

## Asymmetric synthesis using chiral-at-metal complexes as catalysts – Underpinning molecular understanding through diffraction & NMR spectroscopy

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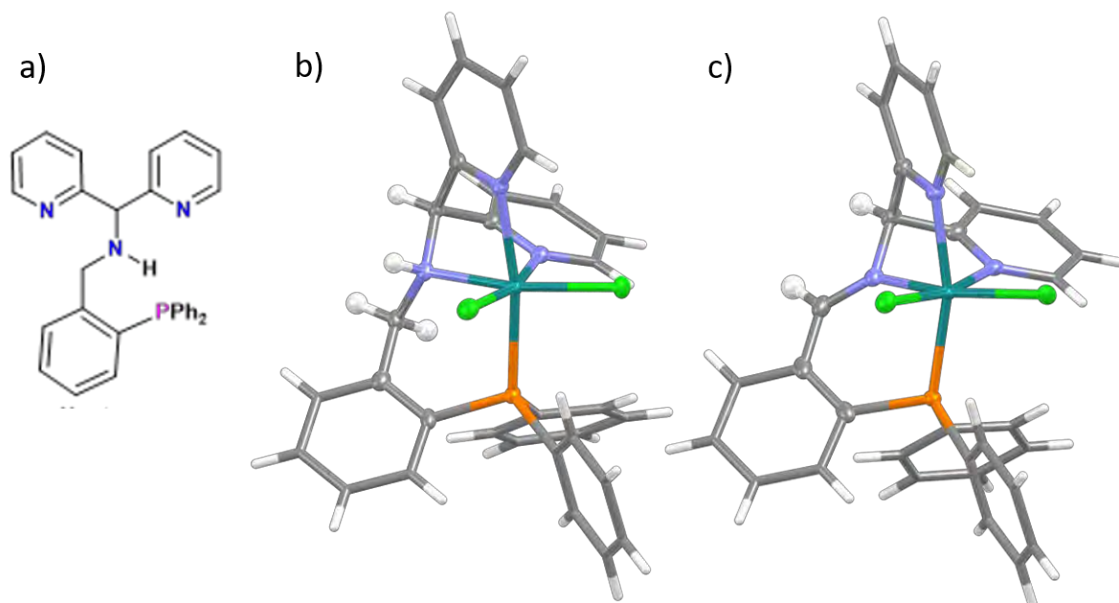
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Chiral metal complexes, an important tool in asymmetric synthesis, are constituted by the assemblies of ligands around a central metal atom, with the stereogenic element(s) located in the ligand and/or, less frequently, in the metal. The asymmetric induction is usually achieved by the coordination of the reagents to the metal atom. Our research group envisages a new approach in asymmetric catalysis, using the metal as the unique source of chirality.

In this context, the challenging control of the absolute configuration of chiral-at metal complexes has been efficiently achieved using tripodal tetradentate ligand LH (Fig. 1a). [1-3]. We have developed a synthetic route for the preparation of octahedral Ru(II) and Ru(III) complexes, bearing LH through a  $\kappa^4$ -*P,N,N',C* coordination model, where the relative configuration of the  $sp^3$  nitrogen atom becomes predetermined by the configuration at the metal. In this communication we present the combined structural characterization of the cationic Ru(III) amido complex  $[\text{RuCl}_2(\kappa^4\text{-P,N,N',C-LH})]^+$  and the neutral Ru(II) imido compound  $[\text{RuCl}_2(\kappa^4\text{-P,N,N',C-L})]$ , depicted in Fig. 1b and 1c, respectively, through diffraction and NMR spectroscopies. The differences in catalytic performance of Ru(II) and Ru(III) species in dehydrogenation reactions have been rationalized from the structural information.



**Figure 1.** a) Tetradentate ligand LH b) Molecular structure of monocationic Ru(III) amido complex c) molecular structure of neutral Ru(II) imido complex.

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