Organometallic Chemistry Laboratory
Chief Scientist: Zhaomin Hou (D.Eng.)

(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 (FY2021) 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 based on the unique characteristics of rare-earth metal complexes. We have successfully achieved the terpolymerization of ethylene (E) and two different methoxyaryl-substituted propylenes ($A^{Hex}P$ = hexylanisyl propylene; $A^{Pyr}P$ = methoxypyrenyl propylene) by a half-sandwich scandium catalyst (Fig. 1). The terpolymerization took place in a sequence-controlled fashion, affording unique multi-block copolymers composed of two different ethylene-alt-methoxyarylpropylene sequences E-alt-$A^{Hex}P$ (soft segments) and E-alt-$A^{Pyr}P$ (hard segments) and relatively short ethylene−ethylene (EE) blocks (crystalline segments). The terpolymers exhibited excellent elasticity and unprecedented self-healability as a result of microphase separation of nanodomains of the crystalline EE segments and the hard amorphous E-alt-$A^{Pyr}P$ segments from a very flexible E-alt-$A^{Hex}P$ matrix, demonstrating unique synergy of the three different components.

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.

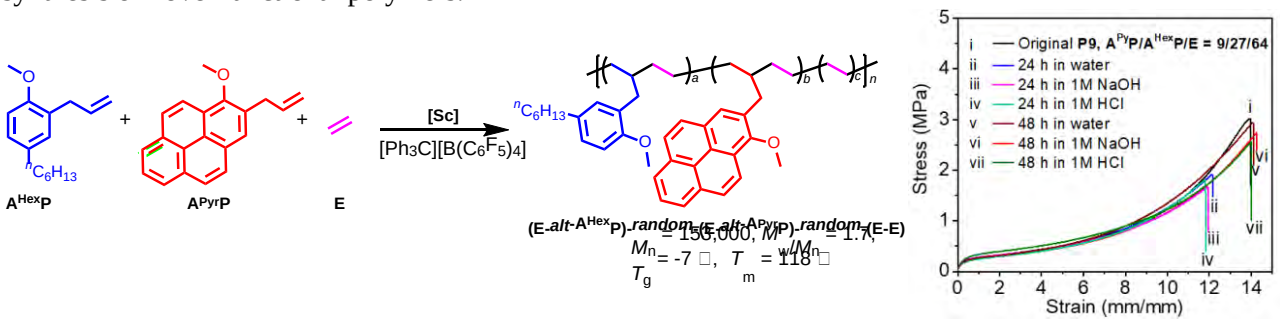
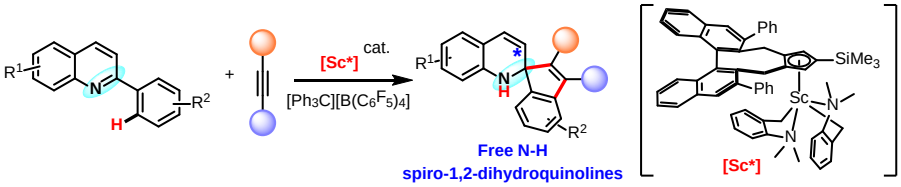


Fig. 1 Synthesis and self-healing property of terpolymer of ethylene and methoxyaryl-substituted propylenes

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

The catalytic enantioselective construction of three-dimensional molecular architectures from planar aromatics such as quinolines is of great interest and importance from the viewpoint of both organic synthesis and drug discovery, but there still exist many challenges. By using chiral half-sandwich scandium catalysts, we have succeeded in



High yiled; High regioslelctivity; High enantioslectivity; 100% atom-efficiency; Broad substrate scope; Well-defined reaction mechanism

Fig. 2 Scandium-Catalyzed Dearomative Spiro-Annulation of Arylquinolines with Alkynes

developing the dearomative spiro-annulation of a wide range of 2-arylquinolines with diverse alkynes (Fig. 2). The reaction is based on a unique combination of the scandium-catalyzed C–H activation, alkyne insertion, and dearomative nucleophilic 1,2-addition of alkenyl species to the C═N unit of a quinoline moiety, standing in sharp contrast with the previously reported late-transition-metal-catalyzed transformation of similar substrates. This protocol features 100% atom-efficiency, broad substrate scope, high yield, high enantioselectivity, and well-defined reaction mechanism, offering an efficient and selective route for the synthesis of a new family of N–H free spiro-dihydroquinoline derivatives which are of great interest and importance in medicinal chemistry and drug discovery but were previously difficult to access by other means.

Multi-substituted aminocyclopentanes are important components in many natural products, bioactive molecules, and pharmaceuticals. In principle, the [3+2] annulation of aliphatic aldimines with alkenes, which involves the activation and addition of an aldimine β-C(sp^3)–H bond to an alkene unit followed by intramolecular addition of the resulting alkyl species to the imine group, would constitute a straightforward and atom-efficient route for the synthesis of multi-substituted aminocyclopentanes. By using half-sandwich scandium catalysts, the regio- and diastereoselective [3+2] annulation of aliphatic aldimines with alkenes via β-C(sp^3)–H activation has been achieved for the first time (Fig. 3). This protocol offers an efficient and selective route for the synthesis of a new family of multi-substituted aminocyclopentane derivatives from easily accessible aldimines and alkenes with broad substrate scope, excellent regio-, diastereoselectivity, and 100 % atom-efficiency. The reaction of aldimines with styrenes exclusively afforded the 5-phenyl-trans-substituted 1-aminocyclopentane products through the 2,1-insertion of the styrene unit. In the annulation of aldimines with aliphatic alkenes, the alkene insertion took place in a 1,2-fashion, selectively affording the corresponding 4-alkyl-trans-substituted 1-aminocyclopentane products. In these cases, the addition of a catalytic amount of amines such as $AdNH_2$ significantly enhanced the catalytic activity and diastereoselectivity.

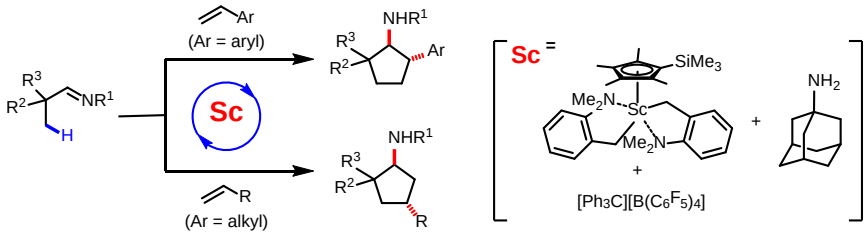


Fig. 3 Sc-Catalyzed Regio- and Diasetereoselective [3+2] Annulation of Aliphatic Aldimines with Alkenes

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.

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

As part of our efforts towards dinitrogen functionalization by multimetallic hydrides, we have recently achieved the activation and functionalization of dinitrogen (N_2) with carbon dioxide (CO_2) by the titanium hydride complex {[(^{acri}PNP)Ti]$_2$(μ-H)$_3$H} affording isocyanate species through N–C bond formation and N–N and C–O bond cleavage. The mechanistic details have been clarified by the experimental and computational studies. A titanium-mediated cycle for the synthesis of trimethylsilyl isocyanate Me_3SiNCO from N_2, CO_2, and Me_3SiCl using H_2 as a reducing agent is also demonstrated.

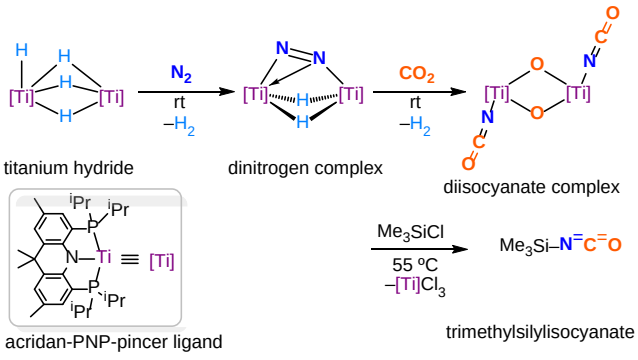


Fig.4 Activation of dinitrogen and carbon dioxide by a titanium hydride

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 as of March, 2022

(Chief Scientist)
Zhaomin Hou

(Senior Research Scientist)
Masayoshi Nishiura, Takanori Shima, Masanori Takimoto, Liang Zhang, Satoshi Kamiguchi

(Postdoctral Researcher)
Qingde Zhuo, Kun An, Aniket Mishra

(Visiting Researcher)
Xiaoxi Zhou, Hao Wang

(Assistant)
Yuka Cowart

(Part-time Worker)
Akiko Karube, Keiko Nakamura

(4) Representative research achievements

1. "Theoretical mechanistic insights into dinitrogen cleavage by a dititanium hydride complex bearing PNP-pincer ligands", J. Yang, Q. Zhuo, Z. Mo, Z. Hou and Y. Luo, ***Dalton Trans.***, *51*, 918-926 (2022).
2. "Regio- and Diastereoselective [3 + 2] Annulation of Aliphatic Aldimines with Alkenes by Scandium-Catalyzed β-C(sp3) −H Activation", X. Cong, Q. Zhuo, N. Hao, Z. Mo, G. Zhan, M. Nishiura, Z. Hou, ***Angew. Chem. Int. Ed.***, *61*, e202115996 (2022).
3. "Synthesis and Structure Diversity of Half-Sandwich Rare Earth Dialkynyl Complexes", G. Xiong, O. Tardif, M. Nishiura, B. Guan, Z. Hou, ***Helv. Chim. Acta***, *105*, e202100197 (2022).
4. "Modular Access to Spiro-dihydroquinolines via Scandium-Catalyzed Dearomative Annulation of Quinolines with Alkynes", S. Lou, G. Luo, S. Yamaguchi, K. An, M. Nishiura, and Z. Hou, ***J. Am. Chem. Soc.***, *143*, 20462-20471 (2021).
5. "Terpolymerization of Ethylene and Two Different Methoxyaryl-Substituted Propylenes by Scandium Catalyst Makes Tough and Fast Self-Healing Elastomers", Y. Yang, H. Wang, L. Huang, M. Nishiura, Y. Higaki, Z. Hou, ***Angew. Chem. Int. Ed.***, *60*, 26192-26198 (2021).
6. "Theoretical Studies of Rare-Earth-Catalyzed [3 + 2] Annulation of Aromatic Aldimine with Styrene: Mechanism and Origin of Diastereoselectivity", P. Wang, G. Luo, J. Yang, X. Cong, Z. Hou, and Y. Luo, ***J. Org. Chem.***, *86*, 4236-4244 (2021).

Laboratory Homepage
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