





Ph.D. position available on 1st October 2025

Synthetic applications of low-valent dizinc(I) complexes

PhD direction: Pr Fabrice Chemla, Pr Franck Ferreira

Place : Institut Parisien de Chimie Moléculaire – Tour 32-42 – Sorbonne Université – 5 place Jussieu – 75005 Paris – France

Key-words : low valent zinc complexes, 1,2-dimetallations, 1,1-dizincio compounds, carbenes

Research context and General objectives

The opportunity to achieve multiple-functionalizations of organic substrates in a single synthetic process (one-pot), is a major endeavor of modern synthesis, as it fosters step-economical sequences.^[1] For this purpose, dimetallation reactions are particularly attractive since they allow for the simultaneous introduction of two organometallic bonds that can then be functionalized sequentially.

Our team has a longstanding interest in **1,1-** and **1,2-bimetallic species** and their applications in synthesis.^[2] We have for instance recently disclosed^[3] an efficient and simple way to prepare out of the glovebox biradical complexes **1**,^[4] bearing an unusual Zn–Zn bond in which each zinc atom is formally at the uncommon (+I) oxidation state. These complexes show a good thermal stability and solubility and were fully characterized by EPR spectroscopy; conditions to achieve the **1,2-dizincation of various alkynes** bearing electron-withdrawing functional groups were also developed :



Specific Research Objectives

The PhD work aims at developing strategies to prepare elusive 1,2-dizincio reagents by examining **the reactivity of bimetallic dizinc(I) complexes such as 1 with activated alkenes**. Using this methodology, **several bimetallic structures of interest** such as 3-zincated enolates and allyl or allyl(vinyl) dizincs will be readily accessible :



In a second part of the work, **insertion of diazo compounds or carbenoids into the Zn–Zn bond of Zn(I) bimetallic complexes** will be considered. This approach will allow the preparation of 1,1-disubstituted 1,1-dizincio compounds which represents a big challenge,^[5] as the corresponding usual diiodo precursors are extremely difficult to prepare:









In both parts of the Ph.D. work, the performance of the 1,2- or 1,2-dizincio compounds obtained by this approach will be evaluated as substrates for double stepwise cross-coupling sequences. Exploiting our experience particular interest will be dedicated to the possibility of designing an efficient enantioselective access to α -substituted benzylketones by a two-step one pot enantioconvergent palladium-catalyzed sequential arylation–acylation coupling of 1,1-dizincio compounds :



Desired skills : Training in organic and organometallic chemistry with an interest in methodology and multistep synthesis.

Start: 1st October 2025.

To apply : Candidates applying for a doctoral position must **first submit their application file**. The FULLY COMPLETED application must be sent electronically to the Director of the Doctoral School (ED) <u>cyril.ollivier@sorbonne-universite.fr</u>, to the secretariat of the ED <u>ED406-Secretariat@sorbonne-universite.fr</u> and to the thesis supervisors (see below), together with MENDATORILY :

• The fully filled information sheet (available here),

- A very detailed CV highlighting the applicant's strong points,
- The transcripts of marks from the M1 (S1 and S2) and M2 (S3) Master's courses and/or the Engineering School,
- Most recent diplomas,
- One or two recommendation letters, one of which must be from the person who supervised the Master's (M1 and, if possible, M2) or Engineering School internship,
- An intention letter (motivations for doing a thesis and motivations for the thesis topic).

The deadline for the electronic submission of applications is 30 April 2025, 12.00. <u>THE APPLICATION MUST</u> <u>BE COMPLETE TO BE CONSIDERED</u>.

All informations can also be found on the Ecole Doctorale ED406 website here.

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¹ Eppe, G.; Didier, D.; Marek, I. <u>*Chem. Rev.* **2015**, *115*, 9175</u>.

² a) Banchini, F.; Leroux, B.; Le Gall, E.; Presset, M.; Jackowski, O.; Chemla, F. Perez-Luna, A., <u>*ChemCatChem*</u>, **2024**, *16*, <u>e202301495</u>; b) Leroux, B.; Beaufils, A.; Banchini, F.; Jackowski, O.; Perez-Luna, A.; Chemla, F.; Presset, M.; Le Gall, E. <u>Beilstein J. Org. Chem.</u> **2024**, *20*, 2834</u>; c) Banchini, F.; Leroux, B.; Le Gall, E.; Presset, M.; Jackowski, O.; Chemla, F.; Perez-Luna, A. <u>Chem. Eur. J. **2023**, *29*, e202301084</u>.

³ Mikael Le Roch, Synthèse et réactivité de complexes bimétalliques de Zn(I) : étude théorique et expérimentale. Ph.D thesis, defended on 18 novembre 2024, Sorbonne Université, under the supervision of Dr. S. Halbert and Pr. F. Chemla. ⁴ Liu, Y.; Li, S.; Yang, X.-J.; Yang, P.; Gao, J.; Xia, Y.; Wu, B. <u>Organometallics **2009**</u>, *28*, 5270</u>; Zhang, R.; Wang, Y.; Zhao, Y.; Redshaw, C.; Fedushkin, I. L.; Wu, B.; Yang, X.-J. <u>Dalton Trans</u>. **2021**, *50*, 13634.

⁵ Seyferth, D.; Lambert, R. L. <u>J. Organomet. Chem. **1973**, 54, 123</u>.