Harnessing Axial Chirality of N-Heterocyclic Carbene (NHC)-Metal Complexes: Applications in asymmetric Catalysis

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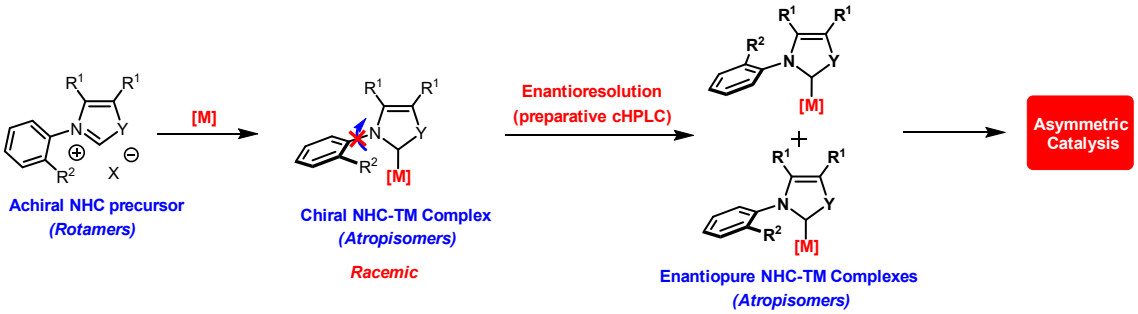
In enantioselective transition-metal catalysis, chiral ligands are key players. The success of N-heterocyclic carbenes (NHCs) as stable electron-rich neutral ligands in homogeneous catalysis led to the development of a wide array of chiral NHCs as stereodirecting ancillary ligands for various asymmetric reactions.[1]

Recently, we devised a new design of chiral NHC-metal complexes based on restricted rotations of dissymmetric aryl groups as *N*-substituents of the NHC ligands.[2] Advantageously, this design does not require the use of chiral synthons since the axis of chirality is created during the metalation step. However, NHC-metal complexes are formed as racemic. Thank to the high chemical stability of most of NHC-metal complexes, a resolution by chiral HPLC at preparative scale enabled to obtain both enantiomers with high yields and excellent enantioselectivities.



Details concerning the syntheses, configurational stabilities and the values of the rotational barriers will be presented. Series of chiral palladium-,[3,4] copper-,[4] gold-[4,5] and ruthenium-NHC[6] complexes have been prepared and their application in enantioselective catalysis allowed to reach high level of enantioselectivities for various reactions.

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