

Title: **Organometallic chemistry with phosphines presenting unconventional coordination modes**

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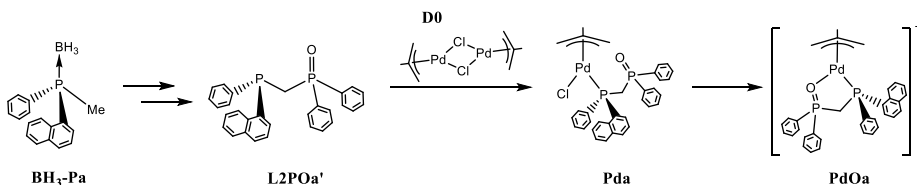
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In this work, two differentiated blocks about the synthesis of complexes containing phosphine ligands presenting unconventional coordination modes are described.

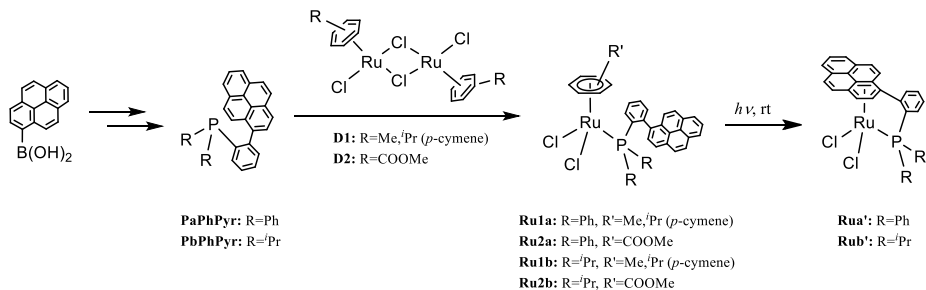
Following and adapting methods from literature, chelated palladium(II) complexes with general formula $[\text{Pd}(\eta^3\text{-2-methylallyl})(\text{P}^*\text{RR}'\text{CH}_2\text{POR}_2\text{-}\kappa^2\text{P}^*,\text{O})](\text{PF}_6)$ were synthesized. Starting from $\text{BH}_3\text{-Pa}$, a *P*-stereogenic phosphine, chiral mono-oxidized diphosphine ligands were prepared and subsequently coordinated to Pd(II) centres by the splitting of a dimer complex of Pd(II), **D0**, resulting in two isomers of **Pda**. The corresponding chelated complexes were obtained from **Pda**, using halide scavengers to force the $\text{P}^*\text{P}(\text{O})$ ligand to act as a bidentate, resulting in a five-membered ring metalocyclic cationic complexes, **PdOa**, which also presented two isomers.



Scheme 1. Sequence for the obtention of the chelated Pd(II) complexes.

The synthesized ligands and complexes were characterized by ^{31}P , $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR.

In the second part, the synthesis of four ruthenium complexes with general formula $[\text{RuCl}_2(\eta^6\text{-arene})(\text{P}(\text{PhPyr})\text{R}_2)]$ and their derived two tethered complexes are described. 1-pyrenyl boronic acid was used as starting material to synthesize two phosphine ligands, **PaPhPyr** and **PbPhPyr**, which were coordinated to ruthenium centres by the splitting of two different metallic precursors, **D1** and **D2**, obtaining **Ru1a**, **Ru2a**, **Ru1b** and **Ru2b**. Later, the corresponding tethered complexes were prepared under mild conditions by means of photochemical processes when they were just exposed to light of a common office lamp at room temperature, obtaining **Rua'** and **Rub'**.



Scheme 2. Sequence for the obtention of the Ru complexes and the corresponding tethered ones.

The ligands and the complexes were characterized by ³¹P, ³¹P {¹H}, ¹H, ¹³C and ¹³C-¹H gHSQC NMR, EA and HRMS, and also by XRD when it was possible.

Keywords: Chiral diposphines, palladium complexes, palladium metallocycles, phosphine oxides, pyrenyl phosphines, ruthenium complexes, tethered complexes, organometallics, bioorganometallic chemistry.