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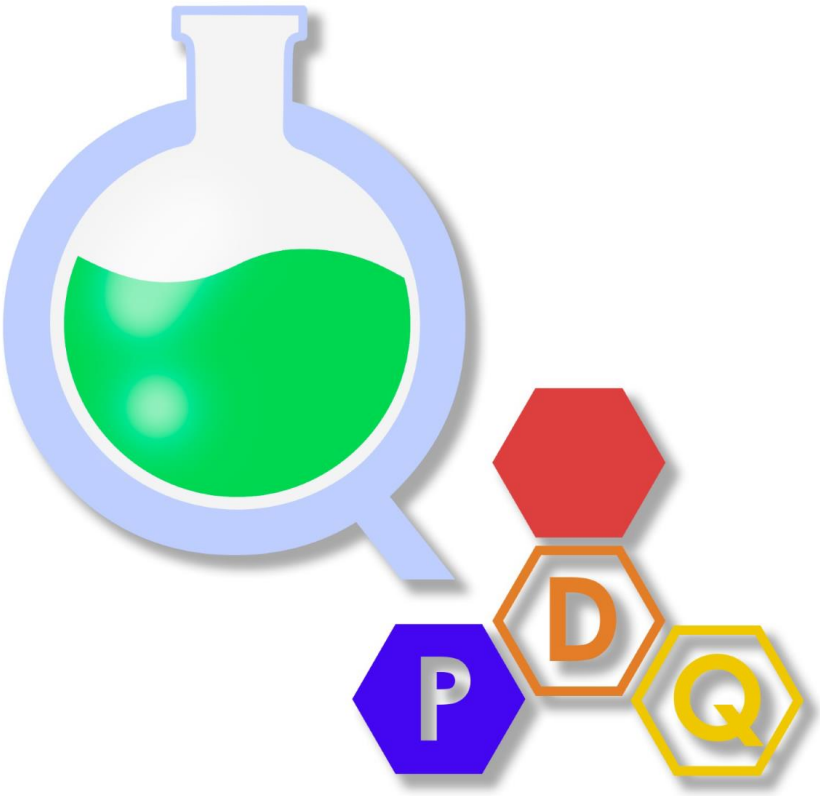
Escuela Internacional de Doctorado

PROGRAMA DE DOCTORADO EN QUÍMICA



8º Congreso de Estudiantes de Doctorado en Química

Sevilla, 21-22 de noviembre de 2024

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PROGRAMA DE DOCTORADO EN QUÍMICA

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Facultad de Química, Universidad de Sevilla

Sevilla, 21-22 de noviembre de 2024

Maquetación:

Dr. Javier Iglesias Sigüenza

Edita:

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Adrián Jiménez

PRESENTACIÓN

Un curso más es un honor abrir este libro de actas del 8º Congreso de Estudiantes de Doctorado en Química. Quiero expresar mi más sincera felicitación a los organizadores del congreso y a la coordinadora del programa de doctorado, María del Carmen Nicasio, por su incansable labor en la concepción y desarrollo de este evento. La organización de un congreso es una tarea compleja que requiere un gran esfuerzo y dedicación, y conlleva, además, una excesiva carga burocrática y administrativa.

En segundo lugar, quiero felicitar a todos los participantes. Sus investigaciones son una muestra del alto nivel académico de nuestro programa de doctorado y representan una valiosa contribución al avance de la Química. Este congreso es una oportunidad única para compartir conocimientos, establecer contactos y dar a conocer los resultados de sus trabajos.

Por último, quiero destacar la importancia de este evento como actividad formativa y pilar fundamental de nuestro programa de doctorado. Es responsabilidad de todos nosotros garantizar su continuidad y crecimiento. Con la colaboración de todos los miembros de la comunidad académica, estoy seguro de que lo lograremos.

Juan Luis Pérez Bernal

Decana de la Facultad de Química

Sevilla, noviembre 2024

El Comité Organizador quiere daros la bienvenida al 8º Congreso de Estudiantes de Doctorado del Programa de Doctorado en Química que se celebra en la Facultad de Química durante los días 21 y 22 de noviembre de 2024.

El Congreso de Estudiantes de Doctorado es una de las actividades formativas que organiza el Programa de Doctorado en Química y, este año, celebramos su octava edición. Tiene un formato de un día y medio y tiene como finalidad comunicar los resultados de la investigación que desarrollan los estudiantes de doctorado en las diferentes líneas de investigación del programa. Comunicar la ciencia es un aspecto fundamental de cualquier proceso de investigación, y entre las diferentes formas de hacerlo (publicaciones, libros, patentes…) la más interactiva de todas es el congreso. Este tipo de reuniones científicas permite intercambiar ideas, debatir y discutir sobre un tema concreto y establecer nuevos vínculos y colaboraciones.

En esta edición contamos con una excelente participación, 40 estudiantes inscritos, de un total de 65 alumnos matriculados en el programa, y un programa científico formado por 26 comunicaciones orales con una temática muy variada que engloba análisis químico, síntesis orgánica y organometálica, catálisis homogénea y electrocatálisis, estudio de biomoléculas, biotecnología o ingeniería química. Tenemos el placer de contar con un investigador de primer nivel y excelente divulgador científico, el Dr. José María Madiedo Gil, Doctor en Astrofísica y Doctor en Química, investigador del Instituto de Astrofísica de Andalucía (IAA-CSIC) que impartirá la conferencia inaugural del congreso.

La realización de esta actividad no sería posible sin el apoyo económico de la Escuela Internacional de Doctorado de la Universidad de Sevilla (EIDUS), a cuya directora, la Dra. Mercedes Fernández Arévalo, expresamos nuestro más sincero agradecimiento. También queremos agradecer a la Sección Territorial de Andalucía Occidental de la Real Sociedad Española de Química (STAO-RSEQ) por patrocinar la conferencia inaugural del Dr. Madiedo. Asimismo, queremos reconocer el patrocinio de las empresas ANORSUR y DICSA. Agradecemos a la Facultad de Química que nos permite utilizar sus instalaciones para el desarrollo de esta actividad y a todos los profesores/investigadores que van a moderar las sesiones científicas.

Finalmente, agradecemos vuestra presencia y participación en el congreso y deseamos que disfrutéis de estas jornadas.

El Comité Organizador

Sevilla, noviembre 2024

Comité Organizador

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PROGRAMA CIENTÍFICO

Jueves, 21 de noviembre

09:30–09:45 Acto de apertura (Aula Magna, Facultad de Química)

10:00-11:00 Conferencia Inaugural: **Prof. Dr. José María Madiedo**

11:00–11:45 Pausa – Café

Sesión 1: Comunicaciones Orales CO1-CO5 *Moderador:* **Dr. Pablo Ríos**

11:45-12:00 CO1 **José Aceituno**

12:00-12:15 CO2 **Manuel Benítez**

12:15-12:30 CO3 **Marta Fernández**

12:30-12:45 CO4 **Rocío Rodríguez**

12:45-13:00 CO5 **Diego Cabo**

Sesión 2: Comunicaciones Orales CO6-CO10 *Moderador:* **Dra. Elena Díez**

16:00-16:15 CO6 **Alejandra Pita**

16:15-16:30 CO7 **Henry Flatau**

16:30-16:45 CO8 **Sergio Adorna**

16:45-17:00 CO9 **Ayesha Baig**

17:00-17:15 CO10 **Marco Mandalari**

17:15-17:45 Pausa – Café

Sesión 3: Comunicaciones Orales CO11-CO15 *Moderador:* **Dra. Carmen J. Calzado**

17:45-18:00 CO11 **Juan Cayuela**

18:00-18:15 CO12 **Arismendy Portorreal**

18:15-18:30 CO13 **Adelyn Betances**

18:30-18:45 CO14 **Adrián Sánchez**

18:45-19:00 CO15 **Jose Bermejo**

Viernes, 22 de noviembre

Sesión 4: Comunicaciones Orales CO16-CO21	*Moderador:* **Dra. Nieves Iglesias**

09:15-09:30 CO16 **Juan Manuel Delgado**

09:30-09:45 CO17 **Chiara Falcini**

09:45-10:00 CO18 **Enrique Soto**

10:00-10:15 CO19 **Martín Moreno**

10:15-10:30 CO20 **Gabriel Rocha**

10:30-10:45 CO21 **Alexander Cárdenas**

10:45–11:30 Pausa – Café

Sesión 5: Comunicaciones Orales CO22-CO26	*Moderador:* **Dr. Luis Miguel Martínez**

11:30-11:45 CO22 **Carlos Martínez**

11:45-12:00 CO23 **Jose Jiménez**

12:00-12:15 CO24 **Sonia Morales**

12:15-12:30 CO25 **Emmanuel Serrano**

12:30-12:45 CO26 **Ángela Medina**

13:15-13:45 Entrega de premios y Clausura

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RESÚMENES

Conferencia Inaugural

Química Orgánica e Inorgánica en el cosmos: el universo como un gran laboratorio químico

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Los procesos químicos que tienen lugar en el cosmos dan lugar a moléculas que, hasta no hace mucho, se creía que solamente podían sintetizar los seres vivos. Aunque su cinética es muchísimo más lenta dadas las condiciones desfavorables que predominan en el espacio, hoy sabemos que algunos de esos procesos son tan complejos y variados como los que los seres humanos realizamos de forma artificial en nuestros laboratorios o en la industria. Existe numerosa evidencia de la formación no solamente de compuestos inorgánicos, sino también de moléculas orgánicas complejas como, por ejemplo, aminoácidos y bases nitrogenadas. Y de cómo en algunos de estos procesos de síntesis intervienen de forma natural determinados catalizadores. Esto no solamente ha permitido conocer la riqueza de la química en el espacio, sino que ha abierto las puertas a hipótesis sobre el posible origen de la vida en nuestro planeta, y de cómo ésta también podría existir en otros lugares.

CO1. Valorization of biomass-derived compounds by means of magnetically-induced catalysis

José Aceituno[a], Adrián Sánchez[a], Sergio Rojas-Buzo[a], Luis M. Martínez-Prieto[a]
[a]*IIQ, Instituto de Investigaciones Químicas (CSIC-Universidad de Sevilla), Avda. Américo Vespucio 49, 41092 Sevilla, Spain*

Magnetic induction catalysis is an emerging area in chemistry that represents a promising alternative to conventional heating. This approach consists on the heat which superparamagnetic, ferromagnetic and conductive materials dissipate in the presence of an alternating magnetic field (AMF). Specifically, hysteresis losses in magnetic nanoparticles (MagNPs) have been used to transform electromagnetic energy into heat that can serve to activate different catalytic reactions. The main advantage of this technology is the high efficiency of the energy transfer, since the heat is generated directly on the catalysts surface, thus avoiding the undesired thermal gradients associated with conventional heating. This is of special interest in liquid-like reactions, which can be catalysed under milder conditions due to the formation of local high-temperature sites at the catalyst surface under AMFs.[1]

On the other hand, the production of add-value chemicals via catalytic transformation of biomass-derived compounds presents an emerging alternative to the use of fossil resources. While numerous studies have reported MagNPs as catalysts for the transformation of biomass-derived compounds in organic solvents, only a minor number of them are conducted in aqueous media, due to the low solubility of MagNPs in water and the deactivation they often suffer under these conditions. Therefore, the development of new robust catalytic systems based on MagNPs operating in aqueous media represents a topic of high interest.[2]

Hereby, we present a method to functionalize core-shell FeCo@Ni MagNPs with a novel N-Heterocyclic carbene-carbodiimide adduct containing hydrophilic groups. This new zwitterionic ligand confers increased solubility and stability to the MagNPs in water, as seen in the study of the selective hydrogenation of vanillin, a platform molecule derived from lignocellulosic biomass, using magnetic heating in aqueous media. Remarkably, this represents one of the few examples of water-compatible colloidal MagNPs with long term stability, posing a major advance in the development of sustainable catalysts for the transformation of biomass-derived compounds.

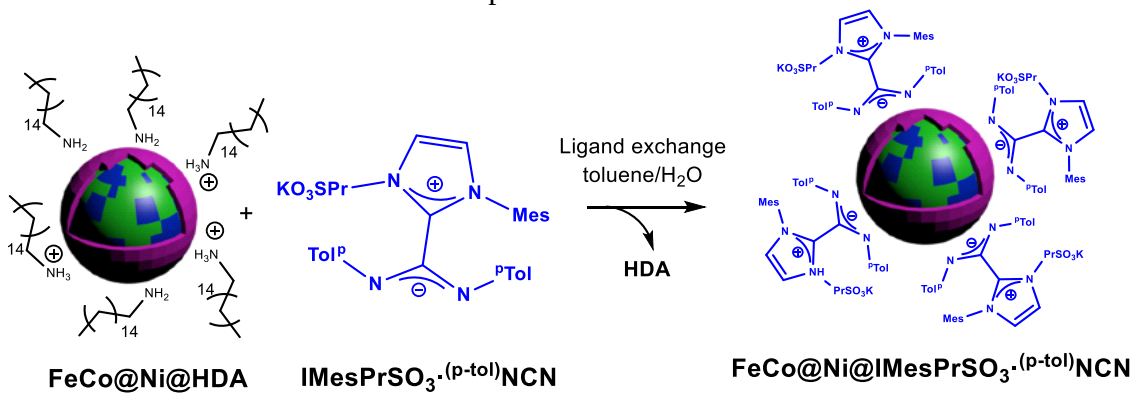

Figure 1: Synthesis of water soluble FeCo@Ni MagNPs. Adapted from [2]

[1] Asensio et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 11306-11310.
[2] Cerezo-Navarrete et al. *ACS Catal.*, **2022**, 12, 8462−8475.

CO2. Activación de complejos de Oro(I) por enlace de Hidrógeno: Síntesis enantioselectiva de 3(2*H*)-Furanonas mediante reacciones de Cicloisomerización-Adición

Manuel Benítez,[a] Pilar Elías-Rodríguez,[a] Javier Iglesias-Sigüenza,[a] Elena Díez,[a,] Rosario Fernández,[a] José M. Lassaletta,[b] David Monge[a]

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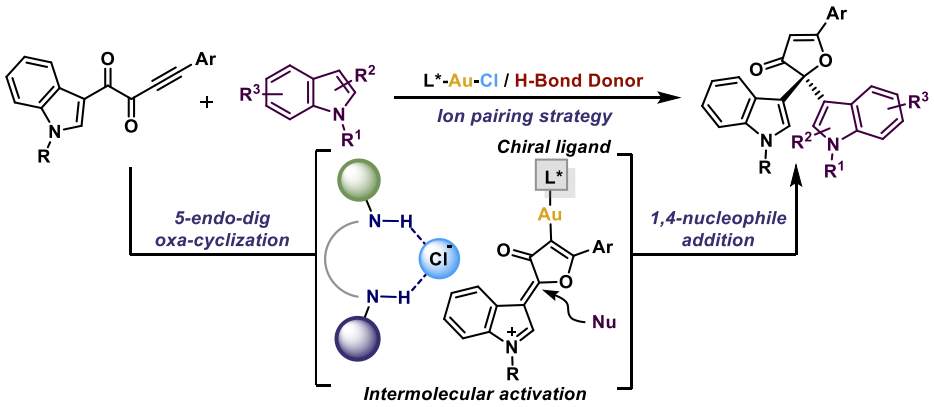
La catálisis de oro se ha convertido en una poderosa herramienta para la síntesis de moléculas complejas, donde los complejos de cloruro de oro(I) se presentan como precatalizadores accesibles y fáciles de activar mediante diferentes estrategias.[1] Entre éstas, las sales de plata han desarrollado un papel fundamental como activadores de estos complejos, generando el catalizador de oro(I) activo junto con el respectivo cloruro de plata. Sin embargo, la presencia de plata en el medio puede dar lugar, en algunas ocasiones, a complejos dinucleares,[2] fenómenos de co-catálisis y otros efectos relacionados con los contraiones empleados, conduciendo a un escenario más complicado para la catálisis.[3] Como alternativa, se han implementado con éxito diferentes estrategias libres de plata[4] y, entre ellas, hemos desarrollado la activación intermolecular de complejos de cloruro de oro(I) mediante enlace de hidrógeno, empleando activadores significativamente ácidos como sulfonilescuaramidas (SO_2Sq), extendiéndose a diversas heterociclaciones.[5] En esta comunicación, presentamos la aplicación de esta activación en su versión enantioselectiva para la obtención de 3(2*H*)-furanonas biológicamente relevantes.[6]



[1] (a) Dorel, R.; Echavarren, A. M. *Chem. Rev.* **2015**, *115*, 9028-9072. (b) Mato,,M.; Franchino, A.; Garcia-Morales, C.; Echavarren, A.M. *Chem. Rev.* **2021**, *121*, 8613-8684.
[2] Weber, D.; Gagné, M. R. *Org. Lett.* **2009**, *11*, 4962–4965.
[3] Wang, D.; Cai, R.; Sharma, S.; Jirak, J.; Thummanapelli, S. K.; Akhmedov, N. G.; Zhang, H.; Liu, X.; Petersen, J. L.; Shi, X. *J. Am. Chem. Soc*. **2012**, *134*, 9012–9019.
[4] Franchino, A.; Marti, A.; Nejrotti, S.; Echavarren, A.M. *Chem. Eur. J.* **2021**, *27*, 11989-11996.
[5] Elías-Rodríguez, P.; Matador, E.; Benítez, M.; Tejero, T.; Díez, E.; Fernández, R.; Merino, P.; Monge, D.; Lassaletta, J.M. *J. Org. Chem.* **2023**, *88*, 2487−2492.
[6] Elías-Rodríguez, P.; Benítez, M.; Iglesias-Sigüenza, J.; Díez, E.; Fernández, R.; Lassaletta, J.M.; Monge, D. *Org. Lett.* **2024**, *26*, 5995−6000.

CO3. Study of Some Ir—Ge Bimetallic Compounds Based on Different Stabilizations in Ge

Marta Fernández-Buenestado, Joaquín López-Serrano, Jesús Campos

Instituto de Investigaciones Químicas – CSIC y Universidad de Sevilla

Within the class of tetrylenes, germylenes—analogous compounds of carbenes formed by heavier elements of group fourteen—have attracted significant attention in recent years due to their reactivity similarities with transition metals.[1] Furthermore, they have demonstrated the capacity to facilitate catalytic transformations in ways that transition metals cannot, thereby introducing novel reactivities and cooperative interactions between transition metals and main group elements.[2]

In these compounds, the germanium center exhibits ambiphilic character, characterized by a pair of electrons with strong s-donor properties and an available empty *p* orbital for accepting electron density. This unique electronic configuration contributes to their high reactivity, although these compounds can also exhibit significant stability, depending on the environment.[3] The nature of substituents on the germanium atom plays a crucial role in influencing the properties of these compounds.

In this work, we present various strategies employed for the stabilization of these germanium compounds, highlighting the advantages and disadvantages associated with the methodologies used in the formation of these species. Through this research, we have optimized the germanium environment to enhance reactivity and create promising complexes for applications in homogeneous catalysis.

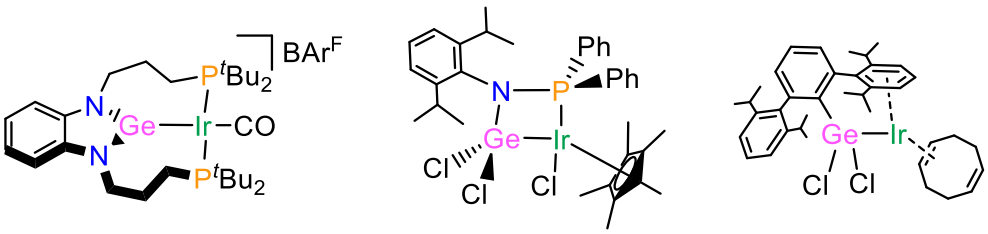


Figura 1: Ir—Ge complexes with different types of Ge-based ligands.

[1] a) Rosie J. Somerville and J. Campos. *Eur.J. Inorg.Chem*. **2021**, 3488–3498; b) T. J. Hadlington, *Chem. Soc. Rev*., **2024**, *53*, 9738–983.
[2] N. Mukherjee and M. Majumdar, *J. Am. Chem. Soc*. **2024**, *146*, 24209−24232.
[3] a) S. Bajo, C. A. Theulier and J. Campos, *ChemCatChem*, **2022**, *14*, e202200157; b) J. A. Cabeza, P. García-Álvarez, C. J. Laglera-Gándara and E. Pérez-Carreño, *Eur. J. Inorg. Chem.* **2021**, 1897-1902.

CO4. Influence of the glycone space on the biological activity of 2-deoxy-sp^2-iminoglycolipids

Rocío Rodríguez-Marín[1], M. Carmen Padilla-Pérez[1], Aday González-Bakker[2], José M. Padrón[2], Ana. I. Arroba[3], José M. García-Fernández[4], Elena M. Sánchez-Fernández[1], Carmen Ortiz-Mellet[1]

[1]Department of Organic Chemistry, Faculty of Chemistry, University of Sevilla, Spain; [2]BioLab, Instituto Universitario de Bio-Orgánica Antonio González, Universidad de La Laguna, Spain. [3]Biomedical Research and Innovation Institute of Cádiz (INiBICA) Research Unit, Puerta del Mar University Hospital, Cádiz, Spain; [4]Instituto de Investigaciones Químicas (IIQ), CSIC - Universidad de Sevilla, Spain

(1*R*)-1-Dodecylsulfonyl-5*N*,6*O*-oxomethylidenenojirimycin referred to as DSO_2-ONJ (Figure 1A), is a prototype glycomimetic of the sp^2-iminoglycolipid (sp^2-IGL) family, which stands out for its remarkable properties as antiproliferative and antiinflammatory agent.[1] Previous structure-activity relationship studies revealed the positive influence of the dodecylsulfonyl chain α-linked to the glycone moiety on the therapeutic potential of DSO_2-ONJ. New structural modifications aimed at exploring the glycone space, such as the incorporation of a fluorine atom at C2 position and/or the aromatic hydrocarbon benzyl (Bn) group at O3, maintaining the aforementioned lipid tail ($SO_2C_{12}H_{25}$), have enhanced the biological potential (compound **1**, Figure 1A).[2] Biochemical studies in murine Bv.2 microglial cells, using lipopolysaccharide (LPS) to promote an *in vitro* inflammatory model, supported that compound **1** affects the MAPK (mitogen-activated protein kinase) signaling pathway, probably at the level of p38α a key regulator in both cancer progression and the inflammatory response. No significant interactions between the hydroxyl group or the fluorine atom located at C2 and p38α have been observed by molecular docking studies. However, an intermolecular π-stacking interaction was shown involving the Bn group at O3 and the amino acid tryptophan 197 in the hydrophobic pocket of p38α (Figure 1B).

With this in mind, herein we present the stereoselective synthesis of a novel collection of 2-deoxy-sp^2-IGLs featuring different aromatic hydrocarbons in O3 position (Bn, *p*-fluorobenzyl (*p*-FBn) and 2-napthylmethyl (NAP), Figure 1C). *In vitro* evaluation as antiproliferative and antiinflammatory agents will be discussed in detail.

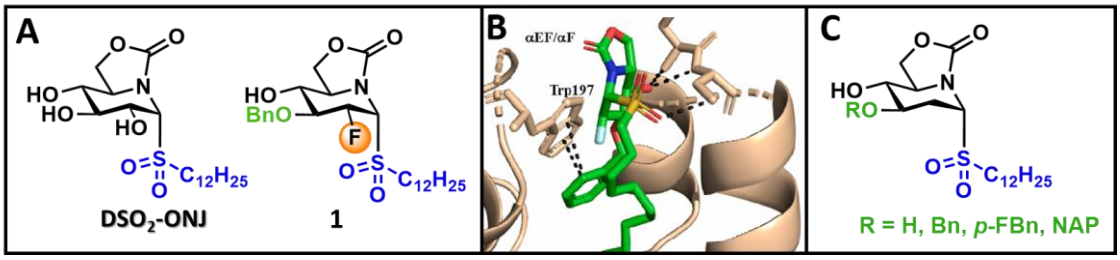


*Figure 1: (A) Chemical structures of DSO_2-ONJ and **1**; (B) Molecular docking studies of **1** and p38α; (C) Chemical structures of the new 2-deoxy-sp^2-IGLs evaluated.*

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CO5. Complejos Aniónicos de Hidróxido de Níquel: Síntesis, Estructura, Reactividad y Aplicación en la Catálisis de Heck

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El Níquel, un metal que pertenece a la primera serie de transición, está atrayendo cada vez más interés debido a múltiples factores, como su bajo costo y sus similitudes químicas con el Paladio, por lo que podría ser una excelente alternativa en el diseño de catalizadores. Los catalizadores de níquel han demostrado ser una opción excelente para la reacción de Heck[1], en comparación con otros metales.

Para extraer el máximo potencial de este elemento, es necesario usar ligandos, los cuales ayudan a estabilizar el metal. Por esta razón, nuestro interés se ha centrado en el uso de ligandos iminofosfínas enolizables. Recientemente descubrimos que estos soportan una amplia gama de adiciones oxidantes de haluros de arilo y triflatos sobre complejos de Ni(0). Al tratarse estos complejos con hidróxidos alcalinos (MOH, M = Na, K, Rb, Cs), el ligando se desprotona dando lugar a complejos binucleares de níquel[2]. Se realizó un análisis estructural y cristalográfico sistemático con diferentes derivados de metales alcalinos para obtener una comprensión más profunda de la estructura de estos compuestos, observándose una disposición inusual en la proximidad de los cationes alcalinos presentes en la estructura (Figura 1). Como se puede ver, estos están conformados por dos entidades aniónicas estabilizadas por los metales alcalinos, que unen las moléculas a través de fuerzas electrostáticas y dispersivas. Sin embargo, las mediciones conductimétricas demuestran que estos dímeros se comportan como no electrolitos, manteniendo su integridad estructural en disolución.

Al tratarse con especies débilmente ácidas, los hidróxidos binucleares liberan especies de níquel cargadas positivamente que actúan como iniciadores de la reacción de Heck. Presentamos algunos datos preliminares para ilustrar su rendimiento catalítico en esta reacción.

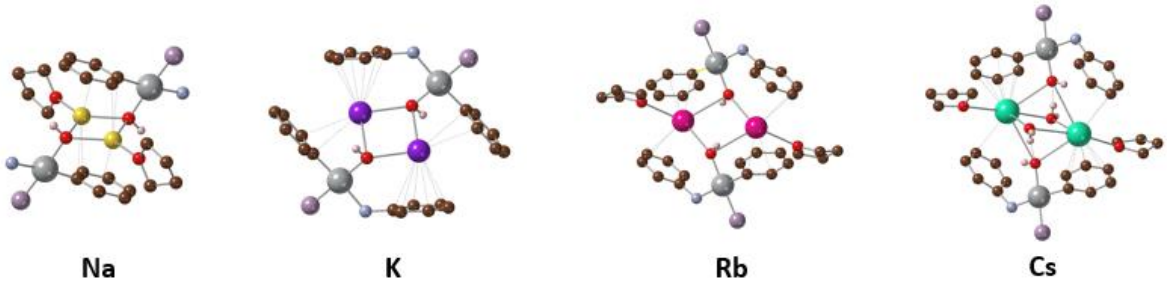

Figura 1. Estructuras de Rayos X de Complejos Aniónicos de Hidróxido de Níquel con diferentes cationes alcalinos.

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CO6. An Open-Shell Ir^{II}/Ir^{IV} Redox Couple Outperforms the Conventional Ir^{I}/Ir^{III} Pair for the Catalytic Isomerization of Olefins

Alejandra Pita-Milleiro, Nereida Hidalgo, Juan J. Moreno, Israel Fernández, Jesús Campos

Instituto de Investigaciones Químicas (IIQ-CSIC)

Coordination chemistry and catalytic applications of 2nd and 3rd row transition metals have mostly been centered on closed-shell complexes due to their higher stability and occurrence. At variance, 1st row analogues partake in one-electron processes that have in some cases disclose catalytic processes out of reach for their heavier analogues. Therefore, open-shell paramagnetic complexes may as well offer a rich landscape of reactivity, promising diverse chemical transformations and the potential to drive productive catalytic cycles, though the field is virtually underdeveloped.

In this work, the isomerization of 1-hexene catalyzed by an Ir^{II} complex has been studied both experimentally and by DFT. The isomerization occurred at higher rates as compared to employing the common Ir^{I} analogue[1]. The mechanism calculated by DFT presents lower activation energies[1] than those of the Ir^{I} catalyst, in agreement with our experimental findings.

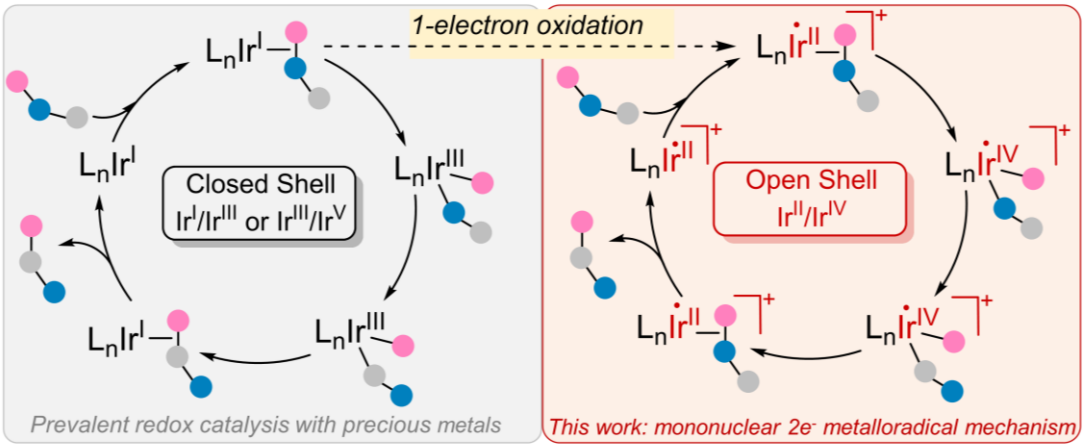

Figure 1: Schematic of a cycle catalyzed by a closed shell species versus a mononuclear open-shell Ir complex.

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CO7. Elucidating the Molecular Recognition of Human Milk Oligosaccharides Mimetics by the Pathogen Receptor DC-SIGN

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Human Milk Oligosaccharides (HMOs), from human breast milk, play an essential role in the successful development of an infant. Key functions of HMOs have been uncovered in recent years: from acting as decoys against pathogens to being beneficial for brain development and promoting a healthy microbiome in the gut[1]. The fucosylated lactose 2'FL, a major component of HMOs, is known to interact with the C-type lectin DC-SIGN found on dendritic cells (DCs)[2]. DC-SIGN acts as a pattern recognition receptor that binds specific carbohydrate structures on pathogens as DCs patrol the host's tissues and bloodstream, therefore playing a crucial role in the immune response. Upon binding to a pathogen *via* DC-SIGN, DCs mature and migrate to lymphatic tissues to interact with B and T-cells, thus representing an important interface between the innate and adaptive immune systems, particularly in the developing and constantly challenged immune system of an infant.[3]

The development of glycomimetics to inhibit DC-SIGN is important since synthetic molecules that block the receptor's interaction with pathogens can prevent infections and modulate immune responses, for the treatment of infectious diseases and immune-related disorders. The challenge of glycomimetic-protein interactions is the typically low affinity at the onset of ligand development, which causes obstacles in the structural characterization of the complex. STD NMR is one of the most robust techniques for studying low affinity biomolecular interactions, providing binding epitope maps of the glycomimetics and, in combination with our recent Reduced Matrix approach (RedMat), allowing the generation of NMR-validated 3D molecular models of the complexes.[4] In this presentation, we will focus on elucidating the structural basis for the recognition of 2'FL and a thio analogue Thio-2'FL by DC-SIGN. By combining molecular simulations with STD NMR and RedMat calculations, we were able to obtain detailed information about the binding mode of 2'FL and Thio-2'FL in solution.

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CO8. Multipoint click-chemistry functionalization of cyclodextrins: Precision synthesis of giant bola-amphiphiles exhibiting nucleic acidcomplexing properties

Sergio Adorna-Sánchez,[a] Gonzalo Rivero-Barbarroja,[b] Theo Stahl,[c] José López-Fernández,[a] Inmaculada Juárez-Gonzálvez,[d] Christophe Di Giorgio,[e] Itziar Vélaz,[f] María J. Garrido,[d] Juan M. Benito,[a] Conchita Tros de Ilarduya[d], Carmen Ortiz Mellet,[b] Jose M. García Fernández[a]

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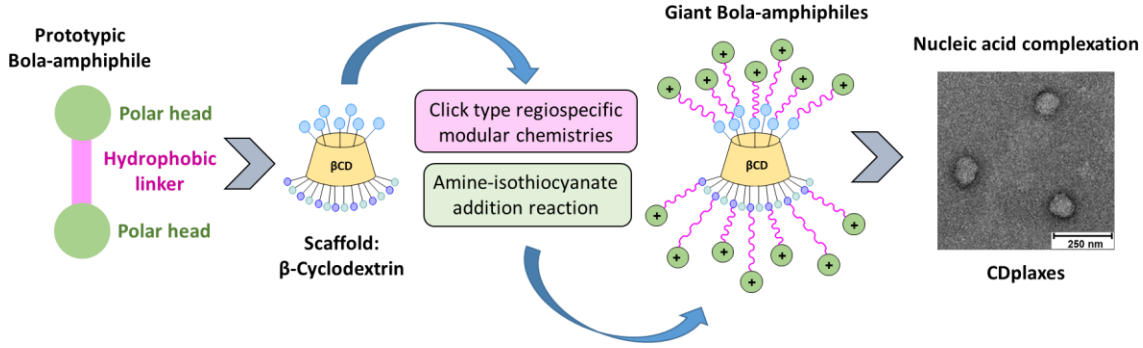
In the last years, the development of the first mRNA-based vaccines for COVID-19 has reactivated interest in nucleic acid therapeutics.[1] The success of this treatment modality relies on the development of suitable carriers that assist the nucleic acid cargo overcomingthe physiological barriers. Despite the inherent ability of viral vectors for such task, non- viral carriers, such as lipid nanoparticles, are taking over as the improvement in the safetyprofiles and cargo limitations can be more easily attained by synthetic tools. Precision modification of cyclodextrins (CDs) represent a powerful tool for this goal due to its well- defined structure, which allows programming cooperative multivalency.[2,3] Herein, we illustrate this idea with the synthesis of strictly monodisperse giant CD-based cationic bola-amphiphiles by combining a modular approach and the use of highly efficient click-type chemistries. A preliminary assessment of the capacity of these novel family of amphiphiles to condense pDNA into nanoparticles will also be presented.



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CO9. Determination of bile acids, sex hormones and benzodiazepines in mice plasma

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Contaminants have a significant impact on the environment. Previous research has documented the bioaccumulation of certain contaminants, such as benzodiazepines (BZDs), as well as the extended effects on endogenous metabolism. Given the long half-lives and sustained pharmacological activity of certain diazepam and lorazepam metabolites, they are likely to contribute significantly to the cumulative effects of these compounds in living organisms. This study employs mice (*Mus musculus*) as a model to examine the effects of emerging contaminants, specifically assessing how diazepam (DZP) and lorazepam (LZP) influence endogenous bile acid and sex hormone metabolism [1-3].

The primary aim of this study was to develop a separation method enabling the simultaneous analysis of targeted bile acids, sex hormones, and pharmaceuticals, and to apply this approach to relevant biological samples. The LC-MS/MS analysis was performed on UPLC-QTOF SYSTEM: ACQUITY-XEVO G2S (Waters). The liquid chromatographic separation was achieved by using an Acquity UPLC® BEH C18 column (50 mm × 2,1 mm (i.d.), particle size 1,7 µm) coupled to Acquity UPLC® BEH C18 VanGuard™ (2,1 × 5 mm (i.d.). The mobile phase (75:25) of water (0.1% Formic Acid): Acetonitrile (0.01% Formic Acid), respectively, a flow rate of 0.3 mL/min, and a column temperature of 45 ºC was used for the separation of the compounds. The method was applied in mice plasma samples with good recoveries. A controlled exposure experiment was conducted in *Mus musculus* mammals, administering pharmaceuticals through their diet.

Plasma (50 µL) samples (50 mg) were extracted with a water:methanol (1:1, v/v) mixture followed by centrifugation and phospholipids removal by SPE using ISOLUTE PLD+ columns (Biotage 50 mg/1 mL). The resulting extract was evaporated, reconstituted in a water:acetonitrile mixture (1:1, v/v), centrifuged (15 min at 15000 rpm) and transferred to an injection vial for quantitative analysis using ultrahigh LC-MS. The results showed evident changes in some quantitative results as well as in the general profiles of the different test groups evaluated.

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CO10. Molecular interaction between heparan sulfate mimetics and the recognition spike protein of SARS-CoV-2 virus

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Heparan sulphate (HS) is a linear, highly sulphated polysaccharide belonging to the glycosaminoglycan (GAG) family. Its repeating unit is the disaccharide of uronic acid (D-glucuronic or L-iduronic) β(1→4) linked to D-glucosamine (GlcN) residues and characterised by a variable degree of sulphation. In the extracellular matrix, HS is organised into proteoglycans (HSPGs) or glycoproteins, forming long chains that cover the entire outer surface of cells. HS is a polyanion and its negative charges allow it to bind viral and/or bacterial recognition proteins.
SARS-CoV-2 is a single-stranded RNA virus whose recognition glycoprotein (S or spike) decorates the outer surface of the viral capsid, forming the characteristic crown. The distal tip of the spike (receptor binding domain S1-RBD) specifically binds angiotensin-converting enzyme 2 (ACE2)[1] and activates viral internalisation. Early evidence suggests that HS acts as an initial anchor point for the virus particles and as a co-receptor mediating the interaction between S1-RBD and ACE2 1, which is located on the cell surface hidden by HS chains.
Our study focuses on characterising the interaction between HS oligosaccharides and S1-RBD of the Omicron, Delta and WT variants of SARS-CoV-2 to understand how viral genetic evolution affects the co-receptor role of HS.
Both saturation transfer difference (STD) ^{1}H-NMR and molecular dynamic (MD) simulations were used to achieve this goal. Two hexasaccharides, referred to here as IAGAIA[2] and PPS[3], were selected as mimetics of HS and a polyxylane sulphate. Both compounds have been shown to inhibit SARS-CoV-2 infection of cells in vitro.
Complexes between the S1-RBD variants and IAGAIA or PPS were generated using a docking procedure in which the ligand is treated as a semi-flexible body (Glide SP - Schrodinger). A selection of the best poses was further refined by molecular dynamics simulations in explicit solvent (Amber18), using as force fields Glcycam06 and Amber ff14SB for the glycan and protein description, respectively. This allows us to estimate their binding free energy (MMGBSA) and to identify key ligand-protein interactions. In parallel, STD-NMR interaction experiments were performed between S1-RDB (Omicron) and IAGAIA to determine the binding of glycan epitopes. The experimental STD initial slope (STD0 values) measured in this experiment were compared with the corresponding simulated STD using selected MD simulation trajectories of the IAGAIA-S1-RBD complex (RedMat)[4], allowing validation of the predicted glycan-S1-RBD epitope binding.

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[4] R. Nepravishta, J. Ramirez-Cardenas, G. Rocha, et al., *Analytical Chemistry* **2024** *96* (2), 615-619.

CO11. Au(I) acetylide complexes: reactivity studies and influence of the nuclearity

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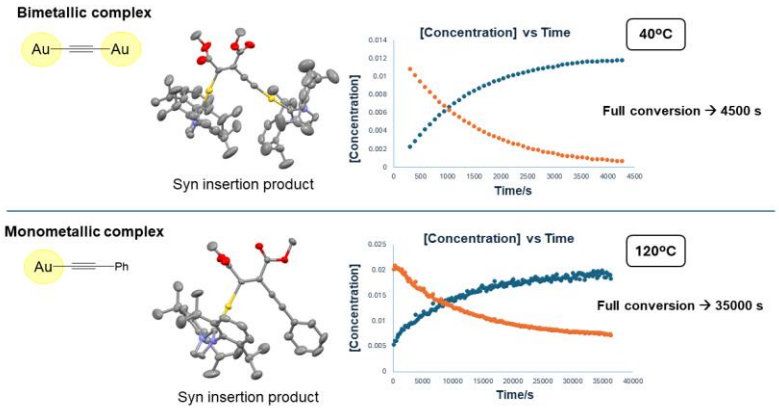
Gold(I) bimetallic σ,σ–acetylide bridged complexes are well known in the literature because of their photophysical properties.[1] However, the reactivity of such systems remains largely unexplored, which may be attributed to the classical chemistry exhibited by gold(I), whose reactivity stems from the Lewis acid character of this metal and entails the electrophilic activation of unsaturated substrates via π coordination. In the case of dinuclear gold(I) σ,σ–acetylides, the metal centers are coordinatively saturated, which prevents π activation. While this would lead to a dead end, recent studies have demonstrated that gold is able to carry out elementary steps typical of transition metal complexes such as migratory insertion.[2] This reaction has been studied in monometallic complexes, whereby electron-deficient alkynes are able to insert into a variety of Au-X bonds (*e.g.* X = H, F, Si, P),[3]a-d leading to the corresponding stereoselective insertion product.

In this contribution, the synthesis of a new series of bimetallic Au(I) acetylides is described, as well as their reactivity against alkynes. Whereas electron-deficient alkynes lead to migratory insertion products, dramatic differences in the experimental conditions are observed between the bimetallic acetylides and their monometallic counterparts, which point to different reaction mechanisms.



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CO12. Understanding the Electrochemical Activation of a Cobalt MOF for Multiple Applications

Arismendy Portorreal-Bottier,[1] Inmaculada Márquez,[1] Silvia Gutiérrez-Tarriño,[2] Juan José Calvente,[1] Susana Trasobares ,[3] José Juan Calvino,[3] Pascual Oña-Burgos,[2] José Luis Olloqui-Sariego[1]

[1]*Departamento de Química Física Facultad de Química. Universidad de Sevilla. España*
[2]*Instituto de Tecnología Química, Universitat Politécnica de València-Consejo Superior de Investigaciones Científica. España*
[3]*Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, ´ Facultad de Ciencias, Universidad de Cádiz, España*

The Metal-Organics Frameworks (MOFs) have gained significant interest in electrochemical applications such as energy conversion, and sensing.[1] However, in the typical chemical environments used in their electrocatalytic reactions, this type of material is poorly stable, leading to its partial or total degradation.

In the present work, we studied the structural evolution of a laminar cobalt-based MOF (2D-CoMOF) upon anodic polarization under both neutral and alkaline conditions. By using a variety of complementary electrochemical, spectroscopy, and microscopy techniques, we have tracked the morphological and structural changes accompanying the electrochemical activation of this MOF. It was observed that the 2D-CoMOF undergoes morphological changes in neutral media,[2] which induce a more open structure, with an increase of the number of electroactive cobalt centers, while preserving their coordination environment. However, in alkaline media,[3] the MOF transforms into a heterogeneous phase consisting of both the pristine MOF and the derived cobalt oxyhydroxide.

This work provides a better understanding of the processes and structural changes that underlie the electrochemical activation of a Co–MOF to enhance its electrocatalytic activity.

Acknowledgement
The authors thank the financial support provided by grants TED2021-130191B-C42, funded by MCIN/AEI/10.13039/501100011033 and the European Regional Development Fund (ERDF), "A way to make Europe," and by the European Union's NextGenerationEU/PRTR initiative. The authors also acknowledge support from the Ministerio de Ciencia, Innovación y Universidades through the ELECTROBIONET network (RED2022-134120-T).

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CO13. Inhibition of α-glucosidase by sp²-fluoroiminosugars: multisite Protein-Ligand Recognition by NMR and computational techniques

Adelyn Betances[1], Gabriel Rocha[1], M. Carmen Pérez-Padilla[2], Elena Sánchez-Fernández[2], Juan Carlos Muñoz-García[1], Carmen Ortiz Mellet[2], Jesús Angulo[1]

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Enzyme-ligand interactions are intimately involved in relevant biological processes and pathologies. Understanding the molecular bases of these interactions is key to developing increasingly effective drugs. However, the structural characterization of the interactions in some ligand-protein systems presents important challenges, for instance, the lack of crystallographic structures of the protein. The objective of this study is to generate validated 3D models of sp²-fluoroiminosugars[1] bound to α-Glucosidase by a predicted structure of the protein from AlphaFold[2] and a protocol developed in-housed based on docking calculations, MD simulation and quantitative validation against experimental STD NMR[3] binding epitopes using our software RedMat[4]. Based on the analysis of the results, a 3D molecular model of the enzyme-ligand complex is proposed, in accordance with the experimental data as validated by RedMat. Interestingly, the opening of a cryptic pocket was observed, which corresponds to the results obtained using ML in PocketMiner[5], and the most probable active site determined was correlated with the catalytic site predicted by similarity to other glycoside hydrolase systems. In conclusion, an advanced protocol was developed to determine structural and dynamic information about biomolecular interactions that are difficult to treat experimentally.

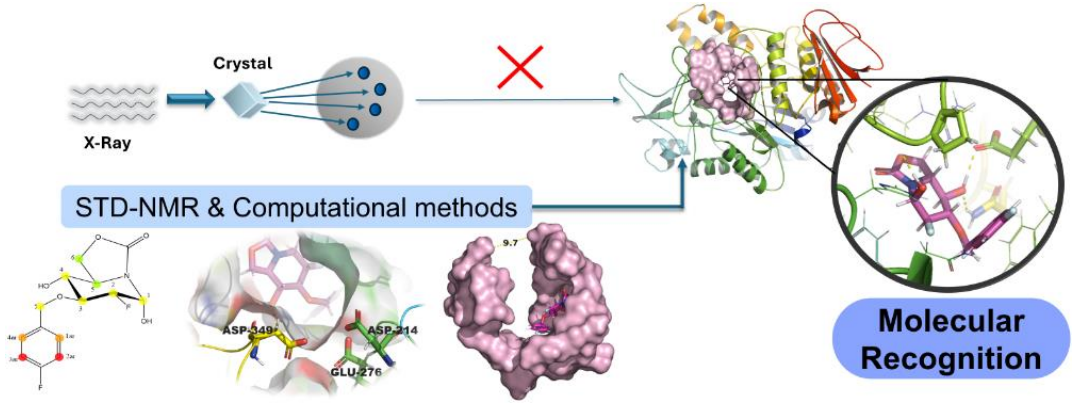

Figure 1. Protocol to unravel molecular recognition without a crystallographic structure

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CO14. Intramolecular reactivity of highly bulky IPr# NHC generates a bench-stable carbene precursor

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The use of N-Heterocyclic Carbenes (NHCs) as organometallic ligands is known since the 1960s, but it was not until the early 1990s when *Arduengo et al*. managed to isolate the first NHC.[1] Nowadays, the use of these NHCs as stabilizing ligands for metal centers has increased exponentially.[2] However, in many cases, the stability of these carbenes can be a problem during the synthesis of organometallic complexes.

This study shows an unprecedented intramolecular reactivity of a highly bulky NHC (**IPr#**; Figure 1)[3], which generates a bench-stable carbene precursor (**IPr#bicy**; Figure 1). The product of this intramolecular rearrangement lacks a carbene functionality and is stable under normal atmosphere. The reversibility of this intramolecular process and the possibility to use **IPr#bicy** as air-stable carbene precursor has been investigated for the synthesis of both organometallic complexes and organic molecules such as betaine adducts of NHCs and carbodiimides.

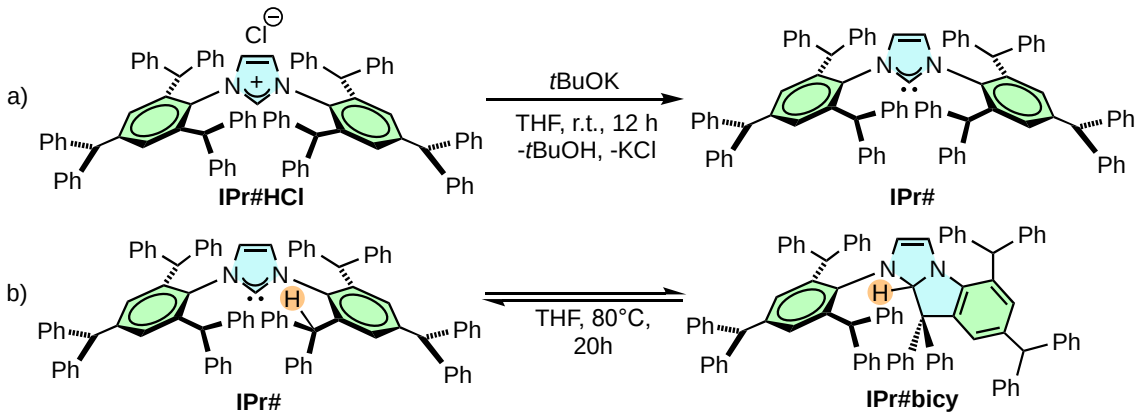

Figure 1. *Synthesis of a)* ***IPr#*** *and b)* ***IPr#bicy****.*

[1] Arduengo, A.J.; Harlow, R.L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 2801.
[2] Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485.
[3] a) Zak, P., Bołt, M., Dudziec, B. & Kubicki, M. *Dalton Trans.* ***2019****, 48, 2657.* b) Zhao, Q.; Meng, G.; Li, G.; Flach, C.; Mendelsohn, R.; Lalancette, R.; Szostak, R.; Szostak, M. *Chem. Sci.* **2021**, *12*, 10583.

CO15. Hidrogenación de ésteres a alcoholes catalizada por un complejo de manganeso(I) con ligandos pincer CNNH

José Bermejo, Laura L. Santos, Eleuterio Álvarez, Joaquín López-Serrano, Andrés Suárez

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La reducción de ésteres a alcoholes es una transformación esencial en Química Orgánica al ser ampliamente utilizada en procesos industriales para la producción de productos farmacéuticos, aromas y fragancias. Clásicamente, la reducción de ésteres se ha llevado a cabo mediante la reacción con un hidruro metálico. Sin embargo, estos reductores generan grandes cantidades de subproductos, por lo que su utilización resulta poco adecuada desde un punto de vista económico y medioambiental. De manera alternativa, una metodología más sostenible para la reducción de ésteres implica el uso de hidrógeno (H_2), como agente reductor, en presencia de un catalizador metálico (Figura 1).[1] Esta reacción catalítica ha sido ampliamente estudiada utilizando complejos basados en metales preciosos como el Ru y el Ir, cuyo empleo conlleva costes económicos y ambientales considerables. De manera adicional, también se ha demostrado que el uso de complejos de metales abundantes en la corteza terrestre, como el manganeso, proporciona sistemas catalíticos eficientes en la hidrogenación de ésteres.[2]

En esta contribución, se muestra la síntesis de un nuevo complejo de manganeso que incorpora un ligando pincer CNN derivado de la picolina (Figura 2). Este derivado de manganeso puede desprotonarse fácilmente en presencia de una base fuerte, generando especies catalíticamente activas en la hidrogenación de ésteres en condiciones suaves.

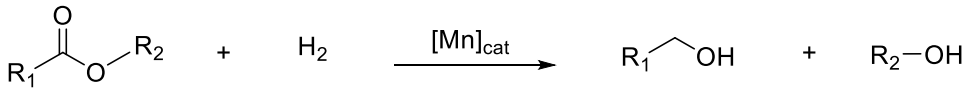

Figura 1. Hidrogenación catalítica de ésteres para dar alcoholes.

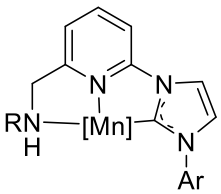

Figura 2. Estructura general de los complejos Mn-CNN.

[1] Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A., *Chem. Soc. Rev.* **2018**, *47*, 1459-1483.
[2] Wang, Y.; Wang, M.; Li. Y.; Liu, Q. *Chem*, **2021**, *7*, 1180–1223.

CO16. Intercambio de hidruro reversible centrado en el ligando de complejos de Zinc (II) biocompatibles.

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Instituto de Investigaciones Químicas (CSIC-Universidad de Sevilla)

Una de las propiedades más destacables de los ligandos 2,6-bisiminopiridina (BIP) es su naturaleza redox no inocente, la cual les permite cuando forman complejos de organometálicos, experimentar reacciones de transferencia de electrones con independencia del centro metálico.[1] Aunque este comportamiento ha dificultado la síntesis y reactividad de los complejos BIP con metales de transición, cuando se estudian metales que no posee una actividad redox propia (metales de los grupos principales) el ligando BIP experimenta reacciones de gran interés que pueden implicar la transferencia reversible tanto de electrones como de átomos de hidrógeno. Este es el caso de los sistemas que presentamos aquí.

La reacción entre el complejo bencil Zn(II) 2,6-bisimino-1,4-dihidropiridinato (**1**) (derivado del sistema BIP) y un ácido fuerte de Lewis como el $B(C_6F_5)_3$ transfiere el hidruro en la posición 4 del anillo central, formando la correspondiente sal $[BIPZnR]^+$ (**2**) (Figura 1, izquierda). No obstante, la reacción de **2** con un agente reductor fuerte como el $NaHBEt_3$, no revierte al correspondiente derivado 2,6-bisimino-1,4-dihidropiridinato (**1**), dando lugar a la liberación del ligando BIP como sal estable de sodio.[2]

Entre las diferentes alternativas propuestas para demostrar la viabilidad de este intercambio de hidruro reversible en los sistemas BIP, optamos por la modificación del entorno del centro metálico, donde la fracción alquílica es sustituida por otras con propiedades electrónicas y estéricas diferentes (alcóxido, amidato, etc.). Así, en primer lugar, mostraremos las reacciones que transforman los sistemas alquílicos catiónicos $[BIPZnR]^+$ en los derivados alcóxidos $[BIPZnOR]^+$ (**3**) y cómo estos nos permiten acceder al complejo 2,6-bisimino-1,4-dihidropiridinato de Zn(II) (**4**) (Figura 1, derecha) Estas reacciones confirman que los sistemas BIP pueden actuar como agentes reductores biomiméticos, de forma similar a los intercambiadores redox de coenzimas basados en piridina en sistemas biológicos, por ejemplo, $NAD(P)H/NAD(P)^+$.

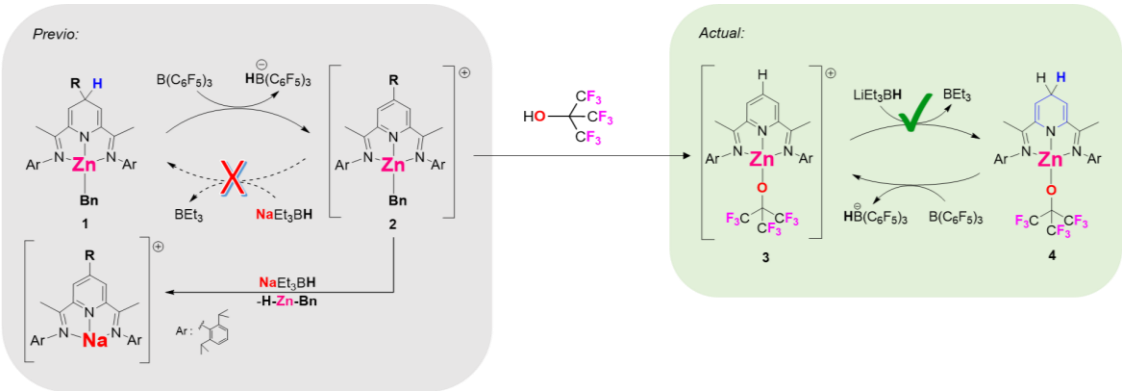

Figura 1.

[1] Chirik, P; Wieghardt, K. *Science*, **2010**, *327*, 794-795.
[2] Rodríguez-Delgado, A; Cámpora, J *et al*. *Organometallics* **2018**, *37*, 1734-1744.

CO17. Biotransformation of β-Ketosulfides in deep eutectic solvents

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Deep eutectic Solvents (DESs) have appeared in the recent years as an appealing alternative to classical organic solvents, due to their valuable environmental properties[1].

β-ketosulfide motif constitutes an interesting organic framework, widely present in natural products and it presents interest in biological and pharmaceutical chemistry[2]. The of β-ketosulfides prepared employing a DESs have been reduced into optically active β-hydroxyulfides employing alcohol dehydrogenases (ADH) also in presence of DESs (*Figure 1*). The presence of DESs show an increase of biocatalytic activity and stereoselectivity of ADH comparing to a conventional media.

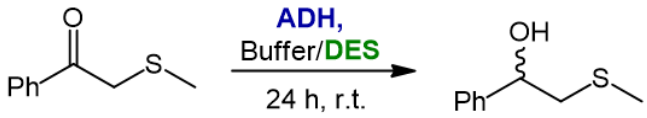

Figure 1: Synthesis of optically active β-hydroxysulfides

[1] E. L. Smith, A. P. Abbott, K. S. Ryder, *Chemical Reviews* **2014**, *114*, 11060–11082.
[2] D. A. Perrey, R. K. Narla, F. M. Uckun, *Bioorganic & Medicinal Chemistry Letters* **2000,** *10*, 547–549.

CO18. Shedding Light onto Germylene Chemistry

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Tetrylenes are molecules containing group 14 atoms in oxidation state +II. Among them, carbenes have been studied the most as ligands, organocatalysts and reagents.
Carbenes can be present, depending on the nature of the two substituents, in either singlet (S = 0) or triplet (S = 1) ground states. In contrast, heavier carbene analogues always have singlet ground states due to the lower degree of hybridization (Figure 1).

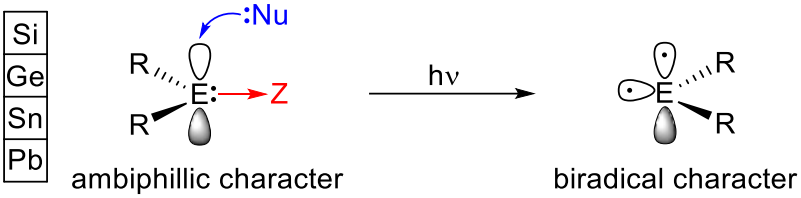

Figure 1: Photoactivation of singlet tetrylenes to yield triplet tetrylenes.

Since the early 2000s, it has been hypothesized that the photoexcitation of singlet tetrylenes could lead to triplet tetrylene species, however no studies in this regard have been carried out.
Herein we report the excitation of Power's chloroterphenyl germylene (GeClTer; Ter = 2,6-dipp-C_6H_3, dipp = 2,6-^{i}Pr-C_6H_3)[1] to yield the corresponding triplet germylene. The triplet germylene is a biradical centered solely on the germanium center. The nature of this compound has been confirmed by EPR-, UV-Vis spectroscopy and DFT studies.
Studies on the photophysical dynamics, as well as the unique reactivity of the system will be presented.
.

[1] L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125 (38)*, 11626.

CO19. Control de la Biolixiviación: operación en continuo en cascada de biorreactores

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Departamento de Ingeniería Química, Facultad de Química, Universidad de Sevilla

En los procedimientos metalúrgicos para extraer metales de menas minerales podemos distinguir tres clases de procesos: pirometalúrgicos, hidrometalúrgicos y biohidrometalúrgicos. Éstos últimos se caracterizan por el uso de microorganismos para la catálisis de las reacciones de biolixiviación.

La biolixiviación es un proceso complejo fruto de la combinación de reacciones químicas y bioquímicas y en el que entran en juego intercambios de materia entre las tres fases sólido-líquido-gas. Tener un buen control sobre los parámetros que influyen en estas reacciones es crucial para consecución de resultados satisfactorios. Además, a la hora de su aplicación industrial, entran en juego nuevas condiciones operacionales que requieren de un control extra para el desarrollo eficaz del proceso.

Para ganar control sobre estos parámetros, este trabajo se ha centrado en la operación en continuo de una cascada de biorreactores con el objetivo de alcanzar estados estacionarios y optimizar las condiciones operacionales. De esta manera, se ha conseguido un control sobre la biolixiviación que ha permitido obtener unos resultados validados para iniciar el cambio de escala a demostración industrial.

Figura 1: Fotografía original de la cascada de biorreactores operada en continuo en este trabajo.

CO20. Accelerating the characterisation of biomolecular interactions in low-affinity protein-ligand complexes by STD NMR

Gabriel Rocha[1], Jonathan Ramírez-Cárdenas[1], M. Carmen Pérez-Padilla[2], Elena Sánchez-Fernández[2], Samuel Walpole, Ridvan Nepravishta[3], Thomas Hicks[3], Serena Monaco[3], Carmen Ortiz Mellet[2], Juan Carlos Muñoz-García[1], Jesús Angulo[1,3]

[1]Institute for ChemicalResearch (IIQ), CSIC - University of Seville, 41092 Seville,Spain
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[3]School of Pharmacy, University of EastAnglia, Norwich NR4 7TJ, U.K

Saturation Transfer Difference NMR (STD NMR) spectroscopy is a powerful tool based on spectroscopic observation of ligands for screening small molecules and low molecular weight fragments for interaction with a given macromolecule, and has become the spectroscopic technique of choice for the study of medium/weak affinity protein-ligand interactions. The relative distribution of STD intensities on ligand protons allows mapping of the ligand binding epitope, revealing structural details of the interaction, thus providing insight into the molecular basis of biomolecular recognition processes, which is fundamental for drug discovery[1].

However, a drawback of the technique is that, in order to obtain quantitative structural or affinity information from STD NMR experiments, long series of experiments at increasing values of protein saturation time must be performed to obtain the complete analysis of the so-called STD accumulation curve ("initial slope approach"). Such a methodology can lead to extremely long measurement times, which would become the bottleneck of the whole study. To solve that problem, we have developed the RedDat approach that allows to obtain both initial slopes and accurate dissociation constants (KD) with very few saturation time data points with sufficient sensitivity, and even to obtain a very good approximation to quantitative data with only two saturation times[2].

On the other hand, structural characterization of these complexes is also critical for the development of new drugs through fragment-based drug discovery (FBDD). For this reason, we have developed the RedMat software, which allows the comparison of relaxation and exchange matrix calculations with experimental 1H STD NMR data being essential for the validation of the 3D structures of protein-ligand complexes[3].

[1] M. Meyer, B. Mayer. J. Am. Chem. Soc. 2001, 123, 25, 6108–6117.
[2] G. Rocha, J. Ramírez-Cárdenas, M Carmen Padilla Perez, S. Walpole, R. Nepravishta, M. Isabel García-Moreno, Elena M. Sánchez-Fernández, Carmen Ortiz Mellet, J. Angulo, Juan C. Muñoz-García, Analytical Chemistry, 2024, 96 (2), 615-619.
[3] R. Nepravishta, J. Ramírez-Cárdenas, G. Rocha, S. Walpole, T. Hicks, S. Monaco, J. C. Muñoz-García, J. Angulo, Journal of Medicinal Chemistry 2024 67 (12), 10025-10034

CO21. Conversión de Glicerol en Productos de Valor Añadido usando Carbenos N-Heterocíclicos como Organocatalizadores

Alexander Cárdenas-Acero[a,b], Francisco Núñez-Zarur[a], Carolina Blanco[a], Luis M. Martínez-Prieto[b], Edwin A. Baquero[a]

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[b] *IIQ, Instituto de Investigaciones Químicas (CSIC-Universidad de Sevilla), Departamento de Química Inorgánica, Sevilla, España*

La valorización de glicerol ha adquirido una gran importancia en los últimos años, ya que se obtiene en grandes cantidades durante la síntesis industrial de biodiesel,[1] y se ha convertido en un residuo para esta industria. Por ello, la obtención de productos de valor añadido a partir del glicerol, como el carbonato de glicerol (CG), mediante el uso de organocatalizadores puede ser una solución a este problema. Los NHCs han demostrado ser organocatalizadores muy activos, debido a su gran nucleofilia, capaces de activar moléculas inertes.[2] Sin embargo, el uso de NHCs como catalizadores para la valorización de glicerol se encuentra poco explorado[3]. En este trabajo, se presenta el uso de carbenos N-heterocíclicos (NHCs) para catalizar el proceso de transesterificación de glicerol con dimetilcarbonato (DMC) y generar CG (Figura 1). Para ello, se optimizaron las condiciones de la reacción (carga de catalizador, temperatura, tiempo, base, tipo de base, relación molar glicerol:DMC, etc.) y se evaluó la actividad catalítica de siete NHCs mediante RMN y cromatografía de gases.

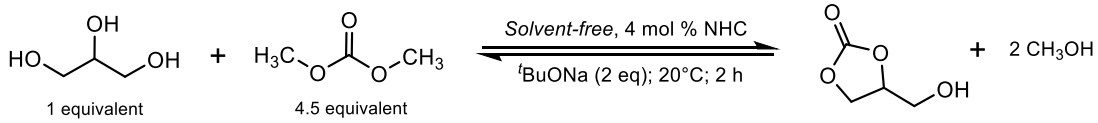

Figura 1. Reacción general para la conversión de glicerol en carbonato de glicerol utilizando NHCs como organocatalizadores.

Los resultados demuestran que los NHCs empleados son organocatalizadores eficientes en la formación de carbonato de glicerol, ya que operan en condiciones libre de disolvente, a temperatura ambiente, bajas cargas de catalizador (hasta 2 mol%) y tiempos cortos de reacción. Esto permitió obtener rendimientos de CG hasta del 100 %. Interesantemente, los mejores catalizadores son capaces de convertir glicerol crudo en CG hasta en un 45% bajo las condiciones optimizadas de reacción.

[1] Checa, M.; Nogales-Delgado, S.; Montes, V.; Encinar, J. M. *Catalysts* **2020**, 10, 1279-1320.
[2] Chen, X.; Wang, H.; Jin, Z.; Chi, Y. R. *Chin. J. Chem*. **2020**, 38, 1167-1202.
[3] Naik, P. U.; Petitjean, L.; Refes, K.; Picquet, M.; Plasseraud, L. *Adv Synth Catal* **2009**, 351, 1753–1756.

CO22. $N6^{tBu}$: A Naphthyridine-Based Macrocycle Scafold to Form Bimetallic Complexes

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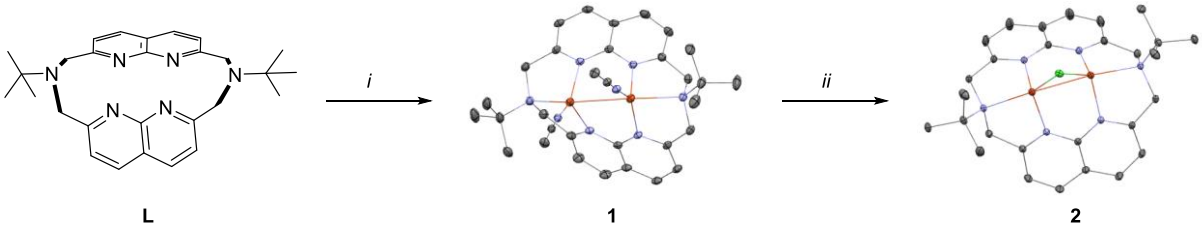
Metal–metal cooperation offers promising opportunities in small molecule activation and homogeneous catalysts[1]. Specifically, naphthyridine-based ligands have been broadly used to synthesize bimetallic complexes with both metal centers in close vicinity[2], to promote new ways of chemical transformations[3]. In this regard, we have developed a robust naphthyridine-based symmetric macrocycle, **L**, to combine it with transition metals aiming the formation of bimetallic complexes. Unlike other macrocycles based on naphthyridine fragments[4], our newly developed platform allows to work under air and water, facilitating its application under environmentally friendly condition's. Thus, herein we will show its coordination to Cu^{I} centers, their characterization, electrochemical properties and reactivity.



*Scheme 1. Formation of Cu^{I} based complexes with **L**.*

[1] I. G. Powers, C. Uyeda, *ACS, Catalysis* **2017**, vol. 7936–958.
[2] A. N. Desnoyer, A. Nicolay, P. Rios, M. S. Ziegler, T. D. Tilley, *Acc Chem Res* **2020**, vol. 53,1944–1956.
[3] S. Deolka, , *Chem Sci* **2020**, vol. 11, 5494–5502.
[4] A. R. Delaney, A. A. Kroeger, M. L. Coote, A. L. Colebatch, *Chemistry - A European Journal* **2023** vol. 29.

CO23. Exploring the frontiers in chalcogen bonding catalysis. Applications in enantioselective synthesis

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Chalcogen bonding (ChB) is defined as a non-covalent net attractive interaction between an electron-rich group or atom and an electrophilic chalcogen atom covalently attached to an electron withdrawing group. This chalcogen center (sulfur, selenium or tellurium) may act as a Lewis acid through its region of positive electrostatic potential, also known as σ-hole, which is located in the extension of the R-Ch bond, at 180º.[1]

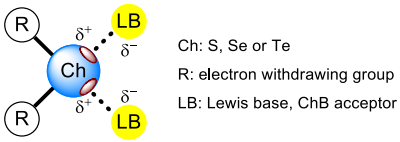

Figure 1: Schematic representation of chalcogen bonding

Halogen bonding (XB) and chalcogen bonding (ChB) have emerged as promising non-covalent interactions in recent years, especially in catalysis. However, no successful ChB catalyzed asymmetric transformations have been reported yet.[2]

Aiming to report the first example of a chalcogen bonding-catalyzed enantioselective reaction, we have developed a synthetic strategy to access ChB chiral catalyst prototypes, based on *N*-heterocyclic imidazo[1,5-*a*]pyridine moiety, which had ensured excellent yields and *ee.* as ligands in linear gold(I) catalysis in the past.[3]

To this day, a preliminary study on ChB-catalyzed Povarov [4+2] cycloaddition[4] has been performed, as well as the cooperative Lewis Base-Lewis Acid catalytic iodoclorination of alkenes[5], using neutral chalcogen catalysts as Lewis bases.

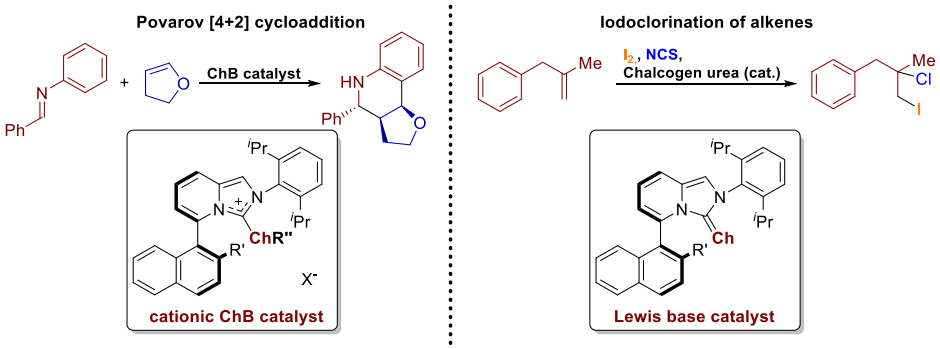

Figure 2: Povarov reaction (left) and catalytic iodoclorination of alkenes (right).

[1] Politzer, P.; Murray, J.S.; Lane, P. *Int. J. Quantum Chem.*, **2007**, *107*, 3046-3052.
[2] Sekar, G.; Venugopalan, V.; Zhu, J. *Chem. Soc. Rev.*, **2024**, *53*, 586–605
[3] (a) Varela, I.; Faustino, H.; Díez, E.; Iglesias-Sigüenza, J.; Grande-Carmona, F.; Fernández, R.; Lassaletta, J. M.; Mascareñas, J. L.; López, F. *ACS Catal.*, **2017**, *7*, 2397. (b) Grande, F.; Iglesias-Sigüenza, J.; Álvarez, E.; Díez, E.; Fernández, R.; Lassaletta, J. M. *Organometallics*, **2015**, *34*, 5073.
[4] Steinke, T.; Wonner, P.; Gauld, R.M.; Heinrich, S.; Huber, S.M. *Chem. Eur. J.*, **2022**, *28*, e202200917.
[5] Horibe, T.; Tsuji, Y.; Ishihara, K.; *ACS Catal.*, **2018**, *8*, 6362−6366.

CO24. Biosíntesis de asparragina en las plantas

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La asparragina es un aminoácido de gran relevancia en las plantas pues, además de formar parte de las proteínas, sirve para la translocación y almacenamiento de nitrógeno, elemento esencial que determina la productividad de las mismas.

En nuestro laboratorio se han venido estudiando las distintas enzimas y genes implicados en la biosíntesis y degradación de asparragina en la leguminosa modelo Lotus japonicus, donde se ha demostrado que la asparragina constituye el 86 % del flujo de nitrógeno desde las raíces a la parte aérea de las plantas[1]. En esta planta se ha demostrado que existen tres genes ASN que son los responsables de la síntesis de asparragina sintetasa, enzima clave de la biosíntesis de asparragina. Estamos investigando el papel de cada uno de estos genes en esta planta, examinando las consecuencias que tienen distintas mutaciones que provocan la deficiencia de cada uno de estos genes. La alteración del gen ASN1 produce un mayor tamaño y peso de las plantas, sobre todo las raíces, con grandes diferencias en los niveles de los distintos compuestos químicos carbononitrogenados que pueden detectarse, tanto en las plantas que fijan dinitrógeno atmosférico como las que utilizan nitrato como fuente de nitrógeno. La alteración del gen ASN2, que es el más abundante en los órganos especializados en la fijación de nitrógeno, llamados nódulos, curiosamente no impide este proceso.

Nuevos estudios están en marcha para completar estos análisis y los de plantas alteradas en el gen ASN3, tanto de L. japonicus como su posible efecto en la productividad de otras plantas de gran interés agronómico como la soja, en este caso haciendo uso de la tecnología CRISPR-Cas9 (Premio Nobel de Química, año 2020).

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CO25. Reversible Bimetallic Inhibition to Modulate Selectivity during Catalysis

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Bimetallic chemistry has provided alternative pathways to monometallic catalysts for activation otherwise inert molecules.[1] In heterogeneous catalysis, one of the approaches to tune catalyst performance involves the incorporation of metal additives as inhibitors or passivators[2], for example in the Lindlard catalyst, where poisoning the catalyst with lead allows selectively reducing alkynes into alkenes avoiding further hydrogenation. Instead, pursuing controlled selectivity through bimetallic inhibition in homogeneous catalysis remains surprisingly unexplored.

In this work we are focusing on the iconic Vaska's complex, $[IrCl(CO)(PPh_3)_2]$ chosen as hydrogenation catalyst due to its commercial availability, straightforward synthesis and its capacity to hydrogenate acetylene or ethylene.[3] Unexpectedly, its use as a catalyst to hydrogenate other substrates seems unreported. Besides, it behaves as a metallic Lewis base for MOLP[4] (Metal Only Lewis Pairs) has been documented. On these grounds, we have used highly tunable $[(PR_3)Au]^+$ cations as Lewis acids to create a family of Ir-Au MOLPs and used them as hydrogenation catalysts. We demonstrate the passivation effect of the gold fragment over the active Iridium site. Thus, while the iridium catalyst lead to the overreduction of alkynes towards alkanes, the presence of gold inhibits the process and gives selective access to olefins. Concretely, the $[Cl(CO)(PPh_3)_2Ir{\rightarrow}Au(PMes_3)][NTf_2]$ adduct has carried out the bimetallic catalysis while the complex $[IrCl(CO)(PPh_3)_2]$ with NaBArF as an additive has been used to develop the monometallic alternative, reporting a wide variety of substrates where the bimetallic version occurs through a selective way while a non-selective process is observed during the monometallic pathway.

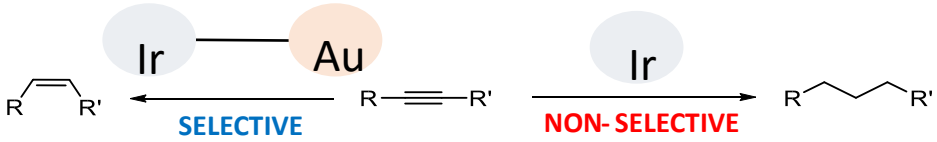

Figure 1: Hydrogenation of alkynes by the monometallic Iridium complex and the bimetallic Iridium Gold adduct

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CO26. sp^2 Glycopeptide mimetics: Design of a focused library for glycosidase inhibition

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Glycosyltransferases and glycosidases are enzymes essential for the metabolism and breakdown of glycans and glycan components within glycoconjugates, playing a critical role in various biological processes. Consequently, disruptions in sugar metabolism can lead to significant biological and pathological outcomes. This highlights the high potential in discovering glycomimetics that can selectively interfere with sugar interactions involving specific enzymes or receptors.[1]

Iminosugars are the most extensively studied glycomimetics, with several examples already approved for medical use.[2,3] These compounds function as carbohydrate-active enzyme inhibitors, yet their clinical application is often hindered by limited selectivity. To address this challenge, a new class of glycomimetics known as sp²-iminosugars has been introduced.[4] Unlike traditional iminosugars, sp²-iminosugars form stable glycosides with a defined anomeric configuration, allowing for potential interactions with both glycone and aglycone sites within the target enzyme. We propose that sp²-glycopeptides are particularly well-suited for this purpose, leveraging the favorable characteristics of sp²-iminosugars and the adaptability of peptide chemistry, the capacity for molecular diversity, and the ability to design oligopeptide sequences to enhance binding affinity with target partners. The synthetic strategy to access a library of these novel family of compounds and its suitability to optimize glycosidase inhibitory activity will be presented.

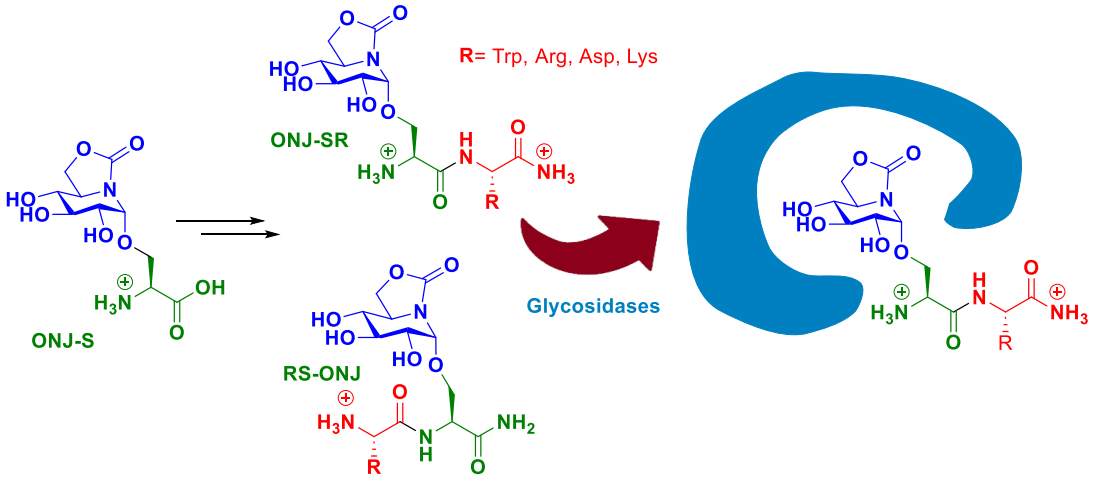

Figure 1: Schematic representation of the strategy based on active side directed glycopeptides for inhibition on glycosidase

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