

**Project Title:**

**Computational Studies on the Electronic Structures and the Reaction Mechanisms of Rare-Earth- and Transition-Metal Complexes**

**Name:** Yi Luo

**Laboratory at RIKEN:** Organometallic Chemistry Laboratory

**1. Background and purpose of the project**

The search for new catalysts for more efficient, selective chemical transformations and for the synthesis of new functional materials has been a long-standing research subject in both academia and industry. To develop new generations of catalysts that are superior or complementary to the existing ones, exploring the potential of untapped elements is an important strategy. Rare-earth elements, including scandium, yttrium, and the lanthanides (La–Lu), constitute one important frontier in the periodic table. Rare-earth elements possess unique chemical and physical properties that are different from those of main-group and late-transition metals. The development of rare-earth-based catalysts by taking the advantage of these unique properties is of great interest and importance.

An understanding of the exact reaction mechanism is an essential aspect of chemistry in general, which would be helpful for improving the reactivity and selectivity of the reactions, as well as for designing more efficient reagents/reactions. However, it's always difficult to clarify the mechanisms or detect related intermediates experimentally. As a powerful tool, quantum chemical theory planted into available programs was used to investigate the detailed mechanisms and the relationship between electronic structure and properties, and hence predict and design new complexes. Therefore, based on the experimental results, we carried out a series of calculations for better understanding of the related mechanisms which would benefit for designing new catalysts or reactions.

**2. Specific usage status of the system and calculation method**

During the fiscal year 2015, large part of specified computational resources was used.

The structures were optimized by DFT methods using Gaussian 09 software. Some molecular orbital analyses were carried out with NBO calculations using some programs such as Gaussian 09, ADF and so on.

The B3PW91, B3LYP, M06, and M06-2X functionals were utilized. Dispersion corrections were also treated with the D3 version of Grimme's dispersion with Becke–Johnson damping (GD3BJ).

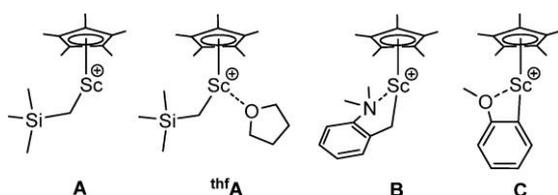
The QM/MM ONIOM Methods was also used for exploring larger systems, such as the third monomer insertion reaction and the interaction between the counter-anion and cationic active species.

**3. Results**

**(a) Computational Analyses of the Effect of Lewis Bases on Styrene Polymerization Catalyzed by Cationic Scandium Half-Sandwich Complexes.**

Stereospecific synthesis of polystyrene is of great importance for meeting various applications. *Syndio*-PS (syndiotactic polystyrene) discovered by Ishihara and co-workers in 1986 currently plays an irreplaceable role in industrial production and in our daily lives because of its high crystallization rate, good electrical properties, and excellent heat and chemical resistance. In the recent decade, novel rare-earth metal catalysts have been developed for highly efficient and selective (co)polymerization of styrene. The rare-earth metal complexes as precursors often bear a THF ligand and have various

alkyls such as  $\text{CH}_2\text{SiMe}_3$ , aminobenzyl, and anisyl. While their polymerization activity and selectivity attracted considerable interest, the effects of the THF ligand and the alkyl groups on the chain initiation efficacy and chain-end microstructure have received much less attention, although such an effect is crucial not only for a better understanding of the chain initiation efficiency and analysis of chain-end microstructure but also for the design of more efficient precursors. We have carried out DFT calculations on the styrene polymerizations catalyzed by cationic half-sandwich rare-earth metal complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sc}(\text{CH}_2\text{SiMe}_3)(\text{THF})_n]^+$  ( $n = 0$  (**A**), 1 (**thfA**)),  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})]^+$  (**B**), and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sc}(\text{C}_6\text{H}_4\text{OMe-o})]^+$  (**C**). (see Scheme 1).



**Scheme 1.** Cationic Scandium Alkyl Species Initiating Styrene Polymerization.

It has been found that THF as an external Lewis base has no effect on the regioselectivity in the chain initiation step. However, it can make activity lower toward styrene insertion. THF is computationally proposed to move away from the Sc center during chain propagation and thus has no effects on stereoselectivity. Aminobenzyl as an internal Lewis base in **B** results in no regioselectivity at the chain initiation stage and has no effect on syndioselectivity during chain propagation. The internal Lewis base anisyl induces high-isotactic chain-end microstructure. The discrepancy in chain-end microstructures induced by aminobenzyl and anisyl groups could be ascribed to the different coordination capability of oxygen and nitrogen atoms to Sc metal. The size of the metal-involved ring in the bare cationic species plays an important role in the control of chain-end microstructure of the resulting

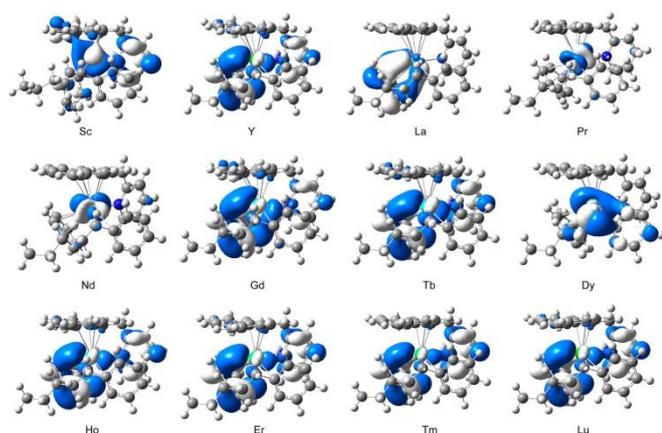
polystyrene. (Published in *Organometallics* **2015**, *34*, 5540.)

**(b) Computational Analyses of the Effect of Metal Ions on Styrene Polymerization Catalyzed by the Entire Range of Rare Earth Metal-Based Cationic Catalysts.** In addition to the Lewis bases, the metal ions are also important factor to the styrene polymerization catalyzed by cationic rare-earth metal complexes. Through cooperation with Cui's group, we performed computational analyses of the effect of metal ions on styrene polymerization catalyzed by the entire range of rare earth metal-based cationic catalysts.

As far as styrene coordination polymerization is concerned, the electron-donating  $\pi\text{-C=C}$  bonding to the empty orbital of the active metal center is generally dominant. Thus, the energy gap ( $\Delta E$ ) between the HOMO level of styrene ( $-0.22588$  au) and the LUMO level of the active species should reflect the catalytic activity on the basis of the frontier molecular orbital theory. It is generally accepted that the cationic active species of styrene polymerization is the metal center coordinated by the last inserted styrene in  $\eta^3$ -allyl mode and the phenyl ring of the penultimate inserted styrene. This allowed us to establish the mode of the active species  $[(\text{Flu-CH}_2\text{-Py})\text{Ln}(\text{C}_{17}\text{H}_{19})]^+$  where the growing polystyrene chain is simplified as a methyl group and two phenyls of styrene are distributed on both sides of the metal center.

The LUMO energies of  $[(\text{Flu-CH}_2\text{-Py})\text{Ln}(\text{C}_{17}\text{H}_{19})]^+$  ( $\text{Ln} = \text{Sc, Lu, Tm, Er, Ho, Y, Dy, Tb, Gd, Nd, Pr, or La}$ ) were analyzed on the basis of its optimized geometry. The cationic scandium species  $[(\text{Flu-CH}_2\text{-Py})\text{Sc}(\text{C}_{17}\text{H}_{19})]^+$  possesses the lowest LUMO energy, leading to the smallest energy gap ( $\Delta E$ ) ( $0.05276$  au) between it and the HOMO energy of styrene. While the LUMO energy of the other cationic rare earth metal species  $[(\text{Flu-CH}_2\text{-Py})\text{Ln}(\text{C}_{17}\text{H}_{19})]^+$  increased from  $-0.16752$  to  $-0.16328$  corresponding to  $\text{Ln} = \text{Lu, Tm, Er, Ho, Y, Dy, Tb, Gd, Nd, Pr, and La}$ , respectively, quite

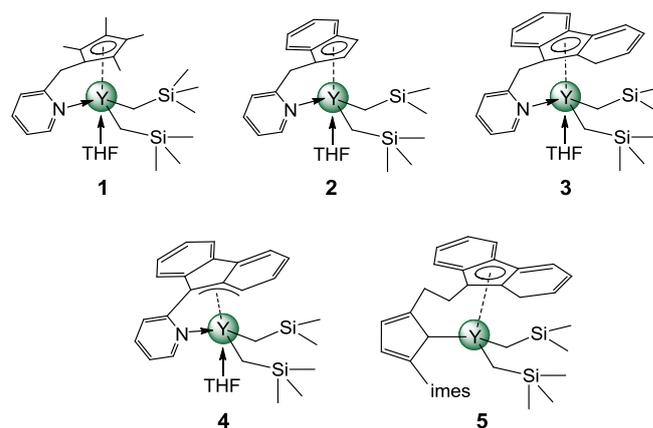
consistent with the kinetic behavior of precursors: the lower the LUMO energy, the higher the activity. As shown in Scheme 2, the LUMOs of the highly active species  $\{[(\text{Flu-CH}_2\text{-Py})\text{Ln}-(\text{C}_{17}\text{H}_{19})]^+\}$  based on the rare earth metals varying from Lu to Gd are formed by atomic orbitals (AOs) from the metal, the ligand, and the growing polystyrene chain, while those of the weakly active La, Pr, and Nd species have no contribution from the ligand, suggesting that the participation of the ligand orbital could reduce the energy of LUMO and therefore make the LUMO energy closer to the HOMO of styrene. (Published in *ACS Catal.* **2016**, *6*, 176.)



**Scheme 2.** LUMOs of  $[(\text{Flu-CH}_2\text{-Py})\text{Ln}-(\text{C}_{17}\text{H}_{19})]^+$  complexes.

**(c) Computational Study of the Ligands Dominate Polymerization of Styrene: Mechanism, Selectivity, and Origin of Difference in Activity.** As the experimental observations, an intriguing feature is the strong dependence of catalytic performance on the nature of ligands and the side-arm groups on the cyclopentadienyl. Thus, understanding the correlation between the structure of ligand and catalytic performance is vital for the design of catalysts. The aim of the present contribution on styrene polymerization mediated by the five complexes (1-5) was to explore the molecular origin of styrene that operates in these polymerizations. The relationship between the structures of the ligands and catalytic performances has been unveiled by DFT calculations. Both the

polymerization process and its tacticity have been studied in details. We employed the same side arm complexes **1**, **2**, and **3** to explore the effect of electron donating nature of the ligands to styrene polymerization. The complexes **3**, **4**, and **5** were employed to explore the effect of the side-arm groups of the cyclopentadienyl on the observed catalytic performance of styrene polymerization. In order to exclude the influence of different metal center, the Y metal was used to the all complexes.

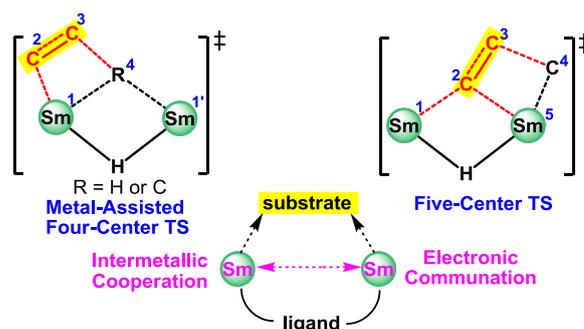


**Scheme 3.** Rare earth metal alkyl complexes 1-5.

We have computationally investigated the chain initiation and propagation during styrene polymerization catalyzed by five cationic rare-earth metal complexes. On the basis of the calculated energy profiles, the experimentally observed difference in styrene polymerization performance has been rationalized. The insertion of the first monomer into the Y-C bond of **1**<sup>+</sup>, **2**<sup>+</sup> and **3**<sup>+</sup> has similar energy barriers, suggesting that there is no significant activity difference in the chain initiation step promoted by precursors **1**, **2** and **3**. It has been found that 2,1-insertion reaction is more favorable than 1,2-insertion since the latter has higher free energy barriers and is less exergonic. The free energy profiles have been computed for both migratory and stationary insertions during the chain propagation and the results indicate a clear kinetic preference for frontside second insertion, resulting in a syndiotactic enchainment of the monomer units. The backside insertion resulting in an isotactic

enchainment needs to overcome significant higher energy barrier in comparison with the case of frontside insertion. This advantage of frontside insertion could be responsible for the experimentally observed preference of highly syndioselectivity. The current results suggest that the Mulliken charge on the central metal and the chemical hardness is good agreement with the activity of the precursors **1**, **2** and **3**: the higher the charge of the central metal and the chemical hardness are, the higher the activity is. The low activity of precursor **4** could be attributed to the coordination of THF molecule to the central metal and thermodynamically less favorable generation of the active species. In the case of precursor **5**, the resulting product of the first styrene insertion is stable ( $\Delta G = -23.0$  kcal/mol) with the central metal surrounded by the bulky ligand and phenyl ring group, which could be responsible for the absolutely insert of styrene polymerization. (under preparation for publication)

**(e) Mechanism of Ethylene Polymerization by a Binuclear Samarium Hydride Complex.** The cooperative effect in bi- and multi-nuclear metal complexes is of great interest in catalysis since such a cooperative effect often renders the complexes unique catalytic performance, unavailable in mononuclear analogues. However, the related mechanism of bi- and multi-nuclear cooperative catalysis remained almost unexplored. Herein, the detailed mechanism of ethylene polymerization by a binuclear samarocene hydride complex has been computationally modeled. We have carried out DFT calculations on the mechanism of ethylene polymerization by a dinuclear samarium hydride complex  $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_3\text{-}3\text{-Me}_3\text{Si})_2\text{SmH}]_2$  (**Sm2**) (see Scheme 4).



**Scheme 4.** Ethylene polymerization by **Sm2**.

The calculations found that, in the chain initiation stage, ethylene insertion into Sm–H bond goes through a metal-assisted four-center transition state. While in the chain propagation stage, ethylene continuously inserts into Sm–C bond rather than Sm–H bond because of thermodynamic factor. Ethylene insertion into Sm–C bond proceeds via a five-center transition state to achieve chain propagation. Additionally, during the chain propagation stage, the bridging hydrogen ligand and the  $\alpha$ -agostic interaction of C–H...Sm play an important role in electronic communication and stabilizing of transition state, respectively. These results could help us to get a better understanding of the mechanism of olefin polymerization by bi- or multi-nuclear catalysts. (Published in *organometallics*, in press)

#### 4. Conclusion

With the help of RICC system, the mechanisms of olefin polymerization catalyzed by a series of cationic rare earth complexes have been investigated. In these studies, we focused on the mechanism, selectivity, and activity of olefin polymerization. During these studies, the interaction between central metal and other moiety such as assisted metal and counterion have been also investigated. Firstly, the effect of metal ions on styrene polymerization catalyzed by the entire range of rare earth metal-based cationic catalysts has been studied by DFT calculations. Secondly, we have computationally investigated the origin of ligand-induced catalytic performance for styrene

## Usage Report for Fiscal Year 2015

polymerization based on DFT calculations. Thirdly, the effect of Lewis bases on styrene polymerization catalyzed by cationic scandium half-sandwich complexes has been analyzed. Additionally, the mechanism of ethylene polymerization by a binuclear samarium hydride complex has been investigated. These studies were successful in unveiling the mechanism, activity difference, and origin of selectivity of olefin polymerization catalyzed by rare earth metal complexes.

### **5. Schedule and prospect for the future**

In the future, the mechanisms of a series of activation of  $\sigma$ -bond and unsaturated bond by rare earth and transition metal complexes will continue to be studied. We will focus on the multimetal cooperation effect and the behavior of bridging ligands during the reactions. In addition, we continually focus on the mechanism of polar and nonpolar monomer polymerization catalyzed by rare-earth metal complexes.

We wish to continue to use RICC system for the current long-term project. At this stage, only primary results were obtained. More systematic results on the mechanism of newly discovered reactions activated by rare earth and transition metal complexes are expected.

Usage Report for Fiscal Year 2015

**Fiscal Year 2015 List of Publications Resulting from the Use of the supercomputer**

**[Publications]**

(1) Xiaohui Kang, Atsushi Yamamoto, Masayoshi Nishiura, **Yi Luo\***, **Zhaomin Hou\***. “Computational Analyses of the Effect of Lewis Bases on Styrene Polymerization Catalyzed by Cationic Scandium Half-Sandwich Complexes” *Organometallics*, **2015**, *34*, 5540–5548.

(2) Gen Luo, **Yi Luo\***, **Zhaomin Hou\***, Jingping Qu. “Intermetallic Cooperation in Olefin Polymerization Catalyzed by a Binuclear Samarocene Hydride: A Theoretical Study” *Organometallics*, in press.