XL GEQO conference
Organometallic Chemistry Group

BARCELONA

7th - 9th September 2022

BOOK OF ABSTRACTS

Scientific Committee

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WELCOME

Dear colleagues and friends,

As chair and on behalf of the local organizing committee, I invite you to the XL GEQO Conference, which will be held in Barcelona (Spain) from September 7th to 9th, 2022. We hope that the covid pandemics will be over and we can meet to enjoy not only science, but also friendship and our very nice city.

We encourage the organometallic chemistry community to attend this meeting, considering it as a platform to embark into fruitful scientific discussions, exchange new ideas and establish new scientific collaborations.

We wish you a pleasant stay in Barcelona, discussing science, but also admiring architecture, culture, excellent Mediterranean cuisine and the many exciting places the city offers.

Finally, we would like to thank all the plenary and invited speakers for accepting our invitation to participate in this conference and all the participants for attending to XL GEQO. Also, all the people of the organization, the organizing committee, the scientific committee and the session chairs are warmly acknowledged. We are extremely grateful for the support obtained from our sponsors.

We hope you enjoy XL GEQO conference and have a great time in Barcelona!

Laura Rodríguez

Chair of the Organizing Committee of the XL GEQO Conference

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Wednesday, September 7th

12:00-16:00	**Registration**
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Chair: L. Rodríguez (BARCELONA ROOM)

16:30-17:30	PL1	**Pedro J. Pérez.** *An Organometallic View of Catalytic Processes Involving Hydrocarbon Functionalization*
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Thursday, September 8th

Chair: A. C. Albéniz (BARCELONA ROOM)

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Chair: A. C. Albéniz (BARCELONA ROOM)

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Chair: M. Monge (CIUTADELLA ROOM)

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10:50-11:05	OC4	**João Carlos Lima**. *Supramolecular gold(I) aggregates: the effect on photophysics*
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Chair: C. Claver (BARCELONA ROOM)

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Chair: C. Claver (BARCELONA ROOM)

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Chair: M. Gómez (BARCELONA ROOM)

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Chair: J. Pérez-Torrente (BARCELONA ROOM)

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Chair: G. Aullón (CIUTADELLA ROOM)

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Chair: E. Fernández (BARCELONA ROOM)

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Chair: E. Fernández (BARCELONA ROOM)

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Chair: M. Diéguez (CIUTADELLA ROOM)

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Chair: A. Lledós (BARCELONA ROOM)

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12:05-12:35	INV9	**Xavi Ribas**. *Tetragonal Prismatic Nanocapsules as Supramolecular Masks for Regioselective Functionalization of Fullerenes*

Chair: A. Lledós (BARCELONA ROOM)

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13:10-13:25	OC27	**Joel Nadal-Moradell**. *A Versatile and Commercially Available Iron Catalyst Active in Carbene Transfer Reactions*
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Chair: M.C. Nicasio (BARCELONA ROOM)

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18:10-18:30	**Closing Ceremony & Awards** (BARCELONA ROOM)
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P04 **Ane I. Aranburu**. *Iridium Based Cation Sensor*

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P06 **Unai Prieto**. *Selective Synthesis of Hydrosilanols and Hydrosiloxanes Catalyzed by di-Silyl Rhodium and Iridium Complexes*

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P17 **Sonia Bajo**. *Mechanistic Investigations on Hydrogenation, Isomerization and Hydrosilylation Reactions Mediated by a Germyl-Rhodium System*

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P60 **Susana Ibáñez**. *Clippane: A Mechanically Interlocked Molecule (MIM) Based on Molecular Tweezers*

P61 **Marcos Rúa-Sueiro**. *Coordination study of diphosphine dppm with platinum cyclometallated thiosemicarbazones*

P62 **Francisco Reigosa**. *Synthesis of double [C, N; N, C] Schiff base palladacycles functionalized with crown ethers*

P63 **Basma Al Janabi**. *Cyclopalladated compounds derived from imine ligands: Synthesis, characterization, and catalytic activity for the Suzuki-Miyaura cross-coupling*

P64 **Concepción López**. *To have and have not: The importance of the* $–CH_2–$ *unit on the properties of Ru–aminoalcohol complexes*

P65 **Eduard Balaguer-Garcia**. *Radical Alkylation Reactions with Metal Enolates*

P66 **Gustavo Espino**. *Rational Design of Mitochondria Targeted Thiabendazole-based Ir(III) Biscyclometalated Complexes for a Multimodal Photodynamic Therapy of Cancer*

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PLENARY LECTURES

An Organometallic View of Catalytic Processes Involving Hydrocarbon Functionalization

Pedro J. Pérez

Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva, 21007 Huelva, Spain
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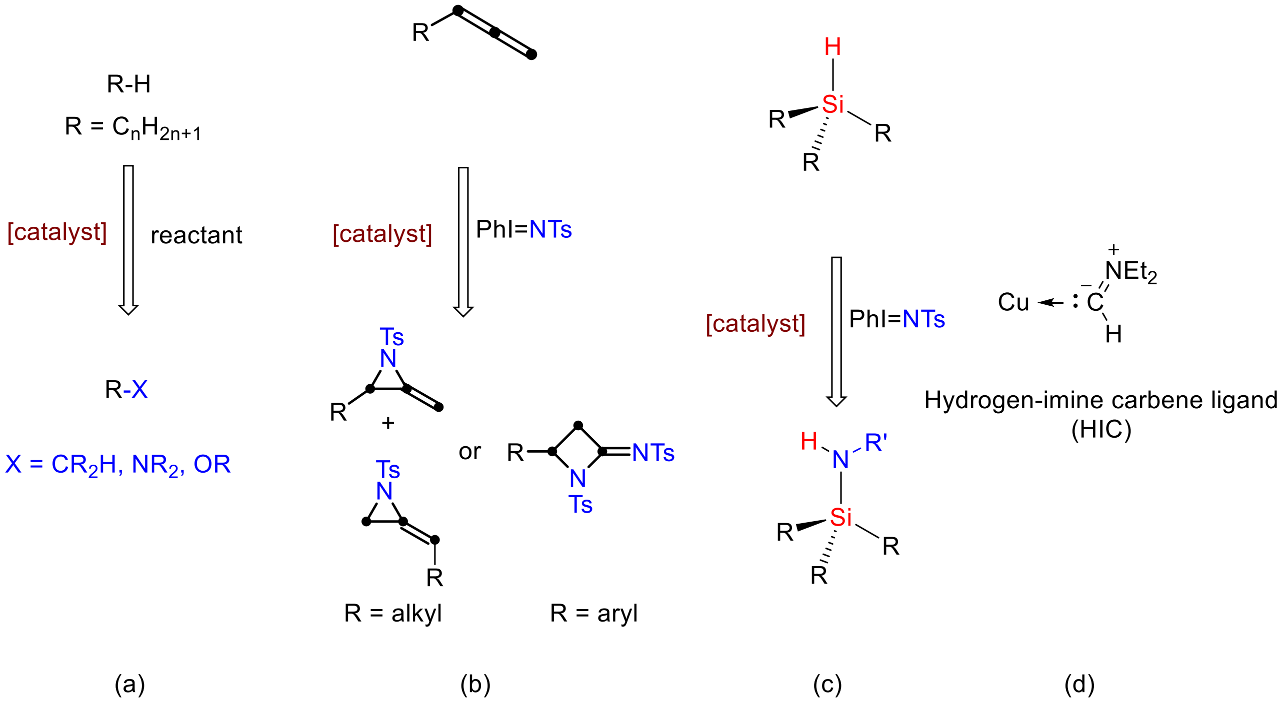
One of the continuous challenges in modern chemistry consists in the conversion of available and affordable raw materials into value-added products. In this context, alkanes C_nH_{2n+2} are yet far of being employed as reactants in synthetic procedures, mainly due to their high bond dissociation energies and low C-H bond polarity. Following our research in the field, the results derived of the functionalization of such hydrocarbons through reactions involving the formation of C-C, C-N or C-O bonds will be presented (Scheme 1a), with particular emphasis in the role of the metal and the reaction mechanisms. Extensions to other substrates such as allenes or silanes, referred to the incorporation of nitrene groups will also be shown (Scheme 1b, c). Finally, the recent discovery of a new hydrogen-imine carbene ligand (HIC) with singular properties will be presented (Scheme 1d).



Scheme 1

PL2

MANGANESE (I)- AND COPPER(I)-CATALYSED TRANSFORMATIONS: DEVELOPMENT, MECHANISMS AND APPLICATIONS

Syuzanna R. Harutyunyan[a]

[a]*Stratingh Institute, University of Groningen, Netherlands, Nijenborgh 4, 9747 AG, Groningen, Netherlands.*

The research program in our group is aimed at the development of novel catalysis concepts for asymmetric synthesis of chiral functional molecules using chiral complexes of earth-abundant transition metal complexes. In recent years we have shown a remarkable ability of copper(I) based catalysts to promote enantioselective alkylations of carbonyls and imines, followed by the development of Lewis acid promoted copper(I)-catalyzed enantioselective dearomatisation reactions. Very recently we have also found that chiral Mn(I) complexes are capable of H−P bond activation. This activation mode enabled us to develop highly enantioselective catalytic methods for synthesis of various chiral bisphosphines that can be used as efficient ligands for both manganese and copper catalyzed enantioselective transformations. During this lecture I will discuss shortly our recent developments in copper chemistry followed by more detailed presentation of our progress in novel Mn-catalyzed enantioslective transformations.

Steering Asymmetric Catalysis with Metal-Centered Stereogenicity

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Over the past few years, our laboratory has advanced the design and application of a novel class of powerful asymmetric catalysts in which the required overall chirality originates solely from a stereogenic metal center [1,2]. Such chiral-at-metal catalysts are of interest due to their intrinsic structural simplicity (only achiral ligands) and provide untapped opportunities with respect to novel catalysts architectures and properties.

Our initial design consisted of bis-cyclometalated Ir(III) [3] or Rh(III) [4] complexes. More recently, we expanded the family of chiral-at-metal catalysts with Ru(II) [5] and Fe(II) [6] bis-(pyridyl-NHC) complexes (Figure 1). Most of these propeller-type complexes feature C_2-symmetry with either Λ-(left-handed screw) or Δ-configuration (right-handed screw).

The presentation will provide insight into the design, synthesis, and applications of such chiral-at-metal catalysts including asymmetric photocatalysis [7-9], electrochemistry [10], enantioselective C(sp^3)-H aminations [11,12], and a recently developed new synthesis of α-amino acids [13].

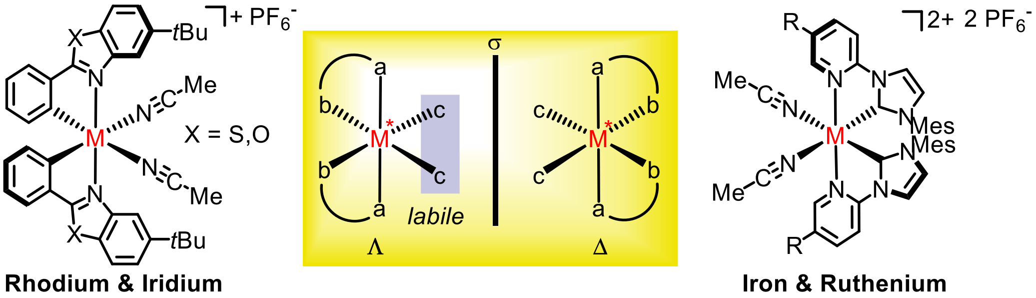

Figure 1. Selection of chiral-at-metal asymmetric catalysts developed in the Meggers lab.

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PL4

Modulation of the Properties of Gold Complexes through Ligand Design

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The chemistry of gold has experienced a great development mainly because the discovery of the properties of its complexes [1]. Gold compounds have been well known to be useful catalysts for small molecule activation and in organic synthesis, while their impacts in materials science and medicine is continuously increasing. To facilitate this extraordinary progress in the chemistry of gold, the synthesis and design of novel strong donor ligands have been crucial. Such strong donor ligands combine electronic and steric properties that are easily modulated, which is a key point to stabilize and to confer the gold complexes with interesting properties.

This presentation will highlight the design of several types of gold complexes that have been developed in our group. Ligand selection is a crucial factor to obtain complexes with the desired properties. In first place, looking for the preparation of gold compounds with biological activity, the use of ligands favoring complexes with improved stability and solubility in the biological media could provide better activities [2]. Functionalization of these ligands to achieve an easier localization of the target by the complex appears as an excellent approach towards gold metallodrugs. The presence of two metallic fragments exerts a cooperative effect in the cytotoxic activity and properties of the final complexes, which could overcome cellular resistance because of the possibility of combining the different intrinsic mechanism of action of each metallic fragment. Additionally, the possibility to move from single to multi-targeted therapy for cancer treatment have revolutionized the concept of oncological medicine. The single-target therapy is vanishing in favor of a multi-target approach, where new drugs can simultaneously target different molecules and gold complexes are excellent examples for this type of approach.

In the second place, research in light emitting materials have experienced a substantial growth during the last few years and it has become one of the most important topics in transition metal chemistry. Potential applications of luminescent compounds in sensors, OLEDs, photocatalysis and medicine (among other areas) explain the growing research in such species [3]. The synthesis and potential applications of gold complexes will be commented. The variety of ligands with different donor centers that can coordinate to gold in their different oxidation states will permit the tuning of the emission energy almost over the whole of the visible spectrum.

Additionally, within the gold complexes with biological activity the incorporation of an organic or organometallic chromophore group would give rise to luminescent complexes, which would allow visualizing the localization inside the cell, providing crucial information such as cellular uptake, biodistribution and/or bioaffinity. This combination of a visualization agent with a selected therapeutic, known as an optical theranostic or a trackable agent, would be able to provide relevant information regarding its biological interplay [4].

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PL5

Synthetic Chemistry with Laughing Gas

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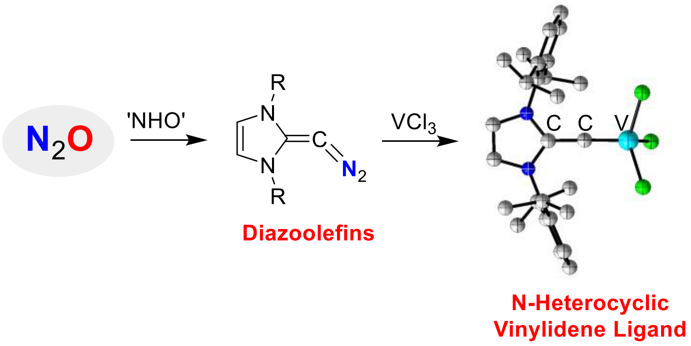
Nitrous oxide (N_2O, 'laughing gas') is rarely used as a reagent in synthetic chemistry. On the contrary, industrially produced N_2O is destroyed by catalytic decomposition into the elements, because the release of N_2O is problematic from an environmental point of view. In the lecture, I will show that N_2O can be used as a nitrogen-atom donor for the synthesis of diazoolefins [1], organic reducing agents [2], triazenes [3], and azo dyes [4]. The latter are interesting precursors for novel carbene ligands [5]. Diazoolefins, on the other hand, display a rich organometallic chemistry. Notable, they can serve as precursors for N-heterocyclic vinylidene ligands (Scheme 1) [6].



Scheme 1. The reaction of N-heterocyclic olefins ('NHOs') with nitrous oxide gives diazoolefins. The latter can serve as precursors for N-heterocyclic vinylidene ligands.

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INVITED COMMUNICATIONS

Light-Induced Reactions of Cyclometalated Pt(II) and Pt(IV) Complexes

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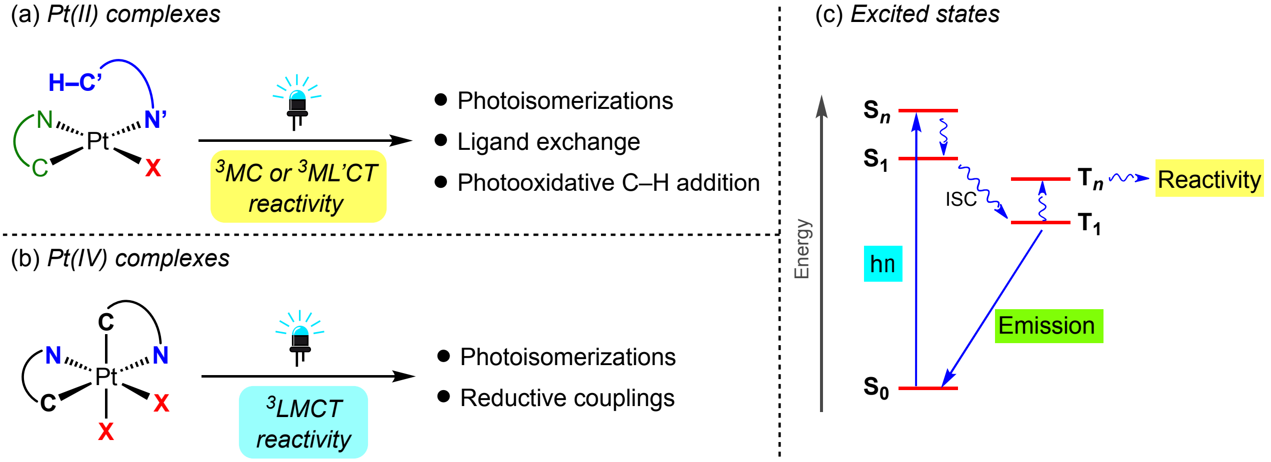
The discovery of chemical transformations that incorporate light-induced (photochemical) steps is mainly motivated by the need to develop novel and more energy-efficient synthetic methodologies. In this context, the excited-state reactivity of transition metal complexes is playing an increasingly important role.[1]

Although cyclometalated Pt(II) complexes bearing 2-arylpyridines and related ligands have been intensely investigated for their luminescence,[2] studies on their photochemical reactivity are scarce and based solely on their strongly reducing character in the excited state, which has enabled photoinduced oxidative additions of alkyl halides[3] and photocatalytic reductive transformations.[4] These complexes present ^{3}LC/MLCT excited states (mixed ligand-centred/metal-to-ligand charge-transfer) from which phosphorescent emissions or electron-transfer reactions can occur. Our recent studies have shown that thermal population of other excited states from the ^{3}LC/MLCT state can lead to different processes, including an unprecedented C–H activation mechanism.[5]

On the other hand, cyclometalated Pt(IV) complexes present ^{3}LC excited states that can produce intense luminescence.[6] However, in certain cases, ligand-to-metal charge-transfer (^{3}LMCT) excited states can be thermally populated from the ^{3}LC state and trigger chemical transformations, including reductive couplings that are not possible under thermal conditions.



Scheme 1. C^N = cyclometalated 2-arylpyridine ligand.

Acknowledgements

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INV02

Exploring the Chemistry of Palladium(I) Stable Radicals

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It is well known that palladium chemistry is dominated by the even oxidation states 0, II, and IV. Although there are also numerous examples of palladium(I) complexes, these are usually dinuclear species with metal-metal bonds and, therefore, diamagnetic.[1] On the other hand, palladium(I) radicals are involved as intermediates in some palladium-catalyzed organic transformations in which Pd^0-Pd^I-Pd^{II} single electron transfers (SET) replace the classical Pd^0-Pd^{II} two-electron transfers.[2] Recently, it has been shown that palladium(I) mononuclear complexes can be stabilized, isolated, and characterized by sterically shielding the paramagnetic metal center.[3] The study of the reactivity of this type of metallo-radicals is of obvious fundamental interest, but has so far hardly been addressed.

We have recently synthetized new mononuclear palladium(I) complexes of $[PdL_2]$+ stoichiometry stabilized by N-heterocyclic carbene ligands (NHCs) of high steric hindrance (an example shown in Figure 1).[4] These metallo-radicals are very stable against air and humidity in solid state and are very convenient and active precatalysts in Suzuki-Miyaura cross-coupling reactions. Experimental evidence, supported by theoretical calculations, shows that the unpaired electron is essentially located on the palladium atom. We will show the usefulness of ^1H and ^{13}C NMR spectroscopy, together with electron spin resonance (ESR) spectroscopy, for the characterization of these paramagnetic compounds. The high donor capacity of NHC ligands favors the oxidation of palladium(I) to palladium(II), inducing an interesting reactivity towards small molecules. In this presentation, we will describe the results obtained on dioxygen activation. Thus, the reaction of $[Pd(NHC)_2]^+$ complexes with dioxygen produces the reversible oxidation of palladium(I) to palladium(II) with formation of superoxide complexes of formula $[Pd^{II}(NHC)_2(O_2^{\bullet})(L^{'})]^+$. The evolution of these superoxides is highly dependent on the L' ligand.

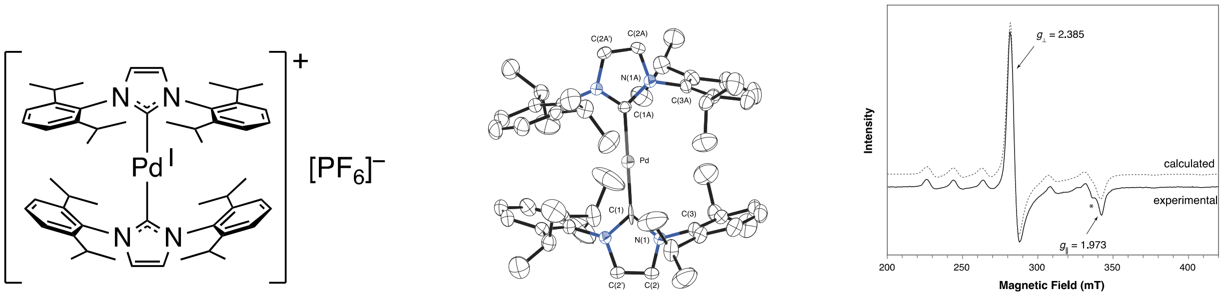

Figure 1

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INV03

LOW-COORDINATE Ni(0) COMPLEXES AND APPLICATIONS IN CATALYTIC C-C BOND FORMATION

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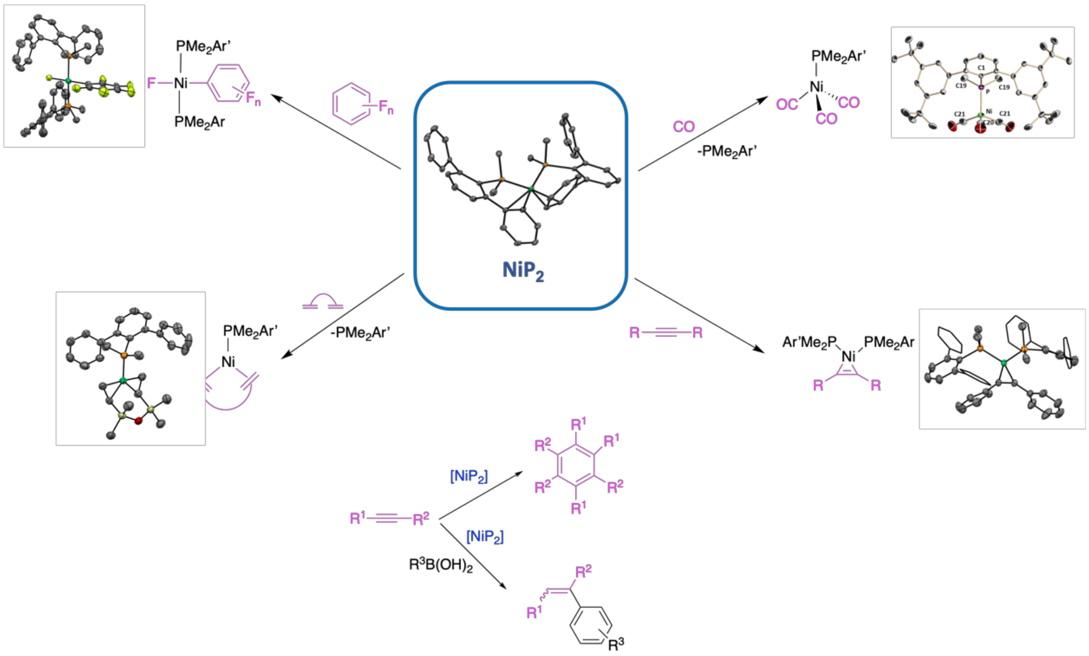
Low-coordinate, zero-valent, transition-metal complexes of group 10 (Ni, Pd and Pt) have attracted widespread attention for their capability to activate unreactive bonds via oxidative addition.[1] On this basis, these species are postulated as intermediates in catalytic transformations that proceed through a M(0)/M(II) pathway, including cross-coupling and C-H activation reactions. Among many examples of M(0) complexes of group 10 metals in low coordination numbers, those of two-coordinate ML_2 complexes are limited to Pd and Pt bearing bulky phosphanes, N-heterocyclic carbenes (NHCs) and isocyanide ligands.[2] However, two-coordinate Ni(0) analogues are rare and instances known are largely restricted to compounds supported by large NHC ligands. So far, two-coordinate bis-phosphane nickel(0) complexes remain unknown.[3] This presentation will focus on the use of dialkylterphenyl phosphanes[4] as ancillary ligand to stabilize homoleptic MP_2 complexes of the nickel triad, with special emphasis in the reactivity of NiP_2 derivatives with unsaturated molecules and their applications in catalytic transformations involving alkynes as reactants.



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Metal-based nanoparticles immobilized on unusual phases: a catalytic survey

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Nanocatalysis emerged as a new concept that combines both colloidal catalysis and engineered nano-objects, showing defined structures and composition. Like most metal nanoparticles (MNPs), aggregation during the catalytic reaction can lead to structure modifications, impacting their unique properties and consequently precluding their expected reactivity. A way to avoid these drawbacks is to use solid supports with the purpose of immobilizing the nanocatalysts, favoring their recycling, but adding plausible effects due to metal-support interactions. With the purpose of preserving the surface state, the immobilization of MNPs in a liquid phase has been considered. In addition to environmentally friendly properties, glycerol permits to catch the catalyst and easily extract the organic products thanks to its supramolecular network which favors the dispersion of MNPs; the catalytic phase can be thus recycled, obtaining metal-free target organic compounds [1].

Our team has proved the glycerol ability for the synthesis of both mono- (Pd, Cu and Cu_2O, Ni, Co) and bi-metallic nanoparticles (Pd/Cu), leading to stable colloidal catalytic solutions in the presence of polymers (such as PVP), phosphines and biomass-based stabilizers such as cinchona derivatives [2]. In particular, bimetallic nanoparticles open new horizons in organic transformations, because of cooperative effects between the two partners and structure-reactivity relationships (alloy, core-shell, hetero-dimer…) [3].

In this contribution, an account of our work related to nano-catalysis will be presented, from the synthesis and full characterization of metal-based nanoparticles in different media (mainly glycerol and solid supports) to catalytic applications, together with mechanistic insights.

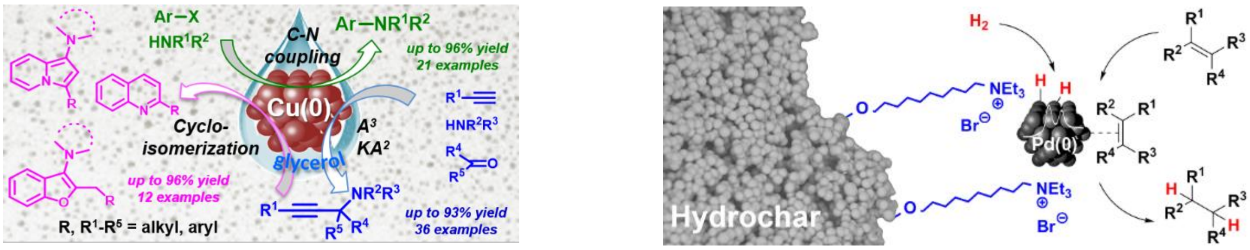

Figure 1. *RIGHT: CuNPs dispersed in glycerol applied in tandem processes. LEFT: PdNPs immobilized on functionalized hydrochars applied in hydrogenation reactions*.

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Exploiting the reactivity of organometallic complexes towards the tailored design of plasmonic hybrid nanostructures

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During the last years, the mild decomposition of noble metal organometallic complexes has allowed achieving a plethora of well-defined nanostructures of controlled size, shape and composition and displaying tailored properties.[1,2] More recently, the research has been focused on exerting this control in the presence of soft matter or solid 2D and 3D materials, giving rise to interesting approaches for the design of multifunctional nanohybrid systems. In such cases, the presence of gold and silver in the nanostructures provides interesting plasmonic properties as, for instance, photothermal heating, optical near field effect or hot-electron injection upon visible/NIR light irradiation.[3,4]

In this communication we show the study of novel gold-based plasmonic nanohybrids formed upon controlled decomposition of organometallic complexes $[Au_2Ag_2(C_6F_5)_4(OEt_2)_2]_n$ or $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) under different reduction conditions (see examples in Figure 1). We will show how the use of an organometallic methodology permits the formation of complex nanostructures such as (i) Pickering emulsion based Au colloidosomes; (ii) core@satellite Prussian Blue Analogue@Au-Ag nanoparticles; (iii) biocompatible polymer stabilized wavy Au-Ag nanorods or (iv) Au-Ag-semiconductor heterostructures. These purposely-designed nanohybrids provide interesting stimuli-responsive properties, photothermal heating and enhanced catalytic or photocatalytic performance. These nanostructures can be applied as highly efficient materials in light-to-energy conversion or in photocatalytic/photothermal environmental remediation fields.

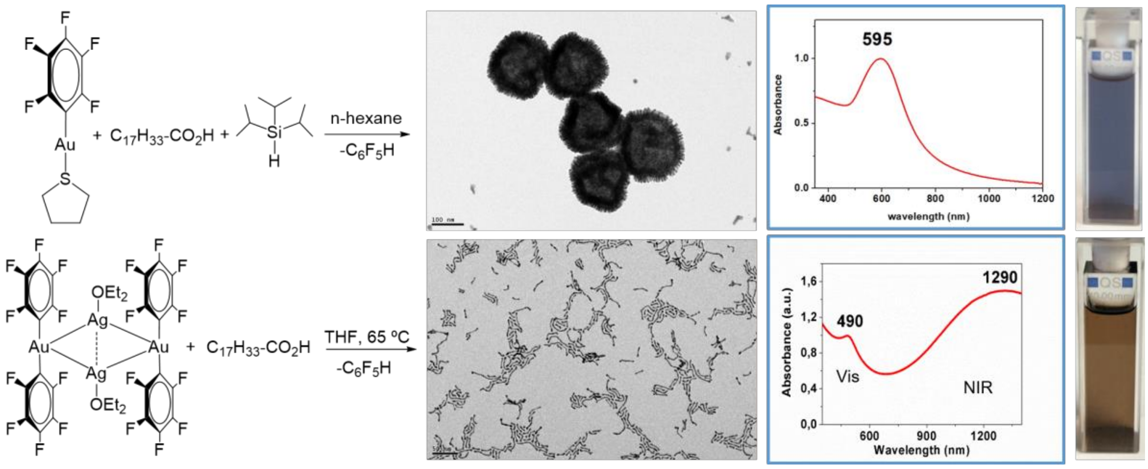

Figure 1. Selected examples of reactivity of organometallic Au(I) and Au(I)-Ag(I) complexes, leading to urchin-like Au colloidosomes and AuAg wavy nanorods, showing LSPR absorptions in the Visible and NIR ranges, respectively.

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INV06

Si-Si Hydrogenolysis and C-C Coupling Rationalized by Theory

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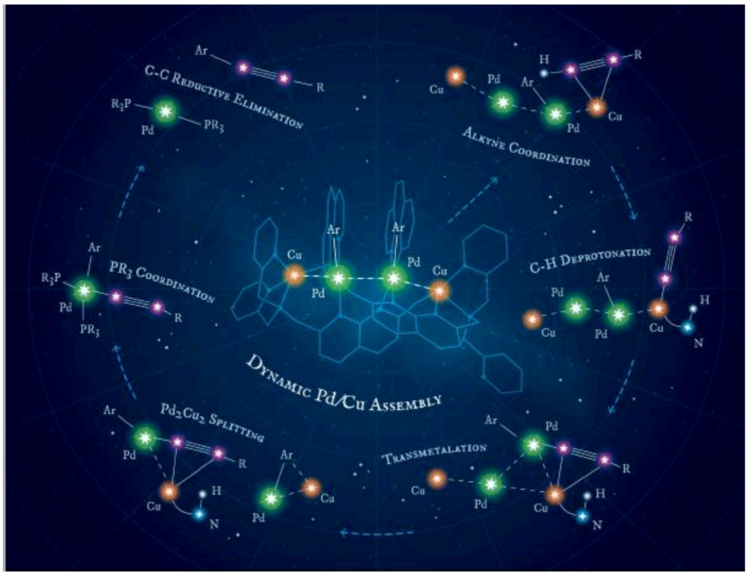
Our recent computational work on organometallic systems evaluated the hydrogenolysis of polysilanes catalyzed by low-valent nickel complexes and the Sonogashira C− C bond coupling reaction by bimetallic Pd and Cu centers.[1,2]

The hydrogenolysis of Si−Si bonds is scarcely studied, requiring harsh conditions and being unselective. In the first part of the talk, we will describe and rationalize via theoretical methods a highly selective catalytic hydrogenation of oligo- and polysilanes proceeding under mild conditions. New low-valent nickel hydride complexes are used as catalysts, forming secondary silane, $RR'SiH_2$, in high purity.[1]

The second part of the talk will focus on the Sonogashira C− C bond coupling reaction. For this reaction, an interaction between the Pd and Cu centers is suggested in the transmetalation step. Still, a detailed understanding of the metal-metal cooperation for this system has remained elusive. Our joint experimental and computational study of Pd/Cu assemblies allows obtaining detailed information on the bimetallic cooperativity, revealing the importance of rearrangements of the highly dynamic multimetallic at the various steps of alkyne activation and transmetalation.[2]



Dynamic Pd/Cu assembly in Sonogashira Coupling

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INV07

Metal Catalysed Transformations at the Surface of Graphene Materials

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Graphene is a particularly interesting material to study superficial phenomena and in particular metal catalysed processes. In the last years, we sought to investigate the role of graphene as support for catalytic transformations. For this purpose, we developed synthetic procedures that allow direct immobilization of well-defined organometallic species and metal nanoparticles onto the surface of graphene.[1–3]

In this communication, we discuss the influence of graphene in catalytic transformations. The catalytic properties with and without the support are evaluated in different benchmark catalytic reactions. The results suggest that the use of graphene as support increases the stability of active species improving the catalytic activity.[4,5]

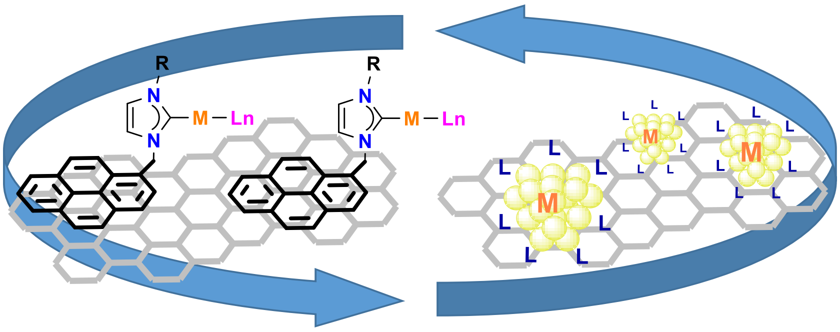

Fig. 1. Immobilization of organometallic complexes and MNPs on the surface of graphene.

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INV08

Bimetallic chemistry featuring low-valent group 13 metals

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Developing new catalytic methodologies to activate otherwise dormant chemical bonds is essential for advancing synthetic chemistry. In this context, transition metals have long dominated catalysis.[1] However, we have witnessed the renaissance of main group systems in recent years as powerful alternatives for redox catalysis.[2] For example, low-valent main-group systems can efficiently activate small molecules (H_2, N_2, CO_2, etc.) and even engage in two-electron redox catalysis.[3]

Our group has been working over the last years towards developing novel bimetallic systems featuring main group metal systems for catalytic applications, in particular, low-valent group 13 systems. This presentation will highlight our latest findings on this topic.[4] These systems feature low-valent Al(I), Ga(I) and In(I) species exhibiting distinctive bimetallic M···M interactions with *s*- and *d*-block metals. Interestingly, these bimetallic systems display unique M···M electronic/structural configurations prime for reactivity with small molecules (H_2, olefins, alkynes) and catalysis. The activation/catalytic mechanism related to their M···M interactions will also be discussed.

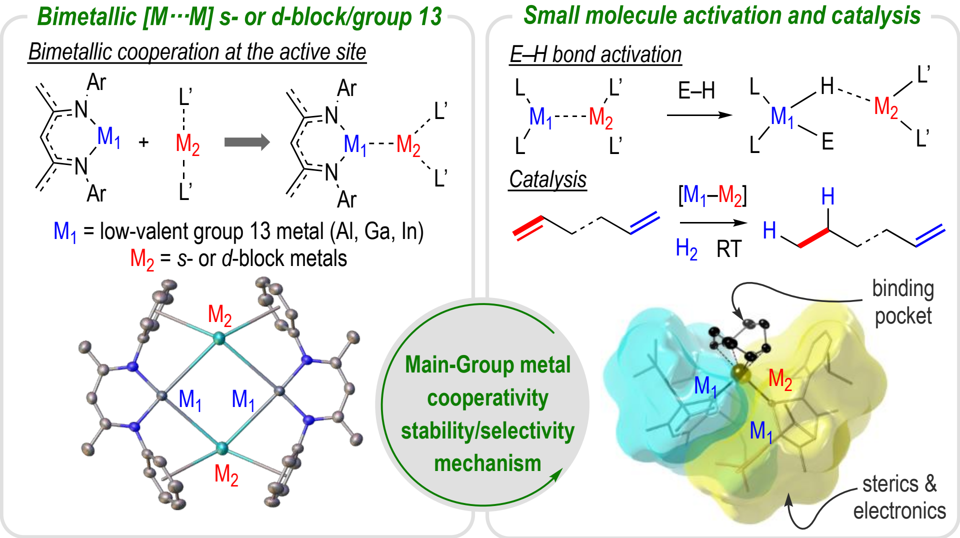

Figure 1. Low-valent group 13 bimetallic chemistry and catalysis.

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Tetragonal Prismatic Nanocapsules as Supramolecular Masks for Regioselective Functionalization of Fullerenes

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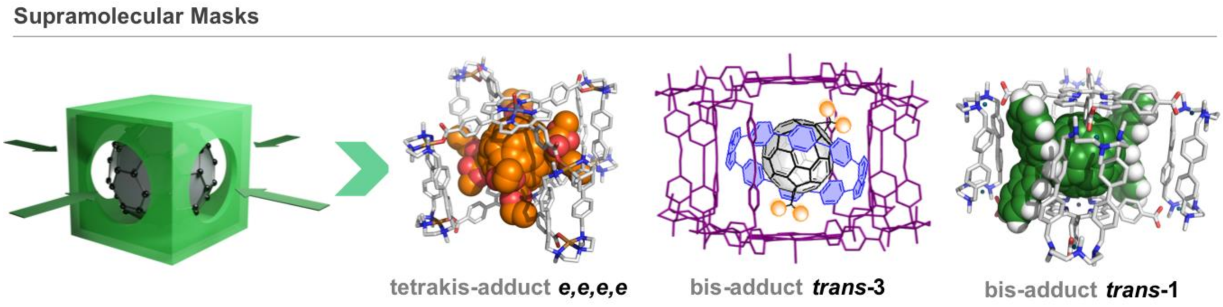
The regioselective functionalization of fullerenes and the control of the number of adducts is highly important to unbar the development of fullerene chemistry.[1] Nowadays, easy-accessible C_{60} and C_{70} fullerene mono-adducts are mainly used in any application due to the hampered accessibility to pure alternative fullerene poly-adduct derivatives. In a general basis, multi-adduct mixtures with uncontrolled regioselectivity (multi-isomers) are obtained, and chromatographic purification is too costly and time consuming to be used in the synthesis of multi-adduct fullerene species. Herein, porphyrin-based supramolecular tetragonal prismatic nanocapsules[2,3] are used as supramolecular shadow masks to tame the over-reactivity of Bingel-Hirsch-type cyclopropanation reactions and, more importantly, to have full control on the equatorial regioselectivity and on the number of additions. Thus, exclusively equatorial bis-, tris- and tetrakis-C_{60} adducts using ethyl-bromomalonate are stepwise obtained and fully characterized (NMR, UV-vis and XRD). Furthermore, the regioselectivity control is finely tuned using a three-shell Matryoshka-like assembly towards the synthesis of a single *trans*-3 bis-Bingel-C_{60} for the first time.[4] Also, the mask strategy is extended to Diels Alder reactions with full control of the regioselectivity in the synthesis of *trans*-1 bis-pentacene-C_{60}. These results, fully attributed to the confinement control imposed by the capsule's cavity, represent a novel and unique strategy to infer regio-control to the synthesis of fullerene multi-adducts. We envision that the described protocol will produce a plethora of derivatives for their implementations in a variety of applications.



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INV10

Bimetallic Frustrated Lewis Pairs and Related Systems

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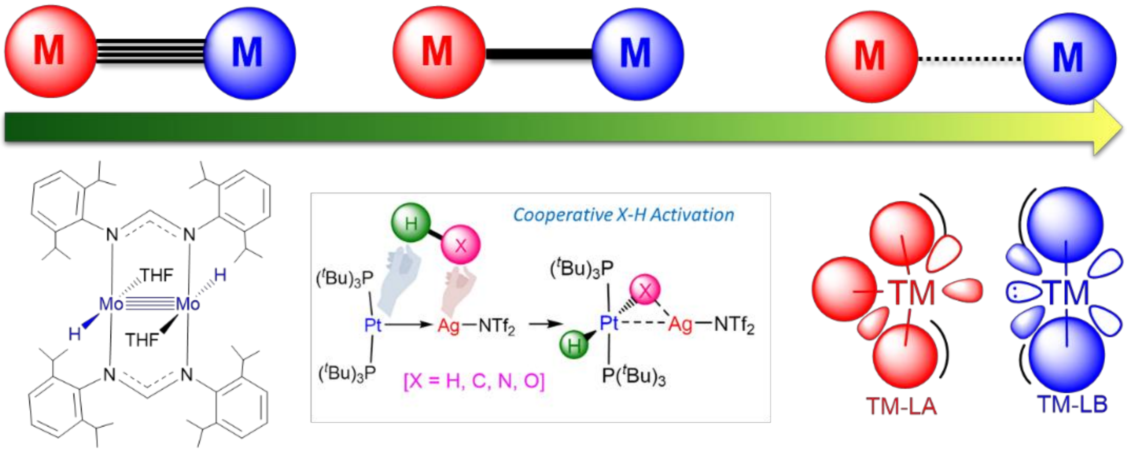
The field of bimetallic cooperation in homogeneous systems has become a hot research topic with a plethora of possibilities for bond activation and catalysis. In fact, there are many important transformations that require the concerted action of pairs of active metal sites, paralleling what is often found in metalloenzymes. Besides, proximal metal sites offer tunable features beyond those found in mononuclear species, as M-M bond order and polarity or single-site versus multi-site activation.[1] Attending to metal bond order, our group has recently explored systems that goes from multiple M-M bonds to single and polarized bonds or even weak interactions in bimetallic Frustrated Lewis Pairs (FLPs) (Figure). The latter systems merge the concepts of bimetallic cooperation and frustration, that is, introduce transition metals into FLP designs, which offer numerous advantages derived from their rich structural diversity and intrinsic reactivity of transition metals.[2] To avoid the formation of metal-metal adducts we have used sterically hindered ligands, mainly phosphines containing a terphenyl (2,6-C_6H_3-Ar_2) substituent. In the last years we have analyzed the effects of modifying the stereoelectronic properties of these terphenyl phosphine ligands in the competition between the formation of M-M bonds versus M···M frustration and investigated the reactivity derived from a variety of bimetallic systems.[3] Our results pertaining the reactivity and potential in catalysis of a number of bimetallic and pseudo-bimetallic pairs will be discussed.



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ORAL COMMUNICATIONS

Filling the gaps in the challenging asymmetric hydrogenation of alkenes with new Ir-P,N catalysts

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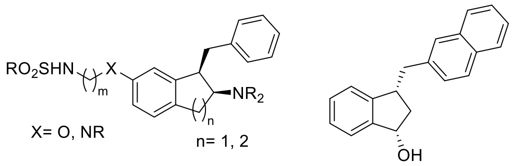
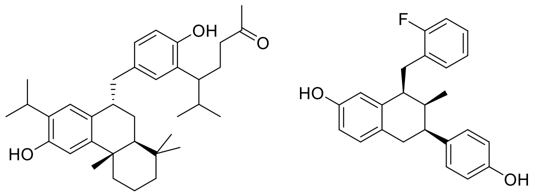
Metal-catalyzed asymmetric hydrogenation is a powerful and sustainable method for preparing chiral compounds due to its perfect atom economy.[1] However, most catalysts are only tested in benchmark substrates, eluding challenging ones that would yield to more appealing compounds, such as exocyclic olefins with a benzofused five/six-membered ring motif, whose hydrogenation products are present in pharmaceutical natural products and key bioactive drug intermediates (Figure 1).



GlyT1 inhibitors[5b,d]
(schizophrenia treatment)

Indatraline analogue[5f]
(treatment of synucleinopathies)



Sugikurojin I[5g]
(from *Cryptomeria japonica*)

Tetrahydronapthalen-2-ol derivative[5e]
(prostate cancer treatment)

Figure 1.

Compared to the considerable number of reports about the reduction of unfunctionalized acyclic and endocyclic olefins, the reduction of unfunctionalized exocyclic olefins is underdeveloped. Only the Ir/In-BiphPHOX catalyst have reported a high catalytic performance in a range of exocyclic benzofused five-membered olefins (93-98% ee).[2] However, the enantioselectivity was lower in the reduction of the parent benzofused six-membered olefin (75% ee). Additionally, the reaction required an additive and a specific solvent (o-xylene), moving away from the commonly used solvents in Ir-catalyzed asymmetric hydrogenation. The difficulty in the reduction of this type of benzofused five/six-membered olefins is even more evident if we consider that PHOX, which are the most successful ligands for Ir-catalyzed hydrogenation, did not work. Herein, we present a new and simple chiral phosphine-triazole ligand for the asymmetric Ir-catalyzed hydrogenation of exocyclic benzofused alkenes.[3] Overcoming previous limitations, the new catalytic system can successfully hydrogenate a series of exocyclic olefins bearing a benzofused five- and six-membered ring motif (ee's up to 99%). The catalyst tolerates well the presence of several substituents and substitution patterns at both aromatic rings. Mechanistic studies explain the origin of this exceptional high catalytic performance.

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Luminescent Pt(II) Complexes with a N^C^C Ligand: Effects of Ancillary Ligands and Aggregation

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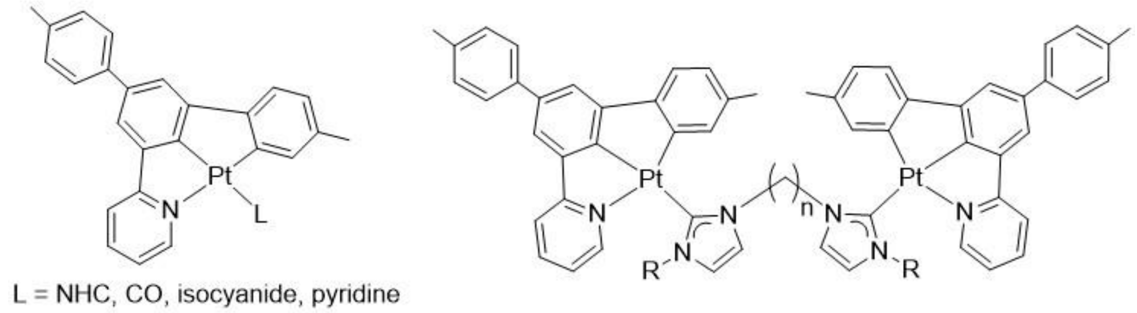
Pt(II) complexes with chelating heterocyclic ligands have been extensively studied for their photoluminescence properties and their applications as phosphorescent dopants for organic light-emitting devices (OLEDs)[1] and probes for cell imaging.[2] Among them, those with cyclometalated 2-arylpyridines have been by far the most studied, whereas derivatives with terdentate or tetradentate ligands have been developed to achieve increased rigidity and enhanced emission efficiencies.[3] Although a few Au(III),[3] Ir(III)[4] and Pd(II)[5] complexes with terdentate N^C^C ligands have been reported, related Pt(II) species are unknown. The presence of two adjacent, strongly σ-donating C-donor moieties is expected to greatly destabilize deactivating ^{3}MC excited by inducing a large ligand-field splitting, leading to enhanced luminescence. Hence, we anticipate that N^C^C ligands could become a great platform for the design of luminescent Pt(II) species.

Here we present the first cyclometalated Pt(II) complexes that bear a terdentate pyridylbiphenylene ligand. An novel photochemical cylometalation methodology has been developed to introduce the N^C^C ligand and different derivatives, including dinuclear species with bridging di(NHC) ligands, have been synthesized (Figure 1). Their photophysical properties will be discussed, with special focus on the influence of ancillary ligands and aggregation on their luminescence.



L = NHC, CO, isocyanide, pyridine

Figure 1

Acknowledgements

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OC03

Heck Reaction: Catalytic Precursors of Nickel (0), (I) and (II) Stabilized with Imino-Phosphine Hybrid Ligands

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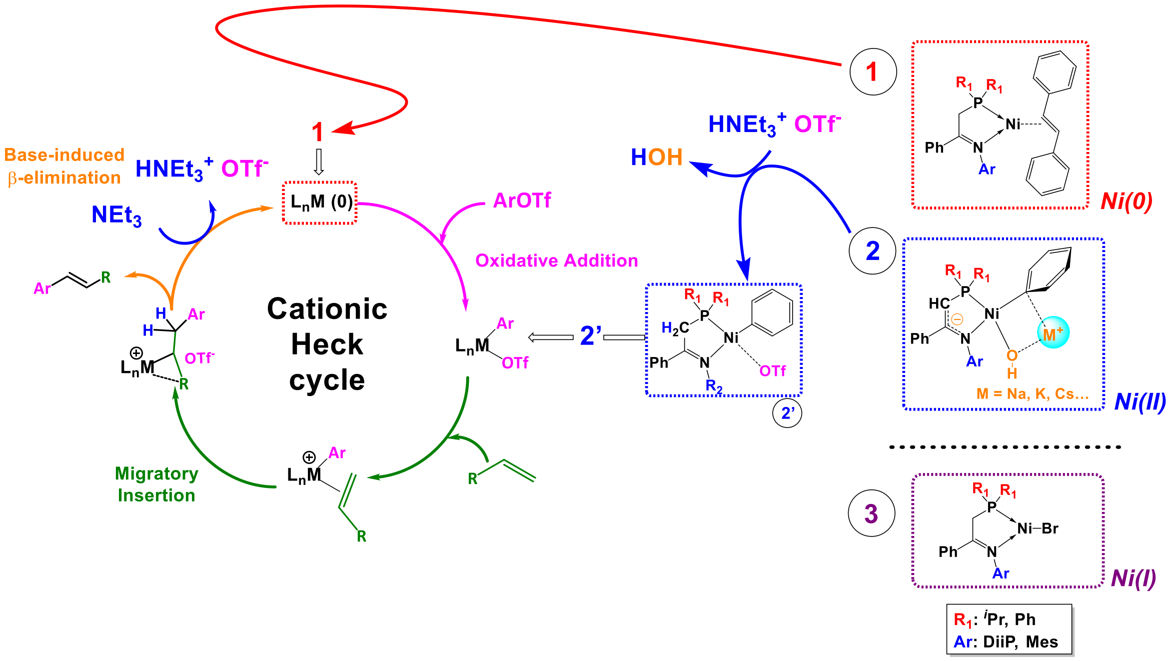
Cross-coupling reactions mediated by transition metals are a powerful tool for the formation of Carbon-Carbon bonds, they are versatile and provide a wide field of application in organic synthesis.[1] One of the most important and well-known is the Heck Reaction.

By far, Palladium (Pd) is the most efficient metal to carry out the Heck Reaction. However, the scarcity of this element, and the strong increase in its cost in recent years, makes it advisable to search for alternative catalysts, based on the use of other more abundant and less expensive metals. Among these alternatives, Nickel (Ni) is positioned as the most obvious replacement since both elements share similar and critical chemical characteristics for the process.[2]

Despite the lower catalytic efficiency of Ni with respect to Pd at present,[3] the truth is that an important part of the promotion of this catalysis is the presence of organic ligands that stabilize the metal, providing different reactivity, being able to direct them, towards levels of catalysis not attainable by the metal alone.

Among all the possibilities of hybrid ligands that currently exist, we focus on a series of Imino-Phosphine Hybrid Ligands (PN Ligands) developed in our research group. These can stabilize Ni complexes with different oxidation states and incorporate them as precursors in the Heck Reaction, completing the catalytic cycle.



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Supramolecular gold(I) aggregates: the effect on photophysics

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The formation of gold(I) supramolecular aggregates is an important tool from different perspectives. On one hand, the modulation of the possible assemblies with different sizes and shapes starting from single molecules is a challenge for the chemistry community and even more, trying to have a control on it. On the other hand, when our molecules present a chromophore we can also tune the resulting colors that come upon aggregation.[1]

Regarding this, in the last years we have developed different series of gold complexes that have been explored on this topic. Thus:

- we have managed to obtain very long fibers, rods and vesicles (Figure 1) with yellow, green and red emission;[2]
- we have also been able to modulate the assemblies from a reversible manner by the addition of an external metal cation that can be removed by a sequestrant agent;[3]
- we can form nanomaterials with different sizes by the reduction of gold(I) supramolecular precursors;[4]

Having this background into consideration, we show here the formation of new vesicle structures starting from gold(I) complexes containing a coumarin chromophore and a polyethyleneglycol long chain.[5] The assemblies have been characterized by different techniques (NMR, DLS, SAXS, OM, FM, SEM, CryoTEM). The empty inner cavity of the vesicles has been detected by photophysical assays using a quencher. These assays let us to determine the number of molecules involved in the aggregates. DFT calculations together with photophysical characterization support that the assemblies are established through $\pi-\pi$ interactions between the coumarin units.

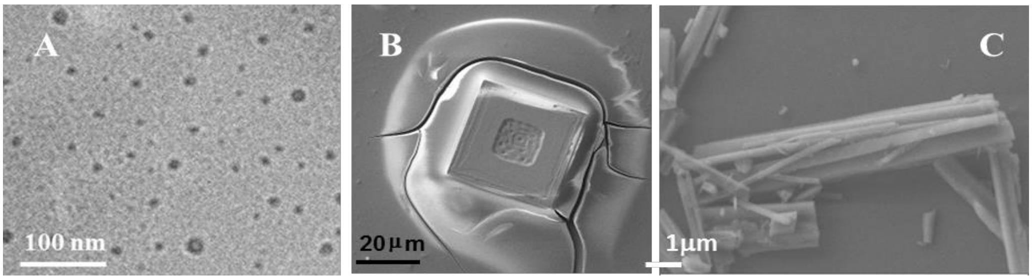

Figure 1. SEM images of the supramolecular gold(I) aggregates previously reported in our group.[2]

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OC05

Metal-allyl Chemistry for the Preparation of Chiral Complex Cyclic Molecules

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Chiral carbo- and heterocyclic cyclic motifs are present in a large number of natural products and drugs. Traditionally, such motifs have been prepared by taking advantage of the chiral pool or by tedious resolution procedures.[1] Over the last decades, Pd-allyl chemistry has become a more sustainable alternative for the preparation of such molecules. [2] In this context, the InnCat group has a long history in the rational development of new chiral ligands for Pd-catalyzed allylic substitution reactions.[3] In this communication, I will show our latest developments in the use of Pd-allyl chemistry for the preparation of an assorted set of chiral carbo- and heterocyclic compounds containing multiple stereogenic centers.

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OC06

Highly Fluorescent Ortopalladated GFP/Kaede-Chromophore Analogues: Synthesis of Organometallic 4-Aryliden-5(4H)-Oxazolones

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Over the past decades, luminescent organic and organometallic compounds have attracted a great deal of attention, especially for their applications in organic light-emitting devices (OLEDs).[1] Unlike iridium and platinum complexes, luminescent palladacycles are exceptions, and it is often found that the palladation of luminescent ligands causes a drastic decrease in luminescence.[2]

In this work we report how the cyclopalladation promotes the amplification of the fluorescent properties of 4-Aryliden-5(4*H*)-oxazolones by suppression of the hula-twist non-radiative deactivation pathway [Figure 1], obtaining fluorescent quantum yields (ϕ) up to 28%, a very good value for a palladium complex. We also study by TD/DFT how the electronic characteristics and position of the substituents in the arylidene ring affects the photophysical properties.

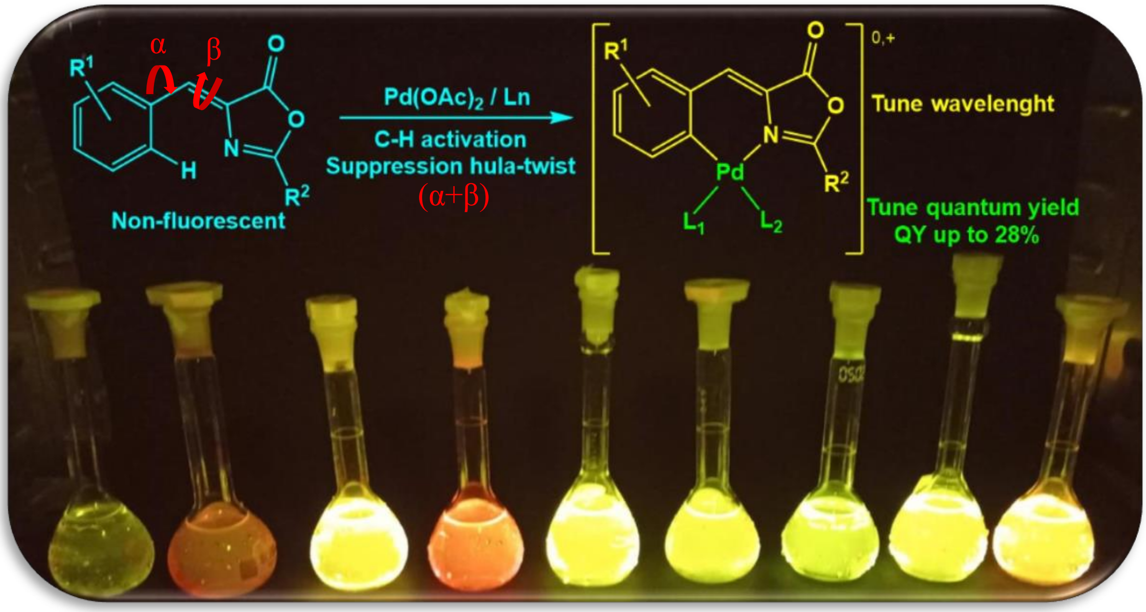

Figure 1. Fluorescence amplification by suppression of “hula twist”

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OC07

Nickel complexes with Chiral *N*-Heterocyclic Carbene: Synthesis and Catalysis.

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N-Heterocyclic carbenes (NHC) are a family of ligands capable to stabilize metal species. They form robust bonds to metals, due to their outstanding σ-donor coordinative nature, and exert steric protection to the M–C bond through the *N*-substituents.[1] We have synthesized enantiomerically pure complexes of Ni from the imidazolium salts and a metal source, and obtained single-crystals of many of them.[2] X-Ray diffraction studies show the carbene ligand in a *C,O*-chelating mode of coordination through the carbenic carbon and the carboxylate group, so that, unlike other complexes found in the bibliography, this type of compounds does not require another counteranion ligands. The structures have also been confirmed by HRMS and appears to be same in solution, according to the NMR data collected.

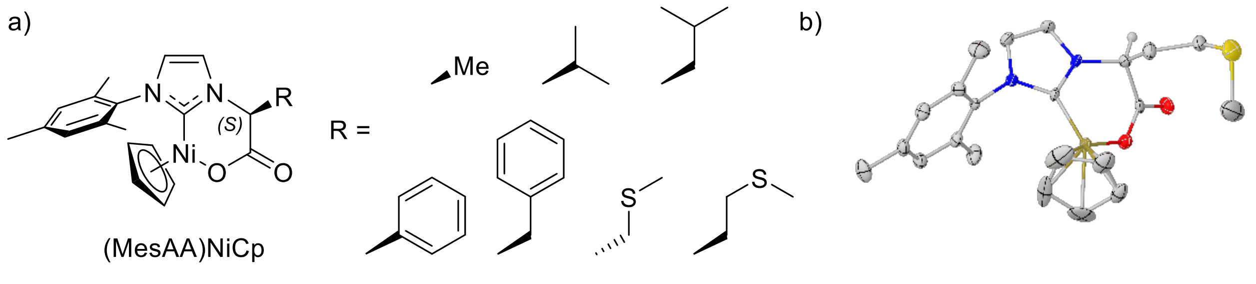

Figure 1. a) Amino acid derived NHC complexes of Ni. **b)** Solid structure of the complex derived from (*L*)-methionine.

Here we will present out results in the synthesis of the new complexes, and preliminary outcomes on their use as catalysts in reactions such as the hydrogenation of ketones in THF, or in water, both with $PhSiH_3$ and in mild conditions.

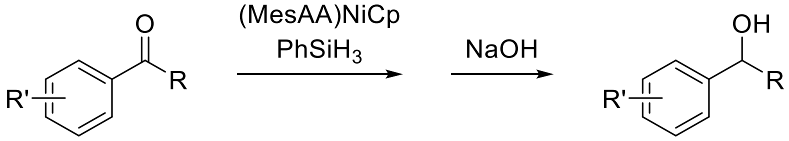

Figure 2. Amino acid derived NHC complexes as catalyst in in hydrogenation.

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Cyclometallated Pt(II)/Ag(I) Luminescent Compounds for the Fabrication of Optical Devices

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Cyclometallated platinum(II) compounds are known to display phosphorescence emission arising from ^{3}IL or ^{3}MLCT transitions at room temperature, with high quantum yields and luminescence lifetimes of a few microseconds. [1] Particularly, [N^C^N] cyclometallated compounds derived from 1,3-di(2-pyridyl)benzene are able to form aggregates through non-covalent interactions such as π-π stacking or metallophilic interactions. The latter are responsible of the formation of ^{3}MMLCT emission bands that appear at lower energies, which is of interest for the fabrication of optoelectronic devices such as OLEDs or solar cells, among others. [2]

Several examples are reported in the literature of the synthesis of heterometallic compounds by the addition of one or several silver(I) atoms to a platinum complex that contains a triple bond. This allows the approximation of two or more cyclometalladed platinum(II), arising in the appearance of new intermolecular interactions that can influence the luminescence of the final compounds. [3]

In this work, starting from several cyclometallated [N^C^N] platinum(II) compounds with aromatic alkynyl ligands, we synthesized a family of heterometallic compounds where two platinum moieties are bound together by a silver atom that coordinates to two triple bonds. For that, the stoichiometry of the final compounds was first determined by titrations followed by luminescence emission. All compounds present an emission in solution shifted to the red with respect of their precursors and a fully red emission in solid state. An exhaustive photophysical study of these compounds both in solution and in thin films revealed their suitability for the preparation of optical devices.

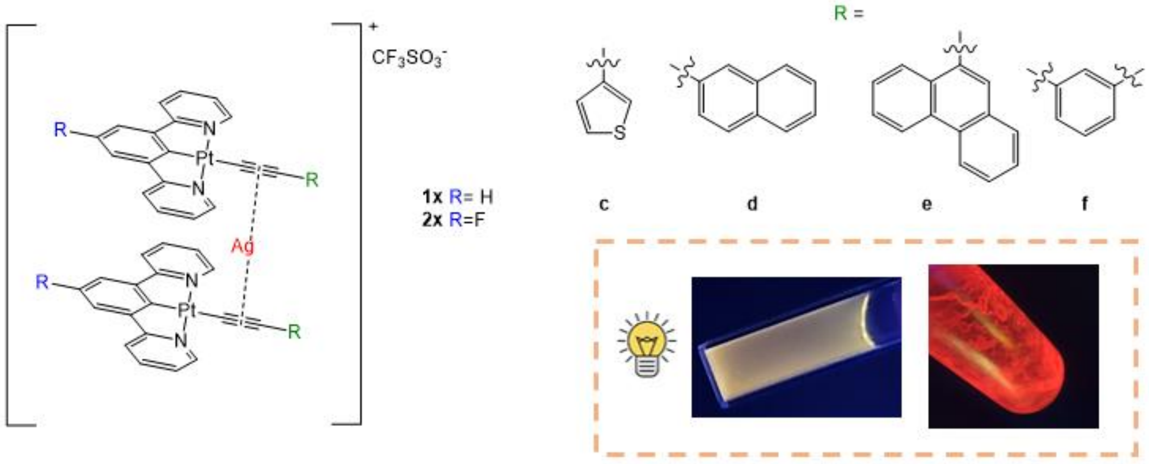

Figure 1. Chemical structure of the synthesized cyclometallated Pt(II)/Ag(I) compounds and their emission in solution and solid state under UV-Visible light.

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OC09

On the Study of the Transmetalation Reaction between [Cu(bipy)(C_6F_5)] and [Fe(Cp)(CO)$_2$I]

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The well-known kinetic inertness of organometallic complexes with electronic configuration d^6 in substitution reactions is due to the loss of stabilization experimented by the "d" electrons when passing from an octahedral geometry to another pentacoordinate or heptacoordinate in the possible intermediates of reaction and transition states. The energy cost of this electronic redistribution significantly increases the activation energy. In organometallic compounds, the predominant mechanism is usually the dissociative one, and substitution reactions are facilitated when the decoordination of the leaving ligand is forced with a third reagent (ie, substitution of carbonyls in the presence of Me_3NO).

Transmetalation reactions are a rather special case of substitution reactions. The entering ligand does not use a non-bonding pair of electrons to start the interaction, instead is a bonding pair of electrons (M-C) that acts as the entering ligand. The transmetalating metal usually acts as an electrophile, extracting electron density from the halide to be substituted, which facilitates its removal. Finally, transmetalation reactions are usually concerted, and often proceed through intermediates and transition states that contain M-M bonds. Thus the substitution reactions cannot be used as models for transmetalation reactions.

Since transmetalations reactions involving octahedral d^6 complexes have been barely studied, we try to find out the pathways of this class of reactions. This communication deals with the experimental and computational study of the transmetalation between the complexes [Cu(bipy)(C_6F_5)] and [Fe(Cp)(CO)$_2$I] to produce [Cu(bipy)I] and [Fe(Cp)(CO)$_2$(C_6F_5)], as an example of bimetallic system involving d^{10} and organometallic d^6 complexes.

OC10

Oxygen Defence Enzymes: from Aza-Macrocyclic Complexes to Nano-Structured Mimetic Systems

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Copper and manganese have prominent biological roles participating in numerous biological processes, most of them related to dioxygen management and electron transfer. Among these functions, these metal ions are involved as the electroactive metal in the active site of protective superoxide dismutases, which are in charge of regulating superoxide radical concentration in mammals, getting rid of excess amounts of superoxide anions through their dismutation into hydrogen peroxide and dioxygen. Superoxide is the first product coming out from the reduction of dioxygen to give water. Imbalances between generation and clearance of superoxide anions give rise to the formation of all other reactive oxygen species (ROS) causing oxidative stress. Oxidative stress is related to a variety of health issues that include neurodegenerative disorders such as Parkinson's, Alzheimer's and Huntington diseases (AD).[1] Administration of SODs is however not useful for therapeutic treatment due to the drawbacks that they present -such as the absence of oral activity. In this respect, it has been reported that several copper complexes of aza-macrocyclic ligands have SOD activities in vitro which rank among the highest ones so far reported for synthetic systems.[2,3] A step forward to improve the activity, the likely-cell uptake and bio-distribution of these low molecular weight mimetics might be their incorporation in non-toxic nanoparticles (NPs). The grafting of the molecules to the surface of the nanoparticles may yield pre-concentration and amplification of the signal.

Here we discuss the chemistry of new Cu^{2+} aza-macrocyclic complexes appropriately functionalized to permit their covalent anchorage to boehmite oxidic nanoparticles,[4] and we examine the parameters regulating the general SOD activity enhancement observed.

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Structure-Function Studies on Fe NHC-based Electrocatalysts for CO_2 Reduction

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The electrochemical reduction of CO_2 is a challenging reaction of interest from a fundamental perspective and as a candidate for converting an environmentally harmful gas into valuable fuels. Application in large scale of this reaction will likely require the use of catalysts based on affordable and abundant metals.

Organometallic ruthenium complexes bearing a 2,2':6',2''-terpyridine paired with a bidentate ligand containing mixed pyridine-N-heterocyclic carbene are well established electrocatalysts for CO_2 reduction to CO (Figure 1, left).[1] We unraveled the mechanism for this system, and we proved that the two geometrical isomers resulting from the asymmetry of the bis-chelating ligand have completely different behavior in the elementary steps of the catalytic cycle, as a consequence the *trans* effect provided by the strongly donating NHC donor.[2] Recently, we synthesized the iron analogues and established similarities and differences between the catalytic cycle performed by iron and ruthenium complexes.[3]

Now in this contribution, we will discuss the synthesis of an iron complex bearing a symmetric bis-carbene ligand (Figure 1, right), as well as the mechanism of this new electrocatalysts in CO_2 reduction.[4] A combination of NMR spectroscopy, cyclic voltammetry, spectroelectrochemistry and DFT calculations have established the effect of the primary coordination sphere on the mechanism of this family of electrocatalysts.

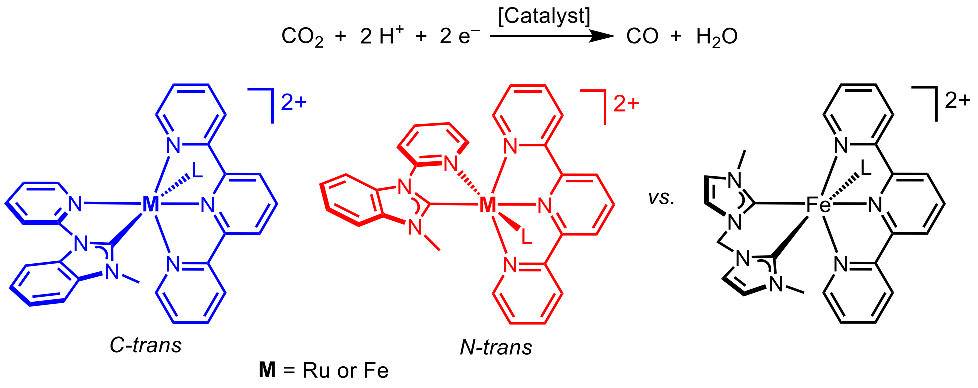

Figure 1

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OC12

DFT and machine learning techniques towards the study of copper-catalyzed Suzuki-Miyaura reactions

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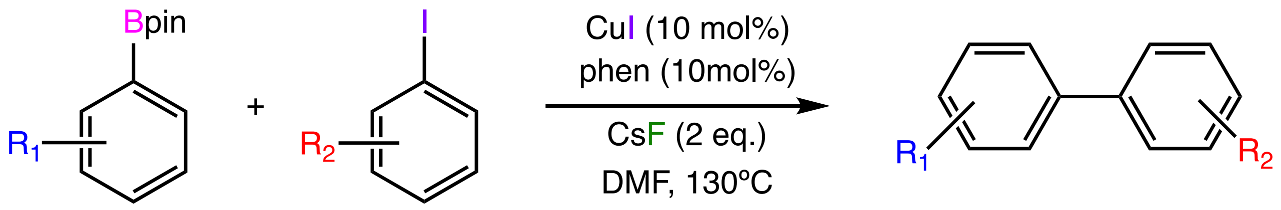
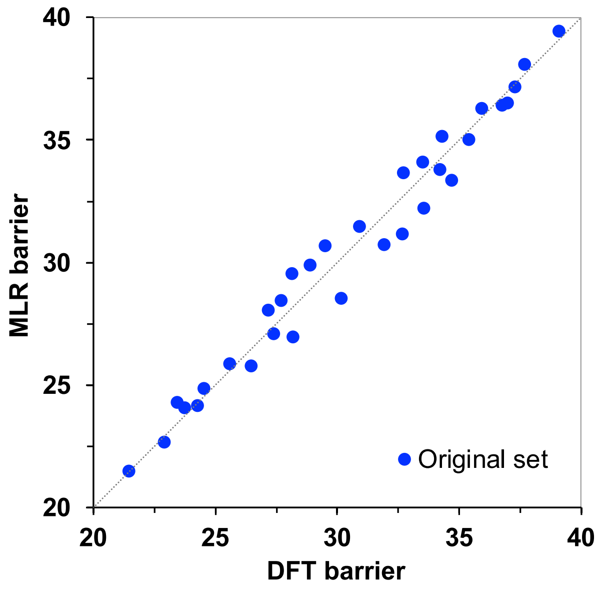
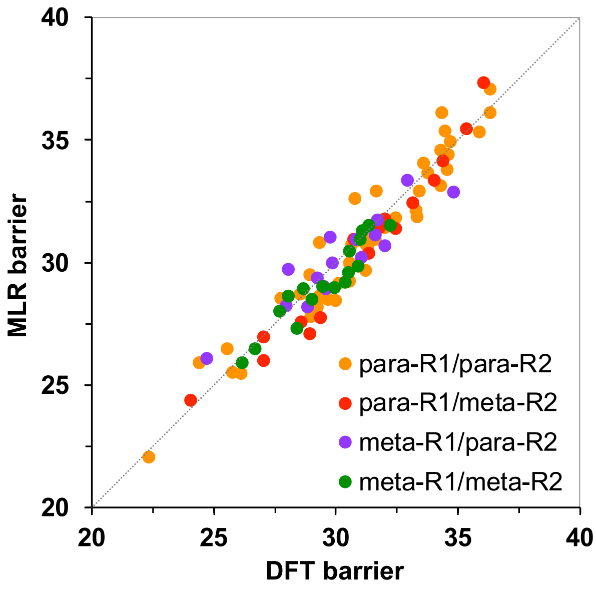
Copper catalysts can be successfully employed as a replacement in reactions employing precious metals such as Pd. A good example of this is the Cu-catalyzed Suzuki-Miyaura coupling between aryl boronate esters and aryl iodides.[1] This reaction has been computationally explored to propose a plausible mechanism that is able to explain the observed reactivity.



Once a reasonable mechanism has been determined, DFT calculations coupled with machine learning techniques have been applied to compute and predict the overall reaction barrier of reactions where the substituents on the boronate ester (R_1) and aryl iodide (R_2), placed in *para*- and *meta*-positions, cover the full range of electronic properties. In this way we can compute and predict the overall reaction barrier of any reaction of the same type by just computing the CM-5 charge of the boron atom of the boronate ester and the charge of the *ipso* carbon of the aryl iodide.





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On the Nature of Gold(I) Vinylidenes

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Gold(I) vinylidenes have been proposed as potential intermediates in some gold-catalyzed transformations [1]. However, their high reactivity has hampered their direct study [2]. Only one gold(I) vinylidene highly stabilized by two silyl groups has been characterized by NMR, although its structure is very different from species proposed as genuine catalytic intermediates [3]. Our group had recently synthesized highly reactive gold(I) carbenes, formed from stable gold(I) carbenoids [4].

Now, we have developed a method to generate gold(I) vinylidenoids from simple gold(I) chloride complexes, which, by reaction with $GaCl_3$ at -90ºC, give rise to (η^2-diarylacetylene)gold(I) complexes via 1,2-aryl migration (Figure 1).

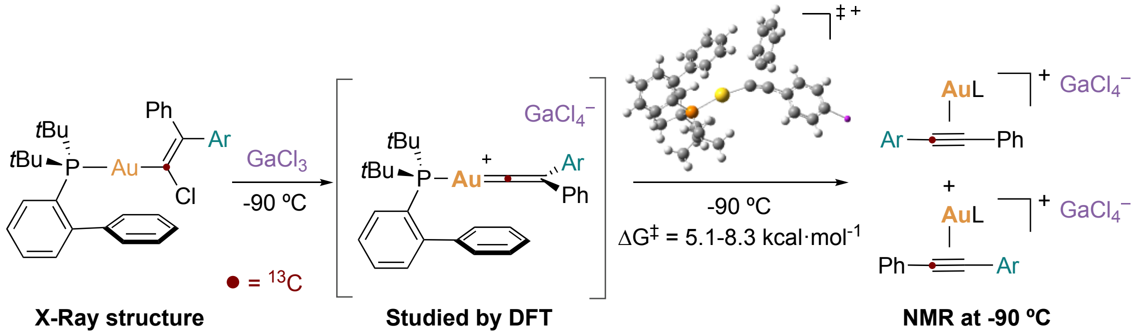

Figure 1. Present study.

The NMR study of this reaction with ^{13}C labelled gold(I) vinylidenoid complexes, combined with DFT studies, allowed us to investigate the mechanism of this transformation.

Acknowledgements

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Hexagonal Planar Complexes: Coordination Chemistry and Reactivity Studies

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The geometry of transition metal complexes is a central aspect of coordination chemistry and has a profound impact on the bonding, reactivity and potential applications of these compounds. Our group recently reported a remarkable 6-coordinate complex featuring an extremely unusual hexagonal planar geometry.[1]

The complex possessed a central Pd atom surrounded by three hydrides and three Mg metalloligands. We now report a deeper study on this unusual complex, as well as two new analogues, including a new hexagonal planar complex with Pt as transition metal. The other analogue has Zn atoms in place of Mg and has a similar but subtly different structure, which is best described as a trigonal planar tris-σ(Zn–H) complex. Insight into this divergent coordination behaviour has been obtained.

With a better understanding of the coordination chemistry of these complexes, we moved to exploring their reactivity and potential in catalysis. The Pd/Mg hexagonal planar complex reacted quantitatively with H_2 gas to afford a new heterometallic complex featuring 4 hydrides and 2 Mg atoms around the Pd centre. This complex possesses a new coordination motif, which was subjected to further study. Analogues with Pt could be independently synthesised and fully characterised.

The reaction with H_2 proved to be reversible and the discovery that both oxidative addition and reductive elimination could be performed by this complex was leveraged to develop an efficient catalytic protocol for H/D exchange reactions, achieving D-incorporations over 99% under mild conditions. In summary, this study showcases how these unusual heterometallic complexes are not only structural curiosities but catalytically relevant species with great potential for reactivity and catalysis.

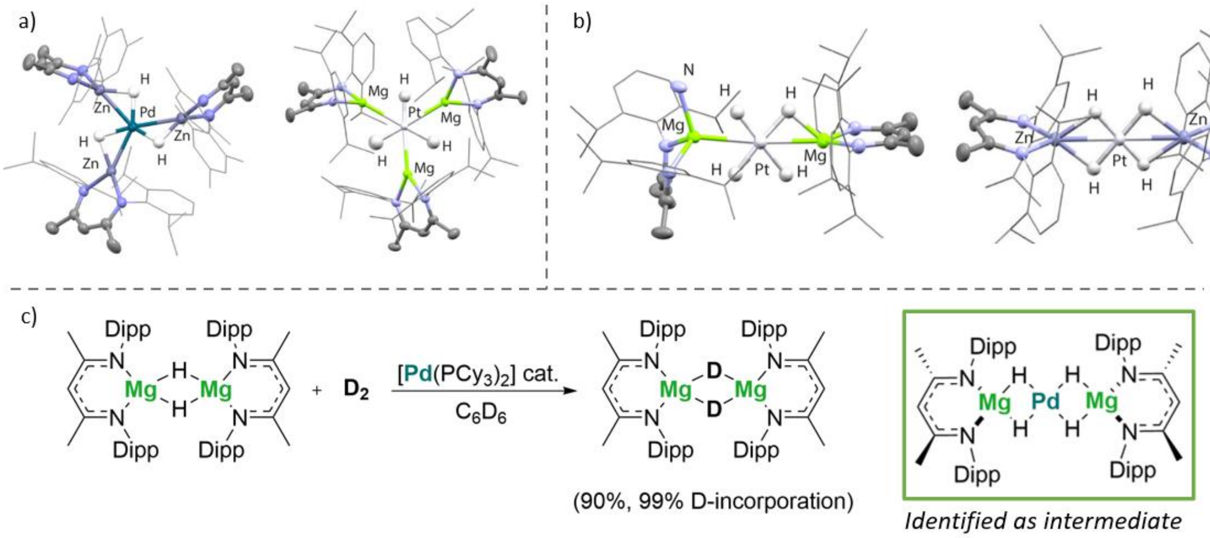

Figure 1. a) X-ray structures for trigonal Pd/Zn and hexagonal Pt/Mg complexes. b) Heterometallic tetrahydride complexes. c) Catalytic H/D exchange reaction.

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Development of a new Non-Innocent platform for Metal-Ligand Cooperative catalysis with group 10 metals

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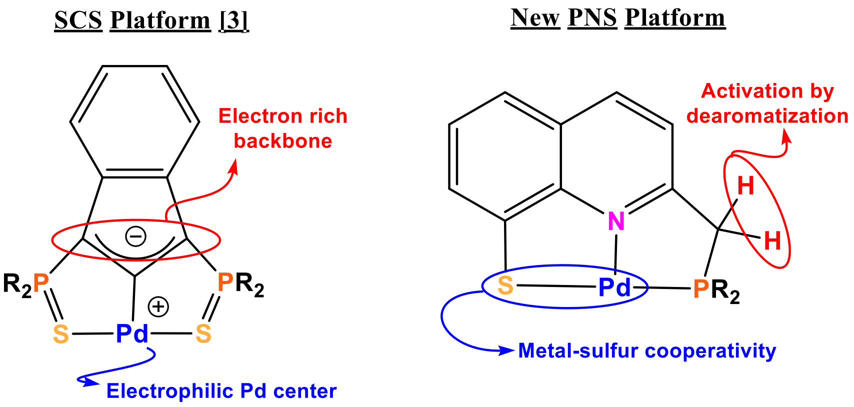
Over the last decade, cooperative effects in transition metal catalysis have attracted increasing interest from the scientific community. Thanks to the synergy between two different catalytic sites, extraordinary improvements in efficiency and selectivity can be achieved. In this context, metal/ligand cooperation (MLC), in which one of the ligands participates actively to the activation of the substrates, can be highlighted [1]. In this domain, pincer complexes of transition metals play an important role. One of the most representative models was reported by Milstein [1], based on an aromatization/dearomatization process of a pyridine-based pincer ligand.

Although group 10 metals are widely used in catalysis, they are much less studied in MLC than metals of group 8 and 9 [2]. Indeed, the two active sites are further away in the square planar geometry of d^8 complexes of group 10 metals. In this context, our group has reported an indenediide Palladium complexes bearing an electron rich backbone [3]. Remarkable results have been obtained in catalytic cyclisation processes involving C-O/C-N & C-C bonds formation.



To further develop MLC with group 10 metals, we are now working on a new platform deriving from the quinoline moiety that can combine two types of non-innocent behavior. The activation can occur either via aromatization/dearomatization of the quinoline moiety or may involve the sulfur atom as described by Ohki & Oestreich [4]. The synthesis of the ligand and its coordination to group 10 metals will be presented. Evidence of the accessibility of both mode of cooperativity will be provided along with emerging catalytic applications.

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OC16

Neutron Scattering: a valuable technique to study metal-mediated processes in water.

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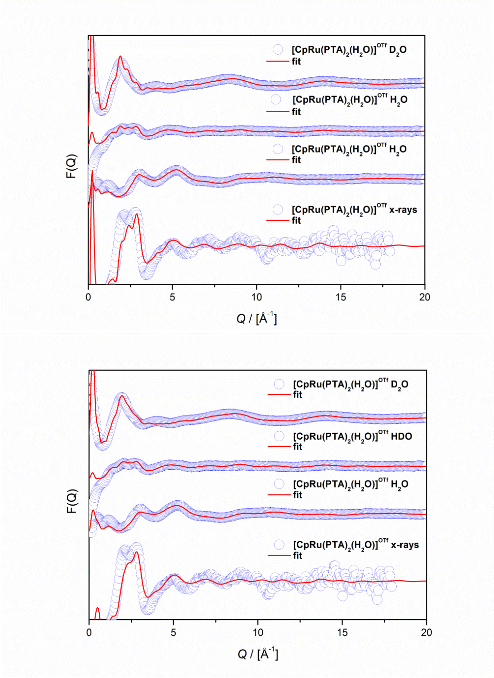
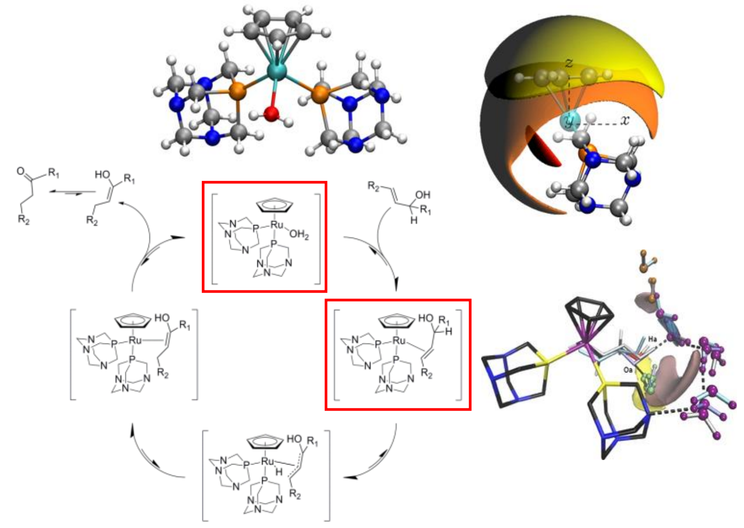
Experimental techniques and theoretical methods such as respectively NMR and DFT calculations can provide some indications on how metal and metal complexes participate in chemical processes in water, which are however typically insufficient. The EPSR (Empirical Potential Structure Refinement) method can refine the structure of the solute and to compute spatial water probability distribution functions by using data from neutron scattering measurements. The combination of NMR, DFT and EPSR (left Figure) offer significant information to propose precise mechanism on how water molecules participate in metal-mediated processes such as synthetic reactions catalyzed by metal complexes. This procedure was used to study the isomerization of lineal allylic alcohols in water catalyzed by the complex [RuCp(PTA)$_2$(H_2O-κO)] (PTA=1,3,5-triaza-7-phosphaadamantane) [1,2]. This reaction can only proceed in presence of a proportion of water more than stoichiometrically needed. The combination of the three techniques reveled that water plays an important role as solvent but also interacting with catalytic reaction intermediates (right, Figure), determining how the reaction proceeds and the final TON and TOF [3,4].





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Redox-Switchable Catalysis with Napthanelenediimide-derived NHC Complexes

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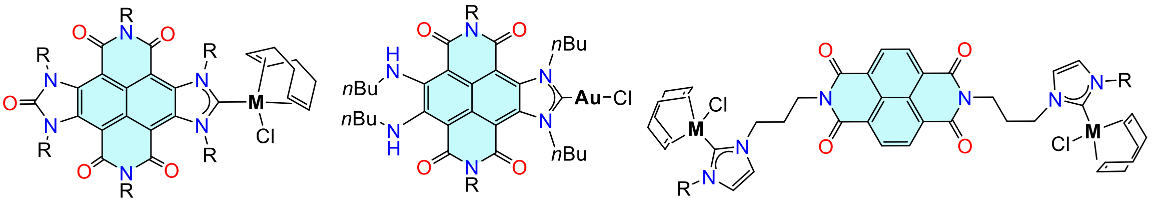
Redox-active ligands can modify their electron-donating character by accepting or releasing electrons. This means that the catalytic activity (or selectivity) of the complex depends on whether the redox-active ligand is acting in its neutral or oxidized/reduced forms, and so the corresponding catalyst may be used to alter a chemical reaction on demand. NHCs have been particularly fruitful in the generation of redox-switchable catalysts, [1] but those containing fluorescent dyes are still scarce and so pose a potential opportunity. [2]

In this regard, we recently described three families of NHC ligands functionalized with a naphthalene-diimide (NDI) dye, which is amenable to reduction, and we studied their behavior as redox-switchable ligands. The Ir and Rh(I) complexes **1** were tested in the cycloisomerization of alkynoic acids, where the one-electron reduction of the ligand produced a great enhancement on the catalytic activity of the process. [3a] The same effect was observed upon the reduction of the dimetallic complexes **3**, bearing an NDI unit electronically disconnected from the two NHC units, which performed excellent even for the most challenging substrate. [3b] Conversely, the activity of the Au(I) complex **2** in the hydroamination of phenylacetylene with anilines was suppressed in the presence of a reducing agent. [3c]

We employed our results for elucidating mechanistic aspects of the two catalytic cycles, as the study of the influence of the electronic-donating character of the ligands in particular steps of the catalytic process could be performed in a more accurate and controlled way by using ligands with tunable electronic-donating power.



1, M = Rh, Ir **2** **3, M** = Rh, Ir

Figure 1. NDI-NHC-based complexes described in this work

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OC18

Modelling Host-Guest Catalysis by Metallocages

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Host-guest catalysis merges the fields of catalysis and host-guest (supramolecular) chemistry.[1] Encapsulation of molecular guests (reactants) into supramolecular hosts (metallocages) is a complex molecular recognition process. In order to enter the host, the guest must displace solvent molecules from the cavity. Moreover, the host must somehow be deformed to let the guest in. A molecular/computational description of the encapsulation process would provide valuable insights into the physicochemical properties that guide it.

For many processes the reaction rate is greatly enhanced when reactants are encapsulated. Here we present a multiscale computational investigation on the encapsulation process as well as the origin of the acceleration rate for several studied processes.[2] We selected the most relevant reactions catalyzed by the tetrahedron metallocage $K_{12}[Ga_4L_6]$ developed by Raymond and coworkers.[3] We will describe how the nature of the guest, the motion of the metallocage, and the presence of the (encapsulated) solvent affect encapsulation and their subsequent reactivity.

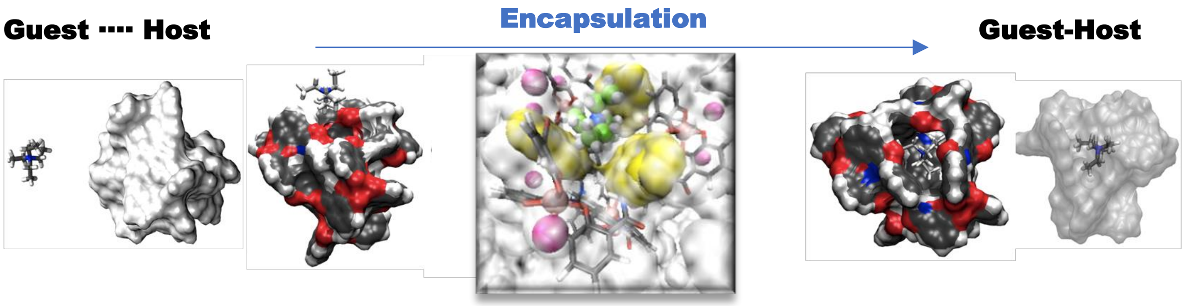

Figure 1: Molecular Dynamics snapshots of a host encapsulation into the guest.

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OC19

The Lord of the Rings. An Extra Ring on a C^N Ligand in Half-sandwich Ir Complexes Changes Dramatically the Orbital Composition and the Photophysical and Biological Properties.

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Photodynamic therapy (PDT) is a clinically approved non-invasive technique to treat cancer. In this strategy, patients are treated with a photosensitizer (PS), which is ideally harmless in the dark, but can be activated upon light irradiation, enabling light-controlled chemotherapy in a spatio-temporal way. The activated PS may generate $^1O_2$ and reactive oxygen species (ROS), which can cause cell death. Octahedral Ir(III) complexes with C^N ligands can act as PSs in PDT due to their outstanding photophysical properties [1]. In this work, new Cp*-Ir(III) complexes with π-extended C^N and imidazole ligands (**Fig. 1**) have been obtained and their photophysical and biological properties studied. They constitute one of the first examples of half-sandwich Ir complexes active in PDT.

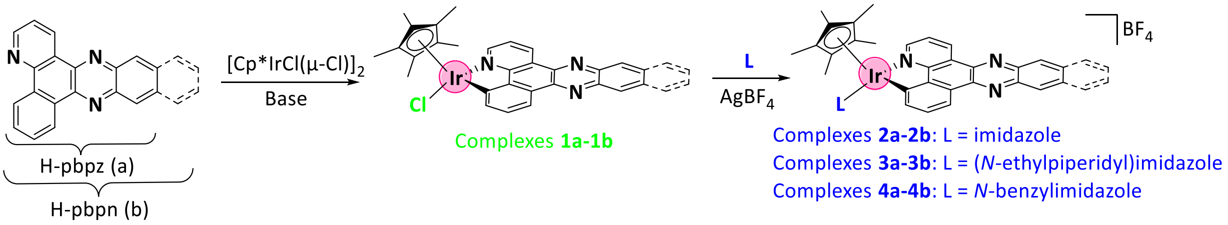

Figure 1. Synthesis of the new half-sandwich Ir(III) complexes.

DFT calculations, carried out for **3a**, **3b**, **4a** and **4b** allows to explain their photophysical properties. The introduction of the extra ring in the C^N ligand in **b** complexes has two important effects: 1) it lowers the LUMO level giving rise to a redshift on absorption and emission and 2) it generates a π molecular orbital (HOMO-1), mainly located on benzoquinoxaline, which is isoenergetic with HOMO. Unlike in **a** complexes, S2 transitions in **b** species, from HOMO-1 to LUMO (π-π*), have the same nature than T1 favouring the intersystem crossing (ISC). The excited state lifetimes, measured by transient absorption spectroscopy (TAS), are much longer for **b** than for **a** complexes (0.976 vs 0.015 μs for **4a** and **4b**) and a different type of emission has also been found: fluorescence for **a** and phosphorescence for **b** species. $^1O_2$ generation studies show a dramatic difference in $^1O_2$ generation quantum yields (Φ_Δ) (0.02 for **4a** and 0.99 for **4b**), due to the most favoured ISC in **b**. According to TAS studies, the interaction with O_2 involves an energy transfer process, which is consistent with the generation of $^1O_2$. Biological studies in the A549 cell line show high cytotoxicity in the dark for the complexes ($IC_{50} \leq 8.0$ μM). Moreover, under blue light, cytotoxicity is hardly improved for **a** species but it is significantly increased for **b** derivatives (PI = 1317 for **3b**) (PI = $IC_{50,dark}/IC_{50,light}$). π-π interactions have been found in the solid state in all the structures determined by X-ray diffraction and also these interactions exist in solution as important changes in the photophysical behavior are observed with the concentration. This outstanding results for pbpn confirm the enormous potential of these complexes as $^1O_2$ sensitizers and as a new class of photoactivatable anticancer drugs.

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OC20

Cooperative sustainable catalysis by scorpionate heterobimetallic Al-Mg complexes

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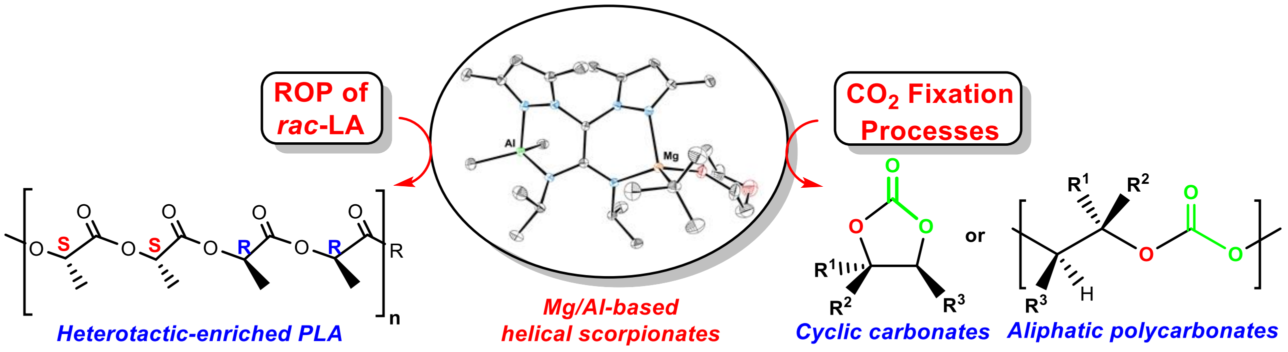
The use of heterobimetallic complexes as catalysts for different organic transformations has emerged as a very promising strategy to increase the efficiency of those processes [1]. The cooperative action between both metal centers arranged in close proximity to each other is crucial for providing higher catalytic performance compared to analogue conventional single-metal systems.

Here, we present a synthetic procedure to obtain a new family of chiral heterobimetallic Mg/Al-based helical scorpionate-based complexes, and describe their use as highly effective catalysts in several sustainable and industrially demanded processes. The presence of a rigid extended planar π-$C_2N_2(sp^2)$–Al/Mg core in these systems enables the cooperation between metals, enhancing their catalytic activity.

We initially studied the use of these compounds as initiators for the ring-opening polymerization of *rac*-lactide, where complete conversion of 200 equivalents is reached after only five minutes at room temperature. Most importantly, a moderate level of control over the stereochemical architecture of the materials produced is reached ($P_r = 0.76$). Interestingly, molecular weight of the obtained polymer samples closely approximates to the expected theoretical calculated values considering one polymer chain per molecule, indicating that both centers do not act independently.

These heterobimetallic scorpionate complexes also display very high efficiency for different CO_2 fixation processes. In particular, they can act, in combination with tetra-n-butylammonium bromide, as excellent catalytic systems in the production of five-membered cyclic carbonates through the cycloaddition of CO_2 and a wide range of epoxides, including mono-, di- and tri-substituted bio-renewable derived substrates, under mild and solvent-free conditions. On the other hand, these complexes were also assessed for the synthesis of poly(cyclohexene carbonate) via ring-opening copolymerization of cyclohexene oxide and CO_2. The materials obtained shows quantitative selectivity for carbonate linkages and the absence of ether linkages.



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OC21

Quadruple Mo≣Mo bonds confronted to *s* and *p* block metals

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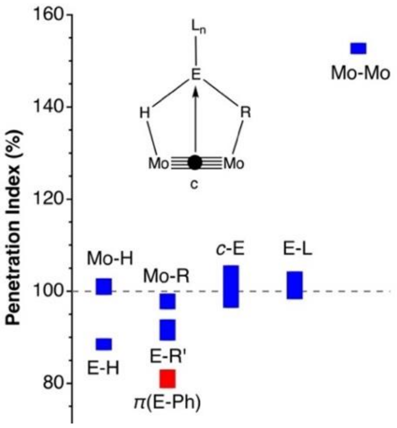
We present a computational-theoretical study of a family of compounds with the common platform $[Mo_2(H)_2(\mu\text{-}Ad^{Dipp2})_2]^{2+}$, consistent of a molybdenum-molybdenum quadruple bond and two bridging amidinato ligands $HC[N(2,6\text{-}{}^{i}Pr_2C_6H_3)]_2$ (Ad^{Dipp2}), that forms with metals of the *s* and *p* blocks H-Mo≣Mo-R-E five-member rings (R = H, Me, Et, Ph; E = Li, Mg, Al, Zn) [1,2].

The bonds that make up these rings are analyzed by means of the penetration indices of the Van der Waals crust [3], that are independent of the atoms' sizes and adopt values close to 100% for two-electron bonds, and smaller for weaker bonds. In that way we can see that the Mo-H and Mo-R bonds are practically single bonds, whereas the E-H and E-R penetrations are smaller and indicative of σ-bond Mo-H and Mo-R coordination to E, as disclosed also by DFT and NBO analyses, that reveal in addition a clear direct coordination of the Mo≣Mo bond to E.



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Organometallic Tools Applied to Metal Nanoparticle Synthesis and Catalysis

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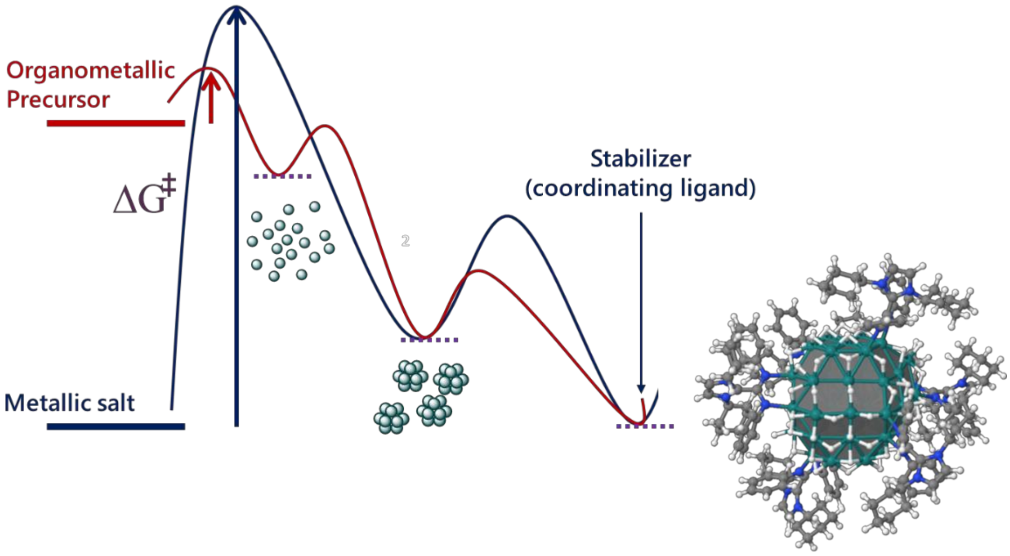
Organometallic chemistry has experienced a tremendous development during the last 40 years, producing very active catalysts in many important catalytic processes, such as asymmetric hydrogenation, C-H activation, methatesis or cross-coupling reactions. It has been possible thanks to a perfect control of the coordination sphere of the organometallic complexes. On the other hand, the catalytic use of metal nanoparticles (**MNPs**) has undergone a spectacular growth during the last 20 years. This is mainly due to the fact that MNPs combine the advantages of heterogeneous (stability and recyclability) and homogeneous (activity and selectivity) catalysts. However, little attention has been paid to the location, binding mode and catalytic influence of the surface ligands of **MNPs**. Therefore, our efforts have focused on the synthesis and characterization of **MNPs** with controlled coordination sphere trying to influence their catalytic properties.

By the controlled decomposition of high energy organometallic complexes in the presence of coordinating ligands, we have access to small, uniform and well-distributed ligand-stabilized **MNPs** (**Scheme 1**). The coordination of ligands at the MNP surface is very similar to that observed in organometallic chemistry, where the ancillary ligand donates a lone pair of electrons to the metal.[1] Thus, efficient ligands for the stabilization of molecular complexes are also effective to stabilize **MNPs** (i.e. N-heterocyclic carbenes; NHCs). In addition, as well as in organometallic complexes, surface ligands are able to modify the electronic and steric properties of the nanoparticles, and thus control their catalytic properties.[2] For example, we have observed that small modifications on the stabilizing ligands are capable of modifying the catalytic properties of MNPs.[3] Finally, supported **MNPs** can be also tuned by modifying their metal surface with ancillary ligands and thereby modulate their surface chemistry and catalytic properties.[4] Therefore, the use of coordinating ligands in MNP catalysis offers a new way to improve the catalytic properties of **MNPs**, until now mainly exploited by homogeneous catalysis.



Scheme 1. Synthesis of ligand-stabilized MNPs following an organometallic approach.

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Facile H_2 Activation by Bimetallic Caesium Aluminyl Anions

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The interest in developing the chemistry of low-valent main group metals has remarkably increased over the last few years.[1] In particular, the landmark discovery of a new class of nucleophilic aluminium Al(I) anions, so-called aluminyls, allowed unprecedented bond activation chemistry at a main group metal center.[2] Furthermore, these Al(I) anions are interesting because of their umpolung reactivity and the cooperative effect they can exhibit in combination with alkali metals.[3] Hence, these aluminyls can be categorized in agreement with the nature and extent of the alkali metal····Al(I) interaction (Figure 1).[4]

In this communication, we will report unique examples of bimetallic sodium, potassium, and caesium aluminyls exhibiting different alkali metal····Al(I) interactions. Interestingly, the caesium aluminyls can activate H_2 under mild reaction conditions, in stark contrast to the sodium and potassium congeners. In addition, we will discuss the nature of the caesium····Al(I) interaction for the challenging activation of H_2.[5]

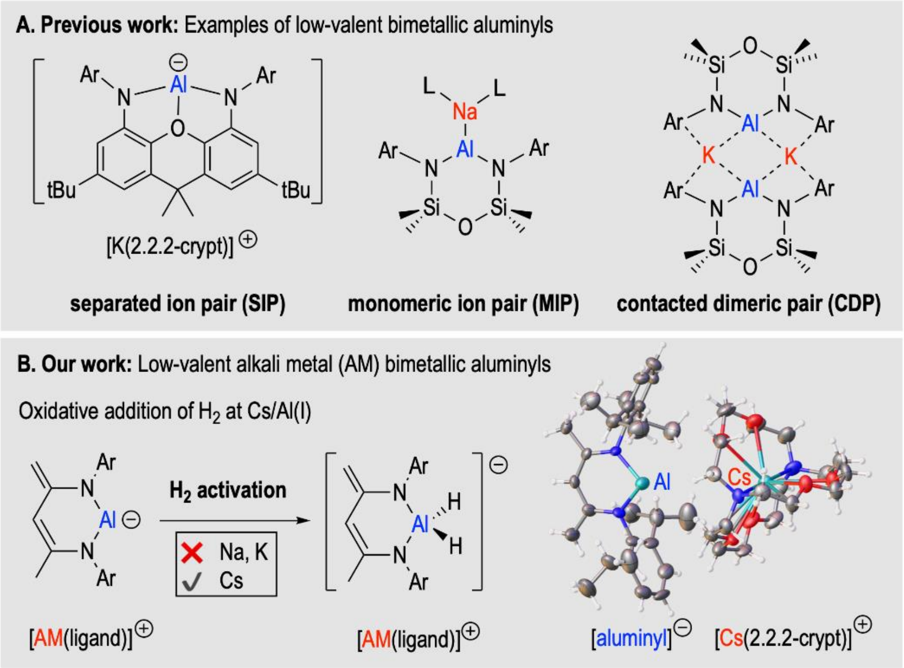

Figure 1. Low-valent alkali metal Al(I) examples and present work.

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OC24

Organolithium Chemistry under Air and with Sustainable Solvents: Synthesis of Guanidines and Amidines

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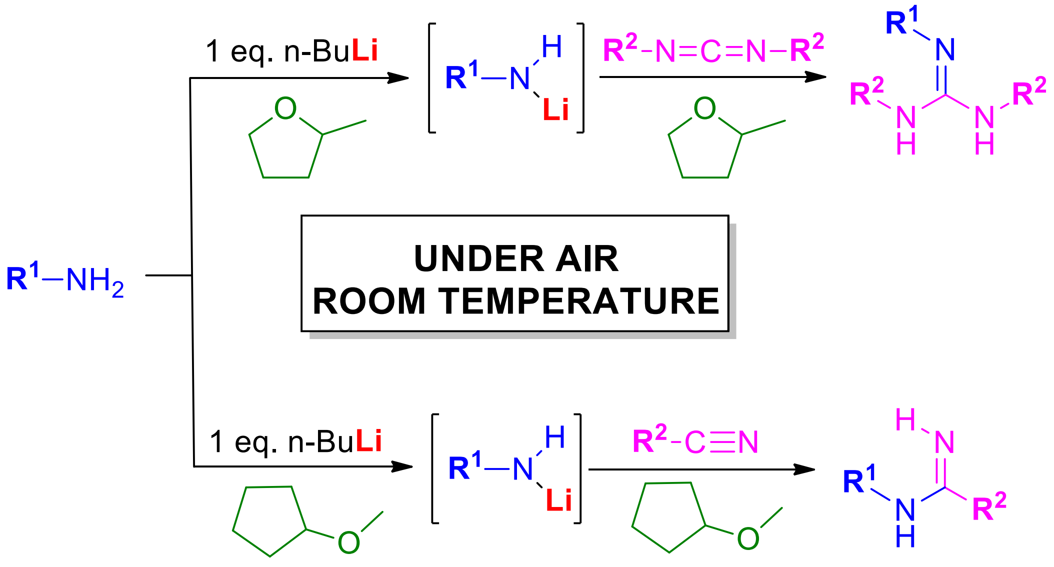
The possibility of using organolithium compounds under-air opens the door to a greener polar organometallic chemistry.[1] In basis to our previous experience in the synthesis of guanidines and amidines,[2] in this work we describe the highly-efficient and selective fast addition of *in-situ* generated lithium amides [LiN(H)R] (obtained *via* acid-base reaction between n-BuLi and the desired amine) into carbodiimides (R-N=C=N-R) or nitriles (R-C≡N), in 2-MeTHF or methylcyclopentylether as ethereal green solvents, at room temperature and in the absence of a protective atmosphere. This alternative synthetic methodology allows the straightforward and successful synthesis of either guanidines or amidines, without the need of isolation or purification steps of any halfway reaction intermediate. The robustness of the method allows the reaction to be carried out on a multigram scale, thus proving that our new and environmentally friendly protocol is amenable for a possible applied synthesis of these highly substituted iminic-type fine chemical products under bench-type reaction conditions.[3]



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OC25

Valorisation of Mixtures of Linear Alkenes Using Cobalt-Mediated Isomerisation and Hydroformylation Chemistries

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Active catalysts derived from cobalt and the Xantphos ligand were synthesised, characterised and tested in the hydroformylation of pure linear alkenes or their mixtures (Fig. 1). The preformed complex [$Co_2(CO)_6$(Xantphos)] (Fig. 2) showed similar reactivity and selectivity towards aldehydes as the active catalyst formed *in situ* from equimolar amounts of [$Co_2(CO)_8$] and Xantphos. In the case of oct-1-ene, the linear aldehyde was obtained with good chemo- and regio-selectivity (linear to branched ratio was up to 75:25). For all octene isomers, tandem isomerisation-hydroformylation processes took place. Regioselectivities for all the studied octene isomers remained practically constant, independently of the position or geometry of the C=C double bond in the starting material. Moreover, by-products were formed in similarly small amounts for all the octene isomers. We also demonstrated that this chemistry is an interesting strategy for valorising mixtures of linear hexenes, heptenes or octenes by transforming the initial mixture into one major aldehyde (addition of a CHO group to the C_1 carbon of the alkene skeleton, up to 73% selectivity). Moreover, these mixtures of alkenes were hydroformylated with low final amounts of non-hydroformylated alkenes, hydrogenated alkenes and alcohols. [1]

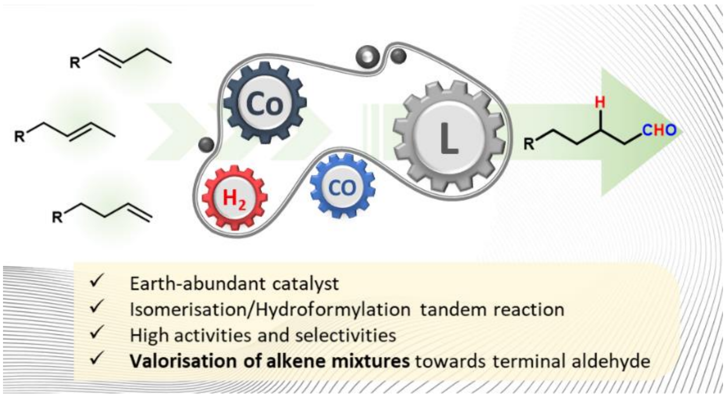

Fig. 1 Scheme of cobalt-mediated isomerisation and hydroformylation chemistries.

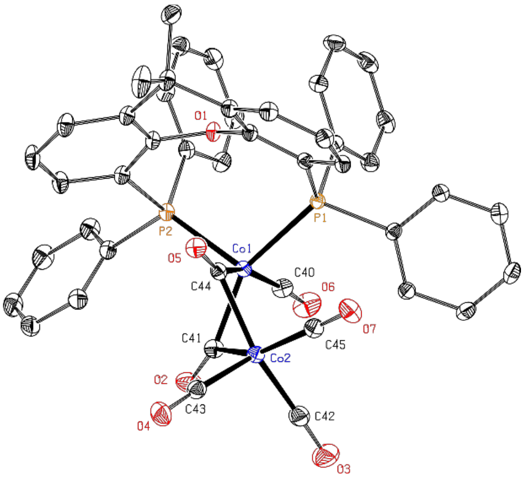

Fig. 2 ORTEP drawing of the crystal structure of [$Co_2(CO)_6$(Xantphos)]. Hydrogen atoms have been omitted for clarity. Color Scheme: C: black, Co: blue, O: red, P: orange.

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Purine-Based NHC Bridging and Terminal Ligands: Polymetallic Clusters and Molecular Wires

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Metallophilic interactions are weak electrostatic attractive forces typically observed between closed-shell (d^{10}) or pseudo closed-shell (d^8) metal centers. They manifest as short metal–metal distances, generally under the sum of van der Waals radii. Such contacts represent an essential driving force in the formation of some host-guest systems.[1] In addition, ligand design and fine tuning of intermetallic distances can be exploited in the modification of luminescent properties[2] and catalytic activity.[3]

We report on a series of group 11 metal-NHC complexes based on purine scaffolds. Selective functionalization of the nitrogen sites in the nucleobase backbone leads to different ligand precursors. Their reactions with accessible metal salts yield a wide variety of complexes. In the solid-state, a broad range of geometries are observed, from linear systems to unusual arrangements. Trinuclear and tetranuclear silver cores are stabilized by strong argentophilic interactions and bridging NHC ligands. Therein, each metallic center is coordinated to two different carbenic carbons from independent ligands, giving raise to triangular and rectangular clusters (Figure 1, left). Unsupported argentophilic contacts are also key in the formation of 1D molecular wires, as they act as the only 'glue' between bimetallic complexes (Figure 1, right).

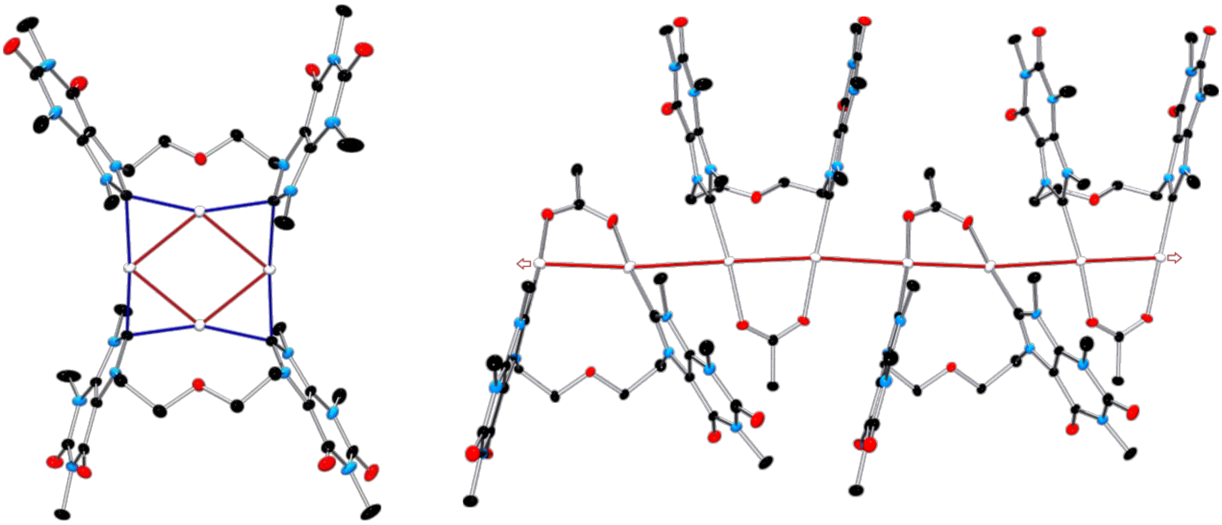

Figure 1. Polymetallic solid-state structures.

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OC27

A Versatile and Commercially Available Iron Catalyst Active in Carbene Transfer Reactions

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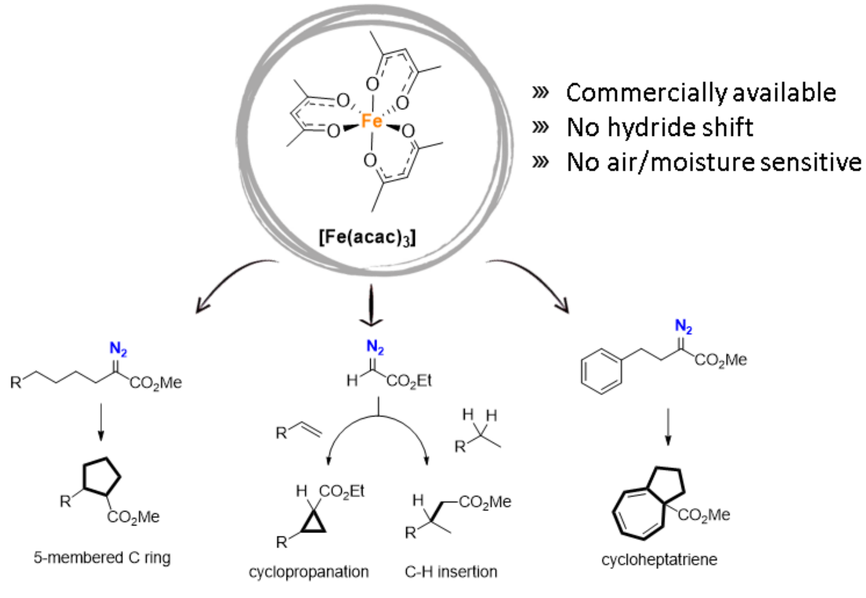
The development of C-H functionalization reactions catalyzed by non-precious metals is an important aim for gaining sustainability in chemical synthesis. In 1992, Hossain reported the first example of carbene transfer reactions using iron as a catalyst, [CpFe(CO)$_2$(THF)]BF$_4$.[1] With this as a starting point, over the past decades iron has exhibited promising results in this field.[2]

Our group has previously described a synergy between an iron catalyst, [Fe(^{F}pda)(THF)]$_2$, and a lithium aluminate salt, Li[Al(OC(CF$_3$)$_3$)$_4$]. The aforementioned catalyst activates azoesters under mild conditions promoting both intramolecular and intermolecular functionalization of strong C*sp*^{3}-H bonds via carbene insertion. [3,4]

During our research we have been able to identify a much simpler and manageable catalyst, [Fe(acac)$_3$], that, upon previous activation, exhibits superior performance. [Fe(acac)$_3$] has shown excellent selectivity practically avoiding the formation of “hydride shift” side products and is able to be operative with only a 5% of Li[Al(OC(CF$_3$)$_3$)$_4$], a 5-fold reduction when compared to our previous system. Of important to note is that [Fe(acac)$_3$] is commercially available, cheap, and air/moisture stable. Finally, [Fe(acac)$_3$] has proven to be a versatile catalyst achieving good yields in intermolecular C-H insertion and cyclopropanations reactions, and it is also able to access to Buchner ring expansion products generating cycloheptatrienes derivatives.



» Commercially available
» No hydride shift
» No air/moisture sensitive

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OC28

Different Approaches of Cyclometalated Ir(III) Complexes in Cancer Therapy

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The development and screening of potential anticancer agents or methods has become an urgent need in our society. Apart from the commonly used cisplatin, there are additional metallodrugs such as those derived from Au(I) auranofin, Ru(III) KP1019 and TLD-1433 Ru(II) among others, that have shown their great prospects as metal-based anticancer agents. In fact, the three of them are nowadays at different stages of clinical trials against diverse cancer diseases. Within this frame, cyclometalated iridium complexes, with the general formula $[Ir(C^{\wedge}N)_2(N^{\wedge}N)]^+$, have also shown their great potential in medicine, not only in chemotherapy but also in photodynamic therapy.[1] On top of that these species are generally emissive; therefore, they can be used as luminescent tags in bioimaging, which allows the collection of key of information using non-invasive techniques.[2]

Herein we present a series of different families of Ir(III) complexes that have demonstrated to be potent anticancer agents in chemotherapy and/or photodynamic therapy, Figure 1.[3] Moreover, preliminary studies revealed that some of the families have great prospects as senolytics, being able to destroy or inhibit selectively the function of senescent cells, and thus, providing an alternative therapy in cancer treatment.

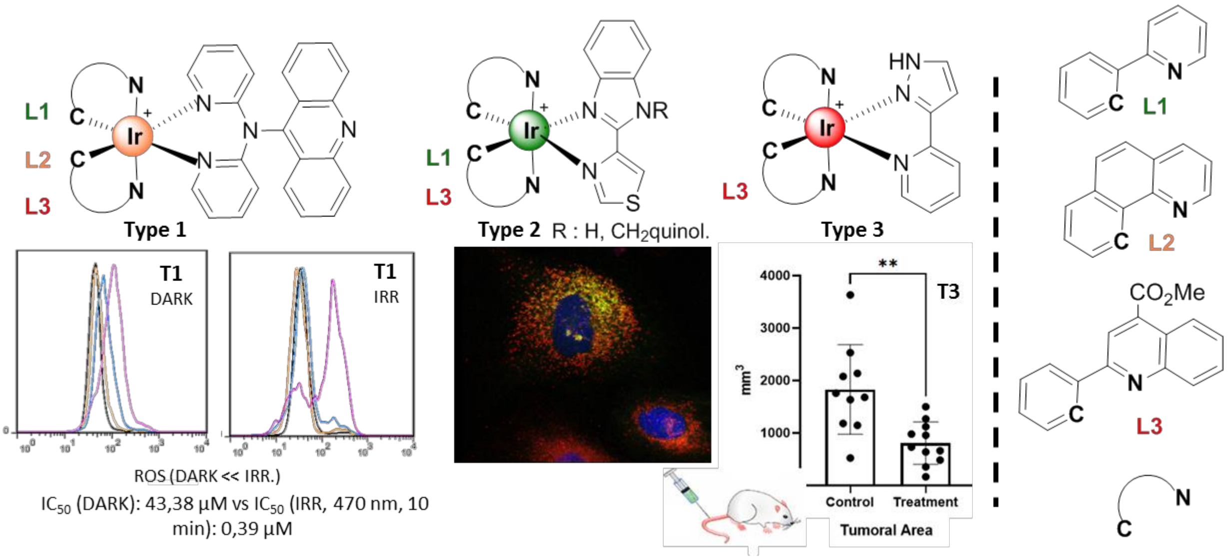

Figure 1

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OC29

Dicoordinate Au(I)–Ethylene Complexes as Hydroamination Catalysts

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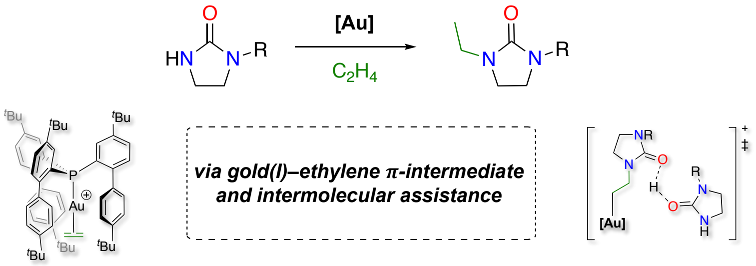
π-Complexes of gold are generally proposed as key intermediates in the functionalization of alkenes, alkynes, dienes or allenes in a wide range of catalytic processes.[1] Thus, the isolation of gold π-complexes holds an intrinsic interest associated with their catalytic relevance and has provided valuable insights during the last years. Cationic gold(I) π-complexes of substituted alkenes have been stabilized by monodentate and bidentate ligands. However, despite significant synthetic efforts, dicoordinate ethylene complexes remain unknown and only by using N- and P-based bidentate ligands the related tricoordinate gold(I) π-ethylene adducts.[2] The use of bulky phosphine ligands has allowed the stabilization, isolation and complete characterization of the first dicoordinate gold(I)–ethylene adducts.[3] The bonding situation of these species has been investigated by means of state-of-the-art Density Functional Theory (DFT) calculations. In addition, the lability of the gold-ethylene bond has also been interrogated. For instance, the use of these sterically congested ligands have proved crucial to stabilize the gold(I)–ethylene bond and prevent decomposition, boosting up their catalytic performance in the highly underexplored hydroamination of ethylene.[4] As a result, the precatalysts bearing the most sterically demanding phosphines showed excellent results reaching full conversion to the hydroaminated products under notably mild conditions, highlighting the high catalytic potential of very sterically crowded catalysts.



via gold(I)–ethylene π-intermediate and intermolecular assistance

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OC30

N-Heterocyclic Carbenes Based on Uracil: Synthesis and Applications

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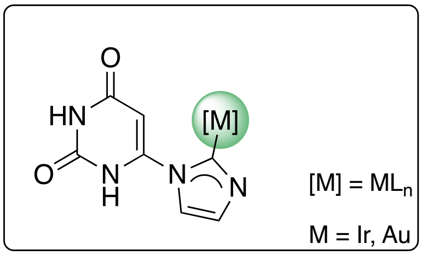
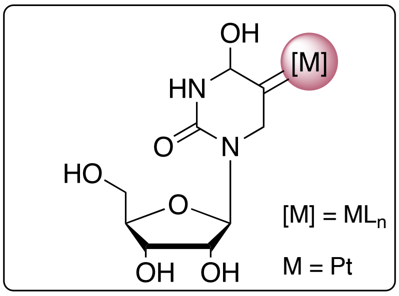
Modified nucleosides are widely used in chemotherapy, acting as antimetabolites that disrupt the synthesis of nucleic acids [1]. Currently, and similarly to cisplatin, they can be applied as a standalone treatment or in combination chemotherapies, to improve effectiveness in treatment by a dual mode of action provided by each drug [2]. Yet, combination therapies are often problematic due to the different pharmacokinetics of individual drugs. To circumvent these issues, one promising strategy is to combine cytotoxic functionalities in one single drug.





Organometallic functionalization is promising strategy previously employed to improve the therapeutic profile of bioactive compounds [3]. Inspired by this, we are currently exploring synthetic methodologies for the development of nucleosides functionalized with transition metals. In this communication, we describe the synthesis of uracil based complexes, bearing iridium, platinum and gold as metal centres.

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OC31

Unusual Reductive Eliminations in Gold(III) Complexes Leading to Formation of Methyl–X bonds (X = Halogen, O, N, P, C)

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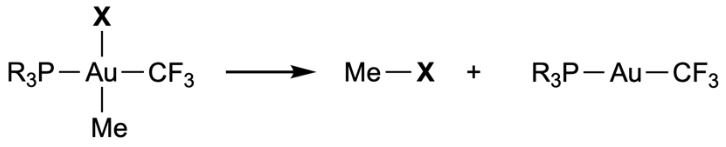
Au(I)/Au(III)-catalyzed C–C or C–X cross-coupling reactions have been intensively investigated in the search for synthetic tools that complement the widespread Pd-catalyzed reactions.[1] Reductive elimination from Au(III) intermediates is a key step in these catalytic cycles, but mechanistic information regarding this fundamental reaction is still scarce. Two main reaction pathways have been disclosed: (a) dissociative pathways with the involvement of unstable tricoordinated complexes, or (b) direct reductive elimination from tetracoordinated complexes.[2]

Very few examples of reductive elimination reactions from well-defined Au(III) complexes leading to formation of carbon–heteroatom bonds have been reported.[2a] In particular, reductive eliminations of organyl triflates, perchlorates or nitrates have never been observed in Au(III) and are very uncommon for most metal complexes.[3]

In this communication we report the synthesis and reactivity of new Au(III) complexes containing a methyl, a trifluoromethyl ligand, and two different anionic or neutral ligands. These complexes undergo thermal reductive elimination reactions leading to the formation of Csp^3–X bonds, including rare examples of formation of methyl esters of triflic, perchloric or nitric acids. The formation of Csp^3–N or –P bonds has also been observed in cationic Au(III) complexes. Mechanistic studies of these reactions suggest the operation of different pathways depending on the nature of the starting complexes.



X = CH_3, OTf, $OClO_3$, ONO_2, F, Cl, Br, Ph_3P^+

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OC32

Iridium catalysts based on N-functionalized NHC ligands for dehydrogenation processes

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In the current paradigm of homogeneous catalysis, the design of catalysts based on NHC ligands is one of the major keys due to the increase of the electronic density at the metallic center along with a remarcable steric influence, which results in the formation of exceptionally strong M-C bonds and thus stabilizing and preventing decomposition of the catalytic species. Functionalization through the wingtips of these NHC ligands provide multiple coordination possibilities including those bestowing a *pincer* behaviour. In addition, the presence and influence of heteroatoms in non-symmetric NHC ligands affords new coordination modes which may increase the catalytic activity of the metallic complexes. [1]

In this sense, Ir-NHC complexes have proven to be among the front row of catalysts regarding hydrogen transfer, hydrogen borrowing or acceptorless dehydrogenation reactions. These processes exhibit great appeal from the environmental standpoint as consequence of their multiple advantages: they allow the valorization of available and inexpensive bulk chemicals such as glycerol, the production of different fine chemicals by transfer hydrogenation, or even, the generation of molecular hydrogen. [2,3]

In the present work, we depict the synthesis of a series of neutral and cationic Ir(I) and Ir(III) complexes bearing non-symmetric NHC ligands functionalized with N-coordinating moieties as well as O-donor fragments, and 1,5-cyclooctadiene, carbonyl or pentamethylcyclopentadienyl auxiliary ligands [Figure 1]. These compounds have shown to be efficient catalysts for acceptorless dehydrogenation and transfer hydrogenation of a range of substrates.

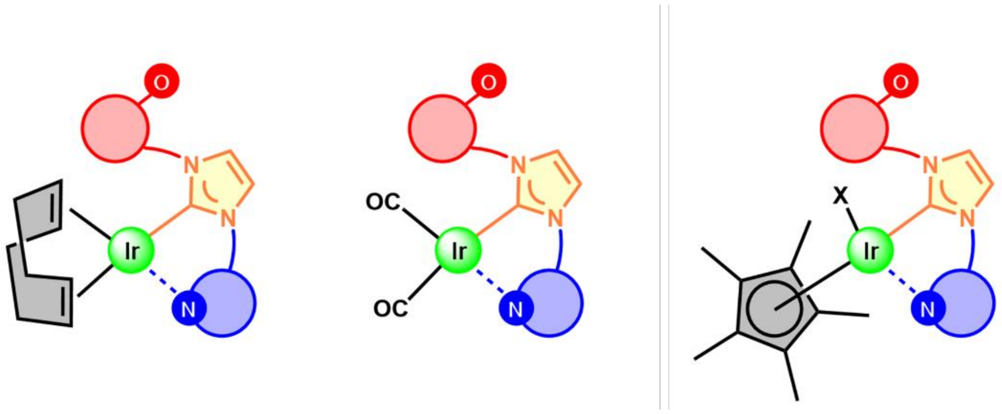

Figure 1. N-functionalized NHC-Iridium catalysts active in dehydrogenation processes.

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OC33

Gold(I)···Lanthanide(III) Bonds in Molecular Heterobimetallic Compounds: A Combined Computational and Topological Study

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The reactivity of the extremely stable dicyanoaurate(I) anion ([Au^{I}(CN)$_2$]$^-$) towards *f*-block metal(III) salts has recently been a subject of sporadic research that mainly has focused on the efficient sensitization of the monochromatic line-like emission of lanthanide(III) cations. [1] It is known, even as textbook knowledge, that lanthanide-based emission is the result of parity-forbidden radiative 4*f*-4*f* transitions proceeding thanks to an energy transfer (ET) from the lowest excited triplet state of a sensitizing (metallo)ligand to the lanthanide atom. [2] Hence, the global emission efficiency strongly depends on the electronic structure of the sensitizer and the lanthanide that requires an appropriate energy match for allowing the whole cascade of intersystem crossings (ISCs) and ETs to occur. Several studies have demonstrated that gold(I) and silver(I) dicyanometallates ([M^{I}(CN)$_2$]$^-$; M^{I} = Au^{I}, Ag^{I}) and platinum tetracyanometallates ([Pt^{II}(CN)$_4$]$^{2-}$) are among the most efficient sensitizers thanks, not only to the similarity between their energy levels and those of the lanthanide(III) acceptors, but also to spin-orbit coupling (SOC) effects. [1]

Despite these synthetic efforts, very little is known about a possible direct interaction between gold(I) and lanthanide(III) atoms. Up to date, an experimental proof of ground-state gold(I)-lanthanide(III) bonds/interactions is lacking, which is even more striking when considering the plethora of structurally-authenticated combinations of other main- and *d*-block metals with lanthanides and even with actinides. [3] This is probably due to the choice of the coordinating dicyanoaurate(I) anion in almost all studies dealing with this subject.

Here, we have theoretically constructed a **Ln$_1$Au$_1$** model (see the **Figure**) featuring a short unsupported interaction between the non-coordinating diphenylaurate anion ([Au^{I}Ph$_2$]$^-$) and three different bis(cyclopentadienyl)lanthanide(III) cations ([Ln^{III}(Cp)$_2$]$^+$; Ln^{III} = La^{III}, Eu^{III}, Lu^{III}). The aims of this communication are (i) to computationally unveil the chemical nature of the Au^{I}···Ln^{III} bond/interaction using energy decomposition analyses and state-of-the-art topological techniques and, (ii) to predict the optical properties due to this interaction and the feasibility to use [Au^{I}Ph$_2$]$^-$ as an efficient emission sensitizer.

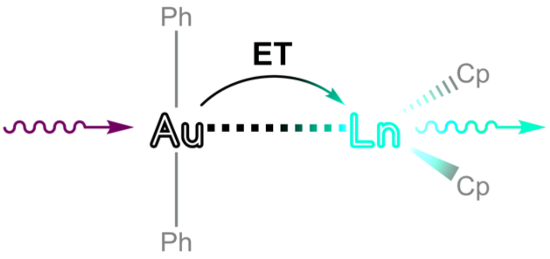

Figure: Schematic representation of the **Ln$_1$Au$_1$** model and the emission sensitization process.

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OC34

Aromatic Trifluoromethylation Through Ag(I)/Ag(III) Redox Manifold

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Despite their ubiquitous use as additives or co-catalysts, silver compounds are generally believed to not interfere with the main metal reactivity and their potential as cross-coupling promoters has long been overlooked. This is most likely due to the erroneous belief that Ag is incapable of undergoing 2e^- redox processes. Our research focus became centered on this old paradigm, and we first targeted the easy access to the organosilver(III) anion $[\mathrm{Ag^{III}(CF_3)_4}]^-$ (**1**), thus bridging the possibility to explore the Ag(III) reactivity in depth. The original Naumann's method for the synthesis of **1** was reported back in 1986, and required the use of $\mathrm{Cd(CF_3)_2}$ (toxic and explosive) as transmetallating agent leading to $[\mathrm{Ag^I}]^+[\mathrm{Ag^{III}(CF_3)_4}]^-$ (**Ag-1**) in modest yield (25% *vs.* initial Ag(I) salt) [1]. In 2018 Menjón revisited this chemistry, and found a safer two step synthesis of $[\mathrm{PPh_4}]^+[\mathrm{Ag^{III}(CF_3)_4}]^-$ (**PPh$_4$-1**) through intermediate formation of $[\mathrm{PPh_4}]^+[\mathrm{Ag^I(CF_3)_2}]^-$ and following 2e^- oxidation with $\mathrm{PhI(OAc^F)_2}$. Yet the yield of **1** was still restricted to 30% and the use of costly hypervalent iodine was mandatory [2]. We herein report the aerobic oxidation of AgF in presence of KF and CF$_3$TMS giving rise to $[\mathrm{K}]^+[\mathrm{Ag^{III}(CF_3)_4}]^-$ (**K-1**) safely, in high yield and multigram scale [3]. The neutral compounds $[\mathrm{(bpy)Ag^{III}(CF_3)_3}]$ (**2**) and $[\mathrm{(phen)Ag^{III}(CF_3)_3}]$ (**3**) where synthetized from **K-1** *via* α-fluorine elimination, and their utility in cross-coupling reactions has been unambiguously proven. Indeed, **3** mediates the trifluoromethylation of arylboron compounds in presence of a base and in aqueous media, this transformation capitalizing on the intermediate formation of $[\mathrm{Ag^{III}(aryl)(CF_3)_3}]^-$ complexes through boron-to-Ag^{III} aryl transfer and the subsequent C–CF$_3$ bond formation.

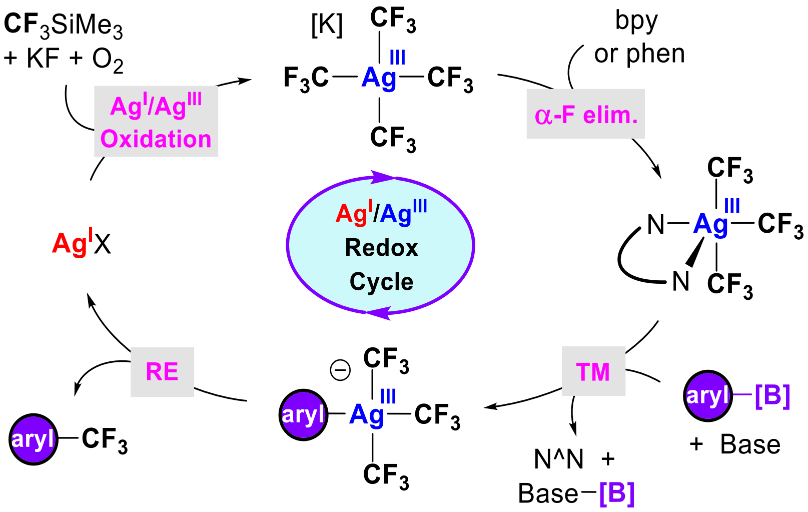

Fig. 1: Mechanistic depiction for the oxidative trifluoromethylation of arylboron derivatives *via* Ag^I/Ag^{III} redox shuttles.

In short, key elementary steps required to implement Ag^I/Ag^{III} redox catalysis were investigated (**Fig. 1**), and definite proof was provided for: *i)* easy Ag^I/Ag^{III} 2e^- oxidation mediated by oxygen; *ii)* bpy/phen ligation to Ag^{III}; *iii)* boron-to-Ag^{III} aryl transfer; and *iv)* reductive elimination of benzotrifluorides from well-defined aryl-Ag^{III}-CF$_3$ complexes. These findings underline the ability of high-valent Ag^{III} to accomplish a given cross-coupling reaction by itself, and subverts old-established stereotypes and misconceptions about the assumed chemical inertness of silver compounds for C–C bond formation along with its restriction to 1e^- transition pathways.

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FLASH PRESENTATIONS

Synthesis and Coordination of *P*-Stereogenic Non-Symmetric Diphosphanes with a Methylene Bridge

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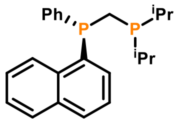
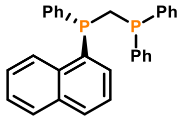
The synthesis of *P*-stereogenic phosphanes has always been a challenge due the lack of available methods. These molecules, however, are very interesting due to their applicability as ligands in a wide variety of enantioselective reactions catalyzed by organometallic complexes. Because of their challenging synthesis and their top-notch performance, new *P*-stereogenic phosphanes are always of interest in both organometallic chemistry and homogeneous catalysis.

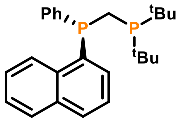
In this contribution, we present an array of *P*-stereogenic diphosphanes with a single-atom (methylene) linker [1], a structural feature that has been very successful with their more basic counterparts [2-4].



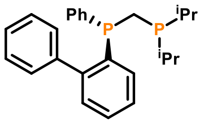
Np^{i}Pr



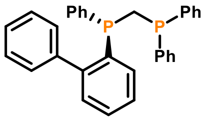
NpPh



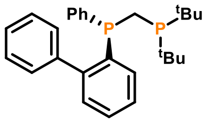
Np^{t}Bu



Biph^{i}Pr



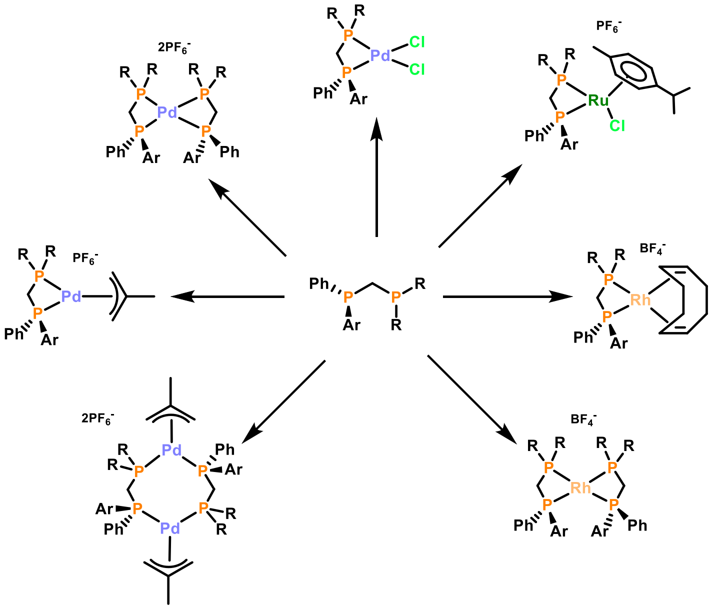
BiphPh



Biph^{t}Bu

These diphosphanes have a very narrow bite angle due to the constraint imposed by the methylene bridge, which makes the ligands very interesting in terms of coordination chemistry [5].

To explore this chemistry, the ligands have been coordinated to Pd, Rh and Ru, affording a wide variety of structures, which showcase the great versatility of the diphosphanes. In addition, some preliminary catalytic studies have also been carried out.



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FL2

Catalyst Design and Reaction Mechanisms in Formic Acid Dehydrogenation

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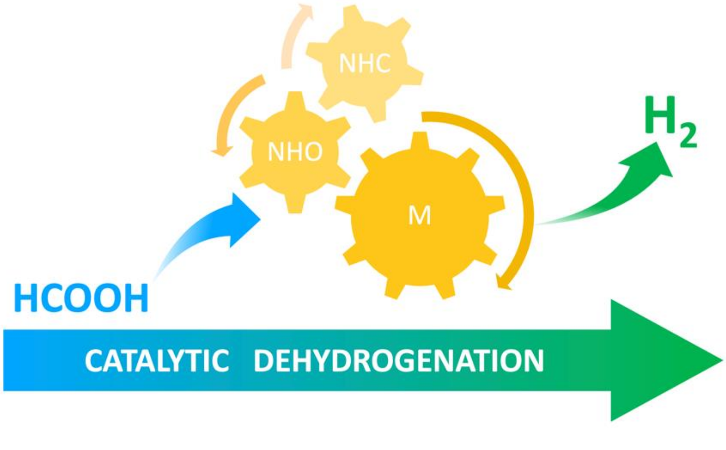
The use of hydrogen as an energy vector presents several issues that need to be addressed in order to implement its use on a global scale. In particular, its storage and transportation problems may be circumvented by the use of LOHC (liquid organic hydrogen carriers). Among them, formic acid has been proposed as a promising hydrogen storage system due to the fact that it is environmentally innocuous, a liquid under ambient conditions, and it presents a higher volumetric energy density and hydrogen content than compressed hydrogen.

This presentation will deal with the design of new catalysts based on NHC (*N*-heterocyclic carbene) and NHO (*N*-heterocyclic olefin) heterotopic ligands. The activity of these catalysts on the dehydrogenation of formic acid was studied under solventless conditions, since the use of solvents drastically reduces the energy density of the reaction mixture, and the presence of volatile organic solvents harms the efficiency of the fuel cell. Furthermore, the proposed reaction mechanisms based on DFT and experimental data—namely, isolation of key putative intermediates of the catalytic cycle, KIE measurements, or in situ NMR experiments—will be discussed [1-4].



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New Perspective in the Ni-Catalyzed Heck Reaction: The Role of Deprotonable P-N Ligands to Assist the β-Hydride Elimination Stage

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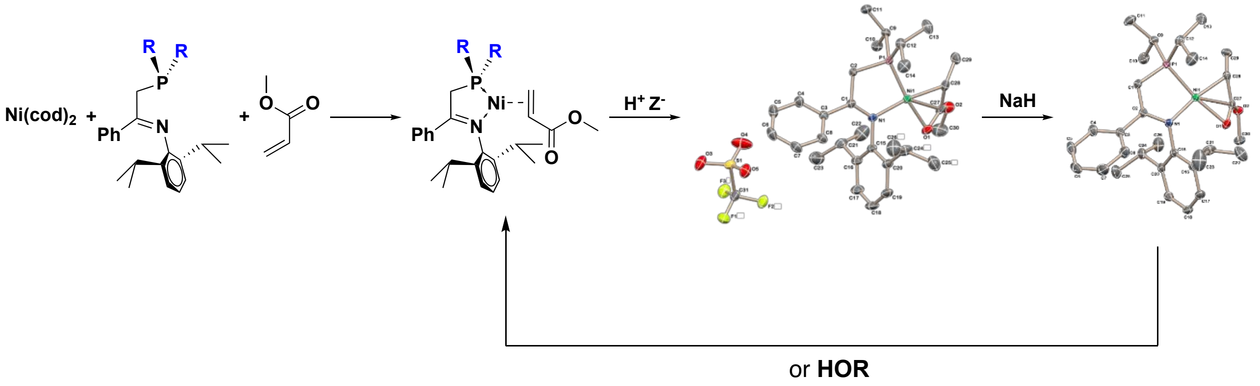
The increasing demands of raw materials by the society, requires not just either more selective or efficient catalysts but cheaper. In this sense, the preparation of organic molecules has led to sustained interest in methods based on homogeneous catalysts, particularly in the development of catalysts assisted by its surrounding.

The properties of a metal complex as a whole are the result of the interaction between the metal center and its ligands, which controls the performance of the catalyst thanks to their steric and electronic properties, playing a spectator role, because the reactivity takes place at the metal center. Nevertheless, recent new approaches make use of cooperative ligands, that can play an active role in the elementary bond activation steps in a catalytic cycle.[1] The central idea is that the metal and the ligand can cooperate in a synergistic manner, and their interplay facilitates the chemical process [2].

Thus, we have been investigating the Heck reaction using Nickel complexes stabilized by iminophosphine ligands. In this context, we recently discovered that the ability of these P,N ligands to be deprotonated with suitable bases, affording the respective phosphinoenaminate species [3], might play a very important role in the nickel-catalyzed Heck reaction, particularly in the third step of the process: β-hydride elimination based induced. In this sense, we discovered that during this last step, the P-N ligands may act as a proton shuttle through an acid/base process so as to assist in the performance of this third step of the catalytic cycle (Scheme 1). For that aim, a model was studied.



Scheme 1

References

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FL4

In-depth photophysical characterization of dinuclear gold(I) complexes

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Gold(I) complexes are an expanding area of investigation due to the possibility of giving rise to supramolecular aggregates thanks to the possibility to establish Au(I) ··· Au(I) contacts. The resulting morphologies can be modulated together with their luminescent properties [1,2]. These properties have found interest in the use of the systems in a wide range of different applications, such as advanced materials, therapeutic drugs, photodynamic therapy agents and sensors, among others. [3,4]

In this work, we are focused on the promotion of the *heavy atom effect*, which has been observed as a crucial phenomenon able to harvest the triplet state, which can lead to phosphorescent emission. [5] To do that, a family of molecules that follow the structure: *Aromatic group-Au-*$(PR_2)_2$*-Au-Aromatic group* has been synthetized. Two aromatic chromophores were combined with different diphosphanes, to see if its rigidity can promote the *heavy atom effect* between two gold(I) atoms by inter- or intramolecular contacts.

Finally, the photophysical characterization by using several techniques such as ns-Laser *Flash Photolysis* and some TD-DFT theoretical calculations were performed, in order to study the influence of the rigidity of these diphosphane ligands in the formation of aurophilic contacts and its consequent luminescence behavior.

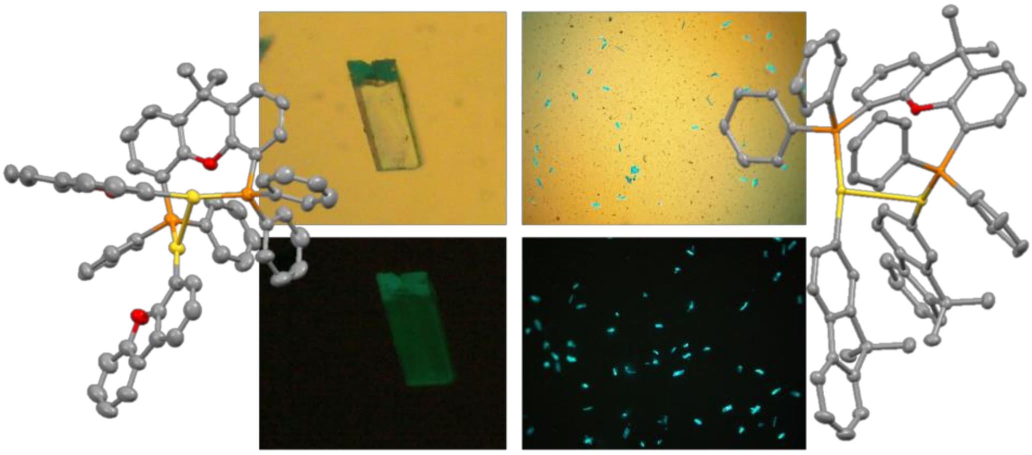

Figure 1. *Crystal of compounds* ***1c*** *(left) and* ***2c*** *(right) under the optic microscope with a visible lamp (upper) and with a fluorescence lamp (down).*

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Gold(I)-Catalyzed Dienyne Cyclization for the Assembly of Decalin Cores

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The potential of cascade polyene cyclization has been demonstrated to be an efficient way for the construction of molecular diversity.[1] Our group reported the gold(I)-catalyzed cyclization of polyenynes for the construction of up to four C–C bonds and applied it to the synthesis of steroid derivatives.[2] Now, we have focused on the development of a new methodology for the assembly of decalin skeletons via gold(I)-catalyzed dienyne cyclization of tetrasubstituted silyl enol ethers in a stereodefined manner. This methodology has led to the formation of building blocks for the synthesis of different natural products such as avarone and avarol, and related compounds.

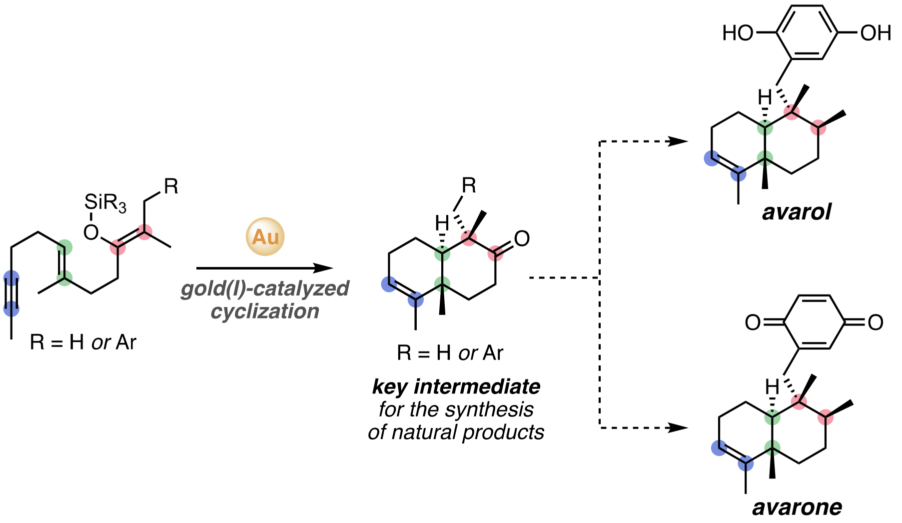

Figure 1. Construction of decalin derivatives by cyclization of dienynes.

Acknowledgements

We thank the MCIN/AEI/10.13039/501100011033 (PID2019-104815GB-I00, CEX2019-000925-S, FPI to I.M.-T.), the ERC (Adv. Grant 835080), the AGAUR (2017 SGR 1257), and CERCA Program/Generalitat de Catalunya for financial support.

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FL6

Asymmetric Hydrogenation: From Benchmark to Elusive Substrates Through Rational Catalyst Design

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Asymmetric hydrogenation has a perfect atom economy and it is operationally simply, which have spurred its use in industry. Thus, asymmetric hydrogenation constitutes ca 10% of all chemical steps in the manufacture of pharmaceuticals, flavors, agrochemicals and fine chemicals.[1] This percentage could be further increased if the new catalyst designs were more specific to challenging substrates rather than based on benchmark ones.[1] Herein I will show our latest improved generation of catalyst designs for the asymmetric hydrogenation of elusive substrates (e.g. exocyclic olefins, cyclic β-enamides, tetrasubstituted olefins …).[2] The hydrogenation of these olefins is of high interest because it led to the synthesis of important chiral synthons, such as chiral benzofused ring motifs, which are present in many natural products and key drug intermediates. Other key advantages of our new generation of catalyst designs are that they are very simple and modular, easy to synthesize and easy to handle (air stale solids). The new catalyst designs have been aided by the combination of computational studies and NMR spectroscopy, together with the analysis of the catalytic results, which have been crucial to rationalize the catalysts' structure, and to ensure the finding of optimal catalyst.

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POSTERS

P01

Three Component One Pot Synthesis of *Endo* Cyclopalladated Imines

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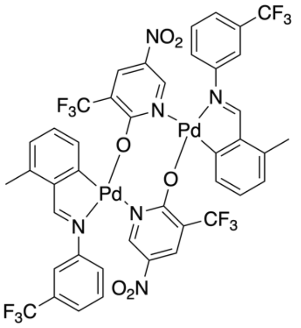
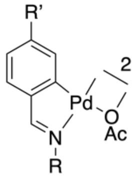
Li et al. reported in 2019 [1] the synthesis of a dinuclear *endo* five-membered cyclopalladated imine containing κ^2-***C***$_{(aromatic)}$,***N***$_{(imine)}$ cyclometallating and μ_2-***N***,***O*** bridging ligands (**A**). This compound was prepared by a four component (aromatic aldehyde, aniline, *ortho*-hydroxypyridine and $Pd(OAc)_2$) one pot method of synthesis. Thus, condensation, cyclometallation, substitution and deprotonation reactions were concatenated in the same medium of reaction to produce **A** in acceptable yield. Previously [2, 3], we have reported the synthesis of *endo* five-membered cyclopalladated imines, containing κ^2-***C***$_{(aromatic)}$,***N***$_{(imine)}$ cyclometallating and acetato bridging ligands (compounds **B**), by three component (benzaldehyde, primary amine (4-nitroaniline or benzylamine) and $Pd(OAc)_2$) one pot methods of synthesis. Therefore, condensation and cyclometallation reactions were concatenated in the same medium of reaction to produce compounds B in acceptable to good yields. Furthermore, in one of these experiments, we detected a small amount of 4-methoxybenzaldehyde (**E**), coming from the oxidation of 4-methoxybenzylamine by palladium(II) [3].

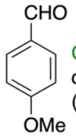
In the poster session, we will report the synthesis of compounds **B**, derived from 2-phenylethylamines, and six-membered *endo* cyclopalladated imines with a palladated aromatic carbon atom (compounds **C**), derived from anthracene-9-carbaldehyde, and with a benzylic palladated carbon atom (compounds **D**), coming from 2,4,6-trimethylbenzaldehyde, by three component one pot methods of synthesis. Furthermore, we will give details on the isolation and characterization of a small amount of the cyclic amide **F**, coming from the reaction between benzylamine, 2,4,6-trimethylbenzaldehyde and $Pd(OAc)_2$. These studies show that three component (aromatic aldehyde, primary amine and $Pd(OAc)_2$) one pot methods of synthesis of *endo* cyclopalladated imines can be a feasible alternative to the classical method of synthesis of these compounds in two steps [4]. Furthermore, these studies can be of interest to chemists working in the field of metal catalyzed C-H bond functionalization using a transient imine as directing group [5].



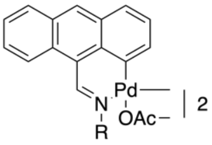
Compound A
(reference 1)



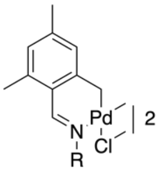
Compounds B
R = $4-NO_2C_6H_4$, R' = H, Me, MeO or OH (reference 2)
R = $C_6H_5-CH_2$, R' = H (reference 3) or OMe (this work)
R = $4-MeOC_6H_4-CH_2$, R' = OMe or NO_2 (reference 3)
R = $C_6H_5-CH_2-CH_2$, R'= H (this work)
R = $4-MeOC_6H_4-CH_2-CH_2$, R' = OMe or NO_2 (this work)



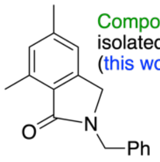
Compound E
detected by ^{1}H NMR
(reference 3)



Compounds C
R = $4-NO_2C_6H_4$ or $C_6H_5-CH_2$
(this work)



Compounds D
R = $4-NO_2C_6H_4$, $C_6H_5-CH_2$, or $C_6H_5-CH_2-CH_2$
(this work)



Compound F
isolated in a small amount
(this work)

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P02

Synthesis and Biological Properties of Palladium(II) Cyclometallated compounds derived from (*E*)-2-((4-hydroxybenzylidene)amino)phenol

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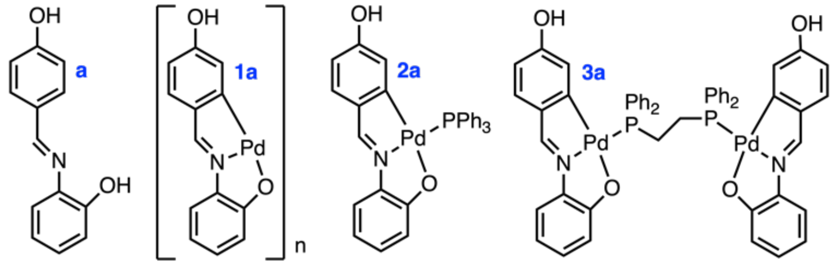
Palladium(II) compounds, containing chelating and good σ-donor or π-acceptor ligands and with steric hindrance around the palladium(II) centres, usually present good profiles as anticancer, antimicrobial and antiparasitic drugs [1, 2]. Therefore, we studied for compounds **a**, their cytotoxicity, antibacterial and antioxidant activities, and their ability to modify the electrophoretic mobility of the pBluescript SK + plasmid DNA in agarose gel, and to inhibit topoisomerases I and IIα. Compounds **a** were prepared by an adaptation of known procedures [3].

Most of compounds **a** were non-cytotoxic or poorly cytotoxic against the MDA-MB-231 and MCF-7 breast and HCT-117 colon human cancer cell lines. Nonetheless, **2a** was moderately cytotoxic against the MCF-7 breast (IC_{50} = 7.8 ± 1.7 μM) and HCT-116 colon (IC_{50} = 31 ± 5 μM) human cancer cell lines and presented a very low cytotoxicity towards healthy human BJ cells (IC_{50} = 86 ± nd μM). Compounds **a** showed also a moderate antibacterial activity against some Gram-positive (B. subtilis and S. aureus) and Gram-negative (E. coli) bacterial strains. In addition, compounds **a** presented a moderate antioxidant activity in the DPPH free radical scavenging assay, having **3a** the best antioxidant activity of the series (IC_{50} = 0.08 mM) in relation to ascorbic acid (IC_{50} = 0.05 mM) in this assay. **1a** was the unique compound of the series that produced a change on the electrophoretic mobility of the pBluescript SK + plasmid DNA in the agarose gel. This change followed the pattern of *cisplatin*, but started to take place at a concentration twenty times higher than with *cisplatin*. In addition, compounds **a** were unable to inhibit topoisomerase I at a concentration of 100 μM, but **1a** – **3a** inhibited topoisomerase IIα at concentrations of 10, 50 and 25 μM, respectively. In the poster session, we will give details on the synthesis, characterization, and biological properties of this series of cyclopalladated compounds derived from imine **a**.



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Orthometallation of Unsaturated Oxazolones: Beyond Palladium

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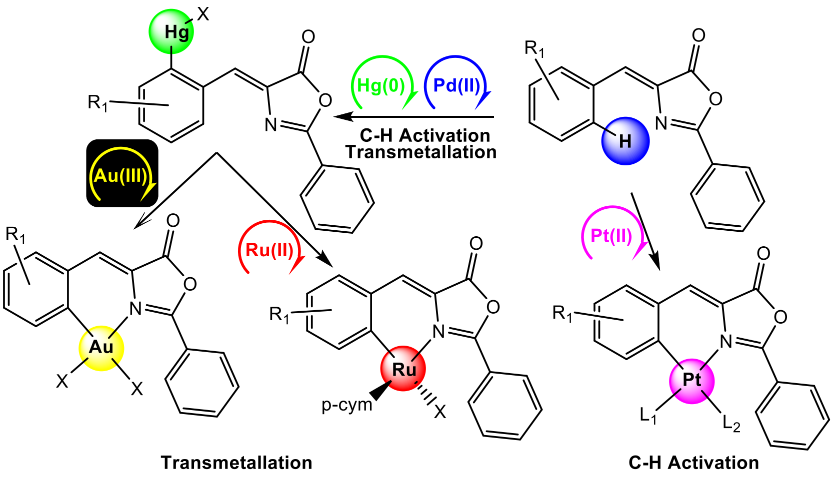
The synthesis of a series of complexes of Hg(II), Ru(II), Pt(II) and Au(III) containing metallated (*Z*)-4-arylidene-5(4*H*)-oxazolones is presented here. The preparation of the target complexes has been carried out through a combination of C-H bond activation and transmetallation strategies, and they have been characterized by NMR and HRMS methods.

The (*Z*)-4-arylidene-5(4*H*)-oxazolones are relevant and interesting synthetic intermediates from the point of view of their pharmacological properties, because they are precursors of phenylalanines. They are also of interest from their remarkable photophysical and photochemical properties. The incorporation of a transition metal to the oxazolone scaffold[1] has allowed a strong development of all mentioned fields due to the remarkable properties exhibited by the resulting organometallic derivatives: (1) the synthesis of *ortho*-functionalized oxazolones has been achieved [2]; (2) the amplification of the fluorescence from the free oxazolone to the metallated derivative reach two orders of magnitude[3]; (3) unexpected photochemical reactions take place on the orthometallated oxazolones using the metal as a template.[4]

In all cases, palladium complexes have been used as synthetic tools. In fact, the only organometallic derivatives from unsaturated oxazolones known up to now contain Pd as transition metal, and no other complexes are known beyond Pd. In this communication we report the first synthetic approximations performed in other metals, such as Pt(II), Au(III), Hg(II) and Ru(II).



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IRIDIUM BASED CATION SENSOR

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Traditionally, techniques such as inductively coupled plasma mass spectroscopy or gas chromatography have been used for cation detection. However, these methods need long analysis times and sophisticated instrumentation. Simpler and faster methods have been developed these days, such us optical methods (colorimetric and/or fluorescent), which can entail easy visualization, high sensitivity and cheaper instrumentation. Among these, ratiometric (bicolour) fluorescent sensors stand out due to the lower limit of detection.[1]

In this area, both organic molecules and metal complexes are being developed as luminescent probes. Indeed, some iridium complexes demonstrated to be selective luminescent sensors for different cations. Different strategies are used to trap or interact with the cation, which permits a rational tuning of the iridium's emission.

In our group, we have been working with iridium complexes for a variety of objectives. In this contribution, an iridium-based sensor for cations will be described including its response to cations in solution and on solid supports.

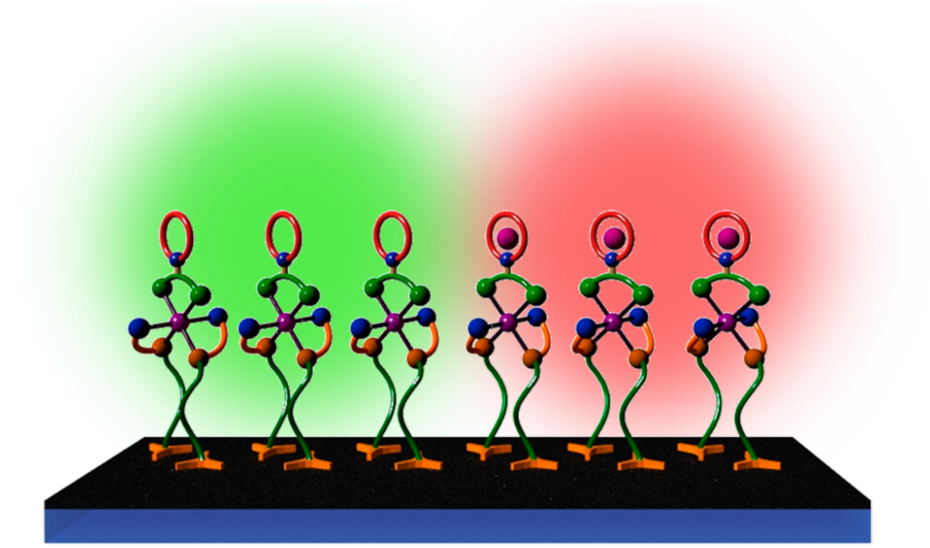

Figure 1. Illustration of the iridium complex's emission color change when trapping the cation.

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P05

Visible-Light-Promoted Aceptorless Dehydrogenation of N-heterocycles Catalyzed by a Standalone Iridium(III) Metal Complex

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The (de)hydrogenation of N-heterocycles catalytically, are considered crucial transformations in organic chemistry due to their presence in pharmaceutical and biological active compounds. Specifically, the acceptorless dehydrogenation of tetrahydroquinolines (THQs) has recently received considerable attention, not only because it avoids the use of stoichiometric oxidants in these organic reactions, but also owed to their prospective use in alternative energy technologies as Liquid Organic Hydrogen Carriers (LOHCs) for hydrogen storage in the liquid form.[1]

Still, the development of effective catalysts for hydrogen-storage has resulted an arduous task so far since they must fulfill a series of technical specifications from the practical point of view. One of the most limiting aspects is hydrogen's discharge temperature from the organic carrier (90-300ºC). Thermodynamically, the dehydrogenation reaction to release H_2 is an uphill process requiring high temperatures. To overcome this obstacle, the use of visible light (400-700 nm) has emerged as a valuable and cleaner alternative. As a result, a successful photocatalytic system for the acceptorless dehydrogenation of N-heterocycles involving a ruthenium-based photosensitizer $[Ru(bpy)_3]^{2+}$ along with the cobalt complex $[Co(dmgH)_2PyCl]$ (dmgH = dimethylglyoximate) has been recently reported.[2] Furthermore, an additional dinuclear iridium catalysts $[\{Ir(Cp^*)(Cl)\}_2(thbpym)]$ bearing (thbpym = 4,4′ ,6,6′-tetrahydroxy-2,2′ - bipyrimidine) as bridging ligand to efficiently catalyze the reverse process (i.e. hydrogenation of N-heterocycles). Herein, the availability of a standalone metal complex capable of catalyzing both transformations under mild conditions to reduce cost is highly desirable.

Thus, the synthesis and catalytic performance of a standalone iridium complex towards the visible light assisted acceptorless dehydrogenation of N-heterocycles and the thermal reverse reaction will be presented in this contribution (Figure. 1).[3]

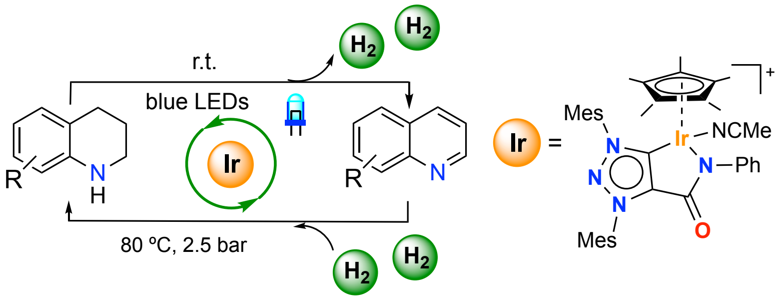

Figure.1 Visible light promoted dehydrogenation and thermal hydrogenation of N-heterocycles catalyzed by a single iridium metal complex.

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Selective Synthesis of Hydrosilanols and Hydrosiloxanes Catalyzed by di-Silyl Rhodium and Iridium Complexes

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Siloxanes and silanols containing Si-H moieties are excellent candidates to control the structure of silicones,[1] because the Si-H bond is one of the most useful functional group in silicon chemistry.[2] Synthetic method for the formation of hydrosiloxanes have been reported, consisting of the reaction of hydrosiloxanes with silanols catalyzed by gold and cobalt complexes.[3,4] However, there are not reported a selective and efficient metal-catalyzed synthesis of hydrosiloxanes and hydrosilanols using water.

Herein we report the synthesis of two neutral ($\{MCl[SiMe_2(o\text{-}C_6H_4PPh_2)]_2\}$; M= Rh, Ir) and two cationic ($\{M[SiMe_2(o\text{-}C_6H_4PPh_2)]_2(NCMe)\}[BAr^F{}_4]$; M= Rh, Ir) complexes and their catalytic activity in the hydrolysis of secondary silanes. The difference in the structure of each complex, and the nature of the dihydrosilane used, allowed us to synthesize different types of related Si-O products selectively. Using the iridium complexes as precatalysts, the obtained product is silanediol, independently of the secondary silane used. However, when rhodium complexes are used as precatalysts, we were able to obtain selectively hydrosilanol and hydrosiloxane depending of the catalyst (neutral or cationic) and the substituents of the silane.

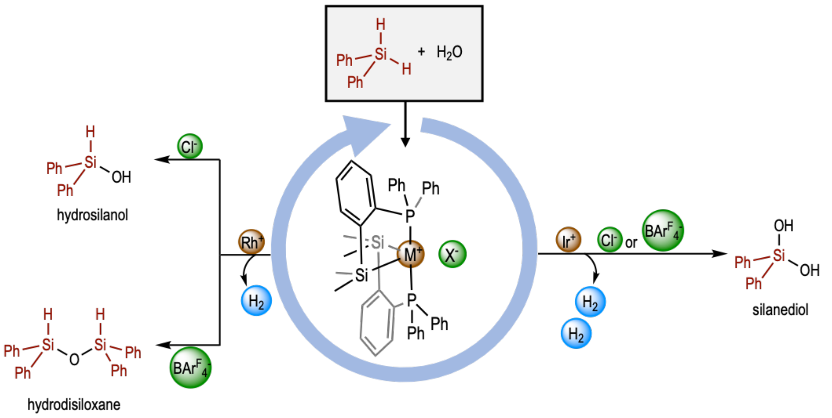

Figure 1

Financial support from the University of the Basque Country UPV/EHU (PIF18/026), Basque Government (IT-11819), the Spanish MICINN (PID2019-111281-GB-I00 and RED2018-102471-T) and IKERBASQUE is gratefully acknowledged.

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P07

ENANTIOPURE IRIDIUM(III) HELICENE COMPLEXES

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Helicenes are aromatic *ortho*-fused polycyclic compounds. When the structure presents more than six fused cycles, these compounds are intrinsically chiral due to their helical out-of-the-plane structure. Chiral helicenes are very well known for their outstanding chiroptical properties (OR, CD, and even CPL). However, they suffer from very poor luminescent quantum yields. Recently, some groups are exploring the coordination of helicene-type ligands to biscyclometalated Ir(III) centers forming species called *iridahelicenes.* These compounds benefit from the outstanding photophysical properties of biscyclometalated Ir(III) complexes and the chiroptical features of helicenic structures.[1,2,3]

In this work we inteded to go one step further. We will present enantiopure chiral-at-metal iridahelicenes synthesised directly from achiral helicenic precursors and chiral-at-metal biscyclometalated iridium complexes. The synthesis, photophysical and chiroptical properties of these new derivatives will be discussed.

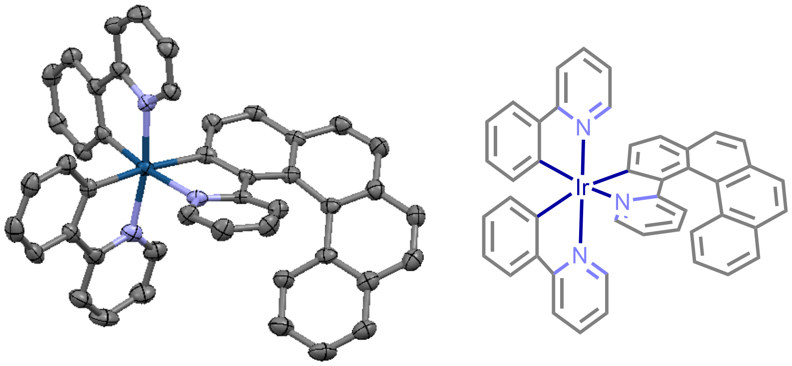

Figure 1: X-ray crystallographic structure and scheme of the iridahelicene

Financial support from the University of the Basque Country UPV/EHU (PIF20/62), Basque Government (IT-1346-19 and IT-1180-19), the Spanish MICINN (PID2019-104772-GBI00, PID2019-111281-GB-I00, RED2018-102387-T and RED2018-102471-T), the European Commission (ERC-2020-SyG-951281) and IKERBASQUE is gratefully acknowledged.

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P08

Hybrid One-pot Tandem Transformation of Ketoximes into Tertiary Alcohols by Combination of Enzymes and RLi/RMgX Reagents in Water at Room Temperature

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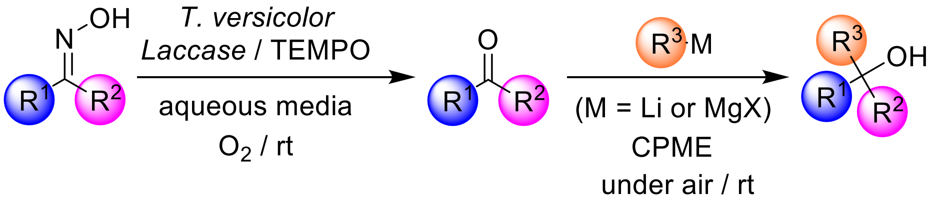
Efficiency and environmental sustainability are central issues in current chemistry [1]. Taking into account this idea, we have previously designed a variety of hybrid one-pot synthetic transformations using sustainable reaction media such as water or *Deep Eutectic Solvents* (*DESs*) [2]. These hybrid one-pot tandem protocols, which combine different instruments from the conventional organic synthetic toolbox (transition metals, main-group elements or organocatalysts) circumvent the need of tedious and time-consuming intermediate purification and separation processes, thus minimizing the generation of residues and simplifying practical aspects. Accordingly, in this communication we will present a new one-pot tandem protocol which combines the biocatalytic laccase/TEMPO deoxymation system with RLi/RMgX reagents in aerobic aqueous media and at room temperature.



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Functionalization of non-activated C−H bonds by carbene transfer reactions catalysed by gold nanoparticles

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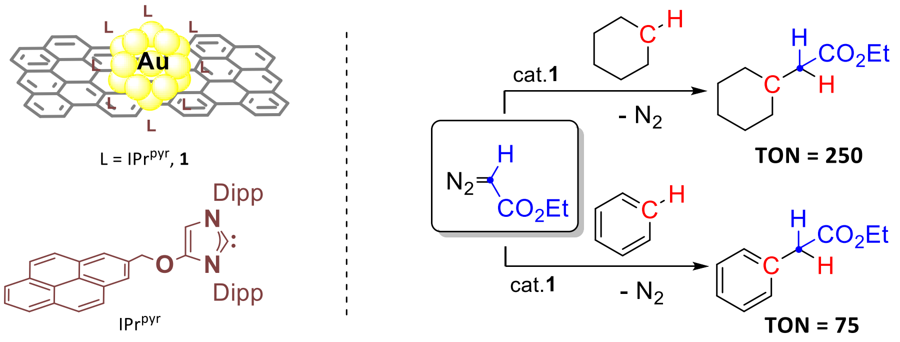
Over the last few decades, carbene transfer reactions from diazo compounds have been widely studied for the functionalization of a broad variety of substrates. Particularly, the functionalization of non-activated C−H bonds of hydrocarbons has significantly emerged from the beginning of this century.[1] Several metals have been reported to catalyze these transformations. Among them, soluble gold-based catalysts have received increasing attention.[2]

At variance with those successful soluble systems, scarce examples can be found regarding the use of heterogenous systems. In fact, no modification of C−H bonds by this methodology is known employing gold-based heterogeneous systems.[3] Herein we present the first example of Au NPs for Csp3−H and Csp2-H bonds functionalization by carbene insertion reaction, where the nanoparticles are stabilized with IPr-like N-heterocyclic carbene (NHC) ligands (IPr^{pyr}) and supported on reduced graphene oxide (rGO), resulting in the material **1**.[4] Finally, recyclability is also effective, reaching an accumulate TON value of 1400 after six consecutive uses in the functionalization of cyclohexane.



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A Novel Catalytic Route To Selective Nitrene Transfer To Enynes

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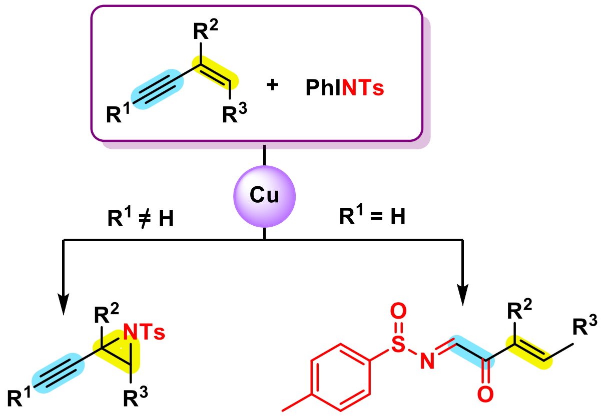
In the last few years, different research groups have developed several catalytic methods for the synthesis of functionalized enynes using copper-based catalysts. This chemistry provides a variety of products where the triple and/or double bonds of the substrate are involved.[1]

Given the experience of our research group in nitrene addition and insertion reactions to substrates of different nature catalyzed by Tp^{x}M (M = Cu, Ag) complexes,[2] we decided to address the nitrene transfer to enynes, a transformation yet unknown in the literature.

In this contribution, we present a new methodology that induces the selective formation of aziridines or sulfinamides derivatives depending on the substituents located at the double or triple bonds. Furthermore, we have carried out the opening and subsequent cycling of these aziridines leading to the formation of pyrroles.



Products derived from the nitrene transfer reaction to enynes

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P11

Chirality Influence on Antitumoral Activity of Anionic Bis(N-Heterocyclic Carbene) Silver Complexes

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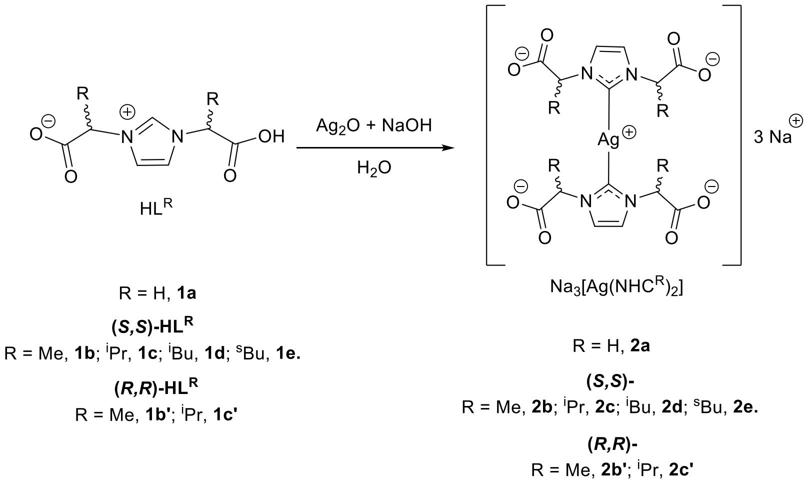
N-Heterocyclic Carbene (NHC) molecules have gained enormous interest in recent decades due to the numerous applications they have demonstrated in various disciplines [1]. Transition-metal NHCs have important applications in medicinal chemistry, for example, as potential drugs against cancer disease. Gold-NHC complexes have a well-recognized anticancer activity, while studies on silver-NHC derivatives are in continuous progress. Specific research on the anticancer activity of enantiopure complexes is still underdeveloped and has focused mainly on platinum derivatives [2]. In fact, to the best of our knowledge, there are no studies on the chiral-anticancer activity relationship for silver-NHC complexes. With these precedents and following our interest in the investigation of complexes containing amino acid-derived ligands and their medicinal applications [3], we decided to explore the preparation of new silver complexes containing chiral NHC^R ligands. Complexes $Na_3[Ag(NHC^R)_2]$, **2a-e** and **2b'-c'**, where NHC^R is a *N*-heterocyclic carbene of the 2,2'-(1*H*-2λ^3,3λ^4-imidazole-1,3-diyl)dicarboxylate type, were prepared by treatment of compounds HL^R, **1a-e** and **1b'-c'** (2-(1-(carboxy*alkyl*)-1H-imidazol-3-ium-3-yl)carboxylate), with silver oxide in the presence of aqueous sodium hydroxide (Scheme 1). They were characterized by analytical, spectroscopic and X-ray methods (**2a**, Figure 1). The cytotoxic activity of these complexes *versus* four human cancer cell lines (melanoma cells MeWo, lung adenocarcinoma A549, bladder cancer cells T24, and gastric cancer cells KATO III) was evaluated and compared with a human non-malignant cell line (skin cells, HaCaT). The study of the cytotoxic activity of the enantiomerically related complexes **2b**/**2b'** and **2c**/**2c'** is unprecedented for silver-NHC complexes and from the comparison of their activities a relationship of chiral-anticancer activity was observed. These and related results will be discussed in this communication.



Scheme 1

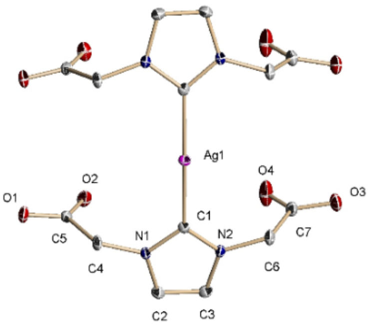


Figure 1

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CATALYTIC REACTIONS OF P$_2$Ni(0) COMPOUNDS WITH ALKYNES

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The transition-metal-catalyzed [2 + 2 + 2] cycloaddition of alkynes is a remarkable atom economy process that provides access to highly substitute benzene derivatives in a single operation, using readily available starting materials.[1] The seminal work of Reppe et al[2] on the cyclopolymerization of acetylene highlighted the central role of nickel complexes in this transformation. On the other hand, hydroarylation reactions of alkynes with arylboronic acids offers a simple and attractive alternative for the preparation of highly substituted alkenes.[2] Second-row transition metals are usually the catalysts of choice for this transformation. However, in recent years, examples of the use of base-metal catalysts, including Ni, have been described[3].

We have recently prepared a series of P$_2$Ni(0) complexes supported by bulky, electron-rich dimethylterphenyl phosphane ligands.[4] In this report, we described the performance of these complexes as catalysts in the cyclotrimerization and hydroarylation of alkynes (Figure 1).

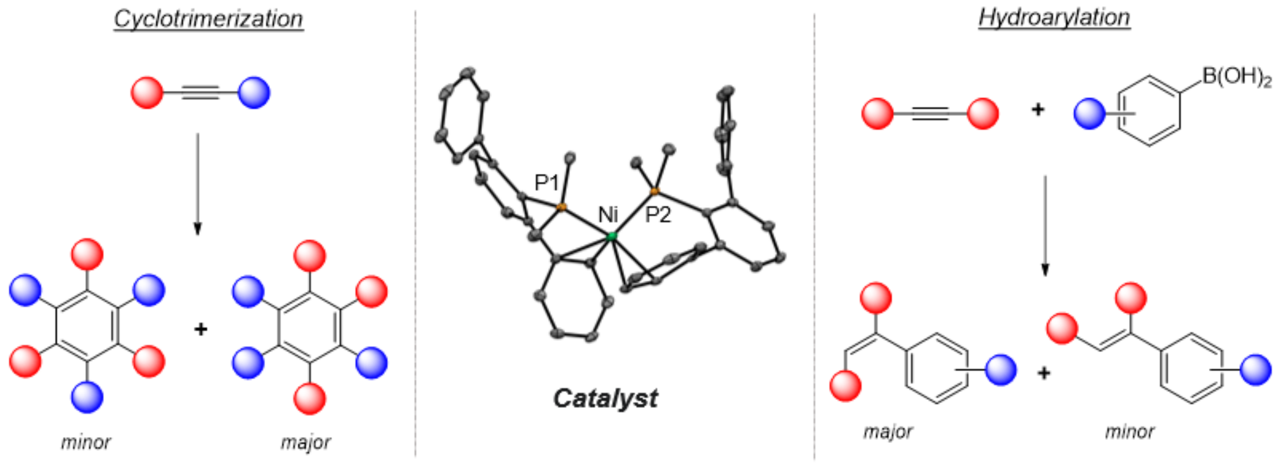

Figure 1. Complex and catalytic reactions described in this work.

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A new series of Pt(II) complexes bearing N^N^N ligands and fluorinated pyridines. Luminescent properties and $^1O_2$ production

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Pt(II) complexes have been extensively studied for their luminescent properties. Tridentate N^N^N ligands permit the synthesis of planar Pt(II) complexes that exhibits interesting luminescence properties by the formation of Pt(II)-Pt(II) interactions, π-π stacking, or aggregated species in solution [1-3]. On the other hand, many Pt(II) complexes have demonstrated to present the ability to produce $^1O_2$, as recently explored in our group [4]. This property is used in several types of applications, such as oxidative reaction, cleaning waste waters, or photodynamic therapy among others.

Herein we present a family of three different triazolyl ligands coordinated to metallic Pt(II) centers and fluorinated ligands. The pincer ligand presents changes in the central ring of pyridine and triazolyl rings in order to analyze the effect of these changes on the luminescent properties in solution and the formation of $^1O_2$.

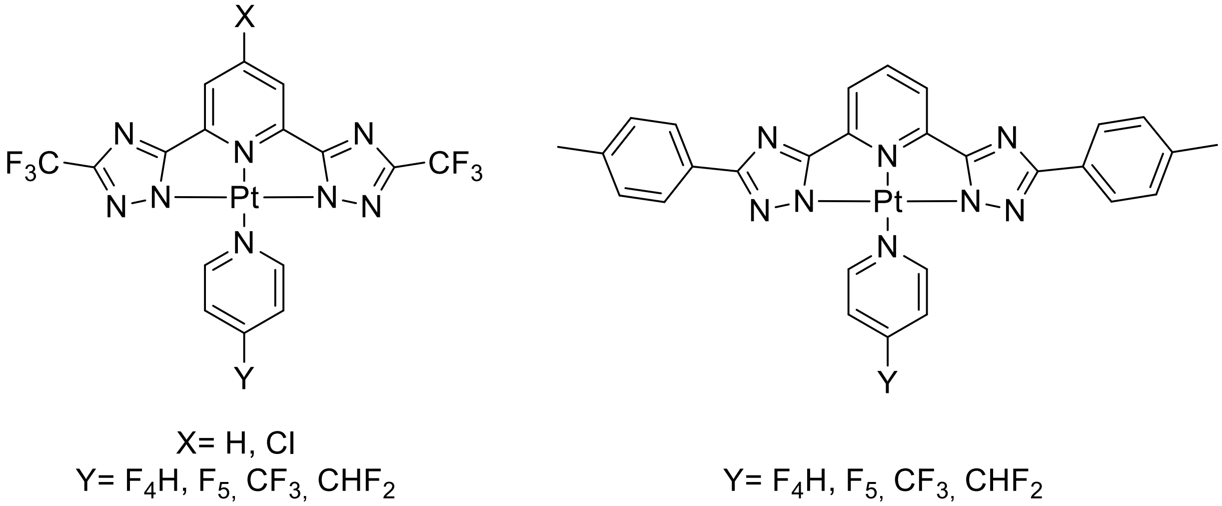

Fig. 1.- Structure of Pt(II) complexes

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Photoinduced C-O Reductive Couplings from Bis-cyclometalated Bis(carboxylato) Pt(IV) Complexes

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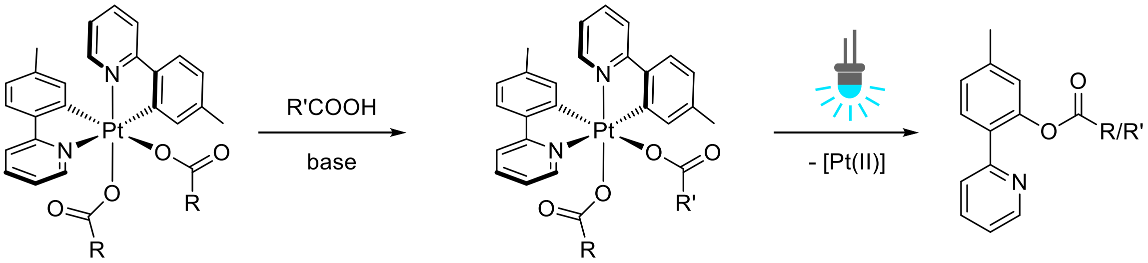
Reductive elimination is a fundamental step in many catalytic cycles and other processes mediated by transition metal complexes for the synthesis of organic compounds. In particular, reductive elimination from group 10 metal complexes has attracted much attention because they enable C–C and C–heteroatom couplings in catalytic reactions.[1] A few C(sp^3)–O reductive couplings from Pt(IV) methyl complexes have been reported, which involve carboxylato, alkoxo or phenolato ligands and usually require heating,[2] whereas the first examples of Ar–O couplings from Pt(IV) complexes were reported in 2020 and proceed under thermal conditions.[3] These precedents suggest that C(sp^2)–O couplings from Pt(IV) complexes are challenging. As far as we are aware, photoinduced C–heteroatom reductive couplings from Pt(IV) complexes have not been reported.

Previous photophysical studies on bis-cyclometalated Pt(IV) complexes featuring an unsymmetrical arrangement of 2-arylpyridine ligands indicated that they may show photochemical reactivity due to the population of triplet ligand-to-metal charge-transfer excited states (^{3}LMCT).[4] In this communication, we present a study on the photoreactivity of bis-cyclometalated bis(carboxylato) Pt(IV) complexes of the type [Pt(tpy)$_2$(O$_2$CR)(O$_2$CR')] [Scheme 1; tpy = cyclometalated 2-(*p*-tolyl)pyridine], which has led to the first photoinduced C–O reductive couplings. The influence of the electronic properties on the carboxylato ligands on the observed regioselectivity will be discussed.



Scheme 1

Acknowledgements
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Computational study of [Cr(indenyl)$_2$] spin-crossover behaviour

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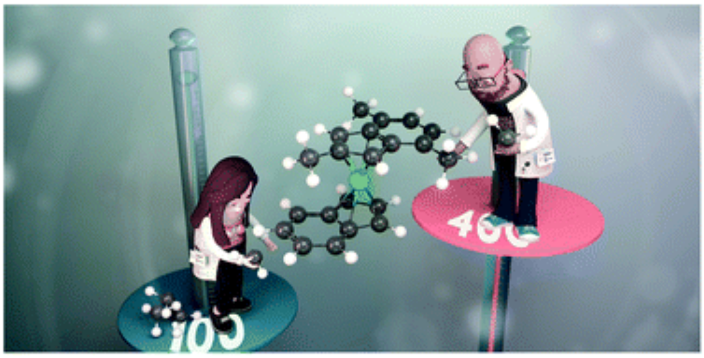
Spin-crossover (SCO) compounds are molecular systems containing first-row transition metal ions that can alternate between two different electronic states which are close in energy. In SCO compounds, an external stimulus (commonly temperature, but also pressure or electromagnetic radiation) is used to change the spin state of the metal centre. The temperature with equal populations of both spin states is defined as the transition temperature ($T_{1/2}$) and is a key parameter in the physical characterization of such systems. This switching behaviour turns such systems in perfect candidates for molecular-level based applications and has raised a lot of attention from the chemistry and physics community over the last years.

In this work, a computational method to study the SCO behavior of the [Cr($^{n\text{-Me}}$indenyl)$_2$] family was carried out. Using the TPSSh/Def2TZVP method with the GD3BJ dispersion correction scheme, we computed the thermochemistry and transition temperatures ($T_{1/2}$) for all members of this family, which are in excellent agreement with the available experimental data [1,2]. Moreover, the computed data allow us to build a model that describes the effect of functionalizing the indenyl ligand in different positions on the spin-state energy gap and transition temperature. Our results show that the C4 and C7 positions of the indenyl ligand have a greater effect on tuning the SCO properties of such complexes. The model quantitatively reproduces the DFT calculations, thus providing a powerful tool to analyze and predict the SCO properties in any member of the [Cr($^{n\text{-Me}}$indenyl)$_2$] family.



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Study of the catalytic activity of (NHC)MCl (M= Cu, Ag, Au) complexes for the nitrene transfer reaction to olefins

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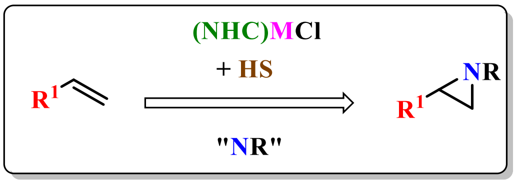
For more than two decades our research group has developed active catalytic systems for the transfer of nitrene groups to substrates of different nature, giving rise to compounds with C-N bonds.[1] In this context however, examples described in the literature usually employ bi- or tridentate ligands, mainly with N-donors. We have now turned our attention to complexes (NHC)MCl (M = Cu, Ag, Au) (NHC = N-heterocyclic carbene ligands) as catalysts for such transformations, in view of the scarce examples reported to date.[2] In this communication we present the results obtained using the (NHC)MCl complexes as catalysts for the nitrene transfer reaction to olefins. The effect of the metal (Cu, Ag, Au), the type of NHC (IPr, IMs) and the halogen scavenger in the chemo- and regioselectivity will be discussed.



M = Cu, Ag, Au

NHC = IPr, IMes

HS = $\mathrm{NaBAr^{F}{}_4}$, AgOTf, $\mathrm{NH_4PF_6}$

"NR" = Nitrene Source

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Mechanistic Investigations on Hydrogenation, Isomerization and Hydrosilylation Reactions Mediated by a Germyl-Rhodium System

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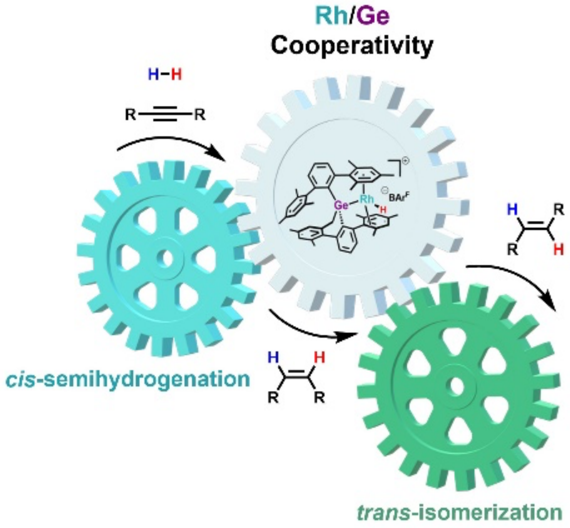
We recently disclosed a dehydrogenative double C-H bond activation reaction in the unusual pincer-type rhodium-germyl complex [(ArMes)$_2$ClGeRh] (ArMes = C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)$_2$).[1] Then, we investigate the catalytic applications of this Rh/Ge system in several transformations, namely *trans*-semihydrogenation of internal alkynes, *trans*-isomerization of olefins and hydrosilylation of alkynes.[2] We have compared the activity and selectivity of this catalyst against other common rhodium precursors, as well as related sterically hindered rhodium complexes, being the one with the germyl fragment superior in terms of selectivity towards *E*-isomers. To increase this selectivity, a tandem catalytic protocol that incorporates the use of a heterogeneous catalyst for the *trans*-semihydrogenation of internal alkynes has been devised. Kinetic mechanistic investigations provide important information regarding the individual catalytic cycles that comprise the overall *trans*-semihydrogenation of internal alkynes.



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P18

Pd(II) PRECATALYST FOR EFFICIENT C-N CROSS-COUPLING OF ARYL SULFAMATES WITH *N*-NUCLEOPHILES

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In recent years, several types of highly efficient Pd(II) precatalysts, able to generate and stabilize monoligated palladium(0) species, LPd(0), have been developed.[1] Among them, the family of 2-aminobiphenyl N, C-palladacycles has been widely studied and modified by Buchwald.[2] The remarkable catalytic activity of these palladacycle precatalysts relies on facile activation, in the presence of a base, to yield the desired monoligated palladium(0) species.

Very recently, we have described the catalytic performance of a series of 2-aminobiphenyl palladacycles stabilized by bulky dialkylterphenyl phosphanes ligands in the amination of deactivated aryl chlorides with a variety of N-nucleophiles.[3] The excellent catalytic properties displayed by this precatalyst bearing the bulkiest terphenyl phosphane, $PCyp_2Ar^{Xyl2}$, encouraged us to investigate their performance in the amination of more challenging electrophiles, such as aryl sulfamates. Contrary to aryl sulfonates (triflates, mesylates, and tosylates), aryl sulfamates have been scarcely used as electrophilic coupling partners in Pd-catalyzed cross-coupling reactions,[4] since they are much less reactive under the same conditions. Reported methods are mainly limited to Ni catalysts, which have some drawbacks such as the high catalyst loading and harsher reaction conditions. Herein, we report an efficient catalytic system for the amination of aryl sulfamates with a variety of *N*-nucleophiles including (hetero)aryl, primary and secondary amines, and *N*-heterocycles under catalytic conditions similar to those reported for more reactive aryl chlorides (Figure 1).

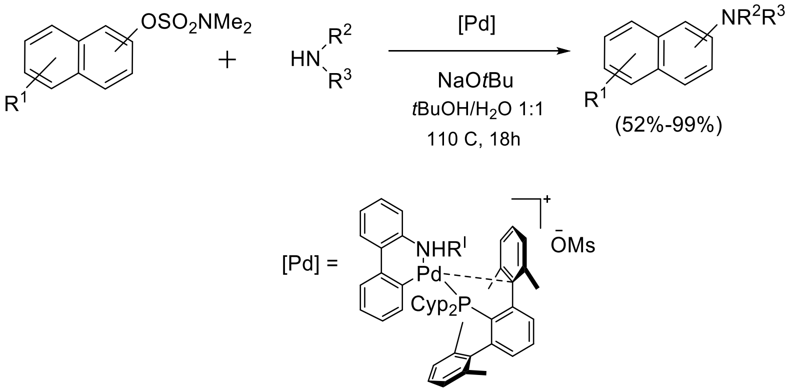

Figure 1. C-N cross-coupling of aryl sulfamates and amines catalyzed by Pd(II) precatalyst supported by dialkylterphenyl phosphane ligand.

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P19

Synthesis and Luminescence of Pt(II) Complexes with a Terdentate C^C^N Ligand

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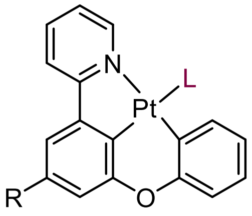
Pt(II) complexes with chelating heteroaromatic ligands have been intensively studied for their excited-state properties, which make them suitable for diverse photochemical, analytical and optoelectronic applications, including their use as luminescent probes for bioimaging,[1] photocatalysts in organic synthesis[2] and phosphors for organic light-emitting devices (OLEDs).[3] Cyclometalated 2-arylpyridines (C^N) have long been the most frequently employed ligands for the design of luminescent Pt(II) complexes because the metalated aryl is a strong σ-donor that induces a large ligand-field splitting, resulting in enhanced stabilities and emission efficiencies with respect to bipyridine (N^N) complexes, and many Pt(II) emitters are of the type [Pt(C^N)(L^X)], where L^X is a monoanionic chelating ligand.[4] Increasing the number of C-donor moieties is desirable to achieve higher emission efficiencies, but the derivatives *cis*-[Pt(C^N)$_2$] are generally not emissive because of geometrical distortions in the excited state. The development of more efficient Pt(II) emitters has often been addressed by using terdentate N^C^N, N^N^C or C^N^C ligands, or tetradentate C^N^N^C or N^C^C^N ligands, which impart rigidity and reduce nonradiative deactivation.[4] However, some of these ligands provide only one C-donor moiety (N^C^N, N^N^C), and other lead to weakly emissive complexes due to a trans arrangement of metalated carbon atoms (C^N^C)[5] or are difficult to introduce in the coordination sphere of Pt(II) (tetradentate ligands).[6]

As far as we are aware, synthetic methodologies for the preparation of Pt(II) complexes with terdentate C^C^N ligands have not been developed, and complexes of other metal ions with this kind of ligands are limited to a few Au(III) or Pd(II) derivatives, which show an enhancement of the emission efficiencies with respect C^N^C analogues.[7] In this communication, the synthesis of a series of complexes of the type [Pt(C^C^N)L] will be presented, which constitute a new platform for the development of efficient Pt(II) emitters with tunable properties.



Scheme 1

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Labile Light-harvesting Ir(III) Complexes

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Targeting iridium complexes able to harvest visible light and create vacant coordination sites to be used in stoichiometric or catalytic reactions, new cationic Ir(III) complexes were synthesized from precursor Ir(IMes”)$(NCMe)_3]PF_6$, which contains a doubly cyclometalated NHC ligand [1]. The new complexes incorporate bidentate L_2 ligands based on either polypyridine (N_2) or mesoionic bis-carbene (C_2) [2] skeletons (see figure) providing extended low-lying π* systems that ensure light absorption in the visible region.

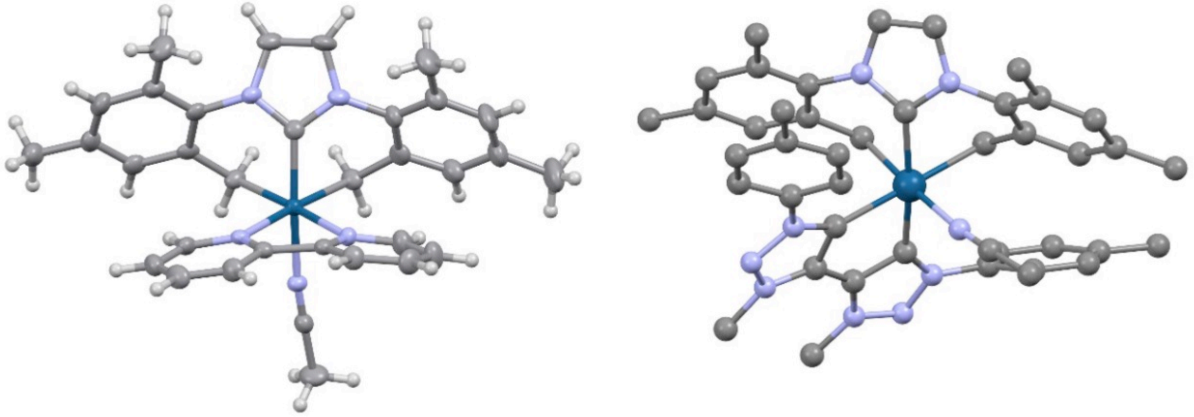

Figure: (left) X-ray structure of the symmetric cation of [Ir(IMes”)(2,2’-bipy)(NCMe)]$^+$ and (right) DFT calculated structure of the asymmetric cation of [Ir(IMes”)(i-bitz)(NCMe)]$^+$ (H atoms have been omitted for the sake of clarity).

The new complexes [Ir(IMes”)(L_2)(NCMe)]PF_6 are generally obtained as two isomers, symmetric or asymmetric, kinetic or thermodynamic, respectively. The isomerization processes and their kinetics in solution have been studied by NMR and interpreted through DFT calculations. The behavior of each complex is ultimately conditioned by the strength of acetonitrile coordination to each of the two different available coordination sites (trans to alkyl or NHC, respectively). The new complexes absorb visible light and show phosphorescent emissions with low quantum yields at room temperature. Calculations indicate that acetonitrile dissociation is favored in the ^{3}MLCT excited states regardless coordination position, suggesting that the energy absorbed from visible light can be directly invested in opening vacant sites at the coordination sphere of the complexes.

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Copper-Catalyzed Olefin Aziridination in Water with an Iminoidonane

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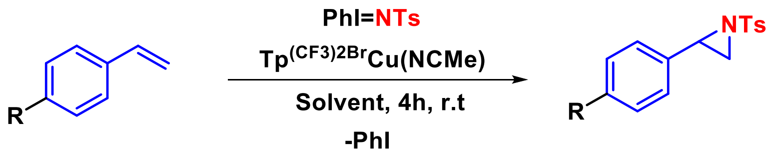
Despite water is the solvent favorite in nature, its application as reaction media is limited in the modern chemistry due to the low solubility of many organic molecules and the low stability in water of many transition metal complexes used as catalysts. However, in the last decades, several strategies have been developed which have allowed that very interesting metal-catalyzed organic transformations can be carried out under mild conditions employing water as solvent.

In this context, our group has previously described a series of metal complexes bearing trispyrazolylborate ligands (Tp^x) as catalysts capable of the functionalization of aliphatic C-H bonds upon inserting $CHCO_2Et$ units from N_2=CHCOEt (ethyl diazoacetate, EDA) using water as reaction media. [1, 2]

Now we have turned out attention to nitrene transfer reactions.[3] In this work, the copper complex $Tp^{(CF3)2Br}$Cu(CNMe) is described as an efficient catalyst for the olefin aziridination using PhI=NTs as nitrene source. Identical activity was observed when dichloromethane and water were used as solvents under same conditions. Competition experiments and Hammett plots show that the behavior of the metal is the same in both reaction media.



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Neutral and Cationic Zinc (II) Alkoxides supported by Non-Innocent BIP Ligands. Synthesis, Structure and ε-Caprolactone Polimerization Catalysis.

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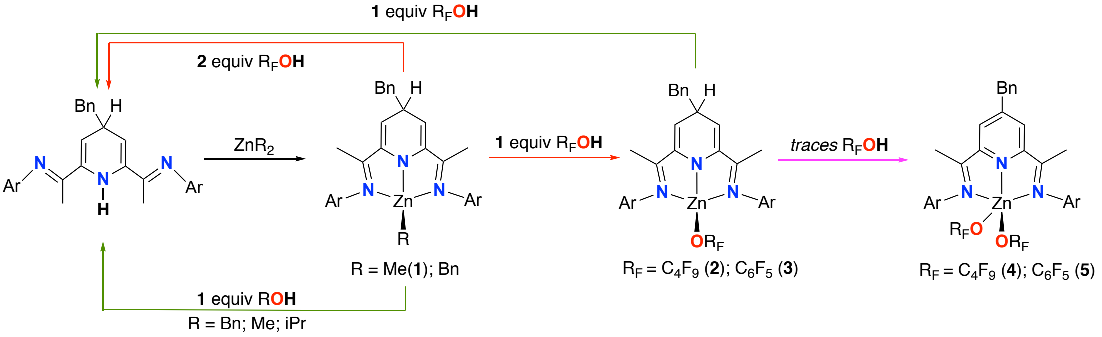
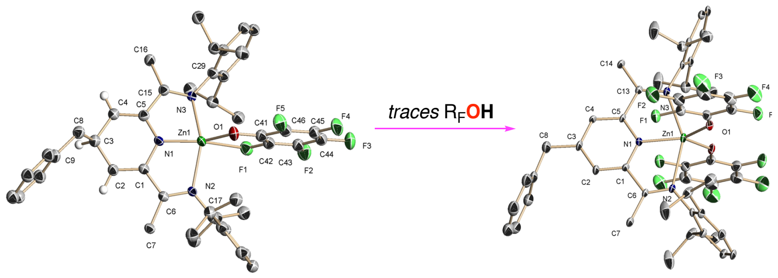
Perfluoro-alkyl and -aryl alcohols react with 2,6-bisimino-4-Bn-dihydropyridinates(-1) zinc (II) alkyls allowing the stabilization corresponding monoalkoxide complexes, whilst equimolar amounts of conventional benzylic alcohol or isopropanol lead to demetallation and clean recovery of the eventually quelated 4-Bn-dihydropyridine ligand as shown in Scheme 1, left. The zinc (II) perfluoro-alkoxide and -aryloxide dihydropyridinates (**2** and **3**) are thermally stable species though they are much more reactive than their precursors (**1** and **Bn**). In the presence of extra amount of alcohol, no matter its nature, **2** and **3** experience transformations that also lead to their complete demetallation and the recovery of 4-Bn-dihydropyridines, whereas if traces of the strongly acidic electrophiles are added to solutions of these 2,6-bisimino-4-Bn-dihydropyridinate monoalkoxide complexes (**2** or **3**), they produce metal-containing zinc dialkoxide 2,6-bisimino-4-Bn-pyridines as the major products of reactions that presumably occur throughout catalytic processes. Together with these reactions and the characterization of the related products, we could also confirm the isolation of the corresponding cationic mono-alkyl and -alkoxide derivatives through different synthetic routes. Some of the neutral and cationic species prepared during these investigations were tested as ε-caprolactone polymerization catalysts offering promising results.





(**3**) (**5**)

From 2-Butyne to Diene and [3]Dendralene Motifs at Triflate Ir(PSiP) Pincers

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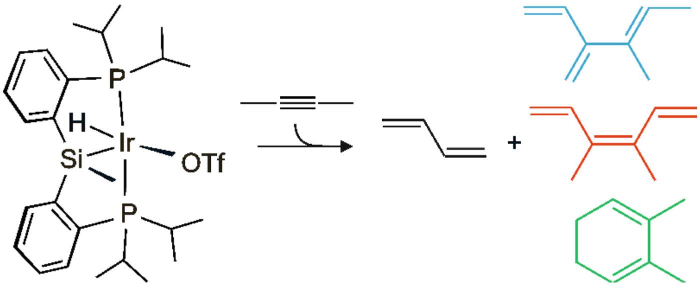
The five-coordinate hydride complex $[\mathrm{IrH}\{\kappa O\text{-}\mathrm{O_3S(CF_3)}\}\{\kappa P,P,Si\text{-}\mathrm{SiMe(C_6H_4\text{-}2\text{-}P}i\mathrm{Pr_2)_2}\}]$ [1] was found capable of catalytically transforming 2-butyne into its more stable 1,3-butadiene isomer, also forming triene: (*E*)-4-methyl-3-methylene-1,4-hexadiene and (*3Z*)-3,4-dimethyl-1,3,5-hexatriene, and 2,3-dimethyl-1,3-cyclohexadiene dimerization products. The reaction only proceeds catalytically in benzene as solvent at high temperature (363 K).



The various reaction intermediates observed by NMR inspired DFT calculations which in turn indicate a key mechanistic role of the triflate as proton shuttle. This is favored in non-polar solvents by ion pairing and the low electronic demand from the metal to the triflate at the coordination position trans to silicon. The shuttling mechanism competes with a more classical one implying hydride intermediates, and with reversible processes of pincer ligand disassembling. Yet, proton shuttling is the only option capable of assisting the determinant release of such strong-coordinating products.

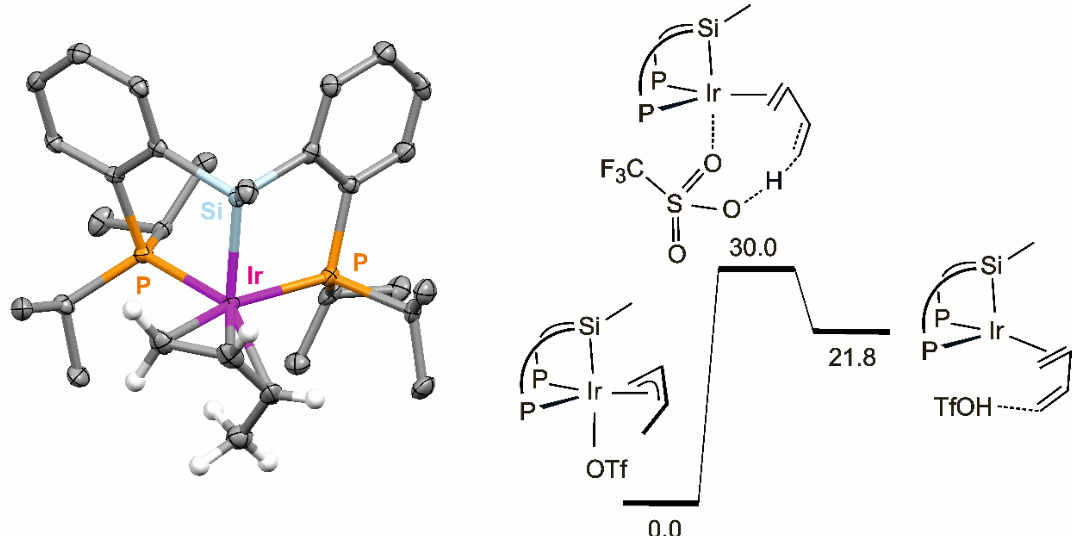


Figure. (left) X-ray structure of the cation of an observed methyl-allyl reaction intermediate. (right) DFT calculated trajectory for triflate-assisted product release (ΔG kcal mol^{-1} in benzene).

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Application and mechanism of the asymmetric hydrogenation of imines with Ru catalysts based on phosphine-phosphite ligands

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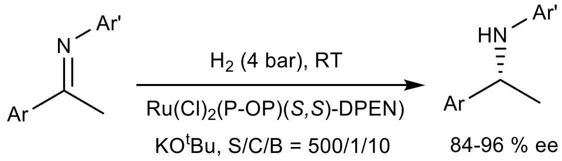
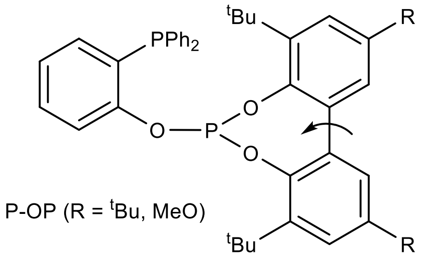
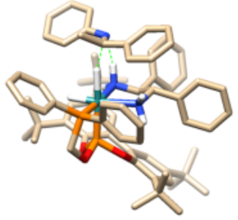
Ru complexes of formula Ru(Cl)$_2$(P-OP)(DPEN) (P-OP: achiral phosphine-phosphite, DPEN: (*R,R*)- or (*S,S*)-1,2-diphenylethylenediamine) provide effective catalysts for the asymmetric hydrogenation of imines under very mild conditions. The catalytic system shows a good substrate range and provides good to high enantioselectivities in the hydrogenation of a broad range of substrates, along with practical advantages, as it is also suitable multigram scale synthesis and it requires commercial DPEN diamine as the sole chiral ligand.





Atropisomerizable (achiral) phosphine-phosphite



cis-dihydride *chiral at metal* catalyst

The mechanism of the reaction has been studied in detail both experimental and computationally. Results agree with a reaction catalyzed by a *cis*-dihydride chiral at Ru species, in contrast with ubiquitous *trans*-dihydrides proposed in ketone hydrogenation. In addition, a substrated assisted process has been calculated as the most favourable one for the activation by hydrogen. Calculations also explain the role of the atropisomerizable phosphine-phosphite ligand and a good agreement between experimental and calculated enantioselectivity.

Acknowledgment: financial support from Spanish Ministry of Science and Innovation (projects CTQ2016-75193-P; AEI/FEDER, UE, RED2018-102387-T, PID2019-110856GA-I00 and PGC2018-100818-A-I00) and Junta de Andalucía (Project US-1380849) is gratefully acknowledged.

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Ligand-Centered Redox Processes and Structural Diversity of Orthophenylendiamido Tantalum Compounds

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Exploring new metal-ligand combinations and its influence on reactivity is essential for applied organometallic chemistry. This is particularly relevant in the case of d^0 early transition metal, in which the selection of the appropriate ligand has enabled multiple application in synthesis.[1]

Remarkable examples are found for group 5 compounds incorporating redox-active ligands capable of mediating multielectron processes.[2] Among the variety of these type of ligands 1,4-disustituted diazabutadiene (DAD) have attracted much attention because of their flexibility in coordination modes and to the possibility of undergoing one or two electron redox processes.[3] Orthophenylendiamido (*o*-PDA) ligands, despite having similar properties, have been comparatively less investigated. A recent report reveals that by simply combining one type of *o*-PDA ligand with [TaCl$_2$Me$_3$] triggers a rich chemistry, involving one electron redox process and two different coordination modes.[4]

Expanding the chemistry of *o*-PDA with tantalum, herein we report our studies on the combination of a variety of redox active ligands with [TaCl$_{5-n}$(η^5-C$_5$H$_4$SiMe$_3$)$_n$] (n = 0, 1). Interestingly, the isolated compounds display three different metal-ligand coordination modes (**Figure 1**) due to the one or two electron oxidations of the redox active ligands.

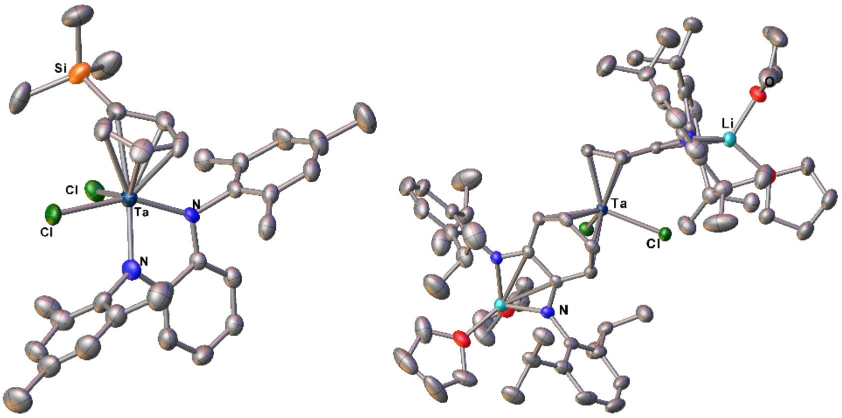

Figure 1. Solid state structures of *o*-PDA-Ta compounds displaying two different coordination modes.

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Synthesis of Ferrocene Based Catalytic Structures and Study of its Properties

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The serendipitous discovery of ferrocene in 1951 is considered an important milestone that allowed the impulse and development of the organometallic chemistry of transition metals, helping this area to take off as an independent field of research.

The excellent properties of this structure have been extensively studied and used for the construction of molecules with greater complexity in multiple areas, from catalysis, materials science, to medicine [1].

Currently, among all of them, the field of catalysis continues to present a high interest since more than 90% of the products derived from the chemical industry include in their synthesis a catalytic stage.

Therefore, as a main objective, this work focuses on the design, synthesis and study of the properties of new catalysts that use the ferrocene skeleton as a support, thus demonstrating the wide versatility of structures that this molecule can offer.

On this point, this work has been divided into two distinct parts:

First, ferrocenyl-organocatalyst type systems have been developed [2], as well as group 11 metal catalysts that use ferrocene-derived structures as ligands [3]. These derivatives (Figure 1) have been characterized by various spectroscopic and/or electrochemical techniques.

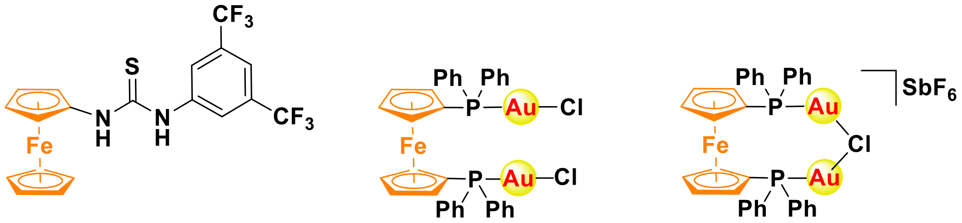

Figure 1. Some of the ferrocene-based structures that have been studied.

On the other hand, an evaluation of the catalytic properties of these structures has been carried out, either in common model reactions in the field of organocatalysis or in catalysis mediated by transition metals, focusing the study on Au(I) complexes.

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Synthesis of NHC-Gold Complexes Featuring a Carbazole Fragment

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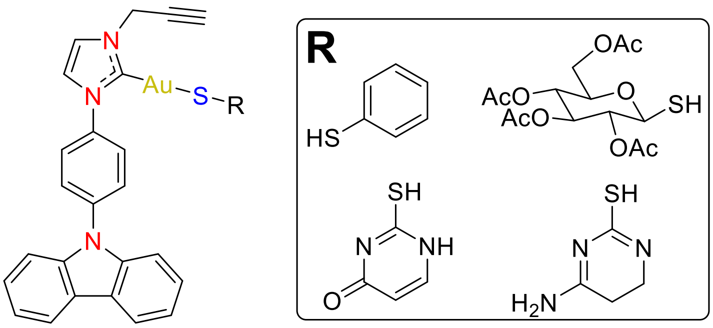
During the last decades, the interest in *N*-heterocyclic carbenes has been increasing since these compounds can find applications in different fields, such as catalysis, pharmaceuticals and organometallic materials.[1] This wide range of applications is a consequence of the great versatility that these compounds present towards the functionalization, being able to modify the nitrogen substituents and therefore, the electronic and steric properties, including the asymmetric induction of the final complexes.

The stability of these compounds with d10 cations such as Au(I) and Ag(I) has led to the development of new M-NHC species with medical applications (as antibacterial and antitumoral agents)[2] or in the field of catalysis, with activation of multiple carbon-carbon bonds.[3]

In this work, we have synthetized a new imidazolium salt featuring a carbazole derivate and its corresponding NHC-Au-Br linear complex. The carbazole fragment gives our complex luminescent properties, aiming to be a good candidate to be used as an imaging agent. The other nitrogen of the imidazolium salt has been functionalized with a propargyl group, which gives the complex more solubility in water and allows further functionalization (either by “click” reaction or by deprotonation of the alkyne).

The gold complex has been derivatized by substitution of the halogen by different thioles with biological interest, such as 2-mercaptopyridine, thioglucose tetraacetate and different DNA-bases derivates.



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Catalytic and Photophysical properties of Gold(I) Complexes bearing the DPPMPY Ligand

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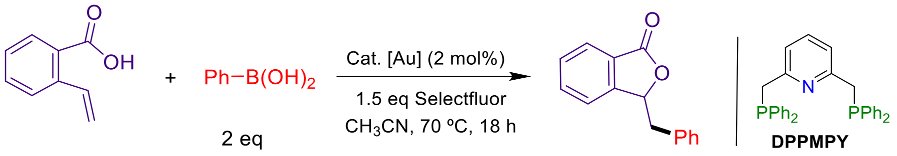
PNP-gold(I) complexes have been used as catalysts in several processes. For instance, Echavarren and coworkers reported carbonylation of primary amines to form ureas catalyzed by polynuclear gold(I) complexes bearing the $[(Ph_2P)_2Py]$ ligand [1] and Toste group described the allylation reaction of aryl boronic acids using the $[(Ph_2P)_2N^{iPr}]Au_2Cl_2$ as catalyst. [2] We wondered if the use of the DPPMPY (2,6-bis(diphenylphosphinomethyl)pyridine) [3] ligand, with a CH_2 group between the phosphorus and the pyridine moiety could introduce different structural characteristics in its gold(I) complexes which, therefore, could influence their catalytic capabilities. In this contribution, we describe the synthesis and characterization of a series of new gold(I) complexes bearing the DPPMPY ligand. We have studied their catalytic activities in the intramolecular oxyarylation reaction of 2-vinylbenzoic acid and phenylboronic acid in the presence of Selectfluor as oxidizing reagent (Table 1). Finally, we have also investigated the photophysical properties of the DPPMPY-gold(I) complexes.

Table 1. Oxyarylation Reaction Catalyzed by DPPMPY-gold(I) complexes



Entry	Catalyst	Yield (%)
1	DPPMPYAu$_2$Cl$_2$(**1**)	50
2	DPPMPYAu$_2$Br$_2$ (**2**)	40
3	[(DPPMPY$_2$Au$_4$Cl$_2$)](SbF$_6$)$_2$ (**3**)	42
4	[DPPMPY$_2$Au$_4$(CH$_3$CN)$_2$](SbF$_6$)$_4$ (**4**)	64
5	[(DPPMPY$_2$Au$_2$Cl$_2$)](BF$_4$)$_2$ (**5**)	40
6	[DPPMPY$_2$Au$_4$(CH$_3$CN)$_2$](BF$_4$)$_4$ (**6**)	60
7	[(DPPMPY$_2$Au$_2$Br$_2$)](BF$_4$)$_2$ (**7**)	61

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Therapeutic applications of Dithiocarbamate Gold(I) complexes derived from Sulfonamides on Colon Cancer cells

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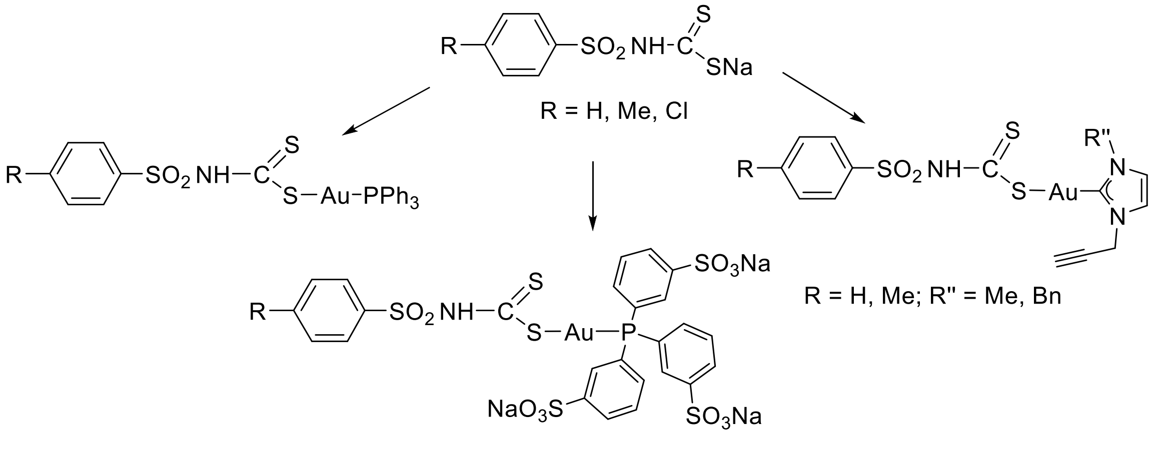
Carbonic anhydrases (CAs) consist on a family of metalloenzymes that catalyse the reversible hydration of carbon dioxide to HCO_3^- and H^+. Some of the isoforms, CAIX and CAXII, are overexpressed in an extensive variety of solid tumours, such as colon cancer, among others [1], being CAIX expression more specific in tumour tissues in comparison to CAXII, what makes it an interesting target for designing chemotherapeutic agents [2].

Dithiocarbamates besides sulfonamide derivatives, compounds with a wide array of biological activities, are considered as CA inhibitors [3]. Combination of both moieties in the same molecule has recently led to sulfonamide-dithiocarbamate hybrids as a potent class of carbonic anhydrase inhibitors [4].

With this background we describe here the synthesis of dithiocarbamate ligands bearing the benzenesulfonamide moiety. Their coordination to gold(I) centres with phosphines or carbene as ancillary ligands (scheme 1) has afforded active complexes against colon cancer cells (line Caco-2). We have studied the anticancer mechanism of selected derivatives which includes the type of cell death, interaction with proteins involved and the targets on which these metallic compounds could act, such as carbonic anhydrase (CA) or thioredoxin reductase (TrxR1). The results suggest that the new complexes could act as multi target drugs, since they inhibit the activity of the enzymes thioredoxin reductase (TrxR) and carbonic anhydrase (CA IX) with alteration of the redox balance and showing a pro-oxidant effect.



Scheme 1

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Strategies for obtaining Thermally Activated Delayed Fluorescence in Gold(I) complexes

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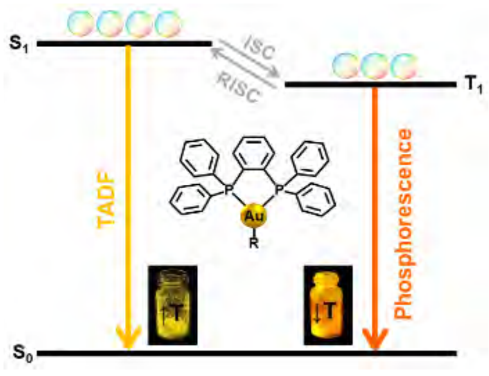
The development of novel materials for their application as electroluminescent devices is nowadays one of the main purposes of many laboratories. In them, one of the main objective is the design of molecules with maxima efficiencies. In this sense, Thermally Activated Delayed Fluorescent (TADF) materials is a very interesting class of emitters because they are able to show extremely high efficiencies due to their ability to harvest the 100 % excitons formed , and when this is achieved at room temperature, the process is undoubtedly of practical application [1].

There are strict requirements that the candidates must fulfil to behave as TADF emitters, for example to present a small difference between the lowest singlet and triplet states; to have a significant rate of Reverse Intersystem Crossing (RISC) from T_1 to S_1 at room temperature; and to present a rigid molecular structure that avoids distortions and, consequently, non-radiative deactivation pathways or roll-off effects.

Gold(I) complexes can be considered a new class of this kind of emitters whose characteristics make them appropriate practical applications. For instance, its heavy-metal nature provokes a very strong Spin Orbit Coupling (SOC) favouring ISC; some of their possible geometries (trigonal planar or tetrahedral) lead to high structural rigidities; and gold(I) with its d^{10} configuration is a very stable and poorly reactive ion towards oxidation.

In this communication we present the different strategies followed to synthesize of a new class of TADF emitters based on gold (I), in which a rational election of ligands derived from bis(diphenylphosphino)benzene (dppBz) and with perhalophenyl) groups, confirmed by theoretical studies, permits the synthesis of very efficient emitters [2,3].



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P31

Influence of Solvent Amount on the Metallophilic Interactions

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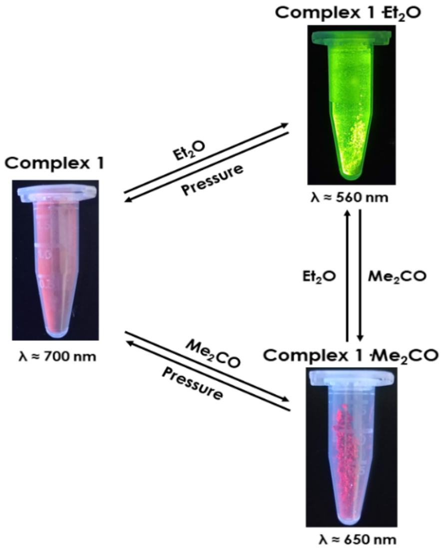
It is known that heavy metal closed shell ions tend to form metal···metal interactions to give rise to polynuclear aggregates with distances between the metals shorter than the sum of their Van der Waals radii.[1] These complexes often show interesting photophysical properties, such as luminescence, which is closely related to the presence of such M···M interactions.[2]

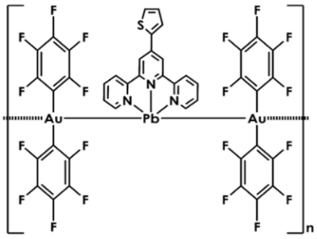
On the other hand, polymorphism can be defined as a "crystalline solid phase of a given compound that gives rise to at least two different organisations of the molecule in space". Within this category is pseudopolymorphism,[3] a subcategory that refers to obtaining a compound in different crystalline forms that differ in nature or stoichiometry by including solvent molecules. Thus, by controlling the factors that can affect the crystallization of a particular pseudopolymorph, the properties of the crystalline solid obtained could be controlled.

In order to study the solvent induced polymorphism, we have synthesized the gold/lead complex $[Au_2Pb(C_6F_5)_4(C_{19}H_{13}N_3S)]$ (**1**), which is obtained as red solid with intense red luminescence (λ ≈ 700 nm). It has been exposed to different solvents, and the effect of the presence, nature and amount of solvent in the structure and photophysical properties of the resulting solids has been analyzed. Thus, the initial red complex **1** turns into the yellow **1**·Et_2O (λ ≈ 560 nm) or the red **1**·Me_2CO (λ ≈ 650 nm) upon treatment with diethyl ether or acetone, respectively (see Figure). Furthermore, treatment of **1**·Et_2O with acetone affords **1**·Me_2CO in a few seconds (and *viceversa*), and shows mechanochromism, since rapidly turns into red by manual grinding.

Interestingly, the slow evaporation of a solution of **1** in diethyl ether afforded three different polymorphs that differ in colour, luminescence and content of solvent, which appeared in the bottom (yellow, **1**·Et_2O), middle (dark green, **1**·0.75 Et_2O) and upper (red, **1**) part of the Schlenk.

The crystal structures of **1**·Et_2O, **1**·0.75 Et_2O and **1**·Me_2CO confirm the relationship between the optical properties of the polymorphs and the homo- and heterometallic distances in the crystal, showing a red shift of the emission as the metal-metal distances decrease.





Complex 1

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P32

Organometallic approach to Au/Ag-2D semiconductor nanostructures and study of their photothermal and photocatalytic properties

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Wet-chemical methods for noble metal nanoparticle synthesis of small size usually require the use of growth directing agents in order to achieve an appropriate control over the nucleation and growth steps. Among these methods, the reduction of organometallic complexes has allowed us and others to control the size, shape and composition of the nano-objects by including ligands or polymers in the nanoparticle formation process.[1-4] However, the ligand/polymer shells may lead to less accessible metal surfaces, reducing the ability of these nanoparticles in catalytic or photocatalytic applications. In order to tackle these drawbacks we have focused on the formation of plasmonic Au-Ag or Au nanoparticles by the reduction of organometallic complexes in the absence of stabilizing agents, directly at the surface of two nanostructured semiconductors such as polymeric carbon nitride (C_3N_4) nanosheets or MoS_2 nanoflowers, which bear stabilizing groups (triazine) or atoms (sulfur) at their surface, respectively. In addition to the metal nanoparticle stabilization provided by these semiconductor supports, their combination into plasmonic metal-semiconductor nanohybrids provide new materials displaying enhanced photothermal and photocatalytic properties.

In this communication we show the synthesis of novel gold-based plasmonic-semiconductor nanohybrids formed by the fast reduction of organometallic complexes $[Au_2Ag_2(C_6F_5)_4(OEt_2)_2]_n$ or $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) on the surface of carbon nitride (C_3N_4) nanosheets or MoS_2 nanoflowers and using triisopropylsilane as reducing agent. These new nanohybrids display interesting photocatalytic and photothermal heating properties that can be applied, for instance, in environmental remediation of wastewater.

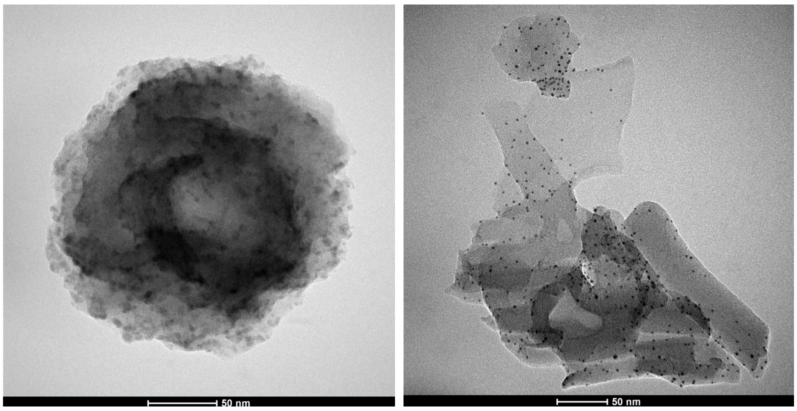

Figure 1. TEM images of plasmonic-semiconductor nanohybrids: AuAg-MoS_2 (left) and Au-C_3N_4 (right)

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P33

Ruthenium catalysts to produce Hydrogen On-Demand using the pair silane/alcohol

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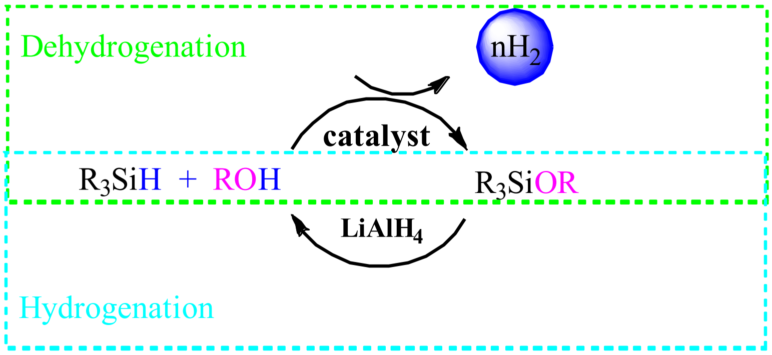
The major limitation of renewable energies is related to its intermittent character, which depends on meteorological factors. To ensure supply and feasibility of renewable energy sources, the creation of efficient energy storage systems is vital. [1] Among them, chemical storage of hydrogen using liquid organic hydrogen carriers (LOHCs) has emerged as an efficient and safe technology, which allows to transport energy safely and use it on-demand. There are several organic pairs that have been considered as potential LOHCs, which include cycloalkanes, N-heterocycles, methanol, formic acid, ammonia-boranes and silanes/ alcohols. [2]

The present work is focused on the coupling of silanes and alcohols LOHC system (Scheme 1). The process generates a silyl ether that can be used in the silicone industry or can be restored to the former hydrosilane by reduction with reactive hydride reagents. [3] The formation of molecular hydrogen from the coupling of hydrosilanes and alcohols is a spontaneous thermodynamic process, although it is kinetically slow, so a catalyst is essential. Previous studies in our research group have showed the feasibility of the pair silane/alcohol as an efficient LOHC using catalysts based on iridium and ruthenium. [4,5].



Scheme 1. LOHC system based on the pair silane/alcohol.

For this reason, three ruthenium complexes that possess different bypiridine ligands have been evaluated as catalysts towards the dehydrogenative coupling of hydrosilanes with different alcohols at room-temperature and low catalyst loadings.

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Synthesis and characterization of Gold(I) complexes of 2-(diphenylphosphino)aniline

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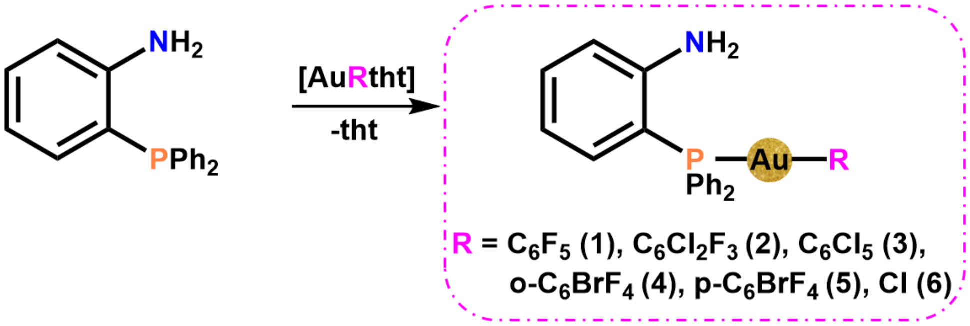
Polynuclear P-, N- or S-donor ligands have been widely employed in the synthesis of polynuclear species that, in the case of gold, may present interesting applications in diverse fields [1]. One such ligand is the P,N-donor 2-(diphenylphosphino)aniline (PNH_2), which offers a P,N donor atom set that can be used to coordinate metals such W, Ni, Pd, Pt, Rh, Os, Re and Mo [2]. In contrast, only a few group-11 metal complexes of PNH_2 have been reported, and very few gold(I) derivates that contain (PNH_2) are known [3].

With this idea in mind, new perhalophenyl and halide coordinated gold(I) complexes using PNH_2 as the chelating ligand and [AuR(tht)] (R = C_6F_5, $C_6Cl_2F_3$, C_6Cl_5, o-C_6BrF_4, p-C_6BrF_4, Cl) as the perhalophenyl–gold(I) and Cl-gold(I) sources, leading to [AuR(PNH_2)] (R = C_6F_5 (**1**), $C_6Cl_2F_3$ (**2**), C_6Cl_5 (**3**), o-C_6BrF_4 (**4**), p-C_6BrF_4 (**5**) and Cl(**6**)) have been prepared. The compounds were fully characterized by HR-MS, IR, ^{19}F NMR, ^{1}H NMR and ^{31}P-{^{1}H} NMR spectroscopy. The crystal structures of compounds **1**, **2**, **3**, **4** y **6** have been determined by X-ray diffraction.

We have also studied their utility as precursor for the preparation of novel homo- and heterometal amine and amide derivatives by reaction with closed shell metal ions in absence/presence of deprotonating agents.

Furthermore, we have carried out topological analysis of electron densities in the [AuR(PNH_2)] complexes by employing the density functional theory (DFT) calculations. With this study, we aim to gain insight into the non-covalent interactions responsible for the supramolecular structures observed experimentally.



Scheme 1. tht = tetrahydrothiophene

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P35

Constructing coordination supramolecular cages using bis- and tris-catecholate 1,2,3-triazole linkers

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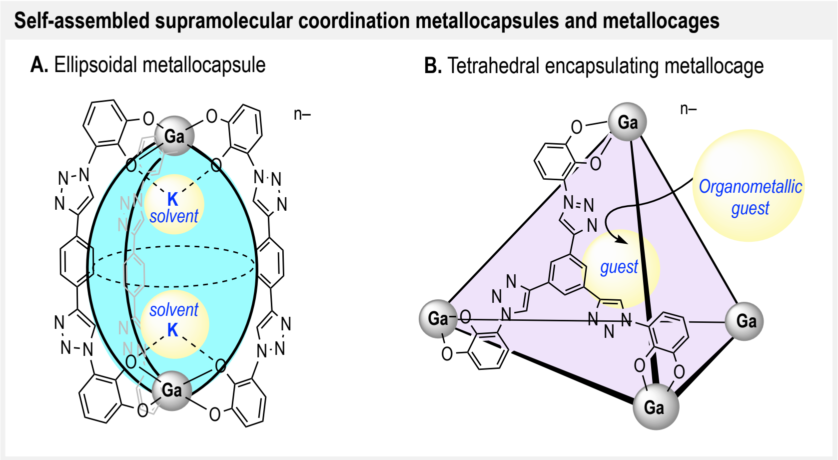
Supramolecular chemistry established itself as a core subject in chemistry since the revolutionary discoveries led by Cram, Lehn, and Pedersen.[1] Since supramolecular hosts are ideal systems to mimic the active site of enzymes, they have attracted interest in catalysis over the recent years.[2] Using appropriate host-guest interactions often results in remarkable reactivity, reaction rate enhancements, and unprecedented product selectivity, overcoming traditional chemical systems.[3] These are features of enzymatic catalysis.[4]

In this communication, we will report the use of two types of organic linkers (di- and tri-topic) in constructing new supramolecular coordination cages with gallium. These are new supramolecular ellipsoidal metallocapsules and tetrahedral metallocages (Figure 1). Whereas the smaller ellipsoidal arrangement does not encapsulate any guest, the tetrahedral metallocage has appropiate dimensions for the encapsulation of organic and organometallic species. In addition, we will account for our NMR encapsulation and hydrodynamic studies and discuss the host-guest affinity.[4]



Self-assembled supramolecular coordination metallocapsules and metallocages

A. Ellipsoidal metallocapsule

B. Tetrahedral encapsulating metallocage

Figure 1. Supramolecular design of novel supramolecular polymetallic coordination architectures.

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Thermally or light-induced hydration of alkynes using few atom gold subnanoclusters as catalysts

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Gold subnanoclusters (Au_n) (SNCs) are species formed by a few gold atoms (n = 3-5) and their use in catalytic systems stems from their ability to act as π-bonds activators[1]. However, this catalytic activity is closely linked to its transient stabilization with organic molecules, through weak dispersive forces such as C-H···Au or π···Au interactions. These unstable subnanoclusters have already been tested by our group in catalytic alkyne hydration reactions[2], in which gold SNCs were in situ prepared by thermally activation. We have checked that functional groups such as alkyl chains with a high number of carbon atoms or aromatic groups in the organic substrate, provide an additional transient stabilization of gold (0) SNCs. Moreover, we have recently observed that another activation route can be employed in order to form the catalyst gold(0) SNCs, which is the use of ultraviolet light. This UV irradiation promotes the formation of SNCs and we have checked selected examples of thermally activated hydration of alkynes (Figure 1).

The Au SNCs species formed by the interaction with alkynes display interesting luminescent properties[3]. The observed emissions arise from quantum size effects through which the SNCs display a molecular-like behaviour, showing different and tuneable absorbance and emission characteristics. Thus, the emissions depend on the number of metal atoms but, in addition, on the type of ligand employed and the corresponding SNCs-ligand interactions. These luminescent properties as well as the catalytic properties of gold subnanoclusters have been evaluated by TD-DFT and DFT calculations.

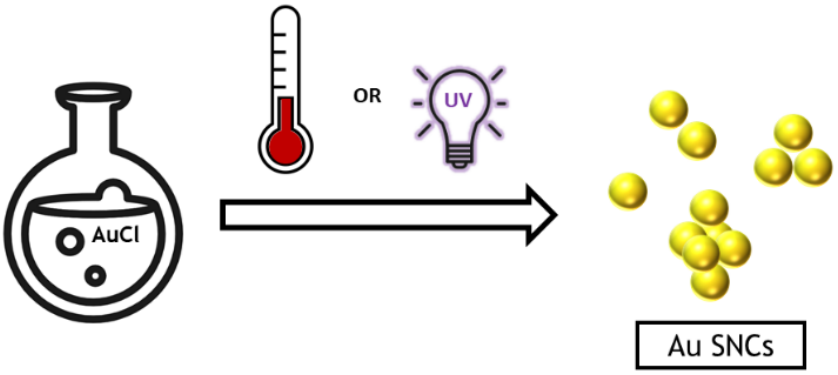

Figure 1: Thermally or light-induced formation of Au SNCs from the AuCl pre-catalyst used for alkyne hydration reactions.

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Fe-Based Deep Eutectic Solvents (*DES*s) for hydration of alkynes in bench-type reaction conditions

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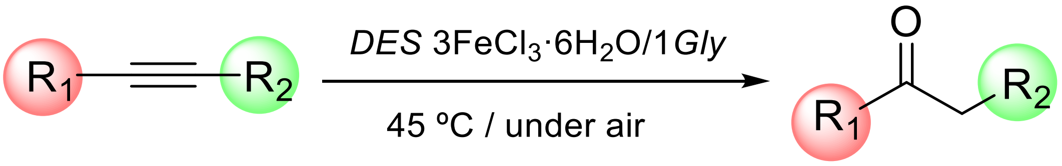
Deep Eutectic Solvents (*DES*s) with Brønsted or Lewis acidity are capable of playing a key role in various transformations such as oxidations, aldol or pericyclic reactions, as well as condensation and multicomponent reactions.[1] In recent years, interest in *DES*s containing metal salts has increased due to their inherent catalytic properties.

In this sense, our research group has previously described a *DES* consisting of $3FeCl_3{\cdot}6H_2O/1$*Gly* capable of promoting the Meyer-Schuster rearrangement of alkynols under bench-type reaction conditions.[2]

In this communication we will present the use of the *DES* $3FeCl_3{\cdot}6H_2O/1$*Gly* as promoter of the hydration of alkynes to produce the corresponding ketones. The process takes place at 45 °C, in the absence of co-catalysts or co-solvents, obtaining up to quantitative conversions (99%).



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Structure-photoluminescence relationship in perhalophenyl-gold(I)-diphosphine complexes. TADF and Phosphorescent behaviour

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Luminescent organo-transition metal complexes have received growing attention recently, as they represent materials for optoelectronic applications. For example, molecular light emitting devices (LEDs) have been increasingly reported to exhibit superior efficiencies when luminescence is enhanced by the presence of a heavy metal because of spin-orbit coupling.

Focusing on gold(I) complexes, the origin of the luminescence can be related to different factors: (i) the presence of aurophilic interactions in polynuclear gold compounds; (ii) the nature of the ligands coordinated to the gold(I) centers and (iii) the geometry around the metal center.[1]

Depending on the coordination environment around the metal center, in the case of diphenylphosphinogold(I) complexes a great variety of molecular structures are obtained leading, consequently, to distinct photoluminescent properties.[2,3]

In the present communication we describe the synthesis, characterization and study of the photophysical properties of new organometallic diphosphinogold(I) complexes. For this purpose, the gold(I) precursor [Au(C_6F_5)(tht)] and three diphosphine ligands with different bite angles and aryl systems have been used.

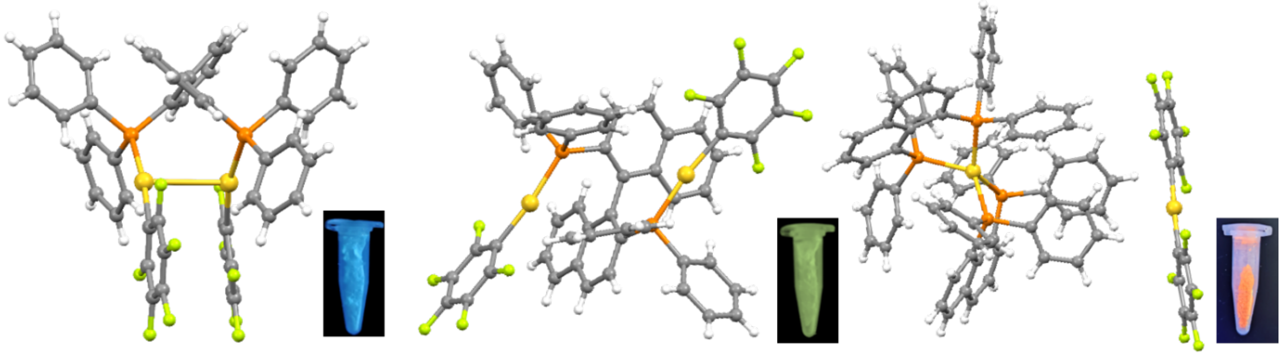

Figure 1. New phosphinogold(I) complexes

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Functionalization of N-Heterocycles with ADAP-Cu(I) Complexes

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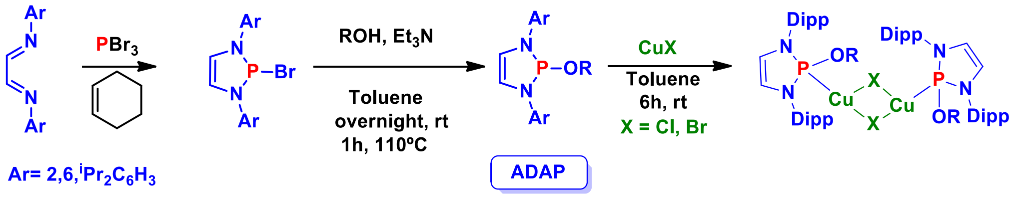
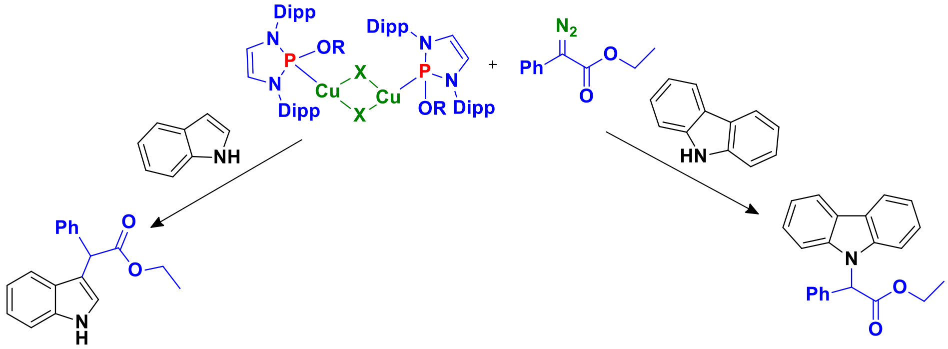
Although N-Heterocyclic phosphine (NHP) ligands have been known for more than 40 years,[1] their use as ligands in metal complexes has generated recent interest derived from their similarities with NHC ligands.[2] Recently in our research group we have described the synthesis of a family of copper complexes with diaminophosphine ligands (ADAP). The synthesis of these new complexes allowed us to prepare chiral copper complexes in a very simple way.[3]



In this contribution, we present the functionalization of indoles and carbazoles with alkyl and aryl diazocompounds. These transformations occur in a chemo- and regioselective manner and, in some cases, with modest enantioselection, affording products with potential biological and pharmacological interest.



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P40

Synthesis, Characterization and Nitrene Generation from Copper and Silver Complexes Bearing Phosphinoazide Ligands

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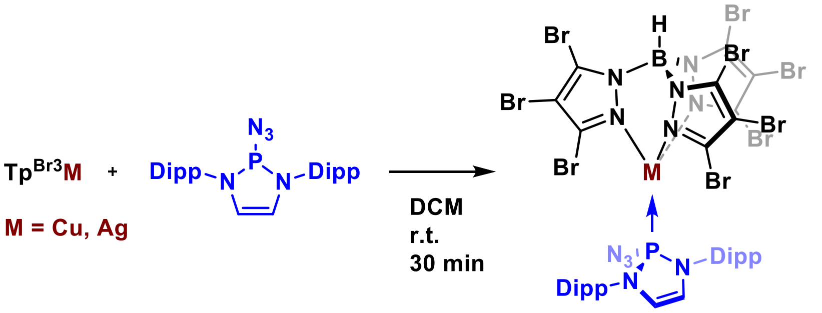
One of the strategies employed for the formation of new C-N bond consists of the transfer of a nitrene group to saturated or unsaturated substrates. During the last decade, our research group has developed several catalytic systems based on a family of copper and silver complexes bearing hydrotrispyrazolylborate ligands (Tp^x) as efficient catalysts for these reactions.[1] However, examples of the key species in these transformations, highly reactive metal-nitrene intermediates, remain scarce.[2]

In this contribution, we describe the synthesis and characterization of two Tp^{Br3}M-L adducts (M= Cu, Ag L= 2-azido-1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-1,3,2-diazaphosphole). Thermal decomposition of both complexes has been studied, showing that copper promotes the formation of the corresponding cyclodiphosphazene by the dimerization of two phosphinonitrene units.[3] This process has been further explored in a catalytic manner by the decomposition of the phosphinoazide in the presence of the Tp^{Br3}Cu(NCMe) complex, allowing the proposal of a mechanism for this transformation.



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P41

Anionic isocyanido iron(II) metallaligands containing azo units

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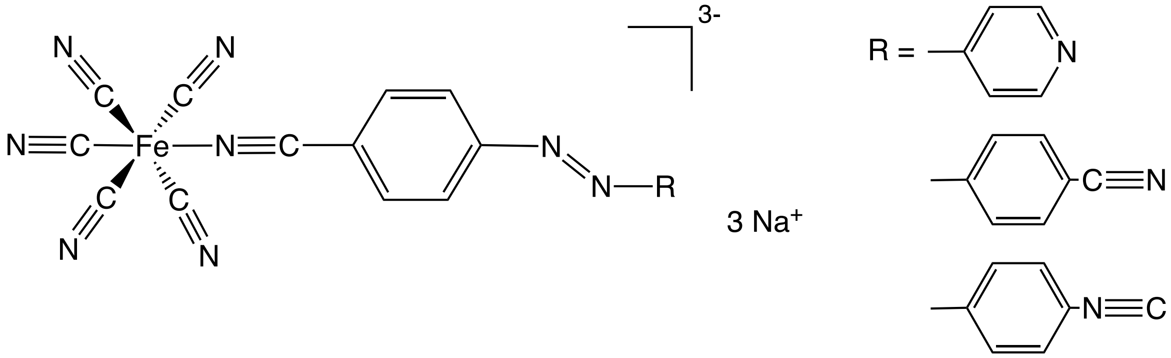
Three different ditopic azo ligands containing terminal isocyanido units and pyridine or benzonitrile fragments have been synthesized. Their coordination to $[Fe(CN)_5(NH_3)]^{3-}$ has allowed the obtention of water soluble mononuclear iron(II) compounds that can act as metallaligands for the obtention of complexes of higher nuclearity with interesting photochemical properties.



The kinetico-mechanistic study of the spontaneous thermal *cis*-to-*trans* conversion in solution of both the ligands and the corresponding Fe(II) complexes, after photochemical excitation, was analysed as a function of solvent, temperature and pressure.

The electrochemistry of the Fe(II) complexes in water solutions indicates that the compounds can be fully reversibly oxidised to the corresponding Fe(III) derivatives. Chemical oxidation with peroxodisulphate results in neat UV-Vis spectral changes that parallel those observed in the spectro-electrochemical titrations. From these time-resolved changes pseudo-first order values of the oxidation rate constants were derived at different oxidant concentrations, temperatures and pressures, allowing for the determination of the thermal and pressure activation parameters for the system.

Low-Valent Monocyclopentadienyl Titanium Complexes for the Activation of Dinitrogen

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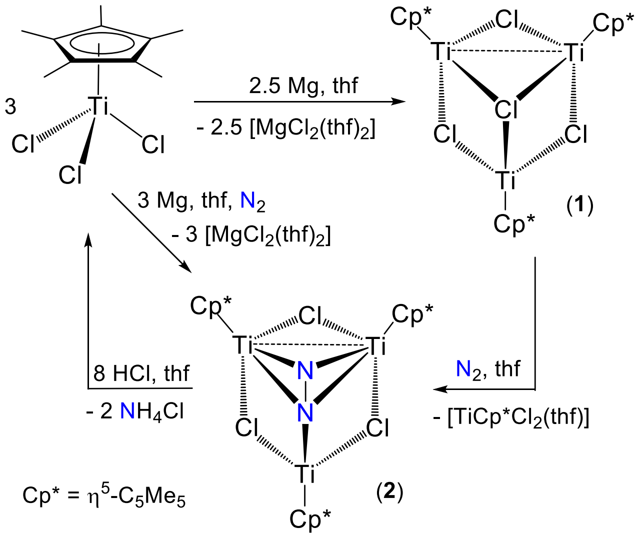
The synthesis of ammonia constitutes one of the most important chemical processes at the industrial level as illustrated by the production of about 150 million metric tons of this molecule in 2021 [1]. Today, the industrial synthesis of ammonia relies on the Haber-Bosch process, developed over 100 years ago, and performed in large-scale plants where dinitrogen and dihydrogen gases are combined under harsh conditions (300-500 ºC and 200-300 bar) in the presence of a heterogeneous catalyst. However, this extremely energy-intensive process consumes about 2% of the world´s total energy and generates ~1% of global CO_2 emissions annually and, unsurprisingly, the development of a sustainable production of ammonia has been identified as one of the IUPAC Top Ten Emerging Technologies in Chemistry 2021 [2].

Inspired in the natural nitrogen fixation carried out under ambient conditions by certain microorganisms, which convert N_2 into ammonia using electrons and protons at nitrogenase enzymes, organometallic and inorganic chemists have long explored homogenous catalysts capable of operating at milder conditions [3]. The fixation of dinitrogen by titanium species has been known for decades, and nowadays a variety of coordination modes of the N_2 unit to the titanium centers is well-documented [4]. While the largest families of titanium-dinitrogen complexes are based in bis(cyclopentadienyl)titanium or tri- and tetradentate PN ligand systems, few examples of monocyclopentadienyl compounds are known [4,5]. Therefore, we have recently begun a research program devoted to the study of dinitrogen activation by low-valent titanium monocyclopentadienyl species. For instance, we have recently reported the reduction of [TiCp*Cl$_3$] to give a mixed-valence trinuclear complex **1** capable of incorporating N_2 under ambient conditions in solution to give the first example of a stable derivative **2** with a μ_3-η^1:η^2:η^2-N_2 ligand (see Scheme) [6]. This dinitrogen complex reacts with excess HCl to regenerate [TiCp*Cl$_3$] with NH_4Cl formation, and several cycles alternating N_2/HCl atmospheres on a [TiCp*Cl$_3$]/Mg(excess)/thf system can be performed to produce NH_4Cl on a relatively large scale. In this communication, we will present new examples of activation and functionalization of dinitrogen at low-valent titanium complexes under mild conditions.



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Quinoline functionalized formamidinato-heavier tetrylenes: Synthesis and first reactivity studies

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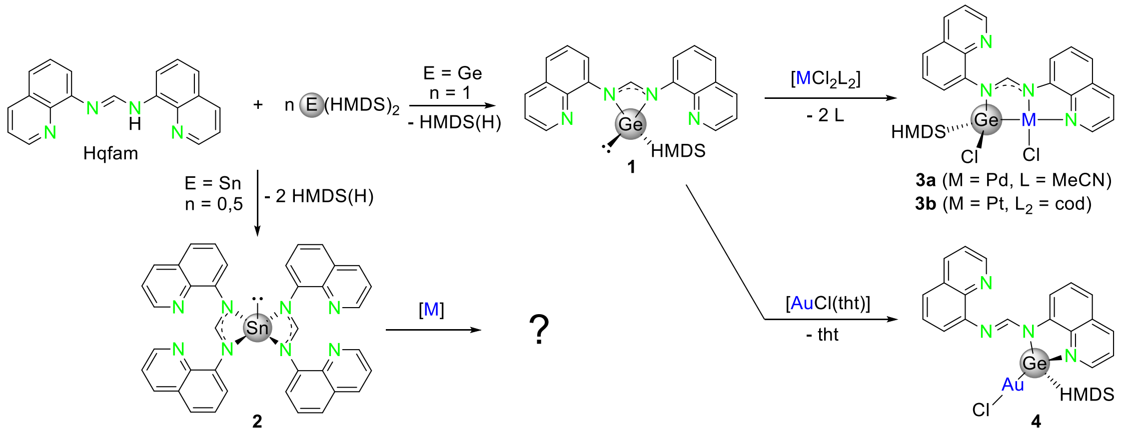
Heavier tetrylenes stabilized by amidinate groups (amidinato-HTs) [1] have been widely used as ligands because they are strong electron-donors [2] while their electronic and steric properties can be extensively tuned. These key features are responsible for the interesting catalytic properties shown by many of their metal complexes, particularly by those featuring polydentate amidinato-HT ligands [3]. This contribution describes two novel polydentate formamidinato-HTs, namely, the mono(formamidinato)germylene **1** and the bis(formamidinato)stannylene **2**, which are equipped with two pendant quinoline groups on both sides of the formamidinate fragment. Compounds **1** and **2** were obtained in high yield reacting *N,N'*-bis(quinol-8-yl)formamidine (Hqfam) [4] with E(HMDS)$_2$ (1:1 mol ratio for E = Ge; 1:0.5 mol ratio for E = Sn; HMDS = hexamethyldisilylamide). Note that the reaction of Hqfam with 1 equivalent of Sn(HMDS)$_2$ did not give the tin analogue of **1**, but led to **2** and unreacted Sn(HMDS)$_2$. The proposed structures of **1** and **2**, which are in agreement with their spectroscopic data, are shown below.

Reactivity studies aimed at evaluating the coordination chemistry of the germylene **1**, which is potentially capable to act as a tridentate κ^3*N,Ge,N*-ligand, are currently underway. For example, the reactions of **1** with [MCl$_2$L$_2$] (M = Pd, L = MeCN; M = Pt, L$_2$ = η^4-1,5-cyclooctadiene (cod)) led to the chloridogermyl complexes [MCl{κ^3*Ge,N,N*-GeCl(HMDS)(qfam)}] (M = Pd (**3a**), Pt (**3b**)), which result from the insertion of the germanium atom into one of the M–Cl bonds. Both analogous derivatives feature a pincer type κ^3*Ge,N,N*-ligand, where the formamidinate fragment is bridging the germanium and palladium atoms, the latter being also linked to only one of the quinoline groups. On the other hand, the reaction of **1** with [AuCl(tht)] (tht = tetrahydrothiophene) led to [AuCl{κ^1*Ge*-Ge(HMDS)(qfam)}] (**4**), which features a monodentate κ^1*Ge*-germylene (no insertion has occurred). Curiously, the germanium atom of **4** is not attached to both N atoms of the formamidinate fragment, being chelated by one formamidinate-N and one quinoline-N atoms. Additional reactivity studies are needed to further investigate the coordination abilities of **1**, which seem to be far from the original κ^3*N,Ge,N* expectations, and of those of stannylene **2**.



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P44

Benzylic Palladium Complexes: Efficient Catalysts for the Synthesis of Vinylic Addition Poly(norbornene-*co*-alkenylnorbornenes)

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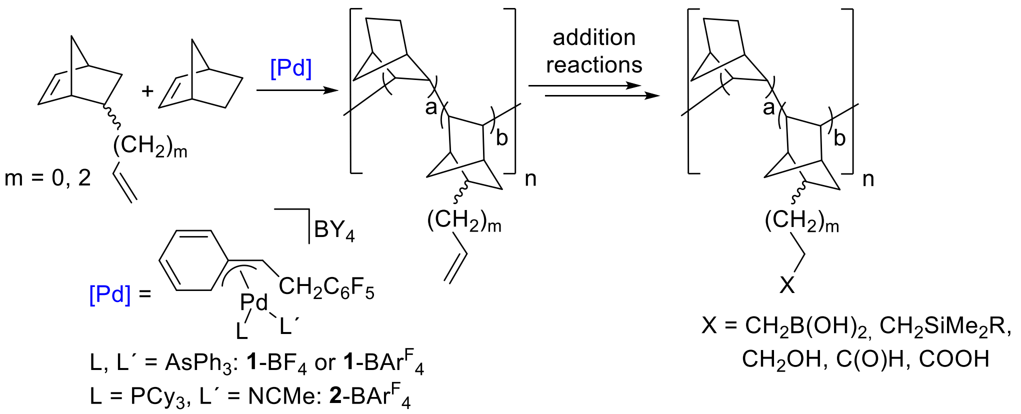
Vinylic addition polynorbornenes (VA-PNBs) are robust materials with high thermal and chemical stability, high T_g and transparency.[1] These features make them convenient supports for several applications but, to extend the range of these applications, the incorporation of functional groups is essential. Functionalization post-polymerization is an attractive alternative to the direct polymerization of substituted-norbornenes where the deactivation of the catalyst is very common. Vinylic addition copolymers of norbornene and alkenyl-monomers (poly(norbornene-*co*-alkenylnorbornenes)) are suitable materials for the introduction of several polar groups. If the polymerization is selective through the endocyclic double bond, the exocyclic one can be transformed in other polar groups by oxygenation or addition reactions (Scheme 1). Not many efficient and well-defined systems are convenient for the selective endocyclic VA-polymerization of alkenyl-monomers.[2] Recently, we have developed a highly efficient benzylic complex of palladium(II) for the VA-polymerization of VNB (5-vinyl-2-norbornene).[3] The use of the benzylic fragment is very convenient to facilitate the initiation of the polymerization since an open coordination site can easily be generated by the transformation of the η^3-benzyl moiety into the σ-benzyl, favoring the coordination-insertion of the monomer to the metal center.

Several η^3-benzylic complexes were tested in the VA-polymerization of norbornene and alkenyl-norbornene giving poly(norbornene-*co*-alkenylnorbornenes) with good to excellent yields (Scheme 1). The molecular weights of the copolymers are in the range 50-90 kDa when L = L' = $AsPh_3$ (**1**-BF_4 and **1**-BAr^F_4). However, the more active benzylic complex where L = PCy_3, L´ = NCMe (**2**-BAr^F_4) generates very high molecular weight PNBs (1.2-1.7 MDa) with just 10 mol ppm of catalyst. The composition of the copolymers can be adjusted by changing the monomer mol ratio in the feed. Furthermore, the reactivity ratios obtained showed the higher preference of norbornene to be polymerized and the distribution of the monomers along the chain indicates a composition drift with a major incorporation of VNB at the latest stages of the copolymerization. Finally, the pendant double bond was transformed in other polar groups by hydroboration and hydrosilylation reactions.



Scheme 1. Poly(norbornene-*co*-alkenylnorbornenes synthesized with benzylic complexes of palladium(II) and the post-functionalization route.

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C-H bond FLUORINATION catalysed by Tp^X Cu^{I}L complexes

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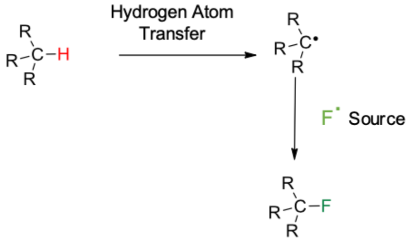
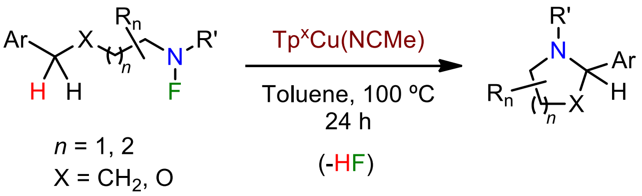
C-H functionalization is crucial in the synthetic process and development of drug discovery and material synthesis. Fluorinated organic molecules are highly important in the pharmaceutical industry or agrochemistry among other areas. Recently, new copper mediated fluorination reactions of alkanes have been reported using N-F reagents, such as N-fluorobenzenesulfonamide or Selectfluor (Scheme 1). [1–3]



Scheme 1. Radical C-H fluorination processes.

In the past, our group has described the intramolecular amination reactions using N-F compounds catalyzed by Tp^{X}CuL complexes (Tp^x = tris(pyrazolyl)borate ligands) (Scheme 2).[4] Based on these precedent, herein we report the study of new intermolecular radical reactions for C-H bond functionalization using Tp^{x}Cu^{I}L as catalyst.



Scheme 2. Copper-Catalyzed N−F Bond Activation for Uniform Intramolecular C−H Amination

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New Molecular Architectures with Metal-Metal donor-acceptor type bonds

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The study of heteropolynuclear complexes with metal-metal donor-acceptor type bonds is highly interesting in connection to bimetallic cooperative catalysis affording C-C or C-X bond forming reactions [1]. Recently, our research group has reported heterodinuclear and heterotrinuclear complexes of general formulas $[(CNC)(PPh_3)MM'(PPh_3)](ClO_4)$ and $[\{(CNC)(PPh_3)M\}_2M'](ClO_4)$ respectively (M = Pt, Pd and M' = Au, Ag), where CNC is a symmetric tridentate ligand [2,3,4]. These new derivatives can be interpreted as intermediates in transmetallation processes of an organic moiety from M to M'.

In this work, we have focused our efforts on the synthesis, characterization and analysis of new heteropolynuclear complexes with Pt-Au and Pt-Ag bonds using a platinum derivative with an asymmetric CNC ligand as a template. Thus, the preparation of the precursor $[(CNC\text{-}Me)Pt(PPh_3)]$, obtained through methylation processes of an orthometallated aromatic ring, and the synthesis and characterization of heterodinuclear and heterotrincuclear derivatives of formulas $[(CNC\text{-}Me)(PPh_3)PtM'(PPh_3)](ClO_4)$ and $[\{(CNC\text{-}Me)(PPh_3))Pt\}_2M'](ClO_4)$ (M' = Au, Ag) will be presented. Special attention will be devoted to determining the most favored coordination spot for the acidic metal fragment, as well as the degree of transfer achieved.

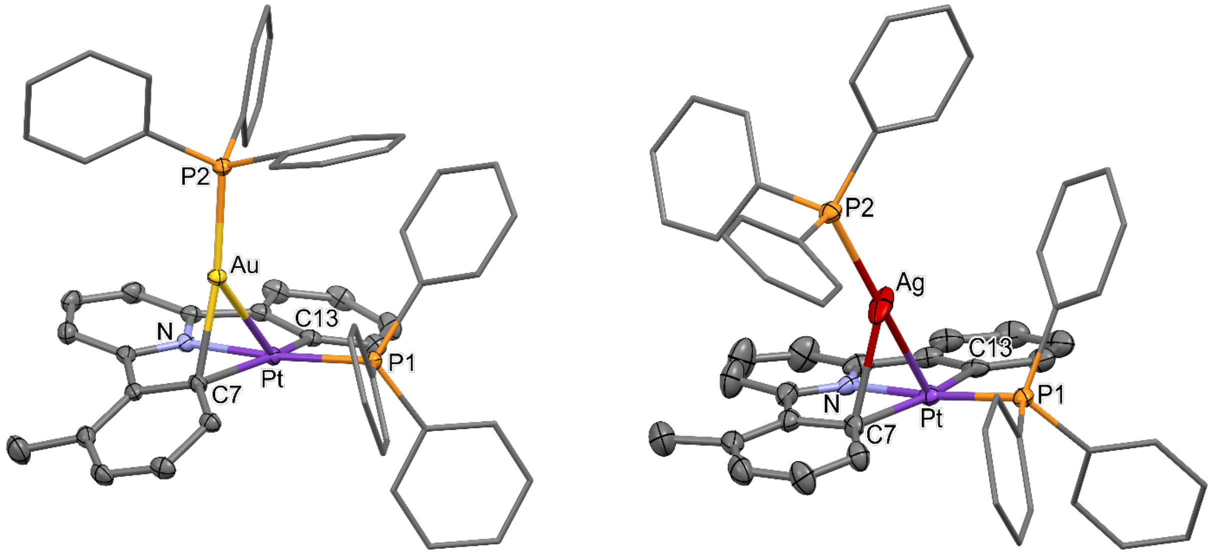

Figure 1. Molecular structures of new dinuclear complexes containing Pt-Au (left) and Pt-Ag (right) bonds and a CNC-Me ligand.

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P47

Luminiscent Cyclometallated Platinum Compounds with N-, P- and O^O-ligands. DFT Studies and Analysis of the Anticancer Potential

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Luminiscent platinum cyclometalated complexes are species of interest due mainly to its applications in the optoelectronic and biological fields, especially what concerns anticancer properties. Information on the influence of the cyclometalated and ancillary ligands in the photophysical properties is important to know how to modulate them. TD-DFT (time-dependent density-functional theory) studies are a valuable tool to get this information. Within these premises, a series of cyclometalated (2-(2'-thienyl)pyridinate, thpy and 2-(2,4-difluorophenylpyridinate, dfppy) platinum complexes with N-donor, PTA (1,3,5-Triaza-7-phosphaadamantane) or chrysin derived ligands (incorporating piperidine or morpholine fragments) were synthetized (Figure 1). The chrysin derived ligands were introduced due to its expected anticancer properties to get a potential dual effect.

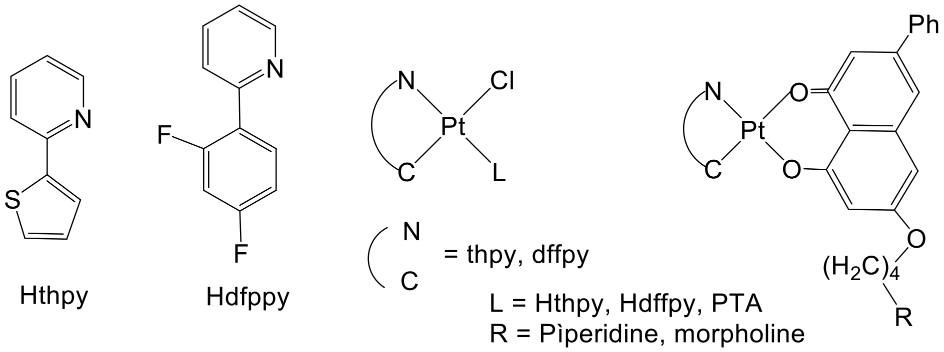

Figure 1

Luminiscence studies showed the complexes exhibit a phosphorescence character with tunable emission wavelengths and quantum yield up to 13.4 %. Supporting TD-DFT studies provided descriptions of the HOMO and LUMO characteristics and information concerning the photophysical properties. In the structure of [Pt(dfppy)Cl(PTA)], determined by X-ray diffraction, $\pi-\pi$ stacking interactions involving the dfppy ligand were found

Biological studies showed that some complexes exerted significant cytotoxic activity against cervical (HeLa) and lung (A549) carcinoma cells, and also the cytotoxicity of one chloride complex increased 2.84-fold after irradiation with blue light, revealing a certain activity in photodynamic therapy Microscopy assays showed accumulation in cytoplasmic organelles, preferentially in mitochondria. Consequently, activity of the complexes disrupted mitochondrial metabolism leading to a decline in adenosine triphosphate (ATP) cellular content.

Overall, these results show an alternative anticancer activity to classical platinum derivatives which could be of great interest in tumors with acquired resistance to DNA-targeted anticancer drugs.

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Coordination chemistry of Bismuth with flexible bis(benzimidazole)amino ligands

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Transition-metal complexes have long dominated the catalytic arena because of their ability to easily switch oxidation states ($M^{n} \rightleftarrows {}^{n+2}$ or $M^{n} \rightleftarrows {}^{n+1}$).[1] However, in recent years, main group systems featuring s- and p-block elements have emerged as powerful alternatives for redox catalysis.[2] For example, low-valent main-group systems (Mg^{I}, Ca^{I}, B^{I}, Al^{I}, Ge^{II}), can activate small molecules (H_2 and N_2) and even engage in two electron redox catalytic cycles (P^{n}/P^{n+2} or Bi^{n}/Bi^{n+2}).[3]

We will report the synthesis of novel Bi complexes bearing tridentate bis(benzimidazole)amino ligands.[4] Mono- or di-nuclear species are obtained depending on the nature of the bis(benzimidazole) ligand (Figure 1). We will show that these species are prone to facilitate ligand exchange reactions at Bi. Future work will develop their uses in redox catalysis.

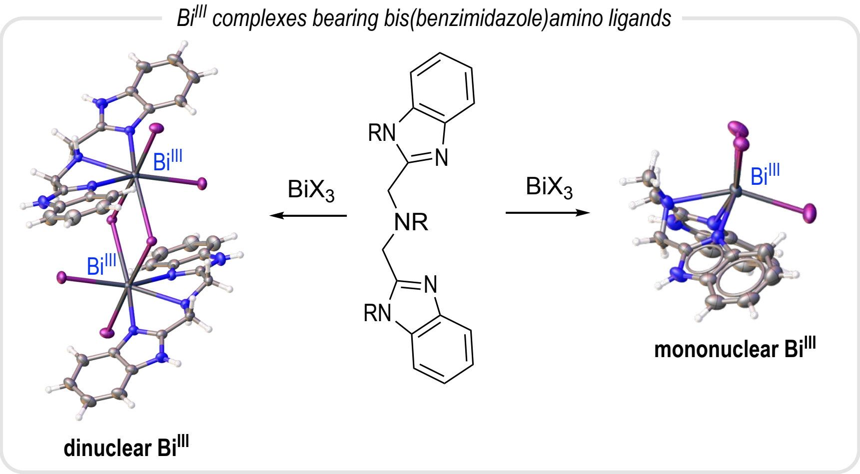

Figure 1. Synthesis of novel mono- and di-nuclear bis(benzimidazole)amino Bi^{III} complexes.

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Pt(II) complexes with terpyridine ligands: effect of π-stacking and interaction with G quadruplex

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Cancer mortality rate has decreased due to a better understanding of tumour biology and improved diagnostic devices and treatments. One of the most successful strategies is chemotherapy. This therapeutic tool is based on the administration of drugs capable of destroying malignant cells or inhibiting their replication to treat the disease.

A fascinating alternative to treat the disease is based on the use of complexes with affinity by G-quadruplex (G4) structure of DNA. This secondary structure of the DNA is formed by two or more layers of guanine tetrads linked through hydrogen bonds. Cancer cells have higher activity of the telomerase enzyme, allowing the replication of cells. The stabilization of these G4 in the telomers inhibits the activity of the enzyme due to the interruption of the interaction with the DNA. Complexes with stabilization of the G4 structure avoid the uncontrolled replication, becoming a selective approach to treat cancer.

Here, a family of Pt(II) complexes with terpyridine ligands are presented (Figure 1) to study the interactions with the G4. An extra phenyl ring is adding into the terpyridine ligand to expand the conjugation of these complexes, affecting not only the photophysical properties of the complexes in solution but also to enhance the intercalation between the planes of the G4.

These complexes were studied with two different cancer cell lines SW480 (colon) and A2780 (ovarian). After 48 h of exposure, these complexes showed IC^{50} values similar to those obtained with cis-Pt. Internalization studies showed higher cellular uptake of complexes **2** and **3**, highlighting the great level of penetration into nuclei of complex **2**. Furthermore, complex **3** showed major stability and selectivity for G4 structures and this can explain the cytotoxicity of this complex towards the cell lines.

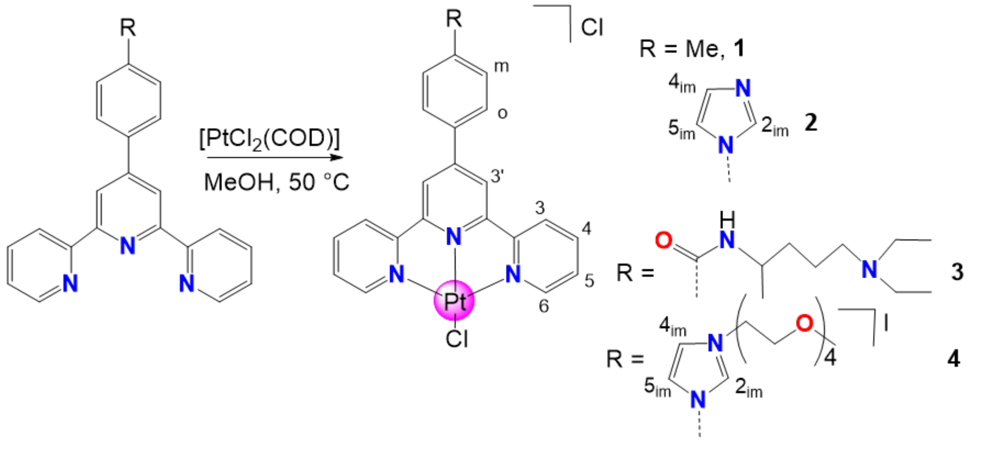

Figure 1. Pt(II) complexes based on terpyridine ligands presented in this work.

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Supported Nickel Nanoparticles on the Surface of Graphene: Synthesis and Applications

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Metal nanoparticles are particularly interesting in the field of catalysis because control of the size and stability allows the rationale design of highly active catalytic systems. The limited stability under reaction condition is one of the disadvantages of nanoparticles. We have previously described the benefits of using graphene as support of molecular complexes for catalytic applications. [1,2]

By supporting nickel nanoparticles (Ni-NPs) on the surface of reduced graphene oxide (rGO) we can avoid agglomeration and deactivation by improving their distribution and particle size, also the stability of this NPs allows the recycling and reuse of catalyst making them appropriate for a potential catalytic application. [3,4] Ni-NPs can performance a variety of organic transformation including catalytic hydrogen transfer, therefore, in this work we evaluate the catalytic properties and the methodologies for the synthesis of functionalized Ni-NPs supported on the surface of rGO.

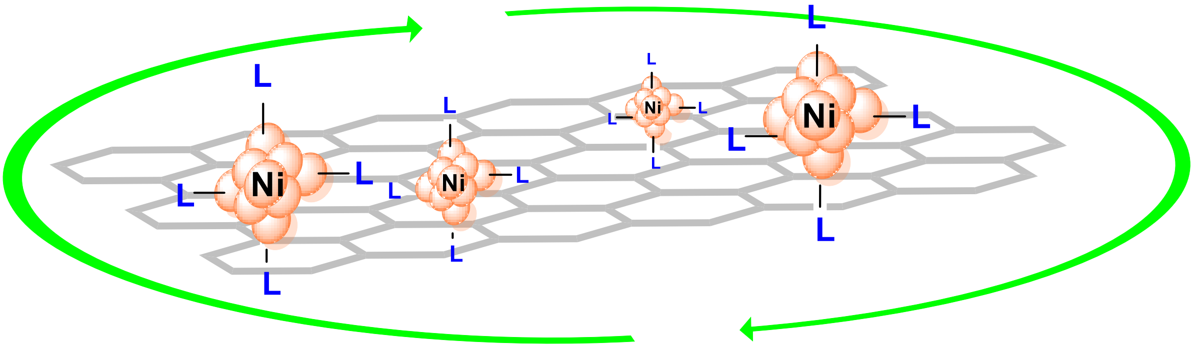

Figure 1. Model representation of Ni-NPs supported on the surface of graphene.

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P51

Study of the Emissive Properties of Copper(I) Heteroleptic Complexes

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In recent years, there has been great interest in the development of low-cost, environmentally friendly metal complexes as dopants for electroluminescent devices. Copper(I) complexes are good candidates due to their luminescent properties and high abundance,[1] and many efforts have been focused on the study of copper complexes that exhibit TADF (time activated delayed fluorescence), which contributes to optimise the efficiency of OLED devices.[2]

This work presents the synthesis of heteroleptic neutral and cationic copper(I) complexes which combine a *closo* or *nido* carborane-diphosphane (P^P) and a diimine (N^N) (Figure 1). The photophysical properties of the complexes have been studied, which include TADF emission for some of them.[3]

The presented complexes have been characterised by different analytical techniques: nuclear magnetic resonance (NMR), mass spectrometry and X-ray crystallography. In addition, the optical properties of the complexes, emission and excitation energies, lifetimes and quantum yields have been analysed.

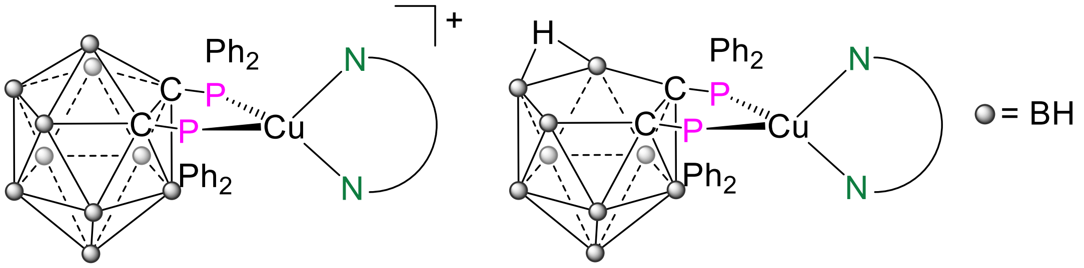

Figure 1. *Schematic representation of the cationic and neutral copper complexes bearing phosphino-carborane and diimine ligands.*

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P52

N-pyridyl-1,2,3-triazole Iridium Derivatives as Precursors for Formic Acid Dehydrogenation.

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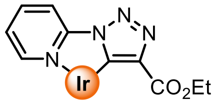
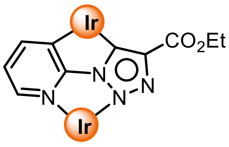
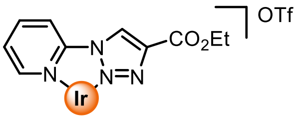
Coordination of N-pyridyl-1,2,3-triazole ligands (L) to the [Cp*IrCl] organometallic fragment has allowed us to prepare mononuclear cationic [Cp*Ir(Cl)k^2-(N,N)L]$^+$ and neutral [Cp*Ir(Cl)k^2-(N,C)L], and bimetallic [Ir]$_2$ complexes containing a bridging triazolylidene ligand. Dinuclear Ir-species exhibit metal to metal electronic communication, which has been previously related to a higher selectivity in catalytic transformations [1].
We have tested these new complexes as catalyst for the selective dehydrogenation of formic acid. In addition, kinetic and NMR studies were carried out to obtain information on the mechanism







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Synthesis and characterization of new chiral ferrocenylphosphanes

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The efficient synthesis of enantiomerically pure compounds is of the most challenging fields of chemistry. Despite the development of many catalytic methods for obtaining chiral molecules, their synthesis still faces problems such as the high cost of enantiopure precursors or the need to separate racemic mixtures, which must be solved to generate more sustainable synthetic methods [1,2].
The most important type of ligands in asymmetric catalysis are phosphanes, however, in general alkylphosphanes are prone to oxidation and difficult to functionalise. A solution to alleviate this problem is the incorporation of an organometallic skeleton such as ferrocene, which allows structural modification with relative ease [3]. Ferrocenylphosphanes appear as a good alternative since the organometallic skeleton of ferrocene allows the modulation of its properties by modification of its structure. In addition, polar functional groups, capable of increasing its interaction with greener solvents, can be introduced.
In this context, incorporation of amino acids emerges as an excellent choice because when coupled to the metallocene fragment, they increase the solubility of the catalytic system in water and introduce chirality into the ligand. Besides, enantiomerically pure amino acids (L-amino acids, the *S* isomers in most cases) are commercially available, avoiding tedious synthetic processes or separations of racemic mixtures [4].

In this work we present new ferrocenylphosphanes including amino (Figure 1) and the study of their coordinating properties against ruthenium fragments for their potential application in homogeneous catalysis reactions in aqueous media.

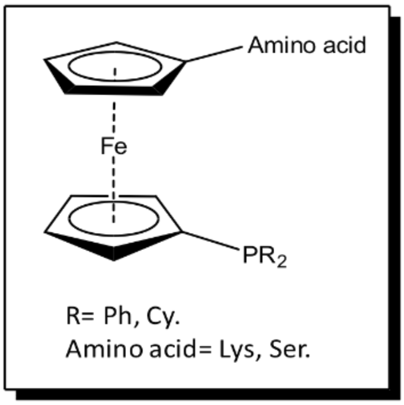

Figure 1 – New chiral ferrocenylphosphanes

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Inner *vs* Outer Sphere Olefin Hydroxylations Promoted by Iridium Complexes

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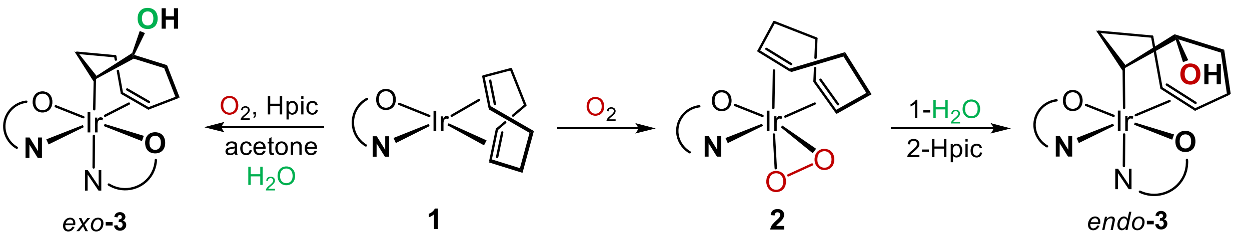
The oxidation of organic substrates is a powerful synthetic tool that provides access to high added-value organic compounds, such as ethers/alcohols, from olefins.[1] Since the publication of the Wacker process for acetaldehyde from ethylene, water, and oxygen, new nucleophilic additions of oxygen-based nucleophiles to olefins have been studied.[2]

Reactions leading to new C–O bonds involve either *outer*- or *inner*-sphere mechanisms, which are intimately related to the selectivity in the products. Thus, the former gives *syn*-stereochemistry, which arises from the nucleophilic attack of the hydroxide/alkoxyde to the external face of the olefin. Conversely, the latter is associated to the *anti*-stereochemistry, typically derived from a nucleophilic attack of a coordinated hydroxide/alkoxyde groups via migratory insertion of the olefin into the M–O bond.[3]

In this context, we have observed *outer*-sphere nucleophilic attacks on olefins promoted by *inner*-sphere oxygen activation. Therein, a novel proton-coupled electron-transfer step connects a superoxide–iridium(II) complex with hydroperoxide–iridium(III) intermediates, rather than peroxide complexes (Scheme, left).[4] Conversely, we have also found that peroxide complexes, such as **2**, can render the *endo*-isomer under appropriate conditions (Scheme, right).



Plausible mechanisms driving the reactions towards one particular isomer will commented. They are based on HR-MS analyses, NMR, IR and labeling experiments.

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Study of the Luminescent properties of Au(I) phosphine complexes

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In recent years, it has been an increasing interest in obtaining room-temperature phosphorescent materials due to their potential applications in a wide range of areas. The design of these materials includes the selection of the chromophore, the metal center, and the auxiliary ligand, which play an important role in the final photophysical properties.

In our group, we have proved that gold(I) complexes can present outstanding luminescent properties because the presence of the heavy atom favors intersystem crossing and the population of the triplet state, increasing the phosphorescent emission of the systems [1-3].

In this work, we describe the synthesis of gold(I) complexes containing different monophosphane and diphosphane ligands in order to evaluate the effect of the proximity of the chromophore and the metal centers in their luminescent properties. All complexes contain a thiol-coumarin ligand as chromophore, and several phosphanes as PPh_3, PEt_3, DAPTA, PTA, Xantphos and DPEPhos have been tested. Luminescent studies show that all complexes analyzed present phosphorescent properties at low temperature.

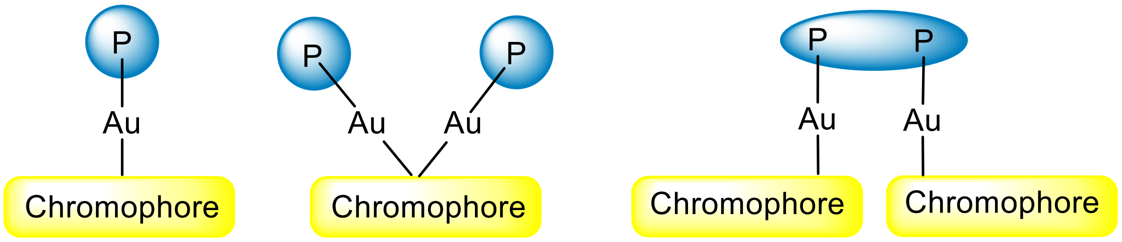

Figure 1. Schematic representation of the structure of the systems obtained.

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P56

REDUCING SMALL MOLECULES ON A Pd(I) BIS N-HETEROCYCLIC CARBENE COMPLEX

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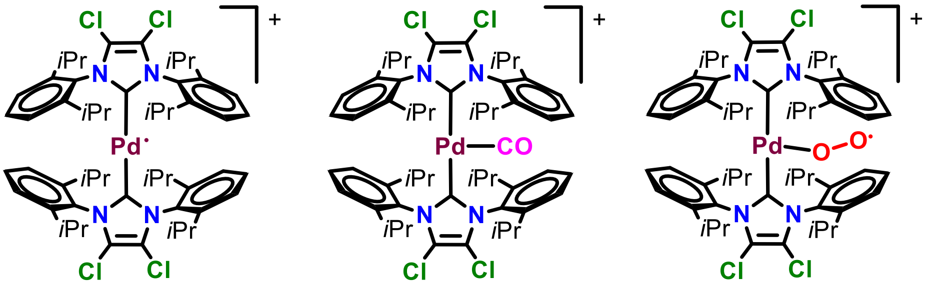
Oxygen binding to metal complexes is relevant to energy conversion, solar fuel production and aerobic oxidation chemistry. The M^n-O_2 interaction occurs with partial cleavage of the O=O bond by one-electron reduction leading to a [M^{n+1}-$O_2^{\bullet -}$] superoxide that could subsequently evolve into [M^{n+2}-O_2^{2-}] peroxide species. For this to occur, bimetallic mechanisms could provide the additional electron needed for the reduction [1,2].

As a result of our recent research activities, we have discovered a general method to prepare stable paramagnetic [$Pd^I(NHC)_2$]$^+$ complexes that have been fully characterized [3]. Here we wish to communicate our recent achievements on the exploration of the reactivity of these Pd(I) cations with CO and O_2 that has allowed us to isolate Pd(II) superoxides and peroxides.



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P57

Redox-Switchable Gold (I) Catalyst: A Convenient Way for Studying Ligand-Derived Electronics Effects

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The use of the naphthalenediimide (NDI) scaffold has allowed us to prepare a family of redox-switchable catalysts with high stability and excellent optical and electronic properties.[1] We previously described an N-heterocyclic carbene (NHC) ligand functionalized with a naphthalene diimide moiety that behaved as an effective redox-switchable ligand in the rhodium- and iridium-catalyzed cyclization of alkynoic acids.[2]

Following this line of research, a new gold complex with NDI-functionalized N-heterocyclic carbene ligand has been prepared and characterized.[3] Our NDI-NHC ligand can modulate its electronic character between three oxidation states, as the neutral ligand is amenable to two successive one-electron reductions. Indeed, these reductions are accompanied by a significant increase of the electron-richness of the metal, as reflected by the *v*(CO)av. of its analogue (iridium−carbonyl complex) and their reduced forms.

Once the redox-switchable properties of this Au(I) complex were proven, the catalyst was tested in the hydroamination of phenylacetylene with arylamines. The activity of the neutral complex was moderate-to-high for this reaction, but the one-electron reduced species did not show any activity. Additionally, we performed kinetic studies that showed a first order dependence on both substrates on the reaction, which suggests that both of them are involved in the rate-limiting step. These results in conjunction with null activity of the reduced species indicate that the rate-determining step of the catalytic cycle is the nucleophilic attack of the amine on the Au-coordinated alkyne. Finally, we demonstrated that the activity of the catalyst could be toggled between an active (neutral) and inactive (reduced) form several times by successively adding a reducing agent (cobaltocene) or an oxidant (acetylferrocenium tetrafluoroborate) during the course of a catalytic reaction.

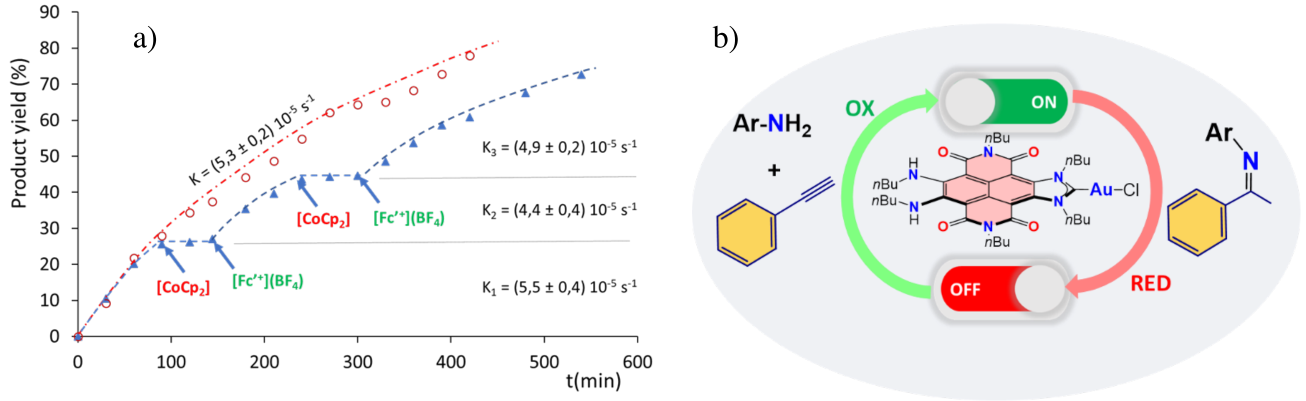

Figure 1–a) Plot showing the hydroamination of phenylacetylene with aniline with sequential additions of oxidant and reductant using as catalyst the compound of the image b).

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P58

Metal Complexes of Small Molecules. Mimicking Antioxidant Enzymes

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Oxidative stress is defined as an imbalance between generation and clearance of reactive oxygen species (ROS) by a biological system through endogenous free radical scavengers [1] and antioxidant enzymes such as superoxide dismutase (SOD), catalase, glutathione peroxidase or peroxiredoxin. Overproduction of ROS has been shown to oxidize various cellular components including DNA, RNA, proteins, enzymes and lipids, causing various forms of damage to cells and tissues. In humans, oxidative stress has been involved in a variety of degenerative processes, diseases and syndromes, including cardiovascular diseases [2], chronic inflammation [3], diabetes [4], neurodegenerative disorders such as Parkinson's and Alzheimer's diseases [5], cancer and a variety of other age-related pathologies.

Synthetic mimetic molecules of low molecular weight based in metallic complexes of polyamine ligands of either cyclic or open-chain topology have been designed as mimetics of SOD enzymes.

In this sense, we have developed different polyazamacrocycles able to complex transition metals such as Fe(II), Mn(II), Zn(II) and Cu(II) at the time that they exhibit antioxidant properties [6]. Here we report on the coordination chemistry of a family of molecules that display antioxidant properties. Furthermore, we have synthetize the molecules changing the electronic properties of the pyridine spacer in order to evaluate their effects on the thermodynamic stability and antioxidant activity.

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P59

Iridium(I) and Rhodium(I) complexes based on NDI-NHC ligands with redox-switchable catalytic applications

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A family of iridium(I) and rhodium(I) N-heterocyclic carbene (NHC) complexes based on a naphthalene-diimide (NDI) scaffold are presented in this work. These complexes were synthesized starting from the bis-imidazolium salts depicted in Fig. 1A, which combine a functionalization that is amenable to reduction (NDI), as we recently proved,[1] with two peripheral imidazolium groups as SMART NHC ligand precursors.[2] In this particular system, the electronic connection between the NDI redox tag and the metal centers is disrupted by the presence of propyl chains. The structural and electrochemical properties of the complexes demonstrate how the redox-active nature of the NDI dye can be used to generate catalysts that can be effectively toggled between their active and lower active forms. One-electron reduction of the ligand produces a great enhancement of the catalytic activity and produces an average Δν (CO) shift of -9.5 cm^{-1} while the second reduction shifts the Δν (CO) by another -3.0 cm^{-1}, as showed by SEC-IR experiments using the corresponding carbonyl derivatives. The most active species are the one-electron reduced-NDI catalysts, followed by the two-electron reduced-NDI catalysts. Lower activities were observed for the neutral species. As an example, iridium(I) one-electron reduced-NDI species increases in over one order of magnitude the constant rate with respect to the neutral form, demonstrating that redox units affect the electronic richness of the metal without being directly attached to the donor atom that binds the metal.

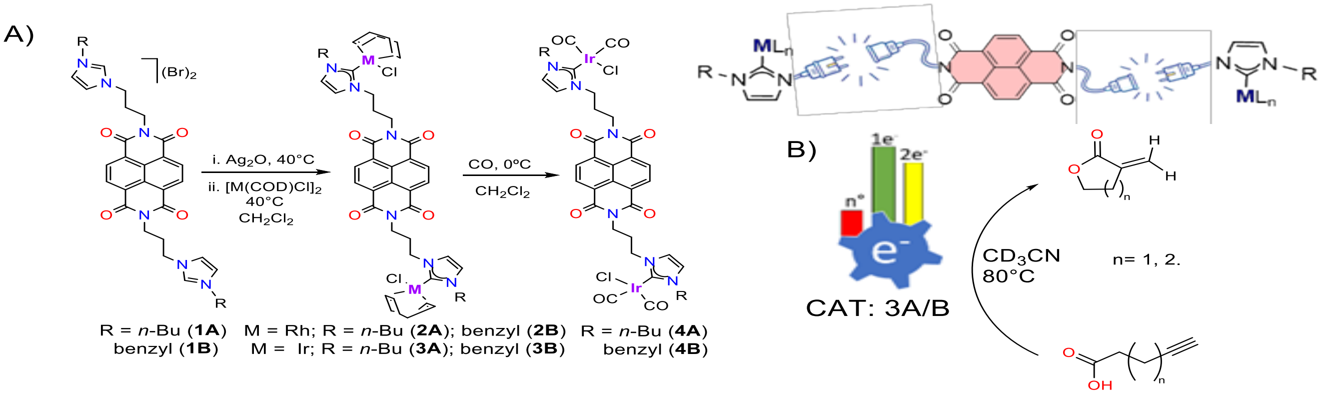

Figure 1. A) Synthesis of bis-NHC-NDI electroactive responsive complexes and **B)** catalytic evaluation reaction model.

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Clippane: A Mechanically Interlocked Molecule (MIM) Based on Molecular Tweezers

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Mechanically interlocked molecules (MIMs) are molecules that are held together because of their topologies, which favor the formation of the so-called mechanical bonds. The inseparability of their components makes MIMs to be regarded as molecules, rather than supramolecules.[1] A mechanical bond, as was defined by Stoddart, is an entanglement in space between two or more components, such as they cannot be separated without breaking or distorting covalent bonds between atoms.[2] We report the preparation of a new mechanically interlocked molecule formed by the self-aggregation of two metallotweezers composed by two pyrene-imidazolylidene gold(I) arms and a pyridine-centered pentacyclic bis-alkynyl linker (see Figure 1).[3] The mechanically interlocked nature of this molecule arises from the presence of the bulky tert-butyl groups attached to the sides of the pyrene moieties of the arms of the tweezer, which act as stoppers avoiding the dissociation of the self-aggregated metallotweezer dimer once it is formed. We tested our metallotweezer for the recognition of polycyclic aromatic hydrocarbons (PAHs), two methanol-functionalized PAHs, three electron-deficient planar molecules and two pseudo-square planar Au(III) or Pt(II) complexes with a CNC pincer ligand.[4] The selection of these guests was performed aiming to determine how different parameters such as the size, the presence of hydrogen-bonding groups or their electron-rich/poor nature could influence the binding with the metallotweezer.

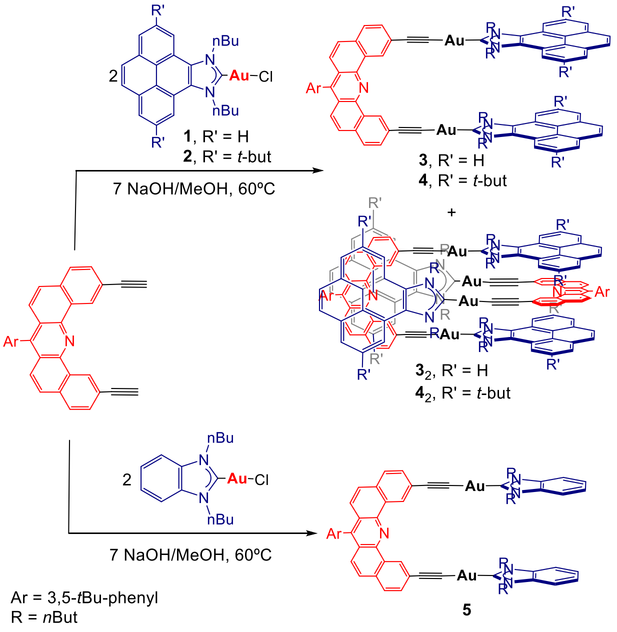

Figure 1. Synthesis of the complexes

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Coordination study of diphosphine dppm with platinum cyclometallated thiosemicarbazones

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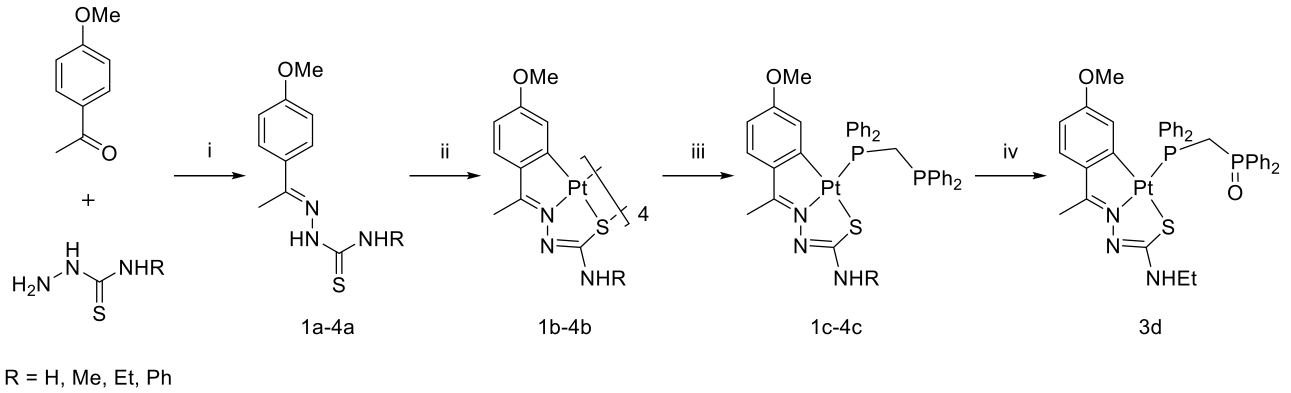
Cyclometallated compounds have been studied for many years because of their potential anticancer activity.[1] Recently, several organometallic complexes with ruthenium, palladium or platinum have shown really promising activity in biological assays.[2]

Synthesis and characterization of platinum cyclometallated compounds containing thiosemicarbazone ligands is discussed herein. Monodentate coordination behavior of the diphosphine dppm makes the compounds obtained even more interesting, being able to act as metalloligands.[3] In addition, some of this kind of compounds have been tested in cytotoxic studies getting promising results.[4]



Scheme 1. (i) HCl(aq); (ii) K_2PtCl_4, EtOH/H_2O; (iii) 1:4 $Ph_2PCH_2PPh_2$, MeCOMe; (iv) MeCOMe

Characterization has been carried by ^{1}H and ^{31}P-{^{1}H} spectroscopies, and by X-Ray diffraction study. X-Ray analysis showed the oxidation of the free phosphorus atom of 3c, giving the novel [O, S] metalloligand 3d.

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Synthesis of double [C, N; N, C] Schiff base palladacycles functionalized with crown ethers

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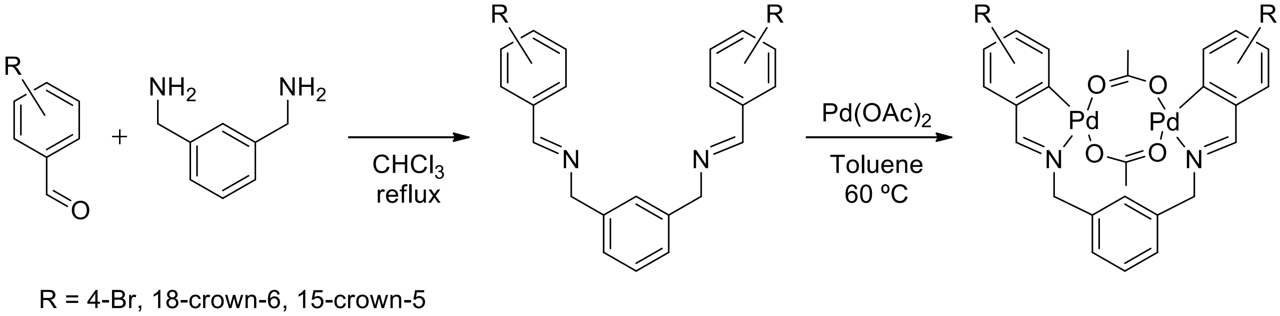
Complexation of crown ether organometallic compounds and different cations have been studied,[1] Recently, our group obtained sandwiched crown ether-bearing palladacycles from thiosemicarbazone ligands, exploiting the crown ether motifs to coordinate metal ions.[2] Acetate bridged palladacycles usually show *anti* disposition of the cyclometallated moieties,[3,4] so in order to get *syn* disposition, constriction of the conformations has to be seek.

Considering this, double Schiff bases were synthesized by the condensation of *m*-xylilendiamine and aldehydes containing bromine and crown ether rings. The resulting ligands were made react with palladium acetate to obtain the corresponding cyclometallated compounds.



Scheme 1. Reaction sequence leading to the synthesis of double [C, N; N, C] palladacycles.

Characterization has been carried by ^1H and $^{31}P-\{^1H\}$ spectroscopies, and by X-Ray diffraction study. X-Ray analysis showed the book structure of the cyclometallated compound, leaving the groups in close proximity.

Acknowledgement: The authors thank funding from Xunta de Galicia (Galicia, Spain) under the Grupos de Referencia Program (GRC 2019/014).

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Cyclopalladated compounds derived from imine ligands: Synthesis, characterization, and catalytic activity for the Suzuki-Miyaura cross-coupling

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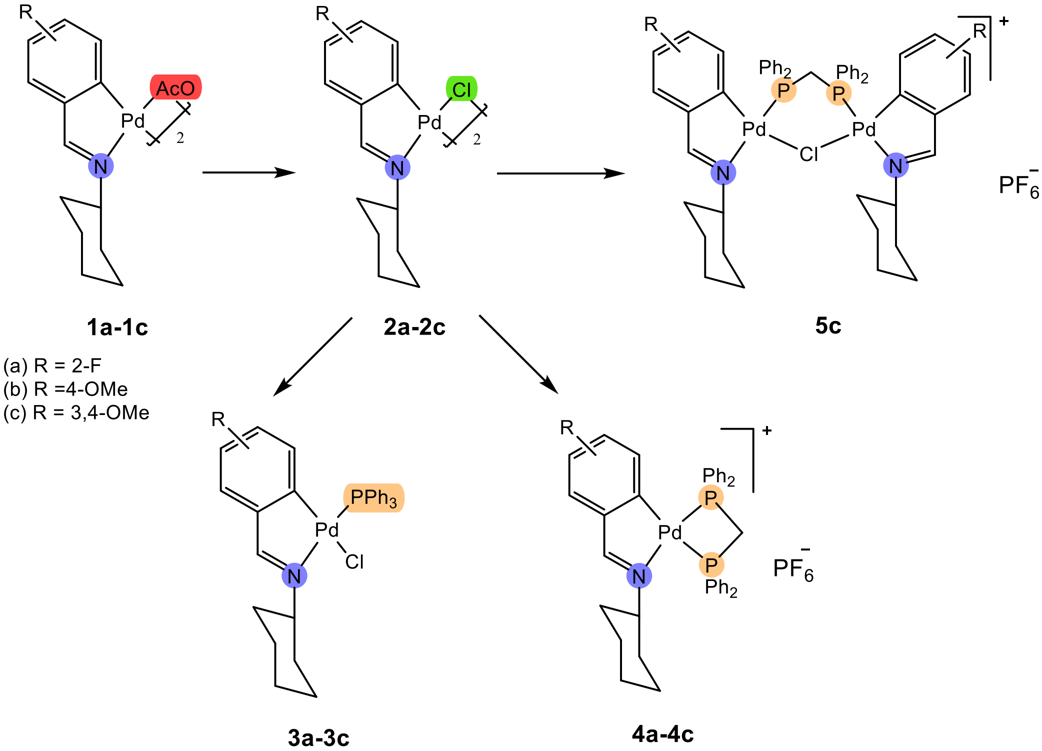
Since Milstein and co-workers developed a wide variety of imine-based cyclopalladated for cross-coupling processes[1], cyclopalladated compounds containing a five-membered ring of [Csp^2,N]Pd(II) have proved to be one of the most efficient tools for organic synthesis in catalytic methods:[2] one of the most significant and often used methods for producing carbon-carbon bonds is the Suzuki-Miyaura cross-coupling reaction, [3] and numerous types of palladacycles with phosphorus-containing ligands were successfully used as catalysts.[4] As a result, this study has mainly focused on the synthesis C,N-cyclopalladated derivatives from imine ligands, some of which contain a variety of phosphine ligands, and on their activity in the Suzuki-Miyaura coupling.

The cross-coupling of 4-bromoacetophenone with phenylboronic acid was performed using compounds **1a-5c** as catalysts under different conditions. In the majority of cases, the results were satisfactory. We may conclude that most of the compounds gave excellent results on average; also, their usefulness stems from the ease of preparation and their more than appropriate stability.



1a-1c **2a-2c** **5c**

(a) R = 2-F
(b) R =4-OMe
(c) R = 3,4-OMe

3a-3c **4a-4c**

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To have and have not: The importance of the –CH_2– unit on the properties of Ru – aminoalcohol complexes

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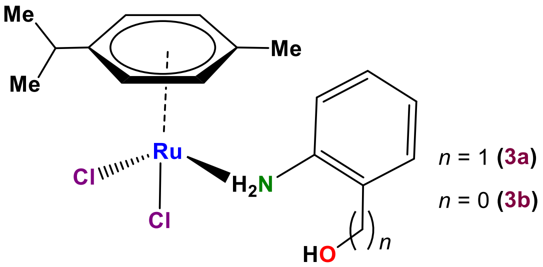
Metallocenes and half-sandwich derivatives are attracting a great deal of interest in Medicinal Chemistry and new drugs discovery [1]. Ru(II)-arene complexes exhibit unique properties (i.e lipophilicity, low toxicity) among others that are valuable for their use in biological media. Compounds of this kind and specially those containing "Ru(*p*-cymene) arrays" are considered as promising candidates to achieve improved chemotherapeutic agents [2].
In this contribution we present the synthesis of the new ruthenium(II) complexes of general formulae [Ru(*p*-cym)$Cl_2\{\kappa^1$-N-(H_2N-C_6H_4-2-$(CH_2)_n$OH)] {n = 1 (**3a**) or 0 (**3b**), shown in the figure} that differ exclusively in the presence (in **3a**) or absence (in **3b**) of the –CH_2– unit between the phenyl and the –OH moieties. Comparative studies of their properties, crystal structures and stabilities, are also presented. Theoretical studies based on Density Functional Theory (DFT) calculations on **3a** and **3b** in vacuum and also in solution have also been carried out in order to rationalize the experimental results and to explain the effect due to the presence (in **3b**) or absence (in **3b**) of the –CH_2– unit.



Additional biological studies on: a) their cytotoxic activities against the normal and non-tumoral BJ cell line and the human adenocarcinoma cell lines [breast (MCF7 and MDA-MB231) and colon (HCT-116)], b) their ability to modify the electrophoretic mobility of pBluescript SK^+ plasmid DNA and, c) to act as inhibitors of cathepsin B and Topoisomerases (I and IIα) have also been investigated. The results obtained provide conclusive evidences of the effect produced by the of–CH_2- moiety on these processes.

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Radical Alkylation Reactions with Metal Enolates

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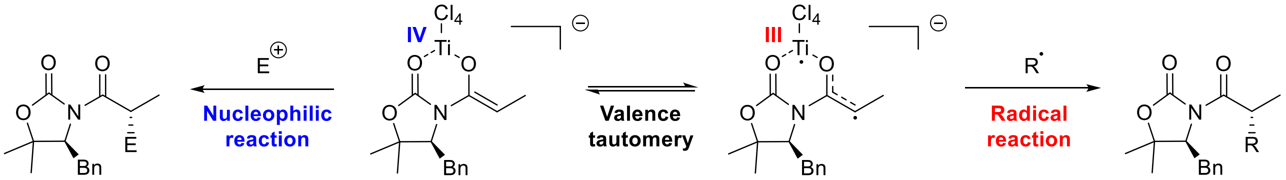
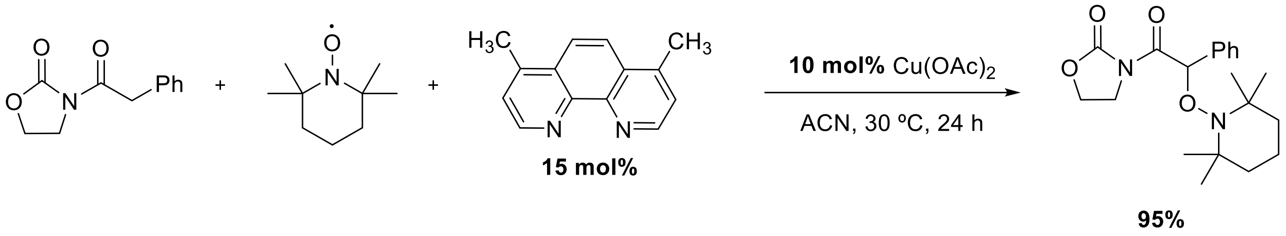
Carbon-carbon bond formation has been in the spotlight of synthetic chemistry. In this context, electrophilic addition to electron-rich metal enolates has been an important strategic approach in the formation of such bonds (**Scheme 1** left part). Nevertheless, this *modus operandi* has to cope with the steric limitations of the electrophiles employed, in the case of S_N2-like procedures, or the lack of electrophilic moieties in S_N1-type reactions. Years ago, our group demonstrated that titanium(IV) enolates have an unexpected biradical character.[1]



Scheme 1. Radical and nucleophilic character of Ti(IV) enolates and its reactivity.

Since then, several species have been used to react with titanium(IV) enolates such as: triclorometilic radical,[2] TEMPO[3] and oxygen (**Scheme 1** right part). More recently, our group reported this reaction with diacyl peroxides[4] as well as *tert*-butyl peresters as a radical source, which allows the alkylation of secondary and tertiary chains, thus circumventing the limitations related to steric hinderance present in previous methodologies.[5]

Unfortunately, the oxophilic character of titanium makes it difficult to develop a catalytic version of this methodology. For this reason, other metals have recently been explored with promising results in the case of copper(II) enolates (**Scheme 2**).



Scheme 2. Reaction of Cu(II) enolates with TEMPO.

During the optimization process, a stable and readily available radical (TEMPO) was employed as a probe to find suitable conditions. Several solvents, temperatures, ligands, bases, and reaction times have been explored.

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Rational Design of Mitochondria Targeted Thiabendazole-based Ir(III) Biscyclometalated Complexes for a Multimodal Photodynamic Therapy of Cancer

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This work describes the synthesis of a new family of Ir(III) complexes of general formula $[Ir(C^\wedge N)_2(N^\wedge N')]Cl$ (N^N' = thiabendazole-based ligands; C^N = ppy (**Series A**), or dfppy (**Series B**)) and their evaluation as potential PDT agents. These complexes are partially soluble in water and exhibit cytotoxic activity in the absence of light irradiation versus several cancer cell lines. Furthermore, the cytotoxic activity of derivatives of **Series A** is enhanced upon irradiation, particularly for complexes **[1a]Cl** and **[3a]Cl**, which show phototoxicity indexes (PI) above 20. Endocytosis was established as the uptake mechanism for **[1a]Cl** and **[3a]Cl** in prostate cancer cells by flow cytometry. These derivatives mainly accumulate in the mitochondria as shown by colocalization confocal microscopy experiments. Presumably, **[1a]Cl** and **[3a]Cl** induce death on cancer cells under irradiation through apoptosis triggered by a multimodal mechanism of action, which could involve damage over mitochondrial DNA and mitochondrial membrane depolarization. Both processes seem to be the result of photocatalytic oxidation processes.[1]

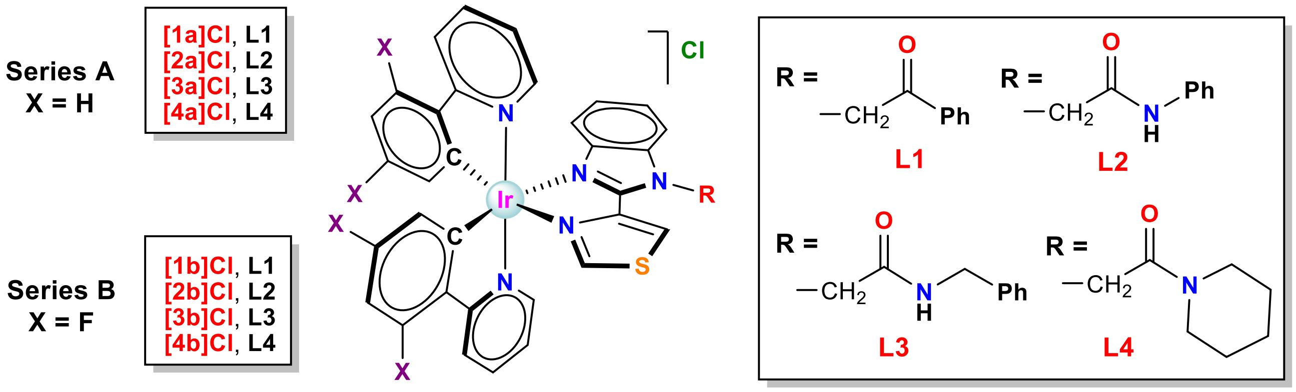

Figure 1. Molecular structures of the new Ir(III) complexes.

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Design and Synthesis of bis-*pincer*-NHC Precursors based on the Naphtalenediimide Core

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NHC-based *pincer* ligand architectures with a central pyridine have been the focus of intense research in the areas of organometallic and coordination chemistry. The combination of the σ-donor abilities of NHCs and the tridentate-*mer* (so-called *pincer*) coordinating mode, provides high stability to the resulting metal complexes.[1] We herein report the design and synthesis of the imidazolium precursor of a bis-*pincer*-NHC ligand based on the naphtalenediimide (NDI) fragment. This unique platform combines the properties of NHC-based pincer ligands with the structural and electrochemical properties of the naphtalenediimide fragment, rendering a promising candidate for a wide variety of applications including supramolecular chemistry, host-guest complexes for molecular recognition and redox-switchable catalysis (RSC).[2] We indeed have recently described two families of NDI-NHC-based complexes that were successfully employed in RSC.[3]

The synthesis of the NDI-NHC ligand precursor was carried out by a two-step procedure. The first step involves the condensation of 2,6-bis(imidazole-1-yl)-pyridine-4-amine with the commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA). The second step involves the N-quaternization of the resulting product with 1-iodobutane. This ligand precursor was characterized by means of NMR spectroscopy and mass spectroscopy. The capability of the isolated salt to act as a tetra-NHC ligand precursor is currently underway in our laboratory.

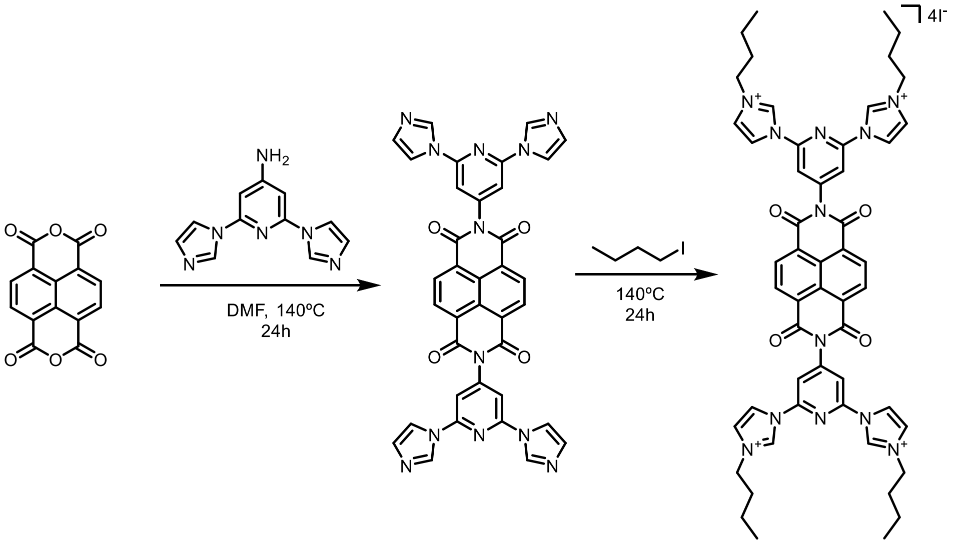

Figure 1. Synthetic route to the tetra-NHC ligand precursor based on NDI

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PARTICIPANTS AND CONTRIBUTIONS

PARTICIPANTS AND CONTRIBUTIONS

Participant	*Contribution*
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Al Janabi, Basma	P02, P63
Albéniz, Ana C.	P44
Albert, Joan	P01, P02
Álvarez, María	P28
Álvarez, Santiago	OC21
Álvarez-Ruiz, Elena	P25
Angurell, Inmaculada	P55
Aranburu, Ane I.	P04
Aullón, Gabriel	OC12
Bajo, Sonia	P17
Balaguer-Garcia, Eduard	P65
Balatov, Evgeny	
Barriendos, Irati	P51
Baya, Miguel	P46
Berbés, Roberto	P27
Blasco, Daniel	OC33
Borrego, Elena	P21
Bosque, Ramon	P64
Cabeza, Javier A.	P43
Cabo, Diego A.	OC03
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