



(0) Research field

CPR Subcommittee: Chemistry

Keywords:

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

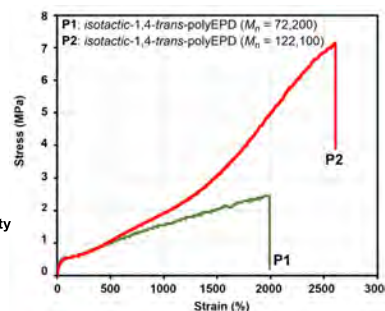
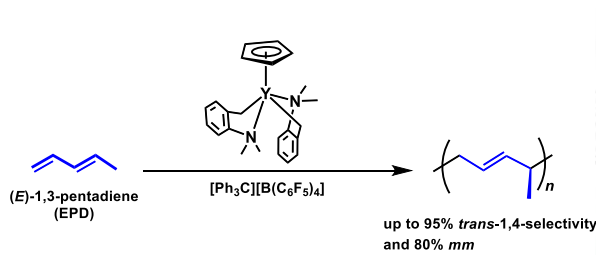
(1) Long-term goal of laboratory and research background

"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 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. By using a C_3H_5 -ligated yttrium catalyst we have successfully achieved the isospecific trans-1,4-selective living polymerization of (E)-1,3-pentadiene (EPD) (Fig. 1). The polymerization mechanism has been clarified by DFT calculations. The resulting well-defined polymers showed good elasticity without vulcanization probably due to the formation of network structures via physical cross-links of highly stereoregular crystalline (hard) segments together with less stereoregular amorphous (soft) segments.



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.

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

The enantioselective C-H alkenylation of ferrocenes with alkynes is, in principle, a straightforward and atom-efficient route for the construction of planar-chiral ferrocene scaffolds bearing alkene functionality but has remained scarcely explored to date. By using a newly prepared chiral half-sandwich scandium catalyst, we have achieved for the first time the enantioselective C-H alkenylation of ferrocenes with diverse internal alkynes (Fig. 2). This protocol offers a straightforward route for the synthesis of a new family of N/alkenylfunctionalized planar-chiral ferrocenes with high enantioselectivity, high yields, broad substrate scope, and 100% atom efficiency. The successful use of the planar-chiral ferrocene as a chiral ligand in the Rh-catalyzed asymmetric 1,4-addition of an aryl boric acid to cyclohexanone

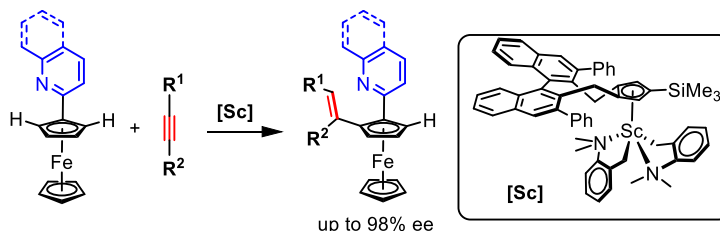


Fig 2. Synthesis of Planar-Chiral Ferrocenes

demonstrates the high potential of the N/alkene-functionalized planar-chiral ferrocene products in asymmetric catalysis.

The regiodivergent catalysis of C–H alkylation with alkenes is of great interest and importance but has remained hardly explored to date. We have achieved for the first time the regiodivergent C–H alkylation of quinolines with various alkenes by using half-sandwich rare-earth catalysts (Fig. 3). The regiodivergence was achieved by fine-tuning the metal/ligand combination or steric and electronic properties of the catalysts. On the basis of the catalyst/substrate-controlled regiodivergence, the sequential regioselective dialkylation of quinolines with two different alkenes has also been achieved. DFT studies revealed that the C–H activation of 2-phenylquinoline at both the C8 position and an ortho position of the 2-phenyl substituent was possible, and these two types of initially formed C–H activation products were interconvertible through the coordination and C–H activation of another molecule of quinoline. The regioselectivity for the C–H alkylation reactions was governed not only by the ease of the initial formation of the C–H activation products but also by the energy barriers for their interconversions, as well as by the energy barriers or steric and electronic influences in the subsequent alkene insertion processes. This work has not only constituted an efficient protocol for the selective synthesis of diversified quinoline derivatives but also offered unprecedented insights into the C–H activation and transformation of quinolines and may help in the design of more efficient, selective, or complementary catalysts.

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.

(C) Novel synthetic reactions by use of NHC-copper catalysts

The catalytic multifunctionalization of unsaturated C–C bonds is a straightforward and efficient strategy for the assembly of densely functionalized chemicals. In view of the numerous applications of organoboron compounds and nitriles as versatile intermediates for various functional molecules, simultaneous incorporation of both a boryl group and a cyano unit into the C=C double bonds of hydrocarbons, such as allenes, in a regio- and stereoselective fashion is of much importance. Recently, we have developed a copper-catalyzed chemo-, regio-, and enantioselective cyanoborylation of allenes which afforded β -boryl allyl nitriles efficiently by the use of a new chiral NHC ligand (Fig. 4). Through the systematic adjustment of the substituents in our newly prepared chiral N-heterocyclic carbene (NHC) ligands, the high enantioselectivity was achieved by installing the isopropyl substituents on the C2 and C6 positions of the naphthalene moieties. This method shows excellent functional group tolerability, therefore, the reactions of a wide range of allenes could afford the enantiopure β -boryl allyl nitriles, which show broad synthetic potentials. Stoichiometric reactions of NHC-Cu complexes were also carried out to prove some mechanistic aspects. DFT calculation studies found that the stability of the borocupration transition states governs the regioselectivity of the current reaction and also revealed that the enantioselectivity was controlled by the steric effects of the chiral NHC ligand. This method sets up an enlightening model for the development of selective catalytic processes through fine-tuning ligand design. In future plan, we will continue to develop novel enantioselective reactions on the basis of our original NHC-copper catalysts by using both the experimental way and computational methods such as designing new ligands based on DFT calculations and machine learning techniques.

(D) Activation and transformation of small molecules by hydride clusters

As part of our efforts towards dinitrogen activation by multimetallic hydrides, we have recently

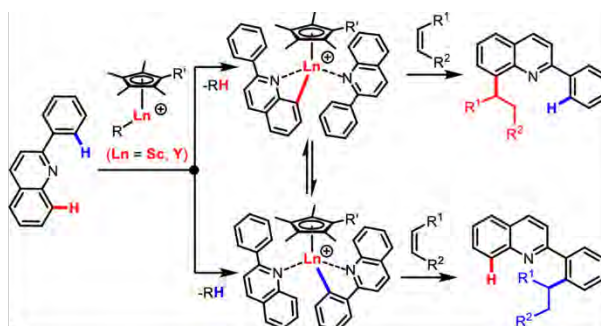


Fig. 3 Regiodivergent C–H Alkylation of Quinolines with Alkenes

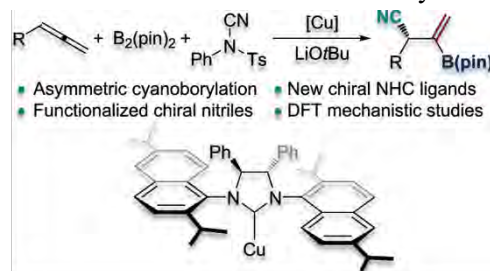


Fig. 4 Enantioselective Cyanoborylation of Allenes

synthesized $C_5Me_4SiMe_3$ -ligated chromium hydride clusters, which enable N_2 cleavage and hydrogenation under mild conditions without the need for any extra reagents. (Fig. 5). DFT study revealed that the overall steps of the reaction of $[(Cp^*Cr)_3(\mu_3-H)(\mu-H)_3]$ with N_2 were comparable to those of the previously reported titanium hydride cluster $[(Cp^*Ti)_3(\mu_3-H)(\mu-H)_6]$ with N_2 , while its energy profiles and final product were in contrast with those of the titanium hydride cluster, reflecting the metal influence.

A titanium hydride cluster showed hydrodeoxygenative cyclotetramerization of CO (Fig. 6). The acidolysis of the product with HCl afforded γ -butyrolactone together with methanol as an organic compound. This work demonstrates that a multimetallic titanium hydride cluster serves as a unique platform for CO transformation.

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

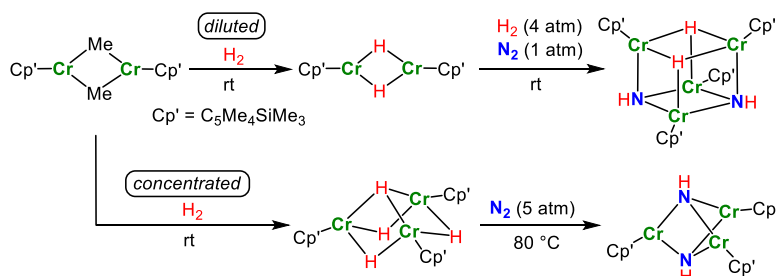


Fig 5. N_2 cleavage and hydrogenation by chromium hydride clusters

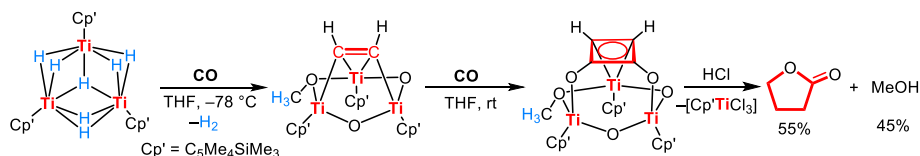


Fig 6. Hydrodeoxygenative coupling of CO by a titanium hydride cluster

(3) Members

(Chief Scientist)

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(Senior Research Scientist)

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(Part-time Worker)

Akiko Karube, Wenjie Zhang

(Student Trainee)

Ryota Owada

as of March, 2021

(4) Representative research achievements

1. "Synthesis of Thermoplastic Elastomers by Yttrium-Catalyzed Isospecific Trans-1,4-Polymerization of (E)-1,3-Pentadiene", K. Nishii, G. Zhou, Y. Saito, A. Yamamoto, M. Nishiura, Y. Luo, and Z. Hou, *Bull. Chem. Soc. Jpn.*, **94**, 1285-1291 (2021).
2. "Enantioselective C–H Alkenylation of Ferrocenes with Alkynes by Half-Sandwich Scandium Catalyst", S. Lou, Q. Zhuo, M. Nishiura, G. Luo, and Z. Hou, *J. Am. Chem. Soc.*, **143**, 2470-2476 (2021).
3. "Hydrodeoxygenative Cyclotetramerization of Carbon Monoxide by a Trinuclear Titanium Polyhydride Complex", S. Hu, T. Shima, and Z. Hou, *J. Am. Chem. Soc.*, **142**, 19889-19894 (2020).
4. "Regiodivergent C–H Alkylation of Quinolines with Alkenes by Half-Sandwich Rare-Earth Catalysts", S. Lou, L. Zhang, Y. Luo, M. Nishiura, G. Luo, Y. Luo, and Z. Hou, *J. Am. Chem. Soc.*, **142**, 18128-18137 (2020).
5. "Enantioselective Cyanoborylation of Allenes by N-Heterocyclic Carbene-Copper Catalysts", Z. Li, L. Zhang, M. Nishiura, G. Luo, Y. Luo, and Z. Hou, *ACS Catal.*, **10**, 11685-11692 (2020).
6. "Dinitrogen Activation and Hydrogenation by $C_5Me_4SiMe_3$ -Ligated Di- and Trinuclear Chromium Hydride Complexes", T. Shima, J. Yang, G. Luo, Y. Luo, and Z. Hou, *J. Am. Chem. Soc.*, **142**, 9007-9016 (2020).
7. "Co-syndiospecific Alternating Copolymerization of Functionalized Propylenes and Styrene by Rare-Earth Catalysts", H. Wang, X. Wu, Y. Yang, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.*, **59**, 7173-7177 (2020).

8. “Dinitrogen Activation by a Titanium/Ruthenium Heteromultimetallic Hydride Complex”,
T. Shima, Z. Hou, *Eur. J. Inorg. Chem.*, 2020, 1418-1422 (2020). (a special issue)

Laboratory Homepage

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

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