

SYNTHESIS AND APPLICATION OF CHIRAL PN³ Pincer Ligands in Transition Metal Catalyzed Borrowing Hydrogen Reactions

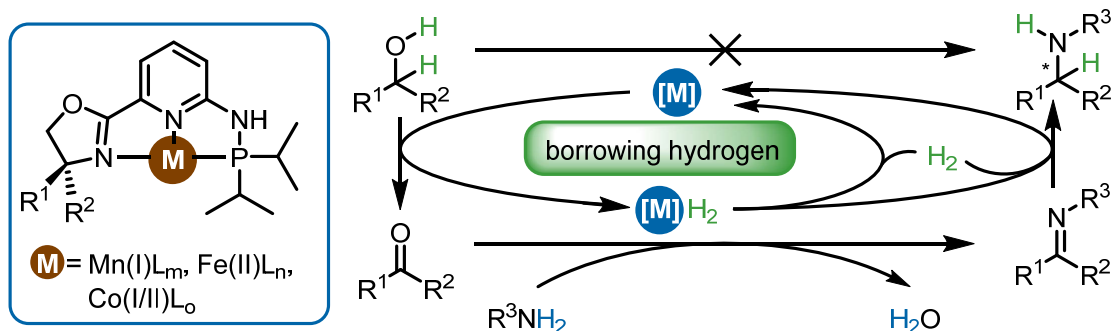
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Nitrogen containing compounds are of great importance in nature and industrial processes and products. As a sustainable and green alternative to established synthetic procedures, the transition metal-catalysed borrowing hydrogen (BH) methodology gained increasing attention over the past few years.[1, 2] A non-symmetric manganese complex utilising a bipyridine scaffold was recently reported by our group to exhibit high catalytic activity towards the N-alkylation of primary and secondary alcohols with aromatic and aliphatic amines under moderate reaction conditions.[3] However, the enantioselective synthesis of amines via BH remains challenging and only few examples utilising precious metals are known to date.[4]



Utilizing chiral oxazoline moieties near the catalytic centre may allow to perform an enantioselective hydrogenation in the final hydrogenation step. This approach offers high tunability of steric hindrance around the metal centre by utilisation of amino alcohols from the chiral pool. Experiments on complexation were conducted with Mn(I), Fe(II) and Co(I/II) precursors. Structural investigation and screening reactions were performed with an achiral model compound on common benchmark reactions for optimisation of reaction conditions. The aldol condensation of secondary alcohols was identified as the main challenge and a way to circumvent this limitation was developed. The findings were applied to catalysis with chiral complexes on various alcoholic and amino substrates.

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