



PhD Proposal 2017

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Collaboration with other partner during this PhD:	
In France:	In China:

Title: New Phosphorous Based Ligands for Organometallic Catalysis: a Combined Theoretical and Experimental Approach
Scientific field: CHEMISTRY: Computational chemistry; Organometallic chemistry
Key words: Ab-initio, simulation, ligand effect.

Details for the subject:

The design of new organometallic species that have unprecedented properties is a challenge for a chemist. The structural and catalytic properties of a complex are obviously related to the metal centre, but they are strongly determined by the nature of the ancillary ligands: those can lead to chemodivergent reactions,⁽¹⁾ and have an impact on stereo- and, more specifically, enatio-selectivities.⁽²⁾

This project aims to predict, analyse and test new kinds of ligands, notably phosphorous based, in connection to metals of the 8-10 groups. Those ligands may incorporate cage structures and possess peculiar acid-base properties, as the Verkade's superbase.⁴⁻⁶ They will be employed to improve some known reactivities, such as gold-catalysed cycloisomerizations. The comprehension of their influence on the metal centre will help to conceive catalytically

active complexes for the first or the second transition line, which are particularly appealing, since more economical than Ir, Pt or Au.

Theoretical studies will be prior and associated to the experimental work. Those allow for a fine understanding of the properties of the complexes and can be used for prediction purposes. A computational ladder of donating and back-donating features will be constructed to compare new to already tested ligands.⁽³⁾ All experimental results (structural properties, spectra, catalytic activity) will be rationalized in terms of quantum mechanical calculations. Modern theoretical methods will be employed and the student will employ several packages of computational chemistry.

This project is addressed to a candidate who would like to combine theoretical and experimental approaches, thus achieving a double expertise.

References:

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- 4) P. Dimitrov Raytchev, A. Martinez, H. Gornitzka, J.-P. Dutasta, J.-P. *J. Am. Chem. Soc.*, **2011**, 133, 2157.
- 5) B. Chatelet, V. Dufaud, E. Jeanneau, H. Gornitzka, J.-P. Dutasta, A. Martinez *J. Am. Chem. Soc.*, **2013**, 135, 18659.
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