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

Title of Project : Development of Novel Catalysts Based on Organo Rare Earth Metal Complexes

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Research Area : Chemistry

Keyword : Organometallic Chemistry, Homogeneous Catalysis, Polymer Chemistry

【Purpose and Background of the Research】

The development of selective, efficient catalysts for chemical synthesis is a very important research subject. To develop new generations of catalysts which complement or are superior to the existing ones, exploring the potential of untapped elements is an important strategy. So far, extensive studies on the utilization of group 4 and late transition metals for polymerization and other chemical transformations have been carried out, whereas rare earth metals have received much less attention. Rare earth elements possess unique chemical and physical properties and are expected to show unprecedented reactivities. This research focuses on the synthesis, structural characterization, and reactivity exploration of a series of cationic rare earth alkyl and related hydride complexes as well as heteropolymetallic complexes containing both rare earth and d-block transition metals (or main group metals), aiming at the development of a new generation of molecular catalysts for efficient chemical transformations and the preparation of functional polymer materials having novel physical, mechanical, and/or optical properties.

【Research Methods】

A series of rare earth dialkyl complexes bearing various mono-anionic supporting ligands will be synthesized and then transformed into the corresponding cationic species by reaction with an equiv molar amount of a borate compound such as $[Ph_3C][B(C_6F_5)_4]$ or $[PhMe_2NH][B(C_6F_5)_4]$. The catalytic activity and selectivity of the resulting cationic rare earth alkyl species in the polymerization and copolymerization of a variety of monomers will be examined. These examinations will lead to understanding of the catalyst structure-performance relation and offer guidelines for the design of better catalysts. The reaction of the dialkyl complexes with H_2 would afford a series of polynuclear rare earth metal polyhydrides. A systematic study on the structure and reactivity of these hydride clusters will also be carried out. Finally, the synthesis and reactivity exploration of heteropolymetallic complexes containing both rare earth and d-block transition metals (or main group metals) will be carried out.

【Expected Research Achievements and Scientific Significance】

This research would yield some novel catalysts showing unprecedented activity and selectivity in various chemical transformations and forge a new frontier in organometallic chemistry. In particular, a new class of single-site catalysts for the polymerization and copolymerization of a wide range of olefins and related monomers would be generated, which would lead to creation of new families of polymer materials with unprecedented physical, mechanical, and/or optical properties.

【Publications Relevant to the Project】

- Y. Luo, J. Baldamus, and Z. Hou, "Scandium Half-Metallocene-Catalyzed Syndiospecific Styrene Polymerization and Styrene–Ethylene Copolymerization: Unprecedented Incorporation of Syndiotactic Styrene–Styrene Sequences in Styrene–Ethylene Copolymers", *J. Am. Chem. Soc.* **2004**, *126*, 8080–8081.
- Z. Hou, M. Nishiura, and T. Shima, "Synthesis and Reactions of Polynuclear Polyhydrido Rare Earth Metal Complexes Composed of "$(C_5Me_4SiMe_3)LnH_2$" Units: A New Frontier in Rare Earth Metal Hydride Chemistry", *Eur. J. Inorg. Chem.* **2007**, 2535–2545.
- L. Zhang, M. Nishiura, M. Yuki, Y. Luo, and Z. Hou, "Isoprene Polymerization with Yttrium Amidinate Catalysts: Switching the Regio- and Stereoselectivity by Addition of $AlMe_3$" *Angew. Chem. Int. Ed.* **2008**, *47*, 2642–2645.

【Term of Project】 FY2009–2013

【Budget Allocation】 163,600 Thousand Yen

【 Homepage Address and Other Contact Information】

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