

**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 development of more efficient and selective catalysts has been attracted numerous attention by scientists in recent decades. Rare-earth and transition-metal have been intensively studied to design new catalyst due to its unique chemical and physical properties. The diverse reactivity of rare-earth- and transition-metal complexes could be attributed to its different geometry structures and electronic characters intrinsically. Although the chemical products catalyzed by some novel rare-earth- and transition-metal complexes have been widely used in industry and daily life, the development of new rare-earth- and transition-metal catalysts featuring high selectivity and efficiency have constantly been a hot topic of researchers.

The fully understanding of the reaction mechanism is an important aspect of chemistry, which is essential for improving the reaction reactivity and selectivity, as well as for further design of new catalyst. However, traditional experiment could not elucidate the exact reaction mechanism generally as a result of these following factors: the related reaction intermediates are too reactive to be isolated or detected in some reaction, the electronic structures of the reaction intermediates remain ambiguous, and the origin for selectivity is difficult to clarify experimentally and so on. The computational chemistry has been used as a powerful tool to investigate the detailed mechanism and explain the reaction reactivity, furthermore predict and design promising catalyst according to the detailed electronic structure and reaction

mechanism. Therefore, based on the experiment results, a series of computational jobs were carried out for better understanding of the related mechanisms which would contributed to the development of new catalysts and reactions.

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

During the fiscal year 2017, about 1,261,000 core\*hours specified computational resources were used. The geometry structures were optimized by DFT methods using Gaussian 09 and Gaussian 16 software. Natural Bond Orbital (NBO) calculations were also carried out using some programs such as Gaussian 09, ADF and so on.

The B3PW91, TPSSSTPSS, M06 functionals were utilized. Dispersion corrections were treated with the D3 version of Grimme's dispersion with Becke-Johnson damping (GD3BJ) as well. The QM/MM Method (ONIOM) was also used for exploring larger systems, such as the third monomer insertion in polymerization reactions, multinuclear transition metal catalyzed reaction and the interaction between the counter-anion and cationic active species.

**3. Results**

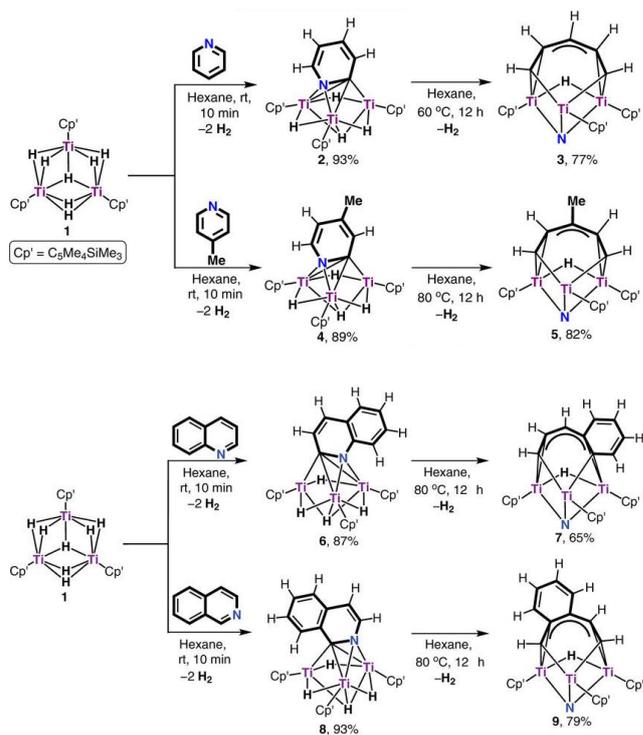
**(a) DFT study on hydrodenitrogenation of pyridines and quinolines at a multinuclear titanium hydride framework.**

The hydrodenitrogenation (HDN) of aromatic *N*-heterocycles such as pyridines and quinolines is an important process in the industrial petroleum refining to remove nitrogenous impurities from crude oil. This transformation is essential not only to

suppress NO<sub>x</sub> emissions upon combustion of the fuel but also to improve the performance of the hydrocracking and other downstream processes. In view of the fact that the industrial HDN process might involve transition metal hydrides as the true active species, investigation of the reactions of molecular transition metal hydrides with aromatic *N*-heterocycles is especially of interest and importance, as this approach may provide a useful entry into homogeneous HDN systems. We have previously shown that multimetallic titanium polyhydride complexes such as [(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Ti]<sub>3</sub>(μ<sub>3</sub>-H)(μ<sub>2</sub>-H)<sub>6</sub> (**1**) exhibit an unusually high activity for the activation of some very stable chemical bonds, such as cleaving dinitrogen (N<sub>2</sub>) and a benzene ring at room temperature. These results promoted us to examine whether titanium hydride clusters could induce the ring opening and denitrogenation of an aromatic *N*-heterocycle. Here, we report our studies on the reaction of the trinuclear titanium heptahydride complex **1** with pyridines and quinolines. We have found that the nitrogen atom in a pyridine or quinoline ring can be extruded under mild conditions at the trinuclear titanium framework through reduction of a HC=N unit followed by cleavage of the two C–N bonds (Scheme 1). The mechanistic aspects have been elucidated by computational studies and the isolation and identification of some key reaction intermediates.

Our studies have revealed both experimentally and computationally that the second C–N bond cleavage is even easier than the first C–N bond scission (pyridine ring opening) at the trinuclear titanium hydride framework, due to the unique synergistic effects of the dynamic and redox-active multiple Ti–H sites. Moreover, the facile formation of **3**, **5**, **7**, and **9** from **2**, **4**, **6**, and **8** suggests that the denitrogenation of an aromatic *N*-heterocycle may not require complete hydrogenation of the aromatic ring. This is different from what was observed previously in the case of solid catalysts, where the

complete hydrogenation (saturation) of an aromatic *N*-heterocycle was believed to be a requisite for C–N bond cleavage. These results may provide hints for designing new catalysts for the HDN of aromatic *N*-heterocycles under milder conditions as well as for other useful chemical transformations. (Published in *Nat. Commun.*, **2017**, *8*, 1866.)

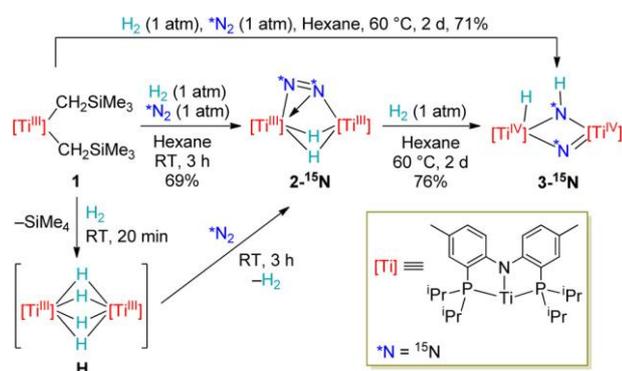


**Scheme 1.** Hydrodenitrogenation of pyridines, quinolines by the titanium hydride complex **1**

**(b) DFT studies on the activation of dinitrogen by transition-metal complexes.**

Dinitrogen (N<sub>2</sub>) is an abundant and easily accessible resource, but it is highly inert under ordinary conditions. The activation and functionalization of N<sub>2</sub> has therefore been a long-standing important research subject. Industrially, the cleavage and hydrogenation of N<sub>2</sub> is achieved by reaction with H<sub>2</sub> at high temperatures (350–550 °C) and high pressures (150–350 atm) on solid catalysts to afford ammonia (NH<sub>3</sub>) (the Haber-Bosch process). In view of the fact that H<sub>2</sub> is the only source of both electrons and protons in the industrial Haber-Bosch ammonia synthesis, the activation of N<sub>2</sub> by H<sub>2</sub> in the presence of a transition metal complex is particularly of

interest. However, studies on the activation and hydrogenation of  $N_2$  by  $H_2$  at the molecular level remained scarce. We have recently reported the hydrogenolysis of the PNP-ligated titanium dialkyl complex  $\{(\text{PNP})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\}$  (**1**,  $\text{PNP} = \text{N}(\text{C}_6\text{H}_3\text{-}2\text{-P}^i\text{Pr}_2\text{-}4\text{-CH}_3)_2$ ) with  $H_2$  (1 atm) in the presence of  $N_2$  (1 atm) afforded a binuclear titanium side-on/end-on dinitrogen complex  $\{[(\text{PNP})\text{Ti}]_2(\mu_2, \eta^1, \eta^2\text{-N}_2)(\mu_2\text{-H})_2\}$  (**2**) at room temperature, which upon heating at  $60^\circ\text{C}$  with  $H_2$  gave a  $\mu_2$ -imido/ $\mu_2$ -nitrido/hydrido complex  $\{[(\text{PNP})\text{Ti}]_2(\mu_2\text{-NH})(\mu_2\text{-N})\text{H}\}$  (**3**) through the cleavage and partial hydrogenation of the  $N_2$  unit (Scheme 1).



**Scheme 2.** Activation and hydrogenation of  $N_2$  by  $H_2$  at a PNP-ligated titanium platform.

The DFT calculations revealed that the transformation of the dinitrogen unit in **2** to the imido/nitride species in **3** is initiated by the hydrogenation of the dinitrogen unit with an external  $H_2$ , followed by release of another molecule of  $H_2$  from the titanium framework and the subsequent cleavage of the N–N bond. This work constitutes the first example of dinitrogen cleavage and hydrogenation by  $H_2$  in a well-defined molecular system without the preactivation of  $N_2$  by other reducing agents. (published in *J. Am. Chem. Soc.*, **2017**, *139*, 1818.)

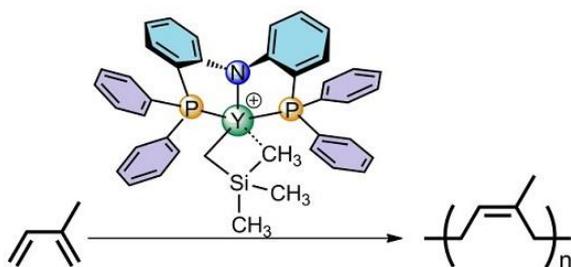
### (c) DFT studies on polymerization of olefins catalyzed by cationic rare-earth metal complexes.

The microstructures of polyisoprene (PIP) and polybutadiene (PBD) have significant influences on its physical and chemical properties, and hence for

certain usage. *cis*-1,4 selective polymerization of isoprene and butadiene is a very important process in the chemical industry to provide products that are among the most significant and widely used rubbers. Generally, it is believed that a slight increase in the *cis*-1,4 regularity of the product leads to a great improvement in the elastic properties. Therefore, the synthesis of PIP and PBD with high *cis*-1,4-selectivity has attracted considerable interest.

Cationic rare-earth metal alkyl species with various ancillary ligands were reported to show high activity and *cis*-1,4-selectivity in the polymerization of isoprene and butadiene. DFT calculations have been carried out for the highly selective *cis*-1,4-polymerization of butadiene catalyzed by a cationic rare-earth metal complex bearing an ancillary PNP ligand (Scheme 3). It has been found that the chain initiation and propagation of butadiene polymerization occurs via the favorable *cis*-1,4-insertion route. The *trans*-1,4 and 1,2-insertion are unfavorable both kinetically and thermodynamically. The chain growth follows the  $\pi$ -allyl-insertion mechanism. The analyses of energy decomposition of transition states indicate that the likelihood of rival insertion pathways is predominantly controlled by the interaction energy of butadiene with a metal center and the deformation energy of butadiene moiety. The electronic factor of the central metal has a decisive influence on the *cis*- vs. *trans*-insertion and the regioselectivity (*cis*-1,4- vs. *cis*-1,2-insertion) is mainly determined by steric hindrance. Tetrahydrofuran (THF) coordination made monomer insertion less favorable compared with THF-free case and had more noticeable impact on the *trans*-monomer insertion compared with the *cis*- case. During the chain propagation, *cis*-insertion of monomer facilitates THF de-coordination and the THF molecule could therefore dissociate from the central metal. To the best of our knowledge, this is the first systematic investigation to explore the

mechanistic details of the *cis*-1,4-polymerization of isoprene and butadiene catalyzed by non-metallocene rare-earth metal complexes. The current results could be helpful for understanding the factors determining the regio- and stereoselectivity of diene polymerization catalyzed by non-metallocene rare-earth metal complexes. (Published in *Polymers*, **2017**, *9*, 53.)

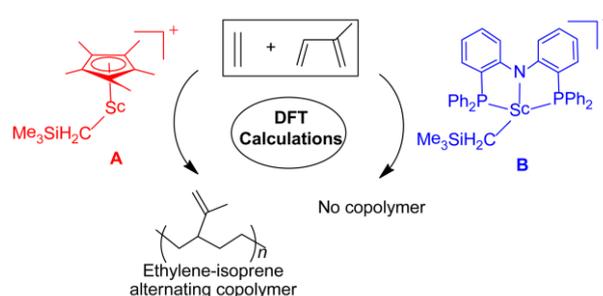


#### Theoretical Insights into the Origin of Selectively

**Scheme 3.** *cis*-1,4-polymerization of dienes catalyzed by a cationic rare-earth metal complex bearing an ancillary PNP ligand.

The development of single-site monoolefin/diene copolymerization catalysts to precisely control the microstructure of the copolymer products can create new opportunities for the preparation of novel polymer materials with desirable properties in industrial applications, and has therefore received significant interest. The copolymerization of monoolefin and conjugated dienes is highly challenging since each monomer typically requires different polymerization conditions. Hou and coworkers reported ethylene/isoprene copolymerization reactions catalyzed by cationic half-sandwich scandium alkyl complexes bearing various cyclopentadienyl ligands generated from the dialkyl precursors. The isoprene/ethylene copolymerization catalyzed by cationic rare earth metal complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sc}(\text{CH}_2\text{SiMe}_3)]^+$  (**A**) had afforded alternating isoprene-ethylene copolymer with rich 3,4-polyisoprene microstructures, whereas no isoprene-ethylene copolymer was observed by using analogous  $[(\text{PNP}^{\text{Ph}})\text{Sc}(\text{CH}_2\text{SiMe}_3)]^+$  (**B**) under the same conditions (Scheme 4).

Theoretical calculations in this work have revealed that, in the case of **A**, successive 3,4-insertion of isoprene resulted in a noncovalent interaction between the C=C double bond of penultimate unit and the metal center, suppressing the further insertion of monomers due to higher energy barrier and endergonic character. On the other hand, the ethylene pre-inserted species with alkyl active site is more suitable for the subsequent kinetically and thermodynamically favorable isoprene insertion and copolymerization is therefore realized. In the case of **B**, the experimentally observed *cis*-1,4-specific homopolymerization of isoprene was the outcome of both kinetic and thermodynamic control. And, the unfavorable ethylene insertion into the isoprene pre-inserted species with allyl active site could account for the experimental finding that no isoprene-ethylene copolymer was obtained. These computational results are expected to provide some hints for the design of rare earth copolymerization catalysts. (Published in *Chin. J. Chem.* **2017**, *35*, 723.)

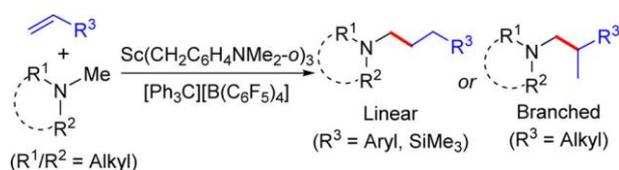


**Scheme 4.** Isoprene/ethylene copolymerization catalyzed by cationic scandium complexes bearing different ancillary ligands

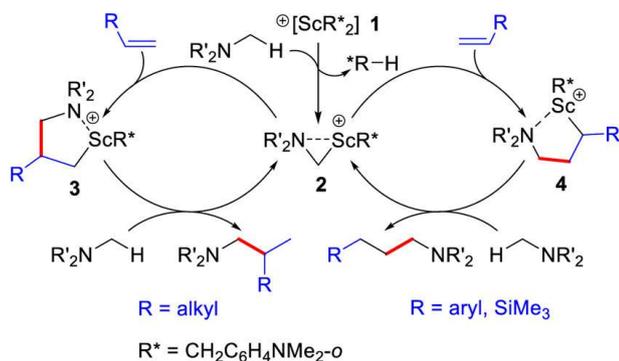
#### (d) Mechanistic insights into scandium-catalyzed hydroaminoalkylation of olefins with amines.

The synthesis of amine compounds has received intense attention for a long time due to the critical function of amine groups in many biologically active compounds and industrial functional materials. Catalytic C(sp<sup>3</sup>)-H bond activation at the position  $\alpha$  to a nitrogen atom has recently attracted much

interest from synthetic organic chemists because this offers new and promising synthetic approaches for the functionalization of simple amines. Very recently, Hou and co-workers reported that a rare-earth alkyl catalyst could promote the intermolecular hydroaminoalkylation of olefins with a variety of tertiary amines under relatively mild conditions and, in particular, with an exclusively substrate dependent regioselectivity (Scheme 5). This reaction could offer an ideal model for mechanistic studies with the purpose of developing regioselective catalytic systems.



**Scheme 5.** Sc-catalyzed hydroaminoalkylation of olefins with amines.



**Scheme 6.** Proposed mechanism of Sc-catalyzed intermolecular hydroaminoalkylation.

DFT calculations have been carried out on the Sc-catalyzed regioselective hydroaminoalkylation of olefins with amines. It has been revealed that the true active species is an amine-coordinated  $\eta^2$ -azametallacyclic complex, and electronic factors play a crucial role in achieving regioselectivity (Scheme 6). The charge dispersion and charge alternation account well for the stability of the olefin insertion transition states and products. The charge distribution of 15 olefin substrates used previously in the experimental studies correlates well with the observed regioselectivity and could thus provide a

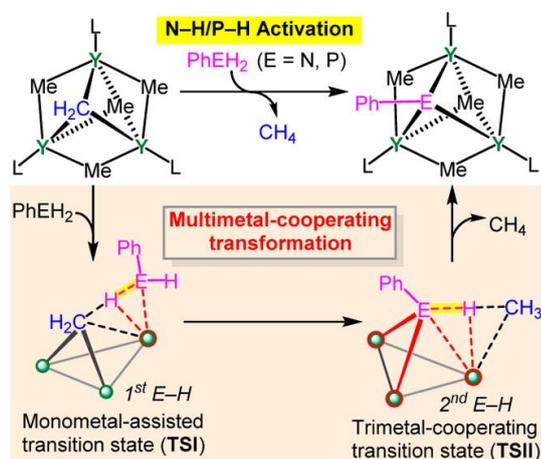
potential model for regioselectivity prediction. The reactivity of different types of C–H bonds was also explored by modeling the reaction of  $(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2\text{Sc}^+$  with  $\text{PrN}(\text{Me})(\text{Et})$ . The suggested reactivity trend for the Sc-catalyzed hydroaminoalkylation follows the order of primary C–H bond > secondary C–H bond > tertiary C–H bond. (Published in *Organometallics*, 2017, 36, 1557.)

**(e) Theoretical study on E–H (E = N, P) bond activation of  $\text{PhEH}_2$  by a trinuclear yttrium methyldene complex.**

Transition-metal-mediated E–H (E = N and P) bond activation as a synthetic elementary step has received intense attention because of its great importance in the transformation of amines and phosphines to value-added compounds in the fields of medicine, agrochemicals, and materials. In past decades, significant progress has been achieved experimentally in N–H/P–H bond activation by transition metal complexes. A deep understanding of the mechanisms of N–H/ P–H bond activation by transition metal complexes is of great importance to establish an effective strategy for functionalization of amines and phosphines. Compared to mononuclear complexes, a multimetallic system may work more efficiently for bond activation owing to the cooperation of multiple metal centers, although the knowledge of cooperative mechanisms is still rather limited. Given the importance of N–H/P–H bond activation, in-depth mechanistic understandings of the related reactions mediated by multinuclear complexes are in great demand, may establish new activation modes, and may inspire us to develop new reactions or catalysts.

E–H (E = N and P) bond activation of  $\text{PhEH}_2$  by a trinuclear yttrium methyldene complex to give a  $\mu_3$ -EPh species has been investigated through DFT calculations (Scheme 7). It has been revealed that the reaction involves three major steps, *i.e.*, activation of one of the two E–H bonds,

intramolecular isomerization, and the subsequent activation of the second E–H bond. The first E–H bond activation is a mono-metal-assisted  $\sigma$ -bond metathesis ( $\sigma$ BM) process, while the second E–H bond activation is achieved by the cooperation of three metal sites. The effect of the phenyl group in PhEH<sub>2</sub> has also been examined. It has been found that the phenyl group in PhNH<sub>2</sub> showed a significant steric effect for the N–H activation, but in the case of PhPH<sub>2</sub>, such steric effect was not observed. The relatively low energy barriers and significant exergonic feature lead us to predict that the trinuclear yttrium methylidene complex should be also effective for activation of NH<sub>3</sub> and PH<sub>3</sub>. In addition, a general behavior of the activation of C=X (X = O and S) and E–H (E = C, N, and P) bonds by multialkyl-bridged trinuclear rare-earth complexes has been described, which could be beneficial for further studies on the chemical transformations at multimetallic frameworks. (Published in *Organometallics*, 2017, 36, 4611.)



**Scheme 7.** Multimetal cooperation behavior of E–H (E = N, P) bond activation of PhEH<sub>2</sub> by a trinuclear yttrium methylidene complex.

#### 4. Conclusion

With the help of HOKUSAI system, (1) the hydrodenitrogenation of aromatic *N*-heterocycles by a titanium polyhydride complexes has been mechanistically investigated. The results may provide hints for designing new catalysts for the HDN of aromatic *N*-heterocycles under milder

conditions; (2) mechanistic aspect of N<sub>2</sub> activation by H<sub>2</sub> and a PNP-Ligated titanium complex have been investigated, offering the mechanistic information of dinitrogen cleavage and hydrogenation by H<sub>2</sub>; (3) the mechanism on polymerization of olefins catalyzed by cationic rare-earth metal complexes, such as *cis*-1,4-polymerization of dienes and monoolefin/diene copolymerization have been studied. The results could be helpful for understanding the factors determining activity and selectivity of polymerization and guide the design of new polymerization systems; (4) we have gained the mechanistic insights into Sc-catalyzed hydroaminoalkylation of olefins with amines by DFT studies, which could be helpful for developing regioselective hydroaminoalkylation reactions; (5) E–H (E = N, P) bond activation of PhEH<sub>2</sub> by a trinuclear yttrium methylidene complex has been theoretically studied, which could be beneficial for further studies on the chemical transformations at multimetallic frameworks. These studies were successful in unveiling the key role of rare-earth- and transition-metal complexes in chemical reactions.

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

In the future, the mechanism of a series of chemical reactions concerning the activation of  $\sigma$ -bond and unsaturated bond mediated by rare-earth and transition-metal complexes will continue to be studied. We will focus on the activation of small molecules by mononuclear or multinuclear transition-metal complexes. Besides, we will concentrate on the polar-monomer/olefin copolymerization catalyzed by rare-earth- and transition-metal complexes.

We wish to continue to use HOKUSAI system for the current long-term project. Although some primary results have been obtained, more systematic studies on the mechanism of newly discovered reactions mediated by rare-earth- and transition-metal complexes are obviously necessary.

**Fiscal Year 2017 List of Publications Resulting from the Use of the supercomputer**

**[Publication]**

- (1) Shaowei Hu, Gen Luo, Takanori Shima, **Yi Luo\***, Zhaomin Hou\* “Hydrodenitrogenation of Pyridines and Quinolines at a Multinuclear Titanium Hydride Framework”, *Nature Communications*, **2017**, *8*, 1866. (SCI, Impact Factor: 12.124)
- (2) Baoli Wang, Gen Luo, Masayoshi Nishiura, Shaowei Hu, Takanori Shima, **Yi Luo\***, Zhaomin Hou\* “Dinitrogen Activation by Dihydrogen and a PNP-Ligated Titanium Complex” *Journal of the American Chemical Society*, **2017**, *139*, 1818. (SCI, Impact Factor: 13.038)
- (3) Xingbao Wang, Xiaohui Kang, Guangli Zhou, Jingping Qu, Zhaomin Hou\*,\* and **Yi Luo\*** “DFT Studies on *cis*-1,4-Polymerization of Dienes Catalyzed by a Cationic Rare-Earth Metal Complex Bearing an Ancillary PNP Ligand” *Polymers* **2017**, *9*, 53. (SCI, Impact Factor: 2.944)
- (4) Xiaojie Hu, Xiaohui Kang, Guangli Zhou, Xingbao Wang, Zhaomin Hou\*, **Yi Luo\*** “DFT Studies on Isoprene/Ethylene Copolymerization Catalyzed by Cationic Scandium Complexes Bearing Different Ancillary Ligands” *Chinese Journal of Chemistry* **2017**, *35*, 723. (invited paper, SCI, Impact Factor: 1.872)
- (5) Fan Liu, Gen Luo, Zhaomin Hou\*,\* **Yi Luo\*** “Mechanistic Insights into Scandium-Catalyzed Hydroaminoalkylation of Olefins with Amines: Origin of Regioselectivity and Charge-based Prediction Model” *Organometallics*, **2017**, *36*, 1557. (ACS Editors’ Choice, SCI, Impact Factor: 3.862)
- (6) Gen Luo, **Yi Luo\***, Zhaomin Hou\* “E–H (E = N and P) Bond Activation of PhEH<sub>2</sub> by a Trinuclear Yttrium Methylidene Complex: Theoretical Insights into Mechanism and Multimetal Cooperation Behavior” *Organometallics*, **2017**, *36*, 4611. (Invited paper, SCI, Impact Factor: 3.862)
- (7) Baoli Wang, Gen Luo, Masayoshi Nishiura, **Yi Luo\***, Zhaomin Hou\* “Cooperative Trimerization of Carbon Monoxide by Lithium and Samarium Boryls” *Journal of the American Chemical Society*, **2017**, *139*, 16967. (SCI, Impact Factor: 13.038)
- (8) Chunxiang Wang, Gen Luo, Masayoshi Nishiura, Guoyong Song, Atsushi Yamamoto, **Yi Luo\***, Zhaomin Hou\* “Heteroatom-assisted Olefin Polymerization by Rare-earth Metal Catalysts” *Science Advances*, **2017**, *3*, e1701011.