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Team Synthèse et Catalyse Organique, Organométallique et Rédox (SCORE)

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PhD position in electrochemical synthesis and catalysis-ANR Grant

MANIAC – MANGanese-catalyzed Intermolecular Alkene Carbofunctionalization

Position details: Fully funded PhD position for 3 years in organic synthesis/catalysis/electrochemistry under the supervision of Dr. J. Vantourout and Dr. M. Médebielle, in the team SCORE (ICBMS, Lyon 1). Open to applicants from all nationalities. Starting date: October 2023.

Scientific context: Decades of improvement in the cross-coupling arena have provided a highly modular toolkit for bond construction in organic synthesis.¹ In addition, the introduction of an alkene as a third component has recently emerged as a viable catalytic strategy to quickly enhancing molecular complexity.² Indeed, in these transformations, two carbogenic partners are distributed across the C=C bond, resulting in 1,2-dicarbofunctionalization offering strategic advantages in synthesis. However, several interrelated challenges such as the nature of starting materials and catalysts as well as the selectivity control still limit the impact such methodologies could afford.³

Project goals: This research proposal aims to develop unprecedented alkene 1,2-dicarbofunctionalization strategies with ubiquitous starting materials using manganese catalysis. Conceptually, every oxidation state will be meticulously controlled to achieve the desired reactivity. The success of this project will require the efficient trapping of a key radical intermediate issued from the addition of a carbonyl to a non-conjugated alkene. Two innovative strategies are envisioned: (i) reaction with an electron deficient heterocycle under Minisci conditions or (ii) radical rebound onto a Mn(III)-Ar complex obtained after oxidative addition of an aryl halide with a Mn(I) complex. The latter will be synthesized from the unprecedented mild reduction of a bench stable Mn(II) catalyst. All mechanistic events will be precisely controlled using electrochemistry. Targeting these new concepts will enable highly attractive transformations and constitute not only a breakthrough in the fields of olefin functionalization but also in the field of manganese catalysis and paired-electrolysis processes.



This project will be carried out using a multi-disciplinary approach involving electrochemical reaction development, catalyst design, organometallic synthesis and mechanistic studies.

Candidate: The applicant should hold a master degree in organic/molecular chemistry and be able to demonstrate a strong interest in all aspects of catalysis. Enthusiasm, autonomy, scientific curiosity and ability to communicate are required qualities. A previous experience in organometallic catalysis and/or electrochemistry would be appreciated but not mandatory. Interested applicants should send a cover letter (1 page), CV, M2 grade sheets and contact details of referents to julien.vantourout@univ-lyon1.fr and maurice.medebielle@univ-lyon1.fr.

References:

[1] Metal Catalyzed Cross-Coupling Reactions and More; De Meijere, A., Brase, S., Oestreich, M., Eds.; Wiley-VCH: Weinheim, Germany, **2014**.

[2] Derosa, J.; Tran, V. T.; van der Puyl, V. A.; Engle, K. M. Carbon-Carbon π -Bonds as Conjunctive Reagents in Cross-Coupling. *Aldrichimica Acta*, **2018**, *51*, 21–32.

[3] Derosa, J.; Apolinar, O.; Kang, T.; Tran, V. T.; Engle, K. M. Recent developments in nickel-catalyzed intermolecular dicarbofunctionalization of alkenes. *Chem. Sci.* **2020**, *11*, 4287–4296.