



LIBRO DE RESÚMENES

(<https://geqonovel01.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. Belderrain	Universidad de Huelva
Joaquín García Álvarez	Universidad de Oviedo

ÍNDICE

Programa	2
Índice de comunicaciones	3
Resúmenes	
Conferencia plenaria	6
Comunicaciones orales	7
Comunicaciones póster. Sesión A	18
Comunicaciones póster. Sesión B	47
Índice de autores	77

PROGRAMA

- 10:30 h** **Presentación.**
(Chairperson: Ana Carmen Albéniz)
- 10:45 h** **Comunicaciones Orales Sesión A (OA1-OA5).**
(Chairpersons: Ernesto de Jesús/Joaquín García Álvarez)
- 12:00 h** **Sesión de pósters A (PA01-PA028).**
- 13:00 h** **Pausa comida.**
- 15:30 h** **Sesión de pósters B (PB01-PB29).**
- 16:30 h** **Conferencia Invitada Prof. A. Radosevic**
*“Organometallic Chemistry of Nontrigonal Tricoordinate Phosphorus
Compounds and Complexes”*
(Chairperson: Ana Carmen Albéniz)
- 17:30 h** **Comunicaciones Orales Sesión B (OB1-OB5).**
(Chairpersons: Ana Carmen Albéniz/Joaquín García Álvarez)
- 18:30 h** **Cierre**

ÍNDICE DE COMUNICACIONES

Conferencia plenaria

- CP1 **Alexander Radosevich.** Organometallic Chemistry of Nontrigonal Tricoordinate Phosphorus Compounds and Complexes. *16:30 h.*

Comunicaciones orales

- OA1 **Laia Vicens.** General access to modified α -amino acids by bioinspired stereoselective γ -C-H bond lactonization. *10:45 h.*
- OA2 **Marta Redrado.** Multifunctional heterometallic Ir(III)-Au(I) probes as promising anticancer and antiangiogenic agents. *10:55 h.*
- OA3 **Unai Prieto.** Study of steric effects in the catalytic tandem isomerization-hydrosilylation of olefins. *11:05 h.*
- OA4 **María Trinidad Martín García.** Zero-valent bis-phosphane complexes of Ni, Pd and Pt. *11:15 h.*
- OA5 **Anabel Moreno Rodríguez.** Enynes as new substrates for the catalytic nitrene transfer reaction. *11:25 h.*
- OB1 **Ana Luque.** Solvent effects and mechanistic considerations on the dehydrogenation of formic acid catalysed by iridium complexes featuring NHC-phosphane ligands. *17:30 h.*
- OB2 **Hellen Videa.** Low valent Group 13 metal carbenoids at Rhodium: Selective hydrogenation of olefins catalysed by Ga(I)-Rh(I) complexes. *17:40 h.*
- OB3 **Araceli de Aquino.** How can we achieve pure room temperature phosphorescence? The key role of heavy atom.. *17:50 h.*
- OB4 **Inés Soldevilla.** Sintonización de la fluorescencia retardada activada térmicamente en compuestos tricoordinados de Au(I). *18:00 h.*
- OB5 **Felipe De la Cruz.** Zinc-catalyzed hydroalkoxylation/cyclization of alkynyl alcohols. *18:10 h.*

Comunicaciones póster

- PA01 **Adriana Sacristán-Martín.** Interruptores moleculares para la asociación de fullerenos basados en ligandos bipyridina poliaromáticos. *12:00 h.*
- PA02 **Alba Sorroche.** Predicción computacional del enlace Au(I)-Pb(II) en complejos de coordinación y estudio de los factores que afectan a la formación de los enlaces covalentes Au(I)-E(II) (E = Ge, Sn, Pb). *12:00 h.*
- PA03 **Andrés Alguacil-Alarcón.** Synthesis, characterization and study of new coordination compounds with water soluble phosphines and anticancer properties. *12:00 h.*
- PA04 **Adrián Alconchel.** Síntesis y estudio de las propiedades luminiscentes de complejos herolépticos de cobre con difosfinas y bisiminas. *12:00 h.*
- PA05 **Ariadna Lázaro.** Anticancer Activity of Luminescent Pt(II) and Pt(IV) Platinacycles Against Multiplatinum-Resistant Metastatic CRC and CRPC Cell Models. *12:00 h.*
- PA06 **Belén López Sánchez.** Significativo avance respecto al mecanismo de isomerización catalítica de alcoholes alílicos secundarios en agua. *12:00 h.*
- PA07 **Blanca Parra.** Derivados luminiscentes de boro e iridio con ligandos amidina. *12:00 h.*
- PA08 **Carlos Gonzalo.** Síntesis de complejos tipo [Cp*IrZ(C[^]N)] con potencial actividad anticancerígena. *12:00 h.*

- PA09 **Daniel Blasco.** Estudio fotofísico, reológico y por dispersión cuasi-elástica de neutrones de nuevos hidrometalogeles de oro(I). *12:00 h.*
- PA10 **Ignacio Pérez-Ortega.** Highly active benzylic complexes of palladium(II) for the vinylic addition polymerization of alqueniil-norbornenes. *12:00 h.*
- PA11 **Javier Quintana.** Control de nanoestructuras anisotrópicas de oro y plata a partir de complejos organometálicos: conversión de luz en energía térmica. *12:00 h.*
- PA12 **Juan Carlos López López.** Luminiscent bis-cyclometalated halo(aryl) platinum(IV) complexes. *12:00 h.*
- PA13 **Juan Diego Pizarro.** Gold-catalyzed selective C-H bond functionalization of arenes. *12:00 h.*
- PA14 **Laura Coconubo.** Síntesis y caracterización estructural de complejos de oro(III) con ligandos fosforo puente y sus precursores de talio(III) y oro(III). *12:00 h.*
- PA15 **Aliah El Astal Quirós.** Nuevos complejos radicales de paladio(I) con ligandos carbeno N-heterocíclico. *12:00 h.*
- PA16 **Nerea Álvarez-Llorente.** Bis-Acetiluros de Au(I) con fosfinas bidentadas como pinzas moleculares. *12:00 h.*
- PA17 **Pablo Alamán-Valtierra.** Alkyne cyclotrimerization mediated by two-coordinate Fe(II) and Co(II)m-terphenyl complexes. *12:00 h.*
- PA18 **Nereida Hidalgo.** Bimetallic Cooperation to Activate Small Molecules. *12:00 h.*
- PA19 **Patricia Rodríguez-Salamanca.** Catalytic Asymmetric Synthesis of Dibenzazepines with Central and Axial Chirality by CuH-Catalyzed Intramolecular Cyclization. *12:00 h.*
- PA20 **Pol De la Cruz-Sánchez.** Readily available Ir/P-S catalysts for the reduction of synthetically relevant olefins. *12:00 h.*
- PA21 **Raquel J. Rama.** Mechanistic Study of Pd-Catalyzed C-N Couplings Supported by Terphenyl Phosphane Ligands. *12:00 h.*
- PA22 **Saúl Alberca.** Pd(II) and pyridine-hydrazone ligands as a versatile catalytic system in asymmetric additions of arylboronic acids. *12:00 h.*
- PA23 **Sergio Gonell.** Mechanistic studies on an Iron pyridyl-carbene catalyst for CO₂ electroreduction. *12:00 h.*
- PA24 **Sonia Moreno.** Aumento del índice de coordinación del ion plomo(II) a alta presión en un compuesto de oro(I) y plomo(II). *12:00 h.*
- PA25 **Tomás G. Santiago.** New Perspective On the Heck reaction: β -Hydride Elimination Assisted by Deprotonable P-N Ligands involving a concomitant Ni(0)/Ni(II)/Ni(0) redox Process.. *12:00 h.*
- PA26 **Jaime Ponce de León.** Wide scope access to luminescent fluorophosphoranes. *12:00 h.*
- PA27 **Álvaro García-Romero.** Cooperatividad Al-Li en sistemas trispiridil aluminato. *12:00 h.*
- PA28 **Alberto Pérez Bitran.** Au(III) does not form hydrogen bonds: the role of ligand-field inversion. *12:00 h.*
- PB01 **Marina Pérez-Jiménez.** Incorporating LiH Molecules into the Coordination Sphere of Mo \equiv Mo Bonds. *15:30 h.*
- PB02 **Agustín Galindo.** Homochiral Imidazolium Based Dicarboxylate Silver Compounds: Structure, Solution Behaviour and Antimicrobial Activity. *15:30 h.*
- PB03 **Agustín Lara-Sánchez.** Ring-opening copolymerization of cyclohexene oxide and carbon dioxide catalyzed by scorpionate zinc complexes. *15:30 h.*
- PB04 **Andrea Monti.** N-substituted aminobiphenyl palladacycles supported by dialkylterphenyl phosphines. *15:30 h.*
- PB05 **Ángela Vivancos.** Phosphorescent tris-cyclometalated Pt(IV) complexes with mesoionic N-heterocyclic carbene ligands. *15:30 h.*
- PB06 **David Campillo.** Reactivity of platinum(II) cyclometalated complexes towards acidic hydrogens. *15:30 h.*
- PB07 **David Dalmau.** Desarrollo de compuestos organometálicos luminiscentes con esqueleto oxazolona. *15:30 h.*
- PB08 **Diego A. Cabo.** Influencia de la presencia de ácidos de lewis de tipo sigma y pi sobre la eficiencia en las reacciones de adición oxidante de triflatos de arilo a complejos de Ni(0) estabilizados por ligando híbridos P-N enolizables. *15:30 h.*

- PB09 **Elena Borrego Blanco.** Hidroxilación directa de benceno catalizada por complejos de cobre (I) con oxígeno molecular. *15:30 h.*
- PB10 **Francisco Montilla.** Synthesis, characterization and antibacterial activity of amino acid-derived N-heterocyclic carbene silver complexes. *15:30 h.*
- PB11 **Francisco Villalba.** Palladium-catalyzed aerobic oxidative Heck reaction of arenes enabled by [2,2'-Bipyridin]-6-(1H)-one. *15:30 h.*
- PB12 **Guillermo Romo-Islas.** Effects of counterion on the photophysical properties of a new series of tetragold (I) complexes. *15:30 h.*
- PB13 **Guillermo Marcos-Ayuso.** Similarities between gold and zinc in aryl by alkyl exchange reaction with palladium dimers. *15:30 h.*
- PB14 **Ignacio Sancho.** Synthesis and chemical reduction of titanium compounds supported by a redox active ligand. *15:30 h.*
- PB15 **Isabel Ortega-Lepe.** Síntesis de complejos de iridio basados en ligandos CNN derivados de la lutidina. Aplicación en la deshidrogenación de NH_3BH_3 . *15:30 h.*
- PB16 **Jesús Damián Burgoa.** Studies of aluminate compounds based on oximate ligands. *15:30 h.*
- PB17 **Jonathan Martínez-Laguna.** Graphene-supported Au-NPs for carbene transfer reactions from diazocompound. *15:30 h.*
- PB18 **José Antonio Castro.** Synthesis of bio-derived cyclic carbonates catalyzed by an efficient aluminum catalyst. *15:30 h.*
- PB19 **Luis Miguel Tarifa.** Dinuclear valence-trapped complexes. *15:30 h.*
- PB20 **Manuel R. Rodríguez.** Intermolecular allene functionalization by silver-nitrene catalysis. *15:30 h.*
- PB21 **Marina Ramos-Martín.** Copper-catalyzed Goldberg-type C–N coupling in deep eutectic solvents (DEEs) and water under aerobic conditions. *15:30 h.*
- PB22 **Marta Navarro.** Bimetallic aluminium scorpionates for coupling of CO_2 and epoxides into cyclic carbonates under mild conditions. *15:30 h.*
- PB23 **Marta Valencia.** Síntesis y caracterización de compuestos N-heterocíclicos de iridio(III). *15:30 h.*
- PB24 **Miguel Palenzuela.** Polylimonene oxide prepared via a catalytic ROP process as biobased plasticizer for PLA. *15:30 h.*
- PB25 **Pablo Molinillo.** Nanopartículas de Pt estabilizadas mediante ligandos de tipo pincer SNS. Síntesis y caracterización. *15:30 h.*
- PB26 **Piedad Herrera.** Palladium-catalyzed cascade reactions for the synthesis of heterocyclic derivatives bearing a phosphonate group. *15:30 h.*
- PB27 **Purificación Cañadas.** Re-Mediated dearomatization and pyridyl ring-opening of a 1,10-phenanthroline ligand. *15:30 h.*
- PB28 **Sara Fernández-García.** Reactivity of seven-membered palladacycles: Insertion reactions of unsaturated molecules into the Pd-C bond. *15:30 h.*
- PB29 **Stephany Zárate-Roldán.** Síntesis de propargilaminas desde alcoholes catalizada por Oro en un proceso one-pot/multicomponente. *15:30 h.*

CONFERENCIA PLENARIA

ORGANOMETALLIC CHEMISTRY OF NONTRIGONAL TRICOORDINATE PHOSPHORUS COMPOUNDS AND COMPLEXES

Alexander T. Radosevich

Department of Chemistry, Massachusetts Institute of Technology
Boston, MA, USA. radosevich@mit.edu.

We have been investigating the extent to which geometric deformation impacts electronic structure and reactivity about tricoordinate phosphorus. Experimental and theoretical results will be presented demonstrating that, whereas phosphorus compounds with local threefold symmetry exhibit pronounced nucleophilic reactivity, symmetry-lowering distortions about phosphorus elicit 'biphilic' reactivity. Consequently, these geometrically distorted P compounds offer new opportunities in organophosphorus reactivity; by enforcing nontrigonal geometries on tricoordinate P(III) compounds, the structural and electronic conditions that facilitate access to higher coordinate phosphorus compounds can be attained. Spectroscopic evidence underpinning the biphilic reactivity of chelate-constrained triamidophosphines and its connection to novel reaction types will be discussed.

COMUNICACIONES ORALES

GENERAL ACCESS TO MODIFIED α -AMINO ACIDS BY BIOINSPIRED STEREOSELECTIVE γ -C-H BOND LACTONIZATION

L. Vicens¹, M. Bietti², M. Costas¹

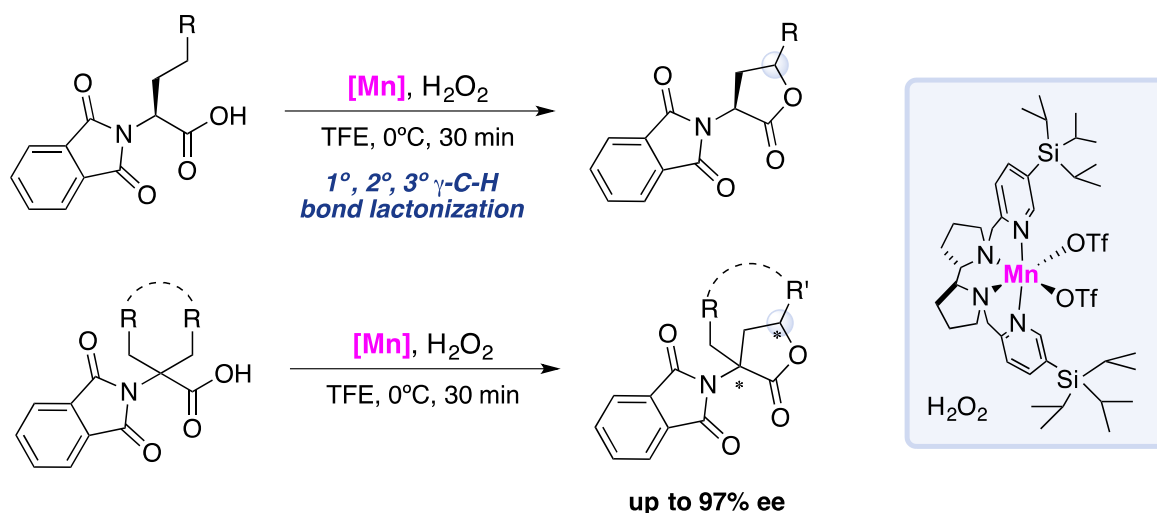
¹ Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Catalonia, Spain, laia.vicens@udg.edu

² Dipartimento di Scienze e Tecnologie Chimiche, Università "Tor Vergata", Rome, Italy

α -amino acids represent a valuable class of natural products employed as building blocks in biological and chemical synthesis. These motifs are of wide interest since they define the skeleton of peptides, which present widespread applications in proteomics, catalysis or drug delivery, among others [1]. As the number of natural amino acids is limited, the design of novel strategies to prepare modified analogues has gained interest in the recent years.

An appealing strategy is the modification of pre-existing natural or synthetic α -amino acids via side-chain C-H bond functionalization; and the most extensively studied methods rely on C-H activation via organometallic intermediate [2].

Herein, we present an alternative strategy to well-established organometallic procedures [3]. We show that the use of bioinspired manganese catalysts and H_2O_2 under mild conditions, provide access to modified α -amino acids via γ -C-H bond lactonization. The system can efficiently target 1^o, 2^o and 3^o C-H bonds of α -substituted and achiral α,α -disubstituted α -amino acids with outstanding site-selectivity and good to excellent diastereoselectivity and, where applicable, high enantioselectivity.



Referencias

- [1] J. B. Hedges, K. S. Ryan, *Chem. Rev.*, **2020**, *120*, 3161-3209.
- [2] W. Wang, M. M. Lorion, J. Shah, A. R. Kapdi, L. Ackermann, *Angew. Chem. Int. Ed.*, **2018**, *57*, 14700-14717.
- [3] L. Vicens, M. Bietti, M. Costas, *Angew. Chem. Int. Ed.*, **2021**, *60*, 4740-4746.

MULTIFUNCTIONAL HETEROMETALLIC Ir^{III}-Au^I PROBES AS PROMISING ANTICANCER AND ANTIANGIOGENIC AGENTS

M. Redrado,¹ V. Fernández-Moreira¹, M. C. Gimeno,¹

¹ Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009, Zaragoza, España. marta.redrado@csic.es

Medicinal inorganic chemistry has attracted great attention in the recent years due to the development of novel metallodrugs derived from gold, platinum and ruthenium species among others.^{1,2} Within this context, a growing interest is devoted to the design of heterometallic complexes with applications in cell visualization and cancer therapy.³ A synergic effect is feasible to take place when both, a bioactive and an emissive metallic fragment are combined and thus, delivering novel trackable metallodrugs.⁴

This work describes the development of a new variety of luminescent and cytotoxic heterometallic complexes based on the combination of both, Ir^{III} and Au^I fragments, **Figure 1**. Their emissive properties, cytotoxic activity, cell distribution, as well as their antiangiogenic ability have been thoroughly investigated. Subsequent modification on the gold ancillary ligand allows modulation of the bioactivity and biodistribution of the final bioprobe.

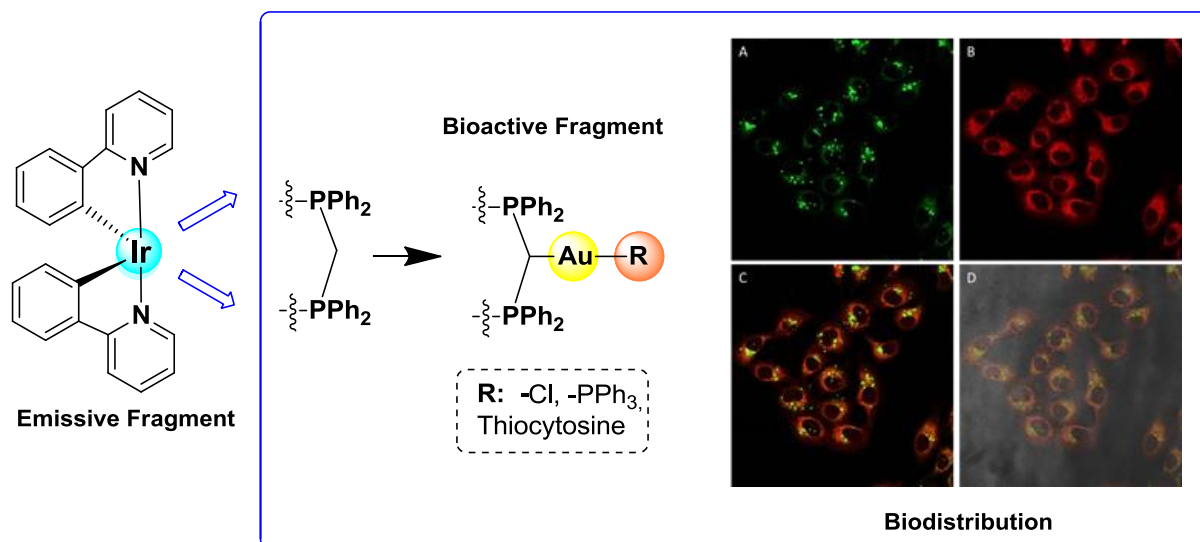


Figure 1.

Referencias

- [1] V. Fernández-Moreira, M. C. Gimeno, *Chem. Eur. J.* **2018**, *24*, 3345-3353.
- [2] M. Redrado, V. Fernández-Moreira, M. C. Gimeno, *ChemMedChem*, **2021**, DOI: 10.1002/cmdc.202000833.
- [3] A. Luengo, M. Redrado, I. Marzo, V. Fernández-Moreira, M. C. Gimeno, *Inorg. Chem.* **2020**, *59*, 13, 8960-8970.
- [4] A. Luengo, M. Reback, I. M. Daubit, I. Marzo, V. Fernández-Moreira, N. Metzler-Nolte, M. C. Gimeno, *Chem. Eur. J.* **2020**, *26*, 12158-12167.

STUDY OF STERIC EFFECTS IN THE CATALYTIC TANDEM ISOMERIZATION-HYDROSILYLATION OF OLEFINS

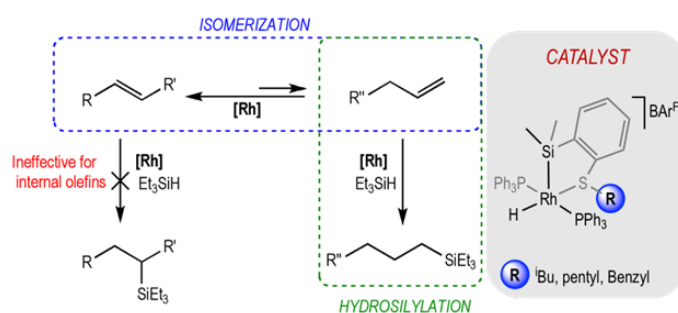
U. Prieto¹, S. Azpeitia¹, E. San Sebastián¹, M. A. Garralda¹, Z. Freixa^{1,2}, M.A. Huertos^{1,2}

¹ Departamento de Química Aplicada, Universidad del País Vasco, San Sebastián, Spain

² IKERBASQUE, Basque Foundation for Science, 48013, Bilbao, Spain.

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

Here we report the synthesis and characterization of new hydrido-silyl-Rh(III) complexes with different substituents on the thioether moiety which have been tested as catalysts in the tandem isomerization-hydrosilylation reaction. In this way, we can study the effect of substituent of the thioether in this reaction.[5]



References

1. I. Fleming in *Comprehensive Organic Chemistry II* (Eds : D. Burton, W. D. Ollis), Pergamon Press, Oxford, U.K. **1979**, p 577.
2. D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter, Z. Huang, *J. Am. Chem. Soc.* **2013**, *135*, 19154 - 19166.
3. S. Azpeitia, M. A. Garralda, M. A. Huertos, *ChemCatChem*, **2017**, *9*, 1901 - 1905.
4. S. Azpeitia, A. Rodriguez-Dieguez, M. A. Garralda, M. A. Huertos, *ChemCatChem*, **2018**, *10*, 2210 – 2213.
5. U. Prieto, S. Azpeitia, E. San Sebastián, M. A. Garralda, Z. Freixa, M.A. Huertos, *ChemCatChem*, **2020**, doi.org/10.1002/cctc.202001699

ZERO-VALENT BIS-PHOSPHANE COMPLEXES OF Ni, Pd AND Pt

M.T. Martín¹, M. Marín¹, R.J. Rama¹, C. Maya,² E. Álvarez², F.J. Molina³, M.C. Nicasio¹

¹Departamento de Química Inorgánica, Universidad de Sevilla, mmarting@us.es

²Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Consejo Superior de Investigaciones Científicas (CSIC) and Universidad de Sevilla

³Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva

Low-coordinate zero-valent complexes of group 10 metals (Ni, Pd, Pt) play a major role in the activation of small molecules as well as in many useful catalytic transformations [1]. Among many examples of three-coordinate M(0) complexes of the Ni triad, those of two-coordinate ML₂ are scarce [2]. The isolation of such unsaturated species requires the use of bulky supporting ligands, which prevent more favorable higher coordination geometries. While examples of zero-valent ML₂ complexes of Pd(0) and Pt(0) complexes with phosphane and N-heterocyclic carbene (NHC) ligands are known [2], those of nickel are restricted to compounds supported by large NHCs ligands [3].

In this communication, we present the synthesis and the structural characterization of bis-phosphane M(0) compounds of the Ni triad supported by bulky terphenyl phosphane ligands (Fig. 1). Linear structures are found for the heavier Pd and Pt complexes whereas for the Ni species coordination numbers greater than two in the solid state are observed due to the existence of Ni-C_{arene} interactions with the terphenyl fragment.[4]

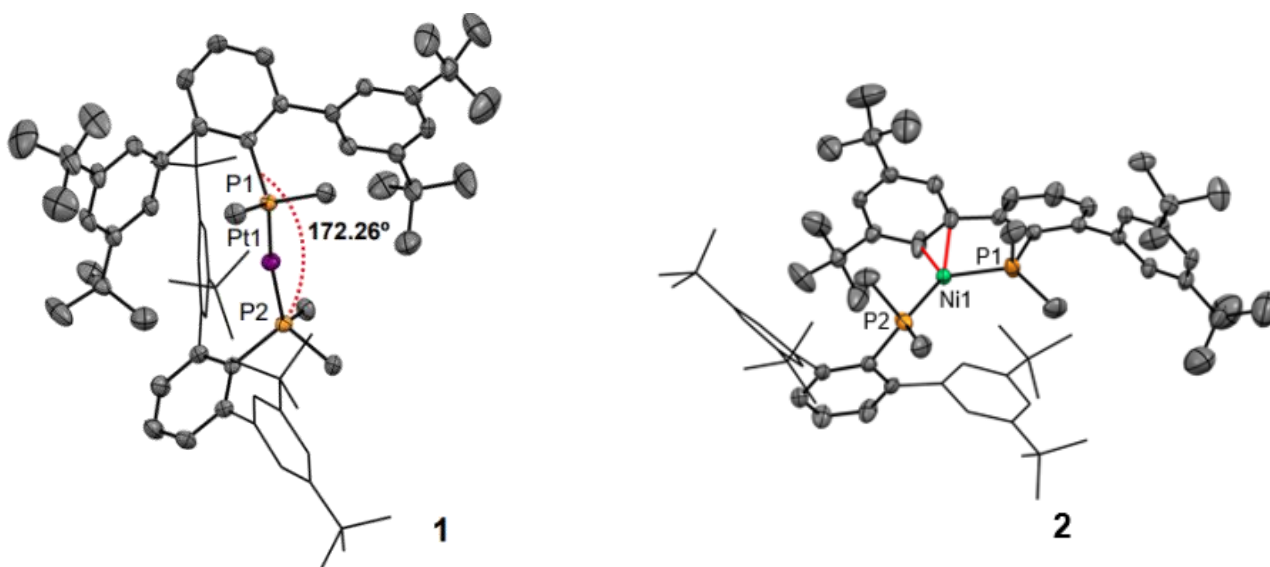


Figure 1. M(PMe₂Ar^{Dtbp2})₂ complexes of Ni(0) and Pt(0).

Referencias

- [1] (a) Colacot, T. J. *New Trends in Cross-Coupling*, RSC: Cambridge, UK, **2015**; (b) Hazari, N.; Melvin, P. R.; Beromi, M. M. *Nat. Chem. Rev.* **2017**, *1*, 0025.
- [2] Rama, R. J.; Martín, M. T.; Peloso, R.; Nicasio, M. C. *Adv. Organomet. Chem.*, **2020**, *74*, 241.
- [3] (a) Arduengo, A. J.; Gamper, S. F.; Calabrese, J. C.; Davidson, F. J. *Am. Chem. Soc.* **1994**, *116*, 4391.
- [4] Martín, M. T.; Marín, M.; Rama, R. J.; Maya, C.; Álvarez, E.; Molina F.; Nicasio, M. C. *Chem. Commun.* **2021**, DOI: 10.1039/d1cc00676b.

ENYNES AS NEW SUBSTRATES FOR THE CATALYTIC NITRENE TRANSFER REACTION

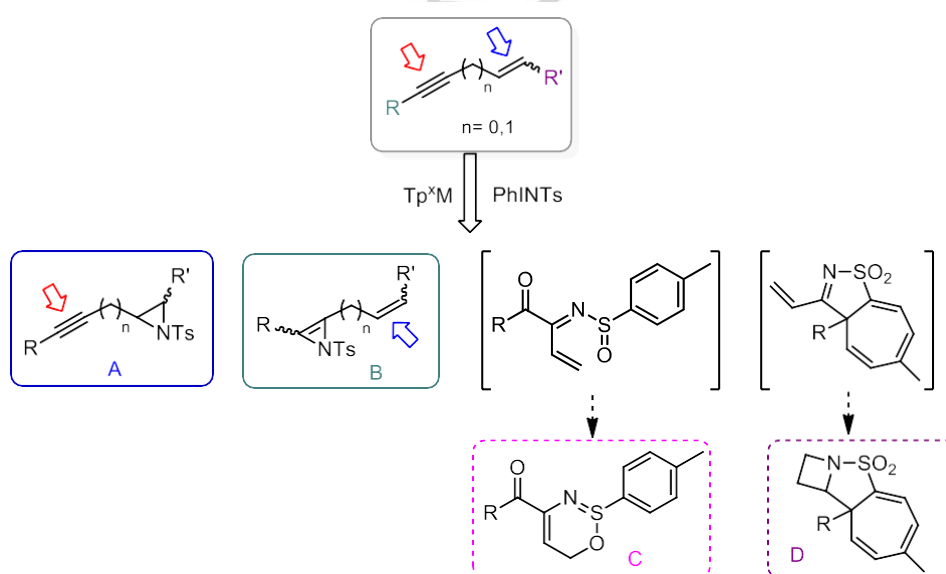
Anabel M. Rodríguez, M. Mar Díaz-Requejo* and Pedro J. Pérez*.

Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible y Departamento de Química, Campus de El Carmen, Universidad de Huelva, 21007-Huelva, Spain.

anabel.moreno@dqcm.uhu.es

The use of enynes as starting materials in different organic transformations has been widely studied by different research groups, although in only one case the triple bond remained unaltered. This is the case of the carbene transfer reaction from a diazo compound catalyzed by Fe, Ag or Ir,[1] a transformation that gives rise to propargylic acceptor-substituted cyclopropanes which are versatile electrophilic building blocks.[1c]

Our research group has developed a family of copper complexes bearing hydrotrispyrazolylborate ligands (Tp^x) as efficient catalysts for the nitrene addition and insertion reactions[2] to substrates of different nature and using PhINTs as the nitrene source. In this contribution we present the preliminary results using enynes as new substrates for the catalytic nitrene transfer reaction.



Possible products of the catalytic nitrene transfer to enynes

Referencias

[1] a) H. Suematsu, S. Kanchiku, T. Uchida, T. Katsuki, *J. Am. Chem. Soc.*, **2008**, *130*, 10327-10337. b) J. F. Briones, H. M.L. Davies, *Org. Lett.*, **2011**, *13*, 3984-3987. c) M.-I. Picher, B. Plietker, *Org. Lett.* **2020**, *22*, 340-344.

[2] A. Caballero, M. M. Díaz-Requejo, P. J. Pérez, *Metal-Catalyzed Oxidation of Alkanes To Give Esters or Amines*, Science of Synthesis: Catalytic Oxidation in Organic Synthesis, Muñiz, K. Ed. **2018**, Chap. 3.

OB-1

SOLVENT EFFECTS AND MECHANISTIC CONSIDERATIONS ON THE DEHYDROGENATION OF FORMIC ACID CATALYSED BY IRIIDIUM COMPLEXES FEATURING NHC-PHOSPHANE LIGANDS

Ana Luque-Gómez¹, Susana García-Abellán¹, Julen Munarriz², Victor Polo³, Vincenzo Passarelli⁴, and Manuel Iglesias¹

¹ Departamento Química Inorgánica–ISQCH, Universidad de Zaragoza–CSIC, C/Pedro Cerbuna 12, 50009 Zaragoza, Spain, analuqgom@gmail.com

² Departamento Química Física y Analítica, Universidad de Oviedo, Avda. Julian Clavería 8, 33006, Oviedo, Spain.

³ Departamento Química Física–BIFI, Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

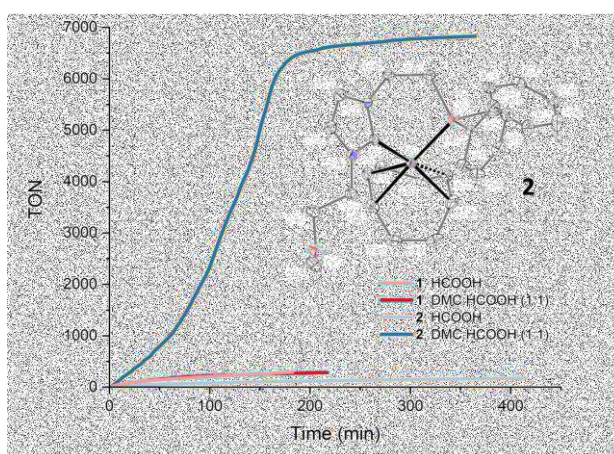
⁴ Centro Universitario de la Defensa, Ctra. Huesca s/n, ES-50090 Zaragoza, Spain

Since in 2008 the groups of Beller [1] and Laurency [2] independently reported the use of formic acid as a hydrogen storage system, a great variety of new catalysts for the dehydrogenation of formic acid have been developed [3].

During the last years, several ways of optimizing the performance of this catalytic systems have been found. Our group recently reported on one of the most active catalysts hitherto reported for the solventless decomposition of formic acid selectively into H₂ and CO₂ [4].

Building on this work, we prepared two iridium catalysts based on a PC^{NHC}P and a PC^{NHC}O ligand, [Ir(COD)(κ³-P,C,P'-PC^{NHC}P)]BF₄ (**1**) and [Ir(COD)(κ-P,C-PC^{NHC}O)]BF₄ (**2**), respectively, which proved active in the solventless hydrogenation of formic acid. Remarkably, the use of organic carbonates as a co-solvent; namely, dimethyl carbonate (DMC) and propylene carbonate (PC), trigger an outstanding enhancement of the catalytic activity for **2** while that of **1** remains virtually unaffected. Indeed, we observed an increase of the TOF_{1h} from 61 to 988 h⁻¹ upon changing from solventless conditions to a 1:1 (v/v) DMC:HCOOH mixture.

Stoichiometric experiments, KIE measurements and DFT calculations were performed in order to shed light on the reaction mechanism. The theoretical and experimental data suggest that the use organic carbonates prevents the deactivation of the catalyst via formation of dinuclear species.



Referencias

- [1] B. Loges, A. Boddien, H. Junge and M. Beller, *Angew. Chem. Int. Ed.*, **2008**, *47*, 3962–3965.
- [2] C. Fellay, P. J. Dyson, G. Laurency, *Angew. Chem. Int. Ed.*, **2008**, *47*, 3966–3968.
- [3] K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurency, *Chem. Rev.*, **2018**, *118*, 372–433.
- [4] A. Iturmendi, M. Iglesias, J. Munarriz, V. Polo, V. Passarelli, J. J. Pérez-Torrente, L. A. Oro, *Green Chem.*, **2018**, *20*, 4875–4879

LOW-VALENT GROUP 13 METAL CARBENOIDS AT RHODIUM: SELECTIVE HYDROGENATION OF OLEFINS CATALYSED BY Ga(I)–Rh(I) COMPLEXES

Hellen Videá and Antonio Martínez-Martínez*

Center for Research in Sustainable Chemistry (CIQSO) and Department of Chemistry,
University of Huelva, Huelva, Spain

Transition metal complexes featuring an E–Metal bond, where E is a main group metal, have attracted recent attention since they realize new molecular transformations, remarkable catalytic activity, and unique product selectivity.[1] In this context, low-valent group 13 main group metals, Al(I), Ga(I), and In(I) species (Figure 1A), are analogues to carbenes as they possess one lone pair of electrons and a formally vacant p-orbital.[2] In addition, they provide unusual electronic and steric environments to transition metals, which are not readily available with standard organic supporting ligands, such as phosphines, amines or carbenes.[3]

This contribution accounts for our recent progress in using low-valent Ga(I) metal ligands as surrogates to carbenes with rhodium organometallic complexes. We demonstrate the utility of low-valent main group metal compounds as supporting ligands for the selective hydrogenation of poly-olefins to mono-olefins mediated by Ga(I)–Rh(I) hydride species (Figure 1B).[4] The catalyst activity, selectivity, stability, and mechanism, controlled by the E–Metal interaction, will be discussed.

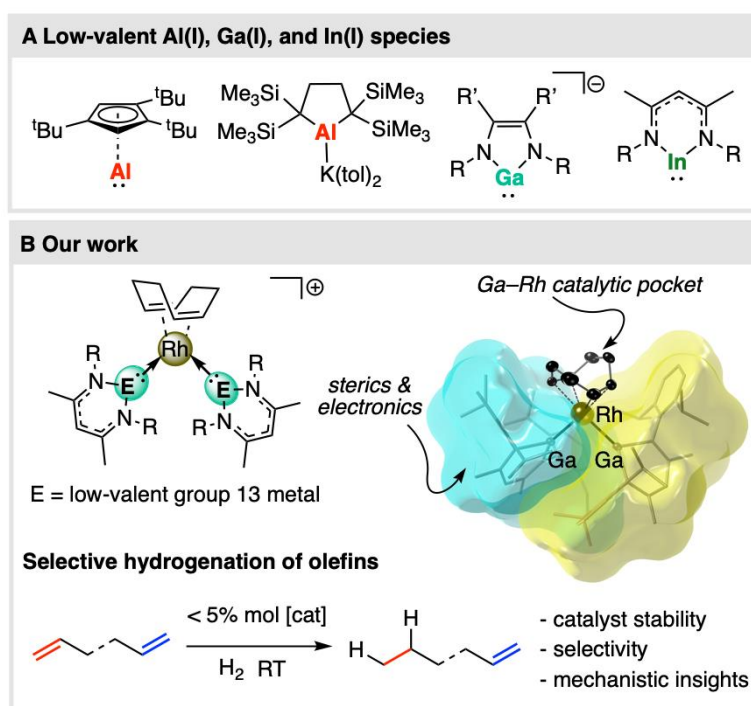


Figure 1. Low-valent group 13 E–Rh(I) organometallic complexes: Selective hydrogenation of olefins.

References

- [1] J. Takaya, *Chem. Sci.* **2021**, *12*, 1964–1981.
- [2] S. Kurumada, S. Takamori, M. Yamashita *Nat. Chem.* **2020**, *12*, 36–39; For a review, see: M. Zhong, S. Sinhababu, H. W. Roesky. *Dalton Trans.* **2020**, *49*, 1351–1364.
- [3] M. Asay, C. Jones, M. Driess *Chem. Rev.* **2011**, *111*, 354–396.
- [4] *Manuscript in elaboration.*

OB-3

HOW CAN WE ACHIEVE PURE ROOM TEMPERATURE PHOSPHORESCENCE? THE KEY ROLE OF HEAVY ATOM.A. de Aquino¹, J.C. Lima², L. Rodríguez¹

¹ Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain. E-mail: aracelideaquino@ub.edu

² LAQV-REQUIMTE, Departamento de Química, Universidade Nova de Lisboa, Monte de Caparica

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

Regarding luminescence, it is known that the heavy atom plays a direct role favouring triplet harvesting being able to observe phosphorescence emission under mild conditions [5].

In our work, we are focused in the synthesis of two families of molecules that follow the structure: PR₃-Au-chromophore or PR₃-Au≡-chromophore. By studying these families of compounds, we can determine if the presence of the alkynyl group (i.e. larger distance between the heavy atom and the chromophore) affects the global emissive properties.

These compounds present supramolecular assemblies based on aurophilic interactions, π - π stacking, ... that allow the formation of the resulting luminescent supramolecular arrays. In order to study their applicability, these compounds were introduced in organic matrixes such as PMMA and Zeonex and their luminescent behaviour was tested. The results show very interesting luminescent properties once the gold(I) compounds are introduced in these thin films.

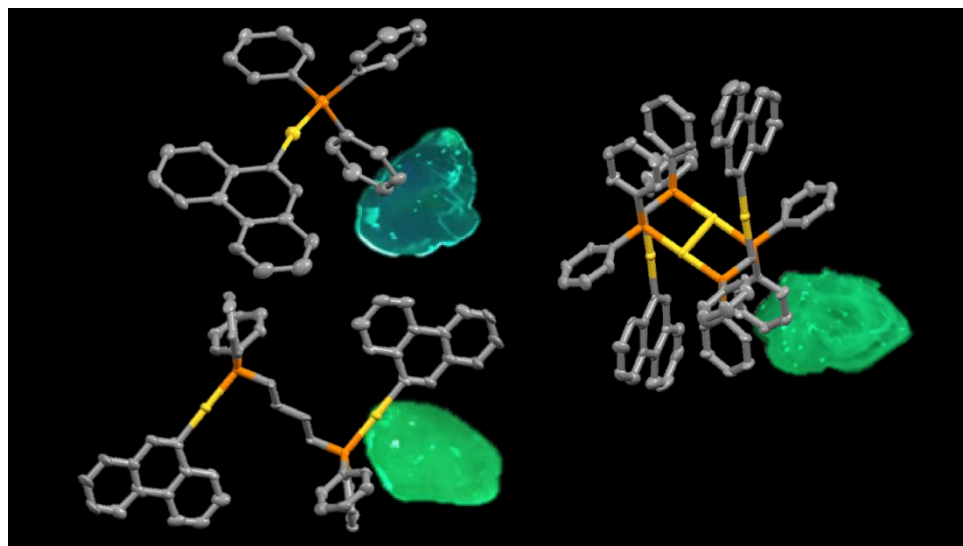


Figure 1. Family of molecules synthesized.

Referencias

- [1] A. Pinto, N. Svahn, J. C. Lima, L. Rodríguez, *Dalton Trans.*, **2017**, 46, 11125.
- [2] J. C. Lima, L. Rodríguez, *Chem. Soc. Rev.*, **2011**, 40, 5442.
- [3] M. B. Nielsen., *Synthesis*, **2016**, 48, 2732.
- [4] X. He; V.W.-W. Yam., *Coord. Chem. Rev.*, **2011**, 255, 2111.
- [5] E. Aguiló, A.J. Moro, M. Outis, J. Pina, D. Sarmiento, J.S. Seixas de Melo, L. Rodríguez, J.C. Lima, *Inorg. Chem.*, **2018**, 57, 13423.

OB-4

SINTONIZACIÓN DE LA FLUORESCENCIA RETARDADA ACTIVADA TÉRMICAMENTE EN COMPUESTOS TRICOORDINADOS DE Au(I)

I. Soldevilla,¹ A. García-Camacho,¹ J. M. López-de-Luzuriaga,¹ M. Monge,¹ M. E. Olmos,¹ M. Rodríguez-Castillo.¹

¹Departamento de Química, Universidad de La Rioja, Centro de Investigación en Síntesis Química (CISQ), Complejo Científico-Tecnológico, 26004, Logroño, Spain

ines.soldevilla@unirioja.es

Un fenómeno fotofísico muy interesante que puede producirse en complejos de oro(I) es el que se conoce como Fluorescencia Retardada Activada Térmicamente (TADF). Este comportamiento se ha estudiado tanto en moléculas orgánicas como en compuestos de coordinación u organometálicos.^[1] En el caso de los metales del grupo 11, se han descrito un amplio número de ejemplos de compuestos de Cu(I) que presentan TADF, siendo mucho más escasos para derivados de Au(I).

Así, a temperatura ambiente la emisión proviene de una fluorescencia retardada, desde el estado excitado singlete, después de haber sufrido un cruce entre sistemas (ISC) en el que primero se accede al estado triplete (en el que se recoge el 75% de los excitones), posteriormente se vuelve al estado singlete (el restante 25%) mediante un cruce entre sistemas inverso (RISC), produciendo emisiones muy intensas (ver figura 1). Por otro lado, a bajas temperaturas la emisión luminiscente se corresponde con un proceso de fosforescencia, con emisión desde un estado excitado triplete.

En esta comunicación se muestra el estudio de compuestos tricoordinados de Au(I) del tipo [Au(R)(dppBz)], con el ligando bidentado quelato 1,2-bis(difenilfosfino)benceno (dppBz) y con distintos ligandos perhalofenilo (R = *o*-C₆BrF₄, *p*-C₆BrF₄, *o*-C₆F₄I, *p*-C₆F₄I). De esta manera, se intenta forzar la tricoordinación de los centros de oro(I) para buscar un alto grado de rigidez estructural que dé lugar a emisiones de alta eficiencia. Además, debido a la presencia de los sustituyentes Br o I en el anillo aromático, se analizará el efecto de la distinta electronegatividad, el efecto de su tamaño y el efecto del átomo pesado, así como la influencia de las posiciones orto o para de estos sustituyentes, para comprobar cómo estas características afectan al comportamiento de fluorescencia retardada activada térmicamente en este tipo de derivados.

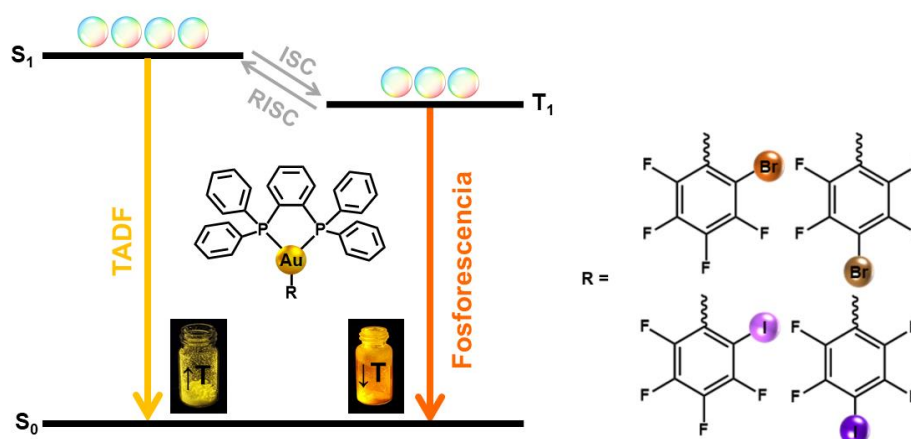


Figura 1. Diagrama de fluorescencia retardada activada térmicamente.

Referencia

[1] J.M. López-de-Luzuriaga, M. Monge, M.E. Olmos, M. Rodríguez-Castillo, I. Soldevilla, D. Sundholm, R. R. Valiev. *Inorg. Chem.* **2020**, *59*, 14236-14244

OB-5

ZINC CATALYZED HYDROALKOXYLATION/CYCLIZATION OF ALKYNYL ALCOHOLS

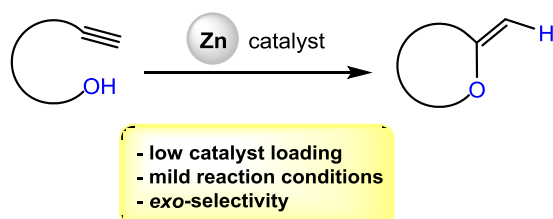
Felipe de la Cruz-Martínez,¹ Juan Fernández-Baeza,¹ Ana María Rodríguez,¹ José Antonio Castro-Osma^{2,*} and Agustín Lara-Sánchez^{1,*}

¹ Universidad de Castilla-La Mancha, Departamento de Química Inorgánica, Orgánica y Bioquímica-Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Ciencias y Tecnologías Químicas, 13071-Ciudad Real, Spain. E-mail: felipe.cruz@uclm.es

² Universidad de Castilla-La Mancha, Departamento de Química Inorgánica, Orgánica y Bioquímica-Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Farmacia, 02071-Albacete, Spain

Transition metal catalyzed processes have attracted much attention over the last few decades since these catalysts allow the synthesis of a great variety of organic molecules and polymeric materials.[1] Hydroelementation reactions allow the introduction of heteroelements into unsaturated carbon-carbon bonds. Among them, hydroalkoxylation reactions of alkenes or alkynes have attracted significant attention over the last years because it is a useful transformation to generate C–O bonds, which are present in natural products.[2] Despite the advances in this field, most of these processes are catalyzed by precious metal catalysts and their selectivity is affected by the structural and electronic nature of the substrate.[3] Therefore, the development of non-precious metal catalysts for this transformation is highly desirable considering sustainability and environmental criteria.[4] In this context, zinc is an abundant, economic and biocompatible metal, so zinc complexes can be plausible candidates to replace precious metal catalysts for the hydroalkoxylation reactions.[5] Although there are many reports on zinc-catalyzed hydroelementation processes,[5] the use of this metal as catalyst for the hydroalkoxylation/cyclization of alkynyl alcohols has not been reported to date.

In this contribution, we describe for the first time the use of zinc complexes as catalysts for the intramolecular hydroalkoxylation of alkynyl alcohols (Scheme 1). Kinetic studies have been performed and confirmed that reactions are first-order in [catalyst] and zero-order in [alkynyl alcohol]. NMR spectroscopy and X-Ray diffraction analysis provided evidence for the formation of alkynyl and alkenyl zinc compounds which has shown to be a key intermediate in the hydroalkoxylation process. Based on the experimental results, a catalytic cycle is proposed.



References

- [1] (a) B. Cornils, W. A. Herrmann, M. Beller, R. Paciello. *Applied Homogeneous Catalysis with Organometallic Compounds*, Wiley, **2017**. (b) Y. Bai, J. Chen, S. C. Zimmerman. *Chem. Soc. Rev.* **2018**, *47*, 1811–1821.
- [2] N. Huguet, A. M. Echavarren, Springer, Berlin, Heidelberg, **2011**, 291–324.
- [3] (a) A. Corma, A. Leyva-Pérez, M. J. Sabater. *Chem. Rev.* **2011**, *111*, 1657–1712. (b) M. Kondo, T. Kochi, F. Kakiuchi. *J. Am. Chem. Soc.* **2011**, *133*, 32–34. (c) J. M. Stubbs, D. E. Chapple, P. D. Boyle, J. M. Blacquiere. *ChemCatChem* **2018**, *10*, 4001–4009.
- [4] (a) N. V. Tzouras, I. K. Stamatopoulos, A. T. Papastavrou, A. A. Liori, G. C. Vougioukalakis. *Coord. Chem. Rev.* **2017**, *343*, 25–138. (b) R. Luque, F. Leung-Yuk Lam. *Sustainable Catalysis*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2018**.
- [5] S. Enthaler, X. F. Wu. *Zinc Catalysis*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2015**.

COMUNICACIONES POSTER SESION A

INTERRUPTORES MOLECULARES PARA LA ASOCIACIÓN DE FULERENOS BASADOS EN LIGANDOS BIPIRIDINA POLIAROMÁTICOS

Sergio Ferrero^a, Héctor Barbero^a, Daniel Miguel^a, R. García-Rodríguez^a, Celedonio. M. Álvarez^a y Adriana Sacristán-Martín^a

¹ GIR MIOMeT, IU CINQUIMA (Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011Valladolid, Spain) adryanasam@hotmail.com^a

La síntesis y diseño de moléculas basadas en hidrocarburos poliaromáticos (PAHs) encaminado al estudio de las interacciones supramoleculares y la síntesis racional de moléculas que pueden interactuar selectivamente con nanotubos de carbono es de máxima importancia.¹ En este trabajo se han preparado ligandos 2,2'-bipiridina derivados de distintos PAHs, y sus complejos de cobre (I) correspondientes (Fig 1), y estudiado la interacción con los fulerenos C₆₀ y C₇₀.

El conformero E de la bipiridinas L1 y L2 es el más estable cuando el ligando se encuentra libre en disolución y tiene una baja capacidad para interactuar con fulerenos. En cambio, la conformación Z de la bipiridina, es capaz de establecer estas interacciones supramoleculares. Para poder fijar esta geometría se ha procedido a la coordinación de cobre. De esta forma, los complejos de cobre actúan como pinzas moleculares y permiten la interacción con C₆₀ y C₇₀. La coordinación y descoordinación del ligando es reversible y puede ser controlada simplemente variando la cantidad de Cu y dppe en el sistema. La adición de dppe a los complejos de cobre permite la liberación simultánea de la bipiridina y el fullereno. La pinza molecular puede regenerarse fácilmente añadiendo más [Cu(NCCH₃)₄]BF₄ al sistema, lo que permite la coordinación de la bipiridina y la formación de los complejos de cobre. De esta forma nuestro sistema funciona como un interruptor molecular donde la actividad para aceptar fulerenos pueda ser 'apagada' o 'encendida' a voluntad simplemente controlando la relación de Cu/ dppe en el sistema.

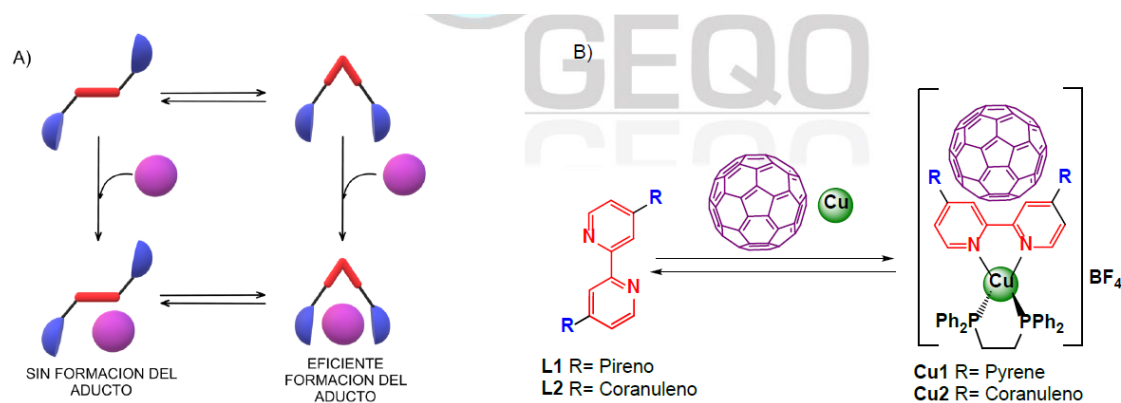


Figura 1. (A) Principio operacional básico en el que se basa la reversibilidad de las pinzas moleculares basadas en PAHs. (B) Representación esquemática del proceso de conmutación.

Referencias

- [1] (a) H. Barbero, S. Ferrero, L. Álvarez-Miguel, P. Gómez-Iglesias, D. Miguel, C. M. Álvarez, *Chem. Commun.*, **2016**, 52, 12964-12967. (b) H. Barbero, S. Ferrero, A. Sacristán-Martín, C. M. Álvarez, *Advances in Chemistry Research*, nº 42, Nova Science Publishers, **2018**. H. Barbero, S. Ferrero, L. Álvarez-Miguel, P. Gómez-Iglesias, D. Miguel, C. M. Álvarez, *Chem. Commun.*, **2016**, 52, 12964-12967. (c) S. Ferrero, H. Barbero, D. Miguel, R. García-Rodríguez and C. M. Álvarez, *J. Org. Chem.* **2019**, *84*, 10, 6183-6190. (d) S. Ferrero, H. Barbero, D. Miguel, R. García-Rodríguez and C. M. Álvarez, *J. Org. Chem.*, **2020**, *85*, 4918-4926

PA-02

PREDICCIÓN COMPUTACIONAL DEL ENLACE Au(I)-Pb(II) EN COMPLEJOS DE COORDINACIÓN Y ESTUDIO DE LOS FACTORES QUE AFECTAN A LA FORMACIÓN DE LOS ENLACES COVALENTES Au(I)-E(II) (E = Ge, Sn, Pb)

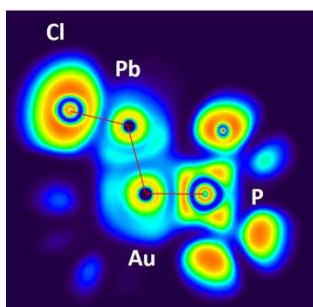
A. Sorroche¹, J.M. López-de-Luzuriaga¹, M. Monge¹, M.E. Olmos¹, M. Rodríguez-Castillo¹

¹Departamento de Química, Centro de Investigación en Síntesis Química (CISQ). Universidad de La Rioja, Complejo Científico Tecnológico, 26006-Logroño (España)
alba.sorroche@unirioja.es

El estudio de la naturaleza del enlace oro(I)-heterometal siendo el heterometal un centro de Ge(II), Sn(II) o Pb(II), constituye un interesante desafío computacional debido a la escasez de este tipo de compuestos tanto desde un punto de vista experimental como del reducido número de estudios teóricos. Los resultados previos sobre compuestos en los que el centro de oro(I) interacciona con iones de metales del grupo 14 muestran que los centros de germanio(II) y estaño(II) presentan una reactividad muy similar frente a precursores de oro(I). Sin embargo, esta similitud en la reactividad de los metales del grupo 14 no se comparte con el elemento más pesado de los tres, plomo.

Con el fin de estudiar las observaciones experimentales, este trabajo está basado en el análisis teórico de los enlaces Au-E en compuestos del tipo $[(PR_3)_3Au-ECI_3]$ (E = Ge^[1], Sn^[2], Pb^[3]; PR_3 = monofosfina terciaria). Así, inicialmente se han construido modelos computacionales simplificados $[(PH_3)_3AuECI_3]$ (E = Ge, Sn, Pb) para llevar a cabo un estudio computacional a nivel MP2 y analizar la naturaleza del enlace heterometálico. Por otro lado, se ha efectuado un análisis topológico de la densidad electrónica sobre los mismos modelos empleando cálculos QTAIM, ELF y DORI.

De manera análoga, aunque en este caso empleando un nivel de cálculo DFT-D3, se ha estudiado el enlace Au(I)-Pb(II) en modelos heterometálicos $[(PR_3)_3AuPbCl_3]$, utilizando ligandos fosfina con diferentes capacidades dadoras-aceptoras (R = CH₃, H, CF₃). Así, se evaluará la influencia del ligando empleado en la fortaleza del enlace Au(I)-Pb(II). Con los datos obtenidos, se podrá predecir la existencia experimental de compuestos que presenten enlaces Au(I)-Pb(II) y, así, corroborar los resultados computacionales.



Referencias

- [1] R. V. Bojan, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, R. Echevarría, O. Lehtonen, D. Sundholm. *ChemPlusChem*, **2016**, *81*, 176-186.
- [2] R. V. Bojan, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, R. Echevarría, O. Lehtonen, D. Sundholm. *ChemPlusChem*, **2014**, *79*, 67-76.
- [3] R. Echeverría, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, *Chem. Sci.*, **2015**, *6*, 2022-2026.

PA-03

SYNTHESIS, CHARACTERIZATION AND STUDY OF NEW COORDINATION COMPOUNDS WITH WATER SOLUBLE PHOSPHINES AND ANTICANCER PROPERTIES

Andrés Alguacil Alarcón^{1,2}, Franco Scalambra^{1,2}, Antonio Manuel Romerosa Nievas^{1,2}

¹ Department of Chemistry and Physics, University of Almeria, Almeria, 04120, Spain, aaa518@ual.es

² Inorganic Chemistry Lab-CIESOL, University of Almeria, Almeria, 04120, Spain

The research on coordination compounds as anticancer drugs raised after the fortuitous discovery of *cis*-[PtCl₂(NH₃)₂] (cisplatin) by Rosenberg in 1965.^[1] From the approval of cisplatin as therapeutic drug in 1978 up to date, new metal complexes with different metals have been synthesized and studied for this purpose. Among these compounds those containing ruthenium(II) showed remarkable antiproliferative activity and low toxicity.

Recently our group synthesised and fully characterized new Ru(II) complexes bearing the ligand dmoPTA (dmoPTA = 3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane), which have shown better cytotoxic profile than those exhibited by cisplatin-like compounds.^[2] The azaphosphine dmoPTA can coordinate metals through the phosphorus atom and the chelating NCH₃ atoms, offering the possibility to synthesise polymeric species. So far, mono- and dimetallic complexes with general formula [RuCp(PPh₃)₂-μ-dmoPTA-1κP:2κ²N,N'-MCl₂]⁺ (M = metal) displayed significant antiproliferative activity and also better selectivity against tumoral cells than cisplatin.^[3]

Herein we present an attempt to improve the cytotoxicity of this family of compounds by N-chelation of Pd(II) or Pt(II) complex units, in order to obtain the bis-metallic complexes [RuCp(PPh₃)₂-μ-dmoPTA-1κP:2κ²N,N'-PdCl₂](CF₃SO₃), [RuCp(PPh₃)₂-μ-dmoPTA-1κP:2κ²N,N'-PtCl₂](CF₃SO₃) and [RuCp(PPh₃)₂-μ-dmoPTA-1κP:2κ²N,N'-PtCl(DMSO-κS)](Cl₂). Also, substitution of a PPh₃ by a PTA ligand was accomplished, leading to a more hydrophilic derivatives based on the [RuCp(PPh₃)(PTA)(dmoPTA-κP)]⁺ scaffold.

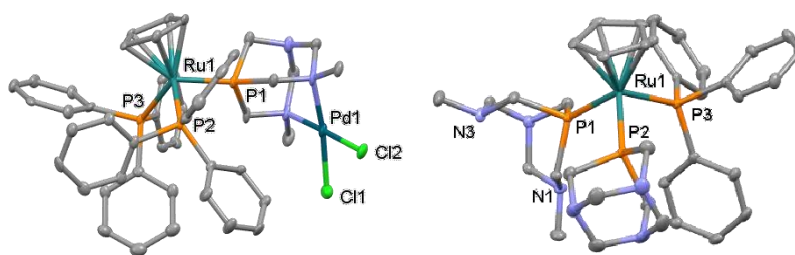


Figure 1. Crystal structures of [RuCp(PPh₃)₂-μ-dmoPTA-1κP:2κ²N,N'-PdCl₂](CF₃SO₃) (left) and [RuCp(PPh₃)(PTA)(dmoPTA-κP)](CF₃SO₃) (right).

Acknowledgements. We acknowledge the Spain Ministry of Economy and Competitiveness (MINECO) and the FEDER program for jointly funding the Project CTQ2015-67384-R, also thanks are provided to the PAI group FQM-317

Referencias

B. Rosenberg, L. Van Camp, T. Krigas, *Nature*, **1965**, 205, 698-699.

Z. Mendoza, P. Lorenzo-Luis, M. Serrano-Ruiz, E. Martín-Batista, J. M. Padrón, F. Scalambra, A. Romerosa, *Inorg. Chem.*, **2016**, 55, 7820-7822.

Z. Mendoza, P. Lorenzo-Luis, F. Scalambra, J. M. Padrón, A. Romerosa, *Dalton Trans.*, **2017**, 46, 8009–8012.

PA-04

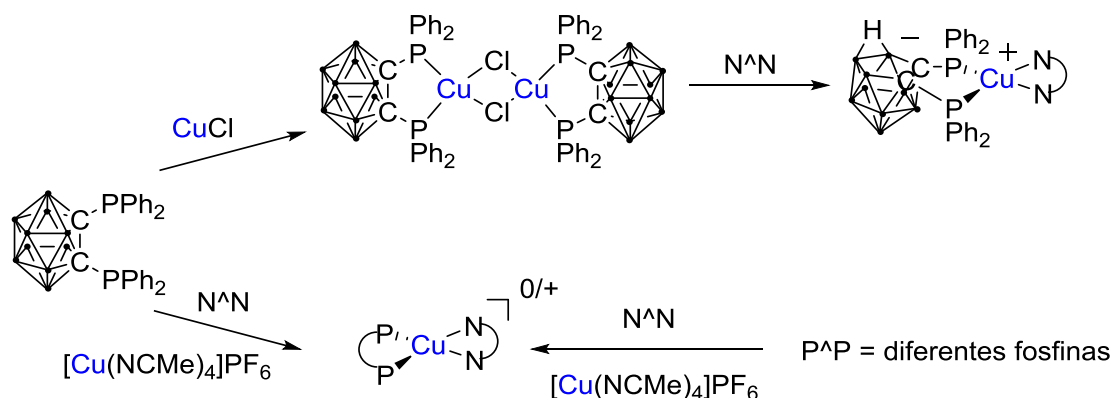
SÍNTESIS Y ESTUDIO DE LAS PROPIEDADES LUMINISCENTES DE COMPLEJOS HEROLÉPTICOS DE COBRE CON DIFOSFINAS Y BISIMINAS

Adrián Alconchel, Olga Crespo, M. Concepción Gimeno

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC- Universidad de Zaragoza, Pedro Cerbuna 12, 50009, Zaragoza, España. alconchel.adrian@gmail.com

En estos últimos años, debido a la gran versatilidad y cantidad de aplicaciones en los que pueden ser usados, los complejos de Cu(I) han generado un gran interés, y más concretamente, los compuestos homolépticos bis-diamina $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$. Sin embargo, estos compuestos tienen diversos problemas, entre los que destaca la posible distorsión en el estado excitado, generando así un quenching de la emisión[1-3]. Para evitar esto se vio que la inserción de un ligando P^P adecuado podrían mejorar la deslocalización electrónica y la rigidez en el entorno metálico, aumentando la eficiencia en el fenómeno de luminiscencia[4,5].

Así, en este trabajo se va a llevar a cabo la síntesis de compuestos heterolépticos $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^{0/+}$ con el uso de diferentes ligandos N^N y P^P quelato a partir de dos vías de síntesis diferentes (Esquema 1). P^P puede representar, entre otras, una difosfina derivada de *orto*-carborano que posee un esqueleto rígido y de gran estabilidad en diferentes entornos y medios de reacción, además de una gran deslocalización electrónica[6]. El objetivo es analizar el efecto de la modificación de la bisimina en las energías de emisión, tiempos de vida y rendimientos cuánticos de los compuestos.



Esquema 1. Síntesis genérica de compuestos de Cu(I)

Referencias

- [1] M. T. Miller, P. K. Gantzel, T. B. Karpishin, *J. Am. Chem. Soc.* **1999**, *121*, 4292-429
- [2] O. Green, B. A. Gandhi, J. N. Burstyn, *Inorg. Chem.* **2009**, *48*, 5704-5714
- [3] Y. Zhang, M. Schulz, M. Wachtler, M. Karnahl, B. Dietzek, *Coord. Chem. Rev.* **2018**, *356*, 127-146.
- [4] F. Brunner, L. Martinez-Sarti, S. Keller, A. Pertgas, A. Prescimone, E. C. Constable, H. J. Bolink, C. E. Housecroft, *Dalton Trans.* **2016**, *45*, 15180-15192.
- [5] S. Igawa, M. Hashimoto, I. Kawata, M. Yashima, M. Hoshino, M. Osawa, *J. Mater. Chem. C* **2013**, *1*, 542-551.
- [6] B. Wang, D. P. Shelar, X. Han, T. Li, X. Guan, W. Lu, K. Liu, Y. Chen, W. Fu, C. Che, *Chem. Eur. J.*, **2015**, *21*, 1184-1190.

Anticancer Activity of Luminescent Pt^{II} and Pt^{IV} Platinacycles Against Multiplatinum-Resistant Metastatic CRC and CRPC Cell Models

A. Lázaro^{1,2}, L. Rodríguez^{1,2}, M. Crespo^{1,3}

¹Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès, 1-11, 08028-Barcelona, Spain

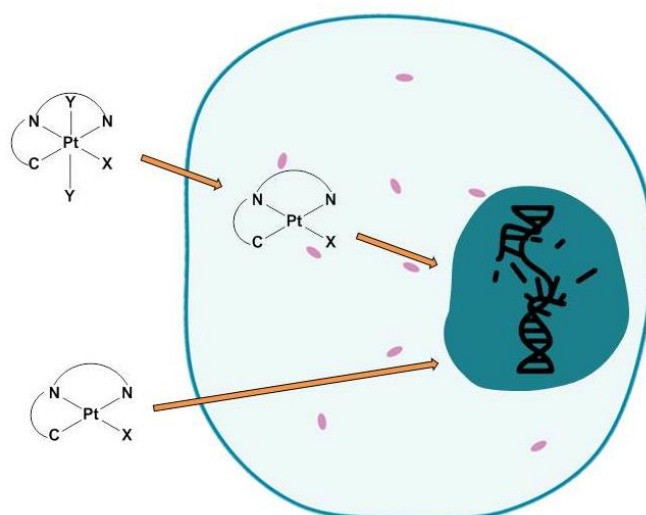
ariadna.lazaro@qi.ub.es

²Institut de Nanociència i Nanotecnologia (IN2UB), Universitat de Barcelona, 08028-Barcelona, Spain

³Institut de Biomedicina de la Universitat de Barcelona (IBUB), 08028-Barcelona, Spain

Platinum-based chemotherapy is widely used as a therapeutic option in a large variety of tumors. However, it is quite common to acquire platinum resistance in time, which leads to the necessity to find alternatives that are effective and non-cross resistant. [1] On the other hand, cyclometallated platinum(II) compounds containing bidentate [C,N] or tridentate [C,N,N'] ligands have displayed interesting properties as novel platinum anticancer drugs. The presence of a $\sigma(\text{Pt-C})$ bond gives these compounds a high stability and increases the lability of the ligands in trans position, favoring covalent coordination to DNA. Furthermore, platinum(IV) compounds have been shown to be a promising class of prodrugs since they are kinetically inert compared to platinum(II) analogues. [2] In this work, [C,N,N'] cyclometallated platinum(II) and platinum(IV) compounds were synthesized in order to evaluate their cytotoxic properties.

Their antitumoral properties have been tested in several cancerous cell lines, including A549 (lung), MCF-7 (breast) and the cisplatin resistant SW-620 (colon) and PC-3 (prostate), as well as in healthy BJ cells as a control. The IC₅₀ values obtained indicate that these compounds display a high potential to be used in chemotherapy. The studied platinum(IV) compounds present enhanced efficacy, capacity to be reduced in solution and a complete absence of platinum cross-resistance against metastatic CRC and CPRC multiplatinum-resistant cell models. [3]



Referencias

[1] T.C. Johnstone, K. Suntharalingam, S.J. Lippard, *Chem. Rev.*, **2016**, *116*, 3436-3486.

[2] I. Omae, *Coord. Chem. Rev.*, **2014**, *280*, 84-95.

[3] A. Lázaro, C. Balcells, J. Quirante, J. Badia, L. Baldomà, J.S. Ward, K. Rissanen, M. Font-Bardia, L. Rodríguez, M. Crespo, M. Cascante, *Chem. Eur. J.*, **2020**, *26*, 1947-1952.

Significativo avance respecto al mecanismo de isomerización catalítica de alcoholes alílicos secundarios en agua.

Belén López Sánchez¹, Franco Scalambra², Antonio Romerosa Nieves³.

^{1,2,3}Departamento de Química Inorgánica-CIESOL, Universidad de Almería, E04120, Almería, España,
¹belenlopezs1993z@gmail.com, ²fs649@inlumine.ual.es, ³romerosa@ual.es.

La ruta sintética de la isomerización catalítica redox de alcoholes alílicos en agua mediada por complejos organometálicos representa un proceso químico muy interesante, ya que se logra catalizar la reacción con un 100% de eficiencia atómica, además de evitar el uso de disolventes orgánicos y condiciones extremas. En esta comunicación se presenta la síntesis y caracterización de un intermedio de reacción de isomerización de 1-octen-3-ol mediante el complejo $[\text{RuCp}(\text{PTA})_2(\text{H}_2\text{O}-\kappa\text{O})](\text{CF}_3\text{SO}_3)$ (PTA=1,3,5-triaza-7-fosfadamantano) (**1**).¹ Por dicha reacción se obtuvieron los complejos *exo*- y *endo*- del intermedio catalítico $[\text{RuCp}(\eta^2\text{-exo-CH}_2=\text{CH-CHOH}-(\text{CH}_2)_4\text{-CH}_3)(\text{PTA})_2](\text{CF}_3\text{SO}_3)$ (**2**), que fueron caracterizados mediante RMN. Dicha técnica mostró la existencia de un equilibrio termodinámico entre dichos conformeros. Notablemente, se han obtenido monocristales del isómero *exo*- de la especie **2**, los cuales han sido caracterizados mediante difracción de rayos X de monocristal. La unidad asimétrica de $[\text{RuCp}(\text{exo-}\eta^2\text{-CH}_2=\text{CH-CHOH}-(\text{CH}_2)_4\text{-CH}_3)(\text{PTA})_2](\text{CF}_3\text{SO}_3)\cdot 2\text{H}_2\text{O}$ (**exo-2CF₃SO₃**) (**Figura 1**), muestra que dicho complejo está constituido por un rutenio con geometría pseudo-octaédrica que está coordinado a un $\eta^5\text{-Cp}$, dos ligandos PTA por su átomo de P y al ligando 1-octen-3-ol a través del doble enlace en forma η^2 , el cual presenta una disposición *exo*.

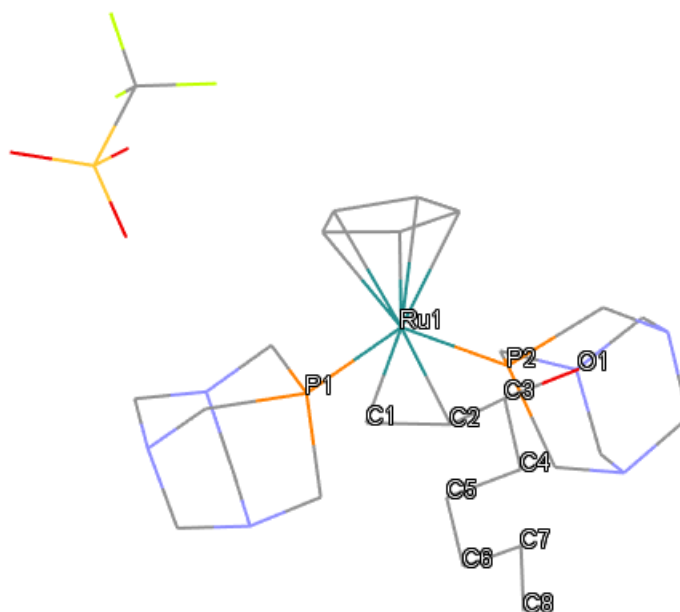


Figura 1. Estructura cristalina de **exo-2(CF₃SO₃)**. Selección de ángulos y distancias de enlace: Ru1-P1 = 2,2852 (8) Å; Ru1-P2 = 2,3084 (8) Å; Ru1-C1 = 2,215 (3) Å; Ru1-C2 = 2,240 (3) Å; C1-C2 = 1,397 (5) Å, C2-C3 = 1,505 (5) Å; C3-O1 = 1,422 (4) Å; Ru-Cp_{cent} = 1,899 Å; P2-Ru1-P1 = 93,47 (3)°.

Referencia

[1] Scalambra, F.; Serrano-Ruiz, M.; Romerosa, A., *Dalton Trans.* **2017**, 46, 5864 - 5871

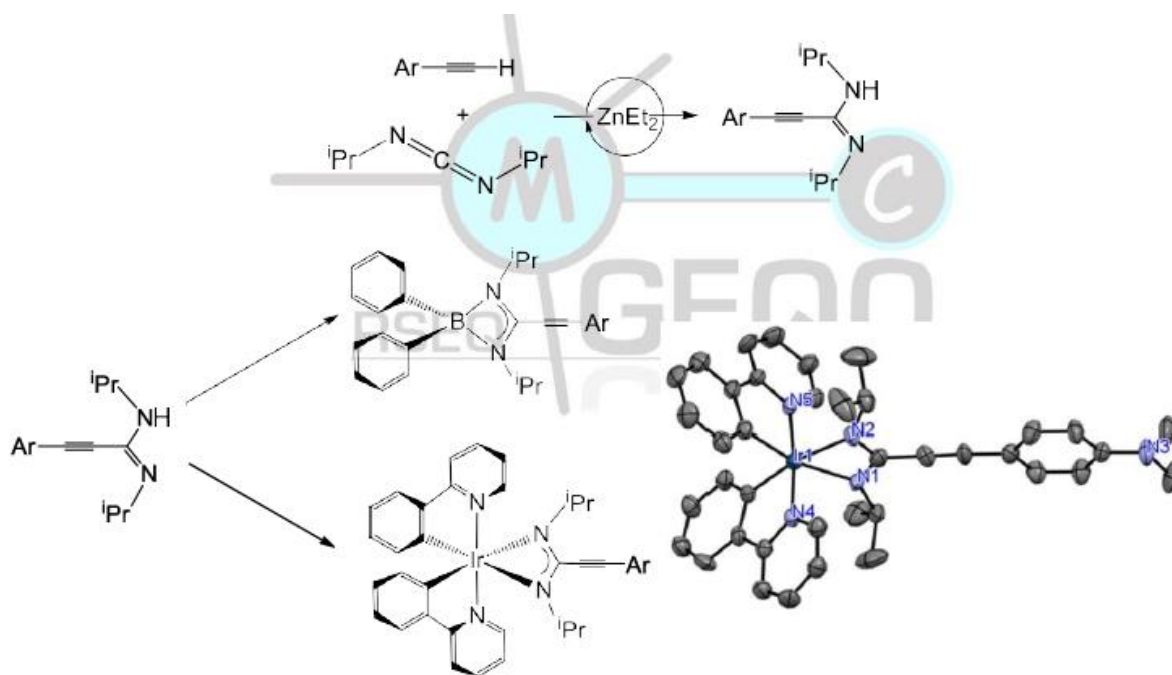
DERIVADOS LUMINISCENTES DE BORO E IRIDIO CON LIGANDOS AMIDINA

Blanca Parra¹, Fernando Carrillo-Hermosilla¹, Antonio Antiñolo¹, David Elorriaga¹, Iván Bravo², Pedro J. Pacheco-Liñán².

¹ Dpto. de Química Inorgánica, Orgánica y Bioquímica, Centro de Innovación en Química Avanzada (ORFEO- CINQA) Fac. de CC. y TT. Químicas. Universidad de Castilla-La Mancha. Campus Universitario, 13071 Ciudad Real. Blanca.Parra@alu.uclm.es

² Dpto. de Química Física, Facultad de Farmacia, Facultad de Farmacia, Universidad de Castilla-La Mancha, Campus Universitario, 02071 Albacete.

Uno de los campos de creciente interés en síntesis química es la obtención de compuestos moleculares luminiscentes, que pueden ser utilizados en la preparación de dispositivos luminosos, o como sondas biológicas [1, 2]. Las propiolamidinas son compuestos orgánicos de fórmula $R^1N=C(C\equiv CR^2)(NHR^3)$, que contienen un enlace tripe C-C conjugado con el sistema amidina. Este tipo de moléculas pueden ser obtenidas de forma muy eficiente, por adición de alquinos terminales a carbodiimidas, utilizando $ZnEt_2$ como precatalizador [3], lo que nos permite conseguir potenciales ligandos con diferentes propiedades electrónicas y estéricas. En esta comunicación, se describe la síntesis de nuevos derivados de boro e iridio del tipo $[BPh_2\{\kappa^2-N,N-ArC\equiv CC(N^iPr)_2\}]$ e $[Ir\{\kappa^2-C,N-(C_6H_4-py)\}_2\{\kappa^2-N,N-ArC\equiv CC(N^iPr)_2\}]$, con propiedades luminiscentes, utilizando este tipo de ligandos nitrógeno dadores.



Referencias

- [1] L. P. Ravano, K. P. S. Zanoni y A. S. S. de Camargo, *Energy Rep.*, **2020**, *6*, 37-45.
- [2] J. L. Donnelly, D. Offenbartl-Stiegert, J. M. Marín-Beloqui, L. Rizzello, G. Battaglia, T. M. Clarke, S. Howorka y J. D. Wilden, *Chem. Eur. J.*, **2020**, *26*, 863-872.
- [3] A. Martinez, S. Moreno-Blázquez, A. Rodríguez-Diéguez, A. Ramos, R. Fernández-Galán, A. Antiñolo and F. Carrillo-Hermosilla, *Dalton Trans.* **2017**, *46*, 12923-12934.

PA-08

Síntesis de complejos tipo [Cp*IrZ(C^N)] con potencial actividad anticancerígenaCarlos Gonzalo¹, D. Martínez¹, A. M. Rodríguez¹, B. R. Manzano¹, G. Durá¹, F. A. Jalón¹¹ Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias y Tecnologías Químicas, Avda. C. J. Cela, 10, 13071 Ciudad Real, UCLM. Carlos.Gonzalo@uclm.es

El cáncer se ha convertido en la segunda causa de mortalidad en el mundo. Sin embargo, su mortalidad ha decrecido gracias al avance de nuevas técnicas de detección y tratamiento, siendo la quimioterapia una de las estrategias más empleadas para el tratamiento del cáncer, si bien presenta varias limitaciones. La fotoquimioterapia o quimioterapia mediada por luz (PCT) ha emergido como alternativa para mejorar los tratamientos actuales y reducir los efectos secundarios. PCT es una técnica no invasiva y supone la administración de un fotosensibilizador, PS, que idealmente es inocuo en ausencia de luz, pero que se activa en presencia de luz, ya que se transforma para dar especies citotóxicamente activas. Esto da la posibilidad de diseñar una quimioterapia controlada por la luz de manera espacio-temporal en un determinado lugar del cuerpo (tumor) y durante un tiempo controlable.

Los complejos de metales de transición han sido empleados como PS debido a sus propiedades fotoquímicas. Se ha descrito el potencial de compuestos de Ir con ligandos ortometalados tipo CN como agentes anticancerígenos. Irradiando con luz, estos complejos tienen la capacidad de generar ¹O₂ y especies reactivas de oxígeno (ROS), las cuales provocan la muerte celular.¹

En este trabajo se presentan complejos tipo Cp*IrZ(C^N), con ligandos CN π-extendidos (Figura 1) para los que se espera capacidad de generar ROS tras ser irradiados con luz. Además, la introducción de ligandos CN π-extendidos posibilita la intercalación de estos ligandos en el ADN, generando un sistema dual, actuando mediante dos mecanismos diferentes.

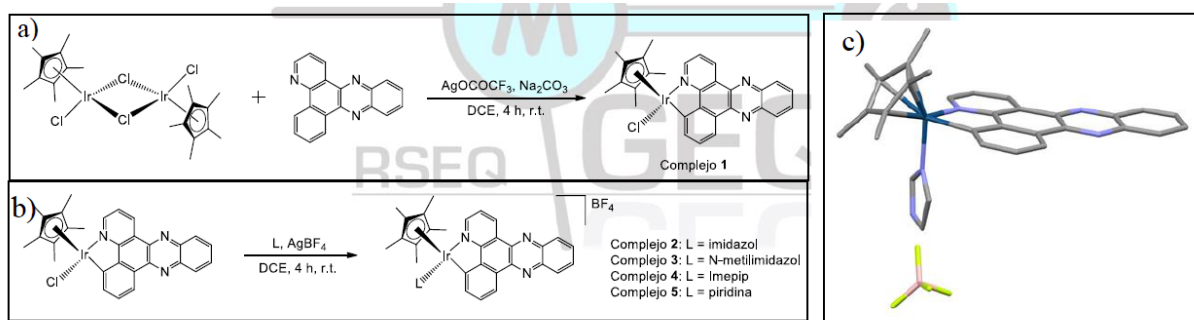


Figura 1. Esquema de síntesis de complejos de Ir con ligandos CN. a) Síntesis del complejo 1 de Iridio a partir del dímero de partida. b) Síntesis de los complejos 2-5 por sustitución del ligando cloruro y coordinación de ligandos N-dadores. c) Estructura de rayos X del complejo 2, con ligando imidazol coordinado al átomo de Iridio. Los átomos de H se han omitido por claridad. (Imepip = (N-etilpiperidil)imidazol).

Referencias

[1] a) J. Li, T. Chen. *Coord. Chem. Rev.* 2020, 418, 213355. b) S. Monro, K. L. Colón, H. Yin, J. Roque, P. Konda, S. Gujar, R. P. Thummel, L. Lilge, C. G. Cameron, S. A. McFarland. *Chem. Rev.* 2019, 119, 797-828. c) L. K. McKenzie, H. E. Bryant, J. A. Weinstein. *Coord. Chem. Rev.* 2019, 379, 2-29.

ESTUDIO FOTOFÍSICO, REOLÓGICO Y POR DISPERSIÓN CUASI-ELÁSTICA DE NEUTRONES DE NUEVOS HIDROMETALOGELAS DE ORO(I) Y ADENINA

D. Blasco,¹ H. Amaveda,² V. García-Sakai,³ J. M. López-de-Luzuriaga,¹ J. A. Martínez-González,³ M. Monge,¹ M. Mora,² M. E. Olmos,¹ y M. Rodríguez-Castillo.¹

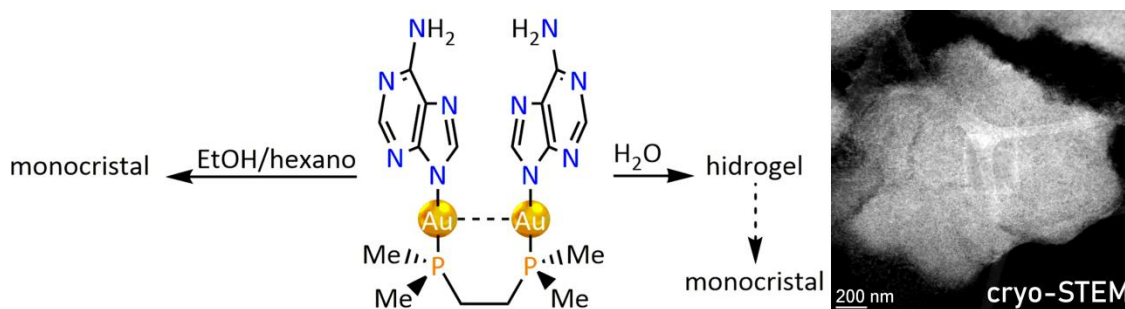
¹ Departamento de Química, Centro de Investigación en Síntesis Química (CISQ), Universidad de La Rioja, Madre de Dios 54, 26004 Logroño (España). e-mail: daniel.blascos@unirioja.es

² Instituto de Nanociencia y Materiales de Aragón, INMA (CSIC-Universidad de Zaragoza), María de Luna 3, 50018 Zaragoza (España).

³ ISIS Neutron and Muon Source, Rutherford Appleton Laboratory (RAL), Harwell Science and Innovation Campus, OX11 0QX Chilton, Didcot (Reino Unido).

La preparación de complejos de oro(I) con capacidad hidrogelificante es una de las áreas de la química de este metal que está experimentando un crecimiento más activo. [1,2] Así, su síntesis supone, aparte de un desafío a las habilidades e intuición química del investigador, una prueba adicional de la acción de las fuerzas débiles “propias” de este metal (aurofilia, $Au^I \cdots Au^I$; enlaces de hidrógeno a oro(I), $X-H \cdots Au^I$, $X = C, N, O$) [3,4] en disolución acuosa.

Nuestra investigación reciente en este campo ha demostrado la utilidad de la coordinación de la unidad catiónica $[Au(PMe_3)]^+$ a la nucleobase adenina, para la obtención de los complejos hidrogelificantes $[Au(^9N\text{-adeninato})(PMe_3)]$ y $[Au(^9N\text{-adenina})(PMe_3)](CF_3CO_2)$. [5] En la actualidad, estamos considerando los complejos dinucleares $\{[Au(^9N\text{-adeninato})]_2(\mu\text{-diphos})\}$ (diphos = dmpe, dmpm, depe) como una nueva familia de hidrogelificantes y/o fotoemisores en fase sólida. Así, en esta contribución se presenta la síntesis, caracterización estructural y estudio de las propiedades fotofísicas de dichos complejos y, en particular, de la hidrogelificación de $\{[Au(^9N\text{-adeninato})]_2(\mu\text{-dmpe})\}$. Para este último propósito, se incluirán medidas reológicas por ensayos oscilatorios, micrografías *cryo*-STEM, y los prometedores resultados preliminares de experimentos de dispersión cuasi-elástica de neutrones (QENS por sus iniciales en inglés), así como su comparativa con $[Au(^9N\text{-adeninato})(PMe_3)]$.



Referencias

[1] L. Rodríguez, J. C. Lima, *Inorganics*, **2015**, 3, 1-18.

[2] N. Mirzadeh, S. H. Privér, A. J. Blake, H. Schmidbaur, S. K. Bhargava, *Chem. Rev.*, **2020**, 120, 7551-7591.

[3] (a) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.*, **2008**, 37, 1931-1951. (b) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.*, **2012**, 41, 370-412.

[4] H. Schmidbaur, *Angew. Chem. Int. Ed.*, **2019**, 58, 5806-5809.

[5] (a) D. Blasco, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, D. Pascual, M. Rodríguez-Castillo, *Inorg. Chem.*, **2018**, 57, 3805-3817. (b) D. Blasco, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, M. Rodríguez-Castillo, *Dalton Trans.*, **2019**, 48, 7519-7526.

HIGHLY ACTIVE BENZYLIC COMPLEXES OF PALLADIUM(II) FOR THE VINYLIC ADDITION POLYMERIZATION OF ALQUENIL-NORBORNENES

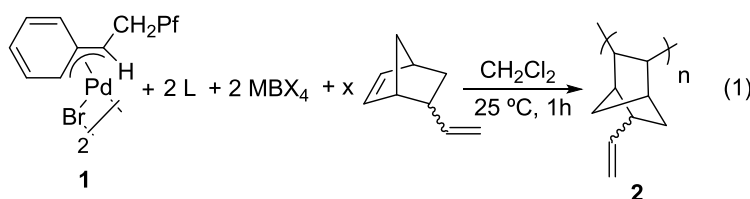
Pérez-Ortega, I.; Albéniz, A. C.

¹ignacio.perez.ortega@alumnos.uva.es

²albeniz@qi.uva.es

Vinyl addition polymerization of norbornene and their derivatives is an important method for the synthesis of polymers with a saturated and rigid structure (VA-PNBs). The most usual and active complexes for the VA-polymerization are nickel(II) or palladium(II) compounds. In general, many complexes show high activities toward the VA-polymerization of norbornene. However, the incorporation of functional groups, such as terminal double bonds, lead to an important decrease in the activity of catalyst that are useful in the polymerización of unsubstituted norbornene. Some recent studies by Bermeshev and Brookhart reported some nickel(II) and palladium(II) complexes with high activity in the vinyl addition polymerization of 5-ethylidene-2-norbornene.¹

In this work, we present a highly active catalytic system for the VA-polymerization of 5-vinyl-2-norbornene and 5-ethylidene-2-norbornene. The catalytic system is based in our previous studies in the synthesis and reactivity of benzylic complexes of palladium(II) bearing a pentafluorophenyl group in the α position.² The dimer **1** in combination of the appropriate phosphine and bromo scavenger makes the catalytic system very effective for the VA-polymerization of alquenil-norbornenes even with very low amount of catalyst (about 10 ppm).



Pf = C₆F₅

L = PCy₃, PPh₃, P^tBu₃,

P(C₆F₅)₃, P(*o*-tolyl)₃

MBX₄ = AgBF₄, AgSbF₆, NaBAR₄^f

The activity of the catalytic system is highly dependent of the counteranion and the phosphine employed. Furthermore, the investigation of the initiation step in the VA-polymerization of 5-vinyl-2-norbornene with the precatalytic system **1**/PCy₃/NaBAR₄^f showed us that the initiation of the polymerization starts by the insertion of the endocyclic double bond into a palladium hydride intermediate generated in situ. The high initiation constant together with the low ratio Pd:ligand are crucial for the high efficiency of this system in the vinyl addition polymerization of alquenil-norbornenes.

References

- [1] a) Farquhar, A. H.; Brookhart, M.; Miller, A. J. M. *Polym. Chem.* **2020**, *11*, 2576-2484. b) Bermesheva, E. V.; Wozniak, A. I.; Fedor A. Andreyanov, F. A.; Karpov, G. O.; Nechaev, M. S.; Asachenko, A. F.; Topchiy, M. A.; Melnikova, E. K.; Nelyubina, Y. V.; Gribanov, P. S.; Bermeshev, M. V. *ACS Catal.* **2020**, *10*, 1663-1678.
- [2] a) Martín-Ruiz, B.; Pérez-Ortega, I.; Albéniz, A. C. *Organometallics* **2018**, *37*, 1074-1085. b) Martín-Ruiz, B.; Pérez-Ortega, I.; Albéniz, A. C. *Organometallics* **2018**, *37*, 1665-1670.

CONTROL DE NANOESTRUCTURAS ANISOTRÓPICAS DE ORO Y PLATA A PARTIR DE COMPLEJOS ORGANOMETÁLICOS: CONVERSIÓN DE LUZ EN ENERGÍA TÉRMICA

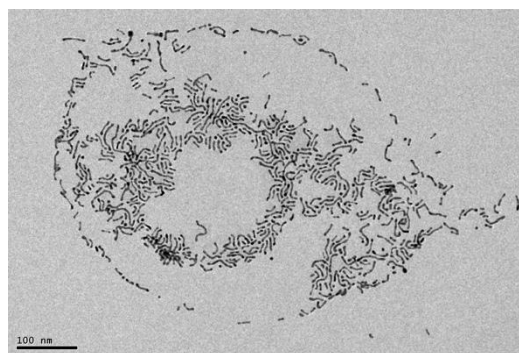
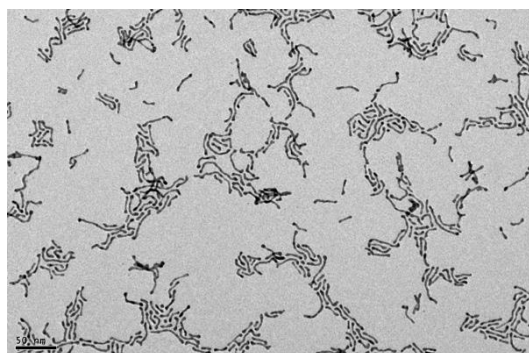
J. Quintana¹, J. M. López-de-Luzuriaga¹, M. Monge¹, M. Rodríguez-Castillo¹

¹ Departamento de Química, Centro de Investigación en Síntesis Química (CISQ), Universidad de La Rioja, Complejo Científico-Tecnológico, 26006-Logroño (España), javier.quintana@unirioja.es

La síntesis de nanopartículas metálicas requiere un control minucioso de su forma, tamaño y composición, ya que a través de ello se podrán modular las propiedades ópticas, biológicas y catalíticas de las mismas.¹ Para ello, una posible ruta es el empleo de agentes directores de forma moleculares que, por una parte, controlen el entorno de coordinación de un precursor organometálico y, por otro, favorezcan el crecimiento anisotrópico de las nanoestructuras obteniéndose morfologías controladas.²

En este contexto, se ha empleado ácido oleico, que junto con un precursor heterometálico de oro(I) y plata (I) como es el compuesto $[Au_2Ag_2(C_6F_5)_4(Et_2O)_2]_n$, favorecen la formación de nanorods de unos 3 nm de diámetro y diferentes longitudes. Estas nanoestructuras presentan una intensa absorción de energía, debida a la resonancia de plasmón superficial longitudinal, en torno a 1500 nm, región del infrarrojo cercano (NIR), lo que hace muy atractivas a estas nanoestructuras por sus potenciales propiedades (foto)catalíticas y biológicas. Además, la modificación de las concentraciones y relación estequiométrica entre el precursor metálico y el ácido carboxílico permite controlar el proceso de pre-ensamblaje para así, poder controlar la longitud de las nuevas nanoestructuras. De esta manera, se obtienen nanorods de diferentes tamaños, cuyas diferentes longitudes (20-30 nm), están directamente relacionados con la sintonización de su resonancia de plasmón longitudinal en el NIR (1300-1700 nm).

Se ha estudiado la capacidad catalítica de estas nanoestructuras en reacciones de reducción y, por otro lado, se ha conseguido biocompatibilizar dichas nanoestructuras con el tripéptido L-Glutationa o el polímero PEG Tiol, obteniéndose nanoestructuras plasmónicas con alta capacidad de conversión de luz en energía térmica lo que las convierten, por ejemplo, en un material idóneo para aplicaciones de terapia fototérmica.



Referencias

- [1] N. Li, P. Zhao, D. Astruc, *Angew. Chem. Int. Ed.* **2014**, *53*, 1756-1789.
- [2] J. Crespo, A. Ibarra, J. M. López-de-Luzuriaga, M. Monge and M. E. Olmos, *Eur. J. Inorg. Chem.*, **2014**, 2383–2388.

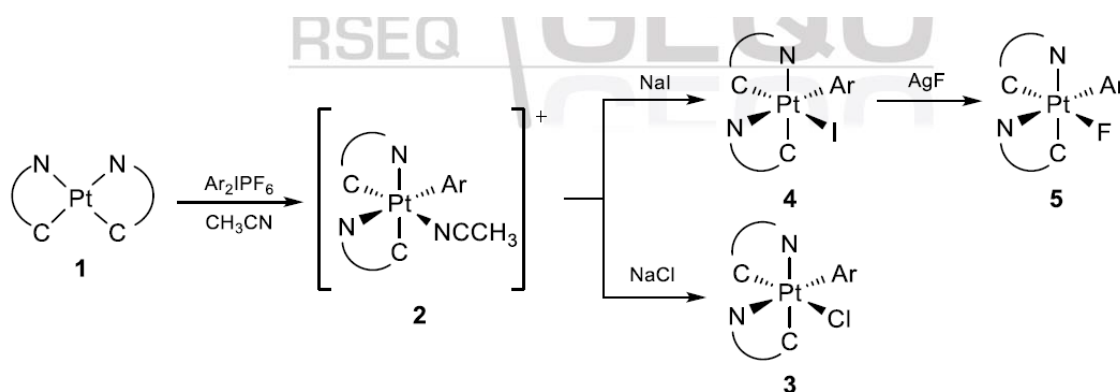
PA-12

LUMINESCENT BIS-CYCLOMETALATED HALO(ARYL) PLATINUM(IV) COMPLEXES

Juan Carlos López López,¹ Delia Bautista² and Pablo González Herrero^{1,*}¹ Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, 19, 30100 Murcia, Spain, jc.lopezlopez@um.es² Área Científica y Técnica de Investigación, Universidad de Murcia, Campus de Espinardo, 21, 30100 Murcia, Spain.

Luminescent transition-metal complexes bearing heteroaromatic ligands have been studied for their long-lived and highly tunable excited states, which make them suitable for important light-based applications.^[1] Most studies have focused on complexes of d^6 [Ir(III), Ru(II), Os(II)] or d^8 [Pt(II), Au(III)] ions. However, Pt(IV) complexes have received very little attention.

Pt(IV) complexes with cyclometalated 2-arylpiperidines (C[^]N) may show efficient and long-lived emissions from triplet ligand-centered (³LC) excited states with a very small metal-to-ligand charge-transfer (MLCT) character.^[2] The MLCT contribution is crucial because it facilitates the formation of the emitting state and accelerates the radiative transition to the ground state due to the spin-orbit coupling effects induced by the metal. To develop Pt(IV) complexes with a higher MLCT admixture into the emitting state, we set out to synthesize complexes of the type [Pt(C[^]N)2(Ar)(X)] (X: Cl⁻, F⁻). The aryl and fluoro ligands can be strong π -donors for the Pt(IV) ion, helping to increase the energy of the metal $d\pi$ orbitals and, hence, the MLCT contribution, which could lead to increased radiative rates and quantum yields. A comparison of luminescent properties between chloro and fluoro aryl complexes will be presented. Complexes [Pt(C[^]N)2(Ar)(X)] with different C[^]N ligands were obtained via oxidative addition of Ar₂I⁺ salts to *cis*-[Pt(C[^]N)2] followed by the addition of NaI or NaCl to give [Pt(C[^]N)2(Ar)(X)] (X: I⁻, Cl⁻). [Pt(C[^]N)2(Ar)(F)] complexes were synthesized by substitution of the iodide ligand by fluoride using AgF (Scheme 1). The photophysical characterization will be presented.



Acknowledgments

Ministerio de Ciencia, Innovación y Universidades (PGC2018-100719-B-I00) and Fundación Séneca (19890/GERM/15).

References

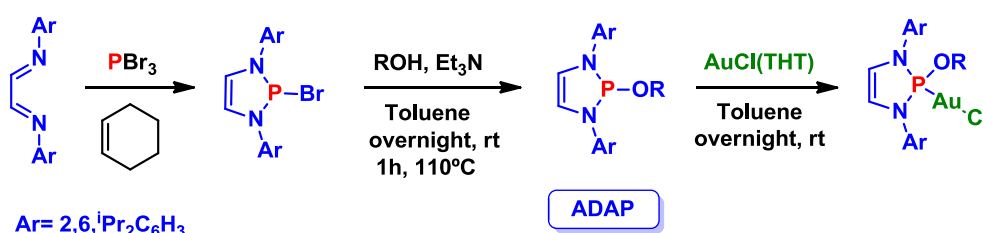
- [1] (a) Yam, V. W.-W. W.; Wong, K. M.-C. *Chem. Commun.* **2011**, 47, 11579–11592. (b) Chou, P.-T.; Chi, Y.; Chung, M.-W.; Lin, C.-C. *Coord. Chem. Rev.* **2011**, 255, 2653–2665.
- [2] (a) Juliá, F.; Bautista, D.; Fernández-Hernández, J. M.; González-Herrero, P. *Chem. Sci.* **2014**, 5, 1875–1880. (b) Juliá, F.; Aullón, G.; Bautista, D.; González-Herrero, P. *Chem. Eur. J.* **2014**, 20, 17346–17359. (c) Juliá, F.; Bautista, D.; González-Herrero, P. *Chem. Commun.* **2016**, 52, 1657–1660.

GOLD-CATALYZED SELECTIVE C-H BOND FUNCTIONALIZATION OF ARENES

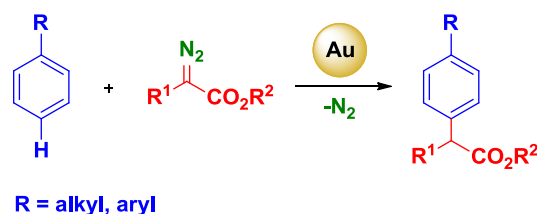
J. Diego Pizarro Javier,¹ Manuel R. Fructos,^{1*} Pedro J. Pérez.^{1*}

¹ *Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible y Departamento de Química, Campus de El Carmen, Universidad de Huelva, 21007-Huelva, Spain.
e-mail: juandiego.pizarro@dqcm.uhu.es*

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



The selective functionalization of C(sp²)-H bonds in substituted benzenes remains as a challenge,^[4] with gold being the metal of choice toward that end.^[5] Herein we present a series of gold complexes with catalytic properties toward the functionalization of such moieties using α -aryl- α -diazooesters as the source of the carbene group to be inserted on the C-H bonds. With the appropriate election of the ligand we have achieved high selectivities toward the *para*-position of the starting arenes.



References

- [1] Fleming, S., Lupton, M. K., Jekot, K. *Inorg. Chem.*, **1972**, *11*, 2534-2540.
- [2] Gudat, D. *Coord. Chem. Rev.* **1997**, *163*, 71.
- [3] a) Pizarro, J. D.; Molina, F.; Fructos, M. R.; Pérez, P. J.; *Chem. Eur. J.* **2020**, *26*, 10330. b) Pizarro, J. D.; Molina, F.; Fructos, M. R.; Pérez, P. J.; *Organometallics* **2020**, *39*, 2553.
- [4] Ma B., Chu Z., Huang B., Liu Z., Liu L. Zhang J., *Angew. Chem. Int. Ed.* **2017**, *56*, 2749-2753.
- [5] Fructos, M. R., Diaz-Requejo, M. M., Pérez, P. J. *Chem. Commun.* **2016**, *52*, 7326-7335.

SÍNTESIS Y CARACTERIZACIÓN ESTRUCTURAL DE COMPLEJOS DE ORO(III) CON LIGANDOS FOSFURO PUENTE Y SUS PRECURSORES DE TALIO(III) Y ORO(III)

L. Coconubo¹, J. M. López de Luzuriaga¹, S. Moreno¹, M. E. Olmos¹

¹ Departamento de Química, Centro de Investigación en Síntesis Química (CISQ), Universidad de La Rioja, Madre de Dios 54, 26006, Logroño (España), e-mail: lacoconu@unirioja.es

La química de los complejos de oro(I) y oro(III) con ligandos fosfuro puente presenta su origen en los trabajos llevados a cabo por R. J. Puddephatt^[1], H. Schmidbaur^[2-4] y nuestro grupo de investigación^[5] durante las décadas de 1970 y 2000. Sin embargo, durante los últimos años, se ha establecido un reducido progreso en este campo de investigación.^[6,7] Particularmente, dicha carencia de compuestos se ve especialmente marcada en el caso de compuestos de oro(III).

Por su parte, las fosfinas secundarias, así como los ligandos fosfuro (PR₂⁻), derivados de su desprotonación, han sido escasamente empleados como ligandos en química de coordinación, debido en parte a su toxicidad, alta reactividad y sensibilidad al aire.^[8]

Considerando esta escasez de complejos de oro(III) con ligandos fosfuro puente usando como precursor fosfinas secundarias, nos propusimos sintetizar fosfino y fosfuro compuestos de oro(III) con difenilfosfina como ligando, haciendo uso para ello del efecto estabilizante de diferentes grupos perhalofenilo, como C₆F₅ o 3,5-C₆Cl₂F₃.

Una primera vía sintética para obtener los compuestos de interés hace uso de los aril derivados de talio(III) [Tl(C₆X₅)₂Cl]_n, algunos de los cuales no eran conocidos hasta la fecha, a partir de los que se sintetizan perhalofenil complejos del tipo [Au(C₆X₅)₃(tht)]. Estos últimos son los precursores de los fosfino compuestos de oro(III) [Au(C₆X₅)₃PPh₂H], los cuales son objeto de pruebas de reactividad a través de su tratamiento con acetilacetato derivados, que actúan como agentes desprotonantes, permitiendo sintetizar fosfuro complejos de oro(III).

Una segunda vía para la obtención de fosfuro derivados de oro(III) parte del anión [AuR₂]⁻ como producto de partida, que tras su oxidación con Cl₂ conduce al precursor de oro(III) [AuR₂Cl₂]⁻. A partir de éste se ha conseguido el nuevo compuesto de oro(III) con doble puente de fosfuro [Au₂(C₆F₅)₄(μ-PPh₂)₂].

Los nuevos compuestos obtenidos han sido caracterizados estructuralmente haciendo uso de diferentes técnicas, tales como espectroscopía de resonancia magnética nuclear (RMN), espectroscopía infrarroja (FTIR), espectrometría de masas (ESI-MS), conductividad molar en disolución y, en los casos que ha sido posible, difracción de rayos x (XRD) sobre monocristal.

Referencias

- [1] R. J. Puddephatt, y P. J. Thompson, *J. Organomet. Chem.*, **1976**, 117(4), 395–403.
- [2] H. Schmidbaur, G. Weidenhiller, O. Steigelmann, *Angew. Chem. Int.*, **1991**, 30, 433.
- [3] E. Zeller, H. Beruda, J. Riede, H. Schmidbaur, *Inorg. Chem.*, **1993**, 32, 3068.
- [4] M. C. Blanco, E. J. Fernández, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, M. E. Olmos, *Angew. Chem. Int.*, **1998**, 37(21), 3042-3043.
- [5] M. C. Blanco, E. J. Fernández, A. K. Fischer, P. G. Jones, A. Laguna, M. E. Olmos, M. D. Villacampa, *Inorg. Chem. Commun.*, **2000**, 3, 163-165.
- [6] S. A. Reiter, S. D. Nogai, H. Schmidbaur, *Z. Naturforsch., B: Chem. Sci.*, **2005**, 60, 511.
- [7] M. C. Blanco, E. J. Fernández, M. E. Olmos, O. Crespo y, A. Laguna, *Organometallics*, **2004**, 23, 4373-4381.
- [8] E. J. Fernández, A. Laguna, M. E. Olmos, *J. Chil. Chem. Soc.*, **2007**, 52(3).

NUEVOS COMPLEJOS RADICALES DE PALADIO(I) CON LIGANDOS CARBENO N-HETEROCÍCLICO

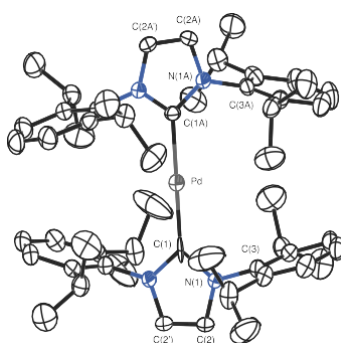
A. El Astal-Quirós, S. de Toro, C. García-Yebra,* E. de Jesús*

Departamento de Química Orgánica y Química Inorgánica, Universidad de Alcalá
Instituto de Investigación Química "Andrés M. del Río", aliah.astal@uah.es

Los complejos de paladio(I), son esencialmente especies dinucleares, diamagnéticas, con enlaces metal-metal [1]. Se han detectado, sin embargo, radicales de Pd^I como intermedios en algunos procesos de síntesis orgánica catalizada, como reacciones de acoplamiento cruzado por transferencia mono-electrónica (single-electron-transfer, SET) [2]. A pesar de estos antecedentes, sólo recientemente ha sido aislado el primer complejo mononuclear de Pd^I, [Pd^I(PtBu₃)₂][PF₆], aunque su reactividad ha sido, hasta el momento, poco explorada [3].

Recientemente, nuestro grupo ha iniciado una línea de investigación centrada en la búsqueda de metodologías generales para preparar complejos mononucleares de Pd(I) estables, el estudio de su reactividad y aplicaciones en catálisis. Los primeros resultados indican que es posible estabilizar estas especies gracias a las particulares características estéricas y electrónicas de los ligandos carbeno N-heterocíclico (NHC) utilizados [4]. Estos complejos están generando resultados muy prometedores en procesos de activación de pequeñas moléculas y como precatalizadores en reacciones de acoplamiento cruzado [5].

En esta contribución se muestran los últimos avances en la preparación de especies de Pd(I) mononucleares de estequiometría [Pd(NHC)₂]⁺ y [Pd(NHC)(PR₃)]⁺ estables, obtenidas a partir de [Pd(0)], que prueban la generalidad del método de síntesis utilizado. Estudios de caracterización de los nuevos complejos, como la voltametría cíclica, permiten predecir su comportamiento químico y relacionarlo con la capacidad dadora de los ligandos utilizados.



Estructura molecular del complejo [Pd(IPr)₂]⁺ [4]

Referencias

- [1] T. Murahashi, H. Kurosawa, *Coord. Chem. Rev.* **2002**, 231, 207.
- [2] P. Chuentragool, D. Kurandina, V. Gevorgyan *Angew. Chem. Int. Ed.* **2019**, 58, 11586.
- [3] T. Troadec, S.-Y. Tan, C.J. Wedge, J.P. Rourke, P.R. Unwin, A.B. Chaplin, *Angew. Chem. Int. Ed.* **2016**, 55, 3754. M.C. MacInnis, J.C. DeMott, E.M. Zolnhofer, J. Zhou, K. Meyer, R.P. Hughes, O.V. Ozerov, *Chem* **2016**, 1, 902.
- [4] Georgiana Dragomir-Maties. Stabilization of Unusual Complexes of Palladium(0) and Palladium(I) with Hindered N-Heterocyclic Carbene Ligands. PhD thesis. Univ. de Alcalá (2020).
- [5] Aliah El Astal-Quirós. Applications of Pd(I) catalysts for the formation of C-C bonds in the synthesis of molecules with biological activity. Trabajo de fin de máster. Univ. de Alcalá (2019).

Bis-Acetiluros de Au(I) con fosfinas bidentadas como pinzas moleculares

N. Álvarez-Llorente¹, R. García-Rodríguez², C. M. Álvarez²

¹ GIR MIOMeT, IU CINQUIMA (Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011Valladolid, Spain), nereaalv96@gmail.com

² GIR MIOMeT, IU CINQUIMA (Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011Valladolid, Spain)

El diseño y síntesis de estructuras basadas en hidrocarburos policíclicos aromáticos para el reconocimiento de diferentes nanoestructuras de carbono es de gran importancia en el campo de la Química Supramolecular[1]. Concretamente, los aductos supramoleculares con fullerenos son de gran interés por sus propiedades electrónicas.

En el presente trabajo se ha sintetizado una familia de bis-acetiluros de Au(I) con diferentes fosfinas bidentadas como ligandos puente (figura 1), siguiendo una modificación de un método previamente descrito en bibliografía[2]. Estos compuestos presentan sustituyentes policíclicos aromáticos, tanto planos (pireno) como no planos (coranuleno). Es de esperar que estos compuestos sean capaces de establecer interacciones supramoleculares con fullerenos, debido a la cooperatividad entre los hidrocarburos policíclicos aromáticos y la capacidad de los átomos de Au(I) de establecer interacciones aurofílicas[3], que permitirían a estos compuestos adoptar una geometría de pinza.

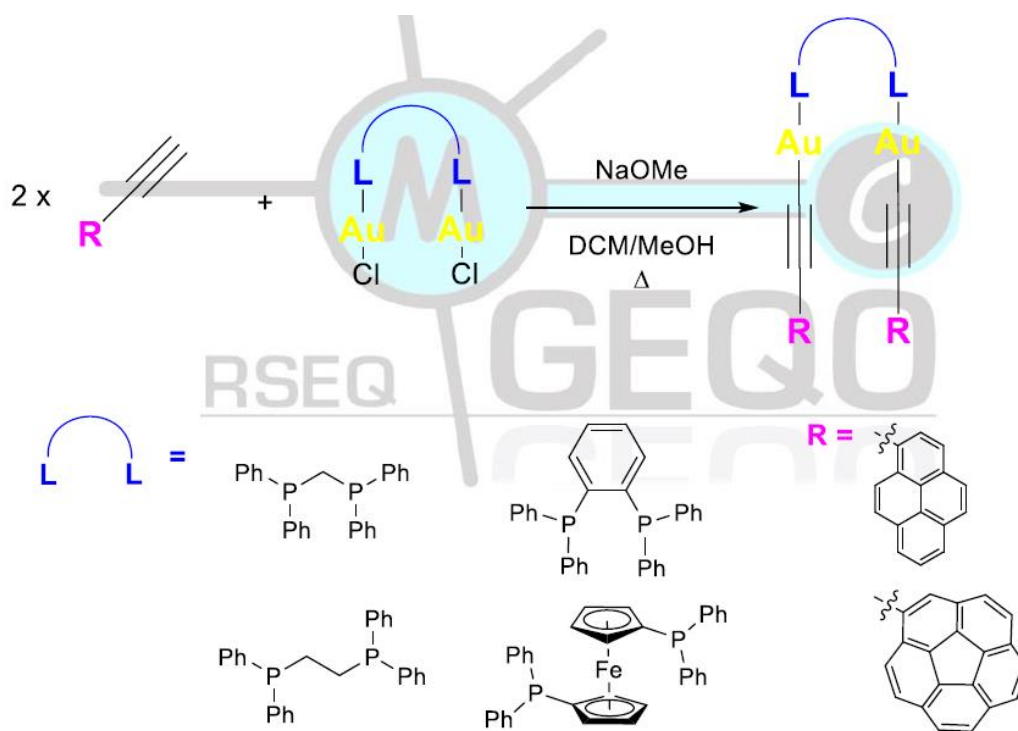


Figura 1. Esquema de síntesis de los compuestos obtenidos en este trabajo.

Se han realizado estudios preliminares que demuestran la interacción de estos compuestos con fullerenos, se proseguirá el trabajo calculando la constante de asociación.

Referencias

- [1] S. Ferrero, H. Barbero, D. Miguel, R. García-Rodríguez, C. M. Álvarez, *J. Org. Chem.* **2020**, *85*, 4918–4926.
- [2] R. Cross, M. Davidson, *J. Chem. Soc., Dalton Trans.*, **1986**, 411-414.
- [3] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.*, **2008**, *37*, 1931-1951.

ALKYNE CYCLOTRIMERIZATION MEDIATED BY TWO-COORDINATE Fe(II) AND Co(II) *m*-TERPHENYL COMPLEXES

P. Alamán-Valtierra¹, W. Lewis², L. J. Taylor², D. Kays², C. Tejel¹, A. M. Geer¹

¹ Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, Zaragoza, 50009, Spain, e.mail: palaman@unizar.es

² School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

The development of new catalytic routes yielding one-ring aromatic molecules from simple feedstocks has a huge importance due to the key role of these molecules in drug development and synthesis of pharmaceuticals, biologically active molecules, materials, polymers, fuel cells, liquid crystals, and natural products.[1] One of the most practical ways to build benzene derivatives is the transition metal-catalyzed [2+2+2] cyclotrimerization of alkynes due to the 100% atom-economy of the reaction. Since Reppe *et al.* discovered the first viable Ni-based catalytic route for the trimerization of propargyl alcohols under mild conditions a wide range of catalytic procedures with decreased side-products formation has been developed. However, many of these catalysts are made of scarce and expensive metals, require harsh conditions, the use of additives or are not regioselective.[2]

Here in the present communication, we showcase two-coordinate cobalt(II) and iron(II) diaryl complexes stabilized by *m*-terphenyl ligands as efficient precatalysts for alkyne cyclotrimerization under mild reaction conditions (Figure 1). The catalysis was found to be regioselective to the 1,2,4-isomer for both aliphatic and aromatic alkynes. Mechanistic studies by *in situ* NMR analysis revealed the reaction to be first order in both catalyst and substrate. A reaction mechanism is proposed to account for these findings.

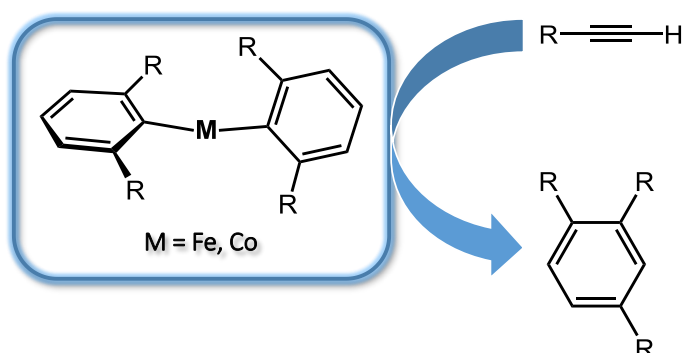


Figure 1. Alkyne cyclotrimerization catalyzed by Fe(II) and Co(II) complexes.

Financial support acknowledgment: MINECO-FEDER CTQ2017-83421-P and GA-FES (Reactivity and Catalysis in Inorganic Chemistry, E50_20D)

References

[1] G. Domínguez, J. Pérez-Castells, *Chem. Soc. Rev.* **2011**, *40*, 3430–3444

[2] Z. Wang, Reppe Alkyne Cyclotrimerization in *Comprehensive Organic Name Reactions and Reagents*, **2010**, Ch 529, pp 2345-2351

BIMETALLIC COOPERATION TO ACTIVATE SMALL MOLECULESN. Hidalgo¹, J. Campos¹

¹ Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA). Consejo Superior de Investigaciones Científicas (CSIC) and Universidad de Sevilla, Avda. Américo Vespucio 49, 41092 Sevilla.

nereida.hidalgo@iiq.csic.es

Homogeneous catalysis has been dominated by mononuclear transition-metal complexes. However, the last decades have evidenced that cooperative effects between metals in close proximity have tremendous utility in bond activation and catalysis.[1]

Considering this, our group recently embarked in the design of less conventional bimetallic designs. Among those, we highlight in this work metal-only Lewis pairs (MOLPs),[2] in which two metal fragments are held together exclusively through a metal-metal dative bond, as well as Transitions Metal Only Frustrated Lewis Pairs (TMOFLPs),[3] that is, combinations of Lewis acids and bases that do not form bimetallic adducts and exhibit FLP-type reactivity.

Our bimetallic combinations are capable of activating small molecules such as hydrogen, alkynes, alcohols or water, providing as well uncommon heterobimetallic structures.[4]

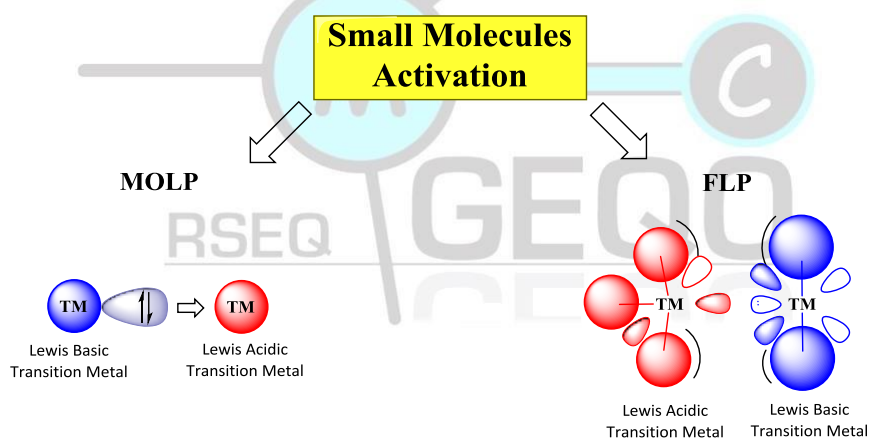


Figure 1: metal-only Lewis pairs (MOLPs) and Metal Only Frustrated Lewis Pairs (TMOFLPs).

Referencias

- [1] a) I. G. Powers, C. Uyeda, *ACS Catal*, **2017**, 7, 936-958. b) D. R. Pye, N. P. Mankad, *Chem Sci.*, **2017**, 8, 1705-1718. c) J. Campos, *Nat. Rev. Chem.*, **2020**, 4, 696-702.
- [2] J. Bauer, H. Braunschweig, R. D. Dewhurst, *Chem. Rev.*, **2012**, 112, 4329-4346.
- [3] a) D. W. Stephan, *Science*, **2016**, 354, aaf7229. b) S. R. Flynn, D. F. Wass, *ACS Catal.*, **2013**, 3, 2574-2581.
- [4] a) J. Campos, *J. Am. Chem. Soc.*, **2017**, 139, 2944-2947. b) N. Hidalgo, C. Maya, J. Campos, *Chem. Commun.*, **2019**, 55, 8812-8815.

CATALYTIC ASYMMETRIC SYNTHESIS OF DIBENZAZEPINES WITH CENTRAL AND AXIAL CHIRALITY BY CuH-CATALYZED INTRAMOLECULAR CYCLIZATION

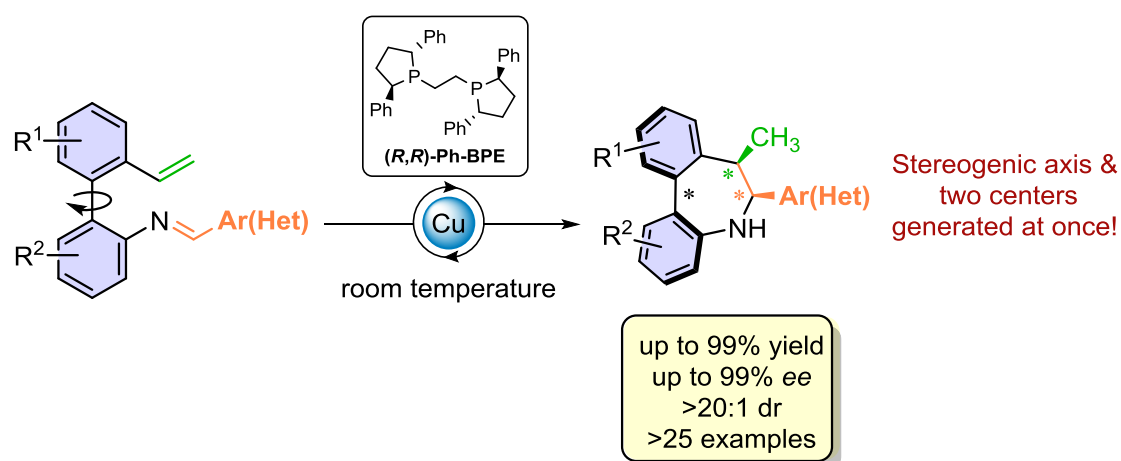
Patricia Rodríguez-Salamanca,¹ Rocío Martín-de la Calle,² Verónica Rodríguez,¹ Rosario Fernández,² José M. Lassaletta,¹ Valentín Hornillos^{1,2}.

¹Instituto de Investigaciones Químicas (CSIC-US) and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Avda. Américo Vespucio, 49, 41092 Sevilla, Spain.

²Departamento de Química Orgánica, Universidad de Sevilla and Centro de Innovación en Química Avanzada (ORFEO-CINQA), C/ Prof. García González, 1, 41012 Sevilla, Spain.

patricia.rodriguez@iiq.csic.es

Chiral dibenzazepines, seven-membered heterocycle rings with a biaryl bridge, are present in numerous biologically active molecules such as immunosuppressants and antidepressants, in ligands for asymmetric metal catalysis and organocatalysts. Despite the increasing importance of this biaryl structures, only a handful of methods have been described for their catalytic asymmetric synthesis. Those approaches consist on the asymmetric reduction of the corresponding imines using a reductase (IRE^d)^{1a} or molecular H₂ and chiral iridium^{1b} or ruthenium catalysts,^{1c} an enantioselective copper-catalyzed intramolecular hydroamination strategy,² and the tautomerization of metastable enamines using a chiral phosphoric acid.³ In this contribution, a copper-catalyzed asymmetric intramolecular cyclization for the synthesis of dibenz[*b,d*]azepines is described. The use of in situ formed [Cu^I/(Ph-BPE)] as the catalyst allows for the synthesis of bridged biaryl amines containing both central and axial stereogenic elements, in high yields (up to 99%) and with excellent diastereo- and enantioselectivities (>20:1 dr, up to 99% ee). The reaction proceeds under mild conditions (rt) and is applicable to various readily available 2'-vinyl-biphenyl-2-imines, including substituted aromatic and heterocyclic compounds.



Referencias

- [1] a) S.P. France, G.A. Aleku, M. Sharma, J. Mangas-Sanchez, R.M. Howard, J. Steflík, R. Kumar, R. W. Adams, I. Slabu, R. Crook, G. Grogan, T. W. Wallave, N. J. Turner, *Angew. Chem. Int. Ed.*, **2017**, *56*, 15589–15593. b) T. Yang, X. Guo, Q. Yin, X. Zhang, *Chem. Sci.*, **2019**, *10*, 2473–2477. c) S. Zhang, F. Chen, Y-M. He, Q-H. Fan, *Org. Lett.*, **2019**, *21*, 14, 5538–5541.
- [2] X-J. Dai, O. D. Engl, T. León, S. L. Buchwald, *Angew. Chem. Int. Ed.*, **2019**, *58*, 3407–3411.
- [3] J. Liu, X. Yang, Z. Zou, J. Nan, Y. Wang, X. Luan, *Org. Lett.*, **2018**, *20*, 244–247.

READILY AVAILABLE Ir/P-S CATALYSTS FOR THE REDUCTION OF SYNTHETICALLY RELEVANT OLEFINS

Pol de la Cruz-Sánchez,¹ Jèssica Margalef,¹ Xisco Caldentey,² Oscar Pamies,¹ Miquel A. Pericàs,² y Montserrat Diéguez¹

¹ Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, C. Marcel·lí Domingo, 1, 43007 Tarragona, España, pol.delacruzsanchez@urv.cat

² Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona, España

One major goal in the fine chemicals industry is to develop synthetic methodologies that produce chiral target compounds with high enantioselectivities and with a minimum environmental impact. For this purpose, asymmetric hydrogenation (AH) has become a key methodology. However, the applicability of catalysts in AH remains an issue. Most catalysts are only tested in standard substrates, eluding challenging substrates that would yield to more interesting compounds. Rh/Ru-complexes have been established as the optimal catalysts for the AH of olefins bearing coordinating functional groups.[1] However, these catalysts are less efficient in the AH of substrates lacking coordinating groups next to the double bond. Pioneered by Pfaltz, Ir-complexes of the type $[\text{Ir}(\text{cod})(\text{P},\text{N})^*]\text{BAR}_f$ were successfully used in the AH of unfunctionalized olefins.[1] We also showed that P-thioether ligands can provide enantioselectivities comparable to the best Ir-P,N catalysts.[2] Along the path from absolutely unfunctionalized olefins to analogues bearing coordinating functional groups, there is a broad range of interesting substrates with intermediate coordinating properties (e.g. α,β -unsaturated esters, amides and ketones), containing functional groups that not form stable chelate rings with the metal, and their reduced products showcase interesting properties.[1] However, most of the methods used for their preparation relied on non-catalytic methods with a limited substrate scope. In contrast, their AH is a highly atom economic approach. However, the efficiency of Ir/P,N-catalysts is still highly dependent on the substitution pattern and the geometry of the substrates. The discovery of a family of catalysts with a wide substrate scope remains a central task in AH of this type of olefins.

To continue the improvement of Ir-catalysts, in this communication we show the successful application of a simple but modular P,S-ligand family for the AH of a broad range of synthetically relevant olefins.[3] The ligands are synthesized in three steps from cheap indene and they are air-stable solids and easy to handle. Their modular architecture has been crucial to maximize the catalytic performance for each type of substrate. Improving Ir-catalysts reported so far, this ligand family presents a broader substrate scope, covering different substitution patterns with different functional groups, ranging from unfunctionalized olefins, through olefins with poorly coordinative groups, to olefins with coordinative functional groups. Acyclic and cyclic esters, ketones and amides were hydrogenated in enantioselectivities up to 99% ee. Enantioselectivities up to 98% ee were also achieved for unfunctionalized 1,1'-disubstituted olefins, functionalized tri- and 1,1'-disubstituted vinyl phosphonates, and β -cyclic enamides.

Referencias

[1] J. J. Verendel, O. Pàmies, M. Diéguez, P. G. Andersson, *Chem. Rev.* **2014**, *114*, 2130–2169 and references there in.

[2] J. Margalef, O. Pàmies, M. A. Pericàs, M. Diéguez, *Chem. Comm.* **2020**, *56*, 10795–10808.

[3] J. Margalef, M. Biosca, P. de la Cruz-Sánchez, X. Caldentey, C. Rodríguez-Esrich, O. Pàmies, M. A. Pericàs, M. Diéguez, *Adv. Synth. Catal.* in press.

MECHANISTIC STUDY OF Pd-CATALYZED C-N COUPLINGS SUPPORTED BY TERPHENYL PHOSPHANE LIGANDS

R. J. Rama,¹ C. Maya,¹ A. Nova,^{2,3} M. C. Nicasio¹

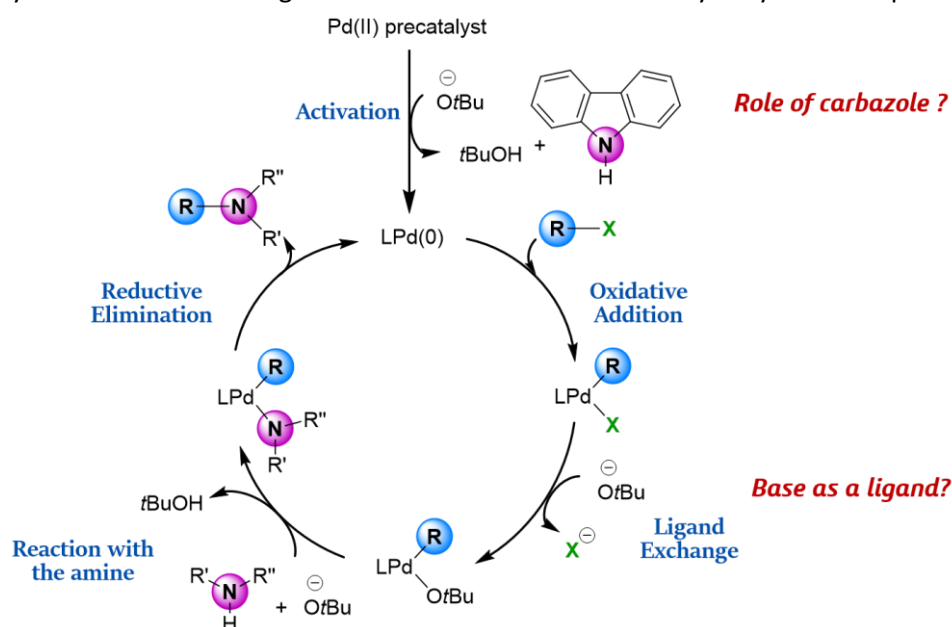
¹Departamento de Química Inorgánica, Universidad de Sevilla, Apdo. 1203, 41071 Sevilla, Spain, e-mail rjimenez17@us.es

²SMN and Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, P. O. Box 1033, Blindern, N-0315 Oslo, Norway.

³Department of Chemistry, UiT-The Arctic University of Norway, N-9037 Tromsø, Norway

Palladium catalyzed cross-coupling reactions are one of the most powerful tools for the formation of C-C and C-heteroatom bonds. [1] The use of Pd precatalysts in these catalytic transformations provides a better control of the influence of the ligand in the catalytic cycle. 2-Aminobiphenyl-derived palladacycles stabilized by dialkylbiaryl phosphane ligands are one of the most successful precatalysts for the Buchwald-Hartwig amination, providing fast activation to catalytically active PdL species under mild reaction conditions.[2] Very recently, we have described the use of terphenyl phosphanes as supporting ligands in Pd-catalyzed Buchwald-Hartwig aminations. [3]

In this communication, we present a thorough computational study of the steps involved in the catalytic cycle of the Buchwald-Hartwig amination catalyzed by Pd species stabilized by dialkylterphenyl phosphanes (Scheme 1). The synthesis of the most significant intermediates of the catalytic cycle is also presented.



Scheme 1. Catalytic cycle studied in this work.

Referencias

- [1] A. De Meijere, S. Bräse, M. Oestreich, *Metal-Catalyzed Cross-Coupling Reactions and More*, Wiley-VCH: Weinheim, Germany, **2014**.
- [2] (a) D. S. Surry, S. L. Buchwald, *Chem. Sci.*, **2011**, 2, 27. (b) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem. Int. Ed.*, **2007**, 46, 2768.
- [3] (a) R. J. Rama, C. Maya, M. C. Nicasio *Chem. Eur. J.*, **2020**, 26, 1064. (b) A. Monti, R. J. Rama, B. Gómez, C. Maya, E. Álvarez, E. Carmona, M. C. Nicasio, *Inorg. Chim. Acta*, **2021**, 518, 120214

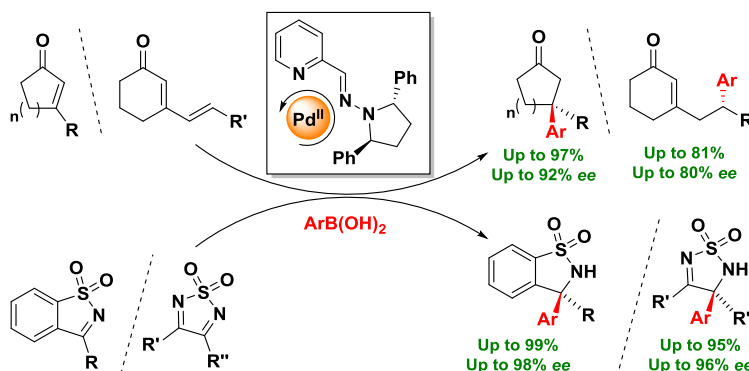
Pd(II) AND PYRIDINE-HYDRAZONE LIGANDS AS A VERSATILE CATALYTIC SYSTEM IN ASYMMETRIC ADDITIONS OF ARYLBORONIC ACIDS

S. Alberca¹, M. Velázquez¹, J. Iglesias-Sigüenza¹, D. Monge¹, R. Fernández¹, J.M. Lassaletta²

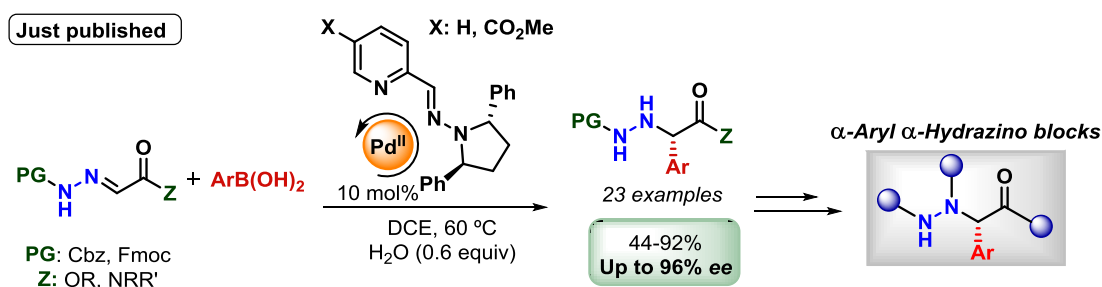
¹ Departamento de Química Orgánica, Universidad de Sevilla, C/Prof. García González, 1, 41012 Sevilla, Spain, salberca@us.es

² Instituto Investigaciones Químicas (CSIC-US), Americo Vespucio 49, 41092 Sevilla, Spain

Catalysts generated by combinations of Pd(TFA)₂ and enantiomerically pure pyridine-hydrazone ligands have been applied to the asymmetric addition of arylboronic acids to different electrophiles. This catalytic system allowed the 1,4-addition to β-substituted cyclic enones with high yields and enantioselectivities. In addition, the most challenging 1,6-addition to dienones was carried out with complete regioselectivity [1]. Other application was developed in the 1,2-addition to saccharin-derived cyclic ketimines and diketimines with a great stereocontrol and high regioselectivities for unsymmetrically substituted diketimines [2].



In this communication, we present the first asymmetric 1,2-addition of arylboronic acids to *N*-carbamoyl (Cbz and Fmoc) protected glyoxylate-derived hydrazones, yielding α-aryl α-hydrazino esters/amides in high enantioselectivities [3]. Subsequent removal of the carbamoyl moiety offers an appealing entry to α-aryl α-hydrazino acids, key building blocks for the synthesis of artificial peptides.



Referencias

- [1] M. Retamosa, Y. Álvarez-Casao, E. Matador, A. Gómez, D. Monge, R. Fernández, J.M. Lassaletta, *Adv. Synth. & Catal.* **2019**, *361*, 176-184.
- [2] Y. Álvarez-Casao, D. Monge, E. Álvarez, R. Fernández, J.M. Lassaletta, *Org. Lett.*, **2015**, *17*, 5104-5107.
- [3] M. Velázquez, S. Alberca, J. Iglesias-Sigüenza, R. Fernández, J.M. Lassaletta, D. Monge, *Chem. Commun.*, **2020**, *56*, 5823-5826.

MECHANISTIC STUDIES ON AN IRON PYRIDYL-CARBENE CATALYST FOR CO₂ ELECTROREDUCTION

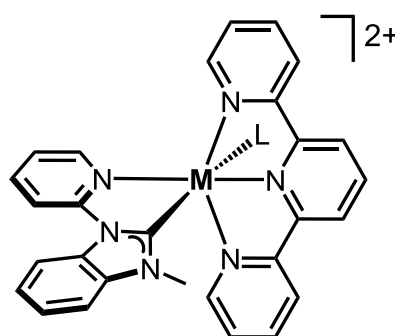
Sergio Gonell,^{1*} Julio Lloret-Fillol,^{2*} Alexander J. M. Miller^{3*}

¹Institute of Advanced Materials (INAM), Universitat Jaume I Av. Vicente Sos Baynat s/n. 12071 Castelló (Spain)
sgonell@uji.es

²Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, 43007 Tarragona, Spain; Catalan Institution for Research and Advanced Studies (ICREA), 08010 Barcelona, Spain

³University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

The electrochemical reduction of CO₂ is a challenging reaction of interest from a fundamental perspective and as a candidate for converting an environmentally harmful gas into a valuable fuel. Application in large scale of this reaction will likely require the use of catalysts based on affordable and abundant metals. Organometallic ruthenium complexes bearing a 2,2':6',2''-terpyridine paired with a bidentate ligand containing mixed pyridine-N-heterocyclic carbene (**1** in Figure 1) are well established electrocatalysts for CO₂ reduction to CO.[1] We recently unraveled the mechanism for this system, and we proved that the two geometrical isomers resulting from the asymmetry of the bis-chelating ligand have completely different behavior in the elementary steps of the catalytic cycle, as a consequence the *trans* effect provided by the strongly donating NHC donor.[2,3] Now in this contribution, we will discuss the synthesis of the iron analogues (**2** in Figure 1), as well as the mechanism of this new family of electrocatalysts in CO₂ reduction.[4] A combination of NMR spectroscopy, cyclic voltammetry, and spectroelectrochemical infrared spectroscopy have established similarities and differences between the catalytic cycle performed by iron and ruthenium complexes.



1, M = Ru
2, M = Fe

Figure 1

Referencias

- [1] Z. Chen, C. Chen, D. R. Weinberg, P. Kang, J. J. Concepcion, D. P. Harrison, M. S. Brookhart, T. J. Meyer, *Chem. Commun.* **2011**, 47, 12607–12609.
- [2] S. Gonell, M. D. Massey, I. P. Moseley, C. K. Schauer, J. T. Muckerman, A. J. M. Miller, *J. Am. Chem. Soc.* **2019**, 141, 6658–6671.
- [3] S. Gonell, E. A. Assaf, K. D. Duffee, C. K. Schauer, A. J. M. Miller, *J. Am. Chem. Soc.* **2020**, 142, 8980–8999.
- [4] S. Gonell, J. Lloret-Fillol, A. J. M. Miller, *ACS Catal.* **2021**, 11, 615–626.

AUMENTO DEL ÍNDICE DE COORDINACIÓN DEL ION PLOMO(II) A ALTA PRESIÓN EN UN COMPUESTO DE ORO(I) Y PLOMO(II)

S. Moreno¹, N. Casati², J. M. López-de-Luzuriaga¹, M. E. Olmos¹

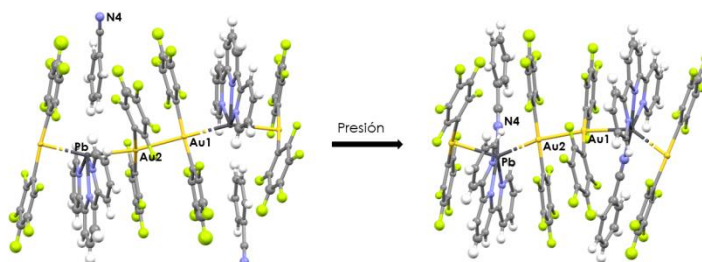
¹ Departamento de Química, Centro de Investigación en Síntesis Química (CISQ), Universidad de La Rioja Complejo Científico-Tecnológico, 26006 – Logroño (España) e-mail: sonia.moreno@unirioja.es

² Paul Scherrer Institute (PSI), Laboratory for Synchrotron Radiation – Condensed Matter, WLGA/229
Forschungsstrasse 111, 5232 Villigen, Switzerland

El efecto de la presión sobre compuestos metálicos es un campo de investigación de creciente interés que proporciona nuevos conocimientos sobre la flexibilidad geométrica, propiedades físicas y sobre la química a alta presión de un gran número de compuestos. [1]

La cristalografía de alta presión es una técnica que permite la manipulación de moléculas en estado sólido. La aplicación de presión sobre las moléculas puede dar lugar a varias respuestas; por ejemplo, puede provocar la aparición de nuevos polimorfos, cambios de color o la formación de nuevas formas moleculares, como polímeros. Este tipo de estudio debe proporcionar información sobre la estructura cristalina en cada punto de presión con el fin de identificar posibles cambios de fase que afecten al empaquetamiento molecular o a las distancias entre los centros metálicos. [2]

En el presente trabajo describimos el estudio del compuesto $[\text{Au}_2\text{Pb}(\text{C}_6\text{F}_5)_4(\text{terpy})]_n \cdot \text{N}\equiv\text{CPh}$ mediante difracción de rayos X sobre monocristal a alta presión para analizar los cambios estructurales al variar la presión. Se obtuvieron monocristales adecuados para este estudio por evaporación lenta de una disolución del compuesto en benzonitrilo. Utilizando una celda de yunque de diamante (DAC) se aplicaron presiones que oscilaron entre 0.0 y 2.1 GPa, recopilando los datos a temperatura ambiente para evitar posibles efectos térmicos. El compuesto cristaliza en el grupo espacial monoclinico Cc. La estructura cristalina consiste en dos fragmentos aniónicos $[\text{Au}(\text{C}_6\text{F}_5)_2]^-$ y un fragmento catiónico $[\text{Pb}(\text{C}_{15}\text{H}_{11}\text{N}_3)]^{+2}$, unidas a través de interacciones homo- y heterometálicas, que dan lugar a una cadena polimérica. Este complejo cristaliza con una molécula de benzonitrilo por molécula de compuesto, que no está conectada a la cadena metálica. Al aumentar la presión, la distancia entre los centros de oro disminuye de 2.969(3) Å a presión ambiente a 2.773(2) Å a 2.1 GPa, con una disminución simultánea del volumen de la celdilla unidad de un 14 %, pero no se observa ningún cambio en el grupo espacial. Un cambio sorprendente observado cuando aumenta la presión (específicamente a 1.0 GPa de presión) está relacionado con la orientación de la molécula de benzonitrilo, en la cual el átomo de nitrógeno cambia su orientación desde el exterior de la cadena metálica a presión ambiente hacia el átomo de plomo, lo que lleva a la formación de un nuevo enlace Pb-N (2.77(7) Å). Este aumento en el número de coordinación del átomo de plomo también conduce a un alargamiento de las distancias heterometálicas Au-Pb si se comparan con las obtenidas a presiones menores.



Referencias

[1] J. P. Tidey, H. L. S. Wong, M. Schröder, A. J. Blake, *Coord. Chem. Rev.*, **2014**, 277-278, 187-207.

[2] A. J. Blake, R. Donamaría, V. Lippolis, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, A. Seal, J. A. Weinstein, *Inorg. Chem.*, **2019**, 58, 4954-4961.

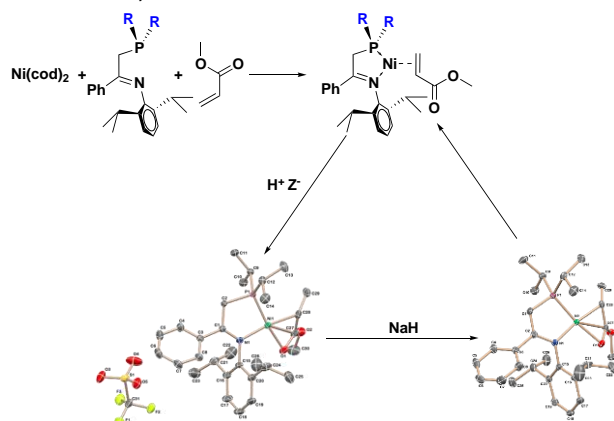
PA-25

NEW PERSPECTIVE ON THE HECK REACTION: β -HYDRIDE ELIMINATION ASSISTED BY DEPROTONABLE P-N LIGANDS INVOLVING A CONCOMITANT Ni(0)/Ni(II)/Ni(0) REDOX PROCESS.Tomás G. Santiago,¹ P. Palma,² E. Álvarez³ and J. Cámpora^{*4}¹ IIQ (CSIC-University of Seville), Américo Vespucio Avenue, 49, 41092, Seville, SPAIN (tomasgsantiago@iiq.csic.es).² IIQ (CSIC-University of Seville), Américo Vespucio Avenue, 49, 41092, Seville, SPAIN (ppalma@iiq.csic.es).³ IIQ (CSIC-University of Seville), Américo Vespucio Avenue, 49, 41092, Seville, SPAIN (ealvarez@iiq.csic.es).⁴ IIQ (CSIC-University of Seville), Américo Vespucio Avenue, 49, 41092, Seville, SPAIN (campora@iiq.csic.es).

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

The properties of a metal complex as a whole is the result of the interaction between the metal centre and its ligands, which controls the performance of the catalyst thanks to their steric and electronic properties, playing a spectator role, because the reactivity takes place at the metal centre. Nevertheless, recent new approaches make use of cooperative ligands, that can play an active role in the elementary bond activation steps in a catalytic cycle [1, 2]. The central idea is that the metal and the ligand can cooperate in a synergistic manner, and their interplay facilitates the chemical process [3].

Thus, we have been investigating the Heck reaction using Nickel complexes stabilized by iminophosphine ligands. We recently discovered that these P,N ligands can be deprotonated with a suitable base affording the respective phosphinoenamine species [4]. This characteristic might play a very important role in the nickel-catalyzed Heck reaction, particularly in the third step of the process: β -hydride elimination based induced. In this sense, we discovered that during this last step, the P-N ligands may act as a proton shuttle through an acid/base process so as to assist in the performance of this third step of the catalytic cycle (Scheme 1). For that aim, a model was studied.



Scheme 1

Referencias[1] Grützmacher, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 1814–1818.[2] van der Vlugt, J. I.; Reek, J. N. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 8832–8846.[3] Lyaskovskyy, V.; Bruin, B. *ACS Catal.* **2012**, *2*, 270–279.[4] Santiago, T. G.; Urbaneja, C.; Álvarez, E.; Ávila, E.; Palma, P.; Cámpora, J. *Dalton Trans.* **2020**, *49*, 322–335

PA-26

EASY WIDE SCOPE ACCESS TO LUMINESCENT FLUOROPHOSPHORANES

J. Ponce de León¹, R. Infante¹, P. Espinet^{1,*}¹ IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Valladolid-47071, Spain.*Corresponding author: espinet@qi.uva.es

Dibenzophospholes are species of wide interest in materials science, due to their luminescent and electronic properties [1]. However, few examples of fluorophosphoranes can be found [2,3].

Herein, a convenient one-step methodology to access luminescent fluorophosphoranes with a dibenzophosphole moiety in almost quantitative yield is presented [4]. These compounds can be easily obtained from biaryl phosphines by an intramolecular S_NAr reaction, and the only requirement is that the phosphine has a F atom at the 2' position of the biaryl.

Their structure in solution and in the solid state was elucidated by multinuclear NMR and X-ray diffraction analysis, and their luminescent properties were also evaluated. A kinetic and DFT study of the process shows that the S_NAr step is rate-determining, and two possible pathways toward the final product are discussed.

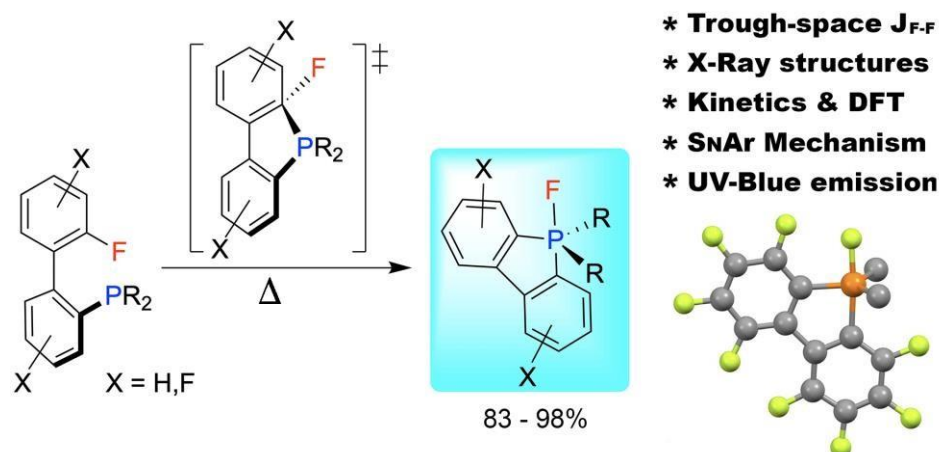


Figure 1. Synthetic protocol to access fluorophosphoranes.

References

- [1] P. Hibner-Kulicka, J. A. Joule, J. Skalika, P. Bałczewski, *RSC Adv.*, **2017**, 7, 9194–9236.
- [2] H. Fujimoto, M. Kusano, T. Kodama, M. Tobisu, *Org. Lett.*, **2020**, 22, 2293–2297.
- [3] S. Lim, A. T. Radosevich, *J. Am. Chem. Soc.*, **2020**, 142, 16188–16193.
- [4] Submitted article.

Cooperatividad Al-Li en sistemas trispiridil aluminato

Álvaro García-Romero¹, Raúl García-Rodríguez¹, Celedonio M. Álvarez¹, Daniel Miguel¹

¹ GIR MIOMeT, IU Cinquima (Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011, Valladolid, España)

alvaro.gar.romero@gmail.com

En las últimas décadas muchos estudios han centrado su atención en los ligandos tris(2-piridil) del tipo [E(Py)₃] (py= 2-piridil) (E= CR, COR, CH, N, P, P=O, Fig 1a) y en el estudio de sus propiedades de coordinación; posicionándolos como una importante familia de ligandos con aplicaciones en diversas áreas como: química de coordinación, química organometálica, catálisis e incluso química bioinorgánica. Uno de los avances más destacados en esta área es la introducción de elementos metálicos como átomo cabeza de puente (E). La incorporación de Al permite la obtención de una familia aniónica que presenta gran afinidad por una amplia variedad de cationes metálicos. La presencia de aluminio permite la obtención de un enlace polarizado (Al-C) capaz de reaccionar de forma inmediata con agua y alcoholes dando lugar a la sustitución de una o varias piridinas por OH o alcóxidos (Fig 1b).^[1]

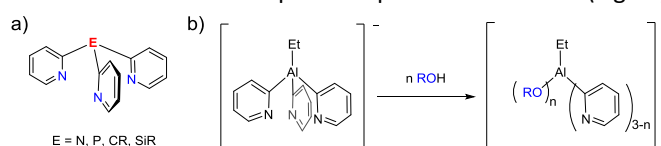


Figura 1. a) Ligandos tris(2-piridil) convencionales. b) Reacción simplificada de [EtAl(2-py)₃]⁻ con ROH.

En este estudio se presenta el primer ejemplo aniónico de la familia de compuestos tris(3-piridil). Este ligando establece interacciones supramoleculares presentando una estructura polimérica en estado sólido. Además, a diferencia de sus análogos tris(2-piridil), el compuesto es estable frente al agua, alcoholes y aldehídos. Para obtener más información acerca de este inusual comportamiento, se han realizado una serie de estudios de ¹H y ⁷Li-DOSY en DMSO (método de Stalke) que atestiguan el diferente estado de agregación de los compuestos [EtAl(2-py)₃]Li y [EtAl(3-py)₃]Li en disolución. Para la especie 2-piridil los estudios sugieren la existencia en disolución de la especie [EtAl(2-py)]Li como un par iónico (Fig 2a), a diferencia de para la especie 3-piridil en los que apuntan hacia una separación de iones y la no formación de un par iónico (Fig 2b).

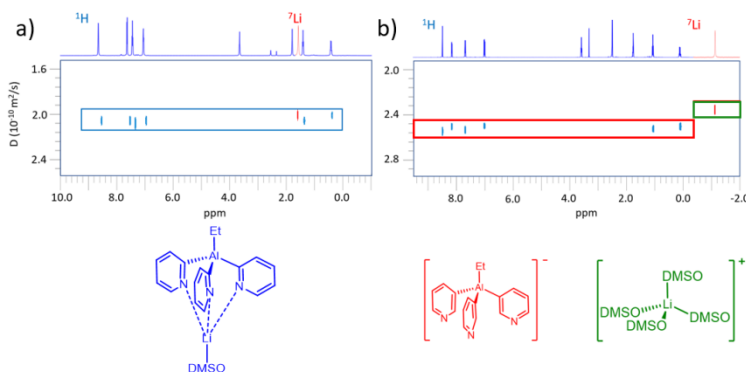


Figura 2. Estudios de ¹H y ⁷Li-DOSY para las especies [EtAl(2-py)₃]Li (a) y [EtAl(3-py)₃]Li (b) en DMSO-d₆.

En base a estos resultados, junto con una serie de cálculos DFT, sugerimos que la coordinación de ORH al Li⁺ facilita la reacción sobre el enlace Al-C, por lo que la incapacidad del tris(3-piridil) de coordinar de Li⁺ en disolución previene la existencia de especies que favorezcan el efecto cooperativo entre aluminio y litio otorgando una gran estabilidad al derivado tris(3-piridil).

Referencias

[1] R. García-Rodríguez, S. Hanf, A D. Bond, D. S. Wright, Chem. Commun. **2017**, 53, 1225-1228.

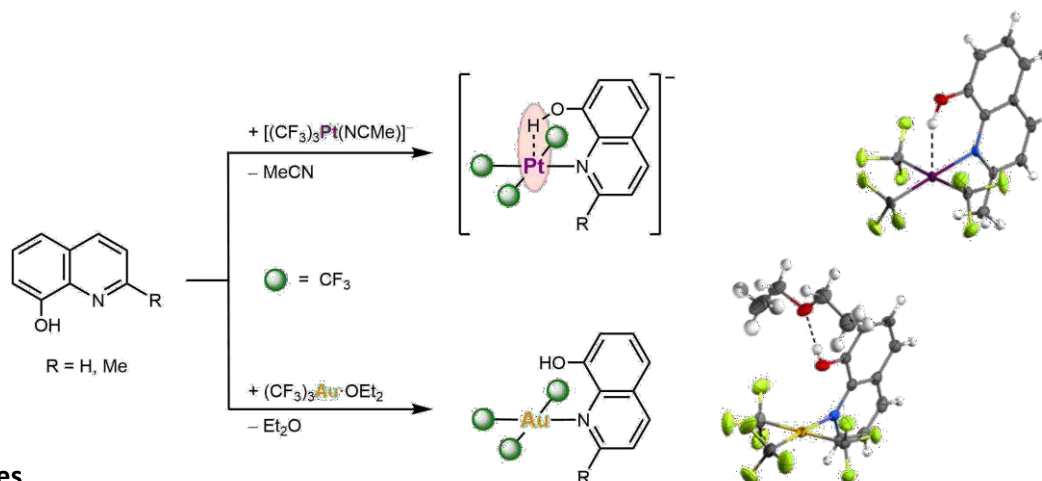
Au(III) DOES NOT FORM HYDROGEN BONDS: THE ROLE OF LIGAND-FIELD INVERSION

A. Pérez-Bitrián,^{1,2} M. Baya¹, J. M. Casas,¹ A. Martín,¹ B. Menjón¹

¹ Instituto de Síntesis Química y Catálisis Homogénea (iSQCH), CSIC-Universidad de Zaragoza, C/ Pedro Cerbuna 12, 50009 Zaragoza (Spain). E-mail: a.perez.bitrian@fu-berlin.de

² Current address: Freie Universität Berlin, Institut für Chemie und Biochemie – Anorganische Chemie, Fabeckstraße 34/36, 14195 Berlin (Germany).

Despite the huge progress accomplished in the development of gold chemistry, the role of gold as a hydrogen-bond acceptor has been a subject of much debate.[1] In fact, the involvement of Au(I) in M...HE interactions (M = metal; E = electronegative main-group element) has been clarified only recently.[2] Nevertheless, no conclusive evidence for Au(III) as a hydrogen-bond acceptor has been found thus far, contrary to the isoelectronic Pt(II) center, which is well known for establishing such interactions.[3] In this communication, the first experimental and theoretical evidence for the reluctance of Au(III) to act as a hydrogen-bond acceptor and a convincing explanation for this observation will be presented.[4] To do so, we have synthesized and characterized two series of isoleptic and isoelectronic (d^8) compounds $[(CF_3)_3Pt(L)]^-$ and $(CF_3)_3Au(L)$, where the ligands L are based on the quinoline frame and have been selected to favor the interaction with the metal center (see figure). Whereas strong hydrogen bonds were actually observed in the Pt(II) compounds, no such interactions were found in the Au(III) derivatives. The explanation for this drastic difference arises from the disparity in the electronic structures of these related species, which reveals ligand-field inversion[5] on going from Pt(II) to Au(III).



References

- [1] a) H. G. Raubenheimer, H. Schmidbaur, *J. Chem. Educ.*, **2014**, *91*, 2024-2036; b) H. Schmidbaur, H. G. Raubenheimer, L. Dobrzańska, *Chem. Soc. Rev.*, **2014**, *43*, 345-380.
- [2] a) M. K. Pandey, H. S. Kunchur, D. Mondal, L. Radhakrishna, B. S. Kote, M. S. Balakrishna, *Inorg. Chem.*, **2020**, *59*, 3642-3658; b) S. K. Verma, S. N. Ansari, P. Kumari, S. M. Mobin, *Organometallics*, **2019**, *38*, 2591-2596; c) M. Straka, E. Andris, J. Vícha, A. Růžička, J. Roithová, L. Rulíšek, *Angew. Chem. Int. Ed.*, **2019**, *58*, 2011-2016; d) M. Rigoulet, S. Massou, E. D. S. Carrizo, S. Mallet-Ladeira, A. Amgoune, K. Miqueu, D. Bourissou, *Proc. Natl. Acad. Sci. U. S. A.*, **2019**, *116*, 46-51.
- [3] J. Kozelka, in *Noncovalent Forces*, Ed. S. Scheiner, Springer, 2015, Ch. 6, pp. 129-158.
- [4] A. Pérez-Bitrián, M. Baya, J. M. Casas, A. Martín, B. Menjón, *submitted*.
- R. Hoffmann, S. Alvarez, C. Mealli, A. Falceto, T. J. Cahill, III, T. Zeng, G. Manca, *Chem. Rev.*, **2016**, *116*, 8173-8192.

COMUNICACIONES POSTER SESION B

INCORPORATING LiH MOLECULES INTO THE COORDINATION SPHERE OF Mo≡Mo BONDS.

M. Perez-Jimenez¹, N. Curado¹, C. Maya¹, J. Campos¹, J. Jover², S. Alvarez^{*2}, E. Carmona^{*1}

¹Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Consejo Superior de Investigaciones Científicas (CSIC) and University of Sevilla, Avda. Américo Vespucio, 49, 41092 Sevilla, Spain.

²Department de Química Inorgànica I Orgànica, Secció de Química Inorgànica, and Institut de Química Teòrica i Computacional Universitat de Barcelona Martí i Franquès 1-11, 08028 Barcelona, Spain.

Molecular hydrides of the s-block elements have been intensively investigated in recent years, although examples of lithium hydrides are scarce. [1-3] The reactions of LiAlH₄ as source of LiH with complexes that contain (H)Mo≡Mo and (H)Mo≡Mo(H) cores [4], stabilised by coordination to two bulky Ad^{Dipp₂} ligands (Ad^{Dipp₂} = HC(NDipp₂)₂; Dipp = 2,6-ⁱPr₂C₆H₃), result in the respective coordination of one and two molecules of LiH, with formation of complexes containing H–Mo≡Mo–H–Li five-membered rings. Attempts to construct a [Mo₂{HLi(thf)H}₃(μ-Ad^{Dipp₂})] molecular architecture led to spontaneous trimerisation and formation of a Mo₆Li₉H₁₈ cluster structure (Figure 1).

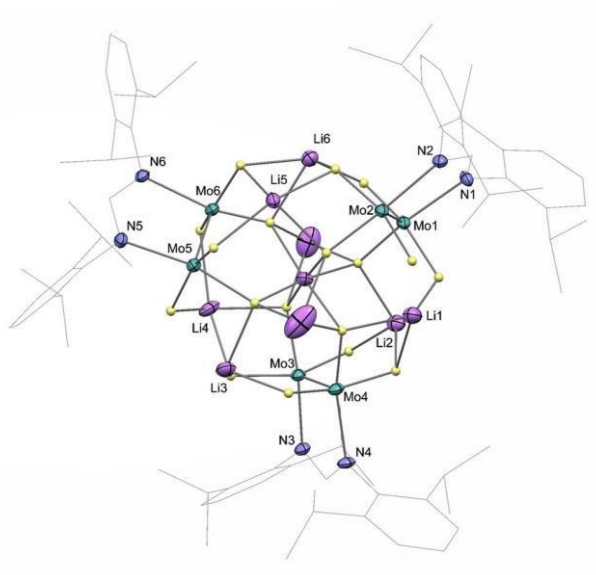


Figure 1: Solid molecular structure of [Mo₂{HLiH}₃(μ-Ad^{Dipp₂})]₃·(thf)₈.

References

- [1] A. Stasch, *Angew. Chem. Int. Ed.*, **2012**, *51*, 1930-1933.
 R. Campbell, D. Cannon, P. García-Alvarez, A. R. Kennedy, R. E. Mulvey, S. D. Robertson, J. Saßmannshausen, T. Tuttle, *J. Am. Chem. Soc.* **2011**, *133*, 13706-13717.
 S. D. Robertson, A. R. Kennedy, J. J. Liggat, R. E. Mulvey, *Chem. Commun.* **2015**, *51*, 5452-5455.
 (a) M. Perez-Jimenez, J. Campos, J. Lopez-Serrano, E. Carmona, *Chem. Commun*, **2018**, *54*, 9186-9189; (b) M. Perez-Jimenez, N. Curado, C. Maya, J. Campos, E. Ruiz, S. Álvarez, E. Carmona, *Chem. Eur. J.* **2021**, *27*, 1-11.

PB-02

HOMOCHIRAL IMIDAZOLIUM-BASED DICARBOXYLATE SILVER COMPOUNDS: STRUCTURE, SOLUTION BEHAVIOUR AND ANTIMICROBIAL ACTIVITY

A. Galindo,¹ F. Montilla,¹ E. Álvarez,² M. M. Conejo,¹ A. Pastor,¹ M. Pérez-Aranda,^{3,4} G. Martínez-Muñoz,³ B. Begines,³ A. Alcudia,³ and E. Pajuelo.⁴

¹ Departamento de Química Inorgánica, Universidad de Sevilla, Aptdo. 1203, 41071 Sevilla, galindo@us.es

² Instituto de Investigaciones Químicas, CSIC - Universidad de Sevilla, Avda. Americo Vespucio 49, 41092 Sevilla

² Departamento de Química Orgánica y Farmacéutica, Universidad de Sevilla, 41012 Sevilla

³ Departamento de Microbiología y Parasitología, Universidad de Sevilla, 41012 Sevilla

Chiral imidazolium-based dicarboxylate compounds have gained a renewed interest in last decades. They are convenient starting precursors for the synthesis of enantiopure substrates (e.g. NHC-carbene ligands and ionic liquids), employed as chirality inductors in asymmetric catalysis and also as linkers in the construction of homochiral coordination polymers [1-3]. In this communication, we present the synthesis of compounds $\{Ag[(S,S)\text{-}L^{\text{iPr}}]\}_n$ (**1s**), and $\{Ag[(R,R)\text{-}L^{\text{iPr}}]\}_n$ (**1r**), which were prepared by treatment of Ag_2O with (S,S) - and (R,R) -1-(1-carboxy-2-methylpropyl)-3-(1-carboxylate-2-methylpropyl)imidazolium compounds, respectively. They were obtained in good yields and characterized by analytical, spectroscopic and X-ray methods (for **1s**, Fig. 1a). At the solid state, they are one-dimensional coordination polymers in which silver cations are connected via chiral 2,2'-(imidazolium-1,3-diyl)bis(3-methylbutanoate) anion with an unprecedented $\mu_4\text{-}\kappa^2O, \kappa^1O', \kappa^1O''$ coordination mode (Fig. 1b). In solution, NMR showed partial dissociation and an H-D exchange was observed at the C²-H atom of imidazolium ring. In order to explain this behaviour, a transient carbene intermediate was proposed and corroborated by DFT calculations (Fig. 1c).

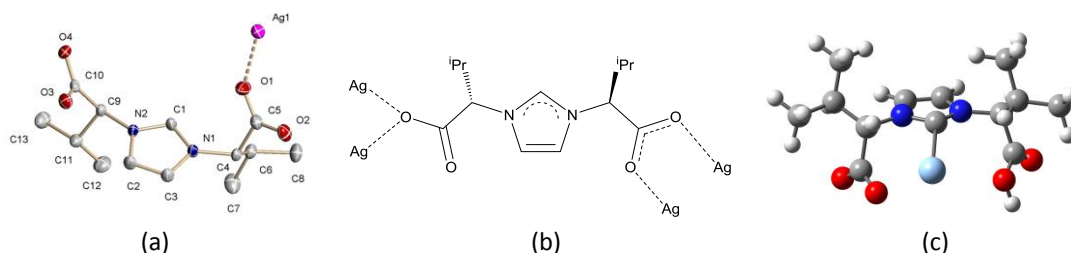


Fig. 1. (a) Asymmetric unit of $\{Ag[(S,S)\text{-}L^{\text{iPr}}]\}_n$ (**1s**). (b) Coordination mode of $[(S,S)\text{-}L^{\text{iPr}}]^-$ anion in the coordination polymer. (c) Optimized structure of carbene intermediate, isomer of **1s**.

Silver(I) complexes are well-known to possess antimicrobial activities and, for this reason, the activity of **1** complexes against selected bacteria (*E. coli* and *P. aeruginosa*) was evaluated by minimum inhibitory concentration (MIC), minimum bactericidal concentration (MBC) and biofilm development studies (see for example Fig. 2 for *P. aeruginosa*). These results clearly show that eutomer is complex **1r**.



Fig. 2. (A) *P. aeruginosa* control. (B) *P. aeruginosa* with **1r** at the MIC. (C) *P. aeruginosa* with **1r** at the MBC.

Referencias

- [1] P. Caballero, R. M. P. Colodrero, M. M. Conejo, A. Pastor, E. Álvarez, F. Montilla, C. J. Carrasco, A. I. Nicasio, A. Galindo, *Inorg. Chim. Acta*, **2020**, *513*, 119923.
- [2] E. Borrego, A. I. Nicasio, E. Álvarez, F. Montilla, J. M. Córdoba, A. Galindo, *Dalton Trans.*, **2019**, *48*, 8731-8739.
- [3] A. I. Nicasio, F. Montilla, E. Álvarez, R. P. Colodrero, A. Galindo, *Dalton Trans.*, **2017**, *46*, 471-482.

RING-OPENING COPOLYMERIZATION OF CYCLOHEXENE OXIDE AND CARBON DIOXIDE CATALYZED BY SCORPIONATE ZINC COMPLEXES

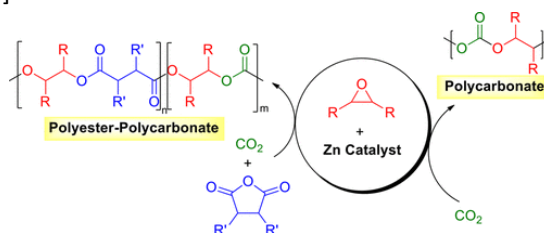
Agustín Lara-Sánchez^{1,*} Felipe de la Cruz-Martínez,¹ Javier Martínez,¹ Marc Martínez de Sarasa Buchaca, Juan Fernández-Baeza,¹ and José A. Castro-Osma^{2,*}

¹ Universidad de Castilla-La Mancha, Departamento de Química Inorgánica, Orgánica y Bioquímica-Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Ciencias y Tecnologías Químicas, 13071-Ciudad Real, Spain, e-mail: Agustin.Lara@uclm.es

² Universidad de Castilla-La Mancha, Departamento de Química Inorgánica, Orgánica y Bioquímica-Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Farmacia, 02071-Albacete, Spain.

The transformation of carbon dioxide into high-value added organic chemicals and polymers has received much attention in recent years as carbon dioxide is seen as an alternative carbon feedstock for a sustainable chemical industry.[1] One of the most relevant processes is the reaction of carbon dioxide with epoxides to afford polycarbonates.[2] The polycarbonates obtained using this methodology are a potential alternative to traditional aromatic polycarbonates, which involve the use of phosgene and Bisphenol-A, and to the polyether–polyols used to produce polyurethane foams. Several companies are currently working to commercialize the production of polycarbonates produced by ring-opening copolymerization of epoxides and carbon dioxide.

In view of the potential large-scale production of polycarbonates, it is highly desirable that catalysts for polycarbonate production are derived from biocompatible metals such as zinc as the quantity of catalyst present in the isolated polymers is usually high and may cause potential health issues associated with the toxicity of some metal-based residues.[3] Herein, we report the synthesis of new bimetallic NNO-scorpionate zinc acetate complexes $[\{Zn(\kappa^3\text{-NNO})\}\{\mu\text{-O}_2\text{CCH}_3\}_3\{Zn(\text{HO}_2\text{CCH}_3)\}]$ as catalysts for the production of polycarbonates from cyclohexene oxide and carbon dioxide and polyester-polycarbonate materials from the terpolymerization of cyclohexene oxide, phthalic anhydride, and CO_2 (Scheme 1).[4]



Scheme 1. ROCOP processes catalyzed by scorpionate zinc complexes.

References

- [1] M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.*, **2014**, *114*, 1709–1742; (b) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.*, **2015**, *6*, 5933–5948; (c) B. Yu, L.-N. He, *ChemSusChem*, **2015**, *8*, 52–62.
- [2] (a) X.-B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.*, **2012**, *41*, 1462–1484; (b) S. Paul, Y. Zhu, C. Romain, R. Brooks, P. K. Saini, C. K. Williams, *Chem. Commun.*, **2015**, *51*, 6459–6479; (c) C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.*, **2015**, *5*, 1353–1370.
- [3] J. Martínez, J.A. Castro-Osma, A. Lara-Sánchez, A. Otero, J. Fernández-Baeza, J. Tejada, L. F. Sánchez-Barba, A. Rodríguez-Diéguez, *Polym. Chem.*, **2016**, *7*, 6475–6484.
- [4] F. de la Cruz-Martínez, M. Martínez de Sarasa Buchaca, J. Martínez, J. Tejada, J. Fernández-Baeza, C. Alonso-Moreno, A. M. Rodríguez, J. A. Castro-Osma, A. Lara-Sánchez, *Inorg. Chem.*, **2020**, *59*, 8412–8423.

N-SUBSTITUTED AMINOBIPHENYL PALLADACYCLES SUPPORTED BY DIALKYLTERPHENYL PHOSPHINES

A. Monti¹, R. J. Rama¹, B. Gomez¹, C. Maya^{1,2}, E. Alvarez², E. Carmona², M. C. Nicasio¹

¹ Departamento de Química Inorgánica, Universidad de Sevilla, Aptdo 1203, 41071, Sevilla, Spain, e-mail: mandrea@us.es

² Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Consejo Superior de investigaciones Científicas (CSIC) and Universidad de Sevilla, Avenida Americo Vespucio 49, 41092, Sevilla, Spai

In recent years, several types of highly efficient Pd(II) precatalysts, able to generate and stabilize monoligated palladium(0) species, LPd(0), have been developed.[1] Among them, the family of 2-aminobiphenyl N,C-palladacycles has been widely studied and modified by Buchwald.[2] The remarkable catalytic activity of these palladacycle precatalysts rely on facile activation, in the presence of base, to yield the desired monoligated palladium(0) species.[3] Very recently, we have reported [4] on the synthesis and catalytic properties in C-N cross-coupling reactions of a series of 2-aminobiphenyl palladacycles stabilized by bulky dialkylterphenyl phosphines ligands. As an extension of these studies, neutral and cationic N-methyl- and N-phenyl-2-aminobiphenyl methanesulfonate palladacycles stabilized with dialkylterphenyl phosphines have been prepared and characterized (Fig. 1). The complexes have been evaluated for activity in C-N cross-coupling reactions and their activity compare to those of the unsubstituted 2-aminobiphenyl analogues.[5]

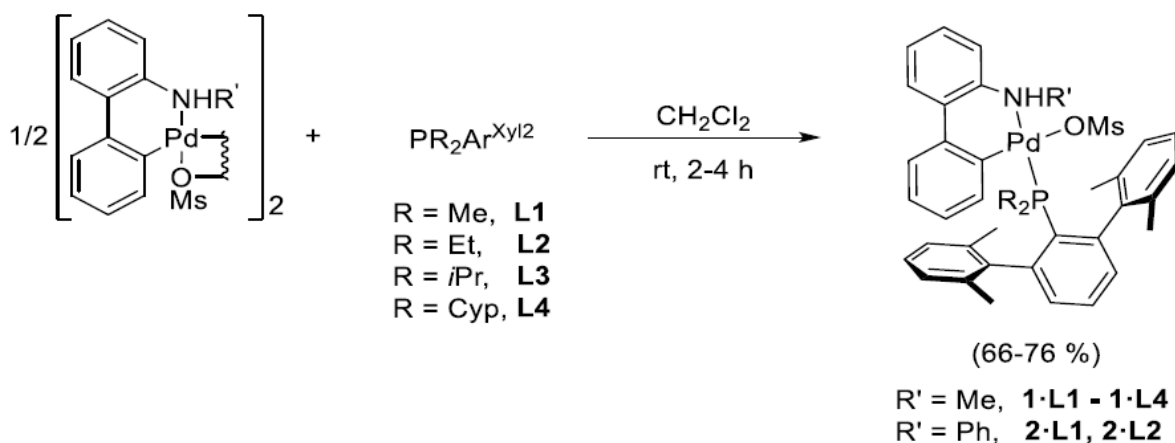


Figure 1: General synthesis of palladacycles

References

- [1] N. Hazari, P. R. Melvin, M. M. Beromi, *Nat. Chem.*, **2017**, *1*, 0025; (b) K. H. Shaughnessy, *Isr. J.Chem.* **2020**, *60*, 180.
- [2] (a) M. R. Biscoe, B. P. Fors, S. L. Buchwald, *J. Am. Chem. Soc.*, **2008**, *130*, 6686; (b) T. Kinzel, Y. Zhang, S. L. Buchwald, *J. Am. Chem. Soc.*, **2010**, *132*, 14073; (c) N. C. Bruno, M. T. Tudge, S. L. Buchwald, *Chem. Sci.*, **2013**, *4*, 916; (d) A. Bruneau, M. Roche, M. Alami, S. Messaoudi, *ACS Catal.*, **2015**, *5*, 1386.
- [3] (a) N. C. Bruno, S. L. Buchwald, *Org. Lett.*, **2013**, *15*, 2876; (b) N. C. Bruno, N. Niljianskul, S. L. Buchwald, *J. Org. Chem.*, **2014**, *79*, 4161.
- [4] R. J. Rama, C. Maya, M. C. Nicasio, *Chem. Eur. J.*, **2020**, *26*, 1064.
- [5] A. Monti, R. J. Rama, B. Gomez, C. Maya, E. Alvarez, E. Carmona, M. C. Nicasio, *Inorg. Chim. Acta*, **2021**, *518*, 120214.

PHOSPHORESCENT TRIS-CYCLOMETALATED Pt(IV) COMPLEXES WITH MESOIONIC N-HETEROCYCLIC CARBENE LIGANDS

Á. Vivancos,¹ D. Bautista,² and P. González Herrero.¹

¹ Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apdo. 4021, 30071, Murcia, Spain, angela.vivancos@um.es

² SAI, Universidad de Murcia, Apdo. 4021, 30071, Murcia, Spain

The synthesis, structure and photophysical properties of the first examples of tris-cyclometalated Pt(IV) complexes bearing chelating aryl-NHC ligands (C[∧]C*) are presented. Pt(IV) complexes with cyclometalated heteroaromatic ligands exhibit a notable combination of properties, including high-energy, long-lived luminescence and a strongly oxidizing character in the excited state.[1] Recently, we have reported the first Pt(IV) complex bearing a cyclometalated aryl-N-heterocyclic carbene ligand, demonstrating that the donor properties of the carbene moiety benefit the emission efficiencies of cyclometalated Pt(IV) complexes by increasing the energy of deactivating excited states of LMCT character in a greater extent than do 2-arylpyridines.[2]

In this study, we have developed a method to obtain the bis-cyclometalated species [Pt(C[∧]C*)₂Cl₂] with a C₂-symmetrical arrangement of C[∧]C* ligands. This complex is an excellent precursor for the synthesis of tris-cyclometalated complexes [Pt(C[∧]C*)₂(C[∧]N)]OTf upon heating it up with different 2-arylpyridines in the presence of silver triflate. Although the synthesized species present a meridional configuration of metalated aryls, they are photostable and photoluminescent, in sharp contrast to the related, nonemissive *mer*-[Pt(C[∧]N)₃]OTf complexes containing only 2-arylpyridine ligands.[1,3] The new species have proved efficient emitters in dichloromethane solution and poly(methyl methacrylate) (PMMA) matrices at room temperature.

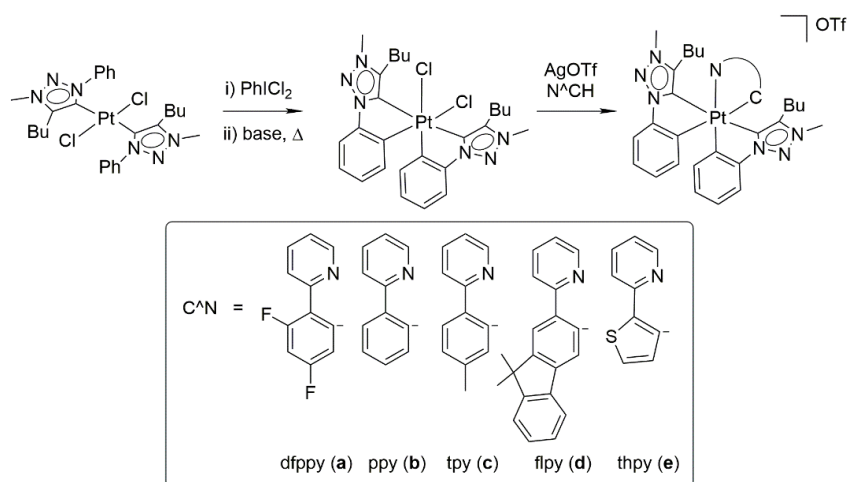


Figure 1. Synthesized [Pt(C[∧]C*)₂(C[∧]N)]OTf complexes.

Acknowledgements

We gratefully acknowledge the financial support from Ministerio de Economía y Competitividad (PGC2018-100719-B-I00) and Fundación Séneca (19890/GERM/15). A.V. thanks Fundación Séneca for a Saavedra Fajardo Fellowship (20398/SF/17).

Referencias

- [1] F. Juliá, D. Bautista, J. M. Fernández-Hernández, P. González-Herrero, *Chem. Sci.* **2014**, *5*, 1875–1880.
- [2] Á. Vivancos, D. Bautista, P. González-Herrero, *Chem. Eur. J.*, **2019**, *25*, 6014-6025.
- [3] F. Juliá, G. Aullón, D. Bautista, P. González-Herrero, *Chem. Eur. J.* **2014**, *20*, 17346–17359.

REACTIVITY OF PLATINUM(II) CYCLOMETALLATED COMPLEXES TOWARDS ACIDIC HYDROGENS

D. Campillo¹, A. Martín¹

¹ Departamento de química inorgánica, Facultad de Ciencias – ISQCH, Universidad de Zaragoza – CSIC, Zaragoza (Spain), davidcp@unizar.es

The basicity of the Pt(II) center in their square planar complexes has been advantageously used in the preparation of heteropolinuclear complexes containing Pt-M' donor-acceptor bonds,[1,2] being M' an acidic metal such as Ag(I), Tl(I), Au(I)... Recently, some of these complexes containing cyclometallated ligands at the Pt environment, [Pt(CNC)L], have been investigated as possible models of arrested intermediates in bimetallic catalysis,[3] since they show short interactions in the solid state between the C_{ipso} of the platinum cyclometallated ligand and the acidic metal Ag(I) or Au(I).

With this results in mind, we have now explored the behaviour of the basic [Pt(CNC)L] substrates towards a different electrophile such as acidic hydrogens. There is a well-known isolobal relationship between the "M(PPh₃)⁺" fragment, being M a group 11 metal with oxidation state of 1, and the proton.[4] Therefore we present in this contribution the study of reactivity of neutral cyclometallated platinum complexes [Pt(CNC)(PPh₃)] (**1**) and [Pt(CNC)(dmsO)] (**2**) (CNC = 2,6-diphenylpyridinate) towards acidic hydrogens.

We can relate these results with the formation of the Pt(II)-M(I) complexes mentioned above. In the protonated complexes reported here, a similar initial Pt-H complex could be formed which quickly evolves giving rise to the protonation of one of the rings. This process is being investigated by computational means.

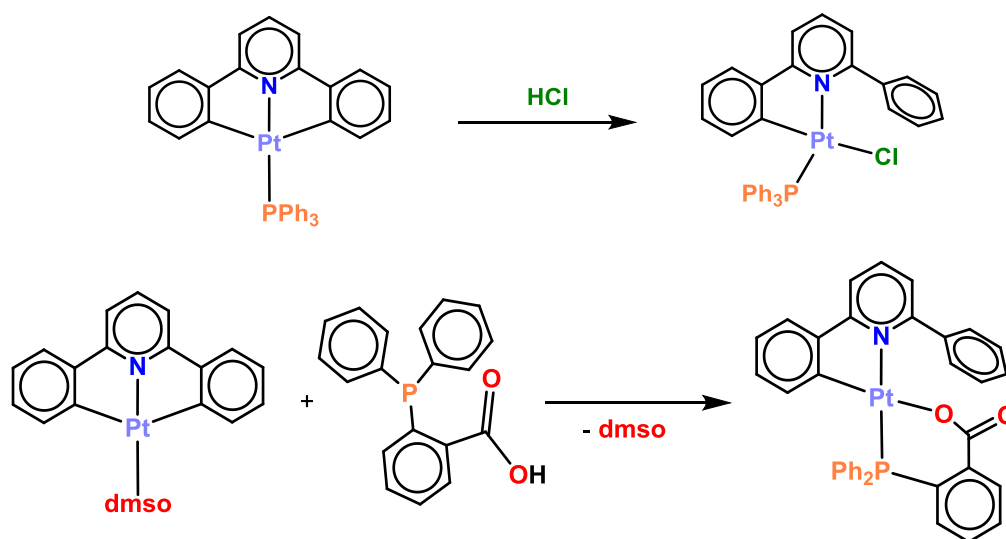


Figure 1.- Examples of protonation reactions

References

- [1] A. Díez, E. Lalinde, M. T. Moreno, *Coord. Chem. Rev.*, **2011**, 255, 2426-2447.
- [2] D. Campillo, Ú. Belío, A. Martín, *Dalton Trans.*, **2019**, 48, 3270-3283.
- [3] M. Baya, Ú. Belío, D. Campillo, I. Fernández, S. Fuertes, A. Martín, *Chem. Eur. J.*, **2018**, 24, 13879-13889.
- [4] H. G. Raubenheimer, H. Schmidbaur, *Organometallics*, **2012**, 31, 2507-2522.

PB-07

DESARROLLO DE COMPUESTOS ORGANOMETÁLICOS LUMINISCENTES CON ESQUELETO OXAZOLONA

D. Dalmau¹, A. Pop², C. Silvestru², A. I. Jiménez¹, O. Crespo¹, E. P. Urriolabeitia,¹

¹ Instituto de Síntesis Química y Catálisis Homogénea (ISQCH, CSIC-Universidad de Zaragoza), Pedro Cerbuna 12,50009 Zaragoza, 683763@unizar.es

² Supramolecular Organic and Organometallic Chemistry Centre, Departament of Chemistry, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Str. Arany Janos 11, RO-400028 Cluj-Napoca, Romania

La búsqueda de nuevos compuestos luminiscentes es un tema de investigación de gran interés debido a la gran cantidad de aplicaciones industriales que presentan este tipo de compuestos: electroluminiscencia en televisiones, fotoluminiscencia en sondas y marcadores biológicos, etc.[1]

Un tipo concreto de compuestos organometálicos objeto de estudio en nuestro grupo de investigación son los que presentan un esqueleto de tipo oxazolona[2], cromóforo análogo al encontrado en la GFP (Green Fluorescent Protein) y que presenta una intensa fluorescencia. A pesar de su gran interés, el comportamiento fotofísico de estos cromóforos en disolución está muy condicionado a la presencia de un entorno rígido para la obtención de una alta luminiscencia, y por ende es preciso eliminar vías de desactivación no radiativa, como el "hula-twist" (Figura 1 izda), por anclaje intramolecular del anillo 4-arilideno y del heterociclo azlactona.[3,4]

En nuestro grupo de investigación se ha llevado a cabo el anclaje intramolecular por incorporación de un metal a la estructura de la oxazolona, uniendo el anillo arilideno y la azlactona. La unión al grupo arilideno se produce por activación C-H directa o por transmetalación (Figura 1, dcha). Esta ortometalación genera un entorno rígido, cuya consecuencia directa es la amplificación de la fluorescencia. El posterior intercambio de ligandos en el producto ortometalado final lleva a una modulación adicional de dicha fluorescencia.

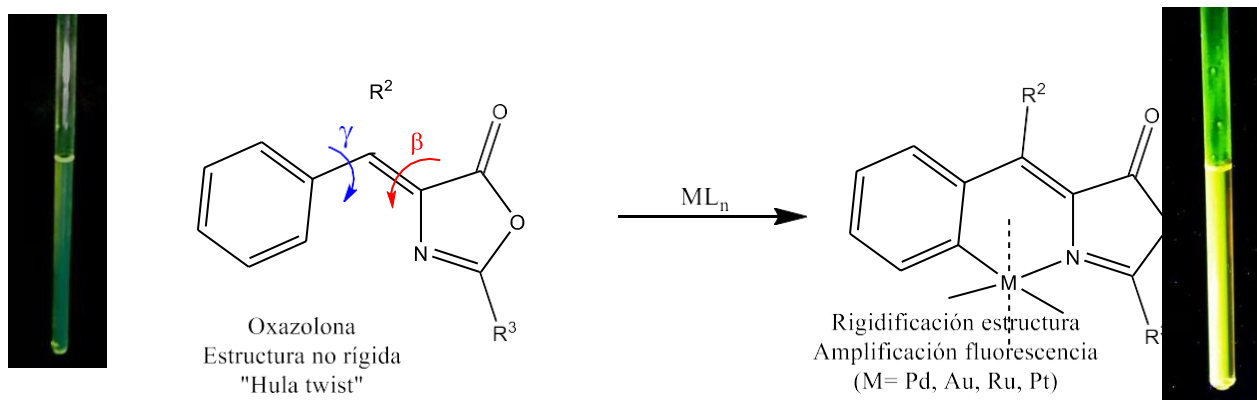


Figura 1. Anclaje intramolecular de oxazolonas y amplificación de la fluorescencia

Referencias

- [1] S. O. Kasap y P. Capper, Eds., *Springer handbook of electronic and photonic materials*. New York: Springer, 2006.
- [2] G.-D. Roiban *et al.*, «Regioselective Orthopalladation of (Z)-2-Aryl-4-Arylidene-5(4 H)-Oxazolones: Scope, Kinetic-Mechanistic, and Density Functional Theory Studies of the C–H Bond Activation», *Inorg. Chem.*, **2011**, vol. 50, n.º 17, pp. 8132-8143.
- [3] S. Collado *et al.*, «Orthopalladation of GFP-Like Fluorophores Through C-H Bond Activation: Scope and Photophysical Properties: Orthopalladation of GFP-Like Fluorophores Through C-H Bond Activation: Scope and Photophysical Properties», *Eur. J. Org. Chem.*, **2018**, vol. 2018, n.º 44, pp. 6158-6166.
- [4] L. Wu y K. Burgess, «Syntheses of Highly Fluorescent GFP-Chromophore Analogues», *J. Am. Chem. Soc.*, **2008**, vol. 130, n.º 12, pp. 4089-4096.

PB-08

INFLUENCIA DE LA PRESENCIA DE ÁCIDOS DE LEWIS DE TIPO SIGMA Y PI SOBRE LA EFICIENCIA EN LAS REACCIONES DE ADICIÓN OXIDANTE DE TRIFLATOS DE ARILO A COMPLEJOS DE Ni(0) ESTABILIZADOS POR LIGANDO HÍBRIDOS P-N ENOLIZABLES

Diego A. Cabo, Tomas G. Santiago y Juan Campora*

Departamento de Química Organometálica y Catálisis Homogénea. IIQ-CSIC

La adición oxidante representa uno de los procesos más básicos y utilizados en química organometálica. Este término es usado para designar un tipo de reacción en la cual la oxidación de un complejo metálico por parte de un electrófilo está acompañada por un incremento de su número de coordinación y de su número de oxidación en dos unidades [1,2].

En nuestro grupo hemos emprendido un estudio experimental comparativo de las reacciones de Heck catalizadas por Ni, cuyo objetivo principal es establecer los puntos en los que este metal resulta inferior al Pd, el metal que se emplea de manera habitual en este tipo de reacciones. Para ello nos centramos en un sistema modelo constituido por complejos de Ni(0), estabilizados por ligandos híbridos iminofosfina e iminopiridina enolizables, los cuales permiten investigar de manera separada cada una de las etapas del proceso catalítico. En este trabajo abordamos el estudio de la primera etapa de este proceso, la adición oxidante de triflatos o haluros de Ni a especies de Ni(0) estabilizadas por ligandos híbridos P-N.

Hemos estudiado la influencia de diferentes factores en la optimización de la adición oxidante, como la concentración de olefina (acrilato de metilo) o la presencia de sales de litio en el medio de reacción. Se observa que las adiciones oxidantes realizadas con triflatos son reacciones más complejas que con haluros, debido a la labilidad del enlace de triflato con el Ni, frente a la mayor estabilidad de los haluros con el metal. De igual modo, se aprecia que la velocidad de la adición oxidante es inversamente proporcional a la cantidad de olefina en el medio. Esto puede apreciarse en vista a los seguimientos obtenidos por medio de equipos de RMN.

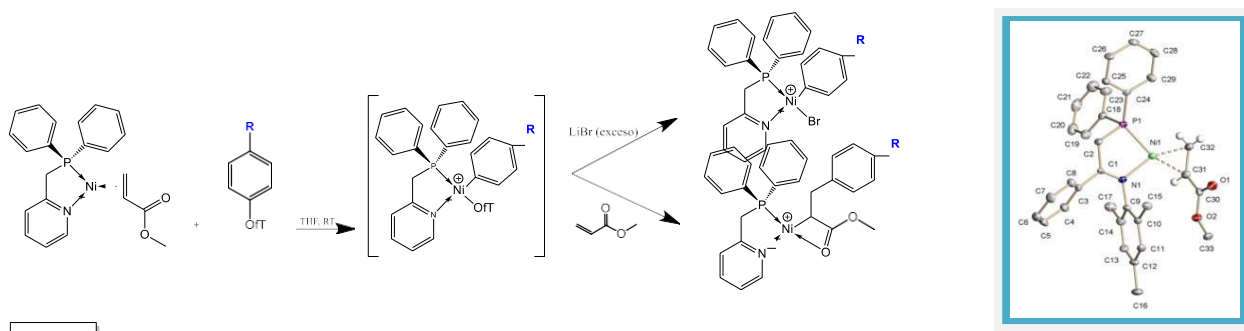


Figura 1. Esquema de formación de complejos con LiBr y Acrilato de metilo, tras reacción de adición oxidante del ligando de piridina con triflato aromático, junto a imagen estructural por Rayos X, de compuesto de Ni(0) con ligando híbrido P-N enolizable análogo al ligando de piridina.

Referencias

[1] Sarah Z. Tasker*, Eric A. Standely* and Timothy F. Jamison, *Nature*, **2014**, *509*, 299-309 [2] T.T. Tsou, J. K. Kochi, *J. Am. Chem. Soc.*, **1979**, *101*:21, 6319-6332

HIDROXILACIÓN DIRECTA DE BENCENO CATALIZADA POR COMPLEJOS DE COBRE (I) CON OXÍGENO MOLECULAR

Elena Borrego Blanco¹, Agustí Lledós², Ana Caballero^{1*}, Pedro. J. Pérez^{1*}

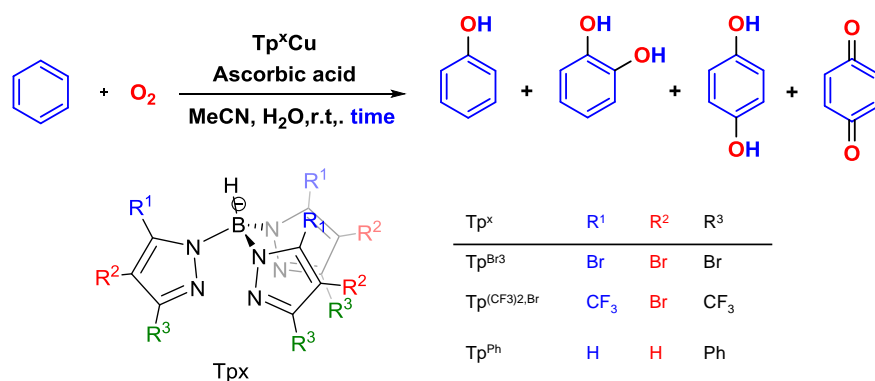
¹ Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva, 21007-Huelva, España

² Departament de Química, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Barcelona, España

El fenol es un intermedio de gran valor industrial cuyo proceso de síntesis, el proceso del cumeno, presenta diversos problemas entre los que destaca un rendimiento global inferior al 5% con respecto al benceno. Esto ha provocado, que el desarrollo de nuevos catalizadores capaces de producir la conversión directa de benceno a fenol usando como oxidantes, el O₂ o el H₂O₂, entre otros, constituya un área de interés constante.

Nuestro grupo ha logrado describir una serie de complejos bio-inspirados de cobre con ligandos de tipo trispirazoliilboratos (Tp^x) como catalizadores capaces de llevar a cabo la oxidación de enlaces C-H alifáticos [1] y aromáticos en presencia de H₂O₂ [2,3]. Recientemente, se ha demostrado que este tipo de complejos pueden ser capaces de producir la activación de O₂ bajo presión y temperatura ambiente [4].

En este trabajo se describen varios complejos de cobre con ligandos Tp^x, Tp^xCuL, como potenciales catalizadores para la oxidación de benceno con oxígeno molecular, usando mezclas homogéneas de acetonitrilo/agua como medio de reacción. Se ha observado que estos complejos son capaces de dar lugar a transformaciones (sub)estequiométricas directas de benceno a fenol al reaccionar con oxígeno a temperatura ambiente en presencia de ácido ascórbico. Los estudios DFT y los resultados experimentales, donde la cantidad máxima alcanzada de producto es la mitad de la de catalizador, sugieren que tanto la formación de fenol como la activación de oxígeno requiere la presencia de dos unidades de cobre.



Referencias

- [1] Conde, A.; Vilella, L.; Balcells, D.; Díaz-Requejo, M. M.; Lledós, A.; Pérez, P. J. *J. Am. Chem. Soc.*, **2013**, *135*, 3887-3896.
- [2] Conde, A.; Díaz-Requejo, M. M.; Pérez, P. J. *Chem. Commun.* **2011**, 47, 8154–8156.
- [3] Vilella, L.; Conde, A.; Balcells, D.; Díaz-Requejo, M. M.; Lledós, A.; Pérez, P. J. *Chem. Sci.* **2017**, *8*, 8373.
- [4] Álvarez, M.; Molina, F.; Frutos, M. R.; Urbano, J.; Álvarez, E.; Sodupe, M.; Lledós, A.; Pérez, P. J. *Dalton Trans*, **2020**, 49, 14647-14654.

SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF AMINO ACID-DERIVED N-HETEROCYCLIC CARBENE SILVER COMPLEXES

F. Montilla,¹ A. Sánchez-Hernández,¹ C. Carrasco,¹ A. Galindo,¹ M. Pérez-Aranda,^{2,3} G. Martínez-Muñoz,² B. Begines,² A. Alcudia,² E. Pajuelo.³

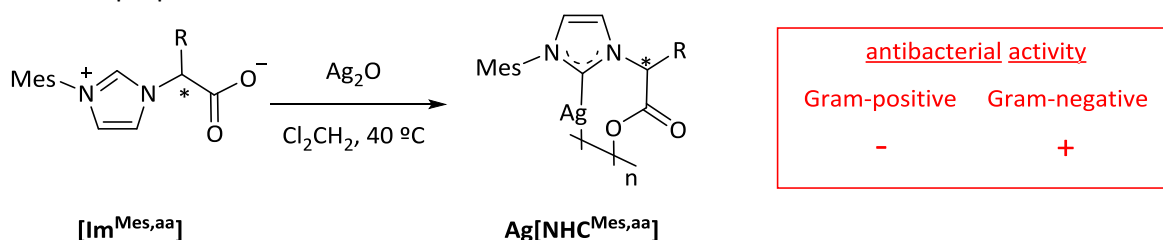
¹ Departamento de Química Inorgánica, Universidad de Sevilla, Aptdo. 1203, 41071 Sevilla, montilla@us.es

² Instituto de Investigaciones Químicas, CSIC - Universidad de Sevilla, Avda. Americo Vesputio 49, 41092 Sevilla

² Departamento de Química Orgánica y Farmacéutica, Universidad de Sevilla, 41012 Sevilla.

³ Departamento de Microbiología y Parasitología. Universidad de Sevilla, 41012 Sevilla.

The antimicrobial properties of silver has been known since ancient times, a use that continued until middle of the past century, when antibiotics (e.g. penicillin) replaced silver in most bacterial infection treatments. However, the evolution of antimicrobial resistance to most of common antibiotics led to resurgence in the use of silver as biocide agent [1]. Thus, during recent decades, different silver(I) complexes have shown excellent antibacterial activity (e.g. silverfulfadiazine is usually used in burns treatments). Particularly, silver(I)-N-Heterocyclic carbene (Ag(I)-NHC) complexes have shown strong antimicrobial properties against many Gram-negative as well as Gram-positive bacterial strains [2]. On the other hand, the use of amino acids for the synthesis of ligands is a simple strategy to generate bio-inorganic metal systems. In this regard, our group have recently reported the use of chiral amino acid-derived imidazole-type compound (imidazolium-dicarboxylate and/or imidazole-carboxylate) as ligands for the synthesis of chiral coordination polymers [3] or as chiral inductors in asymmetric catalysis [4]. In this communication, we present the synthesis of silver(I)-NHC complexes ($\text{Ag}[\text{NHC}^{\text{Mes,aa}}]$), which were prepared by treatment of Ag_2O with amino acid-derived imidazolium precursors, $[\text{Im}^{\text{Mes,aa}}]$ (Mes = 2,4,6-trimethylphenyl; aa = glycine, L-alanine, D-alanine, L-valine) [5]. The biocide effectiveness of the Ag(I)-NHC complexes were tested on Gram-positive (*Staphylococcus pseudintermedius* y *Staphylococcus aureus*) and Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteria. The minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) values showed that these complexes are really active against the Gram-negative strains. Furthermore, it was observed that the structure-activity relationship was important in the display of antimicrobial properties.



Referencias

- [1] S. Chernousova, M. Epple, *Angew. Chemie - Int. Ed.*, **2013**, 52, 1636–1653.
- [2] A. Kascatan-Nebioglu, M. J. Panzner, C. A. Tessier, C. L. Cannon, W. J. Youngs, *Coord. Chem. Rev.*, **2007**, 251, 884–895.
- [3] E. Borrego-Blanco, A. I. Nicasio, E. Alvarez González, F. Montilla, J. M. Córdoba, A. Galindo, *Dalton Trans.*, **2019**, 48, 8731–8739.
- [4] C. Carrasco, F. Montilla, A. Galindo, *Molecules*, **2018**, 23, 1595.
- [5] J. Thongpaen, T. E. Schmid, L. Toupet, V. Dorcet, M. Mauduit, O. Baslé, *Chem. Commun.*, **2018**, 54, 8202–8205.

PB-11

PALLADIUM-CATALYZED AEROBIC OXIDATIVE HECK REACTION OF ARENES
ENABLED BY [2,2'-BIPYRIDIN]-6(1H)-ONE

Francisco Villalba, Ana C. Albéniz

IU CINQUIMA/Química Inorgánica. Universidad de Valladolid. 47011 Valladolid (Spain) francisco.villalba@uva.es;
albeniz@qi.uva.es

The palladium-catalyzed aerobic oxidative Heck reaction of simple arenes has been developed using atmospheric pressure of molecular oxygen as the sole oxidant. The employment of oxygen as a cheap and non-toxic oxidant in the absence of co-oxidant is an environmentally benign route over other metal oxidants since it generates water as a by-product. This reaction is promoted by the [2,2'-bipyridin]-6(1H)-one (bipy-6-OH) ligand developed by our group.¹ The deprotonated coordinated ligand acts as an internal base and assists the cleavage of the C–H bond in a cooperating way.

Direct coupling of non-prefunctionalized arenes with olefins represents an important reaction to create molecular building blocks in organic synthesis. Our approach is useful to a number of simple arenes with different intrinsic electronic features (Figure 1). Finally, some mechanistic details are discussed with all the results collected from this reaction.

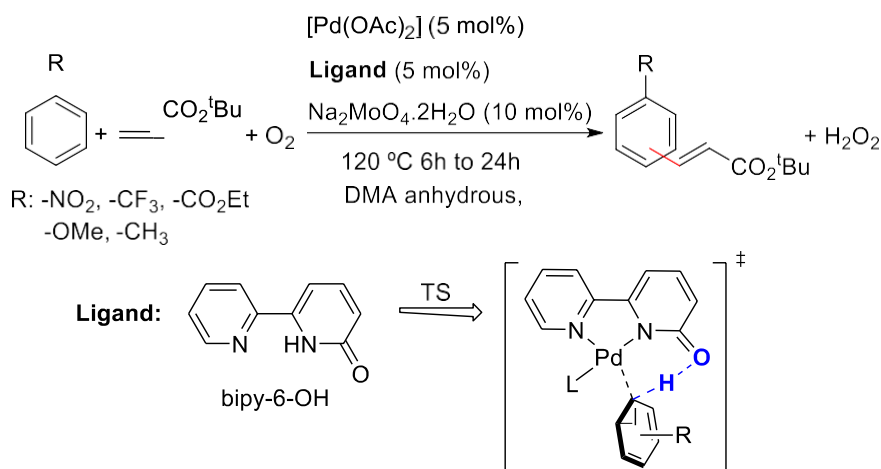


Figure 1. Aerobic oxidative Heck reaction of simple arenes with *tert*-butylacrylate catalyzed by palladium complexes with the bipy-6-OH ligand.

Referencias

[1] Salamanca, V.; Toledo, A.; Albéniz, A. C. [2,2'-Bipyridin]-6(1H)-one, a Truly Cooperating Ligand in the Palladium-Mediated C–H Activation Step: Experimental Evidence in the Direct C-3 Arylation of Pyridine. *J. Am. Chem. Soc.* **2018**, *140*, 17851-17856.

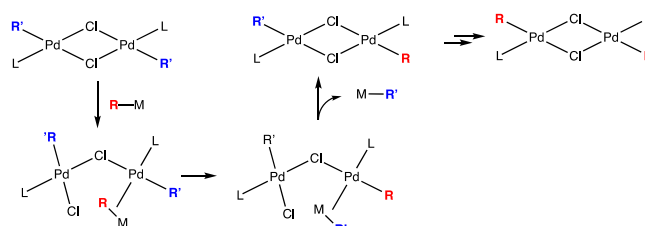
SIMILARITIES BETWEEN GOLD AND ZINC IN ARYL BY ALKYL EXCHANGE REACTION WITH PALLADIUM DIMERS

G. Marcos-Ayuso¹, D. Carrasco¹, J.A. Casares¹

IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071, Valladolid,
Guillermo.marcosayuso@gmail.com

The widespread use of bulk ligands in palladium catalyzed cross-coupling reactions has extended the scope of this synthetic methodology and usually allows mild reaction conditions. The particularity of these ligands is that the geometry of the intermediates changes as consequence of their steric requirements, changing almost all the steps of the reaction mechanisms. For instance, very often after the oxidative addition the expected square-planar intermediate is not able to accept two bulky ligands producing instead tricoordinate intermediates or dimeric structures with halides acting as bridges between the palladium centers. The transmetalation on these intermediates is quite different than the transmetalation on classical square planar complexes of the type $[PdXRL_2]$, which have been profusely studied.

The main objective of the present work is the study of transmetalation reactions between palladium dimers with halogen bridges of the type $trans-[Pd_2(\mu-X)_2Rf_2L_2]$ ($L = PPh_3, PCy_3, PMe_3$) and organozinc or organogold(I) complexes. Transmetalation experiments on the isolated intermediates show that, irrespectively of the reagent used, the reaction lead to the exchange of the organic radicals between the metals instead of the substitution of the halide and the subsequent reductive elimination.



Scheme 1

Kinetic experiments indicate that the mechanism involves the rupture of one bridge chlorine in the dimer by the incoming nucleophilic reagent and the exchange of the organic radicals in the palladium frame that bears the nucleophile (Scheme 1). The preference for this reaction site is derived from the fact that substitution of the phosphine should provide a ΔG_{323}^\ddagger value about 23 kcal mol⁻¹ while the halogen-bridge rupture should be much less energetic, with a ΔG_{323}^\ddagger value found for this reaction of only 17.7 kcal mol⁻¹.

DFT calculations carried out show a low barrier to the exchange reaction from the intermediate containing an M-M' bond, as shown in Figure 1.

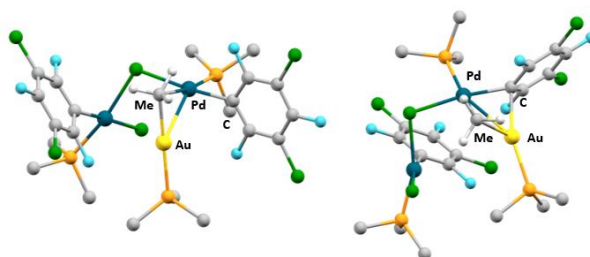


Figure 1. DFT optimized structures of M-M' intermediate between $trans-[Pd_2(\mu-Cl)_2Rf_2(PMe_3)_2]$ and $[AuMePMe_3]$ and TS1 for the exchange reaction.

Referencias

- [1] delPozo, J.; Gioria, E.; Casares, J. A.; Álvarez, R. and Espinet, P. *Organometallics*, **2015**, 34, 3120–3128.
[2] Pérez-Temprano, M.; Casares, J. A.; deLera, A. R.; Alvarez, R. and Espinet, P. *Angew. Chem. Int. Ed.* **2012**, 51, 4917–4920.

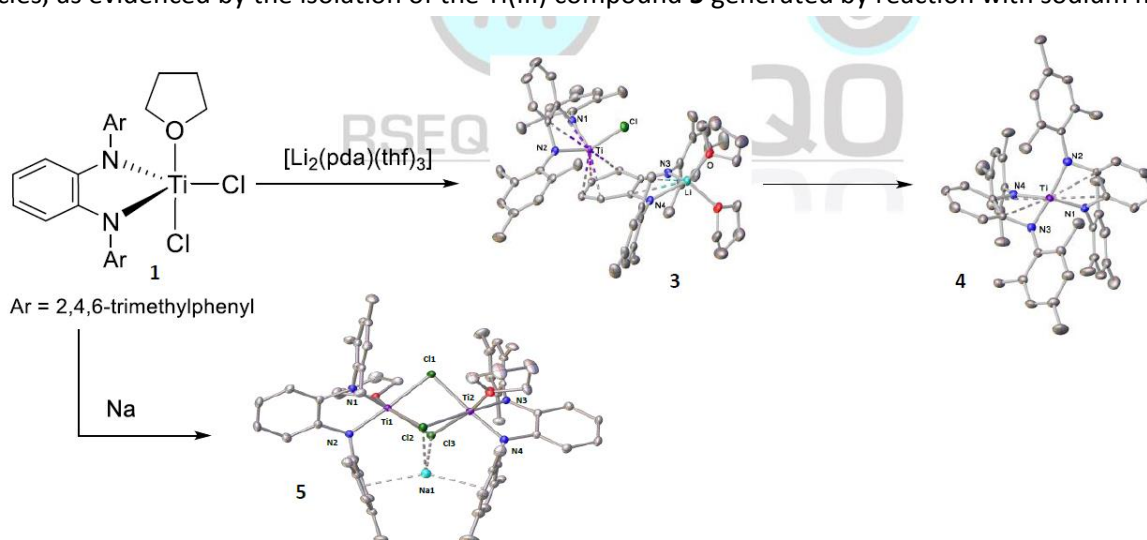
SYNTHESIS AND CHEMICAL REDUCTION OF TITANIUM COMPOUNDS SUPPORTED BY A REDOX ACTIVE LIGAND

A. Hernán-Gómez,¹ M. Mena,¹ I. Sancho,¹ C. Santamaría¹

¹ Department of Organic and Inorganic Chemistry, University of Alcalá, i.sancho@uah.es

Reduced early transition metals supported by redox-active ligands are very attractive species due to their ability to enable multielectron redox reactions such as activation of molecular nitrogen or oxygen.^[1] This has been attributed to a cooperative effect in which the provided electrons come from both the electron-rich metal and the ligand able to adopt multiple oxidation states, acting as an additional electron reservoir. In this context, *ortho*-phenylenediamine (H₂pda) ligands, that can behave as the dianionic *o*-phenylenediamido (pda²⁻), monoanionic *o*-diiminosemiquinonate (pda⁻), or neutral *o*-benzoquinonediimine (pda⁰), have proved to be very effective in stabilizing low oxidation state compounds of main group and late transition metals.^[2] In contrast, studies on the synthesis of reduced group 4 metal compounds using these pda ligands have not been reported.

Herein, we present a family of titanium species supported by one (**1**) or two pda ligands (**4**) prepared via transmetalation reactions. According to a more energetically demanding second transmetalation, it was possible to isolate intermediate **3** in which only partial substitution occurred. Preliminary studies on the chemical reduction of **1** confirm the ability of the pda ligand to stabilize low oxidation state titanium species, as evidenced by the isolation of the Ti(III) compound **5** generated by reaction with sodium metal.



Referencias

[1] a) C. Milsmann, S.P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.*, **2014**, 136, 12099-12107. b) P. J. Chirik, K. Wieghardt, *Science*, **2010**, 327, 794-795. c) W. B. Tollman, *Activation of Small Molecules: Organometallic and Bioinorganic Perspectives*, Ed: Wiley-VCH, **2006**.

[2] For a recent article see: M. Ma, L. Shen, H. Wang, Y. Zhao, B. Wu, X.-J. Yang, *Organometallics*, **2020**, 39, 1440-1447.

SÍNTESIS DE COMPLEJOS DE IRIDIO BASADOS EN LIGANDOS CNN DERIVADOS DE LA LUTIDINA. APLICACIÓN EN LA DESHIDROGENACIÓN DE NH_3BH_3

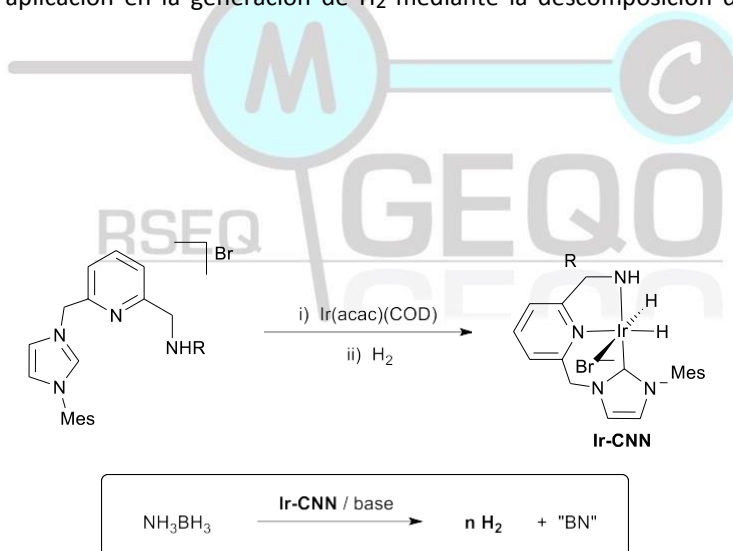
I. Ortega-Lepe, P. Sánchez, L. L. Santos, N. Rendón, E. Álvarez, A. Suárez

Instituto de Investigaciones Químicas (CSIC y Universidad de Sevilla) Centro de Innovación en Química Avanzada (ORFEO-CINQA)

Isabel.ortega@iiq.csic.es

El empleo de complejos metálicos basados en ligandos que incorporan una función ácido/base de tipo Brønsted ha conducido a catalizadores muy eficientes en una amplia diversidad de procesos de hidrogenación y deshidrogenación.¹ Entre estos derivados, cabe destacar los complejos que poseen ligandos pincer derivados de la lutidina,² así como aquellos que incorporan un grupo donador amino secundario.³ El tratamiento con una base adecuada de estos complejos produce la desprotonación reversible de los metilenos de la lutidina o del grupo amino, respectivamente, dando lugar a especies que pueden participar en la activación de enlaces X-H (X = H, heteroátomo).

Recientemente, nuestro grupo de investigación ha sintetizado complejos de rutenio basados en ligandos derivados de la lutidina que incorporan un grupo donador carbeno N-heterocíclico y otro de tipo amino (CNN).⁴ Estos derivados han dado lugar a catalizadores eficientes para la hidrogenación y la deshidrogenación de N-heterociclos. En esta contribución se describe la síntesis de nuevos complejos de iridio basados en estos ligandos CNN, así como un estudio preliminar de su aplicación en la generación de H_2 mediante la descomposición del aducto de borano del amoníaco.⁵



Referencias

- [1] Khusnutdinova, J. R.; Milstein, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 12236.
- [2] Milstein, D. *Philos. Trans. R. Soc. A* **2015**, *373*, 20140189
- [3] Zhao, B.; Han, Z.; Ding, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 4744.
- [4] Sánchez, P.; Hernández-Juárez, M.; Rendón, N.; López-Serrano, J.; Santos, L. L.; Álvarez, E.; Paneque, M.; Suárez, A. *Dalton Trans.* **2020**, *49*, 9583.
- [5] Rossin, A.; Peruzzini, M. *Chem. Rev.* **2016**, *116*, 8848.

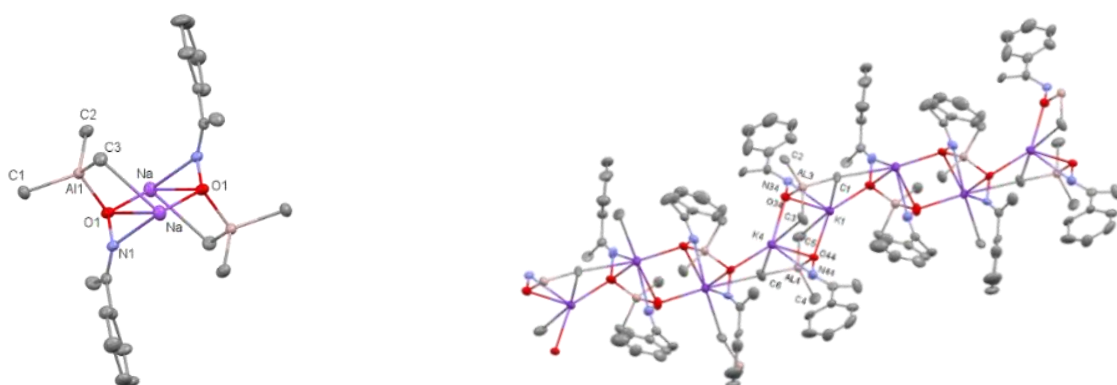
STUDIES OF ALUMINATE COMPOUNDS BASED ON OXIMATE LIGANDS

Jesús. Damián Burgoa¹, Tomás. Cuenca¹ and Marta. E.G. Mosquera¹

¹Departamento de Química Orgánica y Química Inorgánica. Instituto de Investigación en Química "Andrés M. del Río". Universidad de Alcalá. Alcalá de Henares, Madrid. jesus.damian@edu.uah.es

Aluminium is the most abundant metal on Earth's crust and displays a very attractive chemical behavior.[1] Aluminates are a very interesting type of species where the aluminium atom is combined with a more electropositive metal, such as an alkaline metal, frequently through a bridging ligand. A type of ligand that has been rarely explored for the preparation of these heterometallic species is the oximate, in fact there is only another example reported for aluminates.[2] In this communication, we present the synthesis of new aluminate compounds with oximates acting as bridging ligands.

Using the methodology frequently employed in our group,[3] we initially treated the oxime with an alkali metal base and an insoluble solid precipitate. The addition of AlMe_3 to this solid leads to the formation of the new oximate derivatives **1** and **2** that present unprecedented solid-state structures. A different outcome is observed for the sodium and potassium compounds. In the first case, the derivative $[\text{NaAlMe}_3(\text{OR})_2]_2$ (**1**) is formed as the only product of the reaction (figure 1). However, when potassium is the alkali metal, the final species isolated **2** is an aggregate of the derivatives $[\text{KAlMe}_2(\text{OR})_2]_2$ and $[\text{KAlMe}_3(\text{OR})_2]_2$ that are combined generating a chain (figure 2). These chains are arranged in layers via $\text{Me}\cdots\text{M}$ interactions in the crystal packing.



References

- [1] P.P. Power, *Chem. Rev.*, 1999, 99, 3463. S. Woodward, S. Dagorne, *Modern Organoaluminum Reagents*, Springer, 2012; H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* 1980, 18, 99; E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* 2000, 100, 1391.
- [2] Fernandez-Millan, M.; Temprado, M.; Cano, J.; Cuenca, T.; Mosquera, M. E. G. *Dalton Trans.* 2016, 45, 10514–10518.
- [3] M. T. Muñoz, C. Urbaneja, M. Temprado, M. E. G. Mosquera, T. Cuenca, *Chem. Commun.* **2011**, 47, 11757; M. T. Muñoz, T. Cuenca, M. E. G. Mosquera, *Dalton Trans.* **2014**, 43, 14377. F. M. García-Valle, V. Tabernero, T. Cuenca, J. Cano, M. E. G. Mosquera, *Dalton Trans.*, **2018**, 47, 6499.

GRAPHENE-SUPPORTED AU-NPs FOR CARBENE TRANSFER REACTIONS FROM DIAZOCOMPOUND

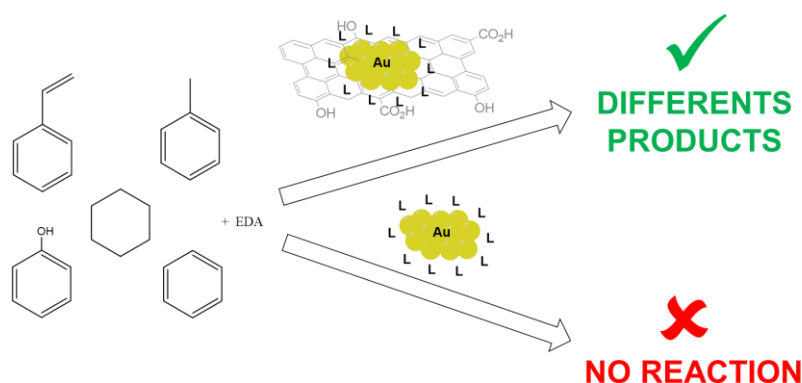
J. Martínez-Laguna¹, A. Mollar-Cuni², D. Ventura-Espinosa², A. Caballero¹, J. Mata², P. J. Pérez¹

¹ Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva, Campus de El Carmen s/n, 21007-Huelva, Spain, E-mail: jonathan.martinez@ciqso.uhu.es

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

In the last few decades, the use of transition-metal catalysts for the carbene transfer reaction from diazo compounds has been extensively studied. Several metals have been reported to mediate this transformation, establishing this methodology as a powerful tool in organic synthesis.[1] In this work, gold nanoparticles were tested as catalyst for the functionalization of several substrates by carbene transfer reactions using ethyl diazoacetate (EDA) as the carbene source.

Gold nanoparticles (Au NPs) functionalized with N-heterocyclic carbene (NHC) ligands[2] supported on reduced graphene oxide (rGO) and the non-supported Au NPs counterpart were tested as catalysts in cyclopropanation, carbene insertion into O-H bonds and C-H bonds reactions.



The non-supported Au NPs did not catalyse these reactions. However, the graphene-supported Au NPs showed superior catalytic activity in comparison to the non-supported parent catalyst, feature that can be attributed to a decrease in electron density at the metal center due to a remote net electronic flux from the gold nanoparticle to the graphene surface.

Referencias

[1] M. Doyle, M. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, 1998.

[2] D. Ventura-Espinosa, S. Martín, J. Mata, *Journal of Catalysis*, 2019, 375, 419-426.

SYNTHESIS OF BIO-DERIVED CYCLIC CARBONATES CATALYZED BY AN EFFICIENT ALUMINUM CATALYST

José A. Castro-Osma,^{1,*} Felipe de la Cruz-Martínez,² Javier Martínez,² Juan Fernández-Baeza,² and Agustín Lara-Sánchez^{2,*}

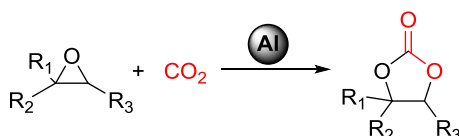
¹ Universidad de Castilla-La Mancha, Departamento de Química Inorgánica, Orgánica y Bioquímica-Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Farmacia, 02071-Albacete, Spain, e-mail: JoseAntonio.Castro@uclm.es

² Universidad de Castilla-La Mancha, Departamento de Química Inorgánica, Orgánica y Bioquímica-Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Ciencias y Tecnologías Químicas, 13071-Ciudad Real, Spain

The development of bio-based high-value added chemical products to replace petrol-based molecules is one of the main objectives for the scientific community and industry. During the last decades, great efforts have been made to shift from a petroleum-based industry to biorefineries in order to meet the social demands for sustainable and environmentally-friendly economic development.[1] In this context, a range of new platform molecules derived from waste biomass have been developed and used as monomers for the production of polymeric materials, as solvents and as chemical intermediates.[2]

One of the most abundant form of carbon on Earth is carbon dioxide (CO₂) and it is a potential sustainable feedstock for the chemicals industry.[3] The most important transformation of carbon dioxide is its catalytic coupling with epoxides to prepare cyclic carbonates.[4] This reaction has been widely studied over the last decade with the development of a wide range of highly efficient metal- and organic catalysts for this reaction.[4]

In this contribution we report the aluminum catalyzed coupling reaction of carbon dioxide with bio-derived epoxides under mild reaction conditions to afford highly-substituted natural-derived cyclic carbonates with excellent diastereoselectivity, obtaining in some cases one diastereoisomer as the major product.[5]



**Highly diastereoselective synthesis;
Excellent yields; Earth-abundant catalyst**

Scheme 1. Synthesis of highly-substituted cyclic carbonates.

References

- [1] D. Esposito, M. Antonietti, *Chem. Soc. Rev.*, **2015**, *44*, 5821–5835.
- [2] (a) V. Froidevaux, C. Negrell, S. Caillol, J.-P. Pascault, B. Boutevin, *Chem. Rev.*, **2016**, *116*, 14181–14224. (b) L. T. Mika, E. Cséfalvay, Á. Németh, *Chem. Rev.*, **2018**, *118*, 505–613.
- [3] (a) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.*, **2014**, *114*, 1709–1742. (b) A. W. Kleij, M. North, A. Urakawa, *ChemSusChem*, **2017**, *10*, 1036–1038.
- [4] H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, *Top. Curr. Chem.*, **2017**, *375*, 50. (b) G. Fiorani, W. Guo, A. W. Kleij, *Green Chem.*, **2015**, *17*, 1375–1389. (c) C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.*, **2015**, *5*, 1353–1370.
- [5] F. de la Cruz-Martínez, M. Martínez de Sarasa Buchaca, J. Martínez, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Rodríguez-Diéguez, J. A. Castro-Osma, A. Lara-Sánchez, *ACS Sustainable Chem. Eng.*, **2019**, *7*, 20126–20138

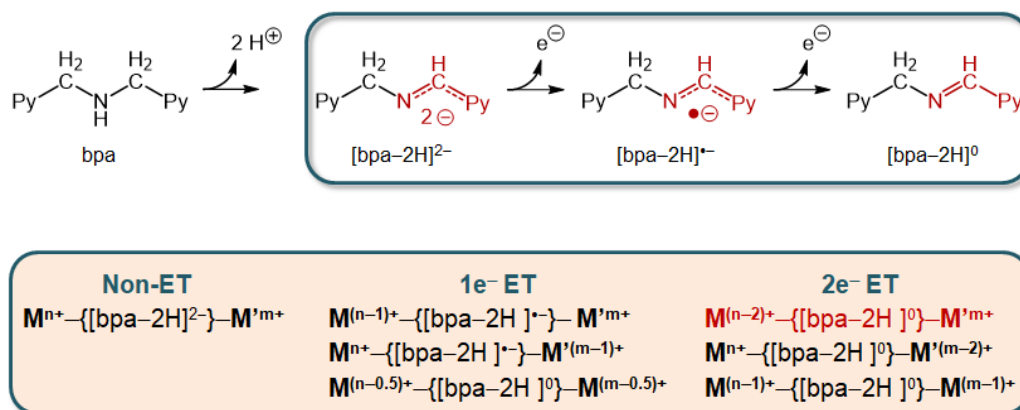
DINUCLEAR VALENCE-TRAPPED COMPLEXES

L. Tarifa, A. M. Geer, José A. López, C. Tejel

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, Zaragoza, 50009, Spain, e-mail: luistarifa@unizar.es

The dilemma between valence-trapped and valence-averaged complexes is an interesting subject of research from both, fundamental and practical levels.[1] Indeed, moving electrons from one metal to other or from the metal to the ligand (and *viceversa*) can finely tune the physical and chemical properties of the complexes, which mainly arise from the major prevalence of one of the canonic forms of the complex. In particular, three-center bridged situations such as M–NIL–M' –containing a 'non-innocent' redox active ligand (NIL) and redox active transition metals–, could provide relevant insight into electronic and spin interactions of the generated complexes. Moreover, tuning the electron-donating and redox properties of the non-innocent bridging ligand, complexes at these formal oxidation state limits may be obtained and therefore, fundamental aspects of intramolecular electron transfer processes could be evaluated.[2]

In this context, we are interested in the potentiality of a doubly deprotonated bis(picoly)amido ligand ($[\text{bpa-2H}]^{2-}$, see figure) in electron-transfer reactions when interacting with similar/dissimilar metallic ions. Since this ligand is suitable to undergo two-sequential one-electron reductions, the three-spin arrangement $\text{M}^{n+}-\{[\text{bpa-2H}]^{2-}\}-\text{M}'^{m+}$ can result in various spin states, depending on the number of transferred electrons from the ligand to the metals (0, 1, or 2) as well as the distribution of the electronic charge between both (see figure).



Herein, we will showcase the synthesis and full characterization of some dinuclear valence-trapped complexes as the result of a neat two-electron transfer reaction from $[\text{bpa-2H}]^{2-}$ to a **sole** metal center (in red in the figure). Furthermore, even in homometallic complexes, this asymmetric electronic distribution $\text{M}^{(n-2)+}-\{[\text{bpa-2H}]^0\}-\text{M}^{n+}$ was found to be preferred relative to the quite more common valence-averaged situation $\text{M}^{(n-1)+}-\{[\text{bpa-2H}]^0\}-\text{M}^{(n-1)+}$. The origin for this particular behavior will be also discussed.

Financial support acknowledgment: MINECO-FEDER CTQ2017-83421-P and GA-FES (Reactivity and Catalysis in Inorganic Chemistry, E50_20D)

References

- [1] J.-P. Launay, *Eur. J. Inorg. Chem.*, **2020**, 329-341.
 [2] W. Kaim, A. Paretzki, *Coord. Chem. Rev.*, **2017**, 344, 345-354.

INTERMOLECULAR ALLENE FUNCTIONALIZATION BY SILVER-NITRENE CATALYSIS

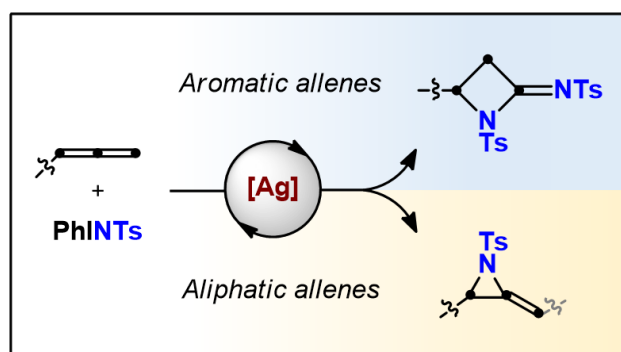
M. R. Rodríguez¹, M. Besora², P. Molina¹, F. Maseras^{2*}, M. M. Díaz-Requejo^{1*}, P. J. Pérez.^{1*}

¹Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva, 21007 Huelva, Spain.

²Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, 43007 Tarragona, Spain.

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

In this contribution, we describe the first example of an intermolecular nitrene transfer to terminal or internal allenes. The use of the [Tp^x,BrAg]₂ complex as catalyst has led to a novel transformation in which azetidines or methyleneaziridines are formed depending on the substrate employed. Furthermore, computational studies have been able to explain the nature of the reaction products allowing us to propose a general mechanism for the transformation.



References

[1] a) Díaz-Requejo, M. M.; Caballero, A.; Fructos, M. R.; Pérez, P. J. Chapter 6. In *Alkane C-H Activation by Single-Site Catalysis*; Pérez, P. J., Ed.; Springer, **2012**. b) R. Fructos, M., Álvarez, E., Díaz-Requejo, M. M., Pérez, P. J., *J. Am. Chem. Soc.* **2010**, 132, 4600 – 4607 c) Llaveria, J., Beltrán, Á., Sameera, W. M. C., Locati, A., Díaz-Requejo, M. M., M. Matheu I., Castellón, S., Maseras, F., Pérez, P. J., *J. Am. Chem. Soc.* **2014**, 136, 5342 – 5350 d) R. Rodríguez, M., Beltrán, Á., Mudarra, Á., Álvarez, E., Maseras, F., Díaz-Requejo, M. M., Pérez, P. J., *Angew. Chem. Int. Ed.* **2017**, 56, 12842 – 12847.

COPPER-CATALYZED GOLDBERG-TYPE C–N COUPLING IN *DEEP EUTECTIC SOLVENTS* (*DESs*) AND WATER UNDER AEROBIC CONDITIONS

Marina Ramos-Martín,¹ Luciana Cicco,^{1,2} Jose A. Hernández-Fernández,¹ Antonio Salomone,³ Paola Vitale,² Javier González-Sabín,⁴ Alejandro Presa-Soto,¹ Filippo M. Perna,² Vito Capriati*² and Joaquín García-Álvarez*¹

¹Laboratorio de Compuestos Organometálicos y Catálisis (Unidad Asociada al CSIC), Departamento de Química Orgánica e Inorgánica (IUQOEM), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain. uo237467@uniovi.es

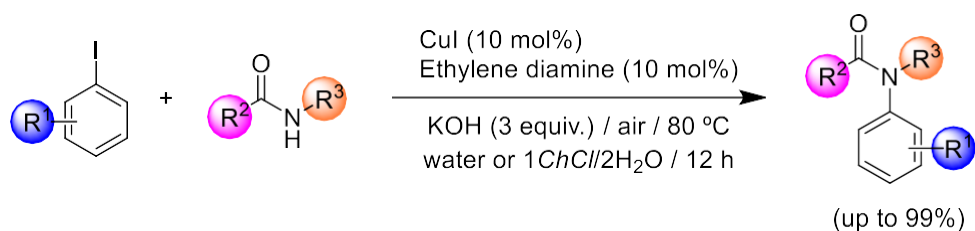
²Dipartimento di Farmacia-Scienze del Farmaco, Università di Bari “Aldo Moro”, Consorzio C.I.N.M.P.I.S., Via E. Orabona 4, I-70125 Bari, Italy.

³Dipartimento di Chimica, Università di Bari “Aldo Moro”, Via E. Orabona 4, I-70125 Bari, Italy.

⁴EntreChem SL, Vivero Ciencias de la Salud, Santo Domingo de Guzmán, E-33011, Oviedo, Spain.

The search for organic transformations catalyzed by first-row, cheap and earth-crust abundant transition metals, like Cu, is nowadays playing a pivotal role in synthetic organic chemistry [1]. In the same vein, the employment of sustainable reaction media in organic synthesis is today highly sought after in order to fulfill one of the most important *Principles of Green Chemistry* [2].

In this context, our research group has recently reported on a variety of highly selective and effective transition-metal-catalyzed organic transformations promoted by Ru, Au, or Pd complexes [3], which have been performed in a new family of sustainable reaction media, that is the so-called *Deep Eutectic Solvents* (*DESs*). Thus, in this communication we will present an efficient and selective *N*-functionalization of amides *via* CuI-catalyzed Goldberg type C–N coupling reaction between aryl iodides and primary/secondary amides run either in *Deep Eutectic Solvents* (*DESs*) or water as sustainable reaction media, under mild and bench-type reaction conditions (absence of protecting atmosphere). Higher activities were observed in an aqueous medium, though the employment of *DESs* expanded and improved the scope of the reaction to include also aliphatic amides. Additional valuable features of the reported protocol include: *i*) the possibility to scale up the reaction without any erosion of the yield/reaction time; *ii*) the recyclability of both the catalyst and the eutectic solvent up to 4 consecutive runs; and *iii*) the feasibility of the proposed catalytic system for the synthesis of biologically active molecules [4].



Referencias

- [1] R. Trammell, K. Rajabimoghadam, I. García-Bosch, *Chem. Rev.*, **2019**, 119, 2954.
- [2] P. T. Anastas, J. C. Warner, *Green Chemistry Theory and Practice*, Oxford University Press, Oxford, UK, **1998**.
- [3] (a) M. J. Rodríguez-Álvarez, C. Vidal, J. Díez, J. García-Álvarez, *Chem. Commun.*, **2014**, 50, 12927; (b) L. Cicco, M. J. Rodríguez-Álvarez, F. M. Perna, J. García-Álvarez, V. Capriati, *Green Chem.*, **2017**, 19, 3069; (c) M. J. Rodríguez-Álvarez, C. Vidal, S. Schumacher, J. Borge, J. García-Álvarez, *Chem. Eur. J.*, **2017**, 23, 3425; (d) L. Cicco, N. Ríos-Lombardía, M. J. Rodríguez-Álvarez, F. Morís, F. M. Perna, V. Capriati, J. García-Álvarez, J. González-Sabín, *Green Chem.*, **2018**, 20, 3468; (e) B. Saavedra, J. M. Pérez, M. J. Rodríguez-Álvarez, J. García-Álvarez, D. J. Ramón, *Green Chem.*, **2018**, 20, 2151.
- [4] L. Cicco, J. A. Hernández-Fernández, A. Salomone, P. Vitale, M. Ramos-Martín, J. González-Sabín, A. Presa-Soto, F. M. Perna, V. Capriati, J. García-Álvarez, *Org. Biomolec. Chem.*, **2021**, DOI: 10.1039/D0OB02501A.

BIMETALLIC ALUMINIUM SCORPIONATES FOR COUPLING OF CO₂ AND EPOXIDES INTO CYCLIC CARBONATES UNDER MILD CONDITIONS

Marta Navarro,¹ Luis F. Sánchez-Barba,^{1,*} Andrés Garcés,^{1,*} Juan Fernández-Baeza,² Agustín Lara-Sánchez²

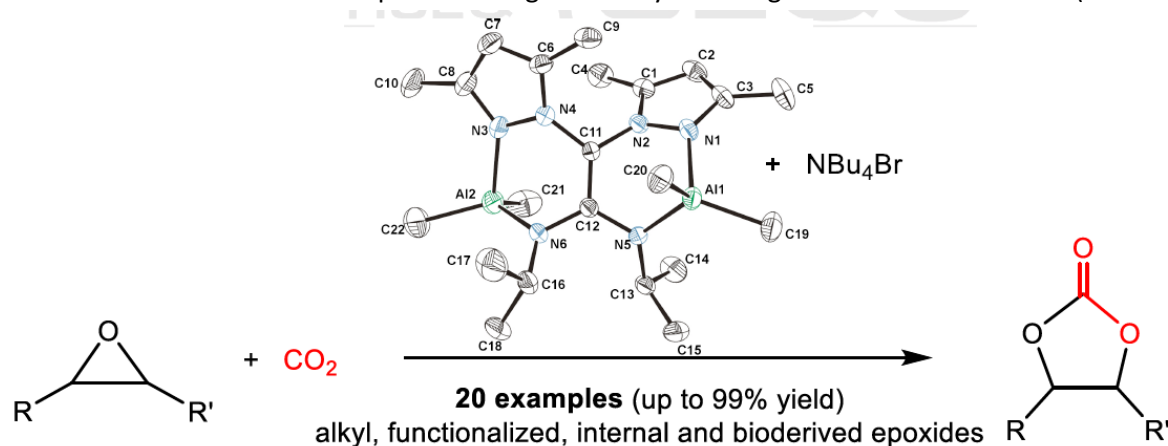
¹Universidad Rey Juan Carlos, Departamento de Biología y Geología, Física y Química Inorgánica, Móstoles-28933-Madrid, Spain

²Universidad de Castilla-La Mancha, Departamento de Química Inorgánica, Orgánica y Bioquímica, Centro de Innovación en Química Avanzada (ORFEO-CINQA) Campus Universitario, 13071-Ciudad Real, Spain
marta.navarro.sanz@urjc.es

In recent years, carbon dioxide has attracted significant attention as a sustainable C1 feedstock for various types of chemical reactions, which help to mitigate global warming. Thus, one of the most successful and widely studied processes is the 100% atom economical cycloaddition of CO₂ and epoxides to produce cyclic carbonates, given their important commercial applications such as electrolytes in lithium-ion batteries sustainable polar aprotic solvents and chemical intermediates in organic synthesis.

Several catalytic systems have been developed during the last years, particularly, organoaluminium complexes have been reported as this metal represents a nontoxic, earth abundant and an effective Lewis Acid to produce highly very active catalytic systems. In this context, bimetallic aluminium complexes have been successfully described as catalyst for the synthesis of cyclic carbonates at ambient temperature and 1 bar CO₂ pressure. Among these catalysts, we have recently reported very efficient systems based on scorpionate complexes in combination with quaternary ammonium salts.¹

Here we report the simple synthesis of a new family of NNN-scorpionate bimetallic aluminium complexes as efficient catalyst to produce cyclic carbonates by coupling reaction of CO₂ with different mono- and disubstituted as well as biobased epoxides using low catalyst loadings under mild conditions. (Scheme 1).²



Scheme 1. Synthesis of cyclic carbonates by using catalyst [Me₂Al(κ²-pbpamd)⁻AlMe₂]

References

- [1]. Martínez, J.; Castro-Osma, J. A.; Alonso-Moreno, C.; Rodríguez-Diéguez, A.; North, M.; Otero, A.; Lara-Sánchez, A. *Chem. Sus. Chem.* **2017**, *10*, 1175-1185.
- [2]. Navarro, M.; Sánchez-Barba, L.F.; Garcés, A.; Fernández-Baeza, J.; Fernández, I.; Lara-Sánchez, A.; Rodríguez, A. *Catal.Sci.Technol.* **2020**, *10*, 3265-3278.

SÍNTESIS Y CARACTERIZACIÓN DE COMPUESTOS N-HETEROCÍCLICOS DE IRIDIO(III)

M. Valencia¹, M. J. Cuenca¹, C. García-Yebra,¹ E. de Jesús.¹

¹ Universidad de Alcalá, Madrid-Barcelona Road, Km 33.6
28805 Alcalá de Henares, marta.valencia@uah.es

Las síntesis de ligandos 1,2,3-triazoles basadas en reacciones regioselectivas de cicloadición de alquinos con azidas se ha incrementado notablemente en la última década. De igual forma, también se ha producido un incremento en el número de complejos metálicos que contienen dichos sistemas. [1]

El tipo de sistemas polimetálicos conocidos que contienen estos ligandos N-heterocíclicos está limitado de forma general a unidades triazol-metal o triazolilideno-metal unidos a través de diversos espaciadores, [2, 3] o ningún espaciador entre las unidades metal-ligando[4]. También se han descrito sistemas heterobimetálicos asimétricos, en los que la unidad triazol-metal poseen sustituyentes ferroceno,[5, 6] así como otros modos de coordinación de sistemas bimetálicos poco habituales.[7, 8]

En este trabajo presentamos nuevos modos de coordinación de sistemas triazol-Iridio(III).

Referencias

- [1] A. Vivancos, C. Segarra, M. Albrecht. *Chem. Rev.* **2018**, *118*, 19, 9493–9586.
- [2] S. Bertini, M. Albrecht. *Organometallics* **2020**, *39*, 3413–3424.
- [3] A. Vivancos, M. Albrecht. *Organometallics* **2017**, *36*, 8, 1580–1590.
- [4] M. F. Pinto, M. Olivares, A. Vivancos, G. Guisado-Barrios, M. Albrecht, B. Royo. *Catal. Sci. Technol.*, **2019**, *9*, 2421–2425.
- [5] M. G. Avello, M. C. de la Torre, M. A. Sierra, H. Gornitzka, C. Hemmert. *Chem. Eur.J.*, **2019**, *25*, 13344–13353.
- [6] M. Frutos, M. Gómez-Gallego, E. A. Giner, M. A. Sierra, C. Ramírez de Arellano. *Dalton Trans.*, **2018**, *47*, 9975–9979.
- [7] L.-H. He, Y.-S. Luo, B.-S. Di, J.-L. Chen, C.-L. Ho, H.-R. Wen, S.-J. Liu, J.-Y. Wang, W.-Y. Wong *Inorg. Chem.* **2017**, *56*, 10311–10324.
- [8] M. Valencia, H. Müller-Bunz, R. A. Gossage, M. Albrecht. *Chem. Commun.*, **2016**, *52*, 3344–3347.

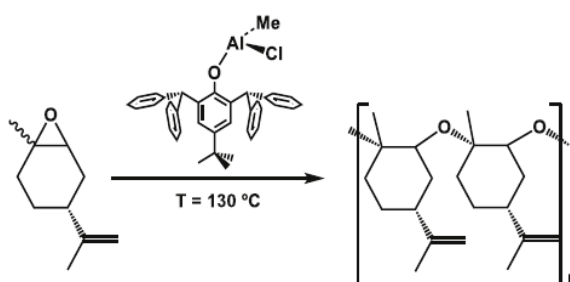
POLYLIMONENE OXIDE PREPARED VIA A CATALYTIC ROP PROCESS AS BIOBASED PLASTICIZER FOR PLA

Valentina Sessini, Jesús Damián, Marta E. G. Mosquera* and Miguel Palenzuela

Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigación Química "Andrés M. Del Río", Campus Universitario, E-28871, Alcalá de Henares, Spain

The use of renewable sources is gaining more and more presence in the production of materials such as plastics. The production of green polymers is attracting attention worldwide in recent years due to an increasing demand of sustainable alternatives to oil-based plastics.[1,2] In this context, terpene derivatives, such as terpene oxides, are a very interesting renewable feedstock. Although these multifunctional molecules are very attractive building blocks to prepared monomers, they had not been widely studied probably due to the diversity in this family of compounds.[3,4] In particular, limonene oxide (LO) is a readily available terpenoid that can be easily produced from limonene, an abundant monoterpene which is extracted from the peel of citrus fruits and is already widely used as a solvent, fragrance, and insecticide.[5,6] The study of the copolymerization of limonene oxide and anhydrides or CO₂ as comonomers to produce polyesters and polycarbonates, respectively, have been already reported. However, surprisingly, the homopolymerization of LO by ROP has only been reported by Park et al. in 2012 in a photoinitiated not very well controlled process.[6]

In this work, we present the homopolymerization of (+)-Limonene oxide by ring-opening using an aluminium-based catalyst that we have reported previously as very active catalyst in ROP of glycidyl methacrylate (GMA).[7] The commercially available mixture of *cis* and *trans* (+)-Limonene oxide was used as monomer in the presence of the aluminium catalyst. The obtained LO-based polyether (PLO) have low molecular weights and low glass transition temperature, which make them suitable for its use as an additive.[8] Hence, we studied the behaviour of the PLO prepared as plasticizer additive for PLA, a biodegradable polymer with very attractive properties, but whose brittleness and rigidity impede its application in some fields, thus, additives are needed to improve its processability.[9,10]



Scheme 1. Catalytic polymerization of (+)-limonene oxide.

References

- [1] A. Gandini, T.M. Lacerda, *Prog. Polym. Sci.*, **2015**, 48, 1–39.
- [2] Y. Zhu, C. Romain, C.K. Williams, *Nature*, **2016**, 540, 354–362.
- [3] P.A. Wilbon, F. Chu, C. Tang, *Macromol. Rapid Commun.*, **2013**, 34, 8–37.
- [4] M. Winnacker, B. Rieger, *ChemSusChem*, **2015**, 8, 2455–2471.
- [5] R. Ciriminna, M. Lomeli-Rodriguez, P. Demma Cara, J.A. Lopez-Sanchez, M. Pagliaro, *Chem. Commun.*, **2014**, 15288–15296.
- [6] H.J. Park, C.Y. Ryu, J.V. Crivello, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, 109–117.
- [7] M.T. Muñoz, M. Palenzuela, T. Cuenca, M.E.G. Mosquera, *ChemCatChem*, **2018**, 10, 936–939.
- [8] V. Sessini, M. Palenzuela, J. Damián, Marta E. G. Mosquera, *Polymer*, **2020**, 210, 123003.
- [9] M. Maiza, M.T. Benaniba, G. Quintard, V. Massardier-Nageotte, *Polímeros*, **2015**, 25, 581–590;

[10] M.P. Arrieta, J. López, A. Hernández, E. Rayón, *Eur. Polym. J.*, **2014**, 50, 255–270.

PB-25

NANOPARTÍCULAS DE Pt ESTABILIZADAS MEDIANTE LIGANDOS DE TIPO Pincer SNS. SÍNTESIS Y CARACTERIZACIÓN.

P. Molinillo, P. Lara, N. Rendón, A. Suárez

Instituto de Investigaciones Químicas (CSIC, Universidad de Sevilla) pablo.molinillo@iiq.csic.es

La síntesis de nanopartículas (NPs) metálicas a partir de la descomposición de un precursor organometálico en condiciones suaves de presión y temperatura, y en presencia de un ligando como agente estabilizante (método organometálico)¹ es un método eficiente de preparación de nanopartículas homogéneas en términos de tamaño y dispersión. Así, el empleo de ligandos de distinta naturaleza hace variar enormemente la estabilidad, el tamaño, el grado de recubrimiento y la forma de las NPs.

En esta comunicación se describe la preparación, mediante el método organometálico, de diferentes nanopartículas de platino estabilizadas por ligandos de tipo SNS (ver Figura 1) y caracterizadas principalmente mediante Microscopía Electrónica de Transmisión (TEM). Se analizará la influencia de la estructura del ligando en el tamaño, y el grado de dispersión de los coloides obtenidos.

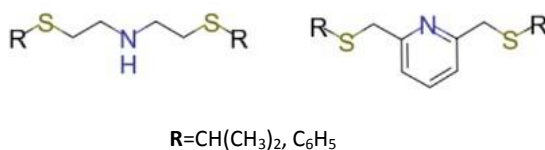


Figura 1. Estructura de ligandos SN^HS y SN^{PY}S empleados en la preparación de Pt-NPs

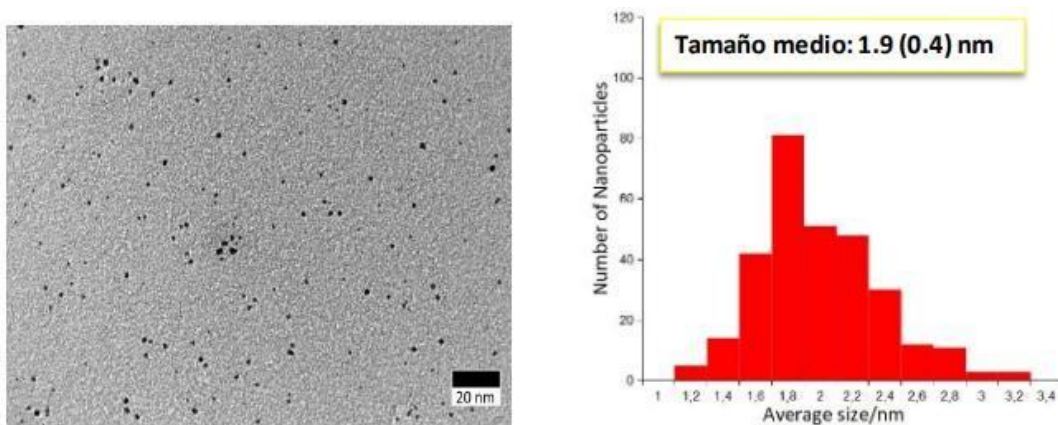


Figura 2. Imagen de TEM e Histograma de tamaño obtenidos utilizando un ligando SN^{PY}S.

Referencias

[1] Chaudret, B, and Philippot, K., in *Comprehensive Organometallic Chemistry III*, ed. R. Crabtree and M. P. Mingos, Elsevier **2007**, 12, 71-99.

PALLADIUM-CATALYZED CASCADE REACTIONS FOR THE SYNTHESIS OF HETEROCYCLIC DERIVATIVES BEARING A PHOSPHONATE GROUP

P. Herrera¹, J.-A. García-López¹

¹Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Campus de Espinardo, Universidad de Murcia, 30100.

Cascade reactions represent a straightforward synthetic strategy to obtain complex molecular structures from simple substrates. Different palladium-catalyzed cascade processes have been developed by trapping σ -alkyl Pd^{II} intermediates generated *in situ* with diverse coupling partners, showcasing the exceptional versatility of Pd catalysts in organic synthesis [1].

In this work, an optimization process was carried out by analyzing different catalytic conditions that favour the formation of phosphorylated heterocycles, which were generated from the coupling of halogenated starting materials with dimethylphosphite. It has been proven that ether- as well as amide-type substrates were particularly well suited for an efficient development of these reactions [2].

Moreover, organometallic σ -alkyl Pd^{II} intermediates were isolated stoichiometrically in order to verify that the initially proposed reaction mechanism for the synthesis of the new coupling products obtained was compatible with the cascade processes outlined above.

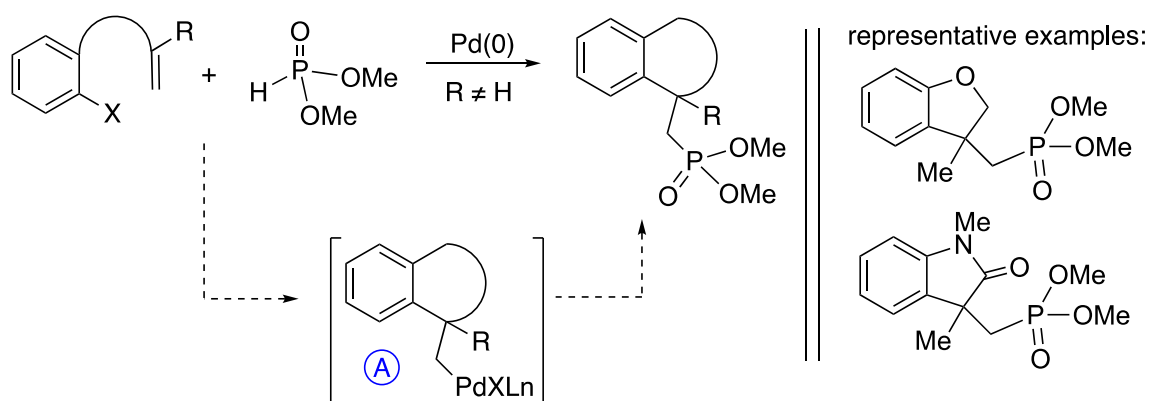


Figure 1. Pd-catalyzed synthesis of phosphorylated heterocycles.

Acknowledgements

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

Referencias

- [1] Pérez-Gómez, M.; García-López, J.A., *Angew. Chem. Int. Ed.*, **2016**, *55*, 14389–14393.
- [2] Lu, G.; Huangfu, X.; Wu, Z.; Tang, G.; Zhao, Y. *Adv. Synth. Catal.*, **2019**, *361*, 4961–4965.

Re-MEDIATED DEAROMATIZATION AND PYRIDYL RING-OPENING OF A1,10-PHENANTHROLINE LIGAND

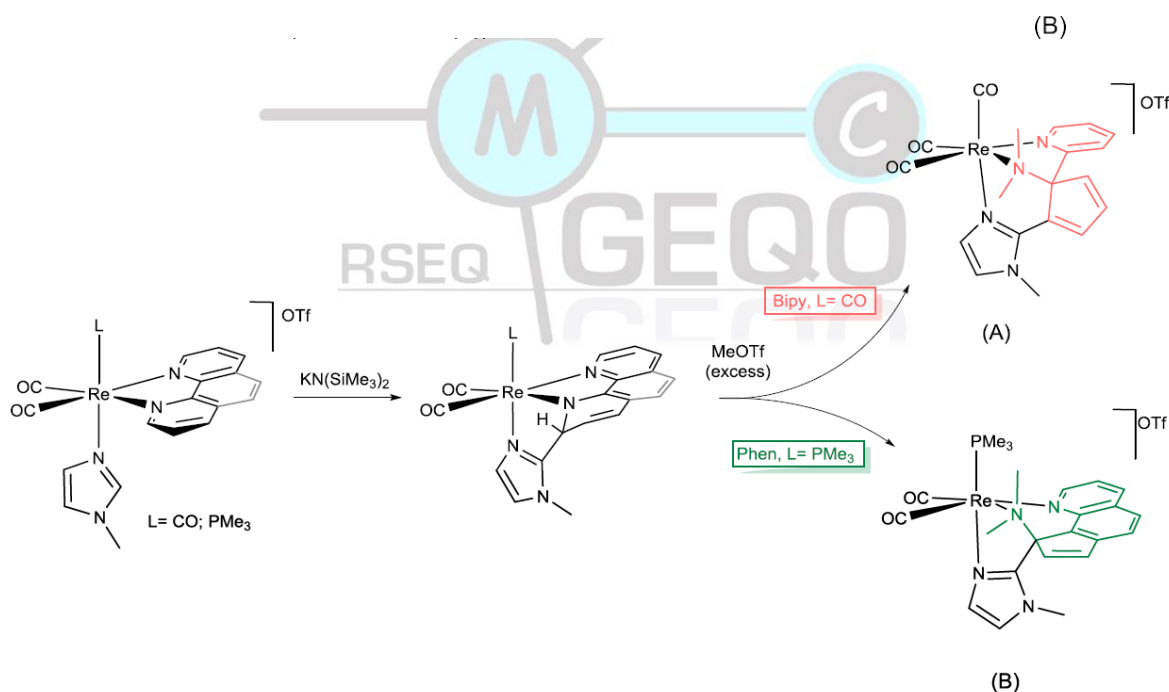
Purificación Cañadas,¹ Julio Pérez,^{1,2} and Lucía Riera²

¹Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, Julián Clavería 8, 33006 Oviedo
uo268976@uniovi.es

²Centro de Investigación en Nanomateriales y Nanotecnología (CINN), CSIC-Universidad de Oviedo-Principado de Asturias, Avda de la Vega 4-6, 33940 El Entrego (Spain)

2,2'-Bipyridine (bipy) and 1,10-phenanthroline (phen) have been widely employed in all areas of coordination chemistry; however, prior to our work, examples of dearomatization of transition metal-coordinated bipy and phen under mild conditions were hardly known.[1] We had previously found that for $[\text{Re}(\text{CO})_3(\text{bipy})(\text{N-Melm})]\text{OTf}$ (N-Melm= N-methylimidazole), the deprotonation of the central CH group of the imidazole ligand triggered the nucleophilic attack onto the C6 atom of bipy, which became dearomatized. Afterwards, two successive methylations of the dearomatized pyridyl moiety promoted the cleavage of a C-N bond, leading to a pyridyl ring-opening product (see Scheme 1 (A)).[2]

Herein we report the extension of this reactivity to more electron rich *cis*- $[\text{Re}(\text{CO})_2(\text{N-Rlm})(\text{phen})(\text{PMe}_3)]\text{OTf}$ (N-Rlm= N-alkylimidazole) compounds, in which ring opening of a pyridyl moiety of a phen ligand is achieved for the first time (see Scheme 1 (B)).



Scheme 1. Reactivity of $[\text{Re}(\text{CO})_2(\text{L})(\text{N-N})(\text{N-Melm})]\text{OTf}$ ($\text{L} = \text{CO}$, PMe_3 ; $\text{N-N} = \text{bipy}$, phen) compounds

References

- a) S. Leelasubcharoen, K.-C. Lam, T. E. Concolino, A. L. Rheingold, K. H. Theopold, *Organometallics* **2001**, *20*, 182-187;
 b) L. M. Kobriger, A. K. McMullen, P. E. Fanwick, I. P. Rothwell, *Polyhedron* **1989**, *8*, 77-81; c) C. Weetman, M. S. Hill, M. F. Mahon, *Polyhedron* **2016**, *103*, 115-120.
 M. A. Huertos, J. Pérez, L. Riera, *J. Am. Chem. Soc.* **2008**, *130*, 5662-5663.

REACTIVITY OF SEVEN-MEMBERED PALLADACYCLES: INSERTION REACTIONS OF UNSATURATED MOLECULES INTO THE Pd-C BOND

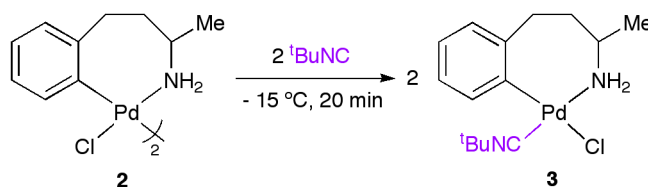
S. Fernández-García¹, M. Pérez-Gómez¹, I. Saura-Llamas¹

¹ Department of Inorganic Chemistry, Faculty of Chemistry, University of Murcia, 30100, Murcia, Spain

Email: sara.fernandez4@um.es

Palladacycles are very versatile compounds that have arisen great interest since their discovery due to their stability and reactivity. The most common palladacycles are those that contain N-donor ligands and five- or six-membered rings, unlike the seven-membered palladacycles which are scarce in the literature. The synthesis of these compounds by C–H bond activation using a Pd(II) salt and the study of their reactivity are subject of great relevance because they provide information about the course of the catalytic cycles in which they are involved.

According to a general method previously described,[1] the triflate of 1-methyl-3-phenylpropyl ammonium (**1**) reacts with one equivalent of Pd(OAc)₂ in acetonitrile at 80 °C to afford, after the addition of NaCl, a dimeric seven-membered palladacycle containing chloro bridges. In this reaction, Pd(0) and a bis-amino complex of Pd(II) are also obtained, which decrease the yield of the desired product. This research work describes an experimental modification of the general method that allows the synthesis of the complex [Pd₂{κ²(C,N)-C₆H₄(CH₂CH₂CH(Me)NH₂)-2}₂(μ-Cl)₂] (**2**) with a good yield. The seven-membered palladacycle **2** reacts with ^tBuNC to give the mononuclear derivative **3**.



Scheme. Reaction of complex **2** with ^tBuNC.

When 2,6-dimethylphenyl isocyanide is used in a similar reaction, a iminoacyl derivative is obtained, which contains a coordinated isocyanide ligand and another one inserted. When this complex reacts with TlOTf and the reaction mixture is heated to 110 °C, the organometallic intermediate decomposes to give an amidinium salt, resulting from the C–N coupling, and Pd(0).

The reaction of **2** with styrene generates a nine-membered palladacycle containing hydrogen in β position to the metal center. This compound decomposes to give (*E,E*)-[PdCl₂{4-(2-(styrylphenyl)butan-2-amine)₂}] and Pd(0). When MeO₂CC≡CCO₂Me is used for the insertion reaction, a nine-membered alkenyl- palladacycles is isolated.

References

[1] R. Frutos-Pedreño, E. García-Sánchez, M. J. Oliva-Madrid, D. Bautista, E. Martínez-Viviente, I. Saura-Llamas, J. Vicente, *Inorg. Chem.*, **2016**, 55, 5520-5533.

SÍNTESIS DE PROPARGILAMINAS DESDE ALCOHOLES CATALIZADA POR ORO EN UN PROCESO ONE-POT/MULTICOMPONENTE

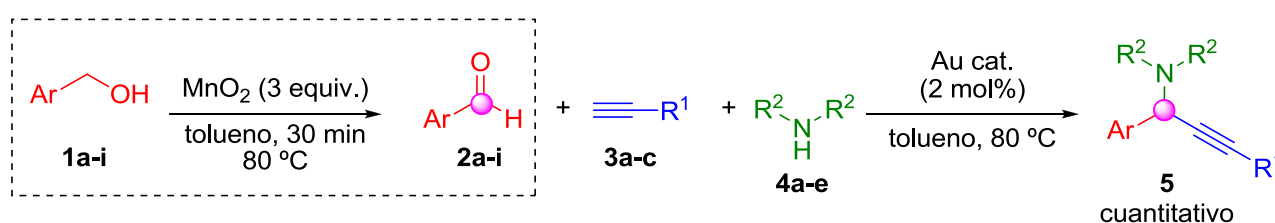
Stephany Zárate-Roldán,^{1,2} M. Concepción Gimeno*¹ y Raquel P. Herrera*²

¹ Departamento de Química Inorgánica. Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza. E-50009 Zaragoza, España. e-mail: szarate.roldan@gmail.com

² Laboratorio de Organocatálisis Asimétrica. Departamento de Química Orgánica. Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza. E-50009 Zaragoza, España.

La síntesis de propargilaminas es un claro ejemplo de una reacción multicomponente, donde a partir de un aldehído, una amina y un alquino terminal se produce un acoplamiento A³, catalizado por un metal de transición.[1,2] Este tipo de síntesis es muy versátil y ha sido ampliamente usada en el desarrollo de compuestos de interés para la industria, especialmente la farmacéutica.[3]

En este trabajo queremos mostrar una aproximación novedosa para la síntesis de estos compuestos partiendo de alcoholes.[4] Así, tras una oxidación inicial de un alcohol usando MnO₂, en un proceso *one-pot*, se lleva a cabo posteriormente un paso catalítico con oro en una reacción multicomponente (Esquema 1).



El dióxido de manganeso activado (MnO₂) fue elegido debido a su alta selectividad y eficiencia en la conversión de alcoholes a aldehídos. [5] Los productos finales se obtienen con muy buenos rendimientos en tiempos cortos de reacción, lo que es de gran interés para la síntesis de fármacos. La utilidad y eficiencia de nuestra metodología se compara con éxito con la misma reacción a partir de aldehídos, demostrando la utilidad, versatilidad y sencillez de esta aproximación.

Referencias

- [1] V. A. Peshkov, O. P. Pereshivko, E. V. Van der Eycken, *Chem. Soc. Rev.*, **2012**, *41*, 3790–3807.
 [2] M. Aliaga-Lavrijsen, R. P. Herrera, M. D. Villacampa, M. C. Gimeno, *ACS Omega*, **2018**, *3*, 9805–9813.
 [3] B. V. Rokade, J. Barker, P. J. Guiry, *Chem. Soc. Rev.*, **2019**, *48*, 4766–4790.
 [4] S. Zárate-Roldán, M. C. Gimeno, R. P. Herrera, *manuscrito enviado*.
 [5] J. V. Alegre-Requena, E. Marqués-López, R. P. Herrera, *Adv. Synth. Catal.*, **2018**, *360*, 124–129.

ÍNDICE DE AUTORES

Alamán-Valtierra, P.	PA17	Conejo, M. M.	PB02	Gonell, Sergio	PA23
Albéniz, Ana C.	PA10 PB11	Costas, M.	OA1	González Herrero, Pablo	PA12 PB05
Alberca, S.	PA22	Crespo, M.	PA05	González-Sabín, Javier	PB21
Alconchel, Adrián	PA04	Crespo, Olga	PA04 PB07	Gonzalo, Carlos	PA08 PA01
Alcudia, A.	PB02 PB10	Cuenca, Marco J.	PB23	Hernán-Gómez, A.	PB14
Alguacil Alarcón, Andrés	PA03	Cuenca, Tomás	PB16	Hernández-Fernández, Jose A.	
Alvarez, E.	OA4 PA25 PB02 PB04 PB15	Curado, N.	PB01		PB21
		Dalmau, D.	PB07	Herrera, P.	PB26
		Damián Burgoa, Jesús	PB16 PB24	Herrera, Raquel P.	PB29
Alvarez, S.	PB01	de Aquino, A.	OB3	Hidalgo, N.	PA18
Álvarez, Celedonio M.	PA16 PA27	de Jesús, Ernesto	PA15 PB23	Hornillos, Valentín	PA19
Álvarez, M.	PB12	de la Cruz-Martínez, Felipe	OB5 PB03	Huertos, M.A.	OA3
Álvarez-Llorente, N.	PA16		PB18	Iglesias, Manuel	OB1
Amaveda, H.	PA09	de la Cruz-Sánchez, Pol	PA20	Iglesias-Sigüenza, J.	PA22
Antiñolo, Antonio	PA07	de Toro, Samuel	PA15	Infante, R.	PA26
Azpeitia, S.	OA3	Díaz-Requejo, M. M.	OA5 PB20	Jalón, F. A.	PA08
Barbero, Héctor	PA01	Diéguez, Montserrat	PA20	Jiménez, A. I.	PB07
Bautista, Delia	PA12 PB05	Durá, G.	PA08	Jover, J.	PB01
Baya, M.	PA28	El Alstal-Quirós, Aliah	PA15	Kays, D.	PA17
Begines, B.	PB02 PB10	Elorriaga, David	PA07	Lara, P.	PB25
Besora, M.	PB20	Espinet, P.	PA26	Lara-Sánchez, Agustín	OB5 PB22
Bietti, M.	OA1	Fernández, Rosario	PA19 PA22		PB03 PB18
Blasco, D.	PA09	Fernández-Baeza, Juan	OB5 PB03	Lassaletta, José M.	PA19 PA22
Borrego Blanco, Elena	PB09		PB18 PB22	Lázaro, A.	PA05
Bravo, Iván	PA07	Fernández-García, S.	PB28	Lewis, W.	PA17
Caballero, Ana	PB09 PB17	Fernández-Moreira, V.	OA2	Lima, J.C.	OB3
Cabo, Diego A.	PB08	Ferrero, Sergio	PA01	Lledos, Agustí	PB09
Caldentey, Xisco	PA20	Freixa, Z.	OA3	Lloret-Fillol, Julio	PA23
Campillo, D.	PB06	Fructos, Manuel R.	PA13	López, José A.	PB19
Campora, Juan	PA25 PB08	Galindo, A.	PB02 PB10	López de Luzuriaga, J. M.	OB4 PA02
Campos, J.	PA18 PB01	Garcés, Andrés	PB22		PA09 PA11
Cañadas, Purificación	PB27	García-Abellán, Susana	OB1		PA14 PA24
Capriati, Vito	PB21	García-Álvarez, Joaquín	PB21	López López, Juan Carlos	PA12
Carmona, E.	PB01 PB04	García-Camacho, A.	OB4	López Sánchez, Belén	PA06
Carrasco, C.	PB10	García-López, J.-A.	PB26	Luque-Gómez, Ana	OB1
Carrasco, D.	PB13	García-Rodríguez, Raúl	PA01 PA16	Manzano, B. R.	PA08
Carrillo-Hermosilla, Fernando			PA27	Marcos-Ayuso, G.	PB13
	PA07	García-Romero, Álvaro	PA27	Margalef, Jèssica	PA20
Casares, J.A.	PB13	García-Sakai, V.	PA09	Marín, M.	OA4
Casas, J. M.	PA28	García-Yebra, Cristina	PA15 PB23	Martín, A.	PA28 PB06
Casati, N.	PA24	Garralda, M. A.	OA3	Martín, M.T.	OA4
Castro-Osma, José Antonio	OB5	Geer, A. M.	PA17 PB19	Martín-de la Calle, Rocío	PA19
	PB03 PB18	Gimeno, M. Concepción	OA2 PA04	Martínez, D.	PA08
Cicco, Luciana	PB21		PB29	Martínez, Javier	PB03 PB18
Coconubo, L.	PA14	Gomez, B.	PB04		

Martínez de Sarasa Buchaca, Marc	PB03	Pérez-Gómez, M.	PB28	Tejel, C.	PA17 PB19
		Perez-Jimenez, M.	PB01	Urriolabeitia, E. P.	PB07
Martínez-González, J. A.	PA09	Pérez-Ortega, I.	PA10	Valencia, Marta	PB23
Martínez-Laguna, J.	PB17	Pericàs, Miquel A.	PA20	Velázquez, M.	PA22
Martínez-Martínez, Antonio		Perna, Filippo M.	PB21	Ventura-Espinosa, D.	PB17
	OB2	Pizarro Javier, J. Diego	PA13	Vicens, L.	OA1
Martínez-Muñoz, G.	PB10 PB02	Polo, Victor	OB1	Videa, Hellen	OB2
Maseras, F.	PB20	Ponce de León, J.	PA26	Villalba, Francisco	PB11
Mata, J.	PB17	Pop, A.	PB07	Vitale, Paola	PB21
Maya, C.	OA4 PA21	Presa-Soto, Alejandro	PB21	Vivancos, Á.	PB05
	PB01 PB04	Prieto, U.	OA3	Zárate-Roldán, Stephany	PB29
Mena, M.	PB14	Quintana, J.	PA11		
Menjón, B.	PA28	Rama, R. J.	OA4 PA21		
Miguel, Daniel	PA01 PA27		PB04		
Miller, Alexander J. M.	PA23	Ramos-Martín, Marina	PB21		
Molina, F.J.	OA4	Redrado, M.	OA2		
Molina, P.	PB20	Rendón, N.	PB15 PB25		
Molinillo, P.	PB25	Riera, Lucía	PB27		
Mollar-Cuni, A.	PB17	Rodríguez, Ana María	OB5 PA08		
Monge, D.	PA22	Rodríguez, Anabel M.	OA5		
Monge, M.	OB4 PA02	Rodríguez, L.	OB3 PA05		
	PA09 PA11		PB12		
Monti, A.	PB04	Rodríguez, M. R.	PB20		
Montilla, F.	PB02 PB10	Rodríguez, Verónica	PA19		
Mora, M.	PA09	Rodríguez-Castillo, M.	OB4 PA02		
Moreno, S.	PA14 PA24		PA11 PA09		
Mosquera, Marta E. G.	PB16 PB24	Rodríguez-Salamanca, Patricia			
Munarriz, Julen	OB1		PA19		
Muñoz, J. M.	PB12	Rodríguez-Belderrain, T.	PB12		
Navarro, Marta	PB22	Romerosa, Antonio M.			
Nicasio, M. C.	OA4 PA21		PA03 PA06		
	PB04	Romo-Islas, G.	PB12		
Nova, A.	PA21	Sacristán-Martín, Adriana	PA01		
Olmos, M. E.	OB4 PA02	Salomone, Antonio	PB21		
	PA09 PA14	San Sebastián, E.	OA3		
	PA24	Sánchez, P.	PB15		
Ortega-Lepe, I.	PB15	Sánchez-Barba, Luis F.	PB22		
Pacheco-Liñán, Pedro J.	PA07	Sánchez-Hernández, A.	PB10		
Pajuelo., E.	PB02 PB10	Sancho, I.	PB14		
Palenzuela, Miguel	PB24	Santamaría, C.	PB14		
Palma, P.	PA25	Santiago, Tomás G.	PA25 PB08		
Pamies, Oscar	PA20	Santos, L. L.	PB15		
Parra, Blanca	PA07	Saura-Llamas, I.	PB28		
Passarelli, Vincenzo	OB1	Scalambra, Franco	PA03 PA06		
Pastor, A.	PB02	Sessini, Valentina	PB24		
Pérez, Julio	PB27	Silvestru, C.	PB07		
Pérez, Pedro J.	OA5 PA13	Soldevilla, I.	OB4		
	PB17 PB09	Sorroche, A.	PA02		
	PB20	Suárez, A.	PB15 PB25		
Pérez-Aranda, M.	PB02 PB10	Tarifa, L.	PB19		
Pérez-Bitrián, A.	PA28	Taylor, L. J.	PA17		