

Applications of “planar-chiral” heterocycles in asymmetric catalysis*

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Abstract: Planar-chiral derivatives of pyridine function as efficient catalysts for processes such as the kinetic resolution of primary amines and the desymmetrization/ring-opening of meso epoxides. Planar-chiral pyrrolyl and phospholyl derivatives serve as effective chiral ligands for a range of metal-catalyzed reactions, including the copper-catalyzed ring-expansion of oxetanes and the rhodium-catalyzed isomerization of allylic alcohols.

INTRODUCTION

At the time that we initiated our program in 1995, there were no applications of “planar-chiral” heterocycles in asymmetric catalysis (Fig. 1). During the past six years, we have been developing the chemistry of this intriguing family of molecules.

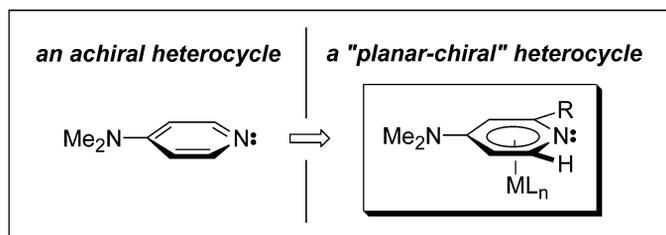


Fig. 1 From an achiral heterocycle to a “planar-chiral” heterocycle.

PYRIDINE-DERIVED CATALYSTS

Pyridines and pyridine-*N*-oxides catalyze a wide range of reactions, including the acylation of alcohols and amines, the rearrangement of *O*-acylated enolates, and the ring-opening of epoxides. Until recently, there were very few reports of *asymmetric* catalysis of such transformations [1].

We have synthesized an array of planar-chiral pyridine-derived complexes (e.g., Fig. 2), and we have determined that they serve as effective enantioselective catalysts for a broad spectrum of processes (Fig. 3) [2].

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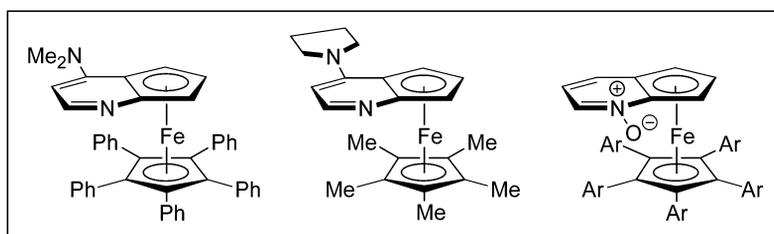


Fig. 2 Planar-chiral pyridine-derived catalysts.

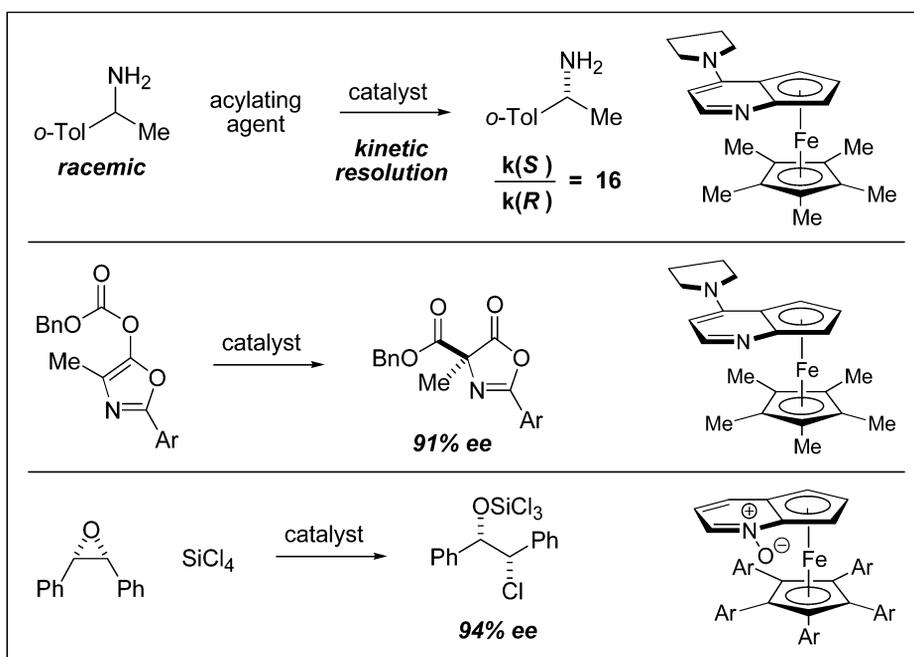


Fig. 3 Asymmetric catalysis with planar-chiral pyridine derivatives.

CHIRAL LIGANDS

We have also been exploring the use of planar-chiral heterocycles as chiral ligands for transition metals. Two examples of the ligands that we have synthesized are the bisazaferrocene and the phosphazaferrocene illustrated in Fig. 4.

We have established that these new ligands are effective in reactions such as the copper-catalyzed ring expansion of oxetanes and the rhodium-catalyzed isomerization of allylic alcohols (Fig. 5) [3].

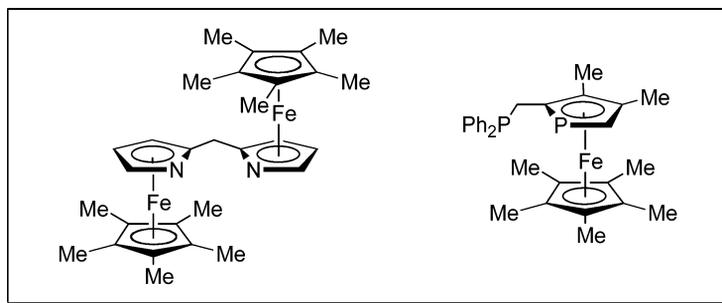


Fig. 4 Planar-chiral heterocycles as bidentate ligands for transition metals.

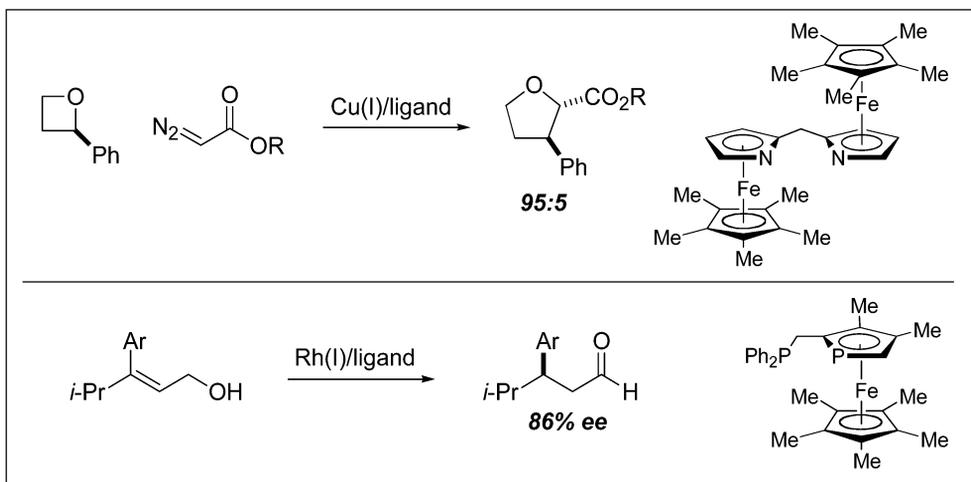


Fig. 5 Applications of planar-chiral heterocycles in transition metal-catalyzed processes.

CONCLUSION

Planar-chiral heterocycles can serve as effective chiral ligands for transition metals and as useful asymmetric catalysts in their own right. Ongoing efforts in this laboratory are directed at expanding the range of applications of this interesting family of compounds.

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