XXXVI GEQO CONGRESS ORGANOMETALLIC CHEMISTRY GROUP

Book of Abstracts

Zaragoza, 5-7th September 2018

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WELCOME

On behalf of the Organizing Committee, it is our great pleasure to welcome you to Zaragoza, to the **XXXVI Congress of the Specialized Group of Organometallic Chemistry (GEQO)** of the Spanish Royal Society of Chemistry that will take place in the Auditorium of Zaragoza between the 5th and the 7th of September 2018.

This is already the XXXVI edition of this series, which started in 1981 in Alcalá de Henares and was also celebrated in the Aragón Community in 1985 in Jaca (Huesca). Now, it comes to Zaragoza, in which a long standing tradition in the Organometallic Chemistry research exists.

GEQO2018 will cover a wide range of topics in and around the field of Organometallic Chemistry. As organizers, we are very proud of the Top-Quality Researchers we were able to gather as plenary and as invited speakers in this edition of GEQO2018. Moreover, we are confident that the selected 16 oral communications as well as the almost 150 posters presented will also contribute to the scientific excellence of this edition. We hope that you can find within this meeting the optimum environment to discuss and exchange stimulating ideas that could culminate in fruitful collaborations.

Moreover, for those who have not visited yet Zaragoza, remember that our city has a rich heritage of historical monuments such as Basilica of El Pilar, San Salvador Cathedral, Aljafería Palace, the paintings of Goya or the Mudejar–UNESCO Heritage of Mankind as well as renewed infrastructures from the 2008 International Expo (Water Tower, Bridge Pavilion or river Aquarium). Additionally, you will be able to enjoy our exquisite gastronomy.

Finally, we would like to thank all the plenary and invited speakers for accepting the invitation to participate in this conference and all the participants for deciding to attend GEQO2018. Also, all the persons that have collaborated in the organization, starting from the organizing committee, the scientific committee, session chairs and the Jury for posters/oral prizes are warmly acknowledged. We are extremely grateful for all support obtained from all our sponsors.

Have a great time in Zaragoza and enjoy the XXXVI GEQO Congress.

M. Concepción Gimeno,
Chair of the Organizing Committee of XXXVI GEQO Congress

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Wednesday 5th

11:00-16:00 Registration

16:00-16:30 Opening Ceremony

Chairwoman: ***Carmen Claver***

16:30-17.30 PL 1 **Walter Leitner (ChemPubSoc Europe Lecture)** : *Metal nanoparticles in suspported ionic liquid phases (M@SILP): a molecular approach to multifunctional catalyst materials*

17:30-18:00 INV 1 **Jesús J. Pérez-Torrente**: *Functionalized bis(N-Heterocyclic carbene) metal complexes: Synthesis, reactivity and catalytic applications*

18:00-18:20 SP1 **Anne Deveson**: *"Behind the Scenes at Chemistry – A European Journal and its Sister Journals: A Day in the Life of an Editor"*

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Thursday 6th

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Chairman: ***Miguel Monge***

10:00-10:30 INV 2 **Gilles Gasser**: *Organometallic compounds as antiparasitical and antifungal drug candidates*

10:30-10:45 Oral 1 **Antonio J. Martínez-Martínez:** *Catalytic upgrading light hydrocarbons: solid-state molecular organometallic chemistry (SMOM)*

10:45-11:00 Oral 2 **Alberto Pérez-Bitrián**: *Synthesis and Properties of Organogold(III) Fluoride Complexes*

11:00-11:30 *Coffee Break*

Chairman: ***Juan Cámpora***

11:30-12:00 INV 3 **Igor Larrosa**: *Transition metal catalyzed C-H activation: reactivity and selectivity control and late-stage functionalization*

12:00-12:30 INV 4 **Eva Hevia**: *Towards a paradigm shift in main group polar organometallic chemistry*

12:30-12:45 Oral 3 **José María Muñoz-Molina**: *Transition metal-catalyzed radical reactions: Strategies for C-N and C-C bond formation*

12:45-13:00 Oral 4 **Gustavo Espino**: *Selective photooxidation of sulphides catalyzed by biscyclometalated* Ir^{III} *photosensitizers bearing 2,2'-*dipyridylamine *based ligands*

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13:30-15:30 Lunch

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15:30-16:30 PL 3 **Luisa de Cola**: *Luminescent Pt(II) complexes: assemblies and sensing*

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16:30-17:00 INV 7 **David Balcells**: *Minimizing off-cycle species in palladium and nickel-catalyzed cross-coupling reactions*

17:00-17:15 Oral 5 **Mario Marín**: *Coordinatively unsaturated* $Ni(CO)_2(L)$ *complexes bearing dialkyl terphenyl phosphines: an experimental and DFT study*

17:15-17:30 Oral 6 **Lucía Álvarez-Miguel**: *Copper complexes in the promotion of aldol addition to pyridine-2carboxaldehyde: synthesis of homo- and heteroleptic complexes and stereoselective double aldol addition*

17:15-17:30 Oral 7 **Susana Ibáñez**: *Cation-driven self-assembly of different discrete, oligomeric and polymeric structures from a di-gold metallo-tweezer*

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18:00-19:30 Poster Session and *vino español* (**Even poster**)

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Chairman: ***Félix A. Jalón***

10:00-10:30 INV 8 **Miquel Costas**: *Selective aliphatic C-H oxidation reactions guided by medium effects and metal catalysts*

10:30-10:45 Oral 9 **Pilar Borja**: *Fom biomass to added-value chemicals*

10:45-11:00 Oral 10 **Cintia Ezquerro**: *White-emitting organometallo-silica nanoparticles for sun-like light-emitting diodes*

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17:00-17:15	Oral 15 **Marta E. G. Mosquera**: *Earth abundant metal catalysts for renewable monomers polymerization*
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17:30-17:45	Closing Ceremony
17:45-19:30	GEQO GROUP Meeting
21:00	Conference Dinner

ABSTRACTS

PLENARY SESSIONS

Metal Nanoparticles in Supported Ionic Liquid Phases (M@SILP):

A Molecular Approach to Multifunctional Catalyst Materials

Walter Leitner[a,b]

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Metal nanoparticles are of major importance in catalysis and essential elements in multifunctional catalytic materials. Their controlled synthesis from organometallic precursors has emerged as fruitful link between the traditional fields of “homogeneous” and “heterogeneous” catalysis. Whereas the ligands control the reactivity of isolated metal centers in coordination compounds, the stabilizing matrix (e.g. polymer, solvent, or support) becomes a critical control factor for the metal assemblies on a nanoscale.

In the present talk, we will discuss the potential supported ionic liquid phases (SILP) for the design, preparation, and application of such materials [1]. In particular, the potential of combining the stabilizing effect of IL-type matrices with the controlled introduction of additional molecular functionalities will be highlighted [2]. It will be demonstrated how the molecular approach to assemble the individual components offers the opportunity to generate catalytically active materials with tailor-made activities and selectivities for challenging synthetic transformations involving in particular hydrogenation and hydrogenolysis reactions [3,4].

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Borametallomimetics – Activation of Small Molecules by Low-valent Boron Species

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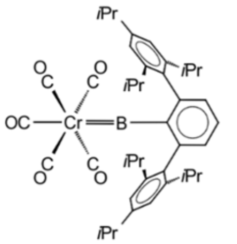
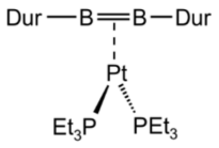
The activation of small molecules is generally associated with transition metals (TM) and constitutes the basis of catalysis. It was believed that TM catalysts are required to facilitate processes such as the activation of H_2 and other unreactive substrates. However, recent years have witnessed exciting developments in main group element chemistry, and the discovery of carbenes, FLPs and heavy main group species that are capable of TM-like activation reactions.[1]

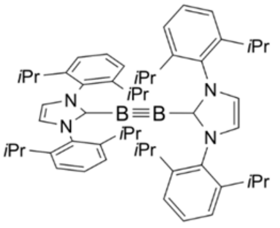
Our ongoing studies on borylenes, diborenes, and diborynes have shown that these low-valent species exhibit a very rich chemistry, which is distinctly different from that of common compounds deriving from boron in oxidation state +3. Particularly interesting is the metal-like behavior of some borylenes and diborynes, which form CO complexes analogous to TMs, bind H_2 and unsaturated organic substrates under mild conditions and even activate N_2.[2]



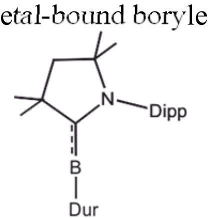
metal-bound borylene



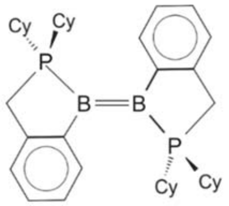
metal-bound diborene



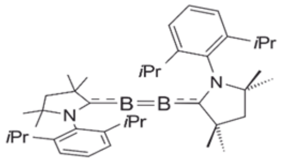
NHC-stabilized diboryne



transient borylene



phosphine-stabilized diborene



CAAC-stabilized cumulene

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Luminescent Pt(II) complexes: assemblies and sensing

Luisa De Cola

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Luminescent molecules that can undergo self-assembly are of great interest for the development of new materials, sensors, biolabels…. The talk will illustrate some of the recent results on soft structures based on metal complexes able to aggregate in fibers, gels and soft mechanochromic materials [1]. The emission of the compounds can be tuned by an appropriate choice of the coordinated ligands as well as of their aggregation in different structures. The formation of soft assemblies allows the tuning of the emission color, by pressure and temperature leading to a new class of materials possessing reversible properties. The monitoring of the different emission properties, used as fingerprint for each of the assembled species, allowed an unprecedented real-time visualization of the evolving self-assemblies [2]. The assemblies can be employed as very sensistive labels for the detection of toxins and drugs [3]. Indeed even though sensing based on fluorescent and luminescent probes are commonly used, the use of aggregates in water allows to distinguish between analytes possessing very similar electronic properties. Sensing can also be done using electrochemiluminescence, ECL. We have recently achieved the first example of aggregation induced ECL showing that assemblies in solution and in the solid state (deposited on the electrode) can generate bright emission [4].

Finally I wish to close my talk showing novel capsules that can be realized using a unique approach to template virus proteins to reconstruct virus-like particles. We use luminescent Pt(II)-complex amphiphiles, able to form supramolecular structures in water solutions, that can act as templates of viruses capsid proteins. The platinum assemblies can have different morphologies and extremely high emission of which the color depends on the assembly. Interestingly we are able to change the size and shape of the particles even though we use the same natural proteins. The obtained virus-like particles can be visualized by their intense emission at room temperature, generated by the self-assembly of the Pt(II)-complexes inside the capside [5].

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Gold(I)-Catalyzed Decarbenation

Antonio M. Echavarren

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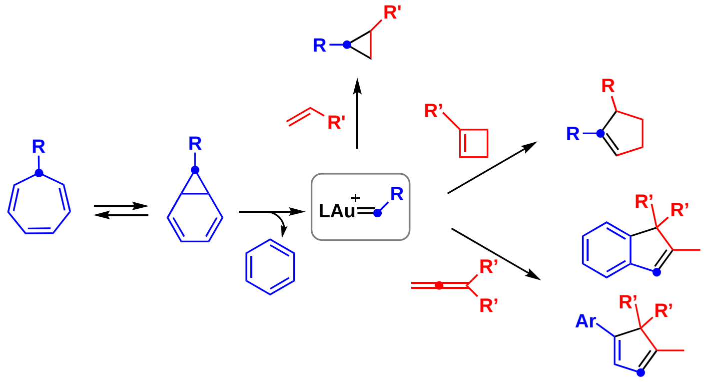
Gold(I) carbenes can be generated by retro-Buchner (decarbenation) reaction of 7-substituted cycloheptatrienes, which give rise to cyclopropanes in the presence of alkenes [1]. By using cyclobutenes as the reactive partners, cyclopentenes are obtained in a formal 4+1 cycloaddition process [2], whereas the reaction with allenes leads to indenes or cyclopentadienes [3]. Indenes and fluorenes are also obtained in intramolecular reactions of gold(I) carbenes with alkenes and arenes [4]. In contrast, 7-ethynyl-1,3,5-cycloheptatrienes form fluxional barbaralyl gold(I) intermediates, which after a series of rearrangements lead to 1- or 2-substituted indenes [5]. When the reaction was performed under oxidative conditions, barbaralones were obtained [5].



New studies on the reactivity of gold(I) carbenes as well as our efforts at performing the decarbenation reaction under milder conditions will be presented.

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Bioorganometallic Chemistry: Synthetic Strategies and Biomedical Applications for Metal-Peptide Bioconjugates

Nils Metzler-Nolte[1]

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Our group uses the unique spectroscopic and chemical properties of organometallic complexes in metal-peptide conjugates for biomedical applications.[1,2] The experimental challenge is to identify air- and water stable organometallic compounds with the desired properties, and to devise methods for the mild, biocompatible synthesis of bioconjugates with these metal complexes. Similarly, biomedical properties of peptides have been tailored by their conjugation to organometallic moieties.[7]

This presentation will highlight various synthetic strategies to obtain bioactive metal-peptide bioconjugates that have been developed in our group, and will present some exemplary biomedical applications of such metal-peptide conjugates. I will show how the versatile reactivity of metal complexes can be matched with peptide chemistry and purification techniques. Potent novel anticancer agents based on a number of different metals such as Fe, Ru, Re, and Au were developed, characterized and tested for their antiproliferative activity against a range of different cancer cells.[1, 2] In-depth studies were carried out to study uptake and intra-cellular localization of the compounds, as well as their potential mode of action.[3] In the second part, I will present novel organometallic-peptide conjugates with very potent antibacterial activities that even surpass that of a last-resort antibiotic, vancomycin.[4] Importantly, these organometallic-peptide conjugates have a novel mode of action, allowing them to avoid the common mechanisms of bacterial resistance.[5] As a promising outlook towards clinical applications, these conjugates can be optimized to have little toxicity against human cells and low hemolytic potential.[6]

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INVITED COMMUNICATIONS

Functionalized bis(N-Heterocyclic carbene) metal complexes: Synthesis, reactivity and catalytic applications

Raquel Puerta-Oteo, M. Victoria Jiménez, Jesús J. Pérez-Torrente

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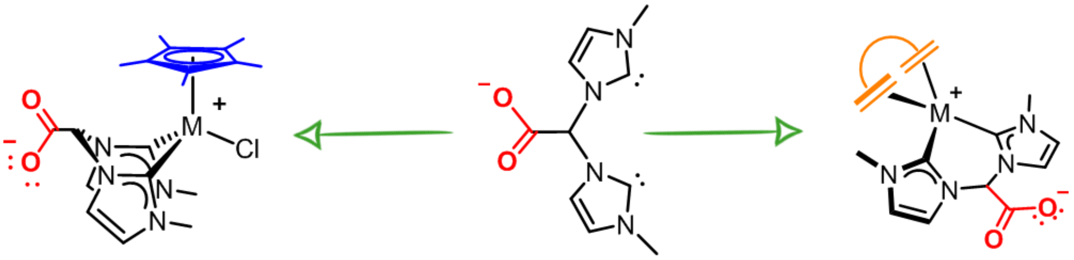
The modulation of catalyst properties through the ancillary ligands is crucial in the field of homogeneous catalysis. In this context, N-heterocyclic carbene ligands (NHC) have shown a great versatility due to the possibility of fine-tuning of their steric and electronic properties which has allowed for the design and synthesis of highly thermally stable transition-metal based homogeneous catalysts. In this context, the chelate or pincer effects derived from coordination of multidentate NHC ligands results in the formation of stable metal-ligand platforms with application in catalysis. However, the number of functionalized methylene-bridge bis-NHC ligands is rather scarce and in most of their complexes the bis-NHC ligands exhibit a κ^2*C*,*C* bidentate coordination mode with an uncoordinated functional group in the skeleton.

This presentation will focus on the synthesis and reactivity of zwitterionic water soluble rhodium and iridium complexes featuring a carboxylate-functionalized methylene-bridged bis-NHC ligand. The carboxylate moiety in these complexes might play very different roles in catalysis: i) the transient stabilization of catalytic intermediates, ii) the activation of substrates by promoting an outer sphere mechanism, or iii) the establishment of a stable metal-ligand platform resistant to harsh reaction conditions through the κ^3-*C,C'O*-tripodal coordination mode. Selected examples on the catalytic applications of this type of complexes in diverse areas of fine and energy chemistry including carbon dioxide reduction and water oxidation will be also presented.



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INVITED 2

Organometallic Compounds as Antiparasitical and Antifungal Drug Candidates

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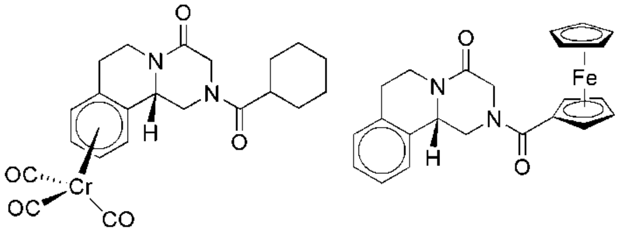
Pioneered by the works of Brocard, Biot and co-workers, the use of organometallic compounds to fight parasitic diseases such as malaria is nowadays a hot topic in medicine.[1,2] Our group has been working over the last years towards the development of novel organometallic drug candidates against the human parasitic disease schistosomiasis[3-7] (see Fig. 1 for examples of compounds investigated in our group), against parasites of livestock animals[8-10] as well as fungal infections.[11] During this talk, we will present our latest *in vitro* and *in vivo* results, emphasizing the role of the metal in the action of the metal-based drug candidates.



$Cr(CO)_3$-PZQ **Fc-PZQ**

Figure 1. Structures of organometallic compounds studied as antischistosomal drug candidates in our group.

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INVITED 3

Transition metal catalyzed C-H activation: reactivity and selectivity control and late-stage functionalization

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The development of greener and more efficient synthetic methodologies is essential for organic chemistry to reach its full potential in its application to many applied and fundamental scientific problems. Biaryls are structural motifs predominant in numerous pharmaceuticals, agrochemicals, chiral catalysts, liquid crystal displays, and even molecular switches and motors. The most common methodology for their synthesis involves the traditional cross-coupling between an organometallic compound, Ar-M, and a haloarene, Ar-X. In the last few years, two promising alternatives to these cross-couplings have emerged: *direct C–H arylation*, where a readily available Ar-H is coupled with Ar-X, and *oxidative double C–H activation*, where two different Ar-H are cross-coupled. These approaches use non-prefuntionalized starting materials, thus eliminating several synthetic steps and consequent chemical waste associated to traditional cross-couplings. However, several challenges have to be resolved before this new approaches can be widely applied: 1) the development of mild reaction conditions with a broad scope, 2) the control of the regioselectivity of C–H activation and, in the case of oxidative couplings, 3) the control of the selectivity of homo- versus cross-coupling, and 4) the development of conditions that can be safely used in industry.

In this talk I will present some of our group's approaches towards addressing these challenges. In particular, we will discuss the use of bimetallic Pd/Ag,[1] Pd/Cr[2] and Au/Ag[3] synergistic systems and the development of novel Ru-catalysts for late stage functionalization.[4]

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Towards a Paradigm Shift in Main Group Polar Organometallic Chemistry

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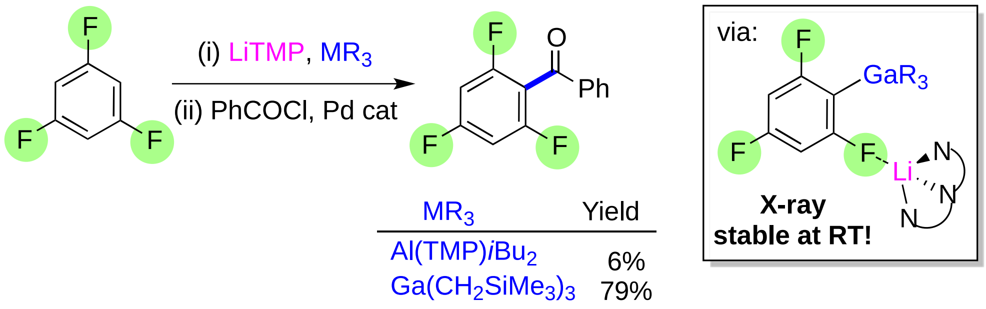
Organolithium compounds (*e.g.*, alkyls, aryls and amides) have been and remain pivotal to the development of synthetic chemistry.[1] Staple reagents in academic laboratories and chemical industries worldwide, their extensive utilization reflects their high reactivity and selectivity (notably in directed *ortho*-metallation). However, in many cases this high reactivity can also compromise their functional group tolerance, imposing the use of severely restrictive protocols (*e.g.*, moisture- and oxygen-free organic solvents, inert atmospheres, extremely low temperatures *etc.*) and frequently the lithiated organic intermediates can be unstable and decompose.

This presentation will explore alternative organometallic strategies to overcome some of these major drawbacks faced by standard organolithium reagents. This includes the use of bimetallic combinations for deprotonative metallation reactions, which operating in tandem enable the trapping of sensitive anions such as metallated diazines or fluoroarenes (see Scheme).[2] Furthermore, the promising use of non-conventional solvent systems such as Deep Eutectic Solvents (DESs) in organolithium chemistry will also be discussed,[3] edging closer towards developing greener and air and moisture compatible methodologies.



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INVITED 5

Catalytic transformation of methane in non-conventional reaction media

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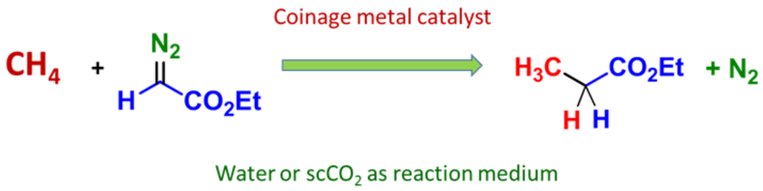
Currently, one of the main problems in the world is the decrease in the oil reserves and an alternative source must be searched. The most convenient one is methane,[1] given the vast reserves of this gas that exist in the Earth crust. However, there are few known examples where this hydrocarbon is transformed, a consequence of the high inertness of its C-H bonds, becoming one of the remaining challenges of modern Chemistry.

Most of the catalytic systems known for the conversion of this molecule into valuable products, leading to the formation of C-O, C-C or C-B bonds,[1] employ harsh conditions such as corrosive media or high temperatures.

During this decade, our research group has focused on the study of the reaction of diazoacetates with gaseous alkanes of formula C_nH_{2n+2}, toward the insertion of a carbene group into the C-H bonds of the hydrocarbon, with special emphasis in methane.[2] Since the latter displays the highest bond dissociation energy of the alkane series, its functionalization must be performed in the absence of any other more reactive C-H bond. In this contribution, the results obtained in the methane functionalization reaction using supercritical carbon dioxide or water as the solvents, to avoid competitive reactions with other C-H bonds, will be presented.



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Minimizing Off-Cycle Species in Palladium and Nickel-Catalyzed Cross-Coupling Reactions

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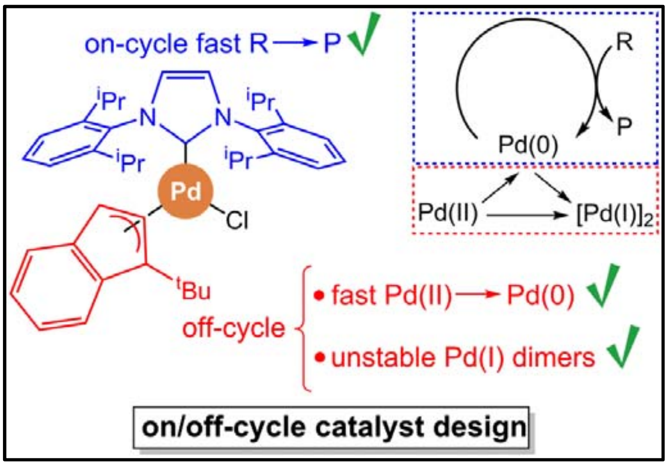
This talk presents an overview on recent experimental and computational studies on the off-cycle reactions of palladium- and nickel-catalyzed cross-couplings.[1,2] Several reactions entering and leaving the catalytic cycle have been characterized, including precatalyst activation by an H-shift mechanism and deactivation by comproportionation into dimeric species. The molecular-level understanding of off-cycle reactions has enabled new catalyst design strategies, including the stereoelectronic fine-tuning of the ligands aimed at maximizing the activation of the precatalyst meanwhile preventing its degradation. Despite several challenges, which concern both experiments (*e.g.* isolation and characterization of transient species) and computations (*e.g.* comprehensive mapping of the potential energy surface), this approach has already been applied with success in the optimization of popular catalytic platforms, including NHC–Pd–allyl precatalysts, and shows promise for the development of highly active and robust catalysts based on nickel.



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Selective aliphatic C-H oxidation reactions guided by medium effects and metal catalysts

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Selective oxidation of unactivated aliphatic C**–**H bonds constitutes a potentially very useful reaction because it introduces functionality in otherwise inert aliphatic skeletons.[1] Intense research efforts have been devoted to uncover the factors that govern C–H bond reactivity against hydrogen atom transfer (HAT) reagents, pointing toward the important role played by bond strengths as well as by steric, electronic, stereoelectronic, and torsional effects in these processes.[2] On the basis of these elements, C–H bonds are recognized to bear an innate relative reactivity against oxidizing agents,[1,2] which defines the site selectivity in the oxidation of molecules containing different C–H bonds. However, this is basically unaffected by the nature of the oxidant, a factor that effectively limits the potential of the reaction.

Our research efforts have been placed in the design of metal catalysts based in iron and manganese coordination complexes. These complexes react with hydrogen peroxide producing high-valent metal-oxo species, which are powerful oxidants and can perform the oxidation of aliphatic C-H bonds via an initial HAT process. Aliphatic C-H oxidation with these catalysts has been pursued with the final goal to set predictable C-H site selective oxidations, alternative to the innate C-H relative reactivity. Two different strategies have been followed towards this goal; a) via catalyst design, incorporating steric bias[3] and/or substrate recognition units in the catalyst architecture,[4] and b) exploiting the polarity reversal exerted by strong H-donor fluorinated alcohol solvents.[5]

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The importance of “weak” interactions

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One of the most important topics in chemistry is that that explains the union between them, *i.e.* the chemical bonding. The classical covalent or ionic classifications are designed for bonds between open- or closed-shell species with opposite charges, respectively. Nevertheless, these never appear in pure form and in the description of the bonding between elements the dispersive forces (that include van der Waals ones) should be taken into account.[1]

In other occasions, these dispersive forces are the only interactions that are responsible for the approximation that suffer atoms with zero charge or between cations of s^2, d^8 or d^{10} electronic configurations.

In those “weak” interactions that appear between heavy metals like gold(I), platinum (II) mercury(II), etc., a very important role is played by their large relativistic effects making them, not so weak. In fact, these interactions are directly related to the properties that many complexes that contain them show. For instance, polymerization of neutral gold(I) subunits; unusual host-guest heterometallic structures; catalytic gold based systems; or metal-centred luminescent materials, among others.

Thus, in this communication examples of systems displaying metallophilic and other weak interactions leading to tailored properties, or the study of the metallophilicity in different media and under extreme external conditions will be described. Relationships between energy of the emissions, potential energy curves and lengths of the interaction distances will be rationalized.

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Approaches to a more sustainable palladium catalysis

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Palladium catalysis is present in most synthetic protocols. A mature area in many ways, it is also continuously expanding not only in the range of reactions that can be catalyzed by this metal, but also in the way the available methodology is transformed to make these reactions more sustainable. We have contributed to this goal, working in two different aspects. First, trying to avoid waste by means of the use of vinylic addition polynorbornenes (VA-PNBs) as polymeric supports for palladium catalysts or reagents (recycle). Two examples are the use of recyclable polymeric tin reagents in the Stille reaction,[1] and the preparation and use of recyclable supported palladium catalysts on these polymers.[2]

On the other hand, the use of reagents that do not need pre-functionalization is a viable approach to increase sustainability (elimination of extra synthetic steps). The direct arylation of arenes with aryl halides to give biaryls is one of the reactions that use non-prefuctionalized arenes as reagents. We have prepared new palladium complexes with a bifunctional 2-2'-bipy-6(1H)-one ligand that catalyze this reaction and are more active than other analogous catalytic systems. The mechanistic study of the reaction reveals that the ligand is favoring the rate limiting C-H cleavage step and this is the origin of the substantial acceleration observed.

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INVITED 10

Gold *versus* Silver Towards Domino Processes

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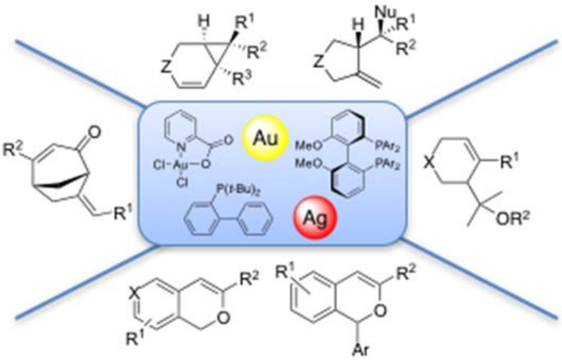
Over the past few years, significant research has been directed toward the development of new methodologies for synthetic efficiency and atom economy processes in the presence of gold and silver catalysts.[1] We have been engaged in a wide project dedicated to the development of catalytic methodologies for the synthesis of original and functionalized carbo- and heterocycles. Our interest has been focused on the cyclization and/or functionalization of alkynes including enynes,[2,3] alkynyl silyl enolethers[4] and o-alkynyl benzaldehydes.[5] We also got interested in cycloisomerization reactions of allenols and developed sustainable catalytic systems.[6] Despite significant progress in the development of enantioselective gold(I) catalysis,[1,7] challenges still remain largely as a result of the high substrate-dependency and the linear geometry the chiral gold(I) complexes.[8] We also This presentation will show an overview of the latest results implying achiral and chiral gold and silver complexes.[9]



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ORAL COMMUNICATIONS

Catalytic Upgrading Light Hydrocarbons: Solid-State Molecular Organometallic Chemistry (SMOM)

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Low-temperature catalytic processes for the valorisation of light hydrocarbons (alkanes and alkenes) are desirable methods for the selective production of valuable chemical building blocks (aromatics, upgraded olefins).[1] Although a variety of systems for selective catalytic functionalisation of light hydrocarbons have been developed, methods that operate at low energy profiles with high selectivity represent a real challenge in heterogeneous catalysis.

In this context, C–H bond activation protocols on well-defined organometallic molecular species via single-crystal to single-crystal solid/gas transformations offer new opportunities in catalysis.[2] We account here our latest advances on the use of well-defined, isolable rhodium sigma-alkane and alkene complexes that behave as "molecular nanoreactors" for the catalytic transfer dehydrogenation of alkanes and the isomerisation of alkenes at room temperature, low pressures and high recyclability (Figure 1). The use of diverse chelating phosphines and various non-coordinating anions on these solid-state molecular organometallic catalysts (SMOM-cats) allows us to evaluate the influence of phosphine bite and solid cone angle, and the structural frameworks provided by the solid-state packing of anions.[3] Thus, we can establish structure/activity relationships in solid-state catalysis. Moreover, the combination of single-crystal X-ray crystallography, gas-phase and solid-state NMR spectroscopy and periodic DFT calculations provide useful insights in studying catalyst speciation and reaction pathways.

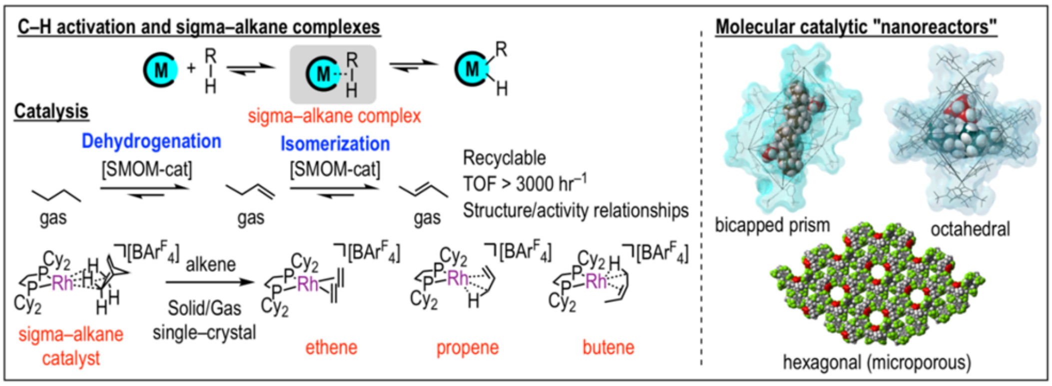

Figure 1. Solid-State Molecular Organometallic Catalysis with light hydrocarbons (SMOM-cat).

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Synthesis and Properties of Organogold(III) Fluoride Complexes

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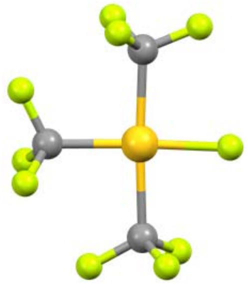
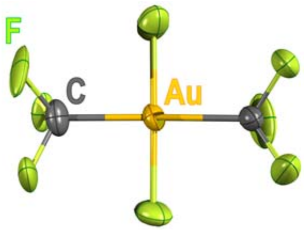
The chemistry of organogold fluorides is a fascinating topic entirely developed within this century.[1] No organogold fluorides were known by the time Roesky *et al*. published their comprehensive review on *Organometallic Fluorides*.[2] Despite its freshness, or rather because of that, the subject is evolving at a breathtaking path. Furthermore, organogold fluorides are frequently proposed as intermediates in a number of gold-mediated fluorination processes of the most varied organic molecules.[3]

The trifluoromethyl group, CF_3, has proved to be especially suitable to stabilize organogold fluorides. In fact, a series of $[(CF_3)_xAuF_{4-x}]^-$ compounds ($x = 1, 2, 3$) were detected in solution by Willner *et al.* but were not isolated from the reaction mixture.[4]

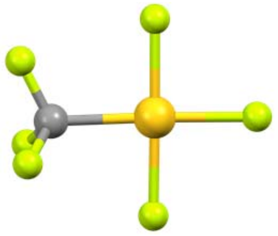
We report here on our efforts to prepare and isolate the components of this interesting series of compounds.[5] Various synthetic strategies will be discussed and the properties of the isolated compounds will be described in detail. In particular, ^{19}F NMR spectroscopy is an invaluable tool to enable the identification of the obtained products and the correct assignment of their stereochemistry. The combined use of tandem mass spectrometry and theoretical calculations also provides useful information on the stability and chemical behaviour of both the isolated compounds and other related species derived therefrom.



$[(CF_3)_3AuF]^-$



$[trans\text{-}(CF_3)_2AuF_2]^-$



$[CF_3AuF_3]^-$

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Transition Metal-Catalyzed Radical Reactions: Strategies for C-N and C-C Bond Formation

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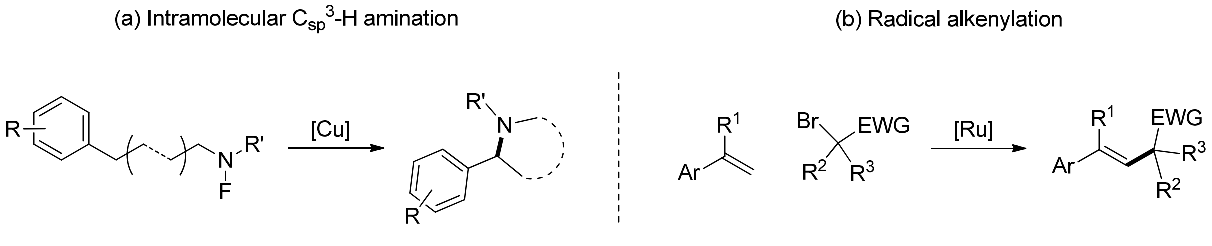
Radical-based transition metal catalyzed reactions have become an essential tool for the construction of carbon-carbon and carbon-heteroatom bonds in organic synthesis. Some of the advantages of radical processes are the use of mild and neutral reaction conditions, functional group tolerance, and the capability of inducing cascade reactions that increase the molecular complexity. Consequently, radical reactions have attracted considerable attention in the synthesis of many natural products during the past decades.[1]

Our group have been involved in the study and the development of transition metal-catalyzed radical reactions over the last years.[2] Here, we present our recent results on this field for the construction of C-N and C-C bonds. First, a novel copper-catalyzed intramolecular $C_{sp}{}^3$-H amination method has been developed for the synthesis of pyrrolidines and piperidines (*Scheme 1*(a)). Second, a highly active ruthenium-based catalytic system for radical Heck-type alkenylation of alkyl bromides will be presented (*Scheme 1*(b)).



Scheme 1. C-N and C-C bond formation through metal-mediated radical reactions.

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Selective Photooxidation of Sulphides catalyzed by Biscyclometalated Ir^{III} Photosensitizers Bearing 2,2'-dipyridylamine Based Ligands

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A new family of heteroleptic biscyclometalated Ir^{III} complexes with formula $[Ir(C^\wedge N)_2(N^\wedge N)]Cl$, **[1-4]Cl**, ((C^N) = 2-phenylpyridinate and (N^N) = 2,2'-dipyridylamine or N-benzylated-2,2'-dipyridylamine) have been synthesized and fully characterized (Fig. 1 (A)). Moreover, these derivatives have been successfully used as photosensitizers (PS) in the catalytic photooxidation of an array of dialkyl, dibenzyl, alkylaryl and diaryl sulphides, as well as S-containing aminoacids. Furthermore, the reactions proceeded with optimal chemo-selectivity and atom economy under smooth conditions (Fig. 1 (B)). Experimental observations support a dual mechanism where singlet oxygen plays a role as the main oxidant, though the radical anion superoxide also takes part in the process.

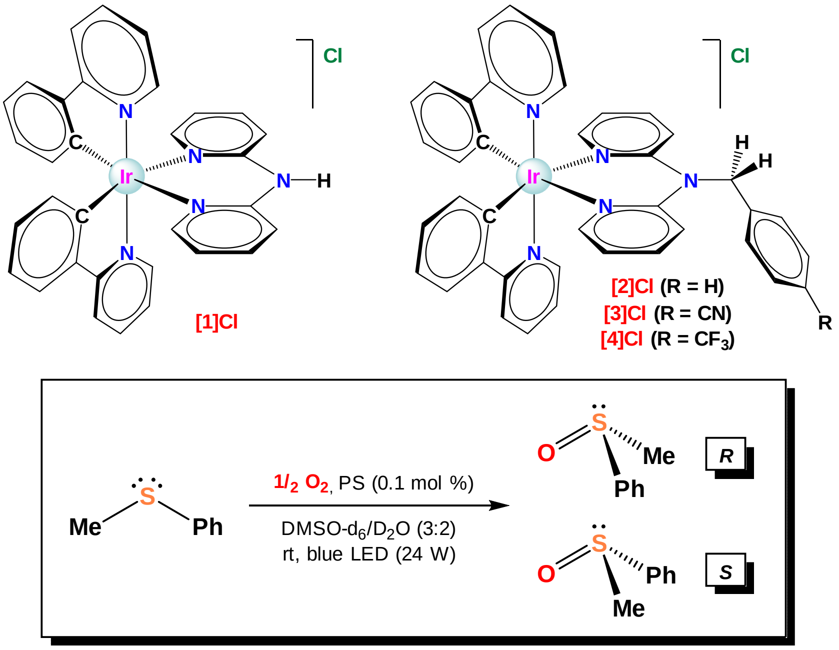

Figure 1. (**A**) Structure of complexes **[1]Cl-[4]Cl** used as photosensitizers (PS). (**B**) Photo-oxidation of thioanisole under an O_2 atmosphere and blue-LED irradiation.

Coordinatively unsaturated $Ni(CO)_2(L)$ complexes bearing dialkyl terphenyl phosphines: an experimental and DFT study

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Ancillary ligands play a key role in homogeneous metal-catalysed transformations, as they remain bound to the metal centre throughout all the elementary steps that make up the catalytic cycle. The ligands most typically used in cross-coupling reactions are monodentate and bidentate tertiary phosphines.[1]

A series of dialkyl terphenyl phosphines, closely related to Buchwald's dialkyl biaryl phosphines,[2] have been recently synthesised in our group (Figure 1). During the study of the electronic properties of these ligands by the measurement of their Tolman electronic parameter (TEP),[3] an interesting reactivity for the bulkier members of this series was discovered (Figure 2). A computational study was performed in order to ascertain the mechanism of this reaction.

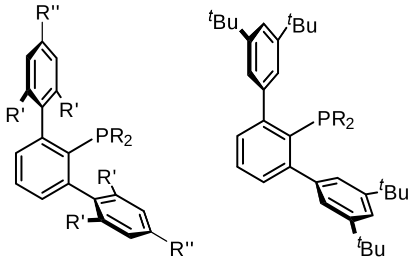

Figure 1. *Phosphine ligands used in this work.*

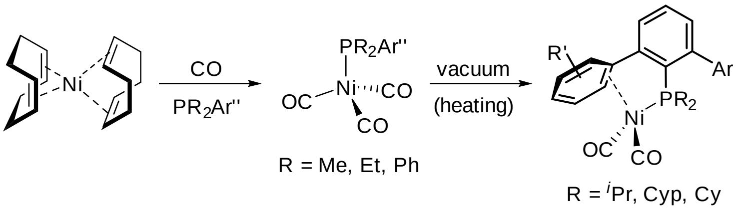

Figure 2. *Reactivity of the phosphines against $Ni(CO)_4$ source.*

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Copper Complexes in the Promotion of Aldol Addition to Pyridine-2carboxaldehyde: Synthesis of Homo- and Heteroleptic Complexes and Stereoselective Double Aldol Addition[1]

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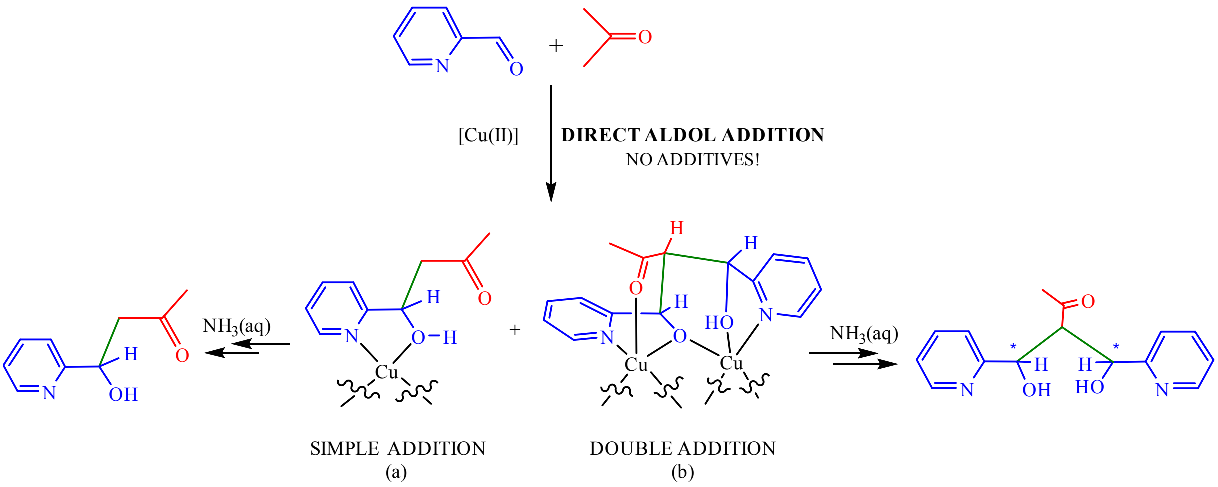
$CuCl_2 \cdot 2H_2O$ and $Cu(ClO_4)_2 \cdot 6H_2O$ are able to promote aldol addition of pyridine-2-carboxaldehyde (pyca) with acetone, acetophenone, or cyclohexenone under neutral and mild conditions (scheme 1a). The general and simple one-pot procedure for the aldol addition to Cu(II) complexes accesses novel Cu complexes with a large variety of different structural motifs, from which the aldol-addition ligand can be liberated by treatment with NH_3. Neutral heteroleptic complexes in which the ligand acts as bidentate, or homoleptic cationic complexes in which the ligand acts as tridentate can be obtained depending on the copper salt used. The key step in these reactions is the coordination of pyca to copper, which increases the electrophilic character of the aldehyde, with $Cu(ClO_4)_2$ leading to a higher degree of activation than $CuCl_2$, as predicted by DFT calculations. A regio- and stereoselective double aldol addition of pyca in the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with acetone leads to the formation of a dimer copper complex in which the novel double aldol addition product acts as a pentadentate ligand (scheme 1b).



Scheme 1. Synthesis of aldol addition products in the sphere of Cu(II) moiety from pyca ligand and ketone. **a)** Example of simple aldol addition product. **b)** Double aldol addition product

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Cation-driven self-assembly of different discrete, oligomeric and polymeric structures from a di-gold metallo-tweezer

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The existence of metallophilic interactions in supramolecular assemblies has given rise to a large number of materials exhibiting photoluminescence and vapochromic properties, of great relevance for the applications in luminescence signaling and vapochemical sensing. Gold alkynyls are recently being regarded as an extremely interesting type of organometallic-based metalloligands due to their potential binding abilities via the alkynyl ligand and through aurophilic/metallophilic interactions.[1,2,3] Self-assembly allows the preparation of highly complex molecular architectures from relatively simple materials. An in-depth understanding of supramolecular transformation is of key importance for the construction of smart functional materials. The careful control of the construction of materials through tunable supramolecular interactions is expected to allow the generation of specific outputs, such as tailored properties or functions. In this work, the complex supramolecular landscape of a di-gold metallo-tweezer (Figure 1) is successfully controlled by adding a series of metal cations. As can be seen in Figure 1, this metallo-tweezer has a strong tendency to form interesting supramolecular structures upon addition of Tl^+, Ag^+ and Cu^+. The choice of the cation is used to directing the formation of the designated molecular architecture.

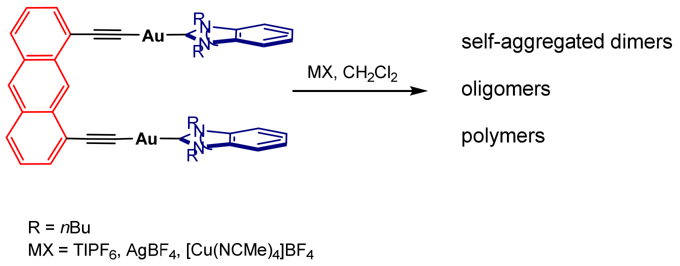

Figure 1

Acknowledgements

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Beneficial Cooperative Effect on scorpionate dizinc complexes for the catalytic production of biodegradable polymers

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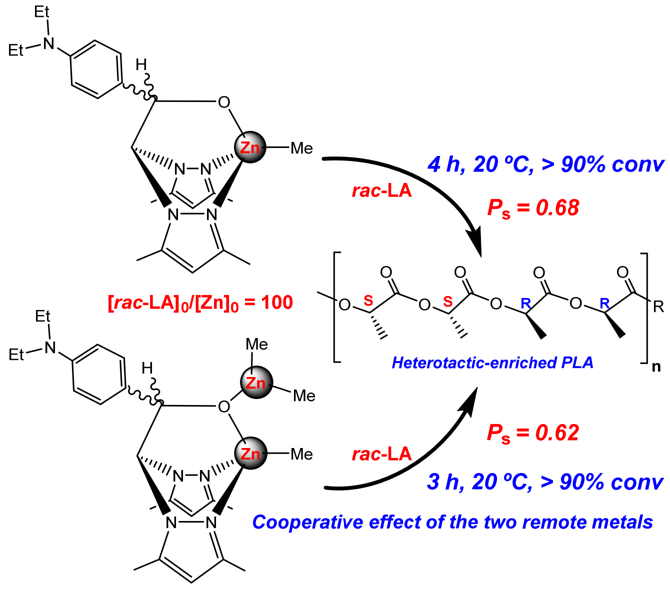
Bio-based poly(lactide) (PLA) is considered an excellent material for many applications in different fields mainly due to its outstanding advantages over other polymers, such as its renewability, biocompatibility, processability or energy saving [1]. PLA is typically synthesized by ring-opening polymerization (ROP) of the inexpensive bioderived monomer of lactide with the assistance of an organometallic complex as catalyst. Over the last decades, numerous efforts have been made to develop efficient metal catalytic systems to promote the ROP of lactide with good activities but also in a controlled manner. In addition, the search of biologically benign metal-based catalyst systems (*i.e.* Zn, Mg, Ca) is desirable to solve the potential pollution problems caused by heavy metal catalysts employed industrially in the process.



Herein, we describe the huge potential in ROP of a new family of alkyl-containing mono- and bimetallic scorpionate zinc catalysts to produce in hours at room temperature medium-low molecular weight PLA materials in a well-controlled and living manner [2]. For all the cases, the dizinc catalysts significantly out-perform the monozinc analogues. This enhanced performance can be attributed to the beneficial catalytic cooperative effect between the two remote metal centres in the bimetallic complexes. A greater level of control of the polymerization process is achieved when more sterically demanding catalysts are employed ($P_s = 0.68$).

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Fom biomass to added-value chemicals.

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Modern life and fossil fuels are inevitably related. However, the abuse of fossil fuels involves important economic, environmental and social costs. Some renewable energy sources (hydropower, photovoltaic energy, wind, hydrogen) have emerged to decrease the use of fossil fuels [1].

A wide variety of commodity chemicals can be synthetized by oxidation of carbohydrates. Non-petroleum carbon sources, such as biomass is an excellent alternative in the production of fine chemicals [2]. During the last years, the oxidation of biomass using well-defined metal catalysts has received great attention among the scientific community (figure 1) [3].

In this presentation, we report a new methodology for the catalytic transformation of carbohydrates in organic acids with the concomitant hydrogen production. A plausible mechanism for the conversion of glucose into gluconic acid is proposed based on experimental evidence and supported by DFT calculations.

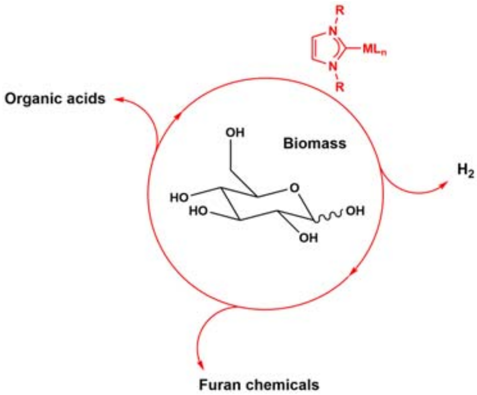

Figure 1. Catalytic transformation of biomass using organometallic carbene complexes.

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Financial support acknowledgment: The authors thank the financial support from MINECO (CTQ2015-69153-C2-2-R), and Universitat Jaume I (P1.1B2015-09). P. Borja thanks the Universitat Jaume I for the postdoctoral grant. The authors are very grateful to the 'Serveis Centrals d'Instrumentació Científica (SCIC)' of the Universitat Jaume I.

White-emitting organometallo-silica nanoparticles for sun-like light-emitting diodes

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In the last years, new architectures for the production of white artificial illumination have been developed. Among all of them, hybrid inorganic/organic emitting diodes (HWLEDs) have attracted much attention since they overcome the limitation presented in other architectures.[1]

On this regard, and taking advantage of our experience in the design of hybrid luminescent materials, [2] we present a new route to synthetize monochromatic and white-emitting organometallo-silica nanoparticles, and their successful integration in color down-converters devices. They have been prepared by developing a new synthetic approach, based on the kinetic control of the formation of organometallic dots (**OD**), built via the condensation of three emitting iridium(III) complexes ($[Ir(dfppy)_2(PPETS)_2]OTf$, $[Ir(ppy)_2(PPETS)_2]PF_6$, $[Ir(ppy)_2(dasipy)]OTf$. Fig. 1), previous to the formation of the mesoporous silica around them. These emitting nanoparticles have been implemented into single-component hybrid light-emitting diodes, achieving a high quality sunlight source that is stable over thousands of hours.

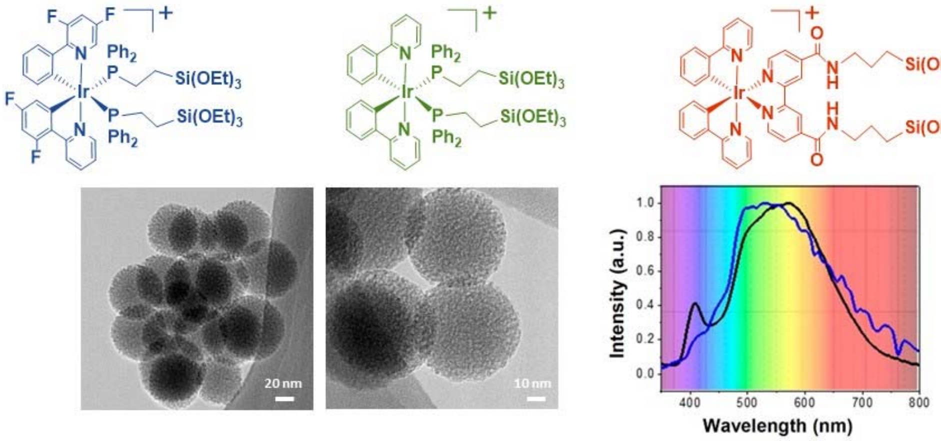

Figure 1. Upper part - Schematic view of the iridium complexes. Lower part – left: TEM images of the white emitting nanoparticles. Right: Electroluminescence spectrum of single-component HWLEDs compared with the visible part of the sunlight spectrum.

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The n → π* interaction in metal complexes

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Although the importance of the n → π* interaction has been recognized in recent years, its presence to date was confined to biomolecules and organic materials [1]. We have recently reported, for the first time, the existence of n → π* donor-acceptor interactions in transition metal complexes containing carbonyl ligands [2]. This new interaction has been observed to be surprisingly abundant and to stabilize certain molecular conformations that maximize the overlap between the donor and acceptor orbitals. Furthermore, it displays some signatures of the similar n → π* interaction in proteins as well as other new features typical of metal complexes, as, for instance, the loss of linearity of the M-C=O angle associated to the acceptor carbonyl. Further structural and theoretical analysis has shown that the n → π* interaction can also be of intermolecular nature and, thus, important for the formation of solid-state structures [3].

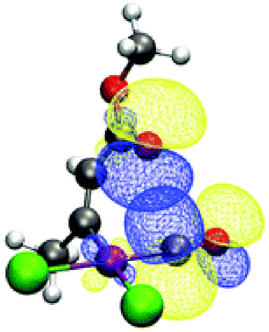

Figure 1. Overlap between the donor lone pair (n) and the empty π* antibonding orbitals in a Pt(II) complex.

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Remote Alkene Catalytic Hydrosilylation or Dehydrogenative Silylation Depending on the Metal Centre

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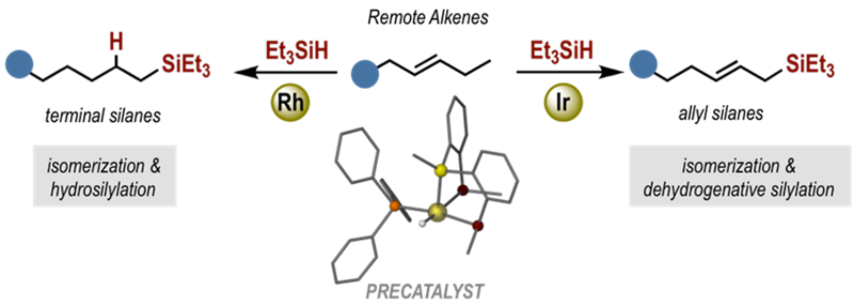
Numerous catalysts have been reported for the hydrosilylation of α-olefins,[1] there are still very few examples of effective catalysts in synthesis of linear silanes from internal olefins or olefin mixtures.[2] Recently we reported an unsaturated 16 electron hydrido-silyl-Rh(III) complex as an efficient catalyst for a tandem catalytic alkene isomerization-hydrosilylation reaction at room temperature under solvent-free conditions.[3] Such a process would be of value to the chemical industry, because mixtures of internal aliphatic olefins are substantially cheaper and more easily available than the pure terminal isomers.

We report here the synthesis of analogue cationic rhodium and iridium complexes supported by a tridentate hydrosilane-thioether proligand, and their catalytic activity in tandem isomerisation-hydrosilylation reactions with various terminal and internal alkenes. The unsaturated hydrido-silyl-Rh(III) complex, $\{Rh[SiMe(o\text{-}C_6H_4SMe)_2](H)(PPh_3)\}[BAr^F_4]$, is able to catalyse tandem alkene isomerization-hydrosilylation reaction at room temperature under solvent-free conditions efficiently, while analogue hydrido-silyl-Ir(III) complex is selective for the dehydrogenative silylation, leading to the formation of terminal allylsilanes from remote alkenes.[4]



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POP-Osmium Polyhydrides in Chemical Hydrogen Storage

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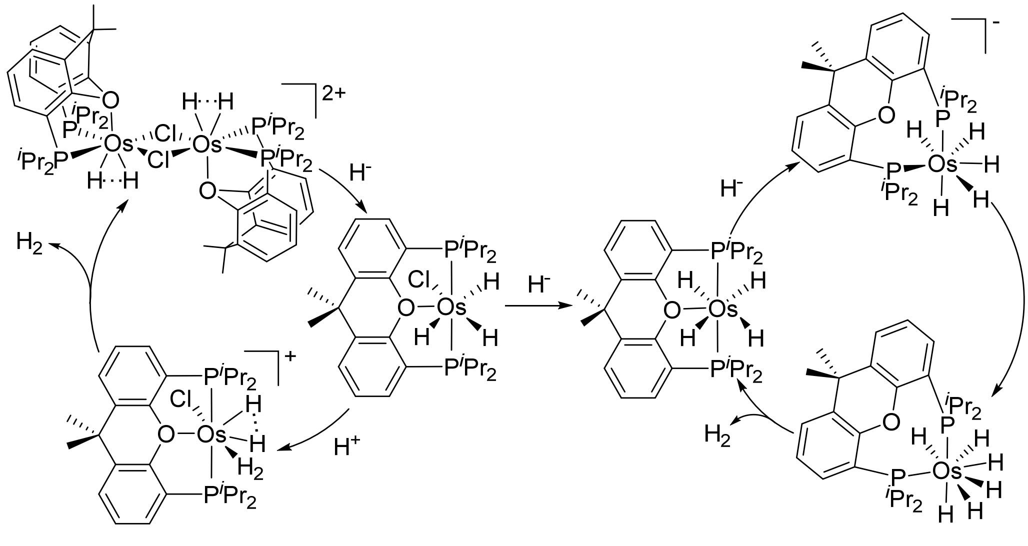
The ever-increasing demand for energy worldwide means that new and economically sustainable energy sources are urgently required. Molecular hydrogen could be a good alternative to replace fossil fuels due to its energy content per unit mass and availability, although problems concerning transport and handling of this low density and highly diffusible gas have to be resolved first. In this regard, recent advances in chemical hydrogen storage methods offer new possibilities in this field.[1]

Osmium polyhydrides have shown their versatility to act in both various catalytic reactions and in the activation of C-H, N-H, C-N, B-H or H-H bonds, amongst others.[2] In the field of hydrogen storage, catalytic dehydrogenation of amine-borane has been achieved using the unsaturated dihydride complex $OsH_2(CO)(P^iPr_3)_2$.[3] We have recently found that the flexibility of a POP pincer ligand allows the stabilization of osmium polyhydride species in which different stages in the activation of H-H and B-H bonds have been fully identified,[4] and show their ability to generate molecular hydrogen in a kinetically controlled cyclic manner (Figure).

Herein we present our recent results in the field of hydrogen storage and production using POP Os-polyhydrides as catalyst.



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Antitumor Activity of Ru-arene Complexes with Monophosphines

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Cancer represents the first cause of death in developed countries, and the second in developing countries, which explain the enormous effort directed to obtain more effective and less harmful chemotherapeutic drugs. Platinum-based drugs, including the archetypical cisplatin (**Figure 1**), are still the most important chemotherapeutic agents, but present severe side effects and limited effect due acquired tumor resistance.

In the search of alternatives to platinum-based drugs, ruthenium-based complexes are among the most promising candidates due to the relatively low toxicity of Ru and its versatility regarding to oxidation states and coordination chemistry [1]. One of the most important examples is RAPTA-C (**Figure 1**), which is a piano-stool Ru(II)-arene complex showing anti-tumoral and anti-metastatic properties [2].

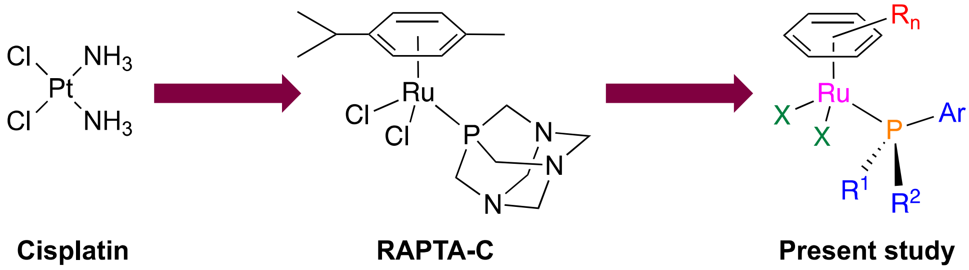

Figure 1. Structures of cisplatin, RAPTA-C and the Ru complexes with tailored phosphine ligands.

Following preliminary studies [3], in this communication we present the synthesis of new $[\mathrm{Ru}(\eta^6\text{-arene})\mathrm{X}_2(\mathbf{P})]$ complexes with monophosphines along with their *in vitro* biological activities. We have found marked structure-activity relationships between the different functionalities of the complexes (arene ligand, halide and the phosphine substituents) and the antitumoral activity, which have assisted in the synthesis of very active systems.

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Earth abundant metal catalysts for renewable monomers polymerization

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In the past few decades, there has been a significant focus on the use of renewable feedstock as raw materials to prepare chemicals. Particularly, in the field of polymers access to a new generation of polymers from renewable resources with good biodegradability and at the same time keeping the high performance of the fuel-based polymers is paramount. In this context, one type of polymers that have attracted a lot of interest are polyesters derived from renewable cyclic esters such as lactide or butyrolactone. Besides, these polymers can be biodegradable and biocompatible and can show a wide range of applications.[1]

One of our ongoing research areas is focused in the preparation of main group metal complexes as catalysts for the Ring Opening Polymerization (ROP) of cyclic esters to generate biodegradable polymers. Within main group metals, aluminum stands out as the most abundant metal on Earth crust and also has well known catalytic properties, in fact recently aluminum is living a renascence as catalysts.[2] As well alkali metals such as Li, Na and K are particularly interesting not only for their abundance but as well due to their low toxicity.

We have prepared a series of aluminum and alkali metal complexes with phenoxide ligands that bear different substituents in the aromatic rings to assess their influence on the catalytic activity.[3] These compounds have shown to be very active in catalytic ROP processes of *rac*-lactide and ε-caprolactone and also in the ROP of a monomer quite reluctant to polymerization such as β-butyrolactone. Furthermore, to enlarge the family of polyesters from renewable feedstock a good strategy is to perform the copolymerization of anhydrides and cyclic ethers derived from renewable resources such as terpene epoxides. In these processes our compounds have also shown to be very active generating efficiently terpene derived polyesters.

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Unravelling the effect of additives on promoting the access to reactive cobaltacycle intermediates: Implications in Cp*Co-catalyzed C–H functionalization reactions

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Over the past decades, transition-metal-catalyzed directed C–H functionalization processes have emerged as a powerful tool for the synthesis of relevant organic scaffolds. Until recently, the majority of these transformations were achieved employing noble metals, such as palladium or rhodium. However, in the recent years, more cost-effective first-row metals have shown their potential to construct C–C and C–heteroatom bonds. In this context, major advances have been accomplished with Cp*Co^{III} catalysts [1]. Despite this significant synthetic progress, Cp*Co^{III}-catalyzed C–H functionalization is still at its infancy, in part, due to the limited fundamental organometallic understanding of these systems. This is likely due to the proposed reversibility of the C–H activation step using Cp*Co^{III} complexes which hampers the isolation and characterization of reactive transient reactive intermediates (Figure 1).

This presentation will describe our recent efforts on accessing previously elusive reactive cyclometalated Cp*Co^{III} complexes [2], the crucial role of additive to overcome the reversible nature of the C–H metalation step, and the use of these metallacyclic Co^{III} intermediates to develop more efficient catalytic processes [3].

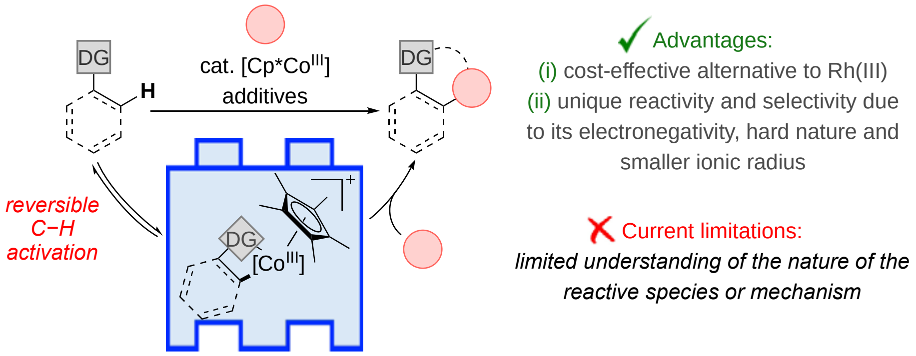

Figure 1. Cp*Co^{III}-catalyzed directed C–H functionalizations

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POSTERS

Zirconium scorpionates as greener catalysts for a more efficient industrial production of valuable biosustainable materials

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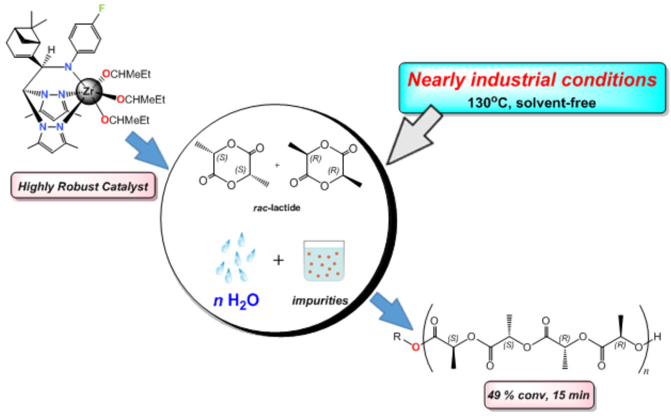
Poly(lactic) acid (PLA), an aliphatic polyester derived from the bioresourced lactic acid, has attracted great interest due to its wide variety of biomedical and pharmaceutical applications, considering its biocompatibility with human tissue and bio-absorbable nature. In fact, the production of PLA is estimated to grow to over 1.2 million tonnes in 2019. The most useful strategy to produce PLA involves the use of metal-based catalysts as initiators for the Ring-Opening Polymerization (ROP) of lactide (LA) monomers, and particularly, the use of group 4 complexes as initiators has increased in interest given its the low toxicity, high activity and good control. However, very few examples have been reported to be effective under the more industrially relevant solvent-free conditions and, in addition, capable to tolerate air and the levels of moisture and impurities present in the monomer.



To address this challenging requirement, our group has prepared a series of enantiopure scorpionate zirconium tris thio-/alkoxides of the type [Zr(ER)$_3$(κ^3-*R*,*R*-fbpza)] (**1–6**) [*R*,*R*-fbpzaH = *N*-p-fluorophenyl-(1*R*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethylamine] for use as thermally stable and robust single-site initiators for the living ROP of *rac*-LA both in solution and in the melt [1]. Importantly, complex [Zr(OCHMeEt)$_3$(κ^3-*R*,*R*-fbpza)] (**2**) exhibits the highest activity reported to date for a group 4-based initiator in the ROP of *rac*-LA under the industrially preferred melt and solvent-free conditions. Surprisingly, initiator **2** is still highly active in the melt when using an unpurified monomer and it shows an unprecedented tolerance to water and impurities (49% conv., 15 min, 130 °C).

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Gold(I) complexes derived from flavonoids as anticancer drugs

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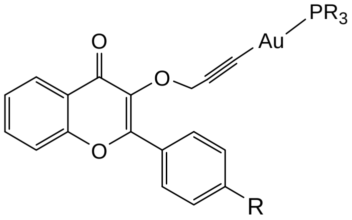
The interest in the development of metallic derivatives as therapeutic agents has been increasing during the last decades after the success of cisplatin in solid tumor treatment. Nevertheless, the occurrence of some drawbacks and limitations, have encouraged researches to find alternatives in order to minimize these negative side-effects. An extensive number of metal-containing compounds were described as cytotoxic agents, which display different mechanism of action. Among them, gold-based complexes have emerged as new chemotherapeutic agents.[1]

The majority of biologically tested gold derivatives comprises gold(I) atoms bonded to thiolates, phosphanes and N-heterocyclic carbene ligands. Recent attention merits alkynyl gold complexes[2] that display improved stability compared to the traditional gold drugs based on the relatively higher bond dissociation energies around the gold centre.

In addition, flavonoids, a class of antioxidant found in fruits, vegetables, tea and red wine have demonstrated their anticancer activity in *in vitro* and *in vivo* studies. Here we present the synthesis of alkynyl phosphane gold(I) complexes obtained from alkylated 3-hydroxyflavonoids, which have been studied as cytotoxic agents against colon cancer cell lines. Preliminary studies on their mechanism of action that comprise the type and mechanism of cellular death, its implication in cell cycle progression, the interaction with BSA, as well as their influence in the ROS formation are also included.



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Boron guanidinato compounds for CO_2 chemical fixation

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Chemical fixation and transformation of carbon dioxide (CO_2), which is an inexpensive and renewable carbon source, is one of the greatest scientific and technological challenges.[1] The development of both new reactions and new catalysts is needed to overcome the kinetic and thermodynamic stability of CO_2.[1] Guanidinato compounds of the main and transition metal groups have been actively studied in recent years for their applications in a variety of attractive areas. As part of our continuous research into the chemistry of guanidine derivatives,[2] we present here the straightforward high-yield synthesis of boron guanidinato adducts of CO_2, $\{R(H)N\}C\{N(R')\}(NR)(CO_2)BC_8H_{14}$ (R = iPr; R' = Ph, p-MeC_6H_4, o-MeC_6H_4, p-$tBuC_6H_4$, p-$CF_3C_6H_4$; R = Cy; R' = p-MeC_6H_4), and isocyanides, $\{iPrHN\}C\{N(p\text{-}MeC_6H_4)\}(NiPr)\{CNR''\}BC_8H_{14}$ (R'' = p-$MeOC_6H_4$, 2,6-$Me_2C_6H_3$), obtained by one-pot selective coupling with borylamines and carbodiimides, through guanidinato intermediates with frustrated Lewis pair-type reactivity (Figure 1). The molecular structures of some borylamine and CO_2 and isocyanide adducts were established by X-ray diffraction analyses.

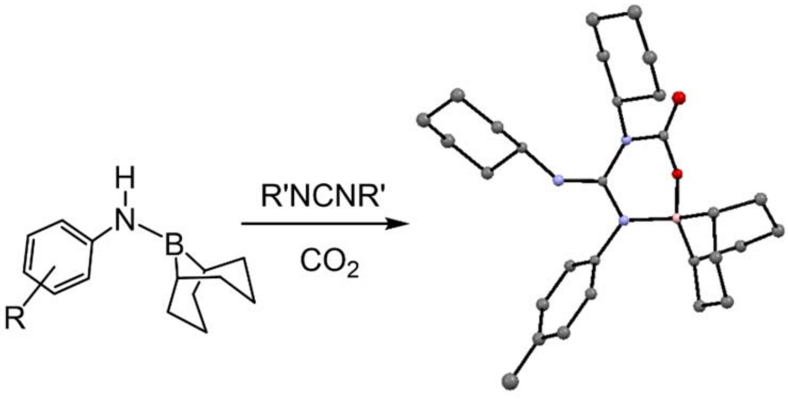

Figure 1. Synthesis of CO_2 boron guanidinato adducts by selective coupling.

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Financial support acknowledgment: MINECO Project nos. CTQ2016-77614-R, CTQ2016-81797-REDC and CTQ2015-63726-P.

Silver-mediated intermolecular nitrene transfer to allenes

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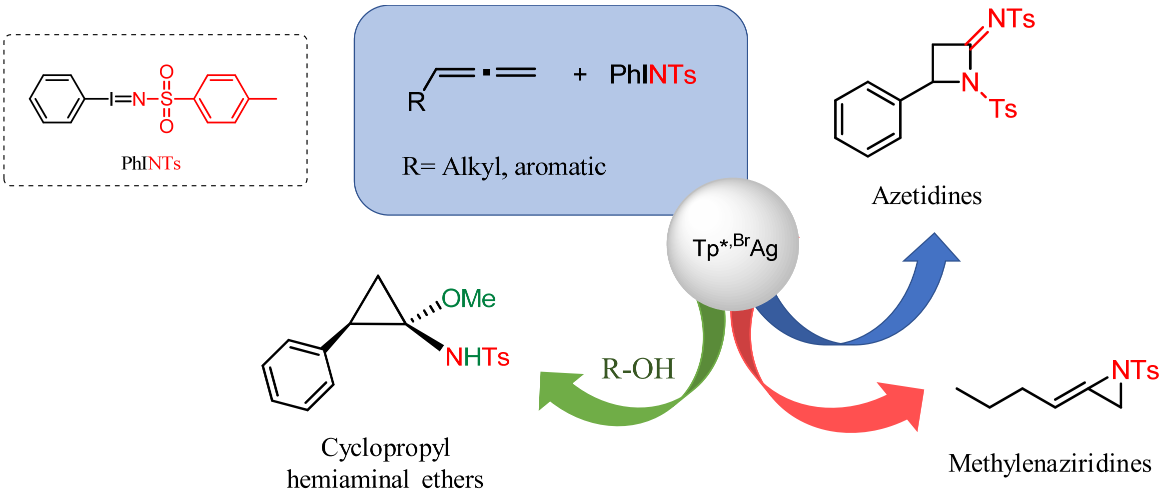
One of the strategies employed for the formation of new C-N bond consists of the transfer of a nitrene group to saturated or unsaturated substrates. Our research group has developed a family of metal complexes bearing hydrotrispyrazolylborate ligands (Tp^x) as efficient catalysts in the nitrene (NTs, Ts = *p*-toluensulfonyl) addition or insertion reactions to substrates of different nature such as alkanes, olefins, alkynes, dienols, furans or aromatic compounds.[1] In our search for other substrates suitable for such transformation we have found that allenes, albeit being widely used in organic chemistry, have not yet been employed as substrates in intermolecular nitrene transfer reactions.

In this contribution, we describe the first example of an intermolecular nitrene transfer to terminal or internal allenes. The use of the $[Tp^{*,Br}Ag]_2$ complex as catalyst has led to a novel transformation in which azetidines, methyleneaziridines and cyclopropyl-hemiaminal ethers are formed.



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Synthesis of Group 6 metal-tris(ethylene) complexes with a PNP-type pincer ligand. Reactivity studies towards carbon dioxide.

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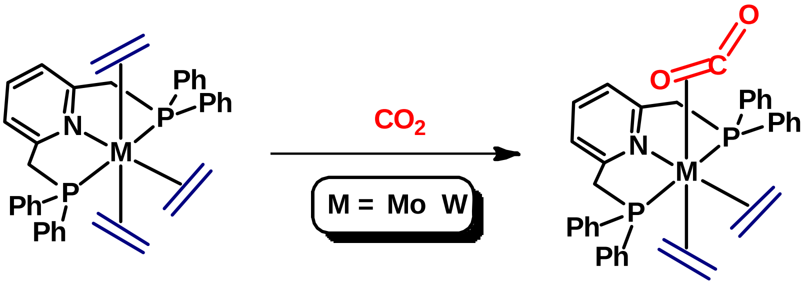
In the last few decades, ethylene complexes of transition metals have become relevant due to their industrial importance as intermediates and catalysts in a wide range of reactions.[1] In the context of the ethylene-carbon dioxide coupling reaction en route to acrylic acid derivatives, very few complexes have been described to promote such transformation.[2] Whereas nickel-based systems have provided catalytic reactions, molybdenum and tungsten derivatives are yet restricted to stoichiometric transformations between C_2H_4 and CO_2 [3].

In this communication, we present the synthesis and characterization of the first tris(ethylene) complexes of Mo(0) and W(0) bearing a PNP-type pincer ligand and the study of their reactivity with carbon dioxide. Preliminary studies have shown that mono-(carbon dioxide), bis(ethylene) complexes are formed (Scheme 1), both in solution as well as in the solid-state.



Scheme 1

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Functionalization of Azaheterocycles with NHP-Cu(I) Complexes

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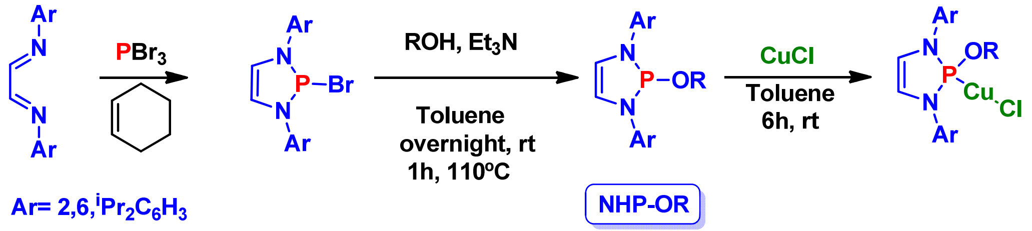
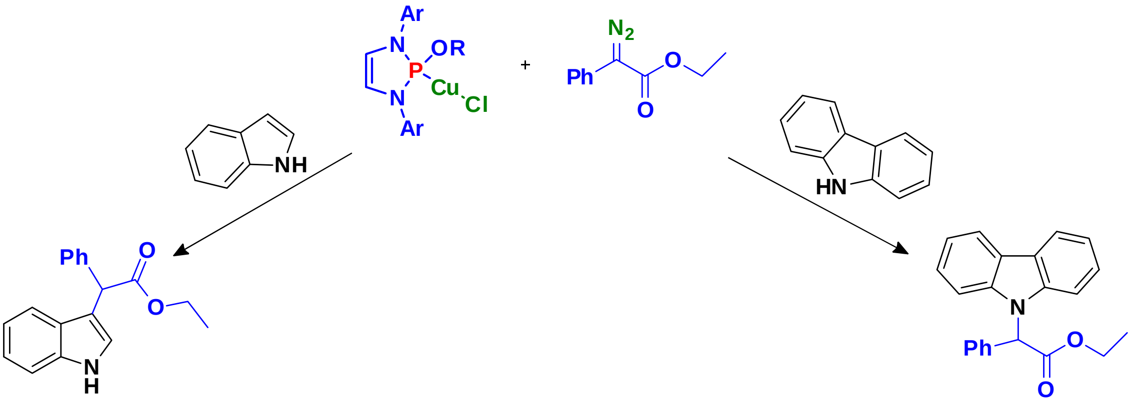
Although N-heterocyclic phosphite (NHP-OR) ligands have been known for more than 40 years,[1] their use as ligands in metal complexes has generated recent interest derived from their similarities with NHC ligands.[2] The modification of the substituents in the N and O atoms allows the preparation of a wide range of ligands with different electronic and steric properties. In addition, chiral versions can be prepared for enantioselective catalysis[3]. In this contribution we present the synthesis and characterization of several Cu(I) complexes with this type of ligands based on chiral alkoxydiazafosfolidenes.



We have also found that these complexes catalyse the derivatization of indoles and carbazoles through carbene insertion reactions with diazo compounds. These transformations occur in a chemo-, regio- and, in some cases, with modest enantioselection, affording products with biological and pharmacological interest.



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POSTER 7

Catalytic C-H functionalization of azulene by carbene and nitrene insertion

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Azulene, a natural hydrocarbon $C_{10}H_8$ consisting of a five- and a seven membered ring fused, has attracted the interest of many research groups due to its unusual properties.[1] It shows a beautiful blue color, the ability to undergo redox processes easily, and a large dipole moment, related with an asymmetric π-polarization between both rings. These properties explain their synthetic utilities and have led to the development of interesting modern applications, mainly in the construction of advanced organic functional materials.

Thus, simple functionalization methods for azulene and its derivatives are highly desirable. The functionalization of the 5-member ring by formation of carbon-carbon bonds have been studied by metal-catalyzed processes, obtaining results in arylation, alkylation, alkenylation, alkynylation, propargylation or carbonylation reactions.[2]

As a different alternative, we have focused in the incorporation of CR'CO_2R units by carbene insertion to the azulene using copper or rhodium catalyst (Figure 1). Additionally, we have also studied the metal-catalyzed nitrene insertion in the C-H bonds of the azulene to get directly carbon-nitrogen bonds. So far, nitration and further reduction it is necessary to obtain amino azulene derivatives.

In this contribution our most recent results regarding the azulene functionalization by carbene and nitrene insertion and further applications in the preparation of degradable azulene-based materials will be presented.

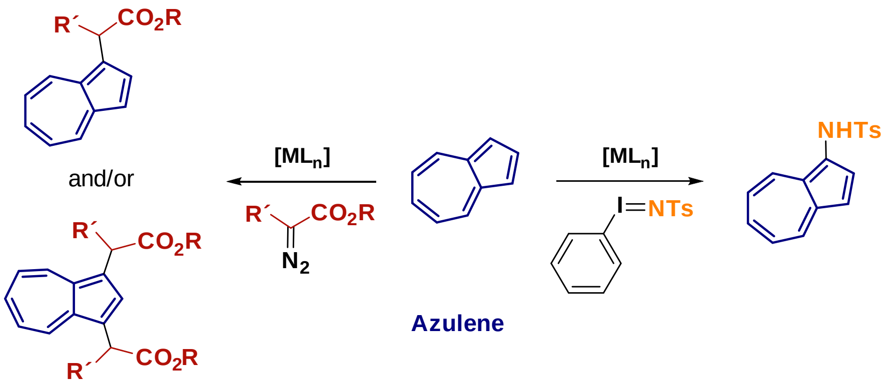

Figure 1

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Copper-Catalyzed Intermolecular Amidation of Light Gaseous Alkanes Using Supercritical CO_2 as Reaction Media

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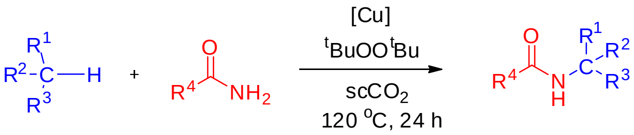
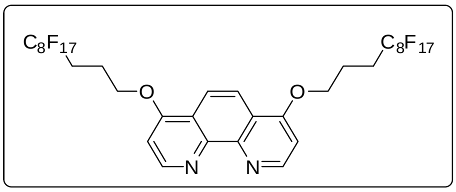
The functionalization of light alkanes is one of the most influence lines of research in the field of chemistry. The importance of finding techniques to achieve this fact is due to the abundance of these substrates in nature makes of them good starting materials but, in spite of it, they have a very low reactivity that makes it difficult to convert them in other molecules.

An unusual metal-catalyzed reactions is the intermolecular amidation of unactivated alkanes using a simple copper catalyst and a peroxide to form the corresponding N-alkyl products.[1] Furthermore, to achieve the objective of functionalizing light gaseous alkanes, including methane, the chosen reaction media is the supercritical CO_2 ($scCO_2$) which improves the solubility of the catalyst and allows the reaction to take place and it that has been employed in previous works to functionalize light gaseous alkanes.[2]





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Metallosupramolecular Cages: Computational Description of Encapsulation

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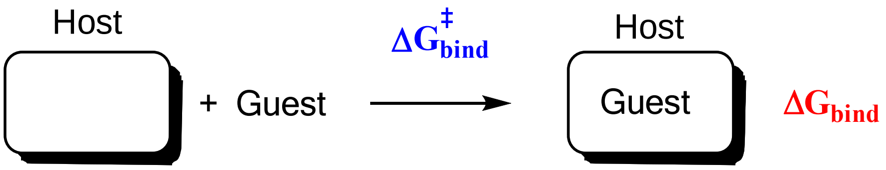
The self-assembled supramolecular hosts have been applied successfully in catalytic transformations.[1] In these processes the encapsulation of the guest into the host is a crucial step. This involves several molecular events one of those being the dynamical complementarity between the binding of the guest and the supramolecular hosts. There are several self-assembled coordination cages have been synthesized from ligands and metal ions (i.e. Raymond[2], Fujita[3]). Nevertheless, the exact contribution of the flexibility of the host in the recognition process is not yet clear.

Here we present our results obtained in the simulation of the host-guest binding process of several cages by Molecular Dynamics. The binding energies as well as the Gibbs energy barrier for this process will be presented for several examples selected from literature.



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Copper-catalyzed selective pyrrole functionalization by carbene transfer reaction

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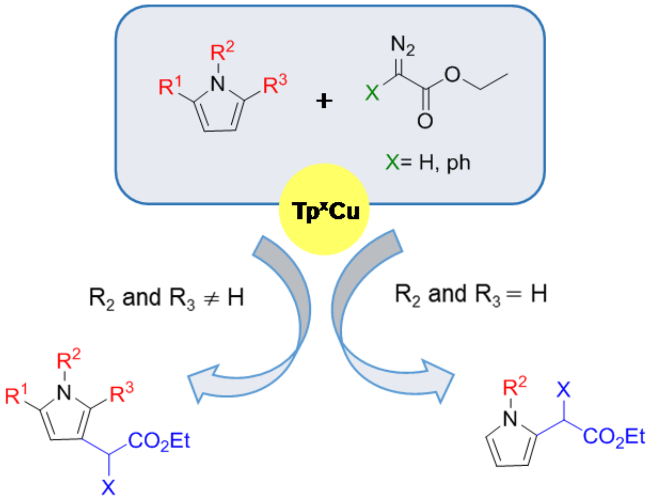
Pyrroles are very abundant heterocycles in natural products and pharmaceutical agents, and are also high-value synthons in organic synthesis.[1] The direct functionalization of C-H bonds of unprotected pyrroles is considered as the most convenient approach toward derivatization of these heterocycles. The high electronic density and the acidic hydrogen (pK_a = 17) on the nitrogen atom, provide additional reactivity with respect to those of other 5-member heterocycles.

The carbene transfer reaction from diazocompounds is a well-established strategy for the formation of new C-C or C-X bonds. However, the examples described in the literature with pyrroles as substrates, mainly based on Rh-catalysts, present low selectivity due to the tendency of pyrroles to difunctionalization in both positions 2 and 5 of the ring, and are restricted to a few cases.

Given the high activity displayed by the complexes Tp^xM (Tp^x = hydrotrispyrazolylborate ligands, M = Cu, Ag) for the catalytic carbene addition and insertion reactions [2], we herein describe the use of Tp^xCu as catalyst capable to promote the C-H bond selective functionalization of a series of different pyrroles by the carbene transfer from diazocompounds.



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Sistemas multimetálicos con ligandos sulfuro: una estrategia cooperativa en la activación de moléculas pequeñas

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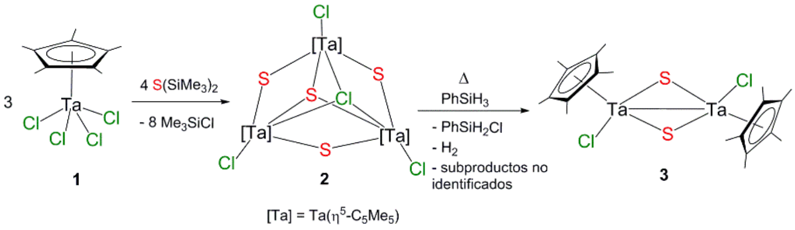
La utilización de sistemas multimetálicos ha despertado un gran interés en los últimos años y la razón hay que buscarla en el efecto sinérgico que surge cuando múltiples sitios reactivos trabajan de forma concertada y cooperan para facilitar diversos procesos de activación y funcionalización.[1]

En esta comunicación se presenta la síntesis, caracterización y el estudio del comportamiento químico de especies sulfuro de tántalo. Así, el derivado $[Ta(\eta^5\text{-}C_5Me_5)Cl_4]$ (**1**) reacciona con $(SiMe_3)_2S$ para generar el compuesto trinuclear $[Ta_3(\eta^5\text{-}C_5Me_5)_3Cl_3(\mu_3\text{-}Cl)(\mu\text{-}S)_3(\mu_3\text{-}S)]$ (**2**), susceptible de reducción posterior, en presencia de $PhSiH_3$, para dar el complejo dinuclear de Ta(IV) $[Ta(\eta^5\text{-}C_5Me_5)_3Cl(\mu\text{-}S)]_2$ (**3**) (**Esquema 1**). El tratamiento de **3** con organolitiados o magnesianos adecuados permite obtener las especies alquilo/arilo correspondientes $[Ta(\eta^5\text{-}C_5Me_5)R(\mu\text{-}S)]_2$ (R = Me, Et, C_3H_5, Ph, CH_2Ph, CH_2SiMe_3). Por otro lado, la reacción del compuesto $[Ta(\eta^5\text{-}C_5Me_5)(CH_2Ph)(\mu\text{-}S)]_2$ con dihidrógeno conduce a la eliminación de tolueno y la hidrogenación parcial del anillo aromático del otro grupo bencilo (**Figura 1**). También se presentarán los resultados obtenidos del estudio teórico de tan singular proceso cooperativo.



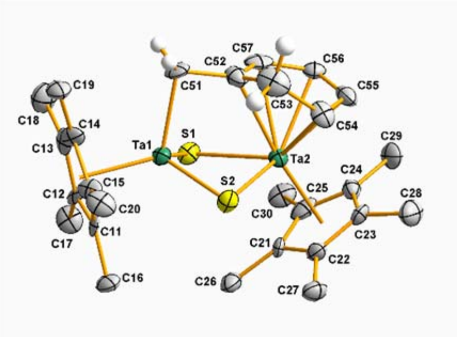


Figura 1

Agradecimientos: MINECO (CTQ2013-44625-R y CTQ2016-80600-P)) y Universidad de Alcalá (CCG2017-EXP/036). C. H.-P. y J. I. G.-P. agradecen a la Universidad de Alcalá la concesión de una beca predoctoral.

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Synthesis of titanium polyhydride complexes with borane derivatives

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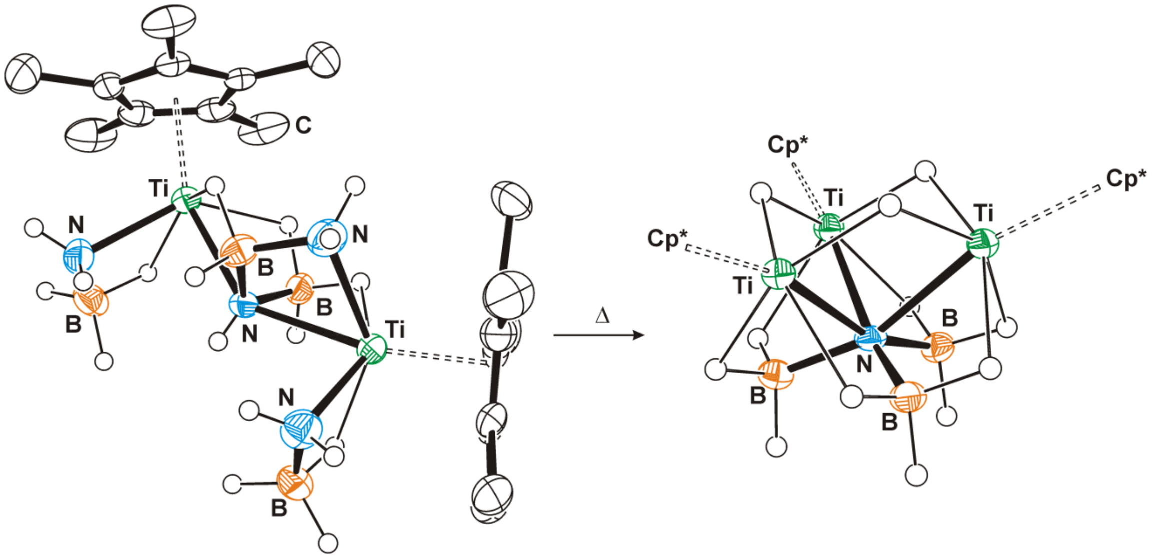
Early transition-metal hydride compounds are receiving increasing attention because of their implication in the activation of inert molecules (eg., N_2, C_6H_6). In this context, we have isolated several zirconium hydride complexes in reactions involving the dimethylamine-borane adduct.[1] Additionally, we have also reported the synthesis of the titanium tetrahydride system [{TiCp*(μ-H)}$_3$(μ$_3$-H)(μ$_3$-NMe_2BH_2)] (Cp* = η^5-C_5Me_5) by the treatment of [TiCp*(CH_2SiMe_3)$_3$] with excess $NHMe_2{\cdot}BH_3$, or with three equivalents of dimethylamine-borane under a hydrogen atmosphere.[2] However, the octahydride species [(TiCp*)$_4$(μ-H)$_8$] is obtained *via* hydrogenolysis of the trialkyl titanium reagent.[2]

In this communication, we will describe further reactivity of monopentamethylcyclopentadienyl titanium complexes [TiCp*R_3] with borane derivatives. As example, the treatment of trialkyl compound [TiCp*Me_3] with the adduct $NH_3{\cdot}BH_3$ in toluene affords a dimetallic complex (see scheme), which decomposes in solution at high temperature to give a trimetallic system. Theoretical studies on these species suggest that both can be seen as titanium(III) hydride units, [TiCp*H(NH_2BH_3)] or [TiCp*H_2] respectively, connected by bridging borazane ligands.



We are grateful to the Spanish MINECO (CTQ2013-44625-R) and Universidad de Alcalá (CCG2017-EXP/021) for providing financial support. E. H. thanks the Universidad de Alcalá for a fellowship.

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Reactivity of imido and nitrido ligands on polynuclear titanium complexes

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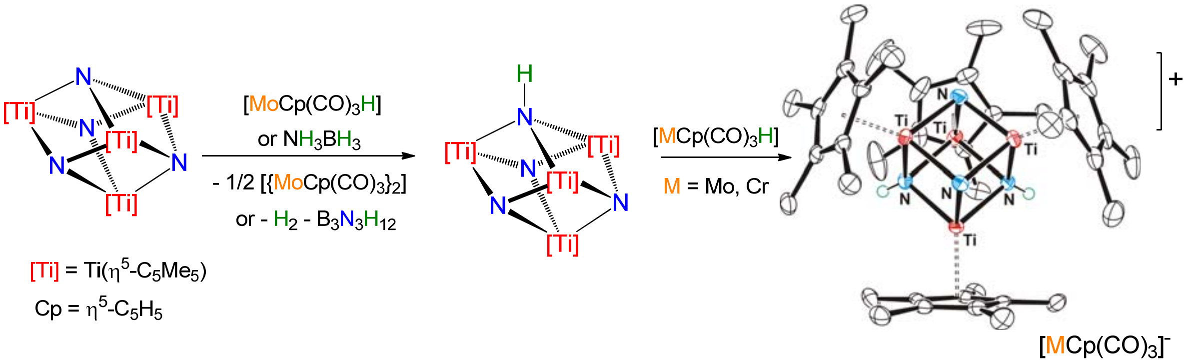
Multimetallic molecular species with μ_n-N nitrido and μ_n-NH imido groups are relevant to the bridging modes of the chemisorbed nitrogen atoms in the heterogeneous catalytic Haber-Bosch ammonia synthesis. Transition-metal imido and nitrido complexes are also implicated in the catalytic conversion of N_2 into NH_3 by homogeneous systems in which the cooperation of multiple metal sites may be beneficial in the activation and hydrogenation of the dinitrogen molecule. In particular, Hou and co-workers reported that polynuclear hydride titanium complexes are capable of breaking the strong $N\equiv N$ triple bond to give imido and nitrido species under mild conditions.[1] More recently, we have described the cleavage of dinitrogen under ambient conditions to give a tetranuclear nitrido complex by simple exposure of $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$ to commercially available and inexpensive forming gas (H_2/N_2 mixture, 13.5-16.5% of H_2.[2]

In this context, our laboratory has a long-standing project devoted to developing a family of polynuclear imido-nitrido complexes,[3] and in this communication we will present new reactivity patterns of the imido and nitrido ligands supported on organometallic trinuclear and tetranuclear titanium systems. For instance, we will show that the treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ and $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ with group 6 hydride complexes $[MCp(CO)_3H]$ (M = Cr, Mo; Cp = η^5-C_5H_5) leads to derivatives resulting from hydrogenation and protonation of the imido or nitrido groups in the starting materials (see Figure). The functionalization of these bridging ligands with amine-borane adducts NHR_2BH_3 (R = H, Me) will be also discussed.



We are grateful to the Spanish MINECO (CTQ2013-44625-R) and Universidad de Alcalá (CCG2017-EXP/021) for financial support. P.B. thanks the Universidad de Alcalá for a fellowship.

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Hydrido-Silyl-Thioether-Rh(III) Complexes to Catalyse Tandem Isomerization-Hydrosilylation Reaction

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The hydrosilylation of alkenes is an important academic and industrial procedure because this reaction leads to the formation of valuable precursors for silicon based polymers, lubricants and water repellent coatings, among others.[1] One of the highest limitations of catalytic hydrosilylation of alkenes is the necessity of using α-olefins to obtain linear alkylsilanes.[2] We have recently reported a series of hydrido-silyl-thioether rhodium(III) compounds capable to catalyse the tandem isomerization-hydrosilylation reaction to obtain linear silanes from internal alkenes or alkene mixtures.[3,4]

Here we report the synthesis and characterization of new hydrido-silyl-Rh(III) complexes with different substituents on the thioether moiety which have been tested as catalysts in the tandem isomerization-hydrosilylation reaction.

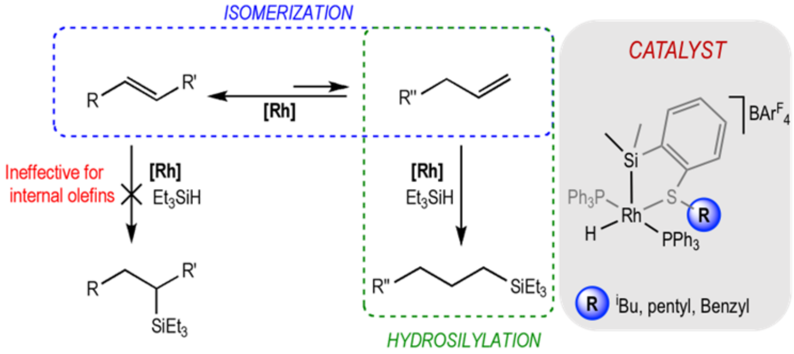

Figure 1. Tandem isomerization-hydrosilylation and catalysts used in this work.

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Iridium Boryl Complexes Stabilized by a Xantphos-Type Ligand

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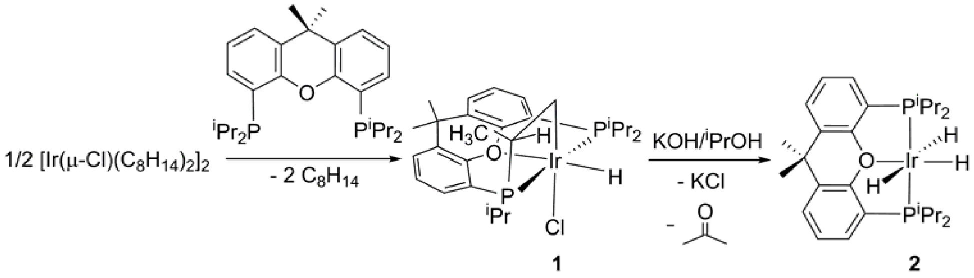
Catalytic reactions involving boranes and diboranes, such as the borylation of organic molecules [1] and the dehydrocoupling of ammonia-borane,[2] among others, are very significant processes in the current chemistry. Many of these processes involve the activation of the B-H bond of a borane, or the B-B bond of a diborane, at a transition-metal center. Within this context, a thorough understanding of these fundamental reactions can be highly valuable in the design of new catalysts.

Complexes containing diphosphine POP-pincer ligands have the ability to stabilize uncommon species as a consequence of the disposition of their donor ligands, and have a particular interest due to the hemilabile properties of the central oxygen atom.[3] These interesting features have prompted us to initiate a research program on POP-complexes of groups 9 metals, looking for new behaviors and applications in catalysis.[4] Within this program we reported the synthesis of IrHCl{κ^4-P,O,P,C-xant(P^{i}Pr$_2$)([^{i}PrPCH(Me)CH$_2$]} (**1**) and IrH$_3${κ^3-P,O,P-xant(P^{i}Pr$_2$)$_2$} (**2**).[4a] In this contribution we show the preliminary results of the reactivity of derivatives **1** and **2** with boranes and diboranes.



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Insights into the Mechanism of the Transmetalation Reactions of Protic N-Heterocyclic Carbenes and Diamino Carbenes from Mn(I) to Au(I)

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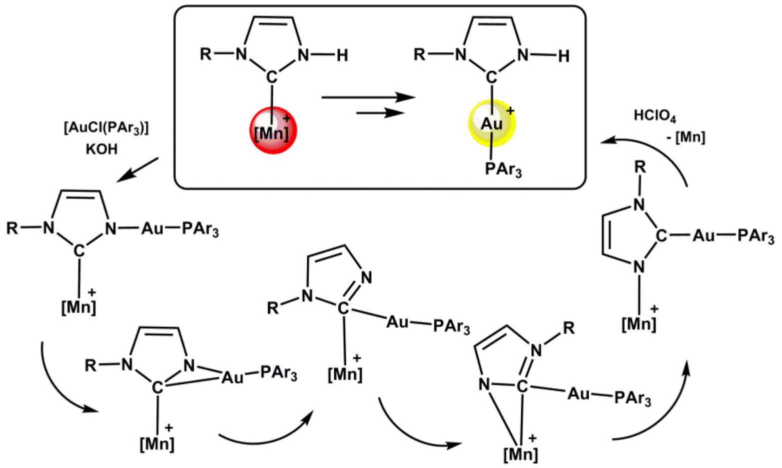
Reactions that involve the use of NHC-complexes of metal such as Ag^I, Cu^I or Au^I as carbene transfer agents have been applied to the preparation of many transition-metal NHC-complexes by transmetalation [1]. Among NHC complexes, those containing one or two N-H moieties (also called protic NHCs or pNHCs) have been little studied, and direct reaction transfer of these carbenes has not been described yet. In our group it was showed that Mn^I-NHC complexes can serve as pNHC transfer agents from Mn^I to Au^I with the mediation of bases [2], a process that we now have studied in depth with new experimental insights and DFT calculations [3]. The reaction mechanism involves the formation of key reaction intermediates bearing a pure bridging imidazolyl ligand between manganese and gold, as well as transition states showing dihapto-coordination of this ligand, first to gold and then to manganese. In addition, similar DFT calculations have been carried out on protic acyclic diamino carbene complexes, showing analogous transferring of the carbene from Mn^I to Au^I to provide noteworthy mangana-N-heterocyclic carbenes of gold [4].



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Novel approach to the synthesis of tertiary α-aryl oxindoles via enantioselective Pd-catalyzed decarboxylative protonation

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Chiral oxindoles are endogenous aromatic substances that are found in the body fluids and tissues of mammals. The oxindole backbone is also present in many natural products with antiviral, antibacterial and anticarcinogenic effects.[1]

Chiral oxindoles can be prepared by Pd-catalyzed intramolecular cyclization. However, this strategy only allows the preparation of quaternary α-aryl oxindoles with ee's up to 71%,[2] being the synthesis of the corresponding tertiary α-aryl oxindoles not feasible. As alternative, the direct metal-catalyzed α-arylation of carbonyl compounds have been attempted but again the asymmetric α-arylation of oxindoles has not been reported yet because of the easy racemization of that tertiary stereocentre in the α-position to the amide group.[3]

In this communication our efforts towards the development of the first catalytic asymmetric preparation of sterically hindered tertiary α-aryl oxindoles via enantioselective Pd-catalyzed decarboxylative protonation will be discussed. The reaction occurs under very mild conditions and in short reaction times, providing excellent yields and good enantioselectivities. We will also discuss our combined experimental and theoretical investigations of the reaction mechanism.

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Pd-catalysed C–H arene metallation with main group hydrides.

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Merging main group chemistry with transition metal catalysis is a rather underexploited strategy in synthesis. Despite the recent renaissance of applications using main group complexes, catalytic applications are often limited to simple transformations such as hydrogenation or hydroelementation of unsaturated substrates.[1] Recently we have found that the reactivity of Al, Mg and Zn reagents can be widely expanded using transition metal catalysis.

While investigating the reactions between [$Pd(PCy_3)_2$] and β-diketiminate supported Mg- and Zn-complexes, we discovered some well-defined intermetallic complexes with extremely unusual coordination geometries and remarkable bonding configurations. The same Pd bisphosphine complex can catalyse the transformation of the C–H bonds of arenes to either C–Mg or C–Zn bonds.[2] For example, the *BDI*Zn–H complex efficiently effects the C–H zincation of a wide range of fluoroarenes, to afford robust and versatile arylzinc reagents. Initial mechanistic studies suggest that the C–H bond activation occurs *via* intermediates with metal–metal bonds. This new reaction is the first direct zincation procedure that does not rely on stoichiometric amounts of other metals (Na, Li, Mg…).[3,4]

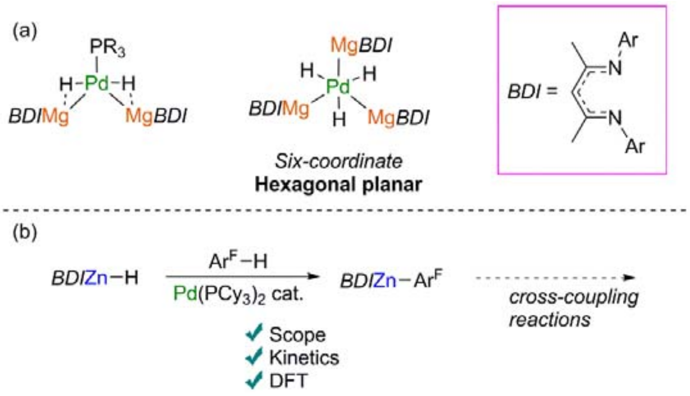

Figure 1. (a) Novel intermetallic Pd-Mg complexes. (b) Direct C–H zincation of fluoroarenes.

The analogous system with Mg does not even require activating groups and can achieve the magnesiation of benzene at ambient temperature. This may ultimately offer an alternative to Grignard formation from carbon–halogen bonds.

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Co(II)-catalyzed alkene cyclohydroamination of primary amines

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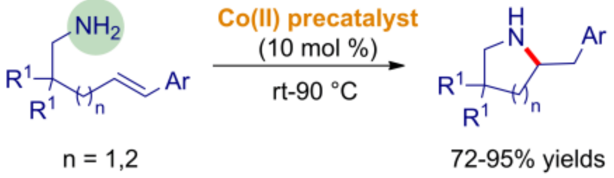
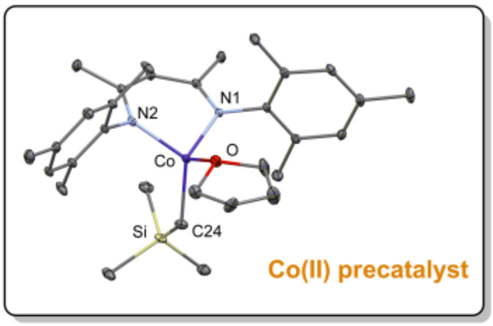
The general concern for sustainable metal catalysis has recently stimulated the exploration of earth-abundant, first-row late transition metals as hydroamination catalyst [1]. In this communication we present the first example of cobalt-catalyzed alkene hydroamination reaction of unprotected and electronically unbiased primary amines. It is reported that a β-diketiminatocobalt(II) complex is an efficient precatalyst for the hydroamination under mild and co-reagent free conditions of unprotected primary amines tethered to an aryl alkene. The reaction mechanism has been investigated by deuterium-labeling, kinetics, and stoichiometric experiments and in-depth DFT studies [2].





- ✓ Protecting-group free
- ✓ No co-reagent required
- ✓ Mechanism studies

The outcome of this work will help guide the rational design of base metal hydroamination catalysts with improved reactivity and alternative selectivity patterns.

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Tailor-made catalyst libraries for the effective preparation of elusive high value chiral compounds

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Asymmetric catalysis is one of the most powerful and sustainable approaches for the preparation of chiral compounds. Usually new catalysts are only tested in standard substrates, eluding systematically challenging substrates that would yield to more interesting compounds. In this communication we present our recent investigations in the design of new efficient catalyst libraries for the elusive and challenging asymmetric hydrogenation (AH) of cyclic β-enamides and tetrasubstituted olefins.[1] These reactions led to the formation of important chiral synthons, such as aminotetraline and aminochromanone derivatives, which can be found in numerous therapeutic agents and biologically active natural products (e.g. rotigotine, alnespirone,...). Despite this, they are underdeveloped compared to the AH of the most studied and solved α-enamides and trisubstituted olefins. Finally, we would also show the developement of new efficient catalyst libraries for the preparation chiral (poly)carbo- and heterocyclic compounds by using straighthforward sequences of allylic substitution and ring-closing metathesis or Pauson-Khand reactions.[2] The combination of theoretical studies and NMR spectroscopy were crucial to rationalize the catalysts' structure, identify the species responsible for the catalytic performance and to improve the catalysts performance.

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Acknowledgements

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Isomerization and Dehydration of Aldoximes catalyzed by (η^6-*p*-cymene)-Ruthenium(II) Complexes Containing Guanidiniumphenylphosphines

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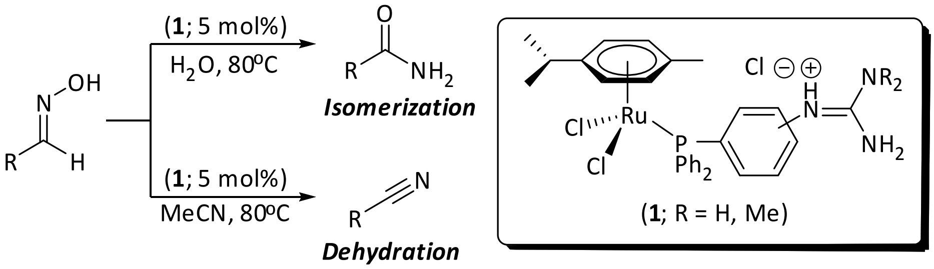
For reasons of cost, safety, and environmental concerns, the development of organic transformations in aqueous media has become one of the major cornerstones in modern chemistry. Following this general trend, the design of transition-metal catalysts for organic reactions in water has arisen a growing interest in recent years.[1] In this sense, introduction of hydrophilic ligands in the coordination sphere of a transition-metal is probably the most popular method for the preparation of water-soluble catalysts.[1,2] Thus, a wide variety of functionalized phosphine ligands containing highly polar sulfonated, hydroxyalkyl, ammonium, phosphonium, carboxylate, carbohydrate or phosphonate groups are actually known and their effectiveness in biphasic catalysis largely demonstrated.[1,2]

Cationic phosphines containing guanidiniumphenyl moieties possess highly polar functions which confer them a pronounced solubility in water. Moreover, the anion binding capacity of the guanidinium groups should exert some precoordination and preorientation of anionic substrates in the periphery of catalyst complexes containing these ligands. Although all these potential advantages, as far as we know there are only few examples of metal complexes containing guanidiniumphenylphosphines in their coordination sphere, as well as their use as catalysts in different organic reactions.[3]

With this situation in mind, we decided to accost the synthesis of various (η^6-*p*-cymene)-ruthenium(II) complexes (**1**) containing different guanidiniumphenylphosphines as ligands. These complexes were subsequently tested as potential precursors in the isomerization or dehydration of several aldoximes employing water or acetonitrile as solvent, respectively.



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Rh(III)-Catalysed Dehalogenation of Chloroform by Silanes

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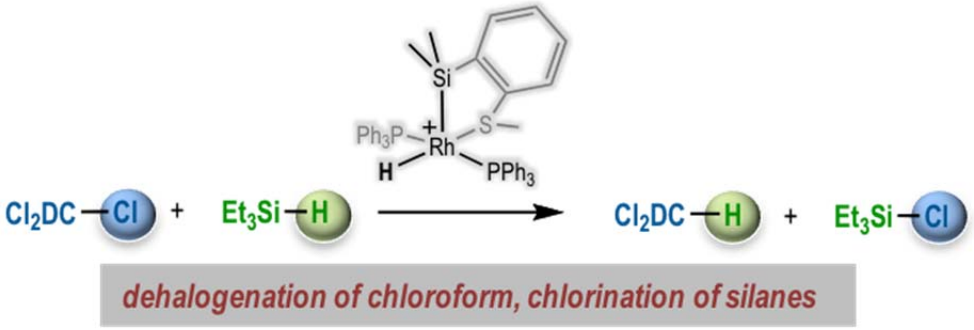
The carbon-halogen bond cleavage has become of interest in recent years due to the growth of compounds containing halides. Many methods for hydrodechlorination of organic compounds employ heterogeneous catalysis and severe reaction conditions are often necessary. Alkyl halides can be reduced by organotin hydrides, the use of hydrosilanes instead of hydrido stannanes results attractive because these compounds are more readily available than organotin hydrides. Only a few transition metal compounds have been reported as efficient catalysts for reduction of a broad spectrum of alkyl halides by silanes.[1-3]

The reaction of [Rh(PPh_3)$_3$Cl] with the bidentate ligand $SiMe_2H(o\text{-}C_6H_4SMe)$ and $NaBAr^F_4$ [Ar^F=3,5-$(CF_3)_2C_6H_3$], leads to the cationic hydrido-silyl-Rh^{III} complex, {Rh(H)[$SiMe_2(o\text{-}C_6H_4SMe)$]($PPh_3$)$_2$}[$BAr^F_4$].[4] This complex has been tested as catalyst for the dehalogenation of chloroform with different silanes such as triethylsilane, dimethylphenylsilane, methyldiphenylsilane and triphenylsilane at temperatures between 40 and 55 °C. With the aim to unravel the mechanism of this process, the kinetic behaviour of the reaction between chloroform or bromoform and triethylsilane catalysed by hydrido-silyl-Rh^{III}compund has been studied. The study of the kinetic isotope effect with deuterated triethylsilane has also been undergone.



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New trispirazolylborate silver complexes for the selective functionalization of primary C-H bonds of non-activated alkanes

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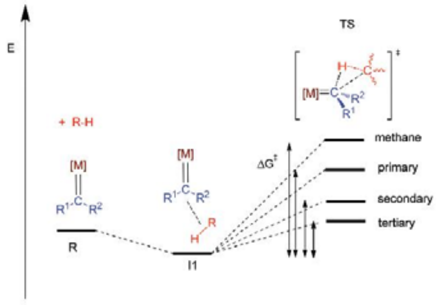
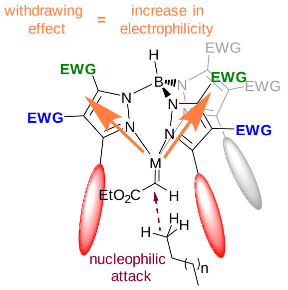
Hydrocarbons are abundant, cheap and easily accessible raw materials. However, their use in the chemical synthesis is rather limited. Their main application is the production of energy through combustion and, in the case of methane, the preparation of *syngas*, a mixture of carbon monoxide and hydrogen used in the production of methanol. The main drawback when facing the functionalization of alkanes is their high inertness derived from the high dissociation energy (ranging from 95 Kcal mol^{-1} of cyclopentane to 105 Kcal mol^{-1} of methane or cyclopropane) [1] and the low polarizability of their carbon-hydrogen bonds that forces the use of harsh conditions to effectively functionalize them. These compounds can be functionalized through carbene insertion reactions using highly electrophilic metal complexes. However, the main drawback of this methodology is the lack of selectivity, especially when the functionalization of primary C-H bonds is faced. Primary C-H bonds have dissociation energies higher than secondary and tertiary C-H bonds, more prone to be functionalized. Following this objective a new family of Tp^x ligands that combine high electrophilicity and small catalytic pocket has been developed.





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Coordination Cages Based On “Click Chemistry” Derived Mesoionic Triazolylidene Ligands

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Supramolecular coordination chemistry enables the formation of complex structures that potentially can be used in multiples applications such as the stabilization of reactive species, molecular recognitions, catalysis and biomedical applications [1].

Our work research focuses on mesoionic 1,2,3-triazol-5-ylidene ligands (MICs) [2]. Their salt precursors are ready available via “click chemistry” [3] followed by alkylation [4]. Treatment of the salts with silver oxide enable the preparation of several coordination cages ($[Ag_3L_2]X_3$, X= Cl, Br, BF_4) which have been isolated and fully characterized. The related trimetallic gold $[Au_3L_2]Cl_3$ and copper $[Cu_3L_2]Cl_3$ complexes were obtained via transmetalation reactions.

Herein, the synthesis of several coordination cages based on coinage metals (Ag, Au and Cu) (Figure 1), which are obtained from the corresponding 1,2,3-triazolium salts and form organometallic three-dimensional structures with well-defined cavities that potentially may host small molecules or alternatively be used as catalysts will be presented.

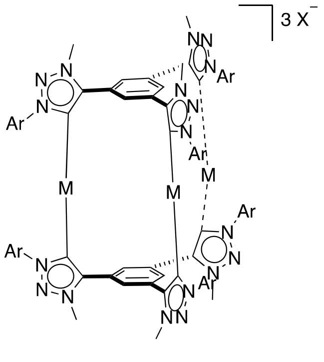

Fig.1: Coordination cages based on “Click Chemistry” derived triazolylidene ligands.

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Palladium-Catalyzed Aerobic Homocoupling of Alkynes: Full Mechanistic Characterization of a More Complex Oxidase-type Behavior

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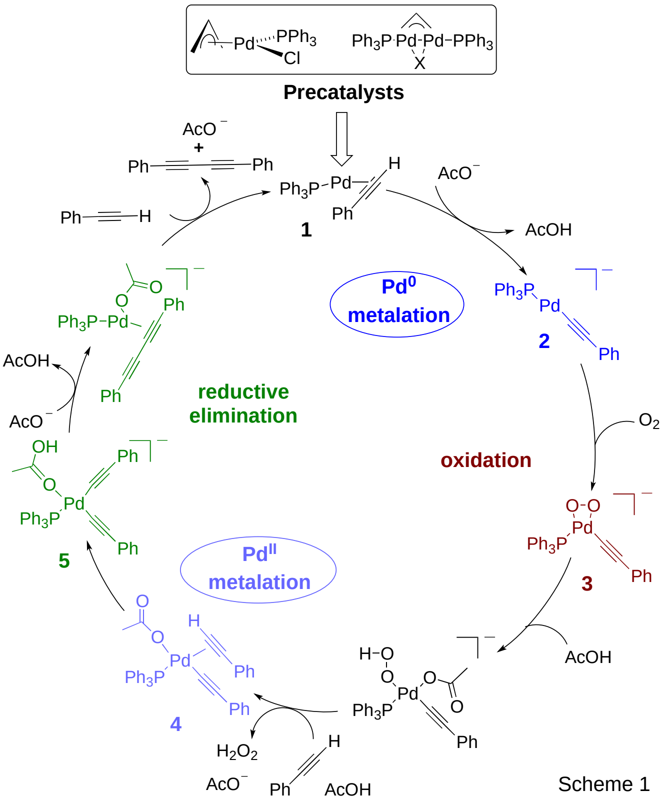
Selective aerobic oxidation of organic substrates features a key challenge in modern chemistry, and homogeneous Pd-catalyzed oxidation reactions are among the most promising strategies to achieve this goal.[1] We have characterized the full mechanism of the Pd-catalyzed oxidative homocoupling of alkynes with O_2 by the use of a combined experimental and computational approach. The controlled generation of a low-ligated [Pd(PPh_3)(alkyne)] complex **(1)** is key in the process, for which allylic Pd^{II} complexes in the presence of a base or Pd^I allylic dimers are suitable precatalysts.

The catalytic coupling (Scheme 1) starts with the alkyne metalation on Pd^0 to give an anionic **[Pd(PPh_3)(alkynyl)]$^-$ (2)** complex that is then oxidized by oxygen. The interaction of O_2 occurs only on this electron rich Pd^0 anionic species and leads to a **κ^2-peroxo Pd^{II} singlet (3)** intermediate that undergoes subsequent protonolysis. The second alkyne metalation occurs on the **Pd^{II} complex (4)** and it is assisted by an external acetate. The resulting **bis(alkynyl)Pd^{II} (5)** complex evolves to the product by reductive elimination.



Scheme 1

This is a more complex oxidase-type reaction where the substrate transformation and the catalyst oxidation are intertwined and dependent of one another, in contrast to most Pd-catalyzed oxidative processes.

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Palladium-catalyzed direct arylation of arenes assisted by a chelating bifunctional ligand.

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Palladium-catalyzed C-C coupling reactions that directly functionalize C-H bonds have led to the development of a large number of transformations aimed at building new C-C bonds without the need of pre-functionalization of every reagent. Here, we report the direct arylation of arenes with electron withdrawing groups (benzonitrile, trifluorotoluene, fluorobenzene and ethyl benzoate) as well as arenes with electron donating groups (anisole and toluene) using [Pd(bipy-6-OH)(C_6F_5)Br] (bipy-6-OH = [2,2'-bipyridin]-6(1H)-one) as catalyst (Figure 1). The results show that arenes with coordinating groups and fluorobenzene lead to faster reactions. The arene can be used as solvent but the reactions can be accelerated by the introduction of polar solvents such as DMF, DMA, dimethylsulfoxide or ketones that increase the solubility of the catalytic species.

Toluene was chosen to carry out a study of the reaction mechanism. It is clear that the ligand bipy-6-OH is assisting the C-H activation step. The substitution equilibria of the halogen by the arene on palladium is dependent on the reaction media and can be crucial in determining the reaction rate.

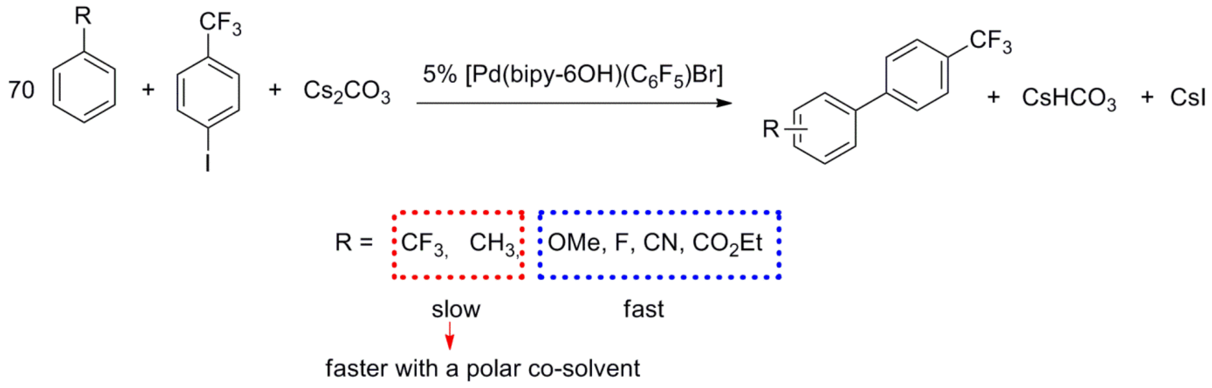

Figure 1. Direct arylation of arenes catalyzed by [Pd(bipy-6-OH)(C_6F_5)Br].

Acknowledgements

We are grateful to the Spanish MINECO (SGPI, grant CTQ2016-80913-P) for financial support.

α-Substituted Benzylic Complexes of Palladium(II) as Precursors of Palladium Hydrides

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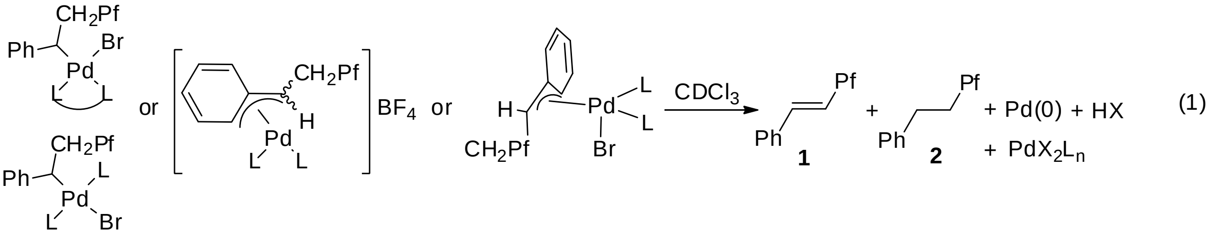
Benzylic palladium complexes are intermediates in catalytic reactions of benzyl derivatives of styrene, and can be considered weakly stabilized alkyls by coordination of the aryl ring in a pseudoallylic (η^3) form. The equilibria between this form and the alkyl σ-benzylic form slows down the β-H elimination reaction, and this could be used as a controlled source of Pd-H fragments. We have previously prepared a variety of benzylic palladium complexes with different ligands and an α-methylpentafluorophenyl substituent.[1] All of them decompose by β-Hydrogen elimination to give pentafluorostilbene **1** and a palladium hydride. This hydride either decomposes or it is transferred to another complex molecule to give, by reductive elimination, the reduction product **2** (eq 1).[2]



L = py, L = tht, L = 1/2(PhSCH$_2$)$_2$,
L = PPh$_3$, L = AsPh$_3$, L = 1/2 dppf,
L = PMe$_3$, L = 1/2 dppe

L = PPh$_3$, L = AsPh$_3$,
L = 1/2 dppf

The stability of the complexes shows a wide variation and it was determined by ^{19}F NMR. The study of the ratio E=[**2**]/[**1**] allows the determination of the effective transfer of the Pd-H between metals. The maximum H-transfer was observed in the presence of a bridging ligand (bromine atom) and low coordinating ligands.

On the other hand, it is possible to trap the Pd-H fragment by insertion of a diene into the Pd-H moiety. Starting from enantiomerically pure R-(+)-limonene, enantiomerically pure palladium allyls can be generated.

Acknowledgements

We are grateful to the Spanish MINECO (SGPI, grant CTQ2016-80913-P) for financial support.

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A Rough Contender is Presented in the Battle against Palladium for the Throne of the Heck Reaction having as Special Weapon Phosphine-Imine Ligands: Mechanistic Studies and Catalysis.

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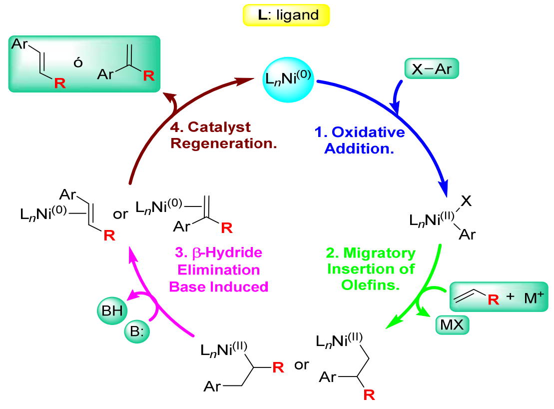
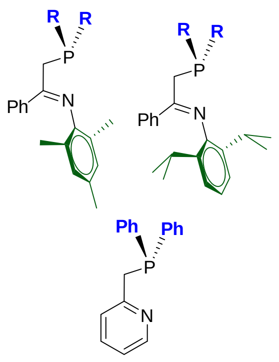
For the uninitiated, nickel might seem like just the impoverished younger sibling of palladium in the field of transition metal catalysis. After all, the use of palladium-catalyzed cross-coupling reaction has skyrocketed over the past half-century: it was honoured with the 2010 Nobel Prize in Chemistry. Nickel lies just above palladium in the periodic table, and as a group 10 metal, it can readily perform many of the same elementary reactions as palladium or platinum. Because of these commonalities, nickel is often viewed solely as a low-cost replacement catalyst for cross-coupling reactions. However, this common misconception is clearly refuted by the numerous and diverse nickel-catalyzed reactions reported in the literature. One of these reactions is the Heck reaction, in which Nickel is the most obvious replacement for Palladium, since both elements share many similar chemical features that are critical for the process [1]. Furthermore, Ni can activate certain substrates (e. g., unreactive aryl sulfonates or chlorides) much more readily than Pd, which suggests that Ni Heck catalysts could represent much more than a cheaper replacement for Pd. In spite of this, very few examples of Ni-catalyzed Heck reactions have been reported. The reasons behind the apparently lower catalytic capacity of Ni complexes in this specific reaction are poorly understood [2].

Hybrid phosphine-imine ligands provide an ideal background for the study of the basic processes involved in the Heck reaction. It is known that both Ni or Pd complexes with hybrid P-N ligands are robust catalysts olefin oligomerization or polymerization reactions [3]. This implies ability to undergo migratory olefin insertion, and relatively stable catalytic intermediates. Thus, we have investigated the following key steps of the Heck catalytic cycle using P-N stabilized Ni complexes (See Scheme): 1) Oxidative addition of several types of aryl halides; 2) Migratory insertion of several olefins, such as methyl acrylate and 3) base-induced β-hydrogen elimination. The relative ability to undergo each of these steps, and their relative importance in a hypothetical catalytic cycle will be discussed.



Ligands



*R: Isopropyl,Phenyl o Anisyl

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Transformation of isocyanides into new organic functionalities assisted by $[Mn(bipy)(CO)_3]^+$ and Ag_2O

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Manganese(I) complexes containing the cationic fragment $[Mn(bipy)(CO)_3]^+$ (bipy = 2,2'-bipyridine) have been successfully applied in several catalytic processes [1]. Some remarkable organometallic reactions promoted by this fragment have been described by our group, and include the tautomerization of imidazoles, oxazole, and thiazole to N-heterocyclic carbenes (NHCs) [2], the formation of NHCs by coupling of isocyanides and propargylamine [3] and the generation of unique metalla-NHCs [4]. In relation with all the above, we introduce herein several reactions of isocyanides coordinated to $[Mn(bipy)(CO)_3]^+$, mediated by Ag_2O, leading to the formation of several organic functionalities such as formamidines, carbodiimides and formimidates.

The isocyanide ligands in complexes *fac*-$[Mn(CNR)(bipy)(CO_3)]^+$ are selectively transformed into formamidines, carbodiimides and formimidates upon nucleophilic addition of primary amines or alkoxides and subsequent treatment with Ag_2O, which promotes tautomerization or oxidation processes of diaminocarbene and alkoxyaminocarbene complexes. Futhermore, the coordinated formamidines and formimidates can be liberated from the metal center, what allows recycling of the starting complexes *fac*-$[Mn(CNR)(bipy)(CO_3)]^+$ [5].

The ability of Ag_2O to transform diaminocabene ligands to formamidines in manganese(I) complexes was extended to cyclic carbenes with similar results [5] and allowing a totally reversible transformation between NHCs and imidazoles [2a].

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New types of luminescent Au(I)-Ag(I) polymetallic systems bridged by the heterobidentate 4-Pyridyl isocyanide ligand.

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Recent papers have established that fluorinated-aryl gold(I) isocyanide complexes produce materials with high level of photo-emission upon mechanical effort (mechanochromism).[1] These complexes have potential application in smart luminescent materials, in the fields of sensing, photodevices, or recording.[2] This has moved us to examine the photochemical properties of some complexes previously reported by the group.[3] Moreover, since they wear an heterobidentate 4-pyridyl isocyanide ligand, we have examined their utility to produce bimetallic complexes, and the photochemical changes induced by the second metal center.

4-Pyridylisocyanide ligand behaves as a simple and effective hetero-bidentate able to bridge chemoselectively Ag(I) and Au(I). We have studied the influence of two different fluorinated aryl groups in the photophysical propierties for Au(I) homometallic systems and also for Ag(I)/Au(I) heterodimetallic systems. Furthermore, the chemical transformation of isocyanide in carbene has been carried out, and the photo-properties of these complexes have been measured.

Acknowledgments

This work was sponsored by the Ministerio de Economía y Competitividad of Spain (Project CTQ2017-89217-P) and for the grant FPI, the University of Valladolid and CINQUIMA Institute.

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New insights into the properties of nucleobase-gold(I) complexes

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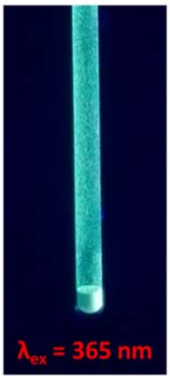
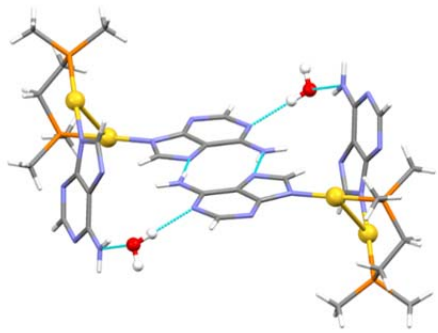
Nucleobase-consisting materials are finding novel and varied *in vitro* and *in vivo* applications mainly due to the self-recognition properties that these molecules manifest. Thus, this self-recognition ability, which relies in the formation of hydrogen bonds and π-π stacking interactions, allows the building-up of supramolecular assemblies with predictable and tuneable properties [1]. As a major example, tailored nano-scaled systems, even up to 300 nm wide, can be prepared by employing the so-called DNA origami strategies [2].

In this regard, the chemical modification of nucleobases through the coordination of linear gold(I) moieties may conduct to the appearance of new and promising properties, *e.g.* stimuli-responsive photoluminescence, that rely on the exclusive behaviour of gold(I) atoms. In fact, $[\mathrm{AuL}]^+$ moieties (where L is a neutral, two-electron donor ligand) are isolobal to H^+ itself, what then may give rise to new supramolecular structures by the additional participation of aurophilic interactions, which are similar in strength to hydrogen bonding but different in nature. We have recently reported that the coordination of certain water-soluble cationic $[\mathrm{AuL}]^+$ fragments (L = mono- or diphosphine) to the adeninate anion is a new approach to the formation of stable luminescent hydrogels, which are formed by the sequential self-assembly through aurophilicity and hydrogen bonding [3]. Thus, new results and perspectives on this subject are presented in this communication.



Luminescent materials

Hydrogelifying complexes



X-ray structure of $\{[\mathrm{Au}(^{9}N\text{-adeninate})]_2(\mu\text{-dmpe})\}$ (fragment) obtained from a single crystal grown in its own hydrogel matrix

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AMINOPHOSPHINE RUTHENIUM(II) ARENE COMPLEXES AS ANTITUMOR AGENTS

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The rapid and modular synthesis of the aminophosphine core has been exploited as tool for rapid development of antitumoral metallodrug candidates.[1] Starting with a series of structurally diverse aminophosphines, all obtained in a single step from commercial amines, a family of Ru(II)-cymene complexes have been generated and tested in vitro for antitumoral activity in a series of cell lines, including the platinum-resistant A2780R. Through this approach, Ru(II)-aminophosphine complexes have been identified with the IC_{50} value range as low as 10-0.8 µM. Several biological assays were carried out to gain insight into the mechanism of action. Cell death by apoptosis and pH-independent action has been demonstrated. In addition, a selective cytotoxity profile for tumoral cells over non-tumoral cells has been identified. Importantly, for the key candidates no loss of activity was observed when applied to the Pt-resistant A2780R, which highlights the potential utility of the bis-phospino-amine scaffold as easily-tuneable auxiliary ligand core in both rapid drug discovery and subsequently logical design of new anticancer metal-containing drugs. The complexes are characterised by NMR spectroscopy, mass spectrometry and single-crystal X-ray diffraction.

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Five-coordinate Pt(IV) species formed by asymmetric splitting of face-sharing dinuclear systems

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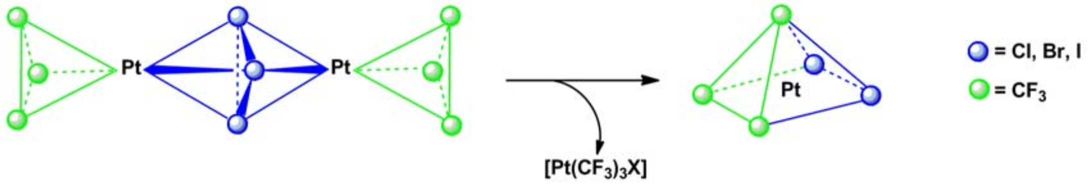
The platinum(IV) derivative $[\{Me_3Pt\}_4(\mu_3\text{-}I)]_4]$ was the first σ-alkyl organotransition-metal compound ever reported.[1] Since this early report, the chemistry of polynuclear organoplatinum compounds in any of the most common oxidation states for Pt (*i.e.*, I, II, III and IV) has received much attention.[2] The vast majority of these species contain double-bridging $Pt(\mu\text{-}X)_2Pt$ systems, which are particularly stable. In contrast, little is known on dinuclear compounds with triple-bridging $Pt(\mu\text{-}X)_3Pt$ systems.

Herein we report on the synthesis and characterization of the $[NBu_4][\{(CF_3)_3Pt\}_2(\mu\text{-}X)_3]$ complexes (X = Cl, Br, I). These compound exhibit face-sharing bioctahedral structures with increasing intermetallic Pt···Pt distance in the order Cl (323.0 pm) < Br < I (354.5 pm). They are one of the very few examples of homodinuclear platinum(IV) complexes with triple-bridging system currently known. Asymmetric cleavage of the corresponding $[\{(CF_3)_3Pt\}_2(\mu\text{-}X)_3]^-$ anions in the gas phase affords the mononuclear five-coordinate platinum(IV) complexes $[(CF_3)_3PtX_2]^-$ in every case. The behavior of these unsaturated, 16-electron species is experimentally analyzed by tandem mass spectrometry (MS^2). The results obtained are rationalized with the aid of DFT calculations. This combined experimental–theoretical approach sheds light on the structural and chemical properties of these unsaturated species, which are frequently suggested as reaction intermediates, but are still less represented.[3]



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Different Emission Colors Obtained by Tuning the Double Rollover Cycloplatinated(II) Structure

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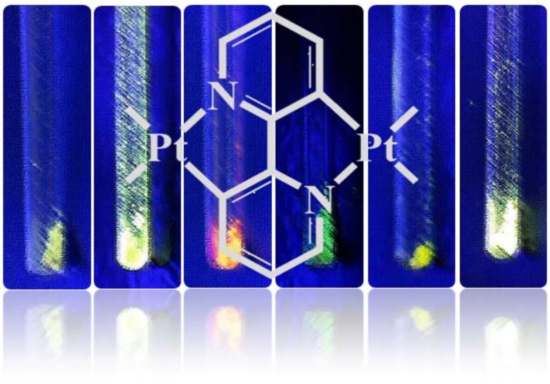
It has been proved that rollover cycloplatinated(II) complexes have shown to be luminescent materials at room temperature [1]. Previously, the reaction of complex $[Pt_2(\mu\text{-bpy-2H})(CF_3COO)_2(PPh_3)_2]$ with halides (Cl, Br and I) resulted in the luminescent complexes in green and yellow regions with the emission efficiency order of Cl > Br > I [2]. In this context, two closely related double rollover cycloplatinated(II) complexes have been prepared with general formula of $[Pt_2(\mu\text{-bpy-2H})(X)_2(PPh_3)_2]$ (X=SCN and X=N_3). The SCN and N_3 ions as two pseudohalides with strong ligand-field have been employed to tune the emission color and raise the efficiency of the products. Besides, a series of chelating ligands such as diethyldithiocarbamate and dicyclohexyldithiophosphate (S^S), and acetylacetonate (O^O) were applied toward the double rollover cycloplatinated(II) structure. The products mostly emit in green area with different efficiencies arising from their different ligand field strengths. The new complexes have been characterized using multinuclear NMR spectroscopy together with single crystal X-ray crystallography. The optical properties of these complexes were determined using the UV-Vis and photoluminescence spectroscopies, and explained by DFT calculations.



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Pyrazolate bridge Pt_2(II,II) and Pt_2(III,III) compounds with cyclometalated N-Heterocyclic Carbenes

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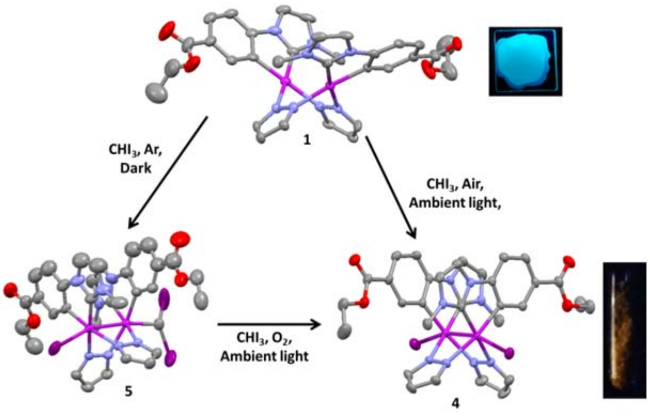

Oxidative-addition (OA) of a molecule AB to d^8 dinuclear complexes has been widely observed for Rh(I) and Ir(I) and the mechanism has been proved to depend on the metal, the ligands or the nature of the added molecule.[1] In the chemistry of binuclear Pt(II) complexes, OA reactions of haloalkanes to lantern or half-lantern complexes displaying short intermetallic distances have been observed but scarcely studied.[2] However, this reaction has been never reported for bis-pyrazolate bridge dinuclear Pt(II) complexes. Here we show a new bis-pyrazolate bridge Pt_2(II,II) complex containing a cyclometalated N-heterocyclic carbene ligand [{Pt(C^C*)(μ-pz)}$_2$] (**1**) (HC^C* = 1-(4-ethoxycarbonylphenyl)-3-methyl-1*H*-imidazol-2-ylidene) and the metal-metal bonded Pt_2(III,III)X_2 compounds, [{Pt(C^C*)(μ-pz)X)}$_2$] (X = Cl **2**, Br **3**, I **4**), resulting from the reactions of **1** with excess of haloforms CHX_3 (X= Cl, Br, I) in the ambient conditions. In the air and in the dark, the reaction with $CHCl_3$ does not work but mixtures of [XPt(C^C*)(μ-pz)$_2$Pt(C^C*)CHX_2] and [{Pt(C^C*)(μ-pz)X)}$_2$] (X = Br, I) were observed in those with CHX_3 (X= Br, I). In case of CHI_3, when the reaction was performed under argon atmosphere in the dark compound [IPt(C^C*)(μ-pz)$_2$Pt(C^C*)CHI_2] (**5**) was formed almost selectively. Mechanism investigation showed that the reaction is a radical-like process thermally or photochemically activated depending on the haloform used, with the O_2 acting as radical (R•) trap and favoring the formation of the dihalocomplexes. The bright blue photoluminescence of compound **1** (ϕ = 98% in PMMA film 5%w/w), disappears upon oxidation, showing the inconvenience of **1** to be treated with halogenated solvents in the ambient conditions.

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Cyclometallated Pd complexes with Pd-M bonds (M = Ag, Au) as models in transmetallation processes

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The study of heteropolynuclear complexes with metal-metal interactions between closed or pseudo-closed shell transition metals (d^8, d^{10}, $d^{10}s^2$) constitutes an important field in inorganic chemistry. As an example these interactions are behind many luminiscent properties and are a powerful tool for crystal engineering.[1] Furthermore, this interest has grown lately because species containing these interactions could play an important role in transmetallation processes in cooperative catalysis.[2,3] For this reason we have focused on the preparation and study of Pd(II)–M complexes which could give more information about the mechanisms of the transmetallation processes involved in catalytic bimetallic systems. In this contribution we present two complexes with Pd(II)-M(I) bonds (being M an acidic metal as Ag(I) or Au(I)) obtained from the cyclometallated neutral compound $[Pd(CNC)(PPh_3)]$ (CNC = 2,6-diphenylpyridinate) as starting substrate. These complexes, $[\{Pd(CNC)(PPh_3)\}_2Ag](ClO_4)$ (**1**) and $[\{Pd(CNC)(PPh_3)\}\{Au(PPh_3)\}](ClO_4)$ (**2**), have been characterized by multinuclear NMR and X-ray diffraction. In solid state, both compounds show a remarkable interaction between the acidic metal bonded to the Pd(II) center and the C_{ipso} of the CNC ligand (see the X-ray structure of **2** in Figure 1). Only in the case of **2** this interaction seems persistent in solution at room temperature, as can be seen from its ^1H NMR spectrum, causing the inequivalence of the two halves of the CNC ligand. X-ray diffraction also shows that this interaction is shorter for **2**, which could be in agreement with the higher carbophilicity of the gold center with regard to silver.

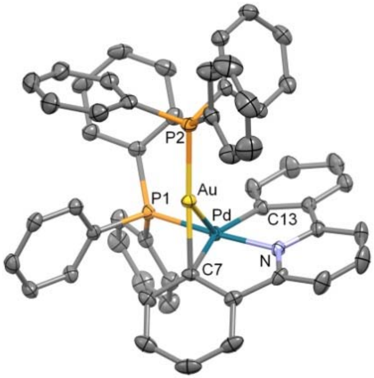

Figure 1

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[Au(IPr)]$^+$-catalyzed assembly of carboxylic acids and alkynes: A new entry to 3-acyl furans

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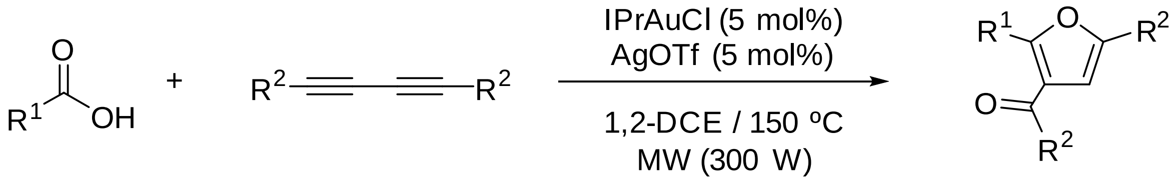
Polysubstituted furans are a very important group of aromatic compounds. They play a central role both in pharmaceutical and material science, as well as in flavour and fragrance industry. In addition, compounds featuring a furan skeleton show practical and diverse biological properties such as anticancer, antiallergic and immunosuppressive activities.[1] For all these reasons, a huge number of synthetic routes have been described to access this type of heterocycles.[2] Over the past years, gold catalysts have emerged as one of the most important tools for furan construction. In this regard, the Au(I)-catalyzed hydration of 1,3-dyines for the synthesis of 2,5-disubstituted furans has been described by different groups.[3]

Inspired by these previous works, we report herein an unprecedented Au(I)-catalyzed MW-assisted synthesis of highly substituted 3-acyl furans employing carboxylic acids and internal 1,3-diynes as starting materials.



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Novel Platinum Complexes with Antitumor Applications

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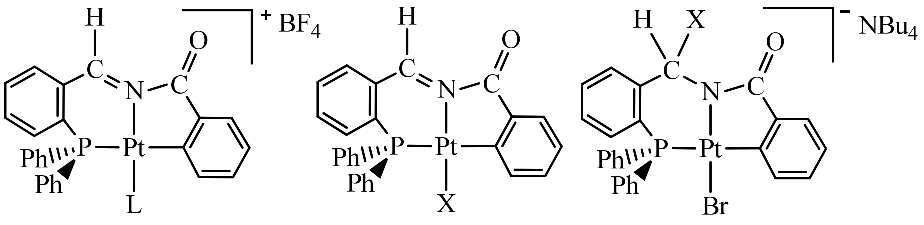
The discovery of the anticancer properties of *cis*-diamminedichloroplatinum (II) (cisplatin) marked the start in the research and use of metallodrugs [1]. However, among the thousands of compounds tested for anticancer applications, only carboplatin and oxalilplatin have reached worldwide approval [2]. These platinum-based drugs are being widely used for the treatment of various types of cancer, in particular head and neck, testicular and ovarian cancers [3]. Despite the success of the referred platinum drugs, their severe toxicities and the drug resistance limit their clinical use [4]. In view of these limitations, research has been extended to the design of novel platinum analogues with the aim of overcoming adverse effects.

In this contribution, we show the syntheses and the study of the antitumor activities of some new pincer platinum(II) complexes. The pincer complex [Pt($Ph_2PC_6H_4CH{=}NC(O)C_6H_4$)(NHC(O)Ph)] (**1**) is formed by an intramolecular coupling between a benzamidate and a diphenylphosphinebenzaldehyde ligand *cis*-coordinated to a platinum center, from which a family of compounds has been prepared (figure 1). Protonation of the starting material occurs on the benzamidate ligand giving rise to 2, which easily affords substitution reactions with neutral or anionic ligands rendering cationic derivatives as 3, 4a, and 4b and neutral ones as 5, 6, and 7. The reactions of complex 6 with nucleophiles render anionic complexes as 8, 9, and 10. All this family of compounds has been tested against HeLa and Jurkat tumor cells with promising results.



L=NHC(OH)Ph (2), PPh_3 (3)
$NCCH_3$(4a),NCPh (4b)

X=Cl (5), Br (6),
TfO (7)

X=OMe (8), H (9),
Me (10)

Figure 1

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Dioxygen activation by Ir(III) Hydride Complexes

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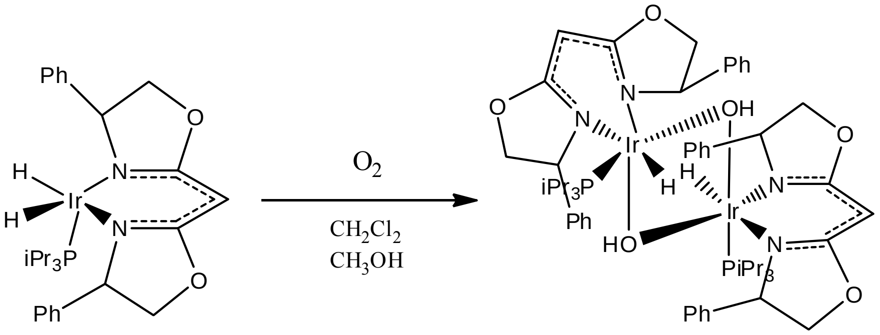
The activation of O_2 by transition metal complexes shows great mechanistic complexity and can potentially involve a number of different intermediates, including monometallic peroxo, superoxo and hydroperoxo species together with species resulting from cooperation of two or more metal fragments.[1] This work describes the reactions with O_2 of Ir(III) hydrides coordinating bis(oxazoline) chelating ligands, which may follow divergent routes depending on the particular features of each precursor complex.



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Bifunctional Aluminum Catalysts for the Chemical Fixation of Carbon Dioxide into Cyclic Carbonates

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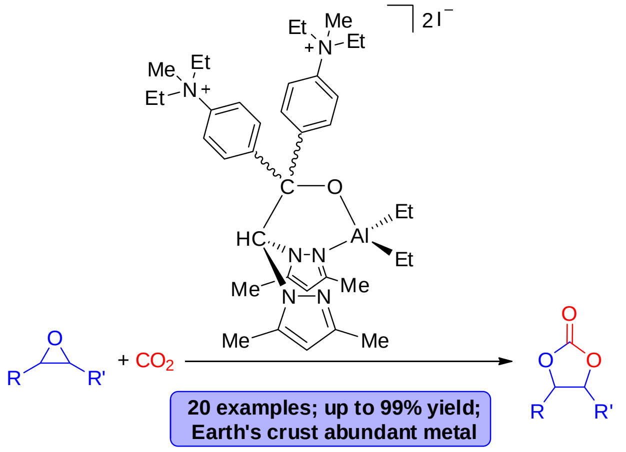
The use of carbon dioxide (CO_2) as a starting material for the production of organic molecules and/or materials has recently received a great deal of attention from the scientific community since carbon dioxide is a cheap, abundant, non–toxic and versatile C1-building block.[1] Therefore, the efficient transformation of CO_2 into fuels, chemicals and polymers would contribute towards a transition from a fossil fuel-based industry to a sustainable and circular one.[2] One of the most important processes that uses CO_2 is the production of cyclic carbonates from epoxides and carbon dioxide as these processes have 100% atom–economy and are highly exothermic (Scheme 1).[1,2]

In this work, we report the development of new bifunctional heteroscorpionate aluminum complexes as catalysts for the synthesis of cyclic carbonates from a broad range of (bio-based) epoxides and CO_2 in good to excellent yields.[3]



Scheme 1. Synthesis of cyclic carbonates catalysed by aluminum complexes

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Reactivity of alkynyl Fischer carbene complexes with isostructural silylene/germylene reagents: Expected and unexpected behaviours

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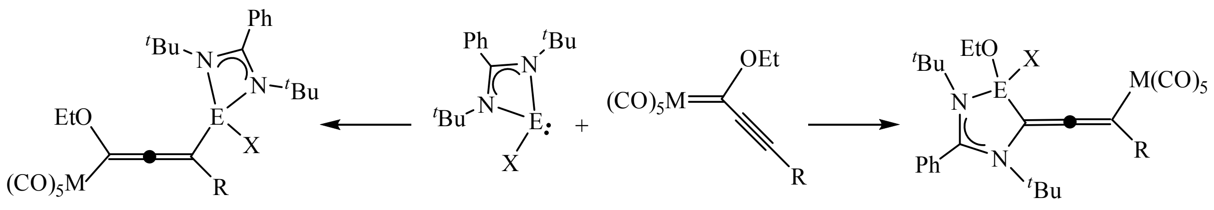
Recent investigations have demonstrated that the reactions of N-heterocyclic carbenes (NHCs) with alkynyl Fischer carbene complexes lead to η^1-allenyl compounds, as a result of the conjugate addition of the NHC to the alkynyl fragment.[1] On the other hand, heavier tetrylenes (HTs), particularly those stabilized with amidinato fragments, are currently playing a prominent role as ligands in Coordination Chemistry,[2] since some of them have been recognized as stronger electron-donating ligands than NHCs.[3]

Aiming at comparing the chemistry of amidinato-HTs with that of NHCs, this communication reports the reactions of E(^{t}Bu$_2$bzam)X (**1**; E = Si, Ge; X = Mes, CH$_2$SiMe$_3$; ^{t}Bu$_2$bzam = N,N'-bis(tertbutyl)benzamidinate) with the alkynyl Fischer carbene complexes [M(CO)$_5${C(OEt)C≡CR}] (**2**; M = Cr, W; R = Ph, Fc; Fc = ferrocenyl). The formation of two types of η^1-allenyl metal derivatives have been observed: *(i)* complexes of type **3**, result from the simple conjugate addition of the HT to the alkynyl fragment (this is the reactivity pattern reported using NHCs as nucleophiles[1]) and *(ii)* the completely unexpected compounds of type **4**, which arise from a series of rearrangements that include: (*a*) an expansion of the ENCN four-membered ring of the original HT to an ECNCN five-membered ring, (*b*) a transfer of the OEt group to the E atom, and (*c*) a 1–3 shift of the M(CO)$_5$ moiety over the C$_3$ chain. The mechanism that leads to compounds of type **4** has been elucidated by DFT calculations.



(**3**) (**1**) (**2**) (**4**)

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En Route to Chiral-at-Metal Ruthenium Complexes Containing Tripodal Tetradentate Ligands

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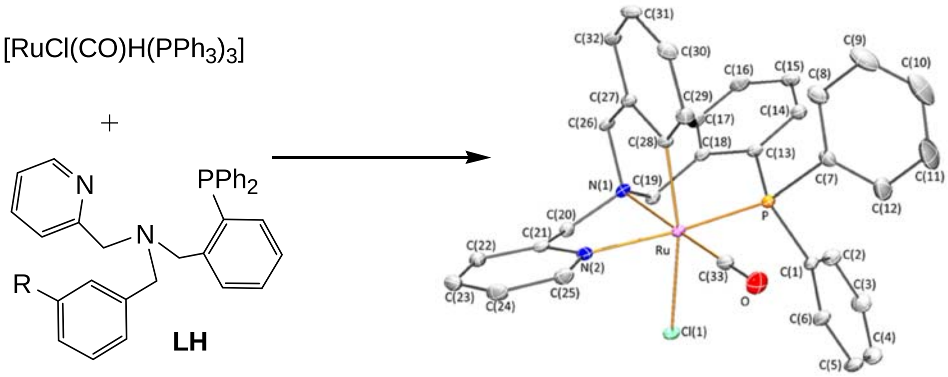
Typically, an asymmetric metallic catalyst consists of a metal surrounded by a chiral ligand together with some ancillary achiral ligands. Activation of prochiral substrates takes place through coordination to the metal and during the catalytic process chirality is transferred from the catalyst to the newly formed stereogenic centers. According to this path, it might be argued that chiral-at-metal catalysts would be well suited to transfer chirality efficiently due to the close proximity between the source and the receptor of chirality.[1]

However, examples of chiral catalysts in which the source of chirality was unequivocally the stereogenic metal center are scarce. Efficient chiral-at-metal catalysts bearing solely achiral ligands have been developed only recently. At this respect, Meggers's group has prepared a new class of efficient asymmetric catalysts consisting of cationic octahedral rhodium(III), iridium(III) or ruthenium(II) complexes containing two cyclometalated achiral ligands. Chirality results from the right-handed (Δ) or left-handed (Λ) propeller defined by the two cyclometalated ligands.[2]

Following our work in this area, here we present our attempts to prepare octahedral chiral-at-metal ruthenium(II) complexes bearing the tripodal tetradentate ligands **LH** (see Figure) displaying a κ^4C,N,N',P coordination mode. Their optical resolution and catalytic applications will be reported in due course.



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Half-Sandwich Complexes of Ruthenium Containing Guanidine-Derived Ligands: Synthesis and Application as Brønsted–Acid Catalysts

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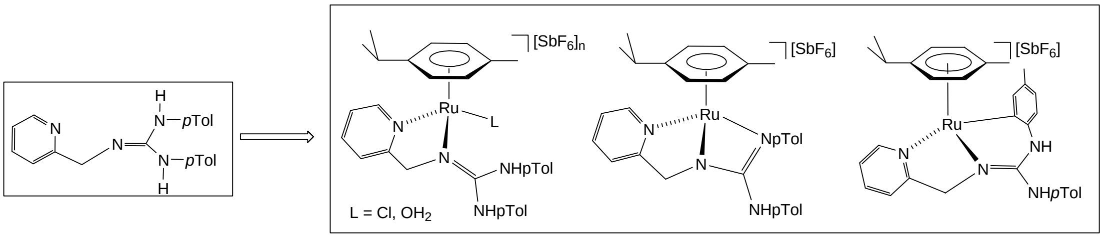
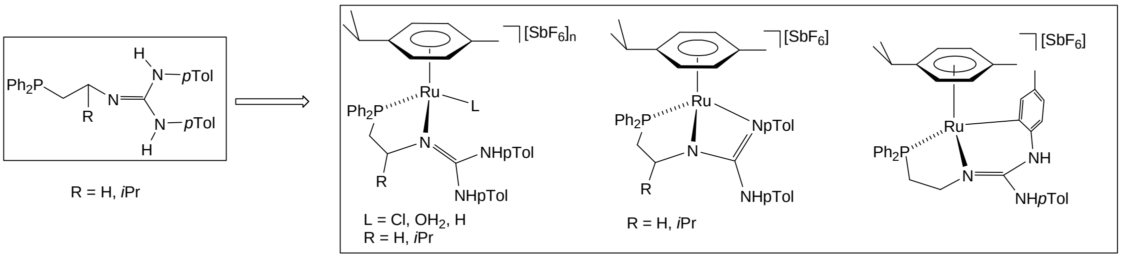
Typically, an homogeneous metallic catalyst activates reagents by coordination to the metal atom. The metallic compound, acting as a Lewis acid, facilitates the reaction steps as well as allows for the dissociation of the formed adduct.[1] In clear contrast, the last years have witnessed the impressive increase of efficient organocatalysts in which weakly acidic small organic molecules are able to act as electrophile activators through either hydrogen bond or Brønsted acid catalysts. Arguably, Brønsted acidity could also be activated by Lewis acid metallic fragments giving place to hydrogen-bond-donor catalysts based upon the second coordination sphere of a metallic complex. Additionally, the metallic portion would provide the resulting entity with the powerful and versatile stereoelectronic features inherent to coordination complexes.[2] However, only recently, it has been demonstrated that OH or NH bonds associated with coordinated alcohols or amines are capable of functioning as hydrogen bond donors to organic substrates.[3]

In the present poster, we show our results about half-sandwich ruthenium complexes capable of acting as Brønsted acids (see scheme). Furthermore, we also present some preliminary results about their catalytic applications.





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Facile H/D Exchange through C(sp^3)−Activation and H_2 Addition in Cp*Rh Complexes Mediated by Rh/N Frustrated Lewis Pairs

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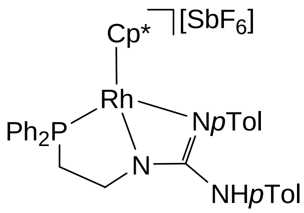
Hydrogen isotope exchange (HIE) reactions have been considered the most fundamental of all functionalization processes. Deuterated products have been widely used in diverse research fields including chemistry, materials science and biology. Homogeneous metallic catalysis dictates current research in HIE and, indeed, a variety of metallic compounds have been successfully applied to HIE reactions on a range of C−H bonds.[1] However, examples of H/D exchange involving the methyl groups of the C_5Me_5 (Cp*) ligand are very scarce.[2]

On the other hand, the last decade has witnessed the development of a new class of systems in which a Lewis acid and a Lewis base do not yield the classical Lewis acid/base adduct for steric and/or electronic factors. In such systems, termed “frustrated Lewis pairs” (FLPs), the coexisting Lewis acid/Lewis base pairs exhibit cooperative behavior rendering excellent results in fields as relevant as those of small molecules activation or catalysis.[3]

In the present communication, we report that the Cp*Rh complex **1**, bearing a tridentate guanidine-derived phosphine, undergoes a reversible H/D exchange process between the methyl groups of Cp* and D_2O. Moreover, complex **1** shows an FLP behavior in the reversible activation of H_2 (or D_2). Mechanistic details of these two transformations are disclosed by means of kinetic studies, NMR spectroscopy and DFT calculations.



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Catalytic properties of iridacycle–MOF hybrid systems

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The seek of heterogeneous catalysts for industrial applications with improved catalytic activity and selectivity, comparable with homogeneous systems, led to heterogeneization of homogeneous catalysts, by immobilizing then on solid supports.

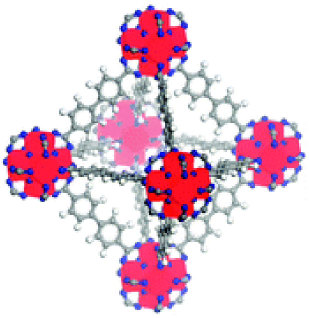

Fig. 1: Octahedral cage of the MOF called UiO-67.

Metal Organic Frameworks (MOFs) are relatively new class of porous materials, formed by metal ions or clusters linked by organic spacers. These structures have attracted increasing attention due to their large surface areas and pore volumes, being studied for various applications such as, separation and adsorption of gases, drug delivery systems, or as heterogeneous catalysts.[1] In recent years, MOFs have also been studied to act as host platforms for organometallic catalysts, where the insertion can be done by direct synthesis or post synthetic modification.[2]

The immobilization of iridacycles on UiO-67, together with the comparative study of its catalytic application in hydrosilylation reactions will be presented.

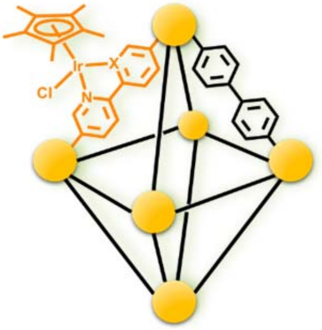

Fig. 2: structure of the catalyst anchored on the MOF UiO-67.

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Acknowledgement

Ikerbasque, Spanish MINECO/FEDER (CTQ2015-65268-C2-1-P), UPV-EHU (GIU16/25) and Gobierno Vasco (BOPV, 01-06-2017)

Hybrid nanomaterial systems containing Au(I) organometallic supramolecular structures

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Gold(I) complexes are very well-known to establish Au(I)···Au(I) contacts responsible for the formation of a wide variety of different 2D and 3D structures (e.g. gels, vesicles, rods…) with a wide variety of applications and that present luminescent properties.[1,2]

One of the less explored applications on this type of complexes and their resulting supramolecular assemblies is their use in the frontier between supramolecular and nanomaterials chemistry. Regarding this, we have taken advantage of the well-alignment of the supramolecular organizations mainly reinforced by the possibility of establishment of metallophilic contacts, to develop simple methodologies for the formation of hybrid organometallic-nanomaterials systems with very interesting applications. In particular, we have developed organometallic-NPs hybrid systems with highly relevant results in fields like hydrogen production,[3] solubilisation of hydrophobic nanomaterials in water[4] and formation of small and very homogeneous nanoparticles[5] among others.

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Mechanisim of manganese-catalyzed synthesis of α,β-dicarbonylhydrazones by aerobic oxidation: new experimental and theoretical insights

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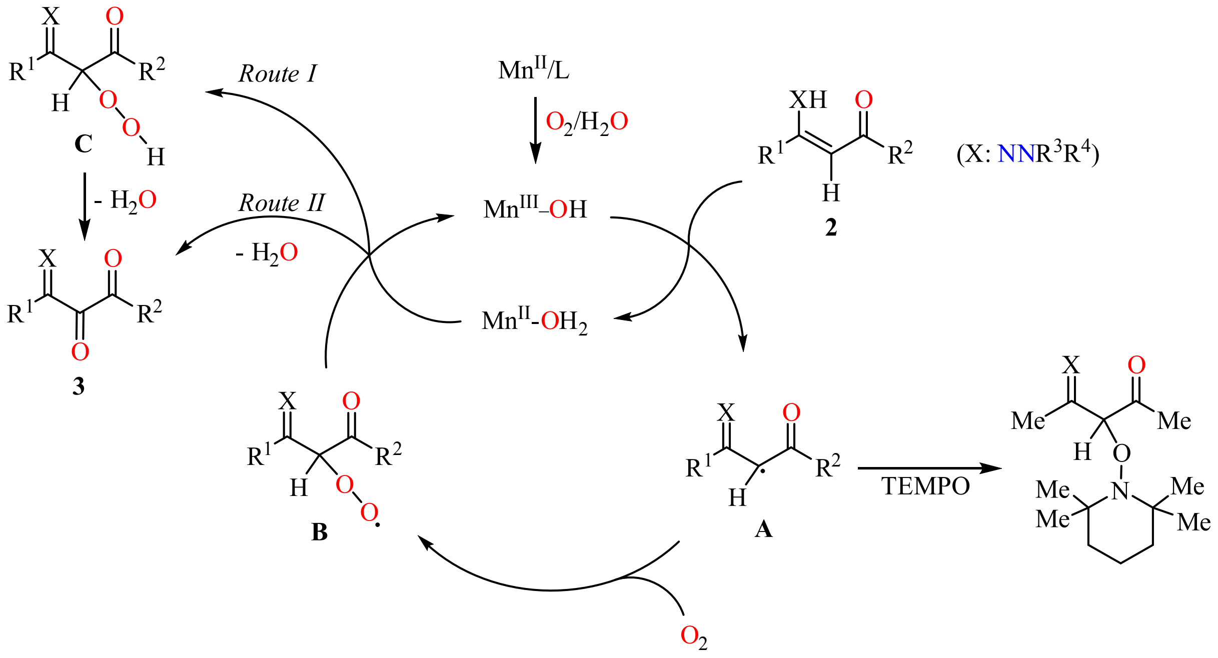
The oxidation of a methylene group α to a carbonyl group to form vicinal dicarbonyl compounds is an important transformation, which has many applications in organic synthesis. They are employed as building blocks for the synthesis of bioactive molecules, especially those containing heterocycles. Conventional reagents for accomplishing this transformation often require stoichiometric or large excess of oxidants and, consequently, generate substantial quantities of waste, which is undesirable due to environmental considerations. Therefore, searching for a mild and green procedure is timely. Following our interest in this area [1,2], here we describe a mild, selective and practical protocol for manganese-catalyzed aerobic oxidation of β-carbonylenehydrazines, **2**, to afford novel α,β-dicarbonylhydrazones, **3**. A combined experimental and theoretical study suggest that the reaction very likely proceeds through a radical pathway via a hydrogen-atom-transfer process promoted by a Mn^{III} species. According to DFT studies, the last step of the catalytic cycle occurs preferentially by elimination of OH radical from a peroxido radical species, **B** (*Route I*).



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Efficient Iridium-Catalyzed N−Methylation of Amines with Methanol by Hydrogen Borrowing Strategy.

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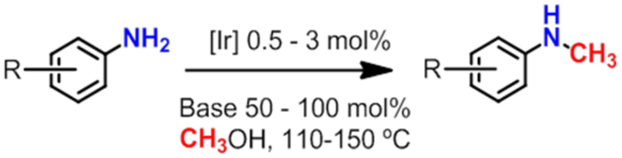
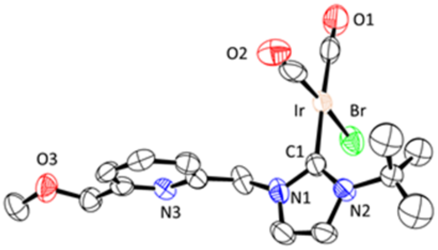
Homogeneous catalysts bearing pincer ligands based on N-heterocyclic carbene (NHC) motifs have played an important role in the last years in the development of highly active and selective catalysts as one of the key points of the contemporary green chemistry. The lutidine-derived pincer-type ligands ability to perform metal-ligand cooperation processes combined with their thermal stability and the easy modulation of the electronical and sterical properties of the NHC ligands[1] make them an interesting set of complexes to study catalytic (de)hydrogenation, transfer (de)hydrogenation and related reactions.[2]





N-methylated amines are important building blocks in the synthesis of fine chemicals, pharmaceuticals, and natural products. The traditional N-methylation procedures, usually using toxic and reactive methyl halides, dimethylsulfate, and diazomethane, have several serious limitations of selectivity and toxicity that block their practical application. Other more environmentally benign reagents, as formic acid, dimethyl carbonate or carbon dioxide in the presence of silanes, boranes or hydrogen require high reaction temperatures (over 150 °C) or excess of reducing agents to achieve high yields. Therefore, the catalyzed direct N-monomethylation of amines with methanol based on the hydrogen borrow methodology is a greener alternative to the C−N coupling reaction of methyl amines with aryl halides employing palladium or nickel as catalysts.[3] In this work we report a novel family of iridium catalysts [Ir(^{t}BuImCH$_2$PyCH$_2$L)] (L = hemilabile fragment) that exhibit good activity and complete selectivity for the methylation of a range of aromatic and aliphatic amines. The most active catalyst is [IrBr(CO)$_2$(κ-*C*-^{t}BuImCH$_2$PyCH$_2$OMe)] that achieves complete selectivity in 5 hours with only 0.5% catalyst loadings.

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Photoswitchable DTE-containing organometallics

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In spite of the importance and versatility of organometallic complexes, smart photo-responsive examples remain rather unexplored in comparison with the plethora of well know light-triggered organic switches. In principle, photo-responsive metal complexes can be obtained by incorporation of organic photochromic units in the structure of their ligands. These photo-sensitive ligands, rather than acting as conventional spectators that tune the properties of their complexes, transform them into dynamic smart entities able to offer a functional response to an external stimulus.[1]

In our group, we work on the development of such photo-responsive organometallics for diverse applications. Our previous studies already showed that the compatibility of the metal coordination and the photo-response of the molecular switch is an issue that needs to be carefully addresses, as it was mostly inhibited in the case of azobenzene derivatives.[2]

As an alternative, in this work we will present the synthesis and characterization DTE organometallic derivatives. The compatibility of the photoswitch and certain properties of the compound will be discussed.

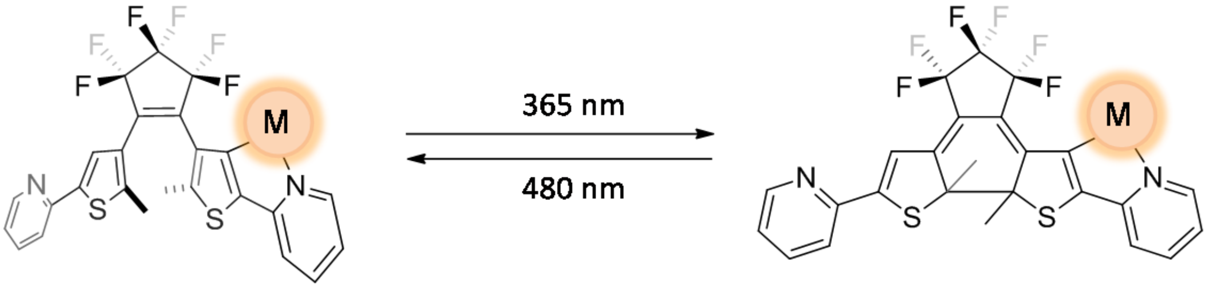

Figure 1. DTE organometallic derivatives

Acknowledgment:
Ikerbasque, Spanish MINECO/FEDER (CTQ2015-65268-C2-1-P), UPV-EHU (GIU16/25) and UPV-EHU (PIFBUR16/29)

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Reduction of CO_2 with Silicon-Hydrides Catalyzed by Ir-NSi Species

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During the last recent years, the catalytic transformation of CO_2 using silicon-hydrides as reductants has emerged as a promising technology that allows the selective reduction of CO_2 to the formate, formaldehyde, methanol or methane level under mild reaction conditions.[1] Moreover, some catalysts have been employed for the formylation and/or methylation of the N-H bonds of secondary and/or primary amines by their reaction with CO_2 and hydrosilanes.[2] Iridium-catalysts have played an important role in this chemistry.[3] This poster contribution summarizes our recent results showing the influence of the nature of the catalyst and the reaction conditions on the performance of the different catalytic processes that have been studied (Figure 1).

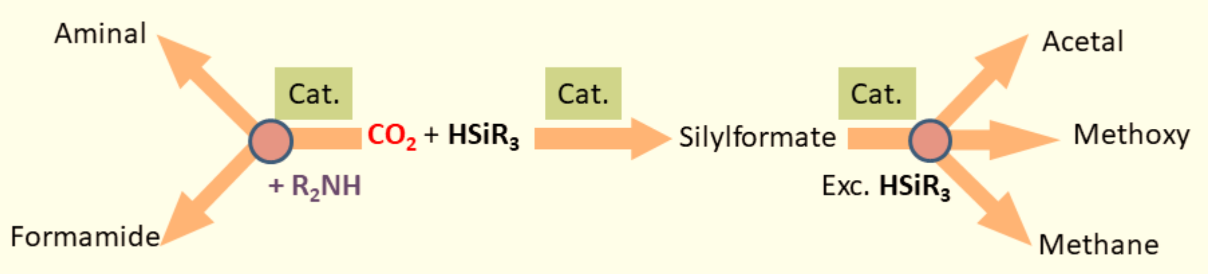

Figure 1. Examples of reaction products that could be obtained from the catalytic reduction of CO_2 with silicon-hydrides.

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Copper(I) complexes as photosensitizers for catalytic water reduction

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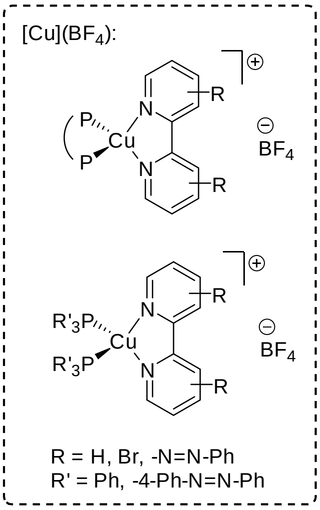
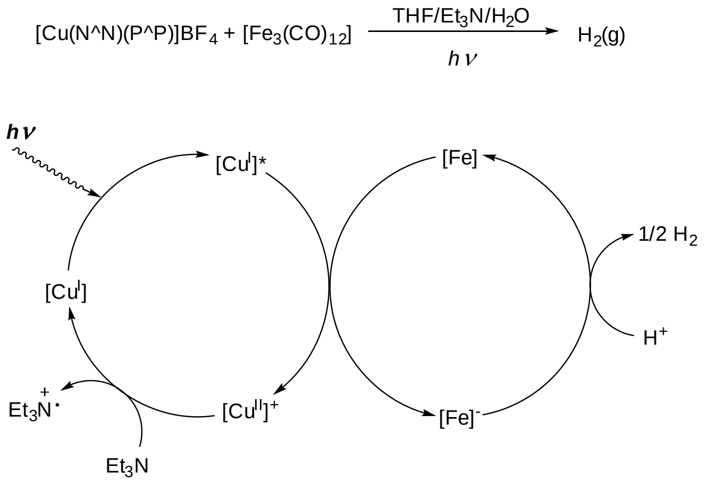
Noble-metal complexes, based mainly on ruthenium(II) and iridium(III), have been extensively studied and employed as efficient photosensitizers for the catalytic reduction of water. In the last decade, as an alternative to these precious photoactive species, copper(I) complexes have emerged giving rise to impressive high performances (long-lived excited-states, high emission quantum yields, tunable emission spectra and adjustable redox properties, among other).[1] The combination of selected bidentate bis(imine) and diphosphine ligands able to form heteroleptic copper(I) complexes of general formula $[Cu(N^\wedge N)(P^\wedge P)]^+$ has been the key to achieve competitive activities.

Herein, we report the synthesis and characterization of a new family of heteroleptic copper(I) complexes of general formula $[Cu(x,x'-R_2-2,2'-bpy)(P^\wedge P)](BF_4)$ and $[Cu(x,x'-R_2-2,2'-bpy)(PR'_3)_2](BF_4)$. UV-visible absorption and photoluminescence studies have been performed in order to determine whether these complexes possess long-lived excited-states that may allow for their application as photosensitizers in the iron-catalysed photocatalytic reduction of water.[2] Thus, those complexes with intense emission spectra have been tested for the generation of hydrogen gas and their performance has been compared to previously known efficient copper(I) photosensitizers.




$$[Cu(N^\wedge N)(P^\wedge P)]BF_4 + [Fe_3(CO)_{12}] \xrightarrow[h\nu]{THF/Et_3N/H_2O} H_2(g)$$

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Reversible vapochromic and mechanochromic behavior of an Au(I) -Pb(II) complex

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Recently, the stability and reversibility of chemical sensors has received great attention. Compounds that suffer a change in their appearance or luminescence when are exposed to different VOCs, have been the focus of many studies due to their wide range of possible applications [1,2].

There are few compounds in the literature that present Au(I)-Pb(II) interactions [3,4], and, in particular, no vapochromic, solvatochormic or mechanochromic compound displaying such intermetallic contact has been reported until now.

Thus, in our research group we synthesized the compound $[Au_2Pb(C_6F_5)_4(C_{15}H_{11}N_3)]$ ("*red polymorph*"), a red solid with intense red luminescence. When it is exposed to vapours of different solvents, like toluene or acetonitrile, its colour and luminescence change to green or yellow, respectively (see **Figure 1**). Furthermore, this change is easily reversible in few seconds by exposition to methanol or by manual pressure.

Thus, we have been able to design a chemical sensor, which modifies its colour and luminescence in the presence of vapours of different VOCs that also displays a mechanochromic behaviour.

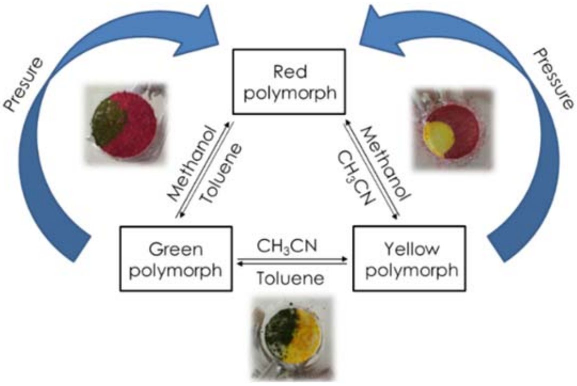

Figure 1. Scheme.

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How Affects the Chelate Effect of the N-Donor Ligands in Iron Catalysed Kumada Reaction?

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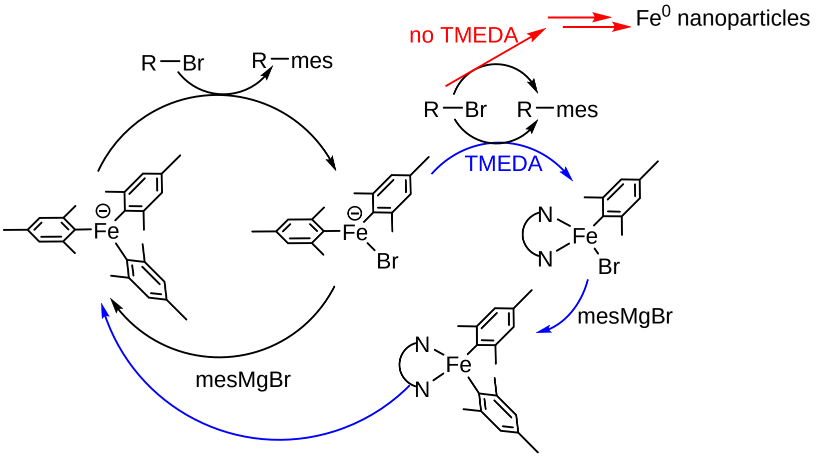
Amine complexes of Iron have been found particularly useful pre-catalysts in a range of Kumada reactions.[1] Especial interest has been focus to TMEDA ligand and the most recent studies[2] have shown that it doesn't play a role in the main catalytic cycle but in an auxiliary one where it prevents secondary pathways.



Whereas these studies were focused using TMEDA and a bulky aryl Grignard reagent (mesityl), in this present work we decided to investigate the effect of varying the amine-donor ligands in presence of a smaller, far more representative aryl nucleophile.

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Luminescent Silver Diphosphane Complexes

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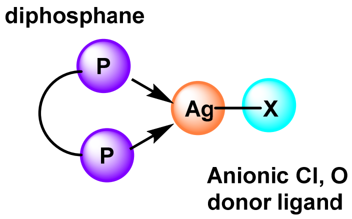
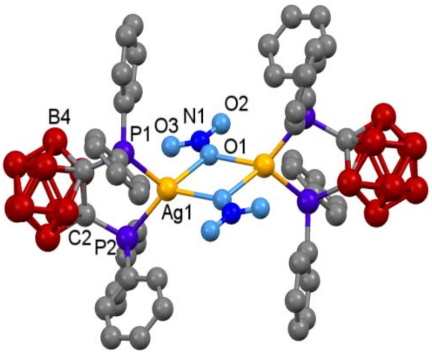
Our interest is focused on the emissive properties of coordination complexes. Among them, silver diphosphane compounds have revealed as interesting emissive species which may exhibit interesting properties as temperature activated delayed fluorescence (TADF) [1] or mechanochromism [2]. We have synthesised derivatives of stoichiometry $[Ag(PP)X]_n$ [P-P = diphosphane, X = Cl, O-donor anionic ligand; n = 1, 2]. The crystal structure of some of the complexes has been elucidated by X-ray diffraction studies.



Analysed systems



Steady state emission and lifetimes of the new complexes have been analysed for both powder samples (both at room temperature and 77 K) and PMMA films (room temperature) in order to study the influence of the anionic ligand and the diphosphane in their luminescent properties. For those emissive at room temperature quantum yield of PMMA films have been measured. TDDFT theoretical studies have been carried out in order to understand the origin of the luminescent behaviour.

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Phosphorescent soft materials based on copper, silver and gold metallacycles

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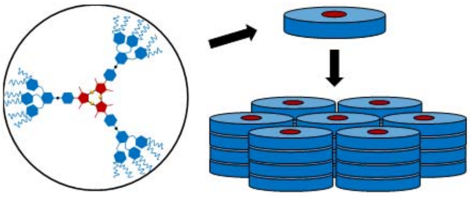
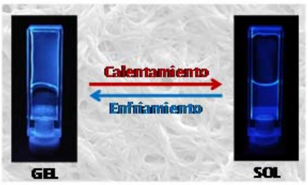
Cyclic trinuclear complexes of the gold group are unique molecular materials that contain a planar or nearly planar nine-membered metallacycle.[1] Some of them show luminescent properties and their emission spectra depend on the arrangement of the molecules in the solid state, which can involve intermolecular metallophilic interactions. Interestingly, these can be easily influenced by external factors such as temperature, ions or solvents.[2] All these properties have opened new perspectives for the development of functional soft materials such as liquid crystals or gels,[3] and new luminescent materials.[4] In this work we describe novel copper, silver and gold complexes using either simple alkyl substituted pyrazolates or complex pyrazolate-based dendritic architectures as ligands. Liquid crystal behaviour, gel forming abilities and luminescence properties are observed. A high dependency of the properties on ligand structure or metal is observed. This allows to withdrawn important conclusions for the optimization of each property. High efficient phosphorescescence, with quantum yields approaching unity at room temperature and color switching by different stimuli, [5] or aggregation-induced emission behaviour (AIEE) are also reported, evidencing their high potential as multifunctional materials.





Acknowledgement

We thank projects MINECO-FEDER CTQ2014-53033-P, MAT 2012-38538-CO3-01, Gobierno de Aragón-FSE and Cátedra IQE.

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Heterometallic Au^I/Tl^I complexes with macrocyclic ligands bearing methylquinoline as *pendant-arms*.

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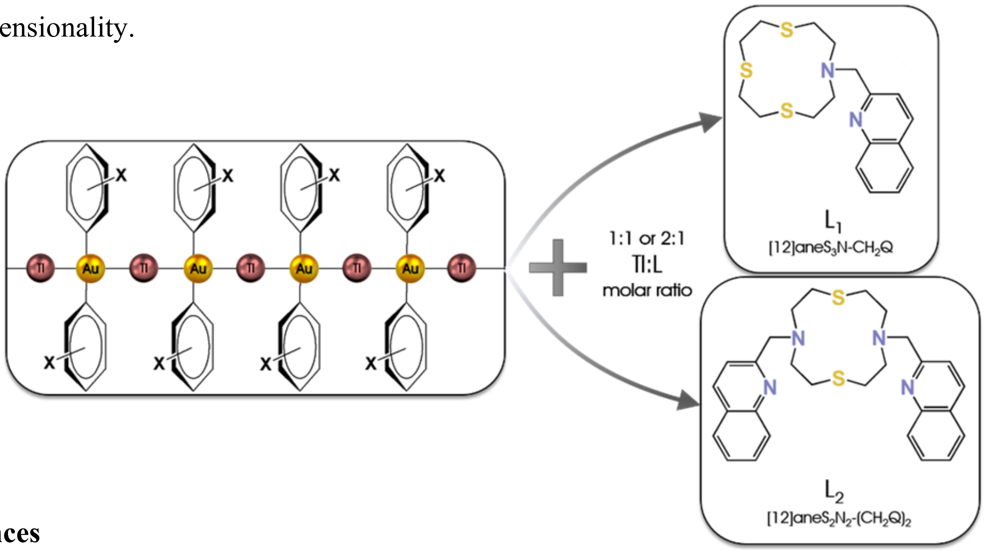
The synthesis of transition metal complexes with tunable photochemical properties is one of the most important challenges in the chemistry of heteropolynuclear extended systems built by secondary interactions. Following the acid-base strategy, and specially by reaction of $NBu_4[Au(C_6X_5)_2]$ with Ag^I or Tl^I salts, a great number of heteropolynuclear extended systems have been synthesized [1].

In addition, the rational design of ligands that can control de self-assembly process in the formation of compounds is a key factor in these studies. In this regard, it is well known the strong binding capability of crown-thioether ligands with transition metal ions since Busch research published in 1978 [2]. Thus, macrocyclic ligands are ideal candidates for this goal, because the size of the macrocyclic ligand controls the coordination chemistry [3], but it can be modified adding pendant substituents that increased the coordination capability of the original ligand.

In this context, we studied the reactivity of the basic gold(I) complex of stoichiometry $NBu_4[Au(C_6X_5)_2]$ (X = F o Cl) against the acid salt $TlPF_6$ in presence of N,S-donor macrocycle ligands with one or two methyl-quinoline groups as pendant-arms (**L_1** and **L_2**, respectively). This allowed us to obtain heterometallic derivatives with different coordination environments, nuclearity and dimensionality.



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Reactivity of POP-Rhodium(I) Complexes with Unsaturated Organic Molecules

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Functionalization of organic molecules is an important challenge actually. The use of transition metal complexes constitute one of the most powerful tools. Insertion, isomerization and C-H bond activation reactions are fundamental processes that are relevant in many organic transformations mediated by transition metal complexes such as the bis(borylation) of unsaturated substrates,[1] and the functionalization of C-H bonds,[2] among many others.

We have recently described the synthesis of the square-planar rhodium(I) complexes RhH{xant(P^iPr_2)$_2$} and Rh(Bpin){xant(P^iPr_2)$_2$} (xant(P^iPr_2)$_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene).[3,4] The monohydride complex is able to activate the B-H bond of boranes, C-H bonds of arenes, fluorobenzene and 1,3-difluorobenzene, and C-H and Cl-C bonds of chloroarenes.[5] Furthermore, it promotes the stoichiometric and catalytic borylation of arenes,[4] as well as the catalytic dehydrogenation ammonia borane.[6] We have demonstrated that benzonitrile and 4-(trifluoromethyl)benzonitrile insert into the Rh-B of complex Rh(Bpin){xant(P^iPr_2)$_2$} to give Rh{C(R-C_6H_4)=NBpin}{xant(P^iPr_2)$_2$} (R = H, *p*-CF_3), key intermediates on the mechanism of the rhodium-mediated decyanative borylation.[7]

In this communication, we present the reactivity of these boryl and monohydride POP-rhodium complexes with different unsaturated substrates, and the results of the combination of insertion, isomerization and C-H bond activation reactions.

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Some reactions of the anionic cluster $[Pt^{IV}Pt_3^{II}(OH)_4(CCl_5)_8]^=$ with Ag^+: neutral and anionic Pt →Ag compounds.

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Mixing transition metal compounds with different coordination number can produce clusters with new structural and chemical characteristics as is the case of the compound $(NBu_4)_2[Pt^{IV}Pt_3^{II}(OH)_4(C_6Cl_5)_8]$ (**1**)]. [1] Its unsual structure (Fig. 1) due to the presence of one Pt(IV) together with the three Pt(II) centers, the C_6Cl_5 groups and its anionic character makes it an interesting starting material for what is expected to be a large family of host guest closed shell metal complexes.

We present some of the compounds obtained in the reaction of **1** with AgX (X = NO_3, SO_3CF_3, SO_3Ph). The influence of the counterion of the silver salt and the solvent medium of the reaction on the nature of the resulting Pt→Ag compounds will be discussed, as well as the intramolecular interactions that contribute to their stability.

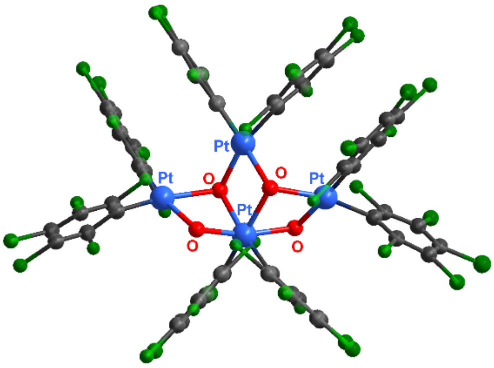

Fig. 1: $[Pt^{IV}Pt_3^{II}(OH)_4(C_6Cl_5)_8]^=$

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Study of the optical properties of a silver-gold-thallium system with a macrocyclic ligand

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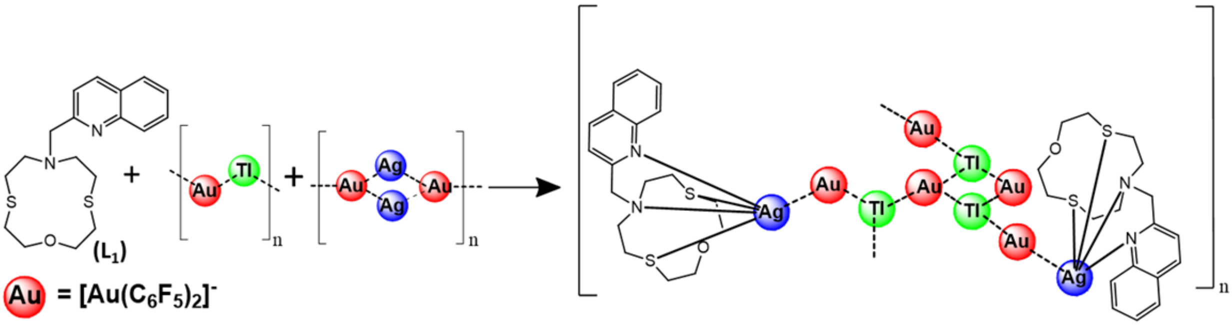
Recently, compounds containing metallophilic interactions between gold(I) atoms and various metal ions having a "closed shell" electronic configuration, [M = Cu(I), Ag(I), Tl(I), Pb(II), Hg(II), Bi(III), Sn(II)] have aroused considerable interest both in terms of theoretical aspects and their physicochemical properties and potential applications. However, despite the numerous materials containing metal interactions Au(I)-Au(I) [1], Au(I)-Ag(I) [2] or Au(I)-Tl(I) [3], very few examples of heterotrinuclear systems are known [4] because of the difficulty in controlling the synthetic process.

In this case, the reactivity of the polymeric compounds $[\{Au(C_6F_5)_2\}Tl]_n$ and $[\{Au(C_6F_5)_2\}Ag]_n$ is studied against N,S,O-donor heterocyclic ligands with a methyl quinoline unit (**L$_1$**). The synthetic idea arises from the possibility of taking advantage of the presence of a high number of donor atoms (and therefore, with different coordination ability to the three metals), and of the tendency of gold(I) to form metallophilic interactions.

This strategy allowed us to synthesize an unprecedented polymeric Ag/Au/Tl system which displays Au···Ag and Au···Tl unsupported interactions.

Theoretical studies have been carried out in order to explain the stability of this system.



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Organometallo-silicas for visible-light promoted iminyl-radical formation

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Visible-light photoredox catalysis is an environmentally friendly and sustainable synthetic technology able to promote a wide variety of nontraditional bond constructions in organic chemistry, including the formation of arenes and heteroarenes.[1] Much of these processes use luminescent organometallic complexes as single-electron transfer homogeneous catalysts. Hybridation of these light-responsive derivatives with solid matrices, as mesoporous silica, offers an attractive route for practical design of efficient catalytic systems easier to recover and reuse.[2]

In the last years, our groups have developed the so-called Sol-Gel Coordination Chemistry, based on the co-condensation of organometallic complexes bearing alkoxysilane terminal groups with a silica source – *i.e.* tetraethyl orthosilicate (TEOS).[3]

In this context, we have chosen the emissive cationic complex [Ir(dfppy)$_2$(dasipy)]OTf (Fig. 1), bearing terminal alkoxysilane groups, to study the influence of the heterogenization of this catalytic species in the formation of phenanthridines from acyl oximes (Fig. 1). This study covers not only different *in-situ* and *post-synthetic* incorporations of the Ir(III) complex to mesoporous silica materials, but also solid self-condensed materials.

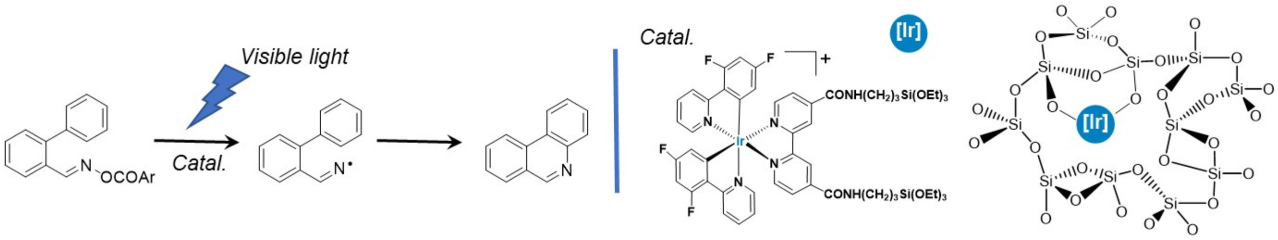

Figure 1

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Activation of a C-Cl bond to form an unprecedented Pt(IV)(μ-CH_2Cl)Pt(II) fragment

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There is a constant quest for novel metal–organic complexes with potential applications in medicine, catalysis, materials science or magnetism. In this context, we have prepared several pentafluorophenyl platinate complexes with some carboxylato ligands in the search of new derivatives with different chemical and structural features. The syntheses of the complexes have been carried out by reacting the derivative $(NBu_4)_2[Pt(C_6F_5)_4]$ with carboxylic acids, namely orotic, malonic, malic, nicotinic or oxalic acids, in refluxing acetone.

The different flexibility and number of donor atoms of the ligands has led to complexes of different nuclearity. Thus, the following complexes have been structurally characterized: $(NBu_4)_2$[*cis*-$Pt(C_6F_5)_2$(Horotate)], (NBu_4)[*cis*-$Pt(C_6F_5)_2$(nicot)(Hnicotinate)], $(NBu_4)_2$[{*cis*-$Pt(C_6F_5)_2$}$_2$(μ-oxalate)] and $(NBu_4)_4$[{*cis*-$Pt(C_6F_5)_2$}$_4$(μ-malonate)$_2$].

When malic acid is used in the presence of CH_2Cl_2, the hexanuclear complex $(NBu_4)_4\{[Pt^{IV}Pt^{II}_2(C_6F_5)_6(malato)(CH_2Cl)]_2\}$ can be isolated, in which activation of a C-Cl bond of a dichloromethane molecule takes place in mild conditions. The complex features an unprecedented bridge of the CH_2Cl moiety between two platinum atoms (fig. 1). The C atom of the chloromethylene unit is bonded to a platinum(IV) center, which is located in a typical octahedral environment, while the Cl atom is bonded to a square-planar platinum(II).

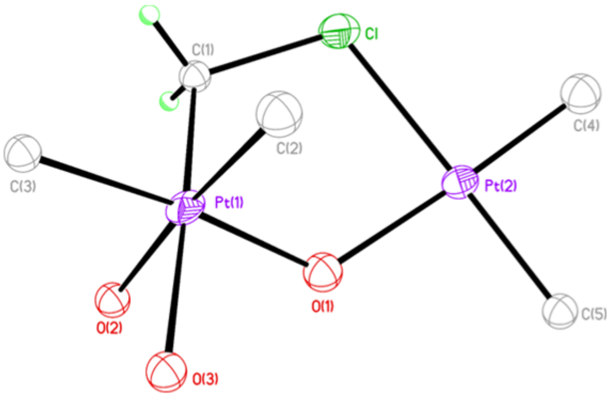

Figure 1

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Tropo-inversion of the biphenyl moiety in chiral bis-amido phosphito ligands

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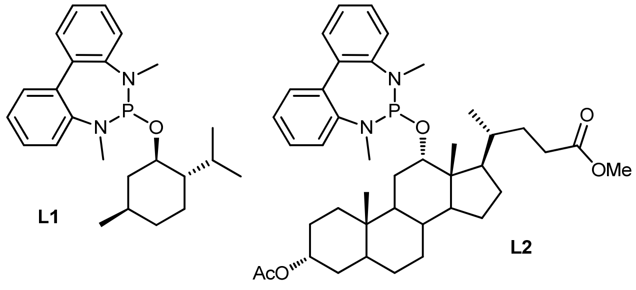
Metal complexes of chiral *tropos* –chirally flexible– ligands have been successfully employed in a number of enantioselective reactions [1]. The incorporation of an enantiopure moiety in the backbone of the ligand is a generally accepted strategy to achieve the conformational control of the *tropos* moiety [2]. Nevertheless, as for now, only a limited number of studies have elucidated the stereodynamics of phosphites and phosphepines [3].

Herein we report a detailed study of the stereodynamic properties of chiral bis-amido phosphites **L1** and **L2** (Scheme 1) and their palladium(II) complexes *trans*-[Pd(μ-Cl)Cl(L)]$_2$ (**1**) and *trans*-PdCl$_2$(L)$_2$ (**2**).

In all the cases NMR spectroscopy indicates that the tropo-inversion is operative at room temperature, all the diastereomers are present in solution and the mechanism of the tropo-inversion is non-dissociative. Further, higher activation barriers are observed upon coordination of **L1** to palladium, and the configuration of the non-inverting ligand has a negligible influence on the barrier of the tropo-inversion in both **1** and **2**. DFT calculations have shed light on the nature of the transition state(s) leading to the tropo-inversion in both free and coordinated ligands.



Scheme 1

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SYNTHESIS AND CYTOTOXICITY OF Pt(II) AND Pt(IV) BIS(PYRAZOLYL)METHANE COMPOUNDS AS POTENTIAL ANTICANCER DRUGS

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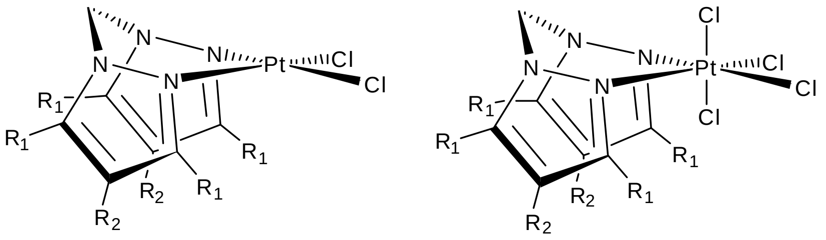
Cisplatin, along with other Pt(II) coordination compounds, has been widely used in cancer treatment due to their great cytotoxic properties. However, these compounds usually have poor selectivity towards tumoral cells, leading to a great number of side effects. Pt(IV) coordination compounds act as a pro-drug, being reduced inside the cells, helping to overcome these problems.

In this work, several Pt(II) and Pt(IV) compounds have been synthesized (Fig 1). In order to force the *cis* configuration, bis(pyrazolyl)methane chelating ligands have been used. Substituents have being added in order to tune their cytotoxic properties.



R_1= R_2= H
R_1= Me, R_2= H
R_1= H, R_2= Me
R_1= H, R_2=Br

Figure 1

The cytotoxicity of these compounds has been studied in order to get information about their potential as anticancer drugs. A549 (Lung), MCF7 (Breast) and HT29 (Colon) cancer cell lines have been used.

Financial support acknowledgment: MINECO of Spain (CTQ2014-58812-C2-1-R), JL thanks to FEDER funds and Plan Propio de I+D+i-UCLM (2014/10340) for a predoctoral contract.

Transfer Hydrogenation Process of Imines Using Ruthenium Catalyst in Biphasic Medium

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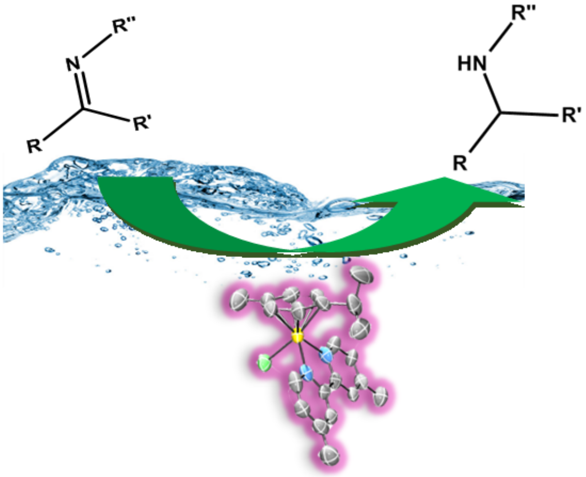
The hydrogenation of organic compounds is a reaction of great importance in many fields like fine chemistry and pharmaceutics. Transfer hydrogenation (TH) is an important alternative to catalytic reduction with H_2, involving the formal transfer of H_2 from a donor molecule to a substrate. Complex $[(\eta^6\text{-p-cym})RuCl(\kappa^2\text{-N,N-dmbpy})](BF_4)$ [1] is water-soluble and active in the catalytic 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.

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Ligand Design for Au(I)/Au(III) Catalytic Cross-Coupling Reactions

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Cross-coupling reactions are arguably the most important transformations to build carbon-carbon and carbon-heteroelement bonds. They are well-known with mid and late transition metal complexes, but the use of gold complexes has just recently emerged.[1] This is due to the reluctance of gold to cycle between its +I and +III oxidation states. Oxidative addition, which is a key elementary step in transition metal chemistry and the entry point to many catalytic transformations, in particular cross-coupling reactions, is not favored for Au(I) complexes.[2]

Our group has overcome the reluctance of gold to undergo oxidative addition[3,4] thanks to the use of (P,P) chelating and (P,N) hemilabile ligands. Together with the easiness of Csp^2–Csp^3 reductive elimination at gold, this has opened the way to gold-catalyzed cross-coupling transformations *via* Au(I)/Au(III) redox cycles.[4,5] Herein, we describe our recent studies on hemilabile *N*-containing ligands to assist the gold center to achieve oxidative addition and Au(I)/Au(III) catalytic cycles.

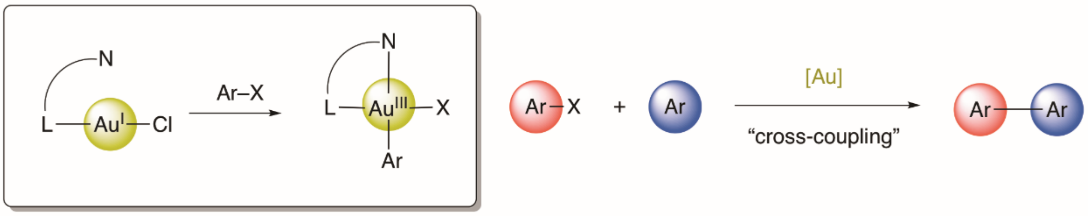

Figure 1. Oxidative addition of aryl halides to Au(I) complex assisted by hemilable *N*-containing ligands as the entry point for Au-catalyzed cross coupling transformations *via* Au(I)/Au(III) redox cycles.

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Reactions of an Osmium Polyhydride with Nitriles

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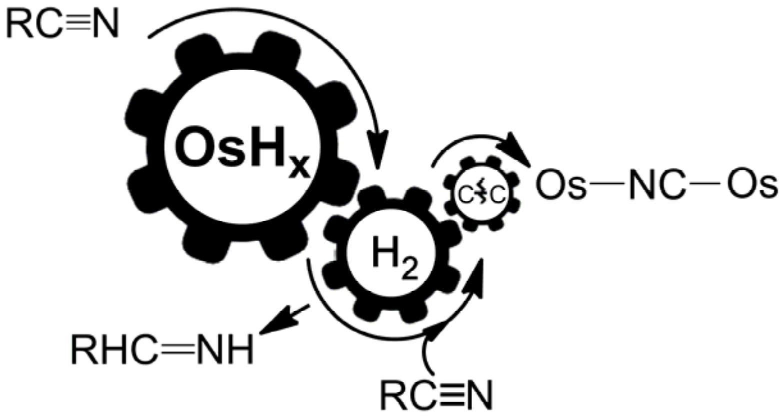
The study of the reactions of nitriles with transition metal complexes is a field of considerable importance due to their connection with catalytic processes such as hydrogenation,[1] hydration,[2] and decyanation.[3] The use of molecular hydrogen for hydrogenation of nitriles is particularly of great interest as it is an efficient, economic and environmental friendly process applied in both academia and industry. Several platinum group complexes have been used for this purpose; nevertheless, isolation of catalytic intermediates is challenging.

Osmium electronic properties allow stabilizing species which are 5d counterparts of complexes proposed as catalytic intermediates in ruthenium-mediated organic synthesis. In this work, we present the study of the reactivity of an osmium polyhydride with nitriles, which allows the rationalization of their hydrogenation catalyzed by ruthenium polyhydrides, between other processes.



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Exploring the Chemistry of an Osmium POP Dihydride with Unsaturated Molecules

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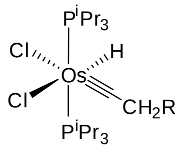
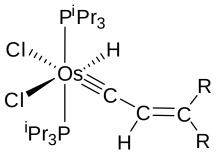
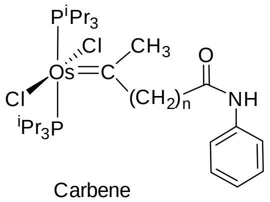
The osmium dihydride complex $OsCl_2H_2(P^iPr_3)_2$ reacts with unsaturated molecules, including terminal alkynes, alkynols, enynes and gem-disubstituted allenes, to give isomeric hydride-carbyne forms.[1] Factors affecting the transformation of osmium hydride-carbyne into carbene species have also been studied.[2] The presence of a distal amide at the alkylic chain of a terminal alkyne allows the preparation of five-coordinate osmium carbene complexes, assisted by coordination of the heteroatom to the osmium center.[3] Different osmium precursors lead to the formation of additional isomeric forms, including hydride-osmacyclopropenes which isomerize into cyclic carbenes.[4]



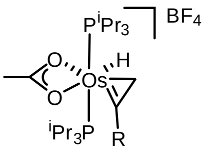
Hydride-carbyne



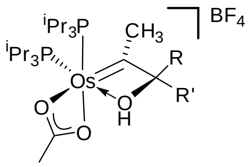
Hydride-alkenylcarbyne



Carbene



Hydride-metalacyclopropene



Cyclic carbene

In this communication, we show the reactivity of a new osmium-POP unsaturated organometallic fragment, $[OsH_2Cl\{xant(P^iPr_2)_2\}]^+$,[5] towards functionalized alkynes and allenes, thus highlighting its structural and electronic similarities with the organometallic complexes mentioned above.

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Metal as Source of Chirality in Octahedral Complexes with Tripodal Tetradentate Ligands

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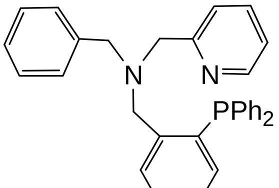
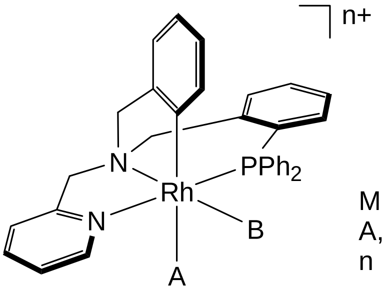
Chiral metallic complexes constitute an important class of asymmetric catalysts that consist of assemblies of ligands around a central metal atom with the stereogenic element(s) located in the ligands and/or in the metal. The resulting chiral entity activates reagents usually by coordination to the metal atom and, in the course of the reaction, the chirality is transferred to the newly formed stereogenic centers.

However, while asymmetric catalysis mediated by metallic compounds bearing chiral ligands is abundantly represented in the scientific literature,[1] enantioselective catalytic systems based on stereogenic metals are much less documented.[2] The demanding requirements of optical resolution, high configurational stability and labile coordination sites can be envisaged as responsible for this scarcity.

Here we present a case in which the challenging control of the absolute configuration of chiral-at-metal complexes is efficiently achieved using the tripodal tetradentate ligand **L**.[3a] The optical resolution of *rac*-$[RhCl_2(\kappa^4 C,N,N',P{-}\mathbf{L})]$ provides access to enantiopure complexes (see Figure) that efficiently catalyze the Diels-Alder reaction between methacrolein and HCp with up to 99% ee.[3b] The nature of the active species, the origin of the enantioselectivity and mechanistic details are disclosed by means of NMR spectroscopy and DFT studies.



L



M = Rh
A, B = Cl, NCMe, H_2O
n = 0, 1, 2

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Unusual rearrangement of a guanidinato-phosphine ligand

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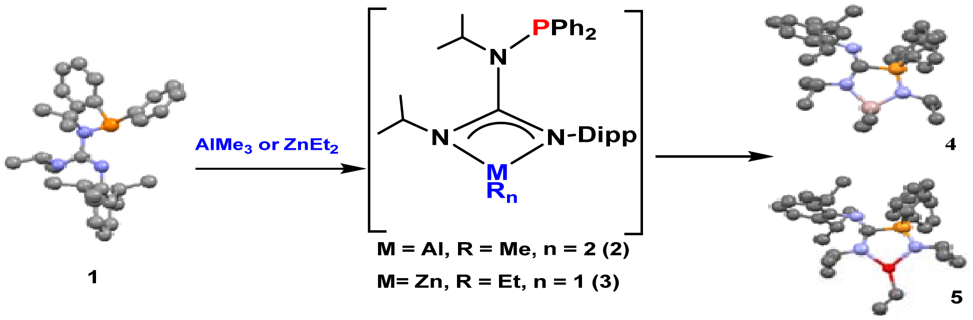
Continuing our study into the chemistry of guanidinate metal complexes,[1] here we describe the results of the synthesis and characterization of new *N*-phosphinoguanidine compound (HN-*i*-Pr)(Ph_2PN-*i*-Pr)C=NAr (Ar = 2,6-*i*-PrC_6H_3, Dipp) **(1)** and its reactivity with $AlMe_3$ and $ZnEt_2$ compounds. In a first stage, the equimolecular reaction generates the κ^2, *N,N*-guanidinato complexes [M{κ^2, *N,N'*-(N-*i*-Pr)(N(Dipp))C(N-*i*-Pr)(PPh_2}R_n] (M = Al, R = Me, n = 2 (**2**); M =Zn, R = Et, n = 1 (**3**)) and immediately give rise zwitterionic NCPNM-heterocyclopentane [Ph_2PN(*i*-Pr)MR_n]((*i*-PrNC=N(2,6-*i*-$Pr_2C_6H_3$)] (M = Al, R = Me, n = 2 (**4**); M =Zn, R = Et, n = 1 (**5**)) complexes. We propose a reaction mechanism by an unusual intramolecular rearrangement of the phosphinoguanidinate ligand via an intramolecular carbodiimide de-insertion, (*i*-PrN=C=N(2,6-*i*-$Pr_2C_6H_3$) followed regioselective insertion into the M-P frustrated Lewis pair.[2]

We also present the study by x-ray diffraction of compound (**1**) and the heterocyclopentane complexes (**4, 5**).



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Study of the Coordination Modes of a BPI Anion in Iridium and Rhodium Complexes

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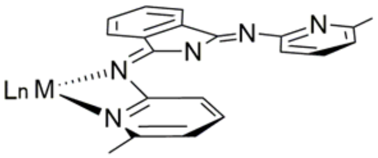
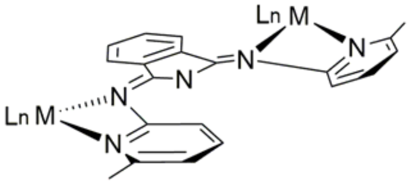
1,3-Bis(2-pyridylimino)isoindolates (BPIs) are a class of polydentate nitrogen-donor monoanionic ligands [1] which usually form κ^3-N_{py},N_{iso},N_{py} complexes with transition metals.[2] BPI complexes are of interest in homogeneous catalysis in different organic reactions including upgrading ethanol to 1-butanol, hydroboration of ketones and nitriles, hydrogenation of alkynes, among others.[3] Recently, we have reported the unprecedented κ^2-N_{py},N_{imine} and μ-(N_{py},N_{imine})$_2$ coordination modes of the 1,3-bis(6'-methyl-2'-pyridylimino)isoindoline anion (HBMePI) in osmium complexes. These complexes are efficient catalyst precursors for the acceptorless and base-free dehydrogenation of alcohols and amines.[4]





With these precedents in mind, we have carried out the study of the different coordination modes of the HBMePI anion in iridium and rhodium complexes.

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Catalytic Dehydrogenative Reactions Catalyzed by Ruthenium Complexes Anchored onto Graphene Surfaces

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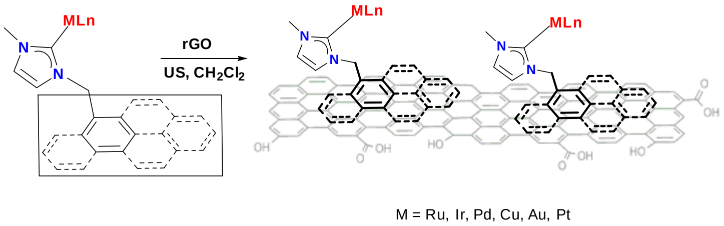
Despite the high activity and selectivity of homogeneous catalysts, its recovery and reutilization is an issue that still needs to be tackled. In the last few years, our group has been focused in the immobilization of molecular complexes onto reduced graphene oxide (rGO) by non-covalent interactions (Scheme 1).[1]



M = Ru, Ir, Pd, Cu, Au, Pt

Scheme 1 Immobilization of complexes onto reduced graphene oxide by π stacking interactions.

In this communication we show the catalytic properties of a ruthenium immobilized complex in three different reactions: the dehydrogenation of alcohols to obtain carboxylic acids;[2] the dehydrogenation of amines to synthesize nitriles;[3] and the dehydrogenative coupling of alcohols and silanes to produce silyl ethers and hydrogen.[4] The results show that the new catalyst can be recycled up to ten times without any loss in activity. Moreover, comparison between the molecular and the supported catalyst show that the activity is increased when the catalyst is immobilized, so graphene is more than a mere support and may play a role in the catalysis.

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The authors thank the financial support from MINECO (CTQ2015-69153-C2-2-R), Universitat Jaume I (P1.1B2015-09) and “Hyproxi” (VAL-2017-05). D. V-E thanks MINECO for a FPU grant (FPU15/03011). The authors are very grateful to the ‘Serveis Centrals d’Instrumentació Científica (SCIC)’ of the Universitat Jaume I.

Relevant Palladium Intermediates in Buchwald-Hartwig Amination

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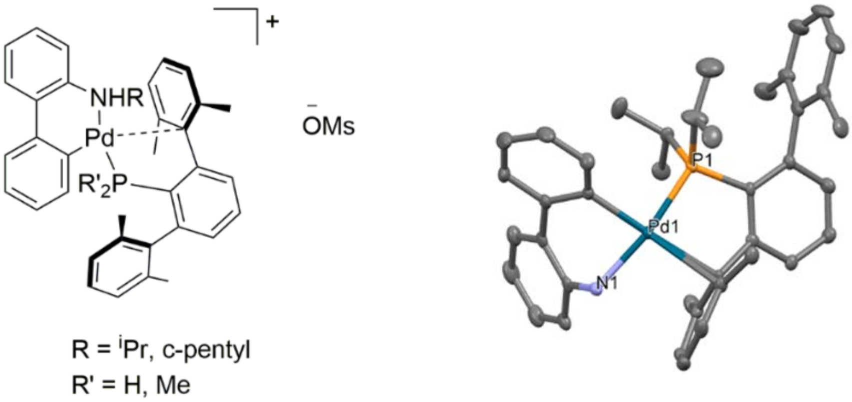
Palladium catalyzed cross-coupling reactions are one of the most powerful tools for the formation of C-C and C-heteroatom bonds.[1] The use of Pd precatalysts in these catalytic transformations provides a better control of the influence of the ligand in the catalytic cycle.[2]

We discuss here the synthesis and characterization of Pd(II)-metallacycles stabilized by bulky dialkylterphenyl phosphine ligands (Fig. 1). These complexes have been used as precatalysts in Buchwald-Hartwig amination reactions. The study of the intermediates in the catalytic cycle is presented.



R = ^{i}Pr, c-pentyl
R' = H, Me

Figure 1. Palladacycles presented in this work.

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Controlling the number of metallophilic interactions in an Au(I)-Pb(II) compound thanks to *puzzle* pieces

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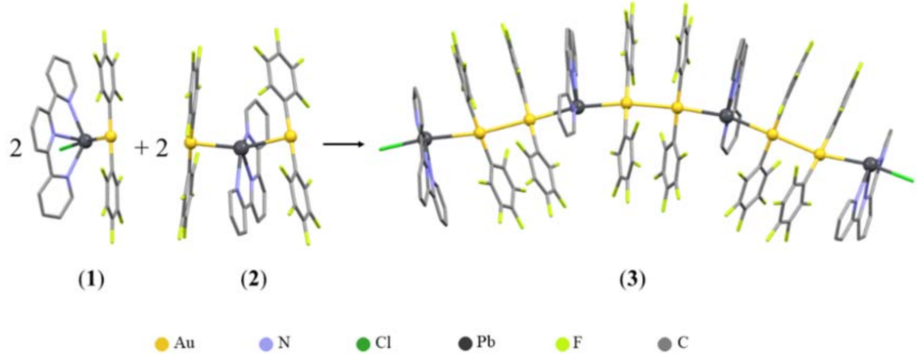
Although intermetallic closed-shell interactions are well known, and there are many examples of gold(I) complexes containing Au···Au or Au··M contacts, there is a few number of gold(I) derivates with group 14 elements, and in particular, with lead(II) [1-3]. Thus, the search of complexes with Au(I)···Pb(II) interactions, and specially avoiding the presence of bridging ligands, thus affording unsupported intermetallic contacts, is of great interest.

By reaction of $[Au_2Ag_2(C_6F_5)_4]_n$ with $PbCl_2$ and terpy in different molar ratios, we have synthesized two new species, $[\{Au(C_6F_5)_2\}\{PbCl(terpy)\}]$ (**1**) and $[\{Au(C_6F_5)_2\}_2\{Pb(terpy)\}]$ (**2**).

Since these complexes display one or two Au···Pb unsupported interactions, and taking into account the tendency of gold(I) centres to form aurophilic contacts, we wondered if these complexes could react in different molar ratios to afford higher nuclearity products. Thus, treatment of **1** with equimolecular amounts of **2** leads to the decanuclear complex $[\{Au(C_6F_5)_2\}_6\{PbCl(terpy)\}_2\{Pb(terpy)\}_2]$ (**3**), which displays Au···Au and Au···Pb interactions. The same compound is alternatively obtained from $[Au_2Ag_2(C_6F_5)_4]$, $PbCl_2$ and terpy in the adequate molar ratios.

We are now trying to combine such puzzle pieces in different molar ratios in order to obtain complexes with longer or shorter chains in an attempt to control the number of metallophilic interactions.



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Polyvinylpyridine Gold(I)-Silver(I) Metallopolymers. Tuning the luminescent properties through Au(I)···M(I) (M=Au, Ag) interactions

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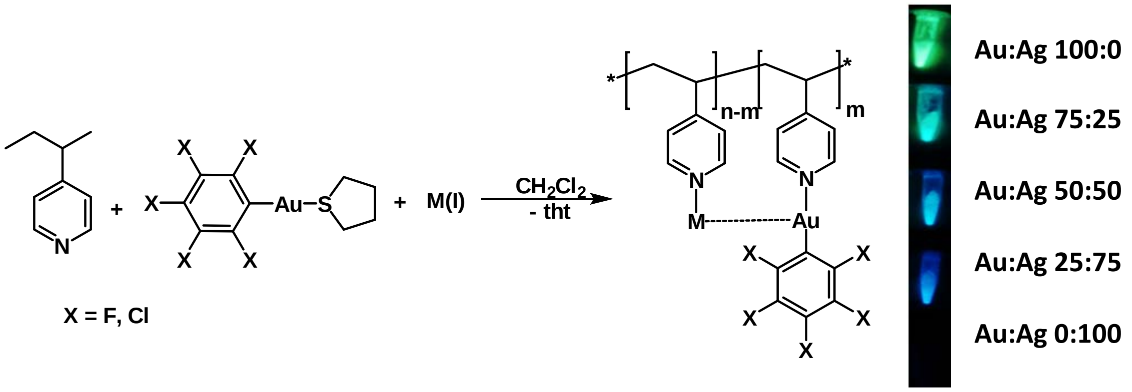
The metallopolymers [Au(C_6X_5)PVP] (X=Cl, F; PVP=poly(4-vinylpyridine)) exhibit very intense luminescent emissions when they are irradiated with UV light.[1] A detailed study of their photophysical properties revealed a fascinating luminescent behaviour which varies depending on the temperature and the excitation energies. This phenomenon is related to the presence of a huge number of aurophillic interactions lengthwise the polymer as well as the different environments for the gold(I) centres.

Therefore, considering that the temperature- and excitation-depending emission energies of the polymers have their origin in the gold(I) centres, it is possible to tune them controlling the gold environment by addition of new metal centres able to generate interactions with them. In this sense, Ag(I) is a perfect candidate since its tendency to form Au(I)···Ag(I) interactions is well known.[2] These assumptions have been confirmed experimentally and new metallopolymers, in which their emission energies depend directly on the Au:Ag ratio present in the polymer, have been synthesized. Therefore, as the silver content increases, the emission energies shift to higher energies. In contrast, when silver is the only metal coordinated to the pyridine groups, the resulting polymers are not luminescent, highlighting the essential role of the gold atoms in the optical properties.



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Iridium complexes with aminophosphano ligands

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In the last years amino-phosphano ligands have raised a lot of interest due to their easy functionalization and their ability to afford metal complexes active both in stoichiometric and catalytic reactions [1]. Motivated by the scarce number of complexes with *N,N′*-diphosphanesilanediamino ligands, we synthetized iridium(I) complexes with the ligand $SiMe_2\{(N(4\text{-}C_6H_4CH_3)(PPh_2)\}_2$ (SiNP, Scheme 1) and we showed that both carbon monoxide and trimethyl phosphite trigger the intramolecular $SiCH_2$-H activation leading to the κ^3C,P,P' coordination of SiNP [2].

Herein we report on the synthesis and characterization of novel iridium(I) and iridium(III) complexes (**1**, **2**; Scheme 1) featuring the Ir(κ^3C,P,P'–SiNP) moiety, and we describe their reactivity towards oxidants and Brønsted acids, respectively. Mechanistic details of the reaction of **2** with either HBF_4 or CF_3COOH have been disclosed by means of NMR spectroscopy.

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Self-Assembled Highly Positively Charged Crowns: Study of the Counterion Effect

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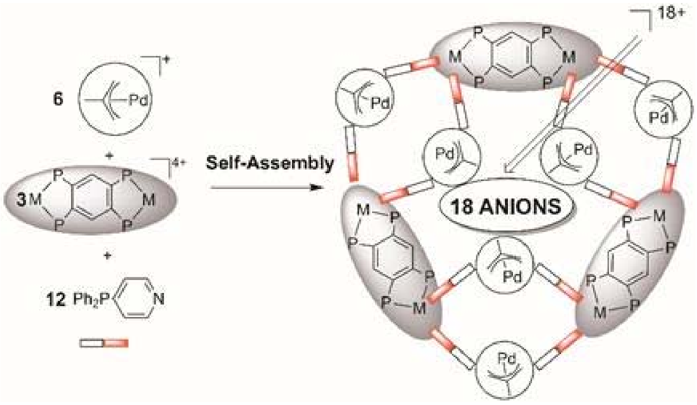
We have prepared and fully characterized a series of self-assembled highly charged homo- and heterometallamacrocycles containing allyl-palladium $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(4\text{-}PPh_2py)_2]^+$ and $[M_2(1,2,4,5\text{-tetrakis(diphenylphosphanyl)benzene})]^{2+}$ (M = Pd, Pt) moieties and fluorinated anions with varied steric and electronic properties, namely BF_4^-, $CF_3SO_3^-$, PF_6^-, SbF_6^- and BAr_F^-.



The new metallamacrocycles have shown remarkable differences both in their NMR and mass spectra depending on the anion. On the basis of the observed differences, the metallacycles have been tested as catalytic precursors in allylic substitution reactions. The anion-depending activity and selectivity has been analysed and compared with that of the corresponding monometallic allylic corners $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(4\text{-}PPh_2py)_2]^+$.

A functional material based on graphene and palladium complexes as catalyst for the semi-hydrogenation of alkynes

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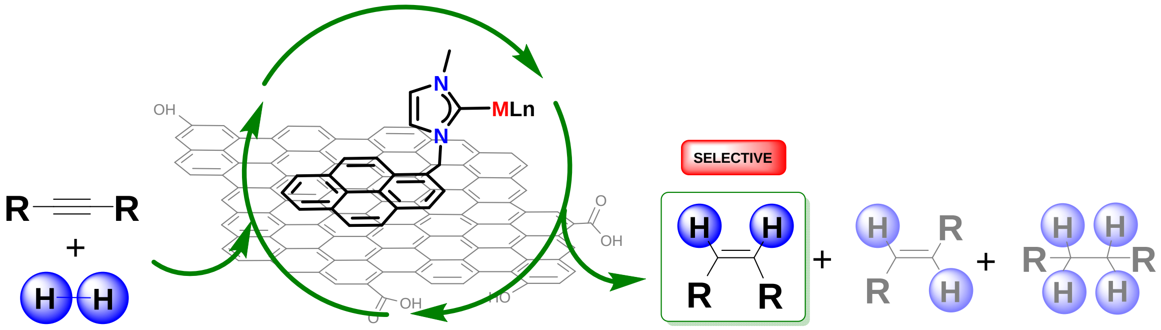
The semi-hydrogenation of alkynes is green approach route to obtain Z-alkenes. The synthesis of Z-alkenes is an important reaction in fine chemistry because this geometry is present in many bioactive natural products such as medicaments, drugs or pheromones.[1] General limitations arise from the lack of selectivity towards the Z-isomer [2] and over-hydrogenation originating the correspondent alkane.[3]

We have developed a functional material based on a palladium complex bearing an N-heterocyclic carbene ligand that efficiently catalyse the semihydrogenation of alkynes in a selective manner. The heterogenization of the palladium complex onto graphene allows the recyclability without activity decrease.[4] A plausible mechanism is proposed based on experimental evidence.



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Plasmonic-assisted and templated-assisted growth of Au-Ag ultrathin nanorods from organometallic precursors

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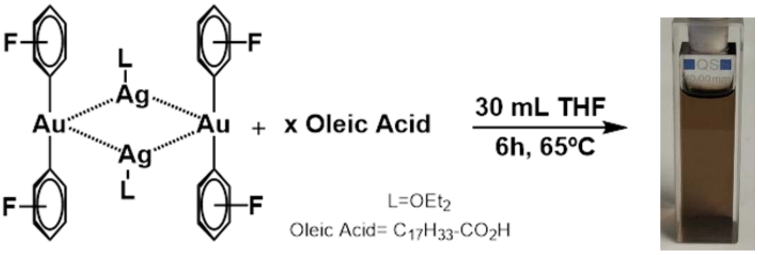
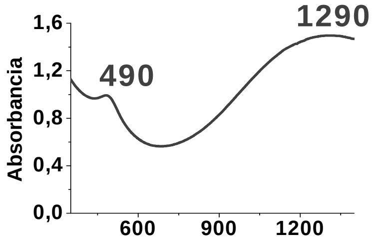
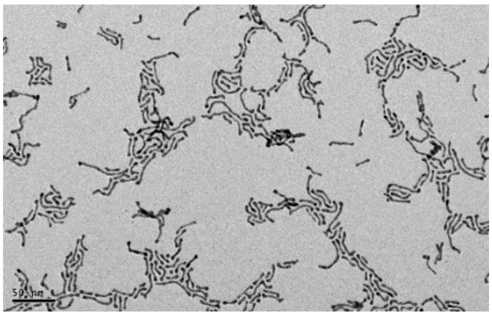
The organometallic approach for the synthesis of metal nanoparticles is based on the rupture of metal-carbon bonds under mild reaction conditions, leaving the metal centre unprotected.[1] If this decomposition takes place in the presence of a molecular template such as oleic acid and/or in the presence of light of different wavelengths a delicate control over the growth of nanostructures of different morphologies can be achieved. We have obtained new gold-silver, ultrathin nanorods by reduction complex $[Au_2Ag_2(C_6F_5)_4(Et_2O)_2]_n$, in the presence of different amounts of oleic acid. The obtained nanomaterials display interesting plasmonic properties in the NIR region. These type of nanostructures would be applied in different areas as, for instance, photocatalysis, photothermal therapy or sensing.[2] In addition, the same type of reactions performed in the presence of LED-light sources of different wavelengths allows a precise control over the length of the obtained bimetallic nanorods.







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Pd/Fe_3O_4 Single-Atom Catalyst for the selective hydrogenation of CO_2 to ethanol

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The conversion of carbon dioxide by hydrogen into value-added chemicals is one of the most investigated methods to reduce CO_2 emissions into the Earth's atmosphere. While the catalytic hydrogenation of CO_2 into methanol and methane are well stablished, the effective and selective transformation of CO_2 into higher alcohols is still challenging.

In this work we have prepared three Pd/Fe_3O_4 catalysts containing 0.11, 0.38 and 3.0 wt% of Pd. HAADF-STEM images show that samples contain, respectively, Pd single-atoms, Pd clusters of 1.2±0.2 nm and Pd nanoparticles of 4.3±0.4 nm. The immobilization of the Pd single atoms and Pd nanoparticles into the surface of magnetite nanoparticles (Fe_3O_4) has been performed by mean of an organic ligand in order to control the size and the homogeneity of the final clusters.

The catalytic tests show that while Pd nanoparticles are more selective to the formation of ethane and methane, SACs present a high selectivity to the formation of ethanol under mild conditions. The influence of the support in the selectivity of the process has also been studied depositing Pd SACs on different supports (CeO_2, Al_2O_3, ZnO), and we have found that a particular interaction is stablish between Pd single atoms and magnetite to construct specific active sites for C-C coupling.

POSTER 80

Encapsulation of Pyridine-based Anionic Ligands in Supramolecular Nanocapsules

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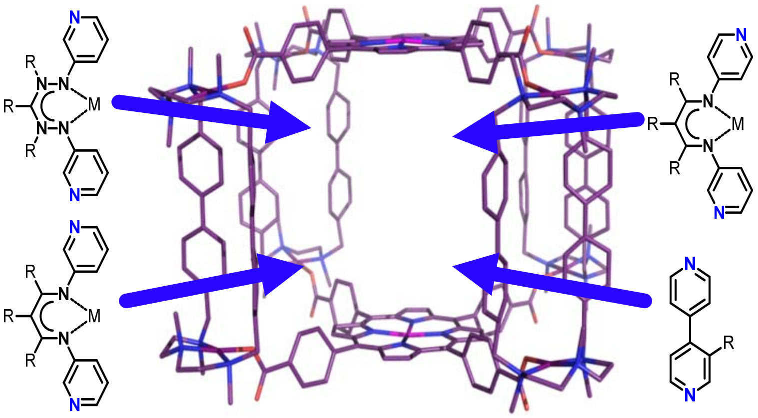
Catalytic reactions taking place in a confined space are found in nature, for example in the active center of enzymes. The special environment around the enzymatic active site leads to a highly selective transformations. In analogy to the spatial constraints imposed by enzymatic centers, the encapsulation of metal-based catalysts by a supramolecular nanocage could modulate their activity and selectivity via the second coordination sphere.[1] The aim of this study is to entrap pyridine-based anionic ligands in a self-assembled nanocapsule taking advantage of the octacationic charge of the nanocapsule that can increase the binding affinity. Formazan, β-diketiminate and bipyridine-like ligands are synthesized, characterized and encapsulated due to the well-known ability of Zn-metalloporphyrins to bind these kinds of pyridine-based ligands.[2,3] Furthermore, comparing the catalytic activity of the metal complexes as a supramolecular catalysts with regard to the catalyst operating in bulk solution, and also the role of the cage as a second coordination sphere of the catalyst is investigated. Although these complexes have been widely explored in stoichiometric studies, their use as catalysts is largely underdeveloped.



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Au^{III}-aryl Species involved in Fundamental Organometallic Processes

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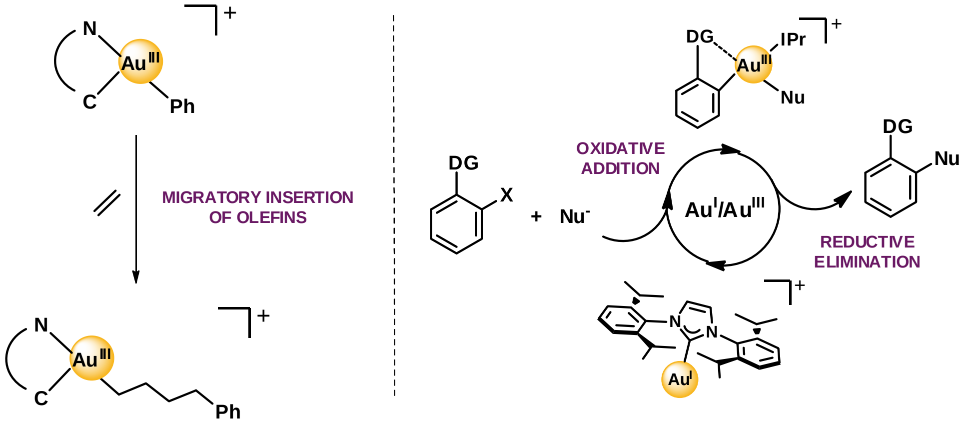
The chemistry of Au(III) complexes has recently caught attention because they display different interesting properties. Herein, we report the migratory insertion of ethylene to a (N,C)-cyclometalated Au(III)-phenyl complex.[1] For our surprise, the product obtained resulted from a selective double insertion. This reactivity is clearly in contrast to the decomposition led by β-hydride elimination observed in related (P,C)-cyclometalated Au(III)-phenyl complexes,[2,3] evidencing that the ancillary ligand plays a key role on the outcome of the reaction. Norbornene insertion will be also discussed to provide further insight into the migratory insertion of olefins at this (N,C)-cyclometalated Au(III)-phenyl complex. On the other hand, our group has developed halide exchange, C(sp^2)-O and C(sp^2)-N bond-forming cross-coupling reactions using different aryl halide model platforms bearing directing groups,[4,5] under a Au(I)/Au(III) 2-electron redox catalytic regime without using external oxidants. Compatible nucleophiles for these cross-coupling reactions included alcohols, phenols, amines, amides and amino acids.



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Immobilized rhodium catalysts for asymmetric hydroformylation under batch and flow conditions

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Hydroformylation of alkenes is one of the most important industrial applications of homogeneous catalysis. Diphosphite ligands have been successfully studied in the rhodium catalysed hydroformylation due to their modular nature [1]. Homogeneous catalysts however present the disadvantage of recycling and reuse. The development of supported catalysis is therefore required to ensure the sustainability of the catalytic processes.

The use of non-covalent interactions is an attractive strategy to attach homogeneous catalysts onto a solid support since it usually does not require additional synthetic efforts. Through this approach the structure of the ligand moiety is maintained. [2] Carbon materials emerged as promising supports due to their unique properties and large surface area.[3] Furthermore, they provide the possibility to immobilise catalysts by π-π stacking, which allow the grafting of molecules containing large polyaromatic systems.[4] In this work, we report rhodium complexes bearing pyrene tagged chiral 1,3-diphosphite ligands. The non-covalent immobilisation of these species onto carbon nanotubes was explored to obtain heterogenised catalysts, which were subsequently tested in the asymmetric hydroformylation of bicyclic alkenes [5]. Recycling experiments in batch and flow mode were carried out to analyse the robustness of these systems.

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Ir-Catalysts Based on N-Heterocyclic Olefins: Synthesis, Applications and Mechanisms

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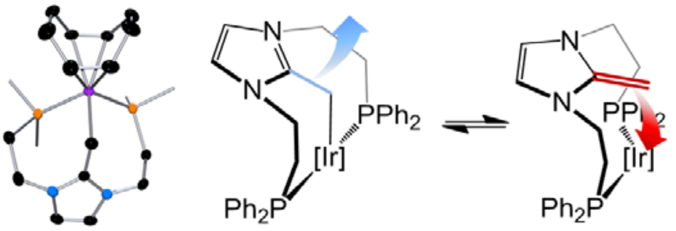
A great variety of pincer complexes has been reported in the literature. In particular, transition metal complexes containing PCP pincer ligands have shown remarkable catalytic activities in relevant reactions, such as, alkane dehydrogenation or transfer hydrogenation. The search for neutral ligands with a strong σ-donating ability has been a continuous endeavour for organometallic chemists in the last decades. The use of *N*-heterocyclic olefins (NHOs) as ancillary ligands for transition metal complexes renders electron-rich metal centers; however, the resulting C–M bond is often labile and leads to decomposition of the complex.[1] This presentation will deal with the preparation of the first PCP-type ligand based on an NHO scaffold and its impact in the activity of iridium complexes in catalysis. The flexibility of this NHO-based PCP-ligand, which can adjust to the geometry of the complex, adopting facial coordination modes in Ir(I) or meridional in Ir(III) complexes, can be attributed to the dual nature (ylide–olefin) of the NHO. This results in a rare case of olefin "slippage" that is supported by X-ray crystallography and DFT calculations.[2]

Iridium(I) complexes featuring this ligand show excellent activities in transfer hydrogenation reactions. The active species ([Ir(κP,C,P'-NHO-PPh_2)(iPrO)]) features an NHO moiety that behaves as a hemilabile ligand, which allows the catalyst to adopt stable square planar geometries in the transition states, thus reducing the energetic barrier of the process.[3]



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Tuning the morphology of plasmonic metal nanostructures through the template-assisted reduction of organometallic Au(I) and Ag(I) precursors

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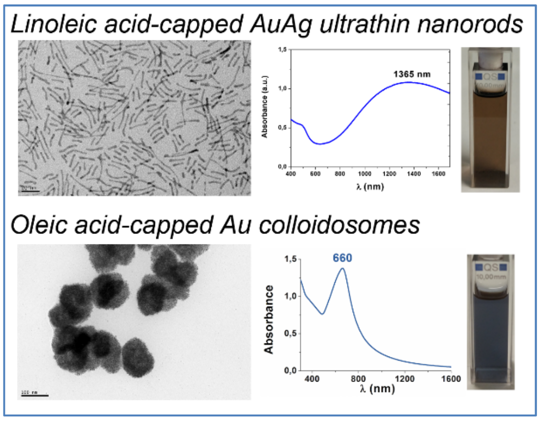
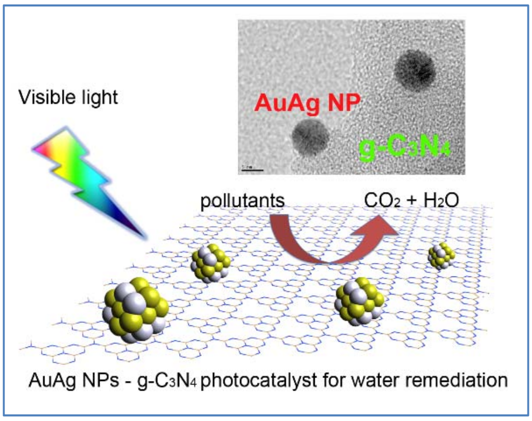
The recent advances in the optimization of synthetic protocols for new metal-based nanostructures have allowed establishing a direct and clear relationship between complex nanoparticle morphologies and their optical, magnetic or (photo)catalytic properties. Organometallic compounds constitute a very interesting class of metal precursors since their decomposition under mild reaction conditions affords a plethora of well controlled nanostructures.[1,2] At this regard, the assistance of molecular or polymeric templates in the transformation of the corresponding organometallic precursors into the final metal nanostructures play a very important role in the development of new hybrid nanostructures displaying enhanced or new properties.

In this communication we show how the template-assisted decomposition of complexes $[Au_2Ag_2(C_6F_5)_4(Et_2O)_2]_n$ and $[Au(C_6F_5)(tht)]$ leads to nanostructures of unprecedented morphologies and compositions. Thus, long alkyl chain carboxylic acids act as stabilizing ligands but also as directing growing agents for the synthesis of plasmonic Au-Ag ultrathin nanorods or Au colloidosomes. The 2D polymeric nanomaterial g-C_3N_4 can also act as a template in the synthesis of new Au or Au-Ag hybrid nanostructures of different compositions giving rise to materials with enhanced plasmonic photocatalytic properties for application in water remediation under visible light.





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New triazolate-bridged organometallic compounds

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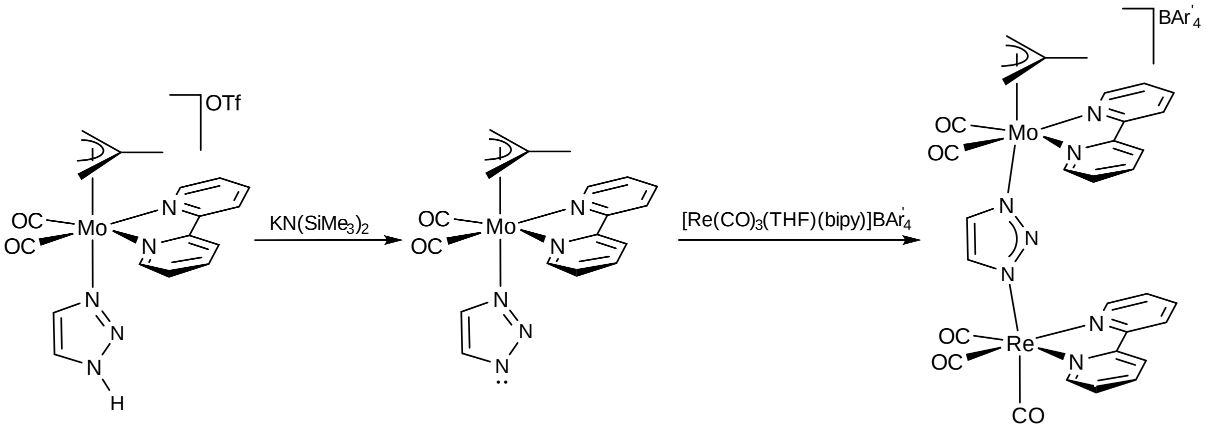
We have recently reported the synthesis of cyclic, bimetallic, dearomatized C-C coupling products by reaction of [Mo(η^3-methallyl)(CO)$_2$(Metz)(N-N)]OTf (N-N= bipy or phen; Metz= 1-methyl-1,2,3-triazole) with the strong base KN(SiMe$_3$)$_2$.[1] The new complexes were obtained as a result of deprotonation of the C5-H group of the triazole ligand, followed by an intermolecular attack to the *ortho* CH group of a bipy or phen ligand. The deprotonation of the parent compound [Mo(η^3-methallyl)(CO)$_2$(Htz)(bipy)]OTf (Htz= 1*H*-1,2,3-triazole) yielded a neutral, terminal triazolate complex, which displays a non-substituted nitrogen atom. The subsequent reaction of this neutral derivative with [Re(CO)$_3$(THF)(bipy)]BAr'$_4$ (BAr'$_4$= tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) afforded a cationic, heterobimetallic complex with a triazolate bridge (see Scheme). Furthermore, other triazolate-bridged compounds were obtained in the reaction of the free 1*H*-1,2,3-triazole ligand with a strong base and the subsequent addition of two equivalents of molybdenum or rhenium metallic fragments.



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Synthesis and photophysical studies of new luminescent heteroleptic bis-cyclometalated Pt(IV) compounds

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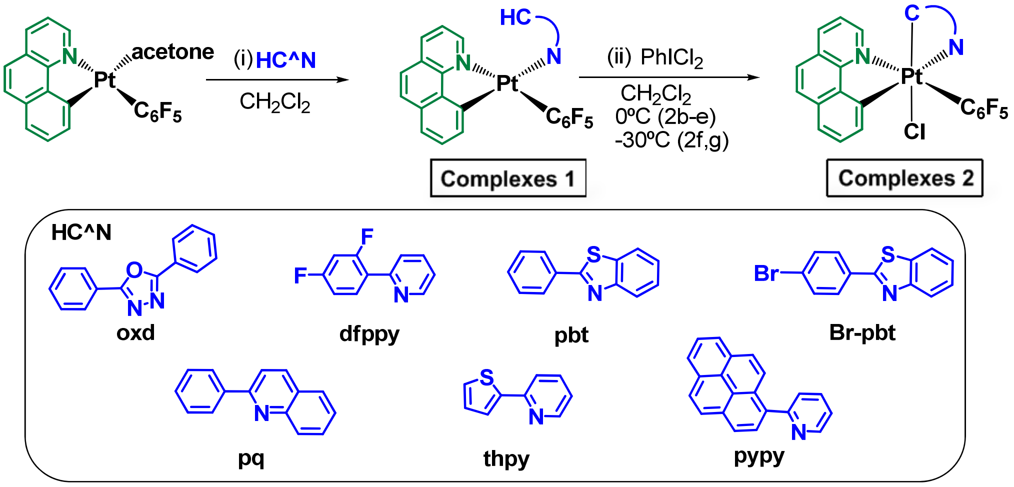
Although numerous studies have been carried out on d^6 phosphors, such as Ru(II), Os(II) and Ir(III) and d^8 such as Pt(II), studies on related luminescent Pt(IV) derivatives have received very limited attention [1,2]. In this context, our research group have recently published the preparation and the study of the optical properties of luminescent homoleptic bis-cyclometalated Pt(IV) complexes with C_6F_5 and Cl^- or CN^- as auxiliary ligands [3].

With the aim of gain more in-depthknowledge on the luminescent behaviour of cyclometalated Pt(IV) systems, a new family of heteroleptic bis(cyclometalated) Pt(IV) compounds with stoichiometry *fac*-[Pt(bzq)(C^N)(C_6F_5)Cl] (**Complexes 2**) containing the same cyclometalated benzoquinoline moiety in all of them and a second heterocyclic ligand C^N (oxd, dfppy, pbt, Br-pbt, pq, thpy, pypy) (see Scheme 1), have been synthesized and fully characterized. The influence in the photophysical properties of the second cyclometalated ligand C^N of **Complexes 2** has been investigated and their emissive properties have been also compared with those of the square-planar Pt(II) precursors [Pt(bzq)(N^C-H)(C_6F_5)] (**Complexes 1**). Besides, DFT and TD-DFT theoretical calculations have been carried out to provide insight into the electronic structures of these new complexes.



Scheme 1. Synthetic route for the heteroleptic bis(cyclometalated) Pt(IV) compounds.

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Role of the isomerism and the extent of Pt···Pt and π···π interactions on the optical properties of cycloplatinated(II) complexes

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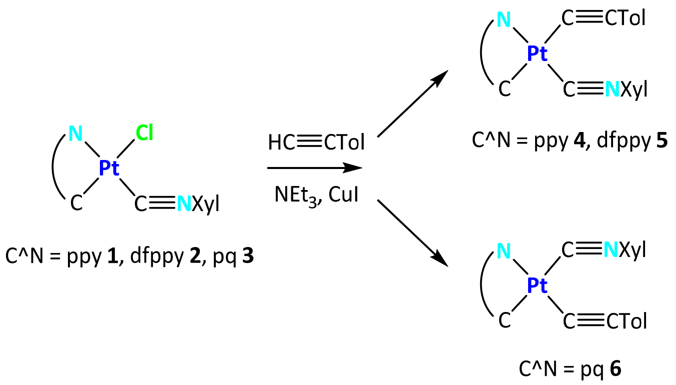
The chemistry of cyclometalated platinum(II) complexes have attracted a great attention in recent years due to their rich chemistry and tunable photophysical properties, with potential applications in light emitting diodes (OLEDs), photocatalysis, dopants chemosensors, bioimaging or solar cells. The presence of planar ligands in these compounds improves their luminescence and enhances their tendency to form aggregates through Pt···Pt and/or π···π interactions. In this context, there are few examples of heteroleptic cycloplatinated(II) complexes bearing isocyanide and alkynyl ligands simultaneously [1].

In this work, we report the synthesis and characterization of a series of luminescent Pt(II) compounds featuring 2-phenylpyridine, 2-(2,4-difluorophenyl)pyridine and 2-phenylquinoline as cyclometalated ligands. The alkynyl/isocyanide complexes [Pt(C^N)(C≡CTol)(CNXyl)] (C^N = ppy **4**, dfppy **5**, pq **6**; Xyl = 2,6-dimethylphenyl) were prepared from the chloride precursors [Pt(C^N)Cl(CNXyl)] (C^N = ppy **1**, dfppy **2**, pq **3**), using Sonogashira conditions. The isomerism of these derivatives (*trans* N_{C^N}-CNXyl or *trans* C_{C^N}-CNXyl) has been studied by NMR and X-Ray diffraction.

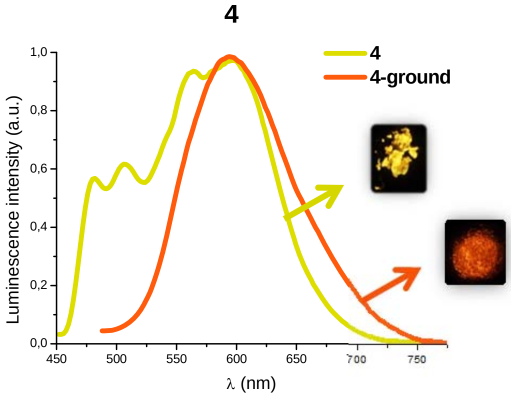
The photophysical properties of all complexes have been examined with the aid of Time-Dependent Density Functional Theory (TD-DFT) calculations. The phenylpyridine-based derivatives exhibit an interesting mechanochromic luminescent behaviour, related to their strong tendency to form stacking structures or aggregates by Pt···Pt and/or π···π interactions.



C^N = ppy **1**, dfppy **2**, pq **3**

C^N = ppy **4**, dfppy **5**

C^N = pq **6**



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Luminescent Pyrazine-based Au(III) pincer complexes

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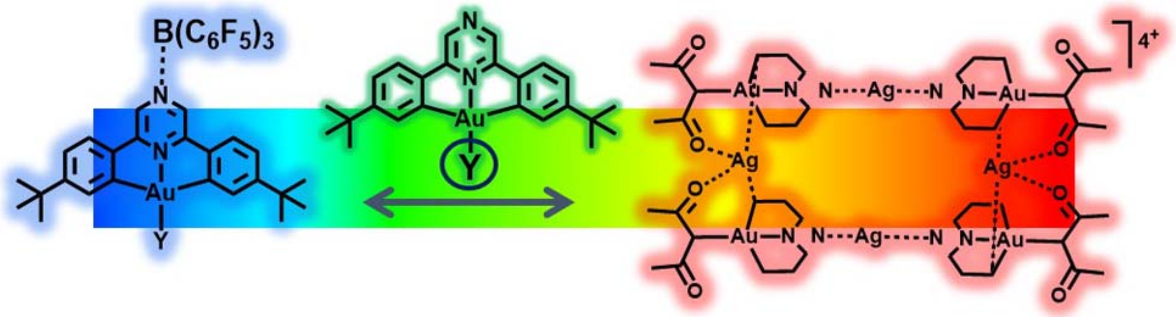
Dianionic pincer ligand based complexes derived from 2,6-diphenylpyridine (C^N^{py}^C) stabilize Au(III) from reductive elimination and show interesting photophysical properties. in particular have been intensely investigated. The development of gold pincer chemistry is however limited by the failure of synthetic routes for heterocycles other than pyridine. We have developed a protocol for the synthesis of pyrazine-based pincers which has opened the route to an unexpectedly large range of photoluminescent complexes, of the type (C^N^{pz}^C)AuX.[1]

This type of pyrazine-based complexes they exhibit better emissive properties that the pyridine analogues and in particular the range of ancillary ligands (X) arising to luminescence is much wider to the lower energy of the C^N^C based orbitals by switching from pyridine to pyrazine.

Besides this, pyrazine-based (C^N^{pz}^C)AuX exhibit a much richer range of photophysical properties associated with supramolecular processes. For example, the thiolate complexes (C^Npz^C)AuSR are the first example of aggregation induced emission ever reported for Au(III).[2] In addition, we have recently probed the viability of the pyrazine based complexes to act as building blocks for the construction of the very first family of Au(III)-Ag(I) aggregates, with a remarkable tuning of the luminescent properties.



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Aggregation studies of hybrid systems containing gold (I) complexes and gold nanoparticles

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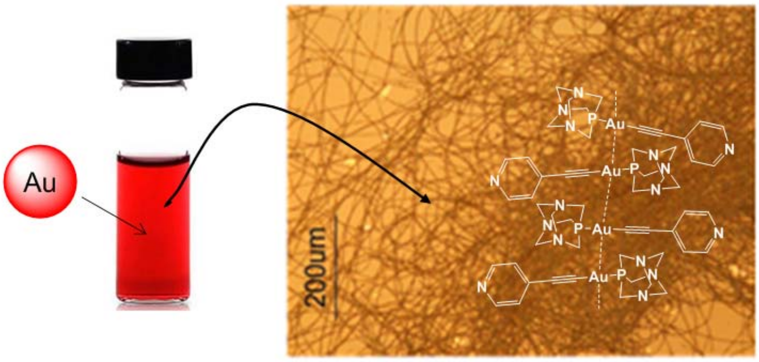
Gold (I) complexes are well known to have luminescent properties and tend to form a wide variety of 2D and 3D structures. The formation of these assemblies are possible due to the capability of these compounds to perform Au(I)···Au(I) aurophilic contacts together with the classical interactions (*e.g.* π-π stacking or hydrogen bonding).[1,2]

The resulting supramolecular assemblies may be affected and play a key role in the iteraction with gold nanopartibles. [3] via metallophilic contacts. In this way, we have developed organometallic-NPs hybrid systems with very interesting applications.



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Rhodium Catalysed Amine-Borane Dehydropolymerisation: Control through Catalyst Design

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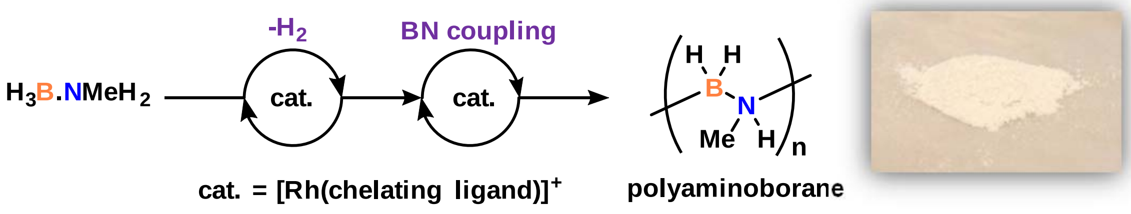
The catalysed dehydrocoupling of amine–boranes potentially allows for the production of B–N oligomeric or polymeric materials via dehydropolymerisation.[1,2,3] Such main–group polymers of empirical formula $(NRHBH_2)_x$, are (valence)isoelectronic with technologically pervasive polyolefins, and are virtually unexplored. In addition, the development of routes for the construction of E–E' (E = p–block element) bonds by catalytic routes lags significantly behind those used for the construction of C–E or C–C bonds. Despite the significant potential for these new materials, the mechanism for, and control of, their construction remains generally ill–defined when compared to analogous olefin polymerisation or other C–C bond forming processes. We describe the development, by mechanism–led design, of well–defined catalysts for the dehydropolymerisation of amine–boranes based upon the $[Rh(chelating\ ligand)]^+$ motif.[4] Through this it will be shown that new catalysts can be designed that have the potential to deliver new polyaminoboranes "to order" in terms of controlled molecular weight and isotopic purity.



Catalyst-controlled Polymerisation

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POSTER 91

Properties and Applications of Novel Metallic Bridgehead Tripodal Ligands

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There has recently been a resurgence of interest in tripodal tris(2-pyridyl) ligands ($Y(2\text{-py})_3$, Figure 1A), particularly in their potential applications as spectator ligands in catalysis. Our interest in this area has focused on heavier, more metallic main group bridgehead species of this type. These ligands now cover almost the entire range of p-block elements, including the heaviest counterpart containing a Bi(III) bridgehead (Figure 1B) and anionic aluminate ligands (Figure 1C). In this presentation we will discuss the effect of the introduction of these metallic bridgeheads, in particular aluminium and bismuth, on ligand properties. The introduction of the heaviest pnictogen element bismuth as the bridgehead has a major influence, both in regard to Lewis acidity and sigma donor character of the ligand set in comparison to the lighter pnictogen elements, and introduces the potential for anion-triggered change of the coordination mode.[1] Aluminum bridgehead tris(2-pyridyl)aluminates [R(2-py)3]- are unusual in having an overall negative charge (rather than being neutral), which results not only in strong affinity for metal cations but also in the easy post-functionalisation of the aluminate ligand, opening the prospect of new supramolecular chemistry and also finding applications in the rapid determination of enantiomeric excess (*ee*'s) of chiral alcohols.[2,3]

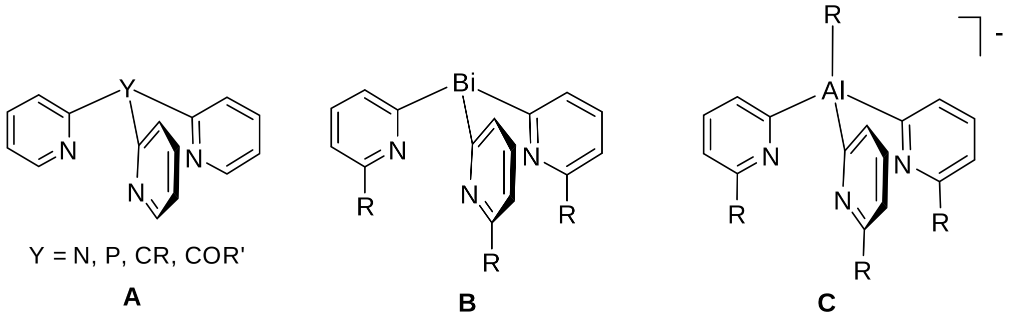

Fig 1

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Urea functionalised NHC gold carbenes as anticancer drugs

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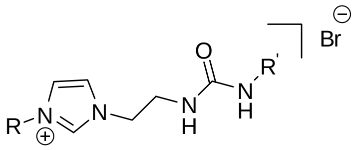
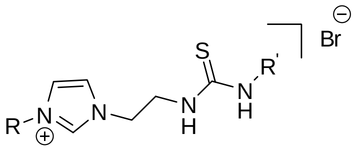
After the development of the *cis*-platinum complexes in cancer chemotherapy, further research was focussed on the synthesis of new metal compounds with less secondary effects and a broader spectrum of activity. In this way, gold and silver compounds showed awesome results to start being studied. Moreover, NHC ligands have allowed the preparation of gold complexes[1] with a huge stability and with a facile synthesis, in addition NHC substituents can be easily modified and because of that, these complexes might offer a wide variety of possibilities both for improving the solubility in serum or for designing compounds which can act again specific targets in cancer cells.

Organic molecules like ureas and thioureas can show biological activity and present a great capacity to form hydrogen-bonds between the sulphur or oxygen atom and the hydrogen atoms of the other molecule. Therefore these compounds have also been used as anticancer drugs[2]. In this work, we report the synthesis of different urea functionalised NHC ligands and their gold complexes; the products obtained have been characterised and their biological properties are being studied.



R: Methyl, Benzyl
R': Phenyl, 3-Fluorophenyl, Benzyl



R: Methyl, Benzyl
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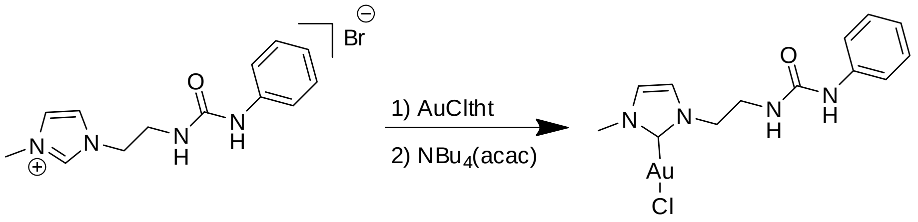

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Gold(I) *N*-Acyclic Diamino Carbenes: Synthesis and Application as Anticancer Agents

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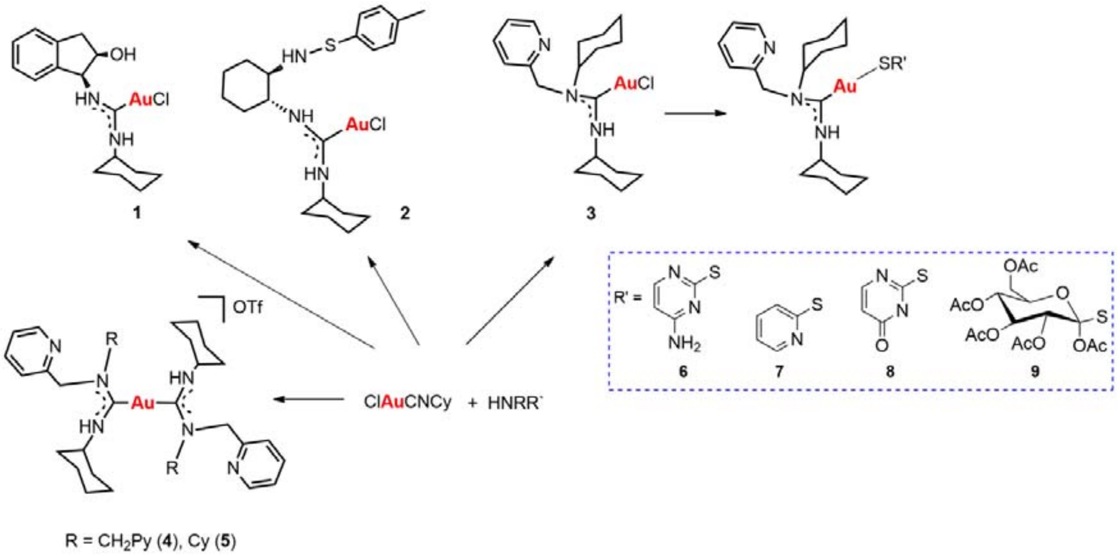
Gold drugs are well known and have been widely studied for their potential chemotherapeutic properties in anticancer treatments [1]. Gold *N*-heterocyclic carbenes display high cytotoxicity in vitro against a variety of human cancer cell lines with different degrees of selectivity. In the search for new alternatives, not only *N*-heterocyclic but *N*-acyclic diamino carbenes (ADC) could be explored [2]. Gold(I) *N*-acyclic diamino carbenes are easily accessible via the reaction between chloro isocyanide gold compounds and different amines. The reaction between the gold carbenes with different thiol derivatives has led to a family of ADC gold(I) thiolate compounds (**Scheme 1**).



Scheme 1. Gold(I) *N*-acyclic diamino carbenes

Cytotoxic activity was measured for the different synthetized compounds in different human cancer cell lines by the MTT assay. The IC_{50} values in the low micromolar range show very promising results.

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Preparation and Pharmaceutical Application of Terpyridine-Silver(I) Complexes: Potential Anticancer Drugs

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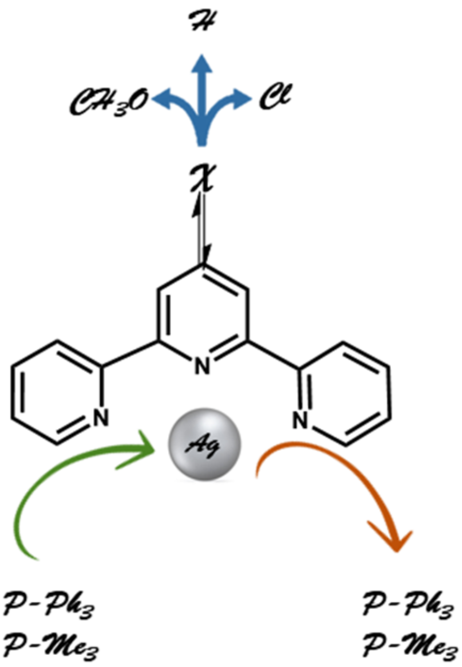
The area of medicinal inorganic chemistry has attracted much attention in recent years. For this reason many research projects have been carried out to design new potential drugs bearing metals like gold, ruthenium, iron, as well as silver[1]. The organic ligands alters physical and chemical properties of the metal ions and contribute, for instance, to inhibit selected metalloenzymes or facilitate metal ion re-distribution, among others[2]. Despite the fact that the some metal complexes with nitrogen donor ligands have been found to be effective in terms of antitumour activity, cell imaging or interaction with DNA, the biological studies that concern complexes with silver(I) and terpyridine are relatively scarce[3]. Therefore, our research project focuses on the study of biological activity of silver (I) complexes bearing phosphines and terpyridine as ligands.

In this study we have synthesized a family of compounds with varying donor-acceptor characteristics of the substituents in the terpyridine ligand. Thus, the presence or absence of phosphine ligands and the number of aromatic rings influence the results. The activity obtained is very promising, since the IC_{50} values show ranges between 3µM and 0,6µM in cell lines such as A-549 and HeLa.



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Heterometallic complexes for diagnosis and therapy

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Medicinal inorganic chemistry has offered many new opportunities for the design of therapeutic agents with excellent biological properties. Within this context, a growing interest is devoted to the development of heterometallic complexes with applications in cell visualization and cancer therapy [1,2]. A synergy effect is feasible to take place when both, a bioactive and an emissive metallic fragments are combined and thus, delivering novel trackable metallodrugs [3].

This work describes the development of a new variety of luminescent heterometallic complexes that are expected to overcome some of the problems associated with traditional trackable drugs, see Figure 1. Specifically, the synthetic procedure, photophysical and bioactive properties of a series of complexes of the type [$Au_2(PR_3)_2(L)MX$], where L is 4,4'-diethynyl-2,2'-bipyridine, PR_3 is either triphenyl phosphine, JohnPhos or 4-sulfophenyl-diphenylphosphine and MX represents a Re(I), Cu(II) or Ag(I) derivative will be presented.

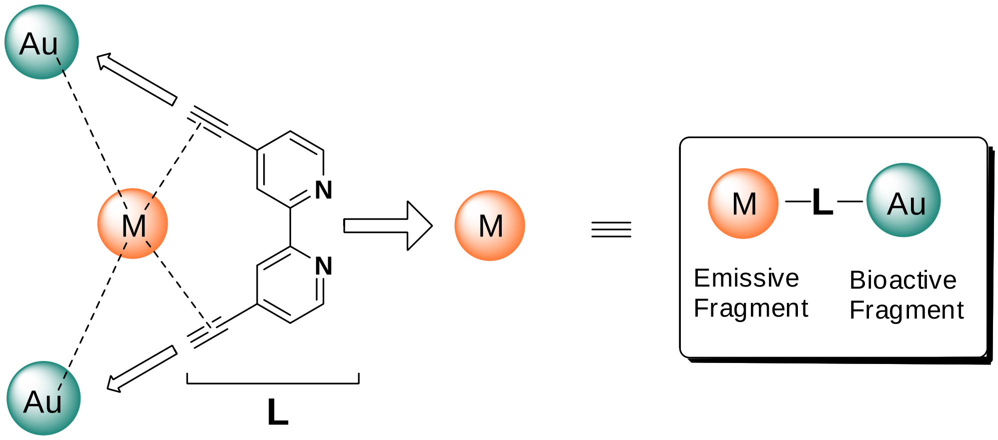

Figure 2

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POSTER 96

Novel Connections Between Rhenium(i) and Gold(i) for Theranostic Agents

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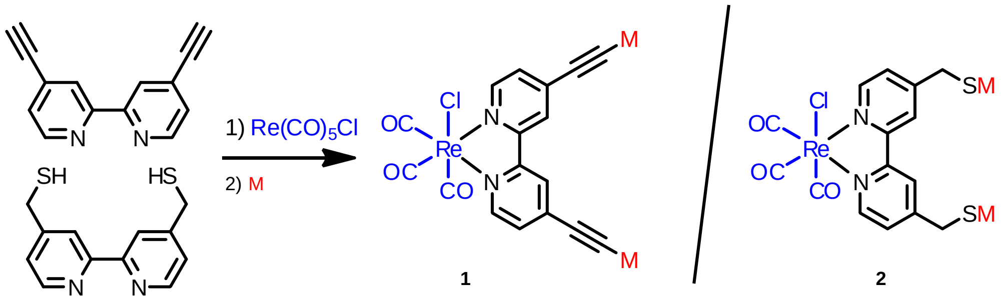
Rhenium (I) complexes of the type *fac*-$[Re(CO)_3(N\^{}N)L]^{+/0}$ are well known to exhibit excellent optic properties derived from a ^{3}MLCT transition, making them suitable for cell imaging applications.[1] Combination of those with a cytotoxic Au(I) fragment delivers novel theranostic bioprobes.[2] While the phenantroline/bipyridine backbone (N^N) typically remains untouched, functionalizations are usually made at the pyridyl/imidazolyl axial ligand (L).[3] However, the axial ligand has shown limited stability in solutions containing halides, and no significant modulation of the luminescence is seen after their funtionalization, suggesting the N^N backbone as the main contributor to the emissive properties. Therefore, two series of bimetallic Re(I)/Au(I) complexes have been synthetized in which the connection between the two metallic fragments takes place through the bipyridyl chelating ligand via either a alkynyl or thiolate moieties. Their emissive and cytotoxic activity has been investigated to assess their suitability as theranostic agents.



Esquema 1

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Functional Gold Materials

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Chiral gold compounds and their aurophilic assemblies have gained increasing interest during the last years due to their unique luminescent properties [1,2,3].

The luminescence of polymeric nanomaterials derived from alternatingly stacked cationic gold(I) and monoanionic coinage metal complexes can be modulated by choice of the metals and ligands [4].

The novel polymeric mixed-valent gold compound $[Au(NCCy)_2][AuCl_4]$ (Cy = cyclohexyl; crystal packing structure in Figure 1) is a candidate for the deposition of ultra-thin gold nanowires [5].

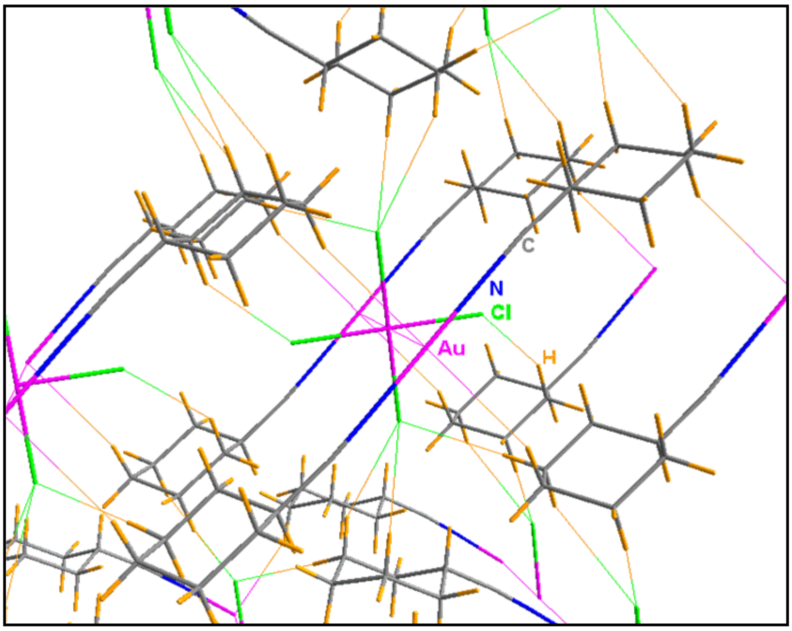

Figure 1. Crystal packing structure of $Au(NCCy)_2][AuCl_4]$; *C*2/m (*R*1 = 0.0262).

We will present the structures and the luminescent and cancerostatic properties of novel polymeric and chiral gold compounds.

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New emissive cyclometalated Pt (II) complexes with potential biological properties

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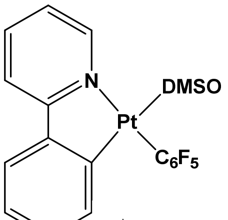
Cyclometalated Pt(II) complexes as phosphorescence emitters have gained increased interest as attractive candidates for use in organic light emitting diodes, oxygen sensors, bioimaging markers and/or antineoplastic agents, because of their remarkable optoelectronic properties[**1**]. Our research group has recently examined the biological activity and biodistribution of two families of neutral platinum complexes having cyclometallating groups and featuring C_6F_5/DMSO or Cl/Phosphine as auxiliary ligands (figure 1), [**2**] showing that this type of complexes are mainly incorporated to the cytoplasm in the perinuclear area.

To expand this research, we present the synthesis and optical properties of new related pentafluorophenyl Pt(II) compounds, bearing functionalized cyclometaled ligands (figure 2). Some of them include alkoxysilane terminal groups, which can enable further incorporation to inorganic oxide supports, such as silica nano-particles, with potential application as luminescent bioimaging probes.



A

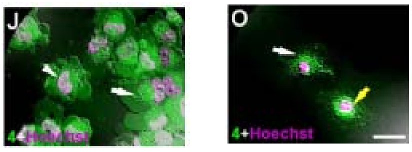
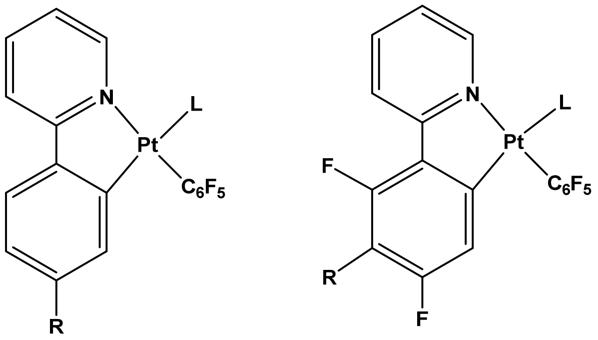


Figure 1: Fluorescence images of A549 (J) and NL20 (O) cells treated with A



R = CHO, CH=N-$(CH_2)_3$-$Si(OEt)_3$
L = DMSO, $PPh_2C_6H_4COOH$

Figure 2: New cyclometalated Pt (II) compounds.

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Assembly of Heterobimetallic Pt^{II}-Au^{I} Complexes with 1,1-Bis(diphenylphosphino)methane Ligand: Luminescence Properties

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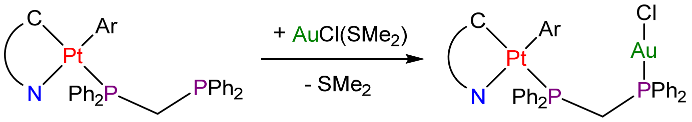
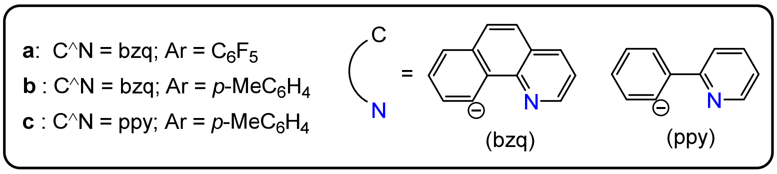
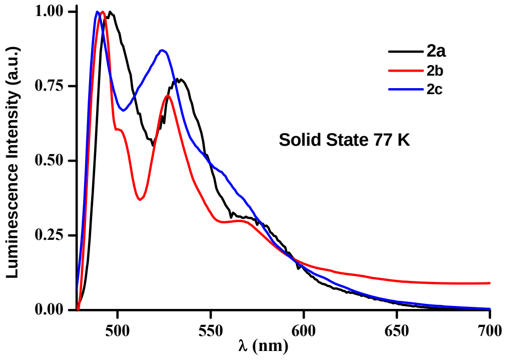
A strategy in the field of optoelectronic consists in the design of heterobimetallic complexes bearing diverse metal centers with distinct photophysical properties [1]. This approach is aimed at exploiting the possible synergism existing among the individual metal centers, which may contribute to overcome the thermally accessible deactivating states [2]. The underlying rationale is that the incorporation of two metals into the same molecule may greatly modify and/or improve the emissive behaviour of the resulting species [3].

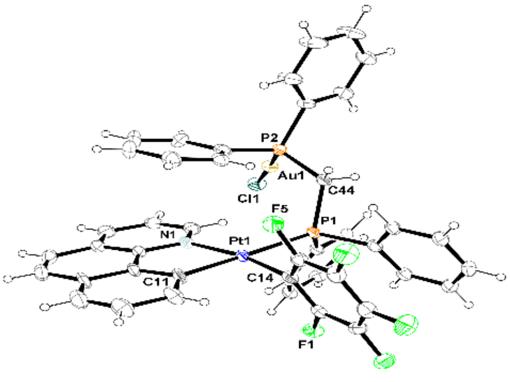
Following our research on synthesis of the heterometallic complexes, in this contribution we report on the preparation, characterization and optoelectronic properties of some bimetallic Pt^{II}–Au^{I} complexes, containing a cycloplatinated(II) moiety and a gold(I) chloride unit linked through the diphosphane ligand, 1,1-bis(diphenylphosphino)methane (dppm).



1a - 1c **2a - 2c**


a: C^N = bzq; Ar = C_6F_5
b : C^N = bzq; Ar = *p*-MeC_6H_4
c : C^N = ppy; Ar = *p*-MeC_6H_4





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Gold(I) derivatives with fluorous and hydrocarbon appendages as potential anticancer agents under hyperthermia

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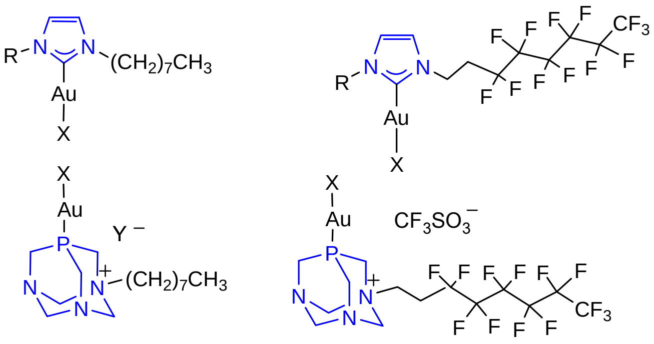
Oncological hyperthermia is an anticancer therapy, based on the use of heat in order to decrease the extension of a solid tumour. The association with chemotherapy can become a great example of synergy.[1] The increase of temperature in a tumour makes the blood request bigger and, for this reason, the amount of anticancer drug that reach the sick tissue increases. Besides, some chemical drugs can change some of their properties like the solubility or the lipophilicity when they are exposed to an increasing of temperature. These temperature dependent changes can improve the bioavailability, the diffusion or the activity of a drug, making it more efficient and selective towards tumor. One recent technique in order to create thermosensitive molecules has been the incorporation of fluor atoms in the chemical structure[2]. Fluor can play a central role enhancing drug activity, by tuning some chemical properties, such as binding affinity or its bioavailability.[3]

Herein we report on the synthesis and characterization of imidazolium salts and phosphanes derived from PTA (1,3,5-7-triazaphosphaadamantane) with long hydrocarbons chains and the homologous fluorinated chains. Coordination to a gold centre afforded the corresponding carbene or PTA gold(I) derivatives and the antitumor activity of some of them against colon cancer cell line Caco-2/PD7 have been studied.



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Reactions of C-halogen Bond Activation Mediated by a Rhodium POP Complex

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The reactions of C-halogen bond activation are fundamental steps in organic transformations mediated by transition metal complexes, such as cross-coupling reactions,[1] as well as in the chemical destruction of halogen-containing organic pollutants,[2] among many others.

We have recently shown that the complex $RhH\{xant(P^{i}Pr_2)_2\}$ ($xant(P^{i}Pr_2)_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) reacts with fluoroarenes to give products resulting from processes of C-H bond activations,[3] while in the case of chloroarenes the C-Cl bond activation takes place (Figure 1).[4] In the present contribution, we will present the preliminary results of the reactivity of the related complex $RhCl\{xant(P^{i}Pr_2)_2\}$ towards halogenated hydrocarbons.

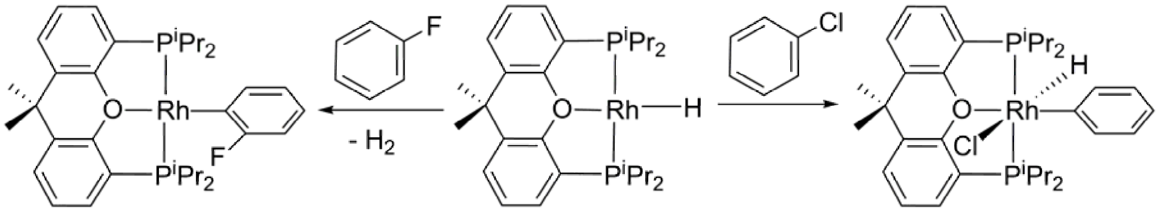

Figure 1

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Síntesis de compuestos de coordinación con ligandos bipiridina funcionalizados con compuestos poliaromáticos para el estudio de interacciones supramoleculares con nanotubos de carbono

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La síntesis y diseño de moléculas basadas en hidrocarburos poliaromáticos (PAHs) es muy interesante para el estudio de las interacciones supramoleculares y la síntesis racional de moléculas que pueden interaccionar selectivamente con nanotubos de carbono.[1,2,3] En este trabajo se han preparado ligandos 2,2´-bipiridina derivados de distintos PAHs, tanto de derivados de pireno como de coranuleno (Fig 1a). En estas moléculas el tamaño de la cavidad resultante entre los grupos R puede adaptarse fácilmente, lo que contribuye a mejorar la interacción y selectividad con fulerenos. Existen dos vías principales para controlar y modular dicha interacción: a) la geometría y naturaleza del sustituyente PAH; y b) la coordinación del ligando bipiridina a distintos fragmentos metálicos y organometálicos, lo que permite la correcta orientación de los sustituyentes PAHs (Fig 2b). Las implicaciones de estas variables en la efectividad de la interacción de la bipiridina con distintos fulerenos, como paso previo al estudio de su interacción con nanotubos de carbono, es discutida en este trabajo.

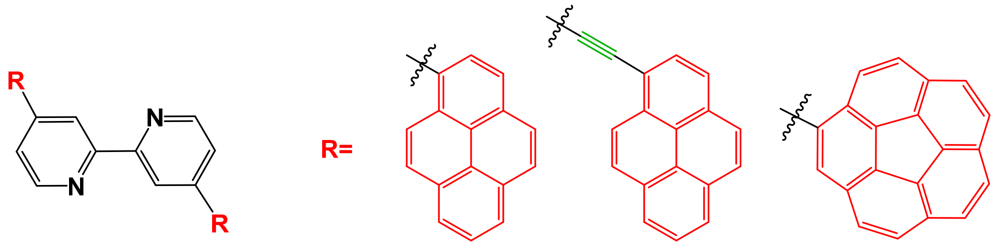

Fig 1a

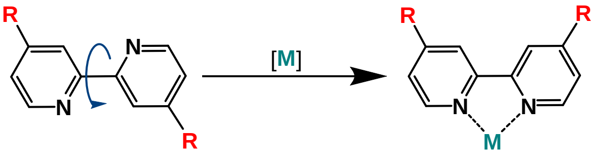

Fig 2b

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Exploring Organolithium Chemistry in Glycerol: Fast and Selective Addition of RLi to Nitriles at Room Temperature and Under Air

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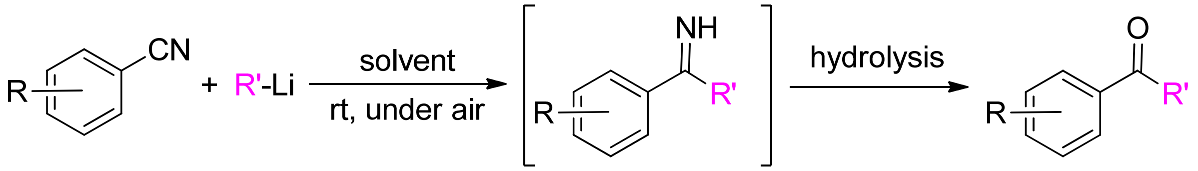
Nucleophilic addition of organolithium reagents to nitriles is a common methodology to access new C-C bonds allowing the synthesis of functionalized ketones or amines [1]. However, all these protocols require restrictive reaction conditions. This includes use of inert atmospheres, dry oxygen-free organic solvents and, in many cases, low temperatures (-78 ºC) in order to avoid intermediate degradation and side reactions. Thus, running polar organometallic chemistry under aerobic and/or using greener solvents (*i.e.*, glycerol) is one of the ultimate challenges to synthetic chemists [2]

In this communication, we present the chemoselective and ultrafast addition of a range of aryllithium reagents to nitriles by using glycerol as a solvent, at ambient temperature and in the presence of air, thus establishing a novel sustainable access to aromatic ketones [3]. Addition reactions occur heterogeneously ("*on glycerol conditions*"), where the lack of solubility of the nitriles in glycerol and the ability of the latter to form strong intermolecular hydrogen bonds seem key to favoring nucleophilic addition over competitive hydrolysis. Remarkably, PhLi exhibits a greater resistance to hydrolysis working "*on glycerol*" conditions than "*on water*". Introducing glycerol as a new solvent in organolithium chemistry unlocks a myriad of opportunities for developing more sustainable, air and moisture tolerant main-group-metal-mediated organic synthesis.



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Triphenylene-Imidazolium Salts and their N-Heterocyclic Carbene Metal Complexes

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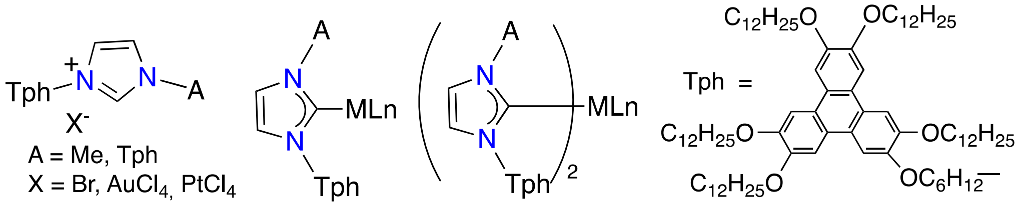
Discotic liquid crystals obtained by self-assembling disc-like molecules into columnar mesophases, is a smart strategy for the development of new functional materials. They present unique electronic and optoelectronic properties associated to their columnar structure, which makes them suitable for potential applications such as conductive devices, field-effect transistors, or photovoltaic solar cells [1]. We have already reported mesomorphic complexes containing triphenylene moieties produce highly stabilized phosphorescent mesophases or semiconducting materials [2].

In order to search for highly versatile systems, we have used imidazolium moieties as modifiers of the promesogenic triphenylene groups; moreover we have exchanged anions and prepared the corresponding compounds with two metallate anions (Scheme 1). On the other hand, imidazolium salts have been used as precursors for the synthesis of N-heterocyclic carbene complexes with a variety of metal fragments (Scheme 1). This leads to hybrid organic/inorganic multi-columnar mesophases as demonstrated by SAXS. We are going to study these compounds not only structurally but if this columnar segregation preserves the triphenylene-centred luminescence or a different luminescence appears. Other properties could also be studied.

Scheme 1.



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Room Temperature C_{sp^2}–C_{sp^2} Bond Formation from Organoplatinum Complexes: Modification in Disulfide Ligands

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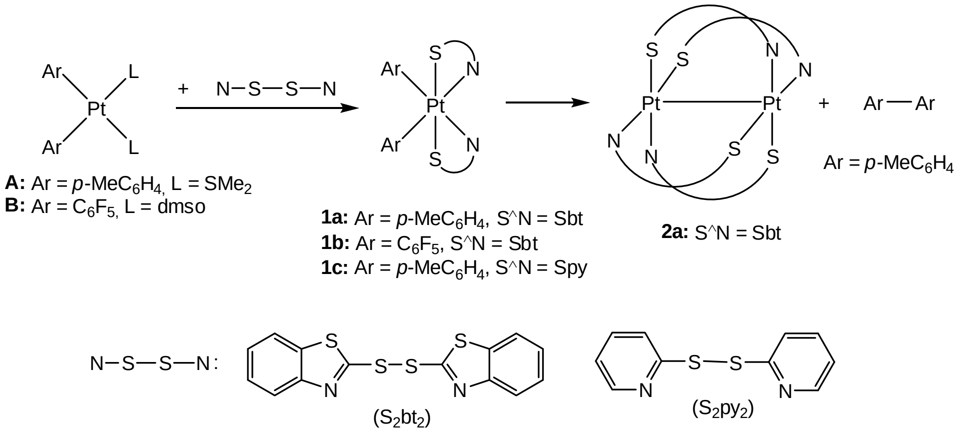
Reductive elimination (RE) is an essential step in many transition metal catalyzed reactions [1]. In particular, understanding the steric and electronic factors controlling the rates of RE to form carbon-carbon and carbon-heteroatom bonds is the most relevant [1b]. The influence of ancillary ligands like phosphine and imine on RE has been widely studied [2]. Disulfide ligands [3] can be emerged as new ancillary ligands on RE by alteration in structural properties.

Herein, we report on the reactions of the bis(aryl) platinum complexes [Pt(*p*–MeC_6H_4)$_2$(SMe_2)$_2$] (**A**) and [Pt(C_6F_5)$_2$(dmso)$_2$] (**B**), respectively, with two different disulfide ligands (S_2bt_2 and S_2Py_2). The reactions evolve with oxidative addition of the S-S bond of the disulfide ligands to give Pt^{IV} complexes [Pt(Ar)$_2$(S-N)$_2$] **1a-c**. The bis(tolyl) derivative **1a** is not stable in solution at room temperature evolving trough a subsequent reductive elimination process to give the corresponding biaryl compound and the dinuclear lantern Pt^{II} complex **2a**. The reactions have been followed up by NMR spectroscopy and all the compounds fully characterized including X-ray for Pt^{IV} (**1b,c**) and **2a** product.



A: Ar = *p*-MeC$_6$H$_4$, L = SMe$_2$
B: Ar = C$_6$F$_5$, L = dmso

1a: Ar = *p*-MeC$_6$H$_4$, S^N = Sbt
1b: Ar = C$_6$F$_5$, S^N = Sbt
1c: Ar = *p*-MeC$_6$H$_4$, S^N = Spy

2a: S^N = Sbt

(S_2bt_2)

(S_2py_2)

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“[Cu($C_6Cl_2F_3$)(tht)]”: Synthesis, Behaviour in Solution, and Reactivity as Arylating Reagent

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In recent years, the synthetic utility of organocopper compounds and their use in catalysis has experienced an enormous grown.[1] One of the fundamental role of organocopper derivatives is the transmetalation in multimetallic catalytic systems, such the Sonogashira Cross-Coupling or the copper assisted Hiyama reaction.[2,3] The mechanistic study of these reactions has been hampered by the extraordinary intrinsic reactivity and the structural complexity of organocopper complexes, up to the point that and nowadays there are no experimental data about the species that actually are involved in the transmetalation, nor about the dependence of the reaction on the auxiliary ligands at the copper.

With the aim of studying the transmetalation of the aryl from aryl-copper complexes to other metals we have prepared the complex of molecular formula “[Cu($C_6Cl_2F_3$)(tht)]”, containing a fluoroaryl ring in which the ^{19}F nuclei do not show any J_{F-F} coupling, making very easy to obtain accurate kinetic data from their ^{19}F NMR spectra. In this communication we report the synthesis of this complex, its RX-structure, the NMR study of its behaviour in solution through DOSY experiments and its reactivity as arylating reagent towards other metals.

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Cyclopalladated (*E*)-*N*,1-diphenylmethanimines with quite unusual substitutions at the aromatic rings

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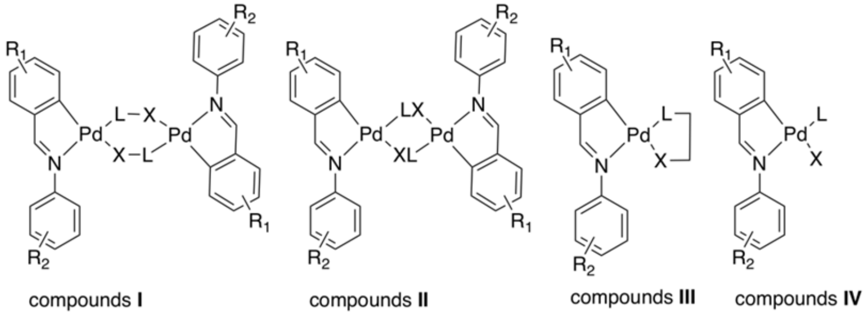
Since Onoue and Moritani in 1972 reported the cyclometallation reaction of (*E*)-*N*-1-diphenylmethanimine ((*E*)-PhCH=NPh) with palladium(II) acetate in acetic acid [1], a myriad of compounds of the general structural formulae **I** – **IV** shown in the Figure has been prepared by cyclopalladation reaction of (*E*)-*N*,1-diphenylmethanimines, and subsequent substitution reactions at the palladium(II) centres of compounds of type **I**, with X-L = OAc, or of type **II**, with XL = Cl. These latter compounds are usually the products of the cyclometallation reaction, when palladium(II) acetate or the system $Na_2[PdCl_4]$/NaOAc are used as metalating agents in this reaction [2]. Interestingly, liquid crystal behaviour has been observed for compounds **II** and **III** with adequate R_1 and R_2 substituents at the aromatic rings and co-ligands at the palladium(II) centres [3], and some compounds **IV** have been used as precatalysts for Heck, Suzuki and Buchwald-Hartwig reactions with good results [4].

In order to further expand the scope of the Onoue and Moritani reaction, we will give details in the poster session on the synthesis of compounds of type **I**, **II** and **IV**, for which R_1 = hydrogen, 4-methyl, 4-methoxy or 4-hydroxy and R_2 = 4-nitro, (compounds **A**), R_1 = 4-methoxy and R_2 = 2-bromo (compounds **B**), and R_1 = 4-hydroxy and R_2 = 3-hydroxy or 4-hydroxy (compounds **C**), by condensation, cyclopalladation and substitution reactions. Compounds **A** - **C** have not been previously reported and present quite unusual substitutions at the aromatic rings of the (*E*)-*N*-1-diphenylmethanimine, which could be interesting for application of these compounds in fields such as medicinal and supramolecular chemistry.



R_1 = 4-alkyl, 4-alkoxy, 4-nitro, 4-dimethylamino, 4-chloro, 2-chloro, …
R_2 = 4-alkyl, 4-alkoxy, 2,4,6-trimethyl, 2,6-diisopropyl, …
X—L = AcO^-, NCS^-, …
XL = Cl^-, Br^-, I^-, N_3^-, OH^-…
X⌐L = $acac^-$, R-CH(NH_2)-CO_2^-, …
X = Cl^-, Br^-, AcO^-, …
L = PPh_3, py, …

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Fluorinated Ni(IV) Organometallics and Aromatic Trifluoromethylation

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Fluorine atoms drastically affect the biological properties of organic synthons, such as lipophilicity, bioavailability and metabolic stability. In fact, 20% of pharmaceuticals and 30% of agrochemicals contain at least one fluorine atom in their structure, typically located in aromatic rings.[1] Among the most common perfluorinated groups, the CF_3 moiety occupies a preferential place. Creating C–CF_3 bond *via* cross-coupling reactions is an appealing strategy. However, the Ar–CF_3 bond formation *via* reductive elimination (R.E.) from [Ar–M–CF_3] fragments represents a challenging task. An original approach to favor the key R.E. step resides in the preparation of high-valent organometallics. In this sense, Sanford reported the isolation of Ni(IV)CF_3 complexes **I-IV** that were found to be good precursors in cross-coupling reactions, including the aromatic trifluoromethylation.[2] Herein, the synthesis, characterization and reactivity of unprecedented Ni(III)CF_3 and Ni(IV)CF_3 complexes, along with their implications in C–CF_3 bond forming reactions, will be presented.[3]

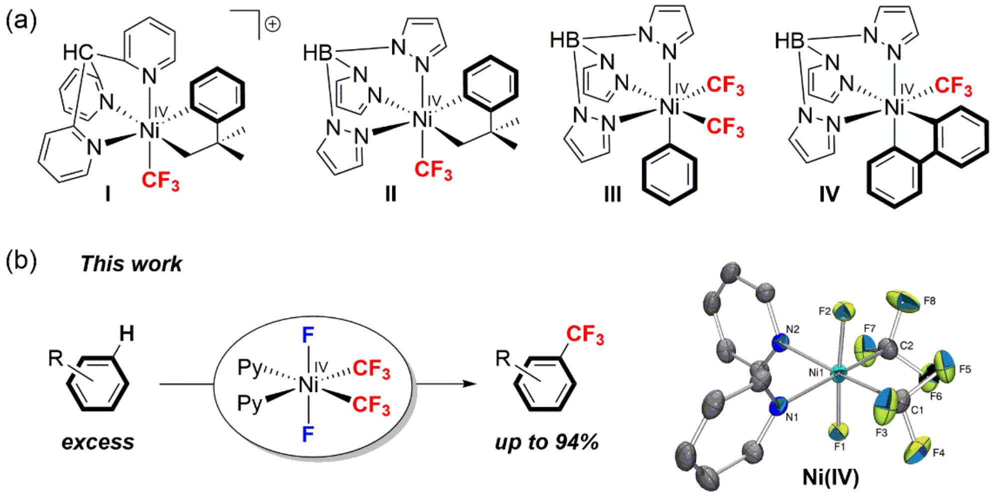

Figure 1. (a) Isolable, coupling-competent Ni(IV)CF_3 organometallics. (b) ***This work***: First C–H bond functionalization of arenes mediated by well-defined, fully characterized Ni(IV) species.

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Design and synthesis of double A-frame tetranuclear complexes

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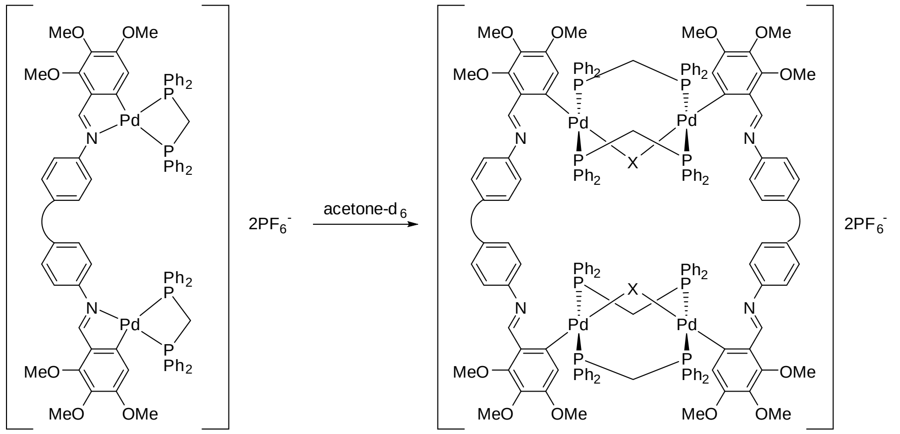
The chemistry of cyclometalated compounds[1] has attracted much research interest in past years. They are known for their ample applications in numerous fields: organic synthesis[2], photochemistry[3], catalysis[4], and as potential biologically active materials[5]. We now report a chelate-to-bridging shift which occurs spontaneously in solution even at low temperature in palladacycles bearing $Ph_2PCH_2PPh_2$-P,P, (dppm).

Palladacycles of the type $[Pd_2(Ph_2PCH_2PPh_2{-}P,P)_2(C,N{:}C,N)]$ (C,N:C,N = bis(N−2,3,4−trimethoxybenzylidene)−4,4′−sulfonyldianiline or −4,4′−oxydianiline) can undergo a spontaneous slow chelate−to−bridging diphosphine coordination shift in solution. Following this strategy a tailor-made synthetic procedure was devised that culminates in isolation of the first crystallographically characterized tetranuclear palladium double A−frame structures hosted in a single molecule.



1a, 1b

= SO_2 **1a-2a** = O **1b-3b**

X = Cl **2a, 2b**
X = Br **3b**

Scheme 1: Reaction sequence leading to the synthesis of the double A−frame complexes.

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Acknowledgements
This work was made possible thanks to the financial support received from the Xunta de Galica (Galicia, Spain) under the Grupo de Referencia Competitiva Programme (Project GRC2015/009). F. Reigosa thanks the Spanish Ministry of Education (grant FPU15/07145).

Dinuclear crown ether palladium complex: a highly effective strategy for encapsulating potassium cations in small crown ether rings

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Crown ethers are ligands that interact with metal ions selectively, depending on the size of the cavity. According to this, they have shown a wide variety of applications related to sensors or membrane ion transport, among others [1]. On the other hand, cyclometalled compounds also display interesting properties as metallomesogens or catalysts [2]. Thus, the combination of both functionalities in the same structure, have been widely studied in order to combine their ample set of applications [3]. However, only in one case were both functionalities combined in the same structure [3b].

In this communication we present the first palladacycle able to entrap a potassium cation through bonding to two 15−crown−5 ether rings in a single molecule. In addition, both moieties where placed on the same aromatic rings, so that the cyclometallated moieties forced the approach of the macrocyclic ligands. This new structure was confirmed by X-ray crystallographic data [4]; thus, giving rise to a new family of main group / transition metal compounds.

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A new dipalladacycle with an hexadentate [*C*, *N*, *S*:*C*, *N*, *S*] imine

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Up to know extensive work has been published on double cyclometallated complexes containing two independent metallated phenyl rings.[1-4] In spite of such an extensive range of publications, relatively few studies deal with double metallation on the same phenyl ring. In order to make this possible, it is necessary that the ligand contains two substituents with potentially donor atoms −nitrogen, sulfur…−, which allow the formation of two five− or six− membered chelate rings.

This communication describes the preparation, characterization and structural study of novel tridentate [*C*,*N*,*S*] bis-cyclopalladated complexes with ligands derived from the condensation of a primary amine −2-(methylthio)aniline− with the corresponding aromatic dialdehyde −terephthalaldehyde−. The compounds are also interesting due to their close-to-planarity arrangement and to the presence of seven fused rings in their structure.

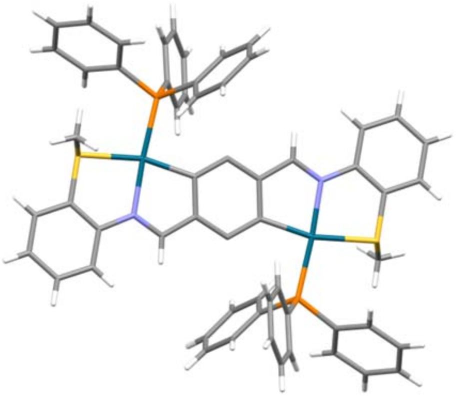

Figure 1. Crystal structure

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F. Lucio-Martínez and F. Reigosa thank the Spanish Ministry of Education (grant FPU13/05014 and FPU15/07145).

Alkyne isomerization and coupling in (PSiP)Ir complexes

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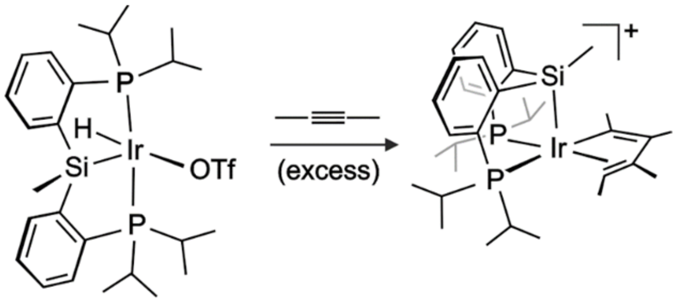
PSiP pincer ligands with central sp^3 silyl functions can adapt their skeletons to coordinate in *meridional* or *facial* modes and, due to their large *trans* influences, favour unsaturated complexes with uncommon structures [1]. Recently, we reported the five-coordinate Ir(III) neutral hydride [IrH{*κO*-$O_3S(CF_3)$}{*κP,P,Si*-Si(Me)(C_6H_4-2-PiPr$_2$)$_2$}] (**1**), which readily dissociates the labile triflate ligand to enable additional coordination and reaction possibilities [2]. The resulting cationic species has been observed to react with internal alkynes such as 2-butyne to form 3,4-dimethyl-1,3,5-hexatriene, after an unusual dimerization-isomerization sequence, though the reaction competes with the mere alkyne isomerization into butadiene. The various organometallic species mediating such transformations will be described.



1

anion = triflate

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The Impact of Protic Ligands in the Ir-Catalyzed Dehydrogenation of Formic Acid in Water

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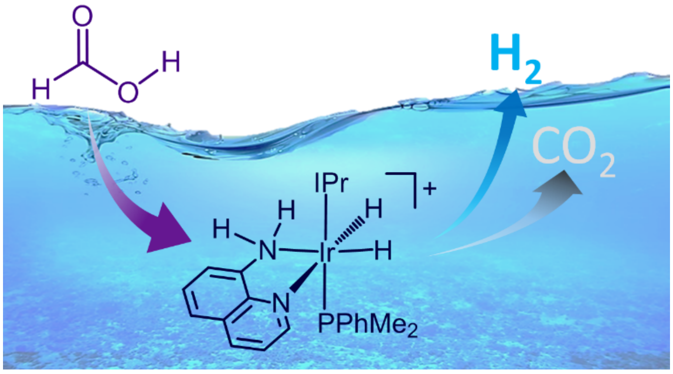
The use of hydrogen as an energy vector has been proposed as a sustainable alternative to fossil fuels; however, it presents several drawbacks, mainly related to its storage and transportation. The catalytic dehydrogenation of formic acid (FA) has been reported to generate fuel cell grade hydrogen, which requires levels of CO below 10 ppm. Furthermore, H_2 and CO_2 are the only reaction products, and the latter can be hydrogenated back to formic acid to render a carbon neutral cycle of hydrogen storage [1]. The use of water as solvent for formic acid dehydrogenation reactions has important implications in fuel cell technology, mainly due to the more straightforward recyclability of CO_2 in aqueous media.

Catalysts based on the Ir-NHC (NHC = N-heterocyclic carbene) scaffold have seen great success in dehydrogenation of alcohols, however, examples that deal with the dehydrogenation of FA are scarce[2]. In this work, new Ir-IPr complexes featuring a variety of chelate ligands, some of them potentially able to establish hydrogen bond interactions, were synthesized. These complexes proved to be efficient catalysts for the dehydrogenation of formic acid in DMF and H_2O. The dehydrogenation rates were dependent on the nature of the ligands that accompany IPr in the coordination sphere of the metal. In fact, complexes that contain protic ligands, show the best activities in H_2O.

$[Ir(aq)(H)_2(IPr)(PPhMe_2)]BF_4$ (aq=8-aminoquinoline), which presents an NH_2 group bound to the Ir center, is not only the most active of the catalysts in water presented in this work but also its high stability permits its reuse without an apparent loss of activity. This behavior can be attributed to the robust ligand system and its ability to stablish outer-sphere mechanisms.



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Selective oxidation of glycerol via acceptorless dehydrogenation driven by Ir(I)-NHC catalysts

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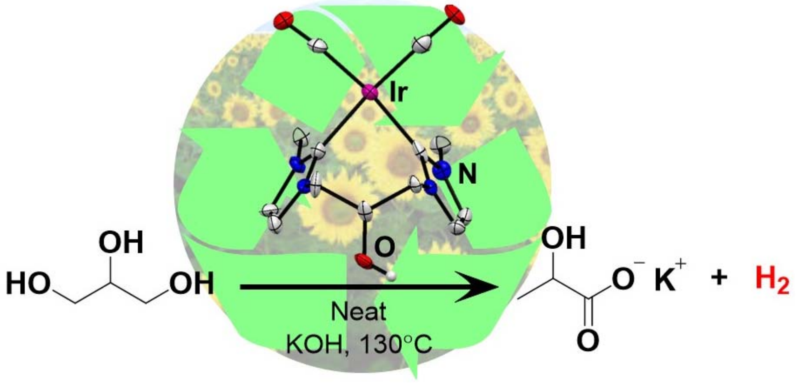
Currently, the mainstream of commodities is produced from non-renewable fossil fuel resources. However, the non-sustainable nature of fossil resources demands the development of cleaner methodologies to produce chemicals from alternative resources.[1] In this sense, the use of biomass in the biodiesel industry has led to a world-wide vast production of glycerol which is readily available in large-scale. Hence, new approaches for the valorization of biomass waste products into value added chemicals are highly desirable. To date, an attractive method is the catalytic oxidation of glycerol to produce lactic acid (LA). In spite of the recent developments on Ir(I) catalysts for acceptorless dehydrogenative alcohol oxidation reactions by Crabtree[2] or Williams[3], more stable catalysts and new protocols for their practical application are required.

The present study focuses on the discovery of highly active and selective catalysts for the acceptorless oxidation reaction of glycerol to LA by addressing: i) solubility of the catalyst in polar media, and ii) inhibition of competitive reactions (*i.e.* hydrogenation). Herein, a series of NHC-Ir catalysts have been designed and synthesized via reaction of functionalized imidazolium salts of the type $[(MeImH)_2CHCOO]Br$, $[\{(MeImH)CH_2\}_2CHOH]Br_2$ and $[(MeImH)(CH_2)_3OH]Br$ with the appropriate iridium precursors. Complexes $[Ir(cod)\{(MeIm)_2CHCOO\}]$, $[Ir(CO)_2\{(MeIm)_2CHCOO\}]$, $[Ir(cod)\{(MeIm)CH_2\}_2CHOH]Br$, $[Ir(CO)_2\{(MeIm)CH_2\}_2CHOH]Br$ and $[Ir(cod)\{MeIm(CH_2)_3O\}]$ efficiently catalyzed the acceptorless dehydrogenation of glycerol in alkaline medium under air to afford $LA^- K^+$ and dihydrogen. These catalysts have shown high stability, selectivity and activity under mild reaction conditions at very low catalyst loading, and can be reused several times without significant loss of activity after consecutive additions.



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Anion-dependent Cytotoxicity of Cationic p-cymene Ruthenium Complexes. Cation-anion Interaction in Solution

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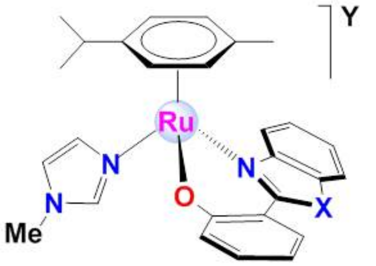
The success of platinum based anticancer drugs has boosted an enormous interest in finding new metal-based potential cytotoxic species that could overcome their associated problems as severe side effects. Ru complexes are receiving increasing attention in this contest [1]. One problem frequently encountered is the inability to be transported through the lipophilic membranes and, thus, an adequate balance of lipo- and hydrophilicity is required. It has been described that the hydrophobic tetraphenylborate anion (TPB) is able to improve drug uptake of some compounds and hydrophobic contacts in ion-pairs are usually proposed to explain their effects.

We report on the synthesis of the complexes indicated in figure 1.



X= NH, Y = Cl
X= NH, Y = OTf
X= NH, Y = BPh_4
X= NH, Y = SbF_6
X = S, X = Cl
X = S, X = BF_4
X = S, X = BPh_4
X = S, Y = SbF_6

Figure 1

Anion-cation interactions in the reported complexes have been studied through dosy experiments (in solution) and DFT-calculations (in gas phase). Moreover, the cytotoxicity of the complexes against a HeLa cancer cell line has been tested and a clear influence of the counteranion and the X group in the ligand has been found.

Financial support acknowledgment: MINECO of Spain (CTQ2014-58812-C2-1-R and CTQ2014-53033-P)

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Cascade Reactions Combining Biocatalysis and Metal Catalysis Employing *Deep Eutectic Solvents* as Superior Green Reaction Media

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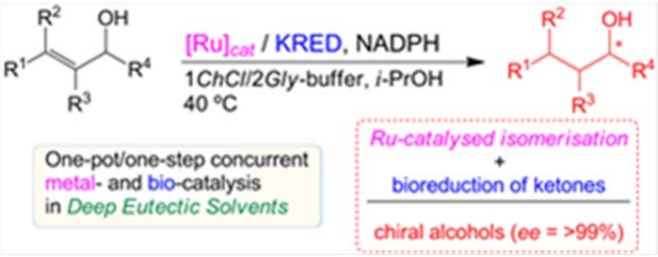
Due to the increasing rate of production of the *Chemical Industry* it is necessary to look for new alternative and greener ways that attempt to minimize the undesired side effects caused to the environment. In this sense, considerable attention has been recently focused on *Deep Eutectic Solvents (DESs)* as an alternative to conventional volatile organic compounds (*VOCs*) in many fields of science.[1]

In this communication, we present the first application of *Deep Eutectic Solvents* (*DESs*) in the asymmetric bioreduction of ketones employing isolated ketoreductases (*KREDs*). The performance of the biocatalysts was enhanced by increasing the percentage of neoteric solvent in *DES*-buffer mixtures. At buffer content of 50% and even 20%, either the combination of choline chloride (*ChCl*)/glycerol (*Gly*) (1:2) or (*ChCl*/sorbitol) (1:1) proved to be most effective for achieving up to >99% conversion and up to >99% enantiomeric excess of the corresponding secondary alcohols. Moreover, this reaction medium was used to perform the first example of chemoenzymatic cascade process in *DES*-buffer mixtures,[2] namely the ruthenium-catalyzed isomerization of racemic allylic alcohols coupled with a further enantioselective bioreduction, in both sequential and concurrent mode.



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Covalent supporting of Rh-carbene hydrosilylation catalysts on graphene-based materials through triazole groups.

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Graphene possesses high conductivity, surface area and tunability, making it an ideal support for the covalent immobilizing of molecular catalysts. Carbon-based nanohybrid catalysts have shown promise both in terms of activity, selectivity, stability and/or recyclability. Graphene oxides (GO) which can be considered as oxidized graphene sheet, or partially reduced graphene oxides (rGO) obtained by thermal treatment of GO at different temperatures, can be easily chemically modified for tailoring materials with the desired functionalities. This approach was successfully applied for the preparation of Ir-NHC hybrid materials through carboxylate/carbonate/acyl bonds that have shown an excellent performance in hydrogen transfer reactions.[1] Unfortunately, related Rh-NHC hybrid materials exhibit a limited applicability for hydrofunctionalization reactions of unsaturated compounds due the presence of reactive C-O bonds that eventually leads to leaching. In order to overcome this setback, we have developed different functionalization strategies using GO and rGO through C-N bond. Decoration of the graphene derivatives with azide groups followed by coupling with alkynes yields triazole rings which are precursors for triazolylidene ligands of the supported of rhodium complexes (Figure 1).

Preliminary results on the application and recycling of the hybrid catalysts compared with related molecular catalysts in alkyne hydrosilylation reactions are presented. For instance, **GO-TRIAZ-I-Rh(cod)** catalyst shows quantitative conversion in the hydrosilylation of 1-octyne with diphenylmethylsilane in 75 minutes and complete selectivity to the *β-Z* vinyl silane, and maintains its activity during at least 5 more cycles.

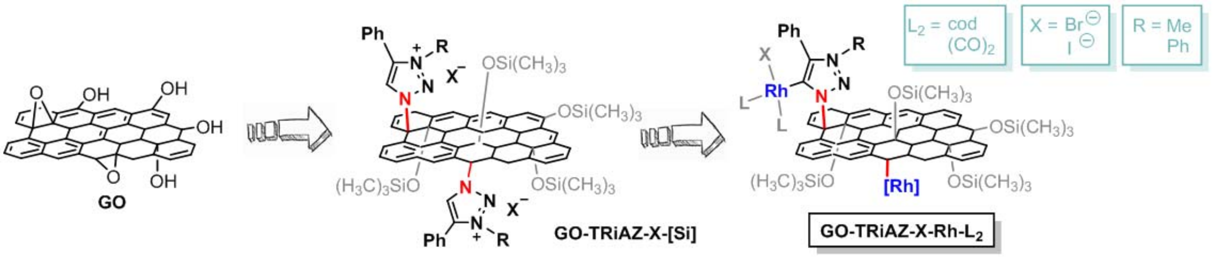

Figure 1. Covalent triazolylidene functionalization strategy for rhodium-carbene hybrid materials.

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Rhodium catalysed aminocarbonylation of alkynes: synthesis and characterization of the key complexes involved in the reaction mechanism

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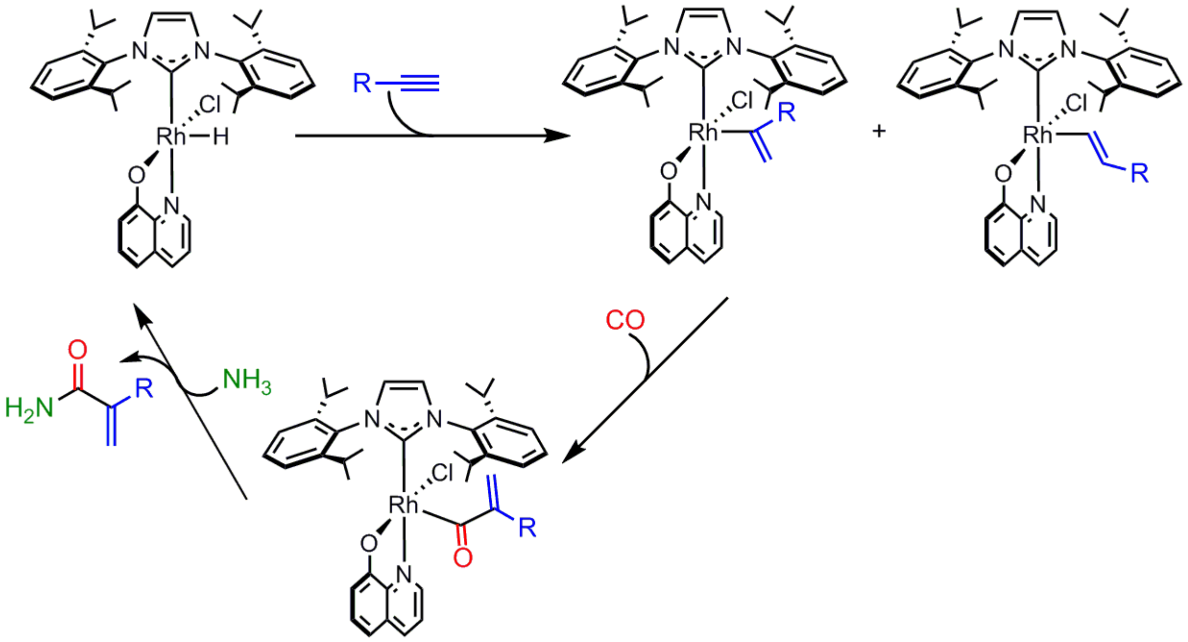
The study of the fundamental steps involved in a catalytic transformation is one of the most important research fields due to its fundamental repercussions on the development of more efficient catalytic systems. Transition metal hydride complexes are specie involved in every hydrofunctionalization reaction of unsaturated substrates. In particular, the insertion of the unsaturated substrate in the metal-hydride bond is often the key step that determines the regioselectivity in the catalytic transformation.
In this work we report on the synthesis and characterization of stable Rh^{III}-alkenyl complexes obtained by reaction of a (NHC)Rh^{III}-H complex and a range of alkynes with different stereo-electronics properties (Figure 1). Experimental and computational studies have allowed us to determine a relationship between the type of alkynes and the formation of the α-gem or β-*E* isomer of the Rh-alkenyl complex. The unusual stability of the latter complexes has enabled us their isolation and to study its reactivity towards small molecules as CO. Carbon monoxide easily inserts in the Rh-alkenyl bond giving NHC-Rh^{III}-acyl complexes that are are really reactive toward the external attack of a nucleophile like NH_3. This research opens the door to the development of new rhodium-based catalytic systems able to perform the regioselective aminocarbonylation of alkynes for the preparation of high added value products as methacrylamides.



Iridium and Ruthenium Complex Using as Catalysts in N-Alkylation of Amines via Borrowing Hydrogen

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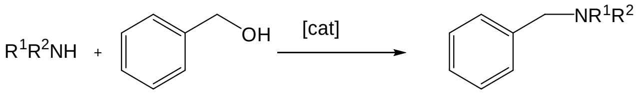
The amination of alcohols by the use of the borrowing hydrogen methodology (Scheme 1) has proven to be a highly atom economical method for the production of amines. No external reductant is required for this process, since the alcohol substrate serves as the hydrogen donor.



Scheme 1. Catalytic Borrowing Hydrogen Reaction Studied for N-Alkylation of Aniline Using Benzyl Alcohol

Our recent efforts along these lines focuses on the development of more efficient/economical catalytic systems for borrowing hydrogen. In the present study, we have tested neutral iridium and ruthenium catalysts in borrowing hydrogen reactions with several amino substrates.

The evolution of the iridium precatalysts in solution has been analyzed by ^{1}H NMR and a hydride complex was detected. The molecular structure of the iridium and ruthenium precursors and of the corresponding iridium hydride compound were determined by monocrystal X-ray analysis.

Financial support acknowledgment: MINECO of Spain (CTQ2014-58812-C2-1-R), MRC thanks to FEDER founds and Plan Propio de I+D+i-UCLM (2014/10340) for a predoctoral contract.

Efecto sinérgico de porfirinas meso-tetraarílicas conteniendo fragmentos de coranuleno y otros restos poliaromáticos planos como huéspedes de fulerenos. Estudio de C_{60} sobre la mezcla de atropoisómeros

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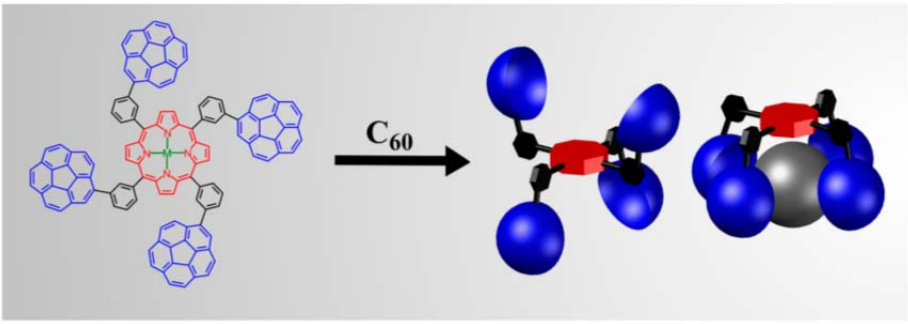
Entre los campos de estudio que implican el uso de fulerenos se encuentra la química supramolecular. En el presente trabajo [1] se han obtenido porfirinas meso-tetrapoliaromáticas simétricas con unidades poliaromáticas planas (fenantreno, pireno) y no planas (coranuleno) en posición meta, cuya disposición espacial es la adecuada para establecer interacciones supramoleculares con C_{60}. El espectro de RMN de ^{1}H muestra el típico patrón de cuatro atropoisómeros no separables por técnicas cromatografías debido a su rápida isomerización. Se ha estudiado el efecto del fulereno sobre la mezcla de isómeros, siendo α_4 el que presenta una mayor constante de asociación.



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First homogeneous catalysts for the selective hydration of cyanamides to ureas

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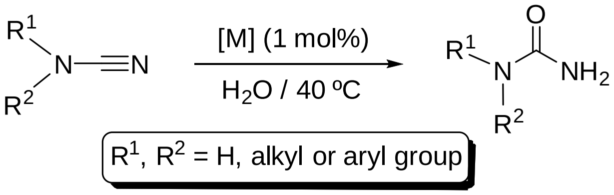
Ureas are important target molecules, particularly in pharmaceutical and agrochemical industries, and are found in many natural products. The traditional synthesis consists in reacting amines with either phosgene (or its derivatives) or isocyanates. However, because of these two reagents are toxic and corrosive, several alternative routes have been developed, involving in most cases the insertion of CO or CO_2 into amino compounds [1]. Given its complete atom economy and the easy access to the starting materials, a more appealing option to synthesize *N*-substituted ureas is the hydration of cyanamides [2]. Such processes are known to be promoted by strong acids and bases under harsh conditions, and very recently different heterogeneous catalysts, allowing the use of milder reaction conditions, have also seen the light [3].

Continuing with our studies on the catalytic hydration of C≡N bonds [4], in this communication we will present the first homogeneous catalysts, namely $[MCl_2(\eta^6\text{-}p\text{-cymene})\{PMe_2(OH)\}]$ (M = Ru, Os), capable to promote the selective hydration of cyanamides to ureas. As shown in the scheme, the hydration process could be successfully achieved for a large variety of mono- and disubstituted substrates employing directly water as solvent, a low metal loading (1 mol%) and mild temperature conditions (40 ºC).



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A theoretical study of the bonding capabilities of the zinc-zinc double bond

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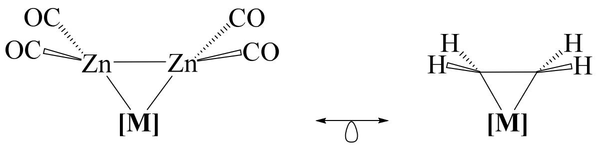
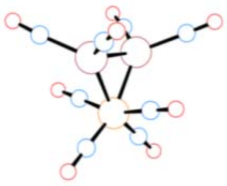
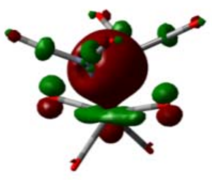
The theoretical knowledge about the zinc-zinc bond has been recently expanded after the proposal by Santiago Álvarez and co-workers of a zinc-zinc double bond in several $[Zn_2(L)_4]$ compounds (*Angew. Chemie - Int. Ed.* 2017, *56*, 10151–10155). They are Zn(0) complexes, which can be compared to olefins by the isolobal analogy. Following our interest on dizinc compounds [1] and prompted by these results, we have selected the $[Zn_2(CO)_4]$ species, isolobally related to ethylene, and investigated the possible η^2-Zn_2-coordination to several first-row transition metal fragments. Complexes $[(\eta^2\text{-}Zn_2(CO)_4)Cr(CO)_5]$, *trans*$[(\eta^2\text{-}Zn_2(CO)_4)_2Cr(CO)_4]$, $[(\eta^2\text{-}Zn_2(CO)_4)Fe(CO)_4]$ and $[(\eta^2\text{-}Zn_2(CO)_4)Ni(L)_2]$ (L = CO, PH_3, PF_3, PMe_3) have been optimized and theoretically studied. The $[Zn_2(CO)_4]$ coordination to the metal fragment produces an elongation of the dizinc bond (2.34-2.43 Å range) and a concomitant pyramidalization of the $[Zn(CO)_2]$ fragment. These structural parameters are indicative of π-backdonation from the metal to the coordinated dizinc moiety, as occurred with ethylene ligand. A QTAIM study of the Zn-Zn bond has been carried out and the properties of identified bond critical points (BCPs) are discussed. A decrease of ρ_{BCP}, $\nabla^2\rho_{BCP}$ $\int_{Zn\cap Zn}\rho$ and delocalization indexes δ(Zn,Zn), relative to corresponding values in the parent $[Zn_2(CO)_4]$ molecule, accompanied dizinc coordination. In spite of the backdonation to the π^* LUMO of the dizinc ligand, the computed δ(Zn,Zn) parameters are indicative of significant electron density sharing between the two zinc atoms.

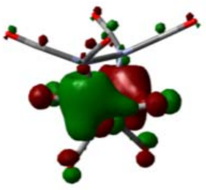




$[(\eta^2\text{-}Zn_2(CO)_4)Fe(CO)_4]$



Donation



Backdonation

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Arene π-Ligation and Terminal Phosphine Coordination to Alkaline Earth Cations

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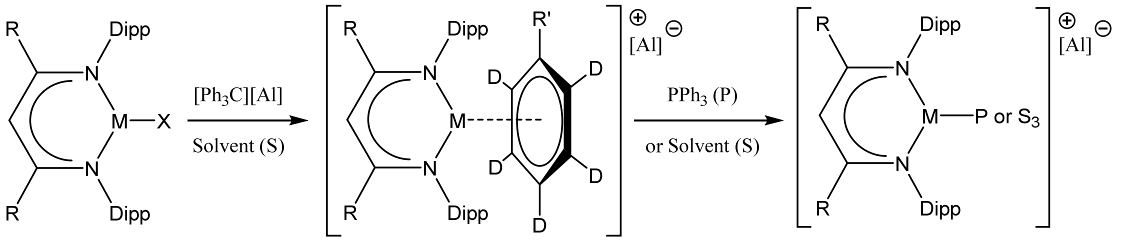
Non-covalent interactions between alkali and alkaline earth metal cations and aromatic π systems have a widespread biological significance.[1] Surprisingly, however, their characterization in the solid state is restricted to a few serendipitously crystallized benzene and toluene solvates of barium.[2] With this in mind and our recent observation that β-diketiminato calcium *n*-alkyls enable the unprecedented nucleophilic substitution of benzene,[3] through engagement of π-systems we provide an assessment of the potential of 'naked' β-diketiminato Mg and Ca cations (**4-7**) to interact with arene π-systems (toluene-d_8 and C_6D_6) when generated in conjunction with Krossing's weakly nucleophilic aluminate anion ($[Al]^-$ = $[Al(OC(CF_3)_3)_4]^-$). DFT calculations carried out on the calcium benzene adduct (**7**) indicate that the arene-metal interaction is, primarily, a consequence of donation from the aromatic arene HOMO into an empty 3d orbital at the alkaline earth metal centre in line with a partial disruption of the π-system.[4]



1: M = Mg, X = *n*-Bu, R = Me
2: M = Mg, X = *n*-Bu, R = *t*-Bu
3: M = Ca, X = $N(SiMe_3)_2$, R = Me

4: M = Mg, R = Me, R' = CD_3, S = C_7D_8
5: M = Mg, R = Me, R' = D, S = C_6D_6
6: M = Mg, R' = CD_3, R = *t*-Bu, S = C_7D_8
7: M = Ca, R = Me, R' = D, S = C_6D_6

M = Mg, P = PPh_3, **8**: R = Me, **9**: R = *t*-Bu
10: M = Mg, R = Me, S = 1,4-difluorobenzene
11: M = Ca, R = Me, S = THF

Although magnesium displays a very low affinity for coordination by phosphine bases since it behaves like as a typical hard Lewis acid, the subsequent reaction of the arene-adducts **4** and **6** with triphenylphosphine generated the respective magnesium phosphine coordination complexes **8** and **9**. Their structures provide the first solid state authentications of terminal phosphine to magnesium coordination.[5] Similarly, reaction of **4** with a stoichiometric excess of 1,4-difluorobenzene provided the complex **10**, which has three coordinated molecules of 1,4-difluorobenzene and constitutes the first observation of a k^1 coordination mode for this fluoroarene.

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Exploring the reactivity of NHC-Ru and NHC-Pt complexes towards organozinc reagents

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Metal-metal cooperativity (MMC) is a widely used strategy for the activation and catalytic transformation of small molecules and it implies that both metals in a bimetallic complex are directly involved in bond activation processes.[1]

Recent studies in our group have shown that complex $[Ru(IPr)_2(CO)(H)]BAr^F_4$ (**1**) (IPr= 1,3-bis-(2,6-diisopropylphenyl-2-ylidene)) reacts with $ZnEt_2$ to afford the complex $[Ru(IPr)_2(CO)(ZnEt)]BAr^F_4$ (**1a**). To our delight, complex **1a** was able to activate small molecules such as H_2.[2] Herein we report the results obtained using alternative sources of zinc, changing the NHC ligand or ultimately, using analogous complexes bearing another metallic centre (Figure 1).

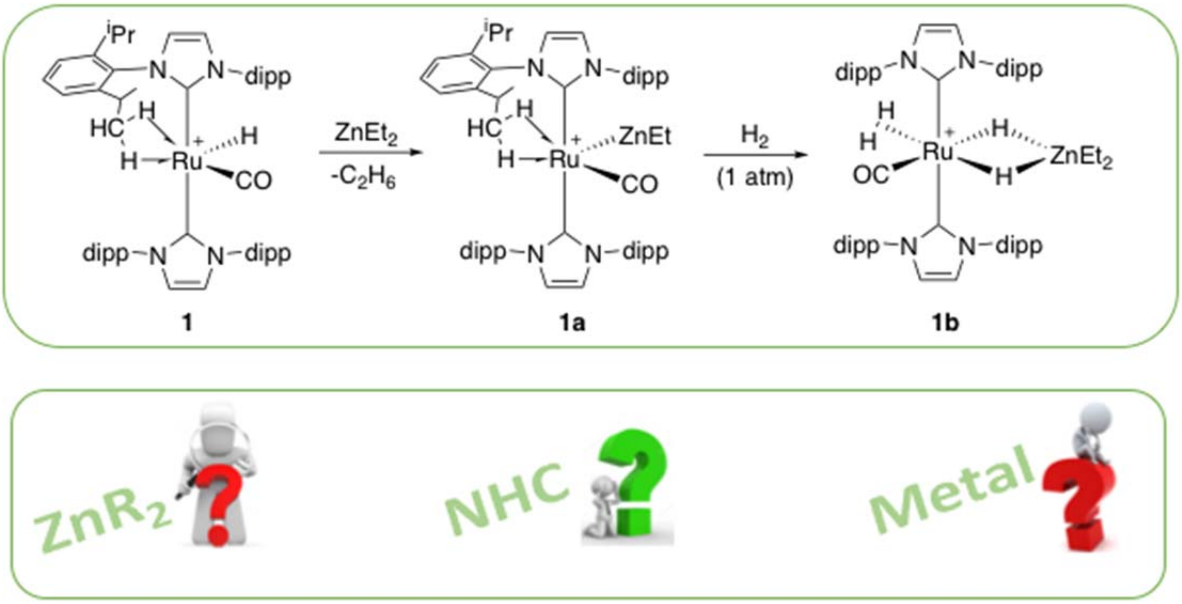

Figure 1. Precedents and extension of the study

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Hydrophosphination Catalyzed by Rhodium Complexes

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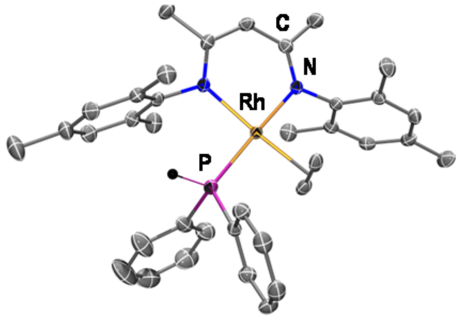
Construction of C–P bonds has been the subject of many investigations, among which net addition of a P–H bond to unsaturated substrates is one of the most attractive strategies because of the safety, selectivity, and 100% atom-economy advantages provided by this approach.[1] In particular, hydrophosphination is a powerful synthetic tool to create a plethora of compounds with a C–P bond such as secondary or tertiary phosphines containing new alkyl substituents.[1b]

A key step postulated in these processes is the activation of the P–H bond, commonly proposed to occur by oxidative addition at late-transition metal centers, which eventually leads to complexes with terminal phosphanido ($M–PR_2$) functionalities as intermediates in such reactions.[2]

For early transition metal systems, the insertion of alkenes into the M−P bond appears to be critical to C−P bond formation, while for late, or electron-rich metal centers, the substrate scope seems to indicate the importance of a Michael-type addition of the highly nucleophilic phosphide at activated, electrophilic alkenes. Thus, an apparent dichotomy exists between catalytic systems participating in inner-sphere, versus outer-sphere, C−X bond-forming reactions.[3]



In this comunication we showcase the catalytic activity of the phosphane rhodium precursors $[Rh(L)(H_2C=CH_2)(PHPh_2)]$ (L = tris(pyrazolyl)borate, Tp; $HC(CMeNMes)_2$, nacnac; see figure) in the catalytic hydrophosphination of activated olefins as well as some clues to account for the different activities of both catalyst's precursors.

Plausible catalytic cycles based on outer-sphere mechanisms as well as extension of these studies to the related hydrosilylation reactions will be also described.

Financial support acknowledgment: MINECO-FEDER (CTQ2014-53033-P, CTQ2017-83421-P) and GA-FEDER (Inorganic Molecular Architecture and Applications group, E70 and E08_17R)

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Activating a Peroxide Ligand for C–O Bond Formation

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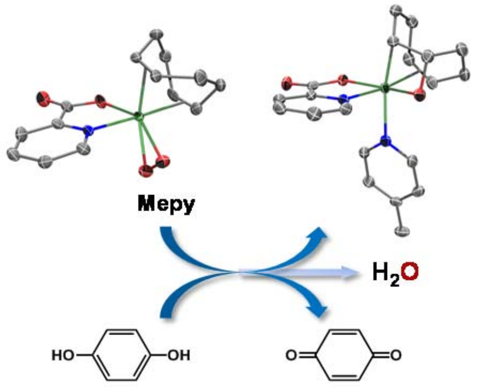
Dioxygen activation for effective C–O bond formation in the coordination sphere of a metal is a long standing challenge in chemistry for which the complicated –sometimes poorly understood– mechanistic panorama slows down the design of catalysts for oxygenations.[1] In this context, olefin-peroxide complexes could be valuable precursors for the study of such reactions, since the simultaneous coordination of oxygen and olefin to a metal center would provide key species to reveal details for the interplay of these ligands in the functionalization of olefins through C–O bond formation. Moreover, knowing the high tendency of iridium(I) complexes to undergo two-electron redox events in their reactions with oxygen –to give peroxide complexes (Ir^{III}-O_2)–, they could be suitable candidates to explore this possibility. Furthermore, those with an olefin as co-ligand are very scarce with very few isolated,[2] or '*in situ*' characterized examples.[3]

In this comunication we first showcase the isolation and full characterization of unusual 'Ir(cod)(O_2)' complexes (cod =1,5-cyclooctadiene) and then the activation of the peroxide ligand for O–O bond cleavage and C–O bond formation to give 2-iradoxetane complexes and water. Such reactivation of peroxide has been achieved by the combined action of 2,4,6-trimethylphenol or 1,4-hydroquinone as hydrogen atom donors and 4-methylpyridine as stabilizing ligand (see figure).



DFT-calculations on the key iridium(II) species, [Ir^{II}(pic)(cod)(Mepy)(OOH)], and a plausible reaction profile will be also commented.

Financial support acknowledgment: MINECO-FEDER (CTQ2014-53033-P, -54071-P, CTQ2017-83421-P) and GA-FES (Inorganic Molecular Architecture and Applications group, E70 and E08_17R)

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Assembling Pieces of a Puzzle: Controlled and Stepwise Synthesis of Iridium Mixed-Valence Linear Chains

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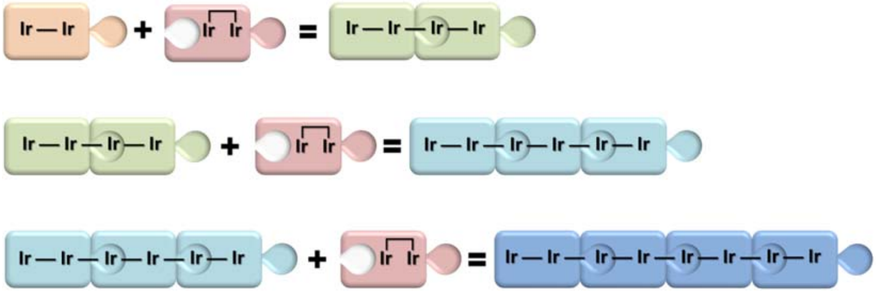
During the recent years there has been a growing interest on the synthesis of discrete chains of metal-metal bonded atoms because of their potential applications as nanoscale devices such as wires or switches.[1] These metallic chains could conduct the electricity as molecular cables allowing the electron transference between two electroactive species.[2] While it would be desirable to have available linear-chain multimetallic compounds with a variety of nuclearities and electronic properties for that purpose, synthetic procedures of thermodynamically stable compounds of this type are scarce due to the tricky synthesis and isolation of this kind of species.



In this communication we will showcase the stepwise synthesis of iridium mixed-valence linear chains from a dinuclear triflate iridium (II) complex by redox comproportionation with a non-oxidized dinuclear precursor as building blocks.[3] We can gradually increase the chain length in solution by a control of the reaction conditions and monitor the growing of the chain by NMR spectroscopy. The metals possess a non-integral oxidation state and, at least, one formally unsupported metal-metal bond in these compounds, although there is a delocalization of electrons along the metallic chain. The isolated compounds were structurally characterized using NMR techniques and their structures were confirmed by X-ray diffraction methods.

Financial support acknowledgment: MINECO-FEDER (CTQ2014-53033-P and CTQ2017-83421-P) and GA-FEDER (Inorganic Molecular Architecture and Applications group, E70 and E08_17R)

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Digging into Nucleophilic Trifluoromethylation at Palladium: from Mechanism to Catalysis Proof

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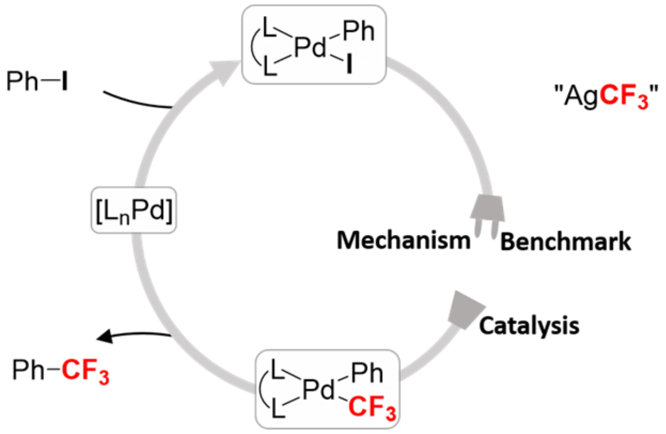
Pd-catalyzed trifluoromethylation reactions remain a largely unresolved challenge and only few examples of cross-coupling methodologies for that have been reported.[1] The main limitation has been attributed to the hampered reductive elimination step, but the transmetalation can dramatically prevent the formation of key palladium intermediate.[2] In this presentation, we not only describe a new family of "$AgCF_3$" complexes as efficient transmetalating agents to a Pd^{II} model system, but also the translation of these findings to a productive catalytic system.



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β-C-elimination in σ-alkyl-Pd pincer complexes arising from C–H activation. A new entry to alkene synthesis

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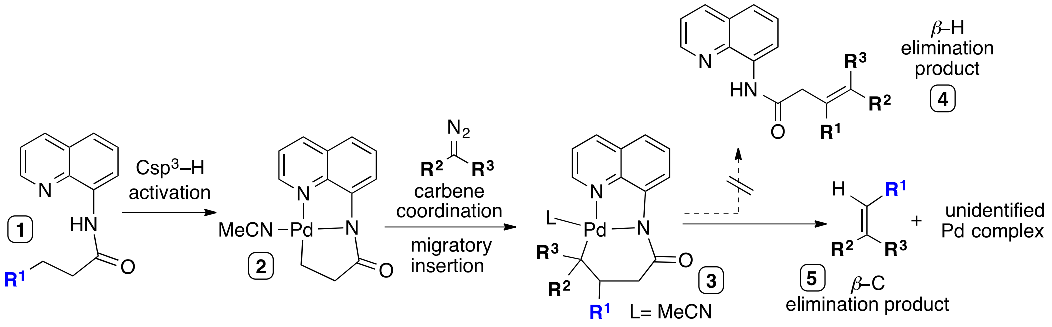
The palladium-catalyzed functionalization of C(sp^3)–H bonds constitute a topic of enormous interest.[1] These types of transformations have been mainly studied using bidentate directing groups such as quinolines, and proceed via palladated pincer intermediates like **2** (Scheme 1).

We have studied the reactivity of pincer-palladium complexes arising from the remote C(sp^3)–H activation of alkyl chains (such as **2**, Scheme 1) toward diazocarbonyl compounds as carbene precursors.[2] From this reactions alkenes **5** can be isolated in good yields. These results are quite surprising, since the alkenes **5** do not correspond to the expected compounds **4**, resulting from the insertion of the *in situ* generated carbene into the Pd–C bond followed by a β-hydrogen elimination. To explain the formation of **5** we propose that after the carbene insertion step, the cleavage of Cβ-Cγ takes place, that is, a β-carbon elimination occurs.[3] To our knowledge, this transformation is an unprecedented way to synthesize alkenes through the coupling of a carbene precursor and an unactivated aliphatic chain. Nowadays we continue with the study of the mechanism of this novel transformation and we are exploring its scope, including aliphatic carboxylic acid derivatives of biological interest.



Scheme 1. Unexpected reactivity of Pd-quinoline complex toward diazocompounds.

Acknowledgments

We thank the Spanish Ministerio de Economía y Competitividad (MINECO), FEDER (CTQ2015-69568-P) and Fundación Seneca (CARM, 19890/GERM/15) for financial support.

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Synthesis and photophysical properties of bis- and tris- cyclometalated platinum(IV) complexes bearing 1,2,3-triazolylidene ligands

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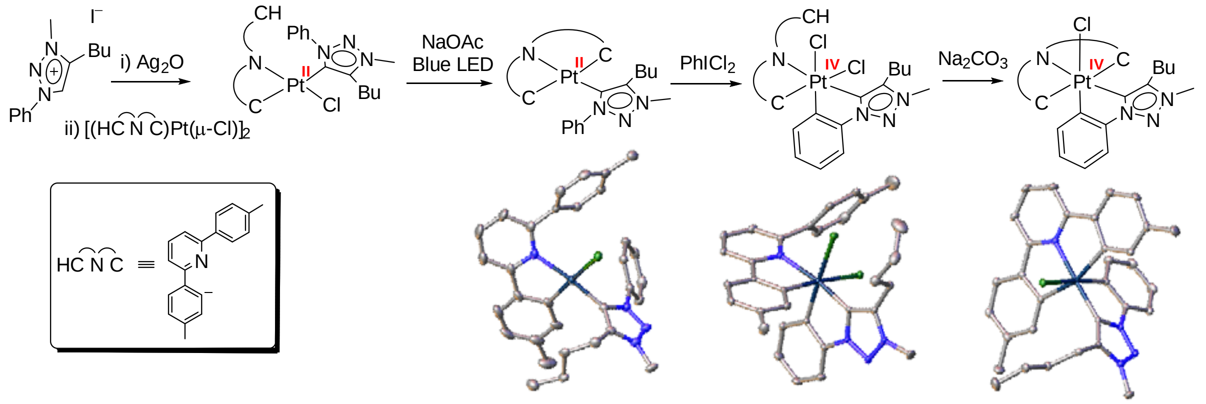
Pt(IV) complexes with cyclometalated heteroaromatic ligands exhibit notable photophysical properties, including high-energy, long-lived luminescence and a strongly oxidizing character in the excited state.[1] On the other hand, 1,2,3-triazolylidene ligands have been recently presented as a powerful NHC-class of ligands in photoluminescence.[2] However, very few examples of platinum species bearing 1,2,3-triazolylidene ligands have been described so far, and no Pt(IV) complexes with this kind of ligands are known.[3] Here we present synthetic routes to Pt(IV) complexes bearing mono- and di-cyclometalated ligands of the 2,6-diarylpyridine type as well as N-heterocyclic carbene ligands. The interesting luminescence properties found for these complexes will be discussed.



Acknowledgements

We thank the Spanish Ministerio de Economía y Competitividad (CTQ2015-69568-P) and Fundación Séneca (19890/GERM/15) for financial support. A.V. thanks Fundación Séneca for a Saavedra Fajardo Fellowship (20398/SF/17).

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Organogold(III) Carboxylate Complexes: Synthesis and Degradation

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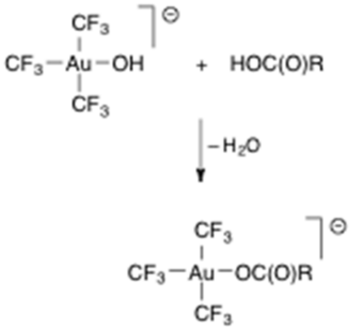
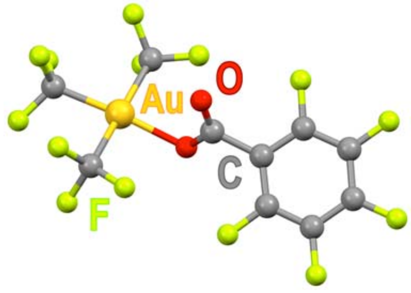
Carboxylate complexes of coinage metals have received renewed attention in the last years mainly because of their involvement in decarboxylative processes.[1] This decarboxylative method has been widely exploited for synthetic purposes.[2] Since it is the reverse process of CO_2 insertion into M–R bonds, it has strong implications in the much sought fixation and functionalization of CO_2.[3]

The decarboxylative method is clean and simple wherever it can be applied.[2] Few organometallic species, however, are stable enough to withstand the high activation energies usually required for decarboxylation to proceed. Since the CF_3 groups are known to endow its metal complexes with substantially enhanced thermal stability, we decided to examine the behavior of a series of carboxylate complexes of the highly acidic $(CF_3)_3Au$ moiety.[4]

Simple salts of the complex anions $[(CF_3)_3AuOC(O)R]^-$ are readily obtained by reaction of the hydroxo-derivative $[(CF_3)_3AuOH]^-$ with the corresponding carboxylic acid HOC(O)R. Representative R substituents were selected to provide a wide range of acidities. Once prepared, isolated and characterized, the thermal stability of the $[PPh_4][(CF_3)_3AuOC(O)R]$ compounds has been checked in the solid state by TGA/DTA. Additionally, the unimolecular fragmentation of their corresponding anions have been studied by tandem mass spectrometry. The obtained results are analyzed and rationalized with the aid of theoretical methods and with especial focus on decarboxylation.





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Mechanistic studies in the formation of C−Si and C−B bonds at 14-electron cationic platinum(II) centers

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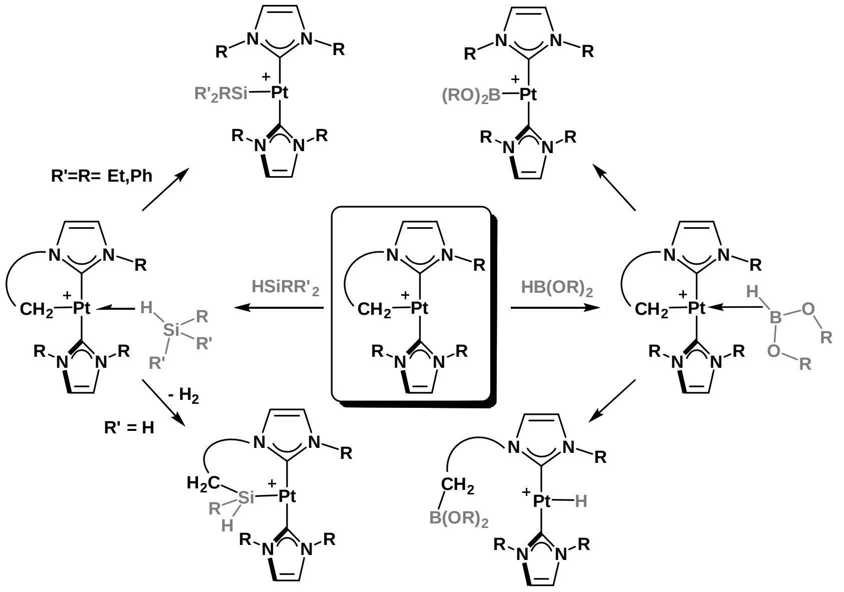
σ-SiH and σ-BH complexes are very well known for most of the transition metals.[1] However, it is rather surprising that platinum complexes of this type have not been isolated to date, in spite of the importance of this metal as catalyst in hydrosilylation and hydroboration reactions. Moreover, cationic systems are expected to be more difficult to detect or isolate as a consequence of the enhanced electrophilic character of the silicon or boron atoms once coordinated to the metal center. Nevertheless, we have been able to isolate some of this type of compounds through a judicious choice of ligands around the platinum center. Thus, silanes interact with cyclometallated 14-electron Pt(II) species [Pt(NHC')(NHC)][BAr^F] leading to "stable" [Pt(σ-HSiR$_3$)(NHC')(NHC)][BAr^F] (R = Et, Ph) compounds that rearrange into silyl derivatives [Pt(SiR$_3$)(NHC)$_2$][BAr^F].[2] In this contribution we have explored the interaction of coordinatively unsaturated Pt(II) complexes [Pt(NHC')(NHC)][BAr^F] with primary silanes, RSiH$_3$, and boranes HB(OR)$_2$. The corresponding σ-complexes have been detected and found that they can rearrange undergoing coupling reactions with formation of C−Si and C−B bonds. The mechanism of the process has been analyzed by DFT calculations.



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Au-NHC Adventures: Synthesis, Reactivity and Catalysis

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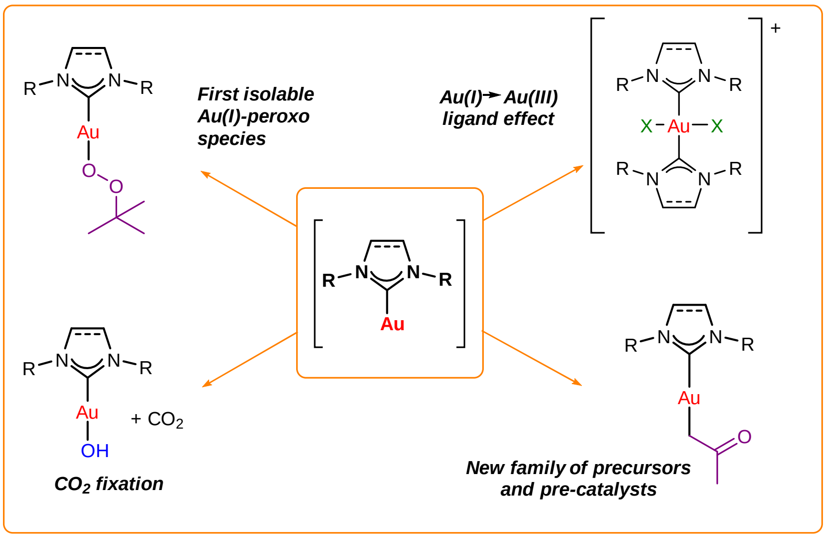
Homogeneous gold catalysis has witnessed an exponential growth in the last two decades.[1] In this field, *N*-heterocyclic carbenes (NHCs) have been widely used as ancillary ligands. NHC-Au halide species have been used as precursors, pre-catalysts and as models to determine the steric properties of the NHC ligand. In this communication, different applications of Au-NHC species will be presented: NHC-Au species have been used for the synthesis of new derivatives as Au-peroxo complexes[2]; and Au-acetonyl species.[3] The former are able to participate in oxygen atom transfer reactions while the latter have shown to be useful pre-cursors and pre-catalysts. NHC-Au-hydroxides have proven to be able to trap atmospheric CO_2[4]; and bis-NHC-Au cationic compounds can be easily synthesised from NHC-Au-Cl species, the ligand effect on the oxidation chemistry of these species towards hypervalent iodine oxidants has been studied.[5]



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Hexanickel cage for selective encapsulation of fullerenes

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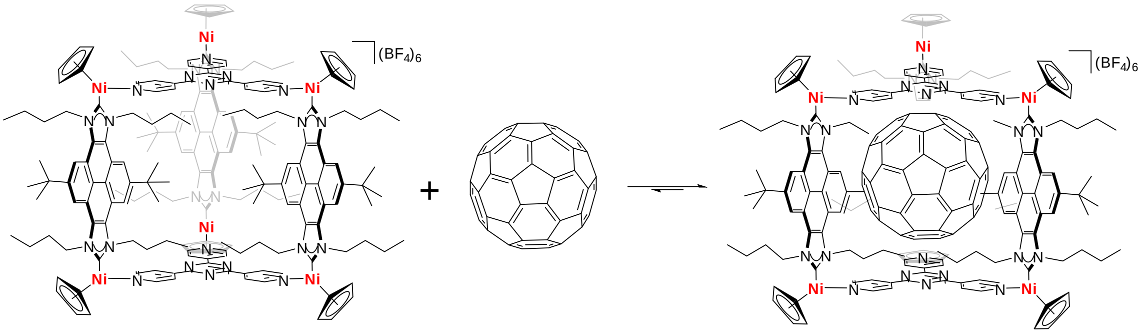
The use of molecular flasks for fullerene encapsulation is an attractive alternative for the separation, solubilisation and chemical transformation of fullerenes.[1] In our group, we have been recently interested in the preparation of metallosupramolecular complexes for the recognition of organic susbtrates.[2-4] In the course of our research, we obtained a nickel-cornered molecular rectangle that showed high affinities for bonding polycyclic aromatic hydrocarbons (PAHs).[5] In a continuation of our research, we now describe a 3-dimensional hexa-Ni(II) cage that shows selective complexation of C_{70} over C_{60}, thus being potentially useful for fullerene separation and purification.



Cage **1**

Fullerene-C 60

Figure 1. Host-Guest equilibrium reaction. Hexametallic Cage **1** is the host and Fullerene-C_{60} the guest.

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Boomerang Activation in Heck-Mizoroki Reactions Catalyzed by Bis(N-Heterocyclic Carbene)Palladium Complexes

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For being attractive for industry, Pd loadings used in Heck-Mizoroki (HM) and other C-C coupling reactions should be reduced from the typical mol% range to the ppm or ppb level.[1] Herrmann et al. found 20 years ago that HM reactions were catalyzed by low loadings of N-heterocyclic carbene Pd(II) complexes (PdNHCs).[2] The utility of NHCs was later brought into question by the development of HM reactions using very low amounts of ligand-free Pd salts.[3] The stability of the M-NHC bond might still help to recycle and reuse NHC catalysts, increasing their productivity. However, a better knowledge of the evolution of the Pd-NHC systems during the catalytical reaction is essential for the rational design of recyclable catalysts.

In the last years, we have studied the behavior of molecular-weight enlarged catalysts such as the chelate Pd complexes shown in Figure 1a.[4] These catalysts can be recovered by nanofiltration membranes in reactors operating under batch or continuous flow operation. When applied to a HM reaction, we observed almost constant conversions for a large number of recovery cycles. We report here that the high recoverability is based in a boomerang initiation mechanism: at the start of the reaction, the excess of base promotes the slow delivery of ligand-free Pd species which are the true active catalyst (Figure1b); at the end of the reaction, ligand-free Pd is trapped again by the NHC ligand avoiding their degradation in the form of Pd black.

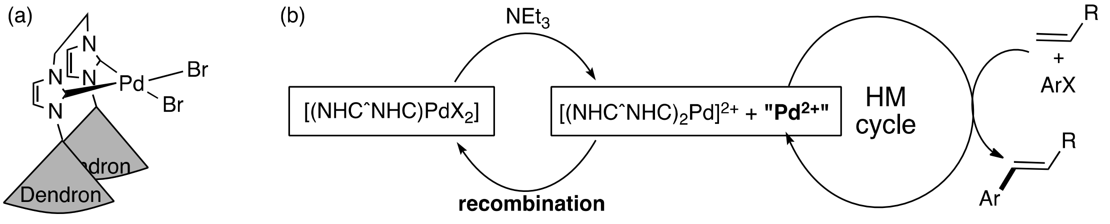

Figure 1. (a) Molecular-weight enlarged bis-NHC Pd catalysts. (b) Boomerang mechanism.

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Rh(III) and Ir(III) Biscyclometallated Complexes with Mitochondria-Targeted Anticancer Activity

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In this communication we report the synthesis and characterization of two pairs of Ir(III) and Rh(III) biscyclometallated complexes with two different ancillary ligands, namely thiabendazole (L1) and N-benzyl-thiabendazole (L2) to study the corresponding photophysical and biological properties (Fig. 1). In the dark, the four complexes exhibit greater cytotoxicity than cisplatin against human colon (SW480) and human lung (A549) adenocarcinoma cells. Moreover, the complexes bearing L2 ([Ir-b]Cl and [Rh-b]Cl) are markedly more cytotoxic than complexes with L1 ([Ir-a]Cl and [Rh-a]Cl), thereby their biological properties were studied further to determine their mechanism of action.

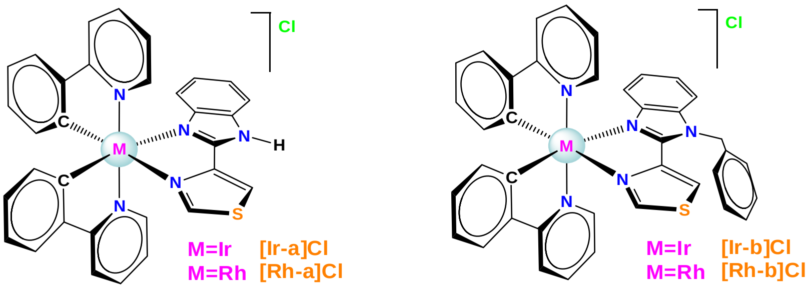

Figure 1. Structure of the complexes described in this work.

Interestingly, [Ir-b]Cl and [Rh-b]Cl bring about the loss of mitochondrial functionality and the activation of apoptotic cell death pathways. Moreover, the Ir complexes [Ir-a,b]Cl exhibit photodynamic activity under visible blue light (460 nm) under soft irradiation conditions (20 min, 5.5 mW cm^{-2}) with PI values of 15.8 and 3.6 for [Ir-a]Cl and [Ir-b]Cl, respectively (PI = IC_{50} nonirradiated/IC_{50} irradiated). On the contrary, the cytotoxic activity of the Rh derivatives is not photo-enhanced. We also demonstrate that only the Ir derivatives are able of photocatalyzing the oxidation of S-containing L-amino acids under blue light irradiation, [Ir-a]Cl being more active than [Ir-b]Cl. These results suggest a reasonable mechanism for their photobiological action (oxidative stress could be selectively promoted through a photocatalytic action). The different anticancer and PDT behaviour observed depending on the metal center and the ancillary ligand may be useful for the rational design of metal-based photosensitizers in the future.

Ir(III) biscyclometallated complexes as selective G-quadruplex stabilizers

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In this work, we describe the synthesis and characterization of two new Ir(III) bis-cyclometallated complexes with 2-phenylpyridinate as the cyclometallated ligand (C^N) and two different pyridyl-imidazo-phenanthroline ligands (N^N) (Fig. 1). Moreover, we have studied their photophysical properties and we have demonstrated that these complexes are very cytotoxic against adenocarcinomic human cells (A549). Interestingly, confocal fluorescence microscopy experiments unveiled that complex [Ir2]Cl is efficiently uptaken into these cells where it exhibits a punctuate yellow staining pattern in a perinuclear region due to its intrinsic phosphorescent emission (Fig. 2.A). In addition, [Ir1]Cl and [Ir2]Cl can promote the formation and stabilization of G-quadruplex conformations in guanine-rich DNA sequences (Fig. 2.B) and catalyze the photooxidation of S-containing amino-acids.

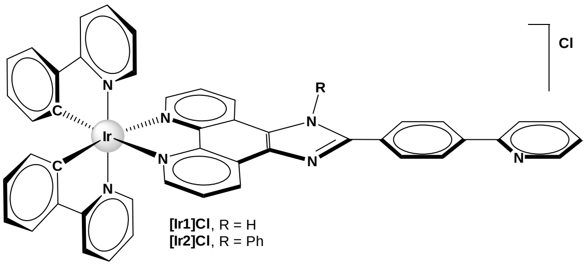

Figure 1. Molecular structures of the synthesized bis-cyclometallated iridium(III) complexes.

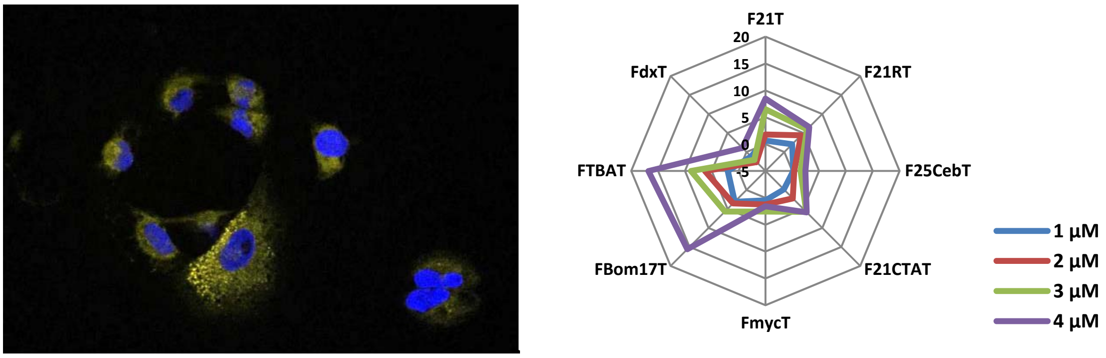

Figure 2. **(A)** Overlaid fluorescence images of **[Ir2]Cl** complex (yellow) and Hoescht (blue) incubated with A549 cells. **(B)** ΔT_m spider plot for the different fluorescent oligonucleotides under increasing concentrations of **[Ir2]Cl**

Catalytic Alkane Functionalization Via Iron-Carbene Insertion Reaction

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Saturated hydrocarbons are nature abundant reagents which upon functionalization constitute a potential vast and low cost feedstock for the synthesis of more valuable chemicals.[1] However, conversion of Csp^3-H into new C-C bonds is a difficult challenge due to their kinetically inert nature. To overcome this lack of reactivity, highly reactive reagents (superacids or radicals) or forcing reaction conditions are required, albeit these approaches usually compromise the selectivity of the process. An alternative to this energetically demanding processes has emerged within the field of Metal-carbene compounds $LM=CR_2$,[2] although it is dominated by precious metals such as rhodium, silver and gold. In replacing these systems by earth-abundant metals, iron rises as an optimal choice since it is of low cost, high natural abundance and low toxicity.[3]

Herein we report our findings investigating the use of a low-valent iron organometallic species as catalysts for Csp^3-H carbene insertion reactions under mild conditions. Optimization of the reaction conditions highlights the role of Lewis acids additives as a source of selectivity. Attempts to identify operative intermediates in these intricate processes are also discussed.

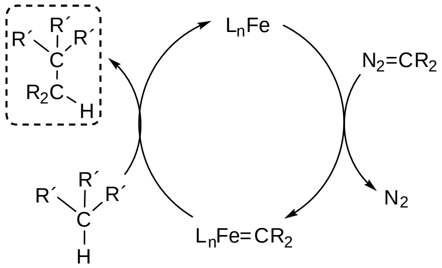

Figure 1. Csp^3-H bond functionalization iron-carbene catalysed.

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Aluminum catalysts for selective polymerization of difunctional monomers

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Aluminium organometallic derivatives containing Al-O bonds are very attractive species because of their remarkable properties in catalytic polymerization. As such, aluminium alkoxides have proven to be very efficient catalysts in ring opening polymerization and copolymerization processes.[1] Also, aluminium heterometallic compounds are appealing catalytic species, as the joint effect of two different metals in the same compound frequently leads to improved catalytic properties, especially when connected by an oxygen atom.[2]

Our research is centered in the preparation of new aluminium homo and heterometallic compounds active in polymerization processes. We have synthesized new aryloxide derivatives bearing functionalized aryl moieties. The presence of the additional functional group in the aromatic ring offers extra coordination points that not only can affect the catalytic behaviour of the complexes, but also can provide them with new structural features. We have achieved a good control of the nuclearity of the compounds prepared by varying the precursors and the reaction conditions. The species synthesized are active in ROP and the influence of their structure in their catalytic activity has been analysed.[3]

Also, well defined heterometallic derivatives bearing aluminium and alkaline metals have been prepared in our group.[4] These species are active catalysts in acrylate polymerization processes, generating syndiotactic PMMA. When we performed the studies with a monomer containing two different functional groups such as glydicyl methacrylate, the homometallic and heterometallic species are both active in the polymerization process but *via* two different paths. Hence, depending on the catalyst used, the selective polymerization of only one functional group is achieved.

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Novel photocatalytic synthesis of amides and thioamides employing blue light and Ir(III) complexes

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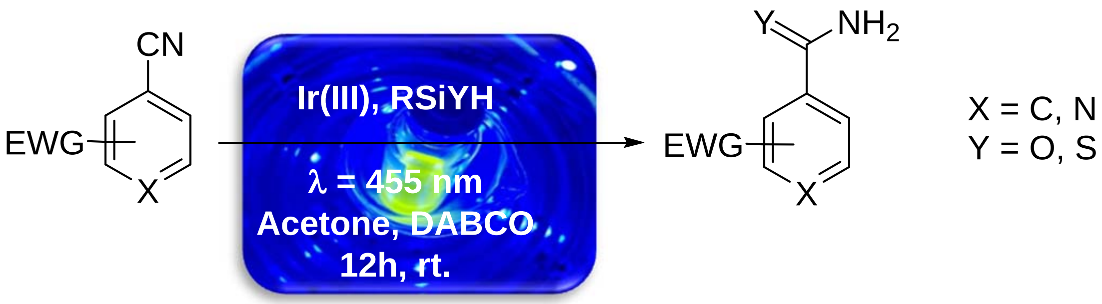
In this work, we present a novel photocatalytic procedure to obtain thioamides and amides. The photocatalysis is one of the most economical strategies for the synthesis of pure small molecules that uses visible light as an environmentally friendly and sustainable way of energy [1]. The iridium complexes have become the most common catalysts [2a-d]. We will present our results on the synthesis of thioamides and amides employing different Ir(III) catalysts under blue light, which show a new strategy to obtain this kind of compounds using mild conditions.



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Trapping enolates in pure water for the synthesis of 4*H*-pyran derivatives and study of their biological activity

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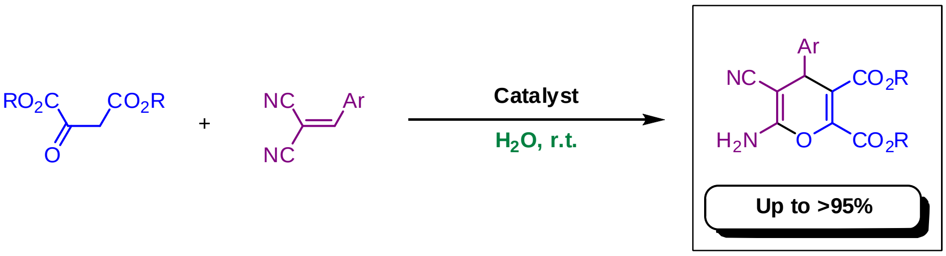
Molecules containing the 4*H*-pyran scaffold constitute a family well studied in chemistry because of their wide range of biological and pharmacological properties [1]. Some of their most interesting applications are as antimicrobial [2], antiviral [3], mutagenic agents [4], antiproliferative [5], sex pheromone [6], or as antitumor agents [7].

The synthesis of potential drugs has an enormous importance and, nowadays, we must try to develop more environmental friendly methodologies leading to these compounds. In this context, reactions in pure water are a keystone in green chemistry, as we can replace more toxic solvents and make these processes more suitable to the pharmaceutical industry. However, there are chemical species that, normally, cannot be used in water, like enolates. In reactions where an enolate form is necessary to perform a nucleophilic addition, water can inhibit this mechanism *via* protonation of these intermediates.



Scheme 1. Synthesis of 4*H*-pyran derivatives.

Herein, we report a synthesis of some interesting 4*H*-pyran derivatives (Scheme 1). This reaction is carried out in pure water, granting us the advantages shown before. In addition, we show some of the biological tests being held in our laboratory concerning these important molecules.

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Hydrogenation of functionalized substrates in water catalyzed by Pt-NPs containing sulfonated NHC ligands

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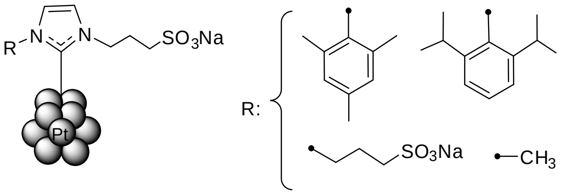
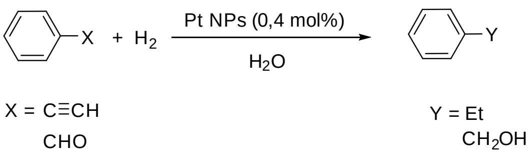
Hydrogenation reactions are one of the most relevant processes in organic chemistry, as they can afford valuable products such as pharmaceuticals and agrochemicals [1]. Transition-metal nanoparticles (NPs) are interesting catalysts in these reactions, due to their high specific surface and the possibility to tune their properties depending on the ligands anchored to them [2]. N-Heterocyclic carbenes (NHC) have proved to efficiently stabilize metal nanoparticles [3], even in water, when conveniently modified with hydrophilic groups [4-6]. Platinum NPs containing sulfonated NHC ligands were unknown until 2014, when we reported the synthesis of NPs **1-4** and their application in the hydrogenation of styrene [4]. Here we present their behaviour in the hydrogenation of other aromatic substrates in water in mild conditions.



Pt NPs = **1-4**



All the NPs are active and selective in the hydrogenation of several substrates, such as phenylacetylene and benzaldehyde. Furthermore, they can be reused for at least eleven consecutive cycles without noticeable loss of activity. The NPs increase in size during the recycling experiments as shown by TEM.

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Aromatic C-H versus C-Br bond activation in iridium olefin complexes

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The activations of C-H and C-halogen bonds by transition metal complexes are a highly important processes due to their connection with the functionalization of organic molecules [1]. Halogenated organic compounds usually have both C-H and C-halogen bonds, therefore their activation is a competitive process. In the case of the homolytic activation of haloarenes, it is observed a transition state of lower energy for the C-H bond activation and a product of lower energy for the oxidative addition of the C-halogen bond, thus supporting the fact that the C-H bond activation is kinetically favored while the C-halogen activation is thermodynamically preferred [2].

In this communication we show, how depending upon the starting iridium material, competitive aromatic C-H and C-Br bond activations take place. It seems that the olefin bonded to the iridium starting products plays a crucial role in the reactivity pattern.

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Experimental and Computational Evidences of the Olefin Insertion and β-Hydride Elimination Processes

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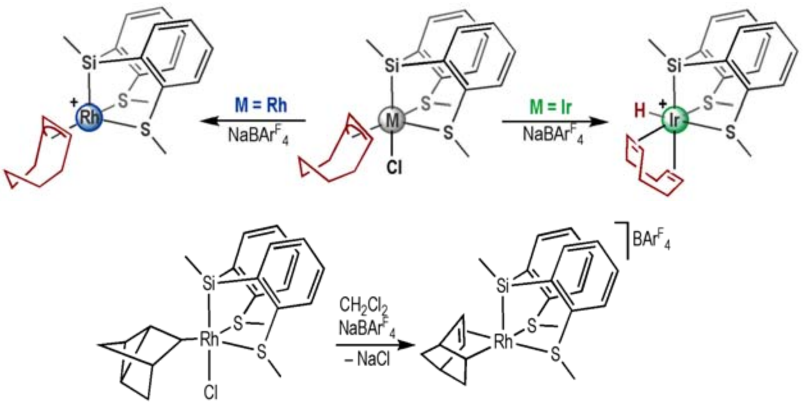
Transition metal complexes have been extensively used as catalysts on olefin functionalization reactions such as hydrosilylation or hydroboration,[1] *via* well-stablished oxidative addition/reductive elimination catalytic cycles. In several processes proposed for these reactions, olefin insertion into a metal-hydrido bond is a key step, leading to the formation of alkyl metal compounds as catalytic intermediates.[2]

Herein we report the synthesis of various Rh(III) and Ir(III) alkyl complexes. Reaction of the silyl-thioether $SiMeH(o\text{-}C_6H_4SMe)_2$ proligand with $[Rh(cod)Cl]_2$ leads to the olefin insertion into the Rh–H bond to yield complex $\{RhCl(\eta^3\text{-cyclooctenyl})[SiMe(o\text{-}C_6H_4SMe)_2]\}$ (**1**). Further reaction with $NaBAr^F_4$ leads to unsaturated compound $\{Rh(\eta^3\text{-cyclooctenyl})[SiMe(o\text{-}C_6H_4SMe)_2]\}[BAr^F_4]$ (**2**). Through reaction of the proligand with $[Rh(nbd)Cl]_2$ (nbd = norbornadiene), $\{Rh(nortriciclyl)[SiMe(\mathit{o}\text{-}C_6H_4SMe)_2]Cl\}$ (**3**) is obtained. The extraction of the chlorine from the neutral nortriciclyl-Rh(III) complex with $NaBAr^F_4$ results in the unusual isomerization from nortricyclyl to norbornenyl forming unsaturated $\{Rh(norbornenyl)[SiMe(\mathit{o}\text{-}C_6H_4SMe)_2][BAr^F_4]$ compound **4**. Finally, by reaction of $[Ir(cod)Cl]_2$ with an equivalent of the proligand $\{Ir(\eta^3\text{-cyclooctenyl})[SiMe(o\text{-}C_6H_4SMe)_2]Cl\}$ (**5**) was also synthetized. The reaction of **5** with $NaBAr^F_4$ led to the formation of $\{Ir(\eta^3\text{-cyclooctenyl})[SiMe(o\text{-}C_6H_4SMe)_2]\}[BAr^F_4]$ (**6**), and due to low stability in solution, this complex undergoes successive ß-hydride elimination and olefin insertion steps, which were elucidated by DFT calculations, to form $\{Ir(H)[SiMe(\mathit{o}\text{-}C_6H_4SMe)_2](cod)\}[BAr^F_4]$ (**7**).



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Aminometilfosfinas: ligandos y estabilizantes de nanopartículas metálicas. Aplicaciones catalíticas

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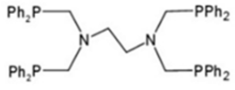

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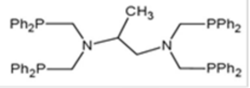

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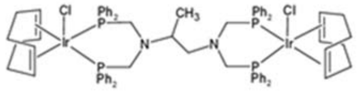
Las aminometilfosfinas tienen especial importancia en la obtención de catalizadores organometálicos [1] y de nanopartículas metálicas [2]. Por reacción de la sal de fosfonio $[PPh_2(CH_2OH)_2]Cl$ con la diamina correspondiente, en presencia de trietilamina, pueden obtenerse las aminometilfosfinas **1** y **2.**

Ambos se coordinan a los metales de forma bidentada quelato mediante los átomos de fósforo para dar los correspondientes complejos bimetálicos. Por reacción de **2** con los dímeros $[MCl(COD)]_2$ (M = Rh o Ir) se obtienen los complejos **3,** pentacoordinado neutro**,** o **4**, plano cuadrado catiónico (en presencia de un anión voluminoso X). A su vez, por reacción con *o*-(difenilfosfino)benzaldehído estos complejos pueden experimentar reacción de adicción oxidativa, y originar complejos análogos a **5**. Los complejos **3-5** presentan propiedades catalíticas en la hidrólisis de amoniaco-borano.



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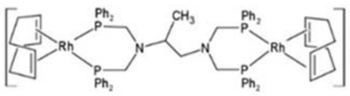

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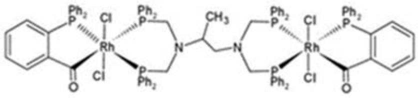

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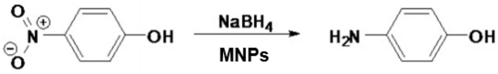
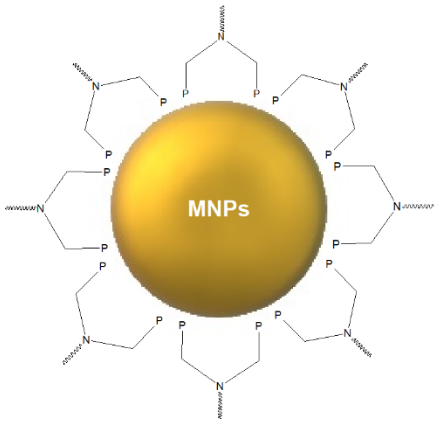
1 y **2** son buenos estabilizantes de nanopartículas de rodio y oro, generadas por reducción de la correspondiente sal metálica con borohidruro de sodio.

MCl_3 + AMINOMETILFOSFINA $\xrightarrow{10\ NaBH_4}$ MNPs

Se plantea que dicha estabilización tiene lugar mediante los átomos de fósforo. Estas nanopartículas son buenos catalizadores en la reducción de *p*-nitrofenol.





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Capturing the Cu(Amyloid-β) complex responsible of ROS production: does it also exist in aggregated forms?

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Nowadays, it is well known that the interaction of metal ions such as Cu, Fe and Zn with the amyloid-β peptide, as well as other amyloidogenic peptides and proteins is involved in the aetiology of neurological disorders.[1,2] Their influence on aggregation and oxidative stress, especially metal-induced ROS production, could be relevant for the development and progress of Alzheimer's disease.

Oxidative stress could be linked to the ROS production of the Cu(Aβ) complex in presence of reductive agents such as ascorbate, present in high concentration in the brain. The redox mechanism of this complex would not be simple: the resting states of Cu(I) and Cu(II) are different. An "in-between" state (IBS) was postulated to be responsible of the ROS production.[3] Recently, we have proposed a coordination structure for the chemical IBS by studying the $^{\bullet}$OH production by the Cu-peptide complexes from a wide series of Aβ mutants.[4]

In this presentation, we will show such a structure, corroborated by a parallel study which used the ascorbate consumption in presence of Cu-peptide complexes. Furthermore, we have observed that in presence of Zn(II), the Cu(Aβ) complex has a slightly faster production of ROS.[5] This could be of importance since Zn(II) is found in the brain in ca. mM concentrations.

In ongoing studies, we want to check if the production of ROS by Cu(Aβ) is still present when aggregates, of different morphologies, are formed and if so, if the IBS could still be applied in this case. Preliminary results show that Cu is still redox active when found coordinated to aggregated forms.

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Acknowledgments: This project is supported by the ERC-2014-StG-638712 aLzINK grant.

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