

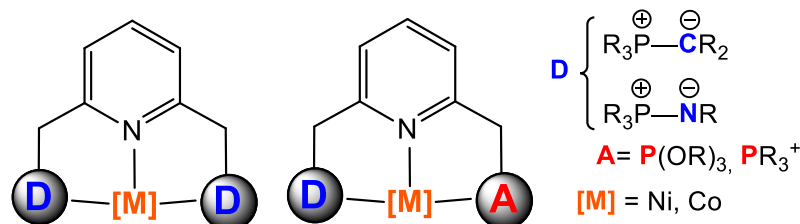
Earth abundant metals and electron rich ligands for catalysis and optics

Keywords: Synthesis, Coordination chemistry, iminophosphorane, base metals, catalysis, optics

Supervision : Dr. Audrey Auffrant audrey.auffrant@polytechnique.edu

Most of homogeneous catalytic processes used at the industrial level rely on rare and expensive metals (Pd, Rh, Ir, Pt) so that those metals will become even rarer and more expensive in the coming decades. This is all the more true as these noble metals are also widely employed in the production of photoactive smart material and optoelectronic devices. Developing alternatives to such metals (Pd^{II}, Pt^{II}, Ru^{II} or Rh^I), commonly referred to as noble metals, is therefore highly desirable. Nevertheless, achieving comparable performances with non-noble metals generally requires an important ligand design. In the past few years electron rich ligands and especially those incorporating N-heterocyclic carbenes (NHC) appeared highly promising for both green catalysis¹ and photophysically active compounds.²

Given our expertise in the development of iminophosphorane ligands, featuring a negatively charged nitrogen atom stabilized by a positively charged phosphorus center, that are more σ -donating ligands than NHCs,³ we wish to prepare iminophosphorane based complexes to develop sustainable catalysts and propose cheaper compounds for photophysics.



We will focus on pincer tridentate ligands associating either two strong electron donors (phosphonium ylide (P=C) and their nitrogen analogue (P=N)) or combining iminophosphorane with an electron poor phosphorus-based function. The goal is to synthesize such ligands and prepare their nickel and cobalt complexes (see above). The latter will be used for catalytic test reactions such as hydrosilylation. Moreover, their photophysical properties will be studied. This will allow theoretical collaborators to identify the energy states and deactivation channels in those complexes.

Techniques used : coordination chemistry under inert atmosphere; GC or NMR monitoring for catalytic reactions; characterizations by multinuclear NMR, X-ray diffraction, UV spectroscopy.

¹ a) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, 510, 485-496 [link](#); b) E. Peris, *Chem. Rev.* **2018**, 118, 9988-10031. [link](#)

² a) T. Duchanois, L. Liu, M. Pastore, A. Monari, C. Cebrian, Y. Trolez, M. Darari, K. Magra, A. Frances-Monerris, E. Domenichini, M. Beley, X. Assfeld, S. Haacke, P. C. Gros, *Inorganics* **2018**, 6, 1-26 [link](#); b) A. Frances-Monerris, P. C. Gros, M. Pastore, X. Assfeld, A. Monari, *Theor. Chem. Acc.* **2019**, 138:86. [link](#)

³ a) T. P. A. Cao, S. Labouille, A. Auffrant, Y. Jean, X. F. Le Goff, P. Le Floch, *Dalton Trans.* **2011**, 40, 10029-10037 [link](#); b) T. P. A. Cao, A. Buchar, X. F. Le Goff, A. Auffrant, C. K. Williams, *Inorg. Chem.* **2012**, 51, 2157-2169. [link](#); c) T. P. A. Cao, G. Nocton, L. Ricard, X. F. Le Goff, A. Auffrant, *Angew. Chem. Int. Ed.* **2014**, 53, 1368-1372.