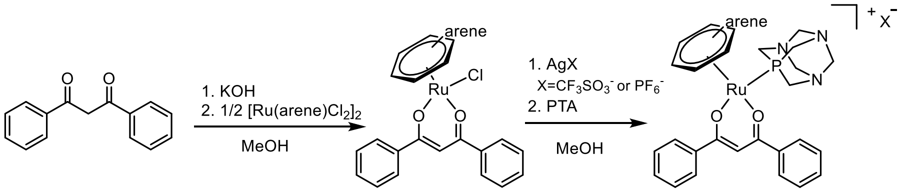
Half-sandwich η^6-arene-ruthenium(II) complexes represent a very important class of organometallic compounds which have been extensively studied and appropriately modified to obtain compounds with various biological properties.[1]

Dibenzoylmethane is a natural β-diketone that occurs in small amount in licorice roots. It exhibits several biological features such as activity against ischemic diseases[2] and different types of tumours.[3]

On the basis of our previous research on Ru(II)-arene complexes with acylpirazolones[4] and curcuminoids[5], in the present work we report the synthesis and the characterization of a series of arene-Ruthenium(II) (arene = *p*-cymene, hexamethylbenzene or benzene) complexes containing dibenzoylmethane and the ionic derivatives with PTA (1,3,5-triaza-7-phosphaadamantane) (Scheme 1).

Preliminary results on their biochemical studies and their antitumor activity evaluated *in vitro* in U266 and RPMI human multiple myeloma cell lines will also be reported.



Scheme 1.

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Poster 44

Syntheses of Ni and Au-N-Heterocyclic Carbene (NHC) Complexes and Their Catalytic Evaluation for C≡N and C≡C Activation

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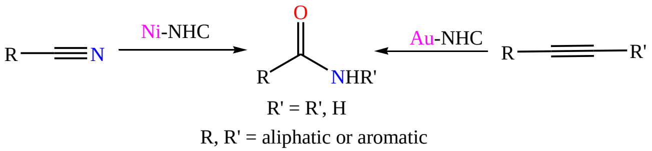
The search for new atom-economical and green synthetic methods for the synthesis of functionalized important molecules has fascinated much attention owing to their potential industrial, medicinal and biological value.[1] Towards this goal new nickel and gold NHC complexes are synthesized and employed for amide synthesis by nitrile hydration and alkyne nitrogenation. Although a number of methods are known for the synthesis of amides, preparation under neutral conditions and without generating any waste is a challenging goal.[2] Nickel-NHC complex is very effective for hydration of nitriles under base free condition. Alkynes are successfully converted to amides by Au-NHC complex (Scheme 1). Industrially important acrylamide and antitubercular agent pyrazinamide are achieved in single step without producing any side product. Mechanisms of nitrile and alkyne activation will be discussed.



R' = R', H
R, R' = aliphatic or aromatic

Scheme 1. Amide synthesis by Ni-NHC or Au-NHC catalyst.

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Poster 45

Photocatalytic water oxidation with iridium catalysts under visible light

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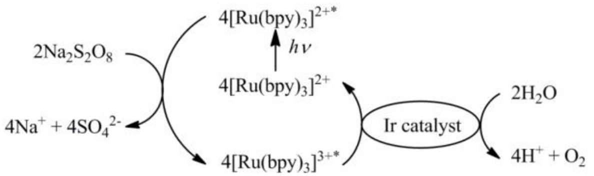
The realization of an efficient apparatus for artificial photosynthesis, aimed at producing solar fuels, is strongly hampered by the difficulty of oxidizing water. Although several iridium complexes have demonstrated to be competent catalysts for water oxidation driven by chemical sacrificial oxidants,[1-6] such as cerium ammonium nitrate (CAN) or sodium periodate ($NaIO_4$), in only one case their photocatalytic activity has been documented.[7] The classical protocol to explore possible photocatalytic activity stems on combining $[Ru(bpy)_3]^{2+}$ as a photosensitizer and $[S_2O_8]^{2-}$ as an electron acceptor as illustrated below.[8-9]



Scheme 1. Representation of a photoactivated cycle for water oxidation.

In this contribution, we report the results of a systematic study aimed at developing highly active molecular iridium photocatalysts and possibly correlating structure/performance using only the $[Ru(bpy)_3]^{2+}/[S_2O_8]^{2-}$ system. Generally speaking, all catalysts were found to be active and O_2 evolution occurred immediately after irradiation of the solution. Chemical and quantum yields varied in the ranges of 35-89%, based on the consumption of persulfate, and 7–22%, respectively, depending on the nature of ancillary ligands bonded at iridium.

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Poster 46

Tripodal Aminophenolate Iron(III) Complexes with Potential Biological Activity

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The quest for cancer metallodrugs with improved pharmacological properties and different mechanisms of action than those of platinum drugs goes on. A possible approach to regulate the cytotoxic responses of metallodrugs is using biologically essential transition metals, such as iron, that plays an important role in many cellular processes. Iron, being redox active is involved in the regulation of cell-growth and differentiation.

Iron(III)-complexes of phenolate ligands with tripodal amines have attracted interest as mimics of enzyme active sites. The tetradentate ligands provide a reasonable analogue to histidine and tyrosinate coordination.[1] Substituents at the phenolate rings as well as the position and nature of the donor atoms are easily tunable features.[2] The introduction of a NN aromatic heterocyclic ligand in the coordination sphere could enforce the biological activity, as metal complexes containing phenanthroline derivatives are reported to be active against various pathologic conditions including cancer, microbial, and fungal infections.[3] A wide array of electronic features and redox potentials are thus available, which can direct synthetic strategies towards attaining complexes with optimal performance. Tripodal aminophenolate iron(III) complexes have a well-developed chemistry, however their application as therapeutics for cancer is still an underdeveloped area of research open for further exploration. We report here the synthesis and preliminary studies on a family of iron(III) complexes composed of a [N,N-bis(2-hydroxy-3,5-dimethylbenzyl)-N-(2-pyridylmethyl)amine] ligand and different substituted phenanthrolines.

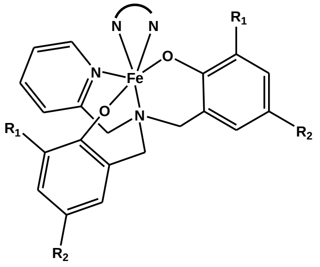

Figure 1.

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Poster 47

Different Generations of Fluorescent PAMAM Dendrimers for Biomedical Applications

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The versatility of polyamidoamine (PAMAM) dendrimers has been demonstrated over these last years with applications in different areas, such as in the biomedical field[1] and, especially, as nanoplatforms for drug/gene delivery and bioimaging. However, these dendrimers are characterized by a weak intrinsic fluorescence which limits their application.[1] Even if fluorescence can be achieved by conjugation oflabeling of fluorescent molecules (e.g. using fluorescein) with the peripheral functional groups of the dendrimer, the intrinsic fluorescent behavior of dendrimers can be further explored, being strongly influenced by the dendritic structure and/or the functional groups at the surface.[1-4] With the aim of exploring the fluorescence of dendrimers, in this work, generations 3 (G3) and 4 (G4) of amine-terminated PAMAM dendrimers were treated with ammonium persulfate (APS). The resulting compounds were characterized by different techniques, namely by Nuclear Magnetic Resonance, Ultraviolet-Visible, Fluorescence and Infrared Spectroscopies. Compounds presented a very intense fluorescence and absorption compared to pure PAMAM dendrimers. Particularly, solutions of the APS-treated dendrimer G3 and G4, when irradiated at 366nm, displayed an intense blue color luminescence (Figure 1). Additionally, preliminary results of the effect of different pHs over the intrinsic fluorescence and the stability of the APS treated dendrimers will be presented and discussed.

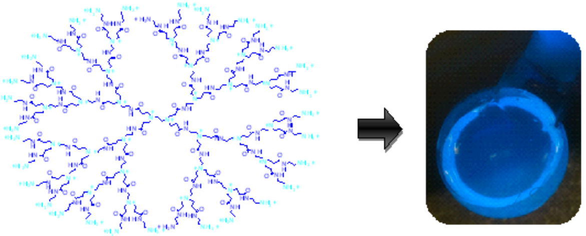

Figure 1. PAMAM G3.NH_2 dendrimer after oxidative treatment a) chemical structure b) irradiated under UV at 366nm.

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Poster 48

Rational Improvement of Molecular Olefin Polymerization Catalysts

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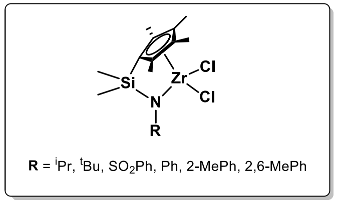
The first challenge in polymer science is the controlled synthesis of macromolecules. In the case of polymers obtained by coordination catalysis, and specifically polyolefins, it is generally possible to tune polymer architecture and microstructure by modifying steric and (to some extent) electronic catalyst properties,[1] but this is still largely achieved by trial-and-error.

In this context, computational chemistry is mainly used to *interpret* – more than *predict* – structure/activity correlations. In the framework of a broader project on molecular design applications in polyolefin catalysis, we are currently investigating the factors which determine molar mass distributions of polymers produced with molecular catalysts, with special focus on electronic effects. A new computational strategy for *rational* average molar mass predictions is proposed. The approach is based on a detailed analysis of local minima "connected" to relevant transition states, and should represent a powerful tool to evaluate the balance between chain propagation and transfer by means of Density Functional Theory (DFT) calculations running in High Throughput Computation (HTC) mode.

To validate / benchmark it, we chose the industrially important class of Constrained Geometry Catalysts (CGC, Figure 1).[2] A number of precatalysts with different ligand substitution patterns have been synthesized, and their catalytic properties are being determined with High Throughput Experimentation (HTE) methods. The thus-obtained experimental database is being compared with the corresponding theoretical one. The first results of our study will be presented here.



CGC(R)$ZrCl_2$

Figure 1. Constrained Geometry Catalysts

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Poster 49

Modulation of the HCOOH / CO Ratio through the Use of Various Brønsted Acids for the Electroreduction of CO_2 Using $[Mn(bpy\text{-}R)(CO)_3Br]$-Type Catalysts

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An efficient transformation of carbon dioxide into higher energy carbon products would make a remarkable impact on global economy, as an environmentally friendly decrease of the CO_2 content in the atmosphere could be coupled with a sustainable approach to gain useful chemicals (e.g. CO, HCOOH and CH_3OH).[1] In recent years, scientific research has primarily directed towards the discovery of new efficient organometallic molecular catalysts, containing abundant and cheap transition metals like Mn[2] and Group VI transition metals.[3]

Taking inspiration from Saveant's[4] work where in the Fe(III) porphyrins, availability of local proton sources is known to greatly enhance the selectivity and the redox catalytic activity for CO_2 reduction to CO, we designed some tricarbonyl Manganese coordination compounds containing polypyridyl ligands[5], $[Mn(bpy\text{-}R)(CO)_3Br]$ (bpy-R = 4-phenyl-6-(1,3-dihydroxybenzen-2-yl) 2,2'-bipyridine **(1)** and 4-phenyl-6-(1,3-dimethoxybenzen-2-yl) 2,2'-bipyridine **(2)**). Our studies showed that the electrochemical of a novel polypyridyl Mn(I) catalyst containing two acidic OH groups in proximity of the purported metal binding site for CO_2 redox catalysis is reported. **1** showed a substantial catalytic activity in anhydrous media induced by the presence of a local proton source. The electrochemical data for **1** highlighted two crucial issues: (1) CV exhibited a strong catalytic effect on the current of the $1^-/2^-$ reduction when the solution was saturated with CO_2, so that the $2e^-$ pathway was supposed to be favoured for **1**. This represents the first reported experimental evidence of an intramolecular proton-assisted catalytic process for a Mn(I) catalyst. (2) Bulk electrolysis at the end of the catalytic plateau (1.8 V) under CO_2 showed an unusual change in selectivity for CO2 reduction by the Mn(I) catalyst, giving a mixture of CO and HCOOH. The catalytic mechanism is under investigation by techniques of IR spectroelectrochemistry and DFT calculations.

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Poster 50

Synthesis of Diketopyrrolo[3,4-*c*]pyrrole -Based Derivatives for Organic Electronics

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Stereoselective In recent years, diketopyrrolo[3,4-*c*]pyrrole (DPP) moiety has been widely used as a building block in the synthesis of a variety of organic semiconductor materials for device applications, particularly for organic thin film transistors (OTFTs) and organic photovoltaics (OPVs).[1] Among all, the thiophene-functionalized DPP moiety TDPP has attracted extensive attention because of its unique properties arising from strong intramolecular charge transfer and good π-π stacking of the resulting conjugating units. A strong influence on these properties is also due to N-substituents of the lactam rings as well as the side chains on conjugate backbone. Recently, interesting materials for applications in organic electronics have been obtained by introduction of hydrophilic oligoether chains as stack-inducing agents on the TDPP units. More relevant, aromatic end-groups appended to the central TDPP core of symmetrically substituted small molecules, typically introduced by cross-coupling reactions,[2] strongly impact on the efficiency of these molecules in BHJ devices. We report the synthesis of new TDPP-based molecular semiconductors in which 1,2,3-triazole rings are conjugated to the central TDPP core (Figure1). The 1,2,3-triazoles are aromatic heterocycles whit high stability which are capable of active participation in hydrogen bonding as well as dipole-dipole and π-π stacking interactions.[3] A variable number of hydrophilic oligoether chains were introduced on the innovative conjugate backbone in order to achieve compounds with a tailored solubility in environmental friendly polar solvents, such as alcohols or water, potentially useful for green OPV or biological applications.

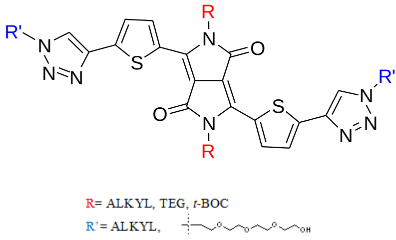

Figure 1.

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Poster 51

Revisiting Ammonium Formate: Chemoselective Transfer Hydrogenation of Aldehydes Catalyzed by Ruthenium Pincer Complexes

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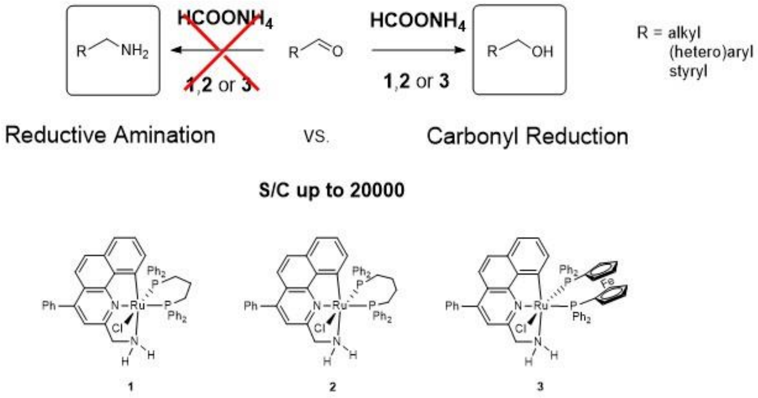
Bis(pyrazolyl)alkanes Ammonium formate (AF) is a cheap, readily accessible and versatile reagent which has been largely employed across a wide range of organic transformations.[1] In the last decade AF has been successfully used in transition-metal-catalyzed reduction processes, particularly in the reductive amination of ketones,[2] given its dual nature of both hydrogen and ammonia donor. Amongst late transition metal compounds, ruthenium complexes have emerged as very productive catalysts for hydrogenative reactions of carbonyl substrates.[3] We have recently studied the catalytic properties of RuCl(CNN^{Ph})(PP) complexes **1**-**3** in the transfer hydrogenation of aldehydes using 2-propanol as hydrogen source.[4] Then we extended the application of RuCl(CNN^{Ph})(PP) compounds in catalytic hydrogenative reactions mediated by different hydrogen sources and we report here the unprecedented use of AF in the chemoselective and highly productive reduction of commercial-grade aldehydes to their corresponding primary alcohols catalyzed by ruthenium pincer complexes **1**-**3**.



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Poster 52

DNA, BSA Binding and Cytotoxic Properties of Iron(III) Complex Bearing Formazan Ligands

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Cytotoxicity of most of the metal complexes has been mainly correlated with their ability to bind and damage DNA or protein.[1] Among them, as alternative to platinum-based drugs, iron(III) complexes have emerged as one of the leading players in this field.[2] However, DNA and protein interacting studies as well as cytotoxic properties of water soluble iron(III) complexes derived from formazan ligands have not yet been reported. Herein we report the synthesis of the Fe^{III} complex [Fe(κN^3-HL^2)$_2$] (**1**) that was isolated by treatment of iron(III) chloride hexahydrate with the new (1*E*,1*E*)-N',2-di(1*H*-1,2,4-triazol-3-yl)diazenecarbohydrazonoyl cyanide (**H$_3$L**), and characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. The interaction of calf thymus DNA (CT DNA) and bovine serum albumin (BSA protein) with complex **1** has been investigated by absorption, fluorescence spectroscopic and viscosity measurement techniques. The observed intrinsic DNA binding constant (1.98(±0.26) × 10^{5}M^{-1}), number of binding sites ($s \leq 1$) of complexes to DNA and viscosity data suggest groove binding and/or a partial intercalative mode of binding to CT DNA. Complex **1** shows good binding propensity to the BSA, giving K_{BSA} values of 1.06(±0.08) × 10^6 M^{-1}. Complex **1** was evaluated for its *in vitro* cytotoxic activity against the human cervical (HeLa) and breast (MCF-7) cancer cell lines as well as noncancer breast epithelial (MCF-10a) cell lines. The results showed that **1** mediates a more strong cytotoxic response to the tested cancer cell lines than normal ones.

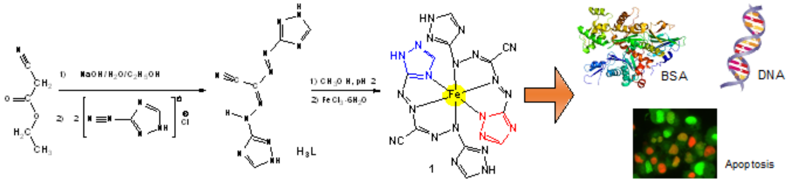

Figure 1. Synthesis of a new Fe^{III} complex with heterocyclic formazan (1) which shows DNA, BSA binding and anticancer abilities.

Acknowledgements: This work has been partially supported by the FCT, Portugal (UID/QUI/00100/2013). N.M.R.M and S.A. are thankful to FCT for the PhD (SFRH/BD/52371/2013) and post-doc fellowship (SFRH/BPD/76451/2011). R.R. is thankful to the CSIR-SRF, India. The authors acknowledge the Portuguese NMR Network (IST-UTL Centre) for access to the NMR facility, and the IST Node of the Portuguese Network of mass-spectrometry for the ESI-MS measurements.

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Poster 53

Novel Hoveyda Type Metathesis Catalysts Bearing Sterically Hindered, Unsymmetrical NHC Ligand

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In 2000 A. Hoveyda developed a new type of olefin metathesis ruthenium catalyst, commonly refered as Hoveyda-Grubbs catalyst. Since than a lot of structure modifications based on this motif were made.[1]

However finding an ideal catalyst that is both active and stable is still a challenge. One of the most promising modifications is the change in NHC ligand. Our group follows that trend and focuses on synthesizing and modifying those types of ligands.[2]

We synthetized a variaty of new Hoveyda type complexes possessing bulky unsymmetrical N-heterocyclic carbene (NHC) (fig.1). Those complexes are potentially interesting in cross methathesis reaction, especially when one of the olefins is ethylene. During the presentation the synthesis and reactivity of the new complexes will be discussed.

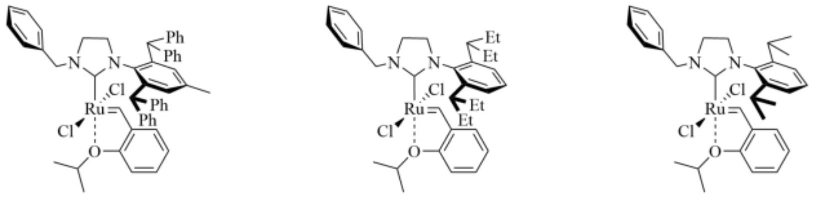

Figure 1.

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Poster 54

Comparing the Catalytic Activity of Cp*Ir Catalysts with bpy and dpa: Insights into the Mechanism of Water Oxidation Driven by CAN

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The rapid depletion of fossil fuels asks for the utilization of alternative and sustainable energy sources. Among them, the sunlight has attracted great attention especially as for the realization of a photosynthetic apparatus aimed at producing solar fuels, exploiting the electrons coming from the catalytic oxidation of water to O_2[1]. Unfortunately, the performances of water oxidation catalysts (WOCs) reported in the literature[2], are far from those required for real applications.

Cp*Ir complexes (Cp* = 1,2,3,4,5-pentamethylciclopentadiene) are highly active and robust WOCs and their performances can be easily tuned by the choice of the ancillary ligand. Herein we report the study of the catalytic behavior of $[Cp^*Ir(dpa)Cl_2]$ (dpa = 2,2’ dipyridilamine) (**1**) using CAN (cerium ammonium nitrate) as sacrificial oxidant. The performances of **1** were strictly compared to those of its analogous $[Cp^*Ir(bpy)Cl_2]$ (**2**) previously reported by us[3,4]. The presence of the –NH bridge substantially increases the activity of **1** (up to 6 times) if compared to that of **2**; this led us to carry on deeper kinetic studies, in order to rationalize such difference. Those studies shed some new insights on the reaction mechanism of water oxidation driven by CAN in general. Indeed, they clearly showed that CAN is consumed before the oxygen evolution starts (Figure 1), thus suggesting a mechanism proceeding through the formation of an intermediate species that maintains the oxidative power of Ce^{4+} or traps the preformed O_2. We believe that such a mechanism might be quite general, since similar results were observed for other molecular catalysts and also for IrO_2.

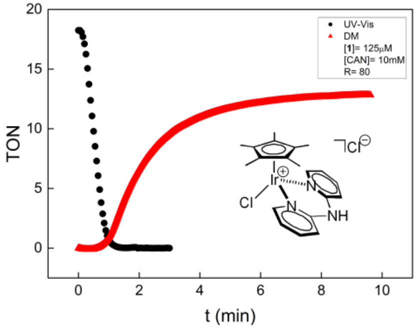

Figure 1.

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Poster 55

Silylated and Germylated Pyrazoleboronic Acids: Synthesis and Characterization

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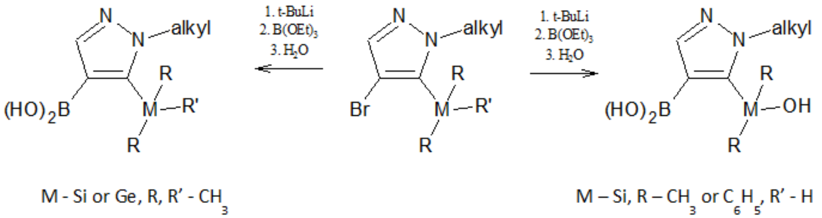
Cross-coupling reactions of organoboron compounds discovered by A. Suzuki are important in various fields of organic synthesis and combinatorial chemistry. Among a relatively wide assortment of available aryl- and heteroarylboronic acids used for Suzuki reaction, the derivatives of pyrazole are still rare species. On the other hand, the pyrazole fragment is present in a large number of natural and synthetic small ligands that interact with various enzymes and receptors of pharmacological significance.

5-Membered nitrogen-containing heteroaromatics (azoles) can often be functionalized efficiently by lithiation of different ring positions and exocyclic α-position. In this work reactions of many 4-bromopyrazole derivatives with LDA were investigated. Obtained lithium derivatives were reacted with various electrophiles as: Chlorotrimethylgermane, Chlorotrimethylsilane or Chlorodimethylsilane to form the corresponding substituted compounds. These products were treated as intermediates for the following reactions with t-BuLi where the bromine was substituted (or not) with lithium. Those which underwent exchange reaction were reacted with $B(OEt)_3$ and hydrolyzed to form finally the corresponding boronic acids.

The structure of diboronic acids was studied using multinuclear NMR spectroscopy and elemental analysis. The crystalline derivatives obtained were suitable for X-ray measurements.



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Poster 56

High Performance Isocyanide Scavengers for Use in Low-Waste Purification of Olefin Metathesis Products

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In recent years, more attention is focused on tackling the problem of metal contamination as early as possible in the synthetic pipeline.[1] Possible approaches include heterogeneous catalysis, self-scavenging catalysts, and the use of metal scavengers.[2] Recently, we reported an olefin metathesis catalyst with quaternary ammonium groups in its NHC ligand, which could be easily removed from the solution by filtration through a short plug of silica gel or extraction.[3]

In this work three isocyanides (**I-III**) containing tertiary nitrogen atoms and between one and three isocyanide groups were used as metal scavengers (Figure 1).[4] These compounds prove to be highly effective at removing ruthenium residues from post-reaction mixtures, in many cases reducing the ruthenium content below 0.0015 ppm and requiring short binding times and low stoichiometric excesses. Finally, we report on the synergy between the scavenger **II** and one of the previously reported self-scavenging catalysts, which allows one to obtain highly pure products even in highly challenging cases. Additionally, isocyanide **II** is shown to be a quenching agent for olefin metathesis, superior to commonly used ethyl vinyl ether.

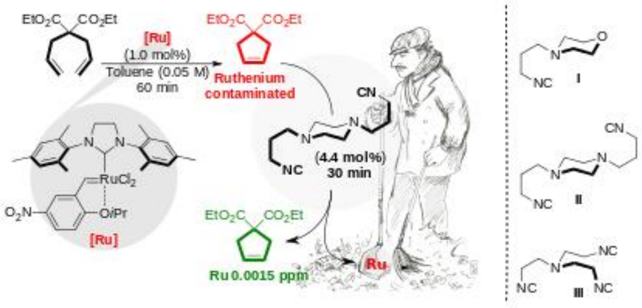

Figure 1

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Poster 57

Synthesis of Thiophene Derivatives in DES

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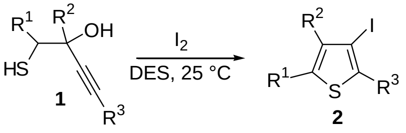
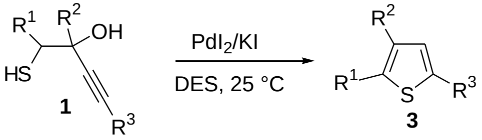
Deep eutectic solvents (DESs), which can be defined as molecular complexes typically formed between a simple halide salt (i.e. choline chloride) and a hydrogen bond donor, have found a wide variety of applications in different fields of modern chemistry, including organic synthesis, biocatalytic reactions, dissolution of metal oxides, electrodeposition of metals, and materials chemistry. However the number of studies reporting the ability of DESs to serve as green and biorenewable reaction media in metal-catalysed organic reactions is still scarce and no examples of iodocyclization reactions in DESs are reported in literature.

We report here the first example of iodocyclisation reaction in DES. Readily available 1-mercapto-3-yn-2-ols **1** are converted into the corresponding 3-iodothiophenes **2** under base-free conditions, at room temperature and in Choline Chloride/Glycerol (1*ChCl*/2*Gly*) such as solvent (eq.1). Products **2** are obtained in good yields (60-79%) and the DES can be recycled different times without lost of activity.



(1)

Starting from 1-mercapto-3-yn-2-ols **1** we have also obtained thiophenes **3** by PdI_2-catalyzed heterocyclization reaction (eq. 2). The reaction is carried out under air, at room temperature and in 1*ChCl*/2*Gl*y such as solvent. Thiophenes **3** are formed in good to high yields (63-81%) and with the possibility to recycle DES-catalyst system several times without affecting the reaction.



(2)

Poster 58

Manganese(II) Complexes with Pyrazole Ligands: Synthesis and Oxidative Catalysis

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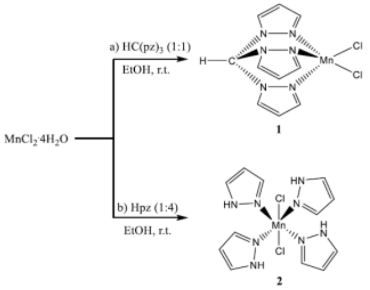
Oxidation reactions catalyzed by transition metal complexes are quantitatively the most important homogeneously catalyzed reactions in chemical industry. The use of metallic complexes with C homoscorpionate poly(pyrazol-1-yl)methane ligands as oxidation catalysts is experiencing significant development, mainly due to their coordinative versatility that allows the electronic and steric features at a metal center to be tuned.[1,2] Herein we report the design of manganese(II) complexes containing the C-homoscorpionate tris(pyrazol-1-yl)methane ligand, $HC(pz)_3$ (pz = pyrazolyl), or pyrazole (Hpz), formed by the reactions depicted in Scheme 1, for application as catalysts for the partial oxidation of saturated hydrocarbons, a field of great interest due to the considerable inertness of the substrates. The effects of some catalytic parameters on the oxidation reactions are also discussed.



Scheme 1.

Acknowledgements: This work has been partially supported by the Foundation for Science and Technology (FCT), Portugal (UID/QUI/00100/2013 and UID/MULTI/00612/2013). Tiago A.G. Duarte is thankful to FCT for his PhD fellowship (PD/BD/105993/2014). The authors acknowledge the Portuguese NMR Network (IST-UTL Centre) for access to the NMR facility, and the IST Node of the Portuguese Network of mass-spectrometry for the ESI-MS measurements

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Poster 59

Straightforward assembly of bis(benzoxaborole) systems from 2-formylphenylboronic acids

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Benzoxaboroles are cyclic, internal hemiesters of phenylboronic acids. These organoboron compounds have found wide applications, ranging from medicine and biological chemistry to materials chemistry and organic synthesis.[1,2] Due to a growing interest in diversely functionalized benzoxaboroles, novel and effective methods for their preparation are highly desirable.

The developed methodology enables a straightforward and efficient synthesis of piperazine-based bis(benzoxaboroles) (Figure 1).[3,4] The method originates from the studies on the reactivity of 2-formylphenylboronic acid towards secondary amines.[5] Herein, the product is formed spontaneously in ethereal solution *via* dehydrative amination of 2-formylphenylboronic acid (or its derivative) with piperazine.

Interestingly, bis(benzoxaborole) **1** was found to have considerable biological activity, being an effective antifungal agent.[6]

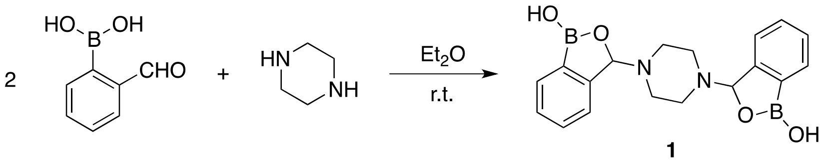

Figure 1.

Acknowledgements: Krzysztof M. Borys acknowledges the Ministry of Science and Higher Education of Poland for financial support within the "Diamentowy Grant" program (grant no. DI 2012 015042 (0150/DIA/2013/42)), as well as the 10th ISOC Organizing Committee for the conference grant.

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Poster 60

Heck arylation of allyl alcohol catalyzed by palladium compounds

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Palladium-catalyzed Heck reaction with allylic alcohols as substrates is interesting because it generates variety of arylated ketones or aldehydes as products. β-Aryl ketones, products of this type Heck reaction can be used for the synthesis of medicinal products, for example 4-phenyl-2-butanones (enzymatic inhibitors).[1] Product A (3-phenylpropionaldehyde) might have synergize effect with trans-cinnamaldehyde for antibacterial and anti-inflammatory effects on H. pylori infection.[2]

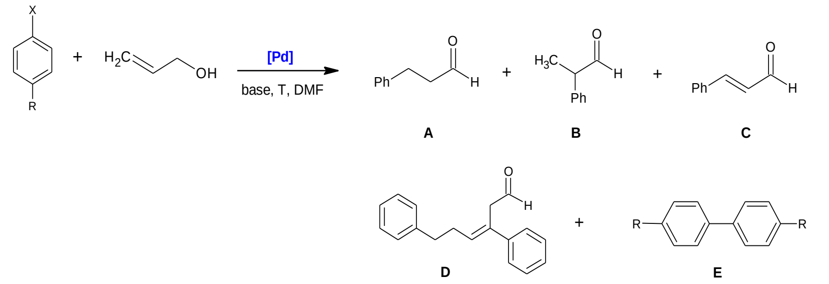

Figure 1. Heck arylation of allyl alcohol catalyzed by palladium catalyst.

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^{o}C - 130^{o}C), time (1.5 h – 24 h) and addition of molten salts (TBAB). We have obtained aldehydes A and B as the main products and they were isolated using extraction and column chromatography on silica gel. The best system for iodobenzene contained NaOAc as base. In 85^{o}C, after 1.5 h, we obtained 79% product A, 13 % B and 2% C. The presence of salt (TBAB) increased yield (49%) of the main product (A) when PhBr was used as aryl halide. We received product A with the yield 48-79% in reaction with para-substituted aryl iodides and the best result were 79% for 4-Iodoanisole and 71% for 4-Iodophenol.

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Poster 61

Formic Acid as an Alternative Hydrogen Source in Ruthenium Catalyzed Transfer Hydrogenation of Olefins

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Catalytic olefin metathesis, as one of the most important methodologies of C-C double bond formation, does not need a particular introduction. Furthermore ruthenium alkylidene complexes were found not only as a great olefin metathesis catalysts[1] but they are well known in literature as active catalysts of numerous non-metathetic reactions.[2]

During our recent study on application of a new nitronate ruthenium complex **1** in olefin metathesis, we have noticed its unexpected non-metathetic activity. Depending on the conditions applied, the same complex promoted efficiently olefin metathesis, cycloisomerization, reduction of a carbonyl group, as well as isomerization of a C-C double bond.[3]

The interesting further results confirmed that complex **1** can also catalyze metathesis and transfer hydrogenation in one-pot sequence without isolation of the metathesis product. Moreover we proved that in this conditions many commercially available ruthenium alkylidene complexes (like **Gru-II**) can catalyze metathesis and transfer hydrogenation sequence or transfer hydrogenation depending on used substrate (**Figure 1**). Methodology was tested on several olefins and more interesting results appeared. The methodology that was developed in our group allows for selective hydrogenation in mild conditions using formic acid instead of dangerous hydrogen gas and does not cleave the benzyl groups.[4]

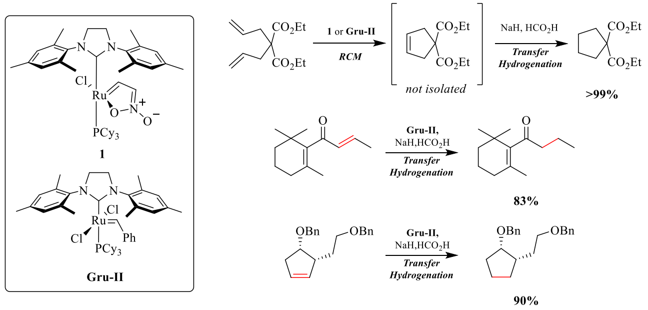

Figure 1.

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Poster 62

CO_2 Reduction to Methanol and Methylamines Using Formic Acid as a C–H Bond Shuttle

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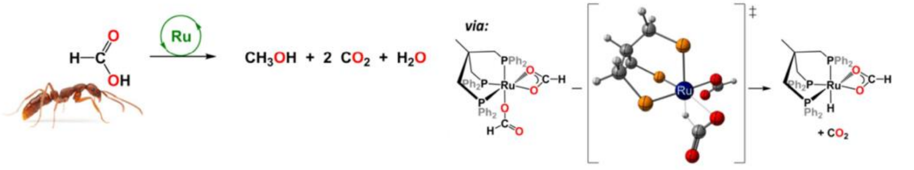
Efficient conversion of CO_2 to methanol is a key process to reach a methanol economy, based on a closed carbon cycle.[1] Such goal could be achieved by the 6-electron reduction of CO_2 or its hydrogenation to methanol. However both solutions currently suffer from low faradaic efficiencies. An interesting alternative would consist in utilizing formic acid (FA) as a C–H bond shuttle in the reduction of CO2 to methanol. This strategy relies on the 2–electron reduction of CO2 to FA, in an electrochemical cell, and this methodology is now technically and economically available, thanks to efficient electrocatalysts.[2] Disproportionation of FA is then required to produce methanol. Miller *et al.* showed, for the first time in 2013, that a molecular complex could promote the disproportionation of FA to methanol.3 Though promising, this strategy currently suffers from the use of expensive iridium catalysts and the yields of methanol do not exceed 1.9 %.[3] We reported the efficient disproportionation of FA to methanol, with methanol yields of up to 50.2 %, using ruthenium molecular catalysts. Different pathways involving transient ruthenium–hydride species have been unveiled, based on mechanistic experimental and DFT investigations.[4]



The utilization of formic acid as a C-H bond shuttle in the conversion of CO_2 can also be extended to the synthesis of fine chemicals. In this respect, the use of CO_2 as a carbon source for the methylamine has been recently unveiled and this methodology requires the use of external reductants such as hydrosilanes and molecular hydrogen.[5] To circumvent the use of additional reductants, we have recently demonstrated that formic acid could be used as the unique source of carbon and hydrogen in the catalytic methylation of amines.[6]

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Poster 63

Zn(II) Homogeneous Supported Catalysts for the Efficient Esterification and Transesterifcation of Vegetable Oils

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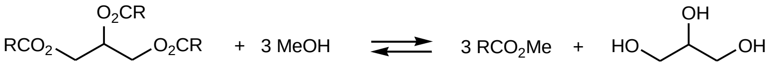
Biodiesel, a mixture of fatty acid alkyl esters produced from vegetable oils (FAME), is a viable alternative to fossil fuels. It is conveniently obtained through simultaneous esterification and transesterification of vegetable oils with high acidity, such as frying oil residues or waste oil of other productions.[1]



$$RCO_2H + MeOH \rightleftharpoons RCO_2Me + H_2O$$

At industrial level, this process is typically promoted by alkaline catalysts, and one of the limits of this approach is their inevitable neutralization because of the acidity of the system. Therefore, the attention has been focused on catalysts Lewis acids, capable of promoting simultaneously the two reactions. However, it has been found that the use of these catalysts in homogeneous phase gives rise to problems related to their corrosive action, which makes the manufacture more complex. A solution to this drawback can derive from their heterogenization, which in addition to eliminate these problems, could favour separation and recycling. In this sense, an often winning strategy is the anchoring on solid supports of traditional homogeneous catalysts, according to the principles of so-called homogeneous supported catalysis.[2] In the light of these considerations, this study has selected as the most promising candidates complexes of Zn(II) which have nitrogen bidentate ligands with a functional group that allows to carry out the anchoring to a solid matrix (as SiO_2). The study of the supported complex **1** in the reaction of esterification and transesterification of a variety of oils, both neutral and with different contents of acidity, has revealed that the catalyst is active and can be recycled several times by simple decantation from the reaction mixture.

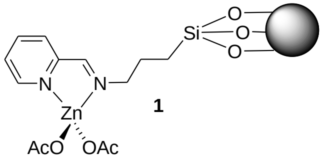


Figure 1.

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Poster 64

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

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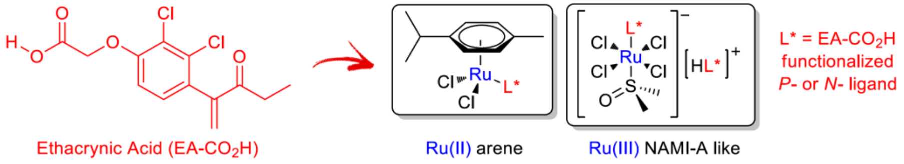
Decades of intensive research established the potential of some families of ruthenium compounds as anticancer agents. Thus, (LH)[trans-RuIIICl4LL'] complexes, *i.e.* KP1019 (L = L' = κ*N*-Indazole) and NAMI-A (L = κ*N*-Imidazole, L' = κ*S*-DMSO), are actually in later stages of clinical trials while several Ru(II)-arene complexes resulted to be very promising in pre-clinical trials.[1,2] Metal complexes can be endowed with higher anticancer selectivity and effectiveness by incorporating, as ligands, organic fragments with complementary biological activity. Following a recent approach,[3] we prepared new *P*- and *N*-donor ligands modified with Ethacrynic acid (EA-CO2H). Ethacrynic acid, a diuretic in clinical use, is a potent inhibitor of Glutathione-*S*-Transferases (GSTs), a class of metabolic enzymes that are overexpressed in many tumors. GST enzymes are not only implicated in the development of drug resistance but also contribute to cancer progression via inhibition of programmed cell death.

In the present study, we synthesized novel EA-modified pyridine- and triphenylphosphine-based ligands, which were then used for the preparation of Ru(II)-*p*-cymene and Ru(III) NAMI-A type complexes. Ligands and complexes were fully characterized by analytical and spectroscopic methods and, in one case, by single-crystal X-ray diffraction. Moreover, some of the compounds underwent *in vitro* tests on ovarian carcinoma cell lines: the obtained results were similar to those previously reported for EA-functionalized Ru complexes.[3]



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Poster 65

Molecular Cages Based on Tris(2-pyridylmethyl)amine Complexes

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Biological and synthetic molecular containers have largely attracted the attention of scientists for their peculiar properties and applications.[1] In particular, supramolecular capsules and cages have offered in recent years the opportunity to draw important guidelines about the interpretation of the confination phenomena. In this communication, we report the formation of a series of new self-assembled cages containing, in the inner part of the cavity, two metals with a coordination site available for binding. We have planned to take the advantage offered by dynamic covalent chemistry (DCC) for the synthesis of molecular cages of opportunely designed *tris*(2-pyridylmethyl)amine **TPy** metal complexes.[2] **TPy** complexes are known to furnish stable species that have been previously used for carboxylic acids recognition.[3] The findings on their molecular recognition properties highlight unprecedented results in the thermodynamic of binding events that have a broad impact in the understanding of the molecular recognition phenomena.

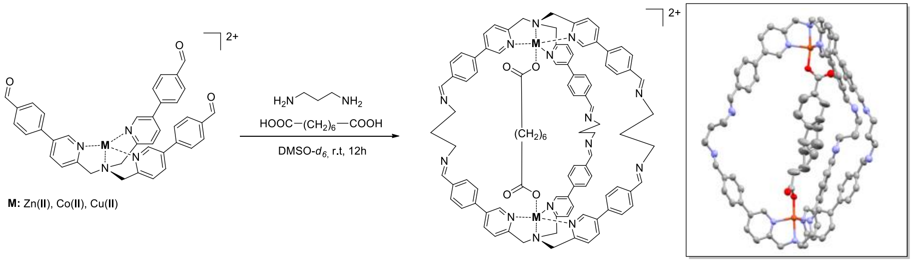

Figure 1. Synthesis and X-ray crystal structure of the tris(2-pyridylmethyl)amine cage.

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Poster 66

Co-Based Heterogeneous Catalysts from Well-Defined Complexes: Synthesis and Applications

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α-Diimines represent a family of nitrogen chelating ligands which found various applications in homogeneous catalysis.[1,2] Here we report the first example of employing these ligands for the synthesis of Co-based supported heterogeneous catalysts starting from their well-defined complexes (Figure 1). The structure of these new materials, elucidated by XRD, XPS, TEM, Raman, TPD and TPR techniques, involves the simultaneous presence of metallic Co and Co oxides nanoparticles in contact with nitrogen-doped graphene (NDGr, derived by the pyrolysis of the nitrogen ligand) in a core-shell structure. These catalysts were successfully applied to the hydrogenation of aromatic nitro compounds. The reaction proceeds with a low catalyst loading (0.5 mol %, 10 mg/mmol) affording substituted anilines in high selectivities and yields. Furthermore, a close correlation with both the amount and the type of nitrogen in the NDGr-based catalytic material was established.[3]

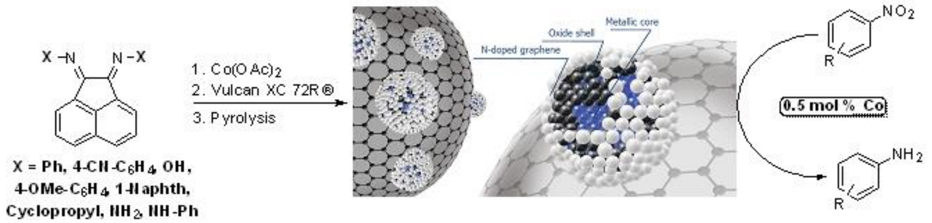

Figure 1.

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Poster 67

A Class of Novel Iron N-Heterocyclic Carbene Complexes for Redox Catalytic Reactions

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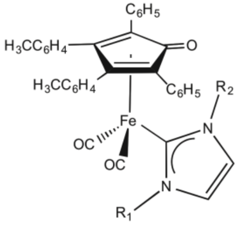
Catalytic hydrogenation and transfer hydrogenation are among the most important reactions in organometallic catalysis. In recent years, cyclopentadienone iron complexes have drawn attention in this field of chemistry due to their air-water stability, availability from cheap starting materials, and unique catalytic features arising from the presence of a non-innocent ligand.[1] Herein, we report the synthesis and characterization of new carbonyl iron complexes combining different ligands, such as cyclopentadienones and N-heterocyclic carbenes (NHC). The unique features of both ligands have been exploited to obtain new metal-ligand bifunctional catalysts to be employed in hydrogenation and transfer hydrogenation, and to be compared with analogous ruthenium complexes previously investigated. [2]



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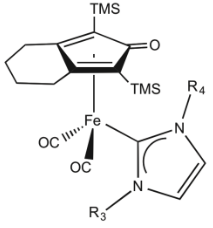

2

1a,2a $R_1=R_2=CH_3$
1b,2b $R_1=R_2=CH_2(C_6H_5)$
1c,2c $R_1=CH_3$, $R_2=(CH_2)_2NH_2$

Carbene coordination occurred through a straightforward transmetallation reaction from the silver carbene intermediate (prepared *in situ* from the corresponding imidazolium salts) to the dicarbonyl acetonitrile iron intermediate (obtained *in situ* from the corresponding triscarbonyl complex) leading to complexes **1** and **2**.

Moreover, a microwaved-assisted method for the synthesis of triscarbonyl precursors has been developed. Microwave conditions resulted in shorter reaction time respect to the reflux reaction, without decreasing the yield.

All the complexes have been characterized by spectroscopy (NMR, IR, ESI-MS) and X-ray studies.

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Poster 68

Ruthenium(0) Cyclopentadienone N-Heterocyclic Carbene Complexes as Transfer Hydrogenation Catalyst: Synthesis and Reactivity

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N-heterocyclic carbenes (NHC) are efficient ancillary ligands due to their strong coordination ability and their tuneable character which allows control of the steric and electronic properties of the metal centre.[1] Herein we report the synthesis, characterization and catalytic application of new carbonyl ruthenium complexes that containing tetraphenylcyclopentadienone and NHC ligands.[2]

The catalytic activity of the imidazolylidenes (**1**) and triazolylidenes (**2**) ruthenium complexes was investigated in homogeneous catalysis: the complexes **1a** (R' = R'' = CH_3), **1b** (R' = Bu, R'' = py) and **2a** were tested as catalyst precursors for hydrogen transfer reactions (Figure 1).

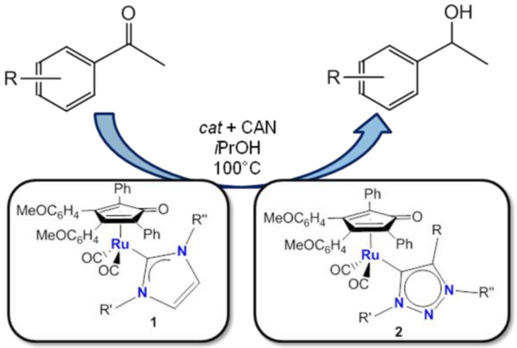

Figure 1.

Transfer hydrogenation of ketones is catalyzed by the ruthenium(0) carbene complexes of type **1** and **2** upon treatment with cerium(IV) ammonium nitrate (CAN) as oxidant.[3] Since the oxidation of the metal center seems to be the key issue for the catalyst activation, a formal oxidation to ruthenium(II) was also obtained by protonation of **1a** and **1b** with trifluoromethanesulfonic acid.

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Poster 69

Catalytic CO_2 Hydroboration with Novel CO_2 Adducts of N/Si+ Frustrated Lewis Pairs

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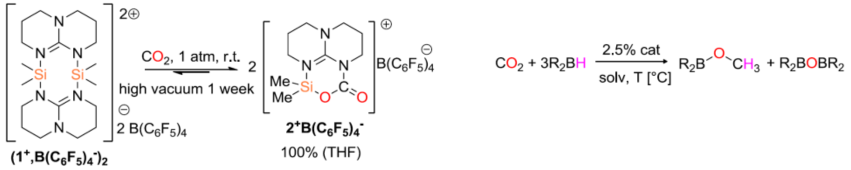
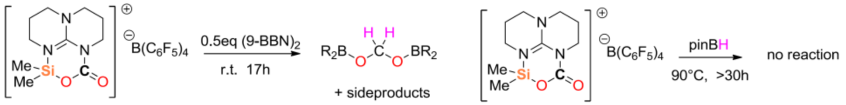
In recent years, cationic +IV silicon species (silyliums) have found application in the design of frustrated Lewis pairs (FLPs) for the activation of small molecules.[1] Highly electrophilic cationic silylium species however are strong σ and π acceptors and tend to undergo unwanted side-reactions (e.g. with solvents). Therefore the use of base-stabilized silyl cations with tunable reactivity is of interest. Although CO_2 inserts readily into N-Si bonds,[2] up today the reactivity of nitrogen/silylium FLPs for the reductive transformation of CO_2 and the activation of other small molecules has not yet been explored.



Scheme 1.

Using a silyl cation stabilized by an intramolecular nitrogen base (Scheme 1), CO_2 can be added to form an isolable N/Si+ FLP-CO_2 adduct. This system was further shown to catalyze the hydroboration of CO_2[3] to methoxyboranes. The influence of the nature of the Si-R groups, as well as the counter-ion on the CO_2-adduct stability and the catalytic performance was investigated and suggest different mechanisms for the catalytic hydroboration of CO_2 depending on the hydride source (Scheme 2). DFT calculations and the isolation of a proposed key intermediate adumbrate a novel electrophilic activation of pinacolborane to form highly reactive base-stabilized silanes and highlight the role of CO_2 adducts during the catalytic cycle of CO_2 hydroboration.



Scheme 2.

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Poster 70

Stereoselective Cyclopropanation of Olefinis Promoted by a C2-Symmetrical Iron(III) Porphyrin Complexes.

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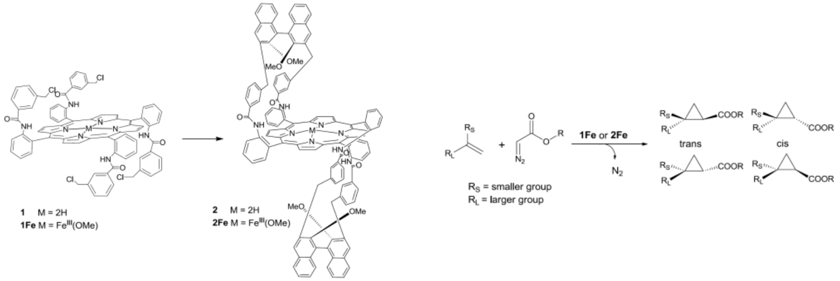
Cyclopropanes are important three-member carbon rings which often represent the active part in biological and/or pharmaceutical compounds.[1-2] Catalytic diastereo- and enantioselective olefin cyclopropanations have been extensively explored and among all the available synthetic methodologies to synthesise cyclopropanes, the one pot reaction of diazocompounds with olefins represents a sustainable and atom-efficient strategy due to the formation of N2 as the only stoichiometric by-product. Considering that metal porphyrins represent a very competent and stereoselective class of catalysts, we are currently studying the catalytic activity of iron derivatives which display a good sustainability for the presence of the eco-friendly, cheap and very efficient metal centre. Thus, we synthesised the new iron(III) complex **1Fe** starting from the porphyrin ligand **1**[3] (*scheme 1*) which has one *C*2 axis within the porphyrin plane and exhibits an open space on each side for the substrate access. Complex **1Fe** demonstrated a very high catalytic activity in cyclopropanations which occurred with excellent *trans*-diastereoselectivities (94-99%). Since positive data, we employed ligand **1** to synthesise the chiral derivative **2**, which shows a steric chiral bulk surrounding the *N*-core of the porphyrin. The free porphyrin **2** was then reacted with iron bromide, in the presence of methanol, to yield the relative iron(III) complex **2Fe** (*scheme 1*) which was completely characterised.[4] Complex **2Fe** showed a very high catalytic efficiency; excellent *trans*-diastereoselectivities, good enantioselectivities and outstanding TON and TOF values were observed in the reaction of cyclopropanation of several olefins by differently substituted diazo compounds (*scheme 1*).[4]



Scheme 1.

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Poster 71

C-H Activation Reactions with Rhodium(III) Complexes Containing Tridentate Ligands

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Over the last few years, various ligands containing chiral dihydrooxazole rings as coordinating units have been reported, and many of them have found successful applications in asymmetric catalysis.[1] A common feature of these ligands is their rather rigid framework with two stereogenic centers in close proximity to the coordination sphere. These ligands are quite attractive since the dihydrooxazole units are easily prepared from enantiomerically pure amino-alcohols, that are commercially available or can be readily prepared from amino acids. More recently, the synthesis of a chiral tridentate ligand containing two dihydrooxazole rings has been reported[2] and its coordination to Zn^{II}, Ni^{II} and Cu^{II} studied.

As part of our ongoing interest in transition metal mediated heterocyclization reactions,[3] we have prepared a new rhodium(III) complex (Figure 1) bearing two chiral dihydrooxazole rings, whose reactivity and selectivity has been studied in different benchmark reactions.

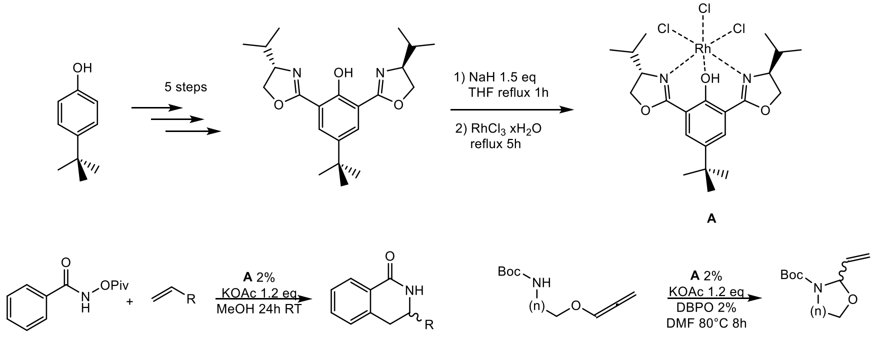

Figure 1.

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Poster 72

Glycoporphyrin Catalysts for Efficient C-H Bond Aminations by Organic Azides

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The activation of C-H bonds represents a '*hot*' topic due to the enormous synthetic potential of this class of organic transformations and the ubiquity of C-H functionalities in almost every molecular scaffold. Among all kinds of C-H bond activations, the C-H bond amination allows the conversion of low cost products, such as simple hydrocarbons, into high added value nitrogen-containing derivatives which often present important biological and/or pharmaceutical features.[1] Amongst all the catalysts active in C-H bond aminations, metal porphyrins have a good catalytic efficiency as well as an acceptable biocompatibility.[2-5] In order to enhance this latter catalyst characteristic it is important to introduce favourable functional groups (such as carbohydrates) on the porphyrin skeleton and low toxicity transition metals into the porphyrin core. We report herein the synthesis of new glycoporphyrin ligands which bear a glucopyranoside derivative on each *meso*-aryl moiety of the porphyrin skeleton. The saccharide unit is either directly conjugated to the porphyrin or a triazole spacer is placed in between the carbohydrate and porphyrin ring. The obtained glycoporphyrin ligands were employed to synthesise cobalt(II), ruthenium(II) and iron(III) complexes which were tested as biocompatible catalysts of C-H bond aminations by organic azides. Two of the synthesised complexes were very efficient in promoting catalytic reactions, up to 19 compounds were isolated in good to excellent yields, and achieved results indicated that ruthenium and iron complexes show an interesting complementary catalytic activity in several amination reactions. The eco-friendly iron catalyst displayed very good chemical stability catalysing the amination reaction for three consecutive runs without losing the catalytic activity.

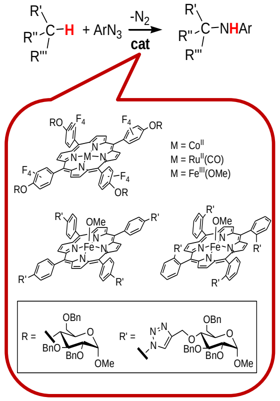

Figure 1.

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Poster 73

Diffusion-Ordered Spectroscopy (DOSY) : a Simple, Promising Tool for Analysing Complex Reaction Systems

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Diffusion-Ordered Spectroscopy (DOSY) is also known as the Nuclear Magnetic Resonance (NMR) chromatography since it allows the separation of a mixture of compounds spectroscopically. It is a simple technique which only requires classical NMR hardware and software. In this work, we report the use of DOSY as a promising tool to estimate diffusion coefficients of copper (I) complexes in solution.

Copper (I) dibenzoylmethane (DBM) complexes are characterized as monomeric species in the solid state. Binap- and Segphos- copper (I) chloride complexes are reported as dimers in the solid state. Their nature in solution is uncertain.[1]

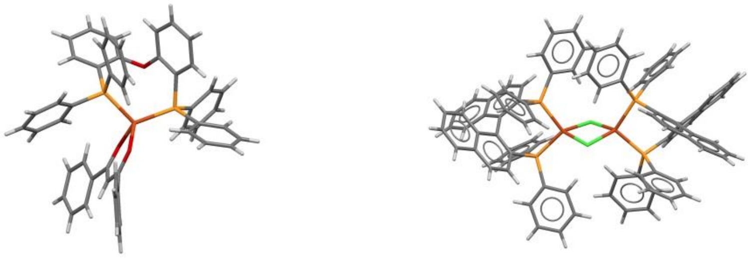

Figure 1. Single crystal XRD structures of dpephosCuDBM and $[BinapCuCl]_2$ complexes

Using the Stokes-Einstein modified equation,[2] it is possible to estimate the diffusion coefficients theoretically. Comparing these values to experimental data, we confirmed the monomeric nature of diphosphine copper (I) DBM complexes and dimeric nature of diphosphine copper (I) chloride complexes in toluene. This method can be applied in the investigation of reaction mechanisms involving these copper (I) complexes.

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Poster 74

Synthesis and Reactivity of Ni-P Carbonyl Clusters

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Over the past years Ni-P supported nanoparticles have been used as catalysts for many reactions,[1-2] and it is known that carbonyl clusters can be used as precursor for the synthesis metallic nanoparticles.[3]

Therefore, we chose to synthesize new carbonyl species containing nickel and phosphorus. There were no homoleptic carbonyl clusters known in the literature and only examples with phosphines as ligands were reported.[4]

The reaction between the $[Ni_6(CO)_{12}]^{2-}$ carbonyl cluster and PCl_3 or $POCl_3$ in different conditions allowed to obtain new species, such as $[Ni_{11}P(CO)_{18}]^{3-}$, $[Ni_{14}P_2(CO)_{22}]^{2-}$, $[Ni_{23-x}P_2(CO)_{30-x}]^{4-}$ (x=0, 1), $[HNi_{31}P_4(CO)_{39}]^{5-}$. Once available, we studied their reactivity and the results showed that these species are strictly related: under the appropriate conditions they can convert one into another (Figure 1).

Finally, we tried to investigate the catalytic properties of these Ni-P compounds, but the studies we carried out have not shown relevant results yet. However it has been confirmed (via TEM analyses) that the controlled thermal decomposition of $[HNi_{31}P_4(CO)_{39}]^{5-}$ leads to the formation of heteroatomical nanoparticles.

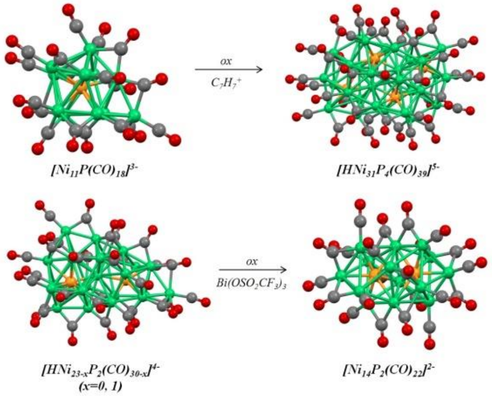

Figure 1.

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Poster 75

^{15}N NMR Spectroscopy Unambiguously Establishes the Coordination Mode of the Diimine Linker 2-(2′-Pyridyl)Pyrimidine-4-Carboxylic Acid (Cpph) in Ru(II) Complexes

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In 2009 Spiccia and coworkers introduced a new diimmine linker, 2-(2′-pyridyl)pyrimidine-4-carboxylic acid (cppH, Figure 1), as an easy-to-make alternative to the widely used – but more tedious to prepare – 4′-methyl-2,2′-bipyridine-4-carboxylic acid (bpyAc, Figure 1).[2]

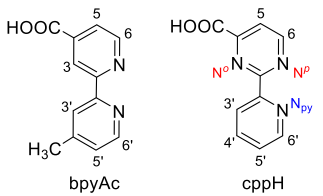

Figure 1. The diimmine ligands bpyAc and cppH with numbering schemes and labels.

This linker can originate linkage isomers, in fact its pyrimidine ring can bind to the metal ion either through the nitrogen atom *ortho* (N^o) or *para* (N^p) to the carboxylate linked to C4. Most of the cppH-Ru(II) conjugates reported so far were prepared following a synthetic route that led selectively to the $\boldsymbol{N^p}$ coordination mode.[1,3-6]

In this work we investigated the reactivity of the Ru(II) precursor *trans,cis,cis*-[$RuCl_2(CO)_2(dmso\text{-}O)_2$] towards cppH. We isolated and characterized two isomers and we reported how {^{1}H,^{15}N}- HMBC NMR spectra recorded at natural abundance of ^{15}N isotope on these compounds allowed us to unambiguously establish the binding mode of cppH, also in the absence of the X-ray structure.

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Poster 76

Copper(II) Complexes of Arylhydrazone of 1*H*-Indene-1,3(2*H*)-Dione as Catalysts for the Oxidation of Alcohols

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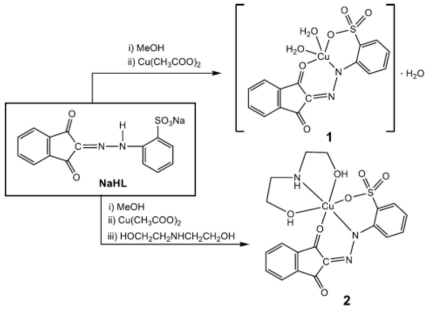
Copper(II) acetate was allowed to react with arylhydrazone of 1*H*-indene-1,3(2*H*)-dione – sodium 2-(2-(1,3-dioxo-1*H*-inden-2(3*H*)-ylidene)hydrazinyl)benzenesulfonate (**NaHL**; see Figure) in the absence and in the presence of diethanolamine, leading to the formation of complexes **1** and **2** which were characterized by conventional methods, as well as by single crystal X-ray diffraction.



Both complexes act as active and selective catalysts for the solvent free oxidation of 1- phenylethanol to acetophenone, using *tert*-butylhydroperoxide (TBHP) as oxidant, under mild conditions. Complex **2** exhibits a higher activity than **1**. An alternative medium [1] (ionic liquid) was also tested and the differences in yield and reaction time are discussed.

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Poster 77

Divergent Intramolecular Hydroamination Reactions of Terminal Alkynes Under Palladium and Platinum Catalysis

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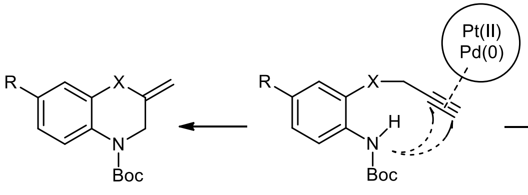
Transition-metal-catalyzed intramolecular reactions involving a C-C multiple bonds have been appreciated as useful processes to obtain heterocyclic systems.[1] Among them palladium in particular has been played a prominent role. For a long time our research group was studying the palladium-catalyzed intramolecular reactions and functionalizations to obtain polycyclic systems[2] and in this contest the hydroamination reactions involving the C-N bonds formation continue to gain our interests.

The present work is regarding the reactivity of terminal alkynes and alkenes tethered to a nucleophilic pendant as a useful scaffolds for intramolecular hydroamination processes with the aim to obtain aza-containing systems. The use of different transition metal-catalysts results in a complete divergent *endo/exo* selectivity depending on the metal catalyst used: in the presence of $Pd(PPh_3)_4$ 6-*exo*-dig cyclization was observed, while with $PtCl_2$ the 7-*endo*-dig cyclization occurred. Moreover working on the allyl derivatives under the same platinum catalysis, the dihydrobenzoxazine rings formation was reported.



X = O, NTs

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Poster 78

The bimca-ligand: Synthesis and Application of its Rhodium and Iridium Complexes

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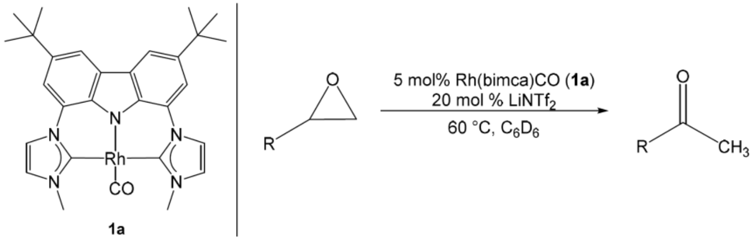
Introduced by Shaw in 1976, pincer-type ligands have become an important ligand class in organometallic chemistry during the last decades.[1] Nearly 15 years ago, they were combined with NHCs either as backbone or side donor moieties. Nowadays a broad range of tridentate mono- or biscarbene ligands are increasingly used in the synthesis of highly active homogenous catalysts.[2]

In 2007 we reported the monoanionic bis(imidazolinylidene)carbazolide (bimca) ligand as anionic pincerligand with two carbene moieties.[3] Since then we established a simplified synthetic access to its precursor and prepared a decent-sized ligand library.[4] Reaction of the lithium carbenes with Rh(I) carbonyl precursors led to the formation of a Rh (bimca)(CO) complex **1a**.



This complex shows a highly nucleophilic reactivity caused by the strong s-donor and weak p-acceptor character of the NHC moieties in addition to the monoanionic carbazolide donor.[3-5] **1a** could be applied in the catalytic rearrangement of epoxides to methyl ketones (*Meinwald* rearrangement), using $LiNTf_2$ as cocatalyst for a preactivation of the epoxides.[5]

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Poster 79

Synthesis of Metal Nanoparticles by Bio-Based Derivatives

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Benzoxaboroles In view of new and important commercial opportunities, it is important to meet the green chemistry principles for the overall procedure of the preparation of metal NPs, minimizing reactant consumption and by-product formation, and using, if possible, renewable materials and benign solvents.

Indeed, in the past, some studies have reported the formation of Au, Ag, Pt and Pd NPs by natural products, like starch, carbohydrates, wood nanomaterials, cellulose nanocrystallites, hydrocolloid gums and various plant extracts[1]. In other studies, NPs were synthesized by the polyol process, where a polyalcohol, generally coupled with a base, acts not only as a solvent but also as a mild reducing agent for the metal salt precursors[2]. In this context, glycerol has successfully employed in the preparation of a variety of metal NPs. However, although the preparation of transition metals nanoparticles has been extensively studied, the literature contains relatively few references on the synthesis of nanoparticles of group 7 transition metals, namely Mn, Tc and Re.

Our main interest in this study was addressed to the green synthesis of rhenium NPs. One of the main drawbacks in the development of a method for the synthesis and also for the potential applications, of Re NPs, is the low stability of the Re colloids generated by chemical reductions.

Our synthetic strategy was based on the reduction of $ReCl_5$ to Re NPs by use of lignin as reductant and stabilizing agent and glycerol or water as media of the reaction; we have to point out that lignin and glycerol are two of the most widely diffused by-products of the agro-industry. For a comparison purpose, we initially synthesized Re NPs employing $NaBH_4$ as reductant and rhenium perrhenate as starting Re source: the reaction was conducted in water or water/glycerol solution. The green synthetic procedures were then developed starting from a water or glycerol solution containing lignin as reductant and rhenium (V) chloride as metal source. In a first protocol, such solution was heated at 80 °C for 3 h while in a second protocol the reaction mixture was sonicated (20 kHz) and heated at 60 °C for 3 h. All the Re NPs were characterized using TEM, UV-vis, XRD analysis. During the characterization of NPs, we noted that glycerol is not only a solvent but it contributes to stabilize the nanoparticles in a synergic effect with lignin.

At the moment, we are studying the application of these nanoparticles, for example in the reduction of succinic acid to 1,4-butadienol.

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Poster 80

Synthesis, Biological Evaluation and Stability Studies of Novel Symmetrical and Non-Symmetrical 11th Group-NHC Complexes

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Recently metallodrug chemistry bearing N-heterocyclic carbene (NHC) supporting ligands has experienced a new rebirth. Our research group, during the last 7 years, has developed different classes of coinage metal-NHC complexes obtained from the precursors $\{[H_2B(BnTzH)_2]Br\}$,[1] $\{[H_2B(pNO_2BnTzH)_2]Br\}$ $\{[HTz(pNO_2Bn)_2]Br\}$[2]. Recently we have focused the research work on the synthesis of new coinage metal-NHCs complexes obtained from the water soluble ligands $Him^{1R,3R}Cl$ (R = $COOCH_3$, $COOCH_2CH_3$ or $CON(CH_2CH_3)_2$)[3] or the zwitteronic symmetrical NHC ligands $NaHIm^{1R,3R,4R''}$ (R = $(CH_2)_3SO_3^-$, R'' = H, CH_3)[4] (Figure 1), $NaHBzim^{1R,3R}$ (R = $(CH_2)_3SO_3^-$) and non-symmetrical NHC ligands $NaHIm^{1R,3R'}$ (R = $(CH_2)_3SO_3^-$, R' = $CH_2C_6H_5$), $\{[HBzim^{1R,3R'}]Br\}$ (R = $(CH_2)_3SO_3Na$, R' = $CH_2C_6H_5$) and the related copper(I)- and silver(I)-NHC complexes.[5] Finally we studied the cytotoxic activity and the stability of the NHC complex classes developed by our research group.

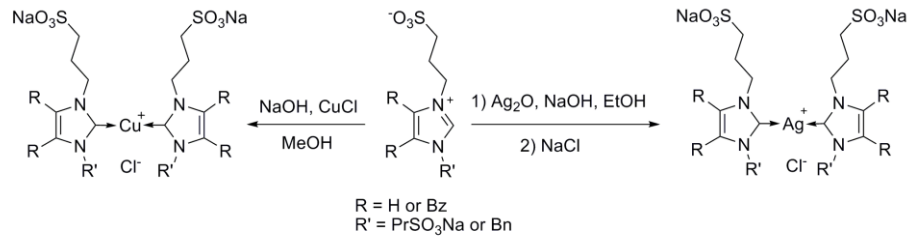

Figure 1.

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Poster 81

Poly(Alkylidenamine)s Dendrimers with Nitrile and Amine Terminal Groups as a Platform to Deliver Metallodrugs

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The acquired immunodeficiency syndrome (AIDS) infected around 78 million of people since the beginning of the epidemic.[1] On the other hand, cancer is one of the leading causes of deaths worldwide. Metal complexes, like ruthenium compounds, present less toxicity when comparing to platinum derivatives and can bind to proteins in the plasma due to their ability to mimic the behavior of iron.[2] The combination of metals with dendrimers, which are highly branched molecules with well-defined structures, provides new nanostructures (metallodendrimers) with improved biological properties.[3,4] These metallodendrimers are under study to be use in a broad range of applications including in the biomedical field to fight cancer and infections.

The aim of this project is to develop a new family of metallodendrimers based on poly(alkylidenamine) dendrimers[5] and ruthenium or platinum complexes, with improved solubility in biological media, and to evaluate their potential as effective drugs against HIV-1 infection/replication and different types of cancer.

In this work, the preliminary results on the preparation and characterization, by NMR, IR and MS, of this new family of poly(alkylidenamine)-based dendrimers having, at each generation, nitrile and amine terminal groups, will be presented and discussed. The nitrile and amine terminal groups on the surface of dendrimers will serve to grow the dendrimer generation and will act as bridging groups for complexation of metallodrugs.

Acknowledgments: This research was supported by Fundação para a Ciência e a Tecnologia (FCT) with Portuguese Government funds through the CQM Strategic Project PEst-OE/QUI/UI0674/2014, the NMR Network – (PTNMR-2014 and PTNMR-2015) and the PhD Grant SFRH/BD/102123/2014 (D.M). The support of the international network CYTED 214RT0482 in the domain of the HIV infection is highly appreciated. We also acknowledge the continuous support of our work by Hotel Vidamar Resorts Madeira.

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Poster 82

Metal Derivatives with 3-(2-sulfonic phenylhydrazo)pentane-2,4-dione, and 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane: Synthesis and Characterization

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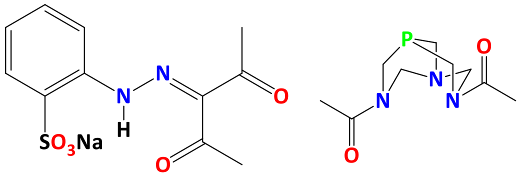
As part of our interest on new water soluble complexes, new set of Transition metal complexes were prepared using two water soluble ligands, which are Sodium salt of 3-(2-sulfonic phenylhydrazo)pentane-2,4-dione (Figure 1a), and 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (Figure 1b).

Transition metal–ADB complexes (ADB = azoderivatives of β-diketones) have been successfully applied as homogeneous catalysts for the peroxidative oxidation of alkanes to the corresponding alcohols and ketones, in a few cases with rather high values of TONs.[1,2] In pursuit of this work, the sodium salt of 3-(2-sulfonic phenylhydrazo)pentane-2,4-dione (**SPPD**) was synthesized, fully characterized, and allowed to react with a metal (Cu or Ni) salt in the presence of amines. On the other hand, one of the most important Cage adamantane-like phosphine derivatives of 1,3,5-triaza-7-phosphaadamantane (**PTA**) is 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (**DAPTA**), which is prepared by reaction of PTA with acetic anhydride, and possess extremely large molar solubility in water.[3,4] New water soluble copper complex was synthesised by reaction of DAPTA with Cu-salt in mild conditions.

The obtained compounds were characterized by IR spectroscopy, elemental analysis and single crystal X-ray diffraction (**SCXRD**).



(a) (b)

Figure 1.

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Poster 83

M–H Bond Repolarization in Hydrogen Bonding and the Proton Transfer Between Two Transition-Metal Hydrides

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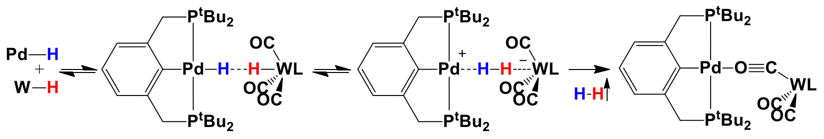
Being formally the sources of either hydride ion H^- or proton H^+ neutral transition-metal hydrides demonstrate different reactivity. A computational study of the intermolecular interaction effect on the M–H bond activation in Group 6 metal hydrides (η^5-C_5H_5)M(CO)$_3$H (M = Mo, W) possessing both acidic and basic properties, was carried out. The electronic structure of adducts of hydride complexes (η^5-C_5H_5)M(CO)$_3$H with the Lewis acid BH_3 and base NMe_3 were analysed.[1] It was shown that the nature of orbital interactions in the complex affects the reaction pathway: the $n_N \rightarrow \sigma^*_{MH}$ interaction leads to deprotonation of the metal hydride and the $\sigma_{MH} \rightarrow n^*_B$ interaction implies the hydride transfer to the Lewis acid. The ease of M—H bond polarization in complexes (η^5-C_5H_5)M(CO)$_3$H explains their reactivity as donor of either proton or hydride ion.

Previously we reported on the unconventional acid–base interaction between tungsten hydride (η^5-C_5H_5)W(CO)$_3$H which acts as an acid, and nickel(II) pincer hydride (PCP)NiH (PCP = 2,6-($CH_2P(t$-$C_4H_9)_2)_2C_6H_4$)) served as a base.[2] Continuing this line of investigation we studied the proton transfer mechanism between their analogous species bearing hydridotris(pyrazolyl)borate ligand (TpW(CO)$_3$H) and palladium metal center ((PCP)PdH). Kinetic and thermodynamic parameters of the proton transfer accompanied by dihydrogen evolution were obtained experimentally by means of IR (ν_{MH}, ν_{CO}) and NMR spectroscopy (^{1}H, ^{31}P) in a wide temperature range (190-300 K). The products and intermediates of the process were established and the peculiarities of their structure were revealed by DFT calculations.



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Poster 84

Catalytic Activity of Copper(I) and Copper(II) 3,5-Dinitro- or 3,5-Bis(Trifluoromethyl)-Pyrazolate Derivatives

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The reaction of [μ-N,N-Cu-(3,5(CF_3)$_2$pz]$_3$ (**1**) with halide sources led to the formation of Cu(II) hexanuclear derivatives such as [(Cu((CF_3)$_2$pz)$_6$(OH)$_6$) ⊃ X][Bu_4N] (**2a**)(Cl^-), (**2b**) (Br^-), (**2c**) (I^-), (**2d**) (NO_2^-).[1] If the reaction occurs in the same conditions but without halides, a highly hydrated hexanuclear metallocycle [(Cu((CF_3)$_2$pz)$_6$(OH)$_6$) ⊃ (H_2O)$_n$], (**3**), was isolated, ruling out the template action of the anions. By replacing the CF_3 groups with NO_2 groups in the pyrazole, neither the trinuclear nor the hexanuclear copper derivatives were obtained, and the dinuclear [Cu-(3,5-(NO_2)$_2$pz)(PPh_3)]$_2$ compound, (**4**), was the only Cu(I) derivative isolated in good yield. Even though CF_3 and NO_2 are both withdrawing groups, a pronounced different chemical behavior was already revealed in the case of similar pyrazolate silver(I) derivatives.[2] All compounds were characterized by elemental analysis, NMR, IR spectroscopy and ESI-MS spectrometry. In the case of compound **4** its crystal structure has been determined by X Ray diffraction analysis, evidencing its dinuclear nature, build up by two bridging ligands which coordinate two copper atoms through nitrogen donors, forming a six member ring with boat conformation. Compounds (**3**) and (**4**) act as catalysts towards the microwave (MW) assisted peroxidative oxidation of cyclohexane to cyclohexanol and cyclohexanone under mild conditions, which is of industrial significance for the synthesis of Nylon-6,6. High yield (up to 51% of oxygenated products) is obtained after 2h of MW irradiation, using a maximum of 0.2% molar ratio of **3** (the best catalyst) relatively to the substrate in the presence of TEMPO. The efficiency of the catalytic systems as well as the influence of various parameters, such as the reaction time, amount of catalyst, temperature and presence of different additives, are discussed. The work was partially supported by the Fundação para a Ciência e a Tecnologia (project UID/QUI/00100/2013)

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Poster 85

Synthesis of Polyboronic Acids Based on Heteroaryl Core – Synthons for Preparation of Microporous Materials

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Boronic acids derivatives are extensively utilized in modern organic synthesis, especially for carbon-carbon and carbon-heteroatom formation via catalytic coupling.[1] Polyboronic derivatives consisting of more than one boronic group are interesting synthons in material chemistry for preparation of ordered networks.[2] Such materials – e.g. Covalent Organic Frameworks (COF)[3] - have potential applications as adsorbents for gas storage and separation. We have focused on synthesis of di-, tri- and tetraboronic acids[4] and respective boronate esters based on thienylsilane, bithienyl, bifuryl and 2,4,6-triphenyl-1,3,5-triazine core (Figure 1). Obtained products will be utilized in synthesis of microporous materials. Preliminary results for these materials will also be included.

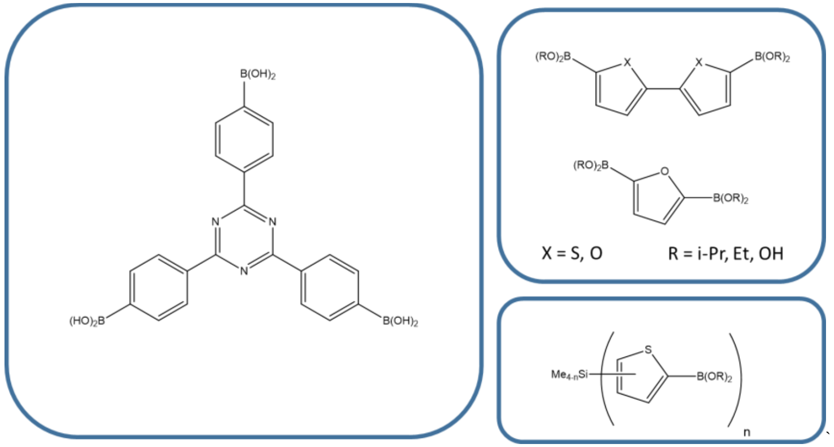

Figure 1.

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Poster 86

Synthesis and Functionalization via Direct Lithiation of α-Aryl-substituted Tetrahydropyrans

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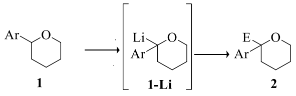
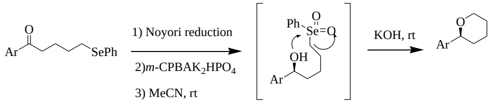
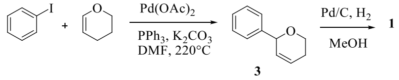
Many biologically active and widely distributed natural products contain a tetrahydropyran moiety. The tetrahydropyran core is, indeed, a useful “building block” not only in organic chemistry, but also in biological and medicinal chemistry.[1] Building on our recent successful α-lithiation-electrofilic interception protocols applied to phenyloxetane[2] and phenyltetrahydrofuran[3] derivatives, we have now extended the result of such an investigation to the preparation of 2,2-disubstituted tetrahydropyrans **2** starting from the parent α-arylated precursors **1** (Scheme 1). The synthesis of racemic **3**, starting α-aryl-substituted tetrahydropyrans has been accomplished exploiting a one-pot strategy, under microwave conditions, which involves a preliminary Heck cross-coupling reaction followed by an hydrogenation procedure (Scheme 2). On the other hand, the preparation of the corresponding optically active substrates was based on a selenium–mediated cyclization starting from δ-phenylseleno ketones (Scheme 3)[2]. In this communication, the influence of the solvent and the temperature, and the nature of the organolithium employed, on the effectiveness of such a direct α-functionalization of these oxygenated heterocycles will be discussed as well as the chemical and configurational stability of the putative anion **1-Li** (Scheme 1).



Scheme 1



Scheme 3



Scheme 2

Acknowledgements: This work was finantially supported by the Interuniversities Consortium C.I.N.M.P.I.S, and by the University of Bary.

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Poster 87

Water Influence in the Preparation and Stabilization of High Quality Phosphorene Flakes

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2D nanomaterials are very promising in nanodevice applications due to their surprising properties such as high electric mobility, outstanding structural properties and large specific surface area.[1] Recently, phosphorene (Figure 1), the all-P counterpart of graphene, has been prepared starting from black phosphorus (BP).[2] Small amounts of single and few layers sheets of the new material have been obtained by either micromechanical cleavage (Scotch tape method) or liquid exfoliation.[3] Herein, we provide a detailed study of the influence of water in the exfoliation of black phosphorus in dimethylsulfoxide, by examining the role played by the amount of water. Three different ranges of molar ratio between black phosphorus and water were considered. Atomic force microscopy, scanning electron microscopy, and transmission electron microscopy gave information on the morphology of black phosphorus nanosheets and their lateral dimension and thickness. X-ray powder diffraction proved the crystalline nature of the samples and also the chemical composition of the material in each condition tested. Comparing the data, an evident and dramatic influence of the concentration of water on the quality of the BP atomic layers is observed and highlights the best working conditions to be adopted in the exfoliation process (Figure 1) in order to get good quality phosphorene flakes.[4]

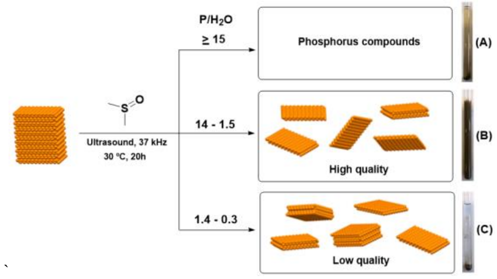

Figure 1.

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Poster 88

Anti-tumor activity of a new ruthenium complex on a model of basal-like breast

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Platinum-based anti-cancer drugs are some of the most effective chemotherapeutic agents in clinical use. In the search for anticancer agents containing metals other than platinum, ruthenium compounds turned out to be the most promising ones and they exhibit unique tumour selectivity and low general toxicity compared to the clinically used platinum-based drugs. We have developed a series of organometallic ruthenium(II)-arene complexes that exert a very low in vitro activity against several tumors cell lines. Here, we show that the prototype compound, [Ru(p-cymene)(bis(3,5-dimethylpyrazol-1-yl)methane)Cl]Cl, (UNICAM-1),[1] when administered in a single dose every three days (52.4 mg kg-1) significantly reduces the in vivo growth of A17 cells, a mouse model of triple negative breast cancer (TNBC), transplanted in FVB syngeneic mice. Pharmacokinetic studies indicate that UNICAM-1 is rapidly lost from the organs and the bloodstream thanks to its high hydrosolubility. In particular, only traces of ruthenium in the liver and kidneys of treated animals clearly demonstrate a high elimination of the metal resulting with minimal side effects. The evaluation of tumour-infiltrating lymphocytes revealed that the therapeutic efficacy of UNICAM-1, beside an impairment of angiogenesis, mainly relies on its capacity to potentiate immune responses by depleting suppressive regulatory T cells. These results provide evidence that UNICAM-1 is a promising anticancer drug for the treatment of TNBC.

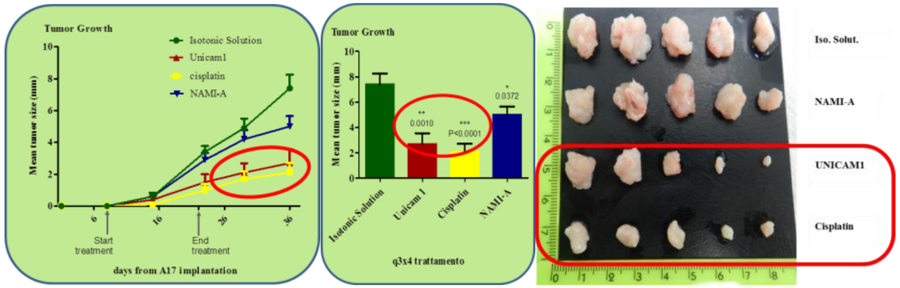

Figure 1.

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Poster 89

Recognition of Prochiral Sulfides in Five-Coordinate Olefin Pt(II) Complexes

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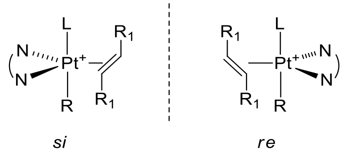
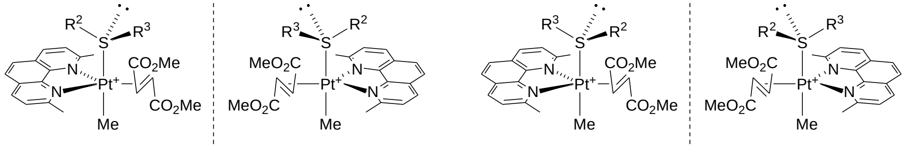
Coordination of *trans*-alkenes in five-coordinate Pt(II) complexes yields a couple of enantiomers (**1**):[1]



1

When even the ligand L in apical position is prochiral, two pairs of enantiomers are generated, whose ratio depends on their relative stability.

The present work is inserted in this topic, with the aim to verify the mutual recognition of the olefin and the ligand L, in case the latter is a sulfide with two different substituents R^2SR^3 (**2**).



2

The study is carried out using an extensive library of sulfides, 2,9-dimethyl-1,10-phenanthroline as nitrogen bidentate ligand (particularly suitable to stabilize the trigonal bipyramidal geometry),[2] and fumaric esters as prochiral alkenes.

The ratio between the diastereoisomers is assessed through NMR spectroscopy, as well as the relative configuration of the prochiral ligands.

Preliminary results show that:

- the measures must be performed at 190 K, because at this temperature the inversion of configuration of the coordinated sulfide is slow;
- in the presence of mixed aryl alkyl sulfides, only one pair of enantiomers seems distinctly privileged, whose geometry will be precisely investigated.

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