PN^3(P)Pincer Complexes: Cooperative Catalysis and Beyond

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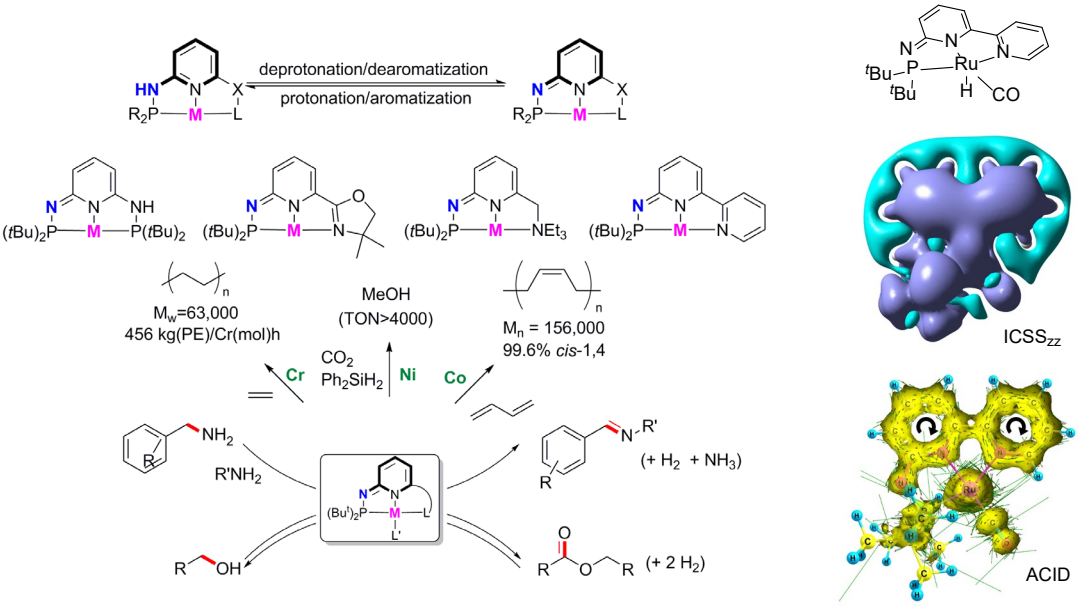
Pincer transition metal complexes have versatile reactivities to catalyze many organic transformations and activate strong chemical bonds. In particular, complexes with ligands derived from tridentate pyridine-based framework exhibit interesting reactivities. We have developed a novel platform of pincer-type PN^3(P)-ligands which are capable of interacting with the substrates during the reaction. We have witnessed that the seemingly small change by replacing the CH_2 spacer in the pyridine-based pincer complex with an NH group has dramatically influenced the thermodynamic and kinetic properties and in some cases the catalytic behaviors of the corresponding metal complexes. Furthermore, unprecedented ligand-centered reactivities (LCRs) were demonstrated. The σ-nucleophilicity of the N atom of the iminic arm was significantly enhanced to reach N-heterocyclic carbene-like nucleophilicity as a catalyst and a ligand. The novel LCR may open a new direction for the catalyst design.



Key References

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