



# SCIENTIFIC PROGRAM





# PLENARY LECTURES





## A computational view on polymetallic homogeneous catalysis

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Polymetallic catalysis, also known as cooperative, dual or tandem catalysis, is a growing field of research that further expands the range of homogeneous catalysis. The simultaneous activation of two substrates by different catalytic entities and their subsequent coupling can lead to rate acceleration and increased selectivity. DFT calculations and microkinetic modeling provide fundamental insights on the substrate activation by metals and on the interactions between different catalysts. In this contribution we will discuss a representative series of computational studies on multimetallic catalysis carried in our group on a variety of systems.



Professor Masera's main research topic is computational homogeneous catalysis, with recent interest in oxidative coupling, single electron transfer, microkinetic simulation and statistical treatments.



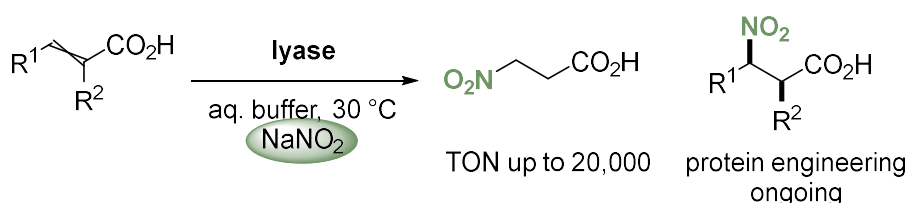
## Enzymatic hydronitration: a unique reaction in the biocatalytic repertoire

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The nitro functionality is one of the major functional groups used in organic synthesis. Its use as enabling tool in synthesis for the production of dyes, polymers, and pesticides, is complemented by its occurrence in a range of compounds (*e.g.*, chemotherapeutic agents and prodrugs). However, access to nitro compounds relies on poorly selective and environmentally unfriendly methods (*e.g.*, use of halogenated compounds and strong acids and oxidants).<sup>[1]</sup> Inspired by the occurrence of nitro compounds in nature,<sup>[2]</sup> we are currently designing innovative enzymatic strategies for nitration reactions in an environmentally acceptable manner.

One methodology under investigation is the biocatalytic hydronitration of  $\alpha,\beta$ -unsaturated carboxylic acids by a lyase. We will provide insights in this unique reaction, which requires only nitrite salt as a nitrating agent and aqueous buffer. Due to the substrate selectivity of the enzyme for fumaric acid, the re-design of the active site is currently being explored in order to expand the substrate scope to a range of conjugated carboxylic acids.



**Acknowledgement** is made to the ACS GCI Pharmaceutical Roundtable Research Grant for partial support of this research. The authors thank the University of Graz for funding.



Professor Hall's research focuses on the development and application of enzymes for sustainable synthesis, with a focal point on asymmetric reactions and the understanding of enzyme catalysis at the molecular level.

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## Phosphine Ligands on Metal Nanocatalysts: Friends or Foes?

Sophie Carencó

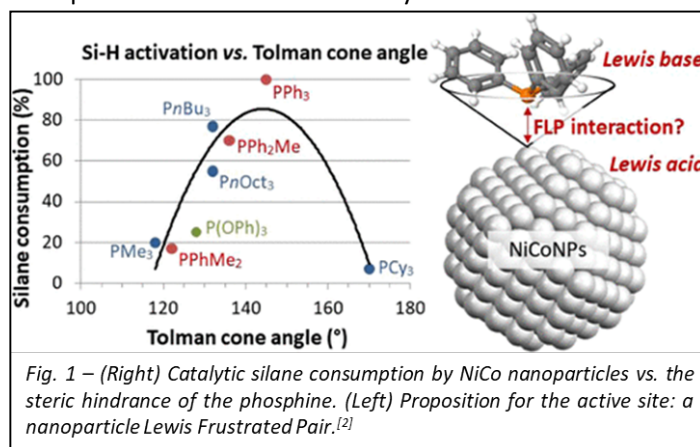
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Metal nanoparticles (NPs) have been used as catalysts in a variety of reactions, involving molecules such as H<sub>2</sub>, CO<sub>2</sub>, aldehydes, ketones, alkynes, alkenes, etc. The selectivity of the catalytic reaction, eg. for the selective hydrogenation of alkynes to alkenes, may be improved by the presence of a surface organic ligand that is coordinated on the metal sites and poisons the most active ones. However, the presence of the ligand generally decreases the catalytic activity of the NPs. It may also lead to unwanted leaching of metallic species into the solution.<sup>[1]</sup>

In order to overcome these limitations, we employed phosphines as bulky Lewis base, in an approach inspired by the Frustrated Lewis Pairs that are well-known in organocatalysis. The metal surface of the NP plays the role of the Lewis Acid. The active site born from the encounter of the phosphine with the surface is expected to favor the heterolytic dissociation of bonds,

such as the H–H bond in H<sub>2</sub>, under mild reaction conditions. Keeping in mind that the ligand is in exchange with the free solution, we investigated a broad range of conditions to delineate when the phosphine was beneficial to the catalytic activity of the particle-ligand couple. In this presentation, I will describe the development of NiCo,<sup>[2]</sup> CoP<sup>[3]</sup> and Ni<sup>[4]</sup> NPs for hydrosilylation (Fig. 1) and hydrogenation reactions. I will

discuss the roles of phosphine concentration, basicity and steric hindrance in relation with the conversion of benzaldehyde and phenylacetylene. I will use stereo-electronic maps as a tool to rationalize the relative reactivity of the nanoparticle-phosphine pairs.



Sophie Carencó works on novel synthetic routes for nanoparticles of metal, phosphides, carbides and oxysulfides. She investigates the optical and magnetic properties of the nanoparticles, as well as their reactivity in catalytic processes such as hydrogenation and CO<sub>2</sub> activation.

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## Never an empty orbital gave for so much reactivity: the boron'ate' versus borata history

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Boron reagents are key players in current organic synthesis due to their easy manipulation to form C-B bonds and their subsequent straightforward functionalization. The impressive evolution of organoboron chemistry, along the recent decades, has at least two main reasons: the parallel development of new accessible boron reagents and the growing application of organoboron compounds in organic synthesis, molecular receptors, sensors, novel materials and biological probes. The versatility of organoboron compounds has been associated with the vacant *p*-orbital of tricoordinated alkyl boronic esters with the fundamental structure R-B(OR)<sub>2</sub>. This accounts for the Lewis acidic properties and the ability to readily react with nucleophiles forming tetracoordinated boronate anions. In parallel,  $\alpha$ -boryl carbanions show a remarkable stability due to the valence deficiency of the adjacent three coordinate boron centre, and they can be also described by their borata-alkene resonance forms, with the delocalization of the electron density of the anion throughout the empty *p* orbital of the adjacent boron. We will highlight the use of boronate anions and  $\alpha$ -boryl carbanions as new and powerful synthetic tool towards efficient C-C bond formation.



Professor Fernández's current scientific campaign is aimed to generate knowledge and awareness about activation modes of borane reagents to be used in selective synthesis of multifunctional compounds.



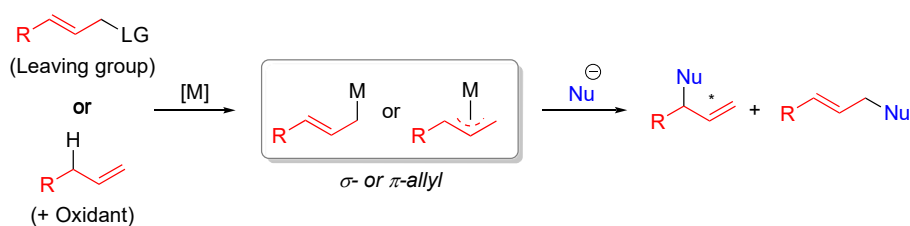
## Transition metal-catalyzed addition of pronucleophiles to alkynes and allenes: an atom-efficient alternative to the Tsuji-Trost reaction

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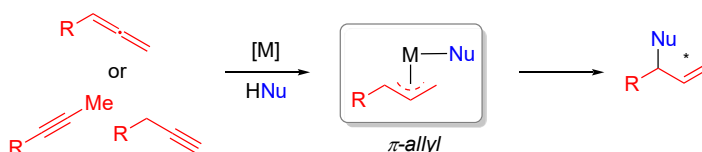
Transformation of simple and readily accessible starting materials to branched allylic derivatives is an important topic in organic synthesis because of the versatility of the allylic moiety for further elaboration and the stereogenic center for asymmetric synthesis.<sup>1</sup> In the last decades, significant progress toward this goal has been achieved, in particular with allylic substitution<sup>1</sup> and allylic C-H oxidation<sup>2</sup> chemistry. However, these methods require pre-installation of a leaving group or stoichiometric amounts of an oxidant, respectively.

**Established:** Tsuji-Trost Allylic Substitution & Allylic Oxidation



**Drawbacks:** Stoichiometric Amounts of LG Couple Product, Oxidants, Base

**Alternative:** Atom Economic Addition of Pronucleophiles to Alkynes & Allenes



As an alternative to these methods, we have developed a set of new reactions enabling the addition of pronucleophiles to alkynes and allenes furnishing branched allylic derivatives in a completely atom-economic fashion under neutral conditions. By choice of the right catalyst, a wide range of regio- and stereoselective C/O, C/N, C/S and C/C-bond-forming reactions could be achieved.<sup>3,4</sup> Applications in target-oriented synthesis will also be presented.



*Professor Breit's research in organic synthesis and catalysis includes pioneering studies on supramolecular concepts in homogeneous catalysis and the development of new catalytic reactions for atomic-economic bond formation.*

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3. Koschker P.; Breit, B. *Acc. Chem. Res.* **2016**, *49*, 1524-1536; L. J. Hilpert, S. V. Sieger, A. M. Haydl, B. Breit, *Angew. Chem. Int. Ed.* **2019**, *58*, 3378-3381.



# ORAL COMMUNICATIONS



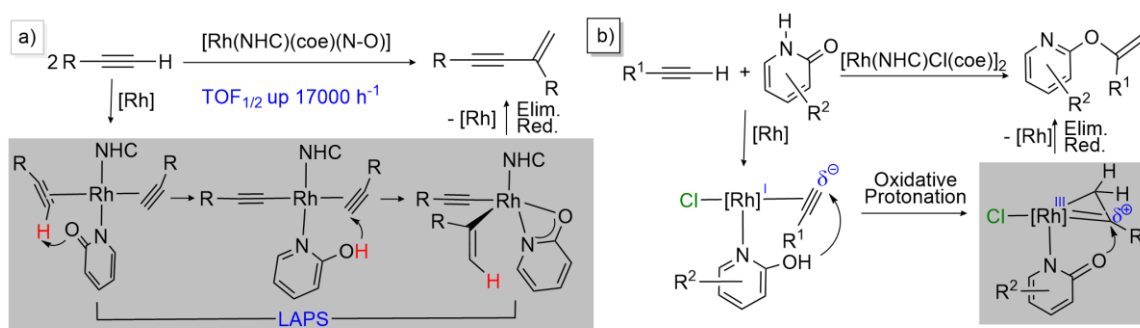


## Mecanistic Insights into Metal-Ligand Cooperation within Rh-NHC Platforms for Alkyne Hydrofunctionalizations

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The concept of Metal-Ligand Cooperation (MLC) has emerged as an essential piece in organometallic-mediated bond cleavage and formation. The synergistic effect arising from MLC generally triggers an enhancement of catalytic activity and provides a better control of selectivity. In this context, *Ligand Assisted Proton Shuttle* (LAPS) processes are nice examples of this cooperation, in which a ligand acts as a transporter of a proton from one substrate to another, coupled with subsequent fast reductive elimination between the newly formed M-X bonds [1]. Particularly, we present here nice examples within Rh-NHC platforms for gem-specific alkyne hydrofunctionalizations [2,3]. Mechanistic details determining the key factors for the improved activity and selectivity will be discussed.



**Scheme 1.** a) Alkyne dimerization via LAPS. b) Alkyne Hydropyridonation

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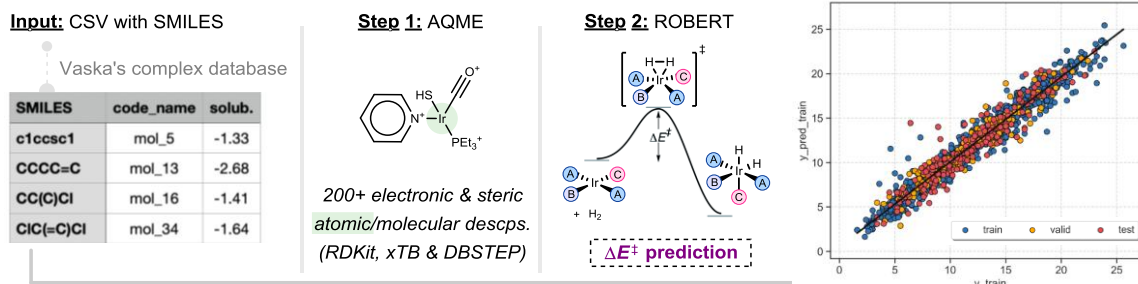
## Automated computational chemistry and machine learning workflows in catalysis

**Juan V. Alegre-Requena, David Dalmau**

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Continued improvements in computer hardware and algorithms have allowed quantum chemical methods to be employed for studying more complex and larger catalytic systems. However, performing the various computational protocols required for high-throughput screening, molecular optimization, and machine learning (ML) model training can be tedious and time-consuming. Automating these workflows minimizes errors, enhances reproducibility, and facilitates storing and reusing the associated data.

In this work, we present AQME,<sup>[1]</sup> an automated end-to-end workflow software that performs multi-step tasks of computational chemistry, and ROBERT,<sup>[2]</sup> a program that automates ML-related tasks such as data curation, hyperparameter optimization, and ML predictor generation. The combination of these programs allows for high-quality reaction energy profile studies and ML predictions to be generated with just one or a few command lines, starting from simple inputs such as databases with SMILES strings.



**One command line:** `python -m robert --csv_name Vaskas.csv --y barrier --aqme --qdescp_keywords "--qdescp_atoms [Ir]"`

## References

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## Fundamental study of the structural dynamics of Pt/CeO<sub>2</sub> catalysts and its use for accelerating the water-gas shift reaction

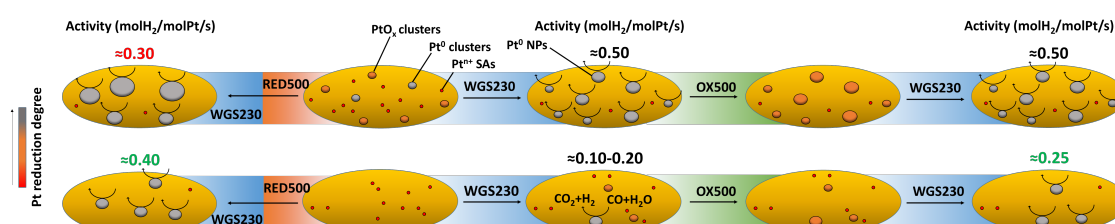
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Pt/CeO<sub>2</sub> is a promising catalyst for the low-temperature water-gas shift reaction (WGS).<sup>1</sup> Moreover, it is “dynamic” since Pt can be dispersed during an oxidative treatment at moderate temperature, leading to single atoms (SAs), while a reducing treatment triggers nanoparticle (NP) formation.<sup>2</sup> Starting from SAs, suitable redox treatments were previously shown to tailor Pt clusters active for the low-temperature CO oxidation in the presence of water.<sup>3,4</sup> In this work, the influence of different redox treatments on the WGS activity of Pt/CeO<sub>2</sub> catalysts has been investigated as a function of the Pt surface density. Relationships between physicochemical and catalytic properties have been established based on several complementary characterization methods including *in situ/operando* techniques.

An optimal H<sub>2</sub> productivity was observed for a Pt coverage higher than 0.1 at/nm<sup>2</sup>, revealing two different behaviors for high and low loadings. It was attributed to the increase in Pt reducibility at higher loadings, enabling the formation of NPs more active than initial SAs (Figure 1). Notably, a reductive pre-treatment or an oxidative post-treatment improves the catalytic performances at low Pt loadings by forming active Pt NPs from stable SAs, while it decreases the catalytic activity at higher loadings. Low-loading catalysts were strongly activated by the increase in Pt and ceria reducibilities, which enhance the formation of Pt<sup>0</sup> NPs under reactive conditions (Figure 1). These results show that Pt reducibility is a critical factor to tune the WGS activity of the catalysts, and this reducibility can be controlled by the Pt content and the applied redox treatments.



**Figure 1:** Scheme of the influence of redox treatments on Pt species formation during the WGS reaction for two different Pt contents (e.g. 0.10 wt% and 1.06 wt%).

### References

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## Enhancing on stream stability in the dehydrogenation of bioethanol to acetaldehyde

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Bioethanol upgrading to valuable platform molecules, is a cornerstone of the emerging “integrated biorefinery” concept. Although active catalysts have already been developed to convert ethanol into acetaldehyde, their rapid deactivation is still an unresolved challenge, which, surprisingly, is largely put aside by the scientific community. In dehydrogenation reactions, catalysts are often deactivated in a matter of seconds. Metal sintering and coking are found to be detrimental for the catalyst lifetime [1]. Whether supported on carbon based materials [2] or on Al<sub>2</sub>O<sub>3</sub>, ZnAl<sub>2</sub>O<sub>4</sub> [3,4], or ZrO<sub>2</sub> [5] state-of-the-art Cu-based catalysts rapidly decay by few hours. Turning our attention to a more inert support, i.e. silica, we recently developed Cu-SiO<sub>2</sub> catalysts that are sintering-resistant, but where coking remains a limitation (that can be solved through appropriate regeneration) [6]. Herein, we propose reaction engineering procedures as well as a wide characterization of the spent catalysts to univocally describe deactivation phenomena and markedly enhance the catalyst lifetime. A single silica supported catalyst, with 8%wt in Cu, has been prepared by Aerosol Assisted Sol Gel (AASG) method [6] and tested in long term experiments (8-24 hours) at fixed temperature, (i.e. 573 K) and constant ethanol feed, in the gas phase ethanol dehydrogenation reaction. Experimental results clearly shown that is possible to prevent coking, introducing small percentages of a gasifying agent and by doing so, stabilize catalytic activity. For example: while A-Cu8SiO<sub>2</sub> rapidly deactivate from a conversion of  $\approx$ 95% to 25%, introducing only 0.44% (V/V) of O<sub>2</sub> allows stabilizing ethanol conversion around 76%. In these conditions, we show that the main reaction (non-oxidative ethanol dehydrogenation) is still occurring, while coke is constantly burned during the reaction without changing the reaction path to acetaldehyde. In fact, selectivity to acetaldehyde always remains higher than 90%. Spent catalysts characterization clearly identify the coke as the main deactivation cause, leading to fouling and pore clogging.

### References

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## Ruthenium nanoparticles as catalysts for chemoselective H/D exchange of E-H bonds

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Nuria Rendón,<sup>\*a</sup> Patricia Lara,<sup>\*a</sup> and Andrés Suárez<sup>\*a</sup>

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Hydrogen isotope exchange (HIE) reactions have attracted much attention in recent years due to the wide variety of applications that isotopically labelled compounds present. For example, they play a key role in the study of chemical reactions mechanisms or in drug development.<sup>1</sup> In this contribution, we describe a series of Ru·MIC nanoparticles prepared using the organometallic approach by decomposition of [Ru(COD)(COT)] with H<sub>2</sub> in the presence of MICs ligands as stabilizing agents (Figure 1). These nanoparticles, which have been characterized by means of TEM, HRTEM, ICP and XPS, have been found to catalyze, employing deuterium gas, the selective deuterium incorporation in E-H bonds (E = Si, B, Ge, Sn) under relatively mild conditions (1 bar D<sub>2</sub>, 55 °C) (Figure 2).<sup>2</sup>

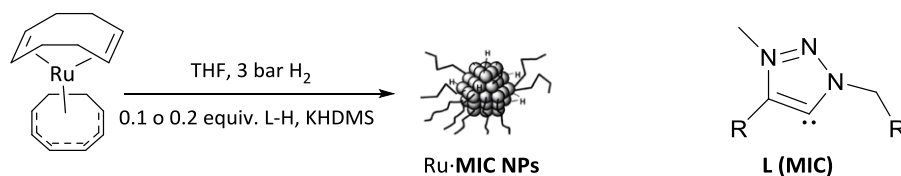


Figure 1. Synthesis of Ru·MIC nanoparticles.

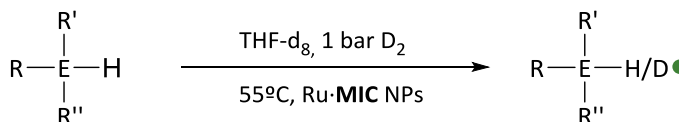


Figure 2. Catalytic H/D exchange.

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# TraPCat<sup>3</sup>

3<sup>rd</sup> Trans Pyrenean Meeting in Catalysis

2-3 November 2023  
Toulouse, France



## One-pot synthesized Rh nanoparticles in polycationic-shell core-cross-linked micelles as efficient catalyst for aqueous biphasic hydrogenation

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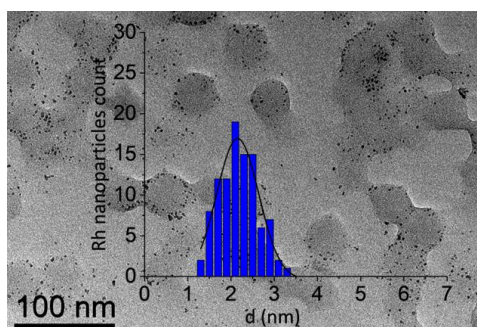
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A well-defined aqueous suspension containing rhodium nanoparticles (RhNPs) has been successfully synthesized using a one-pot method. These RhNPs are confined within the hydrophobic region of core-crosslinked micelles functionalized with triphenylphosphine oxide (TPPO) and surrounded by a hydrophilic polycationic shell, referred to as TPPO@CCM-C [1]. The synthesis was achieved by employing the  $[\text{Rh}(\text{COD})(\mu\text{-Cl})_2]$  precursor in toluene along with hydrogen gas ( $\text{H}_2$ ), where the presence of TPPO eliminated the need for an additional base stabilizer as employed in previous methods used for, e.g. the synthesis of RhNP-TPP@CCM-C (TPP: triphenylphosphine) [2]. The resulting RhNP-TPPO@CCM-C latex displayed remarkably high catalytic activity in the aqueous biphasic hydrogenation of styrene, achieving a turnover frequency (TOF) of  $6400 \text{ h}^{-1}$  based on the RhNP surface atoms. Furthermore, this catalyst proved to be reusable over multiple reaction cycles, with the core-linked TPPO ligands effectively anchoring the RhNPs even during the intermediate product extraction using oxygen-based solvents. The catalyst also demonstrated efficiency in the hydrogenation of various other selected alkenes, alkynes, and carbonyl substrates, achieving TOF values ranging from 1000 to  $3200 \text{ h}^{-1}$ .



**Figure 1:** TEM images of the one-pot-synthesized RhNP-TPPO@CCM-C and (overlaid) the corresponding size distribution of RhNPs ( $d_m = 1.7 \pm 0.2 \text{ nm}$ )

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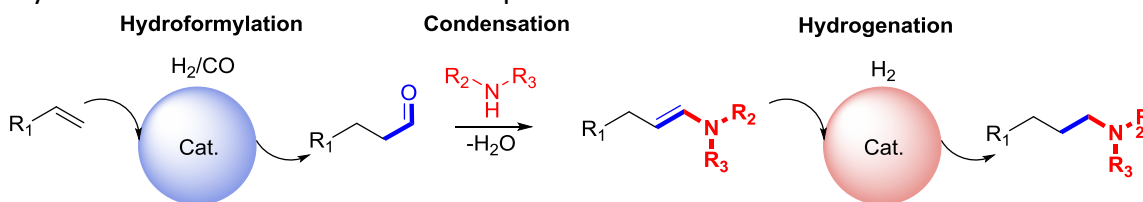
## SYNTHESIS OF PHARMACEUTICALS VIA RHODIUM-CATALYZED ASYMMETRIC HYDROAMINOMETHYLATION OF ALKENES

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Access to chiral amines is of paramount importance for industries which commercialize drugs containing a chiral amine moiety.<sup>[1]</sup> The Rh-catalyzed hydroaminomethylation (HAM) of alkenes is an efficient and atom economic reaction to obtain amines in a one-step reaction (Figure 1).<sup>[2]</sup> Only a few examples of enantioselective HAM were reported to date. Xiao's<sup>[3]</sup> and Han's<sup>[4]</sup> groups developed asymmetric HAM using rhodium complexes with a chiral Bronsted acid and Hantzsch esters, whereas Zhang<sup>[5]</sup> group reported the interrupted intramolecular HAM of 1,2-disubstituted olefins using an external silane as reducing agent. Our group recently published the first examples of efficient asymmetric HAM using a single catalyst of  $\alpha$ -substituted acrylamides<sup>[6]</sup> and  $\alpha$ -alkyl acrylates<sup>[7]</sup> to access chiral  $\gamma$ -aminobutyric acid (GABA) derivatives with high enantioselectivity. In connection with our interest in this reaction, we have studied the synthesis of Tolterodine<sup>[8]</sup> and derivatives via asymmetric HAM. Our latest results in asymmetric HAM are presented in this communication.



**Fig. 1** Rh-catalyzed hydroaminomethylation of alkenes.

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## Structural and Chemical Characterization of Carbon Supported PdIn Bimetallic Nanoparticles from MOFs Processing for Selective Hydrogenation of Alkynes Under Mild Conditions.

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Heterogeneously catalysed processes are widespread in today's chemical technology. Among them, supported monometallic or bimetallic nanoparticles constitute the active phase of most of catalysts employed in many industrial processes. However, these catalysts must possess a tailored sized and dispersed nanoparticles to ensure high active site accessibility and high metal content in order to promote reactivity, selectivity and stability. Conventional strategies to obtain these kinds of materials consist of metal salt impregnation or precipitation on support followed by a reduction step with high thermal treatment with H<sub>2</sub> or N<sub>2</sub> or by chemical reduction with sodium borohydride. However, these strategies lead to a poor control degree in term of size, shape, and composition, especially for high metal loadings. So how to obtain high metal loaded materials while keeping a good active site distribution?

Recently the use of Metal Organic Frameworks (MOFs) as the precursor of tailored supported nanoparticles synthesis has been reported.<sup>[1-3]</sup> The common strategy is to take advantage of the crystallinity, the high metal dispersion, and the high metal loading of MOFs in order to obtain reduced carbon-supported nanoparticles with similar properties. In that context, we have developed the synthesis of bimetallic Pd-based MOFs and we have recently shown a soft<sup>[4,5]</sup> and tailored transformation of a PdM-MOF (M: non-noble metal) into M-doped Pd-NPs supported on a carbonaceous support containing MO<sub>x</sub> clusters, thus improving the nature of the generated material against other synthetic strategies.<sup>[4,5]</sup> Our modified approach consists of the in-situ generation of the amine (i.e., aniline), instead of using it as a solvent, to provide the reaction mixture with a slow supply of amine in the presence of hydrogen (H<sub>2</sub>), in order to reduce metallic species and to lead to nanoparticle formation. Moreover, introducing a second metal would produce a synergetic effect that modifies the surface properties of a Pd-based catalyst, thereby modulating the adsorption energy of hydrogen or oxygen intermediates, increasing the active sites, and ultimately improving the catalyst



performance.<sup>[6]</sup> Recently, we have applied our methodology on PdIn MOF. The resulting material has been used with good catalytic activity, selectivity and stability in the selective hydrogenation of alkynes in mild conditions (ie: 96% phenylacetylene conversion, 95% phenylstyrene selectivity, P=1bar, T=rt).

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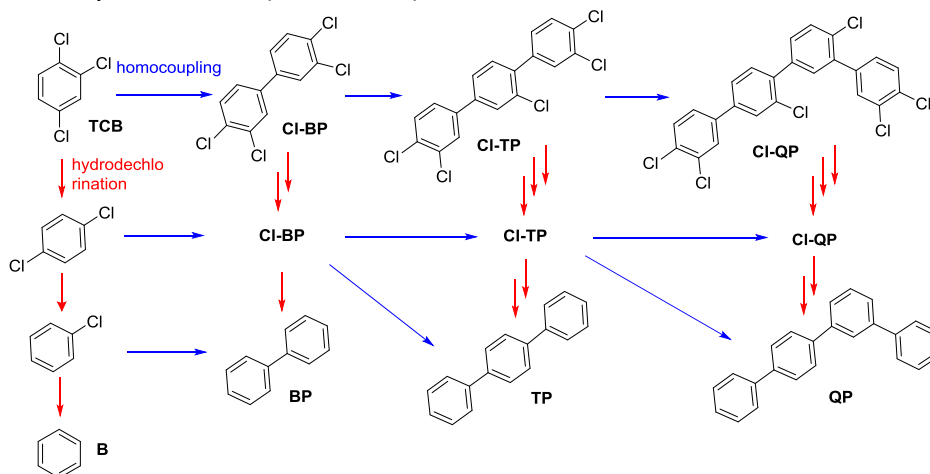


## Pd-catalyzed Ullmann type homocoupling of trichlorobenzenes: transformation of lindane wastes into polyphenylenes

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A method to valorize lindane residues would be the combination of the basic dehydrochlorination to trichlorobenzenes (**TCB**) with the synthesis of biphenyls or larger polyphenylene chains. The Ullmann-type homocoupling of chloroarenes has been described in aqueous phase using Pd/C as catalyst, with a phase transfer catalyst, a strong base and a reductant [1]. In this work we describe the results obtained with 1,2,4-**TCB**, the major product from dehydrochlorination of lindane, and the preliminary tests with real samples from the dismantled Inquinosa factory in Sabiñánigo (Spain). Homocoupling and hydrodechlorination are competitive processes (Figure), leading to final mixtures of benzene (**B**), biphenyl (**BP**), terphenyls (**TP**) and quaterphenyls (**QP**). Factors such as H<sub>2</sub> pressure, temperature, amount of base, amount and nature of phase transfer catalyst, amount of water, amount of sodium formate and loading and amount of Pd/C, have a deep influence on the final result of the reaction. In the optimal case, 75% selectivity to polyaromatic hydrocarbons (**BP+TP+QP**) can be obtained, at full conversion.



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This work was financially supported by Gobierno de Aragón (grant 2023 for research about elimination of lindane residues from the Departamento de Agricultura, Ganadería y Medioambiente, and E37\_23R group) and Agencia Estatal de Investigación (PID2021-125762NB-I00).



## Self-Terminated Surface Reconstruction of Lanthanum Nickelates Promotes Alkaline Oxygen Evolution

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Monitoring the spontaneous reconstruction of the surface of metal oxides under electrocatalytic reaction conditions is critical to identify the active sites and to establish structure-activity relationships. Here we report on a self-terminated surface reconstruction of Ruddlesden-Popper lanthanum nickel oxide ( $\text{La}_2\text{NiO}_{4+\delta}$ ) that occurs spontaneously during reaction with alkaline electrolyte species. Using a combination of high-resolution scanning transmission electron microscopy (HR-STEM), surface-sensitive X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy (sXAS), as well as electrochemical techniques, we identify the structure of the reconstructed surface layer as an amorphous (oxy)hydroxide,  $\text{NiO}_x(\text{OH})_y$ , phase that features abundant under-coordinated nickel sites. Notably, the formation of the reconstructed surface layer increases the material's oxygen evolution reaction (OER) activity by a factor of 45 when compared to that of the pristine crystalline surface. In contrast, a related perovskite phase, i.e.,  $\text{LaNiO}_3$ , did not show noticeable surface reconstruction and also no increase in its OER activity was observed. This work provides detailed insight into a surface reconstruction behaviour dictated by the crystal structure of the parent oxide and highlights the importance of surface dynamics under reaction conditions.

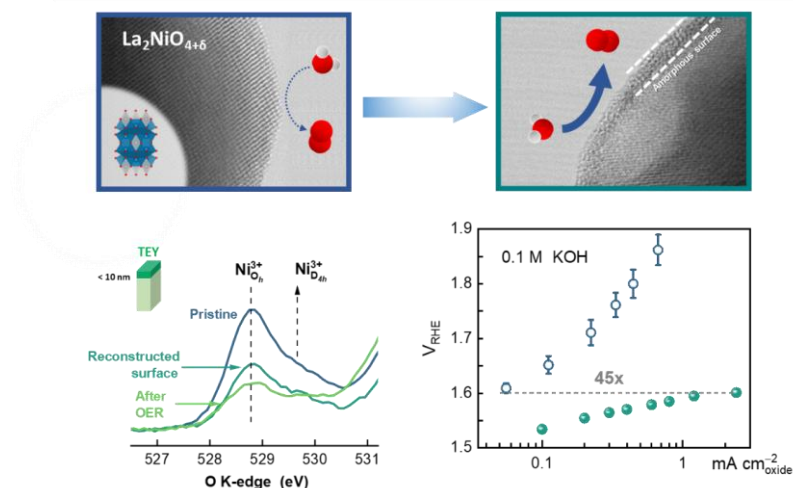


Figure 1 (a) High-resolution transmission electron microscope (HRTEM) images of pristine and self-terminated reconstructed surface of  $\text{La}_2\text{NiO}_{4+\delta}$  in alkaline electrolyte. A clear amorphous layer is indicated by dashed lines. (b) Pre-edge feature of X-ray absorption near edge structure (XANES) at O K-edge of pristine, reconstructed, and post-oxygen evolution reaction surface in total electron yield (TEY) mode. (c) Tafel-plot of pristine and reconstructed surface of  $\text{La}_2\text{NiO}_{4+\delta}$  in 0.1 M KOH.



## Functionalized Ru nanoparticles for (photo)catalytic hydrogen evolution

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As energy demands in the world increase, so does the fossil fuels consumption, the generation of greenhouse gases threaten the climate and living beings in our planet.<sup>[1]</sup> Alternative sources of energy are needed and a way to achieve this objective is taking inspiration from the natural process of photosynthesis. But to be able to produce renewable fuels in a similar way to plants, efficient and selective catalysts are needed.<sup>[2]</sup> Nanoparticles have been proven to be active in a myriad of catalytic processes, thanks to their high surface to volume ratio and their robustness under catalytic conditions.<sup>[3]</sup> However, they have often displayed problems of selectivity and performance. The functionalization of the surface of the nanoparticles with organic ligands allows to tune the catalytic properties and to improve the catalytic performance and selectivity. Moreover, the stabilizing agent can also have secondary roles apart from the stabilization itself, such as providing a bond with a light-absorbing molecule (generating a photocatalyst). In the present communication, the organometallic approach is proposed as a synthetic method to obtain metal/metal oxide nanoparticles that can be used as (photo)(electro)catalysts for the generation of hydrogen by using light. The specific process of synthesis allows the obtaining of different small nanoparticles with a clean surface that are tested under different conditions for the light-driven hydrogen evolution.

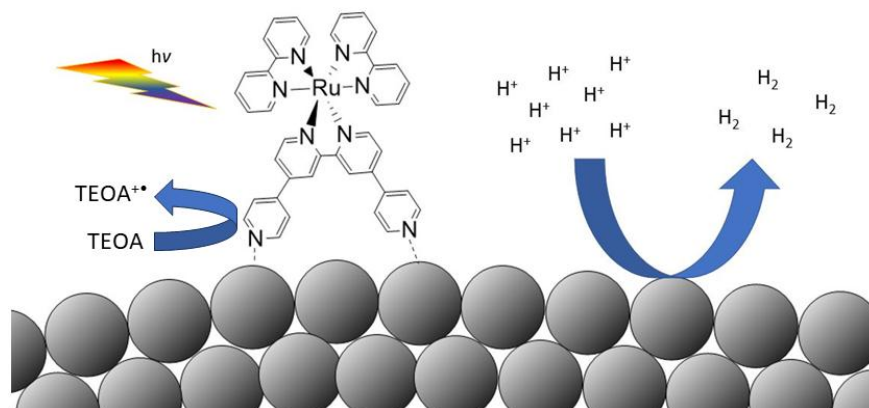


Figure 1. General representation of the photocatalytic process.

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## Organometallic NiCo@Ru Nanoparticles with potential in Magnetic Hydroprocessing of Lignin-based compounds

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Nowadays, scientists work on sustainable chemicals and fuels for a changing energy market increasingly relying on intermittent renewable sources.<sup>1</sup> In that sense, magnetic catalysis combines catalytic function with efficient, localized, and rapid heating, making it ideal for intermittent energy sources. Moreover, it can generate very high surface temperatures, enabling chemical reactions at low H<sub>2</sub> pressures and bulk temperatures.<sup>2</sup> On the other hand, as for sustainable raw materials, lignin is more difficult to convert into fuels and chemicals than cellulose and hemicellulose.<sup>3</sup> Thus, developing efficient catalytic systems for lignin depolymerization, coupled with intermittent renewable power through magnetic induction, is a challenging yet exciting scientific goal.

Herein, we applied an organometallic synthetic protocol to the preparation of ≈14 nm Ni<sub>1-x</sub>Co<sub>x</sub> nanoparticles from Ni[*i*PrNC(CH<sub>3</sub>)NiPr]<sub>2</sub> and [Co{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(THF)]. After finding the right balance between magnetic heating and catalytic properties in the Ni<sub>7</sub>Co<sub>3</sub> composition, a minimum amount of Ru (≈ 0.3 wt.%) was added to decorate the Ni<sub>7</sub>Co<sub>3</sub> nanoparticles (NPs). The NPs were fully characterized by HR-TEM/STEM, XAS, XRD, VSM and SAR. Thereafter, tested in the mild hydrogenolysis of 4-phenoxyphenol, monobenzene, and 2-phenoxy-1-phenylethanol to evaluate the C–O cleavage in lignin 4-O-5, α-O-4 and β-O-4 linkages (Table 1). Excitingly, high C–O cleavage was obtained at low H<sub>2</sub> pressures (3 bar). Fully structural analyses of the Ni<sub>1-x</sub>Co<sub>x</sub> and Ni<sub>7</sub>Co<sub>3</sub>@Ru NPs, kinetics, reusability, and more complex lignin models will be disclosed at the conference.

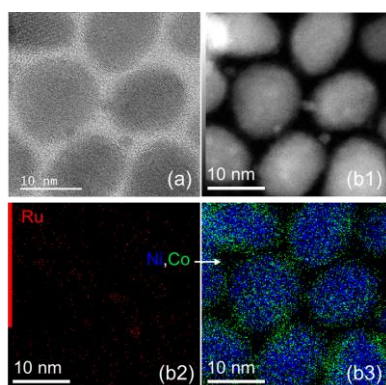
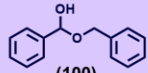



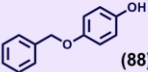



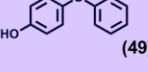




Fig. 1. (a) HR-STEM-BF, (b) STEM-HAADF-EDX

Table 1. Magnetic induced catalysis with Ni<sub>7</sub>Co<sub>3</sub>@Ru on lignin linkage models

Reaction time (h)	Substrate (conversion)	Main Products (yield, carbon basis)	Field (mT)
6	 (100)	 (33)  (21)  (40)	65
13.5	 (88)	 (38)  (51)  (2)	65
8	 (49)	 (30)  (9)	65

R<sub>2</sub> conditions: 1mmol substrate, 0.7 mmol dodecane, 5 mL decane, 8 mg cat (≈0.1 metallic mmol), AMF 300 kHz, 3 H<sub>2</sub> bars.

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## Selective and Adaptive Hydrogenation of Amides using a Magnetically-Responsive Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst Heated by Magnetic Induction

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**Introduction.** The selective reduction of amides to amines is a key transformation for the chemical industry and especially for the pharmaceuticals. However, safety, atom efficiency and waste disposal are still major concerns when using established reagents (e.g. LiAlH<sub>4</sub> and diborane).<sup>1</sup>

**Methodology.** We explore the possibility to achieve selective amide reduction using a multifunctional catalytic system with magnetic heating capabilities. Magnetic induction heating has been shown by others and us to heat suitable materials in a very rapid, localized and energy efficient manner. This technology obviates the necessity of heating the entire reactor environment, leading to reduced energy consumption. We design, prepare and characterize a multifunctional catalytic system composed of Pt/Al<sub>2</sub>O<sub>3</sub> on which iron carbide nanoparticles<sup>2</sup> are immobilized with exceptional induction heating capabilities. This catalyst is used for the selective amide reduction using H<sub>2</sub>.

**Results and discussion.** ICNPs@Pt/Al<sub>2</sub>O<sub>3</sub> was characterized by various techniques. ICNPs@Pt/Al<sub>2</sub>O<sub>3</sub> exhibited high activity and selectivity for the hydrogenation of a scope of tertiary and secondary amides under mild conditions (3 bar H<sub>2</sub>, 160 °C) activated by magnetic induction. The same catalyst heated conventionally up to 200 °C showed no activity. The catalyst's adaptability to intermittent power supply was demonstrated by regularly stopping/re-starting the AC magnetic field. This approach paves the way for the development of magnetically-responsive adaptive systems capable of facilitating challenging transformations under mild conditions via magnetic induction heating.

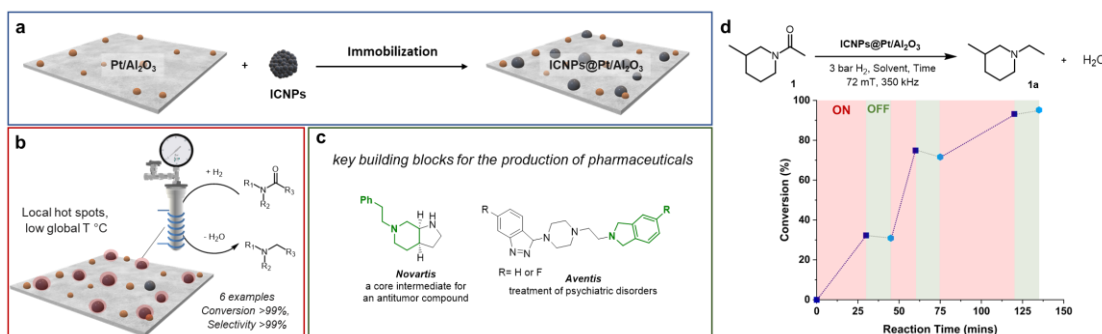


Figure 1. a-c) Illustration the concept of the work. d) Kinetic study of the hydrogenation of **1** using ICNPs@Pt/Al<sub>2</sub>O<sub>3</sub> recorded while regularly switching ON/OFF the power supply of the magnetic induction (red area = power ON; green area = power OFF, 15 min). The product selectivity is >99%.

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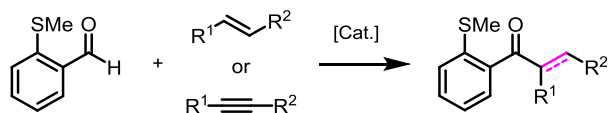


## Hydrogenation and Hydroacylation with *P*-stereogenic Methylene-Bridged Ligands

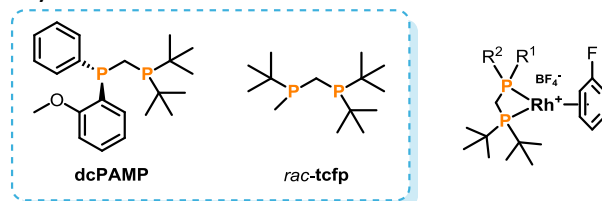
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Catalytic hydroacylation is an efficient method for the synthesis of ketones through the formation of a C—C bond between the carbonylic carbon of an aldehyde and an unsaturated carbon of an alkene or alkyne. The intermolecular version is especially interesting but it has been considerably understudied compared to the intramolecular variant.<sup>1</sup>



A group of methylene-bridged *P*-stereogenic ligands is presented here, along with their application in rhodium-catalyzed enantioselective hydrogenation and hydroacylation.<sup>2</sup> Furthermore, two  $\eta^6$ -fluorobenzene Rh(i) complexes have been synthesized and tested in the intermolecular hydroacylation of 2-(methylthio)benzaldehyde with several alkenes and alkynes. These complexes bear two different ligands, namely trichickenfootphos (**tcfp**), which has proven to be very successful as in enantioselective hydrogenation,<sup>3</sup> and the novel **dcPAMP**, *P*-stereogenic ligand that has been designed with the rationale of accessing the severely underexplored field of enantioselective intermolecular hydroacylation.



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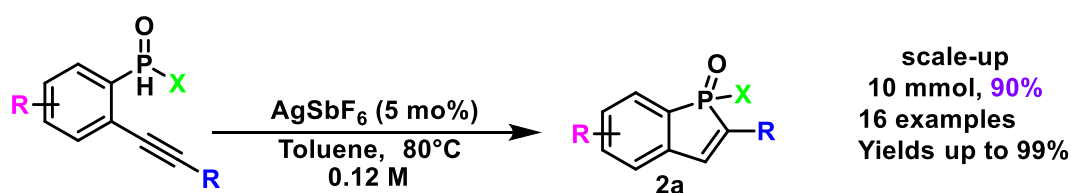


## Silver-Promoted Formation of P-C Bond: Diversifying the Structure of Phosphacycles

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Phosphorus heterocyclic compounds are widely used in fields such as materials science, medicinal chemistry, synthesis or coordination chemistry.<sup>[1]</sup> In particular, five-membered cyclic phosphine compounds have garnered special attention in materials science applications due to their unique optical properties, making them valuable for applications such as OLEDs, cell imaging dyes, and organic photovoltaics.<sup>[2]</sup> Previous work have reported various methods for synthesizing such compounds, including intermolecular oxidative addition of secondary phosphine oxides (SPO) and the cyclization of internal alkynes or alkynyl aryl phosphine oxides.<sup>[3]</sup> However, these methods still possess certain limitations. They require the addition of stoichiometric amounts of strong oxidants, excess of bases, and other additives; there is also selectivity issue in intermolecular addition, often resulting in mixed products and the tolerance of functional groups is also limited.<sup>[4]</sup>

In this work, an efficient and economical intramolecular cyclization for five-membered cyclic benzophosphorus compounds was established promoted by  $\text{AgSbF}_6$  (5 mol%) and under mild conditions. A broad scope of benzophosphorus compounds can be obtained in high yield with good functional group tolerance and without any additional additives. In addition, a plausible reaction mechanism was proposed based on a series of mechanistic experiments, including deuterium labeling and electron paramagnetic resonance (EPR) studies.



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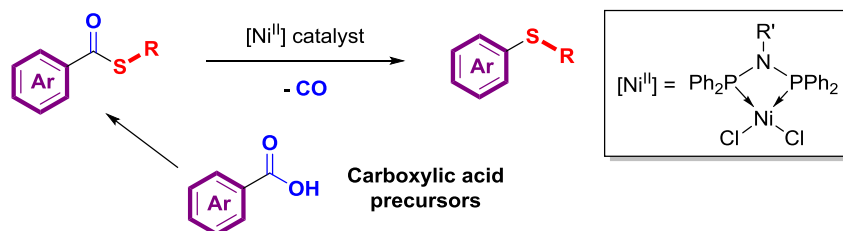


## Nickel-catalyzed synthesis of aryl thioethers via decarbonylation of aryl thioesters

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The diaryl thioether motif is present in many compounds used in pharmaceutical or food industries.<sup>[1]</sup> Classically, such thioethers are synthesized *via* a cross-coupling reaction between aryl halides and thiophenol derivatives and catalyzed by transition metals such as palladium, copper, or more recently nickel.<sup>[2]</sup> Indeed, nickel presents economical and environmental benefits compared to palladium. Another attractive approach to access such compounds, based on the decarbonylation of thioesters, has recently emerged (see Figure).<sup>[3]</sup> Moreover, thioesters are easily obtained from the corresponding abundant and inexpensive carboxylic acids. A few phosphine-stabilized Pd<sup>0</sup>, Ni<sup>0</sup> or Ni<sup>II</sup> complexes have been reported to achieve this transformation.<sup>[4]</sup>



Inspired by these recent findings, we evaluated air-stable Ni<sup>II</sup> complexes of *N*-substituted bis(diphenylphosphino)amine-type ligands (see Figure)<sup>[5]</sup> to mediate the decarbonylation of thioesters to form the corresponding thioethers. Catalysts' synthesis and characterization, optimization and rationalization of the decarbonylation reaction conditions and preliminary mechanistic investigations will be discussed in the present contribution.

The authors thank the ANR for funding the NiCatEther (ANR-22-CE07-0029-01) project.

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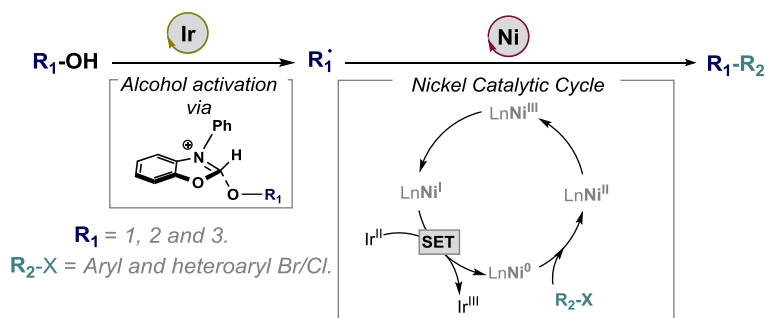




## Computational exploration of the mechanism of metallaphotoredox-enabled deoxygenative arylation of alcohols

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Formation of C-C bonds through cross-coupling reactions are one of the most prominent synthetic transformations in modern-day chemical synthesis. Despite of notable advances that have been reached in cross-coupling reactions, the introduction of commercially available coupling partners such as alcohols is limited in practice. However, this challenge was recently addressed by Macmillan et al. reporting the direct coupling of alkyl alcohols and aryl halides based on the use of N-Heterocyclic Carbene (NHC) salts within a dual photoredox Ir/Ni catalytic cycle.<sup>1</sup> The alkyl radical is generated via the formation of a NHC-adduct and its activation with an Ir photoredox catalysts. Afterwards -in a Nickel based cross-coupling catalytic cycle- this alkyl radical reacts with aryl halide to deliver the final cross-coupling product. In this work we carried out a whole DFT computational study of the dual Ni/Ir-photoredox catalytic cycle. Regarding the alcohol activation, we depicted a full energy profile based on four key steps: a first activation step to form the NHC-adduct, an oxidation step of this adduct via the excited state of Ir(III) photocatalyst, a deprotonation, and a final  $\beta$ -scission to yield the final alkyl radical.<sup>2</sup> We also evaluate the following Ni-catalytic cycle, suggesting that two distinct catalytic cycles operate simultaneously depending on the concentration of the alkyl radical.<sup>3</sup>



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## **Green Hydrogen storage for transport applications: relevant heterogeneous catalyst for the hydrogenation and dehydrogenation steps of Liquid Organic Carriers.**

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### **Keywords:**

Hydrogen storage – Organic liquids – Hydrogenation – Dehydrogenation – Multiphase reactors

For the sake of our planet, energy sources have to be diversified, and the renewable ones are rapidly developing. The use of hydrogen is widely considered to store and transport energy. Hydrogen storage by hydrogenation/dehydrogenation of organic liquids called “LOHCs” (Liquid Organic Hydrogen Carriers) is an interesting alternative to high pressure or liquefied H<sub>2</sub> storages as the use of LOHCs is pointed to be a safe and economical solution.

The described study aimed at identifying relevant organic liquids and catalysts for hydrogen storage in LOHCs through their catalytic reversible exothermic hydrogenation (HYD) and endothermic dehydrogenation (DH), the latter step being poorly studied in literature. The project also focused on relevant innovative designs of multiphase catalytic reactors for this purpose. This 22-months project was funded by the European Commission and managed by the Occitanie region (Défi-clé “Hydrogène Vert”).

Among the literature studies dedicated to LOHCs, a mixture of N-ethyl and N-propyl-carbazole (NEC-NPC) was chosen, as carbazoles are licence-free compounds, and because their mixture has a conveniently low melting point. Several catalysts have been tested for the HYD step, as Ruthenium on carbon, Ruthenium on alumina, Palladium on carbon, Palladium on alumina, Nickel on alumina. For the screening stage, an autoclave batch reactor (~300mL) equipped with a gas induction stirrer was used for HYD runs, and was specifically adapted to DH tests. Then, the best catalysts candidates have been tested in continuous innovative or conventional reactors: a tube reactor filled with catalytic pellets, and a fixed bed reactor. Mild operating conditions were selected to account for industrial application requirements:  $100 \leq T \leq 170^\circ\text{C}$  and  $5 \leq P_{\text{H}_2} \leq 30$  bar for the HYD step, and  $170 \leq T \leq 190^\circ\text{C}$  and  $P_{\text{H}_2} \sim 2$  bar for the DH step. In the batch reactor, H<sub>2</sub> consumption was measured from gauged capacity tanks including T/P probes. However, GC-FID analysis of liquid samples (leading to the concentration of reaction species) was also developed and assessed.

One of the tested catalysts was proved active for both HYD and DH steps with mild T and P: alumina supported nickel developed by Johnson-Matthey Plc. This result allows considering a scenario of great interest, where the carrying organic liquid may be cycled from H<sub>2</sub> storage to H<sub>2</sub> release without removing the catalyst between the HYD and DH steps. The HYD study established that the reaction kinetic law is of first order in regard with the concentration of double bounds in the liquid, with P<sub>H<sub>2</sub></sub>, and with the catalyst amount. Cycles of successive HYD and DH steps were performed in the batch reactor and very good reproducibility and stability was observed.

In the fixed bed reactor, HYD step was applied in up-flow mode and in quasi-isothermal condition, and for various gas and liquid flowrates and various T and P. Reaction yields up to 100% were reached with excellent consistency.

Acknowledgments: the authors thank Johnson-Matthey Plc for providing the nickel on alumina catalyst, European Union and Occitanie Region for project funding through the key challenge “hydrogène vert” (FEDER REACT H2VERT).



## Depleted Uranium Oxide Supported Nickel Catalyst for Autothermal CO<sub>2</sub> Methanation

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The CO<sub>2</sub> methanation reaction converts CO<sub>2</sub> in the presence of hydrogen, produced from renewable energy, into synthetic methane and water. It thus plays the role of an energy storage process according to Power-to-Gas principle (PtG). The reaction is highly exothermic and releases significant heat which calls for catalytic system with high heat management to prevent temperature runaway. Indeed, temperature runaway leads to the uncontrolled catalytic bed temperature increases which induces selectivity loss and severe sintering of the active phase leading to gradual deactivation. Several reactor configurations have been developed to improve the heat management for the industrial implementation of the methanation reaction. It is of high interest to develop new catalytic system with high catalytic performance and stability to operate such reaction.

Here, we reported on the use of nickel-based catalysts supported on depleted uranium oxide which allows one to carry out CO<sub>2</sub> methanation process at extremely low reaction temperature under atmospheric pressure. By adjusting the reaction conditions, the catalyst is able to perform CO<sub>2</sub> methanation reaction under **autothermal process** operated inside a adiabatic (under Joule heating [1]) or non-adiabatic (under induction heating [2]) reactor, **without any external energy supply**. Such autothermal process is possible thanks to the high apparent density of the UO<sub>x</sub> which allows one to confine the reaction heat in a small catalyst volume and to operate the reaction at equilibrium heat in-heat out process. Such autothermal operation mode allows one to significantly reduce the complexity of the heat management of the process. In addition, thanks to the peculiar interaction between the support and the active phase the catalyst displays an extremely high stability as a function of time on stream under either transient or long-term evaluation. It is expected that such new catalyst with unprecedented catalytic performance could open new area in the field of heterogeneous catalysis where traditional supports show their limitations to operate catalytic processes under severe reaction conditions.

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# POSTERS



## Challenges of molecular oxygen as an oxidant in copper exchanged zeolite for the functionalization of methane: a theoretical assessment

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### ABSTRACT

The economic importance of the large quantity of methane available has not been fully utilized because of its inert nature, and methane constitutes about 90 per cent of the natural gases. With the huge amount of resources required for conventional conversions, researchers in both academics and industries have been searching for an alternative route of directly converting methane to high added-value products, such as methanol. The identification of the metal-oxo of copper and iron as active sites used by methanotrophic bacteria has been biomimetic using zeolite matrix to stabilize the active sites to achieve conversion of methane to methanol at 150 °C [1][2]. Nitrous oxide, hydrogen peroxide, or molecular oxygen has been used as an oxidant of the copper or iron exchanged ZSM-5 for the hydroxylation of methane [3]. However, most of the oxidants are expensive (with the exception of molecular oxygen) and may not be economical for industrial purposes. Molecular oxygen is ubiquitous and a cheap source of oxidant that maybe profitable for commercialization of the process. In energy term, oxygen molecule required more energy than other oxidant because four electrons are required to split it into two oxygen atom that would eventually form metal-oxo species. One of the main challenges of the splitting of molecular oxygen is the limited knowledge in the reaction mechanism of the process [4]. Different methods have been proposed in the literature and this work is investigating these findings by means of Density Functional Theory (DFT) calculation using various zeolite frameworks (MFI, Mordenite, Chabazite) to anchor the mono copper-oxo moiety. The thermodynamics and kinetics of the dissociation of O<sub>2</sub> to form active sites for the partial oxidation of methane into methanol is currently being investigated.

**KEYWORDS:** zeolite, methane, methanol, mechanism, oxidant, iron, copper.

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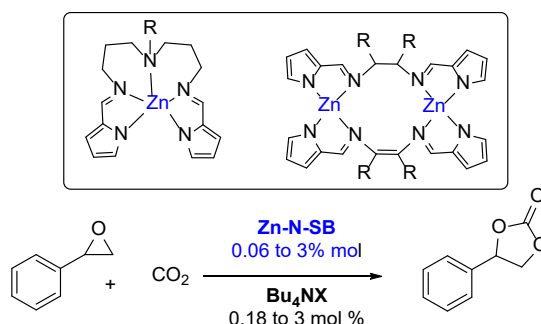


## Robust Zinc complexes as catalysts for the selective transformation of CO<sub>2</sub> into cyclic carbonates

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The selective reaction of carbon dioxide and epoxides to form cyclic organic carbonates requires both, Lewis base and Lewis acid catalysts. Quaternary ammonium halides (such as Bu<sub>4</sub>NX) are often used [1] as Lewis bases, and more recently, zinc complexes proved to be interesting Lewis acids [2] to achieve this CO<sub>2</sub> transformation. Our team developed the easy synthesis of nitrogen ligands using the Schiff condensation method [3] and we herein present a set of robust pyrrole containing Schiff Base zinc complexes (Zn-N-SB). Their XRay analysis showed monomeric or dimeric helical structures, according with the coordination mode of the zinc centre. DFT studies also confirmed if zinc adopts a tetra- or penta- coordinated structure. Combined to Bu<sub>4</sub>NX, these Zn-N-SB complexes led to efficient and selective catalysts for the cycloaddition of CO<sub>2</sub> into styrene oxide. The reaction optimization in solvent free conditions allowed complete epoxide conversions using very small amounts of both catalysts (< 0.2 mol%). Moreover, the robustness of these pyrrole derived zinc complexes allowed various catalytic runs, just adding new styrene oxide loadings, keeping a good catalytic activity along 4 days [4]. The reaction scope was also enlarged successfully to other terminal epoxides.



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# Probing Basal and Prismatic Planes of Graphitic Materials for Rhodium Single Atom Stabilization

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Carbon materials play a dual role as catalyst or catalyst support for chemical transformation reactions due to their large specific surface area, tailorable surface chemistry, high porosity and excellent electron conductivity.[1] Creating defects on the carbon network is often necessary to reach catalytic activity [2] or to use the material as a catalyst support, like in Single Atoms Catalysts (SACs) (Fig. 1).[3] In addition, a better understanding of the surface chemistry of those materials is mandatory, to establish relations between the number and type of defects and the catalytic activity, as well as to understand the change in their properties (magnetism) associated to the implant of defects.

Here we present the study of four different carbon materials showing different ratio basal/edges plan (Fig. 2). Their surface chemistry has been modified to stabilize rhodium single atoms. The catalytic activity of the resulting Rh SACs has been evaluated for various reactions such as hydroformylation, hydrogenation of phenylacetylene and 4nitrophenyl morpholine derivatives.

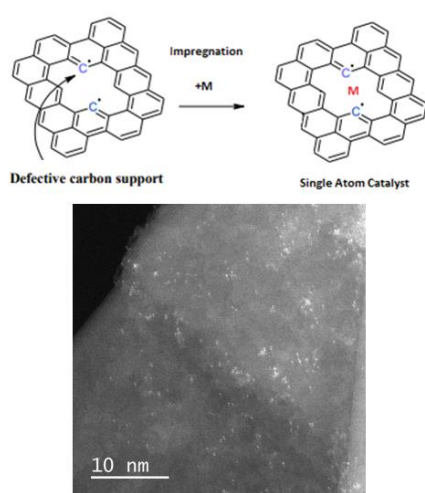


Figure 1 : Rhodium / FLG Single Atom Catalyst

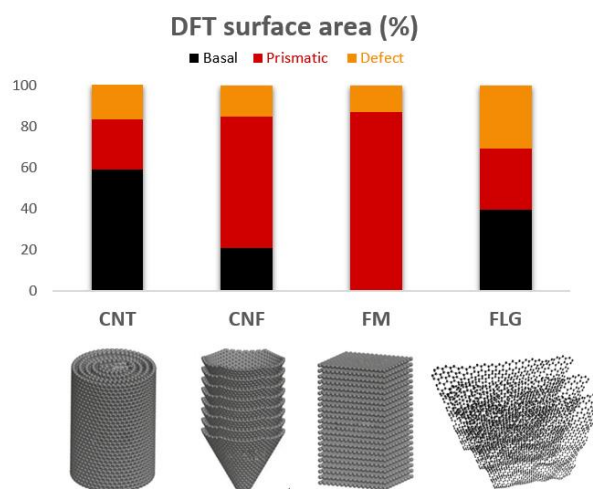


Figure 2 : Carbon materials (CarbonNanoTubes ; Carbon NanoFibers ; Fibrous Material ; Few Layer Graphene)

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## Phosphorous dendrimers asymmetrically functionalized for homogeneous catalysis in special media.

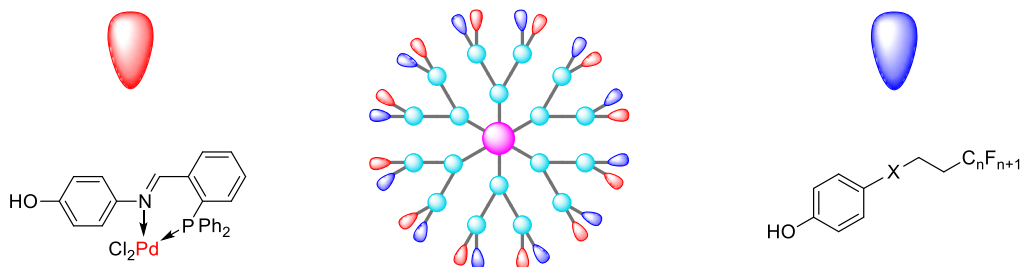
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Phosphorus dendrimers are very strong monodispersed hyperbranched polymers of a great interest for catalytical processes in organic synthesis, due to their property to be easily functionalized on their surface with a wide range of organometallic functions and for their recoverability.<sup>[1][2]</sup> Moreover is known that the solubility of dendrimers, can be modulated grafting the proper functional group on their surface.<sup>[3]</sup> A functionalization strategy is to perform an asymmetrical substitution on the terminal -P(S)Cl<sub>2</sub> function on the surface of phosphorus dendrimers, using distinct phenols or amines.<sup>[4]</sup> Thanks to this phosphorus dendrimers' selective reactivity, two different phenolic substituents were successfully asymmetrically grafted on their surface (**Figure 1**), an organometallic moiety that acts as a catalyst, and an alkylpolyfluorinated moiety that provides solubility in special media. We will present our results in catalysis of cross coupling reactions.



**Figure 1.** Scheme of asymmetrical substitution of phosphorus dendrimers, on the left the catalytic moieties and on the right the moiety that provide solubility of phosphorus dendrimers in supercritical CO<sub>2</sub>.

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## A Computational Perspective of Photoredox Catalysis: from Regioselectivity to Chirality

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In recent years, photoredox catalysis has attracted the attention of the synthetic chemistry community due to the large versatility on organic synthesis. Particularly, the mild and direct access to carbon-centered radical through light-mediated single electron transfer processes has enabled new ways of activating challenging substrates and to create new C-C or C-X bonds. However, the mechanistic understanding of these processes is still very limited comparing to other homogeneous catalyzed methods, such as cross-coupling reactions.

In our research group, we have been exploring photoredox catalysis mechanism during the last years through Density Functional Theory calculations. Herein, we present three different studies that show how polarity match effects and H-bonding platform can induce very high selectivity in radical processes, that are also very tolerant to other functional groups in the target molecules. We will show how functionalization of alkyl tertiary amines can be functionalized selectively using photoredox/thiol catalysis with electron deficient olefins and, complementarily, how minor changes in reaction conditions enable the functionalization of non-activated olefins using dual aminoborane/thiol catalysis.<sup>1</sup> Finally, we will present the extension of this methodology to achieve asymmetric deuterations and formation of C-C and C-X bonds.<sup>2</sup>

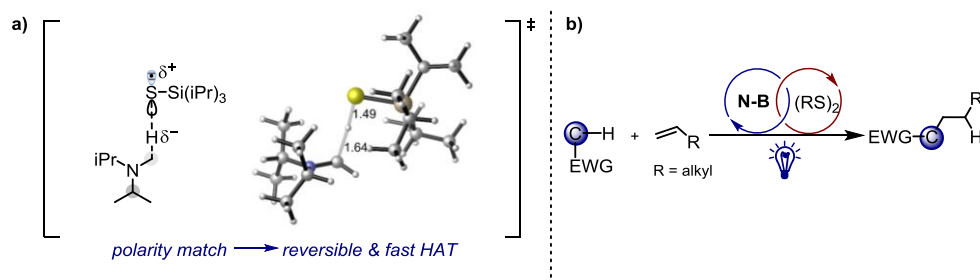


Figure 1. a) Selective functionalization of tertiary alkyl amines. b) Dual-catalyzed functionalization of unactivated olefines.

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## Harnessing Nanocatalysts and Organic Photoabsorbers for Efficient Solar Driven Water Splitting

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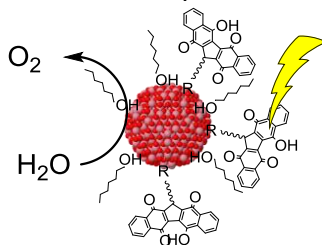
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Addressing global warming requires shifting from fossil fuels to renewables. Water splitting (WS) powered by sunlight is a key solution, but improving the water oxidation (WO) step needs efficient catalysts. Nanocatalysts offer the right compromise between stability and activity.<sup>1</sup> Using first-row metals instead of costly noble metals for WO is desired. Regarding light-absorbers, only few semiconductors absorb visible light. Concerning molecular photoabsorbers,  $[\text{Ru}(\text{bpy})_3]^{2+}$  is widely used but relies on scarce metals. Organic photoabsorbers are nowadays under the spotlight. This work explores oxygen evolution with hybrids materials formed by  $\text{Co}_3\text{O}_4$  nanoparticles<sup>2</sup> and KuQuinones (KuQ)<sup>3</sup> photosensitizers covalently grafted. Photocatalytic tests were done in colloidal cells and on  $\text{SnO}_2/\text{FTO}$  electrodes. Characterization methods include TEM, HRTEM, RAMAN, ICP, and XAS analysis. KuQ- $\text{Co}_3\text{O}_4$  hybrids were active in the photoinduced oxygen evolution. Unusual Co species were observed during synthesis and catalysis. Synchrotron XAS measurements helped understanding the process.



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## CHIRAL-AT-IRIDIUM(III)-SPO COMPLEXES FOR THE ENANTIOSELECTIVE TRANSFER HYDROGENATION OF KETONES

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Since 2010, and triggered by the ground-breaking contributions of the group of Prof. Meggers, enantiopure chiral only-at-metal derivatives of bis-cyclometalated Ir(III) complexes flourished due to their outstanding behavior as catalysts in asymmetric transformations. The use of these complexes in asymmetric catalysis opened a new paradigm in the area, which traditionally relied on the use of enantiopure chiral ligands. One of their most recent examples describes asymmetric hydrogenations using chiral-at-metal complexes that incorporate hydrogen-donors as non-innocent ligands.<sup>[1]</sup>

Secondary Phosphine Oxides (SPO) are amongst the strongest hydrogen-bonding donors described in the literature. This feature has been reflected in many catalytic processes in which a hydrogen-bonding SPO ligand has a key role in the reaction mechanism.<sup>[2]</sup>

In our research group, we have broad experience in the study of SPO-based catalysts for asymmetric reactions using chiral ligands.<sup>[3]</sup> In this communication, a first family of unprecedented chiral-at-metal Ir(III) complexes containing achiral SPO ligands will be presented. The communication includes a comparative study of their application in the transfer hydrogenation of ketones.

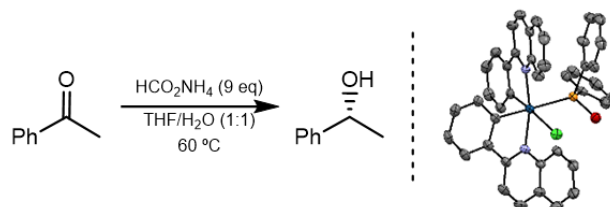


Figure 1: Enantioselective transfer hydrogenation of ketones

Financial support from the University of the Basque Country UPV/EHU (PIF20/62), the Basque Government (IT1180-19 and IT1553-22), the Spanish Ministry of Science and Innovation (PID2019-111281GB-I00 and PID2022-139760NB-I00 funded by MCIN/AEI/10.13039/501100011033) and IKERBASQUE is gratefully acknowledged.

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## Nanoparticles for active and sustainable fuel cell cathodes

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Depletion of fossil fuels and environmental pollution raised interest in new technologies for sustainable energy production, conversion, and storage, among which fuel cell technology is greatly studied, in both academia and industry. Proton exchange membrane fuel cells (PEMFCs) are reputed energy devices, due to their high conversion efficiency and low environmental pollution.<sup>1</sup> Nowadays, Pt-based catalysts exhibit the best electrocatalytic activity towards oxygen reduction reaction (ORR), but enhancing their catalytic efficiency and reducing costs are essential for commercializing fuel cell technology.<sup>2</sup>

Our interest relies with the development of Pt-based nanoalloys<sup>2,4</sup> *via* solution organometallic chemistry approach.<sup>3</sup> This approach allows control over the composition, structure, and morphology of metal nanoparticles, and could lead to increased catalytic activity and long-term stability by revealing more active sites of the catalyst. Additionally, the ability to alloy with a range of metals for producing bimetallic compounds is one of the key advantages of this approach.

In this communication, the synthesis of Pt-based nanoparticles and their characterization by state-of-the-art techniques such as ICP, EA, IR, TEM and HR-TEM will be described. The influence of the Pt complexes used as precursors and of the reaction conditions on the morphology of the Pt nanoparticles will be shown. The obtained nanostructures offer interesting starting materials to incorporate other metals, such as transition or rare earth metals, in order to have nanoalloys and study their performance in ORR in comparison to pure Pt catalysts.

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## N<sub>2</sub>O Hydrosilylation Mediated by RuSNS Nanoparticles

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Nitrous oxide (N<sub>2</sub>O) is a strong greenhouse gas, one of the main contributors to global warming. There is currently great interest in developing chemical processes for the degradation of this gas into non-harmful species. One of these processes is the hydrosilylation of N<sub>2</sub>O,<sup>[1]</sup> which allows its transformation into N<sub>2</sub> together with the formation of different silanols and siloxanes (Figure 1).

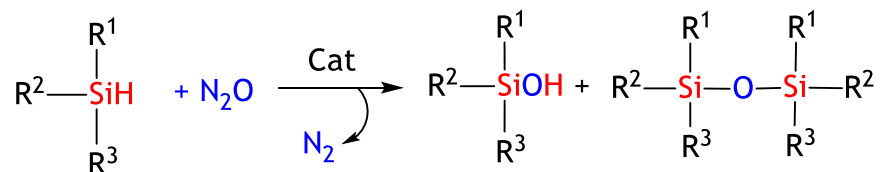
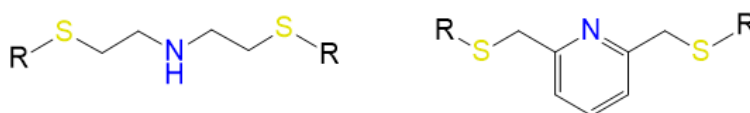


Figure 1. Hydrosilylation of nitrous oxide.

In this contribution we describe a series of RuSNS nanoparticles prepared by decomposition of Ru(COD)(COT) with H<sub>2</sub> in the presence of a SNS ligand (Figure 2) as stabilizing agent (organometallic approach).<sup>[2]</sup> These nanoparticles, which have been characterized by means of TEM, HRTEM, ICP and XPS, have been found to catalyse the reduction of N<sub>2</sub>O to N<sub>2</sub> employing different hydrosilanes under relatively mild reaction conditions (1 bar N<sub>2</sub>O, 55-65 °C).<sup>[3]</sup>



R = CH(CH<sub>3</sub>)<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>

Figure 2. Generic structure of ligands SN<sup>H</sup>S and SN<sup>P</sup>YS.

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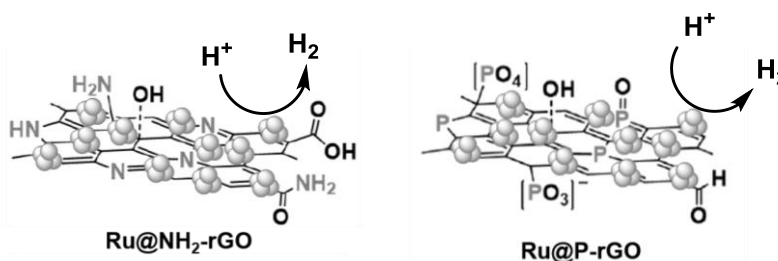


## Ruthenium Nanoparticles Supported on P/N-Doped Reduced Graphene Oxide: Effect of the Heteroatoms in the Hydrogen Evolution Electroactivity

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Metal nanoparticles (NPs) are very promising chemical systems for catalyzing the hydrogen evolution reaction (HER)<sup>1</sup>, amongst which Ru stands as one of the most active and stable metals.<sup>2</sup> In this work, Ru NPs have been synthesized *in-situ* by means of the organometallic approach in the presence of bare reduced graphene oxide (rGO) and its N-doped (NH<sub>2</sub>-rGO) and P-doped (P-rGO) counterparts for their use as HER electrocatalysts. The materials have been characterized by (HR)TEM, EDX, EA, ICP-OES, XPS, XRD, Raman, NMR and IR, and afterwards have been deposited onto a glassy carbon rotating disk electrode to assess their HER electrocatalytic activity at acidic pH. The results show that all three materials are very stable under reductive conditions for at least 12 h, and that addition of the heteroatoms into the graphitic structure extremely increases the activity of the hybrid electrodes, especially for the case of Ru@P-rGO, where the overpotential at 10 mA/cm<sup>2</sup> decreases to only 2 mV. Moreover, DFT simulations of these hybrid Ru@(NH<sub>2</sub>/P)-rGO systems are in full concordance with their electrochemical behaviour.



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## Scanning Tunneling Microscope as a characterization tool for single atom catalysis ? Experimental observations and simulation results

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Single atom catalysts (SAC) have attracted much interest since the last decay. This domain is particularly important in the context of climate change and the necessity to reduce drastically the fossil energy consumption and rare resources employment. However, in spite of important quantity of results already obtained, a real breakthrough in the discovery of effective catalysts is still uncertain. The major bottleneck to optimize the efficiency and the stability of SACs is the lack of understanding about the reaction mechanism of these systems at the atomic scale. Among the available techniques, the scanning tunneling microscope (STM) associated with density functional theory (DFT) calculations could be an interesting means to characterize some model systems [1].

In this work, we present our STM observations and DFT results of two single atoms (Au and Co) evaporated on self-assembled 2D domains of terephthalic acid (TPA) on Ag(001) substrate [2]. By comparing the different behaviors of these 2 single atoms, we have identified that the different contrast of Au atoms originates from its adsorption site and the attachment of diffusing H atoms from the surrounding defects in TPA layer [3]. The reactivity of single Au atom towards the H atoms could eventually explain the desorption of Au adatoms.

The behavior of Co single atom is much simple. Explained by a significant adsorption energy calculated by DFT, Co atom is firmly bounded to the TPA by sitting on top of the center of the benzene ring. In spite of this strong attachment, these single Co atoms are also sensitive to the surrounding H atoms. To illustrate this, the reaction paths of a model system using Co atom as SAC are predicted and simulated STM images of the associated intermediate states are presented.

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## Photo-production of H<sub>2</sub> from ethanol solution over Mo<sub>x</sub>C/g-C<sub>3</sub>N<sub>4</sub> nanocomposites

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The photo-production of H<sub>2</sub> from bio-alcohols could be a suitable route for the obtention of green-H<sub>2</sub>. In this context, photocatalysts based on noble metal onto different semiconductors have been largely studied [1]. However, the development of cheap and available photocatalysts is necessary. We have previously reported new photocatalysts based on the well-known TiO<sub>2</sub> semiconductor and using as co-catalyst Mo and W carbides [2,3]. This background prompted us to report here our results using a visible-light responsive semiconductor, C<sub>3</sub>N<sub>4</sub>, and different Mo carbides, MoC, Mo<sub>2</sub>C and Mo<sub>x</sub>C, as co-catalysts. The H<sub>2</sub> photo-production from an ethanolic solution using new MoC/C<sub>3</sub>N<sub>4</sub>, Mo<sub>2</sub>C/C<sub>3</sub>N<sub>4</sub> and Mo<sub>x</sub>C/C<sub>3</sub>N<sub>4</sub> nanocomposites is here related with the characteristics of Mo carbide phases. Mo<sub>x</sub>C phases were synthesized [2,4], and separately, C<sub>3</sub>N<sub>4</sub> nanosheets were prepared [5]. Mo<sub>x</sub>C/C<sub>3</sub>N<sub>4</sub> photocatalysts were obtained using an ultrasonic-assisted method [3]. The photocatalysts were characterized by B.E.T., XRD, FTIR, TEM-HRTEM and EDX, UV-vis and XP spectroscopy. The photoelectrochemical properties were determined from the transient photocurrent measures and EIS. The photocatalytic tests were carried out at 20 °C in a described set-up [6], using a 25% v/v ethanol<sub>aq</sub> solution and λ>385 nm irradiation. The composite materials kept the structural characteristics of the original carbide co-catalyst after the ultrasonic incorporation onto the C<sub>3</sub>N<sub>4</sub>. The systems containing Mo<sub>2</sub>C were more photo-effective than MoC/C<sub>3</sub>N<sub>4</sub>; the smaller the crystallite size of the Mo<sub>2</sub>C phase the better photocatalytic behavior. The amount of H<sub>2</sub> produced per gram of photocatalyst resulted in very good agreement with the photoelectrochemical properties. The presence of MoC-Mo<sub>2</sub>C heterojunctions could improve the photocatalytic behaviour.

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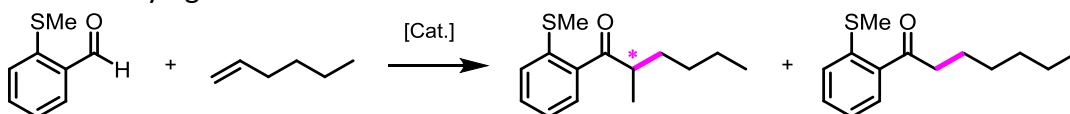


## dcPAMP: a new P stereogenic unsymmetrical ligand for intermolecular hydroacylations

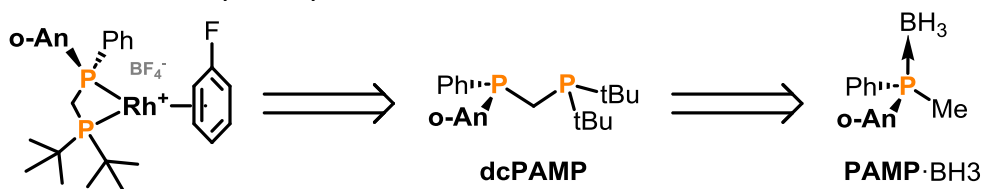
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Hydroacylation is a reaction in which a C—C bond is formed between an aldehyde and a carbon from an alkene or alkyne. In its intermolecular version, the reaction is generally favoured towards the formation of the linear product. This fact makes the obtention of branched ketones—and, consequently, the implementation of an enantioselective version of the intermolecular hydroacylation reaction—a considerable challenge that is worth studying.<sup>1</sup>



In order to pursue this challenge, a new ligand has been designed: a C<sub>1</sub>-symmetric methylene-bridged diphosphane—a structure that has been proven effective in the hydroacylation of internal alkenes<sup>2</sup>—affording ketones which can potentially have a stereogenic carbon. On top of that, the ligand that we have designed, named **dcPAMP**, presents a *P*-stereogenic centre, which makes it suitable for enantioselective intermolecular hydroacylations.



The ligand has been synthesized following the Jugé-Stephan methodology<sup>3</sup> and complexed to [Rh(diolefin)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>−</sup>. Subsequent hydrogenation in the presence of fluorobenzene efficiently led to [Rh(**dcPAMP**)( $\eta^6$ -fluorobenzene)]<sup>+</sup>BF<sub>4</sub><sup>−</sup>. This complex has then been used as a catalyst in asymmetric intermolecular hydroacylation reactions.

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## Sustainable metal-catalyzed pathway for Linalool oxidation

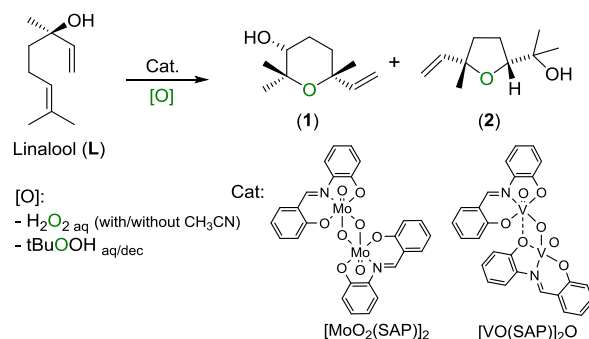
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Among the 12 principles of Green Chemistry, catalysis plays a crucial role in the economic development and expansion of Chemical Industry.<sup>[1]</sup> Thus, products of interest should be obtained under benign conditions and especially from biomass. In this work, we are looking for two heterocycles with potential use in medicine,<sup>[2]</sup> named herein furanoid (**1**) and pyranoid (**2**). Both are currently obtained in big quantity through “non green” synthetic pathways, including huge quantity of waste and solvent.<sup>[3]</sup> Some strategies involve oxidation of linalool, substrate from biomass.<sup>[4]</sup> In the group, [MoO<sub>2</sub>(SAP)]<sub>2</sub> and [VO(SAP)]<sub>2</sub>O complexes have been found to be active oxidation pre-catalysts for natural molecules, under organic-solvent free conditions.<sup>[5–8]</sup> Such significant societal and environmental challenges drive our research. We developed homogeneous catalytic systems based on [MoO<sub>2</sub>(SAP)]<sub>2</sub> and [VO(SAP)]<sub>2</sub>O, for oxidation of linalool using “green” benign oxidant and solvent-free conditions. Catalytic results using those pre-catalysts and several reaction conditions will be presented, as well as green metrics considerations.<sup>[9]</sup>



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## Performance improvement of nanocarbon-supported catalysts for the Fischer-Tropsch Synthesis through different surface treatments

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The Fischer-Tropsch synthesis (FTS) provides an efficient pathway to produce high-quality transportation fuels<sup>1</sup> from synthesis gas, which can be derived from carbon-containing renewable resources. Even though it is a route known for several decades, research is currently focused on developing highly selective catalysts for specific hydrocarbon ranges, thus avoiding expensive post-treatments. Carbon nanomaterials, such as carbon nanotubes (CNTs), are chemically and thermally stable under harsh conditions and have tunable surface chemistry, being gaining interest as catalyst support for FTS.<sup>2</sup> This study aimed to selectively produce sustainable liquid fuels in the C<sub>5-20</sub> range by carrying out different treatments on the CNTs. Pristine CNTs were modified with oxygen and nitrogen-containing species and thermal treatments, strongly influencing their physicochemical properties. The modified CNTs were used to prepare 10% cobalt catalysts by incipient wetness impregnation. The catalysts were tested in fixed-bed FTS. The effect of the different treatments on the CNTs is analyzed regarding their stability and catalytic performance, including CO conversion, specific yield, and selectivity. The results showed that controlling the surface chemistry of the CNT-supported catalysts is essential to produce high-quality synthetic fuels, and the production of synthetic diesel and gasoline with higher isomerization, thus superior quality, is favored.

### Acknowledgments

This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020, UIDP/50020/2020 (LSRE-LCM) and UIDB/00690/2020 (CIMO), funded by national funds through FCT/MCTES (PIDDAC); project “Cat4GTL – Continuous Catalytic reactor for the Gas-to-Liquid process using NETmix technology”, with reference POCI-01-0247-FEDER-069953, co-financed by the European Regional Development Fund (ERDF), through the Operational Programme for Competitiveness and Internationalization (COMPETE 2020), under the PORTUGAL 2020 Partnership Agreement. TS thanks the support through the doctoral Grant (2022.11065.BD.) financed by FCT.

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## Fine-Tuning Ru Nanoparticles with 2,2'-Bipyridine: Size vs. Performance

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Karine Philippot<sup>2</sup>, Jordi García-Antón<sup>1</sup>, Xavier Sala<sup>1</sup>**

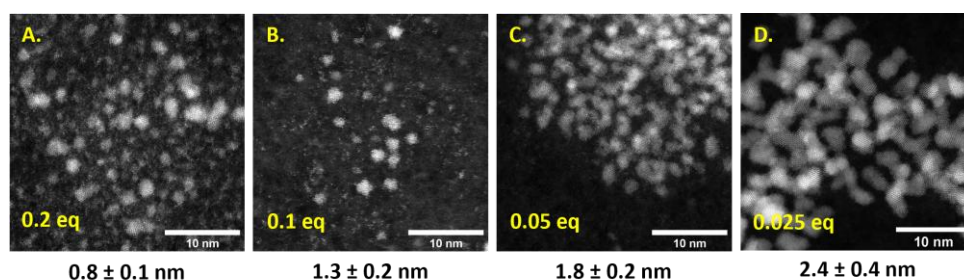
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In recent years metallic nanoparticles (NPs) have increased their popularity for numerous catalytic applications. This is largely due to their size-related properties. When compared to typical homo- and heterogeneous catalysts, metallic NPs gather some of the best properties of both worlds.<sup>[1]</sup> One particularly interesting method for the synthesis of metallic NPs is the organometallic approach. This procedure entails the controlled decomposition of an organometallic precursor in the presence of a stabiliser, usually a ligand of interest, under mild conditions. In this way, the synthesised NPs present a clean surface free of contaminant by-products.<sup>[2]</sup> Interestingly, the ligands attached to the surface of NPs have been shown to alter the physicochemical properties of the system and even increasing their catalytic efficiency, as in the case of Ru NPs stabilised with 4-phenylpyridine ligand for HER.<sup>[3], [4]</sup> Herein we present various systems consisting of Ru NPs stabilised with different amounts of bpy. It was found that there is an inverse relationship between the amount of bpy used and the NP size. These differences in size also translate into their catalytic performances towards HER, being the smallest system the worst and the biggest one the best. This behaviour can be justified by the effect of the bpy ligand on the active sites of the NPs by a combination of experimental and computational studies.



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## Iridium Nanoparticles Deposited onto TiO<sub>2</sub> supports for the Synthesis of 2-Phenylbenzimidazole through Reductive Amination of 2-Nitroaniline and Benzaldehyde

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Selective hydrogenation is crucial in the chemical industry; however, sustainable alternatives to noble metal catalysts are being sought. Auto transfer of H<sub>2</sub> presents a promising option by utilizing organic solvents as a hydrogen source. In this investigation, TiO<sub>2</sub> nanotubes (TNT) [1] and nanoparticles (NPS) were reemployed as supports for Ir catalysts in the synthesis of 2-phenyl-benzimidazole. The reaction involved reductive amination of 2-nitroaniline and benzaldehyde. The nanotubes exhibited excellent support, with the 0.25% Ir/NTs catalyst showing the highest performance at 130 °C. Notably, the support's selectivity towards imine formation was emphasized. Despite decreasing to 80% of maximum conversion, the performance remained consistent after 5 operating cycles. These results suggest a promising approach for the sustainable synthesis of relevant benzimidazoles in pharmaceutical applications.

The catalytic test was performed in a stainless-steel reactor, with 50 mL of cyclohexane as solvent, 50 mg of reduces catalyst in a molar ratio substrate/metal of 100, the conversion of the substrate was followed by GC and all materials was characterized by many techniques, surface, microscopy, and crystallinity.

The main result of the study show that the best catalyst was the Ir0.25%/TNT reaching full conversion of the substrate at the temperature of 130°C with the best selectivity, also the catalyst shows a recyclability of 5 cycles of reaction a activation energy of 5,64 kJmol<sup>-1</sup> on the opposite site the same catalyst supported on titania nanoparticle show also a similar conversion rate but a poor selectivity for the interest product.

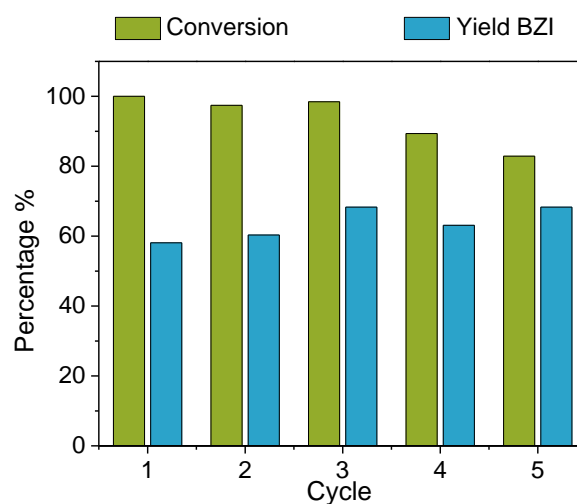


Figure (1) Recyclability for Ir<sub>0,25%</sub>/TNT Catalyst

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## Carbon nitride loaded with Ni, Cu and Pt nanoparticles: effect of g-C<sub>3</sub>N<sub>4</sub> structure on the solar-driven hydrogen evolution reaction

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In last years, semiconductor photocatalysts have been explored to develop new (nano)catalysts that are at the same time stable, inexpensive, visible light responsive and efficient towards solar-driven water splitting. This process is considered a promising technology to deal with energy crisis since hydrogen gas can be produced in an eco-friendly way. The unique features of polymeric carbon nitride (PCN), such as visible-light response, easy synthesis from earth abundant elements, chemical stability and non-toxicity make it a catalyst with great potential for the hydrogen evolution reaction (HER) [1]. However, the activation of the photocatalytic reaction requires the loading of metallic co-catalysts onto the surface of the photocatalyst. The co-catalysts are often metallic nanoparticles (NPs) that promote charge separation of photogenerated electrons and holes and work as active sites for the catalytic reaction [1,2]. Although platinum nanoparticles (Pt NPs) are the most used benchmark co-catalyst for HER, its high cost and scarcity has prompted the search for alternative non-noble metals such as Ni and Cu.

Consequently, in the present work we report the synthesis of two types of PCN (exfoliated and carbon doped) loaded with metallic Ni, Cu and Pt NPs using the organometallic approach [3], which allows to obtain monodisperse metallic NPs of narrow size distribution and controllable surface environment. The prepared catalysts were tested towards photocatalytic HER under simulated solar irradiation (300 W Xe lamp; TEOA 10% V/V) to assess the effect of carbon nitride structure on the photoactivity as well as to check if Ni or Cu NPs can be used as efficient co-catalysts to replace the noble metal Pt NPs.

### Acknowledgments

Eliana S. Da Silva acknowledges the Maria Zambrano fellowship (MAZAM 681136) from the UAB and the Spanish Ministry of Universities, funded by the European Union-Next-GenerationEU.

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## Iron based composite catalyst for magnetically-induced hydrogenation reactions in gas and solution phase

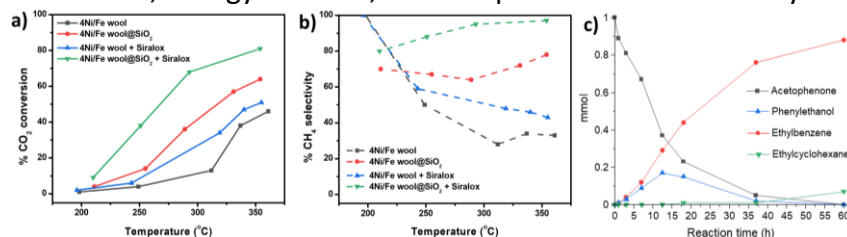
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Recently, magnetically induced catalytic CO<sub>2</sub> hydrogenation has gained lots of attention due to its high energy efficiency and better heat management of exothermic processes as compared to thermal heating.<sup>1</sup> In particular, ferromagnetic nanoparticles (dual heating and catalytic agent) are shown to be active for this process, but the complex synthesis of such nanoparticles hinders their potential to be a commercial success.<sup>2</sup> Herein, a single macroscopic Fe based (SiO<sub>2</sub> and Ni coated) composite with dual functionality was realized and tested for magnetically induced gas-phase methanation and further proved to be active for the liquid phase reactions.

The enhanced catalytic activity (higher CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity) of Ni deposited silica coated Fe wool as compared to the uncoated counterpart could be attributed to the presence of SiO<sub>2</sub> layers, providing more stability to the surface Ni species (Fig. 1).<sup>3</sup> An addition of a Siralox filler in the catalytic bed further improves the CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity, and the stability of the catalyst (30 h on stream). Furthermore, this composite catalyst was demonstrated to be active for solution-phase model hydrogenation (styrene and nitrobenzene) and hydrodeoxygenation (acetophenone and diphenyl ether) reactions with 5mol% Ni loading (Fig. 1c). Herein, the combined XPS, FIB-SEM, and SAR measurements, signifies the judicious choice of SiO<sub>2</sub> coating and the utilization of eddy current mediated heating of Fe wool for the development of stable, energy efficient, and inexpensive Fe based catalyst.



**Figure 1.** Plot of a) %CO<sub>2</sub> conversion as a function of temperature, and b) CH<sub>4</sub> selectivity as a function of temperature, c) solution phase kinetic data for acetophenone hydrodeoxygenation reaction using 4Ni/Fe wool@SiO<sub>2</sub> as a catalyst.

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## Versatile organometallic approach for engineering 2D-Germanane-based electrocatalyst for boosting energy conversion

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The theoretical exploration of graphene and its practical discovery led to enormous interest in the research of two-dimensional (2D) materials.<sup>[1,2]</sup> Succeeding graphene, Xenon as the mono-elemental-based 2D materials has gradually attracted interest in recent years.<sup>[3]</sup> In particular, the appearance of 2D-germanene (2D-Ge) has gained much attention owing to its predicted promising physicochemical features,<sup>[4,5]</sup> similar to the ones exhibited by mainstream graphene, suggesting that it might have multiple applications in the energy conversion field. However, most studies relating to 2D-Ge derivatives are mainly focused on theoretical works, which should be ascribed to the lack of functionalization strategies.<sup>[6,7]</sup>

Otherwise, the organometallic approach is a reliable synthetic strategy for fabricating metallic nanoparticles (M-NPs) from the decomposition of an organometallic precursor under mild conditions.<sup>[8]</sup> This method yields nanoparticles containing metallic atoms with zero oxidation state, which could be effective co-catalysts for improving catalytic efficiency.<sup>[9]</sup> Nonetheless, this synthetic approach has never been utilized for the functionalization of 2D-Ge. In this study, based on the organometallic approach, various metal nanoparticles including Pt-NPs and Au-NPs were loaded on 2D-Ge substrate to reach different electrocatalytic applications, such as Hydrogen Evolution Reaction (HER) and Oxygen Reduction Reaction (ORR). Pivotal electrochemical features of M-NPs@2D-Ge composite were investigated to understand the role of M-NPs during the energy conversion process.

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## 5-Methylene-1,3-Dioxane-2-One: A First Choice Comonomer for Trimethylene Carbonate

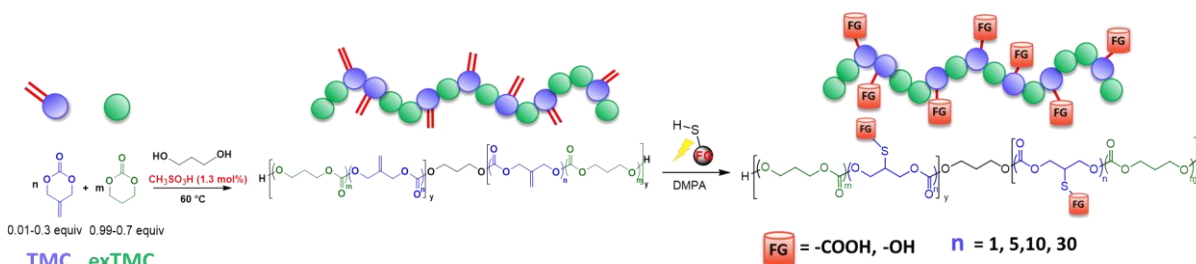
Kamolchanok Sarisuta,<sup>1,2</sup> Miguel Palenzuela Cebrián,<sup>1</sup> Marta Navarro Sanz,<sup>1</sup> Narumi Kumamoto,<sup>1,2</sup> Julien Monot,<sup>1</sup> Hiroaru Ajiro,<sup>2</sup> Blanca Martín-Vaca,<sup>1</sup> Didier Bourissou.<sup>1</sup>

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5-methylene-1,3-dioxane-2-one (exTMC), a six-membered ring cyclic carbonate bearing an exocyclic methylene group, has been investigated as comonomer for trimethylene carbonate (TMC) with the aim to prepare functionalized polycarbonates. Using methane sulfonic acid (MSA) as organocatalyst, exTMC and TMC copolymerize in a controlled manner to lead to copolymers of adjusted composition and high randomness (the corresponding reactivity ratios have been determined by the Beckingham-Sanoja-Lynd (BSL) method as 0.95-0.98 and 1.00-1.06 for exTMC and TMC, respectively). Subsequent thiol-ene reaction on the exomethylene group with thioglycolic acid or thioglycerol provide aliphatic polycarbonates with adjustable amounts of COOH or OH groups randomly distributed along the polymer chains.



**Scheme 1.** Syntheses of PTMC-*co*-PexTMC and functionalization of PTMC-*co*-PexTMC via thiol-ene reaction

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## INHERENTLY CHIRAL CALIX[4]ARENE PHOSPHORIC ACIDS WITH ABHH AND ABCH SUBSTITUTION PATTERNS OF THE NARROW RIM: SYNTHESIS AND ORGANOCATALYTICAL EVALUATION

Eric Manoury,<sup>1</sup> Zoia Voitenko,<sup>1,2</sup> Andrii Karpus,<sup>1,2</sup> Oleksandr Yesypenko,<sup>3</sup> Vyacheslav Boiko,<sup>3</sup> Jean.-Claude Daran,<sup>1</sup> Vitalii Kalchenko<sup>3</sup>

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Calix[4]arenes are bowl-shaped macrocyclic molecules that have attracted great interest in supramolecular chemistry because they are synthesized from accessible and cheap starting materials and because of the possibility for decoration of the calix[4]arene structure with different functional groups, at both wide (upper) and narrow (lower) rims.<sup>1,2</sup> Properly designed molecules can possess useful properties for application in biomedicine, nanoscience, sensor development or catalysis. Among numerous functionalised calix[4]arenes, chiral derivatives are of particular interest but have been much less used in asymmetric catalysis than in other fields.

Recently, we started to test chiral calixarenes in asymmetric catalysis.<sup>3</sup> We now want to report a simple and efficient method for preparation of two types of inherently chiral calix[4]arene phosphoric acids (ABHH and ABCH) with programmed disposition of H-bond donor functional groups on the narrow rim in high yields and the first tests of this Brønsted acids with inherent chirality only in organocatalyzed reactions. To the best of our knowledge, calixarenes bearing phosphorylhydroxy groups have not yet been explored in asymmetric organocatalysis to the best of our knowledge while chiral phosphoric acids have been so successfully used as organocatalysts.<sup>4</sup>

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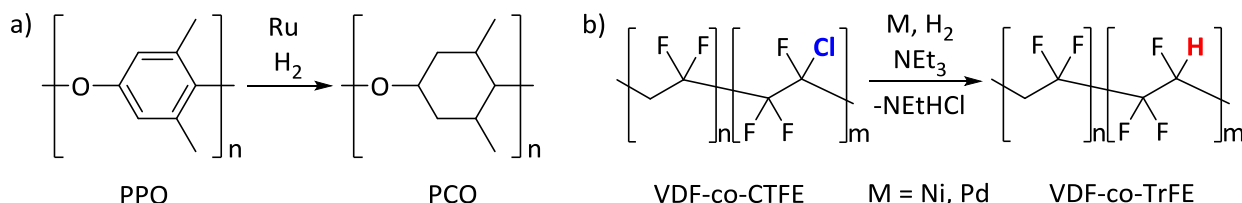
## Supported Metal-Catalyzed Polymer Modification via Hydrogenation and Hydrodechlorination reactions

V. Varela-Izquierdo<sup>1</sup>, G. Mencía<sup>1</sup>, S. Ghosh<sup>1</sup>, B. Chaudret<sup>1,\*</sup>

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**Introduction.** Polymeric structure modification is a well-known methodology providing novel materials with tailored physical properties, thereby increasing the application range of the original polymer.[1] In particular, aromatic polymer hydrogenation catalyzed by Pd and Pt catalysts has been widely used to alter the polymeric chain.[2] On the other hand, Ni and Pd catalyst are commonly used in hydrodechlorination reactions under hydrogen atmosphere for small organic molecule modification[3]. However, in the case of polymers, these catalysts remain unexplored and radical-based reactions are preferred[4]. Those two strategies were applied to modify commercial polymers in the work herein presented.

**Results and discussion.** Ru NPs have been found to be active in aromatic polymer hydrogenation (PS, PPO), with low hydrogenolysis level (scheme 1a). Remarkably, different semi aromatic polymers could be obtained by modifying reaction temperature and support selection. Moreover, Pd and Ni NPs achieved selective hydrodechlorination (up to 80%) of VDF-CTFE, without affecting the fluorine moieties (scheme 1b). All these reactions were carried out under mild conditions (3 - 7 bar of H<sub>2</sub>, 423 K as maximum temp.).



**Scheme 1.** (a) Hydrogenation of PPO and (b) Hydrodechlorination of VDF-co-CTFE.

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## Fischer-Tropsch synthesis by CO<sub>2</sub> hydrogenation on modified Co/TiO<sub>2</sub> catalysts

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Climate change represents the biggest threats of our era. It is mainly due to the increase in greenhouse gas (GHG) emissions, which trap the heat in the earth's atmosphere. CO<sub>2</sub> emissions are responsible for 68% of the global GHG emissions. One of the main goals to reduce GHG is the use of the CO<sub>2</sub> emissions [1]. With this in mind, Carbon Capture and Utilization (CCU) represents a promising strategy to meet the global energy and climate goals.

This research work focuses on the production of C<sub>2+</sub> products by direct CO<sub>2</sub> Fischer-Tropsch synthesis (CO<sub>2</sub>-FTS). In a traditional FTS reaction, cobalt represents one of the best choices for the production of synthetic hydrocarbons. However, in CO<sub>2</sub>-FTS, cobalt catalysts present a low CO<sub>2</sub> adsorption and RWGS thermodynamic constraints [2] leading to low C/H surface ratio and CO coverage, resulting in the preferential production of CH<sub>4</sub> and short chain hydrocarbons [3-4]. Several parameters can be modulated to improve the selectivity towards C<sub>2+</sub> products on Co-based catalysts such as: the choice of cobalt active phase [5], support and metal support interfaces [6], and the addition of promoters [7]. Here, a commercial TiO<sub>2</sub> support was partially reduced leading to the formation of surface defects (O<sub>v</sub> and Ti<sup>3+</sup>). The modified support was used to prepare the Co-based catalysts by incipient wetness impregnation (IWI). The catalysts were used for the direct CO<sub>2</sub>-FTS.

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## Hydrogenation of esters promoted by NHC-phosphine manganese catalyst

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Alcohols are highly valuable synthetic intermediates for the production of pharmaceutical, agrochemical and fine chemical products. Therefore, carboxylic esters, considered as an important class of natural products, are interesting candidates to produce alcohols through their reduction. Hydrogenation catalyzed by transition metal complexes is a well-known method for the reduction of carboxylic esters. Although noble metals are known to be highly efficient in this category of transformation, their scarcity and potential toxicity have prompted chemists to seek a more sustainable alternative: the use of more environmentally friendly and inexpensive Earth-abundant transition metal of the first row such as iron and manganese.<sup>1</sup> In the literature, the catalysts developed so far are mainly based on tridentate ligands involved in a metal-ligand cooperativity.<sup>2</sup>

In this context, we have focused our research on the development of a catalytic system based on a manganese complex carrying a bidentate NHC-phosphine ligand, which is not a priori capable of inducing metal-ligand cooperativity. The results obtained in the hydrogenation reactions of carboxylic esters are presented here. A series of 28 examples of ester were hydrogenated at a catalyst loading of 0.5 mol% in the presence of 50 bar of H<sub>2</sub> pressure and 10 mol% of KBHET<sub>3</sub> at 100 °C.<sup>3</sup> All the results will be detailed in the present communication.

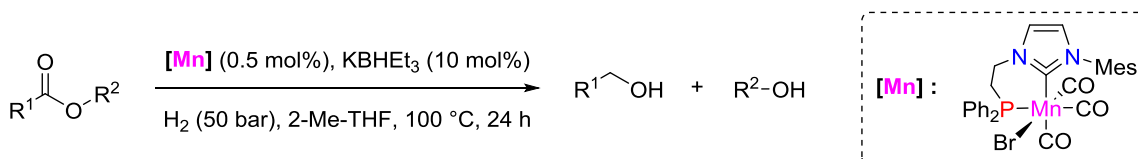


Figure 1

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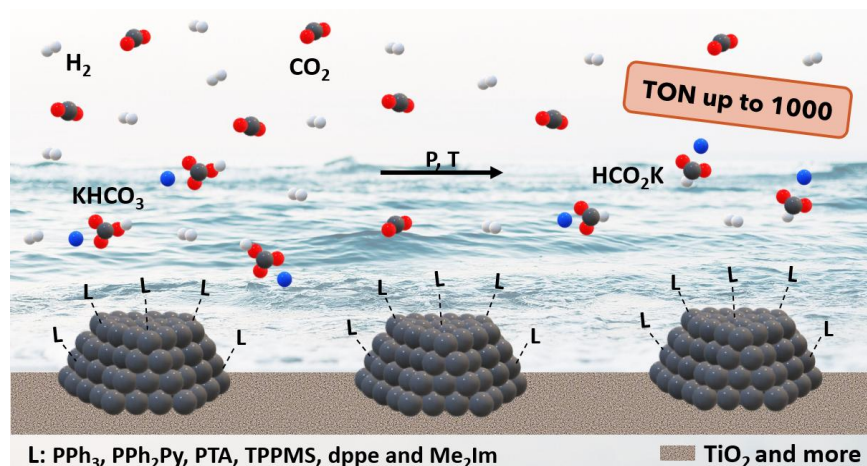


## Modifications of supported $\text{PPh}_3$ -capped palladium nanocatalysts for the hydrogenation of $\text{CO}_2$ into formate

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In this work, a series of heterogeneous palladium catalysts have been developed. The synthesis of the nanoparticles has been carried out by the organometallic method,[1] using ligands and supports of different nature for their stabilization. Indeed, the aim was to modify the surface of these nanoparticles both at a morphological/size and at an electronic level through their interaction with the stabilizer and the support. These catalysts were characterized by several techniques and have been evaluated for the hydrogenation of  $\text{CO}_2$  to formate catalysis with promising results. However, after catalysis, agglomeration of our nanoparticles has been observed. This problem has been solved by making modifications to the catalysts. Modifiers with different elements (P, Si) [2],[3] have been used to deposit them by condensation with the acid centers of  $\text{TiO}_2$ .



**Figure 1.** Catalytic performance of phosphine stabilized palladium nanoparticles for  $\text{CO}_2$  conversion to formate.

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## Catalysis and Green Chemistry for the valorisation of biomass: some examples

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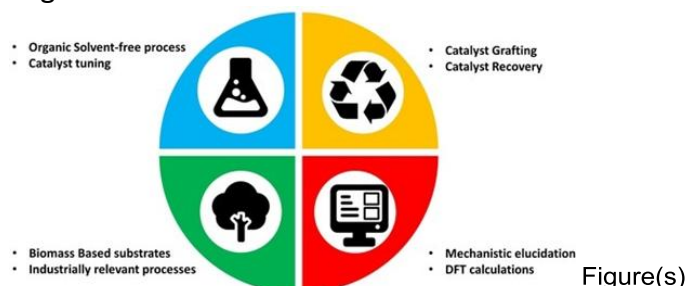
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The current critical situation in terms of available resources on our planet (fossil resources, metals, etc.) and associated consequences with their use (greenhouse gases, global warming, etc.)<sup>1</sup> encourage governments - particularly in Europe - to propose the implementation of sustainable processes to avoid unsustainable future.<sup>2</sup> For reasonable chemical production, implementing processes that are sober in energy/metals/fossil materials is one of the thematic explored by us and presented here.<sup>3</sup> Thus, the study of the catalytic activity of complexes of molybdenum<sup>4,5</sup> and/or vanadium<sup>6,7</sup> for the oxidation of model compounds - in mild conditions and without organic solvent - has made some mechanisms understanding<sup>4,7</sup> and catalysts improvements.<sup>8</sup> The work focused also on valorization of compounds from biomass and grafting of complexes on supports for recycling.<sup>9</sup>



Figure(s)

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## Pallado-catalyzed synthesis of biarylsulfoxides, towards on-surface reactivity studies.

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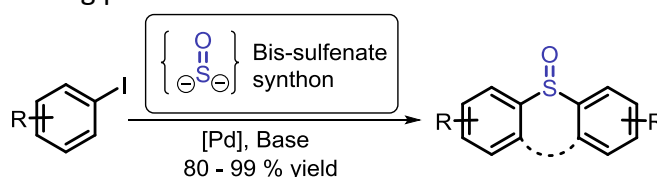
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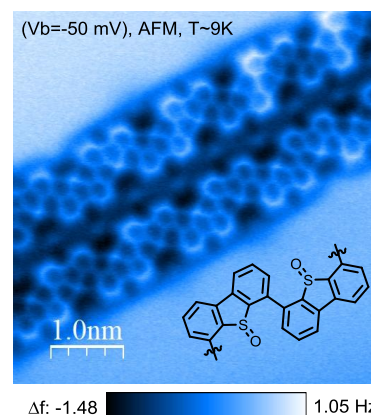
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The analysis of chemical reactions on surface using scanning probe microscopy with subatomic resolution is a blooming research field.<sup>[1]</sup> For such investigations, the molecules studied must be specifically designed, presenting a good adsorption on the surface of choice whilst keeping the desired reactivity. In this perspective, we recognized the biarylsulfoxides as good candidates for surface studies.

The synthesis of biarylsulfoxides typically involves the oxidation of the parent thioether, but in order to ensure the control of the oxidation state of the sulfur atom during their synthesis, we envisioned to use a double pallado-catalyzed coupling of aryl halides with a substrate behaving as a bis-sulfenate synthon. In this communication, we will report the synthesis and evaluation of two new bis-sulfenate precursors, and their use in pallado-catalyzed cross couplings for the synthesis of a large variety of biarylsulfoxides, including potential candidates for on-surface studies.



To this end, in collaboration with the CEMES-Toulouse and the IM2NP-Marseille we are studying the adsorption, reactivity and photochemistry of sulfoxides in solution, as well as on surface by means of Scanning Tunneling (STM) and non-contact Atomic Force (nc-AFM) Microscopies. For example, we could investigate an Ullmann-type reactivity from a brominated dibenzothiophene-S-oxide derivative on a Au(111) surface and show that long polymeric chains could be obtained.



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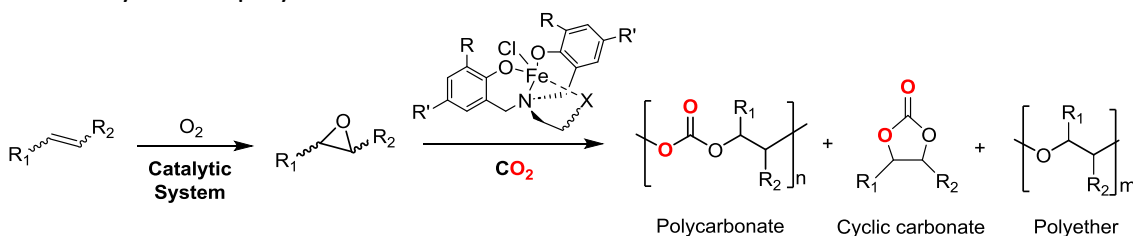


## Copolymerization of terpene-based epoxides and CO<sub>2</sub>: Toward a sustainable production of polycarbonates.

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Polycarbonates are biodegradable, transparent thermoplastic polymers with excellent mechanical properties that can be used for medical and automotive applications. The commercial polycarbonates are mainly produced by the condensation of bisphenol A and phosgene.<sup>[1]</sup> The main disadvantage of these conventional polycarbonates is the use of petroleum based monomers, with phosgene being a highly toxic volatile compound and bisphenol A raising concerns about negative health effects.<sup>[2]</sup> The catalytic copolymerization of CO<sub>2</sub> and epoxides can be a good alternative to produce polycarbonates.<sup>[3]</sup> On the other hand, depending on the epoxide and the catalytic system employed, polyethers chains or/and cyclic carbonates are often generated during the copolymerization reaction, thus suffering from selectivity issues (**Fig.1**). Moreover, in order to produce fully sustainable polycarbonates, the nature of the epoxide plays an important role. In this communication, we wish to report our results concerning the development of efficient heterogeneous catalytic systems for the aerobic epoxidation of terpenes. Cobalt catalysts have been prepared using cobalt acetylacetonate as a precursor and different supports, such as silica and carbon nanotube. We will then discuss the synthesis of new iron based homogeneous catalysts for the CO<sub>2</sub>/epoxide copolymerization and the promising results obtained with a highly selectivity for the polycarbonate.



**Fig. 1** Preparation of green polycarbonates by copolymerization of CO<sub>2</sub> with bio-based epoxides.

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# TraPCat<sup>3</sup>

3<sup>rd</sup> Trans Pyrenean Meeting in Catalysis

2-3 November 2023  
Toulouse, France



## Nickel-copper bimetallic nanoparticles – electrocatalysts for hydrogen evolution reaction

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The hydrogen evolution reaction (HER) is one of the most investigated reactions in electrochemistry, electrocatalysis or/and photoelectrocatalysis.<sup>[1]</sup> The electrode materials in the electrochemical devices containing nickel and copper are the most attractive in the series of transition metals<sup>[2]</sup>, due to their accessibility, electronic and chemical properties.

We have investigated NiCu NPs synthesized by an organometallic method<sup>[3]</sup> as cathode material for anion exchange membrane water electrolysis application. By optimizing the synthesis conditions we obtained alloy-type NiCu nanoparticles with a mean diameter of ca. 4.0–4.3 nm (fig. 1). The composition and structure of the synthesized materials were investigated by ICP, TEM, HRTEM, EDX, XPS and XRD. The nanomaterial was then deposited on a carbon support and evaluated in the electroproduction of hydrogen by a range of electrochemical methods. In alkaline environment, the NiCu electrocatalyst exhibits a good catalytic activity with an overpotential of 273 mV at the current density of  $-10 \text{ mA cm}^{-2}$ , and it shows good stability within 24 h.

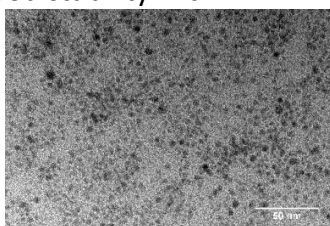


Figure 1. TEM image of synthesized NiCu-NPs

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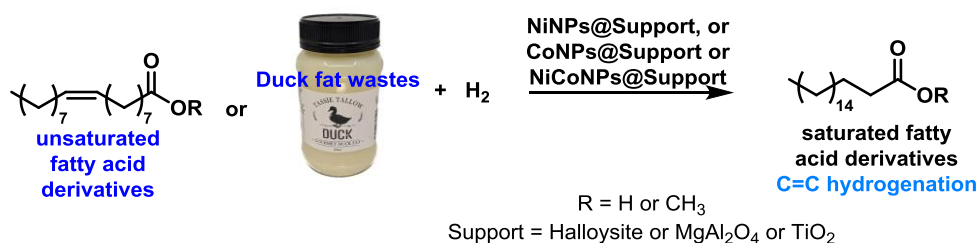


## Fatty waste upgrading via catalytic hydrogenation with Ni and Co-based nanocomposites.

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Saturated fatty acids, like palmitic and stearic acid are widely present in our lives, showing applications as emulsifiers, lubricants, surfactants, cosmetics and plastics [1]. Under catalytic hydrogenation conditions, the triglycerides from animal fats represent an attractive renewable feedstock towards saturated fatty acids [2]. The design of robust catalysts with high selectivity towards C=C hydrogenation capable to withstand the corrosive conditions of carboxylic acid substrates is necessary to achieve such catalytic transformations [3]. Despite the performance of Ni-Raney or Ni-Kieselguhr catalysts towards stearic acid production, the difficult manipulation of this type of catalysts in terms of pyrophoric hazard and toxicity due to formation of Ni-soap and subsequent leaching, are major concerns from both academic and industrial applications [4]. In this context, we focused on the development of Ni and Co-based nanocatalysts supported on robust inorganic materials like  $MgAl_2O_4$  and  $TiO_2$  [5]; as well as halloysite, a naturally occurring nanotubular clay with large surface areas [6]. These resulting nanocomposites have been efficiently applied in hydrogenations of fatty acids, fatty esters, as well as for the valorization of duck fat wastes, with remarkable catalytic performance in terms of selectivity and recyclability.



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## Role of metal-support interaction in the stability of single atoms catalysts under hydroformylation reaction conditions

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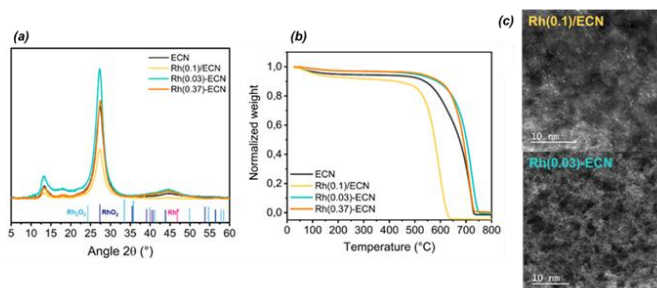


Fig 1. (a) XRD (b) TGA and (c) HRTEM of the synthesized catalysts.

Hydroformylation of olefins to produce aldehydes is one of the most relevant homogeneously catalysed processes at large scale.<sup>[1,2]</sup> Even if biphasic systems have been successfully implemented in industry for the HF of light olefins, the catalyst recovery and the metal leaching are still the major concerns of this approach.

Single atoms highly dispersed over a heterogeneous support are recently emerging as cost-effective alternative, since provide the activity of isolated atoms and facilitate the catalyst recycling.<sup>[1]</sup> Among the supports reported in the literature, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub> or ECN) has been postulated as a promising support for single atom catalysts (SACs), being able to host single atoms in its s-triazine rings.<sup>[3,4]</sup> The resistance to metal leaching of the heterogeneous catalyst will be closely link to the ability of the support in stabilize these single atoms. A way to improve the resistance to metal leaching in heterogeneous catalysts is by creating strong metal-support interactions. In view of that, the present work involves the design of Rh single atoms over ECN with different metal-support interaction and the evaluation of their stability in HF reaction. Accordingly, Rh addition over ECN was conducted or through wetness impregnation (Rh/ECN) or incorporation of Rh into the ECN structure (Rh-ECN). The synthesized catalysts were characterized by several techniques, such as XRD, TGA, XPS, N<sub>2</sub> physisorption, HRTEM, ICP and elemental analysis. At low Rh amount. All catalysts prepared were further submitted to HF reaction using styrene as substrate displaying an aldehyde b:l ratio of 1.4 and very low leaching.

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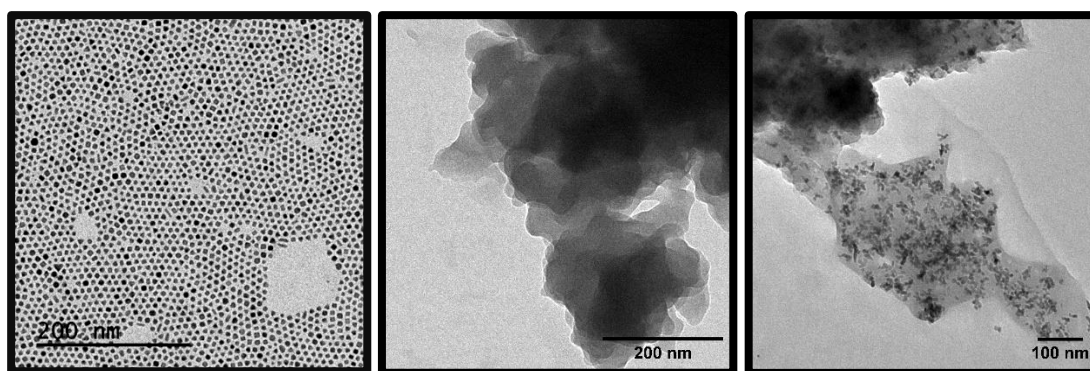
# Synthesis of Surface-Functionalized Ni nanostructures for Energy-Relevant Processes

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Hydrogen is prospected to play a key role in the decarbonization of future societies. Its large availability and high gravimetric energy density make hydrogen a promising element to be used as a vector for storage of renewable energy. Indeed, hydrogen can be produced from the electrolysis of water and consumed in a potentially renewable cycle, effectively storing the intermittent renewable energy in chemical bonds, and rendering it available according to demand. At the present technological state, the main bottleneck that hinders a faster hydrogen production by electrolysis is the slow kinetics of the Oxygen Evolution Reaction (OER), taking place on the anode of an electrochemical cell. Hydrogen production is not the only energy-relevant electrochemical cathodic process that can be exploited in the optic of carbon emissions: CO<sub>2</sub> can also be directly reduced (CO<sub>2</sub>RR) into e-fuels or added value chemicals. The Ni nanostructures presented in this work are produced via the organometallic approach [1], a technique which consists in the decomposition of an organometallic precursor of the metal, and allows great control on the properties of the final product as well as facilitating the functionalization and the characterization of the final material. Ni and Ni-functionalized materials have been showing good results as catalysts for OER [2,3] and can therefore act to speed up the anodic processes in a hydrogen-producing electrochemical cell. Moreover, some of the reported structures are expected to act as catalysts for CO<sub>2</sub>RR [4] anodic processes, possibly allowing the use of the same catalyst for both electrodes of an electrochemical cell.



**FIGURE 1: TEM IMAGE OF DIFFERENT FAMILIES OF Ni NANOSTRUCTURES OBTAINED VIA ORGANOMETALLIC METHOD.**

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## Behaviour of Ru/La/HAP catalysts in the CO<sub>2</sub> methanation reaction

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### ABSTRACT

The clean energy technologies, based on the use of green hydrogen as a fuel, are expected to play a key role for climate neutrality, since they can contribute to an effective reduction of the global CO<sub>2</sub> concentrations to pre-industrial levels [1]. The current global energy crisis further emphasises the importance of green hydrogen not only for the energy transition, to achieve net-zero carbon emissions, but also to reduce dependency on traditional resources markets strongly affected by geopolitical risks. However, numerous challenges seem to delay the application of green hydrogen as energy vector at a large-scale. For instance, it is known that various components of natural gas (NG) transmission and distribution networks are incompatible for hydrogen. Consequently, building gigantic hydrogen pipelines and storage sites require important investments and a long timeframe. On the bright side, this scenario warrants the development of strategies with the aim of taking advantage of the NG storage and transport facilities. In this sense, the re-utilization of the unavoidable emitted CO<sub>2</sub>, through its reaction with hydrogen for synthetic NG (SNG) production is an attractive strategy for implementing *Power-to-Gas* technology [1-2].

Therefore, the development of active and selective catalysts is essential for the methanation process. The efficient formulations must be able to achieve CO<sub>2</sub> conversions close to the thermodynamic equilibrium at relatively low temperatures (< 400 °C) and the selectivity towards CH<sub>4</sub> formation should be maximized as much as possible [1,2]. Ru-based catalysts are widely used for the CO<sub>2</sub> methanation reaction owing to their high specific activity at lower temperatures compared to Ni catalysts. Nevertheless, they suffer from a rapid deactivation due to a loss in their surface active sites, which is considered a major drawback. According to previous reports, the nature of the used support seems to play a crucial role for the distribution and the stability of supported Ru particles. In this sense, it would be essential the design of Ru catalysts exhibiting suitable metal-support interactions in order to provide highly dispersed and resistant active phases.

The present study deals with the investigation on the influence of lanthanum addition on the textural, structural, surface chemistry and catalytic behaviour in the CO<sub>2</sub> methanation reaction of a series of La-modified hydroxyapatite supported Ru samples. The catalysts were prepared by impregnation and characterized by using several techniques (N<sub>2</sub>-physisorption, H<sub>2</sub>-chemisorption, XRD, HAADF, H<sub>2</sub>-TPR, CO<sub>2</sub>-TPD, TPSR and XPS) and evaluated in the CO<sub>2</sub> methanation reaction in a fixed bed reactor at WHSV = 30,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup> in an extended range of temperature.

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### Acknowledgements

The authors are indebted to Spanish Science and Innovation Ministry (CNS2022-135152 and PID2019-105960RB-C21) and Project IT1509-2022 by the Basque Government for the financial support.



## Intramolecular Reactions of Diazo Compounds Catalysed by Redox-Active Ferrocene-Containing Dirhodium(II) Complexes: Chemoselectivity Issues

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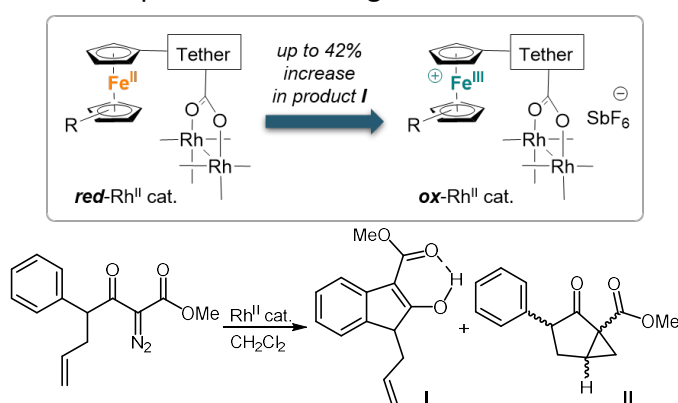
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Redox-active ligands have been used for almost 30 years to alter a catalyst activity toward a given product (redox-switchable or redox-responsive catalysis).<sup>[1]</sup> Many examples rely on ferrocene, which can be easily functionalized and has a very well-known redox behaviour. Some dirhodium(II) complexes bearing ferrocenyl ligands have been reported since 1982, but the redox-active character of ferrocene has been exploited only very recently in this chemistry by our team.<sup>[2],[3]</sup>

We recently demonstrated that the chemoselectivity of the dirhodium(II)-catalysed intramolecular insertion of a carbene into C–H bonds could be tuned by the oxidation state of the ferrocenyl unit in the ferrocenecarboxylate ligands. In this presentation we will describe these findings, as well as the impact of the ferrocenium counter-anion on the chemoselectivity. Several acceptor-acceptor diazo substrates have been studied, with a selectivity switch of up to 42% according to the oxidation state of ferrocene.



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## An insight on recent advancements in ammonia synthesis catalysis

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### Abstract

The invention of the catalyzed industrial process of ammonia synthesis, called Haber-Bosch after the names of the lead researchers, can be considered as one of the most impactful and important of the past century (Appl, 2021). Its most notable effects are the substantial increase of food availability, which greatly accounted for the explosion in human population growth (Thomas & Thomas, 2015). Nonetheless, this molecule also plays vital roles in a wide range of industries, which may employ it as basic building block on the synthesis of complex molecules. Thus, its demand is constant and ever-growing as uses are found.

With growing political interest and tension in the protection and preservation of Earth's ecosystems, many discussions topics center on the use of hydrogen. Hydrogen is regarded as the fuel of the future (International Energy Agency, 2021) due to its high energetic potential, the fact that it is virtually available everywhere on the universe and that its combustion, in theory, should not produce pollutants. However, inappropriate handling of hydrogen may lead to risks to human health and irreversible environmental degradation (Bowker, 1998; Ross, 2012). Careless manipulation of highly pressurized storage tanks may end in explosions and dangerous gas leakages. Furthermore, alteration of the hydrogen proportion on the atmosphere may contribute to a quick destruction of the ozone layer (Ball, 2003). The solution: ammonia.

Ammonia presents certain advantages over hydrogen. It can be condensed at temperatures more easily attainable at ambient pressure, avoiding the danger of dealing with pressurized gas containers. Therefore, ammonia can be more securely used for the storage and/or transportation of hydrogen. Moreover, in its liquid form, ammonia presents an energetic density which is higher than pressurized hydrogen gas, easily enabling it as an alternative fuel. This creates new interest on ammonia synthesis (International Energy Agency, 2021), since the well-known Haber-Bosch industrial process works at high temperatures and pressures, suggesting an optimization in the design of new catalysts. So, this work mainly reviews the last findings on the catalyst development for ammonia synthesis.

**Acknowledgments:** This PhD project is co-funded by RHyO, IMT Mines Albi, and Khimod, and is labelled by BioEco.

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