

Gem-Binucleophilic Linchpins for Orthogonal Multicomponent Asymmetric Reactions

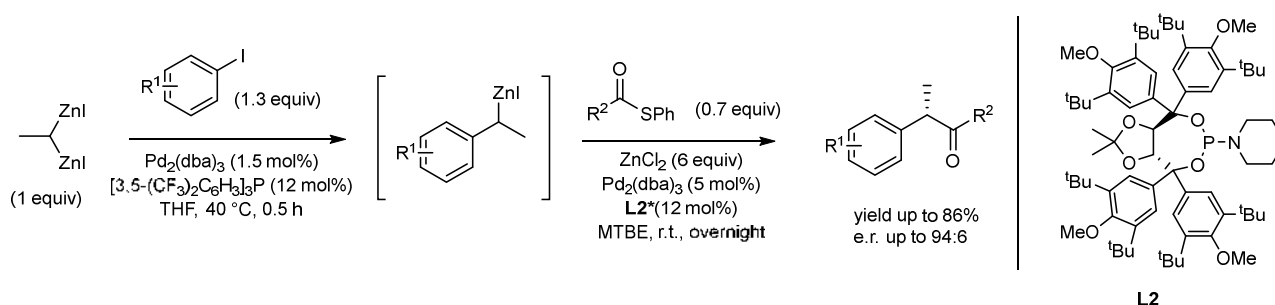
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Multicomponent reactions (MCRs) represent an important trend in the development of more eco-compatible synthetic procedures.¹ Historically, the development of MCRs has been closely related to the use of specific synthetic linchpins (densely functionalized species) enabling the course of domino processes. In this context, the use of metal/metalloid-containing geminal binucleophilic linchpins (*BiLis*) has received very poor attention for the development of asymmetric MCRs (AMCRs) which remain so far largely underexplored. The case of {Zn,Zn} *BiLi*s is particularly interesting because this type of bimetallic linchpin has been largely studied, and has shown easy accessibility and versatile reactivity with reasonable stability using environmentally benign elements such as zinc. However, only one enantioselective transformation was reported,² involving two sequential coupling reactions of a {Zn,Zn} *BiLi* bearing two enantiotopic Zn atoms, but the observed *ee* in the final product was disappointing. Therefore, the present project aims at introducing Zn-containing geminal *BiLi*s in the elaboration of original and versatile AMCRs.

What we present here is the preparation of homobimetallic {Zn,Zn} *BiLi*s (achieved by reductive metalation of *gem*-diiodo derivatives) and used as potential reagents for successive one-pot bi-directional functionalization. We developed enantioselective one pot sequential multicomponent reactions by encompassing successive C–C cross-coupling with two achiral electrophiles: based on Matsubara's seminal work,^{2,3} we achieved selective mono-arylation of CH₃CH(ZnI)₂ by reaction with several (hetero)aryl iodides using Pd₂(dba)₃/L1 as catalytic system (see Scheme); and then, for the second C(sp³)–Zn, unreactive under these conditions, we exploited it for acylation with thioesters in an enantioselective Fukuyama coupling using Pd₂(dba)₃/L2* as chiral catalytic system, based on pivotal Maulide's work.⁴ With our optimized mild reaction conditions in hand (see Scheme), we have developed the first general AMCR using homobimetallic {Zn,Zn} *BiLi*s, exploiting the deracemization of racemic secondary benzyl organozinc reagents, which allowed us to obtain several examples of enantioenriched acyclic α-disubstituted carbonyl compounds carrying potentially labile tertiary stereocenters.



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Liquid crystal elastomer (LCE) with re-entrant nematic phase and smectic phase: toward auxetic LCE

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Auxetics are structures or materials that have a negative Poisson's ratio. When stretched, they become thicker in the direction perpendicular to the applied force. Poisson's ratio (PR) is a measure of the Poisson effect, the deformation (expansion or contraction) of a material in directions perpendicular to the direction of loading.

Until now, nearly all existing synthetic materials with auxetic properties are created by carefully structuring porous geometries from positive PR materials. Note that it is the specific geometries of these materials (rather than the specific molecular structures), which cause the auxetic behaviour. Unfortunately, these synthetic auxetics are limited by their porosity, which weakens the material compared to the bulk, and by the fact that such structures must be engineered, for example, by using resource-intensive additive manufacturing processes. Therefore, creating auxetic materials based on molecular auxetics has been a longstanding goal for the auxetics community, however with few successes so far. Liquid crystal polymer materials are considered as the most promising material for displaying molecular auxeticity.

The backbone conformation of a kind of liquid crystalline side-chain polyacrylate was studied by Small Angle Neutron Scattering (SANS) in the isotropic, nematic, smectic A and re-entrant nematic phases. A transition from an oblate backbone conformation (observed in the nematic and in the smectic A phases) to a prolate conformation (observed in the re-entrant nematic phase) is clearly demonstrated. This kind of liquid crystal polymer could be designed to prepare auxetic LCE.

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Novel Catalytic Silylation Reactions with Silyldiazenes

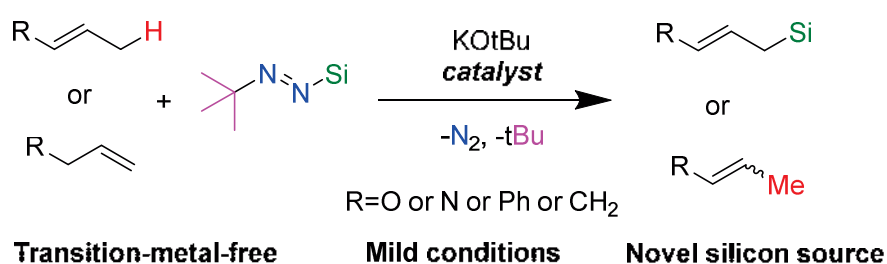
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Compounds containing carbon-silicon (C-Si) bonds have very useful physicochemical properties, and the study of these molecules has important implications in the fields of organic electronics and photonics, drug discovery, nuclear medicine, and complex molecular synthesis.ⁱ Most of the many method reactions currently available for the construction of C-Si bonds rely on the basic step of C-H metallation, which is challenging both in terms of reactivity and selectivity. Transition metal-catalyzed intermolecular carbon-hydrogen (C-H) silylation using rhodium or iridium complexes in the presence of excess hydrogen acceptor is often required, or using stoichiometric amounts of highly reactive Grignard or organolithium reagents.ⁱⁱ For this reason, it is very important to develop new general catalytic methods to construct C-Si bonds that can avoid these limitations, especially direct silanization of unactivated C-H bonds. Here we report an example of cross-dehydroallylic C-H functionalization catalyzed by terrestrially abundant alkali metal species. We found that the direct silylation of allylic C(sp³)-H bonds can be catalyzed using our developed novel silyldiazenes, and we found that in the presence of catalytic amounts of silyldiazenes, repositioning of intramolecular 1,3-hydrogen atoms can be achieved. This new catalytic system is well suited for the silylation and isomerization of a variety of allyl groups, including allyl benzenes, allyl ethers, allyl amines, and low activity olefins, under mild conditions. This catalytic system is also the first case of Csp³-H silylation without transition metal catalysis. The derivatized silane products are easily subjected to a variety of transformations, thus providing new synthetic strategies for pharmaceutical and materials science applications.



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Weak-field coordination of a new iron(0) adduct with an exceptional thermal stability : electronic properties and cycloaddition catalytic activity

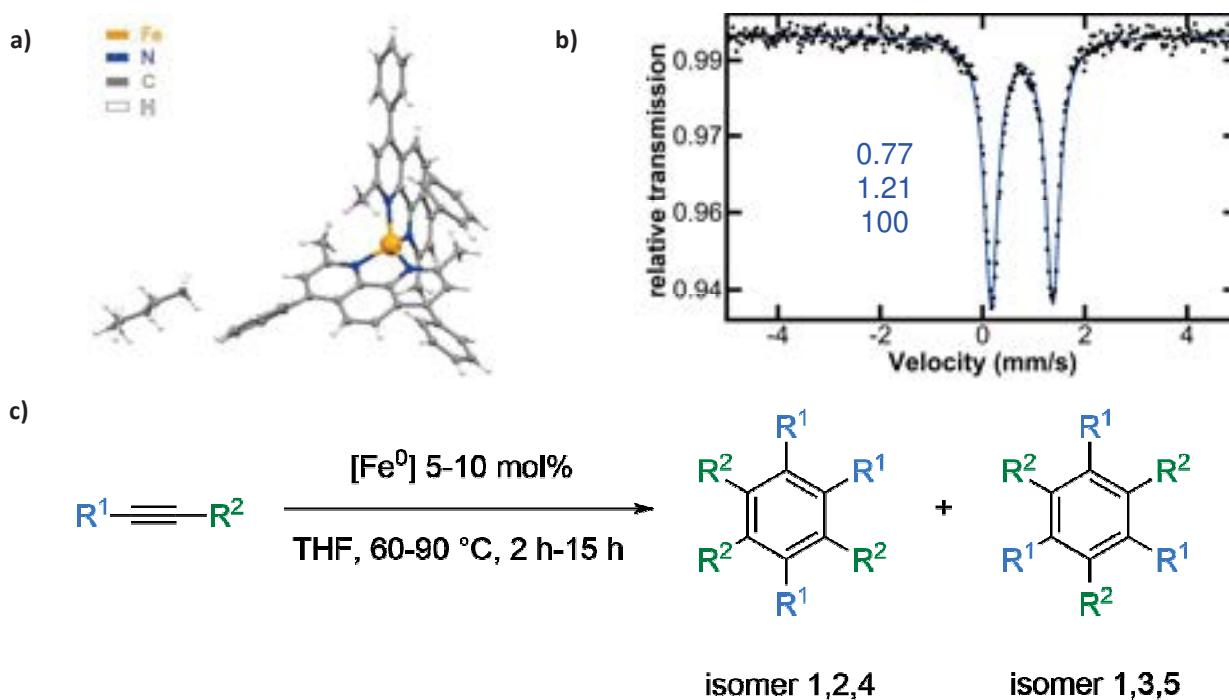
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We report the synthesis of new iron(II) and iron(0) complexes stabilized by a sterically bulky phenanthroline derivative. Unlike the single previous example of such kind of iron complexes,^{2,3} these species have been found to be extremely stable regarding time as well as temperature, and the iron(II) complex is air insensitive. Both species are fully characterized by paramagnetic ¹H NMR, SQUID, elemental analysis, X-ray diffraction, magnetic circular dichroism and Mössbauer spectroscopy (Scheme 1, a and b). The thoughtful study of iron(0) electronic structure also revealed, to a certain extent, a non-innocent behavior. Besides, reactivity of the iron(0) complex is investigated through iron-catalyzed alkyne trimerization reactions (Scheme 1, c). Trimerization of several alkynes, either internal or terminal, and cross-cycloaddition using diyne compounds are performed with excellent results in terms of yield and regioselectivity.

Scheme 1: single-crystal X-ray diffraction structure (a), ⁵⁷Fe-Mössbauer spectrum (b) and catalytic activity (c) of the iron(0) complex.



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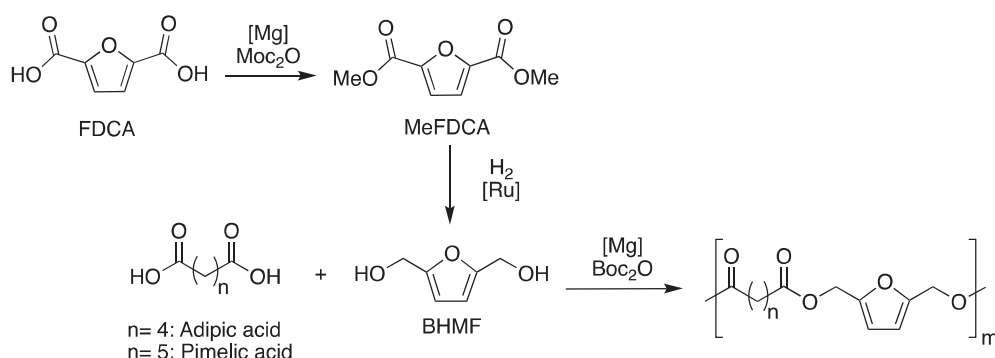
Multicatalysis from renewable resources: a direct route to furan-based polyesters¹

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Due to environmental and availability concerns associated with the use of fossil feedstocks, the production of new types of materials using renewable resources is currently receiving a lot of attention. Furanic materials are one of the most promising classes of bio-based polymers, because their corresponding monomers are widely available in the market. As such, 2,5-bis(hydroxy- methyl)furan (BHMF) which is obtained by hydrogenation of 5-(hydroxymethyl)furfural (HMF), is becoming an interesting building block for the synthesis of high glass transition temperature polymers with good mechanical properties.² However, HMF is generally contaminated by coloured oligomeric impurities called humins, and their purification from HMF remains challenging. To circumvent this contamination issue, we investigated the synthesis of BHMF and the corresponding (co)polymers from bio-based 2,5-furandicarboxylic acid (FDCA), which is a stable monomer produced on industrial scale, and free of humins.³ By a combination of two commercial catalysts, our multicatalytic one-pot procedure allowed the synthesis of two key furanic intermediates, not contaminated by humins. These systems allow the dimethyl 2,5-furandicarboxylate (MeFDCA) formation starting from FDCA, and then its hydrogenation to BHMF, as well as the polycondensation of the newly quantitatively formed monomer with aliphatic diols, providing direct access to furan based-polyesters without needing to isolate or purify any intermediates.



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Organometallic small molecule kinase inhibitors – direct incorporation of Re and ^{99m}Tc into

Opaganib®

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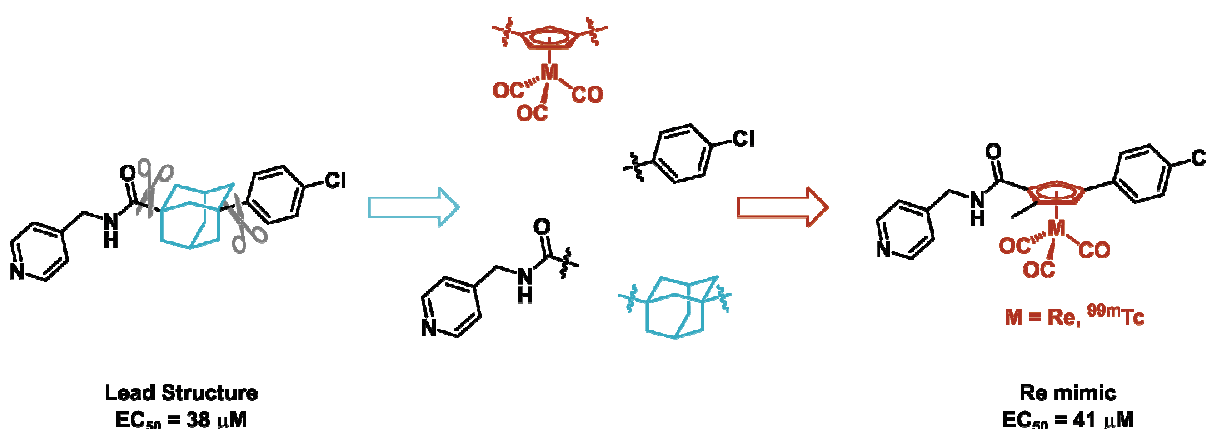
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This work is a collaboration with Prof. Roger Alberto from the University of Zurich (Switzerland)¹ – we have performed the biological evaluation of the compounds prepared in Zurich.

Small molecule kinase inhibitors (SMKIs) have emerged as highly relevant compounds in the clinical treatment of cancer and central nervous system (CNS) diseases.² This is evidenced by no less than 28 SMKIs being approved by the FDA between 2001 and 2015.^{3,4} In this work, $[(\eta^5\text{-Cp})\text{Re}(\text{CO})_3]$ was incorporated into the kinase inhibitor Opaganib®. The resulting bioorganometallic complex showed a similar anti-cancer activity to Opaganib® against PC-3 cancer cells. The IC_{50} value for the kinase SK2 is 30x higher than that of Opaganib®. The ^{99m}Tc homologue was synthesized, completing a matched-pair for molecular theranostics.



Acknowledgments:

Y. W. thanks the China Scholarship Council for financial support.

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Design of a new Microwave-Assisted Continuous Flow equipment for selective catalysis

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The aim of this thesis is to design a new equipment for chemistry synthesis and catalysis, using continuous flow chemistry under microwave irradiation^{1,2}. The goal is to optimize the production of glycerol oligomers and glycerol derivatives. The parameters of the microwaves/continuous flow device were optimized in order to improve the selectivity and the conversion in the desired oligomer. The choice of the reactor geometry was defined, electromagnetic sources layout will be determined and performances of power generating systems were evaluated^{3,4}. In order to optimize those parameters and to design a new equipment, a multiphysics software was used and a preliminary study of the dielectric properties of the oligomers has been carried out in order to know the behavior of the products during the microwave heating^{5,6}. The first results highlighted the selectivity difference between conventional heating and microwave heating and provided the proof of concept for the new device. This work conducted in collaboration with THALES AVS and Chimie ParisTech aimed to design a new equipment for selective catalysis, and a patent filing will take place in the early future.

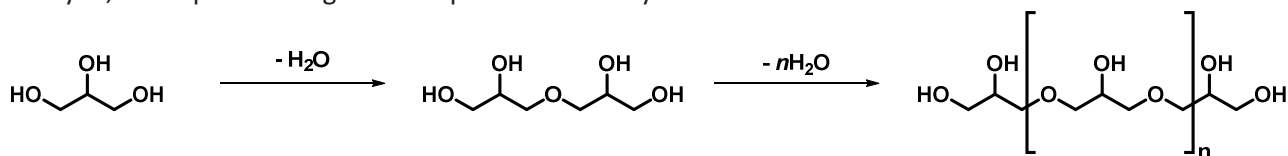


Figure 1 : Glycerol oligomerization

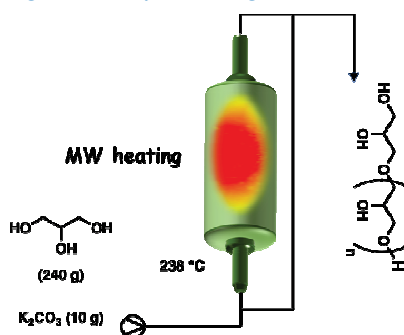


Figure 2: Glycerol oligomerization in continuous flow under microwaves heating

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I thank the CSB2D team and the i-CLeHS group for this collaboration and thank THALES AVS for this collaboration and financial support.

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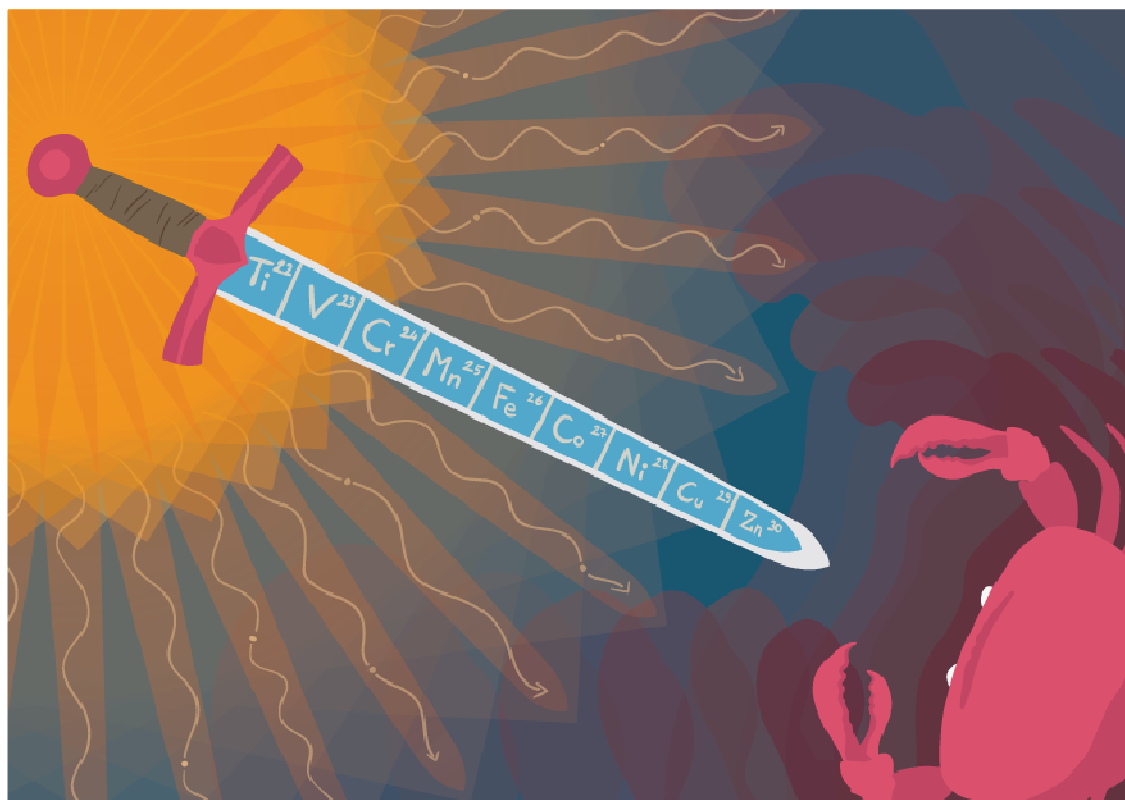
First-row Metal Complexes for Photo-induced Cytotoxicity

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Photodynamic therapy (PDT) and photoactivated chemotherapy (PACT) are therapeutic techniques based on a photosensitizer (PS) and light. These techniques allow to spatially and temporally control the activation of a drug with light. Transition metal complexes are attractive compounds as photoactivatable prodrugs since their excited states can be properly designed by subtle modifications of the ligands, the metal center, or its oxidation state. However, most metal-based PSs contain heavy metals such as Ru, Os, Ir, Pt or Au, which are expensive and non-earth-abundant, contrary to first-row transition metals. In this context, the exploration of the photochemical properties of complexes based on first-row transition metals appears as extremely promising. This presentation will focus on first-row-transition metal complexes in regard to their applications as PSs for phototherapeutic applications.¹



Acknowledgments: ENS-PSL for PhD funding.

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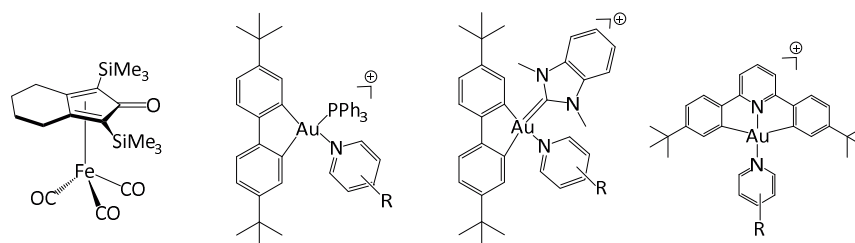
Investigation of ligand electronic effects on organometallic complexes using photoelectron spectroscopy and mass spectrometry

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Organometallic chemistry is a key process in homogenous catalysis and gives access to a wide range of products and reactions. Through their steric and electronic effects, ligands are able to orientate the reactivity of the complexes and can thus influence the selectivity in the chemical transformations. Usually, the metal-ligand bond is depicted by the Dewar-Chatt-Duncanson model^{1,2} involving two opposite interactions, a σ -donor and a π -acceptor effect. Over the years, many experimental methods have been developed to measure these electronic effects, the most common being that of Tolman (Tolman electronic parameter), which is based on the A1-symmetrical CO-stretching frequency shift in carbonyl complexes.³ We have recently developed the use of new experimental gas-phase approaches to measure these effects, one based on photoelectron spectroscopy (PES) coupled to synchrotron radiation, and the other on mass spectrometry using activation by higher energy collision dissociation (HCD). Under the first method, the satisfying results obtained on model systems⁴ have encouraged us to apply this method to catalysts developed for hydrogenation reactions,⁵ and to probe the electronic interaction between the ligand and the metal centre. Results obtained for tricarbonyl iron complexes of the $(\text{Fe}(\text{CO})_3\text{L})$ type, with L being substituted cyclopentadiene ligands, are presented here. The experiments were carried out at the DESIRS monochromatized branch using the SAPHIRS experimental station equipped with the DELICIOUS III double imaging-PEPICO spectrometer. The photoelectron spectra provide access to the ionisation energies and state-selected Fe-CO dissociation energies. This method, as well as that of Tolman are however limited to organometallic complexes possessing probe ligands such as CO. Very few reliable experimental methods make it possible to determine the electronic properties of ligands in complexes that do not possess probe ligands. Therefore, in order to make a direct measurement of the ligand effect, we were interested in their study on gold (III) complexes of the type $[(\text{C}^{\wedge}\text{C})\text{Au}(\text{NHC}/\text{PPh}_3)\text{L}]^+$ and $[(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{AuL}]^+$ with L a differently substituted pyridine ligand. The effect of pyridine substitution on the enrichment of the metal center was evaluated by determining the dissociation energy $\text{M-L} \rightarrow \text{M} + \text{L}$ (bond dissociation energy : BDE) by mass spectrometry. Rationalization of the experimental results is made using density functional theory and bond description methods to get information on the electronic structure of the complexes and thus on the metal-ligand interaction.



Scheme 1. Structures of the studied complexes. R is a variable pyridine substituent (ortho, meta or para position).

Acknowledgments: I gratefully acknowledge the Labex Michem and the Synchrotron center for the financing of this project. Many thanks to our collaborators Jean-Luc Renaud and Benoit Bertrand for the studied compounds in this subject and for their very useful discussions.

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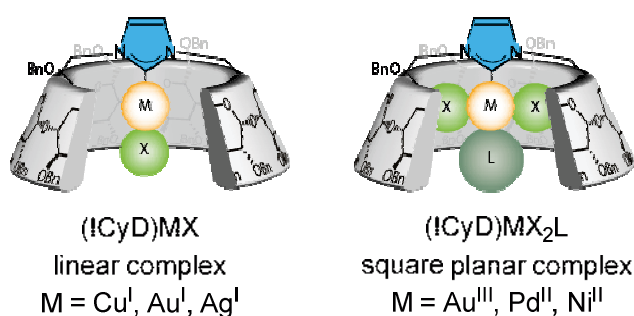
Metal encapsulated inside NHC-capped cyclodextrins: cavity-controlled selective reactions

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Encapsulated metal complexes with well-defined spaces show distinctive properties thanks to the primary and secondary coordination spheres. The association with α , β or γ -cyclodextrin (CD) moiety and *N*-heterocyclic carbene (NHC) ligand, called ICyD, led to the formation of encapsulated complexes in helicoidal distorted cavities¹. Our group reported that this series of ligands allowed to form linear coordination with coinage metals (Cu^I, Au^I, Ag^I), which could induce stereo-^{2,3}, regio-⁴ and chemoselective⁵ reactions. Our group also showed the formation of square planar coordination complexes (Au^{III}, Pd^{II}) inside β or γ -CD cavities⁶.

To get further insight into ICyD-metal complexes, we extend our study to the synthesis and characterization of Ni complexes. Group 8 metal nickel exhibits multiple oxidation states and coordination types. Nickel catalysts could undergo either two electron transfer pathway or radical pathway⁷. Therefore, we synthesized two types of ICyD-Ni^{II} complexes and studied the relationship between their coordination modes and CD cavity.



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Novel Platinum(II) and Iridium(III) Polymetallic Assemblies based on Pyridylidene and π -Extended Ligands

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Cyclometalated platinum(II) and iridium(III) complexes are known for their optical properties enabling their application in a wide range of fields¹. In the last few years, discrete and polymeric coordination assemblies based on π -extended ligands² on one hand and pyridylidene ligands³ on the other hand has been developed by the group, exhibiting interesting luminescent properties.

The deal of my PhD project is the synthesis and characterization of novel platinum(II) and iridium(III)-based bimetallic assemblies incorporating π -extended and pyridylidene ligands.

The π -extended ligands are designed with either pyridine or 2-picolinate moieties (**L**₁ and **L**₂ in Fig.1). Then, their coordination toward C^N chelated platinum(II) and iridium(III) bricks is explored. For platinum(II) a chelating pyridyl-pyridilidene N^C ligand is used and novel bimetallic architectures are obtained and fully characterized (Fig.1a). In the case of iridium(III), first results are obtained with a chelating C^N phenylpyridine, affording a new luminescent bimetallic assembly (Fig 1b). The optical properties of these new luminescent architectures are currently under investigation.

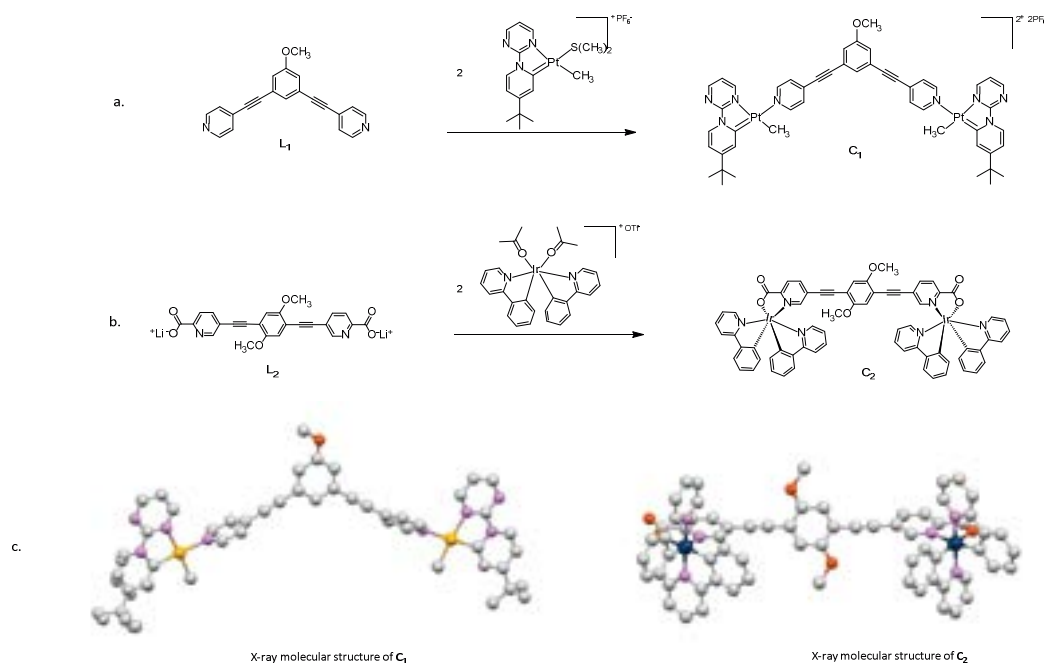


Fig. 1 a. π -extended ligand **L**₁ and its Pt(II) complex **C**₁. b. π -extended ligand **L**₂ and its Ir(III) complex **C**₂. c. X-ray molecular structures of the cationic part of **C**₁ (PF₆⁻ counterions are omitted for clarity) and **C**₂.

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New organometallic gold(III) complexes based on (C[^]C) chelates and NHC ligands: synthesis and anticancer investigations.

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Metal-based anti-cancer treatments appeared in the late 1970s with the appearance of platinum-based compounds.¹ Although these treatments are used in therapy today, they have many limitations. This results in the appearance of side effects or development of resistance.² For this reason, studies have been conducted by replacing platinum(II) by isoelectronic gold(III). Thus, many gold(III) complexes with (C[^]N) or (C[^]N[^]C) ligands have been synthesized and then tested on cancer cell lines. These compounds were found to have anticancer activity in the micromolar range.³ Moreover, the presence of these cyclometalated ligands have improved the redox stability of gold(III) in the presence of strong natural reducing agents such as glutathione.⁴ However, of the four available coordination sites of the complexes, three are blocked by the cyclometalated ligand, leaving only a small possibility for functionalization or for direct coordination of gold(III) with biomolecules. The objective here is to synthesize a new family of gold(III) complexes, replacing the (C[^]N[^]C) ligand. After an initial study of compounds with a biphenyl ligand (C[^]C) and a dinitrogen ligand (N[^]N),⁵ we focused on the synthesis of a new family of complexes composed of a biphenyl ligand (C[^]C), a chlorido ligand and pyridinylNHC ligands based on imidazole and benzimidazole scaffolds. These new organogold complexes have been screened for their anticancer activity on a panel of human cancer cells along with analogs without pyridine ring substituents. A preliminary structure-activity relationship could be established.

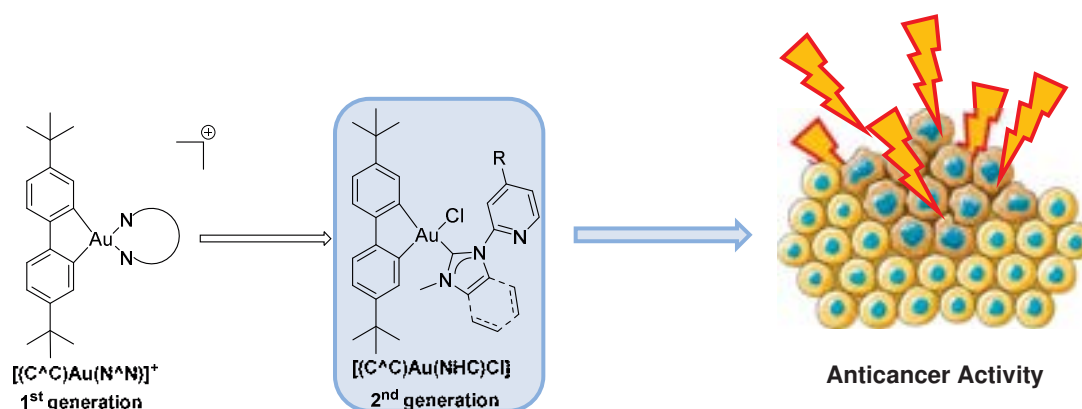


Fig. 1 Optimization of gold(III) complexes with pyridinyl-NHC ligands and assays for anticancer activity

Acknowledgments:

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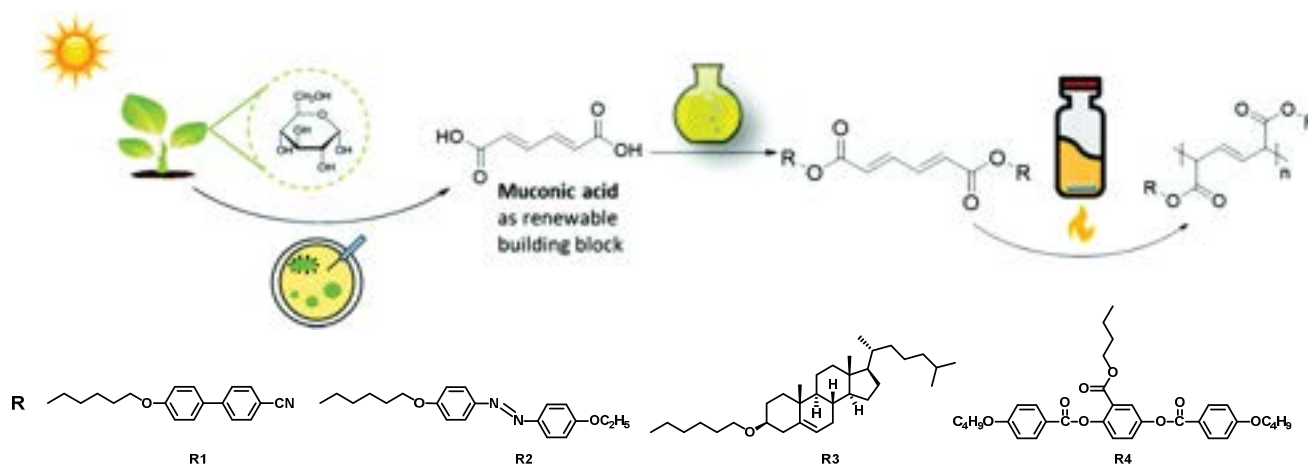
Bio-sourced and biomimetic liquid crystal elastomers as actuators and sensors

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An analysis on the existing liquid crystal elastomers (LCEs) reveals that the mesogens and monomers reported so far are mostly derived from fossil fuels or use them in large quantity for fabrication. Due to ecological and environmental issues, combined with the depletion of oil-based feedstocks, the shift towards greener chemical processes to produce polymer materials is a topical trend. Muconic acid is a promising renewable molecule that can be accessed from bio-fermentation of sugar, lignin or their derived compounds.ⁱ And it features high functionality. The acid groups offer a simple access to graft and modify. On the other hand, the conjugated double bonds present in the structure make the molecule feasible for free radical polymerization. Therefore, we design and synthesize bio-sourced liquid crystal esters from muconic acid. Bio-sourced LCEs actuators and sensors with various shapes will be produced and their biomimetic functions investigated.



Acknowledgments:

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Electrocatalytic CO₂ Conversion to Multi-Carbon Products in Acidic Conditions using a Bipolar Membrane

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Until recently, high-current CO₂ electrolysis has been almost exclusively performed in alkaline and neutral environments. Despite the advantages offered by these conditions, such as the suppression of hydrogen evolution, any electrolyte solution with a pH above the pK_a of CO₂ suffers from CO₂ conversion into HCO₃⁻ and CO₃²⁻, resulting in the loss of a significant portion of reactant.ⁱ An efficient strategy to avoid this issue consists in using an acid catholyte, which prevents permanent (bi)carbonate formation. However, since the local environment of the gas-diffusion electrode remains alkaline due to the CO₂RR, HCO₃⁻ and CO₃²⁻ formation cannot be avoided even in a proton-rich solution. Nevertheless, as these species diffuse in the bulk electrolyte, the low pH effectively converts them back to CO₂, which can then be collected and recycled. Here we present a low-CO₂ inlet flow rate electrolysis setup that allows to separate the carbonate-regenerated CO₂ and the CO₂RR products in two different outlets of a gas-fed flow cell reactor. The outlet CO₂ is highly pure, mixed only with small amounts of H₂. Therefore, it can easily be separated from trace impurities and re-fed to the cell for further conversion. Likewise, the second outlet provides a flow of nearly CO₂-free gaseous reduction products. A bipolar membrane is used to separate the cell compartments, allowing the simultaneous use of an acid catholyte and an alkaline anolyte. The system is able to operate for at least 8 h with an applied current density of -200 mA cm⁻² and a CO₂ inlet flow rate of 1.25 mL min⁻¹, with the latter parameter being the key for efficient separation between regenerated CO₂ and products. In addition, the catalyst is selective towards C₂₊ species (namely ethylene and ethanol) that together account for up to 60% of the total faradaic efficiency.

Acknowledgments:

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Isolated switchable polyoxometalates (POMs) on a highly organized carbon substrate.

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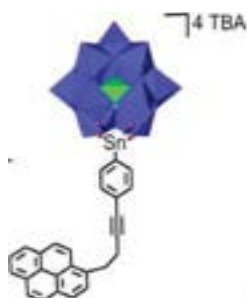
PhD advisor : Florence Volatron, David Kreher

Laboratory : Institut parisien de chimie moléculaire (IPCM)

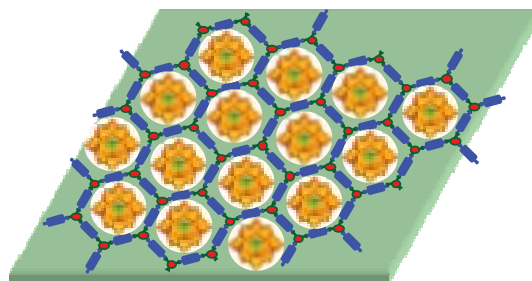
The aim of this research project is to develop a new material constituted of polyoxometalates (POMs) (scheme 1 and 2) deposited onto a highly oriented pyrolytic graphite (HOPG) substrate to achieve a system in which the molecules are isolated from each other and periodically organized on the surface (scheme 3). Different deposition approaches are tried to reach this objective, and several characterization techniques are used in order to demonstrate the organization of the POMs at nanometric scale. To help the organization of the POMs, the surface of HOPG will be nanostructured by deposition of self-assembling molecules forming a 2D network. This system will open the way for data information storage in single molecules. Indeed, POMs display remarkable switchable properties like photoreduction, magnetion...etc. To achieve this aim, several challenges have to be addressed, starting by the synthesis of the POMs and the self-assembling molecules, to the characterization of the monolayer surface to show the periodic organized deposition of POMs.



Scheme 1 : Keggin POM



Scheme 2 : Keggin hybrid POM



Scheme 3 : Organized periodic POMs deposited on HOPG surface

Préparation stéréosélective de 2-alcynyl-hydroxy- ou amino alcools-1,3

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Allenylboranes are important reagents in organic synthesis, allowing, among other things, the stereoselective preparation of alcohols and amines homopropargylic¹ used in the asymmetric synthesis of many natural products. As part of this project, the stereoselective preparation of 2-alcynylaminoalcohols-1,3 from chiral allenylboranes is a strategy considered. Two complementary approaches will be considered. The first will be based on the extension of the previous methodology to the stereoselective reaction of 4-hydroxy-1-allenylboranes with aldehydes and imines to give 2-alcynylaminoalcohols-1,3. In the second approach, we will first study the reaction of diastereoselective silylborylation of acetylene aziridins to access 4-amino-1-allenylboranes.

Acknowledgments:

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