PhD position in organometallic chemistry – *Institut des Sciences Chimiques de Rennes*

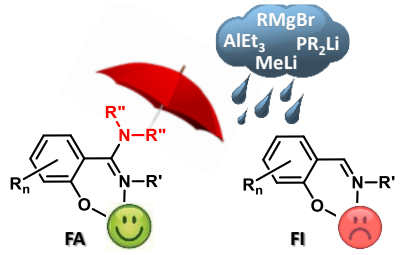
Group 2, 3 and 4 Metal Complexes for Olefin Polymerisation and Hydrophosphination Catalysis

Research topic

Our team in Rennes, France, is composed of 4 permanent researchers as well as 8-10 PhD students and post-doctoral research assistants. We specialise in the design of original organometallic complexes based on oxophilic metals and in their utilisation as molecular catalysts for atom-efficient reactions to produce polymers and fine chemicals. We work in close collaboration with several research groups in and beyond France, and with major industrial partners (Total Energies, Arkema, Bostik, Triskem Int.).

We are seeking to recruit a highly motivated PhD student, starting in between October, 1st 2022 and January, 6th 2023, to pursue our existing program with the oxophilic metals of groups 2 (Ca-Sr-Ba), 3 (Sc-Y) and 4 (Ti-Zr-Hf) (see representative references below). The range of potential applications in homogenous catalysis is virtually boundless. The multidisciplinary project proposed here consists in exploring specific aspects of the synthetic organometallic chemistry of groups 2-4 metals, with a view to producing competent molecular catalysts that will in a second stage be used in olefin polymerisation and hydrophosphination catalysis.

Phenoxyimines (FI) and Salen are ubiquitous ligands that are widely used, particularly in organometallic catalysis, with various industrial applications. However, one inherent drawback of their structure is the presence of electrophilic imine(s), which can react and cause a deleterious drop in catalytic performance. The project aims at developing a related class of FI and Salen ligands, where the imine function will be replaced by a trisubstituted amidine giving rise to new phenoxy-amidine ligands (FA). The amidine moiety should provide higher stability and electron-donating ability making FA ligands particularly well suited for stabilising highly reactive cationic or neutral metal species. FA group 4 metal complexes will be targeted for the production of ultra-high molecular weight polyethylene and for the stereoselective polymerisation of propylene. The σ- and π-donor ability of FA ligands should also contribute to enhance the thermal stability of the catalytic species and thus allow to maintain high reaction rates when more drastic reaction conditions (temperature, pressure) are required. The project aims also at developing FA-based catalysts for hydrophosphination reaction from early transition metals or even the large alkaline earths Ca-Ba. Special attention will be paid to promote asymmetric catalytic hydrophosphination using chiral FA



Phenoxy-amidine (FA) and related Phenoxy-imine (FI) ligands

early metal complexes. FA ligands are expected to be more suitable than FI for this reaction, which otherwise can undergo intramolecular hydrophosphination.

The PhD program will be carried out under the guidance of Prof. JF Carpentier, Dr. E. Kirillov and Dr. Y Sarazin at ISCR in Rennes. The ANR-funded project will be carried out in close collaboration with our partners at ICMUB (Prof. P. Le Gendre and coll., Dijon, France). The experimental work will primarily be conducted in Rennes, but a 6-month mobility to Dijon will also be planned in the course of the PhD to learn about enantioselective hydrophosphination catalysis, phosphine chemistry and ligand design.

Representative references from the group in these research fields

1) *Chem. Sci.* **2021**, *12*, 7098-7114, DOI: 10.1039/D1SC00436K
2) *Angew. Chem. Int. Ed.* **2020**, *59*, 9120-9126. DOI: 10.1002/anie.202001439
3) *Macromolecules*, **2020**, *53*, 8847-8857. DOI: 10.1021/acs.macromol.0c01671
4) *Organometallics* **2019**, *38*, 2664-2673. DOI: 10.1021/acs.organomet.9b00253

About the applicant

Profile: To apply, you must hold an MSc degree (or equivalent diploma) in organometallic chemistry and/or catalysis. The applicant must be able to carry out bibliographic studies and deliver oral and written presentation of the results, and must have team spirit while also being able to carry out his/her work independently in the laboratory. The successful applicant must have a good command of the English language. Previous experience in the handling of air-sensitive compounds and a keen flair for synthetic organometallic chemistry will be an advantage.

Skills and competences: Over the course of the 36-month project, the PhD student will acquire skills in organometallic synthesis under inert atmosphere, chemistry of highly electropositive metals, homogeneous catalysis science, polymer chemistry and analytical tools (multinuclear NMR, FTIR, X-ray diffraction crystallography, gel permeation chromatography, GC chromatography, MALDI-ToF mass spectrometry etc.) for the characterisation of molecular and macromolecular compounds.

ADDITIONAL INFORMATIONS

Hosting team: Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, Université de Rennes 1, Campus de Beaulieu – Team OMC « Organometallics: Materials and Catalysis »

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To apply, please send an up-to-date CV, a cover letter, your MSc transcripts, and the contact details of at least two people who will be asked for reference letters.

Deadline for applications: 2022, October 14th

Expected starting date: Between 2022, October 1st and 2023 January, 6th.

Funding: ANR-funded PhD scholarship (36 months), gross salary: 1866 € per calendar month.