

**2º GEQONOVEL**

Simposio de Investigadores Jóvenes  
del Grupo Especializado de Química Organometálica

Evento virtual

1 de diciembre de 2021

## LIBRO DE COMUNICACIONES

(<https://geqonovel02.navus.io/>)

### COMITÉ ORGANIZADOR/CIENTÍFICO

|                        |                                   |
|------------------------|-----------------------------------|
| Ana Carmen Albéniz     | Universidad de Valladolid         |
| Ernesto de Jesús       | Universidad de Alcalá             |
| Blanca R. Manzano      | Universidad de Castilla-La Mancha |
| Elena Fernández        | Universitat Rovira i Virgili      |
| Tomás R. Belderraín    | Universidad de Huelva             |
| Joaquín García Álvarez | Universidad de Oviedo             |

## ÍNDICE

|                                |    |
|--------------------------------|----|
| Programa .....                 | 2  |
| Índice de comunicaciones ..... | 3  |
| Resúmenes                      |    |
| Conferencia plenaria .....     | 5  |
| Comunicaciones orales .....    | 6  |
| Comunicaciones póster .....    | 20 |
| Índice de autores .....        | 49 |

## PROGRAMA

- 10:30 h.- Presentación**  
Ana Carmen Albéniz. Presidenta del GEQO.
- 10:40 h Comunicaciones Orales. Sesión A (OA1-OA4)**  
(Moderadores: Ernesto de Jesús, Joaquín García Álvarez)
- 11:40 h Pausa**
- 11:50 h Comunicaciones Orales. Sesión B (OB1-OB4)**  
(Moderadores: Joaquín García Álvarez, Elena Fernández)
- 12:50 h Sesión de pósteres A (PA01-PA14)**
- 13:45 h Pausa comida**
- 15:45 h Sesión de pósteres B (PB01-PB14)**
- 16:30 h. Conferencia Invitada.**  
**Prof. Bill Morandi**  
***“Recent developments in shuttle catalysis”***  
(Moderadora: Ana Carmen Albéniz)
- 17:30 h Comunicaciones Orales Sesión C (OC1-OC5)**  
(Moderadores: Joaquín García Álvarez, Tomás Rodríguez Belderrain)
- 18:45 h Cierre**

# ÍNDICE DE COMUNICACIONES

## Conferencia plenaria

- CP1 **Bill Morandi**. Recent developments in shuttle catalysis. *16:30 h.*

## Comunicaciones orales

- OA1 **Daniel Martínez Domínguez**. Ir(III) ortometalated complexes with  $\pi$ -extended C<sup>N</sup> ligand as candidates for theragnosis devices. *10:40 h.*
- OA2 **Diego Alexandre Cabo Palacios**. Reacción de Heck con níquel: búsqueda de complejos de Ni(0) óptimos y bien definidos. *10:50 h.*
- OA3 **Jaime Ponce de León**. Novel strategies for the synthesis of highly fluorinated biaryls. *11:00 h.*
- OA4 **Jonathan Martinez Laguna**. Gold nanoparticles-catalysed functionalization of carbon-hydrogen bonds by carbene transfer reactions. *11:10 h.*
- OB1 **Jorge Faiges Marcos**. Computational guided design of Ir/P,S-catalysts for asymmetric hydrogenation of olefins. *11:50 h.*
- OB2 **Juan Miranda Pizarro**. The first dicoordinate gold(I)-ethylene complex and other unusual species. *12:00 h.*
- OB3 **Laura Carolina Coconubo Guio**. Síntesis y caracterización de compuestos cíclicos de oro(III) con puentes fosforo. una nueva estrategia para generar propiedades luminiscentes. *12:10 h.*
- OB4 **Manting Mu**. Unveiling facilitated ferration of aromatic substrates through intramolecular sodium mediation. *12:20 h.*
- OC1 **Marc Montesinos-Magraner**. Rh(II)-catalyzed alkynylcyclopropanation of alkenes. *17:30 h.*
- OC2 **María del Prado Caballero Espinosa**. Nuevos complejos heteroescorpionato de hierro para la síntesis de productos de interés industrial a partir de CO<sub>2</sub>. *17:40 h.*
- OC3 **María Gil Moles**. Metallo drugs against SARS-CoV-2: Inhibition of the ACE2/S interaction and PLpro protease activity. *17:50 h.*
- OC4 **Piedad Herrera Ramírez**. Palladium-catalyzed cascade reactions for the synthesis of oxindole derivatives through intramolecular carbopalladation and C-C cleavage. *18:00 h.*
- OC5 **Pol De La Cruz Sanchez Badia**. How to overcome substrate and nucleophile limitations. Improved generation of catalysts for the construction of chiral C-C and C-X bonds. *18:10 h.*

## Comunicaciones póster

- PA01 **Alba Sorroche Ezquerro**. Estudio computacional de la estabilidad transitoria de diferentes subnanoclusters de oro con sistemas  $\pi$ . *12:50 h.*
- PA02 **Ana Luque Gómez**. Impact of green cosolvents on the catalytic dehydrogenation of formic acid: the case of iridium catalysts bearing NHC-phosphane ligands. *12:50 h.*
- PA03 **Anabel Moreno Rodríguez**. A new method to obtain pyrroles and sulfinamides through catalytic nitrene transfer to enynes. *12:50 h.*
- PA04 **Andrea Corral Zorzano**. Synthesis and study of luminescent properties of a new family of cyclometalated Pt<sup>IV</sup> compounds with N,N'-donor ligands. *12:50 h.*
- PA05 **Cintya Pinilla Martín**. C-C vs C-N coupling: the importance of the ligand choice in the catalytic functionalization of anilines. *12:50 h.*

- PA06 **David Gómez de Segura.** Synthesis and study of photophysical properties of mono and binuclear cycloplatinated compounds with pyrazole or pyrazolate ligands. *12:50 h.*
- PA07 **Elena Borrego Blanco.** Copper catalyses olefin aziridination in water with an iminoiodonane. *12:50 h.*
- PA08 **Felipe de la Cruz Martínez.** Heteroscorpionate rare-earth catalysts for the low-pressure coupling reaction of CO<sub>2</sub> and cyclohexene oxide. *12:50 h.*
- PA09 **Francisco Villaba de Pando.** Species in the precatalytic mixture of [Pd(OAc)<sub>2</sub>] and cooperating pyridone-type ligands for the C-H activation of arenes. *12:50 h.*
- PA10 **Guillermo Marcos Ayuso.** Copper(I) activation of C–X bonds: Bimolecular vs unimolecular reaction mechanism. *12:50 h.*
- PA11 **Hellen Videa.** Ortho C–H activation assisted by bimetallic Ga(I) systems. *12:50 h.*
- PA12 **Marina Ramos Martín.** Design of one-pot tandem methodologies for chemical synthesis using sustainable solvents: water or deep eutectic solvents. *12:50 h.*
- PA13 **Ramón Lecuna González.** Hydration of alkynes mediated by Fe-based deep eutectic solvents (DESs) under mild and bench-type reaction conditions. *12:50 h.*
- PA14 **Marcos López Aguilar.** One-pot tandem combination of the Cu(II)-catalyzed oxidation of primary alcohol with the addition of RLi/RMgX reagents, at room temperature, under aerobic and aqueous/eutectic conditions. *12:50 h.*
- PB01 **Ignacio Izquierdo Sánchez.** Encapsulation of a cyclopentadienyl Co(III) organometallic complex inside a supramolecular gallium metallocage. *15:45 h.*
- PB02 **Inés Soldevilla Garrido.** Influencia en el mecanismo TADF de los grupos perhalofenilo en complejos de oro(I) con ligandos difosfina. *15:45 h.*
- PB03 **Janira Herce Martínez.** Synthesis of Ir(III) grafted nanoparticles: photocatalytic activity under visible light and recyclability. *15:45 h.*
- PB04 **Joaquín Martínez Sal.** Desarrollo de nuevos complejos Ir-NHC activos en deshidrogenación catalítica de alcoholes primarios a ácidos carboxílicos en ausencia de aceptor de hidrógeno. *15:45 h.*
- PB05 **Jorge Pérez Ruiz.** Formation of fluorinated aziridines by catalytic nitrene transfer reactions. *15:45 h.*
- PB06 **Juan Diego Pizarro Javier.** Functionalization of N-heterocycles with ADAP-Cu(I) complexes. *15:45 h.*
- PB07 **Manuel Ramírez Rodríguez.** Copper and silver trispyrazolylborate complexes bearing phosphinoazide ligands: Synthesis, characterization and nitrene generation. *15:45 h.*
- PB08 **María Álvarez Martínez.** Two copper-carbenes from one diazo compound. *15:45 h.*
- PB09 **María Trinidad Martín García.** Copper(I) complexes as precatalysts in C-S cross coupling reactions. *15:45 h.*
- PB10 **Marina Padilla Langa.** Redox behaviour and UV-Vis of mixed-valent iridium chains. *15:45 h.*
- PB11 **Martina Casciotti.** Synthesis of aminolactones by copper catalyzed aminooxygenation reactions. *15:45 h.*
- PB12 **Sara Fernández Moyano.** Unexplored complexity of simple Au<sup>III</sup> reactions: Striking Cl/aryl scrambling. Driving forces and mechanisms. *15:45 h.*
- PB13 **Selma Miguel Arias.** Síntesis de complejos monofuncionales de ferroceno y platino(II) con potencial actividad farmacológica. *15:45 h.*
- PB14 **Sonia Moreno Infantes.** Empleo de un compuesto de Au(I) y Pb(II) como sensor de vapores de diferentes disolventes orgánicos. *15:45 h.*

## CONFERENCIA PLENARIA

### Recent developments in shuttle catalysis

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In this talk, a series of newly developed shuttle and metathesis reactions will be discussed. This includes for example the concept of e-shuttle for reversible halogenation as well as new functional group metathesis reactions. Interdisciplinary applications of these reactions to the recycling of persistent organic pollutants and synthesis of recyclable porous polymers will also be discussed.

## **COMUNICACIONES ORALES**

## Ir(III) ORTOMETALATED COMPLEXES WITH $\pi$ -EXTENDED C<sup>N</sup> LIGAND AS CANDIDATES FOR THERAGNOSIS DEVICES

Daniel Martínez<sup>1</sup>, C. Gonzalo<sup>1</sup>, J. Ángel Organero,<sup>2</sup> L. Santos,<sup>3</sup> A. Massaguer,<sup>4</sup> F.Á. Jalón<sup>1</sup>, B.R. Manzano<sup>1</sup>, G. Durá<sup>1</sup>

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Photochemotherapy emerges as a new non-invasive technique to improve the selectivity of current cancer treatments and it has special interest in tumours that can be irradiated by light or cannot be removed by surgery (head, neck or skin). In this therapy, a photosensitizer is administered, which is ideally harmless in the dark, and activates in the presence of light, generating  $^1\text{O}_2$  and reactive oxygen species (ROS), producing cancer cell apoptosis. Ir complexes with C<sup>N</sup> ligands have been employed as photosensitizers in photodynamic therapy (PDT) mechanisms due to their photochemical properties and ability to generate  $^1\text{O}_2$ . In this work, a new type of chloro-bridged dimer with a  $\pi$ -extended ligand (C<sup>N</sup>= benzo[a]pyrido-[2,3-c]phenazine; bppz) has been synthesized and new complexes  $[\text{Ir}(\text{C}^{\text{N}})_2(\text{N}^{\text{N}})]^+$  are presented as potential candidates for PDT. Furthermore, fluorescence studies demonstrated that these compounds are luminescent, which can be useful to use them as probes in theragnosis devices. Computational studies have shed light about the photophysical properties and cytotoxicity studies exhibit remarkable  $\text{IC}_{50}$  values under blue light, displaying higher cytotoxicity comparing with cis-platin in A549 cell line.

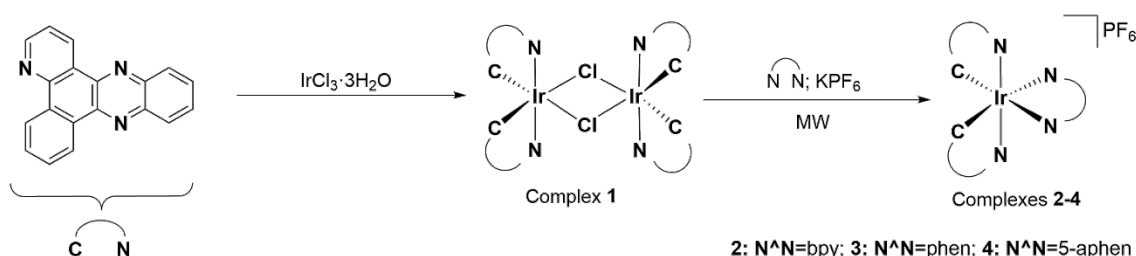


Figure 1. Synthesis scheme of Ir complexes with bppz

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- [1] Orwat, B.; et. al. Inorg. Chem. 2020, 59 (13), 9163–9176.  
 [2] Orwat, B.; et. al. Dalton Trans. 2017, 46 (28), 9210–9226.



## REACCIÓN DE HECK CON NÍQUEL: BÚSQUEDA DE COMPLEJOS DE Ni(0) ÓPTIMOS Y BIEN DEFINIDOS

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El Níquel (Ni) es un metal de la primera serie de transición, el cual, ha creado un interés creciente en los últimos tiempos, debido a sus indudables capacidades para reacciones catalíticas, como la Reacción de Heck. Además de sus capacidades químicas similares al Paladio (Pd), críticas para los procesos catalíticos, también se suman otros factores a su interés por parte de la comunidad científica, estos son su gran abundancia y, en consecuencia, su bajo coste.

Una etapa característica de la Reacción de Heck, es la Adición Oxidante (AO), uno de los procesos más básicos de la química organometálica. Este consiste en la oxidación por acción de un electrófilo sobre un complejo metálico, elevando tanto el número de coordinación, como el de oxidación del metal, en dos unidades [1,2]. Aunque de forma general se admite que el Ni es un elemento eficiente para la AO, lo cierto es que hemos observado de manera cualitativa, que precisa de una serie de condiciones para que se produzca de manera óptima. Para profundizar más en esta cuestión, se precisa de productos de partida bien definidos de Ni(0), que nos ayuden a entender mejor esta cuestión y a cuantificar esta etapa de la Reacción de Heck.

En nuestro caso particular, es utilizado Ni(cod)<sub>2</sub> como precursor de productos de Ni(0), pero este tiene el inconveniente del ciclooctadieno (cod), ya que, se hace difícil su sustitución por otra olefina de mayor interés para la Reacción de Heck.

Nuestro objetivo, por tanto, está enfocado en la síntesis eficiente de complejos de Ni(0) bien definidos estabilizados por ligandos híbridos P-N, sustituyendo el Ni(cod)<sub>2</sub> como fuente de Ni(0) o bien, utilizando otras olefinas capaces de desplazar el cod. Esto permitiría cuantificar la eficiencia de la AO y facilitar el estudio mecanicista de este tipo de reacciones.

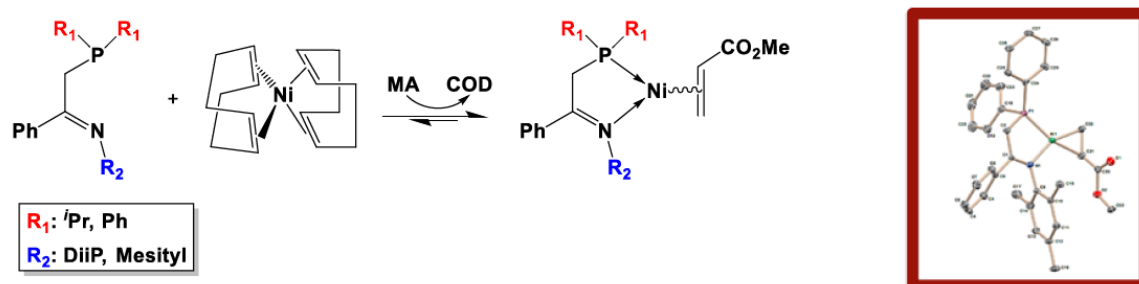


Figura 1: Esquema de formación de complejo de Ni(0) con ligando híbrido PN y olefina, junto a estructura de Rayos X.

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- [1] S. Z. Tasker, E. A. Standely, T. F. Jamison, *Nature*, **2014**, *509*, 299-309
- [2] T.T. Tsou, J. K. Kochi, *J. Am. Chem. Soc.*, **1979**, *101*, 6319-6332

## Novel strategies for the synthesis of highly fluorinated biaryls

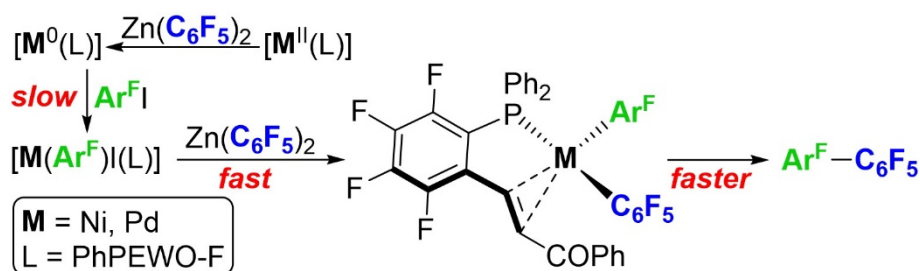
J. Ponce de León<sup>1</sup>, P. Espinet<sup>1</sup>

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The transition-metal catalyzed aryl-aryl coupling reactions are well solved for conventional aryls but have much higher difficulty when polyfluorinated aryls ( $\text{Ar}^{\text{F}}$ ) are involved. These present higher barriers to coupling and become particularly difficult for highly fluorinated aryls possessing  $\text{F}_{\text{ortho}}$  atoms.<sup>[1]</sup> Consistently, the  $\text{C}_6\text{F}_5$ - $\text{C}_6\text{F}_5$  coupling is the most difficult case.<sup>[2]</sup> Recently, we reported that *cis*- $[\text{Ni}(\text{C}_6\text{F}_5)(\text{THF})_2]$  was an efficient synthon to evaluate the ligand ability to promote difficult couplings in Ni.<sup>[3]</sup> The evaluations showed that, while several ligands such as bipyridines or diphosphines gave very stable complexes having very high coupling barriers and dialkylbiaryl phosphines could not prevent hydrolysis, PEWO (Phosphine-Electron-Withdrawing-Olefin) ligands could promote the reductive elimination at temperatures as low as  $-50\text{ }^\circ\text{C}$ .

Therefore, we focused on applying the results of this study to a catalytic system involving the coupling of different fluorinated aryls to a  $\text{C}_6\text{F}_5$  moiety.<sup>[4]</sup> Commercially available aryl iodides and  $\text{Zn}(\text{C}_6\text{F}_5)_2$  were employed as substrates. Again, ligands such as  $\text{PPh}_3$  and XPhos did not afford the coupling product. In contrast, a M/PEWO combination (M = Ni, Pd) gave the desired fluorinated biaryls in good to excellent yields. Following the reaction by NMR confirmed the formation of undesired homocoupling and hydrolysis side products when the aryl iodide is also partially fluorinated. In addition, off-cycle unreactive  $\text{M}^0\text{L}_2$  species were identified, confirming that, in contrast to other ligands that are often used in some excess for better protection of the catalyst, a M:PEWO = 1:1 ratio is required for the good outcome of the reaction.



- ❖  $\text{M}^{\text{II}}$  precatalyst
- ❖ Good to excellent yields
- ❖ High selectivity
- ❖ Mechanistic understanding
- ❖ Ligand promoted coupling

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- [2] E. Gioria, J. del Pozo, J. M. Martínez-Ilarduya, P. Espinet, *Angew. Chem., Int. Ed.* **2016**, *55*, 13276–13280.
- [3] J. Ponce-de-León, E. Gioria, J. M. Martínez-Ilarduya, P. Espinet, *Inorg. Chem.* **2020**, *59*, 18287–18294.
- [4] J. Ponce-de-León, P. Espinet, *Chem. Commun.*, **2021**, *57*, 10875–10878.

## GOLD NANOPARTICLES-CATALYSED FUNCTIONALIZATION OF CARBON-HYDROGEN BONDS BY CARBENE TRANSFER REACTIONS

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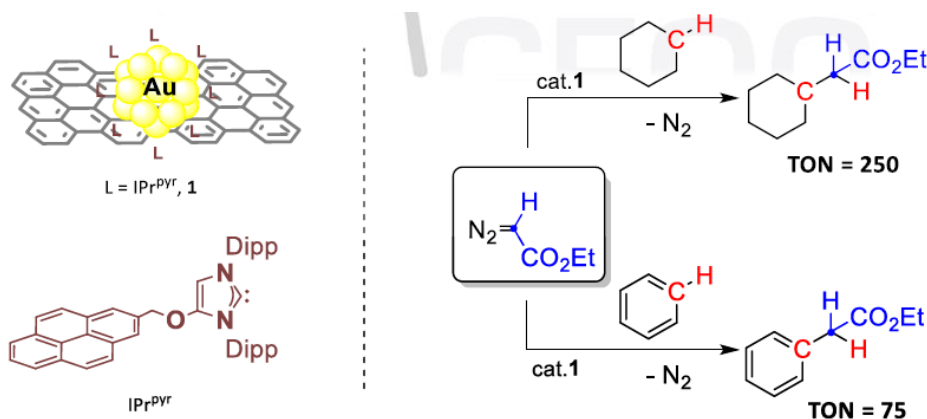
<sup>2</sup>Institute of Advanced Materials (INAM), Centro de Innovación en Química Avanzada (ORFEO-CINCA). Universitat Jaume I, Avda. Sos Baynat s/n, 12006-Castellón, Spain.

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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.[1] Particularly, the functionalization of non-activated C–H bonds of hydrocarbons has significantly emerged from the beginning of this century.[2] Several metals have been reported to catalyse these transformations.[3] Among them, soluble gold-based catalysts have received increasing attention, highlighting the complexes bearing N-heterocyclic carbene (NHC) ligands with aromatic group attached to the N atoms.[4]

At variance with those successful soluble systems, scarce examples can be found regarding the use of heterogeneous systems. So, no modification of C–H bonds was accomplished employing gold-based heterogeneous systems.[5, 6] Based on the above, the first example of Au NPs for Csp<sup>3</sup>–H and Csp<sup>2</sup>–H bonds functionalization by carbene insertion reaction is described in this work, where the nanoparticles are stabilized with IPr-like N-heterocyclic carbene (NHC) ligands (IPr<sup>PYR</sup>) and supported on reduced graphene oxide (rGO), resulting in the material **1** (non-supported nanoparticles of this type are not known).[7] Finally, recyclability is also effective, reaching an accumulate TON value of 1400 after six consecutive uses in the functionalization of cyclohexane.



### Referencias

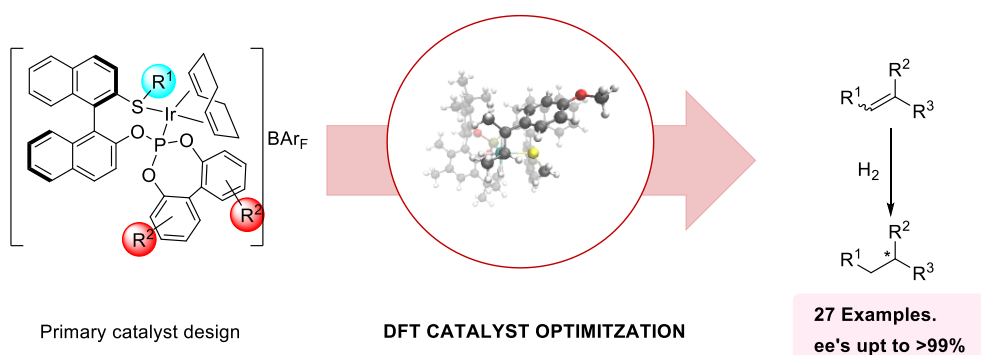
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## COMPUTATIONAL GUIDED DESIGN OF Ir/P,S-CATALYSTS FOR ASYMMETRIC HYDROGENATION OF OLEFINS

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The metal catalysed asymmetric hydrogenation is one of the most powerful tools for the preparation of enantioenriched compounds due to its perfect atom economy.[1] Despite been a deeply studied reaction, still a specific ligand design is required for each substrate class.[1] In this communication we shown the feasibility of in silico optimization of Ir/P,S-catalysts for the asymmetric hydrogenation of broad and diverse type of challenging olefins.[2]



DFT calculations showed that the bulkiness of the thioether has a major role to direct the olefin coordination, thus overcoming very common face selectivity issues and controlling the relative position of the axial hydride and the hydrogen. DFTs also showed that the chirality of the biphenyl phosphite needs to be controlled to maximize the energy gap between the most stable TSs leading to opposite enantiomers. We therefore discovered an Ir-P,S catalysts, which contains an cyclohexyl thioether group and an S-biphenyl phosphite group, as the most enantioselective for the reduction of a range of challenging unfunctionalized olefins and with relevant poorly coordinative groups, regardless of the type of functional groups or their coordination abilities. Appealingly, further modifications on the thioether groups and the biaryl phosphite moiety also allowed the highly enantioselective hydrogenation of olefins with different geometry patterns, such as  $\alpha,\beta$ -unsaturated lactones and lactams, 1,1'-disubstituted enol phosphinates and cyclic  $\beta$ -enamides, present in relevant products (e.g. rotigotine, alnesporine, etc).

To sum up we show the usefulness of an in silico-based catalyst optimization for the discovery of an efficient Ir-P,S catalyst family, whose application in asymmetric catalysis was discarded because early studies failed.

### References

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[2] J. Faiges, C. Borràs, I. M. Pastor, M. Besora, O. Pàmies, M. Diéguez. *Organometallics*, **2021**, *40*, 3424-3435.

## OB-2

THE ACTIVATION OF  $[\text{BAr}^{\text{F}}_4]^-$  BY GOLD(I) CATIONIC COMPLEX: KEY INTERMEDIATESJ. Miranda-Pizarro<sup>1</sup>, J. Campos<sup>1</sup>

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The use of non-coordinating and low interacting counterions has proven to be a powerful tool for the stabilization of highly reactive transition metal species. These anions can also play major role in some bond activation and catalytic processes. In gold chemistry, species of the type  $[\text{LAu}]^+$ , where L is a neutral donor ligand, should be accessible by using counterions with these properties such as  $[\text{BAr}^{\text{F}}_4]^-$  (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate), since it presents an extremely robust character towards many reactive transition metal cations.[1] As a matter of fact, there are only a few examples that provides evidence of the C—B bond activation of the  $[\text{BAr}^{\text{F}}_4]^-$  molecule.[2] In this context, it is not surprising that  $[\text{LAu}]^+$  species can achieve this transformation, but most of the details of this process remains unknown. During our investigation, we were able to observe some key intermediates derived from the activation of  $[\text{BAr}^{\text{F}}_4]^-$  by using dialkylterphenyl phosphines as the auxiliary ligand. Also, the information obtained could be valuable for the synthesis of boranes, compounds widely used as Lewis catalyst, among other applications.

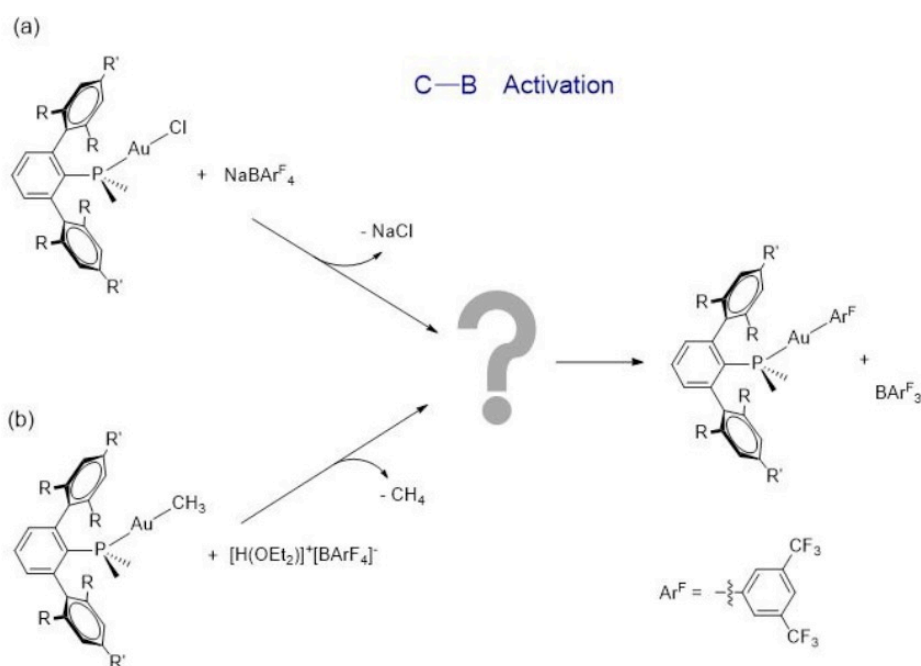


Figure 1. Strategies for the synthesis of electrophilic gold(I) fragments that promote the activation of  $[\text{BAr}^{\text{F}}_4]^-$ .

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## SÍNTESIS Y CARACTERIZACIÓN DE COMPUESTOS CÍCLICOS DE ORO(III) CON PUENTES FOSFURO. UNA NUEVA ESTRATEGIA PARA GENERAR PROPIEDADES LUMINISCENTES

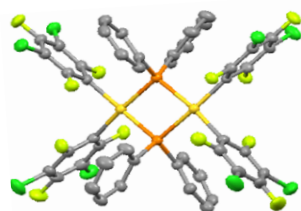
L. Coconubo<sup>1</sup>, J. M. López-de-Luzuriaga<sup>1</sup>, M. Monge<sup>1</sup>, S. Moreno<sup>1</sup>, M. E. Olmos<sup>1</sup>, M. Rodríguez-Castillo<sup>1</sup>.

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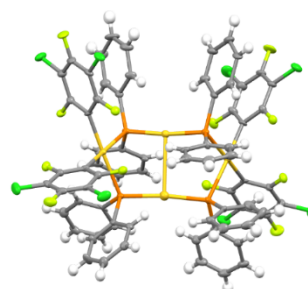
Una gran cantidad de complejos de coordinación de los metales de acuñar exhiben interesantes propiedades ópticas [1]. En particular, los de compuestos de oro(I) han sido ampliamente estudiados debido a su tendencia de presentar interacciones aurofílicas entre los centros metálicos [2]. Por el contrario, las interacciones de oro(III)···oro(III) son raras y han sido menos investigadas, siendo la mayoría de ejemplos de complejos de oro(III) con propiedades emisivas los que emplean ligandos fuertemente  $\sigma$ -dadores, como ciclometalados tridentados o bidentados, u otros no ciclometalados, como alquinilos [1].

Un tipo de ligando clásico en química de coordinación corresponde a los ligandos P-dadores; sin embargo, los complejos polinucleares con grupos fosfuro como ligandos puente han sido poco explorados, siendo pocos los derivados de oro(I) que contienen ligandos  $PR_2^-$  y estando la química del oro(III) aún menos explorada. Adicionalmente, en el caso de los complejos de oro(III) con puentes fosfuro, la luminiscencia no ha sido estudiada.

En este sentido, bajo los anteriores antecedentes, hemos empleado como estrategia para la síntesis de nuevos complejos fosfuro de oro(III) el uso de ligandos fosfuro como dadores  $\sigma$  y perhalofenilo como estabilizantes de este estado de oxidación. Siguiendo esta estrategia, hemos sintetizado el complejo dinuclear con doble puente fosfuro  $[Au(C_6Cl_2F_3)_2(\mu-PPh_2)]_2$  y el derivado tetranuclear mixto de oro(III) y oro(I)  $[Au^{III}(C_6Cl_2F_3)_2(\mu-PPh_2)_2Au^I]_2$ , que presentan interesantes propiedades fotofísicas.



$[Au(C_6Cl_2F_3)_2(\mu-PPh_2)]_2$



$[Au^{III}(C_6Cl_2F_3)_2(\mu-PPh_2)_2Au^I]_2$

### Agradecimientos

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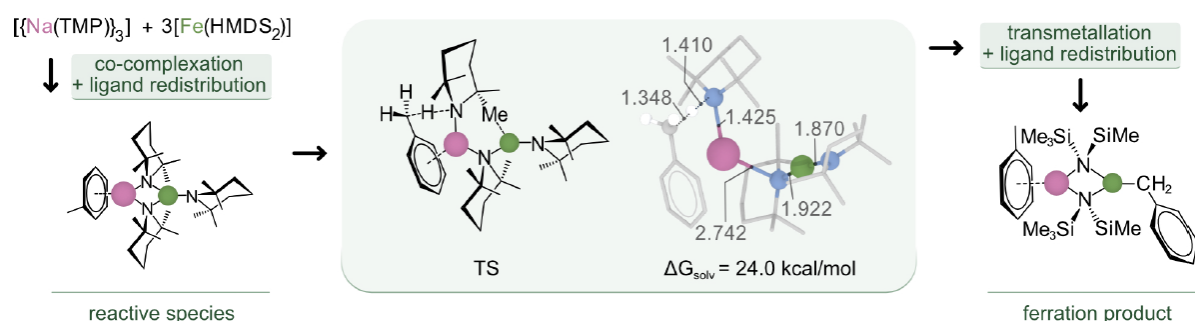
## Unveiling Facilitated Ferration of Aromatic Substrates Through Intramolecular Sodium Mediation

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Heterobimetallic systems utilising the cooperativity of a highly polar alkali-metal amide and a lower polar metal amide (e.g. Al, Zn or Fe) have emerged as a powerful class of reagents for the selective deprotonation of arenes.[1] Previous rationalisation of the underlying mechanism for cooperativity was reported for the reaction of 3-fluoroanisole with LiAl, wherein a stepwise mechanism was proposed.[2] On the contrary, for the reaction of pyrazine with LiZn, a concerted mechanism through a co-complexation intermediate was proposed.[2] Mechanistic studies on direct zincation of benzene have also been reported, although the chemical models chosen for the constitution of the bimetallic base in the computational studies were much simpler than the one employed in experiments.[3] This can lead to deceptive conclusions as we have recently shown for NaFe bimetallic systems, where very bulky bases favour deprotonation of pentafluorobenzene forming a sodiation intermediate, followed by the sequential transmetallation between Na and Fe instead of the direct ferration.[4] In this communication, I will present our recent theoretical insights on the cooperation of [Na(HMDS)] and [Fe(HMDS)<sub>2</sub>] (HMDS = hexamethyldisilazide) to demonstrate the importance of this bimetallic partnership as observed in experiments, which show that neither Na nor Fe amides are able to achieve deprotonative ferration of pentafluorobenzene alone.[4] An unexpected reaction pathway uncovering the cooperativity of Na and Fe in a synchronised manner will be conveyed during the presentation together with the key roles that both Na and Fe play in this reactivity. In addition, I will show how this newly found knowledge has led to the rational design of novel NaFe complexes with [Na(TMP)] (TMP = 2,2,6,6-tetramethylpiperidine), allowing the ferration of less activated substrates such as anisole and toluene, depicted in figure 1, which were confirmed by experimental studies. Overall, this novel NaFe system provides direct regioselective C–H activation metalation reactions at room temperature, creating a valuable tool in organic synthesis, which quantitatively and cleanly produces the desired ferrated product.



**Figure 1.** Ferration of toluene with equimolar [Na(TMP)] and [Fe(HMDS)<sub>2</sub>].

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## Rh(II)-CATALYZED ALKYNILCYCLOPROPANATION OF ALKENES

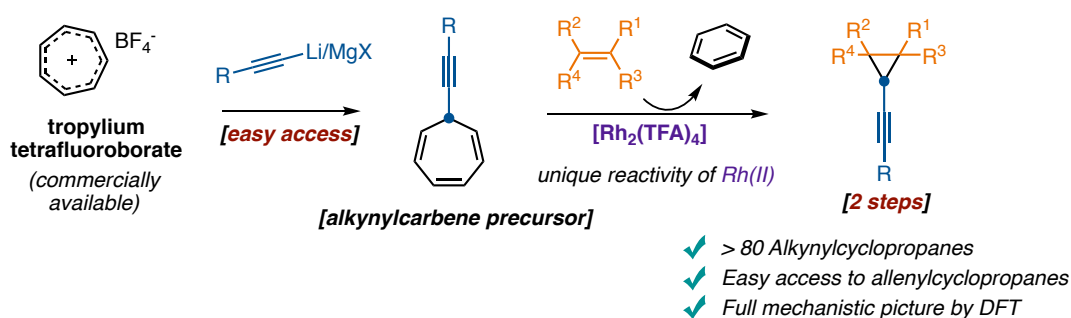
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7-Substituted cycloheptatrienes are interesting precursors of the corresponding carbenes *via* retro-Buchner reaction. This approach allows for the generation of highly reactive donor carbenes under catalytic conditions. Aryl and vinyl carbenes can be formed under Au, Rh or even Zn catalysis, and applied for the synthesis of cyclopropanes, allylsilanes or enals.[1] On the contrary, the engagement of alkynylcycloheptatrienes to produce the corresponding alkynylcarbenes have been impeded by the tendency of these substrates to undergo isomerization reactions.[2]

On the other hand, the alkynylcyclopropane scaffold is present in the structure of several commercialized drugs and natural products, such as Efavirenz or callipeltoside A. Alkynylcyclopropanes (ACs) are also versatile substrates for ring expansion, ring-opening or cycloadditions, among other transformations. Despite their interesting features, a general protocol for the alkynylcyclopropanation of alkenes was missing until very recently.

Herein, we demonstrate the unique reactivity unveiled by  $\text{Rh}_2(\text{TFA})_4$  to generate unprecedented alkynylcarbenes from 7-alkynylcycloheptatrienes under mild reaction conditions.[3] This catalytic system overcomes the tendency of the substrates to undergo isomerization reactions, delivering the carbene selectively, which is then trapped by a variety of alkenes to form the desired ACs. DFT studies were conducted to study the origin of the divergent reactivity observed with  $\text{Rh}_2(\text{TFA})_4$  and Au(I) complexes.



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## Nuevos complejos de hierro para la fijación de CO<sub>2</sub>

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Actualmente, existe un interés creciente en la transformación de los residuos generados por la sociedad en productos de elevado valor añadido. El CO<sub>2</sub> puede ser una materia prima barata y renovable en el ámbito de la industria química, lo que le confiere un gran atractivo en el marco de la economía circular, aunque es una molécula termodinámicamente muy estable y poco reactiva, por ello, es importante el desarrollo de nuevas estrategias o metodologías químicas para activar el CO<sub>2</sub> en condiciones suaves de reacción. Una de las alternativas que más interés está despertando en los últimos años es su uso como fuente de carbono C1 en la síntesis de compuestos químicos de interés a gran escala, como son los carbonatos cíclicos y los policarbonatos.<sup>[1]</sup> La baja reactividad de la molécula de CO<sub>2</sub> precisa del desarrollo de sistemas catalíticos que permitan la activación de esta molécula.<sup>[2]</sup> El hierro es uno de los metales más abundante, es barato y de los llamados “friendly metals” por su baja toxicidad, por lo que el diseño de compuestos de hierro activos en la síntesis de carbonatos cíclicos y policarbonatos es un campo atractivo en estos procesos catalíticos.<sup>[3]</sup> En este trabajo, se han diseñado nuevos complejos de Fe(II) y Fe(III) con ligandos heteroescorpionato como catalizadores de tipo “one component” que no necesitan de co-catalizador para la fijación de CO<sub>2</sub> en carbonatos cíclicos (Figura 1).

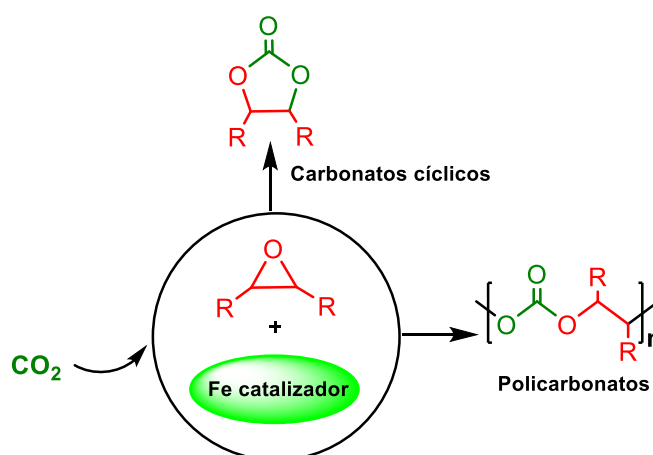


Figura 1.

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## METALLODRUGS AGAINST SARS-CoV-2: INHIBITION OF THE ACE2/S INTERACTION AND PL<sup>pro</sup> PROTEASE ACTIVITY

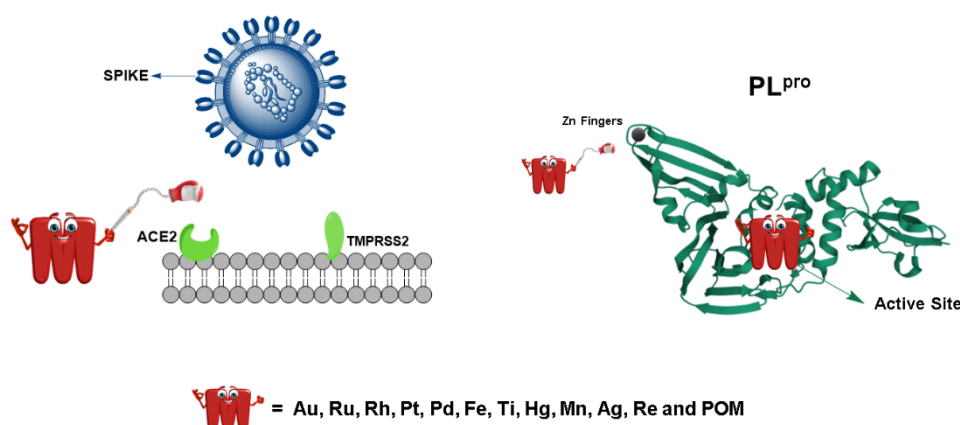
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The global pandemic caused by the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) has led to an unprecedented global crisis health and is requiring major efforts for development of antiviral therapeutics and vaccines. Although vaccines have been available for a year, there is still a huge need for effective therapeutic drugs. In this regard, metal complexes are promising candidates for the development of new antiviral drugs. The antiviral effects of metal-based drugs have occasionally been reported, nevertheless, this area of application has not been studied as intensively compared to the development of metallodrugs against cancer among others<sup>[1]</sup>.

The viral replication cycle of SARS-CoV-2 and several molecular pathways have been in the focus of the search for a possible treatment against COVID-19. In our research group we are analysing the potential ability of different metal complexes to inhibit two different pathways of the viral cycle: 1) The entry of the coronavirus into the host cell: the interaction of ACE2 with the spike protein. 2) The viral replication, in particular the the activity of the papain-like protease PL<sup>pro</sup>. In this regard we conducted a preliminary study with different gold complexes where promising results were observed. The complexes displayed very promising activity against SARS-CoV-2 PL<sup>pro</sup> activity and moderately inhibited the S / ACE2 interaction. In view of these promising results, we decided to extend this study to other metals. We screened over 100 structurally diverse compounds, including: Au(I/III), Ru(II/III), Fe(II/III), Rh(I), Pt(II), Ag(I), Pd(II), Ti(IV), Re(I), Mn(II), Hg(II) complexes and 11 polyoxometalates (POMs). Once the ability of these complexes to inhibit S / ACE2 binding and PL<sup>pro</sup> activity were analyzed, and after cytotoxicity evaluation; several complexes were tested in antiviral SARS-CoV-2 assays confirming activity for some Au, Ag, Ti, or POMs complexes. These preliminary studies may provide starting points for the design of antiviral metallodrugs against SARS-CoV-2 in future studies<sup>[2]</sup>.

More than 100 metallodrugs screened against different targets of SARS-CoV-2



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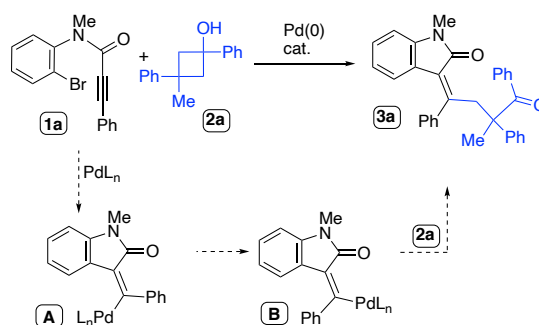
## PALLADIUM-CATALYZED CASCADE REACTIONS FOR THE SYNTHESIS OF OXINDOLE DERIVATIVES THROUGH INTRAMOLECULAR CARBOPALLADATION AND C–C CLEAVAGE

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Cascade reactions represent a straightforward synthetic strategy to obtain complex molecular structures from simple substrates. Palladium-catalyzed cascade reactions have proven to be a versatile and useful tool in organic synthesis for the formation of cyclic structures and new C–C and C–heteroatom bonds through multiple transformations in a single synthetic operation, specially those involving the carbopalladation of alkenes and alkynes. [1] Other innovative cascade reactions are those that imply the C–C cleavage of strained ring systems through a beta-carbon cleavage process. [2]

Recently we have developed a new route to functionalized *N*-heterocycles, including the relevant oxindole nuclei, based on an intramolecular carbopalladation of substrates containing a tethered alkyne group (**1a**). The *E*-alkenyl-Pd intermediate (**A**, Scheme 1) generated initially can undergo isomerization to the corresponding *Z* species (**B**, Scheme 1) and suffer an alkylation process by using cyclobutanol derivatives **2a** as coupling partners. This last step implies the C–C cleavage of the strained cycloalkanol through a beta-carbon cleavage process. [3] This way, a range of interesting heterocyclic compounds bearing a tetrasubstituted olefin moiety have been obtained. Moreover, it has been observed the formation of *E* and *Z* diastereoisomers depending on the steric congestion of the alkenyl-palladium intermediate, and a complete study of structural characterization by NMR has allowed the discrimination between compounds.



**Scheme 1.** Pd-catalyzed cascade involving carbopalladation/alkylation.

### Acknowledgements

Financial support from MICINN (grant PGC2018-100719-B-I00-with FEDER funding) and Fundación Séneca-Agencia de Ciencia y Tecnología Región de Murcia (grant 19890/GERM/15) is gratefully acknowledged.

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## HOW TO OVERCOME SUBSTRATE AND NUCLEOPHILE LIMITATIONS. IMPROVED GENERATION OF CATALYSTS FOR THE CONSTRUCTION OF CHIRAL C-C AND C-X BONDS

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Asymmetric catalysis is a powerful and sustainable method for preparing chiral compounds. Most catalysts are only tested in benchmark substrates, eluding challenging ones that would yield to more appealing compounds. Our group has taken advantage of the adaptability of biaryl phosphite-based ligands to overcome the substrate specificity and low nucleophile scope of the Pd-catalyzed asymmetric allylic substitution reactions. [1-3] Here we present our recent finding in the design of two catalyst libraries. Improving the approaches reported to date, they present a broad substrate and nucleophile scope. [4, 5] Excellent enantioselectivities has been achieved for a broad range of linear (including challenging unsymmetrical di- and monosubstituted) and cyclic substrates with different electronic and steric properties, using many C-, N- and O-nucleophiles (70 compounds in total). [4, 5] Finally, the application of these catalysts for the preparation chiral (poly)carbo- and heterocyclic compounds, with multiple stereocenters, will be demonstrated by the use of straightforward sequences of allylic substitution and either 1,6-enyne cyclization, or ring-closing metathesis or Pauson-Khand reactions.[4,5]

These families of catalysts developed present the advantages of a simple and modular architecture, they have been synthesized in a few steps from unexpensive starting materials and are solid and stable to air and therefore easy to handle. The combination of computational studies and NMR spectroscopy, together with the analysis of the catalytic results were crucial to identify the species responsible for the catalytic performance, to rationalize the catalysts' structure, and to ensure the finding of optimal catalyst. [4, 5]

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## **COMUNICACIONES POSTER**

## ESTUDIO COMPUTACIONAL DE LA ESTABILIDAD TRANSITORIA DE DIFERENTES SUBNANOCLUSTERES DE ORO CON SISTEMAS $\pi$

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La catálisis homogénea con complejos de oro es una disciplina tardía y no fue hasta la década de 1980 que se publicó la primera aplicación catalítica de compuestos de oro(I). Sin embargo, no solo el oro en su estado de oxidación +1 es capaz de ser catalíticamente activo. Las nanopartículas de oro(0) son capaces de actuar como catalizadores mediante la activación de tipo  $\sigma$  para la formación de nuevos enlaces C-C. Sin embargo, cuando el tamaño de las NPs de oro se ve reducido tan solo a unos pocos átomos de oro(0) su comportamiento catalítico cambia, siendo en este caso excelentes activadores de enlaces  $\pi$  [1]. Estas especies se caracterizaron hace unos años, se conocen como subnanoclusteres y su actividad catalítica se ve íntimamente ligada a su estabilización transitoria con el propio sustrato de la reacción.

Los resultados experimentales previos realizados en nuestro grupo de investigación muestran cómo, en reacciones de hidratación de alquinos, grupos funcionales como son cadenas alquílicas con un alto número de átomos de carbono o grupos aromáticos, mejoran la estabilización transitoria de las especies catalíticas de oro(0) [2].

Con el fin de analizar los resultados experimentales, en este trabajo hemos evaluado a nivel computacional la capacidad estabilizante de alquinos que presentan diferentes grupos funcionales, así como de subnanoclusteres con diferente número de átomos de oro. Para ello, se han modelizado sistemas del tipo Aun...alquino (n= 1-6), empleando para ello la teoría del funcional de la densidad DFT.

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## Impact of Green Cosolvents on the Catalytic Dehydrogenation of Formic Acid: The Case of Iridium Catalysts Bearing NHC-phosphane Ligands

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Formic acid is considered a promising material for molecular hydrogen storage. Thus, the catalytic dehydrogenation of HCOOH gives an equimolecular mixture of H<sub>2</sub>/CO<sub>2</sub>, as was independently described by Beller [1] and Laurenczy [2] in 2008.

In this work we focus on the influence of different cosolvents on the dehydrogenation of formic acid. In particular, the study of the activity of two novel iridium complexes based on PC<sup>NHC</sup>P and PC<sup>NHC</sup>O ligands, [Ir(COD)(κ<sup>3</sup>-P,C,P'-PC<sup>NHC</sup>P)]BF<sub>4</sub> (**1**) and [Ir(COD)(κ<sup>2</sup>-P,C-PC<sup>NHC</sup>O)]BF<sub>4</sub> (**2**), under different conditions (**Figure 1**). In this context, the use of dimethylcarbonate as cosolvent (1:1 (v/v)) shows an outstanding improvement of the catalytic activity in the case of complex **2** from having a TOF<sub>1h</sub> of 61 to 988 h<sup>-1</sup>, while complex **1** was barely affected.

The study of the mechanism of this reaction was carried out by stoichiometric experiments, KIE measurements and DFT calculations. These data, both theoretical and experimental, suggest that the use of organic carbonates as cosolvents prevents the deactivation of the catalyst, which occurs after the formation of dinuclear species.

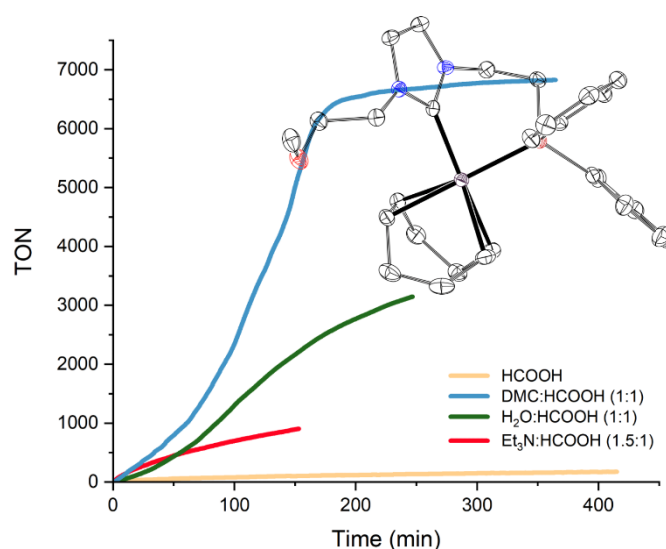


Figure 1: Reaction profiles for the dehydrogenation of HCOOH using **2** with different cosolvents.

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## PA-03

**A NEW METHOD TO OBTAIN PYRROLES AND SULFINAMIDES THROUGH CATALYTIC NITRENE TRANSFER TO ENYNES**

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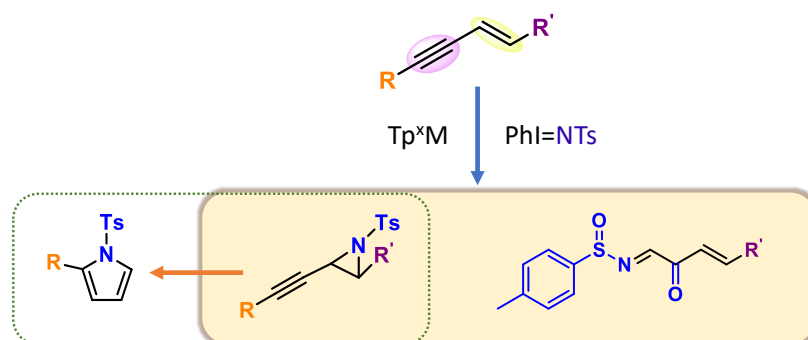
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In the last few years, several research groups have developed different catalytic methods using enynes as starting materials. This chemistry provides a variety of products which the triple and double bonds of the substrate are involved.[1]

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

In this contribution, we will show a new methodology that leads to the formation of aziridines or sulfinamides derivatives from enynes. Furthermore, we have carried out the opening and subsequent cyclizing of these aziridines to induce the formation of a new pyrrole.[3]



**Catalytic nitrene transfer reaction to enynes.**

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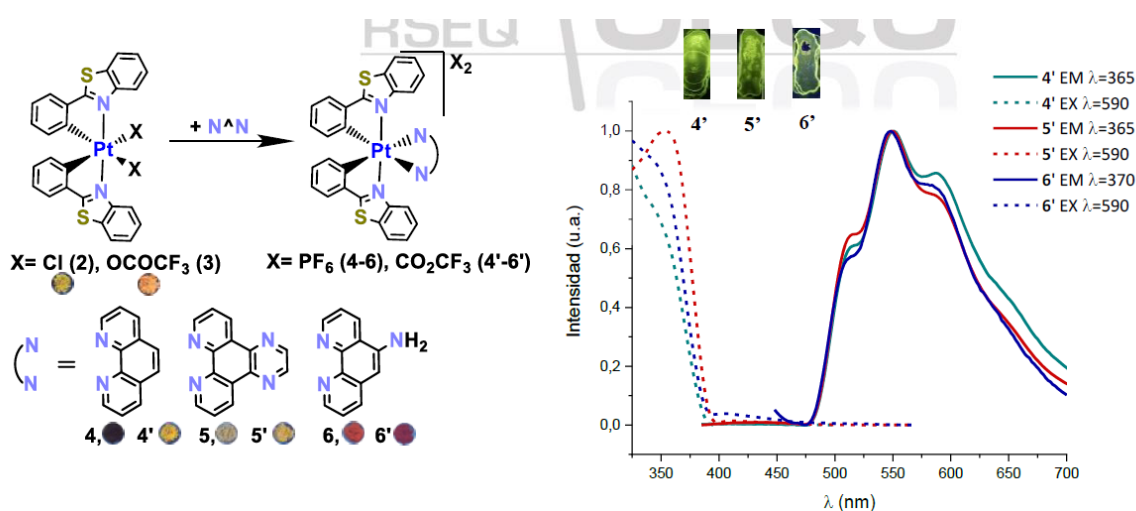
## SYNTHESIS AND STUDY OF LUMINESCENT PROPERTIES OF A NEW FAMILY OF CYCLOMETALATED Pt<sup>IV</sup> COMPOUNDS WITH N,N'-DONOR LIGANDS

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Numerous studies have been carried out on cyclometalated complexes of d<sup>6</sup> (Ru<sup>II</sup>, Os<sup>II</sup> or Ir<sup>III</sup>) and d<sup>8</sup> (Pt<sup>II</sup> and Au<sup>III</sup>) metal ions due to their potential applications in fields such as photocatalysis, biological sensing, photosensitizers and optoelectronic devices. By contrast, related luminescent Pt<sup>IV</sup> derivatives have received less attention<sup>1</sup>.

Our group has recently published two series of neutral bis(cyclometalated)pentafluorophenyl Pt<sup>IV</sup> complexes with Cl<sup>-</sup> or CN<sup>-</sup> as auxiliary ligands<sup>2</sup>. Given the broad applicability of benzothiazole in medicinal chemistry and as a continuation in our ongoing interest on biological activity of cycloplatinated complexes based on 2-arylbenzothiazoles<sup>3</sup>, we have designed two new series of dicationic bis-cyclometalated Pt<sup>IV</sup> compounds based on 2-phenylbenzothiazole cyclometalated (pbt) groups. In detail, we present the synthesis of dicationic compounds [Pt(pbt)<sub>2</sub>(N<sup>^</sup>N)]X<sub>2</sub> (X = PF<sub>6</sub>, CF<sub>3</sub>CO<sub>2</sub>) (N<sup>^</sup>N = phen **4**, **4'**; pyraphen **5**, **5'**; NH<sub>2</sub>-phen **6**, **6'**), using compounds [Pt(pbt)<sub>2</sub>Cl<sub>2</sub>] (**2**) and [Pt(pbt)<sub>2</sub>(OCOCF<sub>3</sub>)<sub>2</sub>] (**3**) as precursors. All new complexes have been fully characterized by spectroscopic techniques, and the molecular structure of **3** has been confirmed X-ray diffraction. A comparative study of their optoelectronic properties in different media (solid state, solution and polymeric film for emission) has been carry out. **2** and **3** exhibit emission based on pbt (3IL), whereas the excited states of phenantroline-based ligands are of mixed 3LL'/CT/3IL/3IL' configuration with remarkable 3IL' (phen-NH<sub>2</sub>) ligand contribution. To insight into the nature of the optical properties, theoretical analysis has been carried out at DFT/TD-DFT level for selected complexes (**2**, **3**, **42+** and **62+**).



**Figure 1.** a) Schematic synthesis of [Pt(pbt)<sub>2</sub>(N<sup>^</sup>N)]X<sub>2</sub> complexes; b) Emission and excitation spectra in polymeric film for complexes **2-6**.

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## C-C VS C-N COUPLING: THE IMPORTANCE OF THE LIGAND CHOICE IN THE CATALYTIC FUNCTIONALIZATION OF ANILINES

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Palladium-catalysed Buchwald-Hartwig amination is a well-known reaction where the C-N coupling products of different amines are obtained with excellent results.[1] The best catalyst for these reactions consists of a palladium precursor and specific phosphines with different bulky substituents. As exemplified in the literature, in order to obtain the C-C coupling product in the presence of amino groups, the protection of the amine is needed before the catalytic reaction.[2] By the use of the ligand bipy-6OH (Figure 1), instead of a phosphine ligand, the C-H activation in the arene ring occurs and the C-C coupling product of non-protected anilines is obtained selectively. The bipy-6-OH ligand has demonstrated before its role in the C-H activation step in the direct arylation of arenes.[3] The coupling product obtained can be selected by changing the catalytic conditions and accelerating one catalytic step over another. The use of a phosphine ligand accelerates the reductive elimination step which leads to the C-N coupling; meanwhile the bipy-6-OH accelerates the C-H activation step obtaining the C-C coupling of anilines (Figure 1). Stoichiometric experiments and DFT calculations on the mechanism will be discussed.

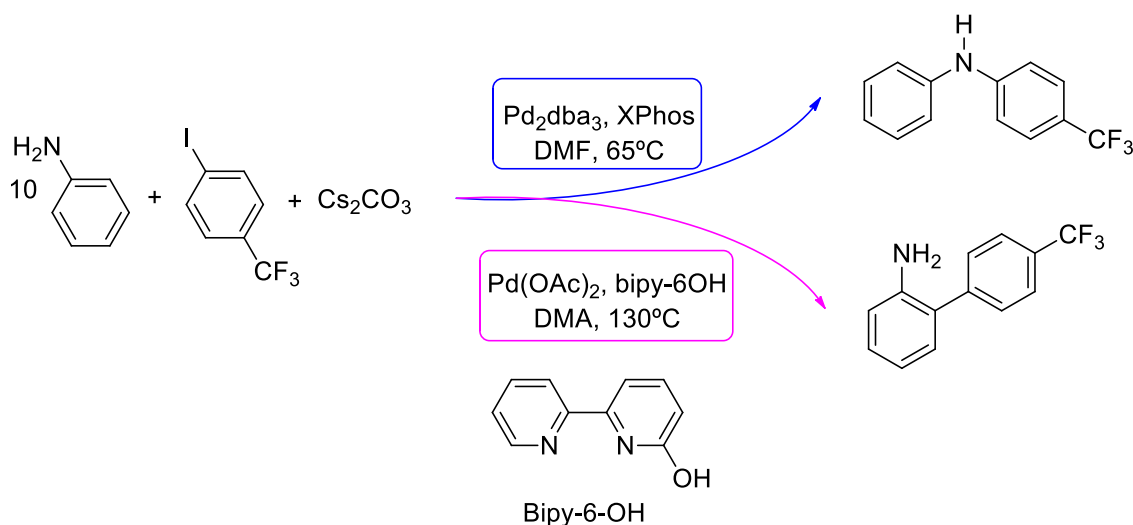


Figure 1. Divergent functionalization pathways for aniline.

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## SYNTHESIS AND STUDY OF PHOTOPHYSICAL PROPERTIES OF MONO AND BINUCLEAR CYCLOPLATINATED COMPOUNDS WITH PYRAZOLE OR PYRAZOLATE LIGANDS

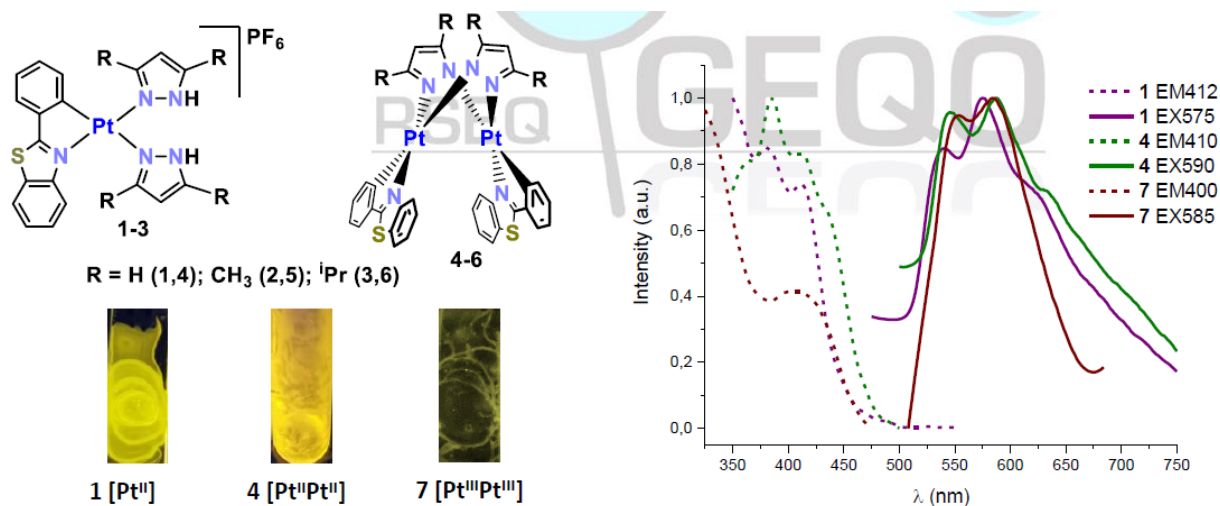
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In the last two decades, the design and study cycloplatinated(II) complexes has undergone a notable development due to their use as triplet emitting materials. In these complexes, the combination of heteroaromatic cyclometalated groups and auxiliary ligands allows the fine-tuning of various mixed ( $\pi$ - $\pi^*$ )/LC/MLCT excited states<sup>1</sup>. In this framework, pyrazole (RpzH)-ligands provide an interesting entry to the design of homo and polymetallic systems with interesting structures and intriguing luminescent properties. Indeed, a great variety of luminescent homo and heteropolynuclear pyrazolate complexes [Pt<sub>2</sub>M<sub>2</sub>] (M = Ag, Cu)<sup>2</sup> and pyrazolate-bridged dinuclear Pt<sup>II</sup> complexes have been recently reported<sup>3</sup>. In the latter, the Pt...Pt distance strongly depends on the steric hindrance of the pyrazolate substituents and modifies the nature of the low-lying emissive state switching from a <sup>3</sup>LC/<sup>3</sup>MLCT to a <sup>3</sup>MMLCT nature. Furthermore, oxidation processes of pyrazolate-bridged Pt<sup>II</sup>Pt<sup>II</sup> are an ease entry to unusual Pt<sup>III</sup>-Pt<sup>III</sup> complexes<sup>3</sup>.

In this work, we present the synthesis, characterization and photophysical properties of a series of mononuclear bis-pyrazole complexes [Pt(pbt)(RpzH)<sub>2</sub>]PF<sub>6</sub> (RpzH = pz **1**, 3,5-Me<sub>2</sub>pzH **2**, 3,5-<sup>i</sup>Pr<sub>2</sub>pzH **3**) and their deprotonation to form butterfly-like bis-pyrazolate bridged diplatinum complexes {[Pt(pbt)( $\mu$ -Rpz)]<sub>2</sub>} (**4-6**). Finally, oxidation of {[Pt(pbt)( $\mu$ -pz)]<sub>2</sub>} **4** afforded the symmetrical Pt<sup>III</sup>-Pt<sup>III</sup> complex {[Pt(pbt)( $\mu$ -pz)Cl]<sub>2</sub>} **7**, which is emissive in rigid media.



**Figure 1.** a) Schematic synthesis of complexes **1-6**. b) Excitation and Emission spectra of complexes **1**, **4** and **7** in polymeric film.

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## Copper catalyses olefin aziridination in water with an iminoiodonane

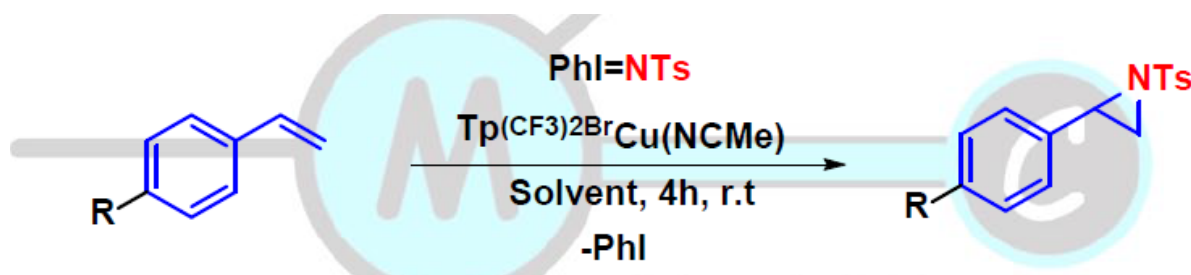
Elena Borrego,<sup>1</sup> Pedro. J. Pérez\*<sup>1</sup> and Ana Caballero\*<sup>1</sup>

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

Our group has described a series of metal complexes bearing trispyrazolylborate ligands (Tpx) as catalysts capable of the functionalization of aliphatic C-H bonds upon inserting  $\text{CHCO}_2\text{Et}$  units from  $\text{N}_2=\text{CHCOEt}$  (ethyl diazoacetate, EDA) using water as reaction media[1][2].

In this work, the copper complex  $\text{Tp}(\text{CF}_3)_2\text{BrCu}(\text{NCMe})$  is described as an efficient catalyst for the olefin aziridination using  $\text{PhI}=\text{NTs}$  as nitrene source. Identical activity was observed with dichloromethane and water were used as solvents under same conditions. Competition experiments and Hammet plot show that the behavior of the metal is the same in both reaction media.



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## HETEROSCORPIONATE RARE-EARTH CATALYSTS FOR THE LOW-PRESSURE COUPLING REACTION OF CO<sub>2</sub> AND CYCLOHEXENE OXIDE

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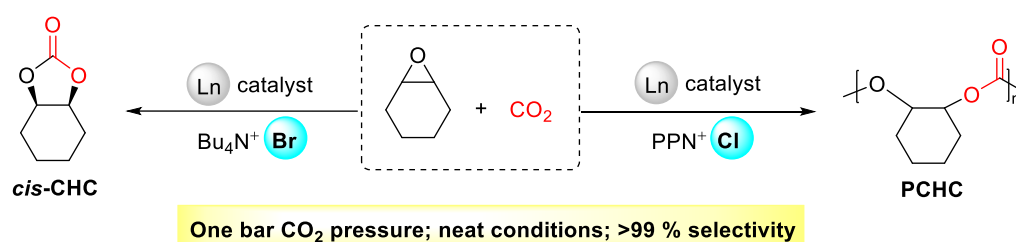
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The transformation of CO<sub>2</sub> into valuable products is a challenge for sustainable chemistry, motivated by the requirement to reduce greenhouse gas emissions and fossil fuel consumption in chemical manufacturing [1]. Metal-catalyzed coupling reaction of CO<sub>2</sub> and epoxides to produce either cyclic carbonates or polycarbonates is one of the most successful and widely studied processes for CO<sub>2</sub> utilization [2]. In terms of operating conditions, many of these catalytic systems have displayed high activity for this coupling reaction under just 1 bar of CO<sub>2</sub> pressure. However, these catalysts are in general limited to monosubstituted epoxides, while those for di- and trisubstituted substrates under these conditions remain rare [3]. Therefore, the development of efficient catalysts for the reaction of internal epoxides and CO<sub>2</sub> under mild conditions is highly desirable. In this context, rare-earth-metal complexes can be promising candidates to produce either cyclic carbonates or polycarbonates from highly substituted epoxides due to their hard Lewis acidity, easy tuning of the steric and electronic environments, and the capacity to bind and dissociate rapidly.

In this work, we report the synthesis of new heteroscorpionate rare-earth metal complexes which have been shown to be very active and selective for the copolymerization of CO<sub>2</sub> and cyclohexene oxide in the absence of a nucleophile source. Moreover, in the presence of the appropriate nucleophile, these compounds allowed the highly selective production of either poly-(cyclohexene carbonate) or *cis*-cyclohexene carbonate at only 1 bar of CO<sub>2</sub> pressure (Scheme 1).



Scheme 1

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## SPECIES IN THE PRECATALYTIC MIXTURE OF [Pd(OAc)<sub>2</sub>] AND COOPERATING PYRIDONE-TYPE LIGANDS FOR THE C-H ACTIVATION OF ARENES

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In recent years, building carbon-carbon and carbon-heteroatom bonds directly from carbon-hydrogen bonds is on the front and center of modern synthetic chemistry<sup>[1]</sup>. Numerous cooperative ligands have been developed to assist the C-H cleavage and lower the energy of the transition state. Among them, our group has experimental and computational studied the ligands [2,2'-bipyridin]-6(1*H*)-one (bipy-6-OH) and 1,10-phen-2(1*H*)-one (phen-2-OH) that have a strong accelerating effect in the functionalization of arenes with no directing groups. This effect is the result of the cooperation of the basic keto group in the C-H activation step. Direct arylation of simple arenes and oxidative Heck reactions has been successfully achieved by this strategy<sup>[2]</sup>. The common procedure in most catalytic reactions is the use of a mixture of [Pd(OAc)<sub>2</sub>] and ligand as precatalyst. There is a lack of information about the species formed from this mixture, but how they evolve to the active species could strongly influence the efficiency of the catalysis. In this work, we have analysed an array of possible scenarios when [Pd(OAc)<sub>2</sub>] and the ligands bipy-6-OH and phen-2-OH are mixed, to determine the complexes formed and their feasibility as a precatalyst for the functionalization of simple arenes in Pd-catalyzed C-H activation reactions (Figure 1).

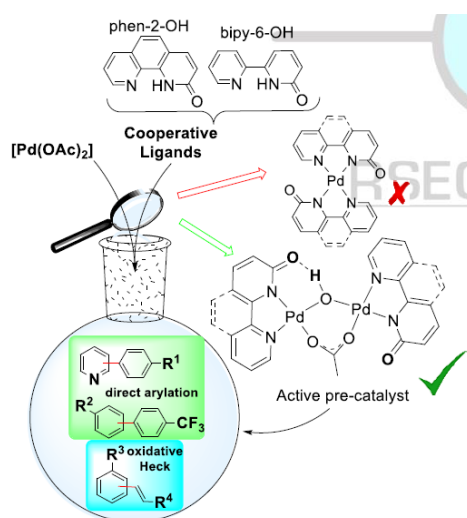


Figure 1.

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## COPPER(I) ACTIVATION OF C–X BONDS: BIMOLECULAR VS UNIMOLECULAR REACTION MECHANISM

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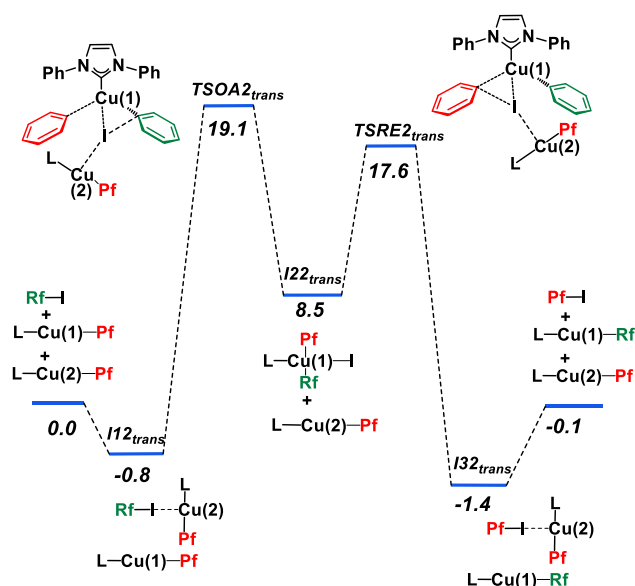
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Activation of C–X bonds (X = halogen or pseudohalogen) is an essential part of copper-catalyzed coupling reactions. Different C–X activation modes have been proposed and discussed. From a mechanistic point of view, C–X activation can be considered an oxidative addition reaction, a homolytic cleavage reaction, or a metathesis reaction. The reaction between [Cu(NHC)(Ar<sup>F</sup>)] (Ar<sup>F</sup> = C<sub>6</sub>F<sub>5</sub>) and allyl or fluorinated aryl bromides yield the expected cross-coupling product. However, when allyl or fluorinated aryl iodides were used, the unexpected metathesis product was obtained.

This unusual behavior was studied using kinetic experiments and kinetic simulations, using Dosy NMR experiments and DFT calculations. About the kinetic experiments, second kinetic order on [Cu(NHC)(Ar<sup>F</sup>)] was measured. The kinetic simulations were consistent with this results. Diffusion experiments shows an association between the fluorinated aryl iodide and the complex [Cu(NHC)(Ar<sup>F</sup>)]. The large change in the <sup>19</sup>F NMR chemical shift of Ar<sup>F</sup>–I when measured under a large excess of [Cu(NHC)(Ar<sup>F</sup>)] further supports this association.

Finally, big differences in the energy profile were detected when a second copper complexes in the DFT calculations was used. The pathway using just one copper complex, an oxidative addition barrier about 22 kcal mol<sup>-1</sup> was obtained for the cis isomer and 24.5 kcal mol<sup>-1</sup> for the trans one. This results were not consistent with the experimental results. Importantly, the presence of the additional [Cu(NHC)(Ar<sup>F</sup>)] molecule reconciles computation with experiment, making trans pathway the favored one, with a barrier matching the experimental  $\Delta G_{\ddagger 298}^{\ddagger}$  (19.9 kcal mol<sup>-1</sup>).



**Figure 1.** Calculated Gibbs energy profiles (kcal mol<sup>-1</sup>) for the reaction between [Cu(NHC)(Pf)] and Rf-I in presence of a second [Cu(NHC)(Pf)] molecule to produce the aryl metathesis (trans pathway). Color code: red aryl = C<sub>6</sub>F<sub>5</sub>; green aryl = 3,5-C<sub>6</sub>F<sub>3</sub>Cl<sub>2</sub>. (DFT at B3LYP-D3/BS2 level, SMD solvent model (DMF), 298K).



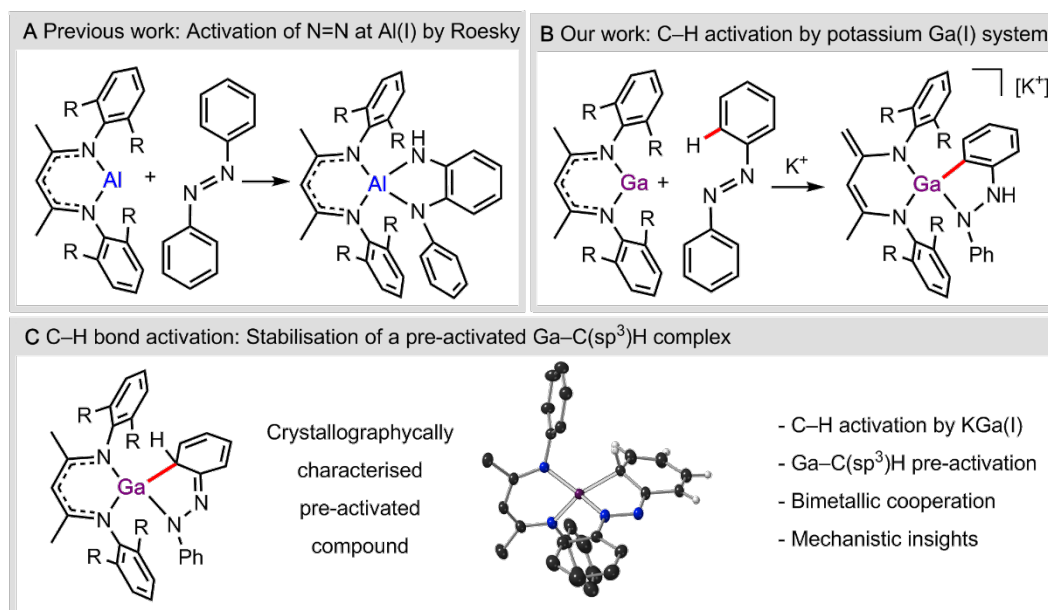
## ORTHO C–H ACTIVATION ASSISTED BY BIMETALLIC Ga(I) SYSTEMS

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Recent studies of the reactivity of group 13 metal systems provide new principles for novel reactivity, showing how diverse is the chemistry of the p-block elements.[1] In this context, the stabilization of low-valent group 13 main group M(I) systems leads to the isolation of Al(I), Ga(I), and In(I) compounds.[2] These low-valent compounds are analogues to carbenes since they have one lone pair of electrons and a vacant *p*-orbital.[3] These compounds have shown applications in activating strong chemical bonds facilitating a range of chemical processes.[4]

We will report the reactivity of a low-valent bimetallic potassium Ga(I) complex in activating an ortho C–H bond of azobenzene (Figure 1). In contrast, the lighter Al(I) analogue activates the N=N bond of azobenzene.[5] We have stabilized, isolated, NMR and crystallographically characterized both the pre-activated Ga(I) compound, which formally results from the 2e<sup>-</sup> transfer from Ga(I) to the azo compound, and also the final C–H activated derivative.[6] We will also account our mechanistic insights into the bimetallic cooperation between Ga and K. This represents a rare example of a C–H bond activation at a low-valent bimetallic group 1/13 metal system.



**Figure 1.** C–H activation by a low-valent potassium Ga(I) system.

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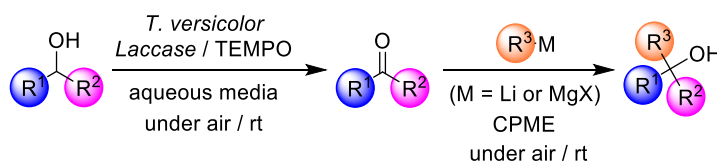
## DESIGN OF ONE-POT TANDEM METHODOLOGIES FOR CHEMICAL SYNTHESIS USING SUSTAINABLE SOLVENTS: WATER OR DEEP EUTECTIC SOLVENTS

Marina Ramos-Martín<sup>1</sup>, Joaquín García-Álvarez,<sup>1,\*</sup> Alejandro Presa Soto<sup>1,\*</sup>

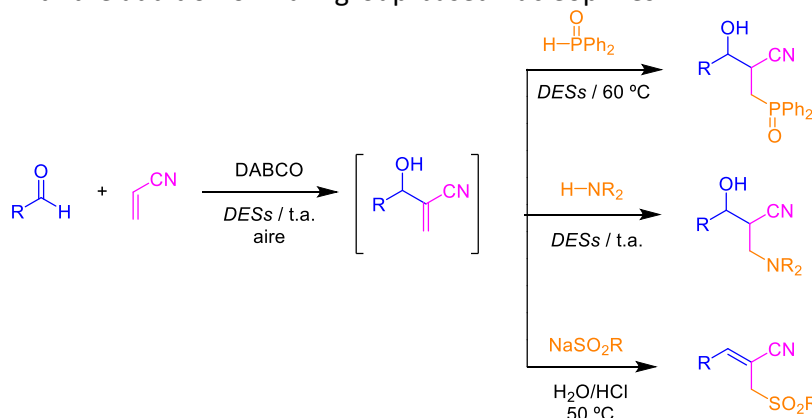
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Efficiency and environmental sustainability are central issues in current chemistry [1]. Taking into account this idea, we have previously designed a variety of hybrid one-pot synthetic transformations using sustainable reaction media such as water or *Deep Eutectic Solvents (DESs)* [2]. These hybrid one-pot tandem protocols, which combine different instruments from the conventional organic synthetic toolbox (transition metals, enzymes, 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 poster we will present two new one-pot tandem methodologies using the aforementioned sustainable solvents:

- a) Combination of the biocatalytic laccase/TEMPO oxidation system with RLi reagents in aerobic aqueous media and at room temperature.



- b) Formation of carbon-heteroatom bonds in Deep Eutectic Solvents (*DESs*) using sequential one-pot tandem methodologies combining the organocatalyzed Morita-Baylis-Hillman synthetic protocol with the addition of main-group-based nucleophiles.



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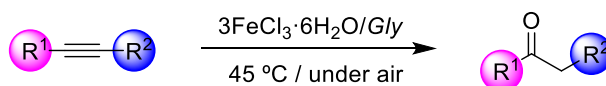
## HYDRATION OF ALKYNES MEDIATED BY Fe-BASED DEEP EUTECTIC SOLVENTS (DESs) UNDER MILD AND BENCH-TYPE REACTION CONDITIONS

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Deep eutectic solvents (DESs) are binary or ternary mixtures comprising at least one hydrogen bond acceptor (HBA) and at least one hydrogen bond donor (HBD) with a melting point much lower than that of either of the individual components and that of an ideal liquid mixture [1]. DESs whose components come from renewable sources have emerged as green solvents due to their low toxicity and volatility and have been progressively replacing toxic and volatile organic compounds (VOCs) in many fields such as catalysis, main-group chemistry, electrochemistry, solar technology, and food and pharmaceutical formulations [2].

DESs showing Lewis- or Brønsted-type acidity as well as other types of catalytic influence in various reactions have been found to display key roles in several cornerstone organic transformations such as oxidations, aldol or pericyclic reactions as well as condensation and multi-component reactions [3]. Among all these DESs, there is growing interest in those containing metallic salts acting as either HBDS or HBAs because of their inherent catalytic properties. In this sense, we have previously described a DES consisting of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and glycerol (Gly) which is capable to promote the Meyer-Schuster-type rearrangement of alkynols under bench type reaction conditions (room temperature and under air) [4]. Going one step further in this chemistry, we will present in this communication the hydration of alkynes to afford the corresponding ketones, working at 300 mM in  $3\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ . The processes under study showed complete conversion after 18 h of reaction at 45 °C in the absence of any co-catalyst/co-solvent, with the possibility to recycle the catalytic system up to 4 runs (conversions 95%).



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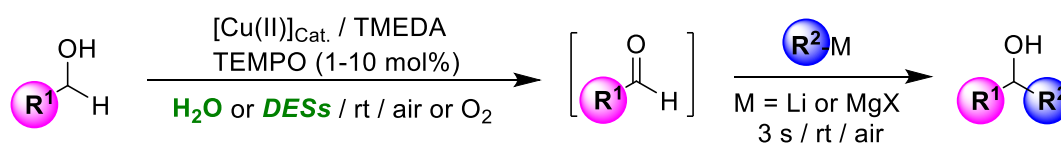
## ONE-POT TANDEM COMBINATION OF THE Cu(II)-CATALYZED OXIDATION OF PRIMARY ALCOHOL WITH THE ADDITION OF RLi/RMgX REAGENTS, AT ROOM TEMPERATURE, UNDER AEROBIC AND AQUEOUS/EUTECTIC CONDITIONS

Marcos López-Aguilar,<sup>1</sup> Marina Ramos-Martín,<sup>1</sup> Alejandro Presa Soto,<sup>1,\*</sup> Joaquín García-Álvarez,<sup>1,\*</sup>

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Since the last decade and in the framework of organic synthesis, the design of one-pot tandem protocols is occupying a strategic place, as new greener substitutions to standard and tedious stepwise processes [1]. In most of the cases, these one-pot tandem transformations employed the same synthetic organic utensil (transition metals, enzymes, main-group elements or organocatalysts) throughout all the tandem process, while the examples that described the amalgamation of different instruments (the so-called *hybrid* tandem protocols) from the conventional organic synthetic toolbox in sustainable solvents, is still scarce [2]. In this sense, our group has previously reported the fruitful combination of polar organolithium/organomagnesium chemistry [at room temperature, under air and in sustainable solvents (water or *Deep Eutectic Solvents* (DES))] with either transition-metal-[3] or organo-catalyzed [4] synthetic transformations.

Going one step further in the design of hybrid one-pot tandem protocols in green solvents and under bench-type reaction conditions (room temperature and under air), in this communication we will present the unprecedented combination of the Cu(II)-catalyzed oxidation of benzylic alcohols into the corresponding aromatic aldehydes with the concomitant addition of highly-polar and highly-reactive main-group organometallic reagents (RLi/RMgX), to yield the desired secondary alcohols without the need of any isolation/purification steps of the intermediates of reaction (aldehydes in this case). At this point it is important to mention that the organolithium/Grignard reagents are able to promote their addition reaction to the *in-situ* generated aldehydes selectively, even in the presence of Cu(II) species or TEMPO in the reaction media, working at room temperature, under air and using water/DESs as green solvents.



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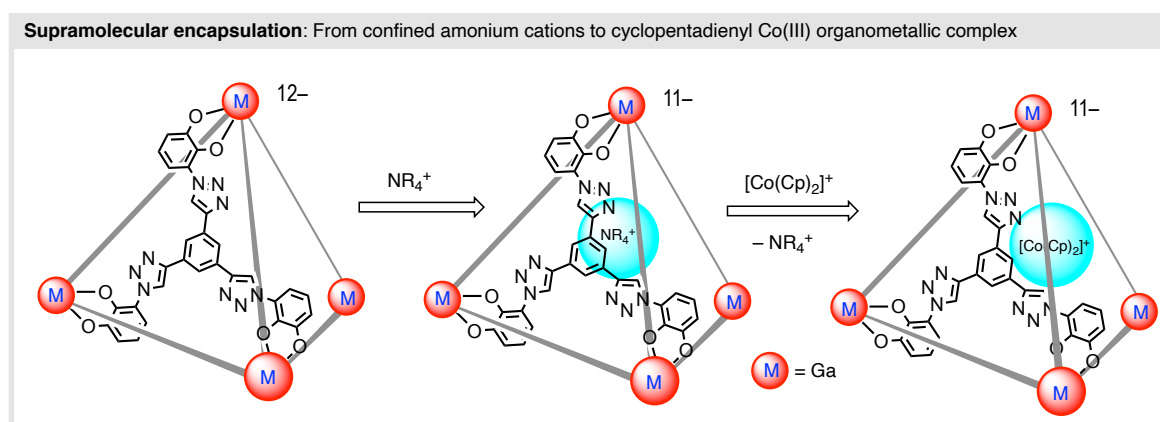
## ENCAPSULATION OF A CYCLOPENTADIENYL Co(III) ORGANOMETALLIC COMPLEX INSIDE A SUPRAMOLECULAR GALLIUM METALLOCAGE

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Supramolecular chemistry established itself as a core subject in chemistry since the revolutionary discoveries led by Cram, Lehn, and Pedersen.<sup>[1]</sup> Supramolecular hosts are ideal systems to mimic the active site of enzymes since they offer unique microenvironments that are not available in conventional molecular chemistry.<sup>[2]</sup> Using appropriate host-guest interactions results in remarkable reactivity, reaction rate enhancements, and product selectivity –overcoming traditional chemical systems.<sup>[3]</sup> These are features of enzymatic catalysis.

In developing new supramolecular host-guest organometallic systems, we will report the preparation of a new supramolecular gallium metallocage. This metallocage contains 1,2,3-triazole scaffolds being isosteric with previous amide linkers.<sup>[4]</sup> Furthermore, this metallocage has been designed to have the appropriate dimensions to encapsulate organic cations and a cyclopentadienyl Co(III) organometallic complex inside (Figure 1). We will also account for solution NMR encapsulation and hydrodynamic studies and discuss the host-guest affinity.<sup>[5]</sup>



**Figure 1.** Encapsulation studies inside a supramolecular gallium metallocage.

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## INFLUENCIA EN EL MECANISMO TADF DE LOS GRUPOS PERHALOFENILO EN COMPLEJOS DE ORO(I) CON LIGANDOS DIFOSFINA

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Uno de los objetivos principales en el desarrollo de nuevos materiales para su empleo como dispositivos electroluminiscentes, es el diseño de estrategias para la preparación de moléculas como emisores luminiscentes de alta eficiencia. Con este fin, surge la tercera generación de OLEDs, basados en el fenómeno de Fluorescencia Retardada Activada Térmicamente (TADF), en el que las moléculas emisoras son extremadamente eficientes, ya que son capaces de generar luz a partir de excitones singlete y triplete, pudiendo alcanzar una eficiencia cercana al 100%, incluso a temperatura ambiente (Figura 1).

De acuerdo con los requisitos para el diseño de materiales TADF, los complejos de oro(I) son prometedores candidatos a emisores TADF, ya que presentan un acoplamiento espín-órbita muy fuerte debido a su naturaleza de metal pesado. También, muestran la posibilidad de sintonizar las energías de emisión en función del entorno estructural del oro(I), y, además, exhiben estabilidad frente a la oxidación.[1]

Teniendo en cuenta lo anterior, en esta comunicación se muestra el estudio de un nuevo tipo de emisores TADF mediante el empleo de la difosfina rígida 1,2-bis(difenilfosfinobenceno) (dppBz) y diferentes fragmentos perhalofenilo de tipo [AuR(tht)] (R = *o*-C<sub>6</sub>BrF<sub>4</sub>, *p*-C<sub>6</sub>BrF<sub>4</sub>, *o*-C<sub>6</sub>F<sub>4</sub>I, *p*-C<sub>6</sub>F<sub>4</sub>I). Se estudia la sintonía de las energías de emisión en función de la posición y la electronegatividad de los halógenos presentes en el anillo perhalofenilo, y se corrobora si este tipo de derivados presentan el fenómeno de TADF. Además, se calculan las constantes radiativas de los diferentes fenómenos, así como la contribución de fosforescencia y TADF a temperatura ambiente en las emisiones observadas.

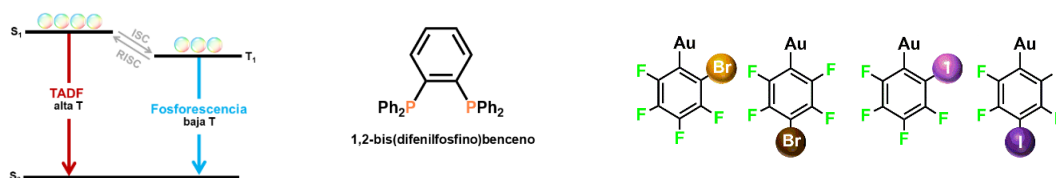


Figura 1. Diagrama de TADF (izquierda), ligando dppBz (centro) y diferentes grupos perhalofenilo (derecha)

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## SYNTHESIS OF Ir(III) GRAFTED NANOPARTICLES: PHOTOCATALYTIC ACTIVITY UNDER VISIBLE LIGHT AND RECYCLABILITY

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Iridium(III) complexes are well known photocatalysts under visible-light irradiation, and their tunable emissive properties make them useful for a wide range of photochemistry reactions.[1] In recent years, attention is increasingly focused on oxidative reactions, which demonstrate the potential of these molecules in other applications such as photodynamic therapy.[2]

This fact prompted us to synthesize a new Iridium(III) complex with pyrazino[2,3-*f*][1,10]phenanthroline, as the bidentate ligand, and two functionalized cyclometalated ligands with triethoxysilane groups (Figure 1, A). These triethoxysilane groups allow the anchoring of the complex on the surface of mesoporous silica nanoparticles (Figure 1, B), for the future recovery and reuse of the photocatalysts. More specifically, the synthesis of two hybrid materials with different nominal percentage of iridium (0.5% and 1%) has been carried out (Figure 1, C).

Finally, these two materials have proven to be efficient photocatalysts in the aerobic oxidative hydroxyformylation reaction of phenylboronic acid to obtain aryl alcohols, using irradiation with blue light and air as an oxidant (Figure 1, D).

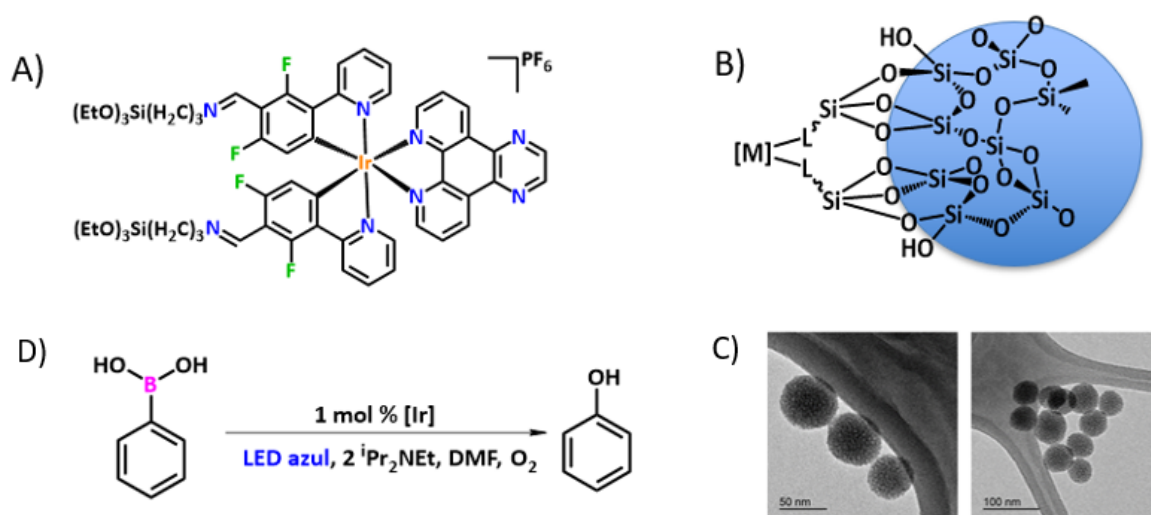


Figure 1

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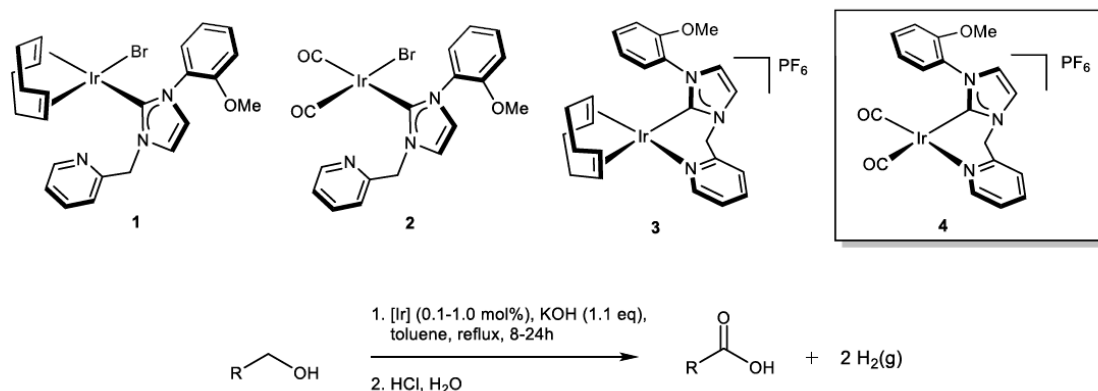
## DESARROLLO DE NUEVOS COMPLEJOS Ir-NHC ACTIVOS EN DESHIDROGENACIÓN CATALÍTICA DE ALCOHOLES PRIMARIOS A ÁCIDOS CARBOXÍLICOS EN AUSENCIA DE ACEPTOR DE HIDRÓGENO

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Las reacciones de oxidación de alcoholes a compuestos carbonílicos y carboxílicos como cetonas, aldehídos, ésteres o ácidos carboxílicos constituyen unas de las transformaciones más esenciales en la síntesis orgánica. Estos procesos suelen llevarse a cabo mediante el uso de oxidantes metálicos en cantidades estequiométricas. En este contexto, la deshidrogenación catalítica de alcoholes en ausencia de aceptor de hidrógeno supone una alternativa más favorable desde el punto de vista medioambiental; por una parte, debido al menor número de residuos generados, y por otra, gracias a la producción de hidrógeno molecular, con un excelente potencial como vector energético. Hasta la actualidad, la deshidrogenación de alcoholes secundarios a cetonas ha sido ampliamente estudiada; sin embargo y debido a su mayor dificultad, la oxidación de alcoholes primarios a ácidos carboxílicos ha recibido menor atención, de modo que únicamente ha sido reportado un reducido grupo de complejos de rodio, rutenio e iridio. [1]

Se ha sintetizado una serie de complejos neutros y catiónicos de iridio(I) funcionalizados con el ligando NHC *pincer* 1-(2-metoxifenil)-3-(piridin-2-il)-2-ilideno. Estos compuestos revelan una alta eficiencia en la deshidrogenación de alcoholes primarios a compuestos carboxílicos en ausencia en condiciones suaves y empleando bajas cargas catalíticas. Estudios preliminares utilizando alcohol bencílico en las condiciones de reacción óptimas: cargas catalíticas de 0.1-1.0%, 1.1 equivalentes de KOH y tolueno calentado a reflujo como disolvente, muestran el excelente desempeño del complejo carbonilo-catiónico **4** en la transformación de un amplio rango de alcoholes lineales y bencílicos a los correspondientes compuestos carboxílicos.



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## PB-05

## Formation of fluorinated aziridines by catalytic nitrene transfer reactions

Jorge P. Ruiz, M. Mar Díaz-Requejo\* and Pedro J. Pérez\*.

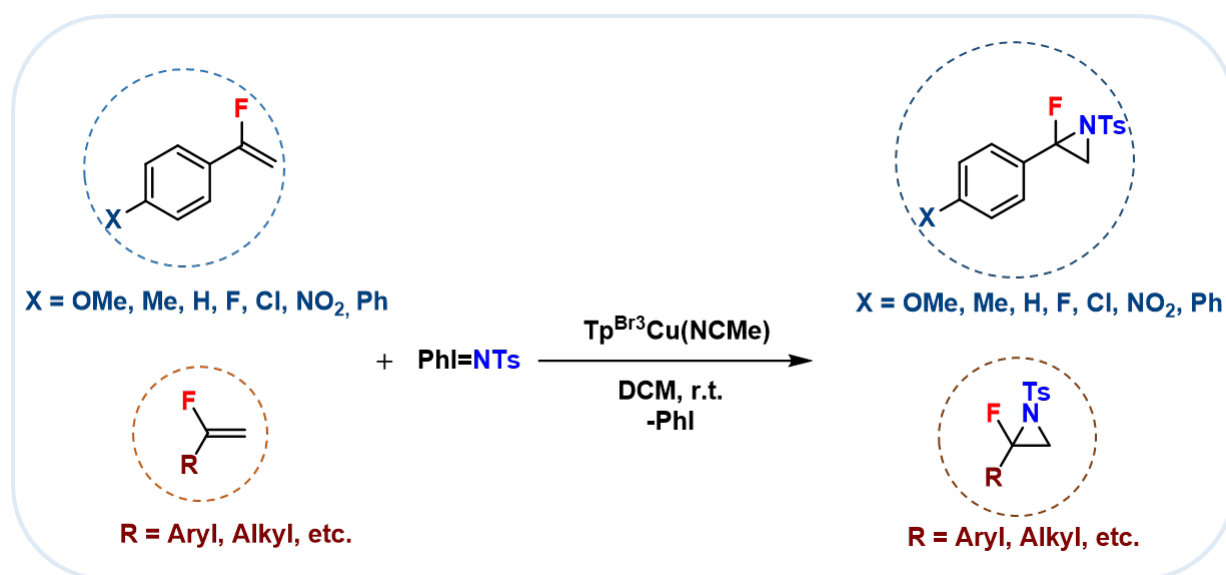
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Our research group has developed for over two decades active catalytic systems for the nitrene transfer reactions to substrates of different nature, using a family of copper complexes bearing hydrotrispyrazolylborate ligands ( $Tp^x$ ) and leading to new compounds with C-N bonds.[1] This catalytic system is especially active for olefin aziridination.

There are practically no described in bibliography any method for the formation of fluorinated aziridines. To the best of our knowledge just one example to obtain a rare monofluoromethyl aziridines is reported involves palladium catalyst.[2]

The catalytic synthesis of fluorinated aziridines represents even today a major challenge in inorganic chemistry, and methods relying on classic nitrene transfer reactions of electron-poor, fluorinated olefins are significantly hampered. For this reason, we are studying this type of reactions.

In this communication, we present the preliminary results obtained using different fluorinated olefins to obtain fluorinated aziridines by nitrene transfer reactions catalyze by  $Tp^{Br^3}Cu(NCMe)$ .



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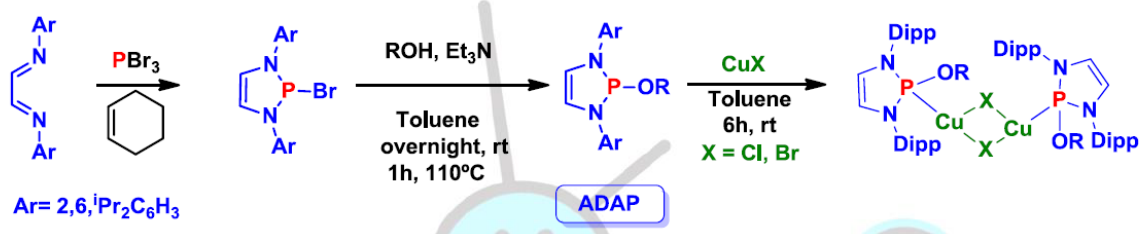


## FUNCTIONALIZATION OF N-HETEROCYCLES WITH ADAP-Cu(I) COMPLEXES

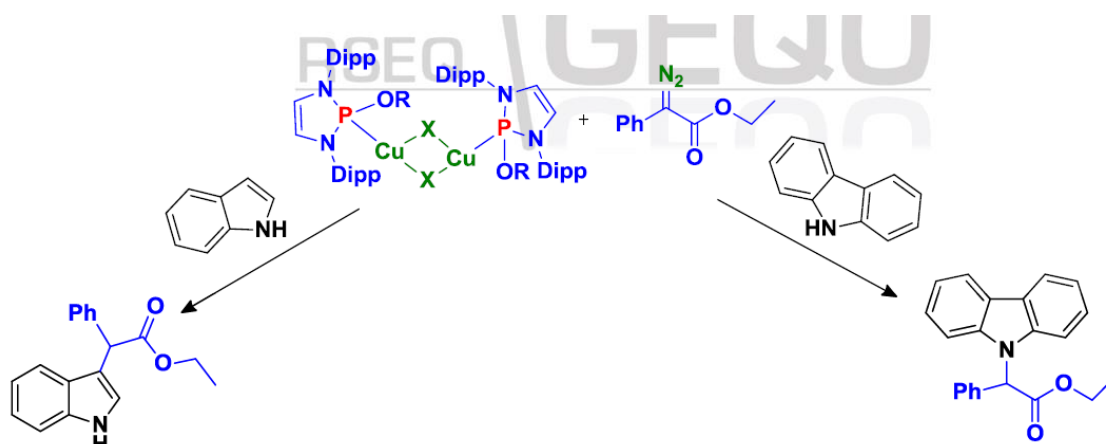
J. Diego Pizarro Javier,<sup>1</sup> Manuel R. Fructos,<sup>1</sup> Pedro J. Pérez,<sup>1</sup>

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



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



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## COPPER AND SILVER TRISPYRAZOLYLBORATE COMPLEXES BEARING PHOSPHINOAZIDE LIGANDS: SYNTHESIS, CHARACTERIZATION AND NITRENE GENERATION

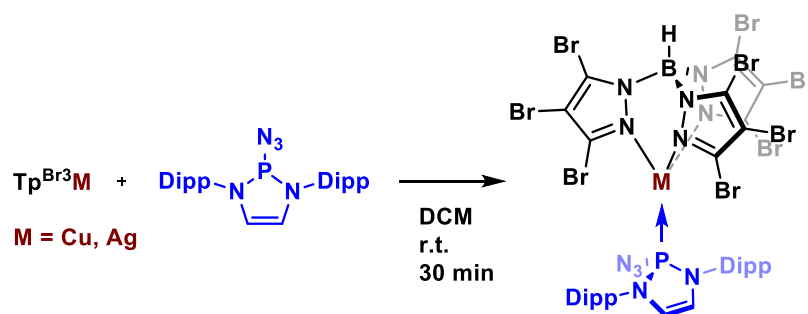
M. R. Rodríguez<sup>1</sup>, F. Molina<sup>1</sup>, M. M. Díaz-Requejo<sup>1\*</sup> and P. J. Pérez.<sup>1\*</sup>

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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 years, our research group has developed several catalytic systems based in a family of copper and silver complexes bearing hydrotrispyrazolylborate ligands (Tp<sup>x</sup>) as efficient catalysts 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<sup>Br3</sup>M-L adducts (M= Cu, Ag and 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, finding 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<sup>Br3</sup>Cu(NCMe) complex, allowing the proposal of a mechanism for this transformation.



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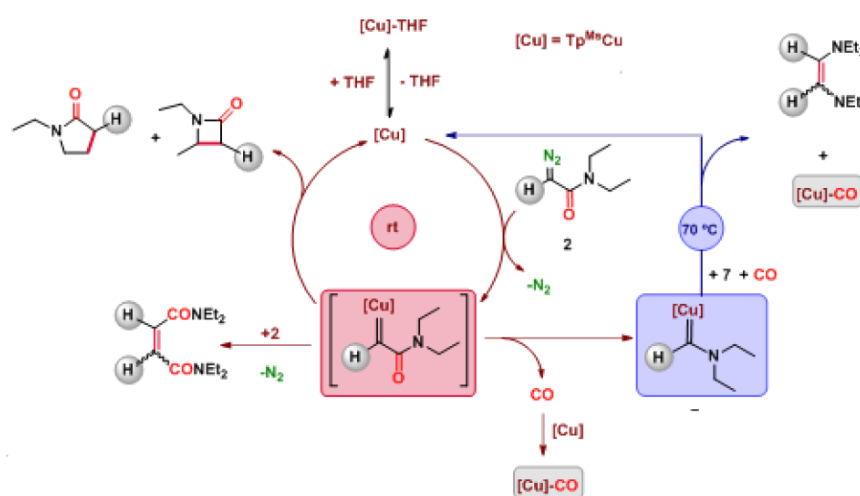
## Two Copper-Carbenes from One Diazo Compound

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Metal-catalyzed carbene transfer constitutes one of the most employed strategies for the functionalization of a wide number of organic substrates.<sup>1</sup> The generation of metal-carbene species from a metal complex of the general formula  $Mn$  and diazocompounds ( $N_2=CR^1R^2$ ) provides an easy access to  $LnM=CR^1R^2$  intermediates, capable of transferring the carbene unit ( $:CR^1R^2$ ). In all these processes, such unit remains unaltered after nitrogen extrusion from the diazo precursor. At variance with that, we have now isolated and characterized<sup>2</sup> the monosubstituted copper-carbene complex  $TpMsCu=C(H)(NEt_2)$ , that is formed by reaction of  $TpMsCu(THF)$  and  $N,N$ -diethyl diazoacetamide [ $N_2=C(H)(CONEt_2)$ ], upon a decarbonylation process from the initially generated  $TpMsCu=C(H)(CONEt_2)$  species, whereas carbon monoxide is trapped leading to  $TpMsCu(CO)$ . The participation of  $TpMsCu=C(H)(CONEt_2)$  in the reaction mixture is evidenced from the formation of products derived from the intramolecular carbene insertion into C-H bonds providing the corresponding functionalization products.



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## COPPER(I) COMPLEXES AS PRECATALYSTS IN C-S CROSS COUPLING REACTIONS

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Metal catalyzed cross-coupling reaction between an organic halide and N-, O- or S-based nucleophiles in the presence of a base represents a valuable tool for the construction of new C-N, C-O and C-S bonds, respectively.<sup>[1]</sup> Despite cross-coupling chemistry is closely associated with the use of palladium, copper-based catalysts enjoy an excellent reputation in the field of C-heteroatom bond formation, particularly in the coupling of substrates that are problematic under its heavier counterpart.<sup>[2]</sup> In this context, copper-catalyzed C-S bond forming reactions has emerged as an attractive alternative to palladium-based protocols for the synthesis of biologically active sulfur-containing molecules, due to the low cost of Cu and its superiority in terms of efficiency and functional group tolerance.<sup>[3]</sup>

In this work, we describe the synthesis and structural characterization of neutral and cationic new Cu(I) complexes containing phosphonites and aminophosphines. Such novel ligands adopt a NPN pincer coordination mode, leading to tetrahedral Cu(I) complexes. Due to scarcity of protocols based on the use of well-defined copper catalysts for C-S bond forming reactions,<sup>[4]</sup> the performance of these new complexes in the thioetherification of aryl halides with thiophenols have been studied (Figure 1).

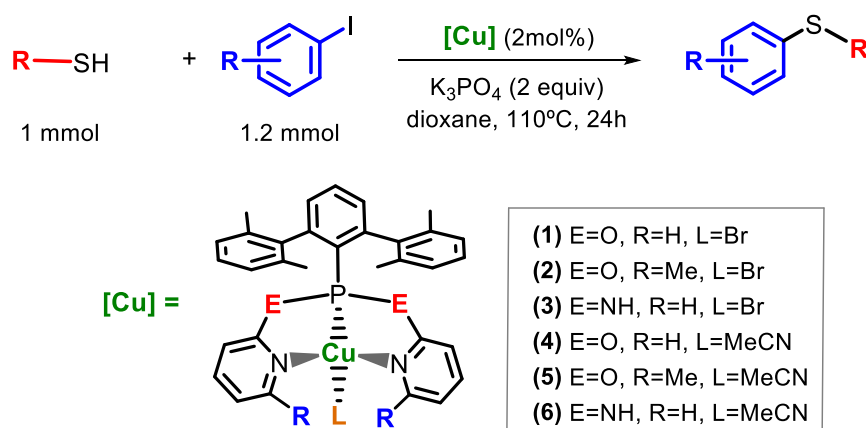


Figure 1. PNP-Cu(I) complexes catalyzed C-S bond formation.

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## REDOX BEHAVIOUR AND UV-VIS OF MIXED-VALENT IRIDIUM CHAINS

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There has been a longstanding interest in complexes containing metal-metal bonds for the development of fundamental chemistry with the purpose of understanding the nature of these compounds. Recently, there have been numerous investigations in relation to these complexes in areas such as catalysis and electronics, especially at the molecular level and nanoscale. [1] Much of the importance of these molecular wires based on transition-metal complexes is their capability of electronic delocalization thorough the whole molecule along the metal backbone. These interesting properties depend significantly on the metal-ligand interactions and, therefore, our group has focused on tuning these metal chains [2] and understanding the relation between the coordinated ligands and the resulting electronic properties.

In this work, redox and electronic properties of several tetranuclear mixed-valence iridium chains of general formula  $[\{X-(Ir_2(\mu-OPy)_2(CO)_4\}_2]$  ( $X = \text{halide or pseudohalide}$ ) will be presented. In addition, the influence of the axial ligand ( $X$ ) on their  $^1H$  NMR chemical shifts, redox potentials, and UV-vis spectra, will be discussed in combination with some DFT studies...

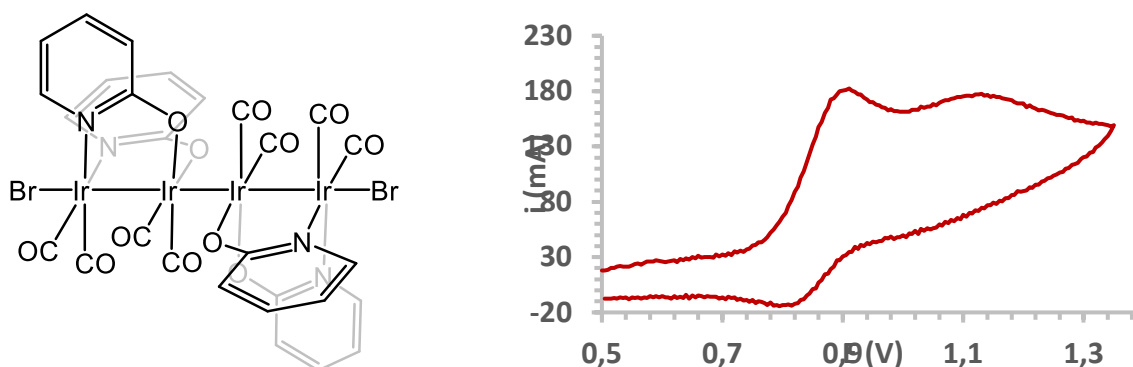


Figure 1. Complex  $[\{Br-(Ir_2(\mu-OPy)_2(CO)_4\}_2]$  and its cyclic voltammetry in acetonitrile at  $500\text{mV s}^{-1}$ .

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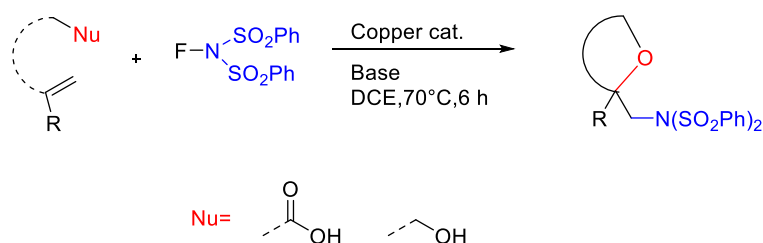
## SYNTHESIS OF AMINOLACTONES BY COPPER CATALYZED AMINOXYGENATION REACTIONS

Martina Casciotti, José M. Muñoz-Molina, Tomás R. Belderrain, Pedro J. Pérez

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Oxygen heterocycles are important structures present in bioactive molecules, pharmaceuticals and natural product [1,2]. Therefore, their synthesis has become a field of great interest in organic chemistry [3]. One of the possible methods consists of the amino oxygenation of alkenes (Scheme 1). A particularly attractive approach uses an electrophilic amino source, which directs complementary chemo- and regioselectivity and eliminates the need of external oxidants [4]. Zhang and Qi reported the copper catalyzed amino lactonization reactions of olefinic carboxylic acids with NFSI (*N*-fluorodibzenzenesulfonimide) which involve radical processes [5].



**Scheme 1.** Aminoxygenation of alkenes

Our group reported the use of well-defined Tp<sup>x</sup>Cu complexes (Tp<sup>x</sup> = hydrotrispyrazolylborate ligand) as efficient catalysts for the atom transfer radical addition (ATRA) of polyhalogenated compounds to olefins [6]. Furthermore, our group described the pyrrolidines and piperidines synthesis by intramolecular C-H amination using *N*-fluorinated precursors catalyzed by Tp<sup>x</sup>Cu [7]. Based on all these precedents, we decided to study the catalytic capabilities of Tp<sup>x</sup>Cu complexes in aminoxygenation of olefinic carboxylic acids using NFSI. In this contribution we show the results of these investigations.

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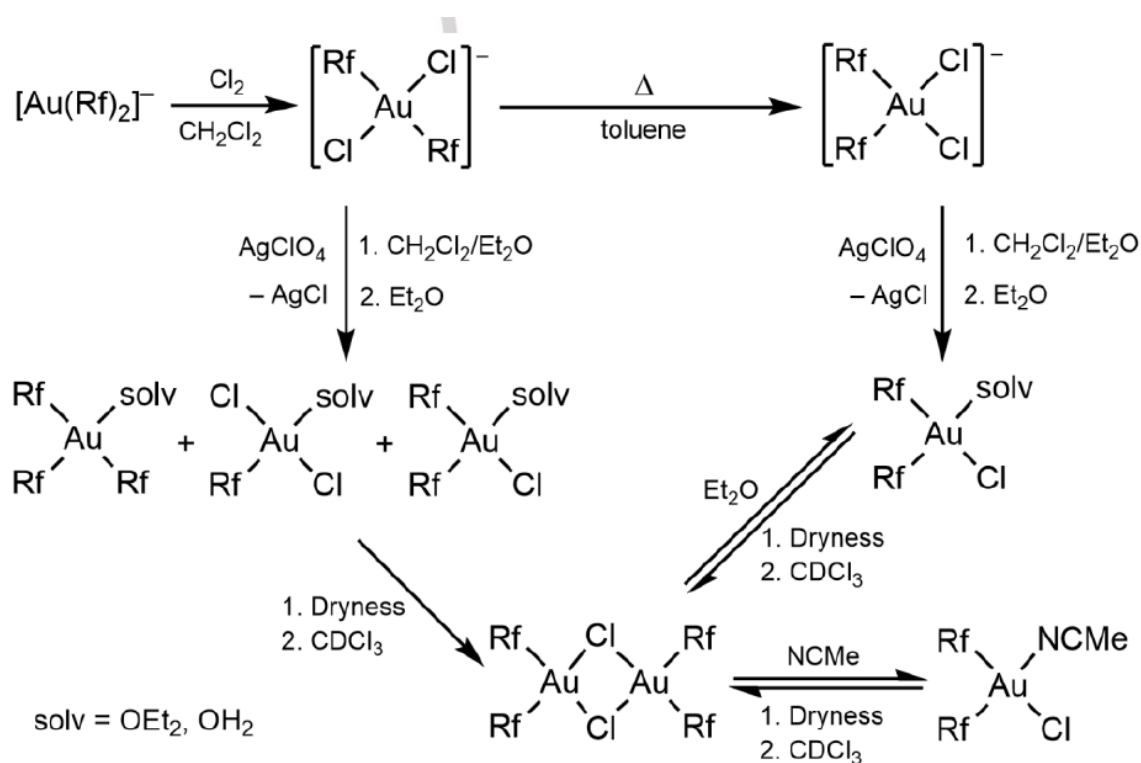
## UNEXPLORED COMPLEXITY OF SIMPLE Au<sup>III</sup> REACTIONS: STRIKING Cl/ARYL SCRAMBLING. DRIVING FORCES AND MECHANISMS

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Aryl rearrangements triggered by Cl<sup>-</sup> extraction from *trans*-[Au<sup>III</sup>Rf<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup> (Rf = C<sub>6</sub>F<sub>3</sub>Cl<sub>2</sub>-3,5), led quickly to a mixture of [AuRf<sub>3</sub>(solv)], *cis*-[AuRf<sub>2</sub>Cl(solv)], and [AuRfCl<sub>2</sub>(solv)] (solv = OEt<sub>2</sub>, OH<sub>2</sub>).<sup>1</sup> The species present in solution in different mixtures were identified by <sup>19</sup>F NMR and X-ray diffraction (Scheme 1), while DFT calculations have been used to get a better understanding of the kinetics and thermodynamics of these almost unreported processes.<sup>2</sup> Very different Rf–Rf coupling rates are found from (μ-Cl)<sub>2</sub>[*cis*-AuRf<sub>2</sub>]<sub>2</sub> or *cis*-[AuRf<sub>2</sub>Cl] species (L = OEt<sub>2</sub>, NCMe, Cl<sup>-</sup>) depending on the coordination strength of the ligand or solvent in the fourth position.



**Scheme 1.** Synthesis of aryl gold (III) anionic complexes and evolution with AgClO<sub>4</sub> (1: 1). The cation is (NBu<sub>4</sub>)<sup>+</sup>.

### References:

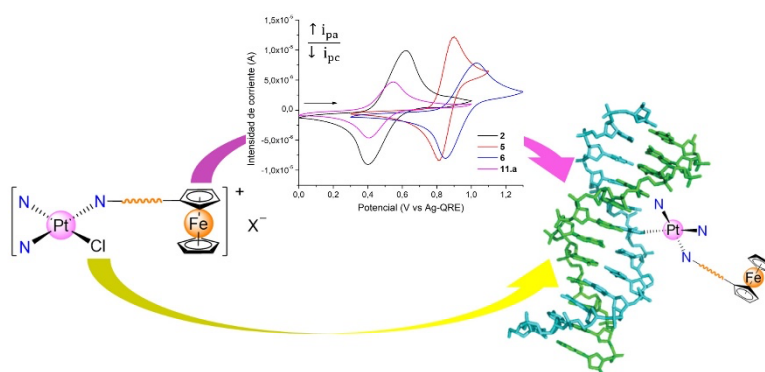
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## SÍNTESIS DE COMPLEJOS MONOFUNCIONALES DE FERROCENO Y PLATINO(II) CON POTENCIAL ACTIVIDAD FARMACOLÓGICA

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Los complejos bifuncionales de platino(II) como el cisplatino, el carboplatino y el oxaliplatino destacan por ser fármacos anticancerígenos al formar aductos intracatenarios con el ADN. Sin embargo, presentan una serie de inconvenientes, siendo necesaria la búsqueda de nuevas alternativas como los complejos monofuncionales de platino(II), que pueden tener una mayor actividad antitumoral y menos efectos secundarios que los complejos bifuncionales [1]. En este contexto, la incorporación en la estructura de un metaloceno, como el ferroceno, supone una opción prometedora debido a su amplia bioactividad y al posible potencial efecto sinérgico que puedan tener ambos centros metálicos [2].

En esta comunicación se presenta la síntesis de nuevos complejos monofuncionales de platino(II) con el ligando *p*-ferrocenilanilina. Estos compuestos se obtuvieron con buenos rendimientos mediante reacciones de sustitución de ligando a partir de complejos bifuncionales de Pt(II), usando diferentes sales de plata para evaluar el efecto de las mismas [3]. Todos los compuestos se caracterizaron mediante distintas técnicas espectroscópicas RMN (<sup>1</sup>H, <sup>13</sup>C y <sup>195</sup>Pt), infrarrojo y espectrometría de masas. También se analizó mediante <sup>1</sup>H RMN la estabilidad de estos complejos en DMSO, al ser un disolvente coordinante ampliamente utilizado para su estudio en disolución.

Adicionalmente, se muestran los resultados del comportamiento electroquímico de los precursores de ferroceno y de los complejos monofuncionales preparados mediante voltametría cíclica (CV) y de onda cuadrada (SWV).

Por último, se ha explorado el perfil energético de las reacciones de síntesis recurriendo a cálculos mecano-cuánticos enmarcados dentro de la teoría del funcional de la densidad, e incorporando las interacciones soluto-disolvente a través de un continuo dieléctrico.

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## EMPLEO DE UN COMPUESTO DE Au(I) Y Pb(II) COMO SENSOR DE VAPORES DE DIFERENTES DISOLVENTES ORGÁNICOS

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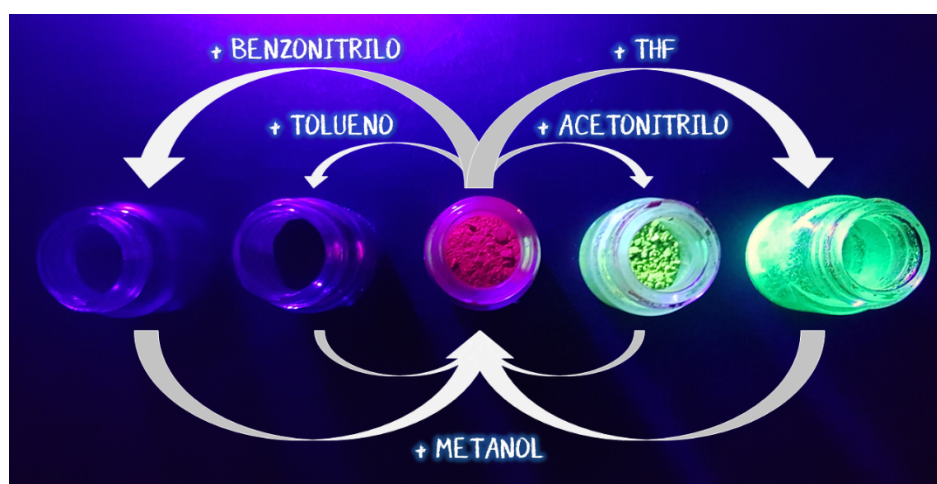
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La detección de vapores orgánicos mediante compuestos que cambian su apariencia o luminiscencia ha sido objetivo de una intensiva investigación en los últimos años [1]. Entre ellos, los materiales vapocrómicos adecuados para detectar compuestos orgánicos volátiles (VOCs) mediante la alteración de las atracciones metalofílicas son muy interesantes, aunque están escasamente representados [2]. Esto es debido a que las interacciones heterometálicas  $Au^I \cdots M$  pueden dar lugar a interesantes propiedades ópticas y su variación puede producir cambios perceptibles al ojo humano.

En este sentido, además, el polimorfismo que presentan algunos compuestos heterometálicos podría facilitar la detección debido a que las propiedades ópticas de estos materiales pueden depender de ligeras variaciones en sus estructuras cristalinas.

En este trabajo se presenta la reversibilidad de un sensor químico de oro(I) y plomo(II) de estequiometría  $[Au(C_6F_5)_2]_2[Pb(terpy)]_n$  (**1**), el cual presenta canales en su estructura cristalina, que permiten que se alojen en su interior pequeñas moléculas [3].

Este compuesto presenta cuatro solvato-polimorfos de igual estequiometría, pero con diferentes moléculas de disolvente en su estructura cristalina. Hemos obtenido complejos con disolventes polares N-dadores como acetonitrilo (**2**) o benzonitrilo (**3**) u O-dadores como THF (**4**), y disolventes no polares como tolueno (**5**), lo que modifica su color y luminiscencia, pudiendo además interconvertirse entre ellos. Por lo tanto, este complejo podría ser un buen candidato como sensor químico reversible de diferentes vapores de compuestos orgánicos.



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## ÍNDICE DE AUTORES

|                                      |             |                               |             |                             |             |
|--------------------------------------|-------------|-------------------------------|-------------|-----------------------------|-------------|
| Albéniz, Ana                         | PA05        | Gonzalo, C.                   | OA1         | Norrby, Per-Ola             | OC5         |
|                                      | PA09        | Herce Martínez, Janira        | <b>PB03</b> | Olmos, M. E.                | OB3         |
| Alcolea, Eduardo                     | PA06        | Herrera Ramírez, Piedad       | <b>OC4</b>  |                             | PB02        |
| Álvarez Martínez, María              | <b>PB08</b> | Hevia, E.                     | OB4         |                             | PB14        |
| Álvarez, Eleuterio                   | OA2         | Iglesias, Manuel              | PA02        | Organero, J. Ángel          | OA1         |
|                                      | PB09        | Izquierdo Sánchez, Ignacio    | <b>PB01</b> | Ortín Fernández, J.         | PB13        |
| Bartolomé, Camino                    | PB12        | Jalón, F. Á.                  | OA1         | Ott, Ingo                   | OC3         |
| Belderrain, Tomás R.                 | PB08        | Jiménez Rupérez, M. Victoria  | PB04        | Padilla Langa, Marina       | <b>PB10</b> |
|                                      | PB11        | Lalinde, Elena                | PA04        | Palma, P.                   | OA2         |
| Berenguer, Jesús R.                  | PB03        |                               | PA06        | Pàmies, Oscar               | OB1         |
| Besora, María                        | OB1         | Lara-Sánchez, A.              | OC2         |                             | OC5         |
|                                      | PB08        |                               | PA08        | Passarelli, Vincenzo        | PA02        |
| Borrego Blanco, Elena                | <b>PA07</b> | Lecuna González, Ramón        | <b>PA13</b> | Peloso, Riccardo            | PB09        |
| Caballero Espinosa, María del Prado  |             | Lledós, Agustí                | PA10        | Peñas Defrutos, Marconi N.  | PB12        |
|                                      | <b>OC2</b>  | López Aguilar, Marcos         | <b>PA14</b> | Pérez Ruiz, Jorge           | <b>PB05</b> |
| Caballero, Ana                       | OA4         | López de Luzuriaga, J. M.     | OB3         | Pérez-Gómez, M.             | OC4         |
|                                      | PA07        |                               | PA01        | Pérez-Torrente, Jesús J.    | PB04        |
| Cabo Palacios, Diego Alexandre       | <b>OA2</b>  |                               | PB02        | Pérez, Pedro J.             | OA4         |
| Cámpora, J.                          | OA2         |                               | PB14        |                             | PA03        |
| Campos, J.                           | OB2         | López, José. A.               | PB10        |                             | PA07        |
| Casares, Juan A.                     | PA10        | Luque Gómez, Ana              | <b>PA02</b> |                             | PB05        |
| Casciotti, Martina                   | <b>PB11</b> | Maddock, L.                   | OB4         |                             | PB06        |
| Castro-Osma, José Antonio            | OC2         | Manzano, B. R.                | OA1         |                             | PB07        |
|                                      | PA08        | Marcos Ayuso, Guillermo       | <b>PA10</b> |                             | PB08        |
| Ciriano, Miguel A.                   | PB10        | Martín, S.                    | OA4         |                             | PB11        |
| Coconubo Guio, Laura Carolina        | <b>OB3</b>  | Martín García, María Trinidad | <b>PB09</b> | Pinilla Martín, Cintya      | <b>PA05</b> |
| Corral Zorzano, Andrea               | <b>PA04</b> | Martín-Martín, Sara           | PA09        | Pizarro Javier, Juan Diego  | <b>PB06</b> |
| Corral, I.                           | PB13        | Martínez Aguirre, Mónica      | PB03        | Polo, Victor                | PA02        |
| de la Cruz Martínez, Felipe          | <b>PA08</b> | Martínez Domínguez, Daniel    | <b>OA1</b>  | Ponce de León, Jaime        | <b>OA3</b>  |
|                                      | OC2         | Martínez Laguna, Jonathan     | <b>OA4</b>  | Presa Soto, Alejandro       | PA12        |
| De La Cruz Sanchez Badia, Pol        | <b>OC5</b>  | Martínez Martínez, Antonio J. | PA11        |                             | PA14        |
| del Amo, Vicente                     | PA13        |                               | PB01        | Ramírez Rodríguez, Manuel   | <b>PB07</b> |
| del Río, M. Pilar                    | PB10        | Martínez Sal, Joaquín         | <b>PB04</b> | Ramos Martín, Marina        | <b>PA12</b> |
| Díaz-Requejo, M. Mar                 | PA03        | Maseras, Felíu                | PB08        |                             | PA13        |
|                                      | PB0         | Massaguer, A.                 | OA1         |                             | PA14        |
|                                      | PB07        | Mata, J. A.                   | OA4         | Rodríguez Castillo, M.      | OB3         |
| Diéguez, Montserrat                  | OB1         | Mato, Mauro                   | OC1         |                             | PB02        |
|                                      | OC5         | Maya, Celia                   | PB09        |                             | PB14        |
| Durá, G.                             | OA1         | Miguel Arias, Selma           | <b>PB13</b> | Rodríguez, A. M.            | OC2         |
| Echavarren, Antonio M.               | OC1         | Miranda Pizarro, Juan         | <b>OB2</b>  |                             | PA08        |
| Espinet, Pablo                       | OA3         | Molina, Francisco             | PB07        | Rodríguez, Miguel A.        | PB03        |
|                                      | PB12        |                               | PB08        | Salamanca, Vanesa           | PA05        |
| Faiges Marcos, Jorge                 | <b>OB1</b>  | Mollar-Cuni, A.               | OA4         | Santos, L.                  | OA1         |
| Fernández Moyano, Sara               | <b>PB12</b> | Monge, M.                     | OB3         | Serrano, Elena              | PB03        |
| Fructos, Manuel R.                   | PB06        |                               | PA01        | Soldevilla Garrido, Inés    | <b>PB02</b> |
| García-Abellán, Susana P.            | PA02        |                               | PB02        | Sorroche Ezquerro, Alba     | <b>PA01</b> |
| García-Álvarez, Joaquín              | PA12        | Montesinos-Magraner, Marc     | PB14        | Sugranyes, Arnau R.         | OC1         |
|                                      | PA13        | Moreno Infantes, Sonia        | <b>OC1</b>  | Sundholm, D.                | PB02        |
|                                      | PA14        | Moreno Rodríguez, Anabel      | <b>PB14</b> | Tejeda, J.                  | OC2         |
| García-Camacho, A.                   | PB02        | Moreno, María Teresa          | <b>PA03</b> | Tejel, Cristina             | PB10        |
| García-López, J.-A.                  | OC4         |                               | PA04        | Valiev, R. R.               | PB02        |
| García-Martínez, Javier              | PB03        |                               | PA06        | Ventura-Espinosa, D.        | OA4         |
| García-Melchor, M.                   | OB4         | Moreno, S.                    | OB3         | Videa, Hellen               | <b>PA11</b> |
| Gil, T.                              | OA2         | Mu, Manting                   | <b>OB4</b>  | Villaba de Pando, Francisco | <b>PA09</b> |
| Gil Moles, María                     | <b>OC3</b>  | Munarriz, Julen               | PA02        | Villaroya, B. Eva           | PB10        |
| Gómez de Segura, David               | <b>PA06</b> | Muñoz Molina, José M.         | PB11        |                             |             |
|                                      | PA04        | Nasibullin, R. T.             | PB02        |                             |             |
| González Vadillo, Ana M <sup>a</sup> | PB13        | Nicasio, M. Carmen            | PB09        |                             |             |