

【Grant-in-Aid for Scientific Research (S)】
Science and Engineering (Chemistry)



Title of Project : Development of New Catalysts Based on Half-Sandwich Metal Complex Structures

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Research Project Number : 26220802 Researcher Number : 10261158

Research Area : Chemistry

Keyword : Organometallic Chemistry, Homogeneous Catalysis, Polymer Chemistry

【Purpose and Background of the Research】

The development of new catalysts for more efficient, selective chemical transformations and for the creation of novel functional materials has been and will remain a long-standing important research subject, in view of the increasing concerns about energy and environment issues and the sustainable development of our society. On the basis of our previous studies on half-sandwich metal complexes, in this research we focus on the synthesis, structural characterization, and reactivity exploration of a new series of cationic alkyl complexes and polyhydride complexes bearing monocyclopentadienyl ligands, aiming at the development of a new generation of molecular catalysts for the activation and transformation of dinitrogen (N_2), the carbon-carbon bond cleavage and asymmetric hydrogenation of aromatic compounds, and the synthesis of new functional polymer materials showing unique chemical, physical, thermal, mechanical and optical properties.

【Research Methods】

At first, we will synthesize a new series of half-sandwich multialkyl complexes of rare earth and group 4 transition metals bearing various monocyclopentadienyl ligands and then transform them into the cationic species by treatment with appropriate borate compounds. The catalytic activity and selectivity of the cationic alkyl species for various transformations, such as the synthesis of functionalized polyolefins and asymmetric C-H bond alkylation of aromatic compounds with alkenes, will be examined. These examinations will lead to better understanding of the catalyst structure-performance relation and offer guidelines for the design of more efficient and more selective catalysts. We will also synthesize various multimetallic polyhydride complexes by the hydrogenolysis of the half-sandwich multialkyl complexes and examine their reactivity for the activation and transformation of dinitrogen and aromatic carbon-carbon bonds. Finally, we will design and synthesize new ligand systems for the immobilization of half-sandwich metal active

species to achieve more efficient chemical transformations.

【Expected Research Achievements and Scientific Significance】

The half-sandwich metal multialkyl complexes and polyhydride complexes developed in this research are expected to show unprecedented activity and selectivity in various chemical transformations such as the synthesis of functionalized polyolefins, asymmetric alkylation of aromatic C-H bonds, activation and transformation of dinitrogen and aromatic carbon-carbon skeletons. The half-sandwich multialkyl and polyhydride complexes immobilized on mesoporous structures could work as unique catalysts showing the advantages of both homogeneous and heterogeneous catalyst systems. This research could make significant contributions to the development of synthetic chemistry, and open a new avenue in organometallic chemistry and molecular catalysis.

【Publications Relevant to the Project】

- T. Shima, S. Hu, G. Luo, X. Kang, Y. Luo, and Z. Hou, "Dinitrogen Cleavage and Hydrogenation by a Trinuclear Titanium Polyhydride Complex", *Science*, **2013**, *340*, 1549-1552.
- M. Nishiura and Z. Hou, "Novel Polymerization Catalysts and Hydride Clusters from Rare-Earth Metal Dialkyls", *Nature Chem.*, **2010**, *2*, 257-268.

【Term of Project】 FY2014-2018

【Budget Allocation】 149,900 Thousand Yen

【Homepage Address and Other Contact Information】

http://www.riken.jp/lab-www/organometallic/engl/index_e.html