



Perspectives

Ten years of research in Chicago

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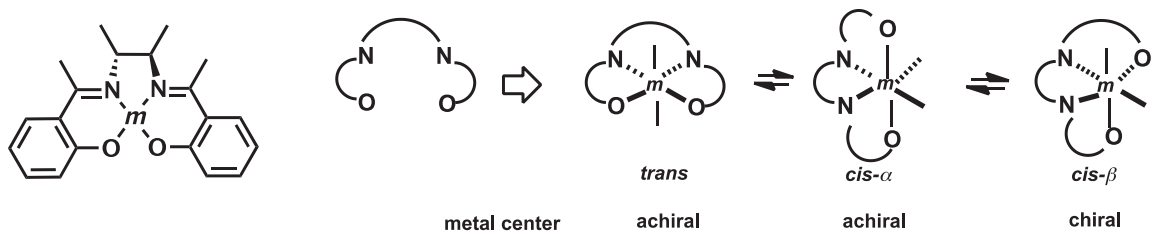
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1. New design of asymmetric catalysts

Jacobsen's concept of a privileged ligand for asymmetric catalysis is popular in catalytic asymmetric synthesis. Among these privileged ligands, probably the one most frequently used would be the salene ligand. Although this ligand is widely used for numerous organic transformations, we believe its conformational equilibrium among trans, cis- α , and cis- β forms may create the existence of multiple possible transition states for the reaction, which could cause undesired by-paths of the transformation compared to the single-pathway process. The equilibrium among these three forms is usually very rapid and it has been believed to be rather difficult to freeze only a single conformer to the others.

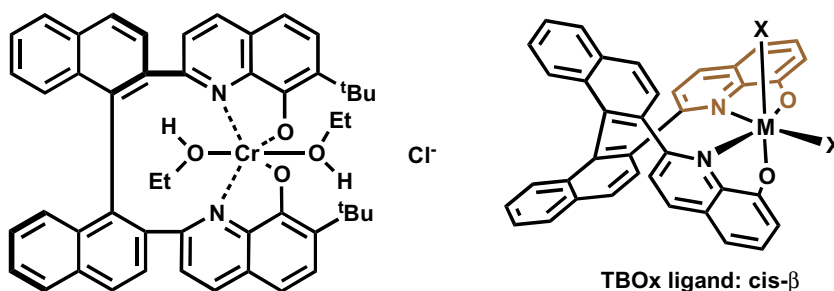
We believed that if we used the longer chains from 7 to 9 carbon-length to bridge the nitrogen–nitrogen atoms, we would be able to freeze such equilibrium with rigorous steric requirements and thus be able to generate a stable and pure single isomer of cis- α or cis- β form without any equilibria. Although such a larger ring bridge might decrease the stability of the metal complex significantly, we felt this problem might be avoided if we chose a coordinating functional group, which was exceedingly strong toward metal ions. 8-Hydroxyquinoline was perfect for our purpose because this group is known to be the privileged heterocycle for numerous metal ions and, in fact, over 50 metal ions are known to coordinate to this ligand forming stable complexes. When we mixed our new ligand with a variety of metal ions, the metal containing the nine-membered ring was generated quite rapidly and quantitatively. As expected, the X-ray crystallographic analysis showed the resulting relatively rigid

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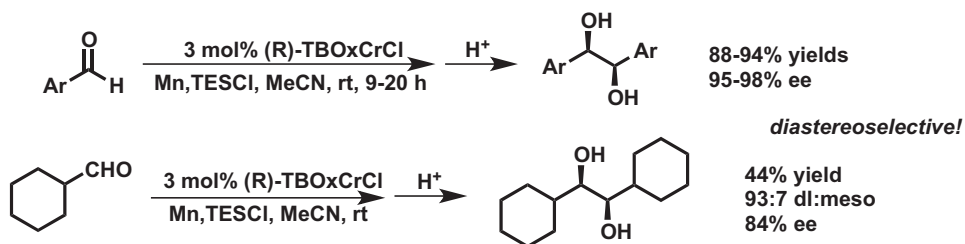


metal complex existed with the expected *cis-β* configurations. In fact, the metal center of these complexes is always chiral and in the case of octahedral metal complexes the remaining two coordinating sites are non-equivalent. Such non-equivalent coordinating sites would provide us both sterically very crowded and less crowded sites on the metal ion, and thus offer asymmetric inductions otherwise unattainable. Based on this

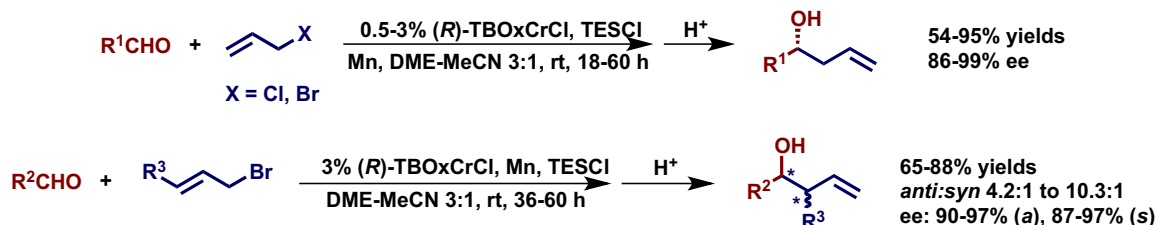
hypothesis, the following asymmetric reactions have been discovered: asymmetric pinacol coupling, NH reactions, allenylation, propargylation, Michael addition, Pudovik reaction, Strecker reaction, and nitroso-hetero-Diels–Alder reactions. Each reaction reduced the possible transition states and also two possible coordinating sites aligned specifically by electric and steric requirements.^{13,28,33,36,39,46,54,56,57}



(1) Catalytic asymmetric pinacol coupling reaction



(2) Catalytic asymmetric Nozaki–Hiyama allylation reaction



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