Japan Academy Prize to:

Zhaomin Hou
Chief Scientist, Organometallic Chemistry Laboratory,
RIKEN Cluster for Pioneering Research
Group Director, Advanced Catalysis Research Group,
RIKEN Center for Sustainable Resource Science

for "Development of Organo Rare-Earth Chemistry and Exploration of New Synthetic Methods"

Outline of the work:

Organometallic chemistry is a scientific discipline that studies the synthesis and reactivity of organometallic compounds, enabling innovations in many fields, such as synthetic organic chemistry, polymer chemistry, catalysis, as well as promoting the synthesis of pharmaceuticals, agrochemicals, and functional materials. Exploring the potential of untapped elements is an important strategy for developing superior or complementary synthetic methods and catalysts to those that already exist. Rare-earth elements, such as scandium, yttrium, and lanthanides (La–Lu), possess unique chemical and physical properties that differ from those of the main-group and *d*-transition metals, forming an important frontier in the periodic table. However, organometallic chemistry of rare-earth elements has received little attention because of the high sensitivity of organo rare-earth compounds, making their handling, structure elucidation, and exploitation of potential reactivities challenging.

Dr. Zhaomin Hou is a pioneer and world leader in organo rare-earth chemistry and catalysis. He has synthesized various organo rare-earth compounds and systematically investigated their structure–reactivity relationships, affording the development of novel enabling catalysts for various useful chemical transformations.

Dr. Hou investigated the reduction of ketones with low-valent lanthanides during the early stage of his studies. Because of a historical report on the one-electron reduction of ketones with alkali metals approximately 130 years ago, ketyl radicals have been postulated as the key reactive intermediate in the pinacol coupling of carbonyl compounds, which are fundamental reactions in organic synthesis. However, ketyl radical species have remained elusive for more than a century because of their extremely high reactivity. Dr. Hou isolated and structurally characterized for the first time a ketyl radical species by reducing fluorenone with a sterically demanding samarium(II) aryloxide complex in 1995. Furthermore, his subsequent study unequivocally demonstrated the reversibility of the pinacol coupling of ketyl radical species, which could be controlled by the careful selection of supporting ligands on the metal center.

Dr. Hou subsequently succeeded in designing and synthesizing a series of previously inaccessible half-sandwich rare-earth dialkyl complexes with monocyclopentadienyl ligands using appropriate metal/ligand combinations based on his early studies on rare-earth metal ketyl complexes. Thus, such half-sandwich rare-earth complexes are accessible; they reveal diverse and

unique reactivities.

The hydrogenolysis of half-sandwich rare-earth dialkyl complexes afforded the formation of rare-earth metal hydride clusters, which was a fruitful investigation along these lines. A series of novel rare-earth metal hydride clusters, which were successfully isolated and well-characterized, demonstrated unique synergistic effects in various chemical transformations, including reversible H_2 addition in a single-crystal to single-crystal state. He also succeeded in the synthesis of novel titanium hydride clusters with remarkable reactivities toward various inactive molecules, such as the cleavage and hydrogenation of dinitrogen at ambient temperature and pressure, skeletal rearrangement of benzene at room temperature, and hydrodenitrogenation of pyridines under mild conditions, by extending his expertise in rare-earth chemistry to *d*-transition metals. These studies have opened up a new avenue in metal hydride cluster chemistry as well as provided unprecedented insights into the mechanistic aspects of some important industrial processes reliant on solid catalysts, such as the Haber–Bosch ammonia synthesis and petroleum refining.

Another important role of half-sandwich rare-earth complexes is in the formation of cationic monoalkyl species, which exhibit unique activity and selectivity in organic synthesis and olefin polymerization. The half-sandwich rare-earth dialkyl complexes could be converted to the corresponding cationic complexes by removing one of the two alkyl groups, providing a unique platform for catalytic C–H addition to various alkenes and related unsaturated compounds. The cationic complexes are also useful for the precise copolymerization of multiple olefin monomers with different properties, such as polar and nonpolar olefins. The key discovery was the significantly enhanced polymerization activity of polar olefins due to the interactions between a metal atom in a cationic half-sandwich rare-earth catalyst and a heteroatom in polar olefins. Unprecedented sequence-control of the copolymerization of polar and nonpolar olefins was realized by tuning the catalyst ligand sterics. The resulting copolymers exhibited remarkable physical and mechanical properties because of their unique microstructure healing. For example, polymers synthesized by the scandium-catalyzed copolymerization of ethylene and anisyl-substituted propylene demonstrated excellent toughness and exceptional self-healing properties, autonomously self-repairing upon mechanical damage in air, water, and acidic and alkaline environments without requiring any external energy or stimulus, demonstrating high potential for various practical applications.

In summary, Dr. Zhaomin Hou addressed the synthesis, structure, and reactivity of various organo rare-earth compounds, affording breakthroughs in many related fields, such as small molecule activation and transformation, C–H bond activation and functionalization, and the copolymerization of polar and nonpolar olefins.

List of Main Publications

I. Papers

1. **Z. Hou**, H. Yamazaki, K. Kobayashi, Y. Fujiwara, and H. Taniguchi, “Novel Crystal Structure of Ytterbium(II)-Benzophenone Dianion Complex and its Reaction with 2,6-Di-*tert*-butyl-4-methylphenol”, *J. Chem. Soc., Chem. Commun.* **1992**, 722–724.
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Sm(ketyl)$(OAr)_2(THF)_2$ and Its Reversible Coupling to a Disamarium(III) Pinacolate", *J. Am. Chem. Soc.* **1995**, *117*, 4421–4422.

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4. **Z. Hou**, X. Jia, M. Hoshino, and Y. Wakatsuki, "First Structural Characterization of a Benzophenone Ketyl Complex", *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1292–1294.
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6. D. Cui, O. Tardif, and **Z. Hou**, "Tetranuclear Rare Earth Metal Polyhydrido Complexes Composed of "$(C_5Me_4SiMe_3)LnH_2$" Units. Unique Reactivities toward Unsaturated C–C, C–N, and C–O Bonds", *J. Am. Chem. Soc.* **2004**, *126*, 1312–1313.
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8. L. Zhang, Y. Luo, and **Z. Hou**, "Unprecedented Isospecific 3,4-Polymerization of Isoprene by Cationic Rare Earth Metal Alkyl Species Resulting from a Binuclear Precursor", *J. Am. Chem. Soc.* **2005**, *127*, 14562–14563.
9. T. Shima and **Z. Hou**, "Hydrogenation of Carbon Monoxide by Tetranuclear Rare Earth Metal Polyhydrido Complexes. Selective Formation of Ethylene and Isolation of Well- Defined Polyoxo Rare Earth Metal Clusters", *J. Am. Chem. Soc.* **2006**, *128*, 8124–8125.
10. L. Zhang, T. Suzuki, Y. Luo, M. Nishiura, and **Z. Hou**, "Cationic Alkyl Rare-Earth Metal Complexes Bearing an Ancillary Bis(phosphinophenyl)amido Ligand. A Catalytic System for Living *cis*-1,4-Polymerization and Copolymerization of Isoprene and Butadiene", *Angew. Chem. Int. Ed.* **2007**, *46*, 1909–1913.
11. X. Li, M. Nishiura, L. Hu, K. Mori, and **Z. Hou**, "Alternating and Random Copolymerization of Isoprene and Ethylene Catalyzed by Cationic Half-Sandwich Scandium Alkyls", *J. Am. Chem. Soc.* **2009**, *131*, 13870–13882.
12. M. Nishiura, J. Baldamus, T. Shima, K. Mori, and **Z. Hou**, "Synthesis and Structures of the $C_5Me_4SiMe_3$-Supported Polyhydride Complexes over the Full Size Range of the Rare Earth Series", *Chem. Eur. J.* **2011**, *17*, 5033–5044.
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15. J. Oyamada and **Z. Hou**, "Regioselective C–H Alkylation of Anisoles with Olefins Catalyzed

by Cationic Half-Sandwich Rare Earth Alkyl Complexes", *Angew. Chem. Int. Ed.* **2013**, *51*, 12828–12832.

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24. Y. Luo, Y. Ma, and **Z. Hou**, "α-C−H Alkylation of Methyl Sulfides with Alkenes by a Scandium Catalyst", *J. Am. Chem. Soc.* **2018**, *140*, 114–117.
25. H. Wang, Y. Yang, M. Nishiura, Y. Higaki, A. Takahara, and **Z. Hou**, "Synthesis of Self-Healing Polymers by Scandium-Catalyzed Copolymerization of Ethylene and Anisylpropylenes", *J. Am. Chem. Soc.* **2019**, *141*, 3249–3257.
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II. Reviews and Book

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2. M. Nishiura and **Z. Hou**, Novel Polymerization Catalysts and Hydride Clusters from Rare-Earth Metal Dialkyls, *Nature Chem.* **2010**, *2*, 257–268.
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