Project Title:

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

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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 Gaussion 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. 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 CH_2SiMe_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 chainend 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 $[(\eta^5\text{-}C_5Me_5)Sc\text{-}(CH_2SiMe_3)(THF)_n]^+$ (n = 0 (**A**), 1 (**thfA**)), $[(\eta^5\text{-}C_5Me_5)Sc\text{-}(CH_2C_6H_4NMe_2\text{-}o)]^+$ (**B**), and $[(\eta^5\text{-}C_5Me_5)Sc(C_6H_4OMe\text{-}o)]^+$ (**C**). (see Scheme 1).
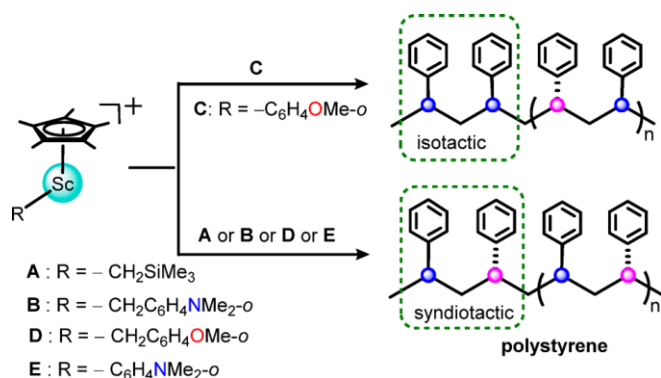

Scheme 1. Cationic Scandium Alkyl Species Initiating Styrene Polymerization.

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 insights into regioselective polymerization of 1,3-dienes catalyzed by a bipyridine-ligated iron complex**. Selective polymerization is one of the main approaches toward the synthesis of functional polyolefin materials. In particular, regioselective polyermization of 1,3-dienes is more attractive since one specific carbon−carbon double bond could be remained (1,2- or 3,4-selectivity) or newly formed (1,4-selectivity) for construction of certain microstructure and subsequent desired functionalization. Although traditional Ziegler-Natta catalysts could effectively polymerize dienes, the selectivity is generally low and hard to control. Systems based on iron complexes with aromatic bidentate amines were also highly active toward the polymerization of various substituted dienes (e.g. isoprene and 3-methyl-1,3-pentadiene) giving novel polymers with various microstructures. Specifically, the system $FeCl_2(bipy)_2$-MAO gives a 3,4-polymer from isoprene (IP) and a 1,2-polymer rather than 1,4-polymer from 3-methyl-pentadiene (3MP), as shown in Scheme 2. Apparently, the methyl substituents of the monomer might affect the observed regioselectivity. However, the molecular mechanism has remained unclear. In view of aromatic bidentate amine being capable of a redox non-innocent ligand, it is worthy addressing the intriguing question of the electronic role of this ligand and the ground state of catalytically active species in the polymerization process and whether this plane-type ligand itself sterically induces regioselectivity. Moreover, the origin of the 1,2- (or 3,4-) rather than 1,4-regioselectivity is also of interest. Simulated by our previous computational studies on olefin polymerization catalyzed by rare earth metal complexes, DFT studies have been conducted for the iron-catalyzed polymerization reactions.
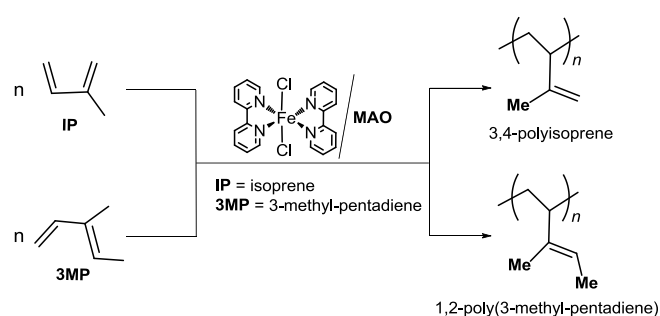
Scheme 2. Selective polymerizations of isoprene (IP) and 3-methyl-pentadiene (3MP) by combination of FeCl$_2$(bipy)$_2$ and MAO.

DFT calculations have been conducted for the regioselective polymerization of isoprene and 3-methyl-pentadiene, catalyzed by a bipyridiene-ligated cationic iron complex. It has been found that the bipyridiene ligand is redox-inert in this system and the open-shell unpaired 3d-electrons are localized on the Fe center. The energetically favourable regioselectivities are in line with the available experimental results, respectively. The steric effect plays a more important role in the regioselectivities during the polymerizations of isoprene in comparison with the electronic factor. During each of the polymerization reactions, the ancillary ligand bipyridiene has neglectable contribution to the deformation energy of active species, unlike most olefin selective polymerizations where non-Cp ancillary ligands themselves are often deformed. (under preparation for publication)

(c) Computational Study of the Ligands Dominate Polymerization of Styrene: Mechanism, Selectivity, and Origin of Difference in Activity. 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.
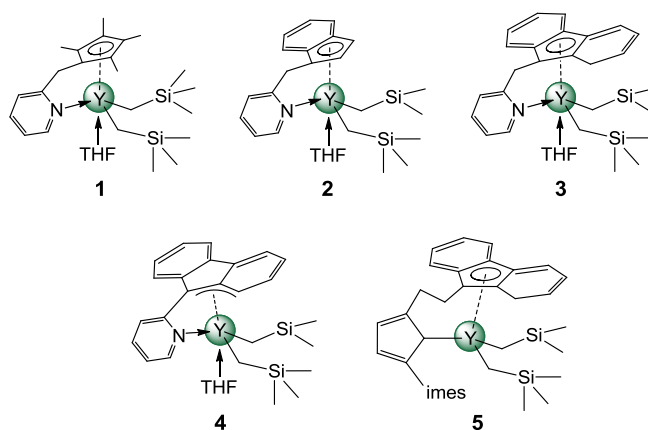
**Scheme 3.** Rare earth metal alkyl complexes **1−5**.

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$^+$**, **2$^+$** and **3$^+$** 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 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)

(d) **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 [Me$_2$Si(C$_5$H$_3$-3-Me$_3$Si)$_2$SmH]$_2$ (**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 (Scheme 4). 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 α-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*, acs.organomet.6b00018)
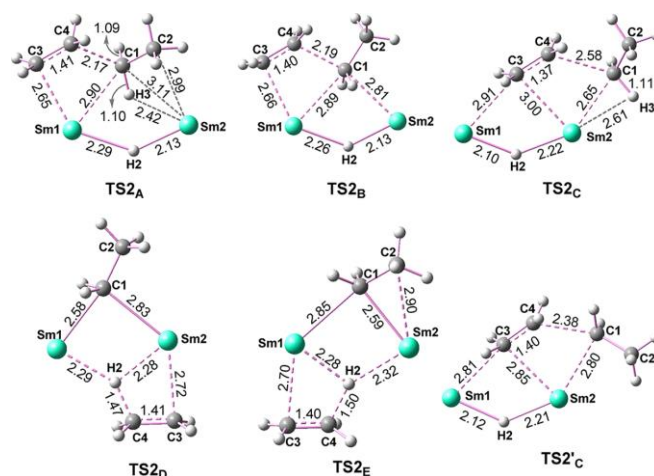
Scheme 4. Computed structures of transition states involved in the second ethylene insertion together with selected structural parameters (distances in Å).

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, DFT calculations have been conducted for the regioselective polymerization of isoprene and 3-methyl-pentadiene, catalyzed by a bipyridiene-ligated cationic iron complex. Secondly, the effect of Lewis bases on styrene polymerization catalyzed by cationic scandium half-sandwich complexes has been analyzed. Thirdly, we have computationally investigated the origin of ligand-induced catalytic performance for styrene polymerization based on DFT calculations. 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 σ-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.

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

[Publications]

(1) Xiaohui Kang, Atsushi Yamamoto, Masayoshi Nishiura, <u>Yi Luo*</u>, **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, <u>Yi Luo*</u>, **Zhaomin Hou***, Jingping Qu. "Intermetallic Cooperation in Olefin Polymerization Catalyzed by a Binuclear Samarocene Hydride: A Theoretical Study" *Organometallics*, acs.organomet.6b00018.