

Searching for Catalytic Enantioselectivity using Metal Complexes with Non-Chiral Ligands. A New Approach with Metals as Unique Stereogenic Centers

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The efficiency of chiral metal catalysts hinges on design. Traditionally, chiral transition metal catalysts have relied on chiral ligands. A more recent approach positions the metal itself as the primary source of chirality. In this strategy, the metal cation is the exclusive stereogenic element, potentially surrounded by achiral ligands. Our research group is exploring this particular novel approach in asymmetric catalysis, using the metal as the unique source of chirality. The structural simplicity coupled with the smart design of the chiral pocket makes these chiral-at-metal catalysts hold great potential for expanding the scope of chiral catalysis and its implementation in asymmetric synthesis.

The main challenge in chiral-at-metal catalysts lies in achieving robust stability at the stereogenic metal center in the presence of labile coordination sites that are essential for substrate activation. Only a few stable chiral-at-metal catalysts with labile coordination sites are known. Most are based on octahedral geometry complexes with d^6 transition metals and robust bidentate ligands that prevent racemization at the stereogenic metal center by ligand dissociation. In this context, the challenging control of the absolute configuration of chiral-ONLY-at metal complexes has been efficiently achieved using tripodal tetradentate non-symmetric ligands [1-3]. We have developed a synthetic route for the preparation of octahedral Rh(III), Ru(II) and Ru(III) complexes, bearing stereochemically restricted ligands bonded through a κ^4 - P,N,N',C , κ^4 - P,N,O,C or κ^4 - P,N,N',N'' coordination modes, where the relative configuration of the sp^3 nitrogen atom becomes predetermined by the configuration at the metal. Some preliminary catalytic results will also be discussed.

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[2] Téllez, J., Méndez, I., Viguri, F., Rodríguez, R., Lahoz F.J., García-Orduña, P., Carmona D. (2018). *Organomet.*, **37**, 3450.

[3] Tejero, A. G., Carmona M., Rodríguez R., Viguri F., Lahoz F.J., García-Orduña, P., Carmona D. (2022). *RSC Adv.*, **12**, 34704.