

Abstract

Phosphorus chemistry is a very broad field with a great range of applications. The goals of this Ph.D. thesis are related to different aspects of low-valent phosphorus chemistry: going from the synthesis of fluorophosphine ligands through a “green” and innovative pathway, to the activation and functionalization of elemental white phosphorus in the presence of late transition metals, and, finally, to the not yet explored synthesis of ruthenium phosphide nanoparticles starting from white phosphorus.

In Chapter 1, different points related to the phosphorus chemistry are mentioned. The opening section reports a general description of the element phosphorus and its allotropic modifications before taking into detailed consideration the reactivity of white phosphorus, emphasizing on the production of organophosphorus compounds through catalytic processes involving the activation of P_4 mediated by transition metal complexes. The second section depicts a brief introduction about the importance of phosphine ligands in catalysis, particularly giving attention to the role of fluorophosphine ligands. Finally, the last section deals with the synthesis of metal phosphides nanoparticles, which are of great interest on diverse fields, particularly in catalysis, aiming at P_4 -derived metal phosphide nanoparticles.

Chapter 2 describes the study of the transformation of phosphorous oxyacids, such as $PhPO(OH)H$, H_3PO_3 , H_3PO_2 , into the corresponding fluorophosphines mediated by $[CpRu(PPh_3)_2Cl]$ under mild reaction conditions using a soft deoxyfluorinating agent, commercially available as XtalFluor-E. The reaction is selective, proceeds with high yields and

can be extended to a wide range of phosphorous oxyacids once coordinated to the ruthenium fragment $\{\text{CpRu}(\text{PPh}_3)_2\}^+$ as their hydroxyphosphine tautomer. Deoxyfluorination of phenylphosphinic acid was also mediated by $[\text{Cp}^{\text{R}}\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$, where Cp^{R} : $\text{Cp} = \text{C}_5\text{H}_5$, $\text{Cp}^* = \text{C}_5\text{Me}_5$, and $\{\eta^6\text{-}(p\text{-cymene})\text{Ru}(\mu\text{-Cl})\text{Cl}\}_2$.

On chapter 3, the coordination chemistry of white phosphorus towards a 16 electron ruthenium organometallic complex $[\text{Cp}^*\text{RuPCy}_3\text{X}]$, where $\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$ is described. The different electronegativity and steric bulk in the series of halogens changes the reactivity with white phosphorus. Migration of the halogen from ruthenium to the P_4 moiety was observed, in the case of chloride and bromide, obtaining bimetallic complexes bearing unexpected P_4X_2 ($\text{X} = \text{Cl}, \text{Br}$) moiety as bridging ligands. In the case of iodide, a completely different structure is proposed, containing the not yet previously reported P_4I ligand as a bridging moiety between two $\text{Ru}(\text{II})$ centers.

Chapter 4 deals with the synthesis and characterization of ruthenium phosphide nanoparticles using white phosphorus as P-source. The novelty introduced is the use of white phosphorus as phosphorus source to react with previously prepared ruthenium nanoparticles. A preliminary catalytic study on hydrogenation of phenylacetylene under mild conditions shows very good catalytic activity and selectivity towards the fully hydrogenated product, ethylbenzene.