

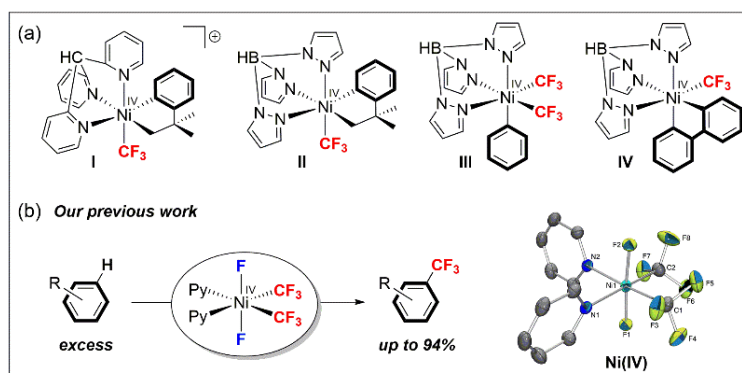


PhD position starting from January 2020

Mastering the Chemistry of Fluorinated Ni^{III,IV} Organometallics.

The biological properties of organic synthons are severely impacted by the introduction of fluorine atoms, especially when located on arene rings.¹ Among the most common perfluorinated groups, the CF₃ moiety occupies a preferential place, these organofluorine compounds possessing multiple applications in pharmaceutical and agrochemical industry, as well as material science.¹ Unfortunately, the lack of efficient methods for installing the CF₃-group in one strategic position impedes further advance in drug discovery. Creating C–CF₃ bond *via* cross-coupling reactions (C.C.R.) is an appealing strategy. However, Ar–CF₃ bond formation *via* reductive elimination (R.E.) from [Ar–M–CF₃] fragments represents a challenging task. An original approach to favor the key R.E. step resides in the preparation of high-valent organometallics. In this sense, Sanford reported the isolation of Ni^{IV}CF₃ complexes **I-IV** that were found to be good precursors in C.C.R., including the aromatic trifluoromethylation (**Figure 1a**).² In addition to the CF₃-groups, in all the cases reported by Sanford the Ni^{IV} complex is stabilized by strong N-donor tricoordinated ligands to the Ni-center in *fac*-fashion.²

In a radically different approach, our group has described the isolation of coupling-competent Ni^{IV}CF₃ species that are exclusively stabilized by simple monodentate ligands (Py, fluoride and the CF₃-group, **Figure 1b**).³ Analogous Ni^{III}CF₃ materials were achieved in selective fashion as well.⁴ The simplicity of our Ni^{III,IV}-platforms in terms of ligand requirements represents a unique entry to explore



the chemistry of Ni^{III} and Ni^{IV} species, which remains scarcely investigated owing to the lack of appropriate precursors. Our expectations for this PhD project dealing with Ni^{III,IV} species are manifold and include: *i*) the synthesis of novel high-valent organometallics bearing perfluorinated groups (F-itself and the CF₃ moiety) to be engaged in C.C.R.; *ii*) their use as organometallic synthons in coordination chemistry; *iii*) the study of elementary processes at unusually high oxidation states at Ni; and *iv*) the unravelling of the mechanistic pathways for trifluoromethylation reactions involving Ni^{III}CF₃ and Ni^{IV}CF₃ intermediates.

Within the frame of the PhD studies, the candidate will acquire the necessary tools in handling highly reactive species (vacuum line and glove-box skills), ligand design, organic and organometallic synthesis, and multiple techniques of analysis and reaction monitoring (NMR, EPR, GC-MS, XRD, React-IR). Mechanistic studies will be carried out combining experimental and theoretical means (NMR, XRD, IR, DFT,...). The candidate should be very enthusiastic and autonomous, and have good knowledge in organometallic chemistry. Interested candidates may send their resume via email (with contact information of two references).

Keywords: Ni^{III,IV} chemistry, coordination chemistry, fluorinated organometallics, trifluoromethylation, fluorine chemistry, cross-coupling reactions, mechanistic investigations.

[1] (a) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881-1886; (b) O. A. Tomashenko, V. V. Grushin, *Chem. Rev.* **2011**, *111*, 4475-4521; (c) T. Furuya, A. S. Kamlet, T. Ritter, *Nature* **2011**, *473*, 470-477.

[2] (a) N. M. Camasso, M. S. Sanford, *Science* **2015**, *347*, 1218-1220; (b) J. R. Bour, N. M. Camasso, M. S. Sanford, *J. Am. Chem. Soc.* **2015**, *137*, 8034-8037; (c) E. A. Meucci, N. M. Camasso, M. S. Sanford, *Organometallics* **2017**, *36*, 247-250; (d) N. M. Camasso, A. J. Canty, A. Ariafard, M. S. Sanford, *Organometallics* **2017**, *36*, 4382-4393.

[3] F. D'Accrisio, P. Borja, N. Saffon-Merceron, M. Fustier-Boutignon, N. Mézailles, N. Nebra, *Angew. Chem. Int. Ed.* **2017**, *56*, 12898-12902.

[4] F. D'Accrisio, G. Nocton, P. Borja, N. Saffon-Merceron, M. Fustier-Boutignon, N. Mézailles, N. Nebra, *in preparation*.