【Grant-in-Aid for Scientific Research (S)】

Broad Section E

Title of Project : Development of Asymmetric Metal Catalysts by Dynamic Stereocontrol of Substitution-Labile Chiral-at-Metal Complexes

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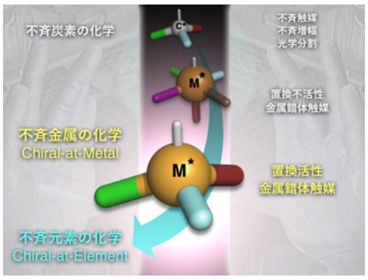
Keyword : Substitution-labile metal complex, Chiral-at-metal complex, Asymmetric metal catalyst

【Purpose and Background of the Research】

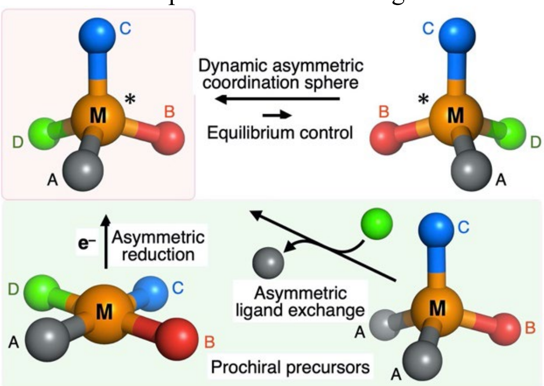
Chiral-at-metal complexes with metal-centered chirality are a group of substances in which the metal directly involved in substrate activation and electron transfer in chemical reactions serves as the chiral center, providing asymmetric reaction fields and chiral properties. In particular, the development of methods that enable the asymmetric induction and stabilization of labile metal centers using only achiral ligands is expected to increase the diversity of chiral metal complexes and promote new developments in the "chemistry of chiral metals"

The aim of this study is to develop a method for asymmetric induction of metal centers based on molecular design and control of ligand substitution activity, and to apply it to asymmetric metal catalysis. Specifically, by controlling the substitution activity of the ligands through the design of achiral ligands and the setting of reaction conditions, we will develop a method for the asymmetric induction and configuration stabilization of labile metal complexes with chirality only at the metal center. Moreover, we will develop highly efficient/selective asymmetric catalytic reactions using labile chiral-at-metal complexes, while solving the racemization problem due to the dynamic properties of coordination bonds and the structural flexibility and diversity.



【Research Methods】

Based on precise molecular design, we will develop synthetic methods and asymmetric induction methods for chiral-at-metal complexes with achiral ligands.



(1) "Equilibrium control" between the two enantiomers of a racemic tetrahedral **M***ABCD using a chiral auxiliary, followed by replacing the chiral ligand with an achiral ligand to synthesize a homochiral tetrahedral **M***ABCD.
(2) Asymmetric reduction of an achiral square-planar **M**ABCD to synthesize a chiral tetrahedral **M***ABCD.
(3) Selective ligand exchange of a prochiral tetrahedral **M***AABC to synthesize a chiral tetrahedral **M***ABCD.
(4) Asymmetric ligand exchange of a prochiral tetrahedral **M***AABC adsorbed on a chiral surface.

We plan to perform various asymmetric reactions (ex. Lewis acid-catalyzed reactions (**M*** = Zn, Ti) using the obtained optically pure chiral-at-metal complexes, and elucidate their catalytic reaction mechanisms from both experimental/measurement and theoretical calculations.

As another approach, we will investigate asymmetric induction at the chiral-at-metal cluster centers by chiral ligands, focusing on the mechanism elucidation of circularly polarized light emission and fluorescence.

【Expected Research Achievements and Scientific Significance】

The aim of this study is to develop a general method for chiral induction and configuration stability of metal centers by experiments, measurements, and theory, and to open up the academic field of "chemistry of chiral metals," which is a twin field to the chemistry of chiral carbon. In this study, we will challenge to discover the unknown properties of metals by precise design of ligands and setting of reaction conditions. Moreover, the "chemistry of chiral metals" and new chiral sources developed in this study are expected to greatly expand the scope of materials science and have great effects on many related fields. This study will provide new perspectives to the basic knowledge and fundamental technologies developed in coordination chemistry, and can also be integrated with cutting-edge fields in catalytic chemistry, bio-related chemistry, supramolecular chemistry, materials chemistry, and theoretical chemistry, leading to great advances in the "chemistry of chiral metals" and even the "chemistry of chiral elements" with expansion of the diversity and functionality of materials.

【Publications Relevant to the Project】

・ K. Endo, Y. Liu, H. Ube, K. Nagata, M. Shionoya, Asymmetric construction of tetrahedral chiral zinc with high configurational stability and catalytic activity, *Nat. Commun*. *11*, 6263 (2020).

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