Ecole Doctorale des Sciences Chimiques ED250

Contrats Doctoraux **2016**

Title :

Theoretical Study on the Ligand-Metal Interaction : Effects on the Reactivity.

Department : Institut des Sciences Moléculaires de Marseille

iSm2, UMR-CNRS-7313

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Team : CTOM

Supervisor : Prof. Stéphane Humbel

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Position : 3-years scholarship available from October 2016 (gross salary: about 1680 euros/month)

Deadline : 20 may 2016 – deadline for sending the candidature to the ED250 (Doctoral School)
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The candidate must contact the supervisor or the co-supervisor before this date for a pre-selection.
31 may 2016 – Interview at the ED250 (Doctoral School)

Project :

The aim of this work is studying the interaction between a metal and an organic molecule (the substrate). The coordination of an alkene or an alkyne to a metal center deeply modifies their nature:[1,2] donation and back-donation (according to the Dewar-Chatt-Duncanson model)[3] cause major changes on the substrate electronic structure, which have a strong impact on the reactivity. This is clear, for instance, in the cycloaddition reactions catalysed by gold, where the coordinated alkyne undergoes a nucleophilic attack, according to a regio-selectivity due to the substituents on the alkyne.[4] Several metal complexes (9-11 group) shall be studied from a computational point of view, in order to quantify factors that impact the activation of double and triple bonds (notably for insertion or cycloisomerization reactions): the role of the ancillary ligands, the role of the substrate substituents, metal type, enantioselectivity.[5] Particular attention will be addressed to the analysis of the nature of the interactions.

These theoretical studies will allow the PhD student to learn a large panel of computational methods, ab-initio and DFT, and to manipulate several computing codes (for instance: Gaussian, TURBOMOLE, Molpro).

Context :

This project continues recent efforts that have been made in our group on the catalytic activity analysis of metal complexes, within established collaborations with the experimentalists of our department.[6,7]

Beside those applications in theoretical chemistry, our group is involved in some method development projects. An access to this expertise is therefore open.

References :

1. P. Nava *et al.*, *ChemCatChem* **2015,** 7, 3791.
2. P. Nava *et al.*, *ChemCatChem* **2014**, 6, 500-507.
3. P. Nava, D. Hagebaum-Reignier, S. Humbel, *ChemPhysChem* **2012**, 13, 2090-2096.