



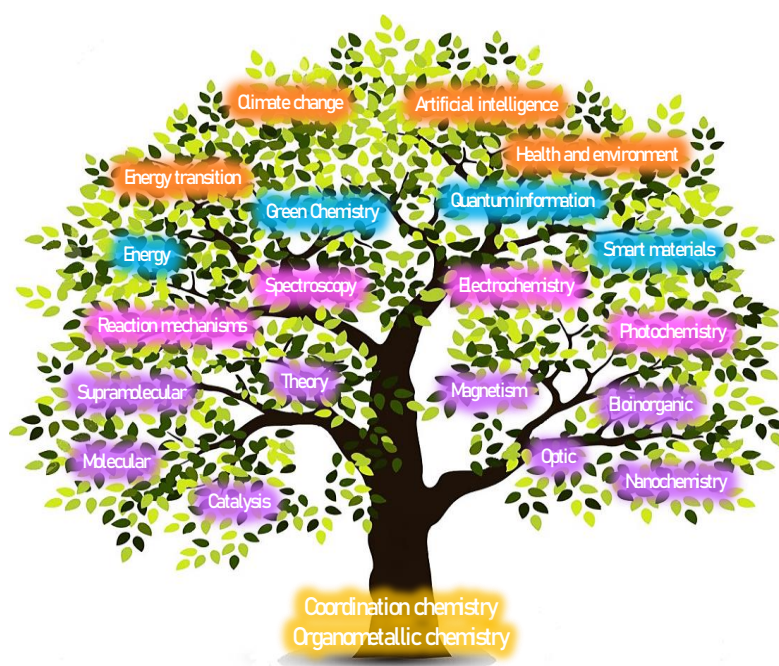
19-24 Mai 2024, Ax-les-Thermes

GECOM-CONCOORD 2024

Groupe d'étude de chimie organométallique
et de la concertation en chimie de coordination

19-24 May 2024

Ax-les-Thermes
Occitanie







GECOM-CONCOORD 2024 Ax-les-Thermes

We are pleased to welcome you all in Ax-les-Thermes, in the beautiful region of Occitanie, for this 2024 edition of the annual meeting of the organometallic chemistry study group (GECOM) and the coordination chemistry concertation (CONCOORD). This annual event brings together the inorganic scientific community interested in coordination and organometallic chemistry, unified around four main fields: i) chemistry and reactivity of coordination complexes, ii) catalysis, iii) coordination and materials chemistry and iv) bio-inorganic chemistry.

We would like to thank all the participants for their interest in this event that gathers 80 researchers and students with 7 invited lectures, 46 oral communications, and 11 posters. We wish to make this conference more than a time for the presentation of scientific results, but also a special moment for scientific (and non-scientific) exchange in a convivial atmosphere.

We wish you a fruitful GECOM-CONCOORD 2024!

The organizing committee.

Nous sommes ravis de vous accueillir à Ax-les-Thermes, dans la magnifique région d'Occitanie, pour cette édition 2024 de la réunion annuelle du Groupe d'étude de chimie organométallique (GECOM) et de la concertation en chimie de coordination (CONCOORD). Cet événement annuel rassemble la communauté scientifique de la chimie de coordination et organométallique, réunie autour de quatre domaines principaux : i) chimie et réactivité des complexes de coordination, ii) catalyse, iii) chimie de coordination et matériaux et iv) chimie bio-inorganique.

Nous tenons à remercier tous les participants pour l'intérêt qu'ils portent à cet événement qui réunit 80 chercheurs et étudiants avec 7 conférences invitées, 46 présentations orales et 11 posters. Nous souhaitons faire de cette conférence plus qu'un simple moment de présentation de résultats scientifiques, mais aussi un moment privilégié d'échanges scientifiques (et non scientifiques) dans une atmosphère conviviale.

Nous vous souhaitons un agréable et bénéfique GECOM-CONCOORD 2024 !

Le comité d'organisation.

Sébastien Bontemps, LCC (chairman)
Vincent César, LCC (chairman)
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Simon Tricard, LPCNO
Dmitry Valyaev, LCC





GECOM-CONCOORD 2024

Ax-les-Thermes

PROGRAM

Monday, 20 May

| | | |
|-------------|------|---|
| 9h00-9h50 | IL1 | Gustav Berggren [FeFe] hydrogenase - a diverse enzyme family with high photo-biotechnological potential |
| 9h50-10h10 | OC1 | Lili Sun A non-macrocyclic thiolate-based cobalt catalyst for selective O ₂ reduction into H ₂ O |
| 10h10-10h30 | OC2 | Léon Escomel Dinitrogen-Bridged Group 6/Al(C ₆ F ₅) ₃ Heterobimetallic Complexes: Design, Characterizations, and Reactivity Studies |
| 10h30-11h00 | | Coffee Break |
| 11h00-11h20 | OC3 | Ewen Bodio WazaGaY: combining Aza-BODIPY and Gallium for the design of efficient NIR-emitting OI/PET innovative bimodal probe |
| 11h20-11h40 | OC4 | Julie Pineau A Competitive Chelating Agent for the Development of Radiopharmaceuticals in Personalized Nuclear Medicine |
| 11h40-12h00 | OC5 | Runqian Yang Chiral tridentate ferrocenyl ligands for asymmetric catalysis |
| 12h00-12h20 | OC6 | Lucie Pedussaut Shedding light on the cyclononatetraenyl ligand and its lanthanides complexes |
| 12h20-14h00 | | Lunch |
| 14h00-14h50 | IL2 | Florence Volatron Mastering the shaping of molecules of interest |
| 14h50-15h10 | OC7 | Vladislava Timofeeva Strong and Tunable Zinc(II) Cationic Lewis Acids: Synthesis and Use in Selective Catalysis |
| 15h10-15h30 | OC8 | Roa Alchamandi Polyoxometalate/polymer composites for the photodegradation of organic dyes |
| 15h30-15h50 | OC9 | Mariia Hruz Room temperature reduction of alkenes with NHC-thioether manganese-complex |
| 15h50-16h20 | | Coffee Break |
| 16h20-16h40 | OC10 | Vladyslav Mudrak Antenna Approach and Acetylacetonate Implementation: On the way to Bioapplication of Ruthenium Nitrosyl Complexes |
| 16h40-17h00 | OC11 | Jean-Claude Berthet Depolymerization of oxygenated plastics with silane reagents |
| 17h00-17h20 | OC12 | Arno Estival Molybdenum Pentahydride Complexes as Catalysts for Hydrogenation of Alkenes and Ketones |
| 17h20-17h40 | OC13 | Fernando Gómez Zamorano Elaboration of high and low-valent Al complexes with a novel N-NON asymmetric ligand for activating small molecules |
| 17h40-18h00 | OC14 | Stanislav Petrovskii Beyond Standard Click Chemistry for Post-Modification of Hexavanadates: Expanding the Diversity of Available Hybrid Structures |
| 20h00 | | Dinner |



GECOM-CONCOORD 2024

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Tuesday, 21 May

| | | |
|-------------|-----------------|--|
| 9h00-9h50 | IL3 | Aude Demessence Advances in d ¹⁰ Coinage Metal Organic Chalcogenolate Coordination Polymers for Optoelectronic Technologies |
| 9h50-10h10 | OC15 | Tatiana Straistari Nickel-copper bimetallic nanoparticles – electrocatalysts for hydrogen evolution reaction |
| 10h10-10h30 | OC16 | Mohammad Ameskaj Unravelling the mechanism of the double alkoxy-carbonylation of butadiene: what is the role of the base? |
| 10h30-11h00 | Coffee Break | |
| 11h00-11h20 | OC17 | Chloé Salis Synthesis of <i>N</i> -Heterocyclic gold(I) complexes with fluorinated ligands for antitumoral activity |
| 11h20-11h40 | OC18 | Maria Dronova Thermally-induced Electron Transfer in CoFe Prussian Blue Analogues using Synchrotron Far-Infrared Spectroscopy |
| 11h40-12h00 | OC19 | Miguel Baya Controlled Degradation of a Pd-CF ₃ Unit as a Methodology for the Synthesis of Palladium Carbene Complexes |
| 12h00-12h20 | Sponsors | |
| 12h20-14h00 | Lunch | |
| 14h00-14h50 | IL4 | Jesús Campos Tuning Synergies by Combining Transition and Main Group Metals |
| 14h50-15h10 | OC20 | Andrea Orellana Ben Amor Lewis acid-mediated radical stabilization in adducts of <i>N</i> -Heterocyclic Carbenes (NHC) with N ₂ O |
| 15h10-15h30 | OC21 | Adrien Normand Poly(vinyl chloride) Dechlorination Catalyzed by Zirconium |
| 15h30-15h50 | OC22 | Alexandre Rico Soft Salts Based on Platinum(II) Complexes with Tunable Optical Properties and Vapochromic Switches |
| 15h50-16h20 | Coffee Break | |
| 16h20-16h40 | OC23 | Orfeas-Evangelos Plastiras Metal-Organic Frameworks: Evaluating cytotoxicity assays and their antiviral activity against coronaviruses |
| 16h40-17h00 | OC24 | Romane Pointis Hydrogenation of esters promoted by NHC-phosphine manganese catalyst |
| 17h00-17h20 | OC25 | Jonathan De Tovar Insights into non-covalent interactions in dicopper(II,II) complexes bearing a naphthyridine scaffold: an anion-dictated electrochemistry |
| 17h20-17h40 | OC26 | Joaquín García-Álvarez Polar s-Block Organometallic Chemistry in sustainable protic solvents (Deep Eutectic Solvents and water) under bench-type reaction conditions |
| 17h40-18h00 | OC27 | Ireneusz Tomczyk Advancing Sustainable Oxygenation and Halogenation via Electrochemical O ₂ Activation with Bioinspired Metal Complexes |
| 18h00-20h00 | Poster Session | |
| 20h00 | Dinner | |



GECOM-CONCOORD 2024

Ax-les-Thermes

Wednesday, 22 May

| | | |
|-------------|------|---|
| 9h00-9h50 | IL5 | Rafael Gramage-Doria Homogeneous Metal Catalysis: from Sustainable Transformations to Supramolecular Approaches |
| 9h50-10h10 | OC28 | Aurélien Béthegnies Nickel catalyzed three-component coupling reactions: A straightforward and atom-economical pathway to homoallylic derivatives |
| 10h10-10h30 | OC29 | Livia Getzner A Novel Family of Multifunctional MOFs Coupling Electron Transfer, Spin Crossover and Redox Activity |
| 10h30-11h00 | | Coffee Break |
| 11h00-11h20 | OC30 | Coralie Duchemin Carboxylate Ligand Role in Cerium Photocatalysis applied to C-centered Radical Functionalization |
| 11h20-11h40 | OC31 | Jean-Michel Grévy Selective cytotoxicity of Ru(II) complexes featuring heterotridentate SNE iminophosphorane ligands (E = S, Se) |
| 11h40-12h00 | OC32 | Luca Demonti Ytterbium-stabilized alkyl palladium(IV) complexes: synthesis and reactivity studies |
| 12h00-12h20 | OC33 | Eder Tomás-Mendivil Merging <i>N</i> -heterocyclic carbene organocatalysis and nickel radical catalysis through a SET event |
| 12h20-12h40 | | Sponsors |
| 12h40-14h00 | | Lunch |
| 14h00-20h00 | | |

Free Afternoon

| | | |
|-------|--|--------|
| 20h00 | | Dinner |
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GECOM-CONCOORD 2024

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Thursday, 23 May

| | | |
|-------------|-------------------------|---|
| 9h00-9h50 | IL6 | Marie Sircoglou Metal-ligand cooperativity and Second-sphere effects in Catalysis |
| 9h50-10h10 | OC34 | Oscar Charpentier Synthesis and study of redox-active bioinspired molecular units for electron transfer and energy storage |
| 10h10-10h30 | OC35 | Gaëtan Quintil Novel iron-based catalysts for photoinduced reversible hydrogen transfer reactions |
| 10h30-11h00 | Coffee Break | |
| 11h00-11h20 | OC36 | Alexandra Loubières Zr(IV) based chelates for innovation in diagnostic techniques |
| 11h20-11h40 | OC37 | Lucie Routaboul Post-synthetic modification mechanism for 1-D spin crossover coordination polymers |
| 11h40-12h00 | OC38 | Faycel Djebbar Exploiting the power of non-innocent iron complexes for C(sp ²)-C(sp ²) bond formation in mild conditions |
| 12h00-12h20 | OC39 | Yongjian Lai From PSM reaction on iron-triazole spin-crossover complexes to their use in catalysis |
| 12h20-14h10 | Lunch | |
| 14h10-14h30 | OC40 | Ulises Carrillo Manipulating the photoinduced electron transfer in iron complexes by chemical design |
| 14h30-14h50 | OC41 | Matteo Mauro Binuclear Copper(I) Complexes for Near-Infrared Light-Emitting Electrochemical Cells |
| 14h50-15h10 | OC42 | Oussama Fayafrou Novel Photoluminescent Ruthenium(II) Bipyridyl Complexes Containing Phosphonium Ylide Ligands |
| 15h10-15h30 | OC43 | Yohan Champouret Synthesis and Characterization of Borohydride Rare-Earth Complexes Supported by 2-PyridinemethanAmido Ligands and their Application towards ROP of Cyclic Esters |
| 15h30-15h50 | OC44 | Gabrielle Mpacko Priso Clustering six electrons within "Dawson-like" Polyoxometalate |
| 15h50-16h20 | Coffee Break | |
| 16h20-16h40 | OC45 | Victoria Mechrouk Sulfoxide functionalized N-heterocyclic carbene complexes of Ru(II): synthesis, coordination mode and catalytic activity |
| 16h40-17h00 | OC46 | Till Neumann Heterobimetallic complexes associating tantalum and 3d transition metals as potential candidates for cooperative bond activation |
| 17h00-17h50 | IL7 | Raluca Malacea-Kabbara Phenoxy-amidines and FAlen ligands, coordination chemistry and catalysis |
| 17h50 | Closing Ceremony | |
| 20h00 | Gala Dinner | |



GECOM-CONCOORD 2024
Ax-les-Thermes

INVITED LECTURES

[FeFe] hydrogenase - a diverse enzyme family with high photobiotechnological potential

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[FeFe] hydrogenases are central to the H₂ metabolism in microorganisms from all domains of life. These enzymes utilize a biologically unique organometallic cofactor, the “H-cluster” (Figure 1, inset), to catalyse the interconversion of protons and molecular H₂. Due to their remarkable catalytic properties these enzymes are explored for a wide-range of biotechnological processes related to renewable energy and serve as blue-prints for the design of molecular catalysts.

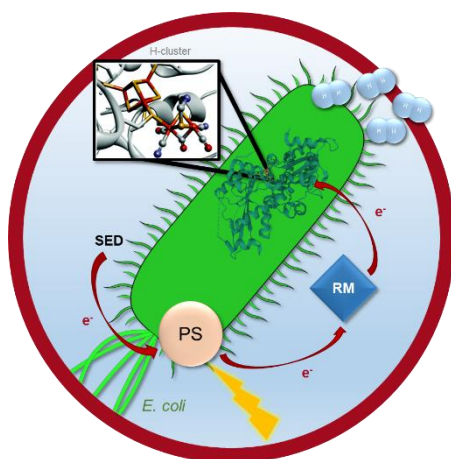


Figure 1. Schematic representation of the bio-hybrid photocatalytic hydrogen evolution system consisting of *E. coli* bacteria, which heterologously express a [FeFe] hydrogenase enzyme, combined with a sacrificial electron donor (SED), an artificial photosensitizer (PS), and a redox mediator (RM).

Here I will present our efforts devoted to mapping out the diversity of this enzyme family,¹⁻⁴ and through rational enzyme engineering using their structural diversity to identify the protein features that enable their outstanding catalytic efficiencies.⁵ Moreover, I will discuss how we employ hydrogenases as a tool for exploring semi-artificial photosynthesis. Through screening efforts, we have identified key factors enabling efficient and sustained hydrogen evolution from biohybrid systems combining *E. coli* bacteria with organic and metal-based photosensitizers (Figure 1).⁶⁻⁸ The photochemistry and associated electron transfer processes of selected combinations of mediators and electron donors are elucidated using transient absorption spectroscopy.

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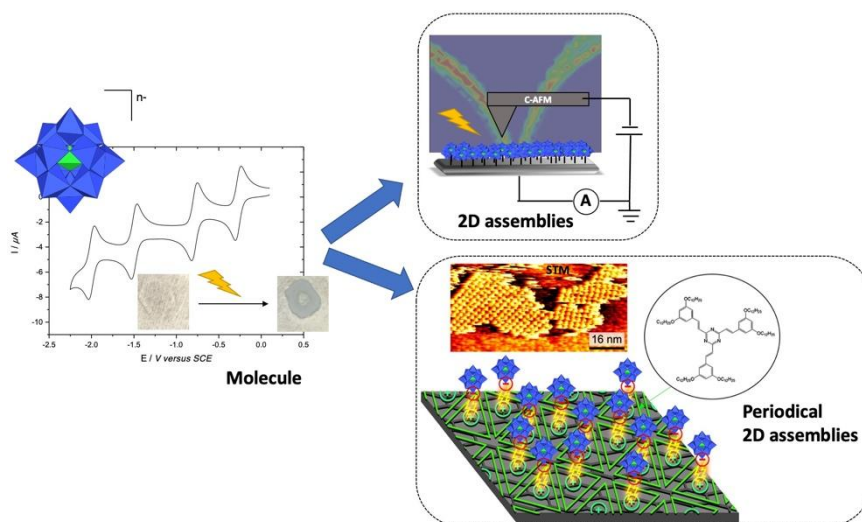
Mastering the shaping of molecules of interest

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These last several decades, the number of synthesized molecules with proper physical properties for applications in molecular electronics, spintronics, quantum computing, sensing... is countless. They can display similar properties as classical materials (conductivity, magnetism, switching, ...), and they bring several added values, as for example their versatility for tailor-made properties, their self-assembly leading to new materials by the bottom-up approach, and their small size to reach the ultimate downscaling. However, to be used in tangible devices, the control of their handling and assembly is crucial to ensure reproducibility and efficiency of the final system.^[1] The shaping step of the molecule of interest is a field in itself: it implies expertise from chemical synthesis to physical chemistry to process the molecules at the material surface in a controlled way and to check their properties in their new environment. In this presentation, I will explain the different steps that lead from the molecule in solution toward the molecule-modified material. I will focus on polyoxometalates, molecular oxide of nanometric size, made of early transition metals in their highest oxidation state that display remarkable physical properties (especially switchable redox and photoredox properties).^[2] I will explain the chemical approach for the elaboration of their 2D assemblies on surfaces with maximum control of their organization in the vertical axis (thickness) but also in the horizontal plane (periodical organization), and how to measure their physical properties once deposited.^[3]



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Advances in d^{10} Coinage Metal Organic Chalcogenolate Coordination Polymers for Optoelectronic Technologies

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Hybrid materials with chalcogenolate ligands ($ER = SR, SeR, TeR$) and d^{10} coinage metals ($M(I) = Cu, Ag$ and Au) are known for a long time in the domains of biology and pharmaceuticals. Indeed, copper-thiolates are present in most of the living organisms as metalloproteins, silver-thiolates are recognized for their anti-bacterial activity and some gold-thiolates, as the Myochrysine, have been used as antiarthritic drugs. Today, the d^{10} coinage Metal Organic Chalcogenolates (MOCs) are gaining a growing relevance in materials science for their semiconductivity and photoluminescence properties.¹ The photoemission of these compounds is attributed to the presence of d^{10} coinage metals and their ability to display metallophilic interactions.

In this presentation, we will show the possibility to tune the dimensionality of the MOC structure as anisotropic 1D or 2D structures and as 3D networks and the resulting photophysical and electronic properties (Fig. 1).² Thus, some MOCs exhibit high quantum yield ($\sim 70\%$) in the solid state, some have intrinsic triple emission associated with luminescence thermochromism allowing optical temperature sensing and some behave as semi-conducting materials with great potentials for thermoelectricity. In addition, MOCs can be shaped as fibers and glasses, and can exhibit phase change behaviors allowing applications in sustainable memory devices.³

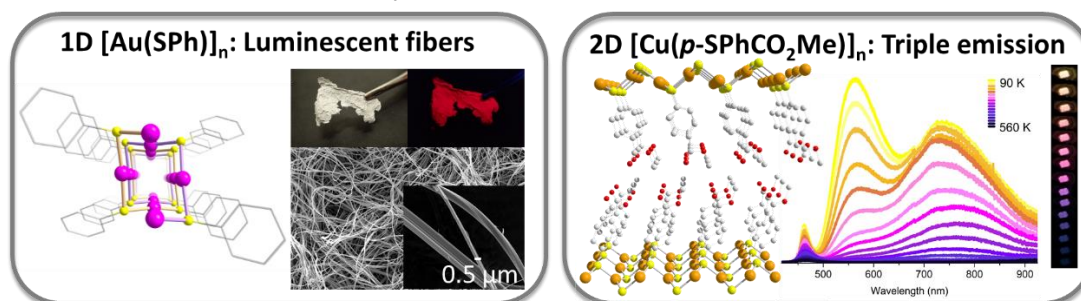


Figure 1 Examples of two luminescent and anisotropic MOCs.

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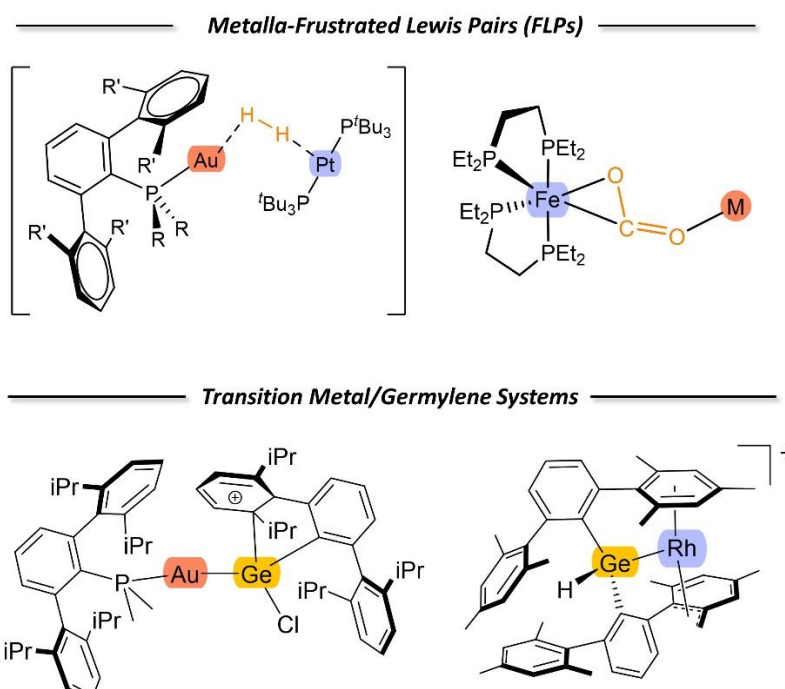
Tuning Synergies by Combining Transition and Main Group Metals

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The organometallic chemistry of transition metals and main group metals has often evolved separately, though many interests and goals are clearly shared. In fact, one of the driving forces in our group has been to explore the interphase between these seemingly independent fields, typically through two approaches. In the first, we have tried to borrow concepts from one area onto the other, with our most representative contributions associated to the concept of metalla-Frustrated Lewis Pairs (FLPs).^{[1],[2]} In those, the idea of frustration originated in the realm of main group chemistry is transferred to transition metals, with important implications in cooperative bond activation and catalysis. In a second complementary approach, we have designed bimetallic chemistry constructed around a late-transition metal (i.e. Au, Rh, Ir, Ni, Pd, Pt) and a low-valent heavier main group metal, mainly germanium(II).^[3] The biphilic character of the low-valent germanium site enables cooperation with the transition metal, a feature that we have exploited for the activation of rather inert bonds (e.g. N–H bond in ammonia) and to subsequently construct catalytic cycles. Some of our results pertaining cooperative reactivity and catalysis within these two approaches will be discussed.



References

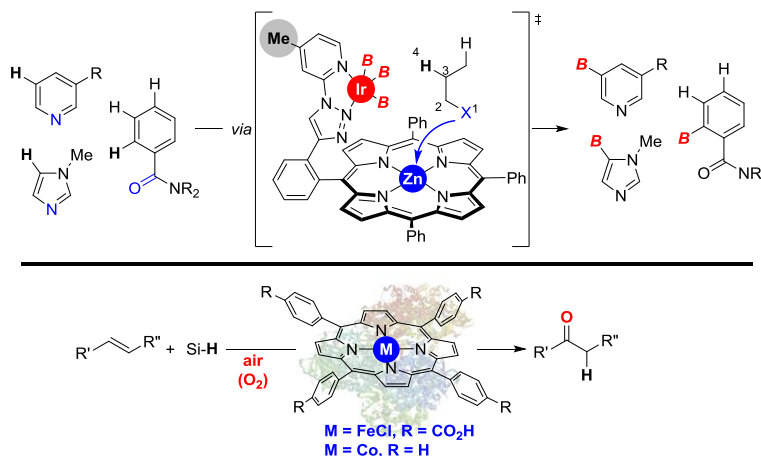
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Homogeneous Metal Catalysis: from Sustainable Transformations to Supramolecular Approaches

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The generation of more efficient, atom- and step-economy transformations is of primary importance to meet the societal challenges associated the 21st century. In this context, transition metal catalysis is an enabling technology and, in our laboratories, we have developed a number of sustainable approaches dealing with C-H bond functionalizations, one-pot multi-step sequences, direct reductive aminations, amongst others.^[1] They aim at minimizing chemical wastes while controlling metal's reactivity. On another hand, we have developed metal-catalysed transformations which are controlled by remote, kinetically labile interactions taking place in the secondary coordination sphere of the metal catalyst.^[2] In particular, we have exploited the reversible coordination bonds between nitrogen- and oxygen-containing substrates and metalloporphyrins as a tool for the design of supramolecular catalysts. These supramolecular catalysts feature unique atom-precise selectivities that enables to tackle challenging chemical transformations besides displaying enzyme-like behaviours such as substrate selectivity and Michaelis-Menten kinetics.^[3] Lastly, the oxidase behaviour of iron- and cobalt-porphyrin catalysts for the industrially-relevant Wacker-type oxidation of olefins into ketones will be shown,^[4] which is important for replacing the scarce, expensive and toxic palladium catalysts.^[5] The oxidation reactions, which involve a complex mechanistic scenario, occur at ambient pressure and temperature with high activity and Markovnikov-selectivity in the presence of an hydrosilane.^[4]



References

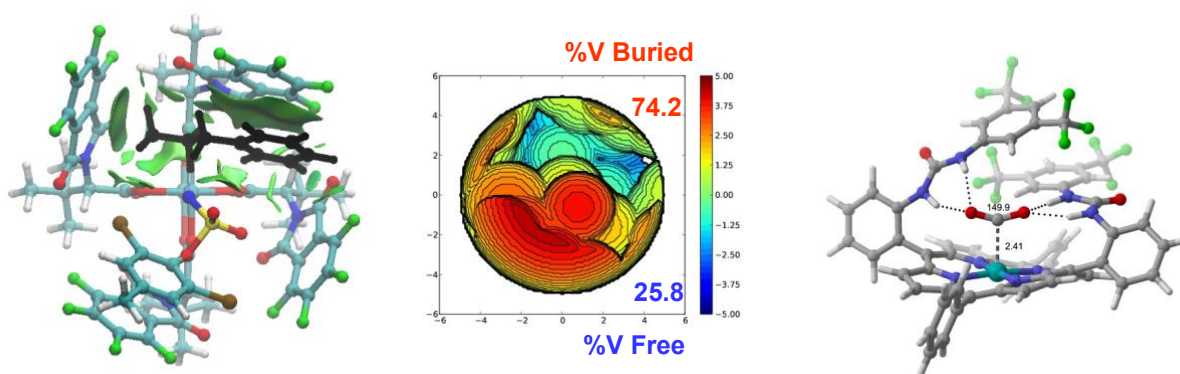
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Metal-ligand cooperativity and Second-sphere effects in Catalysis

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Organometallic catalysis has undergone a significant evolution, starting with the exploration of transition metals and progressing towards the modification of ligands. As the field progressed, attention gradually shifted from the modulation of electronic and steric effects to the design of the second coordination sphere. This strategy has for instance been used to match the reactivity of noble metals with a more abundant alternative or to address challenging transformation with an improved control on the selectivity. In this talk, I will explain how our computational studies have highlighted the decisive role of ligand architecture in several catalytic processes involving oxygen atom transfer reaction, CO₂ to CO reduction or selective C-N bond formation.



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Phenoxy-amidines and FAlen ligands, coordination chemistry and catalysis

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Since few years our team is interested in the coordination chemistry and catalytic activity of a new class of ligands called phenoxy-amidines (FA). These ligands could be considered as a variant of the well-known phenoxy-imine (FI) ligands whose general structure corresponds to a phenol fragment, bearing an imine moiety in *ortho* position (*figure 1*). Replacing the imine moiety with a N,N,N'-trisubstituted amidine allowed us to obtain new phenoxy-amidine ligands with different structures in function of the amidine position. We further described the synthesis of ethylene and a phenylene-bridged bis(salicylamidine) that we called FAlen ligands. The strong σ and π -donor character of the amidine functions was expected to provide additional stability to metal ions, resulting in robust complexes.

The coordination chemistry of these ligands was investigated. Alkane elimination from AlMe_3 and ZnEt_2 was employed to yield new heteroleptic or homoleptic Al and Zn complexes adopting monomeric or dimeric structures. Bidentate, tridentate or tetradentate ways of coordination of these ligands were also confirmed in the solid state by X-ray diffraction studies. DFT calculations were used to understand the fluxional properties and polyvalent denticity of FAlen ligands. Finally, these Al and Zn complexes revealed to be active catalysts for the ROP of *rac*-lactide. We were thus able to compare the influence of various substituents in terms of stability, coordination chemistry and catalytic activity.

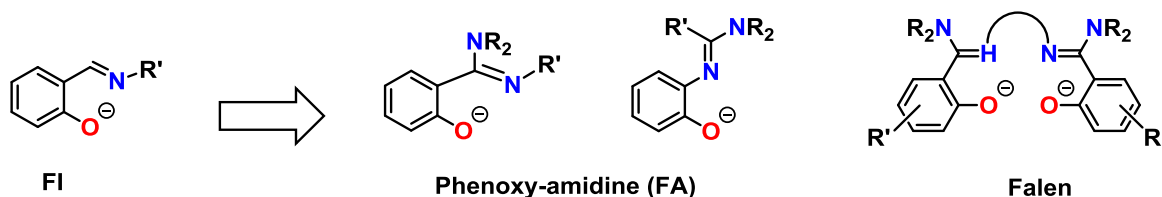


Figure 1 – from phenoxy-imine to phénoxyamidines and FAlen ligands

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ORAL COMMUNICATIONS

A non-macrocycle thiolate-based cobalt catalyst for selective O₂ reduction into H₂O

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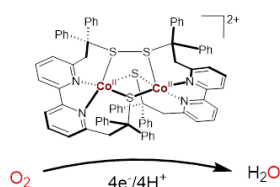
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Oxygen reduction reaction (ORR) is a vital electrochemical process in various fields.¹ To date, precious-metal Pt-based materials are state-of-the-art ORR catalysts, but their large-scale applications are unfortunately limited by their high price and scarcity. The development of non-noble metal-free catalytic systems is thus needed under the premise of ensuring catalytic activity.

In this work, a Co complex coordinated by a bithiolate N₂S₂-donor ligand (2,2'-(2,2'-bipyridine-6,6'-diyl)bis(1,1'-diphenylethanethiolate))² was employed as a homogeneous ORR catalyst. Cyclic voltammetry (CV) and rotating ring-disk electrode (RRDE) techniques were employed to evaluate its electrocatalytic activity towards oxygen reduction in acetonitrile solution. The results demonstrated that the cobalt complex exhibits a good selectivity toward H₂O with a 4H⁺/4e⁻ pathway (0.81 V < η < 1.10 V vs Fc⁺⁰, selectivity between 85 % and 95 %) under electrocatalytic conditions. Its catalytic activity was also assessed under chemical conditions using a one-electron reducing reagent. Remarkably, it displayed an identical catalytic selectivity when compared to electrocatalytic conditions, with 93% selectivity for H₂O and a turnover frequency (TOF) of 3,000 h⁻¹. The selectivity of this cobalt catalyst contrasted with that of previously reported Fe³ and Mn⁴ analogs under chemical ORR conditions, highlighting the influence of the nature of metal ions on the ORR selectivity.



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Dinitrogen-Bridged Group 6/ $\text{Al}(\text{C}_6\text{F}_5)_3$ Heterobimetallic Complexes: Design, Characterizations, and Reactivity Studies

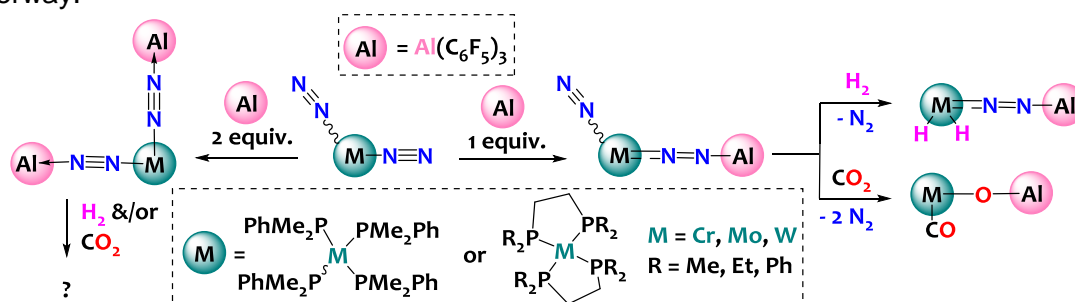
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The discovery of new processes for the transformation of dinitrogen under mild conditions is a holy grail for chemists. One way of achieving this is to develop new molecular design strategies that take inspiration of the Mo-nitrogenase enzymes, which efficiently catalyse the reduction of N_2 to NH_3 at ambient temperature and pressure.^[1] The central idea of this project is to reproduce in synthetic complexes key features of their active site (FeMo-cofactor). One approach to glimpse this chemistry is to combine N_2 complexes with Lewis acids (LAs) to mimic the H-bond donors present in the second coordination sphere of FeMo-co. These LAs interact with metal-bound N_2 resulting in the enhancement of metal backbonding (*i.e.* pulling electron density from the metal) and thus its polarisation and activation - *push-pull* mechanism. In this context, our laboratory reported the coordination of *tris*(pentafluorophenyl)borane (BCF) on Group 6 end-on dinitrogen complexes allowing its functionalisation with mild electrophiles ($\text{R}_3\text{Si-H}$, $\text{B}(\text{C}_6\text{F}_5)_2\text{-H}$) that parallels the Frustrated Lewis Pair (FLP) chemistry.^[2,3] Inspired by these preliminary works, we wanted to investigate how a stronger LA than BCF can induce differences in the resulting chemistry. Consistently, the Lewis Superacid aluminium analogue of BCF, *tris*(pentafluorophenyl)alane – $\text{Al}(\text{C}_6\text{F}_5)_3$ (AlCF)^[4] – is a suitable candidate. We present here a comprehensive study describing the design and characterizations of dinitrogen-bridged group 6/ $\text{Al}(\text{C}_6\text{F}_5)_3$ heterobimetallic complexes (Scheme 1). This new family of compounds features novel single and double aluminium dinitrogen adducts, which have been studied in depth by spectroscopy (NMR, IR), single-crystal X-Ray crystallography, and computational chemistry. The results of this study revealed significant chemical and structural divergences from $\text{B}(\text{C}_6\text{F}_5)_3$ adducts. Then, we tackled reactivity investigations of these adducts with small molecules such as H_2 and CO_2 . The first results of these studies revealed a high reactivity of the Al/M Pair that can promote bond scission of H_2 or reductive cleavage of CO_2 . Extension of this reactivity study is underway.



Scheme 1. Design & reactivity of dinitrogen-bridged group 6/ $\text{Al}(\text{C}_6\text{F}_5)_3$ complexes.

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WazaGaY: combining Aza-BODIPY and Gallium for the design of efficient NIR-emitting OI/PET innovative bimodal probe

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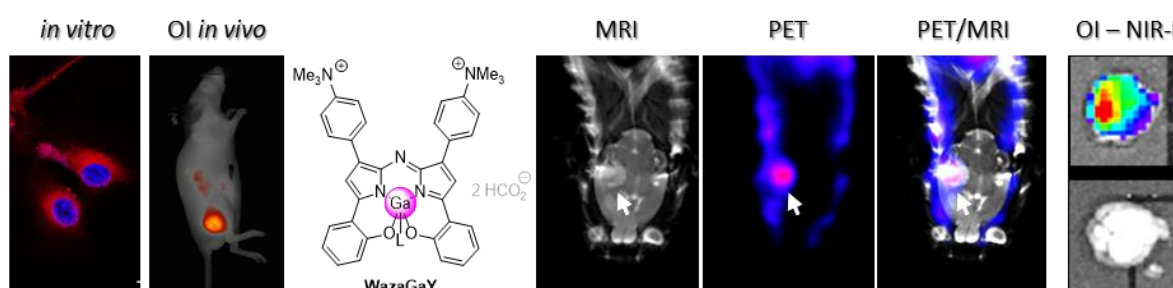
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Aza-boron-dipyrrromethenes (aza-BODIPYs) have gone from being a scientific curiosity to a class of fluorophores of major interest just like rhodamines or cyanines. These *N*-analogues of BODIPYs have built their reputation thanks to their ease of synthesis, their high stability, their good quantum yields, and because they absorb and emit light in the NIR-I (700-900 nm, wavelengths sought after for *in vivo* optical fluorescence imaging or even for surgical assistance).

Some aza-BODIPYs, that we have developed,¹ can even emit in the NIR-II (1000-1700 nm), which allows to further improve the resolution of the images. This area is much more difficult to access and many works have been undertaken to try to reach this area by modifying the substituents of the aza-BODIPYs, by rigidifying them, by extending their conjugated system, but very few groups have focused their attention on the boron atom of the aza-BODIPY core. Indeed, this fluorophore can be considered as an aza-dipyrrromethane ligand chelating a boron atom, which rigidifies this structure. We can wonder what would happen if this boron atom is replaced by a metal?



This presentation will describe the synthesis and the characterization of different aza-Metal-DIPYs complexes.² A focus will be done on the Ga-derivative, that have been water-solubilized and turned to a bimodal probe (NIR-fluorescence/PET). Especially, we will present a NIR-I/NIR-II imaging study of its biodistribution in subcutaneous tumor bearing mice (U87MG, IGROV1, and A375), its potential for fluorescence-guided surgery, its radiolabelling, and the bimodal PET/NIR study of [⁶⁸Ga]-azaGaDIPY in orthotopic brain tumor bearing mice (U87MG).

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A Competitive Chelating Agent for the Development of Radiopharmaceuticals in Personalized Nuclear Medicine

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One of the main challenges in oncology research is the development of targeted diagnostic and therapeutic agents suitable for all types of cancer. Nuclear medicine allows to meet this need through the use of radioelements. Copper-64 (β^+ , $E_{\max} = 653$ keV, $t_{1/2} = 12.7$ h) is attracting growing interest in the field of Positron Emission Tomography (PET) imaging. It forms a theranostic pair with copper-67 (β^- , $E_{\max} = 577$ keV, $t_{1/2} = 62$ h), which offers valuable applications in radiotherapy. Palladium-109 (β^- , $E_{\max} = 1120$ keV, $t_{1/2} = 13.7$ h) is another therapeutic radiometal of interest that can match with copper-64. Its shorter half-life and higher energy than copper-67 allows to target different types of tumors. In order to ensure specific vectorization, the radiometal must be combined with a biological vector through a chelating agent within a structure called a radiopharmaceutical.

Our research group has developed a chelating agent based on cyclam monopicolinate, known as TE1PA (**Figure 1**), capable of forming particularly stable and inert Cu(II) and Pd(II) complexes, avoiding their dissociation in biological environment.^[1, 2, 3] TE1PA has been involved in the construction of several copper-64 and then palladium-109 radiopharmaceuticals, thanks to our academic and industrial collaborations, in France and abroad, allowing us benchtop research up to the preclinical.^[4]

This presentation will focus on the different uses of TE1PA as a versatile and modular chelating agent providing access to efficient radiopharmaceuticals for therapy and diagnosis. Our innovation lies in the ability of TE1PA to be bioconjugated with a variety of vectors targeting different types of cancer, thus providing opportunities for personalized treatment (**Figure 1**).

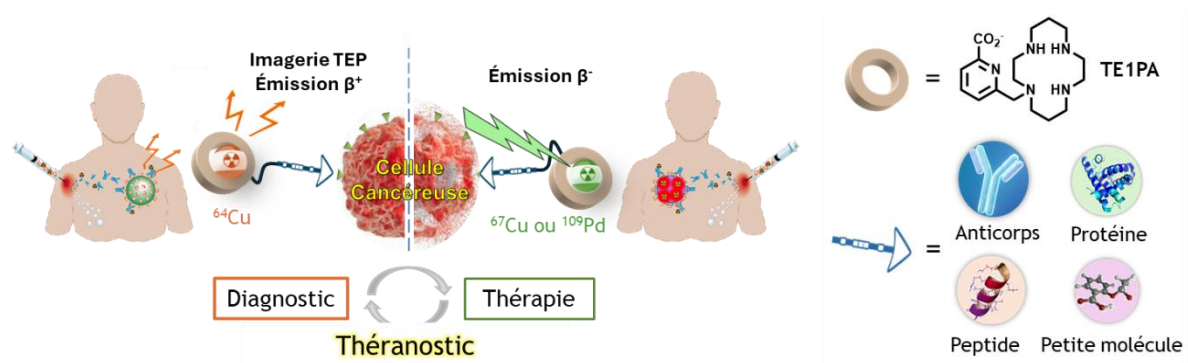


Figure 1: Theranostic approach using TE1PA-based radiopharmaceuticals

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Chiral tridentate ferrocenyl ligands for asymmetric catalysis

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The synthesis of enantiopure compounds is very important for pharmaceutical industry, materials science, agriculture, etc. The study of catalysts that provide high enantioselectivity and productivity is thus of great interest, of which catalysts based on transition metals are proven to be extremely versatile and competent systems in different types of reactions. Due to the need for greener processes and a more responsible use of natural resources, the first-row non-noble transition metals that are more abundant, less costly and less toxic have drawn more and more attention.

Our group develops ligands which participate in enantioselective catalysis with these non-noble transition metals, and we are particularly interested in the synthesis of chiral ferrocenes with a phosphine functional group. Several tridentate ligands have been synthesized, including PNN-type, PSP-type, PNP type, etc., depending on the element of the coordination sites. Recently, we have developed a new promising ferrocenyl PN(H)N ligand family which shows interesting performance in the asymmetric ketone hydrogenation and transfer hydrogenation catalyzed by manganese. Our results on the variations of the ligand structure and the substrate scope will be presented.

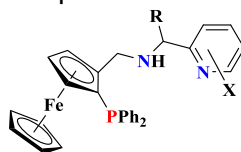


Figure 1 PN(H)N ligands used in this study.

We thank the “Ministère de l’Enseignement Supérieur et de la Recherche” (MESR) from France for a PhD grant to RY and the Indo-French Centre for the Promotion of Advanced Research (IFCPAR/CEFIPRA) for providing a Ph.D. grant to U.B and a Raman-Charpak fellowship to NG.

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Shedding light on the cyclononatetraenyl ligand and its lanthanides complexes

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The cyclononatetraenyl (Cnt) anion is a nine-membered ring aromatic molecule that was first synthesized in 1963 by Katz and Garrat.¹ This compound features two isomers: the *cis,cis,cis,cis*-Cnt and the *cis,cis,cis,trans*-Cnt as depicted in Figure 1. At that time, scientist observed spontaneous isomerization from the *trans* form to the *cis* one. Given the aromatic character of the fully *cis* form, it was considered as the stable form. Unfortunately, the high sensitivity of the Cnt⁻ ligand toward protonation and reorganization into 8,9-dihydroindene precluded further analysis.

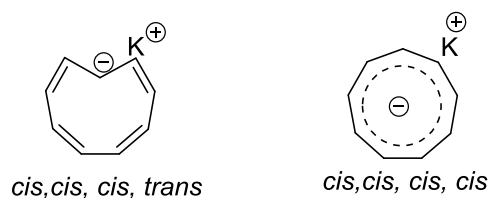


Figure 1: Cyclononatetraenyl anion isomers

Despite all these challenges, the Cnt ligand has regained interest in organometallic chemistry to form sandwich complexes.^{2,3} Our group have expanded this result to a series of lanthanides-containing complexes, where it was shown that a mixture of the *cis* and *trans* isomer complexes were observed.⁴ After careful evaluation of the different stimuli that could cause such species to be isolated, we came to the conclusion that, in certain cases, the isomerization is photo-induced. Thus, this work focuses on how to control the isomerization of the Cnt⁻ ligand and its complexes using light.

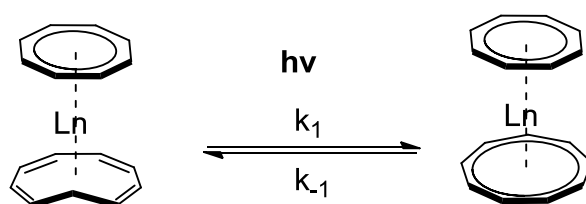


Figure 2: Photoinduced isomerization of Cnt in lanthanide complexes

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Strong and Tunable Zinc(II) Cationic Lewis Acids: Synthesis and Use in Selective Catalysis

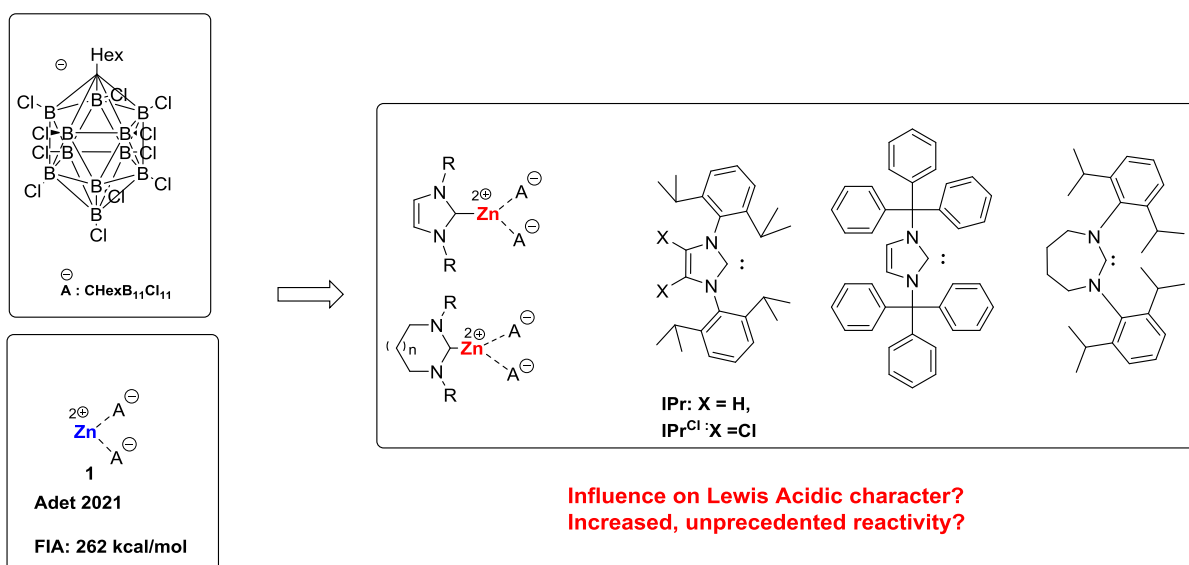
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Functional group activation through Lewis acid catalysis is frequently employed in a variety of organic transformations. The widespread use and versatility of such technique makes it of significant interest in the field of organic chemistry.^[1] In such reactions, the catalytic activity of the metal complex is highly associated with its Lewis acidity, which is directly influenced by its coordination number and the charge of the central atom.^[2] In the case of zinc, neutral diorganozinc species have been recognized as valuable reagents and catalysts in organic synthesis, particularly for modifying unsaturated substrates.^[2] Owing to the fact that Zn(II) is only moderately Lewis acidic (Pearson's HSAB classification), low-coordinated cationic Zn(II) complexes are particularly interesting for their enhanced reactivity.^[3]

In 2021 our group developed the first example of “naked” Zn²⁺ cation (**1**) solely stabilized by weakly coordinating anions. Fluoride Ion Affinity (FIA) calculations reveal an in-solution Lewis acidity of 262.1 kJ*mol⁻¹, higher than that of the landmark Lewis acid B(C₆F₅)₃ (FIA = 220.5 kJ*mol⁻¹). Thus, a question arises: can we further increase its Lewis acidity and, therefore, finely tune the selectivity of the catalytic reactions performed with such catalyst? Based on our preliminary results, NHC ligands, due to their exceptional σ-donating properties,^[4] allow the stabilization and isolation of a broad family of unprecedented NHC-Zn(II)²⁺ organocations with controlled and enhanced Lewis acidity compared to its naked analogue. Furthermore, reactivity studies of such promising Zn(II) platforms for the activation of various small molecules are under active investigation.



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Polyoxometalate/polymer composites for the photodegradation of organic dyes

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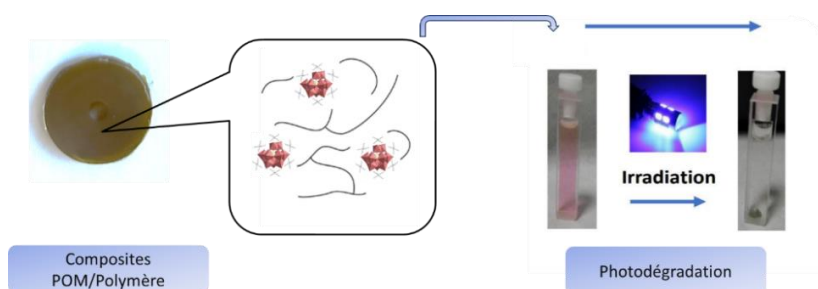
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The expansion of industries generates significant volumes of wastewater, posing severe risks to both human health and the environment ^[1]. Among these industries, the textile sector stands out for its substantial consumption of water, fuel, and chemicals. In particular, Textile effluents typically exhibit elevated levels of dyes and various persistent organic pollutants.

Polyoxometalate compounds constitute a huge family of inorganic compounds displaying various catalytic or photo-catalytic properties. For example, Dumur, Lalevée, and coworkers demonstrated recently that POMs, can be used for the photodegradation of drugs ^[2].

In this context, the photodegradation of dyes with different chemical structures, Rose Bengal, Erythrosine, and methyl blue, was investigated. In this poster, we study the impact of the presence in the aqueous solution of a newly developed POM/polymer ^[3] composite on the removal of these different pollutants from water under visible light irradiation.

Probing further, the POM/polymers were fully characterized by several techniques, including Scanning Electron Microscopy (SEM), Energy-dispersive X-ray analysis (EDX), UV-Visible, Thermogravimetric Analysis (TGA), and Fourier-Transform Infrared Spectroscopy (FTIR). The different methods used to characterize the POM-containing polymers revealed these polymers to exhibit high rigidity as well as exceptional stability for their reuse for many treatment cycles.



Schema 1: Proposed Process for the Photodegradation of Organic Pollutants in the Presence of POM@Polymère Composites.

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Room temperature reduction of alkenes with NHC-thioether manganese-complex.

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One of the primary research goals in modern chemistry is to develop sustainable and selective synthesis techniques employing eco-friendly and efficient catalytic conditions. The scarcity of precious metals, their high price and toxicity diminish their attractiveness for catalytic applications. First-row transition metals such as Fe and Mn, that are inexpensive and environmentally friendly are now of particular interest for catalytic reduction. The hydrogenation of alkenes and ketones is an important chemical transformation that has broad applications in organic synthesis,^[1] industrial processes,^[2] and pharmaceutical production.^[3,4] Only a few manganese catalysts have been reported to date for the hydrogenation of alkenes.^[4-7] After exploring the potential of NHC-phosphine manganese catalysts in hydrogenation,^[8,9] we were interested in developing phosphine-free analogues, and focused on the synthesis and study of bidentate thioether-NHC Mn(I) complexes.^[10] This new generation of manganese complexes was shown to be capable of reducing alkenes under very mild conditions, i.e. at room temperature using a low catalyst loading (Figure 1).

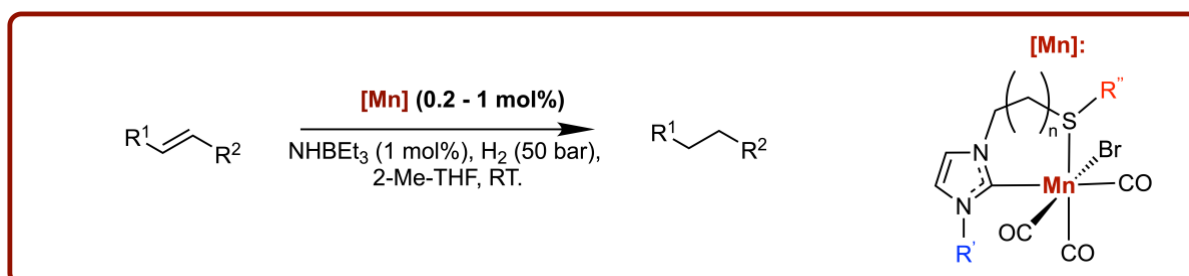


Figure 1: Hydrogenation of alkenes with S-NHC Mn complexes.

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Antenna Approach and Acetylacetonate Implementation: On the way to Bioapplication of Ruthenium Nitrosyl Complexes

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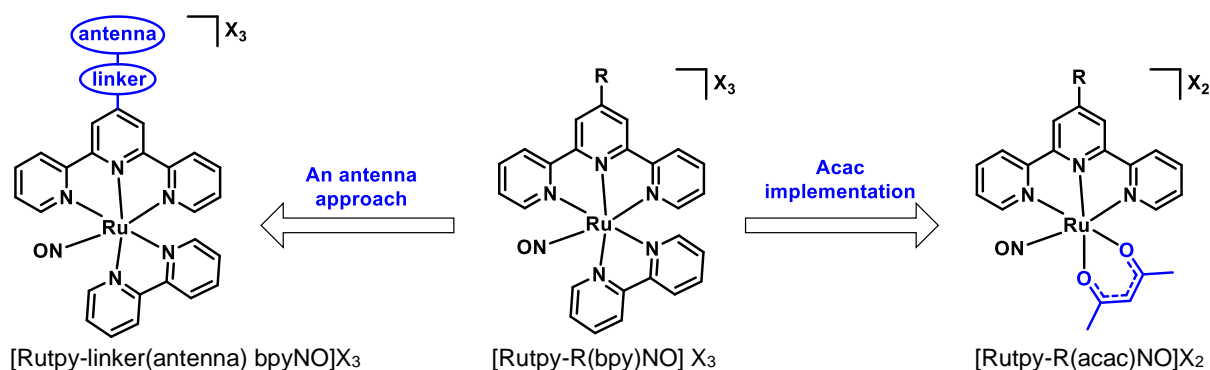
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Ruthenium polypyridyl complexes are intriguing systems with potential applications such as molecular switches, biological sensors, photosensitizers, water oxidation catalysts or anticarcinogenic agents [1]. The transport of the nitric oxide radical which is a physiologically active mediator is one of their additional properties [2]. Besides, the capacity of ruthenium polypyridyl complexes to release active species by absorption of light makes them particularly appealing [3]. In our group, we aim to study photoactive ruthenium nitrosyl complexes based on terpyridine ligand (tpy) with enhanced NO release. Two approaches will be presented:

- The antenna approach in which the introduction of a non-conjugated fluorescent dye (antenna) linked to the tpy ligand leads to a transfer of energy from the antenna to the (RuNO) fragment of the complex, and consequently to a predictable increase in NO release. One system based on fluorene antenna will be presented.
- The second approach concerns the rather poor water-solubility or -stability of some ruthenium nitrosyl complexes. Substitution of the bidentate ligand like bipyridine (bpy) for anionic acetylacetonato (acac) can be the key to the solution of this problem. Synthesis and characterization of a series of new complexes will be presented as well as their NO photorelease capability [4].



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Depolymerization of oxygenated plastics with silane reagents

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Because they are cheap, durable, easy to shape and adjustable properties, plastics have strongly contributed to the post war economic rise by encouraging mass consumption. Driven by innovation and emerging markets, their consumption has quadrupled over the past 30 years to reach 468 million tons in 2022 and should attain 1.2 billion tons by 2060.^{1,2} However, plastics also pose a serious environmental problem. Almost 98% of the world's plastics production is still fossil-based and half of the production is used only once and then thrown away, generating huge quantities (350 Mt/year) of waste.³ Most of these wastes are not recycled (only 8%) and ends up in landfills, nature or oceans.⁴

There is an urgent need to stop the plastic pollution, to solve the waste issue and to favor a circular economy of these matters. Currently, plastic recycling is essentially limited to a narrow range of thermoplastic polymers (**PET**, **PEHD** (High density polyethylene) and **PP**) which are mainly mechanically reprocessed. Chemical recycling technologies can increase circularity by complementing the mechanical process and upcycling hard-to-recycle plastic wastes. Efforts have thus been devoted to develop chemical techniques (depolymerization, cracking...) to convert plastic waste into monomers or practical molecules that could be used as raw materials in the chemical industry.

New efficient catalytic ways and catalytic reductive depolymerization methods using homogeneous or heterogeneous catalysts and a variety of reducing sources (H₂, hydrosilanes,...) have recently shown promise for the treatment of oxygenated and nitrogenated plastics under relatively mild conditions.⁵⁻⁸

Many studies report the ability of iodosilanes to cleave carbon-oxygen bonds in a variety of organic molecules (ethers, esters, carbamates, ketals, ...). We will present our recent results concerning the depolymerization of polyesters with iodosilanes.⁹

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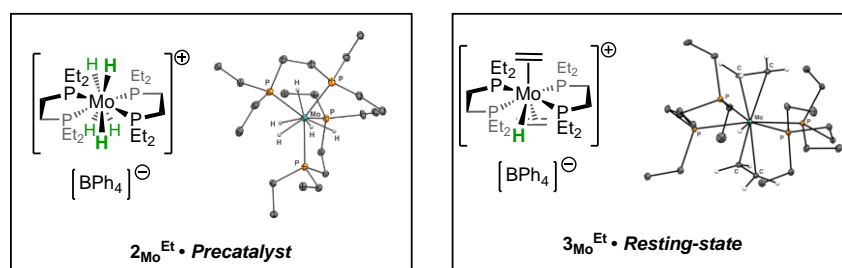
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Molybdenum Pentahydride Complexes as Catalysts for Hydrogenation of Alkenes and Ketones

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The catalytic hydrogenation of unsaturated compounds is a well-known and frequently used reaction in both academic and industrial settings.^{1,2} State-of-the-art molecular catalysts usually rely on platinum group metals (PGMs) such as Ru, Rh and Ir, thanks to the robustness and high activities they offer. However, due to the increasing interest in the development of cheap and environmentally benign catalytic reactions, the application of base metals has recently received considerable attention.³ Several first-row transition metals have shown great promise as homogeneous hydrogenation catalysts with activities rivaling their precious metal counterparts in several instances. Indeed, hydrogenation of unsaturated organic compounds employing Mo and W catalysts has been known since the 1980s, but gained a renewed interest recently with the development of pincer ligands.^{4,5} Several studies have reported that (poly)hydridic group 6 metal complexes can be active hydrogenation catalysts. We have explored the potential of an Mo-based pentahydride complex as hydrogenation (pre)catalyst under mild conditions, and in this presentation, we will show our results with substrates such as alkenes or ketones.

Figure 1 : Hydrogenation precatalyst and identification of a possible resting-state in the hydrogenation of ethylene



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Elaboration of high and low-valent Al complexes with a novel N-N Π N asymmetric ligand for activating small molecules.

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Numerous complexes capable of activating small molecules in multiple industrial processes, such as hydroformylation, metathesis, and catalysis for olefin polymerization, among others are described. Most of these compounds are based on metal centers belonging to the transition group of the periodic table. However, the availability of these metals decreases and is associated with high extraction costs^{1,2}.

This problem has led to the search for inorganic systems based on compounds with metal centers belonging to main groups, such as group 13, which have low production costs and toxicity (mainly aluminum)³.

This project involves the synthesis and characterization of a novel N-N Π N asymmetric ligand, 1,8-diaminonaphthalene derivate, and its coordination properties with metals of the main group, specifically to obtain complexes of aluminum and/or gallium, with high and low oxidation states, for the study of activation of small molecules, such as carbon dioxide (CO₂), molecular hydrogen (H₂), nitrous oxide (N₂O) among others.

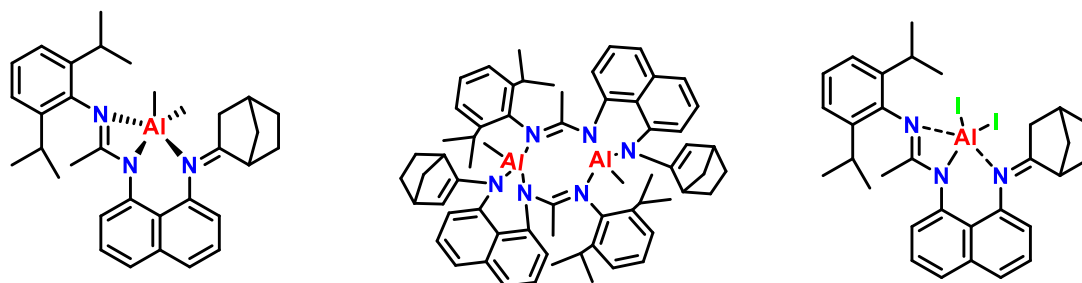


Figure 1: Aluminium complexes synthesized.

On the other hand, both complexes with high oxidation states are being tested as catalysts for the activation of epoxides and CO₂ to cyclic carbonates^{4, 5}.

Acknowledgments

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Beyond Standard Click Chemistry for Post-Modification of Hexavanadates: Expanding the Diversity of Available Hybrid Structures

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Organo-inorganic molecular hybrids bearing fully-oxidised hexavanadate core, ligated by two tris-alkoxo ligands (of the general formula $[(V_6O_{19})((CH_2)_3-R)]^{2-}$) are very attractive class of compounds due to the combination of their electronic properties (including switchable behaviour on the surface¹), considerable stability and solution processability, as well as significant opportunities of structural modifications by modification and post-modification of organic constituents.^{2, 3} The latter transformations are, in turn, the key factor for tuning the steric and electronic properties of hybrid molecules, their affinity to certain surfaces and for giving of desired functional characteristics of molecules and materials. The method of Cu-assisted azide-alkyne click (CuAAC) chemistry adopted for tris-ligated hexavanadates^{4, 5} is one of the most efficient approaches for post-functionalisation, because of generally high yields, tolerance to a great variety of functional groups and general behaviour of the reaction. In this report we present the exploiting of three non-standard click chemistry approaches for tailoring of hexavanadate hybrids affording the synthesis of previously not reported classes of hybrids. First, we have adopted and optimised CuAAC method utilizing Au(I) alkynyl derivatives as synthetic analogues of terminal acetylenes, that afforded a series of Au(I)- $\{V_6\}$ hybrids (Figure 1), demonstrating intriguing behaviour on the surface.^{6, 7} We also demonstrated, that Au(I) azide complexes can be involved in 'click' reaction with ethynyl-derived $\{V_6\}$ hybrids in the absence of Cu(I) ions.

Next, using the solubility factor, we have developed a controlled CuAAC process, which allows, depending on the conditions, convert symmetric $\{V_6\}$ - $(N_3)_2$ hybrid to symmetric bis-triazolyl or asymmetric N_3 - $\{V_6\}$ -triazol derivatives with reasonable yields. The obtained asymmetric product was then involved in subsequent 'click' reaction, which was demonstrated by the synthesis of $\{V_6\}$ - $\{V_6\}$ covalent dimer, bearing hexavanadate core in asymmetric ligand environment.

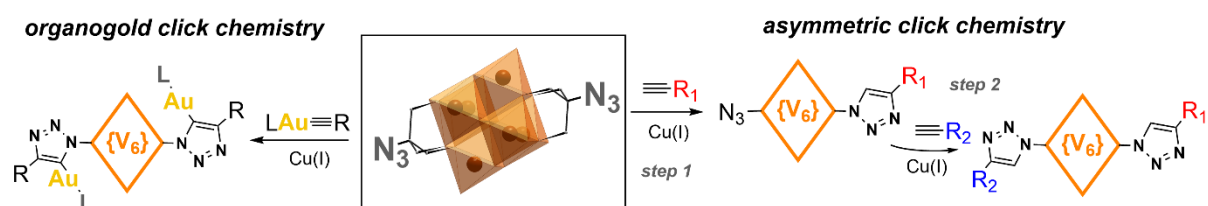


Figure 1. Non-standard click chemistry approaches for tailoring of hexavanadate based structures

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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.^[1] The electrode materials in the electrochemical devices containing nickel and copper are the most attractive in the series of transition metals^[2], due to their accessibility, electronic and chemical properties.

We have investigated NiCu NPs synthesized by an organometallic method^[3] 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 mA cm^{-2} , and it shows good stability within 24 h.

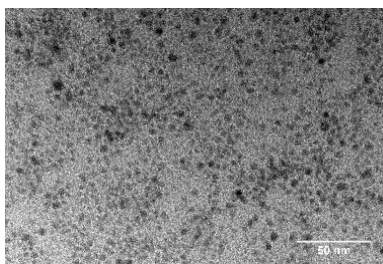


Figure 1. TEM image of synthesized NiCu-NPs

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Unravelling the mechanism of the double alkoxy carbonylation of butadiene: what is the role of the base?

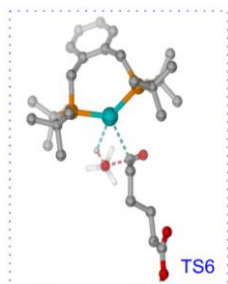
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Adipic acid (AA) is one of the most important building blocks in industrial chemistry. However, its current preparation method raises questions about its energy efficiency and sustainability (such as the use of aggressive oxidants and the generation of large amounts of nitrous oxide, a greenhouse gas).[1] One greener potential alternative involves the one-pot double catalytic carbonylation of butadiene to adipic esters, utilizing butadiene and CO from sustainable sources. While numerous catalytic systems for this reaction have been reported over the past few decades, none have transitioned into industrial processes due to still low activity, selectivity, or inefficient recyclability.[2]

Recently, Beller and co-workers reported a catalytic system based on Pd(TFA)₂ and diphosphine ligands, enabling the double carbonylation of butadiene with remarkable yield and selectivity.[3] Meanwhile, while the mechanism for this reaction is well-documented with simpler olefins like ethene, a noticeable gap exists in our understanding when it comes to butadiene.

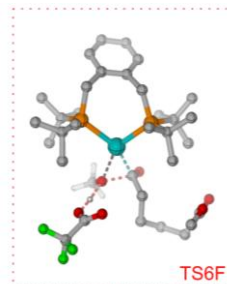
To bridge this gap, the present work combines an experimental study and density functional theory (DFT) simulations to elucidate the mechanism of the double alkoxy carbonylation of butadiene catalyzed by Pd complex with DTBPX as a ligand. We analyse cautiously the observed activity and selectivity in linear versus branched diesters and compare them with the literature as a function of various experimental conditions (proportion of acid and base added).[3] The DFT calculations, at the ωB97XD/TZVP(C,H,P,O)/LANL2DZ(Pd)/CPCM level of theory, providing the first Gibbs energy profile for such reaction and shows that the first methanolysis faces a significant energy barrier of 215 kJ·mol⁻¹, which questions the well-established mechanism involving palladium-hydride species. Moreover, our study indicates that the presence of free base, namely trifluoroacetate, coming from the Pd precursor may impact the free energy profile and influence the barrier for the rate-limiting methanolysis. We finally discuss how this approach can be used to enhance the activity of the alkoxy carbonylation reaction.

Base-free methanolysis



- Unreachable under the reaction conditions
($\Delta G^\ddagger = 215 \text{ kJ}\cdot\text{mol}^{-1}$)
- No change on the oxidation state of Pd
- No need of the acid to regenerate the active species

Base-assisted methanolysis



- Reduction of the kinetic barrier ($\Delta G^\ddagger = 66 \text{ kJ}\cdot\text{mol}^{-1}$)
- Reduction from Pd(II) to Pd(0)
- Need of an acid to regenerate the Pd-H active species, which becomes the rate-determining step
($\Delta G^\ddagger = 182 \text{ kJ}\cdot\text{mol}^{-1}$)

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Synthesis of *N*-Heterocyclic gold(I) complexes with fluorinated ligands for antitumoral activity

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Many studies have demonstrated that gold complexes have inhibitory properties on the Thioredoxin Reductase (TrxR) enzyme present in mitochondria. This enzyme is involved in cell homeostasis, combating oxidative stress which is a key factor in DNA damage. Its inhibition leads to an accumulation of reactive oxygen species, and thus to cell death by apoptosis.^[1] To this end, many complexes have been tested *in vitro* in our team, and the results have shown that biological activity against cancer cells depends on the nature of the groups on the *N*-heterocyclic carbene (NHC) ligands. In addition, our team has recently patented a gold compound including dihydroartemisinin that possesses interesting anti-tumor activity ($IC_{50} < 100$ nM). This compound is a potent inhibitor of NRF2 transcriptional activity, overcoming the chemoresistance induced by NRF2 overactivation.^[2]

For this project, we have chosen to continue on the same type of structures, focusing on NHC ligands featuring a fluorinated aromatic substituent that would increase the lipophilicity of the complexes and their metabolic stability.^[3] Using these fluorinated ligands, we have synthesized four series of gold complexes containing aromatic or nitrogenous groups as quinoline, pyridine, pyrrole and benzyl, followed by one series of gold complexes containing a biologically active group derived from dihydroartemisinin. All these complexes will be subjected to biological cytotoxicity studies on a panel of cancerous and non-cancerous cell lines, as well as mechanistic studies on the molecules with the best activity and selectivity.

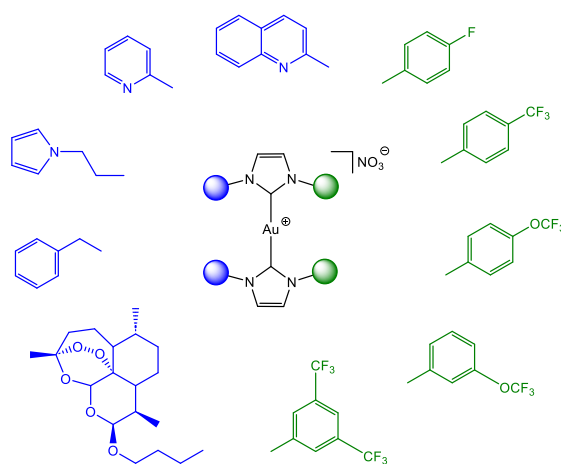


Fig. 1. Structures of NHC-gold(I) complexes with fluorinated ligands.

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Thermally-induced Electron Transfer in CoFe Prussian Blue Analogues using Synchrotron Far-Infrared Spectroscopy

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The CoFe Prussian Blue Analogs (PBAs) have been known for their unique electronic and (photo)-magnetic properties for many years.¹ Nevertheless, the differences observed in the behavior among these PBAs is not yet fully understood. For instance, our previous studies evidenced for $\text{Rb}_2\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3} \cdot n\text{H}_2\text{O}$ and $\text{Cs}_2\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3} \cdot n\text{H}_2\text{O}$ PBAs no thermally-induced electron transfer, but a photo-activated one at low temperatures. It is a marked contrast to $\text{Na}_2\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3} \cdot n\text{H}_2\text{O}$ and $\text{Cs}_{0.7}\text{Co}_4[\text{Fe}(\text{CN})_6]_{2.9} \cdot n\text{H}_2\text{O}$ PBAs, which display both thermally and photo-induced electron transfer properties. For the alkali-cation free $\text{Co}_4[\text{Fe}(\text{CN})_6]_{2.7}$ PBA, a charge transfer is never observed at ambient conditions. Thus, alkali cations likely appears to play a key-role in the electron transfer processes in PBAs, but this role still remains a subject of ongoing discussions.

Here, we present the latest results on our original investigation approach using a synchrotron far-infrared spectroscopy of the two series of CoFe PBAs with the following stoichiometries: (i) $\text{A}_2\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3} \cdot n\text{H}_2\text{O}$ ($\text{A}^+ = \text{Na}^+, \text{Rb}^+$ and Cs^+) and (ii) $\text{Cs}_x\text{Co}_4[\text{Fe}(\text{CN})_6]_{(8+x)/3} \cdot n\text{H}_2\text{O}$ ($x = 0-4$). This study enables to probe the different electronic states involved in the whole temperature range. In addition to a clear assignment of the bands in this FIR region, usually not much investigated for molecular compounds^{2,3}, we could observe that the bands corresponding to the vibrations of the cyanide-bridged CoFe network and to the alkali cations exhibit different thermal behaviors upon cooling in both series. This reveals a characteristic signature of the interaction between the alkali cations and the cyanido-bridged bimetallic network.^{4,5} Our findings show that FIR spectroscopy brings valuable information on these interactions even for PBAs with few alkali cations, where no cooperative effects are present. It also paves the ways towards a deeper understanding of the switching properties in PBAs, where alkali cations clearly play a major role.

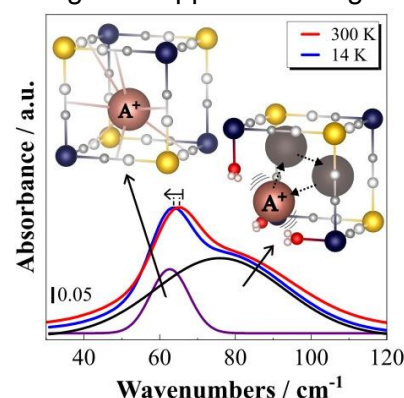


Figure 1. Spectral deconvolution of the alkali cation vibration band over the 30-120 cm^{-1} range, showing two alkali positioning: in the closed (associated with the narrow peak on the spectrum) and opened (the broaden component on the spectrum) cubic cavities.

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Controlled Degradation of a Pd-CF₃ Unit as a Methodology for the Synthesis of Palladium Carbene Complexes

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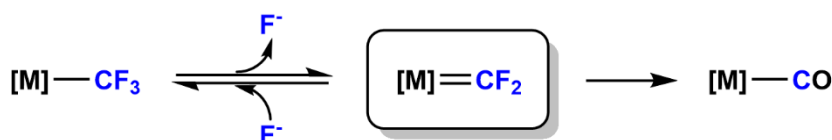
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Trifluoromethyl transition metal (TM) chemistry is emerging as a fast-moving, exciting research field in Chemistry. In the last years, we have focused our studies on highly trifluoromethylated, late TM compounds. In particular, the homoleptic isoelectronic [Ag(CF₃)₄]⁻ (**1**) and [Pd(CF₃)₄]²⁻ (**2**) complexes have recently caught our attention.[1] They present diverging properties, based on the rare inverse ligand field electronic structure of the silver counterpart.

Both homoleptic species, **1** & **2**, show remarkable thermal stabilities, with decomposition temperatures of 188 and 227 °C respectively. In solution, a typical evolution pathway for trifluoromethyl transition metal complexes involves a fluoride dissociation mechanism, thus rendering a highly reactive M=CF₂ moiety prone to evolve into a M-CO unit.[2] Instead, the reverse process constitutes the Fluoride Ion Affinity (FIA) of the putative M=CF₂ species, the FIA being a widely accepted descriptor of the Lewis acidity of chemical species.[3]

DFT calibration of the FIA's in [Ag(CF₃)₃(CF₂)] and [Pd(CF₃)₃(CF₂)]⁻ give an indirect overview of the tendency of **1** & **2** to generate a difluorocarbene complex, a process that potentially opens the door to further reactivity. In this communication we will show our most recent results on trifluoromethyl palladium chemistry, intended to achieve the controlled transformation of a CF₃ into other interesting ligands, including fluoro-heteroatom and bis-heteroatom stabilized carbenes.



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LEWIS ACID-MEDIATED RADICAL STABILIZATION IN ADDUCTS OF N-HETEROCYCLIC CARBENES (NHC) WITH N₂O

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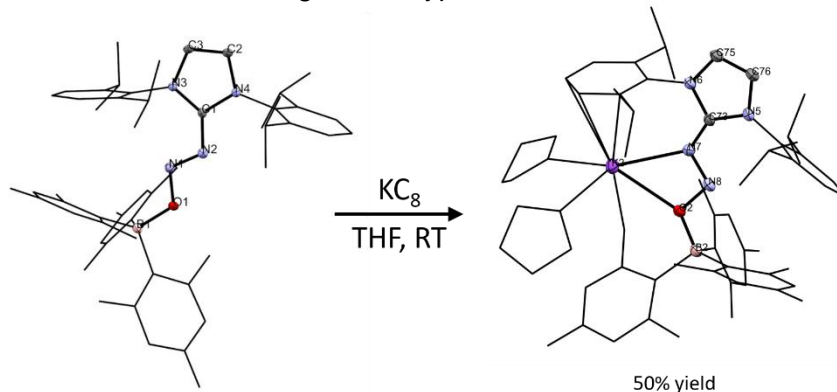
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Nitrous oxide (N₂O) is a minor component of the atmosphere, its concentration steadily increasing since the beginning of the industrial era. Although less abundant than carbon dioxide (CO₂), nitrous oxide's significant contributions to global warming (as the 3rd main contributor) and its role in ozone depletion (as the 1st contributor) have recently attracted considerable attention.^[1,2] Beyond an evolution of agricultural practices (improved nitrogen-containing fertilizers management), mitigating the environmental impact of nitrous oxide necessitates the exploration and advancement of sophisticated methodologies for its efficient capture, destruction or valorization. Although highly oxidizing (E₀=+1.77 V vs NHE), N₂O is nevertheless known for its high kinetic reluctance. Considerable efforts have been made to chemically assist its activation, notably through transition metal complexes.^[3,4] An alternative strategy was reported that relies on the use of N-Heterocyclic Carbenes (NHCs).^[5] Such species are capable to smoothly react with nitrous oxide to give stable adducts in which the N-N-O moiety adopts a bent arrangement. In this configuration, the N-N and N-O bonds are weakened leading to new types of reactivities.



In the course of our investigation, the role Lewis acid partners have to stabilize N-centered radicals was evidenced by cyclic voltammetry, highlighting dramatic changes in the electrochemical behavior of those molecularly activated forms of nitrous oxide. In this presentation, the synthesis and characterization of a new family of N₂O-trapped FLP-type systems will be reported. Modification of the nature of the Lewis acid partner to tune the redox properties of the resulting edifices will be discussed. In particular, the electronic structure of new, stable monoradicals will be described based on 2D-EPR studies and DFT calculations.

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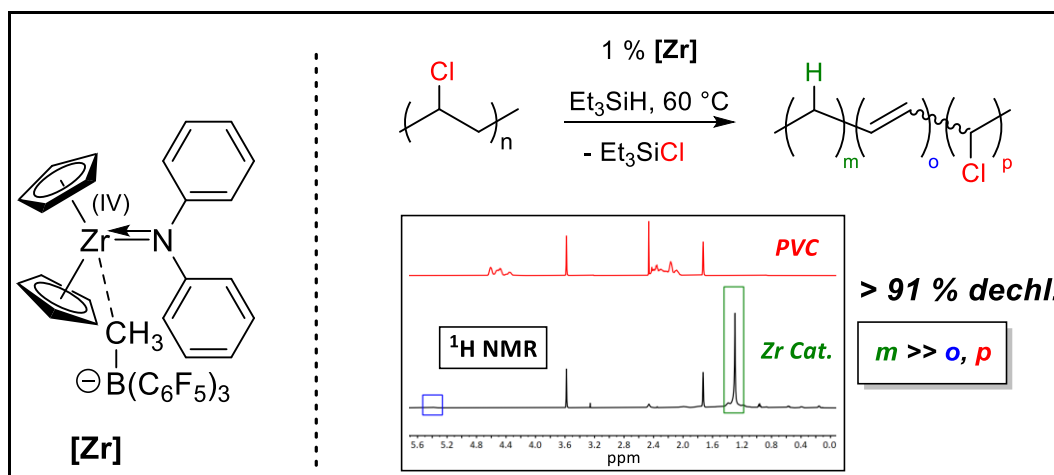
Poly(vinyl chloride) Dechlorination Catalyzed by Zirconium

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The exponentially growing production of plastics, together with the multifaceted challenges associated with their mechanical recycling on industrial scale, have resulted in a colossal — yet increasingly dispersed — amount of plastic solid waste (PSW) in the environment.[1] As one of the main classes of thermoplastics, Poly(vinyl chloride) (PVC) is also one of the most problematic from a waste management perspective, because it releases copious amounts (> 50 % mass balance) of corrosive hydrochloric acid upon thermal degradation. As a result, the economic and environmental viability of mixed plastic waste streams that contain PVC is compromised.[2] Current strategies for the catalytic dechlorination of PVC involve the use of mild hydrogen donors such as silanes or H₂. [3-5] However, these methodologies rely on the use of precious metals (Ir, Rh, Pt) at elevated temperatures (110-200 °C), two features which are disadvantageous in the context of waste management.

We herein report the use of a Zirconium complex **[Zr]**, in the presence of triethylsilane, for the catalytic dechlorination of PVC. This system works with high dechlorination efficiency (> 91 %) at moderate temperatures (≤ 80 °C), whilst generating a by-product with added value (Et₃SiCl). Crucially, complex **[Zr]** also displays interesting activity against customer items (such as PVC piping), and it performs the hydrosilylation of problematic phthalate additives.[6]



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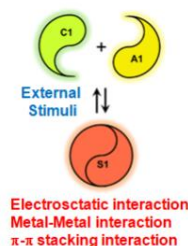
Soft Salts Based on Platinum(II) Complexes with Tunable Optical Properties and Vapochromic Switches

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Luminescent materials exhibiting reversible change of their optical properties under different external stimuli have huge application potentials in various optoelectronic fields. Thus, small molecules, metal complexes, and polymers have been developed as materials with photochromic, mechanochromic, vapochromic, electrochromic, and thermochromic properties. Due to their high photoluminescence quantum yields (PLQY), remarkable stimuli, platinum (II) complexes are potential candidates for constructing luminescent materials.^[1]

Among them, soft salts based on ion-paired cyclometalated platinum (II) complexes are attracting increasing interest as potential candidates for the construction of stimulus-responsive luminescent materials. These complex salts (S1) showed original properties due to Pt(II)···Pt(II) and π - π stacking interactions between anionic (A1) and cationic (C1) complexes enabling selective responses to various external stimuli by accurately regulating various intermolecular interactions.^[2]



In this communication, we will present the synthesis of a series of soft salts based on two oppositely charged cyclometalated platinum complexes **S1-9** ($[\text{Pt}(\text{C}^{\wedge}\text{N})\text{ed}]^+[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{CN})_2]^-$). Appropriate combination of cationic and anionic components allows tuning the photoluminescence properties of the formed salts. Our approach was to investigate the structure-property relationships within a class of Pt(II) soft salts bearing modified C[^]N ligands. The structure-property relationships were highlighted by a comparative study of the photophysical properties of this class of salt (PLQY, AIEE, etc.). To demonstrate the potential materials for anti-counterfeiting applications of these soft salt complexes, vapochromism studies have been successfully explored.

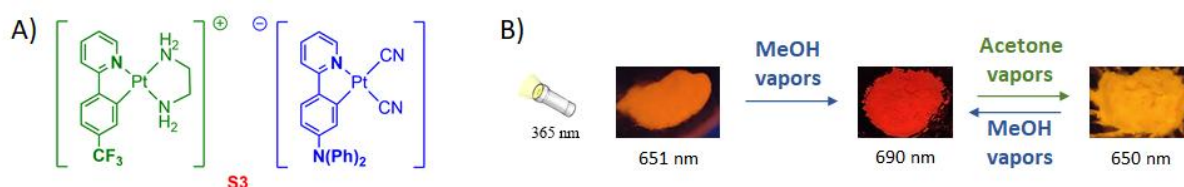


Figure: A) Structure of **S3**; B) Vapochromic behavior of **S3** in the solid state (KBr powder with 1% wt of soft salt). Pictures were taken in the dark upon irradiation with a handheld UV lamp ($\lambda_{\text{em}} = 365 \text{ nm}$).

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Metal-Organic Frameworks: Evaluating cytotoxicity assays and their antiviral activity against coronaviruses

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Severe acute respiratory syndrome coronavirus-2 (SARS-CoV-2) is responsible for the corona virus disease of 2019, or else COVID-19, which originated from Wuhan of China in December of 2019.¹ Up to this day, this disease that was declared a pandemic by WHO on March 11 of 2020 is accountable for 6.8 million deaths and 758 million cases worldwide as of March 6th 2023.²

In this work, five metal-organic frameworks synthesized with different metals (Zr, Cu, Fe, Ti) were used to evaluate different cytotoxicity methods in three cell lines, named MTS, Neutral Red and LDH as cytotoxicity methods and Huh7 TMRSS2, VeroE6 and Vero81.6 as cell lines. Different levels of concentrations were tested and the Neutral Red method was found to be the most precise and accurate, while MTS and LDH gave similar results, but with high standard deviations. 1 mg/mL was the highest concentration that was not toxic for every MOF in every cell line except the one with copper, whose maximum safest value was 0.1 mg/mL. Furthermore, their efficiency against CoV-type viruses (HCoV-229E and SARS-CoV-2) was examined with different tests, that were able to determine both the viral titer and the infectivity of the virus. The Cu and Ti MOFs showed a significant drop of the viral titer of HCoV-229E, while for SARS-CoV-2 the aforementioned MOFs and the Fe MOF exhibited an important decrease.³

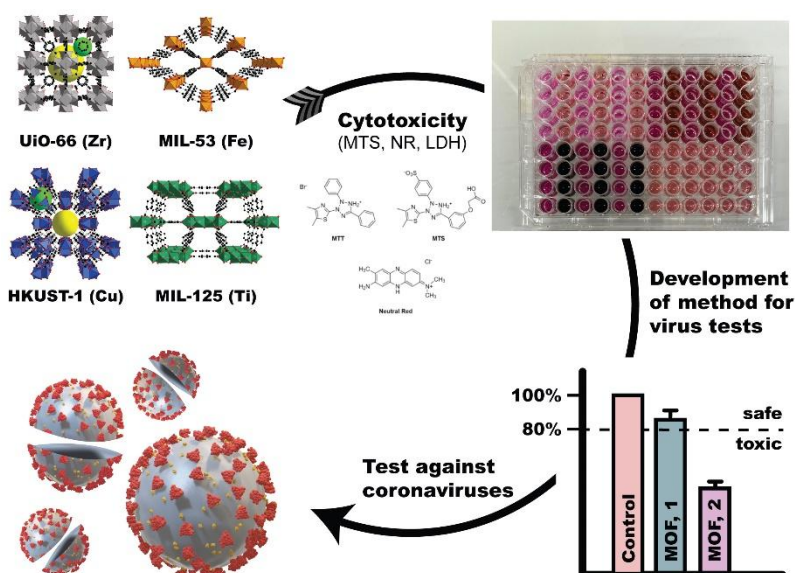


Fig. 1: Representative graphical scheme of the protocol used for the inactivation of coronaviruses.

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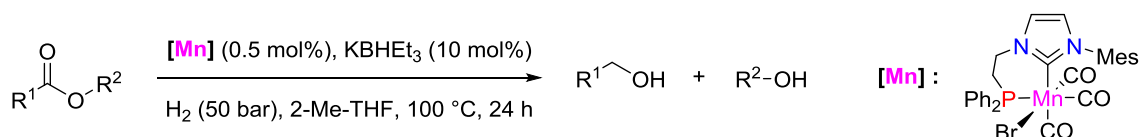
Hydrogenation of esters promoted by NHC-phosphine manganese catalyst

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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.¹ In the literature, the catalysts developed so far are mainly based on tridentate ligands involved in a metal-ligand cooperativity.²

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 H₂ pressure and 10 mol% of KBHET₃ at 100 °C.^{3,4} All the results will be detailed in the present



communication.

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Insights into non-covalent interactions in dicopper(II,II) complexes bearing a naphthyridine scaffold: an anion-dictated electrochemistry

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A family of bis(μ -hydroxido)dicopper(II,II) complexes bearing a naphthyridine-based scaffold has been synthesized and characterized.^[1] Cyclic voltammetry reveals that the nature of the anions present in the complexes plays a pivotal role in their electrochemical properties.^[2] X-ray diffraction, spectroscopic and electrochemical analyses data support the formation of intimate ion pairs through non-covalent interactions^[3] driving to ca. 270 mV difference for the potential required to monooxidize the Cu^{II}Cu^{II} species (Figure 1).

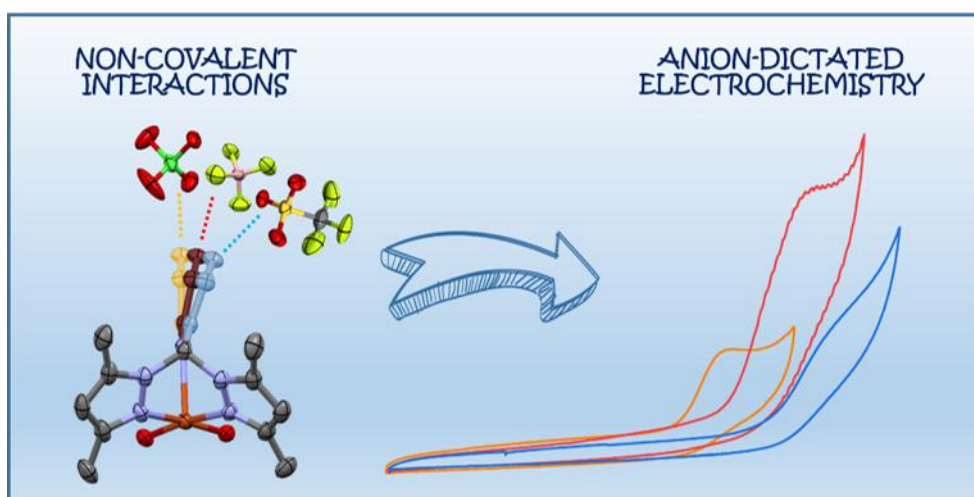


Figure 1. Anions stabilising non-covalent interactions giving dissimilar electrochemical signatures.

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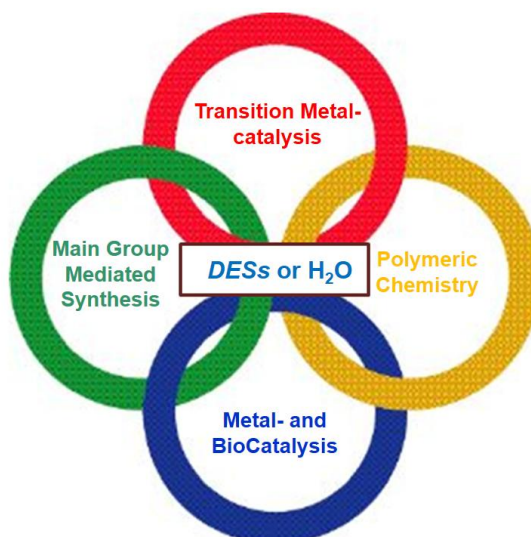
Polar s-Block Organometallic Chemistry in sustainable protic solvents (*Deep Eutectic Solvents* and water) under bench-type reaction conditions

Marina Ramos-Martín, Marcos López-Aguilar, Nicolás Riós-Lombardía, Alejandro Presa Soto* and Joaquín García-Álvarez*

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Due to the increasing rate of production of the *Chemical Industry* it is necessary to look for new alternative and greener ways that attempt to minimize the undesired side effects caused to the environment.^[1] In this sense, considerable attention has been recently focused on *Deep Eutectic Solvents* (DESs) as an alternative to conventional volatile organic compounds (VOCs) in many fields of science.^[2] Our group has an ongoing interest in the study of main-group-mediated organic transformations using biorenewable and biodegradable DESs (or even water) as reaction media.^[3] The implementation of these neoteric solvents has allowed us to work under bench-type reactions (room temperature, under air/moisture) even in the case of highly reactive s-block reagents (RLi/RMgX).

Relatedly, we are pursuing the design of new hybrid one-pot tandem protocols in sustainable solvents and under bench-type reactions conditions which combine RLi/RMgX reagents with other organic synthetic tools (transition metals, enzymes or organocatalysts),^[4] thus circumventing the need of tedious and time-consuming intermediate purification and separation processes, therefore minimizing the generation of residues and simplifying practical aspects, being therefore in agreement with the *Principles of Green Chemistry*.



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Advancing Sustainable Oxygenation and Halogenation via Electrochemical O₂ Activation with Bioinspired Metal Complexes

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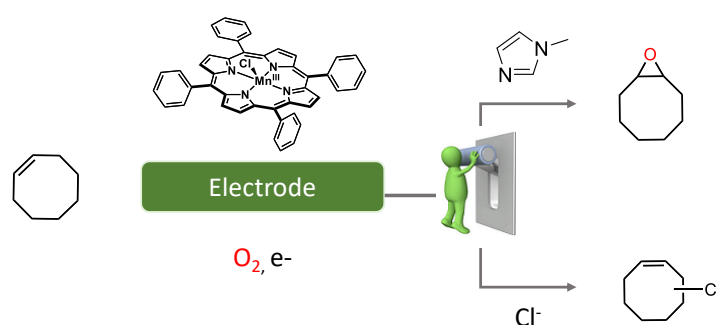
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Oxygenation and halogenation of hydrocarbons are fundamental oxidation reactions allowing for the introduction of functional groups into organic compounds.^[1] Despite their significant synthetic importance, these transformations rely mainly on the use of stoichiometric amounts of oxidants and harsh conditions.^[2] The application of oxygen as a primary green oxidant holds particular appeal. However, the diradical nature of O₂ and thus its ground triplet state renders reactions with closed-shell organic molecules spin-forbidden, resulting in their kinetic inhibition. In this regard, we combined metal porphyrins and electrochemistry to mimic the CYP450 activity.^[3] Following the enzymatic pathway of O₂ activation, where oxidation is driven by sequential and controlled chemical reduction of Fe–O₂ complexes, our methodology utilizes electrical potential to achieve desired transformations of organic molecules.

In the present talk, we will demonstrate how spectroelectrochemical experiments, cyclic voltammetry, and preparative electrolysis are utilized to develop methods for the selective halogenation and oxygenation of cyclooctene via Mn porphyrin catalysis.^[4] Moreover, the reported findings will be complemented by results from ongoing studies aimed at broadening the scope of oxygenation reaction, detecting the generated high-valent Mn active oxidant species, and enhancing our mechanistic understanding of the studied system.



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Nickel catalyzed three-component coupling reactions: A straightforward and atom-economical pathway to homoallylic derivatives

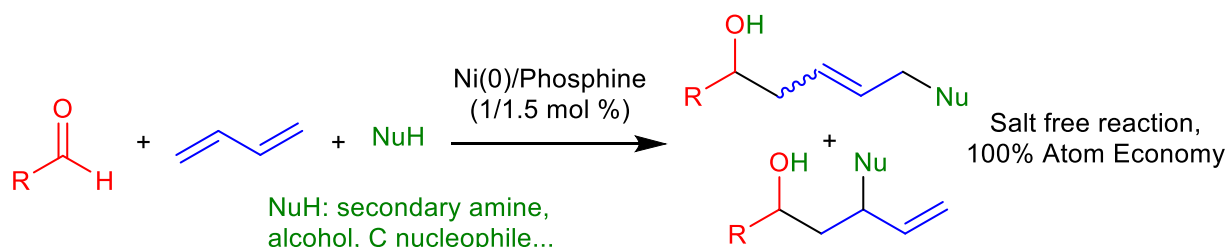
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Homoallylic compounds are attractive building blocks for the synthesis of original molecules of interest in the fields of fine chemistry and drug design. Homoallylic alcohols combine the presence of two functionalities of synthetic interest: the hydroxyl group and the double bond, that can be further chemically modified. They are for example used for the synthesis of a large variety of heterocyclic oxygenated compounds of importance such as polyketides natural products.^{1,2} The synthesis of homoallylic scaffolds typically involves stoichiometric organic transformations and it is clear that **catalytic and more environmentally friendly pathways** would be desirable, particularly if they involve **simple building blocks** such as butadiene which is largely accessible on multiton scale from oil cracking or biomass (bio-ethanol route/Lebedev process³). This latter aspect combined with the development of eco-compatible reaction pathways for homoallylic derivatives, especially alcohols, is particularly relevant for future prospects in the field of **green chemistry** including the incorporation of **renewable carbon**.



We will devote our attention in this study toward the synthesis of allylic derivatives from butadiene and a nucleophile.⁴ Recent works in the group revealed the possibility to synthesize new 1,5-functionnalized homoallylic alcohols starting from very simple building blocks such as aldehydes, buta-1,3-diene and a secondary amine. As example, **1,5-amino homoallylic alcohols**, which are known to be difficult to obtain,⁵ could be synthesized in a very efficient one-step synthesis and a 100% atom economy.

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A Novel Family of Multifunctional MOFs Coupling Electron Transfer, Spin Crossover and Redox Activity

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Hofmann coordination polymers (CPs) that couple a spin transition [1] with an electron transfer (ET) at room temperature are an innovative strategy towards multifunctional metal organic frameworks (MOFs). Here, we developed a family of 2D planar $\{\text{Fe}(\text{R-pbpy}^+)\}_2[\mu_2\text{-M}(\text{CN})_4]_2$ (R= CH₃, Br, COOCH₃ and NO₂, M= Pt^{II} or Ni^{II}) compounds with an unusual structural arrangement, where the axial ligand consists of an infinitely π -stacked, redox-active bipyridinium derivative (R-pbpy⁺) (**Fig. 1**). [2] The materials show vivid thermochromism attributed to ET and/or SCO processes that can occur either independently or concomitantly. This has been observed by UV-Vis-NIR measurements (**Fig. 2**), where a strong band around 580 nm can be attributed to the dimerization of R-pbpy⁺ radicals, known to be stabilized by a MOF structure. [3] These observations are confirmed via temperature dependent single crystal X-ray diffraction, magnetic measurements, Mössbauer, optical and vibrational spectroscopies as well as quantum chemical calculations.

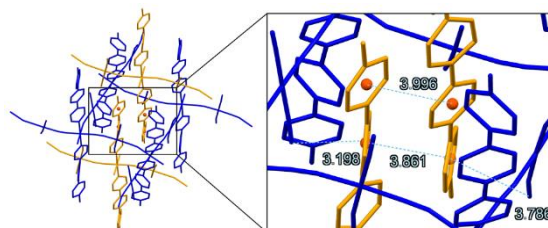


Fig. 1: Crystal packing and π - π stacking in $\{\text{Fe}(\text{CH}_3\text{-pbpy}^+)\}_2[\mu_2\text{-Pt}(\text{CN})_4]_2$.

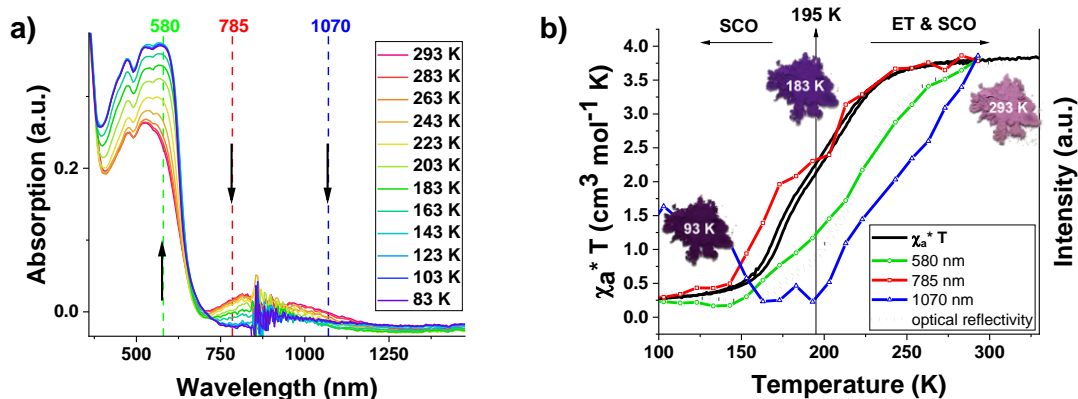


Fig. 2: a) Temperature dependent UV-vis-NIR absorption spectra of $\{\text{Fe}(\text{CH}_3\text{-pbpy}^+)\}_2[\mu_2\text{-Pt}(\text{CN})_4]_2$ upon cooling and b) comparison of the magnetic ($\chi_a T$) and optic behavior with selected absorption intensities as a function of the temperature (inverted band intensity scale at 580 nm). The slight double step in magnetic behavior as well as differences in the absorption band evolution are attributed to a coupling between SCO and thermo-induced ET at higher temperature.

Acknowledgement: This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement N° 101019522).

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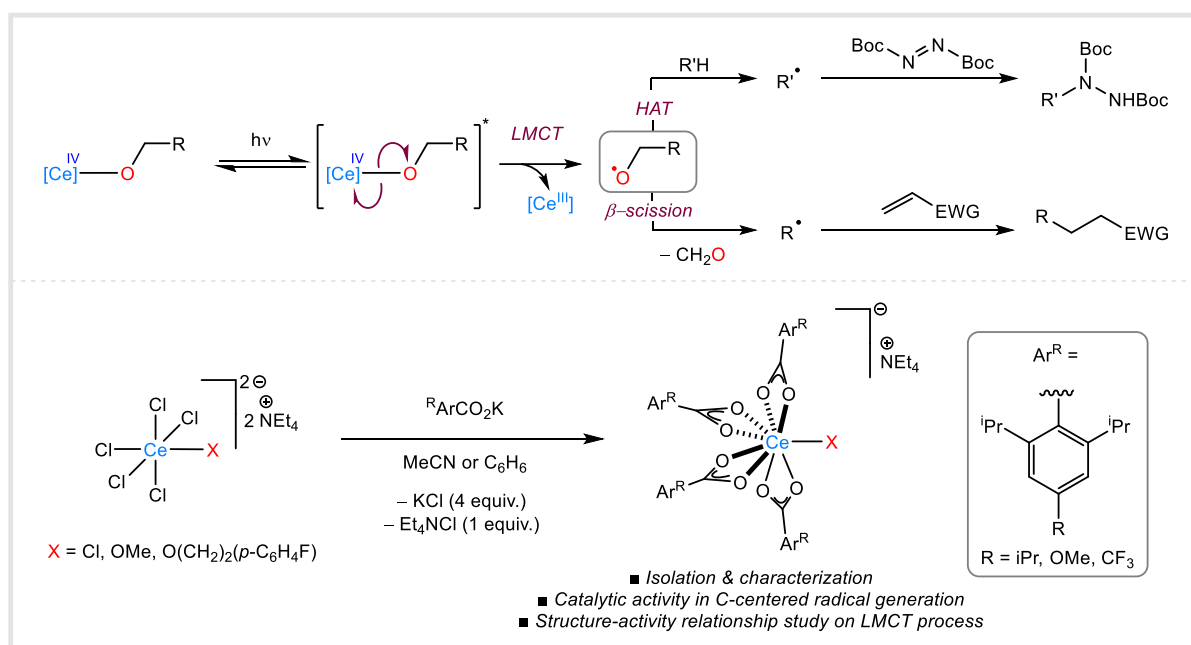
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Carboxylate Ligand Role in Cerium Photocatalysis applied to C-centered Radical Functionalization

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Ligand-to-metal charge transfer (LMCT) under light irradiation is an emerging tool for the development of environmentally friendly transformations using earth-abundant metals. Notably, LMCT from cerium complexes has been used for the functionalization of alcohols (by β -scission) and of C-H bonds by intermolecular hydrogen atom transfer (HAT).¹ Recently, carboxylate ligands have been reported to enable Ce/Ni-catalyzed cross-coupling transformations using abundant alcohol or aliphatic carboxylic acid substrates.^{2,3}

Building a better understanding of the role of carboxylate ligands in cerium catalysis would trigger the development of efficient catalytic systems. Herein, the preparation, characterization and stoichiometric study of a series of well-defined photosensitive cerium(IV) chloride or alkoxy complexes decorated with carboxylate ligands and their catalytic activities will be presented (Scheme 9C). The cerium carboxylate complexes isolated are competent in catalysis for the amination of C-H bonds by HAT. Moreover, a structure-activity relationship study is targeted to explore the effect of the carboxylate ligands on the LMCT process.



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Selective cytotoxicity of Ru(II) complexes featuring heterotridentate SNE iminophosphorane ligands (E= S, Se)

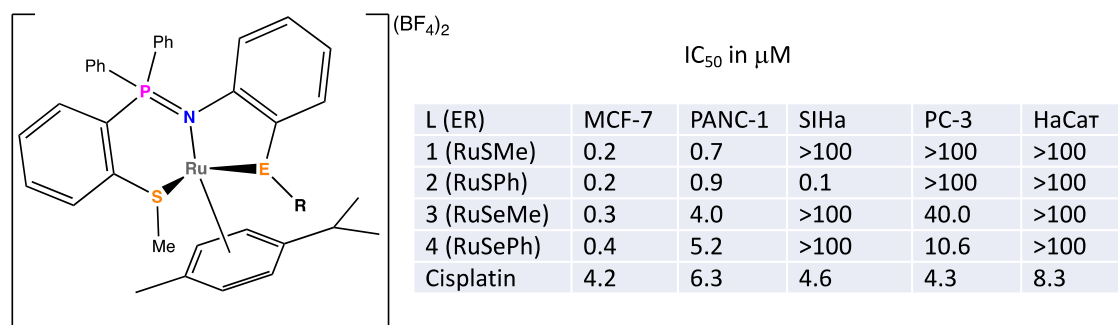
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In our quest to develop novel ruthenium-based anticancer agents with reduced toxicity¹, we synthesized four closely related half-sandwich Ru(II) complexes. These complexes feature neutral heterotridentate iminophosphorane ligands L, with thio and seleno ether pending arms [L= MeSC₆H₄P(Ph)₂=NC₆H₄ER (E= S, Se; R= Me, Ph)]. The dicationic complexes [(η⁶-p-cymene)Ru(L-κ³-SNE)](BF₄)₂ designated as **1** (ER= SMe), **2** (ER= SPh), **3** (ER= SeMe), and **4** (ER= SePh) were obtained with high yields by reaction of L with the (p-Cymene)ruthenium(II) chloride dimer in MeOH. Elemental analysis and common spectroscopic techniques were used for full characterization, with X-ray crystallography of **2** and **4**, confirming their pseudo-octahedral geometry and facial tridentate coordination. Solubility assessments have revealed that **1-4** exhibit excellent solubility in water, MeOH, DMSO, CH₃CN, and aqueous stability was established over a week through ³¹P NMR and UV-Vis spectroscopy. Assessment of the cytotoxicity of complexes **1-4** was performed using the sulforhodamine B (SRB) colorimetric assay² against four human cancer cell lines, namely breast carcinoma (MCF-7), cervical carcinoma (SiHa), pancreatic carcinoma (PANC-1), and prostate carcinoma (PC-3), in addition to noncancerous HaCaT cells (human epidermal keratinocytes). Cisplatin was used as the reference standard drug for comparative analysis, relying on IC₅₀ values³. One of the most remarkable findings of this study is the exceptional selectivity exhibited by the four complexes against the various cancer cell lines examined. Each complex displayed IC₅₀ values in the low micromolar range, surpassing those of cisplatin against MCF-7 and PANC-1, while demonstrating minimal impact on normal HaCaT cells. Furthermore, the structural design of the ligands exerted a significant influence on the selectivity of the corresponding complexes towards specific cancer cell lines. Complexes bearing a selenium donor pending arm (**3-4**) demonstrate notable cytotoxicity against PC-3 cells, whereas those with a sulfur donor (1-2) show no cytotoxic effects. On the other hand, a sulfur-containing pending arm yields IC₅₀ seven times lower than that of the selenium derivatives against PANC-1. Ultimately, only complex **2**, featuring an SPh pending arm, exhibits activity against SiHa, far surpassing that of cisplatin. These findings call for further comprehensive investigations but hold promise for the development of novel anticancer agents with reduced toxicity.



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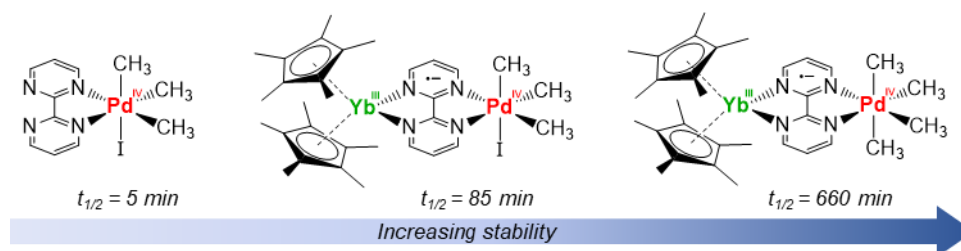
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Ytterbium-stabilized alkyl palladium(IV) complexes: synthesis and reactivity studies

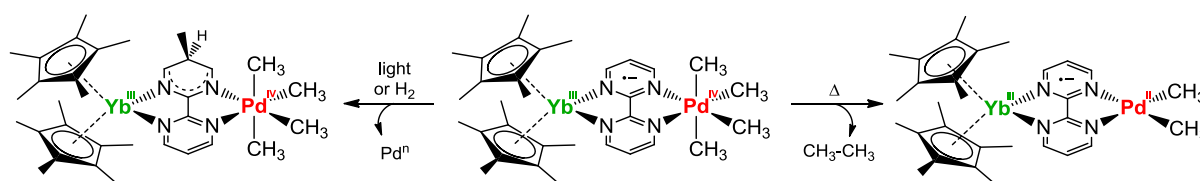
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The chemistry of organometallic palladium complexes is largely dominated by the 0 and +II metal oxidation states due to their central relevance in cross-coupling transformations.^[1] However, higher oxidation states are being explored in an effort to unlock previously precluded transformations and to unveil unprecedented reactivity at the metal centre.^[2,3] Such exploration aims to push the boundaries of our understanding of metal-mediated transformations and to discover unprecedented reaction pathways, however this effort is hindered by the elusiveness and the instability of the scrutinized high-valent species. The coordination of an ytterbium centre to an alkyl-Pd^{IV} species through a redox non-innocent ligand dramatically improves the stability of the resulting complexes.^[4,5] Yet, owing to the presence of labile ligands as halides, such compounds are still susceptible to undergo easy reductive elimination processes.^[4]



Following this effort, here we present the synthesis of an ytterbium-stabilized alkyl-Pd^{IV} species bearing four methyl groups at the palladium centre. Such complex proved to be drastically more stable than its tris-methylated counterpart, with a half-life time in solution of 11 hours at 20°C. Taking full advantage of the increased stability of the resulting complex, its formal reductive elimination to form ethane and its unprecedented reactivity with light and hydrogen gas are explored.



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Merging *N*-heterocyclic carbene organocatalysis and nickel radical catalysis through a SET event.

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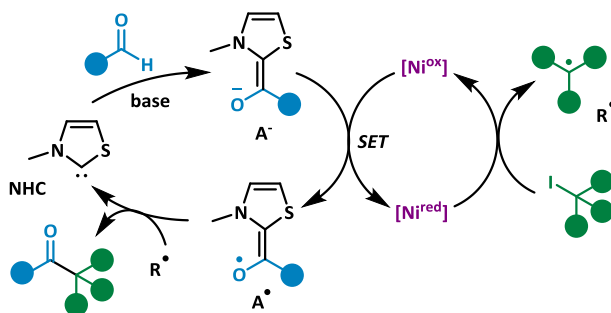
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N-heterocyclic carbenes (NHC) react with aldehydes leading to Breslow intermediates.^{1,2} The deprotonated form of these species (enolates **A**⁻) may behave as single-electron transfer (SET) reagents under certain conditions, a property that can be employed to promote radical transformations.³ Those methodologies that rely on the reducing power of enolates **A**⁻ are limited to redox accessible substrates ($E > -2$ V vs SCE).⁴ Today the barrier is stuck at the activation/reduction of iodoarenes and primary and secondary unactivated alkyl iodides and bromides.⁵⁻⁸ However, none of these methodologies are able to reduce tertiary alkyl halides placing such electrophiles as the new redox barrier.

A possible strategy to activate redox inaccessible substrates is to run cooperative catalysis. The hypothesis is to reduce a metal center by the enolate, which is able to activate the substrate via a mechanism that does not involve a SET event. Following this approach, Ye *et al.* reported (photoredox) cooperative NHC/Pd transformations with tertiary alkyl bromides.⁹

Herein, we present the activation of tertiary alkyl iodides employing a cooperative NHC/nickel catalytic methodology.¹⁰ This allows for the unprecedented coupling between aryl aldehydes and tertiary alkyl iodides leading directly to ketones. The combination of reactivity, electrochemical and spectroscopic studies allowed us to propose a mechanism that merges NHC and nickel catalytic cycles via a SET event.



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Synthesis and study of redox-active bioinspired molecular units for electron transfer and energy storage

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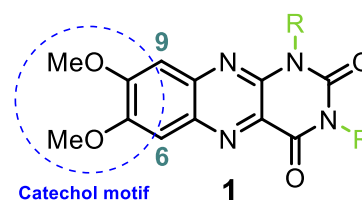
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Redox flow batteries store energy in scalable reservoirs containing redox-active molecules and are the subject of sustained development in the energy storage sector. In order to store a sufficient quantity of electrons, these molecules must be soluble (ideally in water), thermodynamically and electrochemically stable, and have a low molecular weight.^[1]

Flavins (alloxazines/isoalloxazines) are a class of bio-sourced molecules capable of reversibly storing electrons.^[2] They can be solubilized in aqueous media and have a low reduction potential.^[3] However, they have certain limitations, notably poor cycle stability and a tendency to dimerize.^[4] The functionalization of flavins, necessary to modulate their properties through the addition of solubilizing and electron-donor/acceptor groups, is also their major problem, as the only sites that can be modified are the nitrogens of the uracil subunit and the aromatic ring. The latter is difficult to functionalize selectively, and the groups needed to modulate flavin properties generally have to be introduced early in the synthesis and more specifically before the condensation step, leading to the formation of different regioisomers thus causing difficulties in separation.^[3]

We will present our work on the selective functionalization of redox-active bioinspired alloxazine and isoalloxazine derivatives to modulate their redox properties and solubility towards their implementation in redox-flow batteries. A general functionalization method was developed based on methylated alloxazine-catechol (**1**, Figure 1) via a C₉-position selective bromination or bis-bromination (C₆/C₉) sequence followed by Suzuki-Miyaura pallado-catalyzed cross-coupling to introduce different moieties. Several methods were tested to generate water-soluble flavins, yielding a small library of water-soluble molecules under neutral pH, slightly basic and acidic conditions.



A method for flavin functionalization via radical transfer using a copper complex had been developed in the laboratory. In contrast to the mono-bromination set up, which enabled functionalization at C₉ only, selectivity at C₆ via a radical mechanism was elucidated using DFT calculations (Dr. C. Gourlaouen). A high electron density is observed on the C₆ carbon compared to the C₉. Copper is therefore of considerable importance in modulating this selectivity. This mono-functionalization is interesting from a molecular weight point of view (cf. techno-economic constraints of redox-flow batteries).

To meet the structural requirements outlined above, we have set up a method for the selective post-functionalization of flavin at C₉ or C₆/C₉ from flavin ligand, and a selective method at C₆ from the copper complex. A small library of water-soluble molecules has now been synthesized, and redox-flow battery analyses are underway.

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Novel iron-based catalysts for photoinduced reversible hydrogen transfer reactions

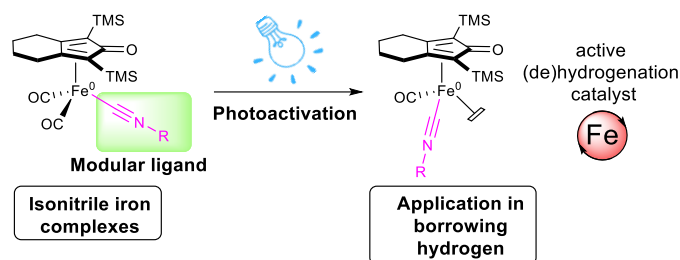
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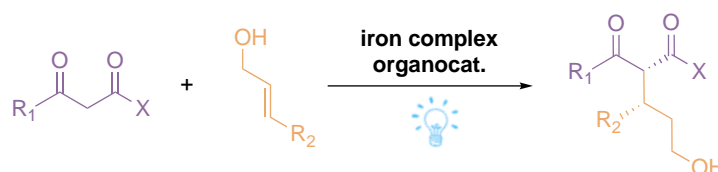
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The quest for sustainable and cost-efficient synthetic processes has led to the development of iron cyclopentadienone catalysts, replacing costly noble metal complexes notably for hydrogen transfer reactions. These catalysts, featuring cooperativity between iron and the cyclopentadienone ligand, provided unique reactivities, particularly in borrowing hydrogen reactions.¹⁻² Modification of these catalysts has mainly focused on changing the cyclopentadienone core, but little has been done with the iron tricarbonyl structure. In order to potentially enhance the activity of these complexes and obtain different reactivities, the CO ligands were replaced by different isonitrile ligands, creating a library of modular complexes.³



These catalysts demonstrated notable activity, surpassing classical catalysts, in a photoinduced multicatalytic borrowing hydrogen process. This enabled easy enantioselective functionalization of allylic alcohols under mild conditions.



To gain a comprehensive understanding of these complexes' reactivity and establish a structure-activity relationship, their behavior was carefully investigated by spectroscopy and computational chemistry. This approach offers profound insights into the catalyst's activity origin and properties.

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Zr(IV) based chelates for innovation in diagnostic techniques

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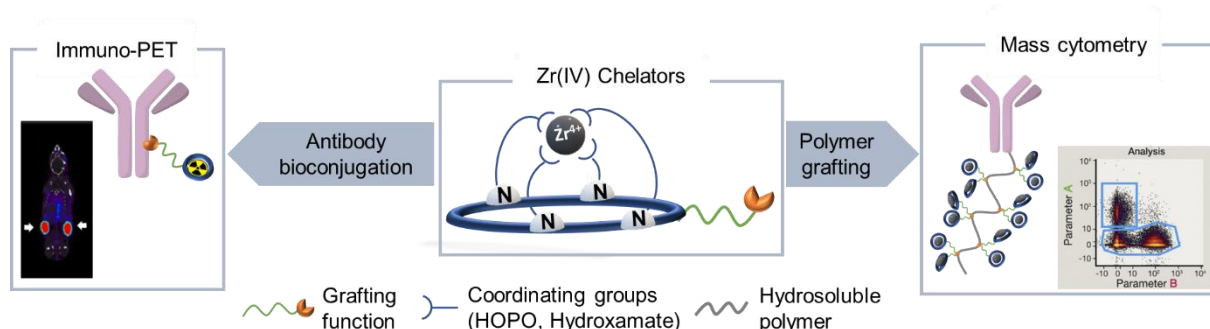
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Cancers and many serious diseases are becoming increasingly complex to study, although it seems judicious to elucidate their origin, behaviour and mechanism to enable earlier and more reliable diagnosis to improve and personalize the associated curative treatment.

Among the imaging modalities, PET-imaging is particularly sensitive and provide anatomic images. In this way, $^{89}\text{Zr(IV)}$ is currently the subject of intense researches since its half-life ($t_{1/2} = 78.4 \text{ h}$) is long enough to be coupled to biological moieties with slow pharmacokinetics (ie. Antibodies) able to detect tumours difficult to reach. The currently used ^{89}Zr chelator, desferrioxamine B (DFO), has however some stability limits leading to the release of free ^{89}Zr that accumulates in bones and causes bones metastasis.^[1]

In the field of monocellular scale diagnostic, mass cytometry (MC) is a particularly powerful technique which reveals the composition of immune system cells (proteins, peptides, DNA, etc.) and therefore their role in both physiology and pathology. The principle derives from flow cytometry but the targeted cells parameters are detected by mass spectrometry. The unique properties of MC enable the identification of rare cellular populations, thanks to antibodies labelled with polymers functionalized with multiple copies of the same metal chelate.^[2] Zr(IV), with its 4 stable isotopes, is interesting for this technique. So far, only one Zr(IV) containing polymer for MC has been synthesized. It employs DFO as Zr(IV) chelator but is limited by a low aqueous solubility.^[3]

The aim of this work is to develop new stable and inert Zr(IV) polyazamacrocyclic chelators functionalized with HOPO or hydroxamates coordinating groups, soluble in biological media and including a reactive chemical function. In this way, there will be usable for the conception of ^{89}Zr radiopharmaceuticals for immuno-PET or for the design of Zr(IV) chelating polymers for mass cytometry.



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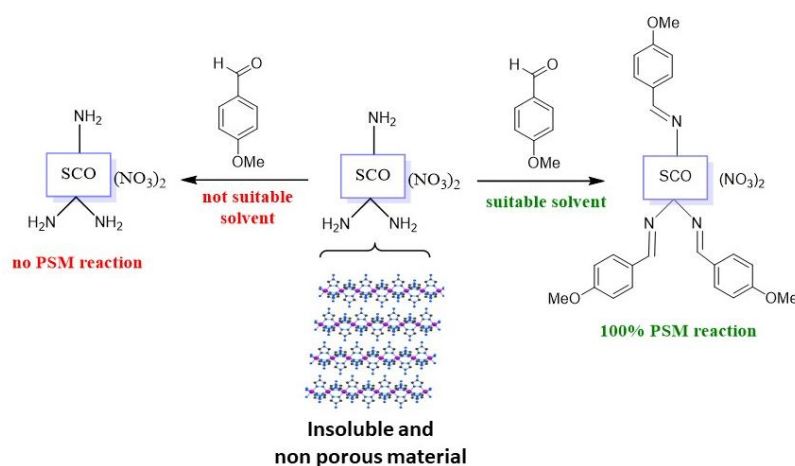
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POST-SYNTHETIC MODIFICATION MECHANISM FOR 1-D SPIN CROSSOVER COORDINATION POLYMERS

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The post-synthetic modification (PSM) of different materials, has emerged as an efficient tool to chemically modify an already prepared material with functional groups that could not be obtained by a direct approach. However only a few reports concerning PSM in chain-like iron-triazole spin crossover complexes has been published.

We have previously demonstrated the attractiveness of PSM reactions of the spin crossover complexes $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{X}_2$ with different functional groups.^[1-2] In most cases we also synthesized the evaluated complexes by a direct synthesis (DS) in order to compare them with their corresponding PSM complexes. We have noted that the spin transition properties of the materials depend on the synthesis method used. Here we present a comprehensive study of the influence of the solvent on the PSM on the $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$ spin crossover complex with p-anisaldehyde. The use of a suitable solvent such as ethanol results in a complete PSM, where the final crystalline material exhibits a gradual conversion just below room temperature in the other hand when an unsuitable solvent such as toluene was used, either no reaction or very long reaction time is needed, leading to undesired Fe(III) species.^[3]



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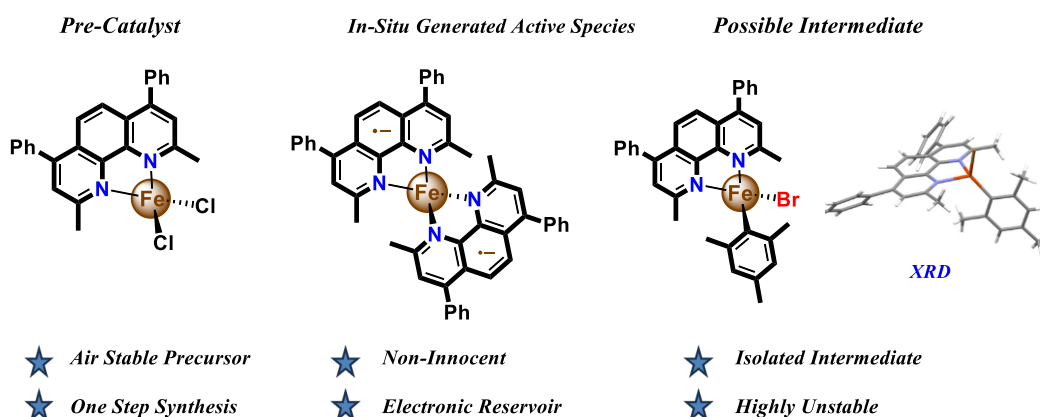
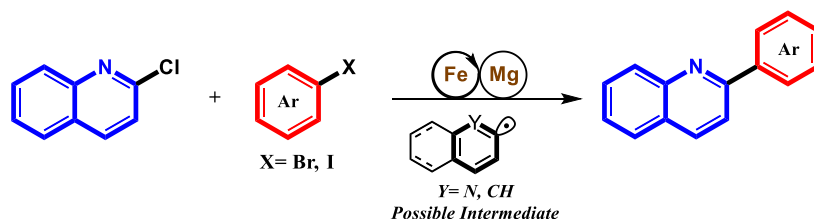
Exploiting the power of non-innocent iron complexes for C(sp²)-C(sp²) bond formation in mild conditions

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Cross electrophile coupling (CEC) reaction is a promising methodology for forging C-C bonds as it involves the use of commercially available starting materials without the need of converting them to hazardous organometallic species. Despite numerous works in this field dominated by nickel¹ and noble metals, this approach has not been extensively studied with iron. In this work, reductive coupling of an aryl halide with a heteroaryl halide is achieved using a new low valent non-innocent iron system² and magnesium as an electron source under mild conditions and straightforward procedure. Preliminary results have shown that the major factor influencing this system is the redox potentials of the two partners. Preliminary mechanistic studies suggest a radical-based process, and reactivity of transient Ar-Fe(II) intermediates will be discussed.



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FROM PSM REACTION ON IRON-TRIAZOLE SPIN-CROSSOVER COMPLEXES TO THEIR USE IN CATALYSIS

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Molecular spin-crossover (SCO) complex represents promising magnetic, dielectric, optical, mechanical, and thermal properties with high potential for applications. These transition metal complexes of certain third-row transition metal ions exhibit reversible switching between their low spin (LS) and high spin (HS) electronic configurations under various external stimuli (such as temperature, pressure, light radiation, etc.)^[1].

In our recent work, we found that SCO complexes are not only promising for post-synthetic modification (PSM) reactions, which have attracted more attention as an efficient tool to perform a chemical transformation on previously synthesized materials^[2-4], but also can be used as reaction catalysts. For example, the presence of this SCO complex allows the quantitative formation of the imine in a few minutes.

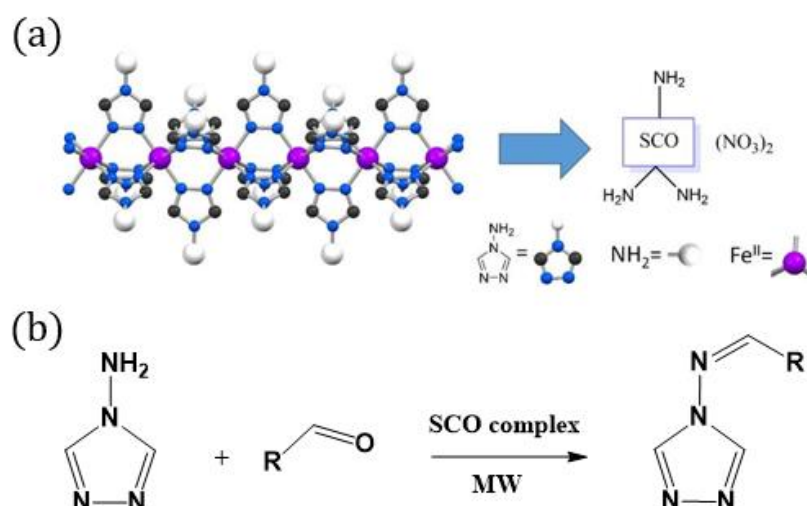


Figure 1. (a) 1D polymeric structure of the [Fe(NH₂trz)₃](NO₃)₂ and its corresponding schematics. (b) Formation of the imine catalysed by SCO complex

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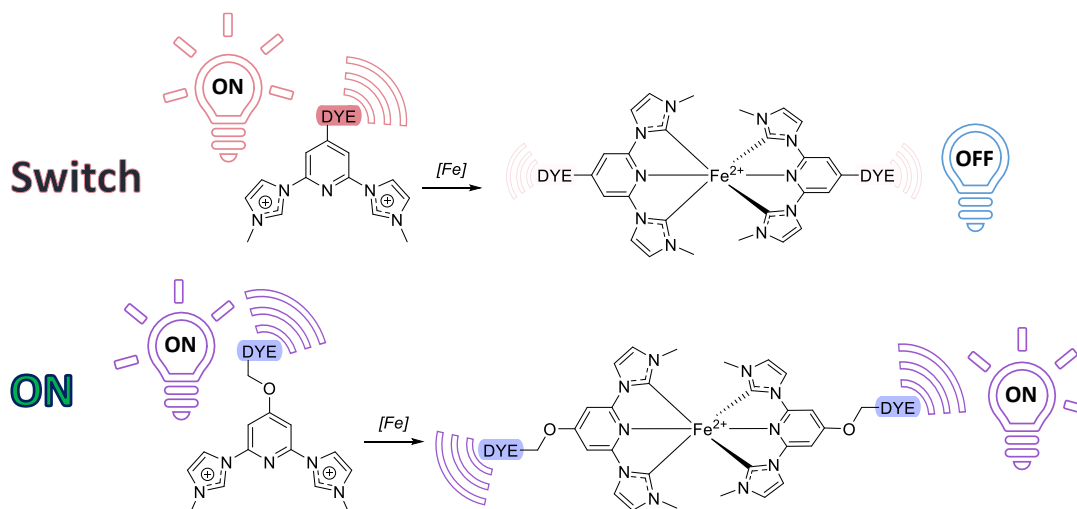
Manipulating the photoinduced electron transfer in iron complexes by chemical design

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Photoactive metal complexes are extensively used in numerous application fields, including drug discovery,¹ bioimaging,² magnetism,³ and so forth. For such applications, Fe-based complexes are desirable due to their low environmental impact and extraction cost,⁴ although controlling their photoactivity is challenging, due to the contracted 3d-orbitals leading to ultrafast non-radiative relaxation,⁵ only a few examples of emitting Fe-complexes with long-lived excited states (nanoseconds) are reported.⁶ Rationalizing the structure-optical properties in Fe(II) complexes is a crucial point to accelerate the development of photoactive Fe(II) complexes and their application.

In this regard, we develop an approach aiming at understanding and controlling the photoinduced energy transfer (PET) processes responsible for the fluorescence quenching properties of the Fe(II) center toward fluorescent dyes (DYE) by chemical engineering. We show that by chemical design, in function of the degree of conjugation of the Dye-ligand-Fe(II) system, it is possible to either quench the fluorescence of a dye, thus acting as a fluorescence turn-off system (switch), or even maintain the emission (ON).⁷



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Binuclear Copper(I) Complexes for Near-Infrared Light-Emitting Electrochemical Cells

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Photoactive complexes based on earth-abundant metal are currently the subject of intensive research that is mainly driven by their appealing applications in the field of photocatalysis, solar energy conversion and light emitting devices. In particular, Cu(I)-based emitters are considered as an attractive alternative to those containing rarer and more expensive metals for the development of electro-luminescent materials. However, due to the much smaller spin orbit coupling (SOC) effect exerted by copper ion compared to Ir and Pt, it results that luminescent Cu(I) complexes typically possess slower radiative rate constants and longer-lived excited states.^[1] This is a severe drawback that needs to be tackled for their suitable application in efficient solid-state light-emitting devices. Furthermore, Cu(I) complexes typically display emission spectra covering the blueish-green to orange region, while designing compounds that efficiently emits beyond 700 nm from deep-red to near-infrared (NIR) region is still highly challenging.^[2,3] This is in spite of the fact that NIR emitters are very appealing for the fabrication of light-emitting devices for night vision display and optical telecommunication technology as well as biological imaging agents.

Herein, a novel class of cationic bimetallic copper(I) complexes with general formula $(\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N}-\text{N}^{\wedge}\text{N})\text{Cu}(\text{P}^{\wedge}\text{P}))^{2+}$, where $\text{N}^{\wedge}\text{N}-\text{N}^{\wedge}\text{N}$ is a *bis*-chelating scaffold based on the thiazolo[5,4-*d*]thiazole unit is presented. The emission maxima in CH_2Cl_2 solution span over almost 100 nm between 700 and 800 nm and X-ray analysis reveals two interligand π - π stacking interactions yielding a doubly locked structure that disfavours flattening of the tetrahedral coordination around the Cu(I) centre in the excited state and keeps enhanced NIR luminescence. These complexes features allowed the successfully fabrication of the first examples of stable NIR light-emitting electrochemical cells (LECs) based on Cu(I) complexes that display electroluminescence maximum $\lambda_{\text{EL,max}}$ up to ca. 780 nm and peak external quantum efficiency (EQE) of 0.43%.^[4,5]

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Novel Photoluminescent Ruthenium(II) Bipyridyl Complexes Containing Phosponium Ylide Ligands

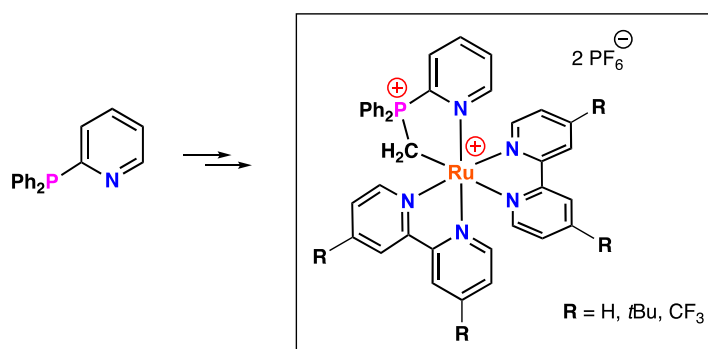
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Taking advantage of their high chemical stability and the relative ease of modifying the nature of their ligands, ruthenium(II) bipyridyl complexes have been extensively studied for their unique redox and photophysical properties.¹ Given the beneficial effect of introducing σ -donating N-heterocyclic carbene ligands (NHCs) such as the destabilization of ³MC states with longer excited state lifetimes,² we considered the incorporation of phosphonium ylides in these octahedral metallic edifices as another class of electron-rich neutral carbon ligands. Indeed, phosphonium ylides are more σ -donating than NHCs³ and moreover, with the exception of very rare cases, have never been evaluated for their photophysical properties.⁴

In this contribution, we report thus the straightforward preparation of the first photoluminescent ruthenium(II) bipyridyl complexes with the general formula [Ru(C⁺N)(bpy-R)₂](PF₆)₂ (R = H, *t*Bu, CF₃) containing C,N-chelating pyridine-phosponium ylide ligands from readily available 2-(diphenylphosphino)pyridine. Structural, spectroscopic, electrochemical and photophysical properties will be discussed. Application of these phosphonium ylide-based Ru(II) complexes in visible-light photoredox catalysis for the formation of C–C bonds through the Aza-Henry reaction will be also detailed.⁵



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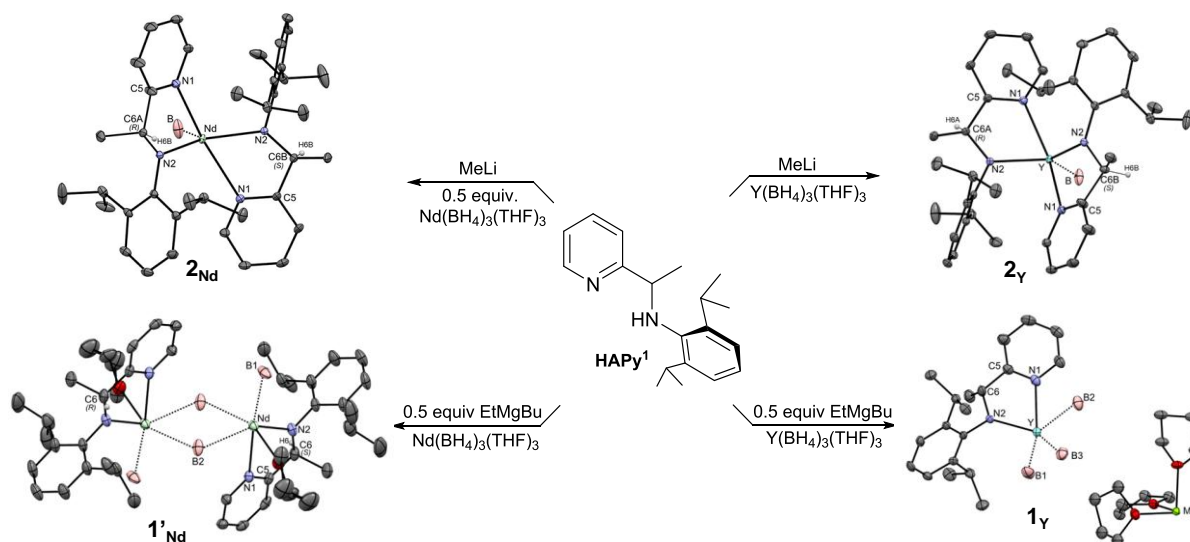
Synthesis and Characterization of Borohydride Rare-Earth Complexes Supported by 2-PyridinemethanAmido Ligands and their Application towards ROP of Cyclic Esters

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The coordination chemistry of non-Cp derivatives of rare-earth (RE) complexes has attracted growing interest over the past three decades, particularly for their diverse applications in homogeneous catalysis [1]. Nevertheless, RE complexes supported by nitrogen-based ligands, in particular those comprising a bidentate 2-pyridinemethanamido chelate of the type C₅H₄N-C(R₂)-(R')N- (where R = alkyl or H; R' = alkyl or aryl), remained scarce [2], despite the fact that these ligands provide a versatile platform that allows a wide variation in the coordination and/or electronic/steric properties of the resulting complexes. Therefore, in this study, we focus our attention on the coordination chemistry of different monoanionic 2-pyridinemethanamido ligands **PyA**¹, **PyA**², **PyA**³ with **ytrium** and **neodymium**, two typical representatives of the “late” and “early” RE sub-group, respectively. The impact of the reaction conditions and the substituent of the **PyA** ligands in the 6-position of the pyridine ring [H for **PyA**¹, Me for **PyA**² and C(Me)=N-(2,6-*i*Pr₂C₆H₃) for **PyA**³] towards the coordination chemistry with **Y** and **Nd** **trisborohydrides** as precursors (see example for **PyA**¹ in **Scheme 1**), as well as the potential application of the resulting complexes in the Ring-Opening Polymerization (ROP) of cyclic esters, will be presented here [3].



Scheme 1: Influence of experimental conditions on the coordination chemistry of Y and Nd with the **PyAH**¹ pro-ligand.

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CLUSTERING SIX ELECTRONS WITHIN “DAWSON-LIKE” POLYOXOMETALATE

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Polyoxometalates (POMs) represent one class of fascinating inorganic molecules built from transition metals in their highest oxidation states (V^{5+} , Mo^{6+} , and W^{6+}). One of the most striking properties of POMs is their ability to exchange massively electrons in aqueous solution, making them highly relevant “electron reservoirs” for developing innovative electrochemical energy-storage systems. For instance, the Cronin's team has recently demonstrated that the classical Dawson-type POMs $[P_2W_{18}O_{62}]^{6-}$ can accept up to 18 electrons without POM decomposition.^[1,2] Curiously, the fundamental investigations about the structure and reactivity of such super-reduced POMs remain unexplored.^[3] The purpose of my PhD project is to fill this lack of knowledge.

In this communication, we will show that the “Dawson-like” POM $[H_2AsW_{18}O_{60}]^{7-}$ can undergo a disproportionation process during its massive electron uptake, leading to species containing three metal-metal bonds as evidenced by single-crystal X-ray diffraction, multi-nuclear magnetic resonance spectroscopy (1H and ^{183}W NMR), extended X-ray absorption fine structure (EXAFS), UV-vis, and voltammetry techniques.^[4] This result evidences that electron storing within metal-metal bonds is not a unique property of Keggin-type POM as postulated since the 70s. Besides, we will demonstrate that the presence of an electron-rich triad in the “Dawson-like” POM allows its post-functionalization with additional tungstate ions, generating a chiral molecule that is also the largest W^{IV} -containing POMs known to date.

If time allows, we will also report the clustering of 12, 18 and 24 electrons within POMs.

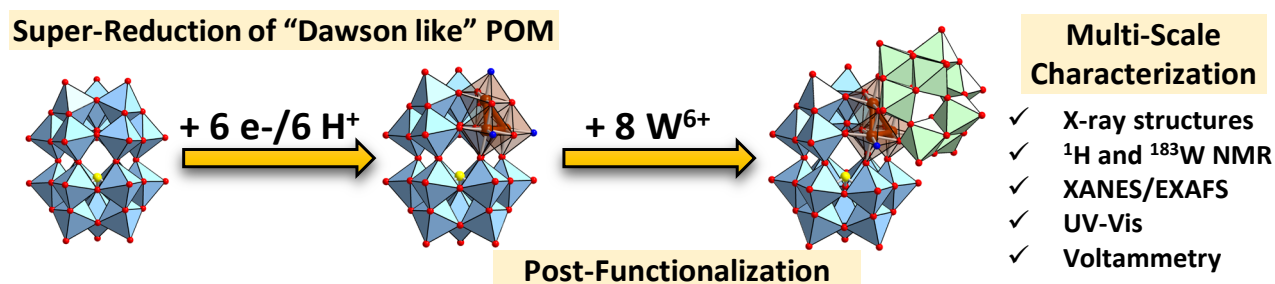


Figure 1: Schematic representation showing the formation of $[H_2AsW^{VI}_{15}W^{IV}_3O_{57}(H_2O)_3]^{7-}$, compound induced by the six-electron reduction of $[H_2AsW_{18}O_{60}]^{7-}$ in acidic solution and its post-functionalization with 8 additional tungstate ions.

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Sulfoxide functionalized N-heterocyclic carbene complexes of Ru(II) : synthesis, coordination mode and catalytic activity

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Keywords: ruthenium, sulfoxide, N-heterocyclic carbene, catalysis

N-heterocyclic carbenes (NHCs) are esteemed ligands due to their notable thermal stability, customizable steric and electronic attributes, and strong sigma-donor characteristics. Their transition-metal complexes offer diverse catalytic applications.^[1] While the majority of NHCs function as monodentate ligands, the chemistry of hybrid NHCs, incorporating an additional Lewis base site typically bound to an N, P, or O atom, has garnered significant attention over the past decade and remains an area of active exploration.^[2] S-functionalized NHCs represent a less explored subset of ligands;^[3] nonetheless, they have demonstrated efficacy as ligands in various metal-catalyzed reactions, particularly for NHC thioether and sulfoxide derivatives.^[4]

Our research focuses on developing N-heterocyclic carbene (NHC) ligands bearing a sulfoxide moiety. Upon coordination, the prochirality or chirality of the ruthenium and sulfur center is anticipated to result in a complex diastereomeric mixture. In this study, we synthesized and fully characterized a series of cationic (κ^2 -C,S)-[Ru(II)(η^6 -cymene)(NHC-SO)][PF₆] complexes. Surprisingly, only one diastereomer (forming an enantiomeric pair) was observed in each case. To elucidate the factors influencing this selectivity, we conducted DFT calculations, variable-temperature NMR spectroscopy (VT-NMR), and X-ray diffraction analysis, considering aspects such as hemilability, sulfur inversion, and steric effects.

Finally, the catalytic activity of these complexes was explored in the β -alkylation of secondary alcohols with primary alcohols.

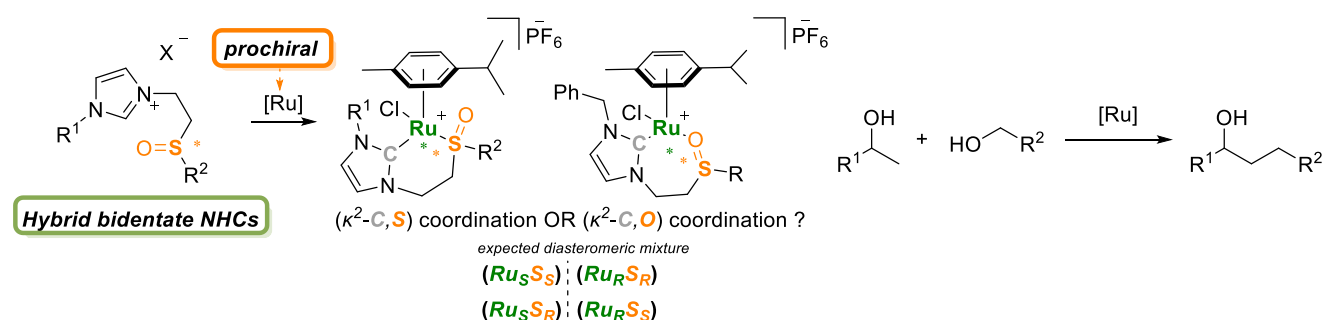


Figure 1 (Ru(II)(η^6 -cymene) complexes) and their applications in catalysis

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Heterobimetallic complexes associating tantalum and 3d transition metals as potential candidates for cooperative bond activation

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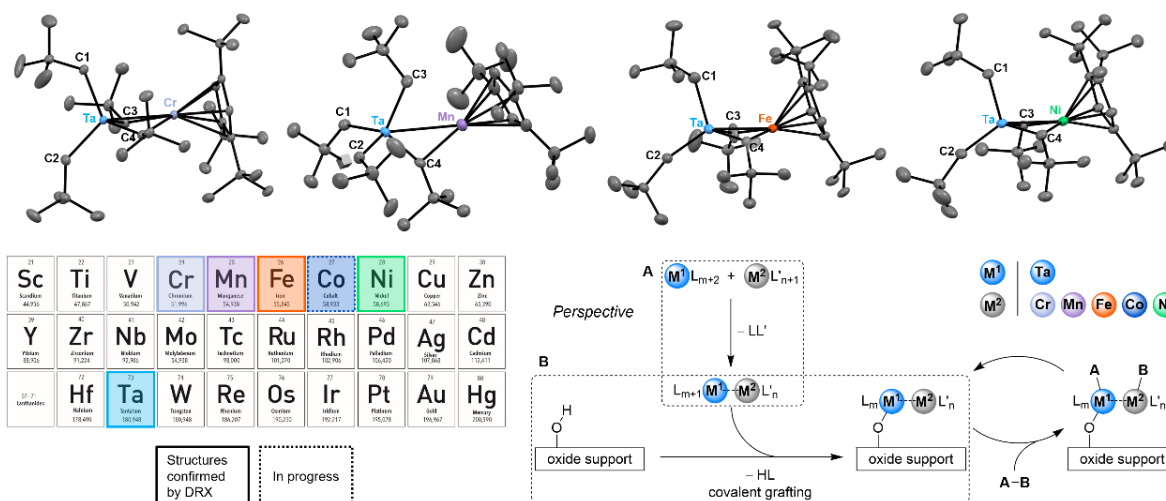
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Over recent years, chemists have sought to tackle the challenging activation of kinetically inert bonds in small molecules and hydrocarbons by developing catalysts combining two different metal centers in a single molecule.^[1–3] Heterobimetallic systems relying on a cooperative interaction between early and late transition-metal centers which feature diverging electronegativities and Lewis acidities are highly promising because the strongly polarized metal pair is expected to enable concerted heterolytic bond cleavage *via* unusual pathways, as highlighted for a tantalum-iridium complex by Camp and co-workers at the CP2M laboratory.^[4,5]

Salt metathesis between an alkali-stabilized tantalate complex, $[\text{Li}(\text{thf})_2][\text{Ta}(\text{C}^t\text{Bu})(\text{CH}_2^t\text{Bu})_3]$, and a series of alkylcyclopentadienyl 3d transition metal halide dimers, $[\text{Cp}'\text{M}(\mu\text{-X})_2]$ ($\text{Cp}' = 1,2,4\text{-}^t\text{BuC}_5\text{H}_2$, $\text{X} = \text{Cl}, \text{Br}$ or I), was developed as a powerful synthetic strategy towards novel perhydrocarbyl-stabilized heterobimetallic Ta—M complexes in which the expensive, heavy 5d transition metal ($\text{M} = \text{Ir}$) is replaced by less onerous first-row transition metal ions ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$ [in progress], Ni). Exploring their solution-state reactivity is particularly interesting as 3d transition metals incorporated into heterobimetallic complexes can promote unprecedented mechanisms of CO_2 and H_2 activation supposedly involving open-shell intermediates, as shown very recently for iron.^[6,7] In this communication, we will discuss and compare the unusual structures as well as the bonding and cooperative reactivity of this series of compounds featuring atypical alkyl / alkylidene / alkylidyne tautomerisms.



Crystal structures of a series of novel tantalum-3d transition metal complexes and project perspectives.

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POSTERS

Thiolate-supported iron-nitrogen adducts relevant to the nitrogenase FeMo-co

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Nitrogen bioavailability is limited by the chemical inertness and stability of N₂ gas. The conversion of molecular nitrogen to ammonia (NH₃) is a fundamental process. In nature, it is carried out at ambient pressure and temperature by bacterial nitrogenases, thanks to the organometallic FeMo cofactor. This catalytic site is a [Mo:7Fe:9S:C]:homocitrate cluster which triggers the N₂ reduction process thanks to a sulfur-rich diiron unit.¹ A number of complexes have been reported to be able to carry out nitrogen coordination and/or stoichiometric or catalytic reduction. However, among them, a small number of these complexes incorporate the bio-inspired sulphur motif.²

In this context, we have investigated the reactivity of bio-inspired bimetallic Fe^{II} complexes supported by a thiolate-rich N₂S₂-ligand (Figure 1) with nitrogenase-relevant substrates. The objective was the detection or isolation of thiolate-iron/nitrogen adducts mimicking possible intermediates in the catalytic N₂ reduction cycle of the FeMo-co. More specifically, the bimetallic [Fe^{II}(LS)]₂^{3,4} and [Fe^{II}(LSMe)]₂ have been used as starting complexes, and their reactivity with N₂H₄, N₃⁻, and N₂ (the latter under reducing conditions) has been explored.

During these studies:

1. We could detect spectroscopically many reduced adducts even if evidences of N₂ coordination/activation are currently lacking;
2. we have observed the formation of an hydrazine adduct ([Fe^{II}(LS)N₂H₄], **Figure 1**) able to react with MeCN to form a Fe-acetohydrizonohydrazide species;
3. We could also isolate the two Fe^{II}-azido adducts ([Fe^{II}(LS)N₃]⁻ and [Fe^{II}(LSMe)N₃], **Figure 1**) and their photoactivation tests to generate Fe-nitride complexes from them are currently in progress.

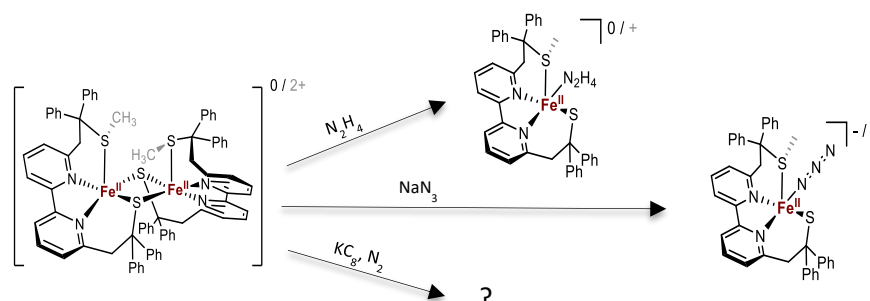


Figure 1: Schematic representation of the synthesis of the reactivity of the initial [Fe^{II}(LS)]₂ and [Fe^{II}(LSMe)]₂ complexes.

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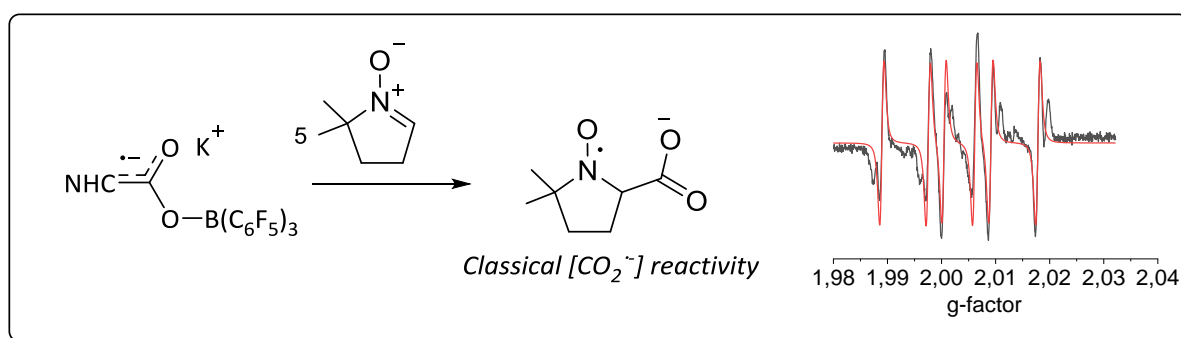
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Synthesis and reactivity of reduced NHC-CO₂-borane adducts

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In the context of utilizing CO₂ as a sustainable carbon source, there is a compelling interest in identifying CO₂ activation methods facilitating a more accessible one-electron reduction to obtain [CO₂^{•-}]. Our focus was on the single electron reduction of Frustrated Lewis Pair (FLP)-type activated CO₂ molecules, achieved through a bifunctional activation involving both Lewis basic and Lewis acidic entities. N-Heterocyclic Carbenes (NHCs) were selected for their significant electronic and steric modularity, along with their known ability to stabilize radical species.^[1] We thus studied the reduction of NHC-CO₂-BR₃ species. We showed that these species undergo mono-electronic reduction at a less negative potential compared to free CO₂ and exhibit similar reactivity as [CO₂^{•-}], nonetheless.^[2]



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Temperature-controlled orthopalladation regioselectivity in (2-indolyl)(diphenyl)iminophosphorane ligands

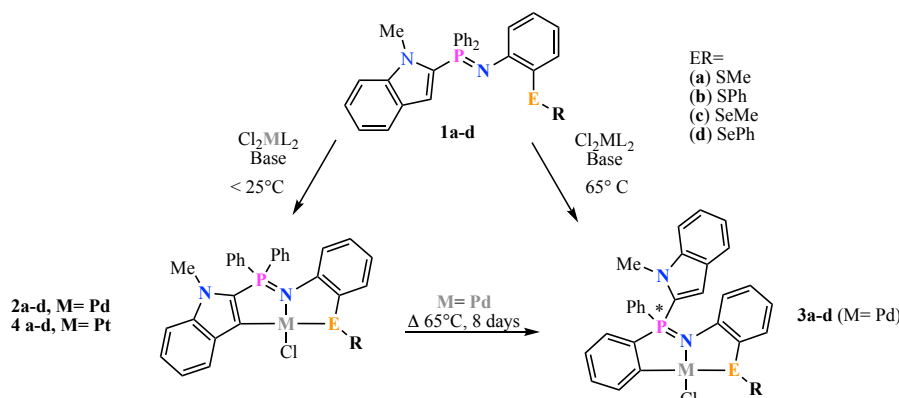
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Four novel tridentate ligands, denoted as (**1a-d**), were synthesized from (2-indolyl)diphenylphosphine¹ and functionalized with thio- or seleno-ether pending arms through the Staudinger reaction using azides of the corresponding thio- and seleno-anilines², resulting in compounds of general formula 2-C₉H₈N(Ph₂P)=NC₆H₅ER [ER= SMe (**1a**), SPh (**1b**), SeMe (**1c**), SePh (**1d**)]. These ligands were obtained with excellent yields and fully characterized. Upon coordination with Pd(II), their reactivity revealed a temperature-dependent metalation regioselectivity. At lower temperatures (< 25°C), palladation predominantly occurred at the 3-position of the indole, forming non-symmetric pincer complexes CNX (X= S, Se) (**2a-d**). Conversely, at higher temperatures (> 50°C), metalation shifted to the ortho position of one phenyl group, resulting in chiral phosphorus centers (**3a-d**). At room temperature, selenium-coordinated complexes **3c,d** displayed a significant inversion barrier, generating a second chiral center within the molecule. All orthometalated complexes showed remarkable stability at elevated temperatures, with no isomerization observed into the indole metalation complex. Conversely, extended heating of complex **2a** at 65°C led to its slow isomerization into complex **3a** over a week. Each complex underwent thorough characterization, with complex **2a** additionally analyzed by X-ray diffraction, confirming the non-symmetric clamp-type structure CNE (E= S, Se) in all cases.

In contrast to palladation, platination was found to be temperature-independent, yielding solely the corresponding non-symmetric pincer complexes **4a-d** CNE-Pt(II) (E= S, Se) through metalation of the indole at its 3-position. These complexes were fully characterized using classical structural analysis methods and complex **4a** additionally analyzed by X-ray diffraction. They all displayed high stability in both solid-state and solution, even in the presence of water, without undergoing isomerization upon heating.

This study represents a rare example of temperature-controlled orthopalladation regioselectivity.



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Rh₂(phesp)₂: a bulky and efficient version of Du Bois' Rh₂(esp)₂ catalyst for carbene insertion into C(sp³)-H bonds

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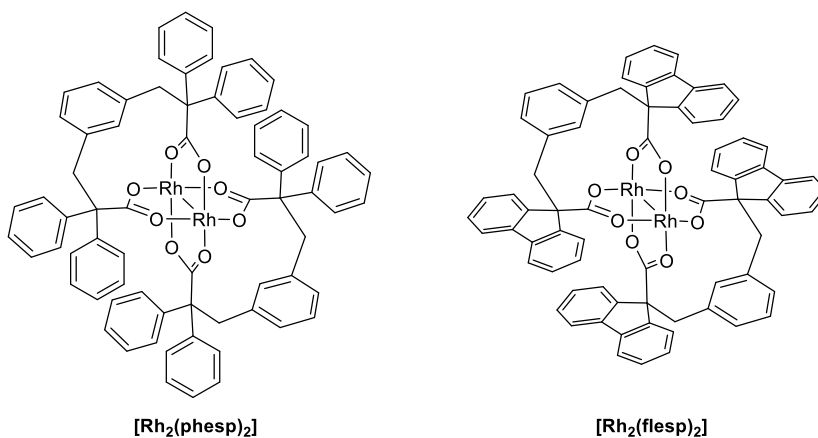
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The selective functionalization of nonactivated C-H bonds, largely inert to chemical transformations, is one of the main challenges in organic synthesis. It becomes even more challenging when selectivity toward one particular C-H bond is required.^[1] Dirhodium(II,II) species are among the best catalysts to carry out such transformations in the presence of suitable carbene precursors. It has been shown that the nature of equatorial ligands around the dirhodium(II) core plays a huge role on the reaction outcome: by carefully tuning electronic and steric properties of the catalyst, significantly different selectivities can be obtained.^[2]

As part of these efforts toward catalyst-controlled selective C-H functionalizations, getting inspiration from robust and highly reactive Rh₂(esp)₂^[3] and of highly selective Rh₂(tpa)₄,^[4] we have designed new ligands. The synthesis of the Phesp and Flesp ligands and their coordination chemistry with dirhodium(II) will be presented. Their potential as catalysts for the intra- or intermolecular insertion of diazo compounds into C-H bonds will also be disclosed.



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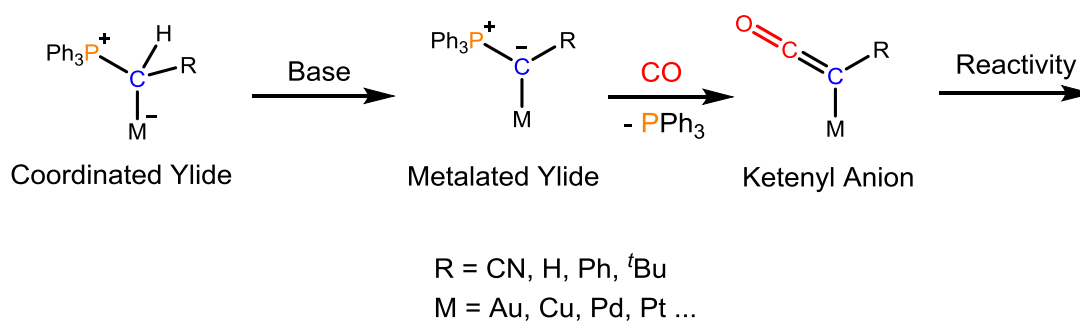
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Synthesis and reactivity of ketyl anions

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Carbon monoxide (CO) is an inexpensive C1 source that is available from fossil resources and biomass in large quantities and is therefore a sustainable building block for synthetic chemistry.^[1] Recent reports have demonstrated metal-free activation of small molecules such as H₂, CO₂, N₂ and CO.^[2] Recently, our group has developed a new synthetic route for the synthesis of stable ketyl anions and then of various functionalised ketenes by the addition of an electrophile. These compounds are synthesised from the reaction between a metalated ylide and CO.^[3] Ketenes are usually generated in situ and directly converted to the final products due to their intrinsic reactivity, demonstrating the power of our strategy. The ketyl anion is synthesised with an electron-withdrawing group (R = P(S)Ph₂,^[3] CN^[4] or SO₂tol)^[5] to stabilise the double negative charge of the metalated ylide. The use of an electron-donating group remains challenging. Ketyl anions have previously been synthesised with an alkaline metal (Li, Na or K) resulting in a weak interaction between the latter metal and the anion. In order to stabilise the negative charge and to gain access to new metalated ylides (R = H, Ph, ^tBu) and ketyl anions, we have switched to transition metals (Au, Cu, Pd, Pt...). The reactivity of these new compounds will be discussed through an experimental and computational investigation.



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Synthesis of Cobalt-Expanded Zirconium- and Cerium-Oxo Clusters as Single Molecule Precursors for Mixed-Metal Oxide Thin Films

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The transformation of current complementary metal-oxide-semiconductor (CMOS)^[1] technology for memory chips and microprocessors into greener electronics requires the development of new approaches to resource- and energy-efficient electron transport and switching materials. Metal^[2] and multi-metal^[3] oxide films play a key role in high-end technical applications; however, their production conventionally involves high-energy, high-temperature processes. Here we present our first attempts to obtain stimuli-responsive mixed metal oxide thin films from solution-processed molecular precursors under milder conditions. A good starting point are carboxylate-supported metal-oxo cluster compounds, which have been proven to offer a viable path to polynuclear and potentially heterometallic coordination clusters.^{[4], [5]}

The targeted compounds were prepared by one-pot reactions of a Co(II) carboxylate complex, triethylamine (Et₃N), N-butyldiethanolamine (H₂bda) and a hexanuclear complex [Ce₆O₄(OH)₄(piv)₁₂] (Hpiv = pivalic acid) or [Zr₆O₄(OH)₄(ib)₁₂(H₂O)]·3Hib (Hib = isobutyric acid) in acetonitrile solution. The resulting charge-neutral, heterometallic coordination compounds have a ligand-supported pentanuclear {Ce^{IV}₃Co^{II}₂} core and a dodecanuclear {Zr^{IV}₆Co^{II}₆} core and exhibit thermal stability up to about 100 °C in air. The dodecanuclear compound {Zr^{IV}₆Co^{II}₆} was deposited and analysed on Au(111) and SiO₂/Si(100) surfaces to explore its potential as a single molecule precursor for the preparation of atomically precise, complex mixed metal oxide thin films. Its adsorption characteristics demonstrate the ability to form stable agglomerates on the examined surfaces (Figure 1).

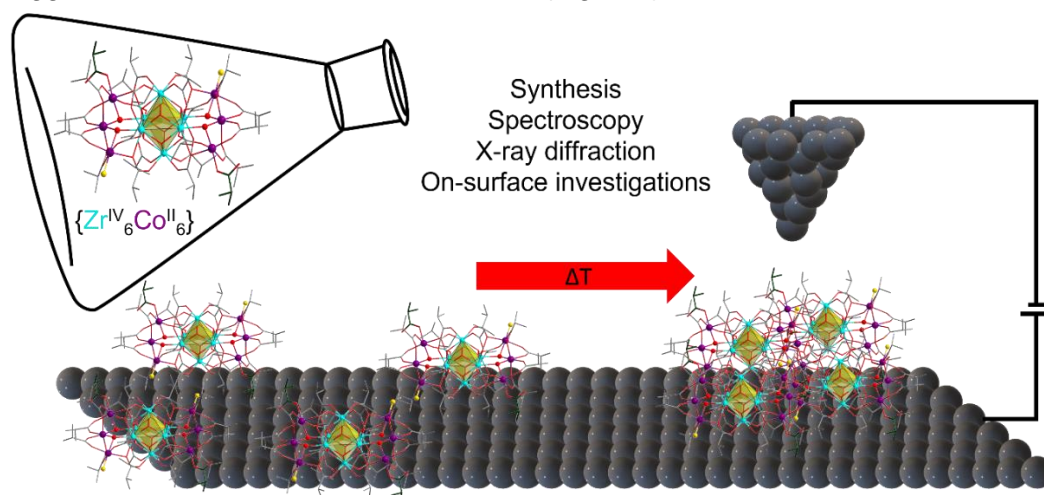


Figure 1. Crystall structure of the {Zr^{IV}₆Co^{II}₆}-based coordination cluster (in flask) and schematic representation of molecular interactions on the surface upon deposition and heating.

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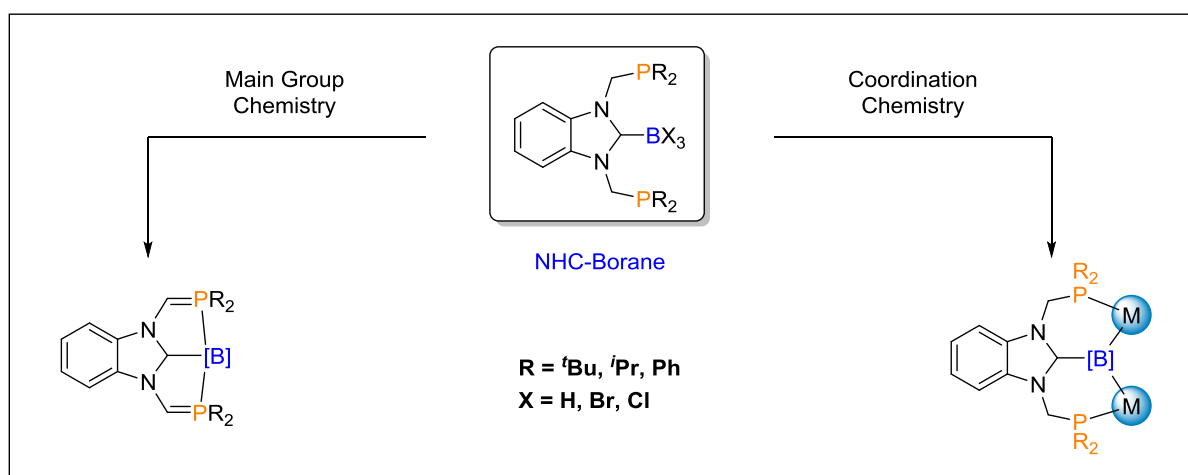
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Study of bisphosphine NHC-borane adducts in coordination and main group chemistry

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Enzymatic catalyzes are prototypical examples of the beneficial role of multimetallic systems for the activation of small molecules. Inspired by this synergetic effect, bimetallic complexes are sought after in the field of small molecules activation.¹ Recently, the synthesis of a bisphosphine [NHC-BH₃] compound was reported in the team as a ligand able to support bimetallic gold structure.² In order to further develop NHC-borane architectures as potential ligands, phosphine and borane substituents were modified. Coordination and main group chemistry were studied and will be presented.



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Use of a geminated dianion as ligand of iron for biomimetic reduction of gas

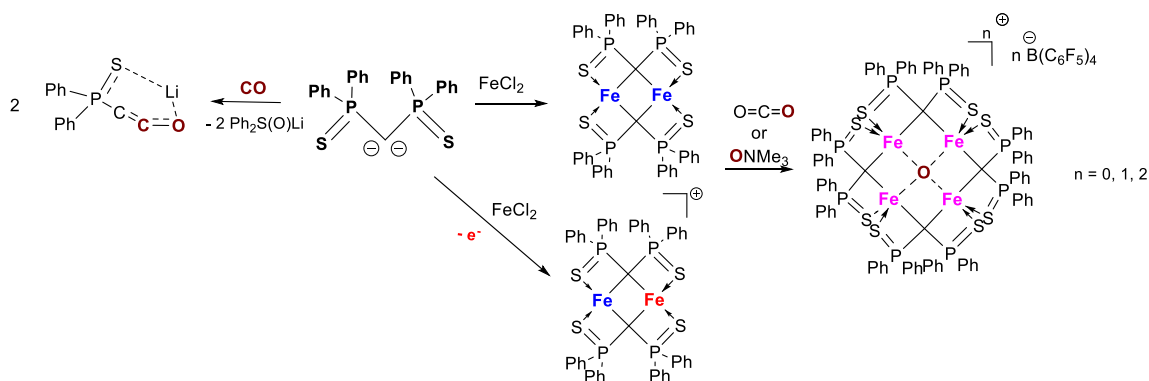
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Nitrogenase cofactors have been extensively studied for their ability to reduce N_2 to ammonia and CO_2 to hydrocarbons.^[1] However, their structure is extremely complex, with a central carbide surrounded by six iron atoms of different oxidation states, which are themselves linked by bridging sulfides. Numerous synthetic models have been proposed to find the simplest structure with relevant reactivity, the carbide ligand being the most difficult to model.^[2]

We propose to use bis-diphenylthiophosphinoylmethanediide as a versatile ligand for the preparation of a variety of tightly bound iron clusters. This gem-dianionic ligand $(S-C-S)^{2-}$ ^[3] enabled us to prepare a range of bimetallic^[4] and tetrametallic^[5] structures, all exhibiting C^{2-} -Fe interactions reminiscent of the structural role of the carbide ligand in FeMo-co. The reactivity of these complexes with CO and CO_2 was studied and compared with this of the nucleophilic, free $(S-C-S)^{2-}$ ligand.^{[6][7]}



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Harnessing Nanocatalysts and Organic Photoabsorbers for Efficient Solar Driven Water Splitting

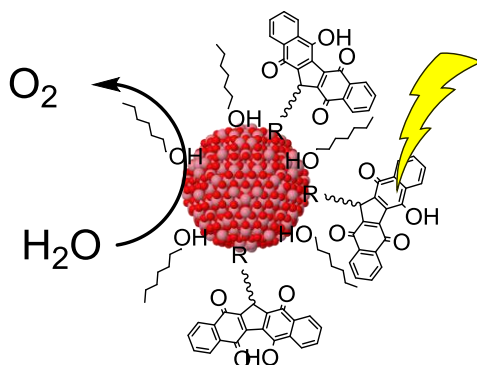
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Addressing global warming requires shifting from fossil fuels to renewables. Water splitting (WS) powered by sunlight is a key solution, but improving the water oxidation (WO) step needs efficient catalysts. Nanocatalysts offer the right compromise between stability and activity.¹ 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, [Ru(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 Co₃O₄ nanoparticles² and KuQuinones (KuQ)³ photosensitizers covalently grafted. Photocatalytic tests were done in colloidal cells and on SnO₂/FTO electrodes. Characterization methods include TEM, HRTEM, RAMAN, ICP, and XAS analysis. KuQ-Co₃O₄ 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, L-shape N-heterobicyclic carbene ligands for asymmetric gold(I) catalysis

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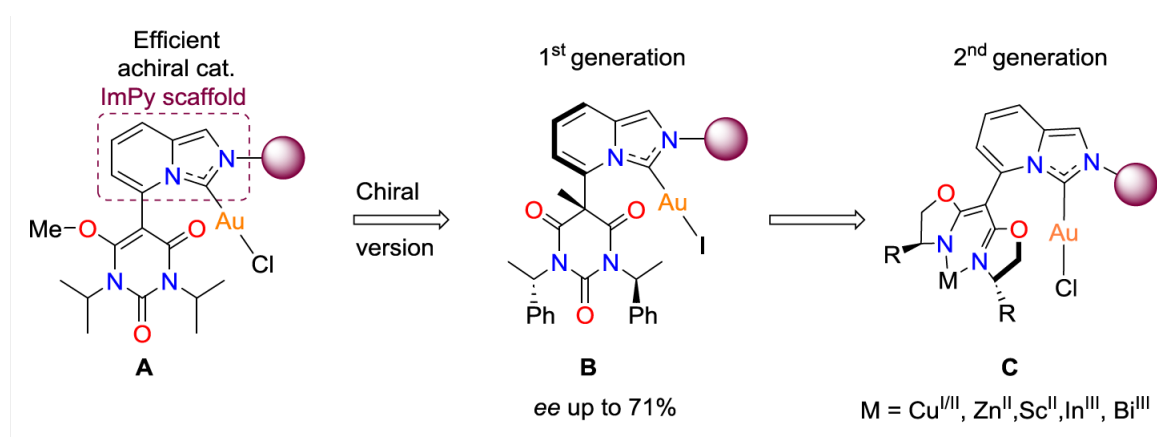
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Despite the outstanding advances realized in homogeneous gold(I) catalysis over the last two decades, the asymmetric version has not experienced the same growth.¹ The main challenge resides in the specific, linear coordination geometry of gold(I) complexes, which limits an efficient chirality transfer from the ligand to the substrate. In 2019, our groups reported that the “achiral”, tunable catalysts **A**, supported by a “L-shape”, bicyclic imidazo[1,5-a]pyridin-3-ylidene (ImPy) ligand laterally-functionalized by a barbituric heterocycle, are highly efficient in gold(I)-catalyzed C-N, C-O, and C-C bond formations.²

We present herein our progresses towards efficient chiral catalysts based on this privileged ImPy platform.³ The first generation is composed of chiral ImPy-Au(I) complexes **B** featuring a chiral lateral barbituric heterocycle obtained from enantiopure (*S*)-1-phenylethylamine. The use of the chiral pre-catalysts **B** in the domino cycloisomerisation/nucleophilic addition of 1,6-enynes with various nucleophiles gave excellent yields and good enantioinduction (up to 72% ee), resulting in functionalized heterocycles.⁴ As a second generation, the ImPy-Au(I) complexes **C** functionalized with a chiral, lateral bis-oxazolinone moiety was developed in order to improve the transfer of the chiral information.



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Intermolecular bimetallic cooperation for highly efficient amine-borane dehydrogenation catalysis

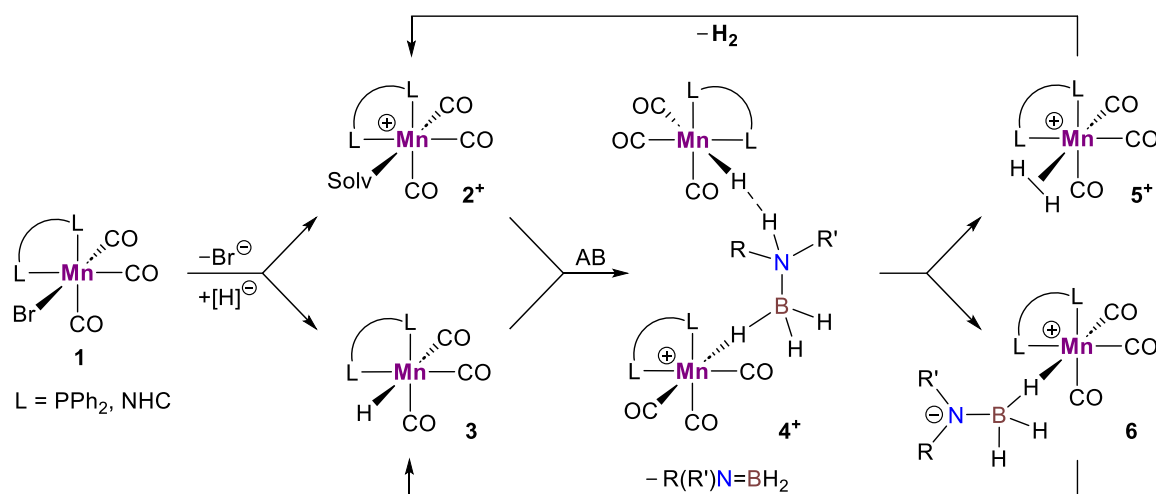
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Cooperative bimetallic activation of inert bonds in organic molecules is one of fundamental principles of coordination chemistry largely exploited in metalloenzymes and related biomimetic systems. While these transformations mostly proceed in *intramolecular* fashion within well-defined binuclear metal complexes, few examples of *intermolecular* cooperative reactivity based on two monometallic species have been recently reported for heterobimetallic Frustrated Lewis Pairs^[1] and Fe/Al radical couple.^[2] We present herein a novel type of intermolecular bimetallic cooperativity observed in Mn-catalyzed dehydrogenation of amine-boranes (see Figure below), in which the concomitant activation of N–H and B–H bonds of the substrate proceeds by a synergetic action between cationic (**2**⁺) and hydride (**3**) metal species generated *in situ* from the corresponding Mn(I) bromide precursors **1**, halide abstractor and bifunctional substrate as hydride donor.^[3] According to spectroscopic, kinetic and theoretical data the formation of the ternary adduct **4**⁺ represents a key step of this process allowing to form dihydrogen and regenerate starting **2**⁺/**3** couple by a sequence of proton and hydride transfers.



The catalytic system based on air-stable Mn(I) bis(NHC) complex **1** and NaBPh₄ shows state-of-the-art performance for a wide variety of amine-boranes at low loading (0.1 mol% to 50 ppm, TON up to 18200) and does not require the activation by strong bases or UV-irradiation typical for other 3d metal catalysts, thus making an important step towards the potential applications in the area of hydrogen storage.

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