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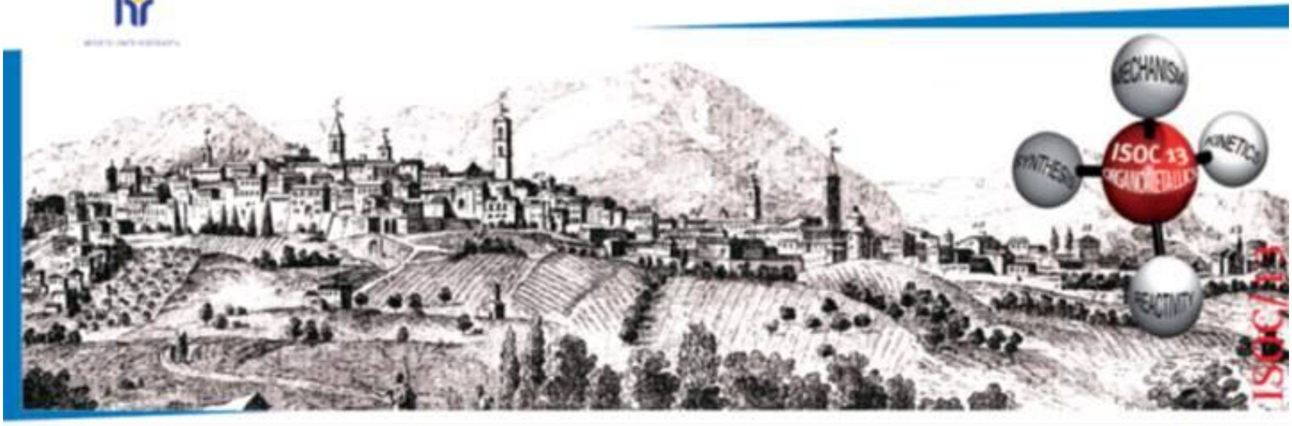

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9th International School of Organometallic Chemistry

Camerino, Italy August, 30 - September, 3 2013

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Interdivisional Group of Organometallic Chemistry

Organometallic Systems To Sustain A Better Future

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INTRODUCTION

“Organometallic Systems To Sustain A Better Future”

Almost all branches of chemistry and material science now interface with Organometallic Chemistry. Organometallics are used extensively in the synthesis of useful compounds on both large and small scales. Industrial processes involving plastics, polymers, electronic materials, and pharmaceuticals all depend on advancements in organometallic chemistry. Many catalytic and non-catalytic stereoselective processes that are key steps in creative and non-conventional synthesis of complex molecules have gained significant advantage from organometallic chemistry.

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 with the aim of encouraging 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 generations of Scientists. The major objective of the ISOC is to promote synergy in organometallic research. The number of participants will be limited to around 120 in order to facilitate maximum interaction among the participants and between them and the lecturers.

The 9th edition of ISOC (ISOC 2013) will focus on the relevance of organometallics systems to sustain a better future. The development of advanced methodologies based on the peculiar properties of organometallic compounds may lead to important changes in the approach of organometallic chemists to the field. A full roster of scientifically distinguished speakers will present their reading keys. In fact, fundamental studies on the mechanistic and structural aspects, as well as new experimental methods and investigation techniques, support the use of organometallic compounds in different application areas including Organometallic Catalysis, Bioorganometallic Chemistry in Biology and Medicine, Green Chemistry (energy and sustainable development), Industrial chemistry and Polymers production, Metal-mediated organic synthesis and Activation of small molecules.

Camerino

The town of Camerino, with about 7,500 inhabitants today, is located 661 meters above sea level, on the dorsal that separates the valley of Chienti from that of Potenza, in the heart of Marche. Of pre-roman origin the town has played an important political and ecclesiastical role through the centuries reaching a notable level of economic and civil development. The wealth of monuments and the vivacity of university life, that pulsates there for almost 700 years, make Camerino a significant center of culture and art.

TIMETABLE

Friday **30 August**	**15,30** Opening Session	**16,00** Prof. K. Tatsumi	**17,30** Coffee break	**18,00** Prof. O. Eisenstein
Saturday **31 August**	**9,00** Prof. P. J. Sadler	**10,30** Coffee break	**11,00** Prof. E. A. Quadrelli	
	14,30 Prof. C. Nájera Domingo	**16,00** Coffee break	**16,30** Prof. E. Schulz	
	18,00 Flash Presentations	**19,30** Poster session	**21,00** Welcome Dinner	
Sunday **1 September**	**8,30** Prof. D. Milstein	**10,00** Prof. M. Albrecht	**11,30** Coffee break	**12,00** Prof. J. Clayden
	15,00 Social Excursion	**20,00** Social dinner		
Monday **2 September**	**9,30** Prof. P. J. Pérez	**11,00** Coffee break	**11,30** Prof F. Ruffo	
	15,00 Prof. A. S. K. Hashmi	**16,30** Coffee break	**17,00** Flash Presentations	**18,00** Poster Session
Tuesday **3 September**	**9,00** Prof V. Cadierno Menéndez	**10,00** Coffee break	**10,30** Prof. G. Reginato	**12,00** Prizes and Closing Ceremony

PROGRAMME

Friday, 30 August:

15,30: Opening Session
16,00: Prof. K. Tatsumi "**Organometallic chemistry of reductases - A clue to building a future sustainable society**"
17,30: Coffee break
18,00: Prof. O. Eisenstein **"Olefin metathesis catalysis with d0 Schrock metal alkylidene complexes: the input from computational studies"**

Saturday, 31 August:

9,00: Prof. P. J. Sadler **"Organometallic anticancer complexes with new mechanisms of action"**
10,30: Coffee break
11,00: Prof. E. A. Quadrelli **"Dinitrogen hydrogenation & cleavage an route to NH3 with a surface coordination chemistry perspective"**
14,30: Prof. C. Nájera Domingo **"Coinage metal complexes as chiral catalysts for 1,3-dipolar cycloadditions"**
16,00: Coffee break
16,30: Prof. E. Schulz **"Hydroamination reactions of unactivated olefins"**
18,00: Flash Presentations
19,30: Poster session
21,00: Welcome Dinner

Sunday, 1 September:

8,30: Prof. D. Milstein **"Sustainable catalysis based on pincer complexes"**
10,00: Prof. M. Albrecht **"Strong donor carbenes and their potential in (oxidation) catalysis"**
11,30: Coffee break
12,00: Prof. J. Clayden **"New reactivity from organolithiums"**
15,00: Social Excursion
20,00: Social dinner

Monday, 2 September:

9,30: Prof. P. J. Pérez **"Catalytic Functionalization of Hydrocarbons: the Methane Problem"**
11,00: Coffee break
11,30: Prof . F. Ruffo **"Sweetness and privilege of metal promoted asymmetric catalysis"**
15,00: Prof. A. S. K. Hashmi **"Gold catalysis - A universe of innovation"**
16,30: Coffee break
17,00: Flash Presentations
18,30: Poster session

Tuesday, 3 September:

9,00: Prof. V. Cadierno Menéndez **"Metal-catalyzed amide bond forming reactions in water: Nitrile hydrations and beyond"**
10,00: Coffee break
10,30: Prof. G. Reginato **"Advances in cross coupling reactions. Synthetic applications in the field of new generation solar cells"**
12,00: Prizes and Closing Ceremony

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SPEAKERS

Martin Albrecht **University College Dublin, Ireland**

Strong donor carbenes and their potential in (oxidation) catalysis

Victorio Cadierno Menéndez **Universidad de Oviedo, Spain**

Metal-catalyzed amide bond forming reactions in water: Nitrile hydrations and beyond

Jonathan Clayden **University of Manchester, United Kingdom**

New reactivity from organolithiums

Odile Eisenstein **University of Montpellier 2, France**

Olefin metathesis catalysis with d0 Schrock metal alkylidene complexes: the input from computational studies

A. Stephen K. Hashmi **University of Heidelberg, Germany**

Gold catalysis - A universe of innovation

David Milstein **Weizmann Institute of Science, Israel**

Sustainable catalysis based on pincer complexes

Carmen Najera Domingo **Universidad de Alicante, Spain**

Coinage metal complexes as chiral catalysts for 1,3-dipolar cycloadditions

SPEAKERS

Pedro J. Peréz **Universidad de Huelva, Spain**

Catalytic Functionalization of Hydrocarbons: the Methane Problem

Alessandra E. Quadrelli **CPE Lyon, France**

Dinitrogen hydrogenation & cleavage an route to NH_3 with a surface coordination chemistry perspective

Gianna Reginato **CNR- ICCOM Firenze, Italy**

Recent advances in cross coupling reactions. Synthetic applications in the field of new generation solar cells

Francesco Ruffo **University of Napoli, Italy**

Sweetness and privilege of metal promoted asymmetric catalysis

Peter Sadler **University of Warwick, United Kingdom**

Organometallic anticancer complexes with new mechanisms of action

Emmanuelle Shulz **Université Paris-Sud 11, France**

Hydroamination reactions of unactivated olefins

Kazuyuki Tatsumi **University of Nagoya, Japan**

Organometallic chemistry of reductases - A clue to building a future sustainable society

Friday, 30 August, h 16,00 *Lecture 1*

Organometallic Chemistry of Reductases: A Clue to Buildinga Future Sustainable Society

Kazuyuki Tatsumi

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Metalloenzymes are essential for all living organisms on earth, as their metal-incorporating active centers play a major role in regulating highly efficient/selective enzymatic functions. In particular, the research on reductases and related metalloenzymes has progressed rapidly in recent years, unraveling novel structures and functions of the cluster active centers and greatly expanding the established knowledge of chemistry. Newly discovered reductases show remarkable activities, exemplified by nitrogenases catalyzing the reduction of dinitrogen into ammonia, hydrogenases reversibly converting dihydrogen into protons and electrons, CO-dehydrogenases generating protons and electrons from CO and water, and acetyl CoA synthase forming acetyl CoA from carbon monoxide, methyl cobalamin, and coenzyme A (CoA). The brilliant functions of these enzymes stand out as a microcosm of the "the mystery of nature" that modern science should strive to understand, and therefore the importance of chemical research on the structure-function relationship of the active sites has been recognized.

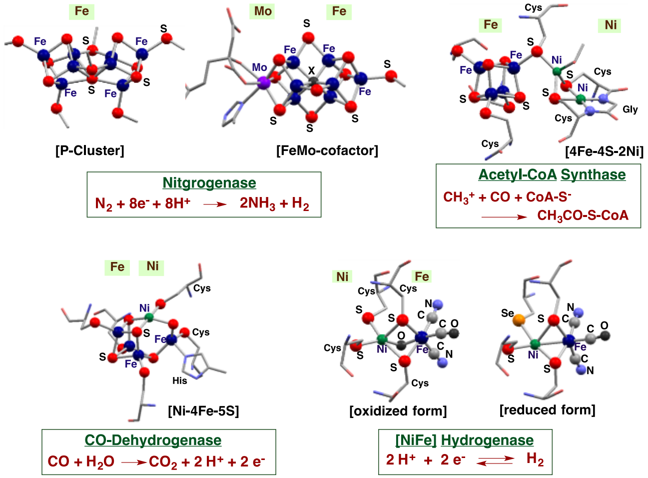

Figure 1. The Cluster Active Sites and Functions of Reductases

These reductases promote "organometallic reactions" in nature. For instance, the function of CO-dehydrogenases is equivalent to the so-called water-gas-shift reaction in organometallic chemistry, and acetyl CoA synthase involves the CO insertion into a Ni-CH_3 bond in its function. Interestingly hydrogenases contain a typical organometallic iron-carbonyls in their active centers. The active sites of reductases are made of unprecedented transition metal sulfide clusters, which have been long-standing targets of synthetic chemists and are extremely challenging due to the instability and complexity of the cluster structures. This presentation shows our recent study on (1) chemical synthesis of the nitrogenase active sites and their electronic properties, (2) chemical synthesis of the [NiFe]-hydrogenase active sites and the model reactions, and (3) chemical synthesis of the active site of acetyl CoA synthase and the functional model.

Friday, 30 August, h 18,00 *Lecture 2*

Computational studies and chemical complexity:
olefin metathesis catalysis with the Schrock alkylidene complexes.

Odile Eisenstein

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Computational studies of reaction mechanism have gained increased visibility and credibility among the community of experimental chemists. It is currently accepted that a reaction mechanism can be determined by computational studies and the large number of mechanistic information obtained by computations, that has been useful to chemists is a daily proof of this success. How to conduct a study and give insight on a reaction knowing that the modeling could be far (even very far) from the experimental system and conditions?

We will illustrate several points of the above by describing our work for the olefin metathesis reaction with the Schrock type metal alkylidene catalysts of the type d^0 M(=CHR)(ER1)(X)(Y) (M = Mo, W, Re; ER^1 = CR^1, NR1, O; X = Y = alkyl, alloxy, siloxy, amido, etc. In this presentation, we will stress the importance of the chemical model (simplified vs closer to the experimental situation), the need to take a global vision of the reaction by including the study of the reactive pathway and that of the side reactions that form by products and could deactivate the catalyst. We will show that the classical Chauvin mechanism holds but needs to be completed.

Some of the experiments were carried out with catalysts grafted on amorphous silica for which solid state NMR is a method of choice. One of the advantages of solid state NMR is to access the dynamics of the catalysts grafted on silica via the measure of the Chemical Shift Anisotropy (CSA) for ^{13}C of the alkylidene group. Mo, W, Re and Ta alkylidene complexes were considered. The decrease of the CSA relative to a static limit suggests that the Mo complexes are essentially immobile, while the three others are relatively mobiles. A computational study of the time average CSA was carried out via a dynamic ab initio calculations of the systems grafted on silica. The methodology will be explained and the dynamics discussed. Remarkably, equal values of the CSA do not mean that the dynamics are of the same nature. The different dynamics will be presented and discussed.

References

The first part will be based on the following papers and unpublished results. The computation studies of the CSA is still unpublished.

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Saturday, 31 August, h 9,00 *Lecture 3*

Organometallic anticancer complexes with new mechanisms of action

Peter J. Sadler

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The periodic table offers potential for discovery of new drugs.[1] I will discuss our work on the design of low-spin d^6 half-sandwich organometallic Ru^{II}, Os^{II} and and Ir^{III} complexes.[2] Initially we synthesised monofunctional Ru^{II} arene complexes that could bind strongly to DNA, by guanine N7 coordination, H-bonding and intercalation of extended arenes, causing different structural perturbations to cisplatin and no cross-resistance.[3,4] However, it has become apparent that redox activity can play a role in activity.[5] For example, thiolato complexes can be activated by oxidation to the sulfenate,[6] and active inert complexes with strong π-acceptor chelated ligands can induce formation of reactive oxygen species (ROS) in cancer cells.[7] The Os^{II} azopyridine complex $[Os(\eta^6\text{-}p\text{-cym})(4\text{-}(2\text{-pyridylazo})\text{-N,N-dimethylaniline})I]PF_6$ exhibits nanomolar potency in a range of cancer cells and is active in vivo.[8] As for Ru^{II}, the iodido and chlorido Os^{II} analogues exhibit marked differences in biological behaviour.[9] Compared to Ru^{II}, Os^{II} arene complexes hydrolyse ca. 100x more slowly and an aqua ligand is ca. 1.5 pK_a units more acidic.[2]

Cyclopentadienyl Ir^{III} complexes with appropriate Cp* substituents and chelated N,N or C,N ligands[10] also possess some remarkable properties: potent anticancer activity[11] and catalytic activity using coenzyme NADH as a source of hydride under biologically-relevant conditions.[12,13] Organometallic arene complexes also offer potential for cancer photochemotherapy.[14]

Acknowledgements: We thank the ERC, EPSRC, Science City (AWM/ERDF) and EC COST action CM1105 for support.

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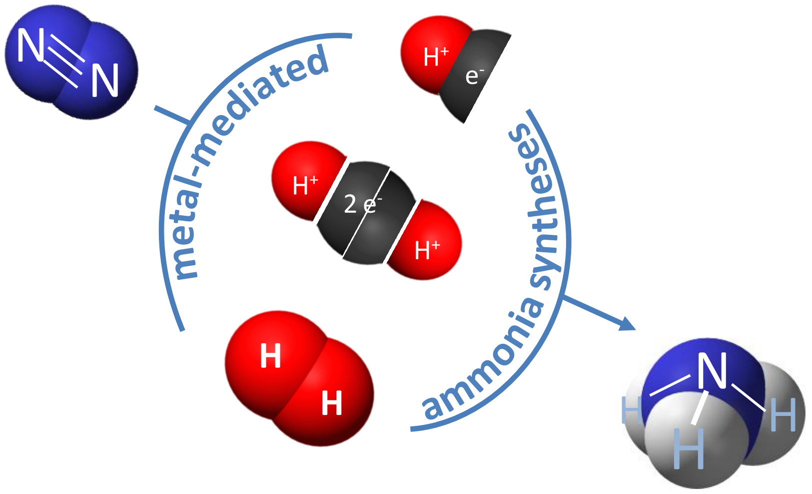
Saturday, 31 August, h 11,00 *Lecture 4*

Dinitrogen hydrogenation & cleavage en route to NH_3 with a surface coordination chemistry perspective:

Elsje Alessandra Quadrelli

Equipe Chimie Organométallique de surface, Laboratoire de Chimie Catalyse Polymères et Procédés (UMR 5265 C2P2 –CPE Lyon CNRS Univ. Lyon 1), Université de Lyon, 43, Bd du 11 Novembre 1918- Villeurbanne, quadrelli@cpe.fr, http://lavande.cpe.fr/lcoms/quadrelli/

Dinitrogen cleavage and hydrogenation by transition-metal centers toward ammonia is central in industry and in Nature. After an introductory section on the thermodynamic and kinetic challenges linked to N_2 splitting, this course discusses three major classes of transition-metal systems (homogeneous, heterogeneous and biological) capable of achieving dissociation and hydrogenation of dinitrogen. Molecular complexes, solid-state Haber-Bosch catalytic systems, silica-supported tantalum hydrides and nitrogenase will be discussed. Emphasis is focused on the reaction mechanisms operating in the process of dissociation and hydrogenation of dinitrogen. Close analysis of the mechanisms at hand in homogeneous, heterogeneous and enzymatic systems reveal the key role played by metal hydride bonds and metal-mediated bifunctional dihydrogen heterolytic splitting in elementary steps equivalent to electron and proton transfers.



Saturday, 31 August, h 14,30 *Lecture 5*

Coinage Metal Complexes as Chiral Catalysts for 1,3-Dipolar Cycloadditions

Carmen Nájera Domingo

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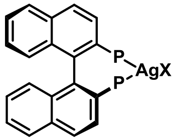
The use of different chiral catalysts derived from binap and phosphoramidites and silver, gold(I) and copper(II) salts for the enantioselective synthesis of highly substituted prolines by 1,3-dipolar cycloadditons (1,3-DC) of azomethine ylides, derived from imino esteres or azlactones, with dipolarophiles is presented. The 1,3-DC using bidentate binap complexes give good enantioselectivities for azomethine ylides when silver salts monomeric complexes **1,**[1] and dimeric gold **2** trifluoroacetates[2] are used yielding *endo*-cycloadducts. Glycine derived azlactones react with maleimides using (*S*)- or (*R*)-dimeric binapAuTFA complexes **2** affording the corresponding *endo*-cycloadducts in good yields and high enantioselections, whereas, silver catalyst **1** failed completely.[3] The intermediate carboxylic acids are treated with trimethylsilyldiazomethane isolating Δ^1-pyrroline methyl esters as final products.

In the case of monodentate phosphoramidites, metal complexes **3** derived from silver salts have been used for the general 1,3-DC of different imino esters and dipolarophiles to afford *endo*-cycloadducts.[4] In the case of using nitroalkenes as dipolarophiles copper(II) triflate complexes **3** are the most appropriate catalysts affording *exo*-cycloadducts.[5] In addition, computational studies have also been carried out in order to explain the high enantioselection exhibited by these chiral complexes. This methodology has been applied to the synthesis of hepatitis C virus inhibitors blocking the viral RNA-dependent RNA-polymerase[6] and for the preparation of 4-nitroprolines, which are excellent chiral organocatalysts for the aldol reaction.[7]



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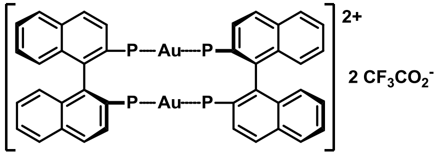
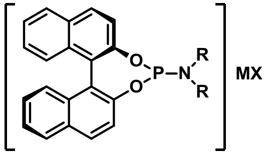


2

P = PPh$_2$



3

MX = AgClO$_4$, AgOTf, Cu(OTf)$_2$

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Saturday, 31 August, h 16,30 *Lecture 6*

Hydroamination reactions of unactivated olefins

Emmanuelle Schulz

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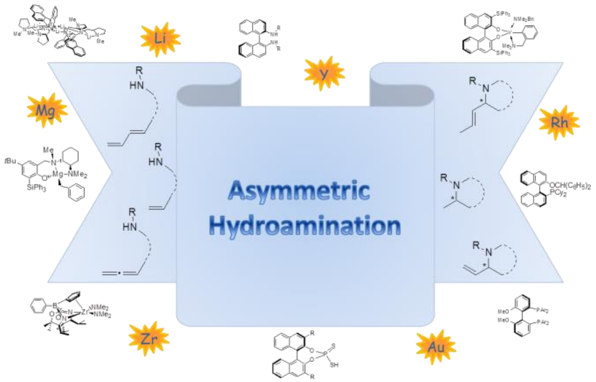
The metal-catalysed hydroamination of olefins, formally the addition of a –NH unit on an unsaturated carbon-carbon bond, perfectly meets the criteria of atom economic reaction.[1] The fine tuning of catalysts to perform this transformation with high enantioselectivities remains at present a real challenge to take up, considering the importance of these compounds in medicinal and natural products chemistry. This transformation is thermodynamically feasible under standard conditions but nevertheless suffers from a high activation barrier. Olefinic activation through catalyst coordination is thus required to diminish the electron density or σ N-H bond activation to increase the nucleophilicity. The last 60 years have seen a huge development of this reaction and numerous catalysts have been reported belonging to alkali bases, but also to the class of alkaline earth metals, rare-earth (actinides), group 4 (and 5) elements, late transition metals and organocatalysts. Recent efforts have been drawn towards the discovery of catalysts able to promote the reaction in an enantioselective manner.



This lecture will give an overview about the development of hydroamination reactions, associated with the optimization of already known promoters or the emergence of new catalysts type. It is organized according to the type of catalyst engaged in the reaction and aims specifically to highlight the most innovative processes for the asymmetric hydroamination of unactivated alkenes, implying either an inter- or an intramolecular pathway. Our contribution in this field will also be presented, concerning the discovery of different new families of efficient lanthanide amide ate complexes based on the binaphthylamido ligand[2] or corresponding simple lithium salts[3] that promoted various hydroamination reactions.

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Sunday, 1 September, h 8,30 *Lecture 7*

Sustainable catalysis based on cooperative pincer complexes

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In recent years, complexes based on "cooperating" ligands have exhibited remarkable catalytic activity. These ligands can cooperate with the metal center by undergoing reversible structural changes in the processes of substrate activation and product formation. Selected examples will be presented.

Our group has discovered a new mode of metal-ligand cooperation, involving aromatization – dearomatization of ligands. Pincer-type, pyridine- and bipyridine- based complexes of Ir, Rh, Ru, Fe, Pd, Pt and acridine complexes of Ru exhibit such cooperation, leading to facile activation of C-H, H-H, N-H, O-H bonds, and to novel, environmentally benign Ru-catalyzed reactions including (a) dehydrogenative coupling of alcohols to form esters and H_2 (b) hydrogenation of esters to alcohols under mild conditions (c) coupling of amines with alcohols to form amides, polyamides and peptides with liberation of H_2 (d) selective synthesis of primary amines directly from alcohols and ammonia (e) direct formation of acetals by dehydrogenative coupling of alcohols (f) generation of imines and hydrogen by coupling of alcohols with amines (g) dehydrogenative amidation of esters (h) dehydrogenative acylation of alcohols with esters (i) hydrogenation of amides to amines and alcohols (j) mild iron-catalyzed hydrogenation of ketones to alcohols (k) iron catalyzed CO_2 hydrogenation to formate salts (l) hydrogenation of CO_2-derived organic carbonates, carbamates, ureas and formates as alternative routes for the conversion of CO_2 to methanol (m) catalytic transformation of alcohols to carboxylic acid salts using water as the terminal oxidant (n) synthesis of substituted pyrroles by dehydrogenative coupling of β-amino-alcohols and secondary alcohols (o) synthesis of substituted pyridines by dehydrogenative coupling of γ-amino-alcohols and secondary alcohols. In addition, we have prepared Fe pincer complexes which exhibit high catalytic activity in hydrogenation of ketones and CO_2. Very recently we have observed a new mode of activation of CO_2 and nitriles by metal-ligand cooperation.

Moreover, metal-ligand cooperation of this type has led to a distinct stepwise approach towards water splitting, based on consecutive thermal H_2 generation and light-induced O_2 liberation, involving a new O-O bond-forming step.

Sunday, 1 September, h 10,00 *Lecture 8*

Strong donor carbenes and their potential in (oxidation) catalysis

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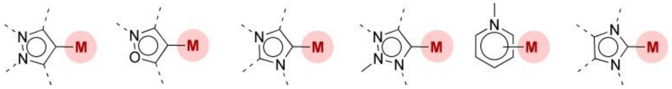
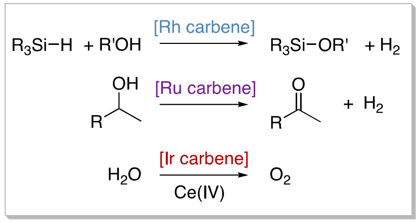
A powerful bond activation strategy relies on oxidative addition of (rather inert) bonds to electron rich transition metal centers. Obviously, the effectiveness of this approach is greatly supported by strongly donating ligands. While phosphine-based ligands have been ubiquitous as strong donors for a wide variety of transition metal-catalyzed reactions, more recently N-heterocyclic carbenes have gained in relevance as potent spectator ligands. Typically, N-heterocyclic carbenes are associated with a largely covalent bonding and strong σ-donor properties, which distinguish them from phosphines. We will discuss the basic impact of N-heterocyclic carbenes, and in particular synthetic opportunities for further increasing the donor ability of this type of ligand (see Figure below).[1]



The lecture will focus specifically on understanding the reactivity and the catalytic activity of such strong donor systems compared to classical Arduengo-type NHC complexes, in particular in redox-type transformations such as direct hydrogenation, transfer hydrogenation with high-valent transition metals, and water oxidation (see Fig right).[2] We will further discuss the scope and limitations of these strong donor carbene ligands, which includes non-innocent behavior and dissociative reactivities.[3]



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Sunday, 1 September, h 12,00 *Lecture 9*

New Reactivity from Organolithiums

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Organolithiums are probably the most widely used organometallics in organic synthesis. From the handful of commercially available organolithiums, a wide range of functionalized organolithiums may be made by regioselective deprotonation, halogen-metal exchange, transmetallation or carbolithiation. The lecture will start with an overview of these methods and will outline some general rules for making effective use of directing effects to construct target molecules effectively. It will stress the importance of solvation and intramolecular coordination effects, as well as stereoelectronic effects, in these regioselective reactions.

Stereoselective features may be introduced by the use of chiral ligands, especially the alkaloid (–)-sparteine and its analogues. The lecture will cover the most useful of these methods, and outline the detailed mechanisms by which asymmetry may be induced in RLi•(–)-sparteine directed reactions. Examples of target-directed syntheses based around this chemistry will be given. Opportunities for catalysis with organolithiums are currently relatively limited, and the state of the art in this area will be described.

Typically, simple organolithiums are used as bases, and more complex organolithiums are used as nucleophiles, with classical nucleophile-electrophile couplings dominating their practical utility. However, more recent work has uncovered some remarkable alternative reactivity patterns that are available to organolithiums under certain conditions of solvation or in certain conformations. These include dearomatising nucleophilic attack on aromatic rings and aryl migration reactions. Effectively, these reactions widen considerably the scope of classical nucleophilic aromatic substitution chemistry to include not only electron-deficient but also electron-rich coupling partners. These organolithium reactions thus provide an alternative, mechanistically unique way to make new C–C bonds, particularly at hindered positions. They allow the construction of unusual or otherwise difficult to obtain structural features in target molecules, and examples of such syntheses will be described.

Organolithium chemistry is relatively easy to understand in terms of a few mechanistic principles, and recently the application of tools such as in situ IR spectroscopy (React-IR) has uncovered previously hidden detail in their chemistry. These advances will be briefly described.

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Background information is provided in *Organolithiums: Selectivity for Synthesis*, Clayden, J. Pergamon, **2002** and in *Dearomatizing reactions using organolithiums* Lemière, G. and Clayden, J. *Science of Synthesis, Knowledge Updates* **2011**, 4, 139-190

For leading recent references, see: *Amines bearing tertiary substituents by tandem enantioselective carbolithiation- rearrangement of vinyl ureas* Tait, M.; Donnard, M.; Minassi, A.; Lefranc, J.; Bechi, B.; Carbone, G.; O'Brien, P.; Clayden, J. *Org. Lett.* **2013**, 15, 34-36; *Intramolecular vinylation of secondary and tertiary organolithiums* Lefranc, J.; Fournier, A. M.; Mingat,G.; Herbert, S.; Marcelli, T.; Clayden, J. *J. Am. Chem. Soc.* **2012**, 134, 7286-7289; *A general synthetic approach to the amnesic shellfish toxins: total synthesis of (–)-isodomoic acid B, (–)-isodomoic acid E, and (–)-isodomoic acid F* Lemière, G.; Sedehizadeh, S.; Toueg, J.; Fleary-Roberts, N.; Clayden, J. *Chem. Commun.* **2011**, 3745-3747.

Monday, 2 September, h 9,30 *Lecture 10*

Catalytic Functionalization of Hydrocarbons: the Methane Problem

Pedro J. Pérez

Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química y Ciencia de los Materiales, Universidad de Huelva, Campus de El Carmen 21007 Huelva, Spain
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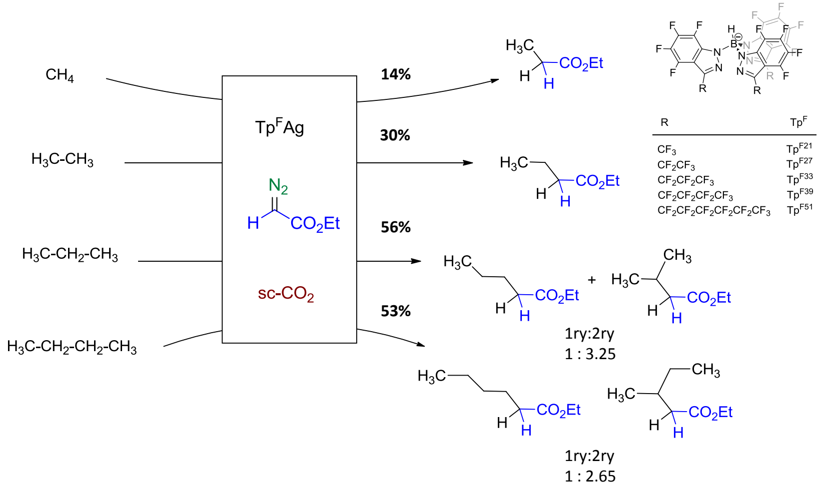
Methane is available in the earth crust either in natural gas (80-90%) or in shale gas (up to 98%), a fact that could make it as an ideal raw material for C1 chemistry. However, the main use of methane from an industrial point of view is restricted to the generation of *syngas*, further employed in the synthesis of methanol, in the Fischer-Tropsch process or in carbonylation/hydrogenation reactions. Examples of the direct functionalization of methane are yet scarce and in all cases confined to the lab scale.[1]

We have recently reported[2] the catalytic functionalization of methane using silver-based catalysts that induce the insertion of carbene units $CHCO_2Et$ from ethyl diazoacetate to the C-H bond of methane through transient silver-carbene intermediates. A family of fluorinated silver catalysts has been developed to promote this transformation, that takes place in sc-CO_2 as the reaction medium. Competition experiments with the C_1-C_4 alkane series have provided the values of the relative reactivity of the C-H bonds of the light alkanes, from which interesting information regarding the mechanism of this transformation have been obtained.



R	Tp^F
CF_3	Tp^{F21}
CF_2CF_3	Tp^{F27}
$CF_2CF_2CF_3$	Tp^{F33}
$CF_2CF_2CF_2CF_3$	Tp^{F39}
$CF_2CF_2CF_2CF_2CF_2CF_3$	Tp^{F51}

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Monday, 2 September, h 11,30 *Lecture 11*

Sweetness and privilege of metal promoted asymmetric catalysis

Francesco Ruffo

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It is nowadays acknowledged the importance of developing convenient methodologies to produce enantiomerically pure products.[1] Within this context, asymmetric organometallic catalysis is one of the most successful strategies. Since the first examples dated 1966,[2] organometallic catalysts have attracted increasing interest in both academic and industrial contexts, for some clear advantages:

(i) the remarkable activity, which allows the use of high substrate/metal ratios;

(ii) the tunability of the coordination environment, that widens the scope of substrates;

(iii) the tolerance to functional groups, which enhances chemoselectivity, and then simplifies the purification of the products.

(iv) the flexibility of the physical properties, which helps separation and recycle of the catalyst.[3]

Objective of this lecture is to provide the essential tools for addressing asymmetric organometallic catalysis. It is first explained the value of this methodological approach, through a brief historical introduction. A careful evaluation of the leading “actors” follows, with the description of the role of the **metal** (the *activating agent*), the **substrate** (from *pupa* to *butterfly*) and the **chiral ligand** (the *conductor*). Then, the research activities[4] of the organometallic chemistry group in Napoli are briefly presented.

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Monday, 2 September, h 15,00 *Lecture 12*

Gold catalysis - A universe of innovation

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In the last decade homogenous gold catalysis has developed into a powerful tool for organic synthesis.[1]In this highly active field the use of diynes as substrates has only recently been explored. Here new cyclisation modes of 1,2-diynearenes to undergo selective intramolecular and intermolecular C-H activation of unactivated C-H bonds are reported (Figure 1).[2-4] The mechanism of this transformation involves two gold centers (principle of “dual activation”), both synergistically activating the substrates for cyclisation *via* π- and σ-coordination. A bifurcation on the potential energy surface gives access to gold-vinylidenes or gold-carbenes, both highly reactive intermediates capable for C-H activation.[5] Depending on the backbone of the diyne system, a change on the bifurcation energy surface to selectively lead to gold vinylidenes or gold carbenes. Both intermediates are highly interesting as they represent a new class of organogold compounds and offer new perspectives for homogenous gold catalysis.

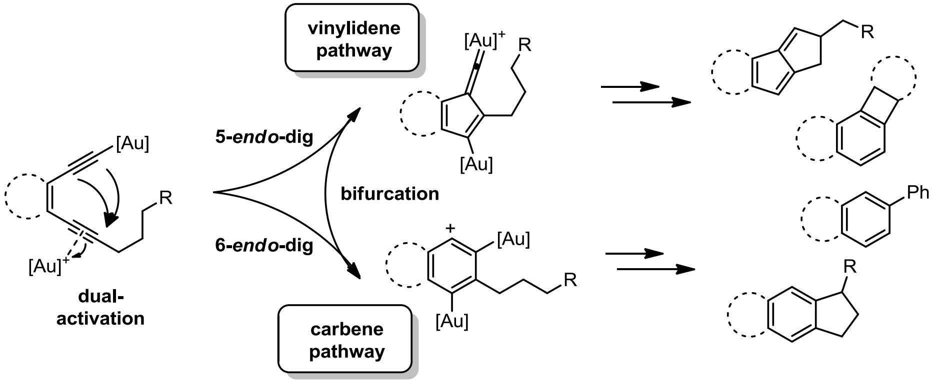

Figure 1. A universe of dual-gold catalyzed cyclizations of diynes

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Tuesday, 3 September, h 9,00 *Lecture 13*

Metal-catalyzed amide bond forming reactions in water: Nitrile hydrations and beyond

Victorio Cadierno Menéndez

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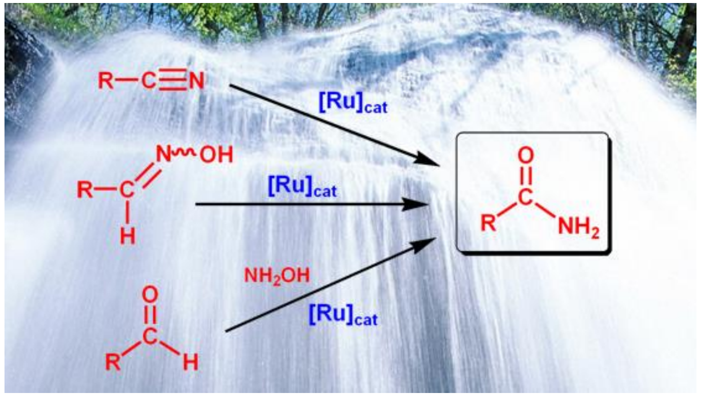
Amides are versatile building blocks in synthetic organic chemistry, present a wide range of pharmacological applications, and are used as raw materials in industry for the large-scale production of engineering plastics, detergents and lubricants. The development of green procedures for the synthesis of this relevant class of compounds is therefore of prime interest in modern chemistry. In the search of improved synthetic methods, metal-catalyzed transformations have emerged in recent years as the most promising alternatives for the atom-economical and cost effective synthesis of amides, opening also previously unavailable routes that start from substrates other than carboxylic acids and their derivatives. In this lecture, a brief overview of metal-catalyzed synthetic approaches of amides conducted in environmentally friendly aqueous media will be presented.[1] Subsequently, the work of our group on the development of hydrophilic ruthenium catalysts for nitrile hydration reactions in water,[2] and related amide bond forming reactions starting from aldoximes and aldehydes,[3] will be discussed in depth.



References

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Tuesday, 3 September, h 10,30 *Lecture 14*

Recent advances in cross-coupling reactions.
Synthetic applications in the field of new generation solar cells

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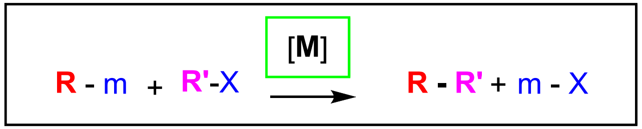
Transition metal-catalyzed cross-coupling reactions between organic halides and organo-metallic reagents constitute one of the most straightforward methods for the formation of carbon–carbon bonds.[1] This has been recognized in 2010 by the awarding of the Nobel prize in chemistry to Richard Heck, Ei-ichi Negishi, and Akira Suzuki "*for palladium-catalyzed cross-couplings in organic synthesis*". Indeed, numerous examples of such process have been developed and exploited as a powerful tool to assemble complex molecular frameworks of a range of interests encompassing total synthesis of natural products[2], medicinal chemistry, industrial process development[3] as well as chemical biology, materials, and nanotechnology. Such an important reaction can be described by the simple equation reported in the following scheme, were **R** and **R'** are organic groups, **X** is an halogen atom or a related heteroatom leaving group, **m** is the metal countercation of the organometallic species involved and **M** is a transition metal.



$$R-m + R'-X \xrightarrow{\boxed{[M]}} R-R' + m-X$$

Despite the simplicity of the process and the huge number of studies and very elegant and efficient examples which are present in the literature, research in this area is still very active. Particular attention is devoted to the development of new and more efficient catalytic systems, which might be able to activate less reactive substrates, to allow a better functional group tolerance, to make possible catalysts recycling. In addition, new environmentally benign reactions conditions aimed to replace expensive reagents, toxic and flammable organic solvents, high temperatures and long reaction times, have been investigated in order to facilitate the application of this methodology in industry. Among the others, cross-coupling reactions represents probably the most widely used method for aryl-aryl bond formation and, more in general, for the synthesis of highly conjugated polyenes and have found a very stimulating field of application in the molecular design of metal-free organic dyes for applications in DSSC[4], a new generation of photovoltaic devices which offer the possibility of low-cost conversion of solar energy.

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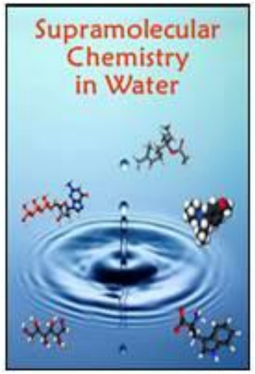

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Poster 1

Glucose-derived Bis(pyridine-2-carboxamide) Ligands for Molybdenum Catalyzed Asymmetric Allylic Alkylations

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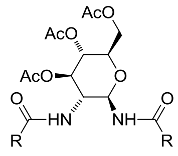
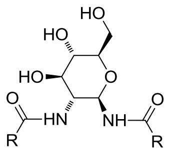
The **elpaN-Py** family of ligands[1] (Figure 1), which represents a subset of the elpaN-type library based on D-glucose,[2] is described. The ligands are structural analogues of the privileged *bis*(pyridine-2-carboxamides) derived from *trans*-1,2-diaminocyclohexane,[3] and differ for the type of substitution in the coordinating functions present in positions 1 and 2. Their ability to induce high enantioselectivity in asymmetric allylic alkylations promoted by molybdenum under microwave irradiation has been successfully demonstrated (Figure 2), starting from both a linear (ee up to 99%) and a branched substrate (ee up to 96%). The multifunctional nature of the sugar scaffold was exploited for the preparation of a polar ligand, through deprotection of the hydroxyl groups in positions 3, 4 and 6. In this version, it was possible to verify the performance in catalysis in alternative solvents, such as ionic liquids and water.



R = R1 **elpaN-py**
R = R2 **elpaN-py-p-OMe**
R = R3 **elpaN-qui**



R = R1 **elpaN-py'**

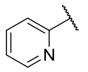
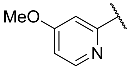
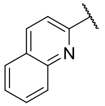
R	STRUCTURE	SUFFIX
R1		**-py**
R2		**-py-*p*-OMe**
R3		**-qui**

Figure 1

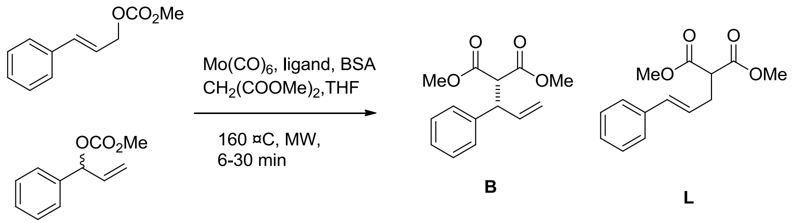


Figure 2

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Poster 2

Synthesis of Organometallic Assemblies from Quinonoid Zwitterions

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Following our previous work on metalla-assemblies,[1] a large cationic triangular metalla-prism $[Ru_6(p\text{-cymene})_6(tpt)_2(L)_3]^{6+}$, incorporating (p-cymene) ruthenium building blocks, bridged by N,N’-R,R-2-amino-5-alcoholate-1,4-benzoquinonemonoiminium zwitterionic ligands (L),[2] and connected by two 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (tpt) subunits allows the encapsulation of various guest molecules. These cationic cages and cationic host-guest systems have been isolated as their triflate salts. The formation of the cages was confirmed by NMR spectroscopy. The properties of these systems were studied in solution by acid-base titrations, allowing the determination of the pH needed to break the cages. Moreover, the solubility and property of the cages can be modified by introduction of different functional groups on the zwitterionic ligand y.

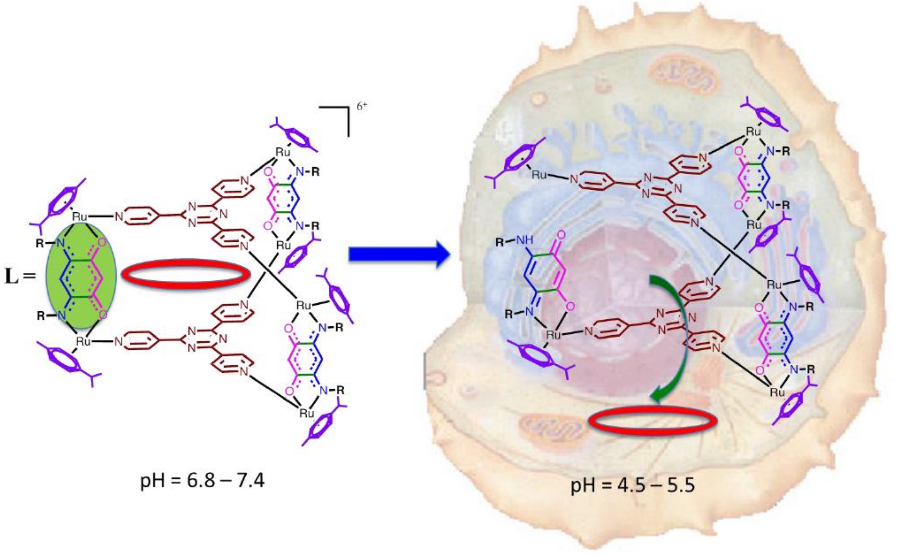

Figure 1

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Poster 3

Electronic Effect in Iron Catalysed C-H Bond Oxidation

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The search for efficient and selective methods to oxidize C-H bonds has been a longstanding goal in organic chemistry. However, it is less than 6 years that this goal managed to become a useful tool in synthetic chemists hands by the use of nonheme iron catalysts. One of the most efficient catalytic systems prepared so far is White's complex,[1] reported in Figure 1 (R=H, the first structure on the left).

With the aim at shedding some light on the mechanism by which this system works, we prepared the three substituted iron (II) PDP complexes shown below. The chosen substituents allow a wide investigation of the electronic effects on the catalytic efficiency of the system.

The results obtained in the oxidation of C-H bonds of some non-activated hydrocarbons substrates will be shown together with the synthetic route and a full characterization of the new iron complexes.

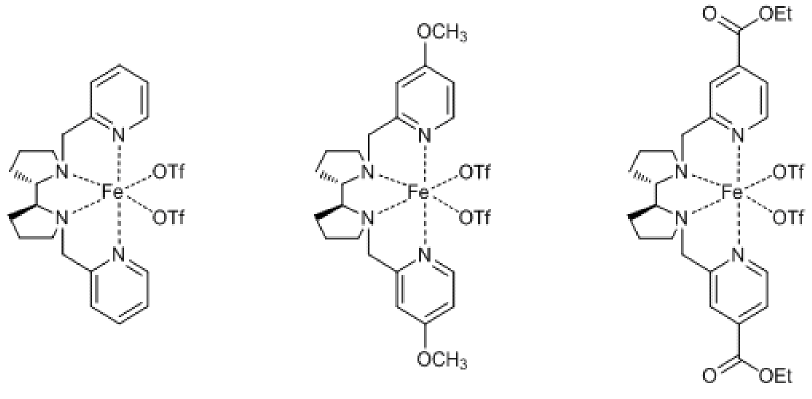

Figure 1

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Poster 4

Synthesis and Oxygenation of Dialkylborane Complexes with Selected O,O'-Bifunctional Ligands

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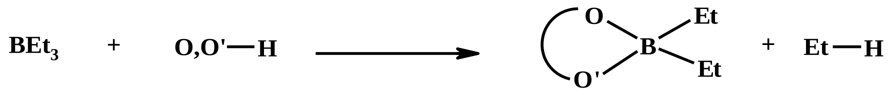
In the recent decades metaloorganic complexes of 13th group elements were shown to catalyze various organic reactions. This type of complexes can also be used as precursors for formation of ceramic materials. In order to rationally design the catalysts and precisely control those reactions, it is important to understand factors controlling structure and reactivity of the molecular complexes. Especially, mechanism of oxygenation of those complexes is very interesting from practical point of view. Lewiński's group has been interested in the oxygenation reaction of the complexes for many years. Systematic investigations performed by our group show, that ligand used for complex formation greatly influences oxygenation mechanism and its products. Therefore, by careful selection of the ligand we may obtain valuable precursors or catalysts. To date most of the work has been concentrated on dialkylaluminum complexes. Much less is known about interaction of dialkyborane complexes with molecular oxygen.



Scheme 1

In the presented work, synthesis of dialkylborane complexes with selected O,O'-ligands (Scheme 1) as well as characterization of their products by ^{1}H and ^{11}B NMR, IR and X-ray diffraction will be discussed. To confirm proposed molecular structures of the complexes, experimental ^{11}B NMR spectra were compared with results of quantum mechanics calculations at the DFT level. Those results confirm that the complexes exhibited both, tetra- and tri-coordinated structures depending on the used ligand.

Subsequently, the synthesized compounds were oxygenated in order to elucidate mechanism of the dialkylborane complexes reaction with molecular oxygen.. On the basis of ^{1}H NMR results one can conclude that only the diethylborane complexes with methyl salicylate and methyl lactate easily undergo the oxidation. These results suggest that propensity of the alkylborane complex toward oxygenation is connected with the asymmetrical structure of ligand containing asymmetric side groups. Our attempts to correlate electrochemical oxidation potentials of the complexes with their tendency to reaction with molecular oxygen will also be discussed.

Poster 5

Synthesis and Characterization of Rhodium Nanoparticles Stabilized by Triphenylphosphine and Application in Catalytic Hydrogenation

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Over the last few decades the synthesis of monodisperse, size- and shape-controlled metal nanoparticles (NPs) has become one of the major goals in nanosciences.[1] Interest was shown toward these nano-sized particles since they form a class of materials with properties distinctly different from their bulk and molecular counterparts.[2] Consequently, metallic nanoparticles found numerous applications, notably in the field of catalysis.[3, 4]

The decomposition of organometallic precursors under mild conditions showed to be a successful synthetic methodology to give well-controlled metallic nanoparticles displaying a very small size.[5] This is a key feature to achieve high catalytic activity due to high surface area of metallic atoms.[6] A stabilizing agent (coordinating ligands,[7] polymers,[1] etc.) is required to prevent the agglomeration of the metal nanoparticles. This stabilizer can also govern the surface chemistry of the NPs as allowing them to be soluble in water for example[vii]

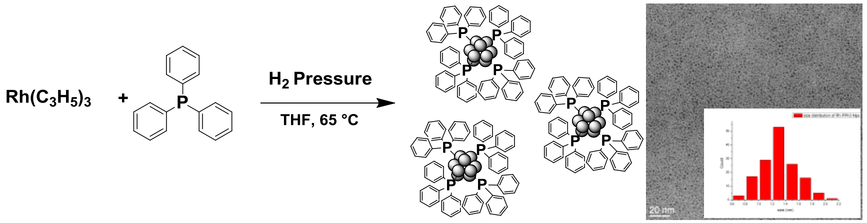

Figure 1

Here in, we will present the synthesis of spherical, ultra small and monodisperse Rhodium nanoparticles synthesized from $[Rh(C_3H_5)_3]$ precursor. The size of these NPs is controlled by a suitable quantity of triphenylphosphine as a stabilizing ligand. Full characterization in terms of morphology and surface state (solution ^1H NMR and ^{13}P NMR, solid state NMR, IR-FT, TEM, HRTEM and EDX, WAXS analysis) for these NPs will be also presented. These systems were tested in hydrogenation reaction of model alkenes and arenes showing high activity under mild conditions.

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Poster 6

Microwave Assisted Synthesis of Shvo's Type Catalysts

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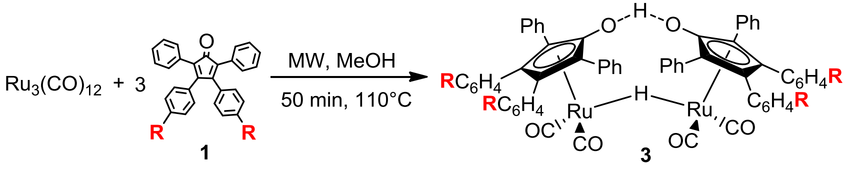
Shvo's catalyst $\{[Ph_4(\eta^5\text{-}C_4CO)]_2H\}\text{-}Ru_2(CO)_4H$ has been applied successfully in a broad scope of hydrogen-transfer processes,[1] therefore development of new protocols for a fast and convenient synthesis of such derivatives is a current challenge. Here we report on a simple, environmentally friendly, expeditious microwave-assisted procedure for the synthesis of Shvo's type complexes through the reaction between $Ru_3(CO)_{12}$ and variously functionalized tetra-arylcyclopentadienones, which provides good yields and purities within 50 min at 110°C (Scheme 1).



R = H (**1a**, **3a**), Br (**1b**, **3b**), OMe (**1c**, **3c**), −C≡CC$(CH_3)_2$OH (**1d, 3d**), −C≡CC$(Ph)_2$OH (**1e, 3e**)

Scheme 1

The reaction is general and leads to yields similar to the conventional refluxing method (ca. 70 %). By far, the most important outcome of this new method concerns the improvement in reaction time from 40 h in the conventional method to 50 min in our microvawe assisted one. Indeed functionalized catalysts maintain the catalytic activity and selectivity toward the reduction of aldehydes and ketones.

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Poster 7

Solid-State Characterization of MOFs for Electroluminescent Applications

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In this communication we report the synthesis and the characterization of different types of Metal-Organic-Framework (MOF). MOFs are a recently-identified class of porous material with a specific three-dimensional structure, consisting of metal ions linked together by organic bridging ligands. Their development represents a new approach on the interface between molecular coordination chemistry and materials science.[1] In fact, MOFs are attracting considerable attention for applications such as gas storage, separations, catalysis, and also, in recent years, for their potential uses in electronic devices.[2] Their potentiality lies on several peculiar properties, such as large pore sizes, high surface areas, selective uptake of small molecules and optical or magnetic responses to the inclusion of guests. More importantly, their synthesis from molecular building blocks holds the potential for directed tailoring of these properties.[3]

This work focuses on MOFs based on copper iodide (CuI), cyanide (CuCN) or thiocyanate (CuSCN) with aza-ligands (DABCO and di-anhydride perilenes) to be used as electroluminescent devices (static host-guest interaction processes). In particular, MOFs synthesis have been carried out especially through a solid-state "solvent-free" approach (*mechanochemical methods*), but also through more traditional techniques such as solvothermal/hydrothermal synthesis and crystallization.

The structural characterization on powder samples has been fulfilled through the following spectroscopic techniques: Solid-State Nuclear Magnetic Resonance (SS NMR), RAMAN and Infrared Spectroscopies, X-Ray Powder Diffraction (XRPD) and, when possible, Single Crystal X ray Diffraction. Concerning the SS NMR analysis, samples characterization was performed through ^{13}C CP MAS to evaluate the ligands coordination, ^{15}N CP MAS to investigate copper-nitrogen interactions, and ^{63}Cu spectra (Hahn-Echo sequence, Solid Echo sequence and Direct Exitation) to analyze metal sites. This represents a very important challenge because of the lack of data reported in literature about copper analysis by SS NMR.

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Poster 8

Novel Water Soluble Symmetrical and Non-symmetrical 11th Group-NHC Complexes: Synthesis, Citotoxicity and SAR Study

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As potential anticancer drugs, N-Heterocyclic Carbene (NHC) complexes constitute a recent and fruitful field of research. Our research group, during the last 5 years, has developed different classes of coinage metal-NHC complexes obtained from the precursors $\{[HB(RImH)_3]Br_2\}$ (R = Benzyl, Mesityl and t-Butyl)[1], $\{[H_2B(BnTzH)_2]Br\}$,[2] $\{[H_2B(p\text{NO}_2BnTzH)_2]Br\}$,[3] $\{H_2C(HTz^R)_2\}$ and $\{H_2C(HIm^R)_2\}$ (HTz = 1,2,4-triazole; HIm = imidazole; R = $(CH_2)_3SO_3^-$ or $(CH_2)_2COO^-$).[4] Recently we have focused the research work on the development of new coinage metal-NHCs complexes obtained from the water soluble ligands $Him^{1R,3R}Cl$ (R = $COOCH_3$, $COOCH_2CH_3$ or $CON(CH_2CH_3)_2$)[5] or the zwitterionic water soluble precursor $NaHIm^{1R,3R}$ (R = $(CH_2)_3SO_3^-$).[6] Here we report the synthesis of the novel zwitteronic symmetrical NHC ligands $NaHIm^{1R,3R,4R''}$ (R = $(CH_2)_3SO_3^-$, R'' = H, CH_3 or NO_2) (Figure 1), $NaHBzim^{1R,3R}$ (R = $(CH_2)_3SO_3^-$) and non-symmetrical NHC ligands $NaHIm^{1R,3R',4R''}$ (R = $(CH_2)_3SO_3^-$, R' = $CH_2C_6H_5$, R'' = H, CH_3 or NO_2), $\{[HBzim^{1R,3R'}]Br\}$ (R = $(CH_2)_3SO_3Na$, R' = $CH_2C_6H_5$) and the related silver(I)-NHC complexes.[3] Finally we report the cytotoxic activity and the SAR study of the NHC complex classes developed by our research group.

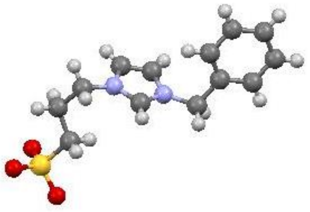

Figure 1. Ortep of $NaHIm^{1R,3R'}$ (R = $(CH_2)_3SO_3^-$, R' = $CH_2C_6H_5$,)

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Poster 9

Synthesis of N-Heterocyclic Dicarbenes Derived from Bis(pyrazol-1-yl)alkane Ligands

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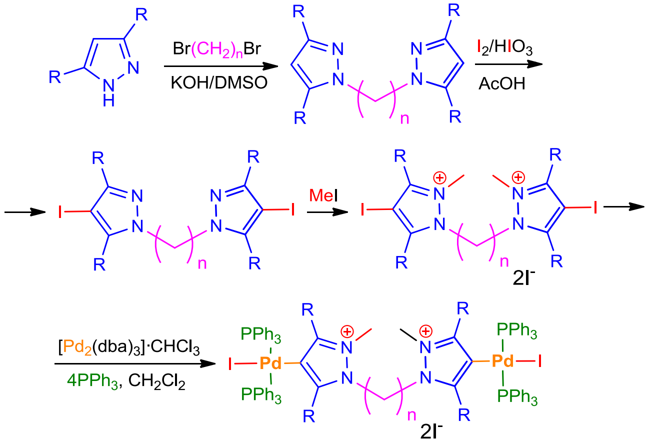
Chemistry of stable N-heterocyclic carbenes (NHCs) is a rapidly developing area of organic and organometallic chemistry. Metal complexes of N-heterocyclic carbenes often demonstrate high catalytic activity.[1] NHCs based on imidazole derivatives are widely known, one of the most important example of their complexes is Grubbs olefin metathesis catalyst.[2] Carbenes based on other azoles, namely pyrazole and triazole are much less studied,[3] especially those containing two or more carbene centers.[4]

Previously we have developed an efficient approach to bis(pyrazol-1-yl)alkane and related ligands by the reaction of azoles with dibromoderivatives in a superbasic KOH-DMSO system followed by pyrazole ring functionalization.[5] Here we report the synthesis of bis(pyrazolium) salts with long aliphatic spacers as precursors for the generation of pyrazole-derived dicarbenes (Figure 1).



R = H, Me; n = 4, 5, 6, 8, 10

Figure 1

Acknowledgements: The reported study was supported by RFBR, research projects Nos. 12-03-31197 and 12-03-98006.

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Poster 10

Novel Copper and Silver Catalysts for Hydrocarbons Functionalization

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One of the most interesting research areas is the development of effective processes for the functionalization of alkanes[1]. Catalysis is an effective method for this goal but it is yet underdeveloped mainly due to the very high dissociation energy of the C-H bonds in these compounds.

Our research group has developed a series of group 11 metal catalysts able to functionalize alkanes by carbene insertion from diazo compounds,[2] a methodology that has recently been applied to methane.[3] With the aim of improving the catalytic activity of this substrate as well as the primary positions of linear alkanes, novel Cu and Ag complexes with new scorpionate ligands have been being developed, their catalytic capabilities being presented herein.

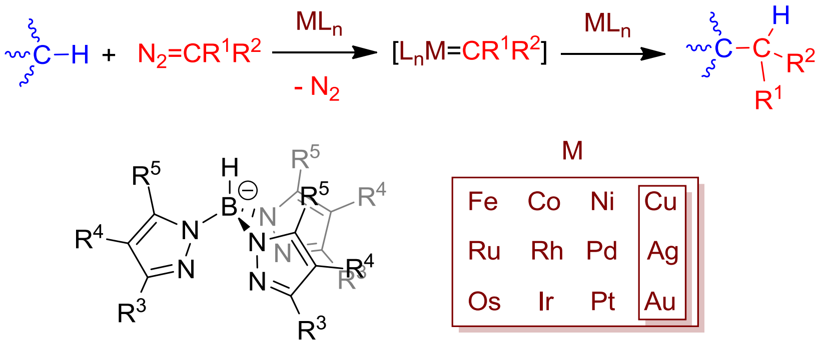

Figure 1

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Poster 11

Fluoroalkyl Allyl Ethers: Useful Building Blocks for the Synthesis of Perfluorinated Molecules

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The insertion of perfluorinated moieties within the structure of more traditional organic compounds confers unique properties that have been largely exploited in several application fields. The readily available allyl perfluoroalkyl ethers can be either converted to vinyl perfluoroalkyl ethers derivatives via a versatile and convenient double bond isomerization reaction or, in a completely different manner, used to build-up multi-block molecules, in which perfluorinated chains are alternated to hydro-ether segments. [2]

In this work we present the ruthenium-catalyzed isomerization of the allyl ethers shown in Figure 1. The isomerization has been carried out under variety of experimental conditions using conventional ([RuClH(CO)($PPh_3)_3$]) and less conventional (CatMETium_RF3™) ruthenium(II) complexes. The activity of the two different pre-catalysts together with the corresponding kinetic studies will be discussed.

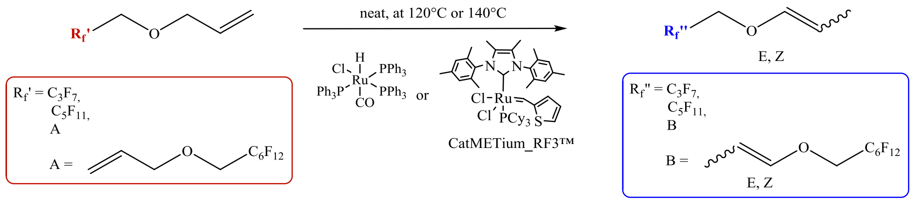

Figure 1

The vinyl perfluoroalkyl ethers derivatives thus obtained can be used as attractive monomers in cationic UV-radiation curing technology.[2]

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Poster 12

Direct *syn* Insertion of Alkynes and Allenes into Au-Si bonds

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During the last 15 years gold chemistry experienced an impressive development regarding catalytic applications and thus gold complexes are no longer considered as chemically inert species.[1] Moreover, recent fundamental studies highlighted that the organometallic chemistry of gold complexes extends beyond the coordination/activation of π-bonds and that gold may offer a more versatile reactivity.[2]

However, our knowledge of gold chemistry is still limited as compared to the other transition metals, which is especially true for elementary steps often involved in transition metal-mediated transformations such as oxidative addition, migratory insertion, etc. We recently started a research program aiming at investigating the fundamental reactivity of gold complexes.[3,4] In this context, we discuss an elementary step which is ubiquitous in transition metal chemistry but unprecedented with gold, namely *syn* insertion.[5] Alkynes and allenes are shown to insert into Au-Si bonds of (phosphine)silylgold complexes to yield vinylgold complexes with high stereo- and regioselectivity (Fig. 1).[6] Based on a combined experimental and theoretical study a mechanistic proposal is presented.

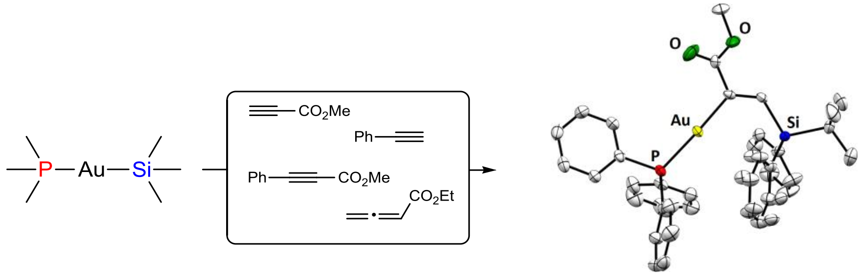

Figure 1: Direct *syn* insertion into the Au-Si bond

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Poster 13

Device Compatible Water Oxidation Catalysts for Solar to Chemical Energy Conversion

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In 2001, the global energy consumption rate was 13.5 TW. In 2050 based on the increasing population and economic growth, this is estimated to reach 27 TW.[1] To meet these future demands, not relying on fossil fuels only, we need sustainable, carbon neutral ways of winning energy. The sun is the most abundant energy source on the planet (regarding current technology) as on average the energy of the sun reaching the earth's surface is estimated to be 1.2·105 TW. Part of this can be directly used by converting it to electricity using solar cell technology, but it is essential to at least partly convert to storable energy, by fixing it in chemical bonds. This can be achieved by using solar energy to convert water into hydrogen and oxygen.

Plants, algae and cyanobacteria already use photosynthesis to convert energy from the sun into chemical energy within Photosystem II at the water oxidation reaction center of the Manganese-Calcium cluster. With Nature serving as a model we try to develop new, rapid and efficient water oxidation catalysts based on Iridium.[2] Application of suitable ligands offer ease of synthetic modification such that these catalysts can be modified to have the ability to integrate them into devices, which are capable to split water into hydrogen and oxygen. This so called Artificial Leaf, if turnover numbers and turnover frequencies are sufficiently high, could provide us with a significant solution towards the upcoming energy problem. In this work we will discuss our endeavors in catalyst modification.

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Poster 14

Study of the Surface Chemistry of Ruthenium Nanoparticles in the Fisher-Tropsch Synthesis

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An ideal solution to the limit stock of natural sources of hydrocarbons and to control the CO and CO_2 emissions is the Fisher-Tropsch synthesis; CO and CO_2 are hydrogenated to produce hydrocarbons (olefins and paraffins) (Scheme 1). Although the activity and selectivity of this process have been improved over several decades,[1] fundamental issues about the mechanism and the structure of the catalyst remain unsolved.

$$CO/CO_2 + H_2 \xrightarrow{\text{catalyst}} C_nH_{(2n+2)}(\text{alkanes}),\ C_nH_{2n}(\text{olefins})$$

Scheme 1

The development of more active and/or selective catalysts for industrial application of this process is still an ongoing field of research. Metal nanoparticles as catalysts are expected to provide more efficient and selective catalysis. In this context, our team has developed for over 20 years the synthesis of metal nanoparticles (NPs) following an organometallic approach (Figure 1).[2] This method allows the tuning of NPs surface chemistry through addition of appropriate ligands as stabilizers. Moreover, the study of NPs surface properties is performed by using a combination of techniques such as IR-FT and NMR spectroscopies. For example, RuNPs prepared in this way can bring useful information on the coordination, dynamics and reactivity of surface ligands such as hydrides and CO [3] which are present in many catalytic processes, like in the Fisher-Tropsch synthesis.

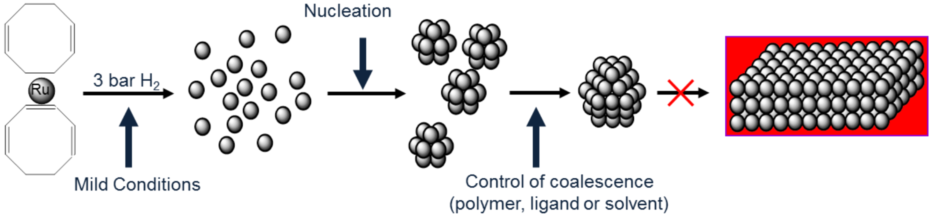

Figure 1

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Poster 15

Selective Synthesis of the $[Ni_{36}Co_8C_8(CO)_{48}]^{6-}$ Carbonyl Cluster by Thermal Decomposition of the $[H_2Ni_{22}Co_6C_6(CO)_{36}]^{4-}$

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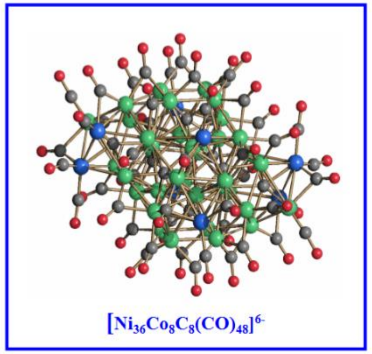
Several bimetallic Ni-Co carbide and acetylide carbonyl clusters are known. They display a random alloy architecture with a very wide variability of the Ni/Co composition. The Ni-Co ratio ranges from 0.33 of $[Co_6Ni_2C_2(CO)_{16}]^{2-}$ [1] to 9 of $[Ni_9Co(CO)_{16}]^{3-}$.[2] The possibility of preparing bimetallic Ni-Co molecular clusters with very different Ni/Co compositions makes these clusters quite attractive for the preparation of bimetallic magnetic Ni-Co nanoparticles, allowing a gradual variation of their properties.[3] In addition, they are interesting also at the molecular level for the study of the relationship existing between composition and proprieties of bimetallic nanoclusters and nanoparticles.[4]



Herein, our recent results in the chemistry of Ni-Co carbonyl clusters are described. The thermal decomposition in thf of the hexa-carbide $[H_2Ni_{22}Co_6C_6(CO)_{36}]^{4-}$ [2] results in the new bimetallic Ni-Co octa-carbide $[H_{6-n}Ni_{36}Co_8C_8(CO)_{48}]^{n-}$ (n = 3-6), which possesses polyhydride nature and can be inter-converted by means of acid-base reactions.[5]

The hydride nature of the $[H_{6-n}Ni_{22}Co_6C_6(CO)_{36}]^{n-}$ (n = 3-6) anions is suggested by the observed shifts of their υ(CO) bands as a function of the basicity of the solvent and/or after addition of acids or bases, and fully confirmed by electrochemical studies. The hexa-anion $[Ni_{36}Co_8C_8(CO)_{48}]^{6-}$ has been isolated in a crystalline state and structurally characterized *via* X-ray crystallography.

The high nuclearity $[H_{6-n}Ni_{36}Co_8C_8(CO)_{48}]^{n-}$ (n = 3-6) cluster approaches the nanosize regime since it displays a diameter of *ca.* 1.61 nm. Thus, it may be viewed as a molecular ultra-small metal nanoparticle.[6]

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Poster 16

Catalytic Hydrogenations Using a Water Soluble Pyridine-Triazole Ligand

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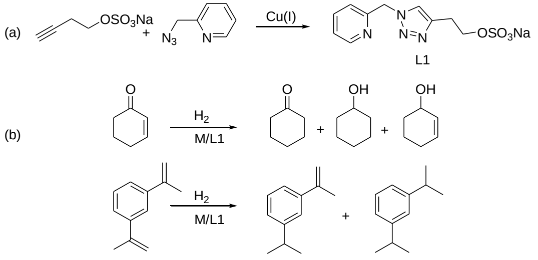
The liquid-liquid two-phase catalysis is at present of great interest because the catalyst is confined in one of the two-phases and the product in the other phase allowing for a prompt recovery of the product and an easy recycle of the catalyst. In particular, the use of water soluble catalysts for aqueous/organic biphasic reactions is increasingly attractive[1]. Our research group has long been interested in the synthesis of triazole ligands for Suzuki-Miyaura (S-M) cross-coupling reaction of aryl halides with arylboronic acids, and recently we have developed a water soluble pyridyl-triazole ligand for S-M reaction in water[2,3,4]. In this work, we wish to report our studies on *in situ* biphasic (water/toluene) catalytic hydrogenation of unsaturated substrates in the presence of triazole ligand (L1) and $[Ir(COD)Cl]_2$.



M: $[Ir(COD)Cl]_2$

Solvents: Water /Toluene

Scheme 1. (a) Synthesis of ligand (L1), (b) Aqueous biphasic hydrogenation of 2-cyclohexen-1-one and 1,3-diisopropenylbenzene.

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Poster 17

Novel dicarbene iridium(III) catalysts for water oxidation reaction

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Light driven catalytic water splitting could contribute to the obtainment of sustainable energy sources alternative to fossil fuels.[1a] This process leads to the green production of H_2 and O_2 molecules, but it has still a bottleneck represented by the development of an efficient catalytic system for the oxidative half reaction, which is endoergonic and mechanistically rather complex.[1] Several transition metals have been employed so far, both in heterogeneous or in homogeneous conditions.[2] One of the most active species is IrO_2 nanoparticles,[3] but molecular complexes are more attractive because their steric and electronic properties can be finely modulated by playing on the metal coordination sphere.[2] In this contribution we report novel dicarbene iridium(III) complexes with different nuclearity depending on the nature of the coordinated N-eterocyclic dicarbene ligands. Some of the synthesized complexes have been employed as catalyst for water oxidation reaction both in dark conditions (Ce(IV) or $NaIO_4$ as sacrificial oxidant) or in a photoactivated cycle ($[Ru(bpy)_3]^{2+}$ as photosensitizer and $Na_2S_2O_8$ as sacrificial electron acceptor). Finally the catalyst fate under turnover conditions has been investigated by combined spectroscopic (NMR, EPR, UV-Vis), kinetic and GC-MS experiments.[4]

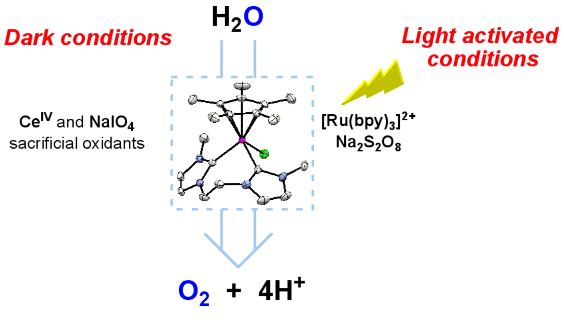

Figure 1

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Poster 18

A new palladium-catalyzed carbonylative approach to isobenzofuran derivatives

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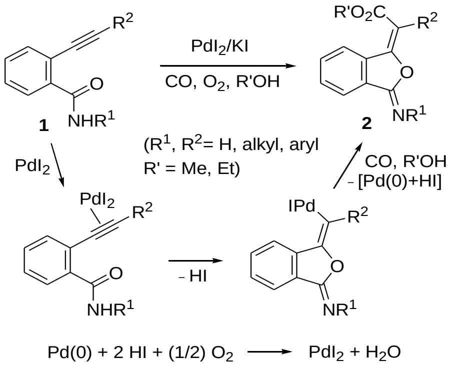
The 3*H*-isobenzofuran unit constitutes the core structure of several biological active compounds having anti-inflammatory, antiviral, and antimicrobial.[1] In this communication, we report a novel approach to the synthesis of functionalized 3*H*-isobenzofuran-1-ylideneamine derivatives **2**, based on PdI_2-catalyzed oxidative heterocyclization-alkoxycarbonylation[2] of readily available 2-alkynylbenzamides **1**, according to Scheme 1.



Scheme 1

Reactions are carried out in alcoholic solvents (R'OH, R' = alkyl) at 80-100 °C and under 40 atm of a 4:1 mixture of CO-air, in the presence of catalytic amounts of PdI_2 (1 mol %) in conjunction with KI (10 mol %), to give carbonylated 3*H*-Isobenzofurans **2** in fair to good isolated yields (50-80%). The structure of the products has been confirmed by X-ray diffraction analysis.

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Poster 19

Intramolecular d^{10}-d^{10} Interactions in Bimetallic Co-Au Carbide Carbonyl Cluster

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Weak d^{10}-d^{10} metal-metal interactions are now widely documented in the chemistry of Au(I) complexes and clusters, and the term "aurophilicity" is commonly used to refer to such interactions.[1] Although positively charged Au(I) ions could be expected to repel each other on the basis of electrostatics, the attractive interactions between these closed valence shell ions result in interatomic distances typically in the range between 2.7 and 3.3 Å, often shorter than the sum of the van der Waals radii.[2]

The M_6C octahedral framework present in several mono-carbide carbonyl clusters seems to be an interesting platform in order to test aurophilicity. In these clusters, the $[AuPPh_3]^+$ fragment might be coordinated to an edge or a face of the octahedron. Moreover, when a second fragment is added, several options arise since it can coordinate to a site close or far from the first one. Aurophilicity favors the proximity of the two Au(I) centers and the formation of intramolecular d^{10}-d^{10} interactions, as exemplified in $Rh_6C(CO)_{13}(AuPPh_3)_2$ and $Co_6C(CO)_{13}(AuPPh_3)_2$.[3,4]

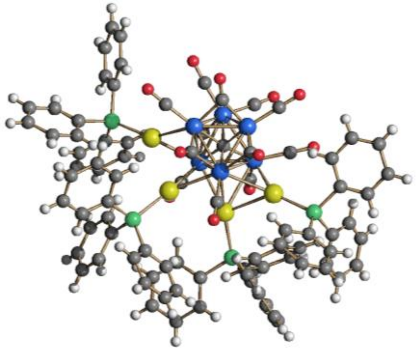

Figure 1

It was, thus, of interest to investigate analogous octahedral M_6C carbonyl clusters containing more than two $[AuPPh_3]^+$ fragments, in order to see if more extended Au⋯Au interactions were formed and to evaluate the importance of such interactions in larger clusters. Herein, we report the study of the reaction of $[Co_6C(CO)_{15}]^{2-}$ with $Au(PPh_3)Cl$ which results in the formation of some new Co-Au carbide carbonyl clusters. Among these, the neutral $Co_6C(CO)_{12}(AuPPh_3)_4$ cluster has been structurally characterized, showing the existence of at least three different isomers possessing the same octahedral Co_6C core and differing for the coordination modes of the $AuPPh_3$ fragments.

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Poster 20

A Cooperative Iridium-bisMETAMORPhos Complex for the Dehydro-genation of Formic Acid

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Hydrogen holds the potential to be one of the major energy carriers for the future. However, a hydrogen-based economy requires technology that allows efficient and safe storage and release of H_2. In this light, the reversible storage of hydrogen in the form of formic acid provides an interesting H_2 storage-release system. Substantial developments in the production of formic acid since the early nineties have stimulated interest in the reverse reaction for hydrogen release on demand.[1] Ideally, catalytic dehydrogenation takes place in the absence of base and additives, thereby maximizing the overall hydrogen storage capacity and preventing hydrogen contamination with traces of volatile amines that may poison the fuel cell. We envisioned ligand cooperativity could provide an interesting approach in this area as metal complexes with an internal base as part of the ligand could be developed.

In this contribution we present a novel iridium-bisMETAMORPhos complex that is active in formic acid dehydrogenation in the absence of external base, and demonstrate that the ligand plays an active role in the mechanism by pre-assembling formic acid, stabilizing the transition state (see figure 1) and the deprotonation of formic acid (see figure 2).[2]

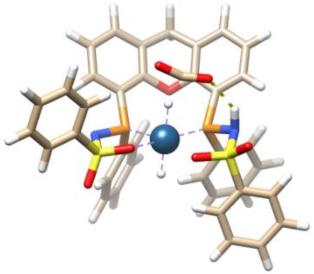

Figure 1

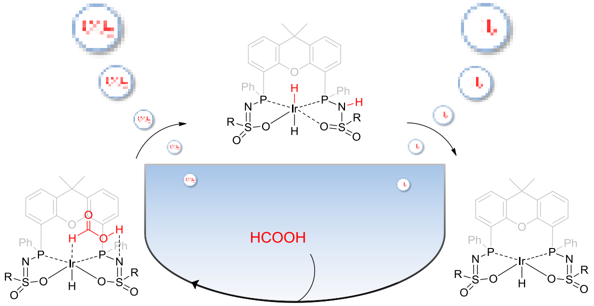

Figure 2

References

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Poster 21

Synthesis of Electron-Rich Uranium(IV) Complexes Supported by Tridentate Schiff Base Ligands and Their Multi-Electron Redox Chemistry

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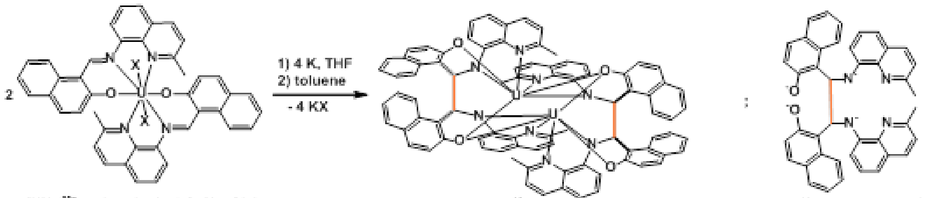
Metal based multi-electron processes remain uncommon in uranium chemistry[1] especially in comparison with the d-block metals, the chemistry of low-valent uranium being dominated by single-electron transfers. In this context, the association of uranium to a non-innocent ligand acting as an independent electron reservoir at a same molecule represents an attractive alternative that should render multi-electron reactivity possible while stabilizing highly reactive formally low-valent oxidation states.[2] We recently reported the synthesis, structure and reactivity of a new complex of U(IV) with the tridentate Schiff base ligand ^{Me}naphtquinolen.[3] The [U(μ-bis-^{Me}naphtquinolen)]$_2$ dimer **2** was isolated from toluene confirms the presence of a U(IV) complex of the reduced ligand. Reactivity studies with molecular oxygen and 9,10-phenanthrenequinone show that complex **2** can act as a multi-electron reducing agent releasing two electrons trough the cleavage of the C-C bond to restore the original imino function of the ligand (Figure 1).



[UX$_2$(^{Me}naphtquinolen)$_2$] X = Cl, I
1-X

[U(μ-bis-^{Me}naphtquinolen)]$_2$
2

bis-^{Me}naphtquinolen^{4-}

Figure 1

References

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Poster 22

Borrowing Electrons to Induce Noble Metal Reactivity on First Row Transition Metal Complexes

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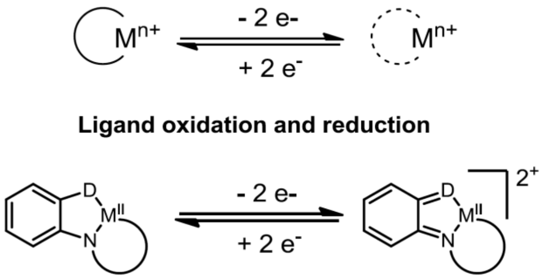
A major challenge in replacing noble metals by earth abundant metals in homogeneously catalyzed processes is the difference in electronic structure and behavior of these subsets of transition metals. First-row transition metals are more prone to undergo one-electron oxidation and reduction reactions, whereas a metal such as platinum often favors two-electron redox changes for bond cleavage or formation reactions.[1]

The use of redox-active ligands as electron reservoirs for first-row transition metal complexes can give them noble metal reactivity. In this scenario, the redox-changes required for elementary reactions, such as oxidative addition and reductive elimination, can be partly or fully ligand centered.[2-4]



Scheme 1

The latest findings on the design, characterization and initial reactivity of new redox-active ligands and their corresponding transition metal complexes will be presented. We will focus on the implementation of an O,N-coordinated o-aminophenolato moiety into a tridentate ligand framework and its chemistry with group 10 transition metals.

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Poster 23

Chelating Heteroditopic Bis-NHCs Complexes: Synthesis and Application in Catalytic Hydrogenation

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Following the success of monodentate N-Heterocyclic Carbenes (NHCs), chelating bis-NHCs have become popular ligands in transition metal catalysis.[1] Two strongly bound NHCs lead to enhanced stability of the complex due to the chelate effect as well as an electron-rich metal center. After reporting zero- and divalent palladium complexes bearing "classic" bis-carbene ligands (Figure 1a),[2] we are now interested in mixed NHC-1,2,3-triazolylidene complexes (Figure 1b). In this system, a well-known and accessible class of mesoionic carbenes (MICs) is combined with a "normal" NHC, leading to heteroditopic bis-NHC complexes. MICs, called that way because a resonance structure with all-neutral formal charges cannot be drawn for the free ligand (Figure 1c), are generally even stronger electron donors than regular NHCs.[3,4] The different NHCs may in synergy induce novel reactivity patterns.

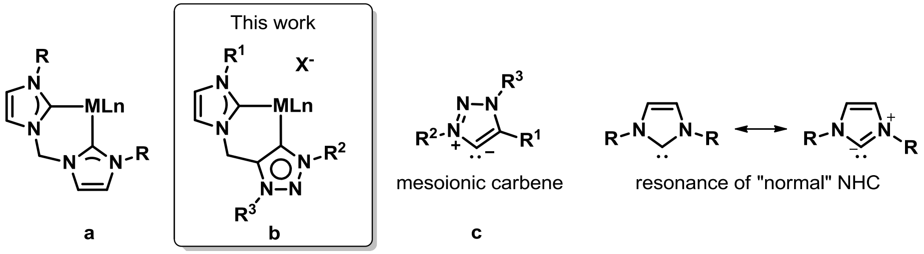

Figure 1: General structure of classic bis-NHC (a), mixed NHC-MIC (b) complex and the free carbene of a 1,2,3-triazolylidene compared to a normal NHC (c), showing its mesoionic character.

The NHC-MIC ligands can be obtained by alkylation of the N-3 position of the imidazolium-triazole salts, that are easily accessible *via* "click" chemistry.[5] The coordination of the ligands to late transition metals and the catalytic reduction activity of unsaturated bonds of the resulting complexes have been studied and will be discussed. Preliminary studies show good activity of the NHC-MIC complexes in the (transfer) hydrogenation of ketones and several esters.

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Poster 24

New Catalytic Systems for the Simultaneous Lipids and Free Acids *Trans*-Esterification/Esterification in non Aqueous Systems

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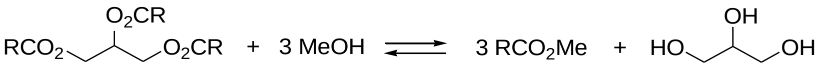
Biodiesel (a mixture of Fatty Acid Methyl Esters, FAME) is the second biofuel produced in the world and the first in Europe. Biodiesel is produced today by *trans*-esterification of triglycerides of refined/edible type oils using methanol and an alkaline homogeneous catalyst (NaOH, NaOMe) (scheme 1):



Scheme 1

The reaction is normally performed at 60–80°C, and glycerol and FAME's are separated by settling after catalyst neutralization. The crude glycerol and biodiesel are then purified. However, homogeneous alkaline catalysts cannot directly be used with waste oils due to the presence of large amounts of free fatty acids (FFA).[1]

Use of Lewis acid catalysts, able to promote the simultaneous esterification of FFA and *trans*-esterification of glycerides,[1-3] is an elegant way solve this problem.[3] Within this frame, we have developed an active supported homogeneous Zn acid catalyst (in figure 1), linked to a solid silica support by an urethane bond. This choice combines the advantage of homogeneous acid catalysis with the possibility to recover and re-use the catalyst by simple filtration. Synthetic and catalytic details will be given in the poster.

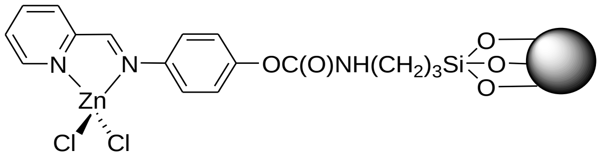


Figure 1

Acknowledgements: Financial support: PON 2007-2013 Project cod. PON 01_01966 (ENERBIOCHEM).

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Poster 25

Synthesis of Biological Aza-Compounds Catalysed by Ruthenium Porphyrins

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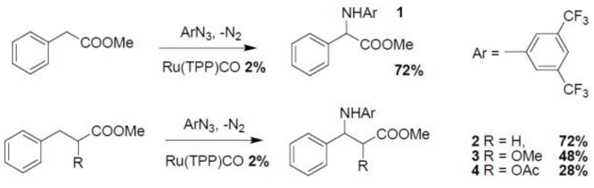
The development of clean and efficient methods to synthesise nitrogen-containing molecules is a topic of high interest in order to obtain valuable fine chemicals in a cheap and environmentally-friendly way. The benzylic amination of hydrocarbons using rutheniumporphyrin complexes as catalysts and aryl azides as nitrene sources is an effective strategy to achieve this aim.[1] The so-obtained good results prompted us to extend the reaction scope to the synthesis of products of pharmaceutical and biological interest. The Ru(TPP)CO-catalysed benzylic amination of methyl phenylacetate and methyl dihydrocinnamate is an efficient synthetic methodology to achieve a and b aminoesters respectively (1,2) (Scheme 1) (TPP = dianion of tetraphenylporphyrin). Furthermore, using methyl 3-phenyllactate derivatives as substrate, α-oxy β-aminoacids (**3**,**4**), useful β-lactames precursors, were obtained in good yields (Scheme 1). All the reactions were carried out in refluxing benzene under nitrogen atmosphere; a high excess of substrate is required, but it can be easily recovered by vacuum distillation.



Scheme 1

During the catalytic amination, a bis-amido ruthenium complex is always formed as a resting state. This complex was isolated and fully characterized in the case of the amination of methyl phenylacetate (Figure 1).

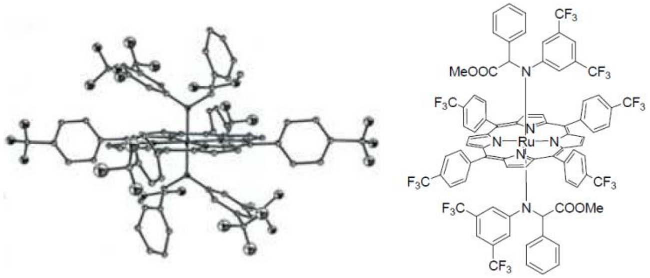


Figure 1

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Poster 26

Copper-Mediated Intramolecular Alkoxychlorination Of Alkynes as a Route to Chloroalkyliden-Substituted Heterocycles

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The formation of oxygen-carbon bonds has a crucial role in organic chemistry.[1] Intramolecular alkoxylation of carbon-carbon multiple bonds represents one of the most effective approaches to prepare oxygenated heterocycles, which are important motifs in many biologically active compounds. This reaction increases its interest when involved in domino processes. In this context, beside the classical use of the hydroxy group, transition metal-catalyzed alkoxylations involving secondary amides[2] or ureas[3] have already been used as a tool to perform oxygenated heterocycles. Following this concept, we tried to perform domino processes involving a cyclization followed by the formation of a carbon-halogen bond. Thus, here we describe a new method to prepare heterocyclic derivatives bearing a chloroalkyliden group by intramolecular alkoxychlorination of alkynes tethered to secondary amides or ureas (Figure 1). The reactions were carried out in acetonitrile at reflux by using copper chloride in stoichiometric amount as both promoter and chlorine source as well as copper chloride in catalytic amount as promoter and NCS as chlorine source.

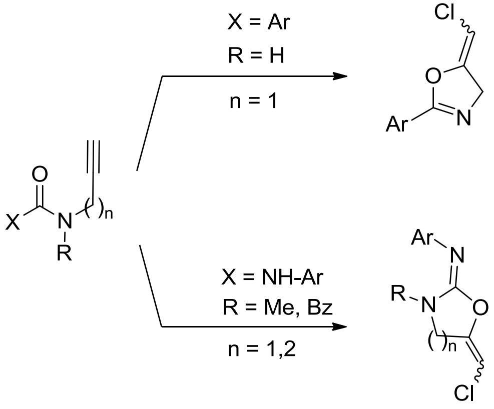

Figure 1

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Poster 27

Nonsymmetric α-Diimines in Pd-Catalyzed Ethylene/Polar Monomer Copolymerization

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One of the major unsolved problems in polymer chemistry is represented by the efficient copolymerization of terminal alkenes with polar vinyl monomers to yield functionalized polyolefins.[1] The main catalytic systems reported in literature are based on palladium(II) complexes with either α-diimines or phosphino-sulphonate ligands,[2] but their productivity is far too low for any industrial application, thus better performing catalyst are strongly needed. Recently, we have reported a new nonsymmetric α-diimine ligand featured by an acenaphthenequinone (Ar,Ar′-BIAN) skeleton with one aryl ring substituted on *meta* positions with electron-withdrawing groups and the other aryl ring bearing electron-donating substituents on the *ortho* positions.[3] The related Pd(II) monocationic complexes were found to be more productive than the complexes with the corresponding symmetrically substituted Ar-BIANs.[3] Now the library of the nonsymmetric Ar,Ar′-BIANs has been extended to two new ligands, both characterized by an aryl ring bearing a methoxy and a methyl group on the *ortho* positions and differing in the positions of the electron-withdrawing groups (CF_3) on the other aryl ring (Figure 1).

The related neutral, [Pd(CH_3)Cl(Ar,Ar′-BIAN)], and monocationic, [Pd(CH_3)(L)(Ar,Ar′-BIAN)][PF_6] (L = CH_3CN or dmso), palladium(II) complexes have been synthesized and fully characterized in solution and, when suitable crystals were obtained, in solid state (Figure 2). The preferentially formed isomer is featured by the Pd-CH_3 bond *trans* to the Pd-N bond of the CF_3-substituted aryl ring. Detailed investigations on the catalytic behaviour of the monocationic derivatives in the ethylene/methyl acrylate copolymerization, carried out at mild conditions of temperature and pressure, will be presented.

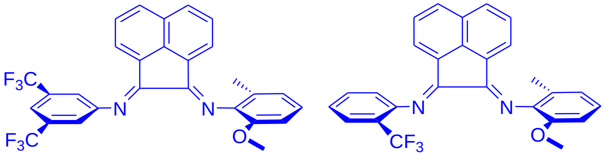

Figure 1

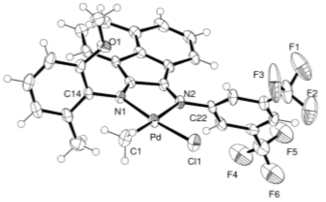

Figure 2

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Poster 28

Mild Regioselective Palladium-Catalyzed Direct C-H Arylation of Azoles

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Arylazoles are important structural units frequently found in natural products,[1a] pharmaceutics,[1b] agrochemicals,[1c] and organic functional materials.[1d] Recently, the transition metal-catalyzed direct arylation reactions of azoles with aryl halides have emerged as an attractive strategy for the effective construction of Csp^2-Csp^2 aryl-heteroaryl bonds.[2] These reactions, unlike the traditional metal-catalyzed cross-coupling protocols involving the use of preformed organometallics, enable the direct elaboration of heteroaromatic cores without the pre-activation of both the coupling partners.

Over the last years we have been interested in studies aimed to broaden the substrate scope of the direct arylation of π-electron-rich heteroarenes and, in particular, to develop efficient protocols for the synthesis of aryl azoles involving palladium-catalyzed regioselective direct C-H arylations of azoles with aryl halides. We have recently found that tetrabutylammonium acetate, an organic base rarely used in direct arylation protocols, is able to promote an effective regioselective direct C-5 arylation of 1-methyl-1*H*-pyrazole, oxazole and thiazole with aryl bromides in the presence of $Pd(OAc)_2$ as the catalyst precursor at a reaction temperature of only 70 °C (**Figure 1**).[3]

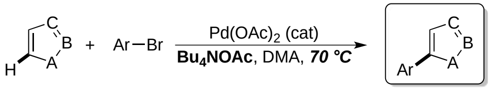

Figure 1

A variety of 5-aryl-1-methylimidazoles was also very efficiently obtained simply rising the reaction temperature to 110 °C.[3] Moreover, we successfully achieved the one-pot sequential C-5 and C-2 direct arylations of oxazole and 1-methylimidazole by pairing this new protocol with our previously reported procedure for the regioselective ligandless direct C-2 arylation reaction. The application of this simple and effective protocol to the preparation of bioactive compounds and of new organic chromophores will be also showed and discussed.

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Poster 29

Organic Chromophores Based on a Fused Bis-Thiazole Core and their Application in Dye-Sensitized Solar Cells

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Dye-Sensitized Solar Cells (DSSC) are one of the most promising technologies to convert solar energy in electric current because of their low cost of production and their colorful and decorative features.[1] The most important component of a DSSC is the sensitizer, which can be a totally organic molecule able to absorb solar light and to convert the absorbed energy into electric current. The organic sensitizer must have an appropriate structure, with a donor (D) and an acceptor (A) group linked by an unsaturated unit (π). Four new D- π -A organic dyes incorporating either a thiazolo[5,4-*d*] thiazole bicyclic system (**TTZ1**–**2**) or a benzo[1,2-*d*:4,5-*d*]bisthiazole tricyclic unit (**BBZ1**–**2**) have been synthesized and fully characterized.[2]

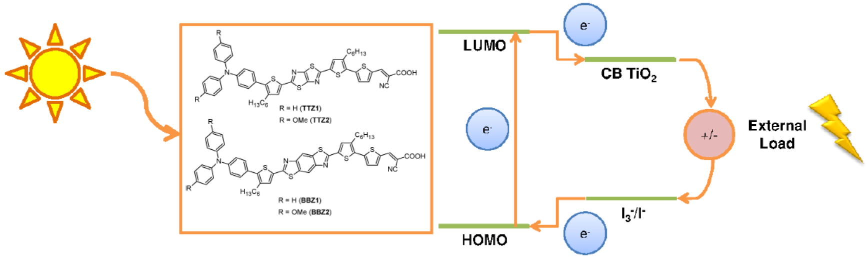

Figure 1

The key steps of the synthesis include an efficient MW-assisted preparation of the thiazole[5,4-d] thiazole core and selective functionalization of two different dihalothienyl derivatives through Suzuki couplings. All the compounds showed photo- and electrochemical properties compatible with their employment in dye-sensitized solar cells. Dye-sensitized solar cells fabricated with those dyes yielded power conversion efficiencies up to 3.53%.

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Poster 30

Water Soluble Calix[4]pyrrole-based Bis[2]catenane

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Calix[4]pyrrole, among many other interesting calixarenes used in supramolecular chemistry, are currently employed and considered for an assorted number of applications (e. g. catalysis, sensors, separations, etc.). We have found that calix[4]pyrroles, such as the nanocapsule shown in Figure 1, can form supramolecular assemblies, and as well recognition of ionic and neutral guest species,[1-3] therefore, applications such as selective binding agents or molecule-separation agents can be envisioned. Many studies, have shown that the intermolecular interactions that form the calix[4]pyrrole supramolecular systems, not only occur in solid state, but also in solution.[4,5] Here, we present our efforts to produce these calix[4]pyrrole supramolecular assemblies in polar solvents, and in order to achieve this, we have included various carboxylic groups in the chemical structures forming the supramolecular assembly.

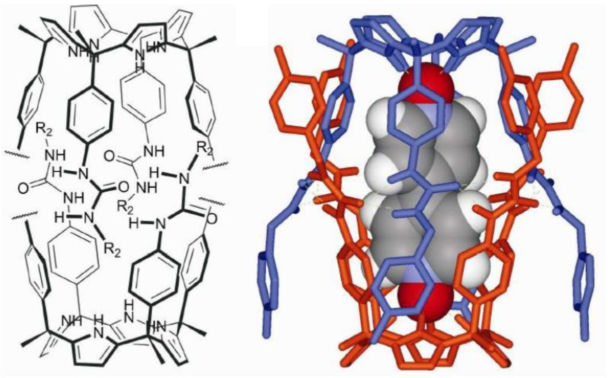

Figure 1

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Poster 31

Design of Photoswitchable Pt(II) and Ru(II) Complexes as Potential Antitumoral Agents

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Dithienylethenes of the type illustrated in Figure 1 are well-known for their promising behaviour as molecular switches, as they undergo reversible ring-closure upon irradiation with UV or visible light.[1-3] However, their potential application in biological systems has not been extensively studied yet. Here we present our first approach to the design of new photoswitchable Pt(II) and organometallic Ru(II) coordination compounds with dithienylethene ligands. These newly obtained compounds exhibit interesting optical properties, and are intended to undergo further studies of biological interaction.

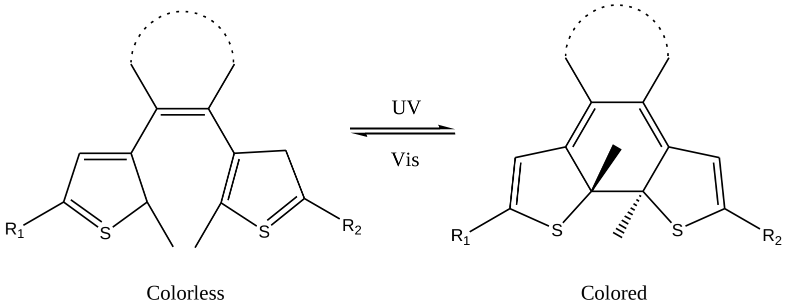

Figure 1

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Poster 32

Carbonylative Synthesis of 10,11-dihydrobenzo[*b*,*f*][1,4]oxazepine Derivatives by Tandem Alkoxycarbonylation-Heterocyclization

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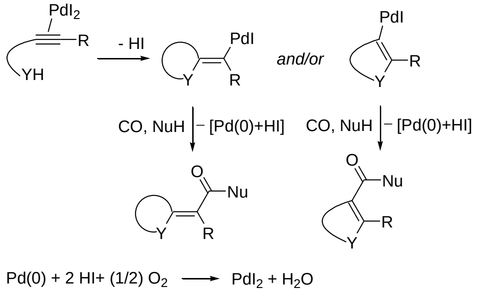
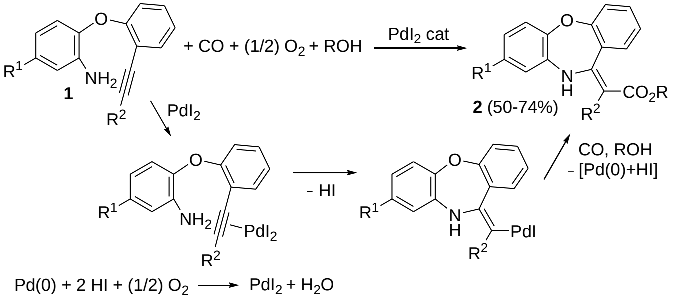
PdI_2-catalyzed oxidative alkoxycarbonylation- heterocyclization of acetylenic substrates bearing a suitably placed nucleophilic group is a powerful methodology for the direct synthesis of carbonylated heterocycles.[1] The process starts with an *exo* or *endo* intramolecular attack by the nucleophilic group to the triple bond coordinated to palladium, followed by carbon monoxide insertion and nucleophilic displacement to give the final product and Pd(0). The latter species in then reoxidized by the action of an external oxidant, usually molecular oxygen (Scheme 1).[1]

In this communication, we report a novel application of this kind of reactivity to the direct synthesis of carbonylated 10,11-dihydrobenzo[*b*,*f*][1,4]oxazepine derivatives **2**, starting from readily available 2-(2-alkynylphenoxy)anilines **1**, according to Scheme 1. Reactions are carried out in an alcoholic solvent under relatively mild conditions (100 °C and 40 atm of a 4:1 mixture of CO-air for 24 h, using 2 mol % of PdI_2 in conjunction with 20 mol % of KI), to afford the desired products **2** in satisfactory yields (50-74%).



Scheme 1



Scheme 2

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Poster 33

Novel Uranyl Salophen Complexes Bearing Anthracenyl Side Arms: Synthesis and Photochemical Behavior

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Fluorescence spectroscopy is a simple and high sensitive technique very useful for the detection of traces of analytes. Actually, in the last years, the design and the development of fluorescent supramolecular materials for sensing has became a target of main importance.[1] Simple uranyl salophen complexes are able to recognize neutral molecules and anions and the recognition event, is easily detected by variations in the UV-Vis and NMR spectra but not in fluorescent emission spectra despite the fact that salophen ligand and uranyl salt are fluorescent if considered independently. In order to obtain uranyl salophen complexes with such characteristic, we tried to introduce fluorescent moieties within the basic skeleton of the receptors as in complexes **1** and **2** (Figure 1)

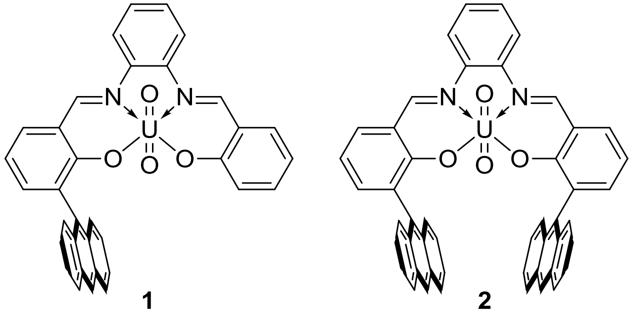

Figure 1

In the presence of anthracenyl moieties, no fluorescence emission was observed for complex **1** and **2**. This can be ascribed to a photoinduced electron transfer process (PET) from the anthracene-localized first single excited state to the metal center. Here we report the synthesis and physico-chemical investigation on the two receptors.[2]

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Poster 34

Bioactive Ru(II)-Arene Complexes with Natural Polyphenolic Ligands as Anticancer Metallodrugs

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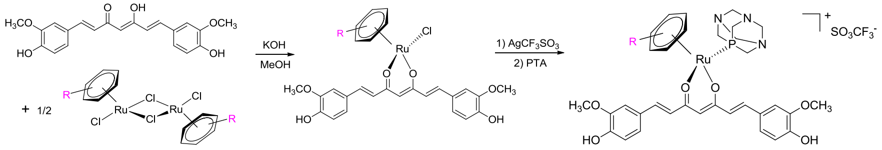
Ruthenium-arene complexes represent a promising opportunity for the design and development of novel bioactive molecules. These compounds display interesting antitumor activity and can be considered valid alternatives to platinum drugs, owing to their lower toxicity and stronger selectivity.[1] We report a systematic investigation of the interaction between arene ruthenium(II) (arene = *p*-cymene, benzene or hexamethylbenzene) and natural bidentate ligands such as curcumin[2] (Figure 1) and quercetin[3] (Figure 2) that are bioavailable polyphenolic compounds well known for their anti-inflammatory, antiviral, and antioxidant activity.[4]

Figure 1

Figure 2



Scheme 1

References

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Poster 35

Hydrophilic Complexes of Pd(0) with Sugar-Derived Ligands: Synthesis, Characterization and Use in Catalysis

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Palladium has an important role in catalysis due to the several reactions in which its complexes are used, such as C-C bond formation, e.g. Suzuki, Stille, Heck and Sonogashira couplings. In order to improve the sustainability of the reaction conditions, our work is focused on the synthesis of sugar-derived ligands, because the carbohydrates (i) are chiral, (ii) many of them are abundant in nature and (iii) can develop lypophilic or hydrophilic complexes according to the protection or deprotection of the hydroxyl groups. This work is focused on the synthesis of type **1** and type **2** hydrophilic complexes of Pd(0) (Figure 1), containing *N*,*P*- and *N*,*N*-bidentate ligands derived from D-mannose and D-glucose:

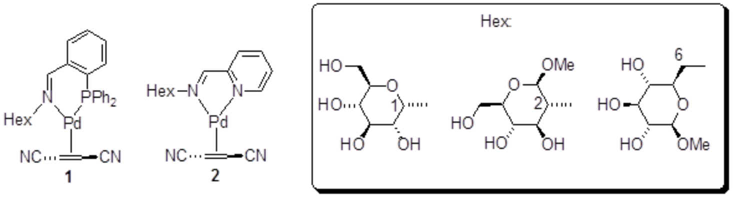

Figure 1

Using bidentate ligands will allow the study of stability and reactivity of donor atoms with different π-acid property. The sugar residues (Hex), from common and easily available carbohydrates, can easily host the iminic function introduced in the positions 1, 2 or 6. The catalytic properties of the complexes will be verified in C-C bond formation reactions, especially Suzuki’s cross-coupling reactions, with special attention towards the easy separation and reuse of the catalyst phase.

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Poster 36

Application of Sugar-Derived Phosphines in the Copper Catalyzed Asymmetric Conjugate Addition to Enones

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The asymmetric conjugate addition (Figure 1) represents an useful method to afford new carbon-carbon bonds for the synthesis of enantiorich fine chemicals.[1]

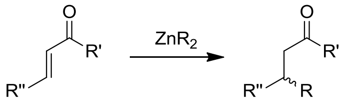
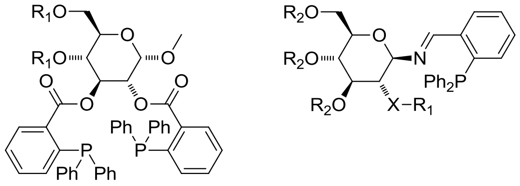


Figure 1

In the last years, a wide range of catalysts has been extensively studied, thus revealing the central role played by copper, as the metal center,[2] coordinated with phosphine ligands.[3] It should however be noted that there are still many issues to be clarified and improved with respect to this reaction, such as those related to improving the performance of the catalysts, the simplification of their synthesis, their easy recycle, the understanding of the mechanism. As part of our studies on the design of chiral ligands derived from sugars, we are currently preparing modular libraries of phosphines based on D-glucose, provided with different stereoelectronic motifs (Figure 2).



X = O, NH
R_1 = H, alkyl, acyl
R_2 = H, alkyl, Ac

Figure 2

Preliminary tests in the methylation of *trans*-3-nonen-2-one promoted by $ZnMe_2$ indicate that, in addition to the effects determined by the main coordinating functions, an important impact is played by the auxiliary functions present in the sugar backbone.

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Poster 37

Glucose-Derived *Salen* Ligands (Elpan-Salen) for the Manganese-Catalyzed Asymmetric Epoxidation of Styrenes

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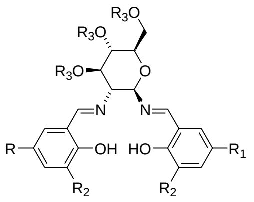
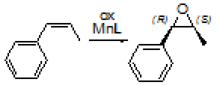
The **elpaN-salen** family of ligands[1] (Figure 1) is presented, which represents a subset of the elpaN-type library based on D-glucose.[2] The ligands are structural analogues of the privileged *salenH₂* derived from *trans*-1,2-diaminocyclohexane,[3] and differ for the position and the number of *t*-butyls in positions 3’ and 5’ of the aromatic portions. All of them, with the exception of **elpaN-salen-aH₂**, show tactical *t*-Bu groups in 3’, *i.e.* ortho to the alcoholic oxygen.

The activity of the Mn(III) complexes of the corresponding *N,N’,O,O’*-deprotonated chelates, [Mn(**elpaN-salen**)]PF_6, has been assessed in the asymmetric epoxidation of *cis*-β-methylstyrene, at 196 K in dichloromethane, by using *meta*-chloroperbenzoic (*m*-CPBA) acid as the oxidant (scheme 1):



elpaN-salen-aH₂: R= R_1= *t*-Bu, R_2= H, R_3= Ac
elpaN-salen-bH₂: R= R_1= H, R_2= *t*-Bu, R_3= Ac
elpaN-salen-cH₂: R= R_1= R_2= *t*-Bu, R_3= Ac
elpaN-salen-dH₂: R_1= H, R= R_2= *t*-Bu, R_3= Ac
elpaN-salen-eH₂: R_1= R_2= *t*-Bu, R= H, R_3= Ac
elpaN-salen-c'H₂: R= R_1= R_2= *t*-Bu, R_3= H

Figure 1



No.	ligand	t (h)	conversion[b]	*cis/trans*[b]	ee(%)[c]
1	[Mn(**elpaN-salen-a**)]PF_6	0.5	>99	50/50	-
2	[Mn(**elpaN-salen-b**)]PF_6	0.5	>99	92/8	84(1*R*,2*S*)
3	[Mn(**elpaN-salen-c**)]PF_6	0.5	>99	92/8	88(1*R*,2*S*)
4	[Mn(**elpaN-salen-d**)]PF_6	0.5	>99	90/10	82(1*R*,2*S*)
5	[Mn(**elpaN-salen-e**)]PF_6	0.5	>99	92/8	86(1*R*,2*S*)
6	[Mn(**elpaN-salen-c’**)]PF_6	0.5	>99	88/12	83(1*R*,2*S*)

Mn/alkene/*m*-CPBA/NMO= 0.024/0.48/0.96/2.40

Scheme 1

The best performing catalyst, [Mn(**elpaN-salen-c**)]PF_6, has then been examined in the epoxidation of other styrenes in the same conditions, substantiating the idea that appropriate functionalization of carbohydrates can produce effective ligands for enantioselective catalysis.[4]

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Poster 38

A Supramolecular Peptide Nanofiber Templated Pd(0) Nanocatalyst For Efficient Suzuki Coupling Reactions Under Aqueous Conditions

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Self-assembly is an important technique for materials design using non-covalent interactions including hydrogen bonding, hydrophobic, electrostatic, metal-ligand, π-π and van der Waals interactions.[1] Various self-organized supramolecular nanostructures have been produced by using these non-covalent interactions. We explore use of peptide nanofibers formed by specially designed short peptide sequences that can form sheet-like hydrogen bonded structures for controlled synthesis of nanometer scale materials. In this work, we explored peptide nanostructures for their further utilization in catalysis and as a template in synthesis of inorganic nonmaterial’s including inorganic catalysts.

We fabricated Pd(0) nanostructures on the surface of self-assembled peptide nanofibers through mimicking biomineralization process. The Pd^{+2} salt was deposited and reduced on the surface of the preformed template. We observed that Pd(0) nanowire formation can be obtained in nanometer precision (Figure 1). The Pd(0) catalyst were employed in model Suzuki coupling reactions.

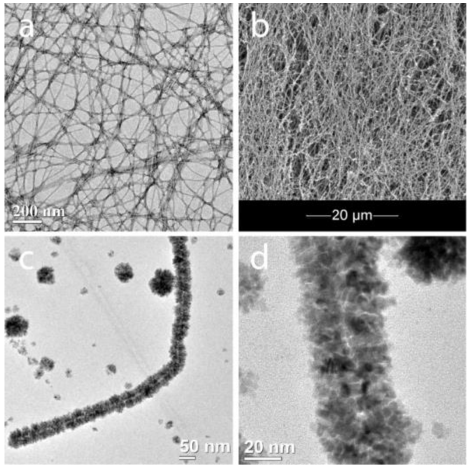

Figure 1. a) TEM image of the peptide nanofibers, b) SEM image of the peptide nanofiber network, c and d) TEM images of Pd nanoparticles on the peptide nanofibers

Acknowledgements: This work is partially supported by grants; TUBITAK 109T603, TUBA-GEBIP, and FP7 Marie Curie IRG

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Poster 39

Palladium complexes as catalysts for synthesis of amines

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Palladium(II) complexes with nitrogen donor ligands have received much attention. These complexes can be applied as catalysts for the carbonylations,[1,2] polymerizations,[3] and other reactions in synthetic organic chemistry.[4] There is a general agreement that catalytic activity of Pd(II) complexes with nitrogen containing ligands depends on electron density on the palladium atom and a strategy to design (and to obtain) more active catalysts is based on incorporation of new ligands to manipulate the steric and electronic effects around the palladium center.

In the present study X-ray characterization and thermal analyses were applied in order to investigate substituent effects on the crystal structures and stability of $PdCl_2(X_nPy)_2$ complexes (where: Py = pyridine; X = Cl or Me; n = 0-2). Electron-donating properties of X_nPy ligands were described by determined experimentally acidity parameter, pK_a. Obtained results were combined with catalytic activity of $PdCl_2(X_nPy)_2$ in the reduction of nitrocompounds to amines by the use of CO/H_2O (scheme 1):

$$ArNO_2 + 3CO + H_2O \xrightarrow{cat} ArNH_2 + 3CO_2$$

Scheme 1

Reduction of nitrocompounds to amines by the use of carbon monoxide is an alternative method for the hydrogenation of nitrocompounds and it allows to eliminate very expensive hydrogen (which is involved in the synthesis of amines nowadays).

We report that nature and position of substituent in the aromatic ring is important to the structure of $PdCl_2(X_nPy)_2$ complexes, however, we did not find a direct correlation between basicity of ligand and the Pd-N distance. Moreover, complexes with methylpyridines are more thermally stable than their analogues with chloropyridines. Thermal stability of $PdCl_2(X_nPy)_2$ complexes is correlated with their catalytic activity in reduction of nitrocompounds to amines by the use of CO/H_2O. We observed an increase of reaction rate with decreasing basicity of X_nPy ligand in the reduction of nitrocompounds. For complexes with *ortho* substituted pyridines significantly lower conversions were observed. On the basis of presented data we propose mechanism of investigated process.

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Poster 40

Use of Diethylaminodifluorosulfinium Salt for the Fluorination of Phosphorus Oxyacids

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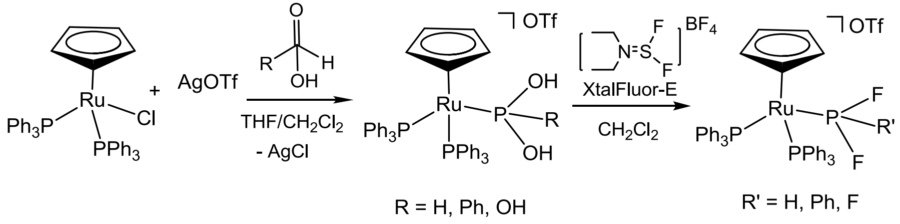
Among the various useful protocols for the introduction of fluorine into organic molecules, electrophilic fluorination is a promising and exciting area of research. Recently, a variety of electrophilic fluorinating reagents has been prepared[1] such as DAST (diethylaminosulfur trifluoride), Deoxo-Fluor, (bis(2-methoxyethyl)aminosulfur trifluoride) and Selectfluor (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)). Moreover, dialkylaminodifluorosulfinium salts have shown to be efficient deoxofluorinating agents for the transformation of a wide range of organic compounds, such as alcohols, ketones, aldehydes and acyl chlorides into the corresponding fluorides, having the advantage of high stability and easy handling.[2]

This work presents the use of diethylaminodifluorosulfinium tetrafluoroborate, XtalFluor-E, for the first time in the transformation of phosphorus oxyacids as H_3PO_2, H_3PO_3 and PhP(O)(H)(OH) into fluorophosphine ligands. The procedure works well in the presence of an unsaturated ruthenium organometallic complex, which stabilizes the pyramidal tautomer[3] of the P-oxyacids i.e. $P(OH)_2(R)$, [R = H, Ph, OH] which are prone to react with XtalFluor-E. (Scheme 1)



Scheme 1

References

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Poster 41

Metathesis Reaction for the Synthesis of Macrocyclic Drug Compounds: Benefits of Nanofiltration Technology for Greener Large Scale Production

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Macrocycles are currently used as Active Pharmaceutical Ingredients (API) in a large number of applications[1]. Compared to their linear equivalent, they are less prone to proteolysis, exhibiting a longer half-life and an improved pharmaceutical activity[2].

Ring Closing Metathesis (RCM) can be of great use in the synthesis of such compounds[3]. Since the pioneering works from Grubbs and co-workers on olefins metathesis, extensive investigations have been done, leading to a better mechanistic understanding and to the development of efficient catalysts for demanding substrates[4].

We report about a real industrial case where olefin metathesis can be successfully used in the synthesis of TMC435, a complex macrocyclic API for hepatitis C treatment (figure 1).

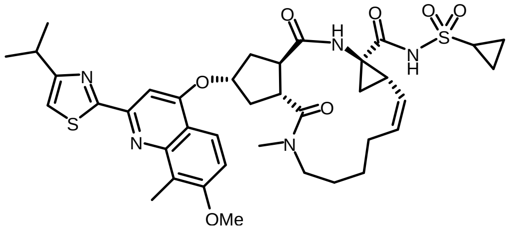

Figure 1. TMC435, API used in the treatment of hepatitis C.

The synthesis of macrocycles is heavily dependent on the dilution conditions: the more diluted a mixture, the higher the ratio between intra- and inter-molecular reactions. Organic Solvent Nanofiltration (OSN) is an attractive technology because, through a separation on a molecular scale and under relatively mild conditions, it allows the isolation and purification of the products and the recovery and recycle of the by-products and the solvent[5].

In our work we aim at coupling it with the metathesis reactions to develop a more sustainable process.

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Poster 42

Tetrathia[7]helicene Phosphane Derivatives: Properties and Characterization

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Tetrathia[7]helicenes (7-TH) are polyconjugated π-systems in which four thiophene rings are orthofused to alternating arene rings to generate a non-planar, chiral, stable helix, allowing the existence of M and P enantiomers.[1] In the course of our studies on the synthesis of 7-TH phosphorus derivatives as potential innovative chiral ligands in asymmetric organometallic catalysis,[2] novel 7-TH-dialkylsubstituted phosphane derivatives **1** and **2** (Figure 1) have been synthesized and fully characterized. Chiroptical properties of borane adducts **1** have been investigated along with the electrochemical properties of phosphine ligands **2** (Figure 1).

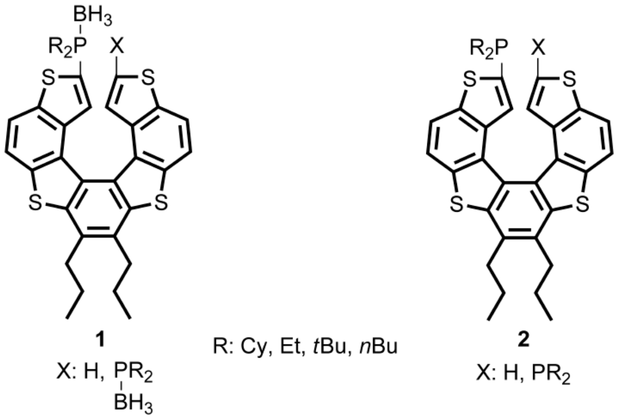

Figure 1

References

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Poster 43

Dinuclear Arene Ruthenium(II) Complexes with 3,3’,5,5’-Tetramethyl-4,4’-Bipyrazole and Modulation of Proteasome Activity

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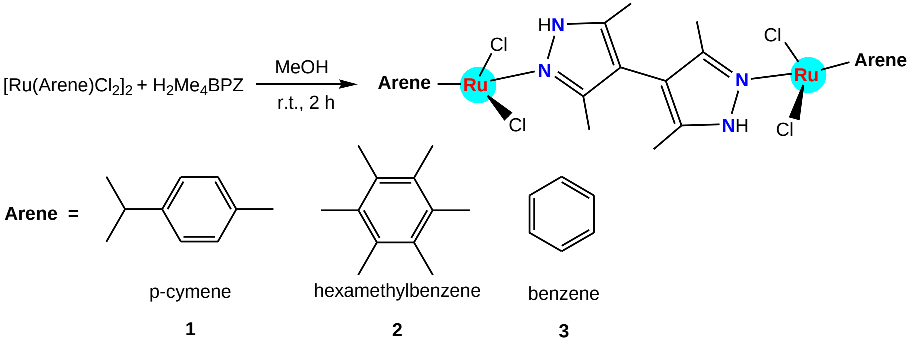
During the last decades, the preparation of half-sandwich ruthenium(II) complexes incorporating π systems has registered a growing attention, especially due to their potentiality as metallo-pharmaceuticals[1] as well as catalyst in synthetic organic chemistry.[2] In the present work, a series of dinuclear arene ruthenium(II) complexes coordinated by the ditopic N-ligand 3,3’,5,5’-tetramethyl-4,4’-bipyrazole (H_2Me_4BPZ) have been prepared (Scheme 1), and preliminary results regarding their ability to modulate proteasome activity are reported.



Scheme 1

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Poster 44

One-Pot Gold-Catalyzed Aminofluorination of Unprotected 2-Alkynylanilines

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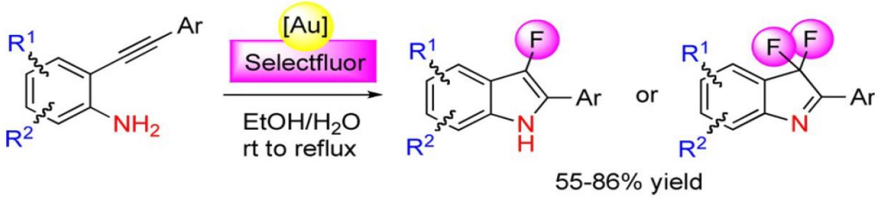
Introducing fluorine into molecules represents a major challenge in organic synthesis.[1] The substitution of hydrogen with fluorine can lead to a dramatic impact in the physicochemical and biological properties of organic compounds, and utilization of fluorine derivatives spans areas as diverse as pharmaceuticals, agrochemicals and polymers.[2] In recent years it has been synthesized a class of stable and easily manipulated fluorinating reagents to which belongs the Selectfluor®.[3] In this work we combine the characteristics of Lewis acid / transition metal of gold, capable of catalyzing the sequential ammination / annulation reaction of the substrate A,[4] with the fluorinating activity of Selectfluor® to obtain the C3 fluorinated indole derivatives according to the scheme 1:



Scheme 1

Depending on the nature of the substituent groups R[1] and R[2] is possible to obtain the final products by operating either through a domino process or through a one-pot/two-steps type process, in which the addition of Selectfluor® occurs after the complete annulation of the substrate A. Furthermore it is possible, by modulation of the stoichiometric ratio between Selectfluor® and starting material, to obtain both C3 difluorinated and C3 monofluorinated products.

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Poster 45

Squaramides as Potent Transmembrane Anion Transporters[1]

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The transport of anions across cellular membranes is an important biological process that is controlled by specialized membrane proteins. Malfunctioning of these proteins has been linked to a variety of diseases, most notably cystic fibrosis.[2] Therefore, there has been an interest in developing synthetic membrane transporters that can substitute these proteins. A large part of these synthetic mobile anion carriers contain urea or thiourea functionalities in their anion binding site. However, there has been a recent interest in the field of medicinal chemistry to use squaramide derivatives as isosteres for ureas and guandinium groups, since it is believed that the stability of bis-squaramides to nucleophilic attack can reduce their *in vivo* toxicity.[3] In addition, squaramides are being increasingly used by supramolecular chemists in the design of ion receptors.[4] We therefore decided to investigate the anion binding and transmembrane anion transport properties of a series of symmetrical fluorinated squaramides and their analogous ureas and thioureas. Squaramides were prepared by the $Zn(OTf)_2$ catalysed reaction between diethoxy squarate and the appropriate aniline. A series of vesicle-based experiments revealed that the squaramide containing compounds are significantly better at transporting anions across a lipid bilayer than the more traditional urea and thiourea derivatives. This behaviour could be rationalized by the superior anion binding properties that were found for these squaramides through NMR titration techniques and X-ray structure determination. Furthermore, it was also shown that the fluorinated squaramides displayed higher transport abilities at much lower concentration compared to the unfluorinated receptors. Both findings promise new guidelines for the design of future anion transporters and transport related drugs.

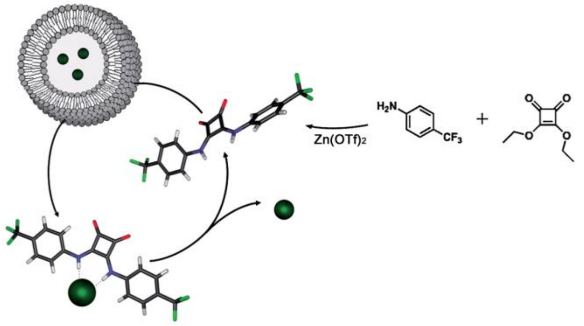

Figure 1

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Poster 46

Ligand Induced Structural and Electronic Variations in Multimetallic Complexes.

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Organometallic rhenium(I) complexes exhibiting phosphorescence have been of interest due to their potential application in fields such as biological imaging, light emitting devices, sensors, and catalysis.[1] Recent investigations have shown that the inclusion of a tetrazole ligand can have a significant effect on the structural and photophysical character of luminescent compounds, and can behave as an effective bridging ligand between multiple metal centres allowing efficient energy transfer.[2] We have previously reported the chemistry and photophysical nature of mononuclear and homo-dinuclear rhenium tetrazole compounds.[2,3] Here we extend the investigation of the versatile nature of the tetrazole ligand to multinuclear and hetero-dinuclear compounds (Figure 1).[3,4]

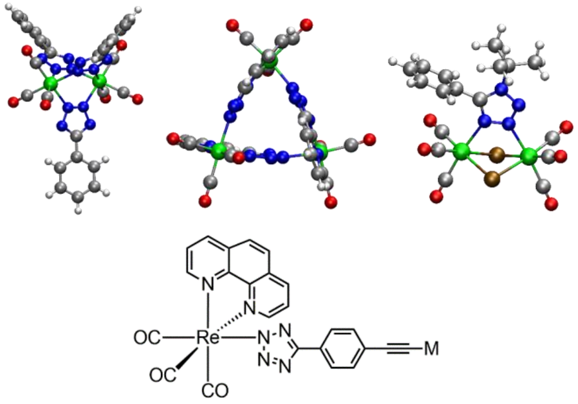

Figure 1

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Poster 47

Silver(I) Acylpyrazolonate Complexes Embedded in Polyethylene with Potent Antibacterial Activity

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Silver ions and its compounds are known to exhibit strong antimicrobial activity towards broad-spectrum bacteria.[1] Silver nanoparticles (NPs) embedded in polymeric matrix have proven to prevent the adherence and proliferation activities of the bacteria at surface of polymeric materials[2] through an efficient Ag^+ release from the surface and direct interactions with the bacterial cell wall. However, an extensive release of the Ag NPs from the materials could lead to environmental hazard.[3,4]

Following our previous research on this topic,[5] here we report some novel complexes of silver(I) containing 4-acyl-5-pyrazolonate ligands with different electronic and steric features and several imidazoles L as ancillary ligands (Figure 1). Their structure have been confirmed by analytical and spectral data (IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS, Elem. Anal.) and X-ray diffraction studies. Specific tests were carried out on all derivatives embedded in polyethylene disks to probe their antimicrobial activity against suspensions of E. coli, P. aeruginosa and S. aureus, but without evident Ag^+ release. Antimicrobial action on contact is under investigation.

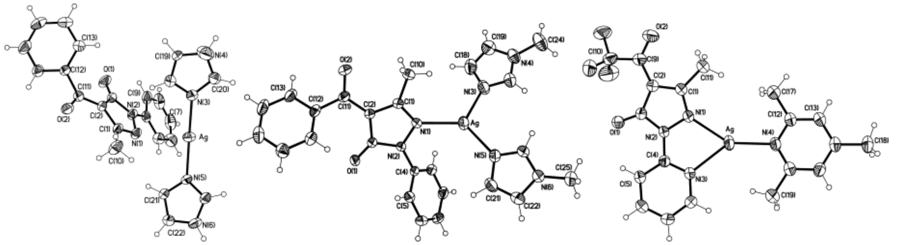

Figure 1

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Poster 48

New Cooperative Ligands for C-H Bond Activations Reactions

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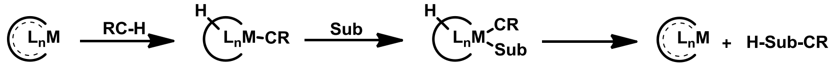
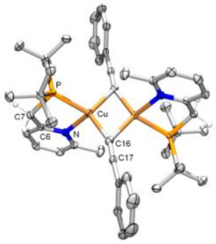
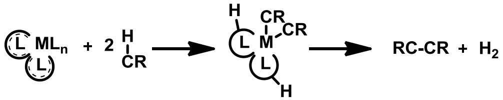
In biological systems, cooperativity between metal and ligands is often employed to mediate proton transfer and redox reactions or substrate activation. Inspired by the versatile application observed in nature, metal-ligand bifunctional catalysts were recently demonstrated to be also useful in a series of activation reactions and catalytic conversions,[1-3] where traditionally chemical reactions are solely metal-mediated. The respective smart ligand systems typically cooperate in substrate binding and activation through secondary interactions like redox non-innocence or proton transfer. Thus, the adaptive ligand can now work as an internal base and this would be a new development in the search of new catalytic routes for functionalization reactions.

One of these functionalization reactions is the catalytic carboxylation reaction which comprises the insertion of CO_2 into C-H bonds, obtaining carboxylic acids as products.[4] This reaction, which uses CO_2 as a C1 building block, is still one of the 'dream reactions' of catalysis, because carbon dioxide is abundant and non-toxic and carboxylic acids are attractive for natural and medicinal compounds.



Here we demonstrate various versatile ligands that are able to operate in a cooperative manner when combined to several late TMs.[5,6] Furthermore, we will discuss studies of these new cooperative complexes [7] towards the activation of C-H bonds. The thus formed metal-carbon bond may then undergo reactions with other substrates to enforce coupling (C-C bond) reactions such as the highlighted carboxylation reactions, but also cross (dehydrogenative) coupling (CDC) or hydroaddition reactions.





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Poster 49

Influence of η^6-Arene Ligand on Asymmetric Transfer Hydrogenation of Imines

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During the last fifteen years, the asymmetric tranfer hydrogenation (ATH) of prochiral imines and ketones via Noyori's piano-stool complexes [RuCl(*S*,*S*)-(TsDPEN)(η^6-arene)] (TsDPEN = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylene-1,2-diamine) has become a user-friendly and relatively well-understood procedure for the preparation of enantiomerically pure amines and alcohols. Yet, up to date, no study has clarified the influence of the η^6-ligand's structure on imine ATH despite the existence of at least four commercially available modifications. Analogous studies exist only for ketones, nevertheless, the 'ketone pathway' strinkingly differs from the imine one.

Our study clearly conludes that reaction rate, enantioselectivity and even solubility is strongly dependent on substitution of the η^6-arene: e.g. in the case of a catalyst with hexamethylbenzene as the η^6-ligand, the reaction proceeds only very slowly, and in cases of ATH of 1-phenyl-substituted dihydroidoquinolines via catalyst with benzene as the η^6-ligand enantioselectivity was close to zero. Studying these modifications can help us to better understand structure-activity relationships and thus help to develop catalytical systems with better properties.

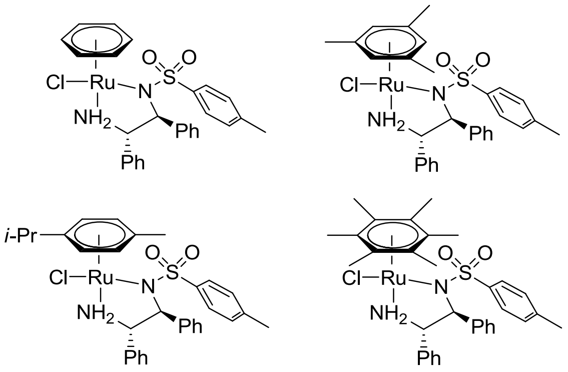

Figure 1

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Poster 50

Synthesis of Nitrogen-Containing Heterocycles via Ring-Closing Ene-Ene and Ene-Yne Metathesis Reactions

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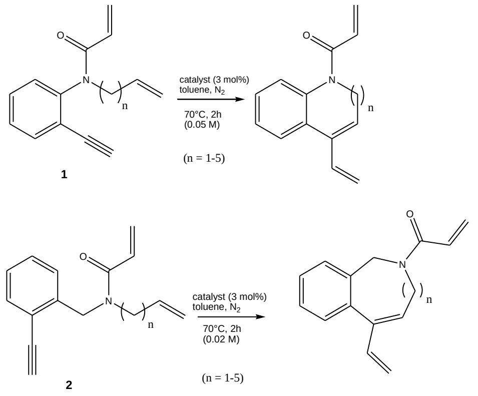
In the last few years ring-closing ene-ene metathesis and ring-closing ene-yne metathesis emerged as a versatile synthetic technique to obtain medium-sized carbo- and heterocycles as well as natural products.[1,2,3]

We recently developed a regioselective ring-closing metathesis approach to the synthesis of highly functionalizable 1-benzazepine and 2-benzazepine scaffolds and five- and six- membered lactams using the second generation Hoveyda-Grubbs catalyst.[4] The synthetic strategy started from compound **1** and **2** (n = 1) to afford respectively 1-benzazepine and 2-benzazepine ring (scheme 1). By changing the alkyl chain an approach to the preparation of large ring nitrogen-containing heterocycles was studied.



Scheme 1

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Poster 51

Bio-derived Chemicals and Fuels: a scientific partnership between Venice and Sydney

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The PhD cotutelle scheme between Venice and Sydney has allowed to couple research on green transformations of bio-based chemicals (including conversion mechanisms from platforms to their derivatives), with catalysts and processes for the improvement of bio-fuels (e.g. derived from algal feedstocks and by new technologies from lignocelluloses).

Bio-based chemicals in Venice. In Venice, the reactivity of bio-based platform chemicals such as levulinic acid and C_4-C_5 lactones,[1,2] with organic carbonates,[3,4] has been studied. This was done with a view of obtaining higher value added chemical compounds[5] by new greener broad-based chemical technologies.[6]

Bio-fuels in Sydney. In Sydney, on-water catalysis was applied to reduce the cloud point of biodiesel (the temperature at which crystals start to form in the fuel). This green innovative methodology was employed to carry out cycloadditions between fatty acids, constituents of biodiesel, and opportune bioderived dienes or dienophiles.

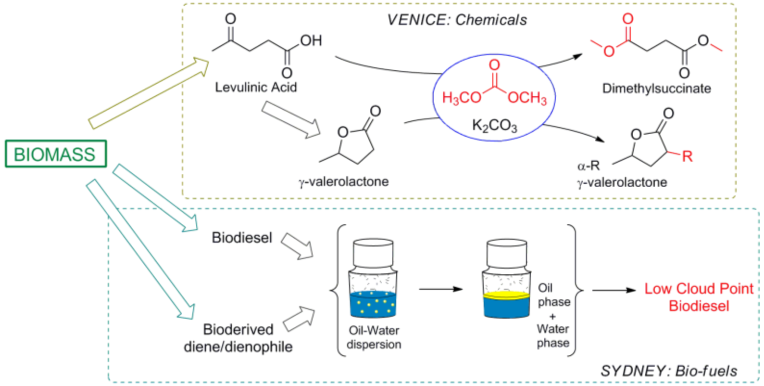

Figure 1. Transformation of chemicals and fuels obtained from biomass.

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Poster 52

Design and Synthesis of New Zinc-Salophen Complexes as Receptors for Biologically Relevant Anions

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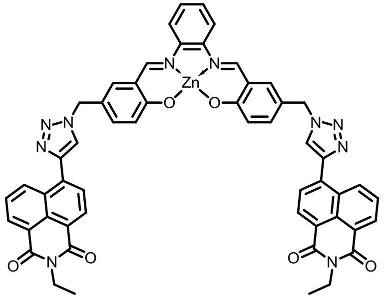
In the recent years, many studies have been focused on the development of synthetic molecular receptors for biologically relevant anions.[1] Among all, phosphates have received considerable attention due to their crucial role in life processes. In particular, nucleotides such as ATP, ADP and AMP are considered the most important due to their implication in energy transfer and storage in living cells.[2] Fluorescent and colorimetric based chemosensors represent useful tools owing the simplicity of the instrumentation and the high sensitivity of their optical response. In this field, zinc-salophen complexes have been widely exploited in anion recognition, and more concretely for phosphate.[3] In this work, we report the synthesis of a new zinc-salophen derivative (**sal 1**, Figure 1) and we show preliminary ^{1}H-NMR spectroscopic studies of its binding affinity towards some anions.



sal 1

Figure 1

Unfortunately, **Sal 1** shows poor solubility in most of the typical organic solvents (e.g. $CHCl_3$, CH_2Cl_2, THF). However, it is highly soluble in DMSO what makes the binding of guests a real challenge. Thus, to increase the solubility of the receptor in common, non-competitive organic solvents we are currently involved in the modification on the skeleton of **sal 1**.

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Poster 53

Oxidative Addition to Cyclometalated Complexes of Pt(II)

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Cyclometalated complexes have been studied in depth and almost every d-block transition metal has its own representative; partly this is because cyclometalation reactions are envisaged as intramolecular analogues of intermolecular C-H activation/functionalization in solution[1] and in gas phase.[2] Rollover cyclometalation is a particular type of C-H activation that involves ligands with at least one heteroatom (usually belonging to group 15 or 16) as donor in order to assist the activation of the relatively inert C-H bond.

Among the wide reactivity offered by Pt(II) cyclometalated complexes is the two electron oxidation to Pt(IV) which opens up a parallel world of possibilities. The importance of the oxidized complexes is well documented in many different fields: from functionalization of saturated and unsaturated hydrocarbons to material science and medicinal chemistry. Our interest in these species is related both to synthesis[3] and reactivity.[4] Here we use CH_3I as oxidizing agent with some cyclometalated complexes of substituted 2-phenylpyridines and 2,2'-bipyridines. The differences in reactivity are striking showing that electronic properties of the coligands are of paramount importance in stabilizing the oxidized metal centre. Pt(IV) rollover complexes, moreover, offer a promising type of chemistry because permit to achieve a rather rare C(sp^3)-C(sp^2) coupling which is still under investigation.[5]

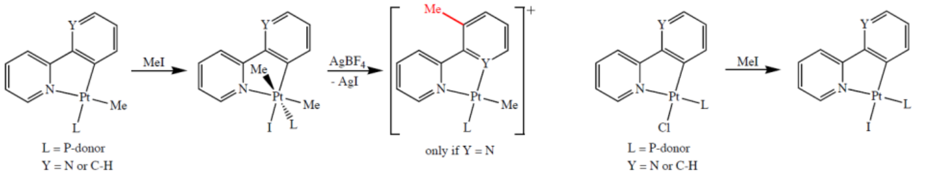

Figure 1

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Poster 54

Hydrogen Bond-Induced Assembly of Supramolecular Bidentate N,N- and N,P-Ligands

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In recent years, combinatorial and supramolecular approaches to the development of new ligands for asymmetric catalysis have gained momentum.[1] Supramolecular ligands contain, besides the atom(s) coordinating to the catalytic metal, an additional functionality capable of non-covalent interactions which can play the following roles: 1) allowing two monondentate ligands to self-assemble into the so-called "supramolecular bidentate ligands"; 2) binding the substrate(s) in proximity to the catalytic metal center, in analogy to metalloenzymes. In both cases, this approach causes reduced degrees of freedom in the metal coordination complexes, which are thus expected to result in more pre-organized systems with a better capacity of controlling the metal-catalyzed reaction.

In the last few years, several powerful supramolecular bidentate ligands with outstanding reactivity and selectivity have been described, but unfortunately, this concept has so far been exclusively confined to the use of phosphorus ligands.[1] We report herein the first example of hydrogen bond-induced assembly of monodentate oxazolines for the formation of supramolecular bis(oxazoline) (SupraBox) ligands (Figure 1) and their application in the copper(II) catalyzed asymmetric acylation of diols.2 In addition we describe also the synthesis of the first supramolecular phosphinoxazoline transition metal complexes (Figure 2).

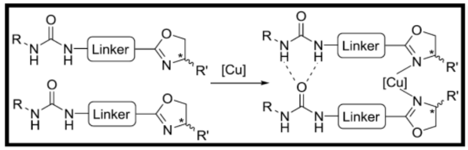

Figure 1

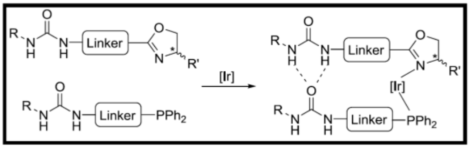

Figure 2

A small library of bifuntional oxazoline ligands was prepared using differently substituted oxazoline nuclei, linkers and different urea substituents. The formation of the transition metal complexes (Cu^{2+}, Pd^{2+} and Ir^{+}) was investigated by MS, UV/Vis and NMR spectroscopy. The SupraBox library was screened in the copper-catalyzed asymmetric benzoylation of vic-diols. Good selectivities were obtained in the kinetic resolution of racemic hydrobenzoin [up to 86%ee and selectivity (s) = 28] and in the desymmetrization of meso-hydrobenzoin (up to 88%ee).

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Poster 55

New Supramolecular Structures Based on Au(I) Luminescent Hydrogels

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Gels are an outstanding group of soft materials lying at the interface of solid and liquid, and find numerous applications in various fields including tissue engineering, biosensors, food processing, cosmetics, photography, controlled drug delivery etc. Amongst the variety of gels, hydrogels (those that entrap water) are of special importance owing to their tremendous potential in biomedicine and supramolecular chemistry. Moreover, gold(I) complexes exhibit interesting self-assembly properties that usually are modulated by the presence of aurophilic (Au···Au) interactions.[1] It has been very recently found that the [Au(4-ethynylpyridyl)(phosphine)] (phosphine = PTA, DAPTA) organometallic complexes forms hydrogels[2,3] and this fact opens a new and promising research field related metallohydrogels obtained with very simple chemical structures.

The small variation on the phosphine structure (DAPTA instead of PTA) (Fig. 1a) has observed to affect the observed properties: i) a great increase on the hydrogel entanglement structure has been observed; ii) the different cross-linking structures give rise to specific emission properties. In this work, we also present how can affect the introduction of different alkylic length chains attached to the PTA phosphine (Fig. 1b) and pyridine (Fig. 1c), on the luminescent and gelation processes (Fig. 2).

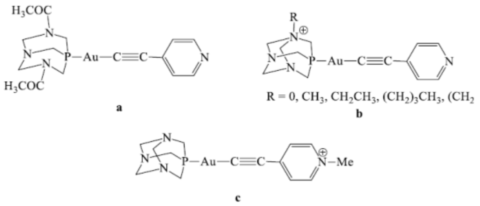

Figure 1. General structures of PTA derivatives

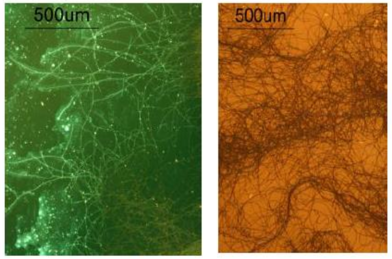

Figure 2. Images of [AuC≡C-C_5H_4N)(DAPTA)] by fluorescence optical microscopy

***Acknowledgements*:**Authors would like to thank funding provided by COST Action CM1005 Supramolecular Chemistry in water

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Poster 56

Gold(I) Complexes Targeting TrxR Enzyme as Anticancer Drugs

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The study of new gold(I) structures is an area of special interest in supramolecular chemistry because of their potential anticancer activity and photophysical applications.[1-3] In this work, we present a series of new dialkynyl, carbene and dicarbene complexes (Figure 1) derived from hydroxycoumarin and imidazolium precursors. These compounds have been characterized by ^1H NMR, IR and mass spectrometry. Their biological properties and those of their corresponding free ligands have been studied by testing their capability to inhibit TrxR and evaluating their IC_{50} and antiproliferative effects in tumor cell lines. For the compounds and free ligands of the dialkynyl series, UV and luminescence studies have been carried out.

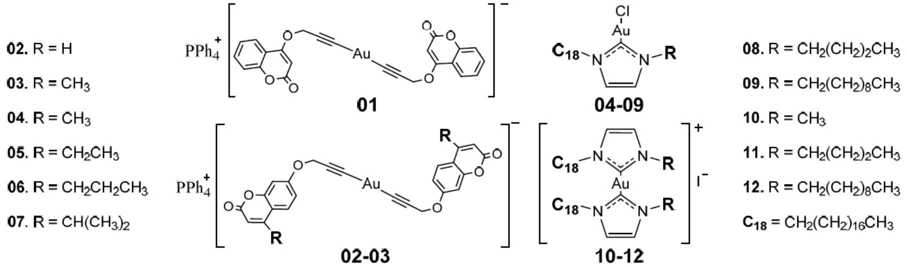

Figure 1. The gold(I) compounds for the dialkynyl series (**01-03**), carbene series (**04-09**) and dicarbene series (**10-12**).

Acknowledgements: Authors would like to thank the COST Action CM1005 for the opportunity to present this work. Financial support from MICINN (project TEC2011-29140-C03-02) and the Generalitat de Catalunya (2009SGR158) is acknowledged.

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Poster 57

Synthesis of New Chiral Tetraaza-Macrocycles and their Use as Ligands for Asymmetric Catalysis

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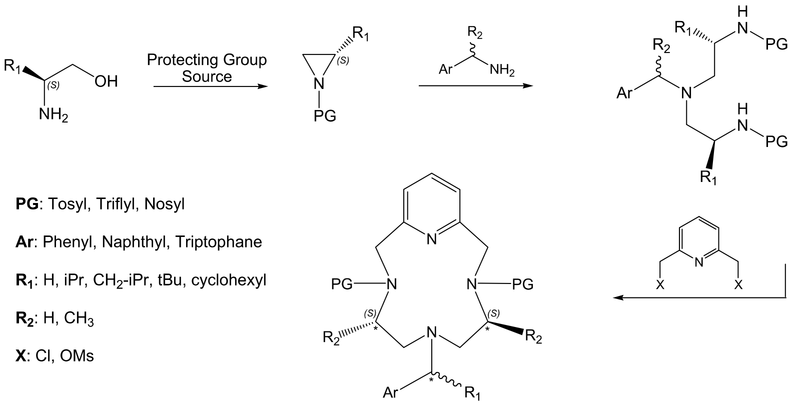
Our group has been focusing for years on the study of new chiral macrocyclic ligand. Their complexes with metal ions – specially copper(I) – are competent catalysts in various organic reactions. We obtained the best results, in terms of yield and enantioselectivity, on the asymmetric cyclopropanation.[1] We made several modifications on the structure of our ligands, to improve their effectiveness and their versatility. Here we reported an overview of these modifications and the preliminary results obtained using the new compounds in catalysis.



PG: Tosyl, Triflyl, Nosyl

Ar: Phenyl, Naphthyl, Triptophane

R$_1$: H, iPr, CH_2-iPr, tBu, cyclohexyl

R$_2$: H, CH_3

X: Cl, OMs

Scheme 1

These compounds could be obtained in moderate to good yields (20-70%) following a simple synthetic path (scheme 1), based on the use of commercially available and enantiomerically pure reagents. We fully characterized the ligands including elemental analysis, MS, ^{1}H- and ^{13}C-NMR. The nosyl protected ligands could easily be deprotected using the Fukuyama conditions[2] to obtain a not-protected dianionic class of macrocycles. We started testing the final compounds as ligands in copper(I) catalysts for asymmetric cyclopropanation with excellent results: in all cases we observed a complete conversion of EDA and, depending on the used ligand, we obtained cyclopropanes with stereoselectivities and e.e. up to 99%

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Poster 58

Cytotoxic Activity on HeLa Tumor Cell Lines of Cu(II) Complexes with Functionalized Quinolines

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In previous studies it was shown how copper complexes with pirazole-pyridine N,N' donor ligands[1] or with 8-hydroxyquinoline derivatives[2] could induce cellular death in human tumor cell lines, by means of intracellular copper overload. This was due to the ability of the ligands to act as ionophores for copper-demanding tumor cells, which accumulated harmful quantities of metal ions inside the cell.

As a continuation of these studies, we wished to investigate how the functionalization of the 8-hydroxyquinoline moieties with an aromatic side arm, with potential coordinating ability, could affect the anticancer activity of their Cu(II) complexes. The different substituents were chosen in order to modulate the overall ligand lipophilicity. A panel of 16 functionalized 8-hydroxyquinolinic ligands (L1-L16) were synthesized and tested for anticancer activity on human HeLa tumor cell line (cervical carcinoma). The ligands were tested alone and in presence of equimolar quantities of $CuCl_2$. A correlation was searched for between the exhibited cytotoxicities and structural features of the ligands. Some of the synthesized Cu(II) complexes were analyzed by means of single crystal XRD to evaluate the coordinating ability of the peripheral aromatic functionalization.

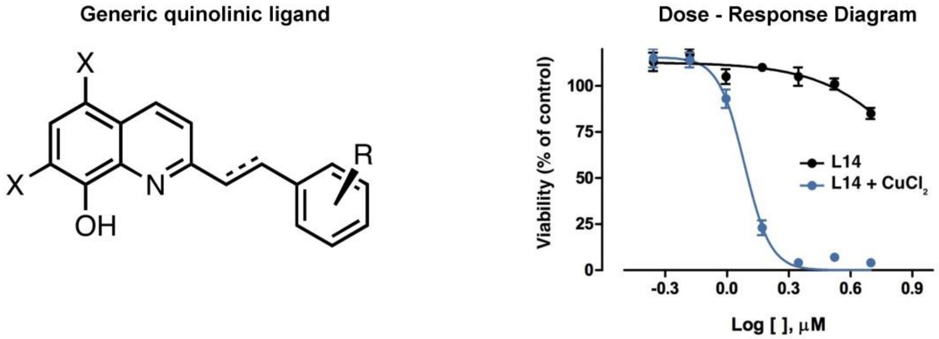

Figure 1

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Poster 59

Catalytic Studies With Model Complexes Mimicking the Hydrogenase Enzymes: Focus on Aromatic Dithiolate Ligand Complexes

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Depletion of fossil fuels in the future is a serious concern. In this regard, hydrogen is being developed as an alternative energy source. Hence, special attention has been paid in recent years to molecular models of the hydrogenase (H_2ase) enzymes due to their remarkable efficiency in H_2 production and activation. Three types of H_2ases are known: the Fe-S cluster containing [FeFe] and [NiFe]- H_2ases and the Fe-S cluster-free [Fe]-H_2ase.[1-5] The [FeFe] and [NiFe] H_2ases participate in hydrogen production and/or oxidation while the [Fe] H_2ase engages mainly in hydrogen activation. The hydrogen evolution and activation has been studied by synthesizing and developing a large number of organometallic complexes.[6-7] But only a few of the complexes are capable of acting as catalysts for proton reduction or dihydrogen oxidation. Hence, the catalytic activities and properties of all the reported aromatic dithiolate (e.g. 1, 2-benzenedithiolate (bdt)) metal complexes will be summarized and reported. Examples of such complexes will include dinuclear organometallic complexes, $[Fe_2(\mu\text{-bdt})(CO)_5L]$ and $[Fe_2(\mu\text{-bdt})(CO)_4L_2]$ where L = Monodentate phosphines (Figure 1).

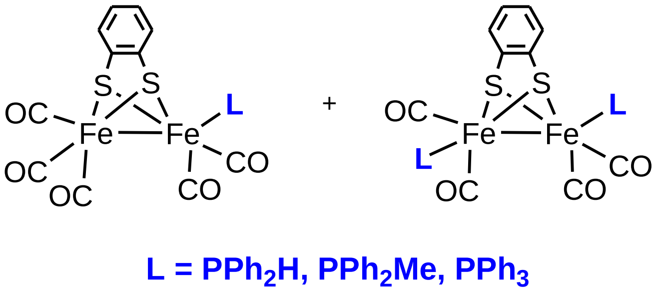

Figure 1

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Poster 60

A Family of Dibenzobarrelene-Based Iridium Hydrides: Structural Peculiarities and the Interaction with Bases and Solvents

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In the last decade cooperative ligands participated actively in reversible structural transformations of catalytic species over the course of a catalytic cycle, have been increasingly used to develop novel efficient catalysts in (de)hydrogenation processes.[1,2] Recently, the new class of polyfunctional dibenzobarrelene-based complexes exhibiting high catalytic activity in alcohol dehydrogenation and hydrofomrylation processes, was reported by Gelman et al.[3]

In this contribution we present the recent results of the combined spectral (IR, NMR) and theoretical investigation of a family of PC(sp^3)P pincer iridium hydrides. The structural deversity of complexes **1** and **2** (Figure 1) was demonstrated on the base of both DFT calculations and experimental data. It was established that their structures had distorted pyramid geometry and differed by the mutual arrangement of ligands in the metal coordination sphere and by conformation of functional groups. The presence of triethylamine leads to the rupture of weak intramolecular interactions in **1** and the stabilization of 5-coordinated complexes by bases and solvents, e.g. DMSO, pyridine, acetonitrile, results in the formation of novel structures. The structural peculiarities of 6-coordinated complexes **3** and **4** will be discussed as well.

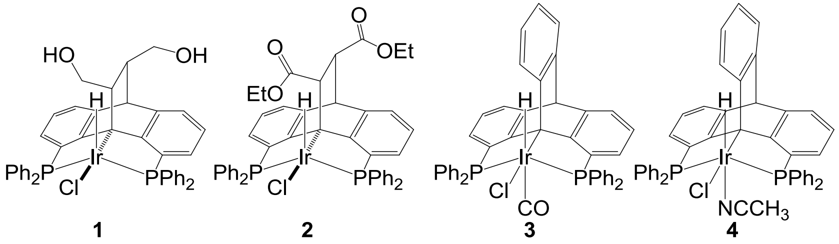

Figure 1

Acknowledgements: This work was financially supported by the Russian Foundation for Basic Research (projects No. 12-03-31326 and 11-03-01210).

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Poster 61

Rerversible Orthometalation as New Mode for Metal-Ligand Bifunctional Catalysis

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The active sites of enzymes often rely on the reactivity of neighboring ligand scaffolds and second coordination sphere interactions. With this cooperativity of the ligands, Nature was able to employ earth-abundant first row transition metals, which incline to undergo one-electron processes, for controlled multi-electron reactions.[1] Recently the use of metal-ligand bifunctional ligands has been recognized as promising tool for the activation of substrates.[2-4] Our group is interested in the targeted design of new non-innocent ligand architectures for cooperative bond activation reactions and catalytic processes.[5]

Many of the metal-ligand bifunctional catalyst that show excellent results in substrate activation, are based on the robust, reactive and easily modified pincer ligands. For a long time, the pincer chemistry was dominated by E-C-E (E = P, N, O, S) ligands with a *ortho*metalated central ring. It is surprising to see that the M-C bond never has been explored as cooperative motif, since C-H activation methodologies provide powerful and efficient pathways for hydrocarbon functionalization.[6]

This poster shows the synthesis of new proton-responsive *ortho*metalated complexes with a phenyl group in the terminal position to avoid steric restrictions (Figure 1). The reactivity of the M-C bond and application in catalytic reactions are explored.

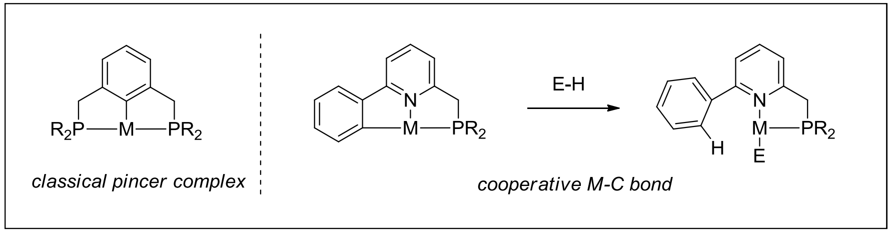

Figure 1

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Poster 62

Nickel-Complexes Bearing Redox Non-Innocent Ligands

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Redox non-innocence allows ligands to become part of the catalytic cycle. These ligands have drawn attention the past decade because they may offer ways to induce new reactivity to metal complexes. Ligands in these complexes are no longer spectators but actors, the key idea behind cooperative catalysis.[1,2]

One way redox non-innocent ligands can be employed is to let them function as an electron reservoir. First-row transition metals often promote one electron redox changes while essential steps in catalysis, such as oxidative addition and reductive elimination are two electron processes.[3] Additionally, redox non-innocent ligands can be employed to generate ligand-based radicals. In this way, interesting ligand-based reactivity can be induced.[4]

Nickel complexes containing a monoanionic PNP-pincer ligand are known to form ligand-based aminyl radicals upon oxidation (figure 1).[5] We are interested in studying the reactivity of these complexes. This relates to their potential to be used for amination reactions and to support relevant intermediates in N_2 reduction pathways.

We will present the latest developments in our research on synthesis, characterization and reactivity of redox non-innocent ligands and their corresponding metal complexes.

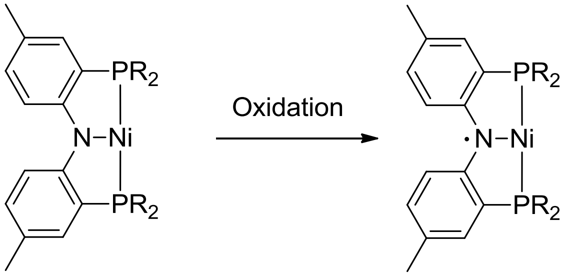

Figure 1

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Poster 63

New Effective Ligands for Cu-Catalysed Aryl Ether Formation in Air

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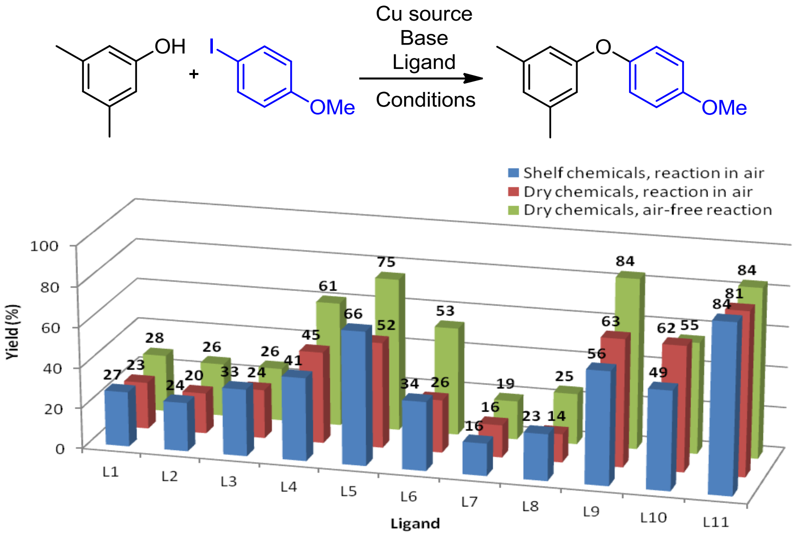
Aryl ethers are important motifs in medicinal chemistry, and the use of Cu-catalysed couplings (Ullmann reactions) for their synthesis is nowadays a common procedure.[1] Typically these reactions require simple neutral or anionic ligands and are performed under inert atmosphere. However, the role of the ligand in these reactions is not totally understood, and only a few structure-activity relationship studies on families of ligands have been reported.[2] Herein, we report investigations on a new class of ligands for Ullmann ether synthesis under mild conditions. Compared with other common ligands (**L1-L10**), ligand **L11** led to higher yields in a model reaction in several condition tested (Scheme 1). In particular, the reaction could be performed in air without any decrease in yield. Optimisation of the reaction, substrate screening and mechanistic investigations aiming to understanding the interactions ligand / metal centre are ongoing in our laboratories.



Scheme 1

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Poster 64

$RuCl_3$ Catalyzed Transfer Hydrogenation of Natural Polyenes Mixture to Monoenes

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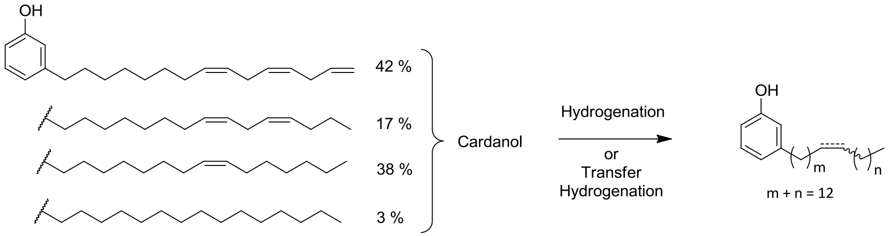
Cashew Nut Shell Liquid (CNSL) a waste from agriculture is rich in Anacardic Acid and Cardol. Technical CNSL is obtained by decarboxylation of CNSL which leads to a mixture mainly composed of Cardanol and Cardol (> 95%). These unsaturated components can be separated by different methods using liquid-liquid extraction or vacuum distillation. These phenolic olefins are mixtures of a triene, a diene, a monoene and a saturated compound.[1] These mixtures of polyenes can be converted into a single monoene by catalytic hydrogenation or transfer hydrogenation using, formic acid or an alcohol as hydrogen source. The reactivity of a number of different catalysts was compared. Very high selectivity was obtained by transfer hydrogenation with $RuCl_3$ using *iso*propanol as reducing agent.

Surprisingly, it was found that $RuCl_3$ is not converted to nanoparticles as expected. Rather, the substrate forms a ligand to the metal. Complexes with one, two or three substrate molecules attached to ruthenium were found. It was also shown that interaction between the ruthenium metal and the aryl moiety is important for activity. As a result, this procedure could also be applied to polyunsaturated fatty acid derivatives, but only introducing a phenyl function. This is the first instance of a catalyst that is activated by the presence of an aromatic ring in the substrate.[2]



Scheme 1

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Poster 65

Methods of Preparing a Chiral Precursor of Mivacurium Chloride

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Mivacurium chloride (Figure 1) belongs to skeletal muscle relaxants with a short duration of action, which are frequently used in surgery under anaesthesia. Like many other relaxants (and drugs in general), Mivacurium is a chiral molecule and must be administered to patients in the form of a single enantiomer. The optically pure fragment of the drug, (*R*)-5′-methoxylaudanosine, is typically produced by separation of racemic mixture.

In this work, we present the synthesis of a precursor of Mivacurium chloride (and other structurally similar relaxants, *e.g.* Gantacurium), which was prepared *via* two different routes. The first way reproduces the procedure established in the industry because no detailed information about the reaction conditions was available hitherto. The second synthesis is based on the asymmetric transfer hydrogenation of a dihydroisoquinoline followed by *N*-methylation. Both methods were feasible, but the asymmetric pathway seemed to be more economical and ecological than the industrial route.

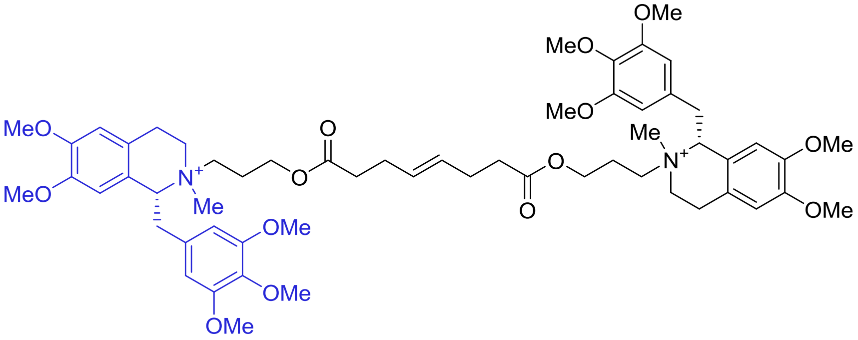

Figure 1. Structure of Mivacurium chloride (the chiral fragment is shown in blue colour).

Acknowledgements: This work has been financially supported by the Grant Agency of the Czech Republic (Grant GACR P106/12/1276), and by grant for long-term conceptual development of Institute of Microbiology RVO: 61388971

Poster 66

On the Mechanism of Asymmetric Transfer Hydrogenation of Imines

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Asymmetric transfer hydrogenation (ATH) of prochiral imines is nowadays a fairly well-documented method for the preparation of optically enriched amines.[1] The reaction is catalyzed by chiral half-sandwich ruthenium complexes [RuCl(η^6-arene)(*N*-arylsulfonyl-DPEN)] (DPEN = 1,2-diphenylethylene-1,2-diamine). The azeotropic mixture of formic acid and triethylamine serves as the hydrogen donor. The mechanism of ATH of imines (and ketones) has been extensively studied since the discovery of the catalytic system. Although the number of publications on this topic is considerably high, one may be easily confused due to a high degree of fragmentation of the findings presented therein. Therefore, the aim of this work is to give a concise but coherent description of the contemporary mechanism (Figure 1). Several contributions of our group on this topic are included, such as calculated geometries of the transition states,[2] influence of the base on the reaction performance,[3] and the formation of the key ruthenium hydride species.

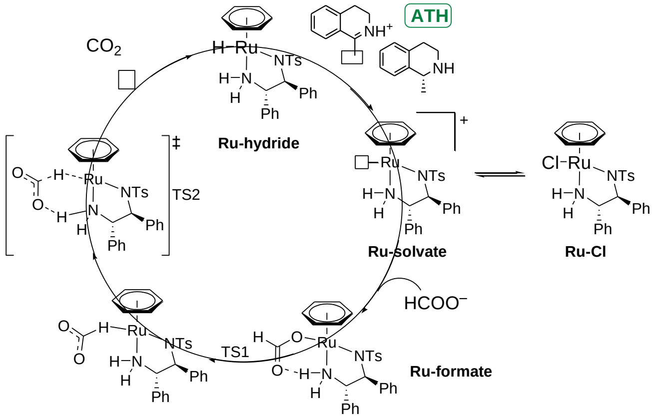

Figure 1. Schematic representation of the mechanism of imine ATH.

Acknowledgements: This work has been financially supported by the Grant Agency of the Czech Republic (Grant GACR P106/12/1276), and by grant for long-term conceptual development of Institute of Microbiology RVO: 61388971

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Poster 67

Novel (arene)Ruthenium(II) Complexes with halogen-substituted Scorpionates: Synthesis and Structural, Electrochemical and Catalytic Studies

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Since their discovery in 1966,[1] poly(pyrazolyl)borates (Bp^x and Tp^x), often indicated as scorpionates, have been extensively employed as anionic σ-donor ligands in a wide variety of metal complexes,[2] as the steric and electronic properties of these ligands are easily modified by changing either the number of pyrazole rings or by substituents thereon or at the boron/carbon center. In recent works, we investigated the interaction of η^6-arene Ru(II) with (pyrazol-1-yl)borates[3] and (pyrazol-1-yl)alkanes,[4] their coordination chemistry and their catalytic behaviour. Here we report some recent results obtained with bis- and tris-pyrazolylborate ligands bearing Br and ^{i}Pr substituents in the pyrazole rings (Fig. 1) and some η^6-arene ruthenium fragments (arene = benzene, *para*-cymene or hexamethylbenzene), together with the spectroscopic and structural characterization of the organometallic complexes. The comparison of the electron-donor character of Bp^- and Tp^- ligands has been supported by electrochemical studies. Furthermore preliminary catalytic results on diastereoselective nitroaldol reaction of benzaldehyde and nitroethane (Henry Reaction) will be reported.

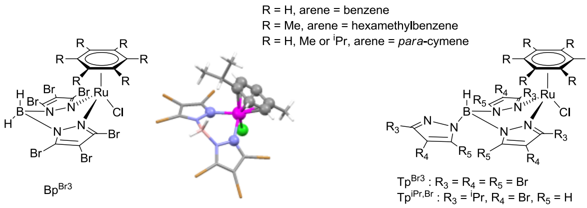

Figure 1

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Poster 68

New Cationic N-Heterocyclic Carbene Gold(I/III) Pyridine Complexes: Synthesis, Characterization and Catalytic Activity

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Since the isolation of the first "free" stable N-Heterocyclic Carbene (NHC) by Arduengo in 1991,[1] organogold chemistry and gold catalysis have taken full advantage from the easy use of this class of ligand.[2] Indeed, the strong electron donor ability and the easy tuning of steric properties of NHCs stabilize gold centers in various oxidation states[3] and many complexes initially thought to be elusive could be isolated and structurally characterized.[4] Therein, here we describe the synthesis and characterization of a new series of stable, cationic NHC gold(I/III) pyridine complexes, as well as their stability and catalytic activity in five well established gold-mediated organic transformations.

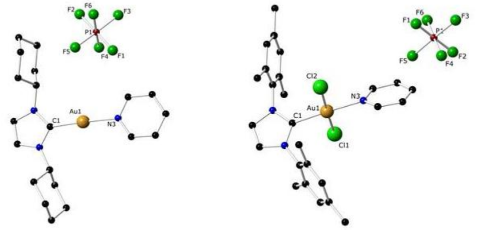

Figure 1

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Poster 69

Sensitization of Monolayer Transparent TiO_2 Thin Films with Metal-Porphyrin Dyes for DSSC Applications. Equilibrium and Kinetic Aspects

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For the best manufacture of dye-sensitized solar cell (DSSC) systems (Figure 1), optimum objectives are represented from very rapid and complete adsorption of single layer of dye on the semiconductor surface.[1,2] Cu(II) and Zn(II) complexes of Coproporphyrin-I or CPI (Figure 2), has been synthesized in our laboratory and tested as sensitizers in DSSC devices.[3,4] A systematic study of kinetic and equilibrium for the adsorption of metal-CPI-dyes onto TiO_2 monolayer surfaces, have permit to establish the best experimental conditions for the adsorption of these dyes and have demonstrated that the metal-CPI-dyes, according to the Langmuir model and with pseudo first-order kinetics, are adsorbed effectively in the support of TiO_2 monolayer without chemical changes. The suppression of the dyes aggregation have permitted the optimization of selective adsorption of one layer of dyes molecules to stoichiometric ratios improving performances in DSSC indicating therefore a powerful experimental strategy, that can be enlarged to other dyes.

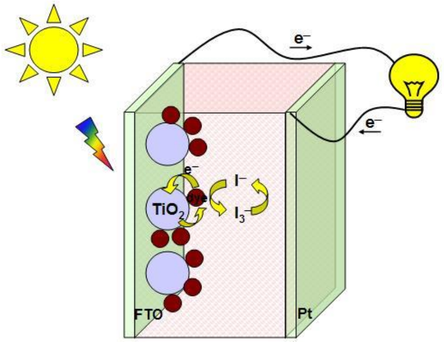

Figure 1. DSSC Process

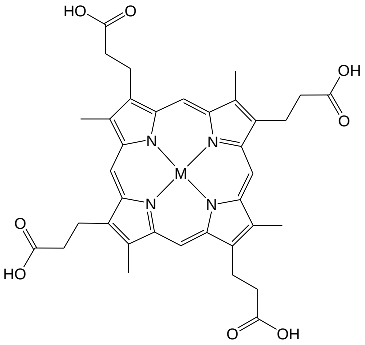

Figure 2. Molecular structures of Coproporphyrin-I sensitizers, CPI = M is no metal, CPIZn =M is Zn(II), CPICu = M is Cu(II).

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Poster 70

Enantioselective Transfer Hydrogenation of Aryl-Ketones and Stereochemistry of the Metal Centre by NMR and CD Spectroscopy

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Ruthenium complexes are the most useful catalyst for AH and AHT of polarized bonds.[1,2] Among the multitude of ruthenium complexes, those gathering a diamine chiral ligand and a diphosphine are particularly efficient. Optically pure 8-amino-5,6,7,8-tetrahydroquinoline (hereafter defined Campy) showed to be a versatile source of chirality, particularly in AHT,[3] with chiral and achiral diphosphine. The great enantioselective efficiency seems to be related to the formation of only one of the possible chiral catalytic species.

In the monohydride complex (inactive in AHT without the presence of $OCH(CH_3)^{3-}$) the formation of the chiral metal centre is stereoselctive and likely proceeds with retention of configuration. We will discuss in detail the relation among CD of LF transitions, NMR NOESY and COSY correlations and the stereochemistry of AHT reduction of prochiral ketons.

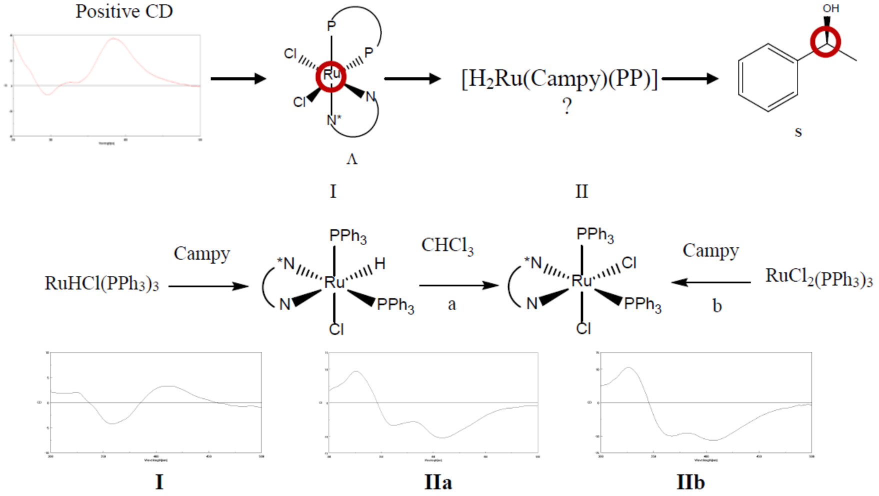

Figure 1

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Poster 71

Zn – Salophen Complexes and Macro Cycles as Hosts in Molecular Recognition of Anions

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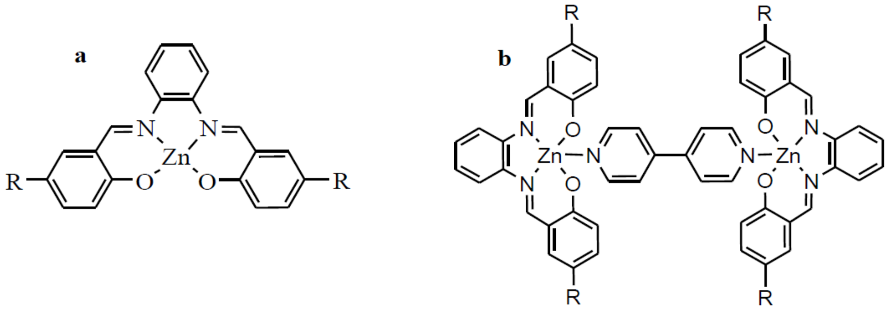
Sensing of anions is an increasing research area in chemistry and even more in biochemistry. Biologically relevant species usually bear negative charges. One strategy to detect this species is to capture them through a coordinative or electrostatic bond that brings the anion near an adequate signaling unit whose fluorescent properties are affected by the coordination. Salophen metal complexes, which bear a vacant coordination position, are very appealing candidates in applications related with anion sensing.[1] In this work, we present the use of different Zn-salophen derivatives that differ on the electronic character of one substituent (Figure 1a). We analyze how this could affect on the molecular recognition processes of anions in solution. Moreover, we present the synthesis of a macro cycle that can host larger anions (Figure 1b).[2]



R = OMe, Br, NO_2, CN

Figure 1

***Acknowledgements*:** Support and sponsorship provided by COST Action CM1005 is acknowledged.

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Poster 72

Synthesis of Novel Salen Ruthenium(II) Complexes

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Salens are distinct ligands that have been applied extensively in asymmetric catatlysis.[1] Their simplicity of preparation and easy accessible dive.[2] Next to the common and widely used “trans” geometry for catalytic systems, also the less common *cis*-α and *cis*-β configurations (see Figure 1) exist. It has been shown that the latter configuration gives rise to *different* and *unique* asymmetric catalytic properties.[3,4] Recently, also binuclear species are shown to enhance catalytical performance5. but not much research has been performed in a combination of these two with ruthenium as a metal.[4,6–9]

Therefore, the two chiral Schiff bases consisting of a bismethylphenyl-(L**1**) or bisnapthyl backbone (L**2**), that are known to favour a non planar coordination geometry, have been prepared. The geometries of these ligands coordinated to ruthenium were investigated, as well as their (cooperative multimetallic) catalytic properties.

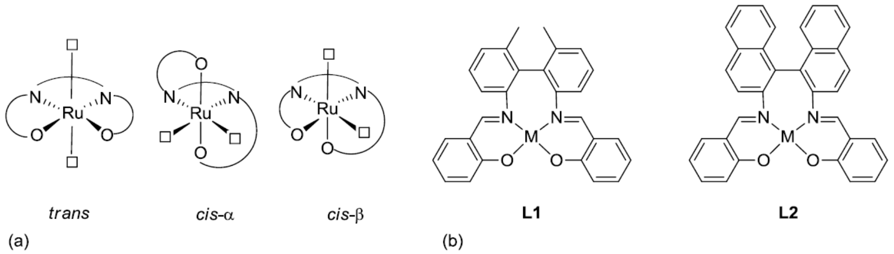

Figure 1. Three different geometries of metallosalens in space (a); Two ligands that favour a non planar coordination geometry (b).

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Poster 73

Cooperative Ligand Effects in Hydride Transfer Catalysis

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Transfer Hydrogenation (TH) is an important and well-studied process in chemistry, which involves stepwise dehydrogenation (hydrogen donor) and hydrogenation (hydrogen acceptor) of substrates. Conceptually relevant reactions in this field include dehydrogenation, dehydrogenative coupling, and hydrogen auto-transfer (borrowing hydrogenation methodology), which are all 'hot topics' in current catalysis research.[1] Transition metal (TM) complexes featuring 'ligand-cooperative effect' to facilitate the hydrogen transfer process have been intensively studied and well developed.[2] Ligands in such systems generally serve as a proton-relay site, while the hydride is typically received and delivered by the metal center. In nature, however, reduction of unsaturated bonds often involves organic hydride donors, with NADH and Flavins among the most well-known examples. Rare cases have been reported in these TH-related catalysis with the ligand of the TM complexes promoting a hydride transfer.[3]

In this poster we present a new concept, in which a new cooperative ligand system is developed that acts an hydride donor/acceptor in transfer-hydrogenation type catalysis. This system is based on the picolyl-amine type scaffold, and allows for a variety of catalytic hydride transfer reactions such as TH and hydrogen autotransfer coupling reactions, thus showing the potential of this new system. On the basis of DFT calculations a new ligand-assisted hydride-transfer mechanism is revealed for this reaction, involving a low-barrier amine to imine interconversion as the key-step of the overall catalytic process (Figure 1). TM Complexes with a new family of PNN ligands have been developed (Figure 2). The ligands can potentially function in the catalysis as a dual shuttle for both protons and hydrides.

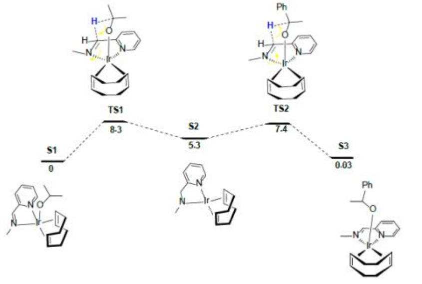

Figure 1

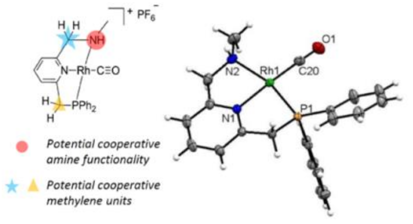

Figure 2

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Poster 74

Closed-shell and Open-shell Group 9 Transition Metal Nitrido Complexes

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Electron rich transition metal nitrido complexes are under great current interest in the context of dinitrogen fixation and catalytic nitrogen group transfer reactions.[1] Open-shell nitrido complexes were postulated as intermediates in nitride coupling, but examples remain scarce.[2,3]

Based on electronically and coordinatively unsaturated iridium and rhodium PNP pincer platforms,[4] we were able to characterize high-valent iridium(V) and iridium/rhodium(IV) nitrido complexes.[5] The electronic structure and reactivity of this class of compounds is discussed,[6] particularly the highly selective nitride coupling reaction of the open shell nitrides which is attributed to a radical coupling reaction due to pronounced nitridyl character.

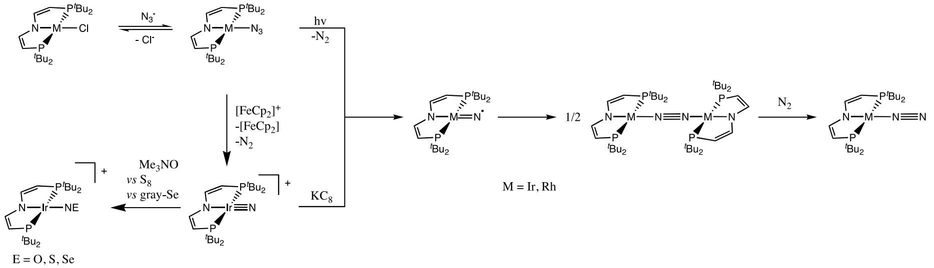

Figure 1

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Poster 75

A New Class of Nanoscaffolds based on Ion Tagged Ti(IV) Amine Triphenolate Complexes

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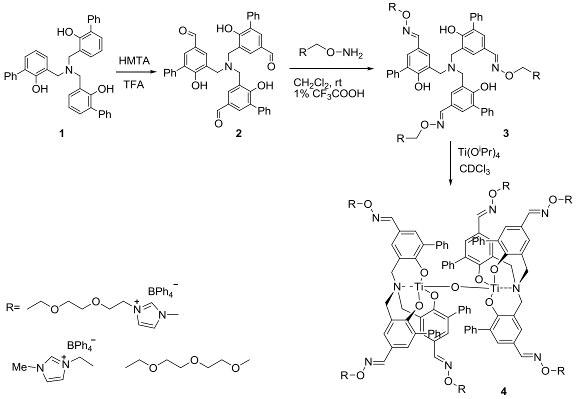
Triphenolamines are highly modular ligands that are able to effectively coordinate to a wide variety of transition metal ions, leading to the formation of a large family of complexes.[1] As referred to Ti(IV) complexes, the nature of the substituent in *para* position to the phenol groups is important to determine the binding mode and the stability of the corresponding complexes in solution. In particular, when the substituent is a phenyl group, the complexation reaction leads to the formation of exceptionally stable S_6-symmetric heterochiral μ-oxo dinuclear complexes (scheme 1).[2]



Scheme 1

Here the synthesis of **1** based on a three-fold reductive amination as well as the highly effective three fold *para* formylation to obtain ligand **2** will be presented. The further functionalization of **2** *via* oxime bond formation allows the introduction of ion tagged and PEG moieties which can tune the solubility of the ligands **3** in polar/protic solvents. Moreover, their corresponding spatially ordered dinuclear complexes **4** can be employed to build up supramolecular systems and molecular scaffolds for further applications in catalysis and material sciences.

Acknowledgments**:** We thank COST Action CM 1005 “Supramolecular Chemistry in Water” for financial support.

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Poster 76

Oldies but Goodies: Back to Ruthenium(II) Complexes

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Following our studies on tetrazolato-based Ru(II)-polypiridyl complexes, which showed remarkable photophysical properties and have also been reported as good emitters for Electrochemilumescent devices,[1] we have developed new Ru(II)-tetrazolate neutral system that might be used either as light absorber for DSSC(dye sensitizer solar cell) or as dopants for OLED type devices (Figure 1).

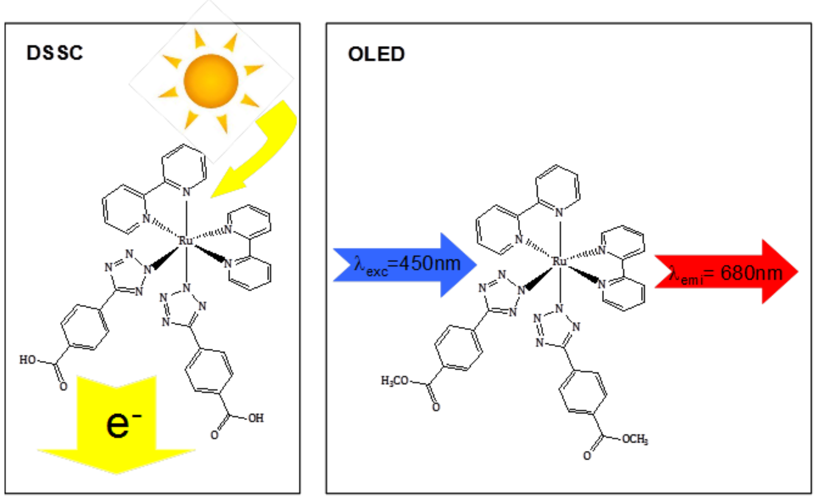

Figure 1

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Poster 77

New Synthetic Methods for Organometallic Ketonyl Derivatives of the Type [PtCl{η^1-$CH_2C(O)R$}(*N-N*)] Starting from the Zeise's Salt

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The reactivity of the Zeise's anion with bidentate dinitrogen ligands (***N-N***) has been the main subject of several studies on the Pt(II) coordination and organometallic chemistry.[1] The chemistry of Pt(II) organometallic ketonyl derivatives it is recognized to be important for many potential applications,[2] where the peculiar properties of ketonyl derivatives with transition metals seem of particular interest[3].

For these reasons we exploit the possible extension of Zeise's anion reactivity, in basic media, to the general synthesis, of organometallic ketonyl derivatives of the type [PtCl{η^1-$CH_2C(O)R$}(***N-N***)], even in the case of aliphatic diamines and sterically hindered diimine ligands. In these conditions we observed the first formation of methastable intermediate complexes of the type *trans*-[$PtCl_2${η^1-$CH_2C(O)R$}(η^2-C_2H_4)]$^-$. Further reaction with dinitrogen ligands (***N-N***) gives [PtCl{η^1-$CH_2C(O)R$}(***N-N***)] complexes (Figure 1). We were able to synthesize for the first time [PtCl{η^1-$CH_2C(O)R$}(***N-N***)] complexes with sterically unhindered or hindered diamine and diimine nitrogen ligands, i.e. **en** (ethylenediamine), **tmen** (*N,N,N',N'*-tetramethyl-ethylenediamine), **Me₂phen** (2,9-dimethyl-1,10-phenanthroline). In particular we could verify the usefulness of this new method for the synthesis, in high yields, of acetonyl derivatives, even in the case of complexes previously obtained by other synthetic pathways, as the complex [PtCl{η^1-$CH_2C(O)R$}(**phen**)], **phen** = 1,10-phenantroline.[4]

This new simple pathway results interesting from the synthetic point of view for the possibility to synthesize ketonyl complexes with several ketones and dinitrogen ligands not suitable for other methods.

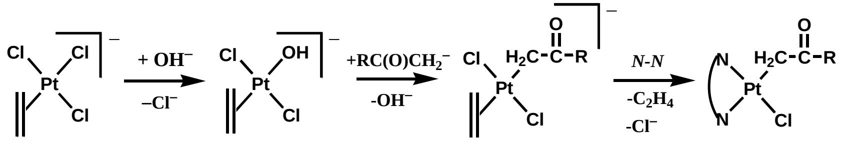

Figure 1

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Poster 78

Solventless VOC chemisorption by silver metallocycles

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Prior work has focused on detection/sensing aspects of VOCs,[1,2] this work proposes a method for their simultaneous filtration and removal through their strong chemisorption to a silver(I) metallocyclic trimer. A solid cyclotrimer can quantitatively remove entire molar integers of VOCs (1-3 equivalents of VOCs per mole of the nitrated trimer) from the vapor phase in a solventless "green" chemical process, which is unprecedented for this class of cyclic d^{10} complexes.

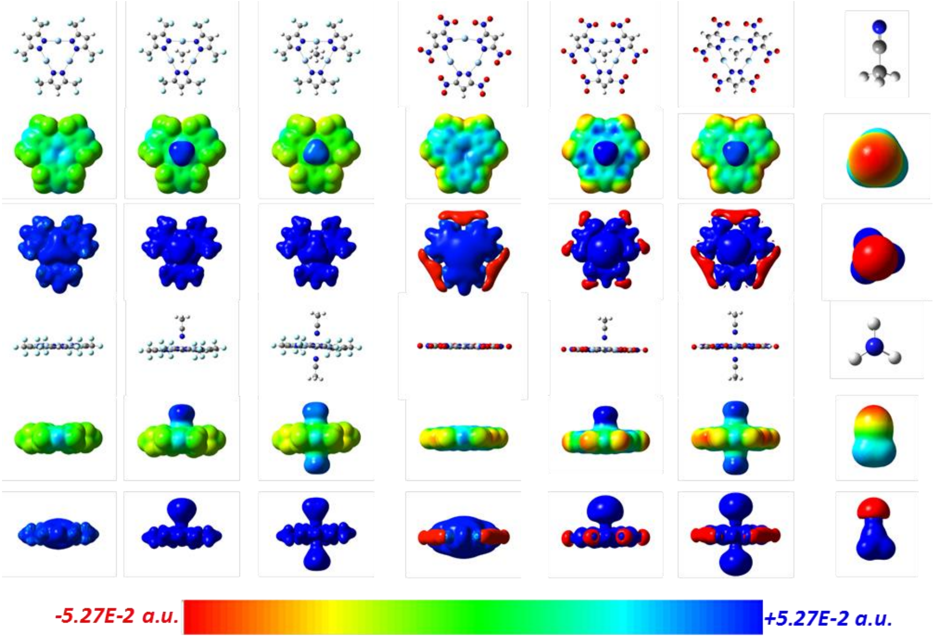

Figure 1. Illustration of quadrupole-dipole interactions involving the [Ag(μ-Pz-2CF_3)]$_3$ or [Ag(3,5-$(NO_2)_2$pz)]$_3$ trimers and acetonitrile using M06/CEP-31G(d). MEP surfaces are plotted in two manners, either mapped on electron density surfaces (rainbow plots with the color scale shown; isodensity = 0.0004) or positive (blue) and negative (red) regions in space (range = ± 2.2 a. u.; isodensity = 0.02)

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Poster 79

Highly Symmetric Dinuclear Ti(IV) Nanostructures

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Mononuclear Ti(IV) complex **1** (R=R'=H), obtained by reaction of Ti(O*i*Pr)$_4$ with amine triphenolate ligand bearing *ortho*-phenyl substituents, has been found to quantitatively and spontaneously reacts with water affording the corresponding heterochiral μ-oxo dinuclear complex **2** (Figure 1).[1] This highly stable and spatially ordered μ-oxo dinuclear complex has twelve potential anchoring sites for the selective functionalization: six correspond to the *meta* positions of the peripheral phenyl moieties (R') and other six to the *para* positions of the phenolate group of the ligand (R). Thus, **2** could be exploited to build up supramolecular self-assembling systems used as molecular scaffolds for applications in catalysis and material science.[2]

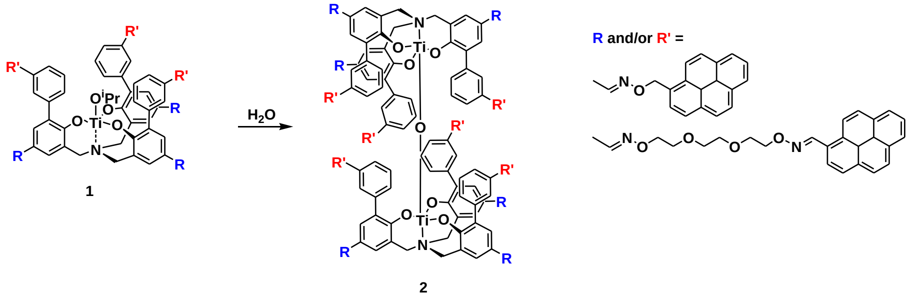

Figure 1

Here we will present the effective synthesis of **2** derivatives bearing pyrenes moieties in different positions and with different linkers, together with their characterization and stability studies and preliminary results related to their applications as multistage redox systems and receptors for C$_{60}$.[3,4]

Acknowledgements: We thank Fondazione CARIPARO Progetti di Eccellenza 2011 (Nano-Mode) and COST Action CM1005 'Supramolecular Chemistry in Water' for financial support.

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Poster 80

A New Synthetic Procedure for Multifunctionalized C_3 Triphenolamines

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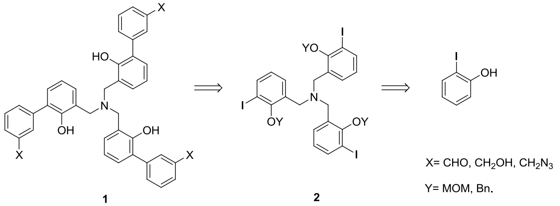
Triphenolamines are highly modular tetradentate molecules that effectively coordinate to transition metal ions[1]. Their highly modular nature allows to obtain a large family of metal transition complexes that have been used as effective catalysts in different processes such as polymerization[2], oxygen transfer reactions[3] and CO$_2$ fixation[4].



Scheme 1

Here we present a novel protocol for the synthesis of **1** based on a three-fold Suzuki coupling starting from the iodo derivative **2** and 3-formylphenylboronic acid. The *O*-protected ligand **2** can be effectively synthesized via three-fold reductive amination of commercially available 2-iodophenol. Different functionalizations in *meta* position of the peripheral aromatic ring can be exploited to tune the properties of the ligands and the corresponding complexes, such as solubility in different solvents, or to insert new reactive moieties for new applications in catalysis and molecular recognition. In particular, we will present the introduction of azide, hydroxo and formyl groups that can be used for the introduction of multiple and ordered functions via *click* chemistry.

Acknowledgements: We thank Fondazione CARIPARO Progetti di Eccellenza 2011 (Nano-Mode) and COST Action CM1005 'Supramolecular Chemistry in Water' for financial support.

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Poster 81

Mechanistic Insights Into Water Oxidation Catalyzed by Ir-Cp* Complexes

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The realization of an efficient apparatus for artificial photosynthesis is strongly hampered by the difficulty of oxidizing water. Several transition metal complexes have been successfully applied as catalysts for water oxidation and those based on iridium attracted much attention in the last five years because they showed remarkable performance both in terms of TOF and TON.[1]

Our group has contributed to the development of new iridium-based organometallic catalysts for water oxidation.[2] Specifically, [Cp*Ir(bpy)Cl]Cl (**1**, bpy = 2,2'-bipyridine), Cp*Ir(bzpy)NO$_3$ (**2**, bzpy = 2-benzoylpyridine) and [Cp*Ir(H$_2$O)$_3$](NO$_3$)$_2$ (**3**) showed to be competent catalysts using cerium ammonium nitrate (CAN) as a sacrificial oxidant, added in a large excess with respect to the catalyst. This contribution deals with the results of our studies on the reactions of **1**-**3** with a small excess of CAN, performed by a multiple technique approach and aimed at shedding some light on the reaction mechanism. Three main findings have been obtained: i) an intermediate species Cp*L$_n$Ir^{IV}–OH was intercepted by UV-Vis spectroscopy; ii) it was concluded that the last oxidative step is most likely the rate determining step of the catalytic cycle (Figure 1); iii) measurements on CO$_2$ formation indicated that catalyst degradation occurs parallel to oxygen evolution, with a minor extent at high concentration of CAN.

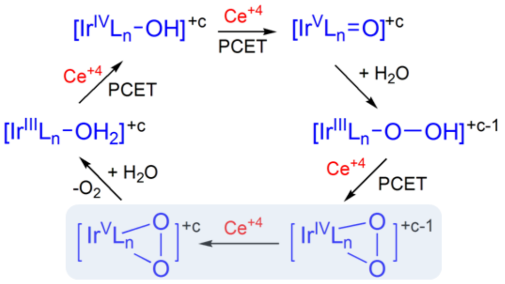

Figure 1

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Poster 82

Dehydrogenation of Ammonia-Borane Catalyzed by Palladium and Ruthenium Complexes

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The increasing quest for efficient and safe hydrogen reservoirs has led to an enormous growth of the hydrogen storage research field in recent years. As far as chemical storage is considered, one of the most promising materials is ammonia-borane (NH$_3$·BH$_3$, AB, 19.6 wt.% H).[1] Homogeneously-catalyzed AB dehydrogenation is the path that the organometallic chemist can follow to exploit AB as hydrogen storage material. Many transition metal complexes have been proposed as possible catalysts.[2] Recent work in our laboratory has been focused on the Palladium(II) PCP pincer complex [(^{tBu}PCP)Pd(H$_2$O)]PF$_6$ [**1**, ^{tBu}PCP = 2,6-C$_6$H$_3$(CH$_2$P^{t}Bu$_2$)$_2$, Figure 1] and on the NP$_3$ Ruthenium(II) hydrides (κ^4-NP$_3$)Ru(H)$_2$ (**2**) and [(κ^4-NP$_3$)Ru(H)(η^2-H$_2$)]BAr$^{Cl}_4$ [**3**, NP$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$, Figure 1]. **1** leads to AB oligomerization and formation of spent fuel of general formula *cyclo*-[BH$_2$-NH$_2$]$_n$ (n = 2,3) as reaction byproducts; one H$_2$ equivalent is released per AB equivalent.[3] Both **2** and **3** produce borazine as a spent fuel, and a total amount of two H$_2$ equivalents per AB equivalent. All the processes have been followed through multinuclear (^{31}P, ^{1}H, ^{11}B) variable temperature NMR spectroscopy; kinetic measurements on the hydrogen production rate and the relative rate constants have also been carried out, along with kinetic isotope effects measured on the deuterated AB analogues (BH$_3$·ND$_3$, BD$_3$·NH$_3$, BD$_3$·ND$_3$). Finally, the reaction mechanism in all cases has been analyzed through a DFT modeling at the M06//6-31+G(d,p) level of theory, with the aim of providing a rationale for the dehydrogenation process.

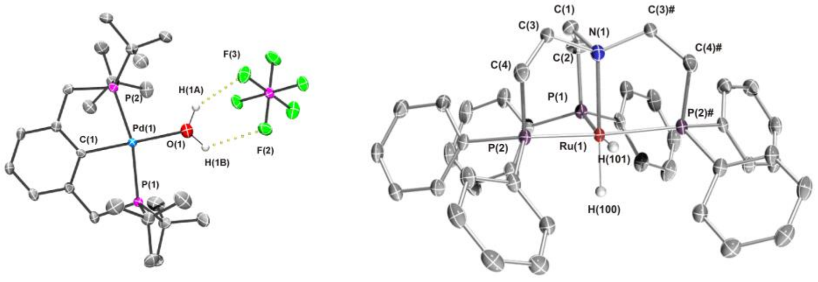

Figure 1. XRD structures of **1** and **2.**

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Poster 83

Organometallic Iridium Catalysts Based on Pyridinecarboxylate Ligands for the Oxidative Splitting of Water

Alberto Bucci,[a]* Arianna Savini,[a] Luca Rocchigiani,[a] Cristiano Zuccaccia,[a] Silvia Rizzato,[b] Alberto Albinati,[b] Antoni Llobet,[c] Alceo Macchioni[a]

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Aimed at producing renewable solar fuels from cheap and abundant reagents (H_2O and CO_2), artificial photosynthesis appears to be a promising solution to the energetic problem of our days. It involves several and complicated processes that have to be properly interfaced between them, but the real bottleneck seems to be the development of an efficient catalytic pool for water oxidation.[1] Ir(III)-Cp* (1,2,3,4,5 – pentamethylcyclopentadienyl)[2] organometallic complexes imposed to the attention of the scientific community as efficient molecular catalysts for water oxidation.[3] Nevertheless, the fastest catalyst reported to date is a ruthenium complex bearing a pyridinecarboxylate ligand.[4] For this reason we decided to synthesize and test **1-4** iridium catalysts containing pyridinecarboxylate ligands (Figure 1, left).[5] Their activity was evaluated by means of different experimental techniques, using Ce^{+4} as a sacrificial oxidant. Although they show similar TOF_{LT} values (long range TOF, between 2.6 - 7.4 min^{-1}), TOF_i values (initial TOF) are very different (Figure 1, right), reaching 287 min^{-1} for **1a** (under optimized conditions). This value is the highest ever reported for an iridium catalyst, and it is about four times higher than the one of Cp*Ir(ppy)Cl (ppy = 2-phenylpyridine), which is considered a benchmark in the literature.[2a]

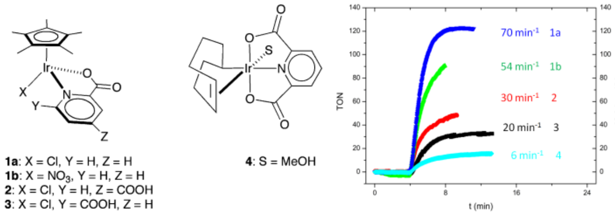

Figure 1

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Poster 84

Bipyridine-type Organometallic Complexes Functionalize Glassy Carbon

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In the past research, silica and alumina (in all their forms) as supports for catalysts have been mostly studied and employed, however, much less attention has been paid to the synthesis and study of catalysts containing transition metals on non-oxide solids. As one of them, carbon is a very interesting low-cost material, and very favourable for electrodes manufacturing. We already bound intact Ru and Ir organometallic molecules to carbon electrode surface by means of electrochemical techniques[1] pioneered by Saveant and co-workers.[2] The present communication aims to extend the technique to Re organometallic complexes of the type (bpy)$Re(CO)_3Cl$. Interest in this class of compounds lies in their activity towards selective CO_2 photo- and electro-reduction, via a reductive quenching mechanism.[3] The reduction of CO_2 emission and the quest for renewable energy are top priorities on the world's strategic research agenda. In the CO_2 Re-photocatalyzed reduction to CO, two 1e electron transfer processes are likely involved, and the use of bimetallic system apparently gave some advantages over the mononuclear Re complex.[4] However, it is not fully clear whether the presence of a second Re unit is needed for only supplying electrons or is involved in the formation of a real Re-CO_2-Re bimetallic intermediate.

The functionalization of intact organometallic complexes over carbon surfaces has thus the advantage to simplify the study of the photocatalytic conversion of CO_2 to CO, since the employment of a potentiostat allows to avoid to use Sacrificial Reagents in the solution. The complex herein presented shows an increased activity towards CO_2 electrochemical reduction with respect the standard (bpy)$Re(CO)_3Cl$ in both homogeneous and heterogeneous (i.e. chemically bonded to Glassy Carbon electrode surface).

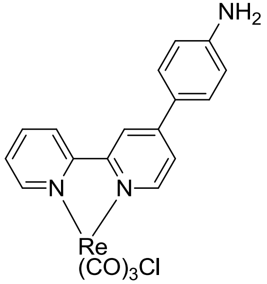

Figure 1

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Poster 85

New Aminomethyl-Substituted Ferrocenes and Derivatives: Efficient Synthetic Routes, and Structural and Electrochemical Characterization

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Functionalized ferrocene derivatives are molecular edifices for which a wide range of useful applications exist, particularly in close relationship with homogeneous catalysis, electrochemistry, material and polymer sciences, and biomedical research.[1] Driven by transition-metal-catalyzed applications, the synthesis of ferrocene derivatives incorporating atoms with donor bonding abilities such as phosphorus atoms has attracted much attention.[2,3] Nitrogen-substituted ferrocenes have been comparatively much less developed, even though a significant amount of works and molecules have been reported since the 1960’s. We report herein the straightforward syntheses of a variety of (aminomethyl)-substituted ferrocenes and parent compounds: (iminomethyl) ferrocenes, *aza*-ferrocenophanes and diferrocenylamines that can be selectively synthesized from reductive amination of 1,1'-diformylferrocene or formylferrocene.[4] The optimized one or two-steps reactions have delivered 13 new compounds, isolated in 65 to 97% yields. X-ray structure of representative members of these ferrocene derivatives families have evidenced the preferred conformation adopted by ferrocene backbones. ^{15}N NMR measurements on (aminomethyl)-substituted compounds established benchmark values ranging from 70 to 95 ppm (nitromethane $\delta = 0$ ppm).[4] The cyclic voltammetry of these species evidences two clearly distinct oxidation potential related to the Fe(II) center and the nitrogen-containing function (Figure1)

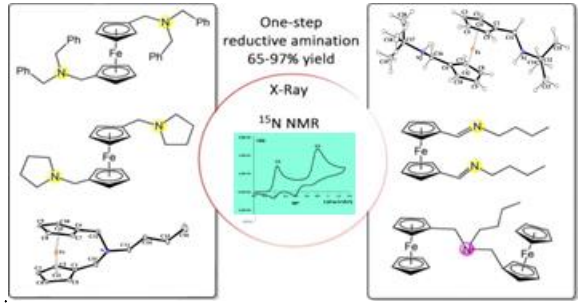

Figure 1. Electrochemical analyses have been achieved in Pr. D. Lucas group and X-Ray analysis done by Dr. H. Cattey (UMR-CNRS 6302, Dijon).

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Poster 86

Synthesis and Electrochemical Study of Re(I) and Mo(0) Complexes with Polypyridyl Ligands for Photo- and Electrocatalytic Reduction of CO_2

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In recent years, the photo- and electrochemical conversion of CO_2 to higher-energy products has been improved by employing transition metal coordination compounds with polypyridyl ligands (e.g. Ru, Os, Re, Mn[1,2]), in the form of molecular or supramolecular organometallic catalysts. In this perspective, our research has mainly focused on the synthesis of a series of novel Re(I)-carbonyl diimine complexes, to be efficiently used as catalysts in both photo- and electrocatalysis for CO_2 reduction. In more detail, this new class of compounds is characterized by the presence of common polypyridyl ligands covalently attached to the highly fluorescent PNI cromophore (N-(diimine)-4-(1- piperidinyl) naphthalene-1,8-dicarboximide), which revealed to be able to provide a huge excited state lifetime enhancement in a Re(I) charge-transfer complex.[3]. This feature may play a key role in the process of catalytic CO_2 reduction (especially in photocatalysis). The spectroscopic characterization (optical and NMR) of the new samples was followed by the study of their electrochemical behaviour either in inert atmosphere and in presence of CO_2, which was finally compared with that of $Re(CO)_3(bipy)Cl$, taken as a reference compound.[4] Photocatalytic measurements are under progress.

On the other hand, looking at a practical use of these systems, the usage of quite abundant first and second row transition metals instead of rare ones is very attractive. For example, to our knowledge there are no reports about the use of tetracarbonyl Mo(0) complexes for the same purpose. This reason lead us to synthesize also a series of $[Mo(CO)_4(L)]$ complexes (L = 2,2’-bipyridyl and derivatives), testing them for electrochemical reduction of carbon dioxide. Our first results are quite promising, showing certain activity and selectivity in reducing CO_2 to CO.

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Poster 87

Ion pairing in cationic NHC and NAC gold(I) η^2--alkyne complexes

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Gold(I) cationic complexes of general formula [LAu$^+$ X$^-$] [L = NAC (Nitrogen-Acyclic-Carbene) or NHCs (N-Heterocyclic Carbenes), X$^-$ = weakly coordinating anion] are successfully employed as catalysts in a large variety of organic reactions involving the activation of unsaturated carbon-carbon bonds.[1] A key role in such reactions is played by the counterion. We have studied the ion pair structure in solution of [NHC-Au(η^2-3-hexyne)]BF$_4$ and [NAC-Au(η^2-3-hexyne)]BF$_4$ by NOE NMR spectroscopy and relativistic DFT calculation. In our previous work,[2] two main orientations were observed for unsaturated NHC ligands: one with the anion close to the carbene backbone (A, most populated) and another with the anion close to the 3-hexyne (B). Here we focus on the effect of different carbenes on the ion pair structure, comparing the aromatic NHC (**1BF$_4$**) with 5 different ligands: a non aromatic NHC (**2BF$_4$**), a polycyclic ligand with an extended aromatic system (**3BF$_4$**) and three different NAC (**4BF$_4$**, **5BF$_4$** and **6BF$_4$**). For **2BF$_4$**, the A:B ratio (observed with NOE NMR spectroscopy) remains almost the same as for **1BF$_4$**, whilst the ion pair structure of the **3BF$_4$** becomes mainly non---specific, with a slight preference for the orientation B. Both cases can be explained analyzing the DFT Coulomb potential map, that shows an attractive region on the backbone of **2BF$_4$** and a flat weak potential around the whole **3BF$_4$**. An interesting result was obtained for **4BF$_4$** that shows a strong attractive region close to the two N-H that makes the IP 100% specific for the orientation A (figure beside). **5BF$_4$** shows a less specific ion pair due to the presence of only one N-H on the back. For the **6BF$_4$** the -OH group on the arm of the carbene introduce a third ion pair configuration, strongly stabilized by the hydrogen bond between the hydroxyl and the anion.

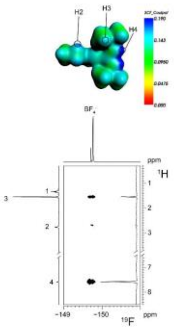

Figure 1. ^{19}F H HOESY

Figure 2. [NHC-Au(η^2-3-hexyne)]BF$_4$ and [NAC-Au(η^2-3-hexyne)]BF$_4$ complexes

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Poster 88

Controlled Self-Assembly of Peptidic Au(I)-Metalloamphiphiles through Cooperative Interactions

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The aim of the work presented herein is to couple Au(I) species to small peptide building blocks in order to prepare new metalloamphiphilic complexes as supramolecular monomers (Figure 1). The peptide sequences are designed in a fashion that prevents the spontaneous formation of aggregates. The non-covalent polymerisation process only becomes thermodynamically favourable through the additional formation of aurophilic interactions.[1] The cooperative effects dictating the self-assembly of these supramolecular polymers in water[2] and their photoluminescent properties will be investigated.[3,4]

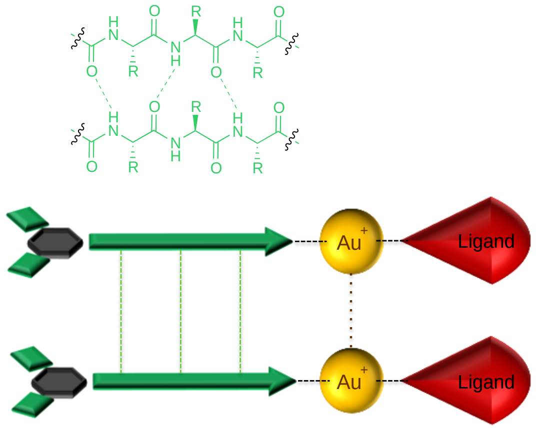

Figure 1: Cooperative interactions during self-assembly.

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Poster 89

Artificial Leaf – Towards Photoactive Electrodes for Hydrogen Production from Water

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As a possible sustainable alternative to the current fossil fuel economy, the production of hydrogen from water by means of solar energy is currently investigated by a large number of scientists. The first functional integrated device that could split water using light (colloquially called an artificial leaf) was shown by Khaselev and Turner.[1] To improve device efficiency and durability, the use of homogeneous catalysts immobilized on a suitable substrate is studied. As opposed to active heterogeneous layers, homogeneous building blocks offer the advantage of having easily tunable properties and a well-defined catalytic character. Using the two inherent constraints of photocatalytic water splitting (the sun’s photon flux and water splitting redox potentials) these catalysts can be straightforwardly optimized.

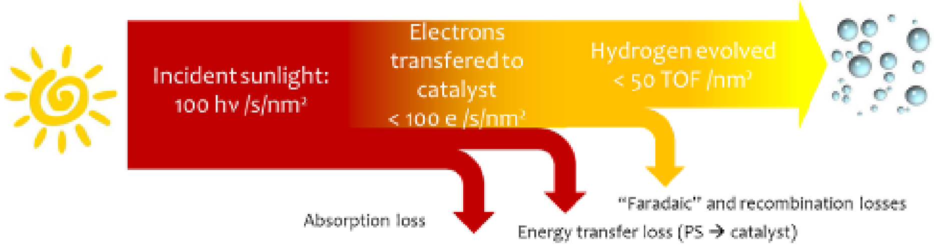

Figure 1. Sankey diagram for matching of photon flux and turnover frequencies.

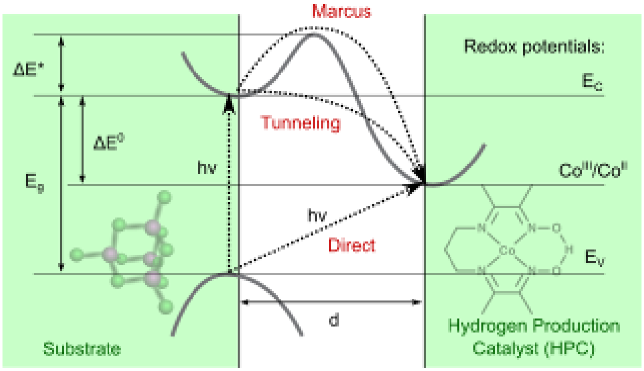

Figure 2. Limiting cases of electron transfer between catalyst and a suitable substrate.

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Poster 90

Bifunctionalized Re(I) Complexes as Luminescent Probes for Bioconjugation

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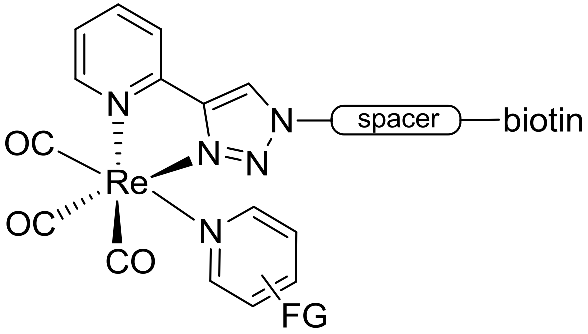
Octahedral Re(I) complexes of the general formula *fac*-$[Re(N^\wedge N)(CO)_3L]^+$, where N^N represents a diimine-type ligand, constitute of promising class of luminescent probes for biological systems.[1] Here, we report the synthesis and characterization of a new class of bifunctionalized Re(I) complexes containing an unconventional diimine ligand (N^N) decorated both with a pendant biotin and a polar subtituent, in order to achieve the formation of luminescent probes for avidin with improved water solubility. (Scheme 1).



Scheme 1

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Poster 91

A ^{33}S NMR-Based Assay to Monitor Transmembrane Sulfate Transport Across Synthetic Phospholipid Bilayers

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The transport of sulfate anions across cell membranes is central to many biological processes,[1] and is facilitated by specialised membrane proteins. However, the malfunction of these proteins can lead to the misregulation of sulfate concentrations, a contributing factor to illnesses such as Alzheimer's disease.[2] Accordingly, there is an ever-present interest in the design and synthesis of synthetic small molecules, which can act as transmembrane sulfate transporters. Transmembrane sulfate transport is particularly challenging due to the high hydrophilicity of the anion.[3] Here we report a novel NMR technique, which is used to directly monitor the transport of sulfate anions across synthetic phospholipid bilayers. This technique gives a definitive yes/no result, allowing the sulfate transport ability of a particular receptor to be investigated. Using the developed ^{33}S NMR method, it was possible to verify that some tren-based (thio)ureas[4] and cyclic peptide-based cryptands[5,6] are able to accomplish the challenging task of sulfate transport.

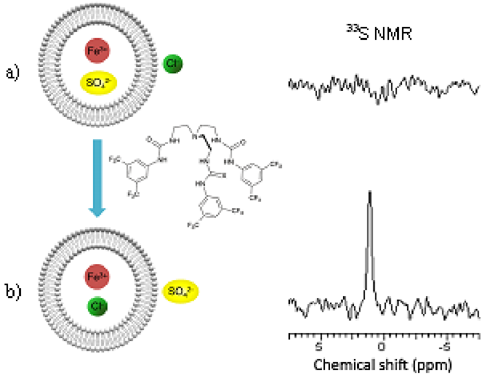

Figure 1

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Poster 92

Phosphine Oxide-Based Supramolecular Complexes from Phosphine Donor

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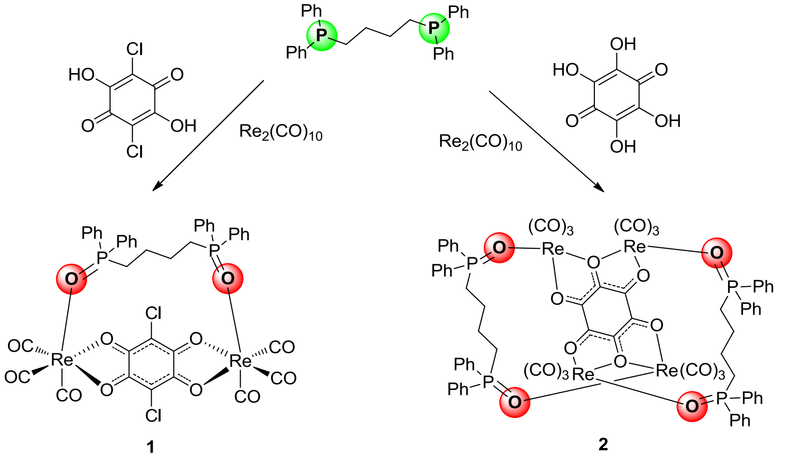
Over the past three decades, significant research interest has been shown in discrete supramolecular coordination complexes (SCCs), because of their properties and potential applications in many fields.[1] The synthesis of SCCs by coordination-driven self-assembly, using predesigned transition metal based acceptors and organic donor precursors, is well established. Recent developments in this field are focused on making complex SCCs, SCCs with functional units, and finding a one-pot strategy for multicomponent assembly. In donor ligands, neutral nitrogen (N) units are widely used as either the whole or part of the organic structure in SCCs. Attempts are being made to use other neutral Lewis base donor in place of the N-donor ligands. As a continuation of the research on Re(I)-based SCCs previously reported,[2-6] the first examples of neutral O-donor, from phosphine oxide, bridged SCCs have been synthesised and are reported herein (Scheme 1).



Scheme 1

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Poster 93

Copper Metallohydrogels: Self-Assembly and Applications in Catalysis

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In recent years, the self-assembly of compounds have gained more and more interest[1] due to their attractiveness in the fields of smart materials, drug delivery, and catalysis.[2] Non-covalent interactions are the driving forces of the molecular self-assembly of compounds such as small peptides. These supramolecular interactions are reversible and may be induced by external or internal stimuli.[3] The design of molecular building units becomes crucial for the structure, properties and function of the resulting assemblies.[4] We have designed a new supramolecular metallohydrogelator (figure 1) presenting alternating phenylalanine/aspartic acid residues. The addition of cooper (II) chloride to a basic solution of **1** leads to the formation of stable light blue and translucent metallohydrogel likely by the interaction of metal-ligand between copper(II) and aspartic acid moieties.[5] Besides elucidate their structure gelation properties and their aggregation mechanisms, we want to study if the formed Cu^{2+} containing nanostructures can function as an asymmetric catalyst for Diels Alder cycloaddition between cyclopentadiene and aza-chalcone[6] (figure 1).

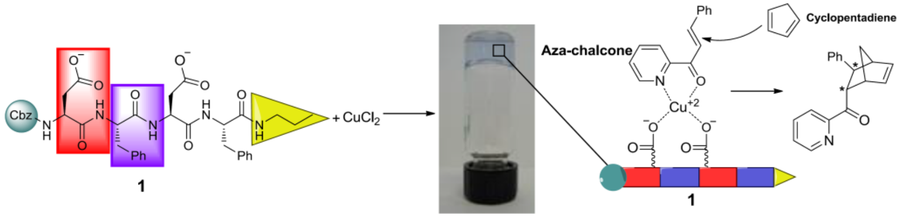

Figure 1

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Poster 94

Bifunctional N-Heterocyclic Carbene (NHC) Complexes and their Catalytic Evaluation

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Early organometallic catalysts contained a metal which was thought to be the active centre where as ligands provided sterically-defined binding sites through association or dissociation for the substrate to bind and undergo transformation. However, with the recent advancements in catalysis, it has been widely recognized that subtle and judicious designing of ligands enable them to participate actively in bond breaking and making processes during the catalytic cycle, thus increasing the tolerance, efficiency and selectivity of the catalyst.[1] N-Heterocyclic Carbenes (NHC's) have gradually emerged as superior counterparts to phosphines over the years due to their robust nature and tunable steric and electronic properties.[2] This work focuses on the incorporation of bifunctional NHC's on transition metals and their effect in homogeneous catalysis.[3]

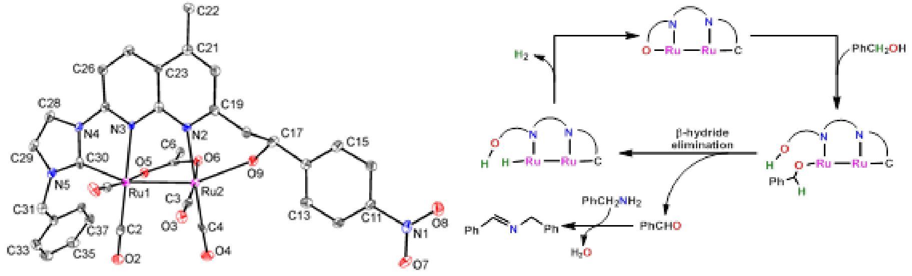

Figure 1

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Poster 95

Synthesis, Characterisation, and catalytic Activity of Novel Pd(II) Complexes Containing 4-Substituted Bis(Pyrazolyl)Methane Ligands

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Among the wide range of bidentate chelating ligands currently used in metal coordination chemistry, bis(pyrazolyl)alkanes are one of the most fascinating family of stable and flexible ligands: they are isoelectronic and isosteric with the well-known bis(pyrazolyl)borates, and were first synthesized by Trofimenko in the seventeen of the last century.[1] The coordinating properties of bis(pyrazol-1-yl)alkanes can be varied over wide range by introduction of various substituents into the pyrazole rings which are able to modify steric and electronic properties.[2] Their metal coordination chemistry with main group and transition metals has been mainly developed in the last twenty years[2] affording a number of transition metal systems with novel interesting properties in the fields of catalysis.[3,4]

Here we report novel bis(pirazolyl)methane ligands bearing 4-substituents (Figure 1) and their coordination chemistry toward $PdCl_2$ and $Pd(OAc)_2$ acceptors. Additionally, some selected derivatives have also been tested for their potential catalytic activity in Suzuki-Miyaura cross-coupling reactions.

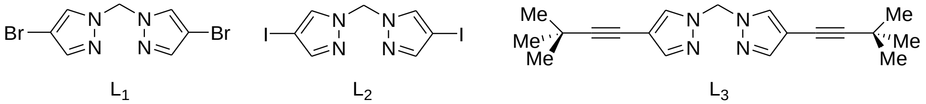

Figure 2

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Poster 96

MW Buchwald Amination as a Key Step in the Synthesis of a new Series of Psensitizers for DSC

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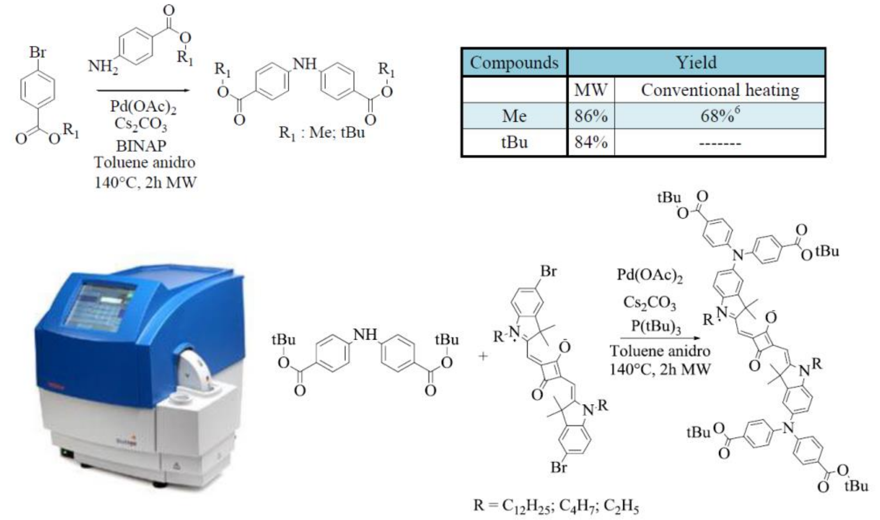
Development of new sensitizers for DSCs[1,2] is a constant challenge to achieve better harnessing of solar energy in innovative photovoltaic devices. In metal-free sensitizers, the triarylamine moiety has a key role as electron donor group. The study of relative synthesis could help the research to obtain triarylamine[3] compounds in a easier, faster, more selective and reproducible way. We studied a synthetic path to obtain these compounds by a Buchwald[4] amination using microwave[5] in order to decrease reaction time and to increase yield compared to a synthetic approach based on conventional heating.[6]



Compounds	Yield	
	MW	Conventional heating
Me	86%	68%[6]
tBu	84%	-------

Scheme 1

References

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Poster 97

Nuclear Spin-Spin Couplings: Recognition and Understanding of «Through-Space » NMR *J* Constants in Organic and Organometallic Compounds

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In NMR the indirect nuclear spin-spin coupling involving very commonly encountered nuclei, such as ^{1}H, ^{13}C, ^{19}F or ^{31}P, provides conclusive data for compound characterization in solution, using the determination and interpretation of nuclear spin-spin coupling. This *electron-mediated* nuclear spin coupling, characterized by the *J* constant, is classically taught as transmitted by *unambiguously* covalently bonded atoms. Yet, since the 1960's, experimental and theoretical NMR studies have highlighted the existence of scalar *J* spin couplings operating through clearly *nonbonded interactions*. These couplings are often called "through-space" internuclear spin-spin couplings (TS couplings). As presented herein,[1] nonbonded spin couplings ("through-space") characterized by high magnitude values of J_{FF}, J_{FX} (X = N, P, Se, C and H), J_{PP} and J_{PX} (X = Se and C) have been authenticated for compounds such as fluorocyclophanes, fluoronaphthalenes, and coordination complexes of ferrocenyl polyphosphines (Figure 1). Semi-empirical quantitative relationships have been discovered which show an apparent exponential dependence of the spin coupling intensity with the internuclear distance.[2] In non-covalently bonded interactions, indirect scalar couplings can be frequently observed across the hydrogen bonding of biomolecules and smaller chemical compounds. Our works aim at clarifying such "through-space" couplings.

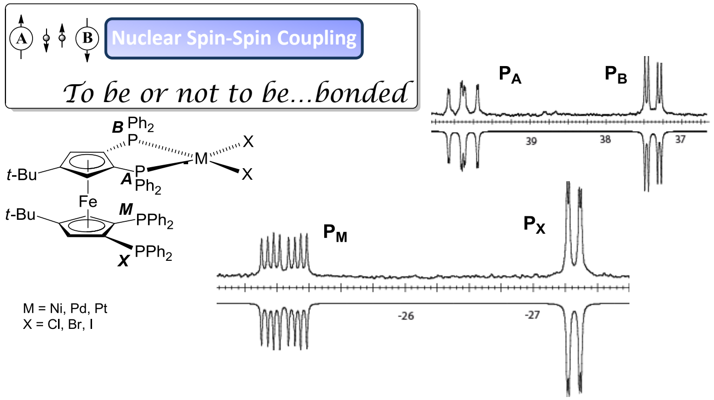

Figure 1

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Poster 98

Synthesis of Phosphine-containing Polymers and their application to Hydroformylation

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Olefin hydroformylation continues to attract interest in view of its industrial importance (oxo process), especially for the conversion of α-olefins to aldehydes with the linear product being preferred. One of the greatest challenges remains the efficient extension of the rhodium-catalyzed low-pressure process to the higher olefins (> C_4) with total catalyst recovery and low separation costs. The typical precatalyst is $Rh(acac)(CO)_2/PPh_3$ (or other more elaborate mono- or multidentate phosphine donors), then transformed in situ to the active catalyst by syngas. Phosphine ligand grafting on polymers has been one of the most investigated approaches to address this challenge.

The effect of the polymer microstructure on the catalytic performance has so far received little attention. On the other hand, the recent phenomenal progress in controlled polymerization makes it possible to build macromolecules with controlled size, architecture, composition and functionality. This therefore gives the opportunity to revisit polymer-supported hydroformylation catalysts. The synthesis and characterization of both linear (A)[1] and star-shaped (B)[2] in-chain functionalized polystyrenes with controlled molecular weight and phosphine density by atom transfer radical copolymerization of styrene and styryldiphenylphosphine (SDPP) will be described. The performance of these macroligands in the hydroformylation of a model α-olefin (1-octene) and the dependence of activity and l/b selectivity on the polymer architecture, phosphine density, chain length and other parameters has been evaluated.

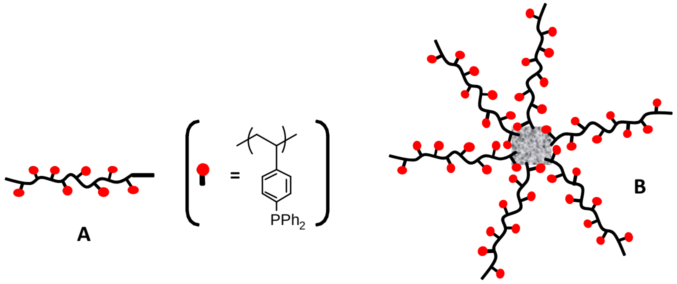

Figure 1

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Poster 99

Studies of Rhodium Complexation into Phosphine-Containing Latexes

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Phosphines are common electron donating ligands that can coordinate many important catalytic metals (e.g. Ru, Pd, Rh...) [1] Wilkinson's work revealed the potential of rhodium phosphine catalysts for the hydroformylation reaction of alkenes[2] and this has become the most important industrial homogeneous catalysis process today.[3] An outstanding challenge is that of extending the existing technology which is well adapted to small olefins (propene, butane) to the higher olefins and for this purpose several strategies are being investigated, including the use of polymer-supported phosphines. In this work latexes containing hydrosoluble polymers (Figure 1) that consist of a nanogel core (blue) and flexible amphiphilic arms with a phosphine-containing hydrophophic bloc (green) and a hydrophilic shell (red) have been used as substrates for coordination studies. We will present complexation studies of the $[Rh(CO)_2(acac)]$ precatalyst into the particles using different P/Rh ratios and different solvents (i.e. $CHCl_3$ and toluene) that help swelling the latex core. The investigations confirm that $[Rh(CO)_2(acac)]$ is transported across the hydrophilic polymer corona to reach the phosphine sites, trapped at the centre of the particles and provides information about the dynamics of the phosphine exchange within the macromolecule.

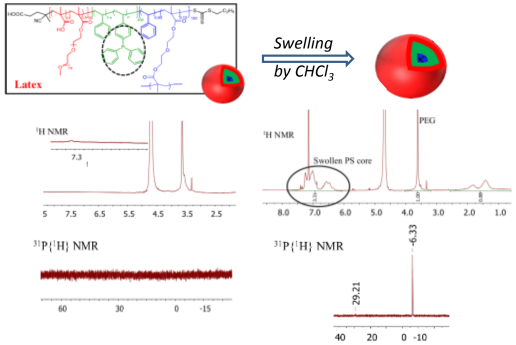

Figure 1

Acknowledgments: We thank the C2P2 team in Lyon, France: Dr. X. Zang, Dr M. Lansalot, Dr F. D'Agosto, Pr. B. Charleux and the ANR BIPHASNANOCAT grant for funding.

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Poster 100

Antiproliferative Activity of a New (Arene)Ruthenium(II) Complex on a Model of Breast Cancer

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Following our previous studies,[1] novel (arene)ruthenium(II) complexes containing neutral chelating nitrogen ligands, with general formula [Ru(arene)(L')Cl]Cl, have been prepared by reacting the ligands L' (L' in general; in detail, L^1 = bis(pyrazol-1-yl)methane; L^2 = bis(3,5-dimethylpyrazol-1-yl) methane) with some dinuclear organometallic acceptors of ruthenium, such as (*para*-cymene)ruthenium(II) dichloride, (benzene)ruthenium(II) dichloride and (hexamethylbenzene)ruthenium(II) dichloride. The solid-state structures of these half-sandwich organometallic complexes were determined by X-ray crystallographic studies.[1] Their antiproliferative properties were assessed *in vitro* and in *vivo* screening assays and it was found that the Ru(II) complexes exhibit potent antiproliferative activity against different human malignant cancer cells, even in comparison with *cisplatin* and NAMI-A (Figure 1). Moreover, our data clearly that some Ru(II) complexes are characterized by a strong ability to block cells migration associated with a low toxicity.

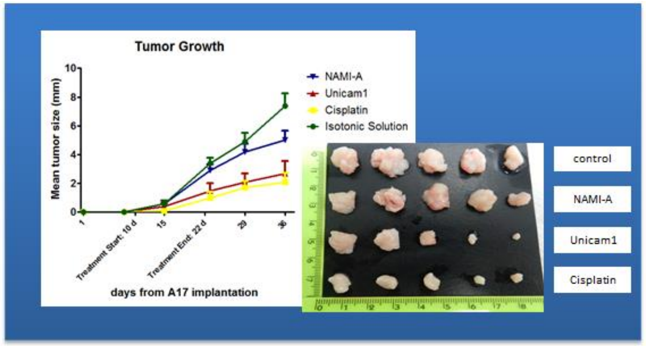

Figure 1

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UNIVERSITY OF CAMERINO

TRADITION

The great literate and jurist Cino from Pistoia, living in Marche in the years 1319-21, and in Camerino in the spring of 1321, remembers the territory blooming with juridical schools. Camerino has been a center of learning since no later than 1200 offering degrees in civil law, canonical law, medicine and literary studies. Gregorio XI took the decision upon the request of Gentile III da Varano with the papal edict of 29 January 1377 directed to the commune and to the people authorizing Camerino to confer (after appropriate examination) bachelor and doctoral degrees with apostolic authority.

AD PERPETUAM

Cum igitur Nobis No

On the 15th of July of the same year, Benedict XIII founds the Universitas Studii Generalis with the faculties of theology, jurisprudence, medicine and mathematics; On April 13 th 1753 the emperor Francesco Stefano I of the of Habsburg Lorena extends the validity of the degrees from Camerino to the whole territory of the Holy Roman Empire and confers to the rector the title of palatine count. In 1861, after annexation by the Kingdom of Italy, the university is proclaimed 'free' and it remains such up to 1958, when it becomes a State University.

INNOVATION AND QUALITY

Attention to the student is the guideline that determines the choices the University of Camerino makes. This permits the continuation of avantguard ideas and proposals being unleashed from the antique heart of this university. For the first time in Italy UNICAM has introduced procedures of quality control in all its institutional activities, identifying objectives and responsibilities in 3 particular areas:

1) Didactics which must work with research, supported by good teaching methods, assured by competent professors (1for 29 students) and facilitated by good building structures (56 laboratories and 15 libraries).

2) services that offer academic assistance as well as academic counseling. These include orientation and tutoring, that is assistance through the entire academic career of the student.

3) services that help the student find work training programs and job placement upon graduation. All this represents a 'system quality management' which was certified in July 2003 according to the international norms UNI EN ISO 9001:2000 by the French certifying company GROUPE AFAQ.

More than 8.000 students attend the University of Camerino today distributed among 7 Schools (Architecture, Pharmacy, Jurisprudence, Bioscience and Biotechnology, Veterinary Medicine, Science and Technology, Environmental Sciences), and 4 campuses (Camerino, Ascoli Piceno, Matelica, San Benedetto del Tronto). The university has 620 employees between professors and administrative technical personnel. UNICAM has an important tradition in didactics and scientific research: there are numerous and innovative degrees being offered in the different faculties including Masters and many professors have received prestigious national and international recognitions.

THE TRUE NATURE OF LEARNING

Besides quality, UNICAM offers the student the necessary tranquility to pursue his studies. The town of Camerino itself which has more students than local residents is like a great university campus immersed in nature.

From the building point of view, UNICAM boasts of structures and equipment in continuous development, such as to render the quality of life and learning unique: modern sports facilities on 20,000 square meters (5,000 of which are covered), dormitories for over 600 students, a new campus which will be able to house and additional 200 students, assistance to the disabled, didactic and scientific libraries with 390,000 books and over 500 study stations, 20,000 square meters of research laboratories and 10,000 square meters of classroom area.

The courses of orientation, integration, and tutoring aim to permit the student to complete his academic curriculum in the pre-established time frame. The job placement office helps the student upon graduation. The numerical relationship between professors and students (1 professor for 29 students) is another fundamental element that guarantees the quality of learning at UNICAM.