



(0) Research field

CPR Subcommittee: Chemistry

Keywords: Asymmetric Catalysis, C-H Functionalization, Carbon Dioxide Fixation, Dinitrogen Activation, Olefin Polymerization

(1) Long-term goal of laboratory and research background

"New Catalysts, New Reactions, New Materials" -this is the main research theme at the Organometallic Chemistry Laboratory. The discovery of novel catalysts can lead to the development of unprecedented chemical reactions and the creation of innovative functional materials that cannot be synthesized by traditional methods. Our research interests cover broad areas of organometallic chemistry, which include the synthesis of new organometallic complexes having novel structures, the development of more efficient, selective catalysts for olefin polymerization and organic synthesis, and the activation and efficient utilization of small molecules. Much of our work lies at the interfaces between inorganic, organic, polymer, and materials chemistry, with an emphasis being placed on the development of our original catalysts for applications in efficient, selective chemical synthesis.

(2) Current research activities (FY2019) and plan (until Mar. 2025)

(A) Regio-, stereospecific polymerization and copolymerization by organo rare-earth catalysts

Aiming towards the creation of novel high-performance polymer materials, a part of our research programs focuses on developing highly active and selective polymerization catalysts on the basis of the unique characteristics of rare-earth metal complexes. Recently, we have achieved for the first time the regio-, diastereoselective and highly stereoregular cyclopolymerization of ether- and thioether-functionalized 1,6-heptadienes and their copolymerization with ethylene by using a half-sandwich scandium catalyst (Fig. 1). The unprecedented diastereoselectivity and stereoregularity could be ascribed to the unique interaction between the catalyst metal center and the heteroatom in a diene monomer, as shown by DFT calculations. By using half-sandwich rare-earth scandium and yttrium catalysts, we have also achieved the co-syndiospecific alternating copolymerization of functionalized propylenes with styrene (Fig. 2), which constitutes not only the first example of co-stereospecific, sequence-controlled copolymerization of prochiral polar and non-polar olefins, but also the first example of co-stereospecific alternating copolymerization of any prochiral monomer pairs with distinctly different functionalities, efficiently affording a new family of functionalized polyolefins with unprecedented regio- and stereochemistry as well as improved thermal and surface properties.

In future plan, we will continue to design and synthesize new organo rare-earth alkyl complexes bearing various types of monoanionic ancillary ligands and develop new regio-, stereoselective transformations for the synthesis of novel functional polymers.

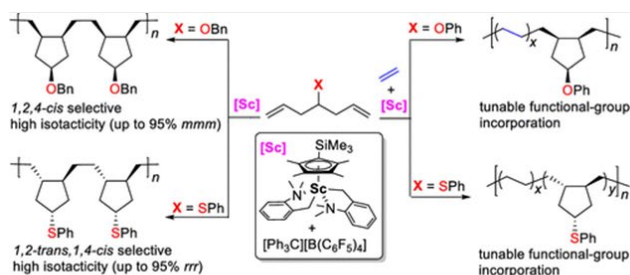


Fig.1 Regio- and Stereoselective Cyclopolymerization of Functionalized α,ω -Dienes and Copolymerization with Ethylene

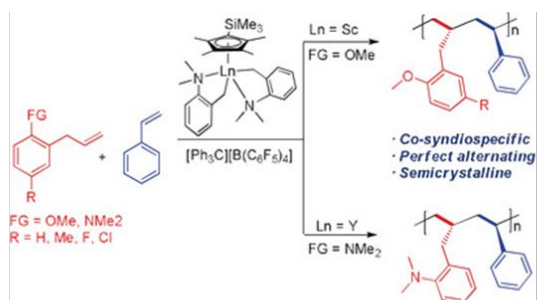


Fig.2 Co - syndiospecific Alternating Copolymerization of Functionalized Propylenes and Styrene

(B) Novel chemical transformations via C-H activation catalyzed by organo rare-earth catalysts

Stereodivergent catalysis is of great importance, as it can allow efficient access to all possible stereoisomers of a given product with multiple stereocenters from the same set of starting materials. By fine-tuning the metal/ligand combination or steric environment of a series of half-sandwich rare-earth metal catalysts, we have achieved for the first time the diastereodivergent [3 + 2] annulation of aromatic aldimines with alkenes via C-H activation (Fig. 3). The combination of a sterically demanding ligand such as $C_5Me_4SiMe_3$ with scandium preferably affords the annulation products in a *trans*-selective fashion. In contrast, the analogous catalyst with a smaller ligand such as C_5Me_4H and yttrium enables the selective formation of the *cis*-diastereoisomers.

Moreover, by using a chiral half-sandwich scandium catalyst, we have achieved for the first time the exo-selective C–H cycloaddition of imidazoles to various alkenes, offering a convenient route for the synthesis of polycyclic imidazole derivatives containing β -all-carbon quaternary stereocenters in a highly enantioselective fashion with 100% atom efficiency (Fig. 4).

In future plan, we will continue to develop regio-, stereoselective and atom-efficient reactions on the basis of our original rare-earth catalysts by making use of the unique activity of rare-earth alkyl species toward C–H activation and C=X insertion (X = C, O, N, S, etc.) together with the unique interaction between rare-earth metal and heteroatom.

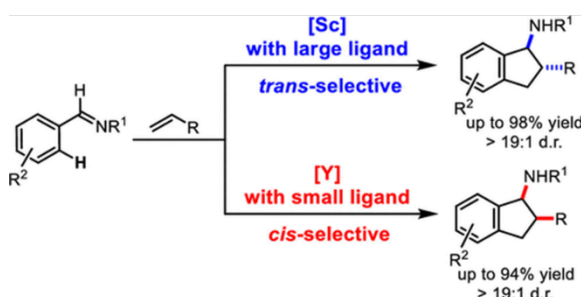


Fig.3 Diastereodivergent [3+2] Annulation of Aromatic Aldimines with Alkenes via C-H Activation

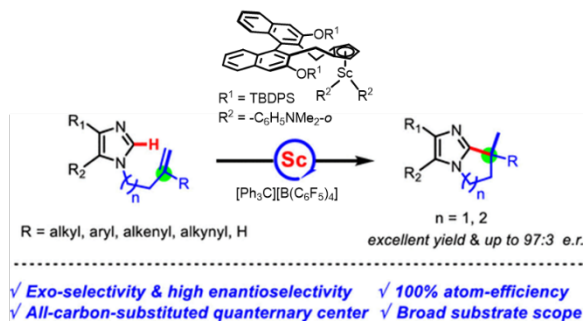


Fig.4 Intramolecular C-H Alkylation of Imidazoles with 1,1-Disubstituted Alkenes

(C) Activation and transformation of small molecules

Carbon dioxide (CO_2) is a naturally abundant, readily available, inherently renewable carbon resource. Thus, the use of CO_2 as a chemical feedstock has attracted much current interest. We have previously reported that N-heterocyclic carbene (NHC) copper(I) complexes can serve as an excellent catalyst for the carboxylation of various substrates with CO_2 . In this fiscal year, we have developed an efficient catalytic difunctionalization of imines by using an NHC copper catalyst (Fig. 5). Experimental and computational studies revealed an α -borylalkylamido intermediate, a metal amide-based Lewis pair formed by borylation of a C–N double bond, and enabled an unprecedented CO_2 fixation pattern that is in sharp contrast to the traditional CO_2 insertion into transition-metal-element bonds. The unique lithium cyclic boracarbamate products could be easily transformed into multifunctional N-carboxylated α -amino boronates. Furthermore, we have developed an efficient protocol for the regio- and stereoselective alkylative carboxylation of ynamides and allenamides with various alkylzinc halides and CO_2 by using a copper catalyst (Fig. 6). A variety of alkylzinc halides bearing functional groups were used for this transformation to afford α,β -unsaturated carboxylic acids, which contain the α,β -dehydroamino acid skeleton, introducing the corresponding alkyl group and CO_2 across the carbon–carbon triple or double bond.

In future plan, we will continue to develop CO_2 fixation reactions that enable the synthesis of a wide variety of value-added compounds.

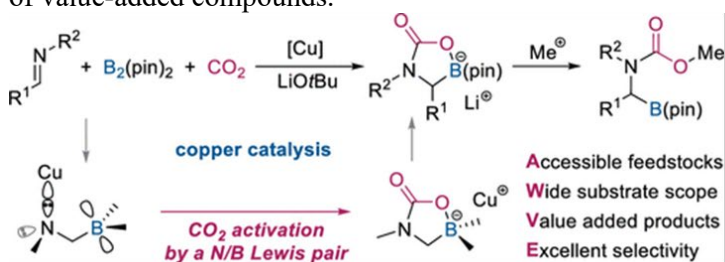


Fig.5 Boracarboxylation of Imines

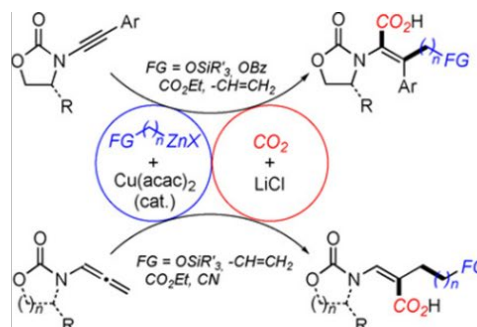


Fig.6 Alkylative Carboxylation of Ynamides and Allenamides

As part of our efforts towards dinitrogen activation by multimetallic hydrides, we have recently synthesized a novel titanium/ruthenium heteromultimetallic hydride complex $[(\text{Cp}^*\text{Ti})_2(\text{Cp}^*\text{Ru})_2(\mu\text{-H})_6]$, which showed synergistic effects for N_2 activation and hydrogenation (Fig. 7). By using a rigid PNP-

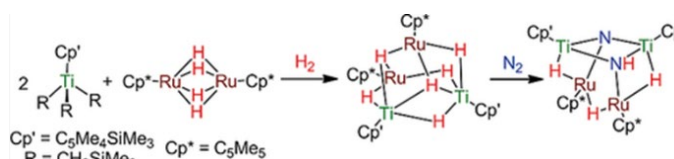


Fig.7 Dinitrogen Activation by a Titanium/Ruthenium Heteromultimetallic Hydride Complex

pincer ligand, we have synthesized a new side-on/end-on dinitrogen complex with two bridging hydride ligands (Fig. 8). This complex reacted with a variety of organometallic compounds in diverse fashions, such as reversible bonding-mode change between the end-on and side-on/end-on fashions, diborylative N=N bond cleavage, the formal insertion of two dimethylaluminum species into the N=N bond, and the formal insertion of two silylene units into the N=N bond, thus revealing many unprecedented aspects of dinitrogen reaction chemistry.

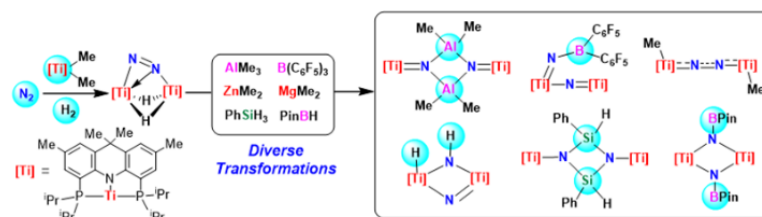


Fig.8 Synthesis and Diverse Transformations of a Dinitrogen Dititanium Hydride Complex

In future plan, we will continue to design and synthesize various multimetallic polyhydride complexes and explore their potential for the activation and transformation of small molecules and inactive skeletons.

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as of March, 2020

(4) Representative research achievements

1. "Synthesis and Diverse Transformations of a Dinitrogen Dititanium Hydride Complex Bearing Rigid Acridane-Based PNP-Pincer Ligands", Z. Mo, T. Shima, Z. Hou, *Angew. Chem. Int. Ed.* **59**, 8635-8644 (2020).
2. "Diastereodivergent [3+2] Annulation of Aromatic Aldimines with Alkenes via C-H Activation by Half-Sandwich Rare-Earth Catalysts", X. Cong, G. Zhan, Z. Mo, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **142**, 5531-5537 (2020).
3. "CO₂ Activation by Lewis Pairs Generated Under Copper Catalysis Enables Difunctionalization of Imines", Z. Li, L. Zhang, M. Nishiura, G. Luo, Y. Luo, Z. Hou, *J. Am. Chem. Soc.* **142**, 1966-1974 (2020).
4. "Construction of All-Carbon Quaternary Stereocenters by Scandium-Catalyzed Intramolecular C-H Alkylation of Imidazoles with 1, 1-Disubstituted Alkenes", S. Lou, Z. Mo, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **142**, 1200-1205 (2020).
5. "Scandium-Catalyzed Regio- and Stereoselective Cyclopolymerization of Functionalized α, ω -Dienes and Copolymerization with Ethylene", H. Wang, Y. Zhao, M. Nishiura, Y. Yang, G. Luo, Y. Luo, Z. Hou, *J. Am. Chem. Soc.* **141**, 12624-12633 (2019).

Laboratory Homepage

https://www.riken.jp/en/research/labs/chief/organometal_chem/index.html

<http://www2.riken.jp/lab-www/organometallic/HP2015e/index.html>