

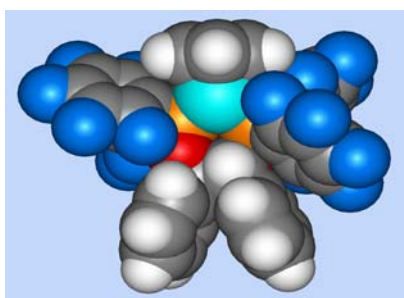
Advances in Transition Metal Lewis Acid - Mediated and – Catalyzed Reactions

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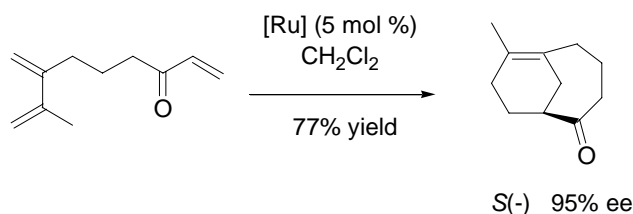
New powerful applications in asymmetric synthesis and catalysis have put half-sandwich complexes of the type MCpL_n and M(arene)L_n into the limelight. Efficient synthetic access and new ligands are instrumental to further development and new applications. This lecture will focus



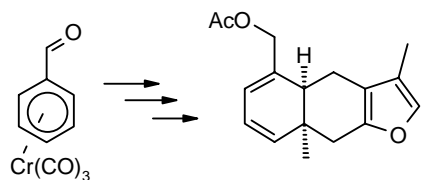
on several aspects of the synthesis of electron-poor half sandwich complexes.

The 16-electron half-sandwich complexes CpM(P*P)^+ ($\text{M} = \text{Fe}, \text{Ru}$) and $[\text{IndRu(P*P)}]^+$ where P*P are electron poor bidentate fluoroaryl-phosphinite ligands are efficient catalysts for asymmetric [4+2] cycloaddition reactions between enals and dienes, and for the [3+2] cycloaddition reactions between enals and nitrones. Attractive features of this family of Lewis acid

catalysts are their straightforward syntheses, well-defined structures and tunable electronic properties.¹ The high stability of the Ru complexes allows quantitative catalyst recovery. New developments include inter- and intramolecular [4+2] cycloadditions involving α,β -unsaturated ketones.²



Temporary complexation of an arene by the electrophilic Cr(CO)_3 group is the key for the transformation of arenes into substituted alicyclic molecules.³



A number of highly asymmetric variants have been developed and have been applied to the synthesis of natural products or fused ring systems of synthetic interest.⁴ An example is the synthesis of both enantiomers of acetoxytubipofuran (**1**).^{4a} Complexation of an arene to an electrophilic metal fragment also provides new opportunities for the enantioselective catalytic desymmetrization of *meso*-complexes.⁵

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