11th International School of Organometallic Chemistry

SUMMER SCHOOL
San Benedetto del Tronto, Italy
02-06 September 2017
http://d7.unicam.it/isoc/

University of Camerino
School of Pharmacy
School of Science and Technology

Interdivisional Group of Organometallic Chemistry

Organometallic chemistry: from theory to applications
INTRODUCTION

“ORGANOMETALLIC CHEMISTRY: FROM THEORY TO APPLICATIONS”

The ISOC series is the most important school on organometallic chemistry at the European level, organized by Camerino University under the auspices of EuCheMS (the European Association for Chemical and Molecular Sciences) and the Interdivisional Group of Organometallic chemistry of the Italian Chemical Society. The aim is to encourage the presence of young researchers and Ph.D students both from University and Industry, including those not directly involved in organometallic research projects, in order to bring together young researchers and distinguished European scientists as a contribution to the important goal of increasing the transfer of knowledge at a high level between different European countries and different generation of scientists.

The 11th edition of ISOC will deal with fundamental principles to their use in novel applications, with a specific focus on the role of organometallic chemistry in finding solutions to many of the major societal challenges in the 21st century: from the development of sustainable energy solutions to the mitigation of climate change, from the synthesis of effective therapeutics to the production of new materials ranging from novel polymers to nanomaterials, from the generation of industrial feedstocks to the remediation of the environment. The scientific community is increasingly being stimulated to tackle problems of practical interest and the society will undoubtedly rely on advances made in the field of organometallic chemistry.
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**Notes:**
- Coffee break and lunch times are provided for breaks in the schedule.
- Flash presentation and poster session times are included for additional presentations and discussions.
- The timetable includes a mix of lectures, presentations, and social events.
- The schedule is designed to accommodate a variety of topics within the field of chemistry and catalysis.
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Prof. Gianna Reginato
Prof. Renata Riva
Prof. Adriana Saccone
SPEAKERS

Prof. David J. Cole-Hamilton
University of St Andrews (United Kingdom)
Greener chemistry through homogeneous organometallic catalysis

Prof. Hansjörg Grützmacher
ETH Zurich (Switzerland)
Metal Ligand Cooperation in catalyzed dehydrogenations

Prof. Peter Fristrup
Technical University of Denmark (Denmark)
Development of the Molybdenum-Catalysed Deoxydehydration of Diols - an example of synergistic use of both experimental and theoretical tools

Prof. Andreas Pfaltz
Basel University (Switzerland)
Asymmetric Hydrogenation with Chiral Iridium Catalysts

Prof. Syuzanna R. Harutyunyan
Groningen University (Netherlands)
Copper Catalysis for Synthesis of Functional Molecule

Prof. Ruben Martin
ICIQ, Institute of Chemical Research of Catalonia (Spain)
Ni-Catalyzed Reductive Carboxylation Techniques
SPEAKERS

Prof. Clark R. Landis
University of Wisconsin-Madison (USA)
High Pressure Operando Kinetic Studies of Homogeneous Catalysts

Prof. Mariola Tortosa
Universidad Autónoma de Madrid UAM (Spain)
Nucleophilic Boron: New Opportunities for Carbon-Carbon Bond Formation

Prof. Wolfgang Kaim
Stuttgart University (Germany)
Organometallic Chemistry Involving Radical-Forming Noninnocent Ligands

Prof. Luigi Cavallo
King Abdullah University of Science and Technology (Saudi Arabia)
Understanding and Controlling Gold Catalysis the Hard Way

Prof. Elisabetta Rossi
University of Milan (Italy)
Catalytic Carbophilic Activation in Synthetic Organic Chemistry: Catalysis by Gold π Acids

Prof. F. Giovanni Poli
University of Paris VI (France)
C-H Activation: Fundamentals and Recent Developments
SPEAKERS

Prof. Julio Loret-Fillol  Institute of Chemical Research of Catalonia, ICIQ (Spain)
Artificial Photosynthesis from Solar Fuels To Solar Chemicals

Prof. Alberto Credi  University of Bologna (Italy)
Molecular Devices: Machines and Motors
Abstracts of Lectures
Homogeneous catalysis is distinguished from heterogeneous catalysis because the catalyst is typically a metal complex dissolved in a solvent rather than an insoluble metal or metal oxide. The metal complex usually contains ligands whose nature can be used to tune the properties of the catalyst to give exquisite chemo, regio and enantioselectivity. A further advantage is that techniques such as in situ NMR and infra-red spectroscopies can be used to gain detailed insight into intermediates in the catalytic cycle and to unravel mechanisms themselves.1,2

In this presentation, we shall discuss the advantages and disadvantages of the different types of catalysis and then show how simple organometallic steps can be used in sequence to build up catalytic cycles using the 16/18 electron rule. A selection of reactions such as hydrogenation, hydroformylation, carbonylation, C-C bond forming reactions and alkene metathesis will be discussed with particular emphasis on the importance of the ligands and mechanism to determining the outcome of the reactions. Commercialised processes will especially be in focus.

The major problem of homogeneous catalysis is the separation of the products from the catalyst and any solvent. New ways of doing this will be described using supercritical fluids, ionic liquids and flow chemistry.

Mention will be made of the use of homogeneous catalysts for the upgrading of bio-derived resources.

References
The transformation of biomass-derived compounds into platform chemicals is one of the possible contributions from chemistry to the realisation of an economy completely independent of fossil reserves. In order for oxygen-rich biomass-derived compounds such as glycerol and sugar alcohols to substitute petroleum, reactions capable of reducing their oxygen content are in demand, and in particular the deoxydehydration (DODH) of vicinal diols into alkenes in the presence of a reductant (“red”) and a catalyst (e.g. a rhenium complex) has received attention (figure 1).

Figure 1: Rhenium catalyzed deoxydehydration of a vicinal diol into an alkene.

The transformation represents a model system for the various hydroxyl groups present in biomass (e.g., in carbohydrates), but is also relevant in itself as a potentially useful transformation of glycerol. Considering the huge amounts of glycerol and sugar alcohols that would have to be processed for the utilization of biomass to make a substantial impact, the development of alternative catalysts, based on elements with higher terrestrial abundance than rhenium, is clearly desirable. In this talk our results from both experimental and theoretical investigations into new DODH catalysts be presented.

Asymmetric hydrogenation with chiral Iridium catalysts

Andreas Pfaltz*

Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056 Basel, Switzerland.

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Iridium complexes with chiral P,N ligands have considerably enhanced the scope of asymmetric hydrogenation. The catalysts are readily prepared, air-stable and easy to handle. In contrast to rhodium and ruthenium diphosphine complexes, they do not require a coordinating group near the C=C bond and, therefore, allow highly enantioselective hydrogenations of a wide range of unfunctionalized tri- and even tetrasubstituted alkenes. In addition, they have also been successfully used for the hydrogenation of various functionalized olefins, heterocycles such as furans and indoles, and imines. In this lecture practical and mechanistic aspects, the scope, and new applications of this catalyst class will be discussed.

References
Lecture of 3 September h 14.30-16.00

Copper catalysis for synthesis of functional molecules

Syuzanna R. Harutyunyan*

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Our research program is aimed at the development of novel catalysis concepts for the asymmetric synthesis of chiral functional molecules. In 2011 we introduced an entirely new role for Cu(I)-based catalysts, facilitating highly enantioselective carbon-carbon bond forming reactions between organometallics and enolisable carbonyl as well as imine compounds. Following this initial discovery, we established Cu(I)-catalysis, in combination with Lewis acids/Grignard reagent, as a powerful tool to tackle the reactivity of inherently unreactive substrates for carbon-carbon bond forming reactions. In this lecture I will focus on how we can use these concepts to access highly demanded and valuable chiral heteroarenes and amides, as well as tertiary alcohols and amines, in catalytic and enantioselective fashion and mechanistic studies.

References

Lecture of 4 September h 9.00-10.30

Ni-catalyzed reductive carboxylation techniques

Ruben Martin*

Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans, 16, 43007 Tarragona, Spain.
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An increased utilization of feedstock materials in catalytic endeavours holds great promise to revolutionize approaches in organic synthesis for preparing added-value building blocks. In this regard, catalytic protocols for incorporating carbon dioxide (CO₂) into organic matter has recently attracted considerable attention in carbon-carbon bond-forming reactions. Among the different alternatives, the ability to design catalytic CO₂ fixation en route to carboxylic acids would be particularly appreciated, as these motifs are important structural elements in a myriad of pharmaceuticals and agrochemicals, among others. In recent years, our research group has reported some progress directed towards the catalytic reductive carboxylation of organic matter with CO₂ (Scheme 1). These methods are characterized by their simplicity, wide substrate scope, including challenging substrate combinations with particularly sensitive functional groups and a diverse set of substitution patterns.

Figure 1

References
Lecture 4 of September h 11.00-12.30

High pressure, operando kinetic studies of homogeneous catalysts

Anna C. Brezny, Katie E. Ziebarth, Spring M. Knapp, and Clark R. Landis*

Department of Chemistry, 1101 University Avenue, University of Wisconsin-Madison, Madison, WI 53706 USA.
landis@chem.wisc.edu

More than 20 million metric tons of product are made each year by transformation of gases (CO, H₂, ethene, propene) in the presence of homogeneous organotransition metal catalysts. Because most of these catalysts are diamagnetic, NMR is an ideal, information rich method for exploring these reactions. This presentation will briefly review different operando methods for studying homogeneous catalysts. The application of operando stopped-flow and high pressure NMR to detailed kinetic analysis of enantioselective hydroformylation, hydroacylation, ethene metathesis, alkene polymerization, and allylic oxidation will be presented.

References

Figure 1

Lecture 4 of September h 14.30-16.00

Nucleophilic Boron: new opportunities for carbon-boron bond formation

Mariola Tortosa*

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Boronic esters are versatile synthetic intermediates for the preparation of a wide range of organic molecules. The development of new methods to create C-B bonds in an efficient, inexpensive, and environmentally friendly way is therefore an important challenge in organic chemistry. Traditionally, the methods to form C-B bonds have mostly been based on the electrophilic nature of boron. While this classical approach works well for reactions with nucleophilic partners, it naturally limits the types of boron compounds that can be prepared. Recently, copper-catalyzed borylations have emerged as a new source of nucleophilic boron. The lower price and toxicity of copper versus other transition metals and the unique reactivity of the boryl-copper intermediates make these processes particularly attractive. Inspired by unsolved problems found in the total synthesis of complex molecules, we have used boryl-copper species to synthesize useful synthetic intermediates such as 1,4-diols, tri- and tetrasubstituted alkenes, dibenzyl derivatives and functionalized small rings. Some of these results will be presented in this talk.

Acknowledgments We thank the European Research Council (ERC-337776) and MINECO (CTQ2012-3957) for financial support.

References
Lecture of 4 September h 16.00-17.30

Organometallic chemistry involving radical-forming noninnocent ligands

Wolfgang Kaim*

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany.
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The potential of organometallics for single electron transfer and for radical reactivity\(^1,2\) is documented for compounds containing redox-active ligands. The diversity of organometallic redox systems with noninnocent ligands\(^3,4\) will be presented in a brief survey, covering reaction mechanisms, the DFT supported experimental identification of stable intermediates, and an outline of some synthetic applications. The value of voltammetric\(^5\) and spectroelectrochemical techniques (esp. IR, UV-Vis-NIR, EPR) will be pointed out.

References

Lecture of 5 September h 8.30-10.00

Understanding and controlling Gold catalysis the hard way

Luigi Cavallo*

KAUST Catalysis Center, King Abdullah University of Science and Technology.
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Methane Acquiring expertise in a new field is like adventuring in an uncanny world. In this lecture we will present our computational work in the field of Gold catalyzed organic transformations. The starting difficult years, within a synergic interaction with an experimental group, will be presented from the backstage.\(^1\) This will give an opportunity to understand the dialectic of a fruitful experimental/theoretical collaboration, and how computational chemistry can contribute during the development of new catalysis.\(^2,3,4\) In the second part of the presentation it will be shown how the expertise acquired during the initial years is then used to rationalize and characterize Gold catalysts, from the single atom complex to nanoparticles.\(^5\)

References
Catalytic carbophilic activation in synthetic organic chemistry:
catalysis by Gold π acids

Elisabetta Rossi*

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Gold(I) and gold(III) salts and complexes are among the most active catalysts for the electrophilic activation of alkenes, alkynes and allenes under homogeneous conditions. In gold-catalyzed reactions, activated systems normally undergo addition of a nucleophile. Nucleophiles can be simple hetero- or carbo-nucleophiles for the synthesis of addition compounds across the unsaturated bond. Moreover, more sophisticated reaction pathways comprise, after the addition of a generic hetero- or carbo-nucleophile, evolution toward the formation of more challenging compounds via enyne cycloisomerization, C-H functionalization, cycloaddition, rearrangement, cascade and multicomponent reactions (Figure 1).

The first part of this lecture will focus on a brief introduction on the general pathways of gold catalyzed reactions with some hints on differences, analogies and complementarities with other historically used transition metal catalysts. The second part will discuss the applications of gold catalysis in synthetic organic chemistry.
Lecture of 6 September h 9.00-10.30

Artificial photosynthesis from solar fuels to solar chemicals

Julio Lloret-Fillol*

*Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Avinguda Paisos Catalans 16, 43007 Tarragona, Spain.

One of the most appealing research areas is the mechanistic understanding of multi-electron multi-proton processes, being central in small molecule activation such as the water oxidation to O₂ (WO) or reduction to H₂ (WR),¹ solar fuels production but also can guide to new chemical transformations. I will present here the basis to understand those processes as well as few selected examples of homogeneous and well-defined catalysts based on 18e-row transition metals, which allows for mechanistic studies. In this regard, we have discovered that well-defined iron coordination complexes based on aminopyridine ligands are highly efficient homogeneous water oxidation catalysts which help us to understand the mechanism.²,³ On the other hand, we developed cobalt complexes based on the same family of ligands that are active catalysts on a variety of reductive chemistry. I will present our last results on the electro- and photo-reduction of water to H₂, CO₂ and how we can also to carry out the photo-reduction of ketones, aldehydes and olefins.⁴-⁹ Finally, I will introduce the extension of this reactivity to the activation of inert C≡C bonds to perform cyclization reactions.

References

Lecture of 6 September h 10.45-12.15

Photoactive nanoscale devices and machines

Massimo Baroncini,a,b,c Serena Silvi, b,d Alberto Credi,a,b,c,g

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c CLAN-Center for Light Activated Nanostructures, via Gobetti 101, 40129 Bologna, Italy.

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The bottom-up design, preparation and characterization of chemical systems that span from molecular scale devices and machines to nanostructured materials is a stimulating challenge of nanoscience.¹ The interest on this kind of systems arises from their ability to perform a (useful) function in response to chemical and/or physical signals. In this context, the use of light stimulation has several advantages, primarily because photons can be used to supply energy to the system (i.e., write) as well as to gain information about its state (i.e., read).²,³,⁴ Here we will present the strategies at the basis of the design, construction and investigation of nanoscale devices and machines that comprise organic and inorganic building blocks, and discuss related challenges and opportunities. Selected examples taken from our research work, such as autonomous molecular shuttles powered by sunlight (see Figure 1),⁵ molecular transporters⁶ and quantum dots with engineered luminescence properties⁷ will be illustrated.

References
Abstracts of Posters
Aerobic intramolecular oxidation of carbon-hydrogen bonds with a Copper (I) complex

María Álvarez, Manuel R. Fructos, Pedro J. Pérez*

Laboratorio de Catalís Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible y Departamento de Química, Campus de El Carmen s/n, Universidad de Huelva, 21007-Huelva, e-mail: maria.alvarez@dqcm.uhu.es

The oxidation of C-H bonds catalyzed by transition metal complexes continues being relevant due to the added value of the oxygenated products. The use of molecular oxygen as oxidant is the most challenging target, for which there are very few examples. Several copper(I) complexes are known to react with molecular oxygen, and detection and/or isolation of reaction intermediates such as dicopper-superoxides, peroxides, and oxides, have been reported. In this contribution, we present the reactivity of a copper(I) complex Tp^III(Cu(THF)) with molecular oxygen, that leads to the formation of a novel trigonal copper complex, in which the intramolecular oxidation of a C-H bond of the ligand takes place (Figure 1).

References

Poster 2
Coordination properties of the zwitterionic ligand EtNHC(S)Ph=P=NPPhC(S)NEt towards Pd(II) and Co(II)

Jacopo Andreo,* Massimiliano Delferro, Claudia Graiff, Daniele Cauzzi*

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The nucleophilic addition of aminophosphane to alkyl- and aryl-isothiocyanate leads to the formation of zwitterionic thiaamidyl-phosphonium (P=C(S)N(R') functional group. Within this family of compounds, EtNHC(S)Ph=P=NPPhC(S)NEt (HeEtSNS) can be prepared by reacting Ph3P=N(NPPh2) (dppa) in EtNCs as the reaction medium. HeEtSNS is a versatile and conformationally flexible mono-, bi- and tri-dentate ligand for a wide range of metal cations. In this work, we present a comparison between Pd(II) and Co(II) complexes (Figure 1), as these two family of compounds show how the ligand may switch from bi- to tri-dentate, and how the atom donors may vary from S-N-S to N-N-N with a conformational adjustment, depending on the metal requirements. Pd^2+ (d^8) is bound to HeEtSNS through S-N coordination, forming [(HeEtSNS)PdCl]Cl. A chloride completes the square planar geometry, the second chloride forming an hydrogen bond with the NH group of the ligand. HCl may be salified with NEt4, thus obtaining the neutral complex [(EtSNS)PdCl] (Figure 1-a). In the presence of NEt4 with a 2:1 ligand-to-metal ratio, complex [(EtSNS)2Pd] (Figure 1-b) is formed, showing a square-planar geometry, the two EtSNS chelating the Pd ion in an S-S bidentate fashion. Co^2+ (d^7), in the presence of NEt4, reacts with HeEtSNS forming two pentacordinate complexes. The neutral complex [(EtSNS)CoCl], analogous to [(EtSNS)PdCl], form the dimer [(EtSNS)CoCl]2 (Figure 1-c), where the two Co^2+ are bridged by two chlorides and the square pyramidal geometry is completed by EtSNS, chelating in an N-N-N coordination fashion. If [(EtSNS)CoCl]2 is crystallized in the presence of HNEt4Cl, the ionic compound [(EtSNS)CoCl]HNEt4+ is formed (Figure 1-d), displaying a trigonal bipyramidal geometry.

References
N,N'-dialkylated cross bridged cyclam: synthesis and bleaching activity of corresponding Mn(II) complexes

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Glyoxal-bridged cyclam based ligands (Figure 1, a) gained a lot of interest in the last decades due to their ability of coordinating mid-late transition metals, forming kinetically inert complexes.1,3 The macrocycles can be easily N-functionalized with various groups, which allows the preparation of a wide range of ligands suitable for important applications such as catalysis,3 the development of metal-based imaging and as therapeutic agents in medicine. Manganese and iron complexes, above all, were targeted as potential oxidation catalysts, in which the all-tertiary nature of the nitrogen atoms minimizes the possibility of ligand oxidation and catalyst destruction. In particular, manganese(II) complexes of formula Mn(L-R,R′)Cl2 (Figure 1, b) show well proven peroxide-based bleaching activity in alkaline solution, which has been the object of extensive studies documented in patent literature.

Because the rigid cross-bridged ligand strongly binds manganese ion, precipitation in the form of MnO2 is prevented; moreover the presence of the alkyl groups R and R’ preclude dimerization and consequent deactivation of the catalyst. Here is extended the knowledge of the cross-bridged cyclam’s family through the synthesis of a wide class of symmetrical and unsymmetrical Mn(II) complexes and the assessment of their bleaching activity at various pH in order to evaluate how steric and electronic effects influence catalytic ability.

References

Poster 3

Poster 4

Allowing the direct interaction of N-aryl α-diimines with a high valent metal chloride: one-pot WCl₄-promoted synthesis of quinoxalinium salts

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While α-diimines (1,4-diaza-1,3-dienes, DADs) have been widely employed in coordination chemistry as redox non-innocent, finely tunable chelating ligands,1 activation reactions of these compounds are very rare, and usually limited to C–C and C–Cl coupling additions at the imine skeleton.2 In the framework of the interest of our group in the unusual activation pathways supplied by high valent transition metal halides to organic substrates,3 the full potential of a high valent metal chloride as both chlorinating and oxidative agent has been explored by allowing WCl₄ to react with DADs, in CHCl₃ at room temperature. Two N-aryl substituted DADs underwent unprecedented conversion to quinoxalinium cations via intramolecular C–N coupling (Figure 1). A plausible reaction mechanism has been outlined with the assistance of DFT calculations.
Post 5

Synthesis of Pechmann derivatives for potential application in organic electronics or photovoltaics

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The synthesis of the (E)-3,3'-bifuranylidene-2,2'-dione heterocyclic system has been first published in 1882 by Von Pechmann.1 Recently promising optical and electronic properties have been demonstrated in some Pechman derivatives and this fact has stimulated further studies concerning the preparation of such scaffold and its incorporation into longer conjugated systems, which might have a potential interest for organic electronics.1 This work, the preparation and spectroscopic characterization of some symmetrical small molecules containing the so-called Pechmann lactone and featuring an extended conjugation, are reported. The absorption and emission spectra of the new molecules obtained have been recorded in solution and clearly show how the photophysical properties can be modulated by a proper choice of the (hetero)aromatic terminal groups. All the compounds prepared in this study have interesting optical properties and could find application as semiconductors in organic electronics or photovoltaics.

References

Post 6

Silatrane as a new versatile alternative anchoring group for Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSSC) have been the subject of constant attention in recent years thanks to the enhancement in their efficiency and stability.1 Metal-free D-π-A dyes are especially interesting since their particular architecture allows a fine adjustment of their photo- and electrochemical properties2 and among the anchoring moiety, the alkoxysilane group was recently recognized as one of the most stable and high-performing anchoring units for DSSC.3 Our work focused on developing an alternative anchoring group to the siloxane, capable of showing the same interesting properties. Our choice has fallen upon the silatrane group. First, we studied an easy and versatile way to introduce the anchoring moiety and we successfully insert the group on three different molecular scaffolds by a simple amide coupling, in comparison for the corresponding trialkoxysilane compounds three different reactions were needed.

Then, the spectroscopic properties and anchoring mode on nanocrystalline TiO2 of the silatrane-dyes were analyzed for a possible application in Dye Sensitized Solar Cells and these results were compared with those already obtained for the corresponding trialkoxysilane compounds.

References
Dye-sensitizer solar cells (DSSC) are currently considered one of the most promising alternatives to traditional silicon solar cells. The research activity in this field is mostly focused on the design and synthesis of new organic dyes with potential application in this kind of devices. The compounds developed in this work are based on a structure well known design where a donor group (D) and an acceptor group (A) are joined by a conjugate bridge (π). In particular, we focused our efforts on the modification of the acceptor group due to his double function: anchoring the dye on the semiconductor (TiO₂) and withdrawing electrons in the excited state of the molecule. We focused on the change of the carboxylic function into the thiocarboxylic and in the dithiocarboxylic ones. The presence of a sulfur atom in the anchoring group shown innovative features such as red-shift of λmax and more generally, a broadening of the absorption spectrum, as predicted by TD-DFT analysis previously carried out. Such improvements against the benchmark (DF15) have been confirmed by UV-Vis and fluorescence analysis on the obtained compounds.

**Figure 1**

**Poster 7**

**Bathochromic shift induced by sulfur-containing anchoring groups of organic dyes for DSSC**

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The effects of global warming caused by burning fossil fuels demand for a sustainable and efficient alternative and the sun is the only source of energy that can meet the current and future energy demand. As a consequence harvesting sun light efficiently is an important quest in science and Dye Sensitized Solar Cells (DSSC’s) proved to be promising candidates. However, existing systems suffer from rapid electron-hole recombination, hampering high efficiencies. It is believed that this is caused by a lack of directionality in electron transfer. To address this problem, redox mediators have been proposed to incorporate directionality of electron transfer. For example, viologen based mediators have already proven to increase photocurrents by Meyer and Willner. Therefore, we propose the rotaxane depicted in figure 1 that contains a ruthenium dye and a viologen based ring as photosensitizer, to show higher photocurrents than the corresponding ruthenium only based DSSC. The question to be addressed is if this rotaxane can be used as redox mediator in future DSSC.

**Figure 1**

**Poster 8**

**Ruthenium(II) complex based rotaxanes for dye sensitized solar cells**

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References

Conversion of CO$_2$ into cyclic propylene carbonate catalyzed by carbamato metal complexes

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The reaction of carbon dioxide with amines affords N,N-dialkykcarbamates, i.e. monoaanionic oxygen donors of formula (O$_2$CNR)$_2$. These species, the in presence of metal halides, allows the straightforward access to a variety of compounds of general formula M(O$_2$CNR)$_2$ (M = non-transition or transition, d or f, element), see Eq. 1.

$$\text{MCl}_n + n\text{NH}_2R_2(O_2CNR)_2 \rightarrow \text{M}(O_2CNR)_2 + n\text{NH}_2RCl$$

The resulting metal carbamates exhibit interesting properties, and in particular group 4 and group 5 compounds show a good capability to catalysle olefins polymerization. Also mixed metal halide-carbamates are able to act as catalysts. In some cases, these compounds display better activities, compared to the corresponding homoleptic carbamates. Convenient synthetic procedures to prepare the former have been recently proposed. Herein, we describe new synthetic strategies for the preparation of a variety of mixed halide-carbamates of high valent metals. The performances of metal carbamates as catalytic precursors for the CO$_2$-propylene oxide coupling reaction will be discussed.

Disperse dyes modification by Pd-catalyzed cross coupling reactions

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Disperse dyes are the most commonly used dyes in tinctorial processes. These dyes possess a very low solubility in water, therefore the use of surfactants is necessary to ensure a good dispersion in aqueous medium. These additives determine a substantial increase in tinctorial costs and their removal from dyeing wastewaters represents a challenge. To enhance the water solubility of disperse dyes, Bianchini and al. developed the naturalization process, consisting in the conjugation of the chromophore to a 6'-piperazinyl-lactose unit through an amide bond. In this work, the previously synthesized 1-amino-2-bromo-4-hydroxy—anthracen-9,10-dione carboxylic acid derivative (C.I. Disperse Violet 17 carboxylic acid derivative 1) was used as substrate in Pd-catalyzed cross coupling reactions (Figure 1).

Different aryl derivatives were used to explore the reactivity in Suzuki, Heck and Sonogashira reactions, to extend the conjugation of the antraquinone unit and to evaluate the changes in the absorption spectrum. The naturalization process was tested on one derivative for each of the three reactions. Only for Suzuki derivative the desired water soluble compound was obtained. The desired Heck derivative was completely insoluble, while for the Sonogashira proce...
Poster 11

V(V) aminotriphenolates as catalysts for effective C-C bond aerobic oxidative cleavage of vicinal diols

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The oxidative C-C bond cleavage of vicinal diols to carbonyl compounds is an important and frequently used transformation in organic chemistry with a wide range of applications. Nowadays this reaction is performed by using stoichiometric amount of dangerous inorganic oxidants (NaIO2, Pb(OAc)2, MnO2). Catalytic procedures have been also reported, but they require stoichiometric amounts of sacrificial oxidants (‘BuOOH, NaClO, H2O2) and rather harsh reaction conditions. More importantly, these oxidants must be used in large excess, with the subsequent production of large quantities of waste. For these reasons, the development of new efficient catalytic aerobic oxidation processes is appealing in order to achieve more environmentally benign and sustainable synthetic procedures. In our research group, we successfully synthesized V(V) aminotriphenolates (1a–e), that have been effectively employed as catalysts in oxygen transfer reactions and for the CO2 fixation. Recently we also discovered that they are able to act as catalysts for the aerobic oxidative C-C cleavage of vicinal diols.

\[
\begin{align*}
1a & : R = R' = \text{Cl} \\
1b & : R = \text{Bu}, R' = \text{NO}_2 \\
1c & : R = \text{Bu}, R' = \text{H} \\
1d & : R = R' = \text{Bu} \\
1e & : R = \text{Bu}, R' = \text{OMe}
\end{align*}
\]

In this communication, we will report on the catalytic activity of 1a in the aerobic C-C cleavage of vicinal diols (Scheme 1), which allows to obtain the relative carbonyl compounds in high yields and selectivity (TON up to 71,000 and TOFs up to 9400 h\(^{-1}\)). The optimization of the catalytic reaction and the scope of the substrate scope will be reported as well.

\[
\text{Scheme 1} \quad 1a \text{ catalyzed aerobic oxidative C-C cleavage of 1,2-diols.}
\]

References


Poster 12

Development of visible-light reductive radical cyclization reactions from unactivated chloroalkanes

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Free-radical generation from organohalides is among the most useful means to access an open-shell reactive intermediate that has found numerous applications in chemical synthesis. The development of new strategies of free-radical generation avoids the use of highly toxic, environmentally hazardous or explosive reagents such as alkyl-stannanes or boranes. A good alternative to the use of these reagents is the visible-light photocatalysis utilizing phototactic transition-metal complexes. In contrast to classical cross-coupling reactions, which rely on two-electron elementary steps, photoredox and metal dual catalysis takes advantage of the ability of first-row transition metals (TMs) to participate in single-electron transfer reactions. In this regard, nickel is at the forefront of photoredox metal dual catalysis, while the rest of the first row TMs pass unnoticed in this field. Thus, we used a family of photogenerated cobalt(I) complexes based on pentacoordinated polyanilinopyridyl ligands that enable radical cyclizations as well as intermolecular C-C bond forming reactions. The use of copper photoredox catalyst, instead of typical Ru and Ir polypyrindyl complexes, makes the developed process appealing for green radical cyclizations. The discovery of highly robust and selective catalytic systems is speeded up by using a parallel photoredox screening platform for high-throughput experimentation.

References

Since their first reports in the 1960s redox-active ligands have attracted much attention thanks to their ability to access unusual chemical properties by coupling the redox activity of the ligand to the coordination chemistry of a metal. In contrast to the nitrogen-containing heterocycles found in dipyrrins and porphyrinoids, studies on the redox activity of sulfur- and oxygen-containing heterocycles are more limited. Following results on uranyl complexes of a donor-expanded dipyrrin, the synthesis and reactivity of thiophene- and furan-derived diarylmethenes are presented (Scheme 1). Deprotonation of the methine bridge in the precursor $HL$ leads to the highly reactive conjugated anion $KL$ which upon reaction with a range of transition-metal halides does not undergo salt-metathesis, instead forming the stable, neutral radical $L$. Alternatively, reaction between the thiophene-derived $KL$ and CuI forms the dicopper complex $\text{Cu}_2\text{I}_2(L^\text{S}\bullet)$ provided with a ligand-centered radical, as confirmed by experimental and computational analysis.

References

Effect of the α-diamine skeleton in Pd-catalyzed copolymerization reactions

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The efficient copolymerization of terminal alkenes with polar vinyl monomers represents a goal nowadays in polymer chemistry. The active catalytic systems for this reaction are based on palladium(II) complexes with α-diamine or phosphino-sulfonate ligands, however they do not reach values of productivity high enough for any industrial application. This means that a catalyst with better performances is strongly needed. In literature, there aren’t many examples on modification of the skeleton of α-diamine ligands, so we decided to explore this field by studying a family of ligands with a phenanthrene-based backbone, the so-called Ar-BIP ligands, and their related Pd(II) complexes (Scheme 1).

Scheme 1

The studied Ar-BIP ligands are symmetrical and have either a simple aryl ring or an aryl ring with electron donating ortho substituent (methyl, isopropyl). The related neutral, [Pd(CH₃)(Cl/Ar-BIP)], and monocatonic, [Pd(CH₃)(CH₃CN)(Ar-BIP)][PF₆] palladium(II) complexes have been synthesized and fully characterized in solution and, when suitable crystals were obtained, in solid state (Figure 1). The monocatonic derivatives generated active catalysts for the ethylene/methyl acrylate copolymerization leading to the expected copolymer. The detailed investigation of their catalytic behaviour, carried out under mild conditions of temperature and pressure, will be presented.

Figure 1

Glycoporphyrins catalysts for nitrene and carbene transfer reactions

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Glycoporphyrins are usually described as efficient photosensitizers to be used in photodynamic therapy (PDT), however, the conjugation between metal porphyrin complexes and glycoside moieties is an attractive approach for developing new efficient, enantioselective and eco-friendly catalysts for organic synthesis. The introduction of saccharide units onto the porphyrin skeleton modulates the catalyst solubility in water or organic solvents and may confer it chiral recognition properties. Among the few reported catalytic uses of metal glycoporphyrins, we have recently shown the catalytic efficiency of ruthenium (II) and iron (III) glycoporphyrins in promoting C-H amination reactions. In order to improve the water solubility of these catalysts, porphyrin 1 (Figure 1) was synthesized with a disaccharide unit directly conjugated onto para position of each fluorinated aryl moiety of the porphyrin ring and the [Ru(1,4-CO)] complex was tested in the catalytic model reaction between 3,5-bis(trifluoromethyl)phenyl azide and ethylbenzene forming the corresponding benzylic amine either in organic solvent or biphasic system. Unfortunately, saccharide units in para position are too far away from the metal center to confer enantioselective properties to the catalyst. Thus, the ligand 2 (Figure 1) with trizole spacer placed in ortho position between the carbohydrates and porphyrin was synthesized. The cyclopropanation of α-methyl styrene, performed in presence of Fe(TPP)(OMe) occurred in good yields but without enantiocontrol due to the high mobility of carbohydrate units. For this reason the more rigid glycoporphyrin 3 (Figure 1), with bridging sugar moieties, was synthesized and tested in cyclopropanation reactions.

References

The organometallic \([\text{Pt}(O,O'\text{-acac})(\gamma\text{-acac})(\text{DMS})]\), I, complex is a recently synthesized compound containing two acetylacetanones (one \(O,O'\)-chelate and the other \(\sigma\)-bonded to platinum(II)) and one dimethylsulphide (DMS) ligand in the metal coordination sphere. Previous studies showed that complex I is very interesting for its biological activity in several culture cells lines, resulting in peculiar interactions with non genomic targets, producing a cytotoxicity about ten times higher than that of cisplatin. In this work, we evaluated the metabolic variations induced in Skov3 (Epithelial Ovarian Carcinoma cells resistant to cisplatin) cell lines, by complex I treatment. At this regard, we analysed by NMR the culture media and the cell fractions aqueous and lipidic extracts. We adopted \(^1\)H NMR metabolomic approach giving us the possibility to evaluate qualit/quantitative variations in the metabolic profile of cells treated and untreated with complex I. In particular, our attention was addressed to the study of the metabolites excreted into the cell culture media, together with the water soluble and lipophilic metabolites extracted from cells. This was made at different times from cell treatment with complex I, at the IC\(_{50}\) lethal dose, evidencing the variations of cellular metabolic profiles upon complex I exposure, with respect to cells treated with cisplatin or untreated, see Figure. Interestingly, in Skov3 cells treated with the \([\text{Pt}(O,O'\text{-acac})(\gamma\text{-acac})(\text{DMS})]\) organometallic complex I, strongly modulating compound I cytotoxicity, have been evidenced. These results acquired in the cisplatin resistant Skov3 cell line, fully confirm the existence of a different mechanism of action between complex I and cisplatin, characterized by peculiar metabolic markers.

### References


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**Poster 17**

**Metabolic response of Skov3 epithelial ovarian carcinoma cells resistant to cisplatin to \([\text{Pt}(O,O'\text{-acac})(\gamma\text{-acac})(\text{DMS})]\) treatment: \(^1\)H NMR analyses**

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The organometallic \([\text{Pt}(O,O'\text{-acac})(\gamma\text{-acac})(\text{DMS})]\), I, complex is a recently synthesized compound containing two acetylacetanones (one \(O,O'\)-chelate and the other \(\sigma\)-bonded to platinum(II)) and one dimethylsulphide (DMS) ligand in the metal coordination sphere. Previous studies showed that complex I is very interesting for its biological activity in several culture cells lines, resulting in peculiar interactions with non genomic targets, producing a cytotoxicity about ten times higher than that of cisplatin. In this work, we evaluated the metabolic variations induced in Skov3 (Epithelial Ovarian Carcinoma cells resistant to cisplatin) cell lines, by complex I treatment. At this regard, we analysed by NMR the culture media and the cell fractions aqueous and lipidic extracts. We adopted \(^1\)H NMR metabolomic approach giving us the possibility to evaluate qualit/quantitative variations in the metabolic profile of cells treated and untreated with complex I. In particular, our attention was addressed to the study of the metabolites excreted into the cell culture media, together with the water soluble and lipophilic metabolites extracted from cells. This was made at different times from cell treatment with complex I, at the IC\(_{50}\) lethal dose, evidencing the variations of cellular metabolic profiles upon complex I exposure, with respect to cells treated with cisplatin or untreated, see Figure. Interestingly, in Skov3 cells treated with the \([\text{Pt}(O,O'\text{-acac})(\gamma\text{-acac})(\text{DMS})]\) organometallic complex I, strongly modulating compound I cytotoxicity, have been evidenced. These results acquired in the cisplatin resistant Skov3 cell line, fully confirm the existence of a different mechanism of action between complex I and cisplatin, characterized by peculiar metabolic markers.

### References


The indole core nucleus is one of the most intensively studied structural motifs, and a crucial building block for the synthesis of biologically active compounds and natural products. Different approaches have been adopted for the synthesis of substituted indoles and intramolecular hydroamination reaction is one of the most powerful and frequently employed synthetic approaches. However, the use of noble metals leads to important issues in terms of methodology sustainability, and the replacement of coinage metals with cheaper metal-free catalytic agents is still highly desirable. In this direction, the employment of strong Brønsted acids as free catalytic agents is still highly desirable. In this direction, the employment of strong Brønsted acids as bases such as $\text{p}$TfOH, TIOH, KOH and $\text{Cs}_2\text{CO}_3$ was found competent in the functionalization of alkynes with hetero-nucleophiles even if the protocols suffered from the requirements of harsh reaction conditions and large and even super-stoichiometric amounts of additives. Alternatively, soft quaternary ammonium salts are known to act as synthetic equivalents of late-transition metal species in activating unsaturated hydrocarbons towards nucleophilic attack. The subsequent replacement of the ammonium fragment by a proton made catalytic variants potentially amenable.

The site selective synthesis of functionalized indoles is presented under environmentally convenient tetrabutylammonium fluoride catalysis. The metal-free approach exploits the combined catalytic efficiency of Bu$_4$N$^+$ and F$^-$ ions in performing a cascade sequence involving intramolecular hydroamination of the C-C triple bond towards the regioselective inter- as well as intramolecular condensation with heteroatom-based nucleophiles. Electrophilic metal species based on Pd, In, Au, Pt, Ag... have found efficient applications in catalytic variants showing good chemical performances and substrate scope. However, the use of cheaper metal-free catalytic agents is still highly desirable. In this direction, the employment of strong Brønsted acids as free catalytic agents is still highly desirable. In this direction, the employment of strong Brønsted acids as bases such as $\text{p}$TfOH, TIOH, KOH and $\text{Cs}_2\text{CO}_3$ was found competent in the functionalization of alkynes with hetero-nucleophiles even if the protocols suffered from the requirements of harsh reaction conditions and large and even super-stoichiometric amounts of additives. Alternatively, soft quaternary ammonium salts are known to act as synthetic equivalents of late-transition metal species in activating unsaturated hydrocarbons towards nucleophilic attack. The subsequent replacement of the ammonium fragment by a proton made catalytic variants potentially amenable.

The selected ligands possess an aromatic and rigid structure that may provide, in principle, an electronic connection between the two metal centres; the latter are expected to play, respectively, a photosensitive and a catalytic role. The prepared compounds have been characterized by analytical methods, and UV-Vis, IR and NMR spectroscopy.

References


Design and synthesis of dinuclear ruthenium(II) complexes with polyazotate bridging ligands toward artificial photosynthetic systems

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Artificial photosynthesis enables the possibility of generating clean and sustainable energy resources through water splitting. This task requires the interfacing of several fundamental but challenging steps such as: light-harvesting, charge separation, electron transfer, water oxidation and proton reduction. Although numerous strategies have been reported, a major drawback to efficient solar water splitting is still represented by the development of robust and long-lasting water oxidation catalysts. We have synthesised new dinuclear ruthenium complexes by linking two different metal moieties with variable N-chelating ligands (Figure 1). The selected ligands possess an aromatic and rigid structure that may provide, in principle, an electronic connection between the two metal centres; the latter are expected to play, respectively, a photosensitive and a catalytic role. The prepared compounds have been characterized by analytical methods, and UV-Vis, IR and NMR spectroscopy.

References

Poster 21
Transfer of Vanadium-based Aerobic Oxidative Cleavage of Diols to Water
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It has already been shown that vanadium amino triphenolate complexes efficiently target the carbon-carbon cleavage of vicinal diols (Figure 1) [1-2]. When considering the transfer to aqueous media of these reactions, micellar media came up as an interesting approach with several advantages. We have successfully executed this transfer and optimization of the conditions allowed to select the chlorinated catalyst V1 incorporated in dodecylphosphocholine (DPC) micelles. The micellar core enables the solubilisation of the hydrophobic catalyst [3] and an additional mechanism of selectivity was introduced by means of the exchange between the micelles and the surrounding aqueous solution.

![Figure 1 Vanadium(V) triphenolate amine catalyst structure (V1) and general reaction](image)

In this work, we will focus on the substrate scope of the reaction in water and compare the results to those obtained in organic solvents. A noticeable result and property of the micellar media was the introduction of a diverse selectivity trend when compared with the reactions in organic phase. Additionally, benzylic vicinal diols were found to be the most reactive. A possible explanation of the phenomenon based on substrate/product/catalyst and oxidant partitioning among the micelles and the surrounding water will be presented, on the basis of kinetic and 2D NMR experiments.

Acknowledgements Special acknowledgement to the Fondazione Cariparo PhD Grant (WD) for funding this research.

References

Poster 22
Catalytic carbene transfer to a cobalt(II) catalyst via sulfur ylides
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Carbenes are found widely throughout organic and inorganic chemistry as fleeting intermediates either in C-H activation reactions or as commercially important precatalysts, such as the Grubbs catalyst. These reactive carbon species are generated via high-energy starting materials, most notably diazo compounds. While proven successful, diazo compounds are notoriously explosive and potentially highly toxic as well. Alternative routes either generate the diazo species in situ or circumvent it altogether, but in all cases, considerable stoichiometric waste is generated. Furthermore, the synthesis of these starting materials is not trivial either. We therefore are investigating the use of sulfuryl ylides as catalytic carbene transfer reagents, starting from primary and secondary alkyl triflates, onto cobalt(II) square planar complexes to generate radical cobalt(III) carbene species. These radical species can then be used in cyclopropanation reactions to demonstrate proof-of-concept (Scheme 1).

![Scheme 1. Synthesis of functionalized cyclopropanes via carbene transfer through catalytic sulfur ylide and radical cobalt(III) intermediates.](image)

References
Hydrogenation and dehydrogenation reactions catalysed by Manganese pincer complexes.

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Catalysis based on metal-ligand cooperation has proven to be a powerful synthetic tool, which has led to several environmentally benign reactions.1 Here, the ligands not only modulate the stereoelectronic properties of the metals but also participate directly in the catalytic process. Hydrogenation and dehydrogenation reactions catalyzed by Mn pincer complexes became a hot area of research, following our initial report on Mn pyridine-based PNP* (the asterisk denotes the dearomatized ligand) pincer ligand (I) catalyzed acceptorless dehydrogenative coupling of alcohols and amines to form imines (I).2 We have recently reported the synthesis and reactivity of the Mn amido complex 2 bearing a pyridine-based PNN pincer ligand.3 Complex 2 shows high catalytic activity for a broad-scope hydrogenation of non-activated esters under mild conditions (II). Lately we have observed also the manganese catalyzed synthesis of cyclic imides from diols and amines (III). These base-metal-catalyzed hydrogenation and dehydrogenative coupling processes yield compounds of high industrial value through atom-economical, sustainable and environmentally benign synthetic routes.

Scheme 1 Solketal synthesis from glycerol

Here we report extremely efficient homogeneous iron(III) catalysts (scheme 2) for the synthesis of solketal from glycerol and acetone. The activities are the highest ever reported so far for this type of reaction, with TOFs up to 10^5 h^-1 at negligible catalyst loading.

Scheme 2 Iron(III) complexes

References
Water oxidation (WO) is considered the bottleneck for the development of an artificial photosynthetic apparatus, aimed at the conversion of solar energy into chemical energy, through the production of renewable fuels. Over the last few years, many molecular,2 heterogeneous1 and heterogenized6 catalysts have been reported. Furthermore, we demonstrated that a ternary system constituted by an Ir(III)-doped ZnAl hydrotalcite-like compound (HTlc) is an efficient and recyclable heterogeneous WO catalyst. Particularly, we showed that \([\text{Zn}_{0.156}\text{Al}_{0.844}\text{Ir}_{0.002}\text{OH}]\text{Cl}_{2.052}\cdot0.4\text{H}_2\text{O}\) is able of catalyzing WO with top performance both in terms of TOF (up to 113 min\(^{-1}\)) and TON (> 11900), in the presence of NaIO\(_4\) as the sacrificial oxidant.2 Herein, we show that both Ir(III) and Ru(III)-doped HTls are efficient and robust heterogeneous catalysts for water oxidation also in electrocatalytic experiments. The HTlc reported herein were synthesized by an isomorphic replacement of Al(III) ions with Ir(III) and one with Ru(III). Their chemical formulas, determined by ICP-OES analysis, are: \([\text{Zn}_{0.156}\text{Al}_{0.844}\text{Ir}_{0.002}\text{OH}]\text{Cl}_{2.052}\cdot\text{H}_2\text{O}\) (1), \([\text{Zn}_{0.413}\text{Al}_{0.587}\text{Ir}_{0.002}\text{OH}]\text{Cl}_{3.107}\cdot\text{H}_2\text{O}\) (2), \([\text{Zn}_{0.156}\text{Al}_{0.844}\text{Ir}_{0.002}\text{OH}]\text{Cl}_{2.052}\cdot0.4\text{H}_2\text{O}\) (3).

The brucitic structure was retained after the incorporation of the noble metal, which was homogeneously distributed throughout the sample, as confirmed by X-ray diffraction patterns and SEM-EDX images. The performances of the HTls toward electrocatalytic water oxidation were evaluated in a standard three electrode-apparatus (KOH 1M), immobilizing the catalysts in carbon paste electrodes. Interestingly, 1 and 3 show a lower overpotential (352mV vs 388mV at 10mA/cm\(^2\)) and twice as high current density with respect to IrO\(_2\) (2.1 vs 1.2 mA/cm\(^2\) at 280mV), used as benchmark (Fig.1). Instead, 2 shows a current density comparable to that of IrO\(_2\). In addition, long-term stability tests, such as chronoamperometry and chronopotentiometry, show that the performances of 1-3 catalysts even increase over time.

**References**


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**Poster 25**

Ir(III) and Ru(III)-doped hydrotalcite-like compounds as suitable heterogeneous catalysts for chemical and electrochemical water oxidation

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**Poster 26**

Electrochemical H\(^+\) and CO\(_2\) reduction processes catalyzed by pyridylamino Co(II) complexes: Experimental and computational mechanistic insights

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The transformation of readily available and inexpensive small molecules into energy-dense compounds is seen as one of the alternatives in order to solve the world’s energy crisis. One approach consists in the reduction of H\(_2\)O to H\(_2\) and CO\(_2\) to CO or carbon fuels following an artificial photosynthetic scheme. However, to be efficient it needs to be coupled to an anodic process that provides the e\(^-\) required for the reductive transformation. In the last years, some pyridine-based cobalt complexes have emerged as active catalysts in both the H\(_2\)O/H\(^+\) and CO\(_2\) to CO reduction processes under photo- and electrochemical conditions.1 However, very few investigations have been devoted to understand the reaction mechanisms under electrocatalytic conditions.2 We have studied the CO\(_2\) electrocatalytic performance of a series of water reduction catalysts based in the tetradentate Py\(^{2+}\)-acen ligand.3 The combination of computational and experimental tools has allowed the identification of a highly stable Co\(^{2+}\)-CO\(_2\) species as the inactive resting state in the CO\(_2\) reduction process at low overpotentials (Figure 1). The mechanistic understanding of the system will be crucial for the design of new strategies to obtain more efficient catalysts for both the CO\(_2\) and H\(_2\)O/H\(^+\) reduction processes.

**References**

**Poster 27**

**Mild N-Alkylation of Amines with Alcohols Catalyzed by Acetate Ruthenium Complexes**

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The formation of C-N bonds for the preparation of amines compounds is a reaction of high relevance for the synthesis of bulk and fine chemicals.1 The preparation of several drug molecules involving N-substitution transformations are usually performed by reaction of amines with alkylating agents or via reductive amination. In this context, the catalytic N-alkylation of amines using environmentally friendly alcohols as alkylating reagents and affording water as only byproduct, is an attractive atom-economic way for the C-N bond formation.2,3

We report here the straightforward synthesis of the carboxylate ruthenium complexes of formula Ru(OAc)2(diphosphane)(CO)2– (n = 0, 1). These compounds are efficient catalysts for the N-alkylation of amines using primary alcohols as both reactant and solvent, with an alcohol / amine molar ratio of 10-100, under mild reaction conditions. Evidence has been provided that in catalysis a monohydride species is formed through an equilibrium reaction.

![Figure 1](image)

**References**


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**Poster 28**

**Steps Towards Sustainable Homogeneous Gold Catalysis: From Neat to Green Solvents.**

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In literature, there are very few examples of gold homogeneous catalysis that works without silver additives, low catalyst loading, mild reaction conditions, simple work-up with the possibility of recovery the catalytic system, and using green solvents or even in neat condition. In this contribution, we obtained a greener pathways through the homogeneous gold catalysis, testing the activity of NHC-Au-X [NHC = (1,3-bis(2,6-di-isopropylphenyl)-imidazol-2-ylidene, X = BF4, SbF6, OTf, NTf2, ClO4, OTs, TFA) as catalysts for the reactions of hydration, alkoxylation and cycloisomerization of alkynes and propargylamines. In our previous works, we notice that the anion plays an important role in the mechanism and in order to obtain a reusable catalytic system, with a low catalyst loading (down to 0.01%), high values of TOF and TON, low Efactor and high EMY, the anion must be choose wisely in neat hydration of alkynes. Once optimized the catalytic system, we extend the study to green solvents, instead of traditional volatile organic solvents (VOS). Utilization of green solvents led us to obtain similar or better results respect to VOS in several reactions mediated by homogeneous gold catalysts.

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**References**

Poster 29

Domino metal-free aminoiidination of olefins in eco-friendly condition

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Intramolecular amination reactions of unactivated alkenes constitute an attractive process for the formation of nitrogen-containing heterocycles with 100% atom-economic result. In addition the possibility of the concomitant functionalization of the heterocycle represents the major challenge of the synthetic pathway. Due to the attractiveness of this field, various efforts have been made in the development of efficient transition metal-catalyzed aminohalogenations. On the other hand, also some examples of metal-free aminoiidination reactions have been studied. Thus, the aim to find more eco-sustainable conditions and to work in step-economical encourage us to investigate metal-free aminohalogenation conditions. In this study we reported the use of hydrogen peroxide and potassium iodide to promote aminoiodination dominio process in the synthesis of functionalized heterocycles. The simple use of these reagents allows us to exploit also greener solvents than the ones traditionally-used.

![Reaction Scheme]

\[ \text{NHTs} + \text{H}_2\text{O} (1.1 \text{ eq.}) + \text{KI} (2 \text{ eq.}) \rightarrow \text{NHTs} \]

**References**


Poster 30

Synthesis, isolation and characterization of the first Palladium-diazo adduct. study of its catalytic properties in the cyclopropanation reaction.

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Transition metal-catalyzed carbene transfer reactions from diazo compounds constitute nowadays a powerful tool in organic synthesis. It is assumed that, previously to the formation of the metallocarbenic species, the interaction of the diazo molecule with the metal centre takes place in different manners, depending on the coordination mode of the diazo compound to the metal. At the time we initiated this work, these type of adducts had been detected and/or isolated for all metals in Groups 8 to 10 with the exception of palladium, that has been widely employed as catalyst in these transformations, especially in olefin cyclopropanation reactions. In this contribution, we present the first example of a diazo palladium(0) complex isolated and fully characterized, with the diazo compound coordinated in a dihapto-η² fashion. In addition, several kinetic and mechanistic experiments have allowed us to propose a catalytic cycle for the palladium-catalyzed olefin cyclopropanation, in which such adduct behaves as a “dead-end” of the catalyst.

![Reaction Scheme]

**References**


Poster 31

Synthesis of Ruthenium(II) Catalysts with Phosphinous Acids: Application in C-H bond activations in water

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Considered for long time as an important challenge in organic synthesis, the C-H activation functionalization reactions have emerged in recent years as powerful tools for the preparation of elaborated molecules from readily available raw materials. In this regard, the use of ruthenium(II) catalysts in the activation of unreactive C(sp3)-H bonds for a variety of C-C coupling reactions has contributed decisively to the advancement of the field. With all these precedents in mind, and continuing with our interest in the application of ruthenium ligand cooperation, we present herein the preparation of new Ru(II) representatives able to catalyze the activation of C-H bonds in pure water.

References

Poster 32

NHC-based Au(I) complexes supported by 1,3,6,8-tetraethynylpyrene

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N-heterocyclic carbene (NHC) based Au(I) complexes containing acetylide and chromophore groups represent an interesting class of luminescent materials. Moreover, acetylide-Au(I) complexes are able to form supramolecular architectures based on their tendency to afford linear geometries and self-assembly structures through aurophilic interactions. Keen to further explore the photophysical properties and recognition capabilities of these NHC-based Au(I) complexes, two Au(I) complexes bearing polyaromatic NHCs have been prepared, and subsequently coordinated to the two-fold ethynyl-substituted chromophore 1,3,6,8-tetraethynylpyrene. The two tetra-Au(I) complexes show fluorescent properties, with emission in the range of 450-600 nm, and quantum yields of 0.38 and 0.87. The self-assembly capability of the complexes has been studied by variable-concentration 1H NMR experiments.

Figure 1 (Left) Scheme of the new family of Au(I)-NHC complexes containing acetylide ligands supported by pyrene. (Right) Luminescent nature of the new complexes.

References
Unexpected cyclisation of Passerini adducts via Tsuji-like allyl transfer – a mechanistic study

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Passerini adducts formed from α,β-unsaturated aldehydes undergo a cyclisation with formal CO₂ insertion when reacted with allylmethylcarbonate in the presence of palladium and an appropriate phosphine. Depending on the reaction conditions, the more expected allylation product may also be formed. Thanks to NMR and electrochemical study, reactivity of both allyl moieties has been compared. The synthesis of putative intermediates, along with a screening of the reaction conditions, leads us to propose a mechanistic pathway for the transformation. The extension of the reaction to chiral phosphines has also been studied.

Cyclic peptides are abundant in nature and display important biological activities. Advantages of cyclic peptides over linear peptides are increased selectivity, biological stability and membrane permeability. Current synthetic methodologies do not give general access to small ( < 15 amino acids) and strained cyclic peptides. We use M₁₂₄₂₄-type spheres as enzyme active-site mimics to facilitate head-to-tail cyclization of small peptides and avoid unwanted intermolecular reactions (Figure 1). The interior of the spheres can be easily modified to allow the design of well-defined cavities that favor difficult cyclization reactions.

References

Figure 1 Schematic depiction of cyclization inside a M₁₂₄₂₄ assembly.
Oxidative dissolution of copper with organic thiol compounds

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Within the concept of circular economy, recycling methods for noble metals (NMs) that are selective and easy to operate have been extensively investigated mainly by using pyrometallurgy or hydrometallurgical methodologies. In our research work metals (Au0, Ag0 and Cu0) are oxidized in organic solutions of heterocyclic thiol ligands in mild conditions (Figure 1). The most reactive ligands for the dissolution have thiol-thione tautomerism in their structure. We were able to dissolve copper in high yields and the mechanism is investigated in more depth. Differences in dissolution rates are observed when changing the reaction media, by varying the ligand concentration and/or by using an accelerator. Interesting mechanistic results were obtained and further details of the dissolution of copper will be presented based on the degradation products and pathways of thiol ligand in different solvents through spectroscopic techniques (1H NMR, ESI-TOF+MS).

References

Alkynylfluoroborates in synthesis: activation pathway

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Herein we present our findings concerning the mechanism of metal-free borylation of terminal alkynes by pentamethylpiperidine and different BF₃-sources published by us earlier (Figure 1).

Mechanism of formation of trialkynylboranes 1 was studied by low temperature NMR. Conditions of further conversion of 1 to tetraalkynylborates 2 were elucidated. Corresponding intermediates were also located computationally. The same mechanism was found to be operative when carrying out the BF₃-assisted activation of potassium alkynyltrifluoroborates and their tetraethylammonium analogues 3. The same rearrangement was also observed with catalytic amount of BF₃-OEt₂ (Figure 2).

In conclusion, we have studied the mechanism of terminal alkynes borylation by pentamethylpiperidine with various BF₃ sources. Analogous reactivity of alkynyl trifluoroborates was found. The mechanism of rearrangement was proven by NMR studies and supported computationally.

References
New hexacopper(I)-iodide cluster and cagelike aminophosphine based 2D coordination network for reversible “turn-on” detection of aniline

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aniline and its derivatives are widely applied in industry, medicine, food control, and agriculture. They are not only key intermediates in the industrial organic synthesis and markers of specific diseases such as lung cancer but are also the recognized environmental pollutants, being carcinogenic via oral or dermal exposure. Unfortunately, until now there is still lack of efficient, simple, and fast detection systems for amine pollutants in both liquid and vapor phase. Thus, an increasing effort has been paid in recent years to design new luminescent “turn-on” sensors based on metal-organic frameworks (MOFs) or coordination polymers (CPs). Such materials can offer advantages of rapid response, simplicity, cheapness, portability, and high sensitivity in various sensing applications. In particular, Cu-based MOFs and CPs represent a remarkable class of materials. Fascinating structural variations, low toxicity, as well as intense luminescence of various [Cu₃L₃] aggregates combined with specific features of water-soluble 1,3,5-triaza-7-phosphadamanate-7-oxide (PTA=O) building block may trigger important implications on the physicochemical behavior and also lead to creation of new stimuli-responsive and sensing materials based on coordination polymers. Hence, we report herein the facile self-assembly synthesis, full characterization, structural features, and stimuli responsive luminescence properties of a novel 2D copper(I) iodide coordination polymer [Cu₃(µ₂-I₂)(µ₂-PTA=O)]₅₅ (1) and a derived 1 paper material. These reveal remarkable capability to detect aniline vapors at a trace level (Figure 1), thus allowing their application as a highly sensitive amine sensor for early stage medical diagnosis and environmental protection.

Figure 1 Schematic representation of aniline sensing properties of 1.

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References

Novel supramolecular approach for photocatalytic applications

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The development of photochemical molecular devices is inspired by nature, where the efficient conversion of light into an exploitable reactive species (e.g., charge-separated or excited state) requires a precise spatial (position of the components) and energy (excited state levels and redox potentials) organization that permit given life-time values of the excited states (rates of competing processes) and protection/recycling of the photoreactive species. Due to the complexity of the photocatalytic system, such an organization can be likely achieved in an artificial architecture by choosing proper molecular modules that spontaneously undergo self-assembly into a suitable structure via non-covalent bonding interactions. In most cases, the artificial systems used to produce light induced functions consist of covalently linked components. This forms photosynthetic architectures in which antenna molecules can fuel donor (D) and acceptor (A) electron mediators via non-covalent recognition sites (Figure 1). Hence, sensitized D* and A* might react independently with the chosen catalysts for the given transformation, depending on the tailored product. In this study we want to focus on designing a self-assembling catalytic system, that can use several sensitzers and catalysts to photocatalytic reactions (e.g. water splitting processes). Further investigations on the photophysical and electrochemical properties of the molecules allow an understanding of the basic phenomena and improve efficiency of the catalytic system.

Figure 1 General scheme of the self-assembling catalytic system. (PS)* photosensitizer, (S) substrate, (C) catalyst, (ET) electron transfer.
Poster 39

Ligand enhanced Cu(I)/TEMPO/NMI catalytic system for aerobic oxidation of primary alcohols

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In this work a new Cu(I)-complex was synthesised and studied for catalytic oxidation of primary alcohols to their corresponding aldehydes. The catalyst is based on CuBr or CuOTf and a Schiff base ligand, which is synthesised out of furfural and 4-fluoroaniline. The resulted complex consists of two ligands coordinating to the Cu(I)-centre. When combined with TEMPO and NMI the complex shows high catalytic activity for the oxidation of 1-octanol or benzyl alcohol and the results are comparable to the already known highly active systems based on bipy as a ligand.

The catalytic reaction was monitored with the help of in situ UV-vis, in situ ATR-IR-spectroscopy and GC during the reaction and further details of the catalytic system will be presented.

Figure 1 in situ ART-IR spectra for the complexation of CuBr with the Ligand (left) and the oxidation of benzyl alcohol with the catalyst (right).

References

Poster 40

Nickel-Cornered Supramolecular Assemblies as Polycyclic Aromatic Hydrocarbon Receptors

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Supramolecular coordination complexes (SSCs) 1 are recently finding a great number of applications in catalysis, 2 molecular recognition, stabilization of reactive species and as a drug delivery/release vectors. 3 In 2008, Hahn and co-workers described a protocol for preparing a series of Ni(II)-based molecular rectangles based on a well-known Janus-type benzo-bisimidazolylidene ligand. 4 Based on this seminal work, we recently described the preparation of two molecular rectangles bearing a pyrene-di-imidazolylidene (Figure 1, complexes [3][X] 4, [4][X] 4) which showed extraordinary binding affinities to polyaromatic hydrocarbons, and high selectivity for binding pyrene and triphenylene. 5 The interest in developing receptors for smaller PAHs resides in the high toxicity and carcinogenic properties of this aromatic molecules. Encouraged by our preliminary results, we now describe the preparation of nickel-cornered boxes (Figure 1, complex [5][X] 6), by combination of a pyrene-di-imidazolylidene with different shapes and sizes. The affinity properties of these supramolecules are studied against small PAHs.

Figure 1 Multi-Ni(II) supramolecular coordination complexes [3][X] 4, [4][X] 4 and [5][X] 6 studied.

References
When Martin’s spirosilane meets a n-heterocyclic carbene (NHC)

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Martin’s spirosilane first synthesized in 1979, has attracted some interest due to its high Lewis acidity, steric hindrance and the intrinsic ability of the silicon atom to become hypervalent. In our study we were particularly interested in the interactions between this spirosilane and different NHCs, known as stable species, with a tunable Lewis basicity and steric hindrance. We started studying the interactions between the two partners that allowed us to obtain different adducts: the normal one with small carbenes (IMe, IMes), and the abnormal one in presence of hindered carbenes (iBu, iPr). This last result can be a hint of a Frustrated Lewis Pair behaviour for the activation of small molecules like H₂, CO₂. We also investigated their potential use as ligands for metal catalysis.

References

Oxidative cleavage of oleic acid with Mo(VI) homogeneous catalysts

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Unsaturated acids derived from vegetable oils are of interest, especially because their oxidation leads to diacids, used to produce polyamides, polyesters, lubricants, and also cosmetics and pharmaceuticals. Among these, azelaic acid is a commodity with an annual output of 1,000 tons. Industrially, the oxidative cleavage of the double bond is carried out by ozonolysis. Recently, we reported an alternative and more sustainable oxidative cleavage system based on the use of tungsten catalyst and hydrogen peroxide. Despite this system is quite efficient, we started to explore the usability of different molecular catalysts based on strong Lewis acid. Here we report preliminary results of the oxidative cleavage carried out using molybdenum based catalysts (scheme 1).

References
Formic Acid (FA) has received significant attention as a promising hydrogen energy carrier due to its high volumetric capacity (53 g H₂/L), low toxicity and flammability under ambient conditions. Particularly, in the last decade, significant advancements have been achieved in the catalyst development for selective hydrogen generation from formic acid. We show herein that the iridium complex [Cp*Ir(pic)Cl] (1, pic = picolinamidate = κ²-pyridine-2-carboxamide), already successfully exploited as catalyst for water oxidation and NAD⁺/NADH transformations, is an exceptional catalyst for formic acid dehydrogenation. Non-optimized turnover frequency (TOF) of 32 000 h⁻¹ at 60 °C and turnover number (TON) of 12 000 (only limited by the amount of formic acid used) were measured, which well compare with the values reported for the best catalysts. Activity seems to be critical affected by the presence of the NH-functionality, as indicated by its drop of about one order of magnitude when complex [Cp*Ir(pic(Cl))]⁺ (2, pic = picolinate = κ²-pyridine-2-carboxylate) is used as catalyst in place of 1. Furthermore, an in-depth mechanistic investigation reveals that the formation of [Ir-H] intermediate is the rate-determining step in the catalytic cycle.

**References**

Metallophilic interactions between gold(I) and other closed-shell metals such as Pb(II) displaying unsupported interactions have been an important matter of study during the few last years. In this contribution, we design a gold(I) organometallic molecular system that is able to encapsulate other heterometals. The trimetallic gold(I)-complex behaves as an empty “basket”. Addition of a lead(II) precursor leads to a heterometallic compound in which appear an Au(I)···Pb(II) metallophilic interaction. Additionally, a B-H···Pb strong interaction also appears. The X-ray structure simulates a gold(I) “basket” accommodating a lead(II) cation (Figure 1). Computational studies allow to know the nature and strength of the interactions present in the complex.

Figure 1

Acknowledgements S.M. thanks the Ministry of Education, Culture and Sport for research project CTQ 2016-75816-C2-2-P.

References

Organic linkers modification in MOFs is a valuable approach to prepare materials with targeted functionalities. Following this concept and given our past experience with pyrazolate-based MOFs, we have prepared, by solvothermal routes, the three novel MOFs [M(BPZ)]∞ (M = Co, Cu and Zn; BPZ = 3-nitro-4,4′-bis(pyrazolate)). Their crystal structures have been solved from powder X-ray diffraction (PXRD). They show 3D (4,4)-connected networks with 1D squared (Co, Zn, Figure 1) or rhombic (Cu) channels decorated by (BPZ)∞ ligands and accounting for an empty volume in the range 14-35%. They are isotypical to the analogues [M(BPZ)]∞, [M(BPZ)]∞, and [M(BPZ)]∞ (M = Co, Zn) containing the 4,4′-bis(pyrazolate), 3,3′-dimethyl-4,4′-bis(pyrazolate) and 3,3′,5,5′-tetramethyl-4,4′-bis(pyrazolate) spacers, respectively. The thermal stability of the [M(BPZ)]∞, MOFs (T_m ~ 470, 370 and 310 °C for M = Zn, Co and Cu, respectively) was evaluated by combining thermogravimetric analyses and variable-temperature PXRD. Their textural properties (BET specific surface area, pore size distribution) and their ability as CO_2 adsorbents were investigated through N_2 and CO_2 adsorption. After thermal activation, [Zn(BPZ)]∞, adsorbs 22 wt % CO_2 at the mild conditions of 298 K and 1.2 bar, hence ranking among the best performing MOFs in this context to date. Moreover, at 298 K [Zn(BPZ)]∞, shows the remarkable CO_2/N_2 selectivity of 25 and a (ΔH_ads)_{CO_2} of 20.3 kJ/mol.

Figure 1

References
Towards the synthesis and application of a neutral cage

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The introduction of a second coordination sphere around a metal catalyst adds an additional handle towards new selectivity and activity in transition metal catalysis.1 However, features such as compatibility and stability of a supramolecular system can lead to several limitations in certain catalytic applications. For example, solubility often narrows the use of metal-coordination cages as catalytic systems. To expand catalytic applications of the encapsulated catalyst, a neutral host system could be used, which is possibly soluble in a wider range and less coordinating solvents. The aim of this work is to encapsulate cobalt porphyrin catalyst in a neutrally charged covalent cage, designed by the group of Kim (Figure 1).2 This encapsulated porphyrin catalyst can be used in catalytic applications such as radical type transformations.3

Figure 1

References

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Gold(I)-catalysed transformations of heterocycle derived 1,3-enynes

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Following our interest in the chemistry of lactam and lactone derived triflates and phosphates as key intermediates in the synthesis of natural compounds, we have previously demonstrated that the gold(I)-catalysed reaction N-Boc protected 6-alkynyl-3,4-dihydro-2H-pyridines affords synthetically useful vinylogous amides (Figure 1).1 On the other hand, when the N-protecting group is a p-toluensulfonyl (Ts), this intramolecular path is prevented. An intermolecular reaction with an external oxidant can then be featured: in the presence of Au(I) as a catalyst and a pyridine N-oxide derivative as an oxidant,2 the synthetic transformation provides access to divinyl ketones in which one of the double bonds is embedded in a heterocycle. These structures are widely represented in natural products and additionally they can be easily converted into polycyclic compounds under feasible electrocyclic Nazarov reaction (Figure 1).

References
Chiral aminoalcohol fragments attached to squaric acid core as backbone for asymmetric borane reduction

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Chirally modified boron complexes have been object of significant interest in recent years due to their ability to induce enantioselectivity in reduction reactions. Asymmetric borane reduction (BH$_3$·SMc$_2$) is one of the most efficient ways for generating enantiomerically pure secondary alcohols. Remarkable success in this reaction has been achieved using chiral oxazaborolidines either formed in situ or prepared separately from natural compound-derived aminoalcohols such as amino acids, terpenoids etc. Interesting results have been reported recently in which squaric acid is used as a backbone to bind chiral aminoalcohol fragments. These structures can be used as chiral catalysts in asymmetric borane reduction. Squaramides are able to form up to four bonds generating chelate complexes with transition metals and particularly boranes. The rigid squaramide skeleton system in combination with chiral aminoalcohol fragments has been used to provide a structurally well-defined chiral environment for asymmetric induction. We have prepared a series of compounds through combination of squaric acid and chiral amines or aminoalcohols, respectively. Within the current comparative study we aim to investigate the contribution of the squaric acid core (bearing different chiral aminoalcohol moieties) on the degree of enantioselectivity achieved by the reduction of ketones.

All of the new compounds were isolated in very high yields and excellent purity. A series of 1D ($^1$H, $^13$C, $^1$B) and 2D NMR ($^1$H,$^13$C HMBC, $^1$H DOSY) experiments were performed in order to investigate the reactivity and stability of the in situ-formed borane complexes.

Acknowledgements This work was partially supported by the Bulgarian Academy of Sciences, Support for the young scientists in BAS (Project DFNP-144/2016) and by Bulgarian National Science Fund (Projects UNA-17/2005, DRNF-02/13/2009).

References

Platinum-based organometallic-folders for the recognition of electron deficient aromatic substrates

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The combination of soluble metal and ligand precursors spontaneously form metal-ligand bonds that generate the thermodynamically favored products in a process that is often referred to as coordination-driven self-assembly. For this reason, metallosupramolecules are often referred to as supramolecular assemblies. Well-defined cavities are often pursued in this kind of complexes. In this context, we have prepared and characterized a series of platinum complexes with cis-oriented polyaromatic N-heterocyclic carbene ligands. The relative disposition of the polyaromatic ligands about the metal make these compounds to behave as metallofolders, with a hydrophobic pocket defined by the void space between the two polyaromatic functionalities. As shown by their molecular structures (Figure 1), these molecules tend to not leave empty the void space formed by the folder.

![Figure 1](image)

Figure 1 a) Platinum complex used in the molecular recognition; b) X-ray structure of host-guest system between a) complex and 1,2,4,5-Tetracyanobenzene (TCNB).

The molecules were tested in the recognition of aromatic substrates, where they showed a selective affinity to bind electron-deficient molecules. This work demonstrates how the presence of the mutually cis polyaromatic ligands may constitute a very useful tool for the preparation of metal-based receptors.

Acknowledgements We gratefully acknowledge financial support from MINECO of Spain (CTQ2014-51999-P and BES-2015-073136).

References
Oxidative carbonylations\(^1\) are useful reactions in synthetic organic chemistry and in the pharmaceutical industry,\(^2\) for their ability to convert unsaturated low cost molecules in highly valuable carbonylated compounds. Although many examples of alkoxycarbonylation reactions of alkenes and alkynes have been reported in the literature,\(^3\) at the best of our knowledge only very few examples regarding the bis-alkoxycarbonylation of internal olefins are known.\(^4\) On the basis of the acquired knowledge on this type of reaction with terminal olefins,\(^5\) we have developed a very efficient catalytic process for the bis-alkoxycarbonylation of internal alkenes.

The bis-alkoxycarbonylation of aromatic, cyclic and aliphatic 1,2-disubstituted olefins, carried out using Pt(TFA)\(_2\); as palladium source, the easily affordable nitrogen ligand 1a and benzoquinone (BQ) as the oxidant, has allowed to obtain esters of succinic acids with complete diastereoselectivity. The geometry of the carbonylated products comes from a syn overall addition of the carboxyl moieties to the olefin.\(^6\) Moderate to excellent yields have been obtained by using methanol, isopropyl alcohol and benzyl alcohol as nucleophiles (Figure 1). These reactions occur under mild reaction conditions: low pressure of palladium source, the easily affordable nitro-rogen ligand d alcohols.

\[ \text{R}_1 \text{CHO} / \text{THF} = 7:1, P_{\text{CO}} = 4 \text{ bar}, \text{rt}, 66h \]

The bis-alkoxycarbonylation of aromatic, cyclic and aliphatic 1,2-disubstituted olefins, carried out using Pt(TFA)\(_2\); as palladium source, the easily affordable nitrogen ligand 1a and benzoquinone (BQ) as the oxidant, has allowed to obtain esters of succinic acids with complete diastereoselectivity. The geometry of the carbonylated products comes from a syn overall addition of the carboxyl moieties to the olefin.\(^6\) Moderate to excellent yields have been obtained by using methanol, isopropyl alcohol and benzyl alcohol as nucleophiles (Figure 1). These reactions occur under mild reaction conditions: low pressure of CO\(_2\) (4 bar) and room temperature (20°C).

**References**

Regioselective access to conjugated and skipped 1-alkoxydienes through Palladium catalyzed coupling between N-tosylhydrazones and alkoxyallenes

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Palladium catalyzed cross coupling involving sulfonylhydrazones represents today a well-established protocol for the synthesis of polysubstituted alkenes and dienes with universal generality with respect to the coupling partners.1 Recently, their ability to undergo nucleophilic addition with in situ formed allyl palladium complexes has been exploited for the construction of 1,4-dienes starting from allyl halides or allenes.2

In this context, we envisioned that the employment of alkoxyallenes could in turn give access to 1-alkoxydienes,3 whose synthetic potential has been largely investigated by our group.4 Surprisingly, we found out that no aryl halide is required for this coupling and that a reactive allyl palladium species directly comes from an initial hydropalladation of the allene. Tosylhydrazones both coming from diaryl and aryl-alkyl ketones smoothly react affording the corresponding dienes in good yields.

Moreover, a wide range of functional groups are tolerated on the phenyl ring, including halides, thus opening to the possibility of carrying out multicomponent and cascade processes.

Interestingly, with enolizable tosylhydrazones, a differing chemoselectivity arises in the final β-hydride elimination, which produces skipped 1,4-dienes through a C(sp²)-C(sp²) coupling.

Figure 1

References

Poster 54

New Ru(II) half-sandwich photosensitizer able to selectively release its 1,8-naphthalimide ligand using blue light

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The research of new transition-metal complexes for anticancer purposes has grown rapidly after the success of Cisplatin (cis-Pt(NH₃)₂Cl₂). In this context, Ruthenium has proved to be one of the most promising elements[5]. In particular, Ru(II) half-sandwich complexes are really interesting since they usually show lower invivo toxicity and higher selectivity toward cancerous cells if compared with other Ruthenium or Platinum derivatives[5]. Following this line of research, Sadler and co-workers designed some Ru(II) half-sandwich complexes able to selectively photo-dissociate one of the ligands when excited with UV-A or white light[5]. This kind of compounds were designed as photosensitizers suitable for the Photo Dynamic Therapy (PDT), a less invasive and not surgical therapy which is yielding excellent results in the treatment of many different diseases[5]. In this work, the synthesis and the photochemical behaviour of a new Ru(II) aren complex are described. This complex acts as a photosensitizer since it has the ability to selectively release its 1,8-Naphthalimide monodentate ligand after irradiation with blue light, a biologically suitable light source [Figure 1].

Figure 1

References
Towards a redox-active cubic assembly using perylene bisimide

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Supramolecular chemistry makes use of non-covalent intermolecular interactions, such as hydrogen bonding, metal-ligand interactions and π-π stacking, to form “cages” from simple building blocks. These cages can function as a second coordination sphere, similar to enzymes.[1] However, in most reports the supramolecular assembly solely acts as a static capsule, rather than an stimulus-responsive or active participant in a (catalytic) reaction.

Figure 1 Schematic representation of a redox-switchable, cubic assembly.

In this research we aim to develop redox-active 3-dimensional (cubic) assemblies from a linear coordinating bispyridine building block (see Figure 1). This ligand contains a perylene bisimide (PBI) core, which is well-known for its redox- and photochemical properties.[2] We envision that these properties allow modulation of the electronics of interior of the cage and, by doing so, perturb any guest inside.

References

Structural patterns in bis(fluorenyl)stannane derivatives

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Organotin derivatives have been intensively investigated in the last decades due to their possible applications in catalysis and synthesis of new organometallic compounds with controlled properties. The stability of the Sn-C bond depends highly on the nature of the organic substituent and can be enhanced by using groups having both electronic and steric effects.

We describe here a series of new stable functionalized bis(fluorenyl)stannane derivatives, symmetrical and unsymmetrical, with the general formula presented in Scheme 1.

Scheme 1 General structure of functionalized bis(fluorenyl)stannane derivatives.

The synthetic pathways used for the preparation of the derivatives are discussed and the structural characterization through the usual spectroscopic methods (NMR, HRMS, etc.). Emphasis is put on the structural differences observed in the solid state and the conformations adopted were interpreted in terms of C-π interactions, that have previously been identified for similar derivatives.1,2,3

References
In the last few years, the use of gold in homogeneous catalysis has experienced increasing attention and progress. Although typically regarded as superior Lewis acids for the activation of multiple C–C bonds towards nucleophiles, transformations involving Au(III) species have recently emerged: catalytic cycles involving a change in the oxidation state of gold could be devised, which have broadened the scope of gold catalysis, particularly in the context of oxidative cross-coupling reactions. In spite of the growing number of examples in this field, the access to key Au(III) intermediates has been limited to harsh sacrificial oxidants, such as I$_3^-$ derivatives or P$_2$O$_5$ sources, as well as using highly electrophilic aryldiazonium salts under photooxidation conditions or via light-driven radical chain reactions. We have recently demonstrated that hemi-labile (P,N) bidentate ligands can provide a suitable balance between reactivity and stability of the key Au(III) species: k$_1$-P coordination to the soft Au(I) center provides a reactive [LAu]$^+$ complex, and upon oxidative addition, the pendant amine group coordinates the resulting hard Au(III) center and tempers its reactivity. The derived cationic Au(I) complex readily promotes oxidative addition of a large scope of ary iodides and bromides. The potential of (P,N) Au(I) complexes in Au(I)/Au(III) catalysis has also been demonstrated by the development of the first gold-catalyzed C–C and C–N cross-coupling from aryl halides.

Figure 1 Ligand design envisioned to trigger oxidative addition of aryl iodides to gold(I) complexes.

References

Homogeneous electrocatalytic reduction of CO$_2$ by selected transition metal complexes

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Since the first industrial revolution the atmospheric concentration of CO$_2$ has grown from 200 ppm to 410 ppm. As it is well known, CO$_2$ is a key greenhouse gas and its excessive atmospheric accumulation cannot be balanced by the earth’s natural carbon cycle, resulting in an uncontrolled global temperature rise and inducing significant non-physiological changes in the planet’s climate. The sustainability and encouraging performance displayed by the electrochemical conversion of carbon dioxide into value-added chemicals, (e.g. CO, HCOOH and CH$_2$OH), which is mediated by transition metal complexes, has attracted growing interest in recent years for the possible positive impact on global economy and environment. The electrochemical reduction of CO$_2$ to fuels and/or fuel precursors still requires low-cost, efficient and selective catalysts for a sustainable energy economy. Most electrocatalytic studies in this field focus primarily on the catalyst/substrate interaction in homogeneous solution even if the heterogeneous electrochemical catalysis could represent an alternative in terms of the large number of potential advantages such as easier recovery of products and catalysts, small amounts of catalyst necessary for efficient electrolysis, deactivation pathways often hindered or suppressed and elimination of solubility problems. In this context, homogeneous electrocatalysis is a suitable method to achieve the goal. The pioneering paper published by Saveant et al. has reported the capability of Fe(0) porphyrins containing pendant phenolic acids of enhancing the selectivity and the activity of this catalysts in the reduction of CO$_2$ to CO. For this reason, two novel poly(pyridyl Mn(I) and Re(I) derivatives containing two acidic OH groups in proximity of the metal center (Mn-OH orto and Re-OH orto) were synthesized, characterized, and investigated as redox catalysts for CO$_2$ reduction in order to deeply investigate the role of a local proton source effect on their catalytic activity. The electroreduction of CO$_2$ of both complexes occurs even in absence of brominated acids and this unique behavior has been ascribed to the structure of dipyridyl ligand (dipyrr-4-phenyl)-2,2'-bipyrindine, in which the pendant phenolic groups near the metal center act as intramolecular proton sources. The results are compared with other Mn and Re complexes in order to demonstrate that little modification in the position of the pyryl-localized phenolic groups is able to produce substantial differences in the reductive mechanism under Ar, even inducing a different reactivity towards CO$_2$.

References
Poster 59

Synthesis, characterization and cytotoxicity of new Rh-Ge carbonyl clusters

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The chemistry of homodi- and hetero-metallic rhodium carbonyl clusters has been widely investigated in the last decades. Nevertheless, there are not so many examples of Rh clusters which interstitially host heavier elements than carbon and nitrogen and, among these, no one presents an inner germanium atom. Therefore, we have focally concentrated our interest on the reactivity of the \([\text{Rh}(\text{CO})_2][\text{NEt}_3]^+\) cluster precursor with Ge\(^{16}\) and Ge\(^{25}\) salts, in order to obtain new Rh-Ge carbonyl clusters, with Ge interstitially hosted. By reacting an acetonitrile solution of \([\text{Rh}(\text{CO})_2][\text{NEt}_3]\) with a solution of GeCl\(_4\) in the same solvent, under N\(_2\) atmosphere and at room temperature, it is possible to obtain \([\text{Rh}_3\text{Ge}(\text{CO})_2]\)\(^{2-}\). Instead, by reacting the same cluster precursor with GeBr\(_2\), \([\text{Rh}_3\text{Ge}(\text{CO})_2]\)\(^{3-}\) could be synthesized. Moreover, this last compound in solution under CO atmosphere undergoes a reduction process, forming the icosahedral species \([\text{Rh}_9\text{Ge}(\text{CO})_2]\)\(^{3-}\). These three new Rh carbonyl clusters have been characterised by IR spectroscopy and ESI-MS spectrometry and their molecular structures determined by X-ray diffraction studies.

Cytotoxicity tests of the two new compounds obtained under nitrogen atmosphere are ongoing.

References


Poster 60

Transfer hydrogenation of imines using water/toluene as biphasic medium

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The hydrogenation of organic compounds is a reaction of great importance in many fields like fine chemistry and pharmaceuticals. Transfer hydrogenation is an important alternative to catalytic reduction with H\(_2\), involving the formal transfer of H\(_2\) from a donor molecule to a substrate. The new complex \((\eta^6-p\text{-cym})\text{RuCl}(\text{C}-\text{N},\text{N}-\text{dmbpy})\)\((\text{BF}_4)^{-}\) is water-soluble and active in the catalytic transfer hydrogenation (TH) of different ketones and imines using aqueous HCOONa/HCOOH as the hydrogen source at pH 4.4. In this communication, we describe the TH of several imines using a mixture of water/toluene as a solvent in a biphasic medium. The system allows an easy separation of the organic products.

In order to obtain a detailed microscopic description for all the steps of the catalytic TH cycle, NMR studies have been carried out. In addition, calculations at this level also support the participation of the stated aqua, formato, and hydrido intermediates in the catalytic reaction and provide a detailed microscopic description of the full catalytic cycle on the basis of DFT calculations.

References

A new class of catalysts has recently brought the attention of researchers, which is generated by pyrolyzing first transition row metal complexes with nitrogen ligands adsorbed on an inert support, such as carbon, silica. The catalysts have a metal/metal oxide core, surrounded by a few nitrogen-enriched graphene layers (NGr). These materials, which only contain cheap and abundant metals such as iron and cobalt, catalyze reactions for which noble metals are usually required; thus representing a cheaper and more sustainable alternative of the costly noble metals. Until now, such catalysts have been employed mainly in the context of hydrogenation reactions. The objective of this work is to expand the field of applicability of this new class of catalysts. We have used Fe₂O₃/NGr@C to catalyze olefin cyclopropanation, a reaction for which the use of these catalysts has not previously been investigated. The activity of Fe₂O₃/NGr@C has been studied by using ethyl diazoacetate and α-methylstyrene as substrates. Various parameters such as solvents, temperature and time were changed. Fe₂O₃/NGr@C-catalysts showed best activity in dimethoxyethane at 60 °C, affording high yields of the desired cyclopropanes (mixture of cis and trans isomers) and only 1-2 % of ethyl maleate and fumarate.

Figure 1 Nanoscaled Fe₂O₃ particles surrounded by nitrogen-doped graphene layers.

References
**Poster 63**

Reactivity of palladacyclopentadienyl complexes toward halogens addition. The influence of the ancillary ligand.

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The organometallic palladacyclopentadiene fragment $\text{Pd(C–COOR)}_3$ is an important synthetic intermediate that is involved in $\text{Pd(0)}$ catalyzed $[2+2+2]$ alkyne cyclotrimerization and cocyclotrimerizations. Palladium complexes bearing the cyclopentadiene fragment easily undergo attack by halogen, interhalogen or organic halides usually yielding a $Z$-$Z$ substituted butadiene fragment $\pi$-coordinated to the metal as a consequence of oxidative addition and subsequent reductive elimination. We have recently studied the reactivity of palladacyclopentadienyl complexes stabilized by different spectator ligands and the information we have gathered can be summarized as follows: i) the nature of the spectator ligands markedly influences the reactivity of their palladacyclopentadienyl derivatives, ii) sometime the spectators may change their obvious role and become actual ligands. In this abstract we report probably the most interesting reaction that is the addition of iodine to palladium $N$-heterocyclic carbene–pyridine palladacyclopentadiene complexes (Scheme 1).

![Scheme 1](image)

The unexpected final products are characterized by a ten term coordinative ring. We have proposed a plausible mechanism on the basis of a dedicated computational approach.

References


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**Poster 64**

Solution structure of AlMe$_2$F and its Reactivity with metallocenes: mimicking cation-anion interactions in metalloocene-MAO inner-sphere ion pairs

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The solution structure of AlMe$_2$F and its reactivity with a prototypical $\alpha$-or $\beta$-metalocene (ETH)ZrMe$_2$ [ETH = rac-(ethylene-bis-4,5,6,7-tetrahydro-1-indenyl)] have been investigated by advanced high resolution 1D, 2D and PGESE (Pulsed Gradient Spin Echo) NMR techniques, with the aim to indirectly shed some light on the "structure and working principles" of methylalumoxane (MAO) mixtures, a key component in homogeneous Ziegler-Natta catalysis. It is found that AlMe$_2$F generates in solutions an equilibrium mixture of oligomeric species differing in the number and arrangement of AlMe$_4$ constituting units. In particular, hexamers, pentamers and two distinct tetrameric species, one of which having an unprecedented heterocubane (Me$_2$Al)$_4$ structure (Figure 1, top), are mainly present in solution. Furthermore, the reaction between (ETH)ZrMe$_2$ and an excess of AlMe$_2$F produces a complex mixture of species in chemical equilibrium. Detailed low-temperature NMR experiments indicate the formation of [(ETH)ZrMe$_2$(μ-$\mu$-F)(AlMe$_2$F)$_n$] (n = 0, 1, 2, 3) inner sphere ion pairs which equilibrate via successive insertions/deinsertions of AlMe$_2$F units into the Zr–(μ-$\mu$-F) bond (Figure 1, bottom). Polymerization tests confirm that, similarly to metalloocene/MAO systems, mixtures of (ETH)ZrMe$_2$ and AlMe$_2$F are capable of polymerizing propene to prevailingly isotactic polypropylene without the addition of other ionizing agents.

![Figure 1](image)

Equilibria involving AlMe$_2$F (up) and species derived from the reaction of AlMe$_2$F with (ETH)ZrMe$_2$ (bottom).

References

Copper(II) coordination chemistry with various carboxylates has been investigated for a long time. Such relationships attract much attention due to the variety of types of coordination adopted by carboxylate ligands. Dimeric carboxylates attract the attention of many researchers not only in interactions between adjacent metallic centers, but also because of their bioactive and biocatalytic functions. An important feature of the biologically active compounds is their solubility in water. One of the most common ways of obtaining water-soluble metal complexes is use of hydrophilic ligands such as 1,3,5-triazine-2,4,6-triactate (PTA) and its derivatives, e.g. PTA = O. Water solubility is also one of the most important properties that allow the use of coordination compounds in medical chemistry as anticancer agents (Cu, Ag, Au, Ru), catalysts (Ru, Rh, Pd) or luminescent materials (Au, Cu, Ag). Moreover, in nature, such metalloproteins (the active center is copper(II)) are very efficient catalysts for the oxidation of o-diphenols to the corresponding o-diaquinones by the electron reduction of molecular oxygen to water. Therefore, studies on the model compounds that can be active as bioinspired catalysts with catecholase activity are promising for the evolution of new catalytic systems. In this contribution we report three new coordination complexes namely a 0D dicopper(II) complex [Cu$_2$(μ-PTA)(MeOH)$_2$](PTA=O)$_2$, a 3D metal-organic framework (MOF) [Cu$_4$(μ-PTA)(μ-PTA=O)$_4$]$_n$, and a mixed-valence copper(II)/III 1D wave-like metal-organic chain Cu$_2$(μ-PTA)$_2$[acetate$_2$(PTA)]$_n$. We report crystal structure, spectroscopic characterization, magnetic properties for I-3, and additionally for complex (1) and (2) catecholase activity study.

References


**Figure 1**

M = Pd$^{2+}$, Y$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$

**References**

Cationic, neutral and anionic hydrides of Iridium with PSiP pincers

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Transition-metal hydride complexes are almost ubiquitous in organometallic catalysis and energy conversion and storage paradigms.1 In particular, those of iridium promote or mediate catalytic transformations of actual or potential industrial importance.2,3 Behind this singular reactivity are factors such as the exceptional mobility of metal-bonded hydrogen atoms,4 and their strong σ-donor character and trans influence as ligands which become less decisive when other strong σ-donor ligands are present, for example silyl-donor (PSiP)5 or boryl-donor (PB) pincers.6 These strong σ-donor pincers have been observed to expedite migratory insertions into M–H bonds, thus being particularly suitable for challenging catalytic transformations such as those involving carbon dioxide.7 This work describes synthetic routes from the known precursor [IrClH{α,P,P,Si(Me)(C6H4–2-PiPr2)}] (Scheme 1) to new hydride and polyhydride derivatives. The range of possible reactions enabled can be extended by replacing the chloride ligand. It leads to obtain a variety the hydrides complex with different charge and different number of hydride ligands.

Scheme 1 Synthetic routes from [IrClH{α,P,P,Si(Me)(C6H4–2-PiPr2)}].

The structures and the NMR spectrums obtained confirm the importance the trans influence of the sylil group to define the coordination environments and the ability of this pincer in the mer coordination mode.

References


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Application of allylic compounds in the Heck reaction catalyzed by palladium compounds

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Palladium-catalyzed C–C coupling reactions with allylic alcohols as substrates is one of the methods of synthesis saturated and α,β-unsaturated aldehydes.2 These compounds can be useful intermediates for the preparation of medicinal products or used in another organic syntheses. Reactions with cinnamyl alcohol and linalool as substrates are not widely described in literature. In the reactions with cinnamyl alcohol we obtained five products-diarylated compounds (a–d). The main product – b was obtained in 57% yield.

Figure 1 Studied Heck arylation of allylic alcohols catalyzed by palladium catalyst.

Pd-compounds such as Pd(OAc)2, PdCl2COD or Pd(acac)2 were used as catalysts. The reaction was studied with variation of parameters such as different temperature (50°C – 120°C) and time (3 h – 24 h). In this reaction we used weak bases - NaHCO3, NaOAc, K2CO3 and Et3N and the best results were obtained with NaOAc. When Et3N was used as the base products a and b were formed. The highest conversions of PhI, 56-93%, were obtained in the mixed solvent, DMF and water in ratio 1:1. The linalool is widely used in cosmetics but it can also provide interesting material for the synthesis of arylated unsaturated alcohols (A and B). Initial experiments showed that we can obtain 68% of product A after 5 h in 120° C with NaOAc as a base. We have also obtained good results with another allylic compounds like as eugenole or estragol. Using mild conditions, such as heating in 100°C for 3h, let us to obtain 100% conversion of Phd and 84-92% of derivatives of 1,3-diphenylpropenes.

References


Among the various nanomaterials, certainly arouse great interest the metallic nanoparticles and specifically the MNPs obtained from noble metals which, thanks to their properties, have potential applications in different fields. Their use is very important especially in nanomedicine in the loading and release of drugs (drug delivery) [1]; or they are used as diagnostic imaging tracers [2]. Other applications are in catalysis [3] and sensors [4]. Fundamentally, in order to obtain reduced size and monodispersion, are the synthetic route and type of binder chosen for stabilization and functionalization. The synthesis used for these nanoparticles of gold and silver, is a single phase synthesis in water where a metallic precursor is reduced from a strong reducing agent in the presence of a hydrophilic ligand (example: cystamine) [2]. The MNPs synthesized have been applied in different fields, for example the nanoparticles stabilized with cystamine have been used to extract the polyphenolic compound in the EVOO matrix.

![Synthesis of noble metal nanoparticles functionalized with hydrophilic ligands for biotechnology application](image)

**Figure 1**

**References**


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**Poster 69**

**Synthesis of noble metal nanoparticles functionalized with hydrophilic ligands for biotechnology application**

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The vast field of metal-organic frameworks (MOFs) and coordination polymers (CPs) has been incessantly developing due to their potentiality in a wide range of key functional applications, e.g. gas storage and separation, drug delivery, biochemistry, luminescence, catalysis, just to mention only a few. A CP is an inorganic or organometallic polymer structure containing metal cation centers linked by organic ligands with repeating coordination entities extending in 1, 2, or 3 dimensions. MOFs occupy a special place amongst porous materials owing to their extraordinary surface areas (routinely > 2500 m²/g) topological diversity and high functional tenability. The properties of MOFs can be changed via the functionalization of the ligand. Poly(pyrazolate)-based spacers have gained increasing attention as an alternative to poly(carboxylate)-based ones in the design and preparation of thermally stable, functional CPs and MOFs. In this work, we have reported, by conventional and solvothermal route, the synthesis, characterization and some applications of novel porous and non-porous coordination polymers based on different bis(pyrazolyl)tagged ligands [M(BPZ₂₃₃₆)₃] (M = Zn, Cu, Ni; BPZ₂₃₃₆ = [4,4'-bipyrazolate]-3-amine), [M(BPZ₂₃₃₆)₃] (M = Zn, Co, Ni; BPZ₂₃₆₂₃₆ = [4,4'-bipyrazolate]-3,5-diamine), and [Ag(BPZ₂₃₆₂₃₆)] (BPZ₂₃₆₂₃₆ = 3,3'-dimethyl-4,4'-bipyrazolate). Figure 1. Their crystal structures have been solved from powder X-ray diffraction (PXRD). They are isotypical to the analogous M(BPZ₂₃₆₂₃₆)₃ and [M(BPZ₂₃₆₂₃₆)] (M = Cu, Zn, Cd). The thermal stability was evaluated by combining thermogravimetric analyses and variable-temperature PXRD. Their textural properties (BET specific surface area, pore size distribution) and their ability as CO₂ adsorbents were investigated through N₂ and CO₂ adsorption. Moreover, at 298 K [Zn(BPZ₂₃₆₂₃₆)] shows the remarkable CO₂/N₂ selectivity of 26 and a (∆Δ(ads))CO₂ of 35.6 kJ/mol.

**Figure 1** Crystal structure of [Ag₄H₃BPZ₂₃₆₂₃₆]PF₆

**References**


Selective oxidation of alkenes catalysed by well-defined [Iron(III)(PcL)] complexes

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The introduction of a pyridine moiety into the skeleton of a polyazamacrocyclic ligand affects both thermodynamic properties and coordination kinetics of the resulting metal complexes.1 Some features have engendered a great interest of the scientific community in recent years. The applications of pyridine-containing macrocyclic ligands ranges from biology to supramolecular chemistry, encompassing MRI, molecular recognitions, materials and catalysis. Much of the efforts in the use of macrocyclic pyridine containing ligands have been devoted to the study of catalytic oxidation reactions. We report here the synthesis and characterization of [Fe(III)PcL’s] complexes (PcL = Pyiridine-containing Ligand) and their catalytic applications in alkene epoxidation or cis-dihydroxylation reactions using H2O2 as the terminal oxidant under mild conditions (Figure 1). Depending on the anion employed for the synthesis of the iron(III) metal complex, we observed a completely reversed selectivity. When X = OTf, a selective cis-dihydroxylation reaction was observed. On the other hand, employing X = Cl, we obtained the epoxide as the major product (traces of aldehyde were observed at very high conversions). It should be pointed out that under otherwise identical reaction conditions, using FeCl3·6H2O as catalyst in the absence of the ligand, no reaction was observed.

References

Iridium water oxidation catalysts based on substituted Pic ligands

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The production of solar fuels has been proposed as a feasible part of the solution to the global energy problem.1-3 The bottleneck in this development is water oxidation, so much effort is devoted to synthesize an efficient water oxidation catalyst (WOC).4 Iridium(III) catalysts with coordinated pentamethylcyclodienyl (Cp*) and pyridinecarboxylate (picolinate = pic) ligands have proven to be highly efficient, reaching all time high turnover frequencies (TOFs) and numbers (TONs) for water oxidation driven by ceric ammonium nitrate (CAN)5 and NaIO4.6 In this project a correlation is sought between the TOF and the electron withdrawing or donating properties of substituted pic ligands, in NaIO4 driven WO experiments. This is done by varying the position and nature of substituents on the pic ligand (Figure 1). Catalytic performance is quantified and qualified by kinetic measurements with differential manometry and Clark electrode, respectively.

References
Towards new cobalt complexes for nitrene generation

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The formation of carbon-nitrogen bonds is an important step in the synthesis of pharmaceuticals and natural products. The generation of nitrene or imidyl intermediates in the coordination sphere of transition metal complexes has been recognized as an efficient approach for the formation of new C-N bonds from C-H bonds. The goal of this research is the development of new cobalt complexes which are suitable for the formation of cobalt-nitrene or -imidyl intermediates. The metal centre in these complexes is supported by new tetradentate nitrogen-based ligands, with either an electron donating or withdrawing character. By this virtue we hope to achieve two goals; (a) a more electron-donating cobalt-catalyst which facilitates azide activation and subsequent radical-type C-H amination and (b) generation of the same nitrene/imidyl intermediates through oxidative PCET-type activation of the N-H bonds in primary amines.

References
**Poster 75**

New synthesis of ruthenium phosphide nanoparticles and their application as hydrogenation catalyst

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Ruthenium phosphides have proved to be effective catalysts for hydrodesulfurization,\(^1\) hydrodeoxygenation\(^2\) and recently they have also been tested as electrocatalyst for oxygen reduction in acidic medium.\(^3\) We report here a new synthetic route to ruthenium phosphate nanoparticles starting from Ru(0) nanoparticles\(^4\) and white phosphorus as a cheap and convenient ‘P’-source, instead of common methods based on metal salt precursors and alkyl phosphine, P(SiMe\(_3\))\(_3\) or NaH\(_2\)PO\(_2\) as phosphorus donors. The nanoparticles Ru\(_2\)P prepared by this route, exhibit a narrow size distribution with average diameter of 2.2 nm. Applications of these nanoparticles in the catalytic hydrogenation of nitroarenes has been investigated and they resulted efficient and selective catalysts (Figure 1).

**Figure 1**

\[\text{Ru(O) NPs} \quad \text{Ru}_2\text{P NPs}\]

References


**Poster 76**

Improving gold catalytic activity by anchoring molecular catalysts onto reduced graphene oxide

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Although it was initially considered as inert, gold has proved his potential in catalysis as nanoparticles, clusters or molecular complexes.\(^1,2\) While homogeneous catalysts are usually more active and selective, its poor stability and difficult recyclability make them useless for industrial applications. Moreover, catalyst separation from the reaction media is an issue that must be tackled, especially in the pharmaceutical industry, where even small amounts of metal in the final product are not acceptable. In the last years, our group has been focused in the immobilization of homogeneous catalysts onto graphene by means of non covalent interactions (Figure 1).\(^3\) The results show that the immobilized catalysts are recyclable and improve the catalytic properties of the molecular entities.\(^4\) Here we show that the immobilization of gold complexes onto the surface of reduced graphene oxide lead to an outstanding increase of the catalyst activity. The interaction between the complex and the surface is strong enough to allow the catalytic reactions without loss of activity. Furthermore, analysis of the new hybrid material before and after the catalysis shows the absence of metal nanoparticles, which indicates that the active species on the surface of the material is molecular.

**Figure 1**

References

Biocatalysis and MCRs: a potential green strategy for the synthesis of high added-value compounds starting from biomass

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In recent years lignocellulosic biomass materials are receiving increased attention as a renewable, economical, and abundant alternative to fossil resources for the production of chemical building blocks. The latter products can be further transformed into high added-value products. For these reasons our group is implementing an overall strategy to access to a variety of drug-like, biobased heterocycles with control of stereochemistry, starting from biomass derivatives. To this purpose the project involves the coupling of three techniques:

- Biocatalysis affords chiral precursors, bearing a variety of alternative appendages, which are used to direct the stereochemical outcome of the multicomponent reaction.
- Diastereoselective Passerini reaction represents a very powerful tool in diversity-oriented synthesis, allowing the introduction of several diversity inputs in a single step. It can afford interesting polyfunctionalized intermediates that could be manipulated to give a variety of heterocycles.
- Post condensation cyclizations allow to broaden the scaffold diversity through the obtainment of heterocyclic systems.

As biomass derived starting material we chose erythritol, a meso natural polyalcohol that can be found in fruit and fermented food. It is well known as non-caloric sweetener and it is biotechnologically produced from common sugars using various microorganisms.

Figure 1

This communication will focus on the synthetic elaboration of the chiral molecules obtained through biocatalysis to give enantiomerically pure building blocks to be used in the Passerini reaction. The preliminary results of the diastereoselective multicomponent reaction and the following cyclizations will be discussed as well.

References

Design, synthesis and iodine capture properties of new non-covalent microporous materials based on heteronuclear clusters

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The effective capture and immobilization of radioactive forms of iodine, namely $^{129}$I and $^{131}$I, formed as side products in nuclear power plants is a growing priority for treatment of nuclear waste forms. Various groups of porous materials have been regarded as promising materials for applications in capture and safe storage of toxic chemicals, including radioiodine. Solid sorbents currently or recently deployed in plants include Ag-loaded zeolites (e.g mordenite or faujasite), however low porosities of these materials result in low iodine loading capacities. Among porous materials iconic zeolitic imidazolate framework-8 (ZIF-8),‡ MIL family, and very recently a new class of COFs (SIOC-COF-7) have been studied for capture and storage of radioiodine. According to the type of bonds between their basic building units we can distinguish materials with strong covalent or coordination bonds like metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). Less common, although very promising materials, are non-covalent porous materials (NPM), where weak interactions between building units are responsible for their porosity and stability. This contribution is dedicated to the study of iodine sorption in noncovalent porous materials as an alternative to zeolites and other porous materials with strong covalent or coordination bonds. We designed and synthesized new NPM materials based on heteronuclear clusters with specific diamond crystal structure. We will demonstrate our approach to the synthesis of these new NPM materials and we will demonstrate the sorption properties for iodine vapors and other gases (N$_2$, Ar, CO$_2$, H$_2$).

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References
Palladium catalyzed functionalization of unsaturated ketones under microwave conditions

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Synthesis of arylated unsaturated ketones is a very important area of interest in synthetic chemistry for many years. Due to their properties, these compounds are used in food industries as a flavoring agents or as intermediates in the synthesis of pharmaceuticals. Currently known organic methods of synthesis of unsaturated ketones are connected with formation of environmentally unfriendly wastes. It motivates to search of new synthesis ways, one of which is a palladium catalyzed tandem Heck arylation of unsaturated ketones (Rys.1):

We performed experiments with unsaturated ketone, 3-buten-2-one and PhI as a model system; using Pd(OAc)$_2$ catalyst. The reaction was carried out in the presence of NaHCO$_3$ as a base and DMF/H$_2$O as a solvent in 160°C and 1h under microwave conditions. After this time we obtained 95% yield of product A. In the second step another aryl iodide (4-iodoanisole) was added to the same catalytic system and the reaction was continued using microwave heating for 2h at 120°C. As a result, 70% of product B was obtained. Product B can be next transformed to saturated diarylated ketone (C), according to two possible pathways, namely hydrogenation or reductive Heck reaction. We optimized reaction condition for reductive Heck reaction by testing various reductive agents. Tripropylamine has turned out to be the best reducing agent for this synthesis and saturated disubstituted ketone (C) was obtained in 67% yield.

Scheme 1 Tandem Heck arylation of 3-buten-2-one.

References


Synthesis of 4,5-fused bicyclocarboline-2-ones through [3 + 2] C-C/N-C bond forming annulation

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Annulation reactions are one-pot two-component transformations that generate cyclic structures via two sequential and mechanistically unrelated bond forming steps between the two components. Although many annulation processes have been reported and some of them are widely used in synthesis, [3 + 2] C-C/N-C bond forming annulation generating saturated pyrrolidine motifs are still missing in the toolkit of the organic chemist. In this context, we have recently discovered that under Pd(0)-catalysis, γ-acetoxy α,β-unsaturated carboxyl compounds 1 react with secondary malonamides 2 to afford 4,5 fused pyrrolidine-2-one derivatives 3. This transformation, that entails an intermolecular carbon acid allylation / intramolecular N-1,4-addition sequence constitutes a [3 + 2] C-C/N-C bond forming annulation. Discovery, optimization, scope and limitations of this method will be presented (Figure 1).

Figure 1

References

Dialkylaluminum alkoxides and aryl oxides stabilized with N-heterocyclic carbenes

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Dialkyl alkoxides and aryl oxides of the group 13 metals stabilized with NHC (N-heterocyclic carbenes) are a new and still poorly developed group of compounds. In recent years, our group have reported several gallium and indium R2MOR(NHC) complexes of interesting catalytic properties in the polymerization of cyclic esters. Despite the importance of NHC gold(I) complexes, there are only few structure-based catalytical studies of this class of complexes in the literature. To further develop our research on the synthesis of unsymmetrically substituted NHC gold species, we herein present detailed study concerning the catalytic activities of NHC gold(I) complexes available by the isonitrile route (Figure 1).

References
Frustrated Lewis pairs (FLPs) is a powerful yet simple concept to activate various chemical bonds through their heterolytic splitting. In order to achieve “frustration”, i.e. prevent formation of classical Lewis adducts, Lewis acid and the Lewis base with sterically bulky substituents are selected. Various parameters such as acid and base strengths, steric hindrance of the reactive centres can be varied to affect reactivity, catalytic activity, selectivity of FLPs. Therefore, FLP chemistry emerged as a powerful tool for activation of a broad range of small molecules, including the molecular hydrogen (H₂). However, sensitivity of FLPs to moisture is considered as one of the serious limiting factors in the widespread application of FLPs as hydrogenation catalysts. The majority of FLP-based catalysts contain highly Lewis acidic organoboron compounds. In light of this, development of water tolerant FLPs for catalysis and other applications remains a big challenge.

Herein we report a new water-stable intramolecular frustrated Lewis pair (FLP) - ansa-phosphinoborane 2. The compound was characterized by ¹H, ¹³C, ³¹P NMR and its structure was determined by single crystal X-ray diffraction analysis. The ansa-phosphinoborane does not react with molecular hydrogen or water at room or elevated temperature. According to performed DFT studies, addition of water or hydrogen to the phosphinoborane are both endergonic but close in thermodynamics. In polar solvents, methanol and acetonitrile, the hydrogen addition is energetically more favourable than the water addition.

![Figure 1](image1.png)  
**Figure 1** Rh¹¹⁰-catalyzed polymerization of ethyl diazoacetate.

The preparation of well-defined, stereoregular polymers bearing a functional group on each backbone carbon is extremely difficult to achieve through classical alkene (C2) polymerization. New avenues to polymers with functional side chains have been opened by coupling of carbene (R1R2C) (C1) monomers derived from e.g. diazo precursors. In C1 polymerization, stereospecificity is still a major challenge and the only catalysts known to catalyze the formation of stereoregular polycarbenes insofar are the cationic Rh¹³⁰ species I (Figure 1). With I, polycarbenes such as poly(ethyl 2-ylideneacetate) could be obtained in a fully syndiotactic fashion in yields up to 85% and Mₚ, up to 770 kDa. As a result of the functionalization of every carbon of the backbone and the stereoregularity (i.e. not a single error in stereospecificity), the tertiary structure of the polymer and therefore its appearance and physical properties are strongly impacted. Whereas atactic poly(ethyl fumarate) is a sticky red oil, its stereoregular carbene analogue (poly(ethyl 2-ylideneacetate)) folds into triple helices held by Van der Waals interactions¹ and the polymer appears an elastic white film (Figure 2). In pursuit of similar stereoregular polymeric materials, we are currently investigating the polymerization of alkyl-substituted diazo compounds derived from N-tosyl hydrazones.

**Figure 2** An illustration of the influence of the secondary polymer structure on its appearance and physical properties.
Silver(I) sulfadiazine coordination polymers as a new effective antimicrobial and antivirus agents.

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Sulfadiazine (4-amino-N-pyrimido-2-yl-benzenesulfonamide) is one of the most effective and safe medicines needed in a health system. It is in the sulfonamide class of medications and it is available as a generic medication used for toxoplasmosis, chancroid, chlamydia and many inflammatory disease. Sulfonamides are still among the most widely used and studied antibacterial agent in the world. Interest in the silver complexes is due to its many possibilities of coordinating, active binding sites are the pyrimidine N atoms, the sulfonamido N and one sulfonic O, it is giving rise to a polymeric arrangement moreover, the various forms of the complex obtained may be dependent on dielectric constant solvents. Another strong antimicrobial agent is silver ions, which already have an effect at low concentrations. Silver ion preferentially binds to cell surface receptors of bacteria, yeast and fungi and it appears to be critical to antimicrobial action. By combining these two agents and creating their derivatives with PTA (1,3,5-Triaza-7-phosphaadamantane), we try to obtain new complexes with desirable physicochemical properties such as water-soluble and persistent to solar radiation. The use of PTA is dictated by its coordinating capabilities and the ability of us to impart the desired attributes to our complexes. PTA and its derivatives have increasing number of interest coordination compounds related to its hydrophilic thereby biological active complexes. Herein the obtained coordinating polymers will be characterized in terms of structure, physicochemical properties and electron analysis. In the further part of the study, it is intend to investigate antibacterial properties.

Figure 1 Sulfadiazine.

References

Rational Design Rule for Molecular Water Oxidation Catalysts based on Scaling Relationships

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Optimizing the water oxidation reaction is of paramount importance for the development of sustainable fuel production. We show that mechanism for water oxidation has an intrinsic influence on the theoretically achievable minimal overpotential, based on scaling relationships. The water nucleophilic attack (WNA) mechanism results in catalysts with a fundamental minimal overpotential of ~0.3 eV. While catalysts operating via a radical oxo coupling (ORC) mechanism do not suffer from this limitation and therefore, design strategies for efficient water oxidation catalysts should focus on the later mechanism. Figure 1 Two possible mechanisms for water oxidation.

References
Poster 87
Cation-driven self-assembly of a gold(I)-based metallo-tweezer

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Gold(I) complexes are known to form stable linear compounds with aryl-acetylide, and this has been extensively used for the synthesis of oligomeric and polymeric materials with attractive photophysical properties.\(^1\) In addition, alkynyl-gold(I) fragments are able to form supramolecular architectures based on their tendency to afford linear geometries and self-assembly structures through aurophilic interactions.\(^2\) Based on these precedents, we envisaged that the parallel orientation of the alkynyl fragments in 1,8-diethynyl-anthracene, in combination with a N-heterocyclic carbene ligand fused with a pyrene fragment (Scheme 1), should allow the formation of a di-gold(I) tweezer with unprecedented recognition properties. The presence of the two arms containing the pyrene moieties, together with the anthracene linker provides two sites with the potential to bind aromatic guests through \(\pi-\pi\) stacking. In addition, the presence of the two gold(I) centers, provides an additional binding motif through aurophilic and metallophilic interactions, thus introducing a new dimension in the recognizing abilities of the tweezer, which may also be sensitive to the presence of metal ions. Indeed, we have demonstrated that the self-assembly of the di-gold(I) tweezer proceeds in the presence of \(M^+\) cations such as Ag\(^+,\) Tl\(^+\) and Cu\(^+,\) giving rise to duplex complexes 3, 4 and 5, respectively.\(^3\)

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