

## Organometallic Chemistry Laboratory (2023)

Chief Scientist: Zhaomin Hou (D.Eng.)



### (0) Research fields

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 (FY2023) and plan

#### (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 based on the unique characteristics of rare-earth metal complexes. We have achieved for the first time the synthesis of tough and fluorescent self-healing polymers by sequence-controlled terpolymerization of 4-[2-(1-pyrenyl)ethenyl]styrene (Pyr), ethylene (E), and anisylpropylene (AP) using a sterically demanding half-sandwich scandium catalyst (Fig. 1). The resulting terpolymers consisted of relatively long alternating E-*alt*-AP sequences, isolated Pyr units and short E-E blocks, which exhibited excellent tensile strength, remarkable self-healability, and high fluorescence quantum yield. Furthermore, the styrenyl C=C bond of the Pyr unit in the terpolymers could undergo [2+2] cycloaddition under photoirradiation, which thus enabled the fabrication of a self-healable fluorescent two-dimensional image on a terpolymer film through photolithography. This work offers an unprecedented efficient protocol for the synthesis of a brand-new family of fluorescent self-healing materials, showcasing the high potential of catalyst-controlled sequence-regular copolymerization of different olefins for the creation of novel functional polymers.

In future, 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.

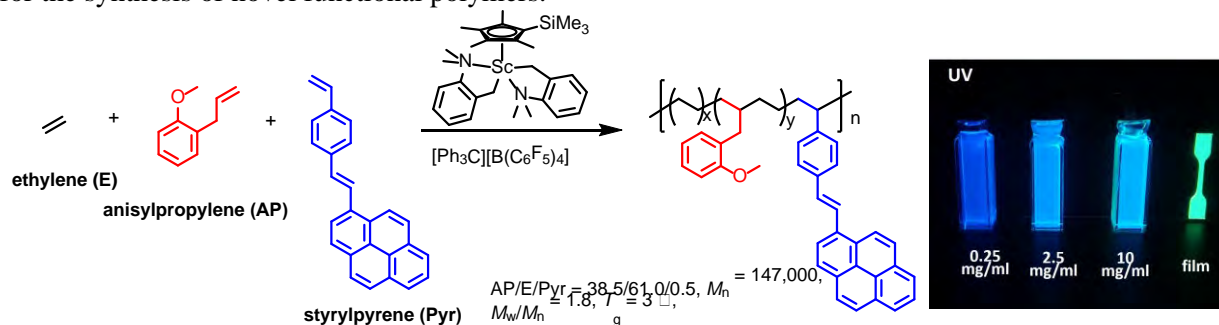


Fig. 1 Synthesis and fluorescence properties of E-AP-Pyr terpolymer

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

Multisubstituted chiral 1-aminoindanes are important components in many pharmaceuticals and bioactive molecules. In principle, the asymmetric [3+2] annulation of aldimines with alkenes through C-H activation is the most atom-efficient and straightforward route for the construction of chiral 1-aminoindanes. By using chiral half-sandwich scandium catalysts, we have achieved for the first time the enantioselective [3+2] annulation of a wide range of aromatic aldimines and alkenes via *ortho*-C(sp<sup>2</sup>)-H activation, which provides a straightforward route for the synthesis of multisubstituted chiral 1-aminoindanes (Fig. 2). This protocol features 100% atom-efficiency, broad functional group compatibility, and high regio-, diastereo-, and enantioselectivity. Remarkably, by fine-tuning the sterics of the chiral

ligand around the catalyst metal center, the diastereodivergent asymmetric [3 + 2] annulation of aldimines and styrenes has been achieved with a high level of diastereo- and enantioselectivity, offering an efficient method for the synthesis of both the *trans*- and *cis*-diastereomers of a novel class of chiral 1-aminoindane derivatives containing two contiguous stereocenters from the same starting materials. Moreover, the asymmetric [3+2] annulation of aldimines with aliphatic  $\alpha$ -olefins, norbornene, and 1,3-dienes has also been achieved.

The asymmetric hydrophosphination of cyclopropenes with phosphines is of much interest and importance but has remained rarely explored to date. We have achieved the diastereo- and enantioselective hydrophosphination of 3,3-disubstituted cyclopropenes with phosphines by using a chiral lanthanocene catalyst bearing the C<sub>2</sub>-symmetric 5,6-dioxy-4,7-*trans*-dialkyl-substituted tetrahydroindenyl ligands, which have been developed in our laboratory (Fig. 3). This novel synthetic protocol offers a selective and efficient route for the synthesis of a new family of chiral phosphinocyclopropane derivatives, featuring 100% atom-efficiency, good diastereo- and enantioselectivity, broad substrate scope, and no need for a directing group.

In future, we will continue to develop regio-, stereoselective and atom-efficient reactions based on 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.

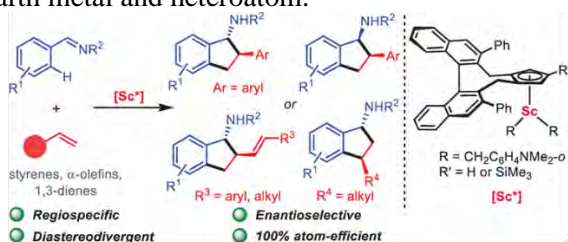


Fig. 2 Enantioselective [3+2] Cycloaddition of Aromatic Aldimines and Alkenes

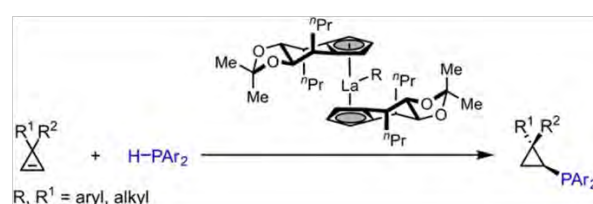


Fig. 3 Enantioselective Hydrophosphination of Cyclopropenes

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

Enamides are an important class of compounds in synthetic organic chemistry. Thus, developing new methods that enable the region- and stereo-controlled synthesis of multi-substituted enamides has been an interesting subject. By using an *N*-heterocyclic carbene (NHC) copper catalyst, we have developed an efficient protocol for the regio- and stereoselective carbozincation of allenamides with dialkylzinc reagents, leading to a straightforward route for the regio- and stereo-selective synthesis of multi-substituted enamides (Fig. 4). This new protocol provides alkenylzinc species introducing the alkyl group to  $\gamma$ -position and the zinc component to  $\beta$ -position of the allenamides in a regio- and stereoselective manner. The resulting alkenylzinc species can be submitted further C-C bond forming reactions, such as allylation, arylation, and benzylation, in one-pot, and this sequential transformation provides various unsymmetrically  $\beta,\beta$ -disubstituted enamides with well-defined configuration.

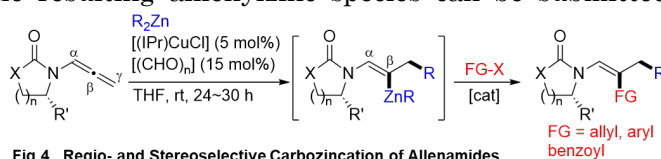


Fig. 4. Regio- and Stereoselective Carbozincation of Allenamides

In future plans, we will continue to develop novel reactions by using unique features of NHC-copper catalysts.

### (D) Activation and transformation of small molecules by metal clusters

Ammonia is globally used in large amounts, and is produced using the Haber-Bosch process under harsh reaction conditions. New catalysts for ammonia synthesis under mild conditions are urgently needed. We have developed a novel supported ultrasmall molybdenum cluster (ca. 0.7 nm in size) by immobilization of a halogen-ligated cluster on a porous support, followed by the removal of the ligands with hydrogen. The resulting supported cluster successfully catalyzed ammonia synthesis from N<sub>2</sub> and H<sub>2</sub> (Fig. 5), and the catalytic activity was highly durable even at a lower temperature (at 200 °C under 5.0 MPa). Mechanistic studies suggested that the cooperation of the multiple molybdenum sites promoted the N≡N bond cleavage.

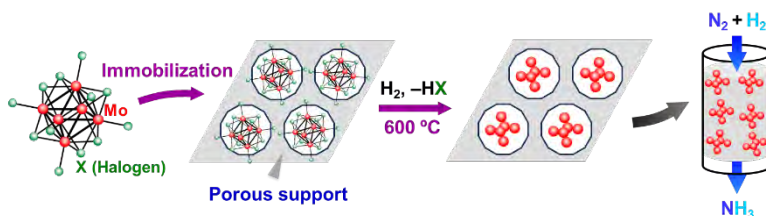


Fig.5 Ammonia synthesis by supported metal cluster catalyst

In future, we will optimize the support for the cluster and use various additives, for further highly efficient ammonia synthesis.

Dinitrogen ( $N_2$ ) is the most abundant nitrogen source, but it is highly inactive and difficult to functionalize. Recently we found that an unprecedented 1,4-conjugated (aza-Michael) addition of  $N_2$  to a variety of  $\alpha,\beta$ -unsaturated carbonyl compounds in a well-defined dititanium framework (Fig.6). The higher nucleophilic reactivity of the  $N_2$  unit than that of the oxymethylene unit in the dinitrogen complex could lead selective N-C bond formation. The resulting 1,4-

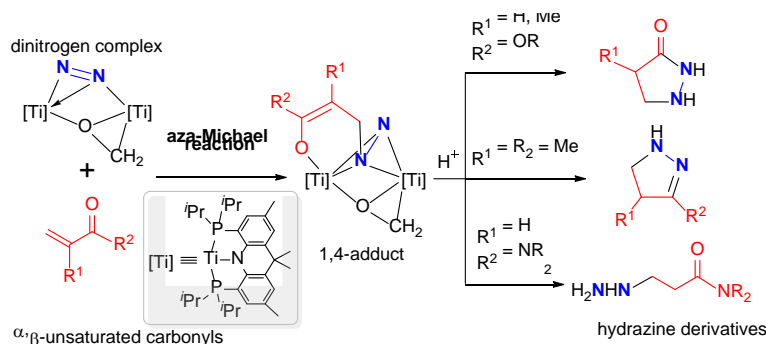


Fig. 6 Aza-Michael addition of dinitrogen to  $\alpha,\beta$ -unsaturated carbonyl compounds in a

metallic framework. The resulting 1,4-adduct easily converted to a diverse range of NN-containing hydrazine derivatives. This work showcases the use of  $N_2$  as a building block for the synthesis of NN-containing organic compounds through activation and functionalization in a molecular metal framework.

In future, we will continue to design and synthesize various multimetallic polyhydride complexes changing the metal combination (or nuclearity) and the steric and electronic properties of the ancillary ligands and explore their potential for the activation and transformation of small molecules and inactive skeletons.

### (3) Members

#### (Chief Scientist)

Zhaomin Hou

#### (Senior Research Scientist)

Masayoshi Nishiura, Takanori Shima, Masanori

Takimoto, Liang Zhang, Satoshi Kamiguchi

#### (Postdoctoral Researcher)

Qingde Zhuo

as of March, 2024

#### (Special Postdoctoral Researcher)

Xiaoxi Zhou

#### (Assistant)

Yuka Cowart

#### (Part-time Worker)

Akiko Karube, Keiko Nakamura

### (4) Representative research achievements

1. "Regio- and Diastereoselective Annulation of  $\alpha,\beta$ -Unsaturated Aldimines with Alkenes via Allylic  $C(sp^3)$ -H Activation by Rare-Earth Catalysts", X. Cong, N. Hao, A. Mishra, Q. Zhuo, K. An, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.*, 146,10187-10198 (2024).
2. "Catalytic ammonia synthesis on HY-zeolite-supported angstrom-size molybdenum cluster", S. Kamiguchi, K. Asakura, T. Shibayama, T. Yokaichiya, T. Ikeda, A. Nakayama, K. Shimizu, Z. Hou, *Chem. Sci.*, 15, 2914-2922 (2024).
3. "Synthesis of Tough and Fluorescent Self-Healing Elastomers by Scandium-Catalyzed Terpolymerization of Pyrenylethenylstyrene, Ethylene, and Anisylpropylene", L. Huang, Y. Yang, J. Shao, G. Xiong, H. Wang, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.*, 146, 2718-2727 (2024).
4. "Aza-Michael Addition of Dinitrogen to  $\alpha,\beta$ -Unsaturated Carbonyl Compounds in a Dititanium Framework", Q. Zhuo, J. Yang, X. Zhou, T. Shima, Y. Luo, Z. Hou, *J. Am. Chem. Soc.*, 145, 22803-22813 (2023).
5. "Enantioselective Synthesis of 1-Aminoindanes via [3 + 2] Annulation of Aldimines with Alkenes by Scandium-Catalyzed C-H Activation", A. Mishra, X. Cong, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.*, 145, 17468-17477 (2023).

### Supplementary

#### Laboratory Homepage

[https://www.riken.jp/en/research/labs/chief/organometal\\_chem/index.html](https://www.riken.jp/en/research/labs/chief/organometal_chem/index.html)

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