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N-Heterocyclic Carbene based Rh and Rh/ZnO nanoparticles for H/D exchange reactions

Period	6 months beginning not later than: ☐ January ☐ February ☐ March ☐ April ☐ May ☐ June ☐ July ☒ September 2021
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Location	135 Avenue de Rangueil, 31077 Toulouse-France
This research master's degree research project could be followed by a PhD	☒ YES ☐ NO

Abstract / work package / illustration & legend

Over the last years, Hydrogen Isotope Exchange reactions (HIE) has gained great importance due to the wide use of deuterated compounds. These products may be used for mechanistic reaction studies, as standards for liquid and gas chromatography, as well as promising drugs.[1] Importantly, HIE reactions can be achieved through one-step C-H bond activation processes. Although this reaction has been catalyzed by homogeneous transition metal complexes (Ir, Ru, Rh, Pd o Pt), and some heterogeneous systems (Pd, Pt and Ru, supported on carbon), metal nanoparticles (MNPs) have emerged recently as promising catalysts for this reaction.[2] This is thanks to the unique properties provided by these systems in catalysis such as high surface/volume ratio, separation and recyclability, as well as control of reactivity and selectivity of the process by adding proper stabilizers and/or doping the surface with another metal (bimetallic NPs). In this sense, N-Heterocyclic Carbene (NHC) ligands have emerged as an important class of ligands due to their outstanding stereoelectronic properties, allowing their application as NP stabilizers.[3] In the last years, our research group has reported different MNPs as catalysts for HIE reactions through C-H bond activation in different heteroaromatic compounds (nitrogen-based molecules, amino acids, etc.). We have worked in different systems for this process: Ru, RuPt, Ni; Ni/NiO NPs among others.[2] Despite their great advantages, the high reactivity of Ru, for example, towards aromatic rings is one of their greatest drawbacks, giving undesirable reduced side products.[4] On the other hand, Rh complexes have been explored in C-H activation reactions in homogenous fashion. Nevertheless, to the best of our knowledge, there is no report about RhNPs as catalysts for this reaction. However, it is well known that RhNPs present similar activities compared with Ru NP regarding reduction process.[5] To avoid these side effects, bimetallic systems capable of diluting this high reactivity are required. In this project we proposed to the applicant to carry out the synthesis and full characterization of Rh and Rh/ZnO NPs stabilized by NHC ligands to study their application as catalysts for HIE reactions through C-H bond activation of different nitrogen-based molecules (pyridines, amino acids, anilines, among others).

References:

1. Leeuwen, P. W. N. M. Van; Claver, C. *Recent Advances in Nanoparticle Catalysis*; Springer, 2020.
2. Lepron, M.; et al. *Acc. Chem. Res.* **2020**, *54,* 1465.
3. Zhukhovitskiy, A. V.; MacLeod, M. J.; Johnson, J. A. *Chem. Rev.* **2015**, *115*, 11503.
4. Bouzouita, D.; et al. *Nanoscale* **2019**, *11*, 16544.
5. Castelbou, J. L.; et al. *ChemCatChem* **2014**, *6*, 3160.

Keywords, areas of expertise	HIE, Nanoparticles, N-Heterocyclic Carbene (NHC) ligands, Rhodium, C-H bond activation.
Required skills for the internship	Knowledge in organometallic chemistry, NHC ligands, catalysis and synthesis and characterization of metallic nanoparticles.