GECOM-CONCOORD 2025

Groupe d’Étude de Chimie OrganoMétallique
et de la Concertation en Chimie de Coordination

May 19th-23rd, 2025

Métabief
Bourgogne Franche-Comté

https://gecom2025.sciencesconf.org/

Dear participants,

We have the pleasure to warmly welcome you to Métabief, France, for the GECOM-CONCOORD 2025 Conference. This meeting was born in 1993 from the merger of the group "*Dialogue in Coordination Chemistry* (CONCOORD)" and "*Study Group in Organometallic Chemistry* (GECOM)". Since then, the GECOM-CONCOORD aims at focusing annually on the latest advances in different areas of Coordination Chemistry and Organometallic Chemistry, including Catalysis. This event is voluntary outside any city in order to stimulate scientific exchange between young researchers (PhD students, postdocs) and more experienced researchers.

Encouraged by the number of participants taking part to this week meeting, we have no doubts that the atmosphere during the course of the meeting will be a lively and friendly one, allowing many new scientific and personal interactions to be established between participants.

We wish you an enjoyable week in Métabief and a fruitful congress!

The organizing committee

Chères participantes, chers participants,

Nous avons le plaisir de vous accueillir à Métabief, au sein des installations du centre *Azureva*, pour l’édition 2025 du GECOM-CONCOORD. Ce congrès est né en 1993 de la fusion du groupe «*Concertation en Chimie de Coordination* (CONCOORD)» et du «*Groupe d'Étude en Chimie Organométallique* (GECOM)». Depuis, le GECOM-CONCOORD vise à mettre annuellement l'accent sur les récentes avancées développées dans les domaines de la Chimie de Coordination et de la Chimie Organométallique, et inclut également le domaine de la Catalyse. Cet événement est volontairement « *hors ville* » afin de stimuler les échanges scientifiques directs entre les jeunes chercheurs (doctorants, post-doctorants) et des chercheurs plus expérimentés.

Encouragé par le nombre de participants prenant part à cette réunion, nous sommes persuadés que l'atmosphère tout au long de la semaine sera animée et conviviale, permettant ainsi de nouvelles interactions scientifiques et personnelles entre les participants.

Nous vous souhaitons une agréable semaine à Métabief et un bon congrès !

Le comité d'organisation

Organizing Committee
Comité d'organisation

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Nous tenons à remercier chaleureusement toute l'équipe du centre *Azureva* de Métabief.

Le Comité d'organisation du GECOM-CONCOORD 2025 remercie vivement les partenaires institutionnels et privés qui ont apporté leur soutien à la préparation de cette manifestation :

Université Bourgogne Europe
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Transition Metal Chemistry (Ed. Springer)
Chemistry Europe

Program of Lectures

Programme

May 2025	Monday 19	Tuesday 20	Wednesday 21	Thursday 22	Friday 23
		Forewords Raluca Malacea Chairman Julien Roger	Chairman Charles Devillers	Chairman Laurent Plasseraud	Chairwoman Raluca Malacea
08:30-09:20		PL1 Yann Sarazin	PL3 Abderrahmane Amgoune	PL5 Carine Robert	09:10 PL7 Chiara Dinoi
09:20-09:40		OC1 Alexis Giraudon	OC16 Loëza Collobert	OC20 Perrine Lambert	
09:40-10:00		OC2 Camille Chartier	OC17 Steven Roldán-Gómez	OC21 Amal Bouammali	
10:00-10:30		Coffee break	Coffee break	Coffee break	Coffee break
10:30-10:50		OC3 David Martins Bessa	PL4 Alexandre Martinez	OC22 Léon Escomel	OC35 Rodolph Jazzar
10:50-11:10		OC4 Carmen Antuña-Hörlein		OC23 Vanessa Delahaye	OC36 Martine Castella-Ventura
11:10-11:30		OC5 Thu Van Nguyen	OC18 Clément Soep	OC24 Thanh Tu Bui	Closing Raluca Malacea
11:30-11:50		OC6 Hussein Tabaja	OC19 Sabine Lam	OC25 Cyril A. Theulier	Lunch
11:50-12:10		OC7 Beatris Onzimba	Sponsors Advion Interchim	OC26 Quentin Pessemesse	
12:10-14:00		Lunch Chairman Michel Meyer	Lunch	Lunch Chairman Ewen Bodio	
14:00-14:50		PL2 Mathilde Bouché	Free time Visits	PL6 Benoît Bertrand	
14:50-15:10		OC8 Dragos-Adrian Roșca		OC27 Luca Antonini	
15:10-15:30		OC9 Louis Le Moigne		OC28 Fatima Awada	
15:30-15:50		OC10 Gwendal Uguen		OC29 Mélaine Wang	
15:50-16:10		OC11 Guillaume Flick		OC30 Maxime Steinmetz	
16:10-16:40	Welcome	Coffee break		Coffee break	
16:40-17:00		OC12 Ming-Yu Chen		OC31 Iulia-Andreea Crețoiu	
17:00-17:20		OC13 Jean-Thomas Pouzens		OC32 Jahja Mehmet	
17:20-17:40		OC14 Vladislava Timofeeva		OC33 Cenna Toullec	
17:40-18:00		OC15 Nour Shalhoub		OC34 Jérémy Leroy	
18:00-18:20		Sponsors OrigaLys, Anton Paar		Sponsors BioLogic	
18:20-20:00	19:00 Opening Raluca Malacea	POSTER SESSION		POSTER SESSION	
20:00	Dinner	Dinner	Dinner	Prizes + Gala Dinner	

Monday, May 19th, 2025 / *Lundi 19 Mai 2025*

16h00-	Registration / *Accueil et enregistrement*
19h00	Opening / *Cérémonie d'ouverture*
20h00	Dinner / *Dîner*

Tuesday, May 20th, 2025 / *Mardi 20 Mai 2025*

Forewords / *Préambule* – Raluca MALACEA

Chairman / *Modérateur de la session* – Julien ROGER

8h30	**PL1**: Beyond the obvious: Unexpected reactivity with main group metals *Yann SARAZIN*
9h20	**OC1**: Tuning the 1D / 2D Dimensionality in Copper(I) and Silver(I) Thiolate Coordination Polymers *Alexis GIRAUDON*
9h40	**OC2**: Influence of the 4*f*-3*d* Metals Pairs on the Synthesis, Structure and Reactivity of Heterobimetallic Siloxide Complexes *Camille CHARTIER*
10h00	Coffee break / *Pause café*
10h30	**OC3**: σ-BH activation of [NHC-BH_3] fragments at dinuclear Cu complexes: a DFT description *David MARTINS BESSA*
10h50	**OC4**: From the Old to the New: Group 9 Metals in Cyclometallation and Ligand Substitution Reactions for C-H Bond Functionalisation *Carmen ANTUNA-HORLEIN*
11h10	**OC5**: Amidine-phenoxy ligands (AF) and their group IV metal complexes for olefin polymerization *Thu-Van NGUYEN*
11h30	**OC6**: Six-membered CO_2-based lactones/lactams towards polyesters and polyamides *Hussein TABAJA*
11h50	**OC7**: Caged Triazacyclononane Ligands: Towards Non-heme Bioinspired Caged Catalysts *Beatris ONZIMBA*
12h10	Lunch / *Déjeuner*

Chairman / *Modérateur de la session* – Michel MEYER

14h00	**PL2**: Light-activatable metal complexes and theranostics *Mathilde BOUCHE*
14h50	**OC8**: Multifaceted reactivity of cobalt and iron-based electron-rich redox active systems *Dragos-Adrian ROSCA*
15h10	**OC9**: Defluorination of discrete molecules and polymers catalysed by titanium *Louis LE MOIGNE*
15h30	**OC10**: Use of Pyridyl cores in biomimetic [FeFe]-Hydrogenases complexes *Gwendal UGUEN*
15h50	**OC11**: Bifunctional nickel catalysts for hydroboration and hydrosilylation reactions via cooperative B–H and Si–H bond activations *Guillaume FLICK*
16h10	Coffee break / *Pause café*
16h40	**OC12**: Mn-Catalyzed Regioselective Alkene Hydrosilylation: Reaction Mechanism Investigation *Ming-Yu CHEN*
17h00	**OC13**: Theoretical investigation of FAlen-Zn complexes coordination: when causes are actually consequences *Jean-Thomas POUZENS*
17h20	**OC14**: Hybrid ambidentate NHC ligand with a dithiolene backbone *Vladislava TIMOFEEVA*
17h40	**OC15**: Unprecedent panchromatic absorption of azaullazine-based Fe(II) complexes *Nour SHALHOUB*
18h00	Sponsors / *Interventions d'Exposants* – ORIGALYS, ANTON PAAR
18h20	Poster Session / *Séance Posters*
20h00	Dinner / *Dîner*

Wednesday, May 21st, 2025 / *Mercredi 21 Mai 2025*

Chairman / *Modérateur de la session* – Charles DEVILLERS

8h30	**PL3**: Controlling Nickel Redox States for Radical Pathways with Photo- & Electro-chemical approaches *Abderrahmane AMGOUNE*
9h20	**OC16**: Design of Luminescent Lanthanide-Based Bioprobes for Two-Photon NIR-to-NIR Imaging in Vivo Applications *Loëza COLLOBERT*
9h40	**OC17**: Modelling the mechanism of Gallium-catalysed recycling of silicone waste with BCl_3 to yield chlorosilanes *Steven ROLDAN-GOMEZ*
10h00	Coffee break / *Pause café*
10h30	**PL4**: Recent developments in the chemistry of hemicryptophane cages: from recognition to confined catalysis *Alexandre MARTINEZ*
11h20	**OC18**: Influence of the ligand on the toxicity, speciation and intracellular localization of Au(III) complexes in lung cancer cells *Clément SOEP*
11h40	**OC19**: Tb(III) Complexation with Hydroxamic and Pyridinecarboxylic Ligands by Affinity Capillary Electrophoresis and DFT Calculations *Sabine LAM*
12h00	Sponsors / *Interventions d'Exposants* – Advion Interchim
12h20	Lunch / *Déjeuner*
14h00	Free time – visit / *Temps libre – visite*
20h00	Dinner / *Dîner*

Thursday, May 22nd, 2025 / *Jeudi 22 Mai 2025*

Chairman / *Modérateur de la session* – Laurent PLASSERAUD

8h30	**PL5:** Ring Opening Polymerization using Organometallic Complexes for the Synthesis of Biosourced Polymers *Carine ROBERT*
9h20	**OC20**: Heterobimetallic Complexes of Photoactive N-Heterocyclic Carbenes *Perrine LAMBERT*
9h40	**OC21**: Synthesis of Polyarylcyclopentadienyl-Based Dysprosium Complexes and Investigation of Their Magnetic Properties *Amal BOUAMMALI*
10h00	Coffee break / *Pause café*
10h30	**OC22**: Lewis Superacid-Mediated Reduction of Dioxygen and Carbon Dioxide *Léon ESCOMEL*
10h50	**OC23**: B_2pin_2-mediated Ligand Deprotonation Enables Selective Iridium-catalyzed C-H Borylations Revealed by Click Ligands *Vanessa DELAHAYE*
11h10	**OC24**: Rare-earth Complexes of Bis(phenoxy-amidinate) FAlen Ligands as Catalysts for Ring-Opening Polymerization *Thanh Tu BUI*
11h30	**OC25**: Zr(IV)-catalyzed Hydrosilylation of Polycarbonates *Cyril A. THEULIER*
11h50	**OC26**: Mechanistic Insights into Copper Hydride Chemistry: Dynamic Structure and Reactivity *Quentin PESSEMESSE*
12h10	Lunch / *Déjeuner*

Chairman / *Modérateur de la session* – Ewen BODIO

14h00	**PL6**: Biphenyl-gold(III) complexes: a promising scaffold for investigations of anticancer drug candidates *Benoît BERTRAND*
14h50	**OC27**: Dinitrogen functionalization: road to ammonia thanks to molybdenum complexes *Luca ANTONINI*
15h10	**OC28**: Synthesis and Characterization of Porphyrinoid-based Molecules and Materials for applications in Gas Sensing *Fatima AWADA*
15h30	**OC29**: Synthesis and Bioevaluation of dicobalt Tetrahedranes, Pt$_2$ A-frame and Pt(0) Complexes bearing a *N*-Heterocyclic fragment *Mélaine WANG*
15h50	**OC30**: Dimerization and Cycloaddition Catalyzed by Tethered Complexes in a Supramolecular Host *Maxime STEINMETZ*
16h10	Coffee break / *Pause café*
16h40	**OC31**: Design of Sulfur Based Pincer Ligands for Stabilization of Low Valent Species *Iulia-Andreea CRETOIU*
17h00	**OC32**: Computational insight into the geometry of amidine-phenoxy early transition metal complexes *Jahja MEHMET*
17h20	**OC33**: New catalytic pathways for carbene insertion into Si-H bonds catalyzed by ruthenium phthalocyanine complexes *Cenna TOULLEC*
17h40	**OC34**: Reactivity of Grignard Reagents towards Nitrile in context of polymerization catalysis *Jérémy LEROY*
18h00	Sponsors / *Interventions d'Exposants* - BIOLOGIC
18h20	Poster Session / *Séance Posters*
20h00	Banquet / *Banquet*

Friday, May 23rd, 2025 / *Vendredi 23 Mai 2025*

Chairwoman / *Modératrice de la session* – Raluca MALACEA

9h10	**PL7**: Reactivity and Catalytic Activity of the Beta-Diketiminato [(BDI)CaH]$_2$ Compound: A Theoretical DFT Study *Chiara DINOI*
10h00	Coffee break / *Pause café*
10h30	**OC35**: Cu-rious Bonds *Rodolph JAZZAR*
10h50	**OC36**: Theoretical Study of the Adsorption of Methyl Pyridine Derivatives in H-ZSM5 Zeolite *Martine CASTELLA-VENTURA*
11h10	**Closing** / *Mots de clôture* – Raluca MALACEA
11h30	Lunch / *Déjeuner*

Plenary Lectures

Conférences Plénières

Yann SARAZIN is a CNRS Research Director at the Institut des Sciences Chimiques de Rennes. He gained his PhD in macromolecular and coordination chemistry in 2004 from the University of East Anglia, UK, under the guidance of Prof. M. Bochmann. After a 3-year postdoc at UEA to study main-group cations, he returned to France in 2007 for a stint as a postdoc for Total Petrochemicals. He joined CNRS in 2008. His main current research interests include the fundamental organometallic chemistry of main group metals, most notably the large alkaline earths calcium, strontium and barium, along tetrel (Sn, Pb) and pnictogen (Sb, Bi) elements, and its applications in molecular catalysis towards selective bond formation, with an emphasis on the investigation of operative mechanisms. The design of unusual metal complexes with controlled coordination spheres and the corresponding structure-function relationship occupy the core of his research program, which stretches from catalyst development to the study of the properties of tailor-made polymers. He has published over 100 papers, patents, and book chapters in these fields.

PL1 | Beyond the obvious: Unexpected reactivity with main group metals

Gabriel Duneș,[1] Peter M. Chapple,[1] Sakshi Mohan,[1] Albert Soran,[1]
Jean-François Carpentier,[1] Jean-Yves Saillard,[1] Yann Sarazin*,[1]

[1] Université de Rennes, CNRS, Institut des Sciences Chimiques de Rennes, UMR 6226,
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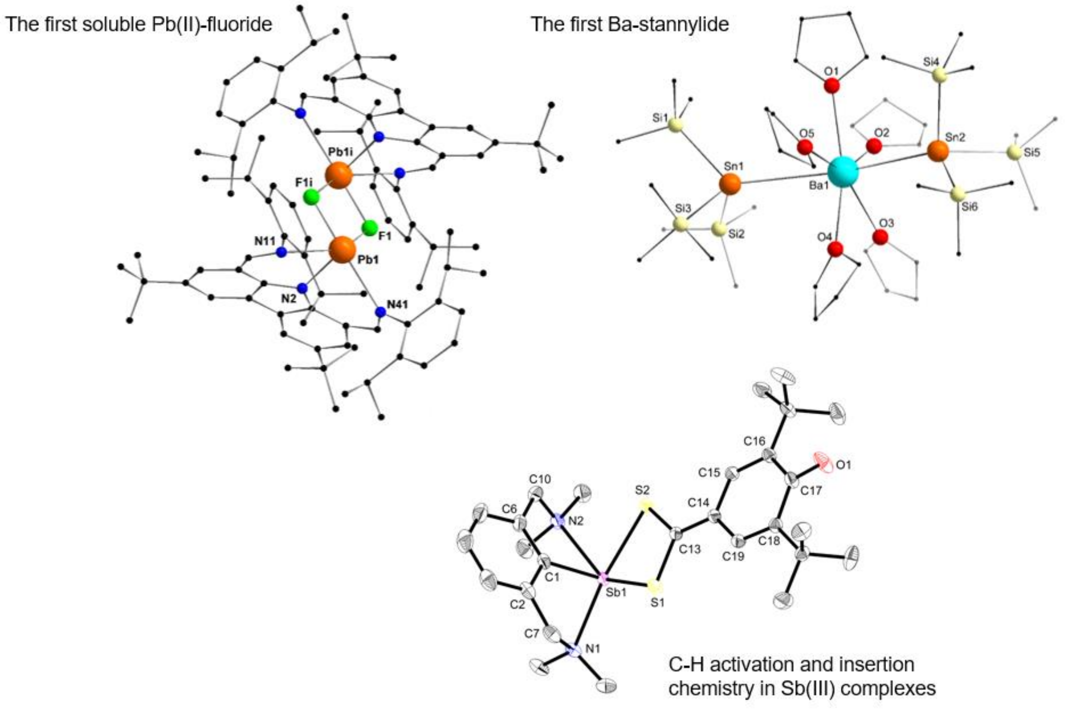
Along the years, we have devoted a substantial part of our efforts to the larger alkaline earths Ca, Sr and Ba, going from the design of complexes with a tailored coordination sphere to their implantation as potent molecular catalysts in functionalisation reactions, e.g. hydroelementations and heterodehydrocouplings.[1-3] Beyond group 2 metals, we also maintain a keen interest in the coordination chemistry of the heavy *p*-block metals, in particular for the heavier tetrels (Sn, Pb) and pnictogens (Sb, Bi) in their low oxidation states.[4-6]

A brief overview of our recent activities will be highlighted. The design of low coordinate alkaline-earth complexes stabilised by bulky monoanionic ligands and non-covalent interactions will be presented. We will see that these complexes, and Ba ones chiefly among them, promote C-H/H-Si and NH/H-Si dehydrocouplings, leading to original materials.[2,3,6] We will dwell into the fundamental organometallic chemistry of the alkaline earths, discussing both unexpected reactivity with *n*-butyllithium and our mixed success towards the synthesis of heterobimetallic complexes combining *s*- and *p*-block metals.[7] Last, a seldom case of C-H bond activation with antimony(III) compounds will exemplify how to leverage new reactivity with heavier pnictogens.[4,7]


The first soluble Pb(II)-fluoride

The first Ba-stannylide

C-H activation and insertion chemistry in Sb(III) complexes

This work was supported by the ANR (ANR-17-CE07-0017-01 POLCADE; ANR-21-CE07-0045-02 BiMeDep). Y.S. thanks his close collaborators at ISCR and elsewhere for their invaluable help.

1. Erwann Le Coz et al., *Chem. Eur. J.* **2021**, *27*, 11966.
2. Peter M. Chapple et al., *Chem. Sci.* **2021**, *12*, 7098.
3. Peter M. Chapple et al., *Angew. Chem. Int. Ed.* **2020**, *59*, 9120.
4. G. Duneș et al., *Dalton Trans.* **2024**, *53*, 15427.
5. Adrian-Alexandru Someșan et al., *Dalton Trans.* **2025**, *54*, 482.
6. A. Soran et al., *Dalton Trans.* **2025**, *54*, 2037.
7. Unpublished results.

Mathilde BOUCHÉ is a CNRS researcher at the L2CM (UMR 7053) at University of Lorraine since 2020. She currently leads a research group on Bioinorganic Chemistry with a strong focus on metal-based complexes for therapeutic and theranostic applications. She studied Chemistry at the University of Burgundy, and obtained a PhD in Bioinorganic Chemistry from the University of Strasbourg (2017) on the development of platinum-based chemotherapeutics under the supervision of Dr. S. Bellemin-Laponnaz. She then completed a two-years postdoctoral stay as Fulbright scholar at Prof. Cormode's lab at the University of Pennsylvania (U.S.A.) in Molecular Imaging, and returned to France for a postdoctoral stay at the University of Lorraine in Medicinal Chemistry.

PL2 | Light-activatable metal complexes and theranostics

Mathilde BOUCHÉ*,[1]

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Drugs based on transition metals ─ metallodrugs ─ substantially impacted medicinal chemistry particularly in cancer therapy, as exemplified by the success of cisplatin and more recently of the photosensitizer padeliporfin.[1] Yet, several pathologies remain particularly challenging to treat, like resistant and inoperable cancers, and require the emergence of more performant therapeutics. To achieve this, metallodrugs active in dual therapy are promising. Particularly when photothermal therapy (PTT) and chemotherapy are achieved simultaneously using metallodrugs that display appropriate photophysics, it offers the possibilities of enhancing their selectivity and therapeutic potential.[2] Iron(II) complexes stabilized with strong field ligands display privileged photophysics for light-to-heat conversion in PTT[3] and fascinating therapeutic effects, thus foreshadowing remarkable therapeutic possibilities by dual PTT-chemotherapy. However, because iron is omnipresent in living systems and displays a large scope of mechanisms of action,[4] exploring the reactivity of the coordination sphere of iron-based metallodrugs in living systems is crucial to design appropriate photothermal agents. To unravel the fate of such iron-metallodrugs in complex media and understand the impact of their coordination sphere on their behaviour in complex media, optical imaging modalities are privileged techniques.[5] We will discuss our recent progress in the development of iron-based photothermal agents and show how optical imaging can be a gamechanger for rationalizing their structure-activity relationship to guide the development of more potent and selective theranostics.

1. M. A. Jakupec, M. Galanski, V. B. Arion, C. G. Hartinger, B. K. Keppler, *Dalton Trans.* **2008**, *2*, 183.
2. C. Yan, Y. Zhang, Z. Guo, *Coord. Chem. Rev.* **2021**, *427*, 213556.
3. (a) M. Delcroix, A. Reddy Marri, S. Parant, P.C. Gros, M. Bouché, *Eur. J. Inorg. Chem.* **2023**, *26*, e202300138; (b) P. Xiang, Y. Shen, Z. Feng, M. Sun, Q. Zhang, S. Li, D. Li, G. Zhang, Z. Wu, Y. Tian, Z. Zhang, X. Tian, *Inorg. Chem. Front.* **2020**, *7*, 2753.
4. M. Bouché, C. Hognon, S. Grandemange, A. Monari, P.C. Gros, *Dalton Trans.* **2020**, *49*, 11451.
5. M. Bouché, P.C. Gros, EP23306807.1.

Abderrahmane AMGOUNE carried out his PhD in 2006 in the field of organometallic chemistry and polymerization catalysis at the University of Rennes under the supervision of Profs. Jean-François Carpentier and Christophe Thomas. He then joined the group of Prof. Stefan Mecking (University of Konstanz, Germany) as postdoctoral researcher (Alexander-von-Humboldt fellowship). In 2008, Abder was promoted CNRS research fellow in Toulouse at LHFA (Laboratoire Hétérochimie Fondamentale et Appliquée). Since 2017 he is full professor at the University of Lyon 1 at the ICBMS (Institut de Chimie et Biochimie Moléculaires et Supramoléculaires). He is interested in the development and understanding of innovative catalytic approaches merging rational design of nickel-based catalysts with the use of photochemical and electrochemical approaches to convert readily available feedstock chemicals efficiently and sustainably to high added value organic scaffold.

PL3 | Controlling Nickel Redox States for Radical Pathways with Photo- & Electro-chemical approaches

Abderrahmane Amgoune*,[1]

[1] *Université Claude Bernard Lyon 1, ICBMS, UMR 5246,*
1 rue Victor Grignard, 69100 Villeurbanne, France
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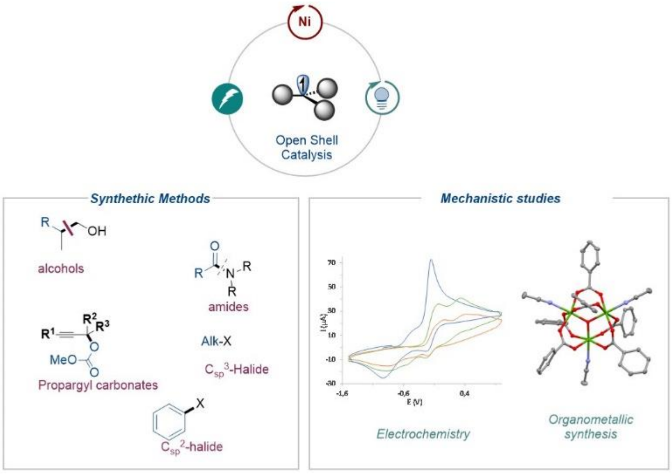
Our research focuses on the development of innovative catalytic approaches that merge rational design of nickel-based catalysts with photochemical and electrochemical methodologies to enable the efficient and sustainable conversion of readily available feedstock chemicals into high-value organic scaffolds. In this presentation, we will highlight our recent progress in developing nickel-catalyzed processes that leverage photochemical and electrochemical activation for challenging cross-coupling reactions and the synthesis of unsaturated substrates. We will discuss several key catalytic strategies recently developed in the group, including: (1) Electrochemically driven cross-electrophile coupling of N-acyl-imides with alkyl halides, (2) Photocatalytic reduction of unsaturated substrates, such as alkynes and propargyl carbonates, mediated by nickel molecular catalysts and (3) the development of a general photocatalytic platform that combines nickel and iron ligand-to-metal charge transfer (LMCT) catalysis for selective deconstructive Csp^2–Csp^3 bond cleavage and arylation of unactivated alcohols. Mechanistic insights gathered from cyclic voltammetry, stoichiometric experiments, and the isolation of catalytic intermediates will be presented, offering a deeper understanding of the key role of nickel redox states in these processes.



Scheme 1. Combining nickel catalysis with photo or electrochemical approaches.

1. (a) Kerackian, T.; Reina, A.; Krachko, T.; Boddaert, H.; Bouyssi, D.; Monteiro, N.; Amgoune, A. *Org. Lett.* **2020**, *22*, 2240; (b) Kerackian, T.; Bouyssi, D.; Pilet, G.; Médebielle, M.; Monteiro, N.; Vantourout, J. C.; Amgoune, A. *ACS Catal.* **2022**, *12*, 12315.
2. (a) Hu, T.; Jaber, M.; Tran, G.; Bouyssi, D.; Monteiro, N.; Amgoune, A. *Chem. Eur. J.* **2023**, *29*, e202301636; (b) Hu, T.; Fagué, V.; Bouyssi, D.; Monteiro, N.; Amgoune, A. *Green Chem.* **2024**, *26*, 6124.
3. Jaber, M.; Ozbay, Y.; Chefdeville, E.; Tran, G.; Amgoune, A. *ACS Catal.* **2024**, *14*, 12757.

Alexandre MARTINEZ He obtained his PhD in 2004 at the CNRS Coordination Chemistry Laboratory (LCC, Toulouse) in the team of Dr. B. Meunier and Dr C. Hemmert. After a postdoctoral Fellowship with Pr. J. Lacour at University of Genève he worked as Graduate Teaching Assistant at IUFM of Nice (University of Toulon). In 2006 he became Associated Professor in Organic Chemistry at Ecole Normale Supérieure de Lyon and since 2014 he is Professor at Ecole Centrale de Marseille. His main current research interests include supramolecular chemistry and catalysis, supramolecular recognition of biologically active compounds with a focus on hemicryptophanes, aza- and proaza-phosphatrane.

PL4 | Recent developments in the chemistry of hemicryptophane cages: from recognition to confined catalysis

Alexandre Martinez*[,1]

[1] *Aix Marseille Univ, CNRS, Centrale Marseille, iSm2, Marseille, France*
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Hemicryptophanes are host molecules, combining a cyclotribenzylene (or cyclotriveratrylene, CTV) unit with another different C_3-symmetrical moiety.[1] Although the synthesis of the first hemicryptophane was described in 1982 by J.-M. Lehn and A. Collet, this class of host received very little attention during the 20 years following this first promising result.[2] Nevertheless, since 2005, hemicryptophanes have aroused growing interest, and new aspects have been developed (Figure 1).[1] Hemicryptophanes revealed able to complex various guests, including charged and neutral species like neurotransmitters or carbohydrates. They can also act as molecular switches leading to stimuli-responsive supramolecular systems. Furthermore, they can lead to supramolecular catalysts: the endohedral functionalization of their cavity providing nanoreactors with improved stability, selectivity or reaction rates compared to their model parents, lacking cavity. Here, recent developments will be described and we will focus in particular on their properties as confined catalysts.

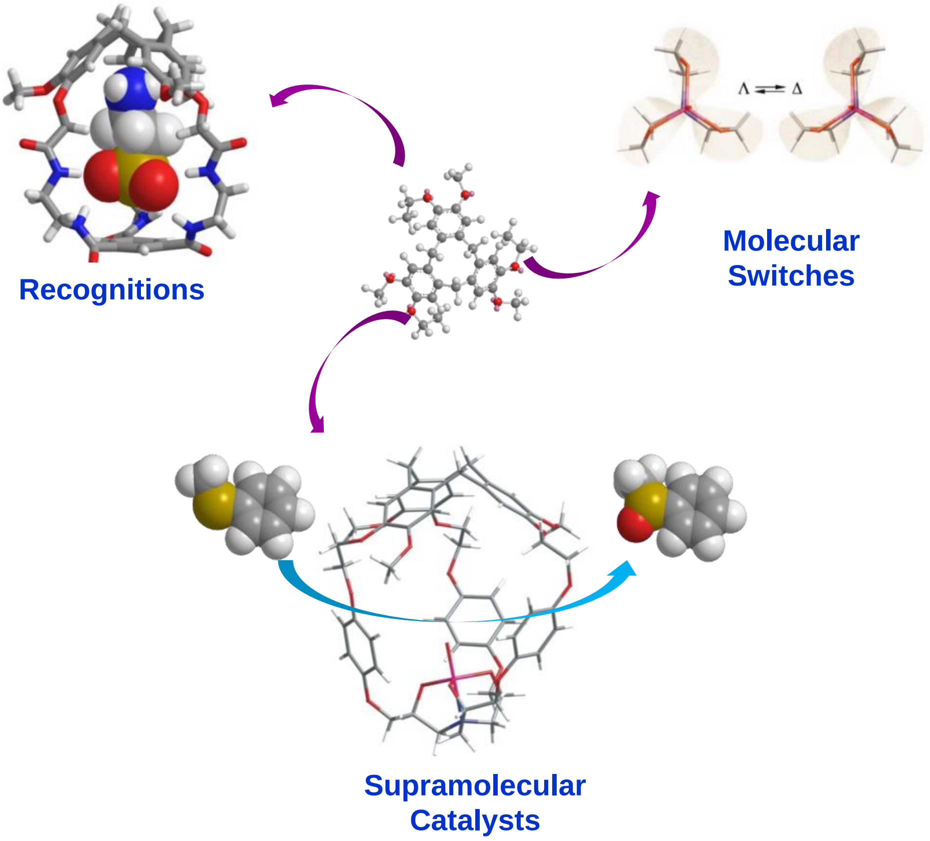

Figure 1. Three different applications of hemicryptophane cages.

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Carine ROBERT obtained her doctorate in 2012 under the supervision of Prof. C.Thomas. She then joined the University of Tokyo (Japan) and worked for a year as a post-doctoral researcher with Prof. K. Nozaki, with the support of the Japan Society for the Promotion of Science. In 2013, she was appointed Lecturer at Chimie ParisTech (Paris, France) in the research group of Prof. Christophe Thomas (IRCP UMR 8247, Organometallic Chemistry and Polymerization Catalysis team) developing extensive skills in polymer chemistry, more particularly in the field of biodegradable polyesters, polyethers and polycarbonates. She is primarily interested in the design of organometallic catalysts capable of carrying out chemical transformations with high degrees of efficiency and selectivity. His established skills in catalysis include polymer synthesis, fine chemical synthesis as well as catalyst characterization and mechanistic aspects. Additionally, she works in all areas of synthesis, from air-stable compounds to derivatives that are extremely sensitive to air and humidity. She also has experience in the catalytic conversion of bio-based derivatives.

PL5 | Ring Opening Polymerization using Organometallic Complexes for the Synthesis of Biosourced Polymers

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The vast majority of commodity materials are obtained from petrochemical feedstocks. These resources will plausibly be depleted within the next 100 years, and the peak in global oil production is estimated to occur within the next few decades. In this regard, biomass represents an abundant carbon-neutral renewable resource for the production of polymers. Among the thermoplastics, aliphatic polyesters are the most interesting polymers since they could be rendered biodegradable under the appropriate conditions. Here we report new strategies, based on catalyzed ring-opening polymerization of cyclic polar monomers, to obtain polyesters with new properties from renewable materials. Newly designed and commercially available organometallic complexes will be presented as efficient catalysts for 1) highly reactive ring-opening polymerizations of cyclic esters under soft reaction conditions to afford controlled microstructures[1][2][3] 2) one-pot and tandem strategies to produce biobased polyesters.[4] New biosourced poly(meth)acrylates from multicatalytic transformation of acrylic acid are also introduced.[5]

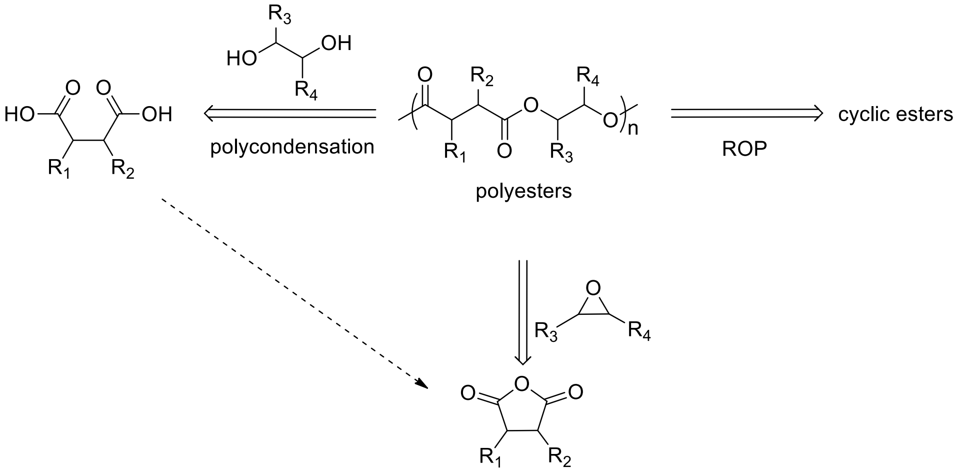

Figure 1. Synthetic approaches to aliphatic polyesters.

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Benoît BERTRAND completed a double PhD degree in 2015 in bioorganometallic chemistry shared between the University of Burgundy (France) with of Prof. Le Gendre, and the University of Groningen (The Netherlands) with Prof. Casini, on the synthesis and anti-tumour activity of gold compounds. He then moved to the University of East Anglia (UK) as a senior postdoctoral research associate in the group of Prof. Bochmann, where he worked on cyclometalated Au(III) complexes as anti-cancer agents. In 2017 he joined the group of Prof. Thorimbert at Sorbonne Université (France) and in 2018 he got appointed at Sorbonne Université as a CNRS junior researcher. His research interests deal with the synthesis, reactivity studies and biological investigations of organogold(III) complexes with a particular emphasis on their intracellular speciation.

PL6 | Biphenyl-gold(III) complexes: a promising scaffold for investigations of anticancer drug candidates

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J. Forté,[1] G. Gontard,[1] M. Salmain,[1] Joëlle Sobzack-Thépot,[3] S. Bohic,[4] O. Proux,[2]
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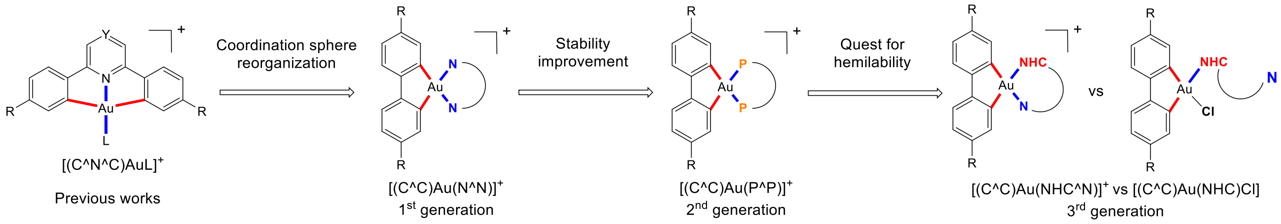
Organometallic gold(III) complexes have attracted a large attention as potential anticancer agents in the last decades. The main advantage of organometallic complexes is their high redox stability in physiological media due to the presence of Au-C bounds. In this respect, bis-cyclometalated [(C^N^C)AuL]$^+$ complexes have demonstrated great potential.[1] However, their main limitations are the large number of coordination site occupied by the pincer ligands leaving only one or no coordination sites for available for other ligands. Moreover, the amount of substitution tolerated on the pincer ligands are quite narrow meaning the possibility of variation of these scaffolds are quite limited. To enlarge the scope of structures that can be tested and potentially explore new modes of actions while preserving the high redox stability of bis-cyclometalated complexes, a reorganization of their coordination sphere appeared as a promising potential. Using a biphenyl ligand giving two Au-C bounds would preserve the high redox stability of bis-cyclometalated complexes while offering two coordination sites available for various ligands to optimize the anticancer properties of the complexes. Our results on the synthesis and anticancer activity of biphenyl-Au(III) complexes presenting N-[2] and P-donor ligands[3] and hemilabile NHC-N ligands[4,5] as anticancer agents will be presented.



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Chiara DINOI obtained her PhD in 2007 in Organometallic Chemistry at the LCC laboratory in Toulouse, working on high oxidation state Mo and W complexes in aqueous media, in the team of Pr. R. Poli. After a first postdoctoral stay at the ICIQ laboratory in Tarragona, in the field of water oxidation catalyzed by Ru complexes, she carried out a second postdoctoral stay at the LPCNO laboratory in Toulouse, where she was introduced to DFT calculations as a complementary deepening of experience. Appointed lecturer in 2010 at the Université Toulouse III-Paul Sabatier, she focused on the chemistry of highly electrophilic complexes of metals from the left of the periodic table, for the activation of inert CH bonds and the catalysis of atom-economic reactions such as ring-opening polymerisation (ROP) and hydroelementation (HE), using an experimental approach. In 2016, she moved full-time into computational chemistry, centering her research interests on the use of DFT calculations to model the electronic structure and reactivity of molecular and grafted organometallic complexes with s-, d- and f-blocks. Her skills in the DFT calculation of energy profiles and spectroscopic properties aim to link theory and experiment.

PL7 | Reactivity and Catalytic Activity of the Beta-Diketiminato [(BDI)CaH]$_2$ Compound: A Theoretical DFT Study

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The last 20 years have seen the more general emergence of calcium-based reagents, primarily as Earth-abundant and inexpensive vectors for homogeneous catalysis.[1] Central to these latter efforts has been the use of a variety of multidentate uninegative supporting anions (L) as spectator ligands in the study of heteroleptic derivatives, LCaX (where X =, e.g., amide, phosphide, alkyl, hydride). While the primary requirements of L are to enhance LCaX solubility in non-coordinating solvents and suppress otherwise deleterious Schlenk-type equilibration, its steric demands must be appropriately and conveniently perturbed to maintain an appropriate level of kinetic reactivity at the Ca–X bonded unit. Instigated by Harder and co-workers' report of the calcium hydride, [(DippBDI)Ca(THF)H]$_2$ (**1**, DippBDI = HC{(Me)CN-2,6-*i*Pr$_2$C$_6$H$_3$}$_2$),[2] □-diketiminate derivatives have been particularly prominent in these advances.[3]

Whitin this class of complexes, the core of this contribution will describe a theoretical DFT study on the reactivity and catalytic activity of the THF-free variant of **1**, the [(BDI)CaH]$_2$ (**2**) compound. A DFT computational study on the mechanism involved in the reaction of **2** with inactivated terminal alkenes will be detailed[4] and compared with that computed for the lighter [(BDI)MgH]$_2$ analogue.[5] The potency of the hydride reagent **2** toward the hydrogenation of C–C multiple bonds will be then discussed, by the reaction of **2** with the 1,3,5,7-cyclooctatetraene (1,3,5,7-C$_8$H$_8$) molecule.[6] This reaction leads to the formation of the dicalcium cyclooctatetraenyl derivative, [(BDI)Ca(μ-COT)Ca(BDI)] (**3**), by reductive aromatization of cyclooctatetraene, highlighting the ability of compound **2** to function as a source of polarized unsaturated insertion (2σ–2π) and metathetical (2σ–2σ) reactivity.

The synthesis, of hydridoaryl- and diaryl-calcium compounds, by reaction of **2** with Ar$_2$Hg reagents, will be then described.[7] These complexes display different types of Ca-μ$_2$Ar-Ca bridging modes, whose stability will be discussed in terms of stabilizing ortho-CH⋯Ca interactions and BDI aryl substituents steric repulsion. The C–C coupling across bis-phenyl calcium dimers will be finally discussed,[8] by taking into account the role of the phenyl anion π-interactions with the two Ca atoms in the decrease of the mutual repulsion of the two carbanionic α-carbon phenyl centers.

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Oral communications

Communications Orales

OC1 | Tuning the 1D / 2D Dimensionality in Copper(I) and Silver(I) Thiolate Coordination Polymers

Alexis Giraudon,[1,2] Oleksandra Veselska,[1] Chloé Andrade,[1,3] Nathalie Guillou,[4] Stéphane Pailhès,[3] Florent Perret,[2] Aude Demessence[1]

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In the past years, coordination polymers (CPs) have gained significant attention due to their potential applications in various domains, such as sensing or energy storage.[1] Among them, d^{10} coinage metal-thiolate CPs, stand out due to their ability to form stable and anisotropic structures thanks to the strong metal-sulfur interaction. However, the relationship between their one- or two-dimensionality and their physical properties, such as electrical conductivity and luminescence, remains poorly understood.[2] According to literature and past studies from our team, it appears that the steric hindrance near the thiolate moiety plays a crucial role in the modulation of the dimensionality.[3]

In this context, we investigated the synthesis of eight new CPs formed from 3-mercaptobenzoic acid (*m*-HSPhCO$_2$H), methyl-3-mercaptobenzoate (*m*-HSPhCO$_2$Me) or the 1- and 2-Naphtalenethiol (1-NT and 2-NT): [M(*m*-SPhCO$_2$H)]$_n$, [M(*m*-SPhCO$_2$Me)]$_n$, [(M(1-NT)]$_n$ and [M(2-NT)]$_n$ with M = Cu or Ag, in order to assess how structural changes in the organic ligand affect the overall CP structure and the resulting physical properties of these new materials (**Figure 1**).

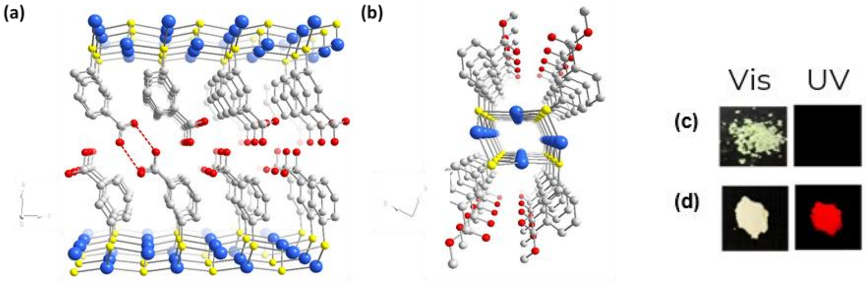

Figure 1. (a) Projection of the 2D [Ag(*m*-SPhCO$_2$H)]$_n$ and **(b)** projection of the 1D [Ag(*m*-SPhCO$_2$Me)]$_n$. **(c)** and **(d)** Photographs of [Ag(*m*-SPhCO$_2$H)]$_n$ and [Ag(*m*-SPhCO$_2$Me)]$_n$, respectively, at RT under natural (left) and UV (right) lights.

Crystallographic data showed that the steric hindrance around the thiolate function induces a 1D dimensionality. This directly affects their photophysical properties : 1D CPs are more susceptible to exhibit intense red-yellow luminescence while 2D CPs are non-emissive at room temperature. Effects of the dimensionality of the CPs on the electrical conductivity will also be discussed.[4]

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OC2 | Influence of the *4f*-3*d* Metals Pairs on the Synthesis, Structure and Reactivity of Heterobimetallic Siloxide Complexes

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The development of heterobimetallic catalysts has attracted growing interest in recent decades to tackle the challenging activation of inert bonds. The combination of two metal centers with complementary properties and functions, in close proximity, aims to promote cooperativity for original and improved catalytic reactivity, not accessible with monometallic species.[1] For instance, our group recently reported the synthesis of original Ta-Ir and Hf-Ir heterobimetallic complexes, both in solution and grafted on silica solids, exhibiting high catalytic performances for H/D exchange reactions compared to the monometallic analogues.[2] However, the number of heterobimetallic catalysts reported so far is limited and mostly restrained to expensive and rare elements.

The objective of this work is to explore new combinations of non-noble metals, associating lanthanides (Ln) as hard, Lewis-acidic metals, with earth-abundant 3*d* metals such as Mn, Fe, Co, Ni, Cu. Using the bulky, electron-rich tris(tert-butoxy)siloxide ligand $(^{t}BuO)_3SiO^-$, suitable for grafting on solid supports,[3] a promising salt metathesis strategy has been developed and allowed the isolation of new heterobimetallic complexes, such as the homoleptic $[EuMn(OSi(O^{t}Bu)_3)_4]$ complex associating divalent Eu and Mn ions. Interestingly, by changing the nature of the 4*f* and 3*d* metals, the synthetic routes as well as the structures and properties of the resulting complexes are affected, as will be presented in this communication.

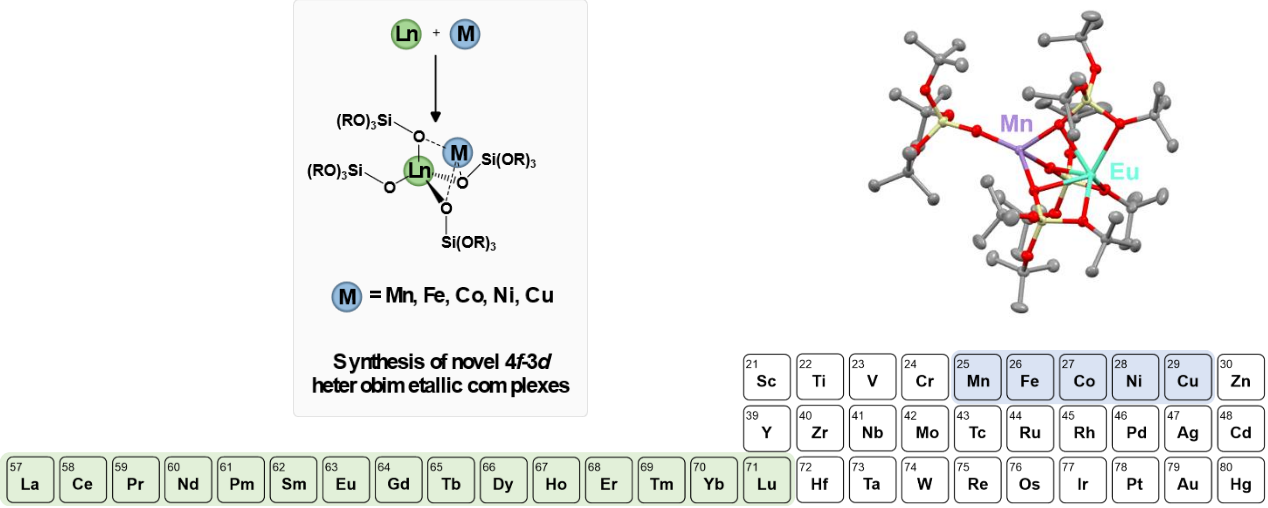

Figure 1. Synthetic strategy to develop 4*f*-3*d* heterobimetallic complexes and crystal structure of a novel Eu-Mn siloxide complex.

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OC3 | σ-BH activation of [NHC-BH_3] fragments at dinuclear Cu complexes: a DFT description

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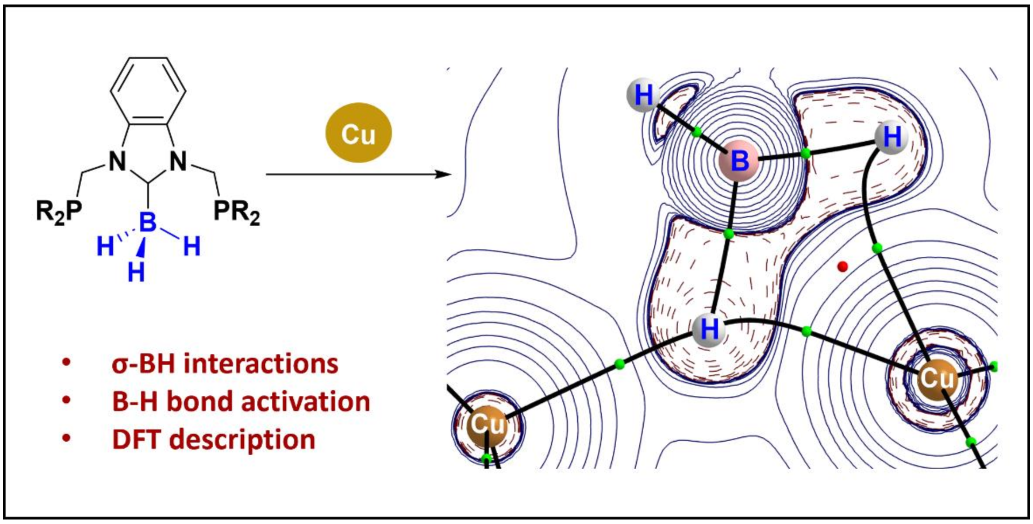
The synthesis of a bisphosphine [NHC-BH_3] compound was recently reported in the team as a ligand able to support bimetallic gold structure.[1] In the present work, the coordination properties of this ligand was explored toward cationic and neutral Cu centers. Dinuclear Cu complexes were synthesised featuring BH fragments involved in various σ-BH interactions with metal centers. DFT investigations supported experimental characterization of these interactions and estimated the level of activation of the B-H bond depending on the coordination environment. The study shows a gradual increase of the activation whether the BH fragment is involved in none, one or two σ-BH interaction with Cu centers.[2]



Scheme 1. DFT characterization of σ-BH interactions of a [NHC-BH_3] dinuclear copper complexes.

This work was supported by the Agence Nationale de la recherche under France 2030 plan (ANR-22-PESP-0010 Projet ciblé "POWERCO2") within the PEPR project SPLEEN

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OC4 | From the Old to the New: Group 9 Metals in Cyclometallation and Ligand Substitution Reactions for C-H Bond Functionalisation

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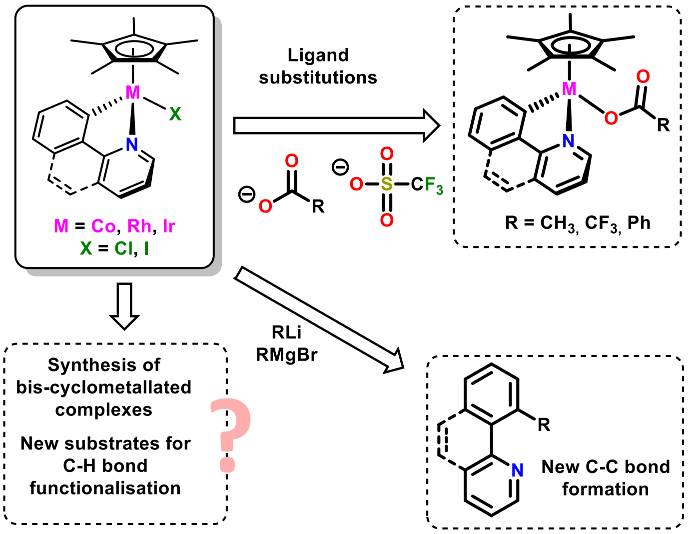
Metallacycles are crucial structures in organometallic synthesis and catalysis: understanding their behaviour and reactivity provides key clues for the development of new and efficient catalytic systems. Synthesised through an initial base-assisted C-H bond activation,[1] Group 9 metallacycles serve as an ideal starting point in order to explore both the synthesis of new complexes and as an example of how the chemistry of 4d and 5d row metals might be recreated using a 3d row metal. Their participation in reactions such as C-H bond functionalisation through novel reaction pathways such as oxidatively induced reductive elimination[2] paves the way for new catalytic systems to be developed using Co, Rh and Ir. The reactivity of these structures has been explored using two approaches: the first one focused on the synthesis of old and new metallacycles, and the second on the use of more labile ligands in order to carry out new chemical transformations.

Thus, a small library of metalacyclic complexes based on the general structure [MCp*(C^N)X] was synthesised, where M = Co, Rh, Ir, Cp* = 1,2,3,4,5-pentamethyl-cyclopentadienyl, C^N is a C,N-chelating ligand and X is generally an anionic ligand.[3] This allowed the exploration of cyclometallation reactions based on ligands with up to two cyclometallation sites, leading to a greater understanding of the constraints that govern these reactions. In parallel, the introduction of carboxylate, alkyl and aryl ligands allowed the study of how the introduced ligand might affect the tendency of the obtained organometallic complex to undergo C-C bond forming reductive eliminations.



Finally, the use of a labile ligand such as the triflate anion also proved to be a promising approach to unlocking new C-C and C-N bond forming reactions, where freeing up a coordination site on a cobaltacycle allowed electrophilic alkyne annulations and C-H bond amidation reactions to take place.

These results are a first step towards optimizing C-H bond functionalisation reactions, clearly proving that there is great potential for Group 9 metals to become key players in this domain, whilst also setting the stage for the development of cobalt cobaltacycle chemistry.

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OC5 | Amidine-phenoxy ligands (AF) and their group IV metal complexes for olefin polymerization

Thu Van Nguyen,[1] Yoann Rousselin,[1] Jérôme Bayardon,[1] Evgeny Kirillov,[2] Jean-François Carpentier,[2] Raluca Malacea-Kabbara,[1] Pierre Le Gendre[1]

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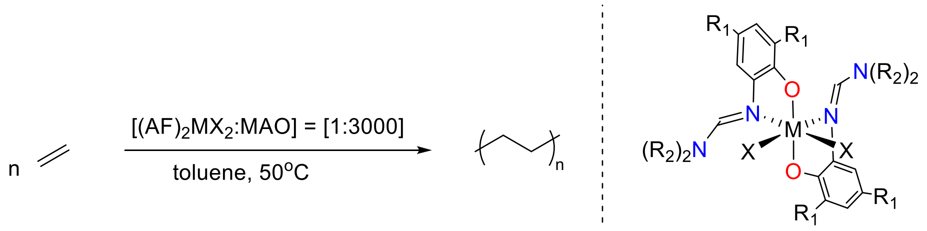
Our group has recently developed a new variant of the ubiquitous phenoxy-imine (FI) and imine-phenoxy (IF) ligands by replacing the imine moiety with an amidine moiety.[1]. We hypothesized that amidine, being more basic and less sensitive to nucleophilic attack than imine, should confer greater robustness to metal-AF catalysts compared with their FI counterparts. In this study, we have described the coordination chemistry of amidine-phenoxy ligands (AF) with the metal ions Ti and Zr and evaluated their catalytic performance in ethylene polymerization. The coordination chemistry was done via two strategies: the salt metathesis of metal precursors with lithium salt of the ligands, and another pathway via silylated ligands. NMR spectroscopy of $(AF)_2MX_2$ complexes in solution shows that all complexes bearing unsubstituted AF ligands (R_1 = H) exist only as the symmetrical C2 isomer. This distinguishes AF ligands from their IF counterparts, which generally give Ti/Zr-IF complexes as a mixture of isomers in solution.[2]. X-ray diffraction analysis of the $(AF)_2MX_2$ complex (M = Ti, Zr) showed that all these complexes exhibit an octahedral geometry around the metal centre with an *O-trans*, *N-cis*, X-*cis* configuration. Furthermore, bond length analysis reflected a strong delocalization on the amidine moiety and highlighted a strong trans influence of amidine functions. Catalytic tests showed that these complexes are active in ethylene polymerization upon activation by MAO at 50°C in toluene. Complexes with ^{t}Bu substituents on the aryloxy ring showed better polymerization efficiency than unsubstituted complexes. The amido **$(L4)_2Ti(NMe_2)_2$** complex gave the highest productivity (229.6 kgPE/mol$_{\mathbf{cat}}$.h).



L1: R_1 = H, $N(R_2)_2$ = CH_3
L2: R_1 = H, $N(R_2)_2$ = pyrrolidine
L3: R_1 = H, $N(R_2)_2$ = piperidine
L4: R_1 = *t*Bu, $N(R_2)_2$ = CH_3
L5: R_1 = *t*Bu, $N(R_2)_2$ = pyrrolidine
X: Cl or NMe_2

Scheme 1. Ethylene polymerization with MAO activation.

This work was supported by ANR (MORFAL, ANR-22-CE07-0011).

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OC6 | Six-membered CO_2-based lactones/lactams towards polyesters and polyamides

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My project focuses on developing six-membered lactones derived from CO_2 and exploring their catalytic transformation into polyesters and polyamides. After introducing the context of my project, I zoomed in on EVP lactone — an unsaturated six-membered lactone synthesized from butadiene and CO_2[1] — which I aim to use as a key platform molecule for generating new CO_2-based synthons and polymers.

In my first project, I explored several methods to produce linear diesters, with the goal of using them to make polyesters via polycondensation with diols. I thoroughly investigated the hydroesterification of EVP using CO/MeOH in the presence of palladium catalysts. I screened different ligands and optimized the reaction conditions to improve selectivity, since the reaction initially gave a broad mixture of products. After a detailed analysis and structural identification of these products, I managed to improve the selectivity for the desired product to 50%. A manuscript based on this work is currently in preparation.

In my second project, I focused on the dimerization of EVP through self-cross metathesis using the Hoveyda-Grubbs II catalyst,[2] which gave me the dilactone in about 50% yield. I then performed aminolysis studies using model mono-amines like benzylamine and morpholine, to understand the best conditions for making polyamides via reaction with polyamines. Interestingly, the amines not only opened the lactone rings but also underwent Michael-type additions, leading to a complex mixture of products, most of which I was able to identify and characterize.

I also initiated the copolymerization of this dilactone with hexamethylene diamine. Although the reaction proceeded, the resulting product was poorly soluble, which made its characterization difficult. This wasn't unexpected, considering that the amine could react at multiple sites on the dilactone, leading to potential crosslinking. I tried a first copolymerization with a diol to make polyesters, but that attempt was unsuccessful.

To address the chemoselectivity issues and avoid side reactions like Michael additions, I hydrogenated the unsaturated dilactone to obtain the saturated version, using Pd/C as the catalyst. This hydrogenation was highly efficient, and I've already started testing the copolymerization of this saturated dilactone with diamines. The initial results look promising, though further optimization and characterization are still needed.

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OC7 | Caged Triazacyclononane Ligands: Towards Non-heme Bioinspired Caged Catalysts

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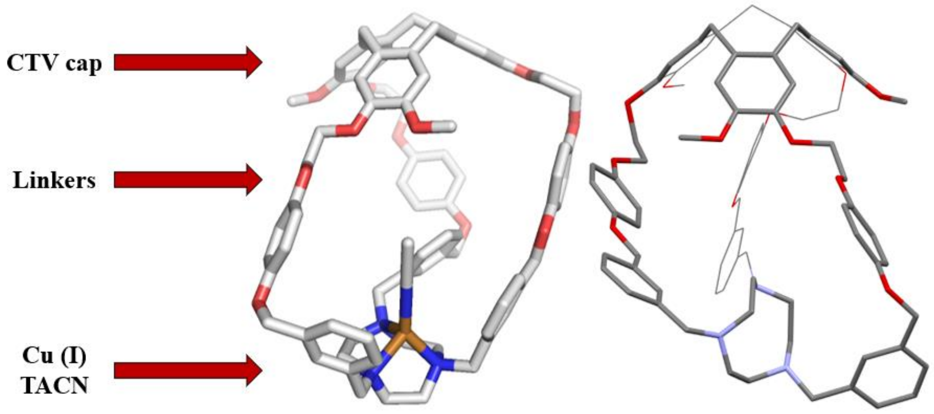
Metalloenzymes are biocatalysts, whose reactivity depends on biologically active metal ions (Cu, Fe, Zn, Mn) supported by oxygen, sulphur or nitrogen donor ligands confined within the enzymes proteic scaffold. Most notably, metalloenzymes catalyse difficult reactions, under mild conditions, with remarkable selectivity and efficiency. For instance, methane monooxygenase (**MMO**) activates molecular oxygen to reach the highly challenging selective oxidation of methane to methanol.

The 1,4,7-triazacyclononane (**TACN**) is a saturated azamacrocycle displaying three nitrogen donor atoms. This ligand is well known for its coordination ability with metal cations, varying from transition metals to lanthanides.[1] **TACN**-based complexes have been widely applied in the development of radiopharmaceuticals and bioinspired catalysts. Especially, it was shown by Tolman and co-workers, that open Cu (I) **TACN**-based complexes, substituted with bulky groups, could activate O_2 to produce powerful oxidizing species.[2]

However, in order to mimic metalloenzyme's activity, it is crucial to not only replicate the first coordination sphere, but also mimic the hydrophobic cavity surrounding the active site. To do so, it is possible to use hemicryptophane ligands, which are cyclotriveratrylene (**CTV**)-based cage structures, that were recently used in our group to develop bioinspired catalysts.[3] On this basis, the goal of this work is to functionalize the canonical **TACN** ligand with the bowl-shaped **CTV** cap, via three linkers, creating a hemicryptophane cage (**Scheme 1**). Here, the synthesis of two **TACN**-based ligands, displaying well-defined cavities of varying volumes and flexibility, will be presented along with the study of their corresponding Cu (I) complexes as potential O_2 activating confined catalysts.



Scheme 1. DFT-optimized structure of the **TACN**-based caged Cu (I) complex (left) and XRD structure of the **TACN**-based caged ligand (right).

This work was supported by the National Research Agency (ANR-22-CE50-0009-01).

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OC8 | Multifaceted reactivity of cobalt and iron-based electron-rich redox active systems

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When developing catalytic processes with open-shell first-row transition metals, the active participation of supporting ligands in bond-breaking and bond-forming events can significantly enhance control over reactivity and selectivity. Active ligands contribute through various mechanisms; for instance, they can assist metal centers in substrate binding and activation.[1,2] Alternatively, they may serve as electron reservoirs, facilitating two-electron redox processes in place of the less controllable single-electron transfer reactions typically favored by these systems.[3] While these strategies have been independently leveraged in catalysis, instances where they operate synergistically remain rare.

Previously, we reported that open-shell iron-based PNN dinitrogen complexes exhibit facile spin-state transitions triggered by either chemical stimuli (*e.g.*, non-nucleophilic bases) or physical stimuli (*e.g.*, vacuum). These spin-state changes are accompanied by alterations in reactivity towards small molecules such as H_2, CO_2, and N_2.[5,6] Building on this work, we have now developed analogous cobalt complexes that display unusual reactivity patterns and magnetic properties.

For instance, singlet (PNN)Co^{n}Bu species are isolable despite the presence of β-hydrogens and vacant coordination sites. These complexes only undergo β-hydride elimination under vacuum or in the presence of weak ligands, such as CO_2. Interestingly, despite their singlet electronic ground state, significant spin-orbit coupling effects contribute to a pronounced temperature-independent paramagnetism. This phenomenon results in dramatically shifted NMR resonances for species like PNNCoH and PNNCoMe compared to standard diamagnetic references.[7] The origins and implications of these effects will be discussed and a comparison with the iron analogues will be presented.[8]

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OC9 | Defluorination of discrete molecules and polymers catalysed by titanium

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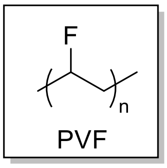
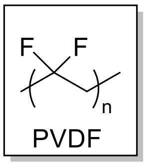
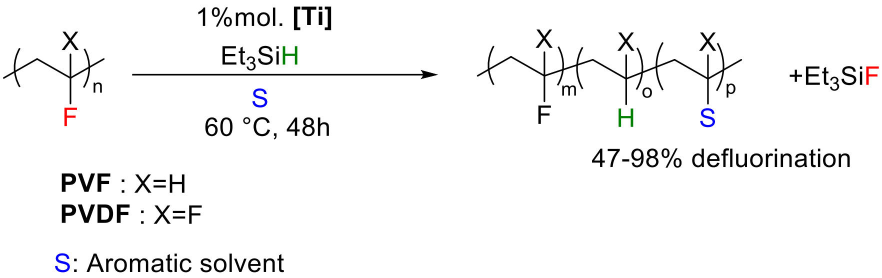
The use of PFAS (per- and polyfluoroalkyl substances) or fluoropolymers like PVF (poly(vinyl fluoride)) and PVDF (poly(vinylidene fluoride)) is very widespread nowadays. However, their growing production has led to the problem of how to process their waste.


PVF


PVDF

Previous work carried out in our laboratory showed the possibility to perform the dechlorination of PVC (Poly(vinyl chloride)) in the presence of a zirconium catalyst, and triethylsilane as a source of hydrogen.[1]

In my talk, I will introduce our work about the defluorination of PVF and PVDF, with group 4 metal catalysts. Good results of defluorination were obtained, between 47 to 98%. Electron-rich aromatic solvents showed the possibility to realise the grafting of solvent molecules onto the polymer by Friedel-Craft Reaction.



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OC10 | Use of Pyridyl cores in biomimetic [FeFe]-Hydrogenases complexes

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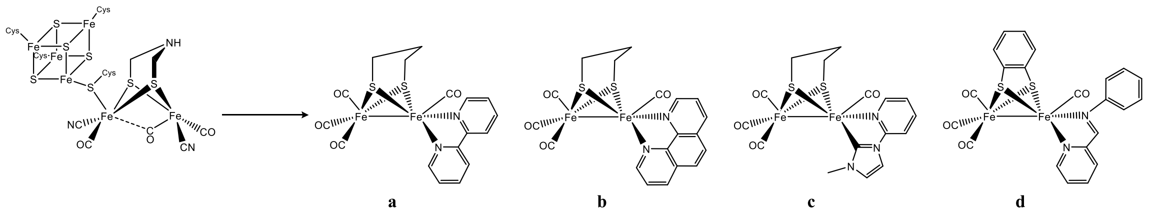
Since several decades, the activation of small molecules, such as H_2, N_2, CO_2, catalyzed by organometallics complexes constitutes an important field of researches. Environmental and economic issues lead to the use of less noble transition metal complexes instead of gold or platinum.

In the nature, the reversible production of dihydrogene from electrons and protons is possible in microorganisms by efficient enzymes called Hydrogenases. In 1998, Peters et al. have highlighted the structure of one [FeFe]-Hydrogenase.[1] Their active site, called the H-cluster (*Scheme 1*) consists of two iron atoms surrounded by terminal ligands (CN, CO) and a cuboidal [4Fe-4S] cluster, a non-innocent redox ligand participating in electron transfers, and bridged by an amino-dithiolato group in which the amine function allows the transport of protons towards the diiron center.

Since then, the design and study of the activity of iron-sulfur complexes mimicking the H-cluster, based on $[Fe_2(CO)_6(\mu\text{-dithiolate})]$ precursors, have been widely developed by combining cooperative ligands for electron and proton transfers or to influence the geometry around the diiron site in the aim to reproduce specificities of the H-cluster.

Pyridine derivatives represent interesting candidates as ligands to combine with a dinuclear iron site, in reason of their possible redox and base properties. A first example of the coordination of pyridine in a complex of general formula $[Fe_2(CO)_5L(\mu\text{-dithiolate})]$ was reported in 2009 [2] but the chemistry of diiron systems with such pyridyl ligands was poorly developed. A limited number of complexes containing chelate ligands with a pyridyl framework have been studied [3],[4],[5],[6] (*Scheme 1*). One on-going project is to design iron-sulfur systems, related to the H-cluster, using polydentate pyridine ligands with specific electron-donating or attracting groups.



Scheme 1. Representation of the H-cluster and some $[Fe_2(CO)_4(\kappa^2\text{-L})(\mu\text{-dithiolate})]$ complexes containing pyridyl cores.

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OC11 | Bifunctional nickel catalysts for hydroboration and hydrosilylation reactions via cooperative B–H and Si–H bond activations

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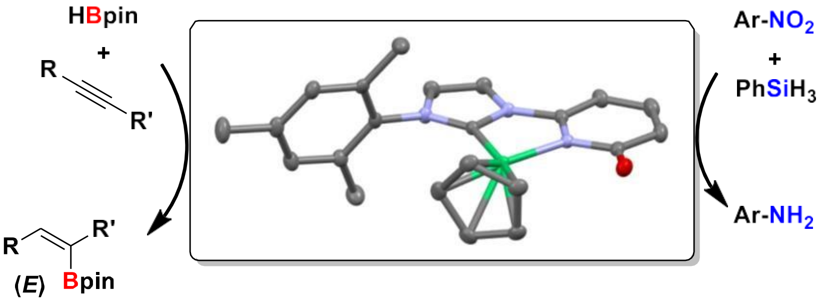
The transition-metal-catalyzed hydroboration[1,2] and hydrosilylation[1,3] are powerful synthetic methodologies because they provide valuable organoboron and organosilicon compounds by straightforward and atom economic synthetic routes. Organoboronate derivatives are widely employed for the construction of C–C, C−N, C−O, and C−S bonds and, as such, are significant feedstocks for the synthesis of pharmaceuticals, agrochemicals, liquid crystals, and organic light-emitting diodes.[1,2] By comparison, organosilicon derivatives are less involved in organic transformations though significant progresses have been made.[4] Such organic compounds are mainly applied in the industrial production of commodity silicones or as pharmaceuticals.[1,3] In addition to these applications, the use of hydrosilanes and hydroboranes is an interesting alternative to hydrogenation, their use as reductants allowing reactions to proceed without any high-pressure equipment or high temperatures. Furthermore, as the reactivity of such boron and silicon reagents and related reaction intermediates is modular and depends on their substituents, hydroboration and hydrosilylation reactions can become highly chemo- and regioselective reduction methods that tolerate various other reducible functional groups.[1,3] The main drawback, however, of the synthetic methodologies involving hydroboration or hydrosilylation is that they are principally developed with noble metal-based catalysts. In addition, whether various organic unsaturations can be reduced through the sole use of a hydrosilane activated by a catalyst, their hydroboration using boranes like catechol or pinacol borane most often requires the combination of a catalyst and a basic activator.

In this context, based on preliminary results,[5] our research project aims at developing bifunctional activator-free catalysts based on nickel, an abundant first-row transition metal. In particular, we target Ni(II)-NHC (NHC = N-heterocyclic carbene) catalysts able to assist hydroboration and hydrosilylation reactions by cooperative E–H (E = B, Si) bond activation and therefore result in effective catalytic processes. A first generation of nickel catalysts has been developed based on a NHC ligand substituted by a pyridone moiety, *i.e.*: based on a NHC ligand bearing a remote metal-unbonded nucleophilic site.[6] Such catalysts are effective without any additive for the selective hydroboration of alkynes to alkenylboronates and the straightforward reduction of nitroarenes to anilines through hydrosilylation (Scheme 1).



Scheme 1. Catalytic hydroboration of alkynes and hydrosilylation of nitroarenes using a Ni(II)-NHC-pyridone complex.

This work is supported by ANR, project BIFUN (2023–2027, ANR-22-CE07-0023-01).

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OC12 | Mn-Catalyzed Regioselective Alkene Hydrosilylation: Reaction Mechanism Investigation

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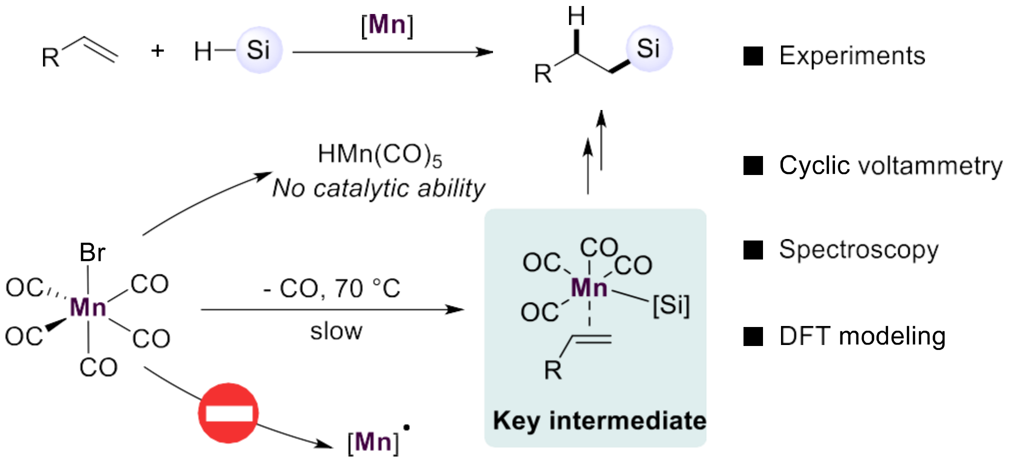
Alkene hydrosilylation is a key reaction for the preparation of organosilicons and functional silanes. Currently, unsustainable platinum-based complexes are still preferred in the industry and although ppm levels of catalyst are used, the difficulty to remove Pt from the reaction products leads to extra costs.[1] One current major trend in this field is thus replacing platinum with earth abundant non-noble metal species. Consequently, in recent years, a major effort has been dedicated to the development of first-row transition metal complexes as catalysts for alkene hydrosilylation. In this context, commercially available and structurally simple Mn complexes were found very promising catalysts for the regioselective hydrosilylation of various alkenes under UV irradiation or under thermal conditions (70°C) with low Mn loadings.[2,3] The most recent catalytic system based on $Mn(CO)_5Br$ was found to tolerate unpurified substrates and could be used in green solvents under air, selectively yielding the anti-Markovnikov hydrosilylated products at 70°C.[3] However, $Mn(CO)_5Br$ exhibits poor solubility in industrially favorable green solvents at low temperatures and deactivates during the reaction. Therefore, there is still a need to raise mechanism understanding to promote the rational design of next generation catalysts.

In this study, through an integrated approach combining NMR spectroscopy, kinetic monitoring, control experiments, cyclic voltammetry studies and DFT modeling, we were able to elucidate the hydrosilylation reaction mechanism.[4] In addition to understanding the molecular origins of the observed selectivities and the potential deactivation pathways, our findings revealed that the initiation step involves specific CO ligand dissociation and substrate coordination to generate an active Mn(I) intermediate that enables the desired transformation via concerted 2-electrons organometallic pathways. Such detailed insights into this mechanism provide a clearer framework for advancing catalysts design and optimizing reaction conditions.



Scheme 1. Mn-Catalyzed Regioselective Alkene Hydrosilylation: from Mechanism Investigation.

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OC13 | Theoretical investigation of FAlen-Zn complexes coordination: when causes are actually consequences

Pouzens Jean-Thomas,[1] Thu-Van Nguyen,[1] Benjamin Théron,[1] Valentin Vaillant-Coindard,[1] Cédric Balan,[1] Jérôme Bayardon,[1] Laurent Plasseraud,[1] Yoann Rousselin,[1] Paul Fleurat-Lessard*,[1] Raluca Malacea-Kabbara,*,[1] Pierre Le Gendre*,[1]

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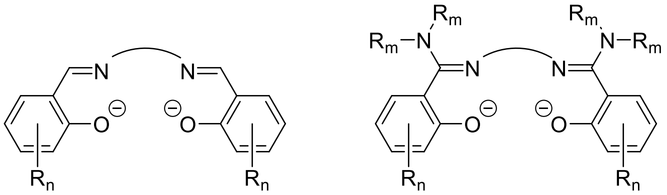
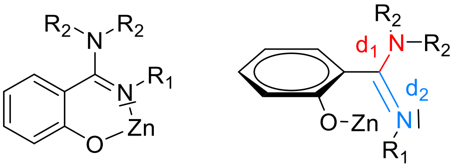
Salen ligands are tetradentate N_2O_2 Schiff-bases. Their metal complexes used in several fields such as catalysis,[1] chemical sensors[2] or energy storage.[3] However, those complexes are sensible to hydrolysis, reduction of alkylation, reducing their efficiency. To overcome this, a new generation of ligand were designed with phenoxy-amidines replacing phenoxy-imines. This so-called FAlen ligand is more robust against reducing or nucleophilic agents and presents improved performances such as the (FAlen-κ²)$AlMe_2$ for ring opening metathesis (Scheme 1).[4]



Scheme 1. Salen and Falen ligands structures.

FAlen ligands offer a great flexibility when it comes to the coordination. Indeed, they can express monodentate to tetradentate behaviours and become bridging to form dimers.[4] This flexibility comes with two main types of coordination: End-on and Side-on (Scheme 2). Moreover, this coordination might lead to an inversion of the bond length (d_2 > d_1) for specific FAlen-Zn complexes.



Scheme 2. End-on and side on coordination modes.

We used DFT and Topological approaches FAlen-Zn complexes as well as different models based on phenoxy-amidine and phenoxy-imines to explain this unusual coordination mode. Our analysis reveals that amidines are not the main drivers of the side-on coordination. On the other hand, the bond length inversion depends on many parameters.

This work was supported by ANR (MORFAL, ANR-22-CE07-0011).

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OC14 | Hybrid ambidentate NHC ligand with a dithiolene backbone

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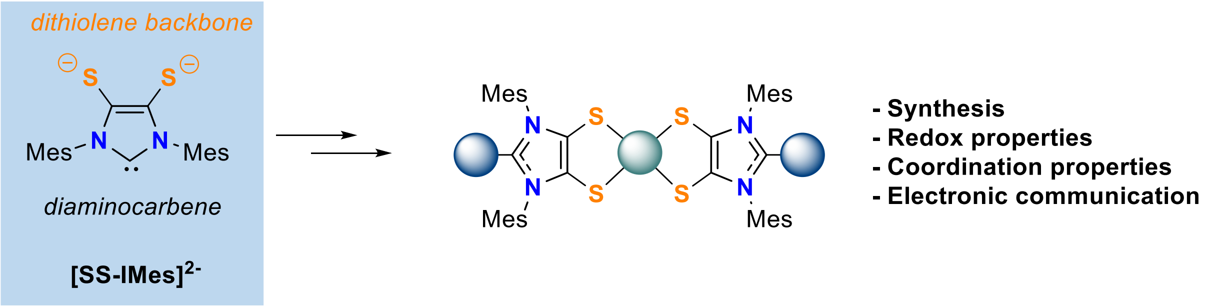
Since the first isolation of a free N-Heterocyclic Carbene (NHC) by Arduengo in 1991, NHCs have emerged as an important class of ligands, widely used and explored in organic and organometallic chemistry.[1] In particular, backbone-functionalized NHCs are especially intriguing, owing to the possibility to drastically tune their electronic properties or to introduce new functionalities such as, chemically, photo-or electro-responsive moieties at C4 and C5 positions of the carbenic heterocycle.[2-5]

In this context, we decided to introduce a very-well known dithiolene moiety as the imidazolyl backbone, as dithiolene complexes have been extensively studied in literature and that they exhibit stable multi-redox states. As relevant examples, the bis(dithiolene) complexes based on imidazolidine-2-thione have shown very interesting photothermal activity,[6] and imidazolidinethione-based dithiolene compounds have shown a vast and rich redox chemistry.[7] We report herein the straightforward introduction of the two sulfur atoms onto the imidazolyl-ring to formally generate the precursor of [IMes-SS]$^{2\square}$, as well as the synthesis and properties of a series of mono-and polymetallic complexes of this ligand.



Scheme 1. Ambidentate NHC ligand with a dithiolene backbone.

This work was supported by the ANR QDotNHC project.

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OC15 | Unprecedent panchromatic absorption of azaullazine-based Fe(II) complexes

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The development of iron-based complexes to substitute ruthenium-based complexes as sensitizers in dye-sensitized solar cells and photocatalysts is an appealing and valuable approach owing to iron respective abundance and low cost. In that context, instead of using classical polypyridyl ligands, the incorporation of N-heterocyclic carbenes (NHC) on the pyridine ring could generate Fe(II) complexes with improved photoactivity, *i.e.* excited-state lifetimes of some tens of picoseconds.[1] Besides, the absorption features of the complexes have to be optimized in order to ideally collect photons of the entire visible window (panchromatic character) particularly, for solar cells applications. Accordingly, the extension of the conjugation and/or the HOMO-inversion concept has been recently reported to be beneficial strategies to significantly improve the spectrum coverage of the respective Fe(II) complexes.[2–5] Recently, our research group developed the synthesis of azaullazine derivatives consisting in a fused and planar heterocycle analogous to the pyridine ring.[6,7] Based on its highly conjugated structure, we were interested to substitute the central pyridine ring in pyridyl-NHC ligands with azaullazine and to evaluate the impact on the photophysical properties of the related Fe(II) complexes. As anticipated, the introduction of that fused heterocycle generates Fe(II) complexes with the broadest and most intense absorption spectrum reported to date in the literature. Transient-absorption spectroscopy, spectroelectrochemistry and DFT calculations have been used as tools to investigate the photophysical and electrochemical properties of that new family of Fe(II) complexes.

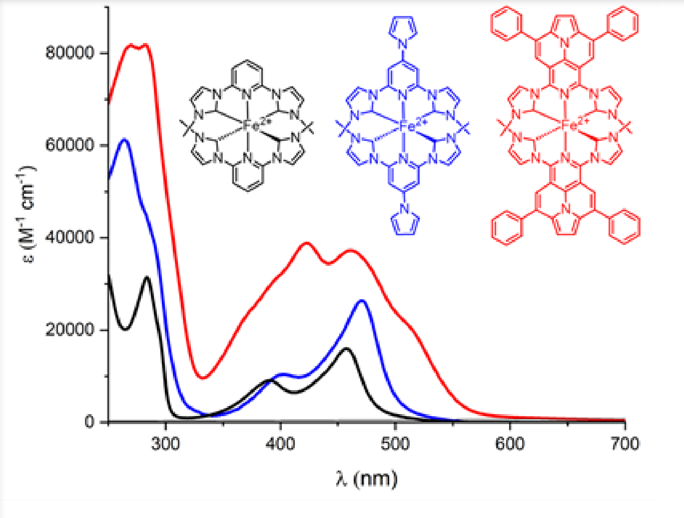

Figure 1. UV-vis spectrum of azaullazine-based Fe(II) complex (red curve) in comparison with analogous Fe(II) NHC complexes.

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OC16 | Design of Luminescent Lanthanide-Based Bioprobes for Two-Photon NIR-to-NIR Imaging in Vivo Applications

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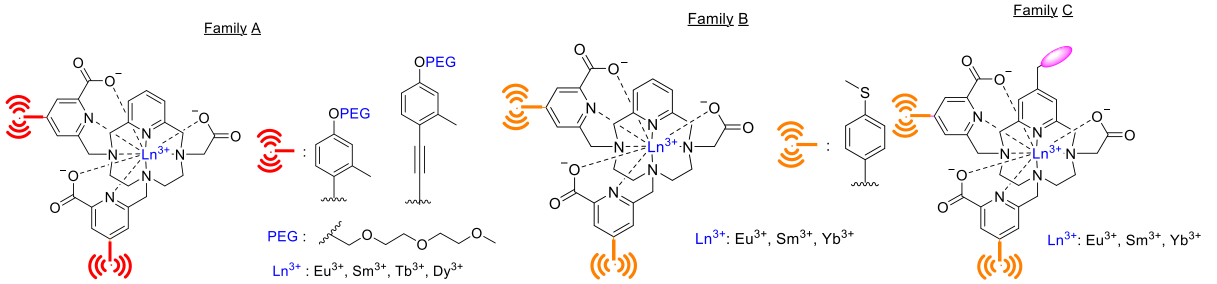
Optical microscopy imaging is limited to the UV-visible range (350 nm to 450 nm) due to absorption by tissue and scattering of light *in vivo*.[1] Two-photon (2P) absorption overcomes some of these limitations by operating within the biological transparency window (650-1100 nm), thereby reducing tissue autofluorescence. Luminescent lanthanide-based bioprobes (LLBs) are particularly promising for optical imaging thanks to the specular properties of Ln(III) ions[2] (specific emission spectra with fine transitions ranging from the visible to NIR, long luminescence lifetimes) associated to π-conjugated chromophores that facilitate 2P excitation.

Polyazacycloalkanes have shown their interest as macrocyclic platforms for the complexation of cations with fine thermodynamic and kinetic properties. Pyclen is specific azacycloalkane with an aromatic pyridine unit. This provides an additional constraint to the structure that can impose coordination environments leading to an improvement of the chelating properties.[3] The pyclen derivatives *N*-functionalized by a combination of picolinate and acetate pendants, have been largely studied in our groups for their photophysical properties.[4] Building on these structures, π-conjugated antennas were introduced, leading to LLBs with outstanding luminescent properties (Scheme 1a). These bioprobes have facilitated the acquisition of high-quality images under two-photon excitation, and *in vivo* imaging experiments have also been conducted on zebrafish models.[5]



Scheme 1. General structures: a) Previously studied pyclen-based LLBs, b) New NIR-to-NIR bioprobes c) New bifunctional bioprobes devoted to targeted optical imaging.

We are now focusing on two new challenges: the design of NIR-to-NIR probes, where both absorption and emission occur in the NIR region. To achieve this, the pyclen macrocyclic platform was functionalized with new π-conjugated antennas optimized for sensitizing ions emitting in the NIR (Sm, Yb) (Scheme 1b). Additionally, we are developing a bifunctional analog with an additional reactive chemical function at the *para* position of the pyclen's pyridine ring, allowing its grafting onto biological vectors (Scheme 1c). The synthesis of the ligands and complexes as well as the associated photophysical studies will be presented.

This work was supported by ANR-21-CE29-0018-02_ACT.

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OC17 | Modelling the mechanism of Gallium-catalysed recycling of silicone waste with BCl_3 to yield chlorosilanes

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Rudy Lhermet,[3] David Gajan,[4] Anne Baudouin,[5] Steven Roldán-Gómez,[5] Marie-Eve L. Perrin,[5]
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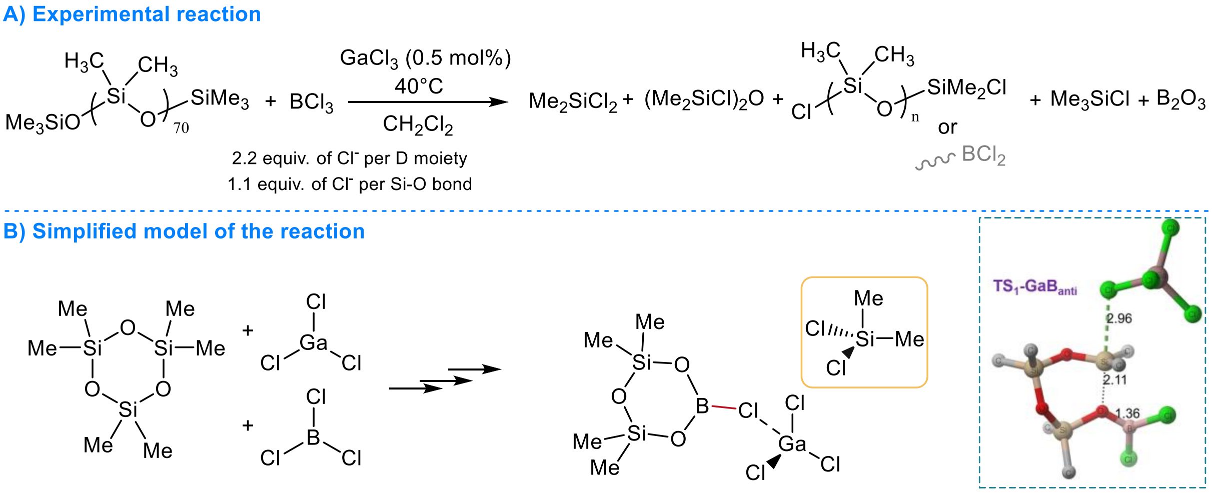
Silicone polymers are omnipresent in modern households as well as in diverse industrial applications due to their useful properties.[1] However, there are not many options available to recycle them. In this regard, it would be ideal to chemically transform them into any of the starting materials involved in their production process. For that purpose, we developed an initially counterintuitive method to depolymerize all types of silicone-base materials including post-consumer silicone waste into methylchlorosilanes, a key intermediate in the silicon industry.[2] The reaction proceeds with $GaCl_3$ as catalyst and BCl_3 as chlorine source and depolymerizing reagent.

To enlighten the way the system cleaves silicon backbone moieties, Si-O-Si bonds, to yield Si-Cl bonds, we performed molecular modeling at the DFT level on a simplified model of silicone, the cyclic dimethylsiloxane trimer (D_3). Based on these results we were able to explain the catalytic role of the gallium chloride acting as a chlorine “shuttle” and the role of the BCl_3 as Lewis acid “activator” of the Si-O bond to cleave. We also explain why the reaction does not proceed in presence of only one of the species, corroborating their synergetic effect on the depolymerization.



Scheme 1. a) Experimental reaction. b) Simplified model of the reaction used for calculations.

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OC18 | Influence of the ligand on the toxicity, speciation and intracellular localization of Au(III) complexes in lung cancer cells

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Platinum is currently the most widely used metal in cancer chemotherapy. However, their lack of selectivity inducing heavy side effects, prompted investigations on other transition metals. This is particularly true of Au (III), which has been considered in recent years as a new alternative.[1] From a mechanistic point of view, two routes of toxicity are generally envisaged: structural toxicity or toxicity due to the reactivity of the complex. In the first case, the complexes present a high degree of intrinsic stability, preventing the decoordination of a ligand. They thus interact with their target via weak interactions such as π-stacking or 'electrostatic' interactions.[2] In the second case, the complex is able to release a ligand, allowing it to react with its target.[3] The strength of the metal-ligand bond therefore plays an important role in the mode of action of the complex towards cancer cells. Its evaluation provides a better understanding of the mechanisms involved, enabling us to improve the complexes toxicity.

In this context, we investigated the role played by different phosphines (L) on the metal-ligand interaction (Figure 1). The effect of phosphine substitution on Au-L bond strength was evaluated by determining the dissociation energy of this bond using mass spectrometry.[4] The results obtained were then compared with data on the toxicity of the complexes towards cancer cells. A relationship between the toxicity of the complex and the strength of the Au-L bond was thus demonstrated. The complex with the most solid Au-L bond were the most toxic. Imaging experiments on individual cells using cryo-micro-X-ray fluorescence spectroscopy were carried out at ESRF to target the localization of the complex in the cell and provided a better understanding of the target of the complexes in the cell. X-ray absorption spectroscopy experiments carried out at ESRF on cancer cell pellets incubated with the complexes informed us on the coordination sphere of the complex in cellulo.

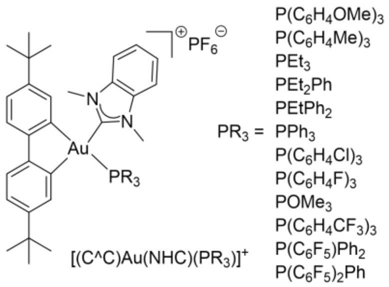

Figure 2. Family of complexes studied.

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OC19 | Tb(III) Complexation with Hydroxamic and Pyridinecarboxylic Ligands by Affinity Capillary Electrophoresis and DFT Calculations

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Needs in new radioisotopes for medical applications are growing, not only in order to increase possibilities of imaging/therapy, but also to better personalise treatments. In order to consider the vectorization of radionuclides towards organs to be treated/imaged, we are interested in the chelation of Tb(III), as interesting appealing and emerging "theranostic" (THERApeutic and DiagNOSTIC) ion, which offers 4 clinically interesting radioisotopes with complementary physical decay characteristics: ^{149}Tb ($T_{1/2}$ = 4.12 h, α therapy), ^{152}Tb ($T_{1/2}$ = 17.5 h, PET), ^{155}Tb ($T_{1/2}$ = 5.32 d, SPECT), and ^{161}Tb ($T_{1/2}$ = 6.9 d, β^- and Auger therapy).[1]

DOTA derivatives are currently widely used as bifunctional chelators for Ln(III) ions, forming extremely stable and inert complexes.[2] However, their full encapsulation by this macrocycle is extremely sluggish at near-room temperatures and involves several low-stability intermediates that can partially dissociate *in vivo.*[3] Thus, it is challenging to find new ligands for the encapsulation of radioisotopes in mild conditions.

In this work, we evaluated the possible Tb(III) complexation with hydroxamic and pyridinecarboxylic ligands. Lanthanide ions exhibit strong affinities for hard, negatively-charged oxygen donor atoms (e.g. carboxylate) and polarizable neutral nitrogen donor atoms (e.g. pyridine). Affinity capillary electrophoresis (ACE) was used for Tb(III) complexation studies. This method was successfully applied to unravel the speciation and measuring the equilibrium constants of labile (kinetically rapid) systems.[3,4] DFT calculations were also performed to characterize the binding properties of studied ligands. This information can be useful for searching new chelators for Tb(III), which can become alternatives to the DOTA derivatives.

This work was supported by the *TTRIP project (2022–2025) of the French National Research Agency (ANR-21-CE19-0037-01) and the MITI project (Mission for Transversal and Interdisciplinary Initiatives) of the CNRS, the French National Centre for Scientific Research.*

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OC20 | Heterobimetallic Complexes of Photoactive N-Heterocyclic Carbenes

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Vincent César,*,[1] Dmitry A. Valyaev*,[1]

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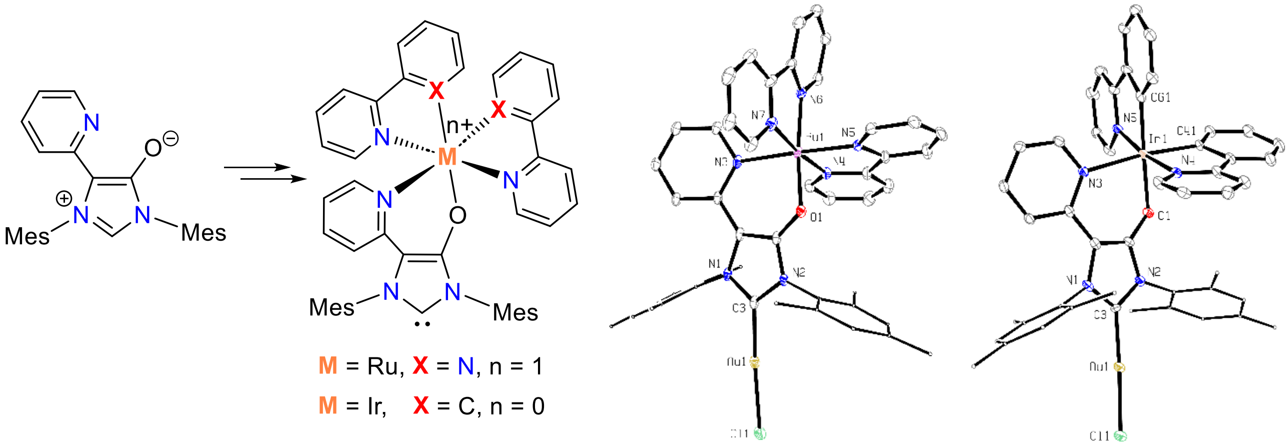
In addition to their extensive use in organometallic chemistry and homogeneous catalysis[1] *N*-heterocyclic carbenes (NHCs) have recently become key components in the design of highly efficient luminescent transition metal complexes suitable for optoelectronic applications.[2] However, the incorporation of organic or organometallic photoactive moiety directly into the NHC backbone remains much less common strategy opening promising opportunities in terms of luminescence[3] and photocatalysis.[4]

We report herein the synthesis of a new class of photoactive NHC ligands based on emblematic IMes scaffold functionalized at the backbone with ubiquitous Ru(II) and Ir(III) chromophores (Scheme 1, left). Their coordination chemistry with gold as well as the studies of photophysical and catalytic properties of the resulting heterobimetallic derivatives (Scheme 1, right) will also be presented.[5]



Scheme 1. Synthesis of NHC ligand precursors bearing organometallic photoactive units at the ligand backbone and X-ray structures of the corresponding heterobimetallic complexes.

This work was supported by CNRS Emergence@INC2022 grant NHC_Lumen (post-doctoral grant for A. D.). P. L. is grateful to French MENESR for a PhD fellowship.

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OC21 | Synthesis of Polyarylcyclopentadienyl-Based Dysprosium Complexes and Investigation of Their Magnetic Properties

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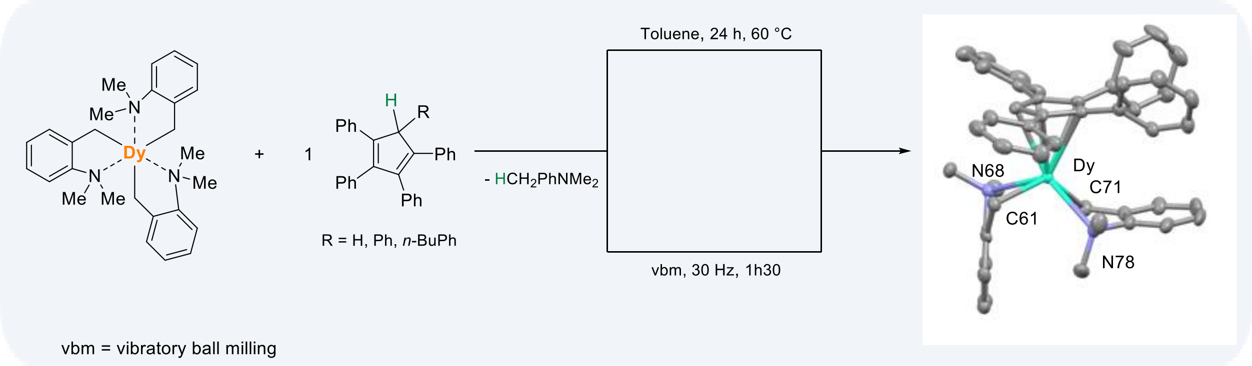
Polyarylcyclopentadienyl ligands have found manifold applications in the synthesis of a large variety of main group, transition and rare-earth metal complexes, related to their steric and electronic properties.[1] Furthermore, functionalizing the aryl groups during the ligand synthesis enables fine-tuning of the complexes' solubility and electronic characteristics.[2] In our research group, we have explored these ligands in the synthesis of various divalent lanthanide complexes, employing different synthetic strategies to achieve specific structural and luminescent properties.[3]

In recent years, lanthanide-based single-molecule magnets (SMMs) have attracted great interest due to their ability to retain magnetic memory at low temperatures, an essential feature for next-generation data storage technologies. Among lanthanide-based SMMs, dysprosium complexes coordinated with two Cp ligands bearing alkyl substituents have demonstrated remarkable performance.[4] To gain new insights into the influence of the electronic and steric influence of polyarylcyclopentadienyl ligands bound to the Dy core on the magnetic properties, we herein report on the synthesis of the first mononuclear dysprosium(III) complexes featuring these ligands. Two synthetic approaches were explored: a traditional solution pathway[5] and an innovative ball-milling method, both leading efficiently to the targeted compounds (Scheme 1). The new complexes were structurally characterized by X-ray diffraction (XRD) and their magnetic properties were extensively studied, revealing promising features for advancing the development of lanthanide-based SMMs.



Schema 1. First examples of polyarylcyclopentadienyl dysprosium(III) complexes.

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OC22 | Lewis Superacid-Mediated Reduction of Dioxygen and Carbon Dioxide

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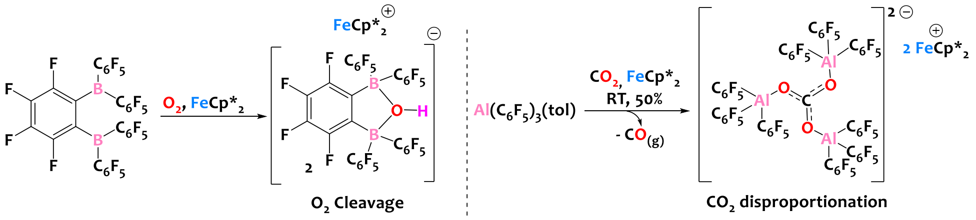
Small molecule activation has become a key focus in main group chemistry in recent years, fueled by the pursuit of using more abundant and benign elements to take on roles traditionally dominated by transition metals.[1] Frustrated Lewis pairs (FLPs) are a key example that has emerged from this area of research.[2] A simplified explanation of their reactivity involves a sterically hindered Lewis acid (LA) and Lewis base (LB), whose combined actions enable the LB's electron pair to attack a substrate that has been electron-depleted due to its interaction with the LA. While most of FLP chemistry can be explained by ionic mechanisms, it has been observed that several FLP-mediated activations of small molecules occur through radical pathways. These pathways can involve $LA^{\bullet-}$ /$LB^{+\bullet}$ systems or homolytic bond cleavage. The recent emergence of frustrated radical pairs (FRPs) and their role in the activation of small molecules has prompted some research focused on controlling electron transfer to small molecules with the assistance of LAs.[3] From this perspective, single electron transfer (SET) by mild reductant to donor/acceptor pairs has recently emerged as a new strategy for small molecule activation (such as O_2 and N_2O) leading to the generation of uncommon anions.[4] One key example, reported by Agapie and coworkers in 2014, is the reduction of O_2 by ferrocene (Fc) or decamethylferrocene (Fc*) in the presence of the LA $B(C_6F_5)_3$ leading to dianionic *bis*(borane) peroxide counter-balanced by two ferrocenium cations.[5] Another key example, reported by Severin *et al*. in 2018, is the one-electron reduction of nitrous oxide (N_2O) promoting by the combination of the Lewis Superacid (LSA) $Al(C_6F_5)_3$ (AlCF) with metallocenes.[6]

Recently, our group has explored the reactivity of Piers' bis(borane) *o*-$\{(C_6F_5)_2B\}_2C_6F_4$ (B_2CF) and the alane AlCF with dinitrogen group 6 metal complexes.[7,8] In continuation of these works and inspired by the above presented studies, we investigated the reduction of O_2 and CO_2 by combining these two LSAs (B_2CF and AlCF) with $FeCp^*_2$. Our study shows i) the pivotal role of the bidentate nature of B_2CF to promote the O-O cleavage (Scheme 1, left). ii) The crucial role of aluminum in facilitating the disproportionation of CO_2 (Scheme 1, right).



Scheme 1. O_2 and CO_2 reduction promoted by the combination of B_2CF/AlCF with Fc*.

This work was supported by the grant ANR-21-CE07-0003.

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OC23 | B_2pin_2-mediated Ligand Deprotonation Enables Selective Iridium-catalyzed C-H Borylations Revealed by Click Ligands

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Iridium-catalyzed C-H bond borylation reactions have revolutionized the way of conceiving chemical synthesis by providing step- and atom-economy methodologies using bench stable boron precursors such as bis(pinacolato)diboron (B_2pin_2).[1] Indeed, the access to boron-containing building blocks is highly attractive since straightforward post-modifications can lead to new carbon-carbon and carbon-heteroatom bond formations. Iridium-catalyzed C-H borylation of aromatics have been developed and the regioselectivity is controlled by the steric and electronic nature of the substrate as pioneered by Hartwig.[2] To bypass the inherent reactivity of iridium at sterically accessible sites, catalyst-to-substrate coordination appears as a promising strategy.[3] For that, well-defined, and typically sensitive, anionic ligands have been developed in order to form catalytically active iridium species allowing substrate-coordination towards proximal selectivity.[4-6] Herein, we present a fundamentally new approach in which the anionic ligand forms *in situ* upon reaction of the iridium pre-catalyst with the boron reagent B_2pin_2. This new action mode has been exploited to control the regioselectivity in unbiased substrates that impose selectivity issues when using standard iridium catalysts. As such, these results disclose the manifold role of B_2pin_2 and raises questions about previous, postulated action modes[7] in which the ligand could eventually *in situ* switch from neutral to anionic during the catalysis.

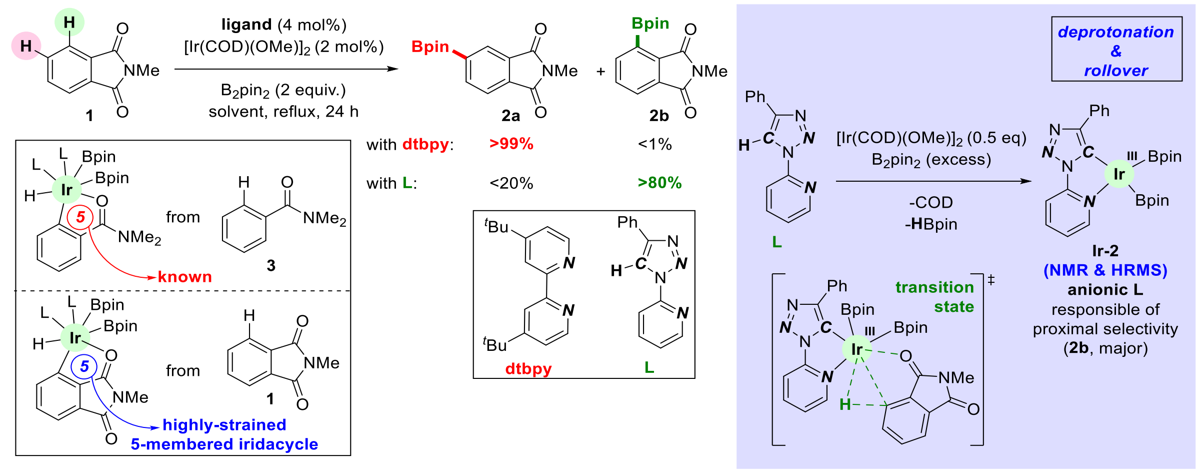

Figure 1. Click ligands enabling proximal C-H bond borylation selectivity via a unique action mechanism mediated by B_2pin_2.

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OC24 | Rare-earth Complexes of Bis(phenoxy-amidinate) FAlen Ligands as Catalysts for Ring-Opening Polymerization

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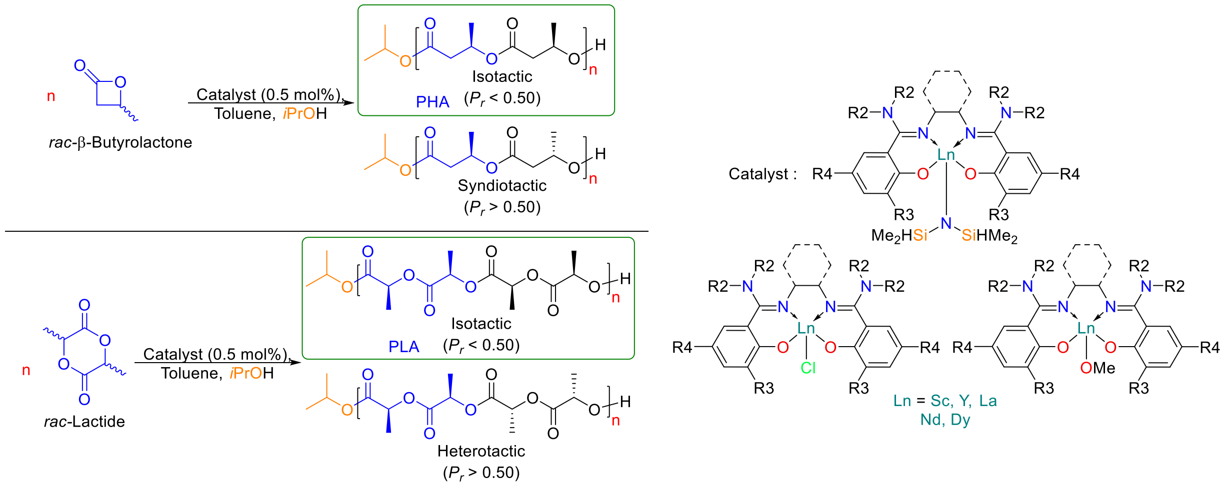
Rare earth metal complexes emerged as highly effective catalysts for ring-opening polymerization (ROP) of cyclic ethers and esters due to their Lewis acidity and diverse coordination environments [1]. In this project, we study the catalytic activity of FAlen-type rare-earth complexes in the polymerization of *rac*-β-butyrolactone (*rac*-BBL) and *rac*-lactide (*rac*-LA). These catalysts demonstrate very high activity, yielding the polyesters with narrow dispersity, and remarkable isoselectivity.



Scheme 3. Ring-opening polymerization of cyclic ester catalysed by rare-earth complexes.

This work was supported by ANR (MORFAL project, ANR-22-CE07-0011).

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OC25 | Zr(IV)-catalyzed Hydrosilylation of Polycarbonates

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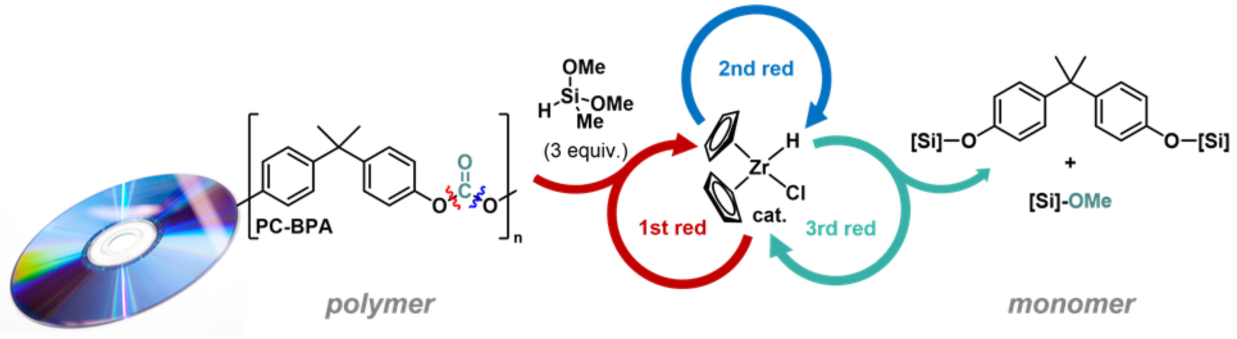
Since the 1950s, manufacturers have increasingly used plastics as their facile and cost-effective mass production allowed to meet the growing demand of the consumer society. Today, plastics are ubiquitous with global annual production reaching approximately 410 Mt in 2023.[1] However, their production still relies mainly on fossil fuels and a lack of sustainable waste management causes significant environmental pollution. Despite the urgent need to integrate plastics into a circular economy, less than 9% of the plastic currently produced stems from recycling. While mechanical recycling remains the most widely employed method, chemical alternatives and complementary approaches have emerged. Among them, chemical recycling is viewed as the deconstruction of plastic materials into valuable monomers, enabling the regeneration of virgin-quality plastic and the recovery of industrial feedstock chemicals.

Recently, reductive catalytic depolymerization using homogeneous catalysts together with a reductive source has shown to be particularly effective for deconstructing oxygenated and nitrogenated plastics, particularly those containing carbonyl functional groups.[2] Our group has demonstrated that the Schwartz's reagent, $Cp_2Zr(H)Cl$, traditionally used as a stoichiometric reductant in hydrozirconation reactions, can be now used catalytically in the presence of a stoichiometric amount of silanes to promote the hydrosilylation of amides and esters.[3] Using Zr(IV)-catalyzed hydrosilylation, we manage to extend the scope to the less reactive organic carbonates. This work led to the identification of an efficient $Cp_2Zr(H)Cl$ / $Me(MeO)_2SiH$ (DMMS) catalytic system that tackles di(alkyl) carbonates, aryl/alkyl carbonates as well as di(aryl) carbonates to afford silylated alcohols. This system also proved to be efficient in the hydrosilylative depolymerization of polycarbonates, thus demonstrating its robustness towards the additives and the dyes contained in the household plastic materials. Notably, the catalytic system displayed selective depolymerization from a mixture containing both polycarbonates and polyesters. Experimental investigations provided evidence for a mechanism involving multiple three-step sequences: (i) hydrozirconation of the carbonyl fragment, (ii) thermal σ(C−O) bond cleavage, and (iii) Zr−OR/Si−H σ-bond metathesis, which regenerates the hydride catalyst.[4]



Scheme 1. Zr(IV)-catalyzed hydrosilylation of organic carbonates and polycarbonates household wastes into alcohol derivatives.

This work was supported by CEA, CNRS, the University Paris-Saclay, the Sun-to-X project from the European Union's Horizon 2020 research and innovation program (grant No. 883264).

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OC26 | Mechanistic Insights into Copper Hydride Chemistry: Dynamic Structure and Reactivity

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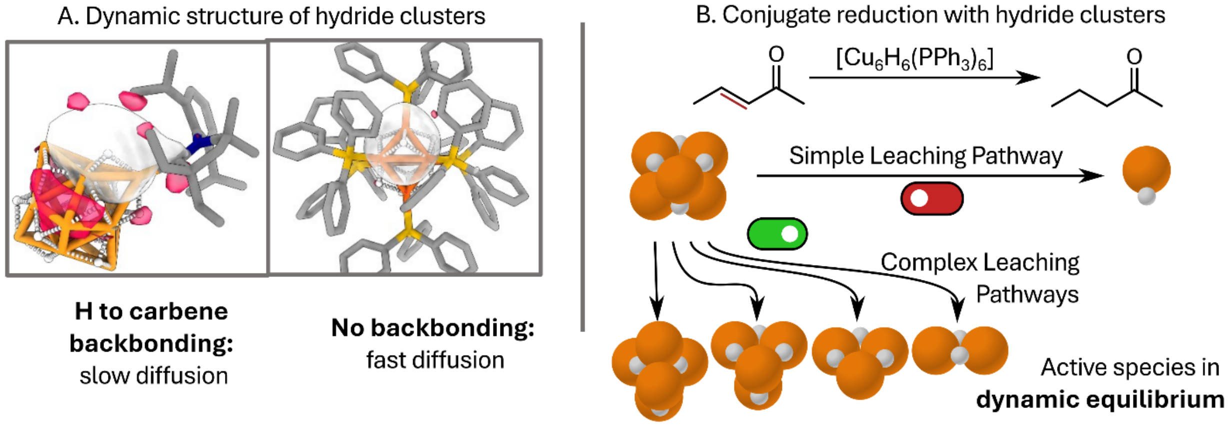
CuH clusters are useful reductants in organic synthesis,[1] as well as promising model systems for heterogeneous catalysts. Despite this, their structure remains under debate, and the knowledge on their reaction mechanisms is limited at best.

Relying on *ab initio* molecular dynamics calculations, differences in the behavior of hydride ligands in phosphine or carbene stabilized [Cu_xH_y] clusters were rationalized.[2] The fast diffusion behavior of hydrides at the surface of hydride clusters was compared to diffusion in hydride-covered Cu(111) facets, effectively bridging the gap between model cluster systems and heterogenous catalysts. Spectroscopic investigations using quadrupolar NMR could confirm the surprisingly fast diffusion of hydrides.

Further DFT calculations were carried out to investigate the role played by low-nuclearity clusters in the reduction of methyl cinnamate by [$Cu_6H_6(PPh_3)_6$] clusters. While the monomeric and dimeric forms are too unstable, the reactivity of larger aggregates is more favorable. This contrasts with the textbook mechanism in which monomeric CuH species are proposed as active species.

Quantum chemistry techniques were instrumental in investigating the multi-faceted role of metal hydrides.



Scheme 1. The dynamic structure of hydride ligands in copper hydrides was investigated, as well as the mechanism of conjugate reduction reactions.

This work was supported by a CDSN grant (Ministère de l'Enseignement supérieur et de la Recherche), by ANR grant CARBHYDRIDE (ANR-23-CE07-0031), and by generous allocation of computational ressources by the CBPsmn of ENS Lyon and the GENCI (n° A0160813435).

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OC27 | Dinitrogen functionalization: road to ammonia thanks to molybdenum complexes

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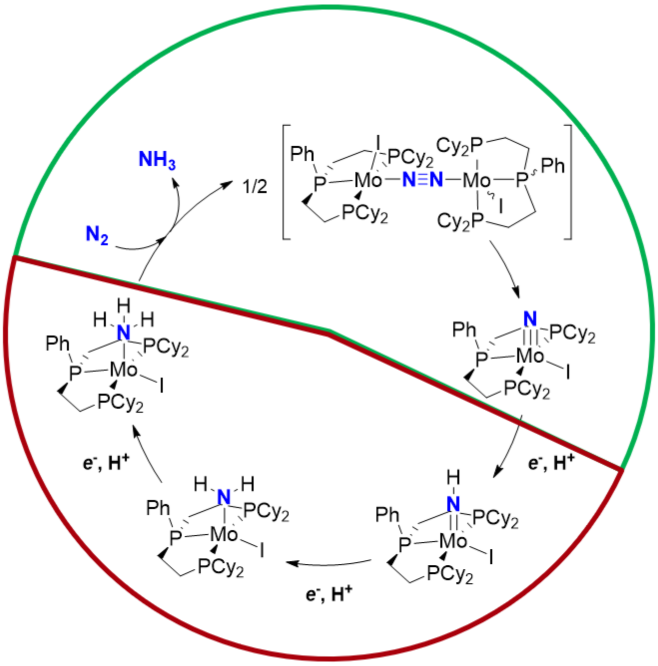
New roads to ammonia are of global interest nowadays, given the awareness of its widespread use in industry (fertilizers, explosives, …) and its potential as energy vector.

However, dinitrogen fixation remains challenging in organometallic chemistry.[1] Both the key steps involved are demanding, the cleavage of the nitrogen-nitrogen triple bond and the subsequent functionalization of the nitrogen atom.

Among a variety of transition metal complexes, Molybdenum phosphine complexes are particularly relevant, having been shown to be able to mediate N_2 conversion under mild reaction conditions.

Indeed, using reducing conditions on a triphosphine Molybdenum complex, dinitrogen splitting was achieved leading to a nitride complex which proved to be competent in different N-functionalizations (silylamine,[2] borylamine[3]).

Using this platform as starting point, direct pathways to ammonia is now under study using protons source an electrons donor.[4] Various synthetic and spectroscopic methods are used for mechanistic investigations.



Scheme 1. Dinitrogen splitting and functionalization towards NH_3.

This work was supported by PEPR SPLEEN/ ECOCHEM.

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OC28 | Synthesis and Characterization of Porphyrinoid-based Molecules and Materials for applications in Gas Sensing

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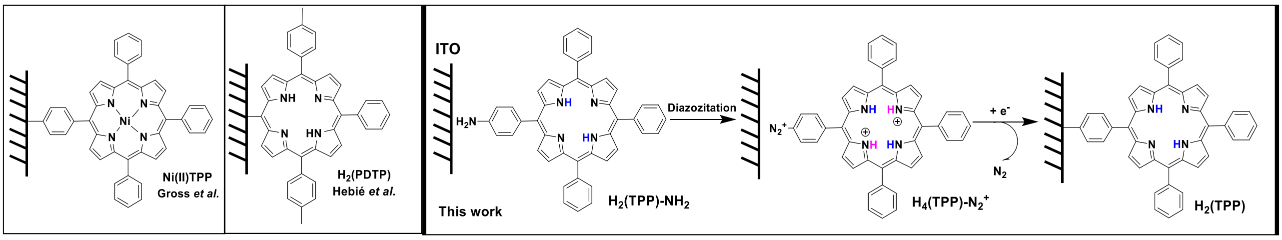
The interest for surface modification[1] with organic films has developed over the years due to their use in various applications such as gas sensing,[2] catalysis,[3] analytical applications,[4] solar and fuel cells applications,[5] energy conversion and storage,[6] and molecular electronics.[7] Thin film of porphyrins have attracted many researchers because of their interesting physicochemical properties allowing these materials to be used in the manufacture of optical devices, in the design of sensors based on photoluminescence,[8] and also as electrocatalytic systems.[9] Covalent grafting of porphyrins can be performed by electrochemical or spontaneous reduction of diazonium-porphyrins. In 2011, Gross *et al.* (Scheme 1, left) have reported on the electrografting of Ni(II) tetraphenylporphyrin in an organic medium[10] *via* the reduction of Ni(II) 5-(*p*-diazonium-phenyl)-10,15,20-triphenylporphyrin. In a more recent study, in 2016, Hebié *et al.* published covalent and direct diazonium electrografting on platinum electrode of the 15-phenyl-10,20-ditolylporphyrin H_2(PDTP) through the electroreduction of the corresponding *meso*-diazonium salt, (Scheme 1, center).[11]



Scheme 4. Electrografting of porphyrins on conducting electrode.

In this work, 5-(*p*-diazonium-phenyl)-10,15,20-triphenylporphyrin and its fluorinated analog are electrografted (Scheme 1, right) on interdigitated electrodes that are tested in bilayer organic heterojunction devices for the detection of NH_3 gas.

This work was supported by ANR Porph4Sens (ANR-22-CE06-0039-01).

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OC29 | Synthesis and Bioevaluation of dicobalt Tetrahedranes, Pt$_2$ A-frame and Pt(0) Complexes bearing a *N*-Heterocyclic fragment

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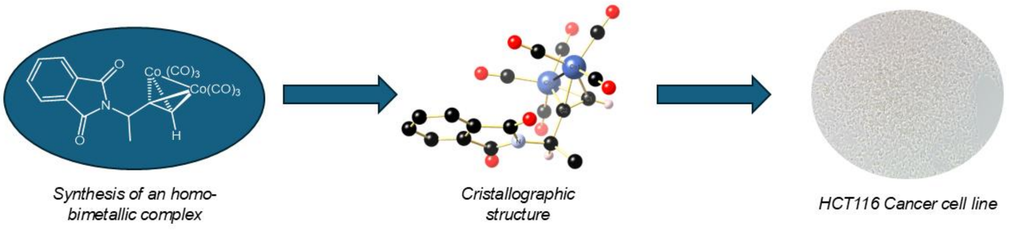
Since the discovery of the anticancer properties of cisplatin in the 1970s, transition metal complexes have garnered significant attention for their potential as metallodrugs.[1] Among the various strategies explored, combining biologically active *N*-heterocyclic frameworks with organometallic fragments has shown great potential. Isoindole-based scaffolds, derived from both natural and synthetic sources, have emerged as versatile scaffolds for the design of pharmaceutical and bioactive compounds.[2]

In this study, we report on the synthesis, characterization, and biological evaluation of homobimetallic scaffolds (Co-Co, Pt-Pt) as well as Platinum(0) complexes incorporating an isoindole moiety. These metal-metal bonded species and the Pt(0) π-complexes were prepared using alkyne-functionalized isoindole ligands, characterized by IR, multinuclear NMR spectroscopy,-and single-crystal X-ray diffraction.[3] Biological assays were also conducted to evaluate their cytotoxic, anti-Alzheimer, and anti-diabetic activities.[4]

Preliminary cytotoxicity tests indicate notable efficacy against several cancer cell lines (HCT116, MCF-7, WM266-4 and LS174T), with IC$_{50}$ analyses. Promising anti-butyrylcholinesterase (BChE) activity was also observed, suggesting a potential application in Alzheimer's disease treatment. However, no significant inhibition was noticed in the □-glucosidase assay, highlighting the selective bioactivity of these complexes.

Our results reveal the ability of bimetallic complexes as multifunctional platforms for the development of innovative metallodrugs with improved biological efficacy.



Synthesis of an homo-bimetallic complex

Cristallographic structure

HCT116 Cancer cell line

Figure 1. Crystal structure of a homo-bimetallic Co-Co dimetallatetrahedrane complex and microscopic imaging of a HCT116 cancer cell line.

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OC30 | Dimerization and Cycloaddition Catalyzed by Tethered Complexes in a Supramolecular Host

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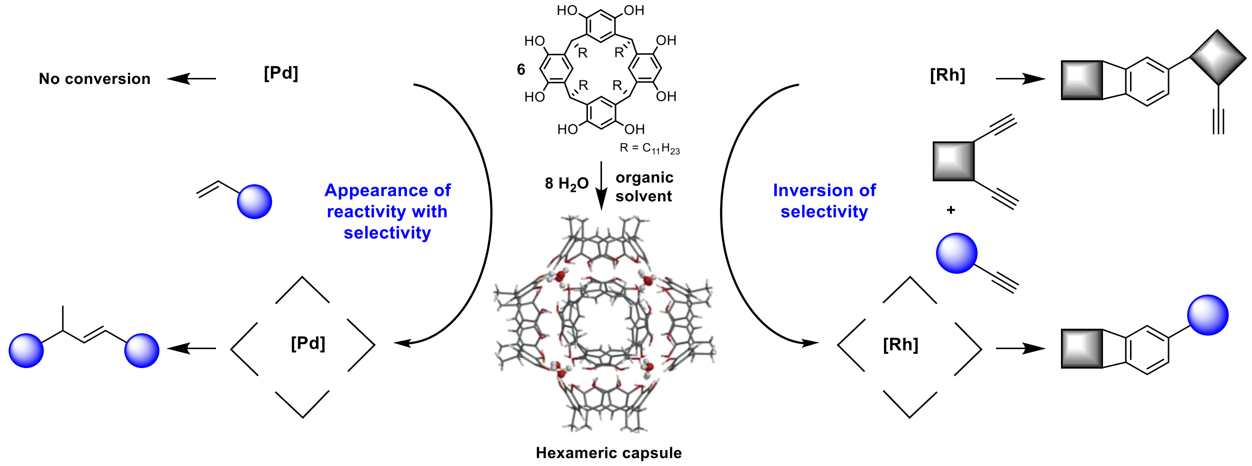
Catalysis with molecular containers is an emerging field due to its similarity with enzymes.[1] Two ways of making large assemblies exist: *i*) the formation of covalent cages or metallo-capsules but their synthesis require several steps, like in the case of the pallado-trimeric-resorcinarene, previously reported;[2] *ii*) supramolecular assemblies, which are easily achievable like the self-assembled capsule based on 2,8,14,20-tetra-undecyl-resorcin[4]arene discovered by Atwood.[3] By using this hexameric host, one palladium and one new rhodium complex were encapsulated. The formation of inclusion complexes was deduced from UV/Vis and NMR (^1H, ^{31}P and DOSY) spectroscopies in the same way as in our previous example based on a neutral ruthenium catalyst.[4] The embedded palladium complex was evaluated in the selective dimerization of styrene derivatives. No reaction was observed in the absence of the host, the catalyst working in a synergic fashion. On the other hand, the rhodium complex was used to modify the catalytic outcome of the [2+2+2] cycloaddition of alkynes. With the unencapsulated catalyst, we mainly observe the formation of the homocycloaddition product, while in the presence of the supramolecular assembly the heterocycloaddition product is favored. These two examples clearly show the beneficial role played by the second sphere of coordination brought by the capsule, which is able to emerge activity of catalyst or to modify the nature of the formed products.



Scheme 1. Hexameric capsule used as a second sphere of coordination to modify catalytic outcome and schematic examples of the reaction studied: dimerization of derivatives (left) and [2+2+2] cycloaddition of alkynes (right).

This work was supported by École doctorale des Sciences Chimiques - ED222 and M.R.T. for a research fellowship.

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OC31 | Design of Sulfur Based Pincer Ligands for Stabilization of Low Valent Species

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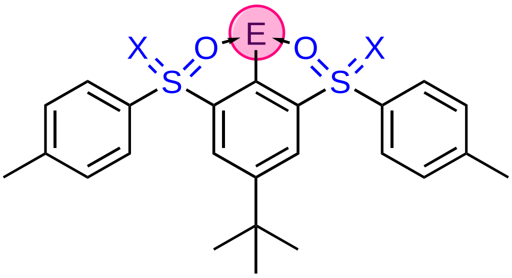
A few decades ago, metallylenes—the heavier analogues of carbenes—were considered little more than chemical curiosities. However, following the successful isolation of several divalent species, interest in their chemistry grew, and they became the focus of an extensive study. Characterized by a lone pair of electrons and a vacant p orbital in the singlet ground state, along with their ambiphilic character, metallylenes have proven to be highly versatile. Initially, research on metallylenes was driven by fundamental scientific inquiry, but numerous discoveries have since highlighted their potential for practical applications, transforming the chemistry of metallylenes into a well-established research field. Pincer ligands were initially employed to form transition metal complexes, where they demonstrated high efficiency and played a significant role in catalytic applications and materials science. Recently, pincer ligands have also been used to stabilize metallylenes, with the literature providing examples of germylenes, stannylenes, and plumbylenes supported by various types of pincer ligands.

Therefore, this study presents the design of pincer ligands functionalized with sulfur donor groups in different oxidation states, i.e. sulfoxides, sulfones, sulfoximines, for the stabilization of metallylenes, enabling the distinct exploitation of hemilabile and stereogenic character.



X = -, O, NR'

Scheme 1. General structure of sulfur-based pincer ligand stabilizing low valent species.

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OC32 | Computational insight into the geometry of amidine-phenoxy early transition metal complexes

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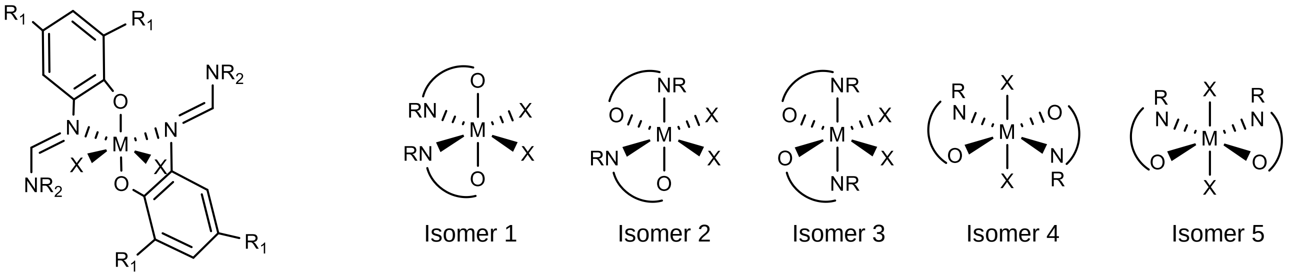
The combination of phenoxy-imine (FI) ligands with Group 4 metal ions has proven to be one of the most efficient and versatile classes of olefin polymerization catalysts.[1] Recently, our group developed a variant of the FI ligands by replacing the vulnerable imine function with an amidine group.[2] These amidine-phenoxy (AF) ligands were then used to obtain (AF)$_2$MX$_2$ complexes (M = Ti, Zr) (Scheme 1, left). The solid-state structures of most of these complexes have been established by single crystal X-ray diffraction analysis. All the complexes showed a distorted octahedral geometry around the metal centre with the same *O-trans*, *N-cis*, X-*cis* configuration (isomer 1). Consistently, NMR spectroscopy of (AF)$_2$MX$_2$ complexes in solution shows that all complexes exist only as a symmetrical C2 isomer. This distinguishes AF ligands from their FI counterparts, which generally give Ti/Zr-FI complexes also as *O-trans*, *N-cis*, X-*cis* isomer in the solid state but as a mixture of isomers in solution.

(FI)$_2$MX$_2$ and (AF)$_2$MX$_2$ complexes can theoretically exist in five isomeric forms (Scheme 1, right). For olefin polymerization, the ideal structure are isomers 1-3 which offer *cis*-positions for the growing polymeric chain and the incoming monomer. On the contrary, isomers 4 and 5 are inactive because they offer *trans* reactive positions which prevents the migratory-insertion step of the reaction. The nature of the isomer (1-3) has also a significant impact on the stereochemical outcome of the polymerization reaction when 1-substituted olefin is used (propene, styrene…). Therefore, it is important to have control over which isomer is formed.



Scheme 5. Typical complex studied as well as its five possible macro-isomeric forms.

These observations drove us to examine the stability and the interconversion of the isomers in FI and AF group 4 metal complexes with Density Functional Theory.

In this communication, we will show that seemingly contradictory experimental results come from the interplay between the electronic structure of the AF ligands and the steric hindrance of the R1 group.

This work was supported by ANR (MORFAL, ANR-22-CE07-0011).

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OC33 | New catalytic pathways for carbene insertion into Si-H bonds catalyzed by ruthenium phthalocyanine complexes

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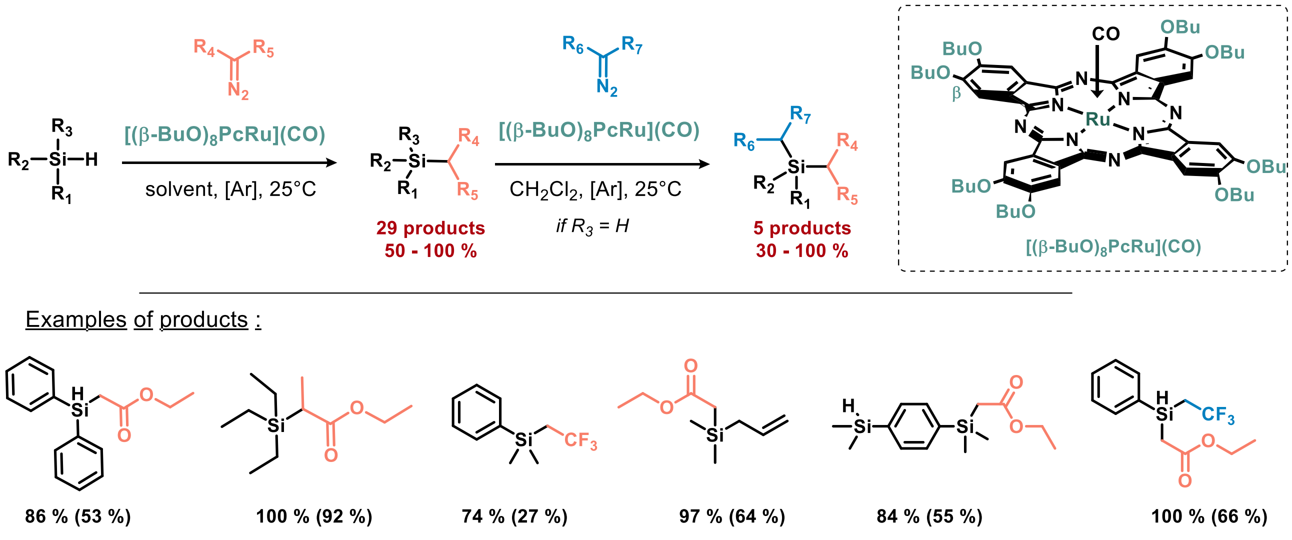
Organosilanes find increasing applications as valuable building blocks in organic, material and medicinal chemistry.[1] Synthetic strategies for introducing silicon motifs to organic molecules such as hydrosilylation of alkenes, nucleophilic, radical and cross-coupling reactions often involve chlorosilanes, expensive organometallic compounds, stoichiometric chemistry and suffer from the use of toxic and unstable reagents, harsh conditions, limited scope and poor atom economy. In this context, the catalytic carbene insertion into Si-H bonds is a straightforward and efficient approach for the construction of Si-C bonds.

In stark contrast to well-known porphyrin-based catalysts, related phthalocyanine counterparts are still unexplored in the carbene insertion into Si-H bonds. These cheap and readily available tetrapyrrolic complexes are efficient catalysts for a variety of reactions.[2] Our recent studies disclosed their promising catalytic activity in N-H carbene insertion and cyclopropanation.[3] Herein, we describe the first efficient functionalization of aromatic, aliphatic and alkylaromatic silanes using different carbene precursors in the presence of ruthenium octa-*n*-butoxyphthalocyanine [(β-BuO)$_8$PcRu](CO). A large variety of the structurally divergent products including non-symmetrical tertiary silanes, quaternary silanes and symmetrical and non-symmetrical disilanes were prepared in high yields (up to 100%) and elevated TON values (up to 15 400) using only a small amount of catalyst (0.025 mol% to 0.5 mol%). The scope and synthetic opportunities of this approach will be discussed.



Scheme 1. Carbene insertion into Si-H bonds catalyzed by [β(BuO)$_8$PcRu](CO).

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OC34 | Reactivity of Grignard Reagents towards Nitrile in context of polymerization catalysis

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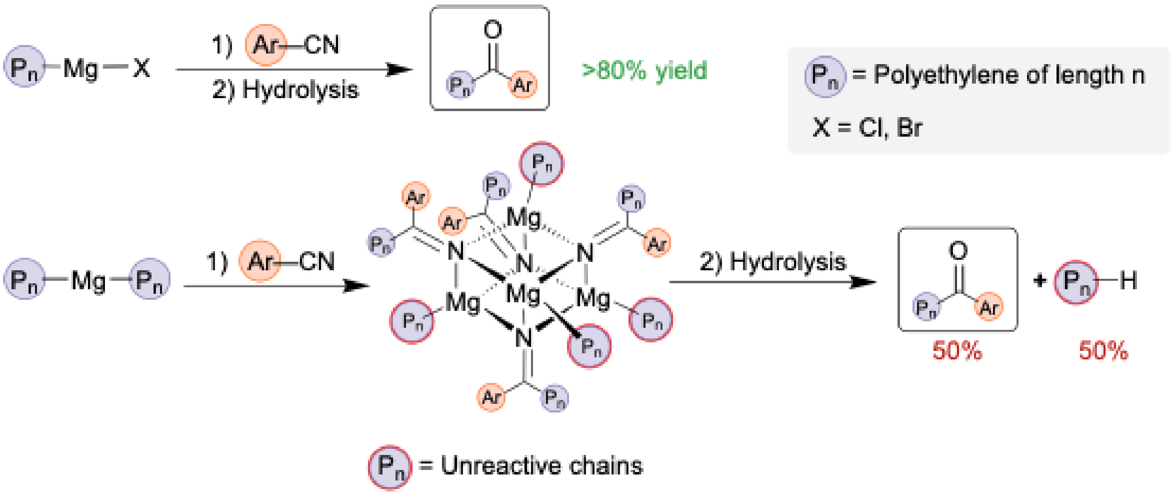
The coordinative chain transfer (CCTP) polymerization of ethylene in toluene and diethyl ether uses neodymocene catalysts and organomagnesium complexes as chain transfer agents including dialkyl magnesium (MgR2) or Grignard reagents (RMgX).[1] Reacting the Mg-C chain ends with nitriles affords ω-functionalized chains, enhancing polymers properties.[2] The nature of the organomagnesium compound plays a key role in the rate of functionalization. Grignard Reagents often aggregates and undergo Schlenk equilibrium which modify the reactivity along the reaction course.[3] This study relies on molecular modelling at the DFT level with extensive sampling to understand the influence of different chain transfer agents for functionalized polyethylene. The functionalization rate and extent can be limited by the formation of stable tetramers which trap unfunctionalized chains. The obstacles to efficient functionalization of polymers chain ends were identified thanks to extensive sampling of aggregation states. The outlined mechanism is not restricted to polymer chain end functionalization but also applies in the context of organic synthesis.



Scheme 1. Reactivity of P_nMgX and P_nMgP_n towards nitrile derivatives.

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OC35 | Cu-rious Bonds

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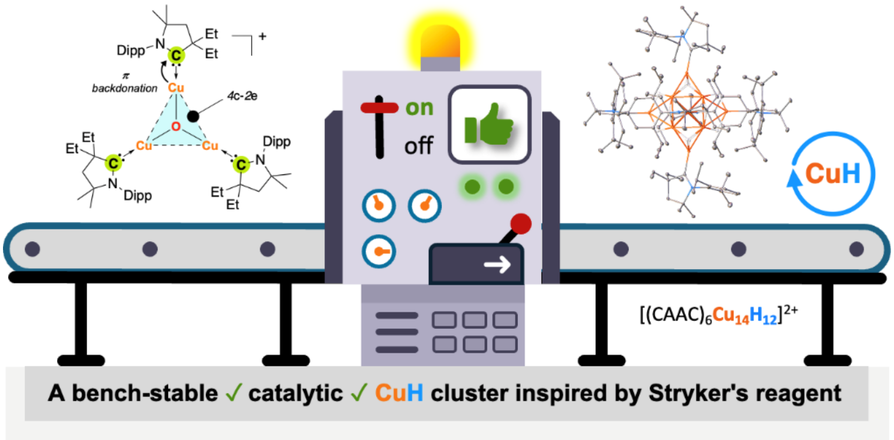
Metal hydride clusters play a crucial role in numerous applications, including hydrogen storage and catalytic hydrogenation. However, their practical use is often limited by their high sensitivity to oxygen and moisture. Thanks to a multidisciplinary collaboration leveraging expertise from teams at the Scripps Research Institute and ICBMS,[1] we recently reported $[(\text{carbene})_6Cu_{14}H_{12}]^{2+}$ (**C_6CuH**), a novel, air-stable copper–hydride nanocluster that combines robustness, efficiency, and broad catalytic applicability.[2]

Unlike conventional approaches that rely on thiol or phosphine ligands, **C_6CuH**'s stability arises from a distinctive hydride-to-carbene bonding interaction. Furthermore, its structure is reinforced by multi-center, multi-electron delocalized bonding, which plays a key role in defining the nanocluster's architecture and reactivity.

Beyond introducing an air-stable Cu–H catalyst, this work sheds light on the impact of ligand-induced hydrogen mobility in metal hydrides. Computational studies reveal that hydrogen dynamics are highly sensitive to ligand types, offering new strategies for tuning structure/activity of these clusters. These insights open pathways for the rational design of next-generation nanomaterial catalysts with applications in fine chemical synthesis and energy storage.



This work was supported by the Agence Nationale de la Recherche (reg. No. ANR-23-CE07-0031-CarbHydride).

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OC36 | Theoretical Study of the Adsorption of Methyl Pyridine Derivatives in H-ZSM5 Zeolite

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The theoretical study of the adsorption of pyridine (PY) and of its methyl derivatives (isomers of methyl and dimethyl pyridines) on the Brønsted acid sites (BAS) in the straight channel of H-ZMS-5 zeolite by cluster and periodic models of 32 and 96 tetrahedral centers (T), respectively, using PBE-D3 calculation method has been investigated (Figure). In this study, realistic cluster models extracted from the siliceous crystallographic ZSM-5 structure have been used. The substitution of one Si atom in two different tetrahedral crystallographic T1 and T7 sites by aluminum atom within the ZSM-5 cavity has been considered.[1-3] The confinement effects resulting from van der Waals dispersion interactions and steric constraints on the energetic and vibrational properties of the adsorption complexes formed have been thoroughly examined.

Our DFT-D3 calculation results clearly show that upon adsorption of any PY derivative, a proton transfer occurs spontaneously from BAS to adsorbed molecule leading directly to the formation of an ion pair complex. Whatever the adsorption complex considered, the calculated structure reflects a compromise between the repulsive interactions due to steric hindrance and the attractive van der Waals dispersion interactions between the atoms of the adsorbed molecule and those of the wall zeolite cluster. Although the isomers of methyl pyridine derivatives have the same stability and the same proton affinity, the stability of their complexes and the adsorption energy of their isomers essentially depend on their steric hindrance due to the fact that for some sites of adsorption, the methyl group of some isomers does not fit well in the void space of the zeolite cavity. Whatever the adsorbed molecule considered, the calculated vibrational frequencies and frequency shifts are in satisfactory agreement with the experimental results available in the literature.

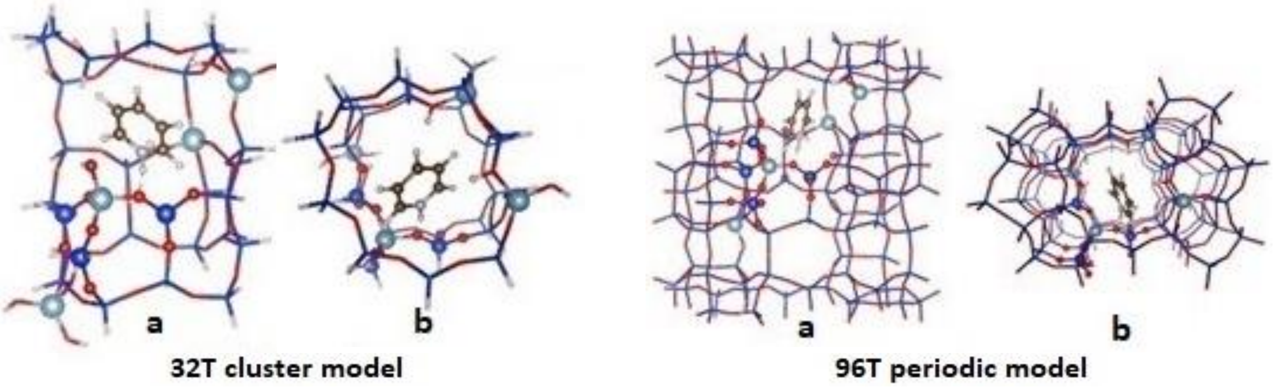

Figure 1. PY chemisorption complexes within the straight channel of H-ZSM-5 zeolite viewed along [001] (a) and [010] (b).

This work was supported by HPC resources from GENCI-CINES/IDRIS (Grants A0040807071, A0060807071, A0080807071, AD010807071R1 (2018-2025).

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Posters

Communications par Affiche

P1 | Depolymerization of polyesters with iodosilanes

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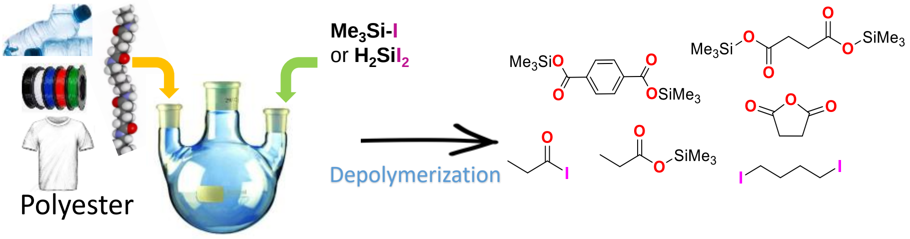
Driven by innovation and emerging markets, plastic materials have strongly contributed to the mass consumption and to the post war economic rise. Their consumption of ~2 million tons in the 1950's now reaches 468 million tons in 2022 and should attain 1.2 billion tons by 2060.[1,2] Currently, over 98% of the world's plastic production is still of fossil origin and accounts for ~11% of the oil consumption with a global carbon footprint of ~1.8 Gt of CO_2 in 2019. The current linear plastic economy, with a steady increase in short-lived disposable materials and an almost uncontrolled end-of-life management (350 Mt of waste/year), poses major environmental and societal issues.[3,4] Recycling is view as one solution to limit the plastic pollution and to favor a circular economy. While mechanical recycling is an industrial way to reuse plastic matter, it is currently limited to materials streams composed of a single type of plastic, which imposes major constraints in terms of sorting. Chemical recycling is a different strategy that consists in depolymerizing polymers into their monomers, to regenerate virgin plastic, or into molecules to feed the chemical industry. While polyesters (> 85 Mt) are the second most widely produced polymers[1a] after the polyolefins **PE**, their chemical recycling is underdeveloped and the search for novel processes is essential. In addition to traditional chemical methods of depolymerisation (solvolysis), routes to deconstruct oxygenated plastics by catalytic reduction, using catalysts and a hydride source (hydrosilanes and hydroboranes) have recently shown promise.[5-7] We revealed now the ability of iodosilanes (Me_3SiI, H_2SiI_2) to depolymerize, in the absence of catalyst, a series of polyesters into functional convenient products involving iodo and Me_3SiO fragments.[8]



Scheme 1. Chemical depolymerisation of polyesters by iodosilanes.

This work was supported by CEA, CNRS, the University Paris-Saclay, and the European Research Council (ERC Consolidator Grant Agreement no. 818260).

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P2 | Expanding the Potential of Aza-BODIPYs: WazaGaY, a gallium-aza-BODIPY derivative, designed for Bimodal NIR Fluorescence/PET Imaging

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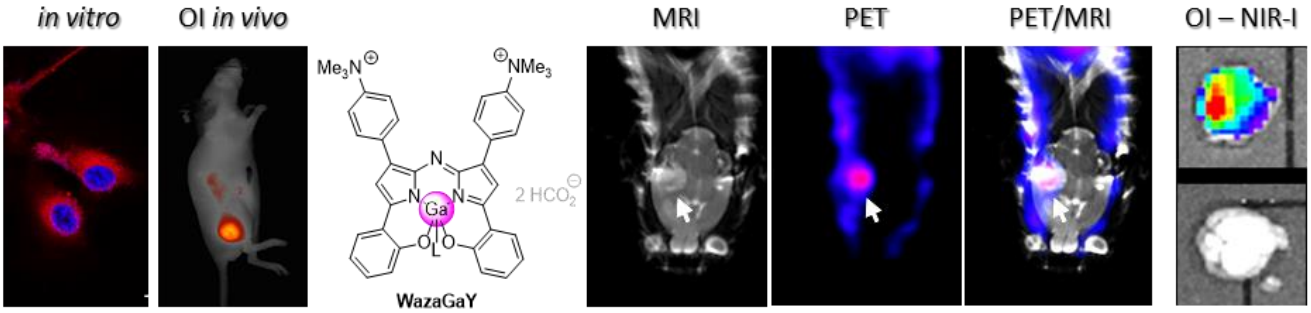
Aza-boron-dipyrromethenes (aza-BODIPYs) have emerged as a class of highly promising fluorophores, comparable to rhodamines and cyanines, due to their ease of synthesis, high stability, and strong fluorescence in the near-infrared (NIR-I, 700–900 nm). These properties make them ideal candidates for *in vivo* fluorescence imaging and surgical guidance. Some of our developed aza-BODIPYs extend emission into the NIR-II window (1000–1700 nm),[1] enhancing imaging resolution.

While structural modifications have focused on tuning the substituents and conjugation of aza-BODIPYs, little attention has been given to the boron center itself. In this work, we explore the impact of replacing boron with metal centers, leading to the synthesis and characterization of novel aza-Metal-DIPY complexes.[2] Special emphasis will be placed on a gallium derivative that has been water-solubilized and designed as a bimodal probe for both NIR fluorescence and PET imaging. We will present its biodistribution in tumor-bearing mice (U87MG, IGROV1, A375), its application in fluorescence-guided surgery,[3] and its potential for PET imaging through radiolabeling with [^{68}Ga]. These results highlight the promise of metal-substituted aza-BODIPYs for advanced bioimaging applications.



This work was supported by the Ministère de l'Enseignement Supérieur et de la Recherche, the Centre National de la Recherche Scientifique (CNRS), and the French Research National Agency (ANR) via project PRC "MAP" ANR-21-CE07-0025. This work was also supported by grants from the Ligue Contre le Cancer, Comité de l'Isère.

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P3 | Synthesis of Novel Nanohybrids Coated with Cell-Penetrating Peptides to Cross the Blood-Brain Barrier

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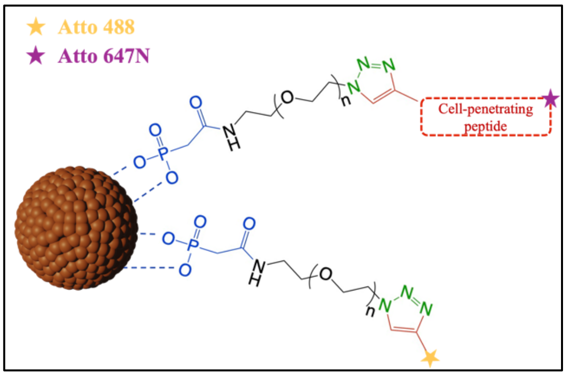
Given the increase in life expectancy, neurodegenerative diseases have become more prevalent, and their highly debilitating symptoms urge for new treatments.[1] Oxidative stress, mainly due to mitochondrial metabolism failure, plays a key role in neurodegenerative diseases physiopathological processes, notably in Alzheimer's disease representing 60-70% of dementia diseases.[2]

In this project, we elaborated hybrid nanoparticles (HyNPs) aimed at targeting mitochondria to deliver an antioxidant compound. HyNP is made of superparamagnetic iron oxide nanoparticles (SPIONs) coated with a biocompatible heterobifunctional polymer (PEG) and further functionalized, by click chemistry,[3,4] with new cell-penetrating peptides (CPPs) that can cross the blood-brain barrier (BBB), target mitochondria and reduce the oxidative stress with antioxidant properties. HyNPs and CPPs were both labeled with a luminescent probe to track them *in vitro* (see Scheme).

We synthesized the HyNPs through a step-by-step method, involving metal-phosphate interaction, amide bond formation, click chemistry. For each step, we purified and then characterized the corresponding nanoparticle conjugate using several techniques such as dynamic light scattering (DLS) for size measurement, thermogravimetric analysis (TGA) for the determination of the organic coating rate, X-ray photoelectron spectroscopy (XPS) for chemical composition and chemical bonds determination and high-performance liquid chromatography coupled to mass spectrometry (HPLC-MS) to evaluate the coupling outcome.

In this poster, we will focus on these new nanohybrids and particularly on i) each step of the synthesis with different characterizations to prove the effectiveness of each coupling, ii) the first biological and BBB crossing tests[5] and iii) the future experiments that will be run in the next months, especially the targeting of mitochondria and the reduction of oxidative stress.



Scheme 1. Synthesized nanohybrid for BBB crossing.

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P4 | Azolium-Porphyrin Electrosynthesis

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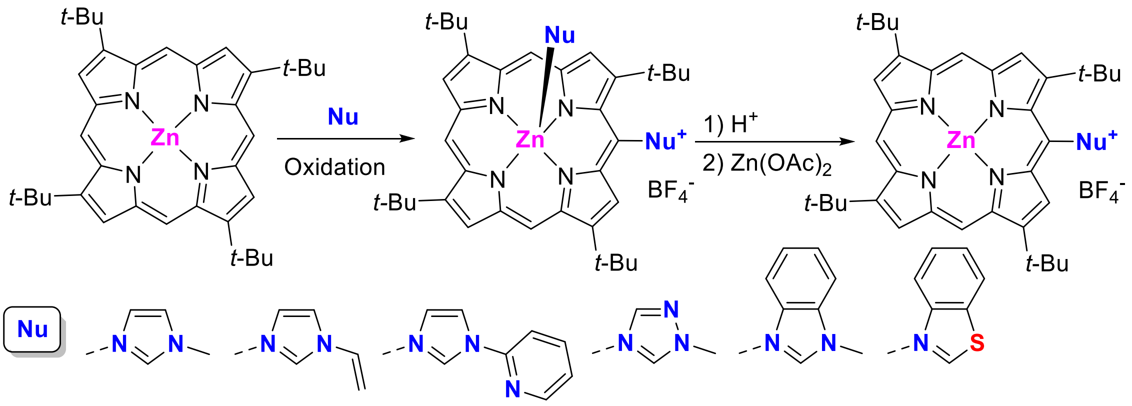
The functionalization of porphyrin is an important research field since this macrocycle is involved in numerous applications ranging from photovoltaic solar cells, electro- and photocatalysis to photodynamic therapy. Despite the considerable efforts that have been devoted to this task for several decades, more efficient and (regio)selective functionalization of porphyrins is still in progress. Recently, the development and applications of imidazolium-porphyrins has motivated novel synthesis strategies that provide moderate to good yields of these cationic compounds.[1] Given the impressive resurgence of electrochemistry as a clean and sustainable way to transform and functionalize organic and organometallic derivatives,[2] we wanted to explore the electrochemical synthesis route, as never done before for porphyrins. This alternative method will provide a new, selective, straightforward and metal-free pathway.

This work thus describes the electrochemical synthesis and characterization of original azolium-porphyrins starting with zinc(II) 2,7,12,17-tetra-*tert*-butylporphyrin (**Zn-1**) and the following nucleophiles: 1-methylbenzimidazole, 1-vinyl-1*H*-imidazole, 2-(1*H*-imidazol-1-yl)pyridine, 1-methyl-benzimidazole, 1-methyl-1*H*-1,2,4-triazole, and benzothiazole.[3]



Scheme 1. Electrosynthesis of azolium-porphyrins.

This work was supported by ANR (ANR-17-EURE-0002, ANR-15-IDEX-03, ANR-15-CE29-0018-01, ANR-19-CE07-0009-02, ANR-23-CE07-0020-02), UBE and CNRS.

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P5 | Bifunctional nickel catalysts for hydroboration and hydrosilylation reactions via cooperative B–H and Si–H bond activations

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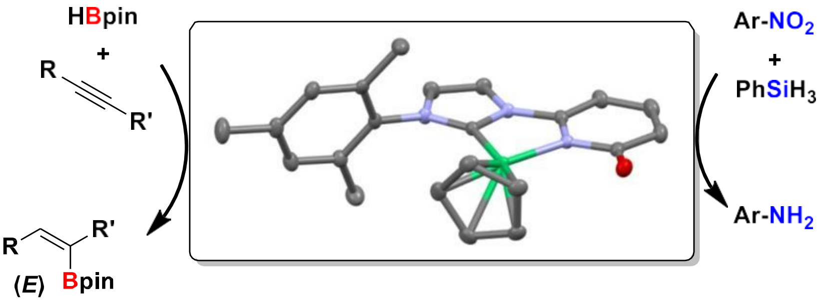
The transition-metal-catalyzed hydroboration[1,2] and hydrosilylation[1,3] are powerful synthetic methodologies because they provide valuable organoboron and organosilicon compounds by straightforward and atom economic synthetic routes. Organoboronate derivatives are widely employed for the construction of C–C, C−N, C−O, and C−S bonds and, as such, are significant feedstocks for the synthesis of pharmaceuticals, agrochemicals, liquid crystals, and organic light-emitting diodes.[1,2] By comparison, organosilicon derivatives are less involved in organic transformations though significant progresses have been made.[4] Such organic compounds are mainly applied in the industrial production of commodity silicones or as pharmaceuticals.[1,3] In addition to these applications, the use of hydrosilanes and hydroboranes is an interesting alternative to hydrogenation, their use as reductants allowing reactions to proceed without any high-pressure equipment or high temperatures. Furthermore, as the reactivity of such boron and silicon reagents and related reaction intermediates is modular and depends on their substituents, hydroboration and hydrosilylation reactions can become highly chemo- and regioselective reduction methods that tolerate various other reducible functional groups.[1,3] The main drawback, however, of the synthetic methodologies involving hydroboration or hydrosilylation is that they are principally developed with noble metal-based catalysts. In addition, whether various organic unsaturations can be reduced through the sole use of a hydrosilane activated by a catalyst, their hydroboration using boranes like catechol or pinacol borane most often requires the combination of a catalyst and a basic activator.

In this context, based on preliminary results,[5] our research project aims at developing bifunctional activator-free catalysts based on nickel, an abundant first-row transition metal. In particular, we target Ni(II)-NHC (NHC = N-heterocyclic carbene) catalysts able to assist hydroboration and hydrosilylation reactions by cooperative E–H (E = B, Si) bond activation and therefore result in effective catalytic processes. A first generation of nickel catalysts has been developed based on a NHC ligand substituted by a pyridone moiety, *i.e.*: based on a NHC ligand bearing a remote metal-unbonded nucleophilic site.[6] Such catalysts are effective without any additive for the selective hydroboration of alkynes to alkenylboronates and the straightforward reduction of nitroarenes to anilines through hydrosilylation (Scheme 1).



Scheme 1. Catalytic hydroboration of alkynes and hydrosilylation of nitroarenes using a Ni(II)-NHC- pyridone complex.

This work is supported by ANR, project BIFUN (2023–2027, ANR-22-CE07-0023-01)

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P6 | DFT Investigation of the Initiation Step in Lactide Ring-opening Polymerization by Al-salan Complexes

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Poly(lactide) properties are highly dependent on its microstructure, and controlling tacticity allows the design of materials with tailored thermal, mechanical and degradability characteristics. Stereocontrol during polymerization achieved by modulating the sequence of monomer insertion plays a key role in defining these properties.[1] Aluminum-based salan complexes have shown promise as stereoselective catalyst for ring-opening polymerization (ROP) of lactide, with the substituents and chirality of the salan ligands being critical for stereocontrol.[2]

To investigate the origin of stereocontrol, we examined the potential energy surface (PES) and initiation mechanisms of lactide polymerization using various of salan-aluminum complexes. Density functional theory (DFT) was used to explore the reaction pathways of the ROP initiation step. PES was carried out with the TeraChem package via relaxed scans and the Nudged Elastic Band (NEB) method while geometry optimizations and transition states and intermediates characterization were performed using Gaussian 16. Free energy, enthalpy, and entropy barriers were obtained with GoodVibes Python program using the quasi-harmonic approximation for low-frequency vibrational modes. All DFT calculations were done at the PBE0-D3/def2-SVP level of theory. A basic salan-H2 system was used to explore the PES, followed by structural modifications to evaluate the influence of ligand substituents and the chirality. In all systems, the spatial arrangement of lactide relative to the complex led to distinct reaction pathways (see Figure 1).

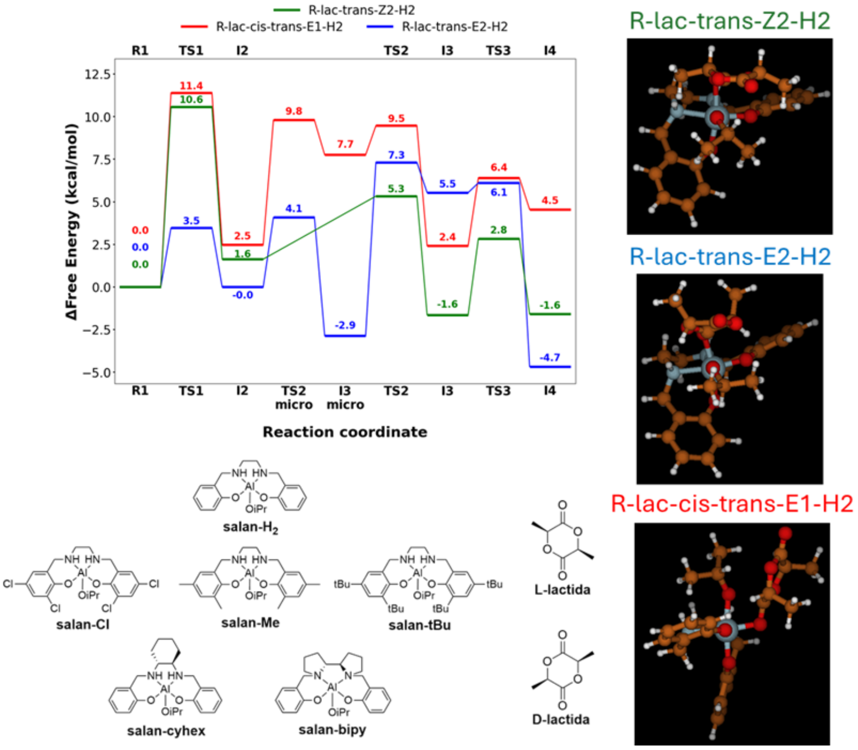

Figure 3. Different reaction pathways obtained for Al salan-H2 complex.

This work was supported by "Beca de Postgrado UdeC".

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P7 | Cooperative *N*-heterocyclic carbene/transition metal redox catalysis

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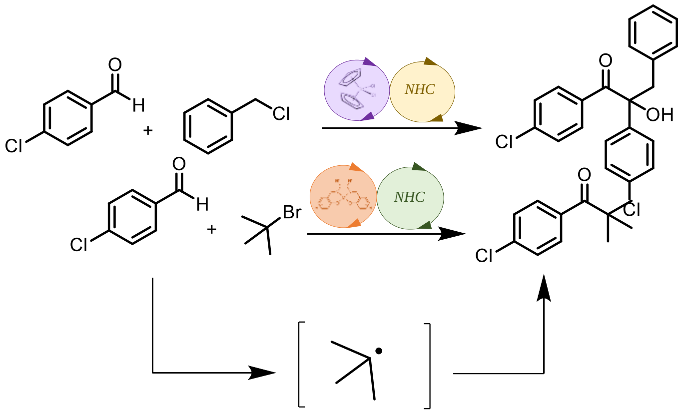
N-Heterocyclic carbenes (NHCs)[1] are well known organocatalysts. They are known for their umpolung reaction with aldehydes to produce Breslow intermediates.[2] These enols are then utilized in the formation of ketones by coupling with other electrophiles. There are two pathways for this reaction: anionic and radical. The reducing power of enolates are limited to redox accessible substrates ($E > -2$ V vs SCE).[3] NHCs can reduce alkyl halides such as primary and secondary alkyl iodides and bromides through both radical and ionic pathway, which are considered challenging substrate to activate.[4,5,6] However this method is still not possible in activating alkyl chloride and tertiary alkyl bromide and iodide.

A possible strategy to activate redox inaccessible substrates is to run cooperative catalysis. Our group showed that tertiary alkyl iodides can be activated by NHC/Ni cooperative catalysis, via SET events.[7] The reduced [$NiBr_2$(Xantphos)] shows a ($E°$Ni(0)/Ni(I) = −0.9 V vs SCE), this potential enables acylation between tertiary alkyl iodides and aldehydes to form ketone.[7] Our approach involves starting with *N*-heterocyclic carbene (NHC) in conjunction with titanocene dichloride to facilitate the activation of alkyl chlorides, beginning with benzyl chloride as the model alkyl chloride.[8]

Using both palladium metal and *N*-heterocyclic carbenes (NHCs) together works effectively to activate alkyl bromides, especially the ones that are secondary or tertiary.[9] We are exploring the use of less expensive metals, such as cobalt complexes, in combination with NHCs to activate tertiary alkyl bromides.



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P8 | Polyoxometalate-based Artificial Photosynthesis

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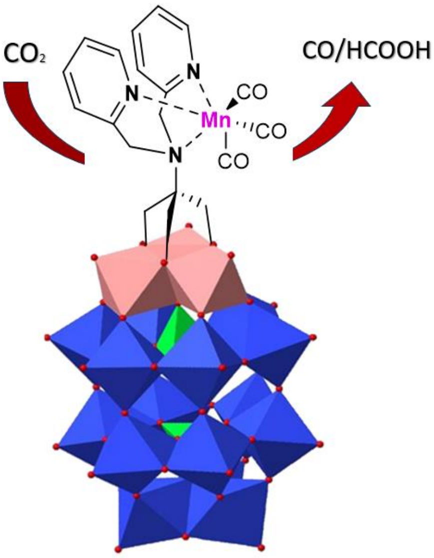
Energy policies in developed nations are pressing. Solar energy, abundant on Earth, could meet global demands if efficiently harnessed. Storing intermittent solar energy is a challenge. An attractive option, however challenging, is to store this energy into chemical bonds, for example (photo)reducing proton into H_2 or carbon dioxide. Due to the intrinsic photoreactivity of the POM, mixed V-W Dawson derivatives functionalized with a Cu-complex could store up to three electrons, and the latter have been used for reductive catalytic applications. In a follow up of our previous work on CO_2 (photo)electroreduction with POM derivatives, the aim of this project is to activate by light the catalytic properties of the grafted complex by replacing the Cu-Dipyridyl moiety by a Co-complex and its Fe- or Ni-analogues, known for their ability to electro-reduce protons or CO_2, and to test the photo-/electro-catalytic properties of these new hybrids.



Scheme 1. Schematic representation of the bioinspired hybrid POM.

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P9 | Intercomparison Study of DGT Devices with Dihydroxamate-Based Binding Gels for Uranium(VI) Sampling in Freshwater

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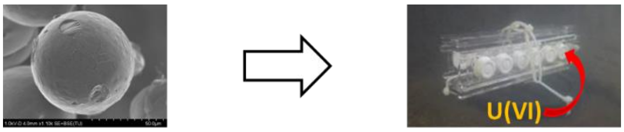
Uranium is released into the environment through mining activities, production and use of nuclear fuel (~65 kt/year), reprocessing of spent fuel and storage of nuclear waste, coal burning, and spreading of phosphate fertilizers. Once discharged, uranium may migrate across various environmental compartments, ultimately leading to the contamination of trophic chains [1]. Monitoring such contamination, particularly in aquatic systems, calls for innovative analytical techniques capable of assessing both the distribution and bioavailability of actinides. In that respect, Diffusive Gradients in Thin Films (DGT) is one of the most promising techniques for determining the concentration of labile metal species in aquatic environments, including wetlands and sediments. Unfortunately, the most widely used and commercially available binding gels for uranium, namely the Chelex-100® ion-exchange resin and the TiO_2-based Metsorb® adsorbing material, are known to underperform in hard, carbonate-rich freshwater and seawater [2,3].

To overcome these shortcomings, we designed a pincer-like UO_2^{2+} chelator bearing two terminal hydroxamate bidentate groups able to coordinate the uranyl cation in its equatorial plane [4]. Potentiometric studies revealed a high binding affinity towards UO_2^{2+} and an excellent selectivity with respect to Ca^{2+} and Mg^{2+} ions. According to PHREEQC speciation calculations, uranium(VI) is efficiently chelated between pH 4 and 8 even in the presence of major competing ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, and HCO_3^-. Hence, the dihydroxamic acid was covalently grafted by amide bond formation onto a hydrophilic organic resin, Sephadex CM-25®, and the resulting extracting material embedded in a binding gel made of agarose. The uranium(VI) uptake performances of the new DGT samplers made thereof were assessed under controlled laboratory conditions, using both mineral waters and synthetic seawater spiked with 20 μg/L of UO_2^{2+}. Accordingly, uranium prevails as $[M_xUO_2(CO_3)_3]^{(4-2x)-}$ triscarbonato species (M = Mg, $x = 1$; M = Ca, $x = 0–2$) in each medium. Results were benchmarked against commercial Chelex-100® and Metsorb® samplers, highlighting the superiority of the hydroxamic acid based extracting resin.



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P10 | Diversity of trifluoromethanesulfonate coordination modes in organotin(IV) complexes

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The first study describing the synthesis of organotin trifluoromethanesulfonates dates back to the 1970s.[1] Since then, this class of compounds has attracted much interest in organic synthesis and homogeneous catalysis. Acting as *Lewis* acid catalysts, organotin trifluoromethanesulfonates are known to be effective in a number of organic reactions, such as: aldol reaction of *Mukaiyama*,[2] *Robinson* annulation,[3] acetylation of alcohols,[4] transesterification of dimethyl carbonate (DMC) with phenol,[5] and direct synthesis of DMC from methanol and carbon dioxide.[6-7] The structural aspect, last reviewed by *J. Beckmann* in 2005, is also of great interest.[8] Based on earlier reports for *p*-block metals, the CF_3SO_3 group can be ionic and act as a counter anion, or it can also be a ligand bound directly to the metal adopting different coordination modes. Examples of mono-, bi- and tridentate CF_3SO_3 groups, as well as terminal, *pseudo*-terminal and bridging groups, have already been reported in the literature (Figure 1).

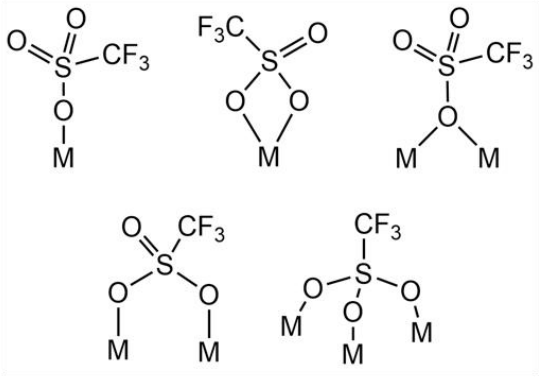

Fig 1. schematic representation of the coordination modes involving the trifluoromethanesulfonate ligand and the *p*-block metals.

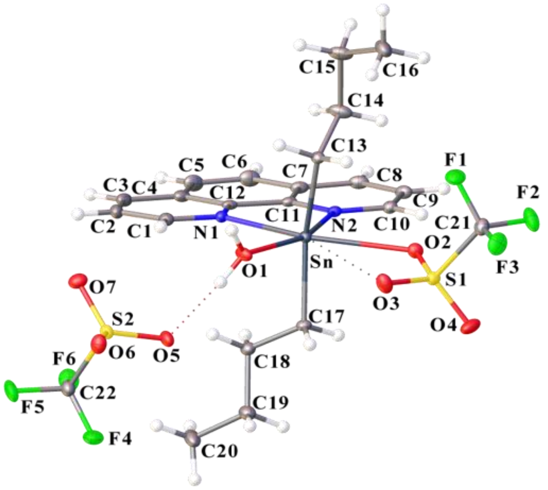

Fig. 2. [n-$Bu_2Sn(OH_2)(phen)(OSO_2CF_3)](O_3SCF_3)$ (ORTEP view) [10].

As part of our past and present studies on the reactivity of organotin(IV) compounds,[9] we have been able to isolate and characterize several trifluoromethanesulfonate derivatives in the solid state that exhibit some of these configurations (a newly identified example is shown in Figure 2). The most remarkable structures of these compounds will be detailed and discussed in the poster.

This work is supported by the Centre National de la Recherche Scientifique and the Université Bourgogne Europe.

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P11 | Discovery of $Ni^{(I)}$ Complexes for CO_2 Insertion Enabled by a Machine Learning-Computational-Selection Sequence

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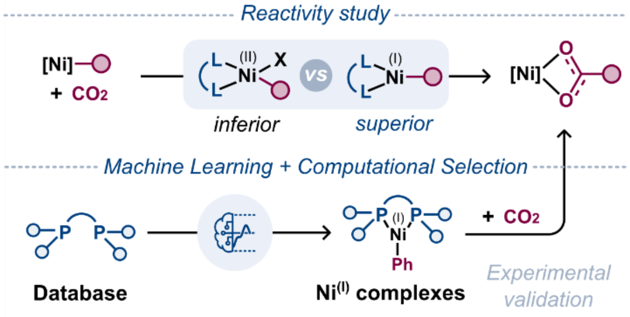
In Ni-catalyzed carboxylation of alkyl or aryl halides, it is thought that $Ni^{(I)}$ is vastly superior to $Ni^{(II)}$ for mediating the CO_2 insertion.[1] *In-situ* speciation of the catalyst is a critical aspect for catalytic efficiency (turn-over, catalyst lifetime, reactivity and/or selectivity). However, it is not possible to predict *a priori* the effect of the ligand on this speciation. In order to select suitable ligands for the desired $Ni^{(I)}$ speciation (instead of trial-and-error approaches), we undertook a machine learning study combined with computational activation barrier predictions to achieve CO_2 insertion at room temperature. After a thorough computational analysis of the reactivity differences between $Ni^{(I)}$ and $Ni^{(II)}$ towards CO_2 insertion, we applied machine learning to identify ligands that stabilize $Ni^{(I)}$-Ph complexes, the least sterically hindered (and most sensitive) key catalytic intermediates. After evaluating CO_2 insertion barriers using DFT, a selection of representative candidates was synthesized and experimentally tested for stoichiometric or catalytic carboxylation, confirming their reactivity and the effectiveness of computational predictions.[2]



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P12 | Rhodacycles Activity in P-directed Rhodium-Catalyzed Synthesis of π-Extended Aromatic Phosphines

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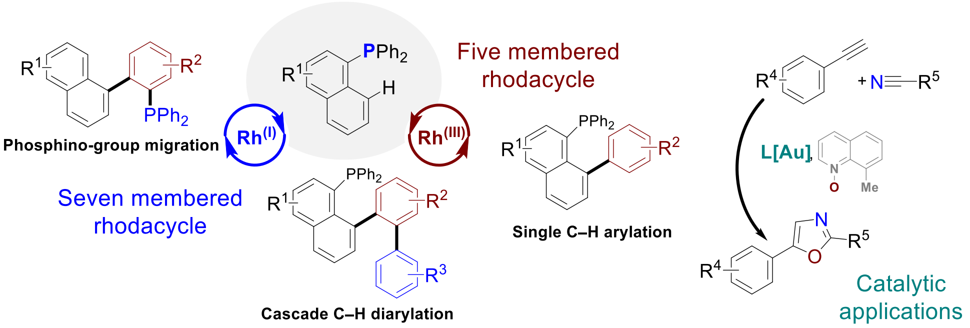
Monophosphine polyaromatic hydrocarbons have demonstrated their interest in numerous applications in the fields of coordination, catalysis (such as Buchwald biphenyl-based ligands), health through their analgesic, anti-inflammatory, or anti-cancer activities, as well as in organic electronic materials. These include planar aromatic derivatives such as pyrene, phenanthrene, fluoranthene, or naphthalene, for which their electronic and geometric characteristics can also favor π-stacking interactions. These can be easily obtained and diversified through selective C–H bond functionalizations using phosphorus as a directing group with the help of transition metals such as rhodium.[1,2] The nature of the rhodium-based metal precursor $Rh^{(I)}$ vs $Rh^{(III)}$ can be essential in controlling the functionalization of polyaromatic derivatives. Thus, the cationic precursor $[Rh^{(I)}(COD)_2]\ BF_4$ allows more efficient introduction of bulkier aryl groups, as well as cascade functionalization, or even migration of the phosphorus group *via* a 7-membered rhodacycle.[2] These (poly)arylated monophosphines have notably improved the catalytic activity of gold in a cyclization reaction towards the formation of oxazoles.[3]



Scheme 1. P-directed rhodium-catalyzed synthesis of π-Extended Aromatic Phosphines.

This work is supported by the CNRS, the Université Bourgogne Europe, the Conseil Régional Bourgogne-Franche-Comté, the Fonds Européen de Développement Régional (FEDER), the French Agence Nationale de la Recherche via the ANR JCJC program 2018 FIT-FUN and the ANR PRC program 2020 CARAPH.

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P13 | Identification of protonated complexes of metal ions by means of affinity capillary electrophoresis: the uranyl-oxalate system

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The protonated complex species of metal ions with various polybasic acids as ligands are difficult to identify by physical methods. In general, these species have been postulated to improve the fitting of potentiometric or spectrophotometric data. This work demonstrates the advantages of affinity capillary electrophoresis (ACE) for the identification of protonated complexes. The case of U(VI) complexes with oxalic acid is studied.

The mobilities of U(VI) are measured in aqueous acid solutions containing oxalic acid at different concentrations (from 0 up to 0,5 M) in the range of pH 1,5-2,5. The observed U(VI) mobility was found to decrease with increasing ligand concentration added to the background electrolyte solution. Since the changes in metal ion mobilities at different pH values reflect the chemical equilibria occurring in solution,[1] the ACE data allowed us to decipher whether or not the ligand was protonated in the metal complexes.

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P14 | Design of efficient nano-catalysts for H_2 release from ammonia-borane

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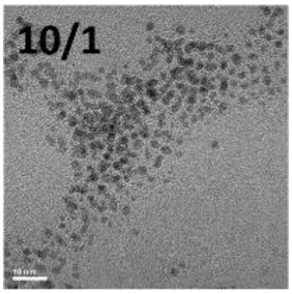
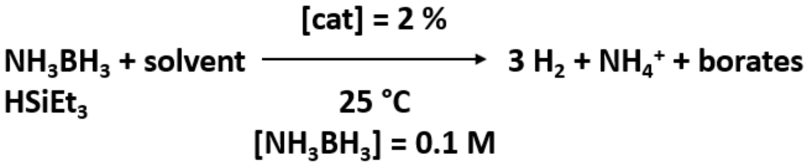
The combustion of fuel produces deleterious gas (CO_2) for which the capture and recycling is mostly not achieved. Conversely, the use of chemical hydrogen storage materials, releasing H_2 –for combustion engines or fuel cells– and liquid or solid by-products, gives the important opportunity to easily capture and handle this co-produced waste.[1] On one hand, ammonia-borane NH_3BH_3 (AB, 19.5 wt% H) and $NaBH_4$ (10.8 wt% H) are able to release H_2 by hydrolysis and alcoholysis, in the presence of a metal catalyst in ambient conditions.[2] These reactions have attracted considerable attention, with special focus on the catalysts for fast H_2 delivery.[3] In comparison, critical aspects for the industrial implementation of this approach, like the nature of the solvolysis by-product(s) have been much less investigated, while their identification and recycling will be needed in a righteous circular approach.[3] On the other hand, organosilicons and specially hydrosilanes –as widely manufactured commercial products– may also be attractive as potential sources of H_2. This, following various catalyzed chemical roads, including hydrolysis and alcoholysis of silanes (R_3Si–H, R_2SiH_2, *etc.*), or their dehydrogenative oligomerization ($PhSiH_3$ dehydrocoupling).[4] Here we will present the development of ruthenium, and iridium NPs for AB and hydrosilane (Et_3SiH) solvolytic dehydrogenation (H_2O, MeOH). The synthesis of Ru, and Ir nanocatalysts stabilized by bulky, rigid, s-donating functionalized adamantane and diamantane ligands will be described and their performances in H_2 production discussed.





$$\begin{array}{l} NH_3BH_3 + \text{solvent} \\ HSiEt_3 \end{array} \xrightarrow[\substack{25\ °C \\ [NH_3BH_3] = 0.1\ M}]{[cat] = 2\ \%} 3\ H_2 + NH_4^+ + \text{borates}$$

This work was supported by the University Burgundy Europe, and the CNRS.

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P15 | Hypervalent Organopnictogen(III) Cations

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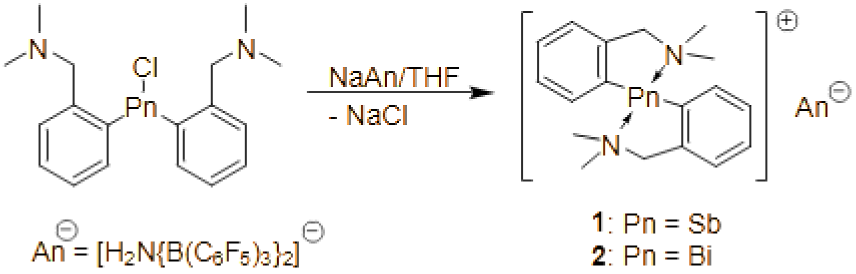
Cationic organometallic species based on antimony(III) and bismuth(III) have shown great interest due to their applicability as Lewis acids[1] or as part of frustrated Lewis pairs, in organic reaction catalysis.[2] Antimony(III) cationic complexes bearing cyclopentadienyl ligands were proved to be strong Lewis acids,[3] some of them even being used as catalysts for the dimerization of 1,1-diphenylethene.[4] Such complexes are water- and air-sensitive and often difficult to synthesize, purify and use. Hypervalent bismuth(III)-based cations bearing a tridentate (C,E,C) ligand (E = S,[5] RN[6]) and another anionic, weakly coordinating ligand {OTf^-, $[B(C_6F_5)_4]^-$} were used, in water, as catalysts for the Mannich reaction.

Perfluorinated arylboron anionic species can be used with great success as low-coordinating anions. In solid state, chemical species such as $[B(C_6F_5)_4]^-$ and $[H_2N\{B(C_6F_5)_3\}_2]^-$ coordinate weakly, if at all, to the metal centre of an organopnictogen cation, while in solution, the coordination is preponderantly absent.[7] This allows a strong Lewis acid to be free in solution, circumventing the decoordination step at the beginning of the catalytic cycle.

We report the synthesis of two salts (**1**, **2**), in which the cation is a hypervalent homoleptic diorganopnictogen(III) complex of the type $[\{2\text{-}(Me_2NCH_2)C_6H_4\}Pn]^+$ [Pn = Sb (**1**), Bi (**2**)] and the counterion is the low-coordinating $[H_2N\{B(C_6F_5)_3\}_2]^-$ amido diborate anion. The reaction required the corresponding diarylpnictogen(III) chlorides and the sodium salt of the anion (Scheme 1).



Scheme 1. Synthesis of **1** and **2**.

Salts **1** and **2** were characterized by multinuclear (^1H, ^{13}C, ^{19}F, ^{11}B) NMR spectroscopy and the molecular structures were determined by single-crystal X-ray diffraction.

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