Advanced Control of Catalytic Activity and Stereoselectivity in Catalytic Asymmetric Reactions

Tamio Hayashi
(Kyoto University, Graduate School of Science, Professor)

【Outline of survey】

One of the significant subjects for developing catalytic asymmetric reactions is the design and preparation of a chiral ligand which will fit in with a given reaction efficiently in both catalytic activity and enantioselectivity. A number of chiral molecules containing phosphorus and/or nitrogen atoms have been prepared and used for transition metal-catalyzed asymmetric reactions, but they are not always useful as chiral ligands because of their low catalytic activity or enantioselectivity. Recently, we found that chiral dienes are very effective as chiral ligands for some catalytic asymmetric reactions, especially for rhodium-catalyzed asymmetric carbon-carbon bond forming reactions. In this research project, we will survey various types of molecules, which have functional groups potentially coordinating to late transition metals, for their ability as ligands for catalytic reactions. They are those molecules bearing olefin, acetylene, carbene, as well as phosphine and amine functionality at an appropriate position. With information on the relationship between the ligands and catalytic activity in hand, chiral ligands which have both high catalytic activity and high enantioselectivity for a certain reaction, will be designed and used to realize the practically useful catalytic asymmetric reactions.

【Expected results】

One of the goals of our research project is to systematically summarize the features of potential ligands with respect to their coordination ability to late transition metals and their electronic characters which are strongly related to the catalytic activity of their metal complexes. Another is to realize practically useful catalytic asymmetric reactions with high efficiency by rational design of chiral catalysts with high catalytic activity and high enantioselectivity at the same time.

【References by the principal investigator】

・A Chiral Chelating Diene as a New Type of Chiral Ligand for Transition Metal Catalysts: Its Preparation and Use for the Rhodium-Catalyzed Asymmetric 1,4-Addition. Hayashi, T.; Ueyama, K.; Tokunaga, N.; Yoshida, K. *J. Am. Chem. Soc*. **2003**, *125*, 11508-11509.
・C_2-Symmetric Bicyclo[2.2.2]octadienes as Chiral Ligands: Their High Performance in Rhodium-Catalyzed Asymmetric Arylation of *N*-Tosylarylimines. Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shintani, R.; Hayashi, T. *J. Am. Chem. Soc*. **2004**, *126*, 13584-13585.

【Term of project】 FY2007− 2010	【Budget allocation】 27,800,000 yen (2007 direct cost)

【Homepage address】 http://kuchem.kyoto-u.ac.jp/orgchem/Top.html