3rd Main Group Metal Chemistry Symposium

12-13 nov. 2025 Paris (France)

Book of abstracts

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3rd Main Group Metal Chemistry Symposium

12-13 nov. 2025 Paris (France)

Wednesday, November 12,2025

13h15-13h50	***Reception of attendees***
13h50-14h00	***Opening***
14h00-14h50	Plenary 1 **Guillaume BERIONNI** (University of Namur, Belgium) *Chiral phosphines, pyridines and boranes: applications in main-group and transition-metal catalysis*
14h50-14h55	FP 1 **Teddy POTEZ** (CARMeN Institute, University of Rouen Normandy, France) *NMR Study of Organolithium Reactivity in Deep Eutectic Solvents*
14h55-15h00	FP 2 **Amal BOUAMMALI** (ICGM, Univ Montpellier, France) *Ansa-effects in octaphenylmetallocenophanes of the alkaline earth metals*
15h00-15h20	OC 1 **Marc PRRESSET** (ICMPE, Université Paris-Est Créteil, France) *Alkylzinc halides in Mannich reactions*
15h20-15h40	OC 2 **Laetitia CHAUSSET BOISSARIE** (CARMeN Institute, University of Rouen Normandy, France) *Flow-Enabled Organolithium Methodologies: From Batch to Scale-Up*
15h40-16h00	OC 3 **Adrian SOMESAN** (SOOMCC, Babeș-Bolyai University, Cluj-Napoca, Romania) *Organotin(IV) chalcogenides – design, synthesis and applications*
16h00-16h45	***Coffee break***
16h45-16h50	FP 3 **Sélène CASTANET** (IPCM, Sorbonne Université, Paris, France) *Self-assembled molecular networks for molecular rectifiers*
16h50-16h55	FP 4 **Alex TOMUTA** (ISCR, Université de Rennes, France) *Hypervalent Organopnictogen(III) Cations*
16h55-17h00	FP 5 **Thu-Van NGUYEN** (ICMUB, Université de Bourgogne, Dijon, France) *Bis(phenoxy-amidine) (FAlen)-Zn Complexes for the Cycloaddition of CO2 to Epoxide and the Ring-Opening Polymerization of Lactide*
17h00-17h20	OC 4 **Marc DEVILLARD** (ISCR, Université de Rennes, France) *Transformation of silacyclopropenes*
17h20-17h40	OC 5 **Morwenna PEARSON-LONG** (IMMM, Le Mans Université, France) *Double addition of organoaluminium reagents onto nitriles to access diethynyl carbinamines*
17h40-18h00	OC 6 **Ewen BODIO** (CEISAM, Nantes Université, France) *From Boron to Metals: Unlocking Aza-BODIPYs for Multimodal NIR/PET Imaging*
18h00	***Photograph***

Thursday, November 13, 2025

8h50-8h55	FP 6 **Fida IBRAHIM** (CARMeN Institute, University of Rouen Normandy, France) *Investigating Mixed Aggregates of Dimethylphenylsilyllithium, Dimethylphenylsilanoxide, and Lithium Chloride in THF: A Comprehensive NMR {^{1}H, 6,7Li, 29Si} Study*
8h55-9h00	FP 7 **Iulia CRISAN** (ISCR, Université de Rennes, France) *Bulky allyls for heavier alkaline-earth chemistry*
9h00-9h50	Plenary 2 **Gabriele MENGES-FLANAGAN** (Fraunhofer IMM, Mainz, Germany) *Organometallics in Flow*
9h50-10h10	OC 7 **Stéphanie HALBERT** (LCT, Sorbonne Université, Paris, France) *Redox-Active Ligands in Low-Valent Complexes: from formation to reactivity*
10h10-10h35	*Coffee break*
10h35-10h40	FP 8 **Tudor M. UNGUREAN** (SOOMCC, Babeș-Bolyai University, Cluj-Napoca, Romania) *Toward new diorganoantimonides: isolation of new azastibocine hydride and distibane*
10h40-10h45	FP 9 **Djemel-Dine BAZILLE** (CARMeN Institute, University of Rouen Normandy, France) *A new dilithiated initiator for anionic continuous flow polymerization of telechelic polymyrcene oligomers*
10h45-11h05	OC 8 **Riccardo PICCARDI** (LCBPT, Université Paris Cité, France) *A Journey from Alkynylalanes to Bioconjugation of Biomolecules*
11h05-11h25	OC 9 **Armelle OUALI** (ICGM, Univ Montpellier, ENSCM, France) *Transfer hydrogenation catalysts based on alkaline-earth metals: applications and mechanistic studies*
11h25-11h45	OC 10 **Clément CHAUVIER** (IPCM, Sorbonne Université, Paris, France) *Organoalkali-Catalyzed C–Si Cross-Couplings with N-tert-Butyl-N'-Silyldiazenes*
11h45-12h05	OC 11 **Sabrina TOUCHET** (L2CM, Université de Lorraine, Nancy, France) *Mg/Li Bimetallic Organomagnesiate Complexes as Tools for the Synthesis of Fused (Hetero)aryl Lactones*
12h05-14h00	*Lunch (free)*
14h00-14h05	FP 10 **Sarah CHAPUIS** (IPCM, Sorbonne Université, Paris, France) *Lewis-base Activation of Grignard Reagents for Enantioselective Catalysis and Continuous Flow Process*
14h05-14h10	FP 11 **Raffaele FONTANA** (SOOMCC, Babeș-Bolyai University, Cluj-Napoca, Romania) *N,C,N-Polypyridinic Bismuth(I) Complexes as Two-Electron Donor Ligands in Cobalt Coordination Chemistry*
14h10-15h00	Plenary 3 **Alexander HINZ** (Institute for Inorganic Chemistry, Karlsruhe Institute of Technology, Germany) *Limits of steric protection: From barium hydride to acyclic silylenes*
15h00-15h20	OC 12 **Laurent CHABAUD** (ISM, Université de Bordeaux, France) *Aminoboranes and Amine–Borane Complexes: Versatile Reagents for the Synthesis of Organoboron Compounds*
15h20-15h40	OC 13 **Béatrice JACQUES** (ICS, Université de Strasbourg, France) *Strong Zn(II) and Mg(II) Cationic Lewis Acid: Synthesis, Structure, and Reactivity in Catalysis*
15h40-16h00	OC 14 **Alexandre VASSEUR** (L2CM, Université de Lorraine, Nancy, France) *Tandem Dual C–C Bond Formation Enabled by LiZn-Based Reagents*
16h00	***Closing words***

Plenary Lectures

PL-1 Chiral phosphines, pyridines and boranes: applications in main-group and transition-metal catalysis – Pr. Guillaune BERIONNI

PL-2 Organometallics in Flow – Dr. Gabriele MENGES-FLANAGAN

PL-3 Limits of steric protection: From barium hydride to acyclic silylenes – Dr. Alexander HINZ

Chiral phosphines, pyridines and boranes: applications in main-group and transition-metal catalysis

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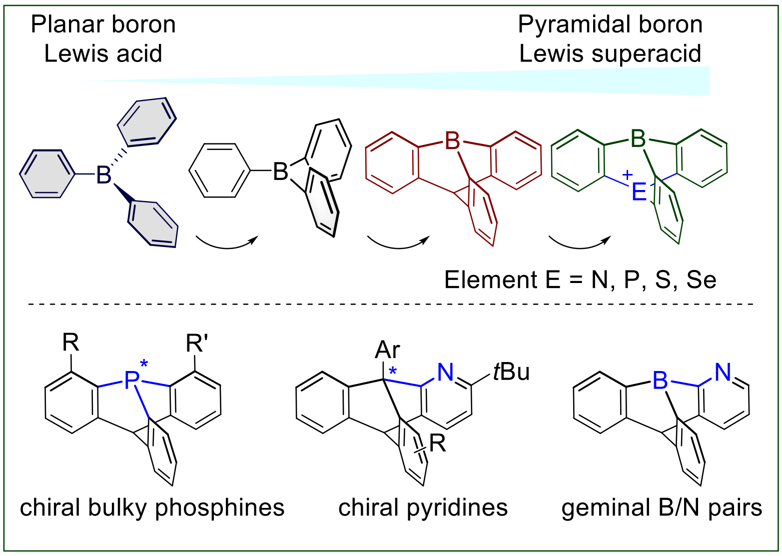
Frustrated Lewis pairs and main-group element / ligand bifunctional compounds mimicking the reactivities of transition-metal complexes are increasingly used as catalysts for small molecules activations and inert bonds functionalization.[1] Our group has recently devoted significant efforts towards the development of new classes of bulky chiral phosphines, pyridines and boranes featuring unprecedented reactivities.[2] Experimental and computational mechanistic investigations of FLPs mediated hydrogenation and C-H borylation reactions proved to be a powerful strategy to design new frustrated Lewis pairs with unusual structures and reactivities and to discover new coordination modes at phosphorus and boron.[3]



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[3] (a) A. Osi, D. Mahaut, N. Tumanov, L. Fusaro, J. Wouters, B. Champagne, A. Chardon, G. Berionni, *Angew. Chem. Int. Ed.* **2022**, *61*, e202112342; (b) A. BenSaida, D. Mahaut, N. Tumanov, J. Wouters, B. Champagne, N. Vanthuyne, R. Robiette, G. Berionni, *Angew. Chem. Int. Ed*. **2024**, *63*, e202407503; (c) T.-H. Doan, A. Chardon, N. Vanthuyne, T. N. Ramos, N. Tumanov, L. Fusaro, M. Albalat, L. Collard, J. Wouters, B. Champagne, G. Berionni, *Angew. Chem. Int. Ed.* **2025**, *64*, e202421931; (d) N. Niessen, L. Mineur, A. Chardon, A. Osi, A. I. Adjieufack, D. Mahaut, N. Tumanov, J. Wouters, B. Champagne, G. Berionni, *Chemistry Europe*, **2025**, accepted.

Organometallics in Flow

Gabriele Menges-Flanagan,[1] Eva Deitmann,[1] Lars Gössl [1]

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Organometallic reagents based on Mg and Zn metal have been used by process chemists to form new C-C bonds in the synthesis of Active Pharmaceutical Ingredients (API), in the agricultural but also the flavors and fragrances industry for over 100 years. Synthesis of such organometallic reagents is, however, impeded by sensitivity to water and oxygen, the high exothermicity of formation in many cases and therewith safety concerns in their production. Over the last nearly a decade, Fraunhofer IMM has worked on fully utilizing continuous processing on varying throughput scales to enable the scalable continuous Grignard and Zn reagent formation and consumption. The goals have always been increasing safety, improving product quality, and allowing a flexible production of exactly the needed and required amounts of reagent and follow-up product. On the laboratory-scale, process investigations enable a fast and cost-efficient evaluation of achievable benefits of switching from batch to continuous processing. On the pilot-scale, Grignard and Zn-based solutions in concentrations ranging from 0.5 to 2.0 mol/L have been processed continuously with up to 18 L/h to allow for industrially relevant throughput scales. Maximum throughputs achievable for a specific organometallic reagent are determined by its concentration and reactivity. Furthermore, follow-up reactions such as Grignard, Negishi, Saytzeff and Reformatsky reactions, have been investigated on varying throughput scales. The continuous producing and consuming organometallic reagents ultimately leads to savings in time, energy and money, accompanied by a reduced time-to-market for new substances. It allows full access to the whole range of organometallic reagents based on Mg and Zn and manages high exothermicities, in-situ metal activation and side product formation. Continuous processing as presented here provides a route to process intensification yielding a safer, more selective and easily scalable way to organometallic reagents and their subsequent consumption in follow-up reactions, even enabling a simultaneous processing (one-pot-synthesis) by performing Barbier reactions in flow.

The presentation will summarize the efforts undertaken at Fraunhofer IMM in the last several years. Besides detailing aspects of reactor design and engineering to enable continuous processing of solids in flow for the formation and consumption of organometallic reagents on varying throughput scales, a more detailed look on the chemistry of these compounds in continuous processing will be presented. Switching from a batch to a continuous processing route will be shown to lead to significant improvements as detailed above. This includes a look at many reagents based on Mg and Zn and even Li metal that have already been successfully prepared on multiple throughput scales (up to 18 L/h) as well as a closer look at some of their follow-up reactions (Grignard, Barbier, Saytzeff, Negishi).

Limits of steric protection: From barium hydride to acyclic silylenes

Alexander Hinz, Pauline Hädinger, Maximilian P. Müller, Lucas Winkler,
Emma Stapf, Lukas Steppe, José Miguel León Baeza, Xiaofei Sun

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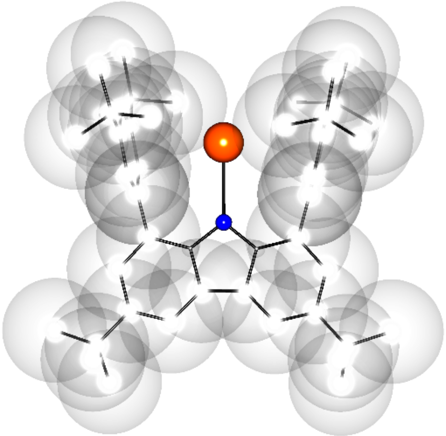
The use of sterically demanding substituents has allowed various developments in p-block chemistry, such synthesis of tetrylenes (silylenes, germylenes, stannylenes and plumbylenes) which display unsual properties and reactivity. In these compounds, the group 14 element is low-coordinated with coordination number 2. Driving this strategy to its logical conclusion, the desired target for low-coordinated compounds is coordination number 1 by involving even bulkier ligands. To this end, we developed a carbazole-based substituent (Cbz) and initially employed it in tetrylene chemistry.[1] The synthesis and properties of low-coordinated group 14 compounds will be discussed in detail, culminating in the mono-coordinated silicon(II) cation [(Cbz)Si]$^+$.[2,3]



The strategy of sterically shielding central atoms to enable unusal properties is not limited to p-block elements. A subsequent line of investigation was aimed at extending the concept to elements of the s-block. In this field, the stabilisation of molecular hydride complexes has been a long-standing challenge. We have employed a monodentate ligand for the synthesis of such hydrides and investigated the reactivity of these hydride compounds.[4,5] Also, with these non-covalent carbazolide compounds, efficient luminescence phenomena were observed and will be shown at selected examples.

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Oral Communications

OC-1 Alkylzinc halides in Mannich reactions – Marc PRRESSET

OC-2 Flow-Enabled Organolithium Methodologies: From Batch to Scale-Up – Laetitia CHAUSSET BOISSARIE

OC-3 Organotin(IV) chalcogenides – design, synthesis and applications - Adrian SOMESAN

OC-4 Transformation of silacyclopropenes – Marc DEVILLARD

OC-5 Morwenna PEARSON-LONG Double addition of organoaluminium reagents onto nitriles to access diethynyl carbinamines – Morwenna PEARSON-LONG

OC-6 From Boron to Metals: Unlocking Aza-BODIPYs for Multimodal NIR/PET Imaging – Ewen BODIO

OC-7 Redox-Active Ligands in Low-Valent Complexes: from formation to reactivity – Stéphanie HALBERT

OC-8 A Journey from Alkynylalanes to Bioconjugation of Biomolecules – Riccardo PICCARDI

OC-9 Transfer hydrogenation catalysts based on alkaline-earth metals: applications and mechanistic studies – Armelle OUALI

OC-10 Organoalkali-Catalyzed C–Si Cross-Couplings with N-tert-Butyl-N'-Silyldiazenes – Clément CHAUVIER

OC-11 Mg/Li Bimetallic Organomagnesiate Complexes as Tools for the Synthesis of Fused (Hetero)aryl Lactones – Sabrina TOUCHET

OC-12 Aminoboranes and Amine–Borane Complexes: Versatile Reagents for the Synthesis of Organoboron Compounds – Laurent CHABAUD

OC-13 Strong Zn(II) and Mg(II) Cationic Lewis Acid: Synthesis, Structure, and Reactivity in Catalysis – Béatrice JACQUES

OC-14 Tandem Dual C–C Bond Formation Enabled by LiZn-Based Reagents – Alexandre VASSEUR

Alkylzinc halides in Mannich reactions

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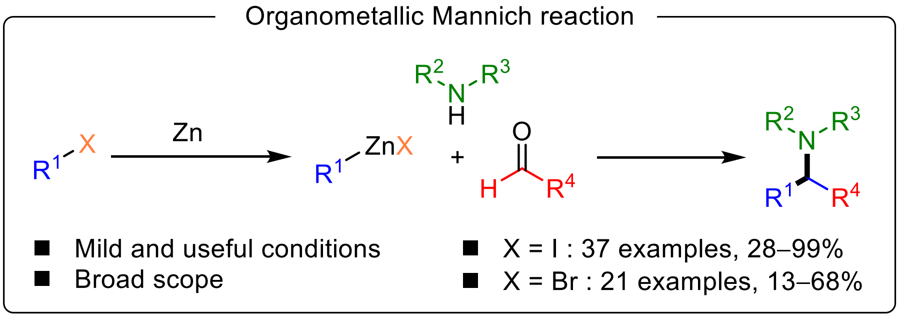
The Mannich reaction is a benchmark in multicomponent chemistry, enabling rapid access to α-branched amines through simultaneous C–C and C–N bond formation. While the use of organometallic nucleophiles has expanded its scope,[1] applications with nonstabilized sp³-hybridized reagents remain rare and challenging.[2]

We report that mixed (heteroleptic) organozinc reagents can efficiently engage in the three-component Mannich reaction.[3,4] These species, readily generated from alkyl iodides or bromides by direct zinc insertion, provide straightforward access to highly substituted α-branched amines. The method tolerates a wide range of organozinc reagents, secondary amines, and both aromatic and aliphatic aldehydes. Remarkably, the observed reactivity trends are strongly influenced by the nature of the alkyl halide precursor and reaction conditions.

This work demonstrates a cost-effective and broadly applicable strategy that significantly expands the scope of the organometallic Mannich reaction, opening new perspectives for the streamlined construction of complex amine architectures.



- Mild and useful conditions
- Broad scope
- X = I : 37 examples, 28–99%
- X = Br : 21 examples, 13–68%

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[3] M. Pinaud, E. Le Gall, M. Presset, *J. Org. Chem.* **2022**, *87*, 49614964.
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Flow-Enabled Organolithium Methodologies: From Batch to Scale-Up

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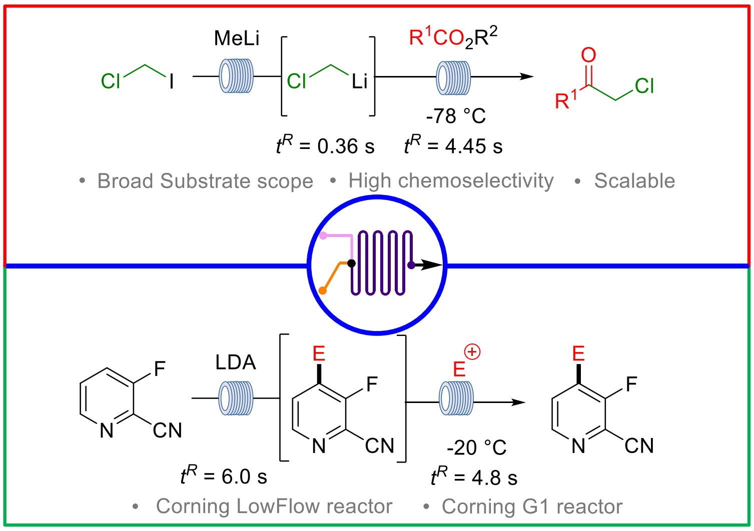
To date, numerous examples demonstrated the advantages of microfluidic systems in terms of reaction efficiency and selectivity, showcasing their value in modern chemical synthesis and manufacturing.[1] Owing to their inherently high surface-to-volume ratio, continuous flow technology enhances heat and mass transfer offering significant benefits for reactions involving very short-lived or highly reactive intermediates. In this context, we report a novel and practical strategy to access α-chloroketones from esters bearing diverse (hetero)aromatic, aliphatic, alkynyl and alkenyl substituents with transient chloromethyllithium under continuous flow conditions. This highly chemoselective method enables a fast (on a time scale of <5 s), efficient and straightforward access to a broad substrate scope (up to 99% yield) with a remarkable throughput of ~10.6 g/h.[2] In addition, we demonstrate the selective functionalization of pyridines via lithiation, illustrating the transition from laboratory-scale experiments to continuous processing in the Corning G1 reactor. This study highlights the advantages of flow chemistry in enhancing efficiency, scalability, and safety, ultimately facilitating the progression from small-scale synthesis to pilot-scale production.



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Organotin(IV) chalcogenides – design, synthesis and applications

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Group 14 chalcogenide frameworks are known hybrid materials that exhibit various pore size and structures such as wormhole or hexagonal honeycomb.[1] This class of compounds has continuously increased attention of the scientific community thanks to their various applications, *i.e.* as gas sensors,[2] precursors for metal chalcogenides or for their specific properties such as luminescence[3] and semiconductivity.

Six-membered ring systems of general formula $(R_2SnE)_3$ E = S, Se, Te; R = Me, Bn, Ph are already reported, but most of them have common organic substituents bounded to Sn and only a few were further investigated for potential applications (single-source precursors for SnS or SnSe semiconductors).

A more attractive family of clusters containing late group 14 elements (Ge, Sn) is the adamantane-type chalcogenide system with the general formula $(RM)_4E_6$, M = Ge, Sn; E = S, Se, Te. These cages display a well-established directionality of the organic fragments, R, provided by the adamantane-like core, which enables the usage of these clusters as building blocks for metal-organometallic networks (MOMNs). Recently, a series of $[(RSn)_4E_6]$ clusters (R = Ph, Bn, Cp, Cy, $(C_6H_4)COOEt$; E = S, Se) were reported as exhibiting nonlinear optical properties.[4]

Adding some functional ligands on these clusters would increase their potential in terms of coordination abilities or reactivity, as shown earlier by Dehnen et al. who validated their reactivity towards hydrazine, hydrazones and related species, and probed their optical and electrochemical properties.[5]

Thus, the aim of the current study is the development of a new generation of organotin(IV) chalcogenide clusters with the general formulae $(R_2SnE)_n$, n = 2, 3 and $[(RSn)_4E_6]$ E = S, Se, Te, decorated with functional aryl substituents (*i.e.* R = $-C_6H_4-CHO$, $-C_6H_4-COOH$, $-C_6H_4-CN$, $-C_6H_4-CH=NR'$) and their usage as linkers for MOMNs.

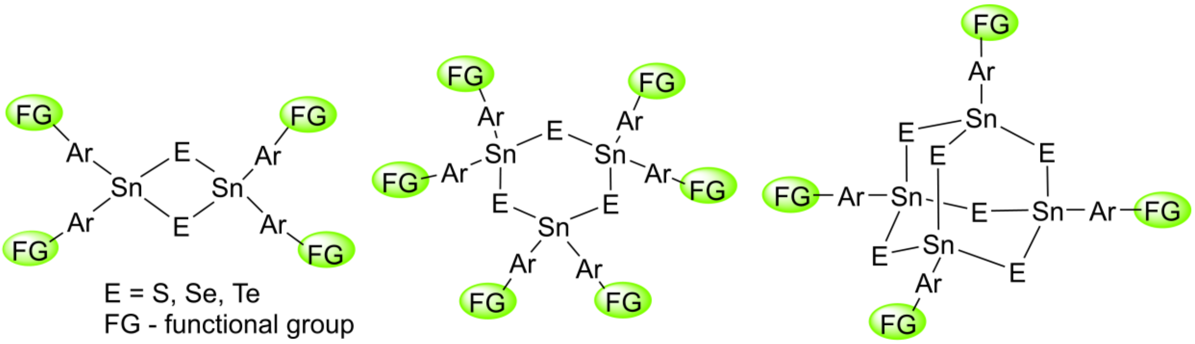

Figure 1. Organotin(IV) chalcogenides target molecules.

References:
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Transformation of silacyclopropenes

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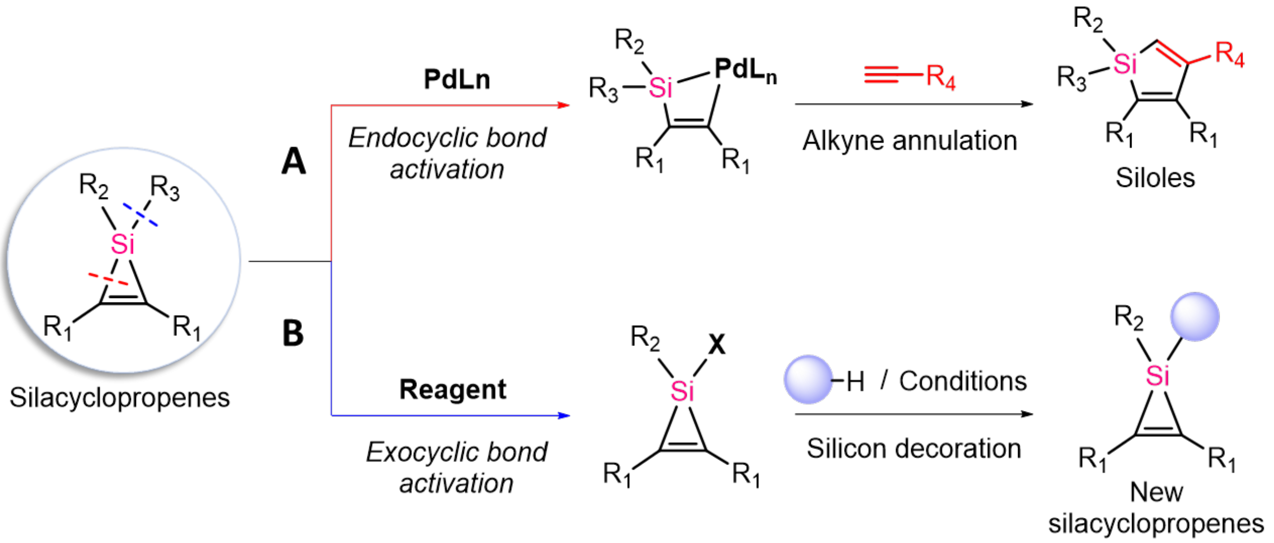
As part of our research program aimed at developing new synthetic methodologies in main-group chemistry, we have been recently focused on the synthetic potential of tight silicon rings as valuable precursors in organic and organometallic chemistry. In particular, we have explored the possibility to address selectively endocyclic and exocyclic Si–C bonds of silacyclopropenes.[1] On one hand, and inspired by seminal findings of Seyferth and others,[2] we have developed a facile route to photochromic siloles based on the 1,2-dithienylethene backbone (Figure, A).[3] The synthesis consists in the annulation reaction of terminal alkynes and proceeds by the activation of endocyclic Si–C bond of a silacyclopropene by palladium(0). On the other hand, we have developed a general strategy to decorate silacyclopropenes by post-functionalization of the ring by activation of exocyclic Si–C bonds (Figure, B). The results obtained in these two directions, including mechanistic studies and limitations, will be discussed.



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Double addition of organoaluminum reagents onto nitriles to access diethynyl carbinamines

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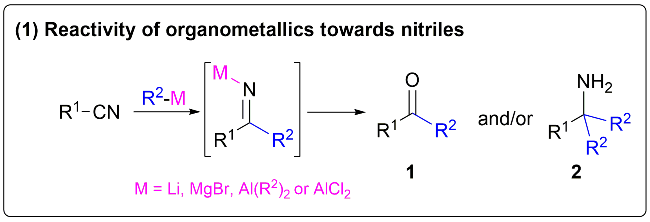
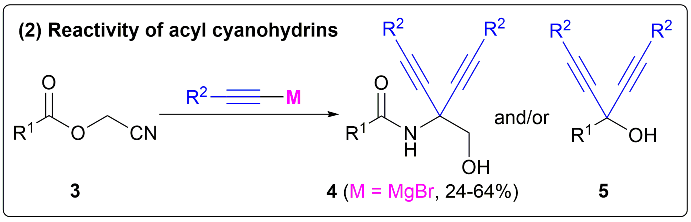
The reactivity of organoaluminum reagents with nitriles has been scarcely studied since the pioneer work of Pasynkiewicz in the 1960s.[1] As for the organomagnesium and organolithium reagents, the addition onto nitriles provides metalated ketimine intermediates which are generally not electrophilic enough to undergo a second addition, and lead to the corresponding ketones **1** after acidic hydrolysis (**eqn 1**). A second addition, leading to tertiary carbinamines **2**, remains possible with organomagnesium or organolithium reagents, by using specific substrates or by adding additives.[2] However, no such double addition reaction of organoaluminum reagents has been reported to date.





Double addition with organoalanes (M = AlMe$_2$)?

Among organoaluminum reagents, dimethylalkynylaluminums have attracted great attention as alkynyl nucleophilic agents (selective alkyne transfer reaction, no β-hydride transfer),[3] and the addition of such reagents onto nitriles was successfully reported by Lee in 2013 to synthesize α,β-alkynyl ketones.[4] As a part of our ongoing research concerning the synthesis of complex tertiary carbinamines by double addition of organometallics onto nitriles,[5] we were interested in the preparation of dialkynyl hydroxyamides structures **4** (**eqn 2**). Unlike other Grignard reagents that added twice onto acyl cyanohydrins **3** to provide the corresponding hydroxyamides in good yields, alkynyl magnesium bromides were less reactive and led to the formation of side-products such as the tertiary alcohol **5** (resulting from the competitive addition onto the ester moiety). In order to overcome this limitation, we explored the reactivity of dimethylalkynylaluminum reagents and we will present in this communication a new and efficient method to build substituted diethynyl carbinamines in mild conditions.

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From Boron to Metals: Unlocking Aza-BODIPYs for Multimodal NIR/PET Imaging

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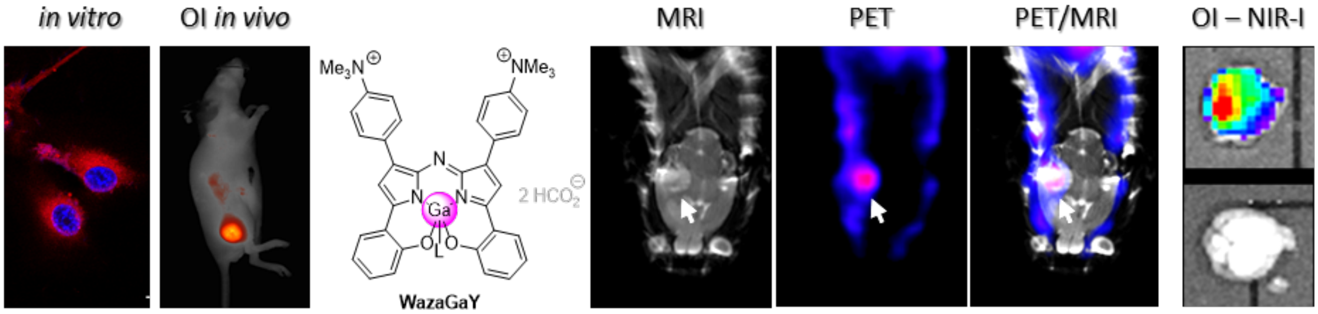
Aza-boron-dipyrromethenes (aza-BODIPYs) are gaining increasing attention as near-infrared (NIR) fluorophores thanks to their straightforward synthesis, high stability, and bright emission. Comparable to rhodamines and cyanines, they are particularly suited for *in vivo* fluorescence imaging and surgical guidance, with some of our recent derivatives even pushing emission into the NIR-II window (1000–1700 nm),[1] offering higher imaging resolution.

So far, most structural engineering has focused on peripheral substituents and extended conjugation, whereas the boron center itself has remained largely unexplored. In this study, we address this gap by replacing boron with different metal centers, giving rise to a new family of aza-Metal-DIPY complexes.[2] Among them, we will highlight a gallium-based derivative that we rendered water-soluble and designed as a bimodal probe for both NIR fluorescence and PET imaging. We will discuss its biodistribution in tumor-bearing mice (U87MG, IGROV1, A375), its successful application in fluorescence-guided surgery,[3] and its potential as a PET tracer through [^{68}Ga] radiolabeling.

Altogether, these findings establish metal-substituted aza-BODIPYs as a versatile platform for next-generation multimodal bioimaging.



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Redox-Active Ligands in Low-Valent Complexes: from formation to reactivity.

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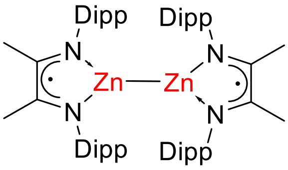
Main-group organometallic compounds featuring a M-M metal-metal bonds are well known in group 13 compounds, particularly in diboranes, which are stable and widely applied in 1,2-diboration reactions.[1] In contrast, since the discovery of Cp*$_2$Zn$_2$,[2] a complex with a strong s Zn–Zn bond in the unusual Zn(I) oxidation state, only a limited number of such Zn(I)-Zn(I) species have been synthesized and characterized, and their applications remain limited. To stabilize such M-M bond in unusual oxidation states, a-diimine ligands are especially effective: owing to their redox non-innocence, they can readily accept or donate one or two electrons, thereby enabling the stabilization of metal centers across multiple oxidation states, including low-valent species.[3]

This communication highlights the role and versatility of redox-active α-diimine (DAD) ligands in the stabilization, formation, and reactivity of a biradical low-valent Zn(I)–Zn(I) complex.[4] Computational studies reveal that the nature of the solvent significantly impacts the stability of these species, which can exist as radical or polar species depending on the oxidation state of the ligand.[5] Furthermore, during the formation of the low-valent complex, the redox-active ligand acts as an electron reservoir, facilitating Zn–Zn bond formation. Finally, the reactivity of the dizinc species toward alkynes is discussed, providing new insights into the role of the ligand.



Low-valent Zn(I)-Zn(I) complex with Redox-Active Ligand

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A Journey from Alkynylalanes to Bioconjugation of Biomolecules

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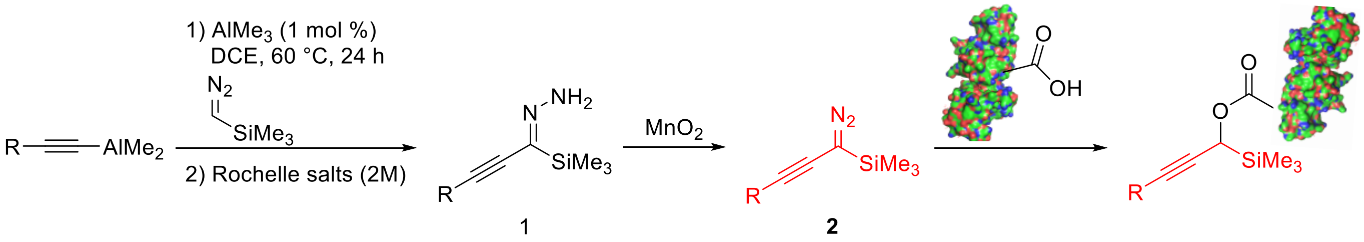
Organoaluminum compounds are an intriguing class of organometallics, characterized by unique selectivity and reactivity arising from the strong Lewis acidity of aluminum and the non-ionic character of the C–Al bond.[1] Within this class, we are particularly interested in studying the reactivity of dimethylalkynylalanes. Traditionally, these compounds are prepared via transmetallation of the corresponding lithium or magnesium derivatives in ethereal solvents.[2] However, this method often reduces their reactivity due to the formation of Lewis acid-base adducts. To overcome this limitation, building on earlier work by Binger[3], a base-catalyzed direct metalation of terminal alkynes has been developed to generate dimethylalkynylalanes in toluene or heptane.[4,5]

$$R{-}{\equiv}{-}H + AlMe_3 \xrightarrow[\text{toluene or heptane}\atop \text{24 h, r.t.}]{NR_3\text{ cat.}} R{-}{\equiv}{-}AlMe_2$$

Since no ethereal solvents are used in this process, the resulting compounds exhibit entirely new reactivity, which we have investigated in our group. Notably, we discovered an unprecedented reaction with trimethylsilyldiazomethane, leading to the formation of hydrazone **1**, a compound that cannot be prepared by other means.[6] This hydrazone serves as a valuable intermediate for synthesizing alkynyldiazosilane **2** via oxidation with MnO_2.

We will demonstrate how this new class of diazo compounds, accessible only through alkynylalanes, can be applied in the bioconjugation of biomolecules.[7]



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Transfer hydrogenation catalysts based on alkaline-earth metals: applications and mechanistic studies

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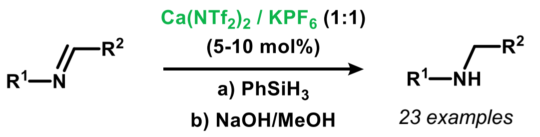
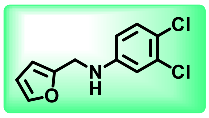
The development of efficient, eco-friendly catalytic systems for organic synthesis is of great importance. This presentation focuses on amine preparation, key building blocks found in natural products, pharmaceuticals, and agrochemicals.[1]

Among the different strategies reported for amine synthesis from readily available precursors via hydrogen transfer processes, the hydrosilylation of imines has emerged as a particularly attractive approach.[1] In this context, a wide range of transition metal-based catalysts have been developed to efficiently promote this transformation.[1]

In this work, we aim to design catalysts based on alkaline-earth metals (Mg, Ca), which are abundant, environmentally benign, and have attracted increasing attention over the past two decades.[2] Here, we show that a simple, readily available, and moisture-stable calcium triflimide catalyst, generated in situ from $Ca(NTf_2)_2$ and KPF_6, efficiently promotes imine hydrosilylation under mild conditions.[3] The corresponding amines are obtained in fair to excellent yields (40–99%), typically at room temperature. To highlight the synthetic potential, a bioactive antifungal molecule was prepared on gram scale in high yield using the green solvent 2-methyltetrahydrofuran.

The reaction mechanism was investigated experimentally and by DFT calculations, supporting an electrophilic activation of the silane by the calcium catalyst.[3] In addition, related Mg and Ca complexes were prepared from sulfonimide ligands with varied electronic and steric properties.[4] Their Lewis acidity was measured using the Gutmann–Beckett method and their catalytic performance evaluated. This study revealed clear relationships between ligand structure and catalytic activity, and provided further insight into the generation of the active species.





gram-scale, 85% yield
bioactive molecule

☑ **commercial precursors**
☑ **mild conditions** (25 °C in most cases)
☑ **no inert atmosphere required**
☑ **easy purification** (no heavy metal contaminant)

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Organoalkali-Catalyzed C–Si Cross-Couplings with *N-tert*-Butyl-*N'*-Silyldiazenes

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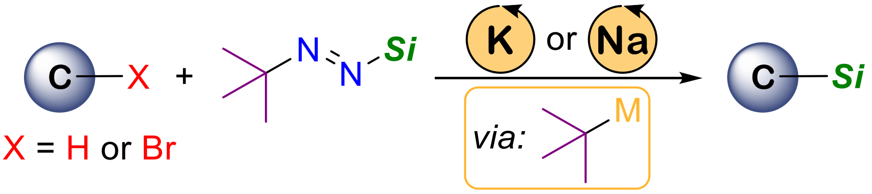
Organosilicon compounds have become indispensable tools in the chemical sciences, as evidenced by their growing applications in organic synthesis, drug discovery, and materials science. Among the conventional methods for C–Si bond formation, cross-coupling reactions provide a particularly versatile route to organosilicon compounds due to the broad range of organic substrates and silylating reagents that can be used.[1] However, many of these methods are limited by the specific nature and/or the amount of promoters required to facilitate the key C–Si bond formation.

This communication will describe the invention and development of a novel C–Si cross-coupling strategy through the design of a new class of silylating reagents, namely silylated *tert*-butyl diazenes (*t*Bu–N═N–SiR_3). The synthetic utility of these reagents will be demonstrated in their ability to rapidly assemble diverse organosilicon compounds *via* silylation of C–H[2] and C–Br[3] bonds upon simple treatment with catalytic amounts of alkali metal alkoxides. Mechanistic considerations highlighting the involvement of alkali metal-stabilized *tert*-butyl carbanion intermediates will be discussed along with their conceptual implications, notably for transposing the stoichiometric metalation chemistry of group 1 polar organometallic reagents (e.g. organolithium compounds) into a catalytic framework.



• General • Catalytic • Transition metal-free • Ambient conditions

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Mg/Li Bimetallic Organomagnesiate Complex as Tools for the Synthesis of Fused (Hetero)aryl Lactones

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Phthalides and derivatives are widespread in biologically active compounds and natural products. These heterocycles can also serve as versatile building blocks for the synthesis of natural and pharmaceutically-important products. Their preparation is widely documented in the literature even though many of their synthetic routes are non-convergent and relied on intramolecular cyclization, requiring relatively complex syntheses of the starting materials in order to bring diversity to the final phthalides. Moreover, fused heteroaryl-lactones (pyridinyland benzothienyl-) are poorly exemplified in the literature. [1,2,3,4]

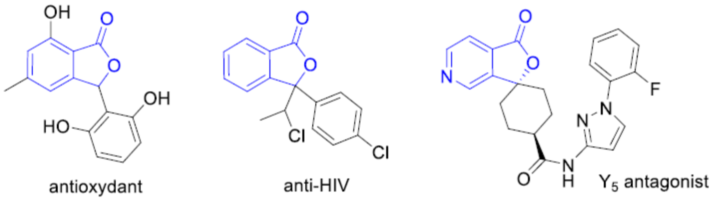

Figure 1. Example of bioactive phthalides and pyridinic analogs.

In the past few years, our laboratory has been focusing on developing chemistry using bimetallic ate complexes composed of a polar organometallic and a "soft" organometallic in metal halogen exchange (MHE) reaction. Based on that expertise, we decided to started a research program with the aim of exploring the reactivity of organomagnesiates for the synthesis of substituted phthalides, azaphthalides and also fused benzothienyl-lactones. Thereby, we showed that BIPHEN or BINOL-based monobutylmagnesiate ((rac)-BIPHENBuMgLi or (rac)-BINOLBuMgLi) can efficiently promote the MHE of easily available 2-iodobenzoate derivatives, followed by the addition of an aldehyde or a ketone, which leads to an intramolecular cyclisation and the formation of a series of new, diversely substituted phthalide derivatives in moderate to good yields. [2,3,4]

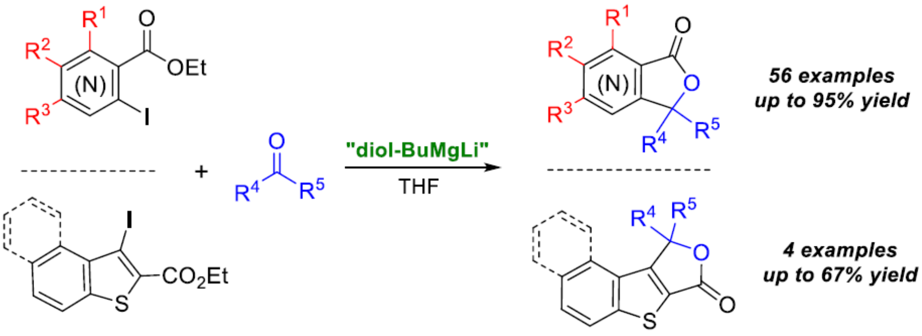

Figure 2. Synthesis of fused (hetero)aryl lactones.

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Diisopropylamine-borane complex : an air and water stable borylating agent

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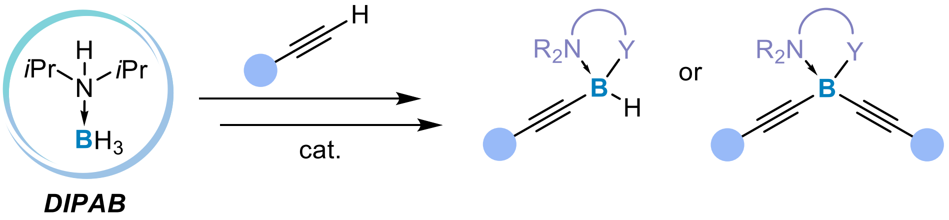
Organoboron compounds, particularly alkynylboranes, are highly valuable synthetic intermediates, yet their preparation remains a significant challenge. Conventional synthetic routes often require air- and moisture-sensitive reagents, limiting their practicality. Catalytic dehydrogenative borylation of terminal alkynes has recently emerged as a powerful and atom-economical alternative.

This talk will present our recent results on a modular strategy for the synthesis of mono- and dialkynylboranes. The first method relies on a magnesium-catalyzed dehydrocoupling of terminal alkynes with the diisopropylamine borane complex (DIPAB) under mild conditions.[1] The second employs diisopropylaminoborane under zinc catalysis.[2] Both approaches allow precise control over reactivity while effectively suppressing undesired hydroboration side reactions. The resulting aminoboranes can then be converted into stable, tetracoordinate boron complexes, thereby broadening their potential applications.



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Strong Zn(II) and Mg(II) Cationic Lewis Acid: Synthesis, Structure, and Reactivity in Catalysis

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Electrophilic Lewis acid metal cations, especially abundant and biocompatible Zn^{2+} and Mg^{2+} dications, stand as reagents of choice for the activation of unsaturated or polar substrates for catalytic applications. *N*-heterocyclic carbene supporting ligands coordinated to the metal center allow for stability through tuned steric protection and/or electronic stabilization thus modulating the reactivity and selectivity of these species in catalysis.[1–3] On the other hand, further enhancement of the Lewis acidity is even possible by accessing “ligand-free” metal cations thanks to the use of chemically inert and weakly coordinating anions[4] such as carborate ions of the type $[R\text{-}CB_{11}Cl_{11}]^-$. In particular, access to unprecedented “pseudo-naked” Zn^{2+} and Mg^{2+} ions is now possible with such anions.[5,6] Experimental studies were combined with classical molecular dynamics simulations and DFT calculations to gain a better understanding of these new species.

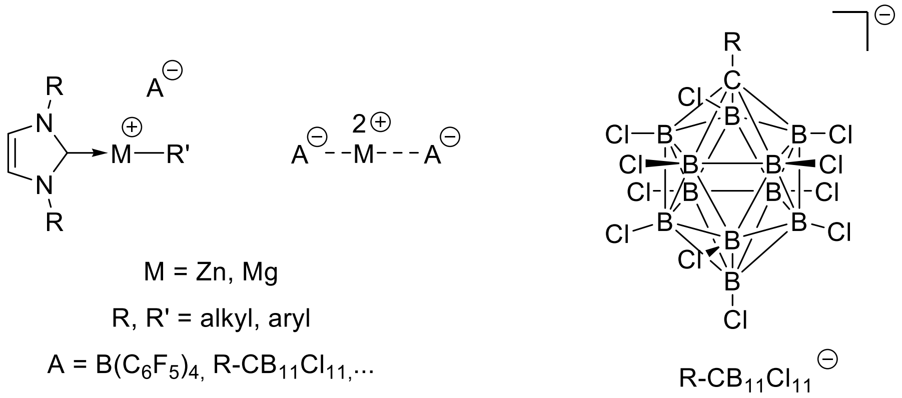

Figure 1. Zn(II) and Mg(II) cations as strong Lewis acids.

These Lewis acid metal cations readily activate alkenes and alkynes for fast catalytic hydrosilylation as well as hydrogenation transfer catalysis at room temperature. Catalytic reduction with silanes was also observed for carbonyl compounds and even for a more challenging substrate, CO_2.

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Tandem Dual C–C Bond Formation Enabled by LiZn-Based Reagents

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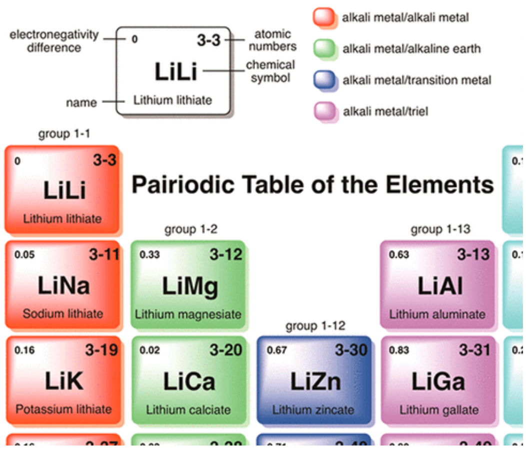
Heterobimetallic complexes have emerged as powerful tools in modern organic synthesis, as the coexistence of two distinct metals within a single molecular framework enables cooperative interactions that generate truly synergistic effects—outcomes greater than the mere sum of their individual contributions.[1] Such heterobimetallic cooperativity between active centers offers new opportunities to achieve regio-, chemo-, and stereoselectivity in organic transformations that remain unattainable with classical monometallic species.[2] It also provides access to divergent reactivity. A representative example is the cooperation between lithium and zinc: the combination of a highly reactive but poorly selective organolithium reagent with a selective but modestly reactive organozinc compound produces a mixed species with enhanced reactivity and selectivity.[3] The synergistic cooperation between the two metals is driven by the existence of a recently computationally characterized heterobimetallic bond, which may be preserved during reaction processes.[4] This type of synergistic interplay illustrates the “PAIRiodic Table” concept,[2] where unique heterobimetallic entities are envisioned as new chemical elements (*e.g.*, the ‘LiZn’ element) in their own right. In this communication, we demonstrate how LiZn-based reagents can orchestrate tandem dual C–C bond formation in benzyl derivatives at sites separated by five atoms with perfect regio- and chemoselectivity.[5] Furthermore, a LiZn element–promoted divergent process that regioselectively forms two C–C bonds five atoms apart in a single reaction vessel, through an electron-count–controlled approach, is presented using a thenyl derivative as a model substrate.[6]

Excerpt from the PAIRiodic table of the elements



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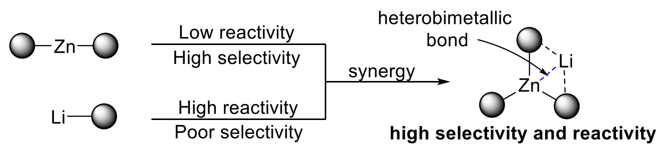
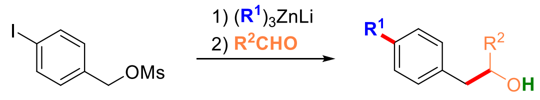
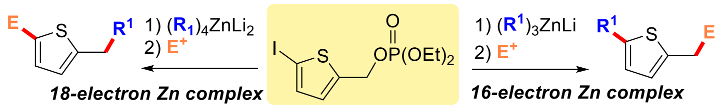
Synthesis and comparative properties of a LI–Zn-based Reagent in relation to R□Znand RLi



Synthetic applications: Tandem dual C-C bpnd formation



Electron-count-controlled regiodivergent strategy for dual C–C bond formation



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Flash Presentations

FP-1 NMR Study of Organolithium Reactivity in Deep Eutectic Solvents – Teddy POTEZ

FP-2 Ansa-effects in octaphenylmetallocenophanes of the alkaline earth metals – Amal BOUAMMALI

FP-3 Self-assembled molecular networks for molecular rectifiers – Sélène CASTANET

FP-4 Hypervalent Organopnictogen(III) Cations – Alex TOMUTA

FP-5 Bis(phenoxy-amidine) (FAlen)-Zn Complexes for the Cycloaddition of CO2 to Epoxide and the Ring-Opening Polymerization of Lactide – Thu-Van NGUYEN

FP-6 Investigating Mixed Aggregates of Dimethylphenylsilyllithium, Dimethylphenylsilanoxide, and Lithium Chloride in THF: A Comprehensive NMR {^{1}H, 6,7Li, 29Si} Study – Fida IBRAHIM

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FP-11 N,C,N-Polypyridinic Bismuth(I) Complexes as Two-Electron Donor Ligands in Cobalt Coordination Chemistry – Raffaele FONTANA

NMR Study of Organolithium Reactivity in Deep Eutectic Solvents

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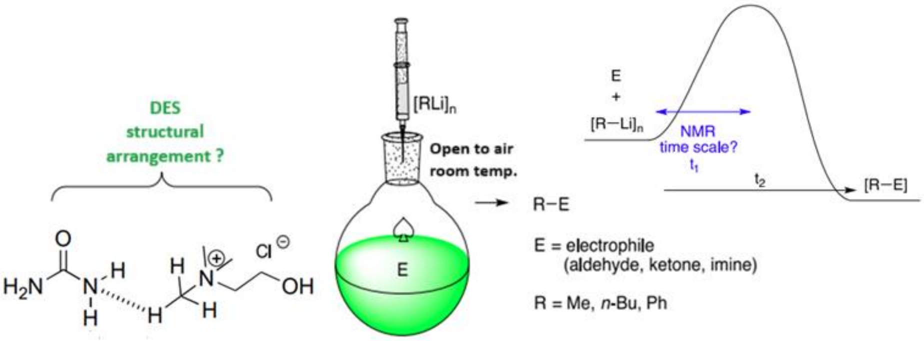
Recent groundbreaking discoveries have revealed that organometallic reagents of group I and II (R-M, M= Li, Na, MgX) can be effectively employed as nucleophiles in unconventional media such as protic eutectic mixtures[1] or even water,[2] under batch conditions, at room temperature, and in the presence of air. Our research focuses on exploring the structure-reactivity relationships of highly polar organolithium compounds and elucidating the molecular-scale mechanisms that govern their behavior in these unconventional reaction environments, particularly in deep eutectic solvents (DES). A key aspect of this work involves addressing several open questions concerning the unique role of water and DES in these transformations. For instance: under what conditions can water act as an effective polar ligand? Can "coordinated" water or DES promote enhanced reactivity compared to traditional ethereal solvents? Moreover, considering the intrinsic self-associative nature of DES through hydrogen bonding networks, how might this property influence the aggregation state of alkyllithium reagents and help preserve their intrinsic reactivity? To answer these questions, NMR spectroscopy represents an ideal analytical tool. NMR has already proven valuable for probing the supramolecular structure of DES,[3] and for assessing the effects of lithium salt addition in such media.[4] In this communication, we present a comprehensive multinuclear magnetic resonance investigation (^{1}H, ^{7}Li, ^{13}C, ^{15}N), both in solution and using high resolution magic angle spinning (HRMAS) techniques. Our goal is to gain deeper insights into the structural and dynamic features of DES at room temperature, as well as to unravel the nature of the interactions between alkyllithium compounds and these novel solvents.



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Ansa-effects in octaphenylmetallocenophanes of the alkaline earth metals

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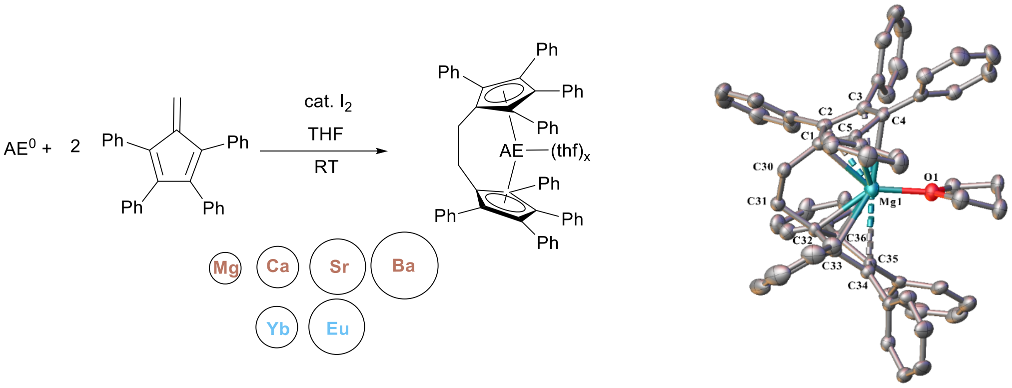
Ansa-complexes or metallocenophanes, i.e. organometallic complexes which have two cyclopentadienyl-type ligands connected via a carbon or heteroatom bridge of various length, have found numerous applications in catalysis, polymerization reactions and medicinal chemistry.[1-3] Compared to their non-bridged analogues, such *ansa*-complexes can have different stability and provide better reactivity or selectivity, often referred to as *ansa*-effect.[4] Among various synthetic pathways, reductive dimerization of fulvene-type molecules is a straightforward approach based on low-valent metal precursors.[3]
We herein report on the synthesis of a full series of ethylene-bridged group 2 metal octaphenylmetallocenes (Mg to Ba) via reductive dimerization of 1,2,3,4-tetraphenylfulvene and their characterization by single-crystal X-ray diffraction (Scheme 1). Their structural features, especially ring-slippage, will be compared to the corresponding lanthanide analogues[5] and also to the non-bridged octaphenyl-sandwich complexes in order to provide some insights into the *ansa*-effects.[6] The Ca *ansa*-complex has also been successfully employed in the transmetallation reaction with $FeCl_2$ to provide a new bent ferrocenophane.[7]



Scheme 1. Synthesis and structure of new *ansa*-octaphenylmetallocenes of the alkaline-earth metals.

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Self-assembled molecular networks for molecular rectifiers

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One of the key challenges in organic electronics is controlling current flow at the molecular level. Molecular rectifiers are necessary components to achieve this. One way to obtain efficient molecular rectifiers is using a bottom-up approach via self-assembled monolayers (SAMs) [1]. However, traditional SAMs face limitations in reproducibility, molecular organization, and tunability of donor-acceptor properties, which hinder their performance and integration into next-generation electronics [2].

To overcome these limitations, we have recently developed novel molecular dyads capable of forming ordered assemblies on graphene-like substrates. Held together by non-covalent interactions, these dyads enable facile mixing and matching of components, resulting in a highly tunable system [3].

In this work we will present a second generation of molecular pedestals based on indium and aluminium phthalocyanine (Pc) derivatives, which will enable us to control the self-assembly on a graphene/ HOPG substrate. Here the metal is key to control the off-plane assembly via the axial ligand. The synthesis and characterization of these novel pedestals will be presented.

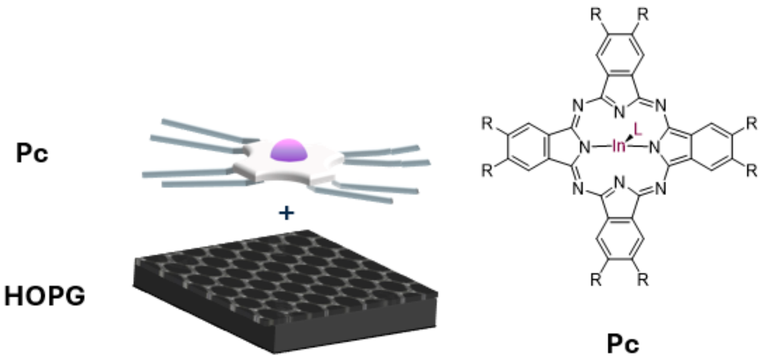

Figure 1 Phthalocyanine molecular pedestal for Self-Assembled Molecular Networks

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Hypervalent Organopnictogen(III) Cations

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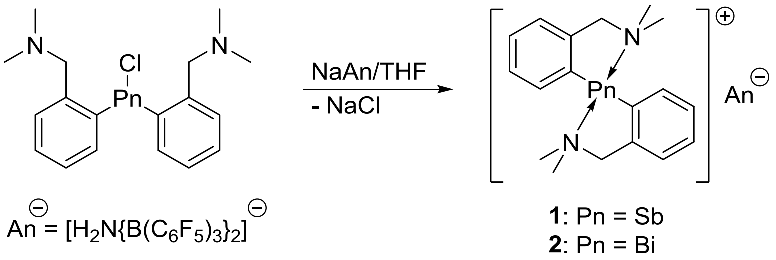
Cationic organometallic species of antimony(III) and bismuth(III) have attracted significant interest thanks to their utility as Lewis acids[1] or as components of frustrated Lewis pairs in organic catalysis.[2] Antimony(III) cationic complexes bearing cyclopentadienyl ligands have been demonstrated to exhibit pronounced Lewis acidity,[3] with some applied as catalysts in the dimerization of 1,1-diphenylethene.[4] These complexes, however, are typically air- and moisture-sensitive, and their synthesis, purification, and application can be challenging. Hypervalent bismuth(III) cations supported by tridentate (*C*,*E*,*C*) ligands (E = S,[5] RN[6]) and paired with weakly coordinating anions such as OTf^- or $[B(C_6F_5)_4]^-$ have been employed in aqueous media as catalysts for the Mannich reaction. Perfluorinated arylboron species are particularly effective as weakly coordinating anions. In the solid state, anions such as $[B(C_6F_5)_4]^-$ and $[H_2N\{B(C_6F_5)_3\}_2]^-$ exhibit little, if any, interaction with organopnictogen cations, while in solution, coordination is essentially absent.[7] This feature enables the Lewis acidic center to remain accessible in solution, thereby circumventing the decoordination step that commonly initiates the catalytic cycle. In this context, we describe the synthesis of two salts (**1** and **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 $[H_2N\{B(C_6F_5)_3\}_2]^-$amido-diborate anion. The reactions (**Scheme 1**) were carried out using the corresponding diarylpnictogen(III) monochlorides and the sodium salt of the counterion.



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

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

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Bis(phenoxy-amidine) (FAlen)-Zn Complexes for the Cycloaddition of CO_2 to Epoxide and the Ring-Opening Polymerization of Lactide

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Our group has recently developed a new variant of the bis(phenoxy-imine) (salen) 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 the catalysts compared with salen complexes. In this study, we have described the coordination chemistry of four bis(phenoxy-amidine) (FAlen) ligands with Zinc and evaluated their catalytic performances in two different reactions: cycloaddition of CO_2 to epoxide and the ring-opening polymerization (ROP) of *rac*-lactide [2]. The coordination chemistry was done by the addition of $ZnEt_2$ to the ligands, resulting in C2 symmetrical complexes in solution. Catalytic tests showed their comparable activities to Salen-Zn complexes in cycloaddition of CO_2 to epoxide under solvent-free condition. These FAlen-Zn complexes also showed outstanding performance in the ROP of *rac*-lactide under mild conditions, delivering high molecular-weight polylactide with excellent control whereas the similar Salen-Zn complex exhibited no activity.

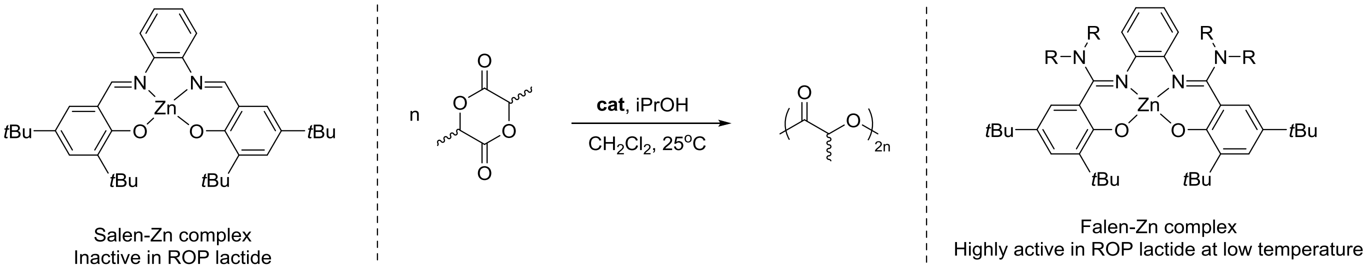

Figure 1: Ring-opening polymerization of rac-lactide catalyzed by FAlen-Zn and Salen-Zn

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Investigating Mixed Aggregates of Dimethylphenylsilyllithium, Dimethylphenylsilanoxide, and Lithium Chloride in THF: A Comprehensive NMR {^{1}H, ^{6,7}Li, ^{29}Si} Study

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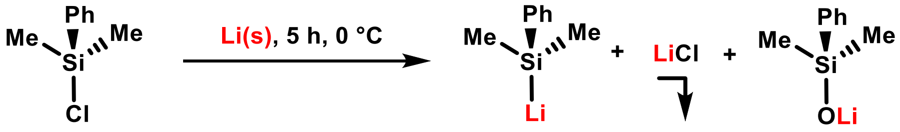
Dimethyphenylsilyllithium ($Me_2PhSiLi$) is a key organometallic reagent widely employed in carbon-carbon and carbon-heteroatom coupling reactions, as well as in deprotonation processes. It is typically synthesized by reacting dimethylphenylsilyl chloride with metallic lithium (Scheme 1).[1] Despite its significance in synthetic chemistry, the aggregation behavior of $Me_2PhSiLi$ in solution is not well understood, particularly in the presence of common by-products such as lithium chloride (LiCl) and dimethylphenylsilanoxide ($Me_2PhSiOLi$), which can influence reactivity [2] and selectivity.[3]

In this study, we employed multinuclear NMR {^{1}H, ^{6,7}Li, ^{29}Si} spectroscopy to investigate the aggregation, solvation, and structural organization of $Me_2PhSiLi$ in THF-d_8 at -78°C, in the presence of LiCl and $Me_2PhSiOLi$. Our findings provide new insights into the mixed aggregation phenomena of $Me_2PhSiLi$ under synthetically relevant conditions, offering a better understanding of their influence on reactivity.



Scheme 1

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Bulky allyls for heavier alkaline-earth chemistry

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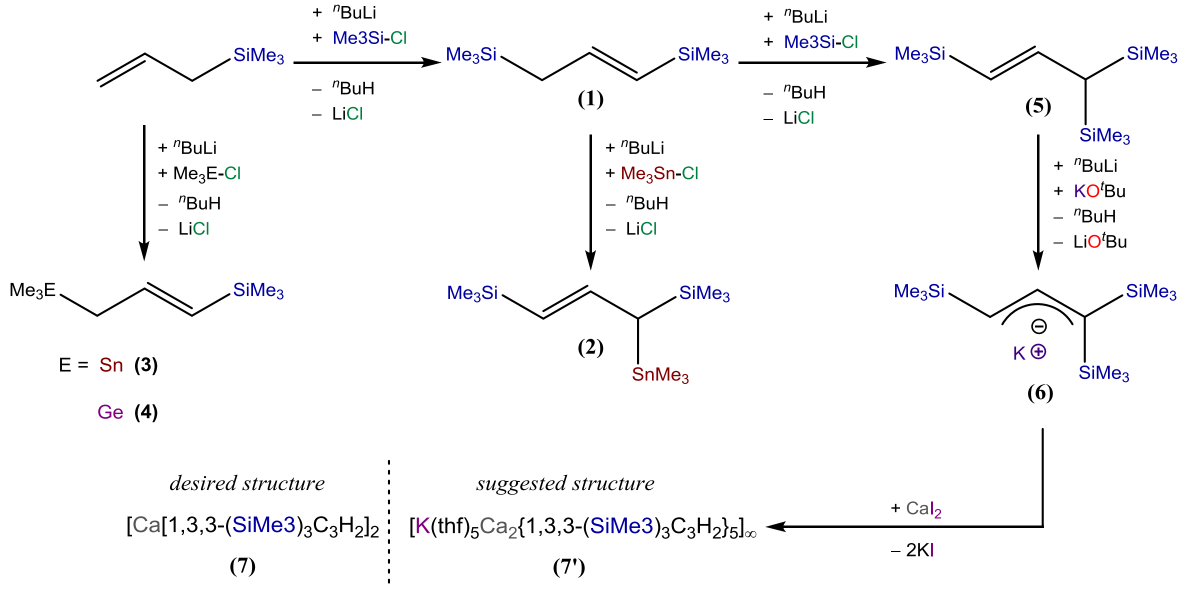
Alkaline-earth organometallic chemistry has received significant attention in recent years, driving interest in the development of structurally diverse species and their implementation in molecular catalysis.[1] While magnesium compounds have been studied thoroughly, gaps in the chemistry of heavier alkaline-earth complexes with Ca,[2] Sr [3] and Ba [4] have only recently begun to be addressed in literature. In particular, allyl complexes containing silyl moieties have proved useful in synthetic main group organometllic chemistry, due to their unique bonding, solubility and stabilization proprieties.[5]

To gain further insight in the use of these allyls and their applications in alkaline-earth chemistry, this study showcases the successful synthesis of five silylated proligands, including three novel compounds that contain germanium or tin substituents, and a new potassium salt. All compounds were obtained in good yields with optimised and reproducible protocols. Structural identification was achieved by multinuclear NMR spectroscopy, with additional characterization by FTIR and elemental analysis. Attempts were made to synthesize the corresponding calcium complex from the potassium precursor. Spectroscopic and EDS analytical data suggest the possible formation of a polymeric mixed-metal species rather than a discrete complex. Single crystals suitable for X-ray diffraction have yet to be obtained for the potassium and calcium species.



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Toward new diorganoantimonides: isolation of new azastibocine hydride and distibane

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Although the chemistry of diorganoantimonides began in the middle of last century,[1] and started to develop in the early years of this century,[2-3] the field remains underdeveloped. The literature describes three principal synthetic approaches for accessing antimonides: (a) reduction of a triorganoantimony compound with lithium,[1] (b) hydride formation followed by hydrogen substitution,[4] and (c) distibane formation followed by alkali-metal insertion.[5] In the present study, an organoantimony(III) bromide (**1**) bearing the rigid C,N,C-pincer ligand [^{i}PrN($CH_2C_6H_4$)$_2$] was selected as the starting material based on the rigidity of the framework.[6] The corresponding hydride **2** was obtained from compound **1**, as illustrated in *Figure 1*, via reduction with either $LiAlH_4$ or K-selectride at low temperature. Reductions employing active metals led to variable outcomes: sodium reduction afforded metallic antimony, whereas magnesium reduction yielded the distibane **3**. Compound **4** remains elusive even after attempts of reduction with strong reducing agents like KC_8 or potassium naphthalenide used in high excess.
Compounds **2** and **3** have been characterized by ^{1}H and ^{13}C NMR spectroscopy. The solid-state structure of compound **3** was determined using single-crystal X-ray diffraction.

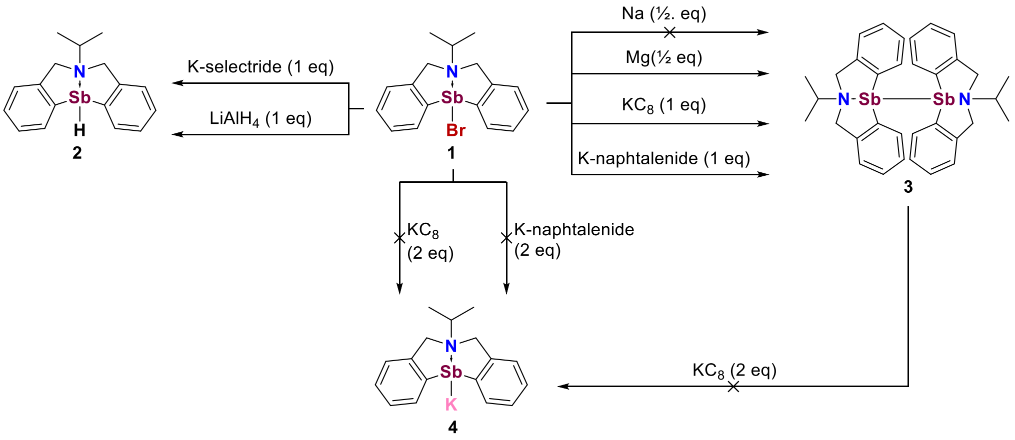

Figure 1*: Synthetic pathways for azastibocine reduction.*

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A new dilithiated initiator for anionic continuous flow polymerization of telechelic polymyrcene oligomers

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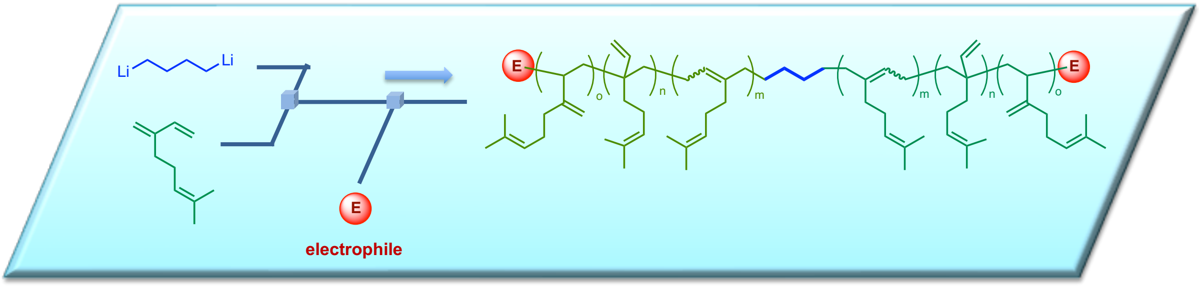

To meet the expectation of an environmentally responsible chemical industry, bio-based polymers are crucial to replace plastics materials [1] often derived from oil, natural gas or coal. With this in mind, telechelic polymers are important structures, they can give access to larger polymers thanks to the functional groups present, improve shelf life or facilitate chain degradation [2]. We already know that continuous flow is mainly used in organic chemistry [3] but it gave an interest in polymerization the two last decades [4-6]. Indeed, that offer many advantages notably length or polydispersity control and classic advantages like exothermicity control and safety reactions [6]. The aim here is to use flow chemistry to achieve polymerization control and a high functionalization degree, via a bio-based monomer (myrcene) and a new dilithiated initiator [7], thanks to microflow reactors. This results in a bidirectional oligomer in the first reactor, which will then react with an electrophile in another reactor to give our telechelic oligomer.

Use the following notation for references.[1]

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Lewis-base Activation of Grignard Reagents for Enantioselective Catalysis and Continuous Flow Process

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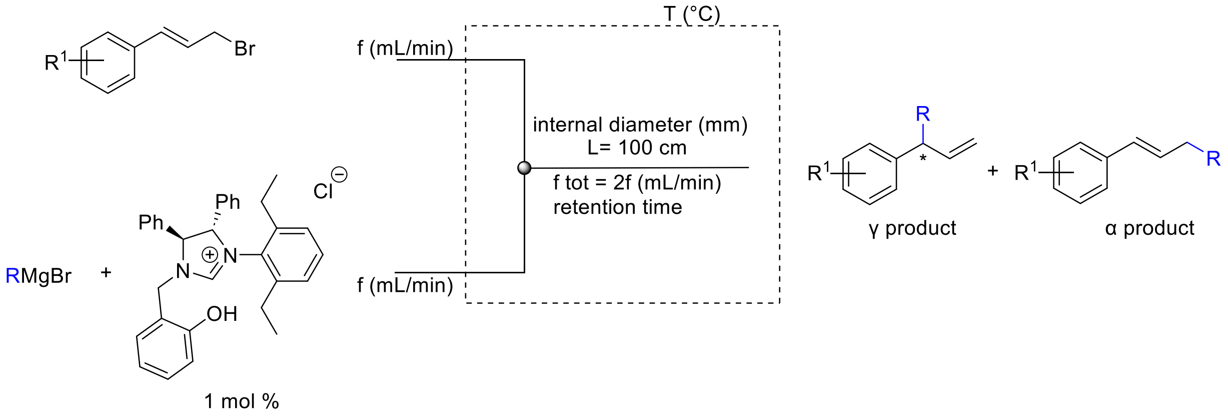
The stereoselective formation of C-C bonds using Grignard and dialkylzinc reagents has been largely developed, particularly in the context of allylic substitution reactions. Traditionally, these transformations require the use of transition-metal catalysts. However, over the past fifteen years, an alternative strategy based on Lewis-base activation of Grignard reagents by *N*-heterocyclic carbenes (NHCs) has emerged, enabling such reactions to proceed under transition-metal-free conditions with good to excellent regio- and enantioselectivities.[1-2]

In this context, we aim to adapt this Lewis base activation strategy to continuous flow chemistry, both in homogeneous and heterogeneous systems, with the goal of improving catalytic performance in enantioselective allylic substitutions. To achieve this, a small library of chiral NHC ligands was synthesized to study the parameters influencing selectivity. So far, the results show improved regioselectivity, comparable enantiomeric excesses while the reactions proceed under milder conditions.



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N,C,N-Polypyridinic Bismuth(I) Complexes as Two-Electron Donor Ligands in Cobalt Coordination Chemistry

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Group 15 compounds of the type RM (R = monoanionic ligand; M = P, As, Sb, Bi), commonly referred to as pnictinidenes, are electron-rich species featuring two lone pairs, making them attractive ligands for transition-metal coordination.[1] While phosphinidenes and arsinidenes are well established, the heavier congeners, particularly bismuthinidenes, have remained challenging to isolate due to their intrinsic instability. In the last decade stable bismuth(I) compounds become accessible, primarily using rigid N,C,N pincer-type ligands.[2] These scaffolds not only stabilize the low-valent bismuth center via intramolecular coordination of pendant imine donors but also benefit from additional aromatic stabilization through the formation bismazole frameworks. To this date, all isolable bismuth(I) species have relied on stabilization by imine donors, carbene ligands, or transition metals, and systematic studies of their coordination chemistry remain scarce.[3]

Herein, we report the synthesis and characterization of a novel family of bismuth(I) complexes bearing N,C,N-polypyridinic ligands, and their coordination behavior toward cobalt (Figure 1), highlighting the ability of these bismuth(I) species to function as two-electron donor ligands.

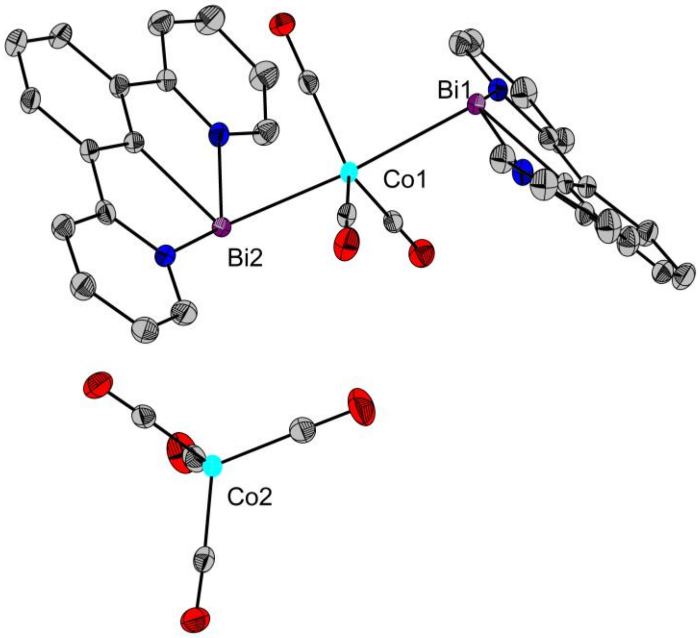

Figure 1. Molecular structure of $[\{2,6\text{-}(2'\text{-Py})C_6H_3Bi\}_2Co(CO)_3][Co(CO)_4]$.

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