

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 complexes 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 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 be clarified experimentally and so on. The computational chemistry has been used as a powerful tool to investigate the detailed mechanism and explain the observed reactivities, furthermore

predict and design promising catalyst according to the detailed electronic structure and reaction mechanism. Therefore, based on the experimental 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 2016, a large number of specified computational resources was used. The geometrical structures were optimized by DFT methods using Gaussian 09 software. Natural Bond Orbital (NBO) calculations were also carried out using some programs such as Gaussian 09, ADF and so on.

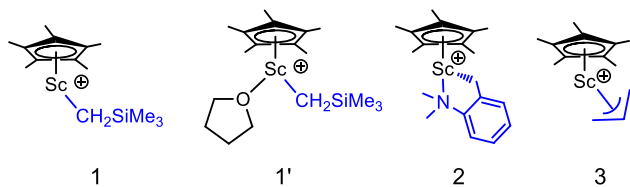
The B3PW91, TPSS/PSS, M06 functionals were utilized. Dispersion corrections were treated with the D3 version of Grimme's dispersion with Becke-Johnson damping (GD3BJ) as well. The QM/MM ONIOM method was also used for exploring larger systems, such as the third monomer insertion reaction, multinuclear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

3. Results

(a) Computational Analyses of the Effect of Alkyl on Chain Initiation Efficiency of Olefin Polymerization by Cationic Half-Sandwich Scandium Catalysts.

High-performance poly(olefins), which play an irreplaceable role in industrial production and in our daily lives, have attracted considerable interest in

academia and industry. The development of highly active olefin polymerization catalysts has become a primary impetus behind the evolution of new polymers. In the last decades, cationic rare-earth alkyl complexes have been reported to be a new family of olefin polymerization catalysts and have afforded a series of novel polymers that were hard to achieve previously. A cationic rare-earth-metal monoalkyl catalyst for olefin polymerization generally consists of four parts: metal center (M), ancillary ligands (L), alkyl (R), and an external neutral Lewis base (X) such as THF. All of these parts affect the polymerization performance. While numerous studies have been carried out to explore the effects of ancillary ligands and metal centers on polymerization performance, the correlation between the alkyls or Lewis base and polymerization properties has remained almost unexplored. In addition, mechanism concerning such alkyl effects on the induction period or chain-end microstructures at the chain initiation stage has remained unclear. We have carried out DFT calculations on the chain initiation of ethylene, propene, 1-hexene, styrene, butadiene, and isoprene polymerization mediated by the half-sandwich cationic rare-earth-metal Sc catalysts $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sc}(\text{CH}_2\text{SiMe}_3)(\text{THF})_n]^+$ ($n = 0$, **1**; $n = 1$, **1'**), $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)]^+$ (**2**), and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sc}(\eta^3\text{-C}_3\text{H}_5)]^+$ (**3**). (see Scheme 1).



Scheme 1. Cationic Scandium Alkyl Species Initiating Polymerization.

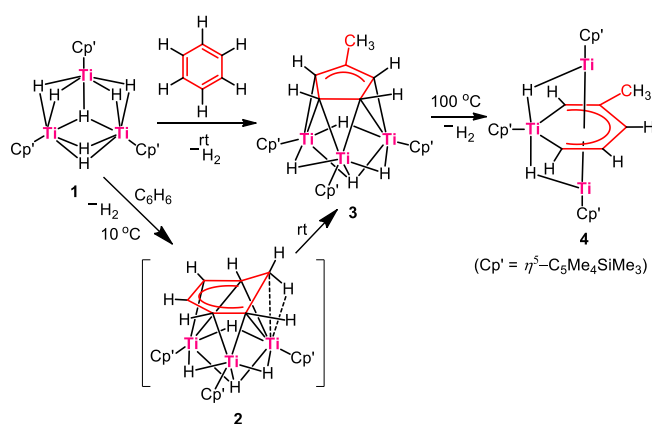
It is found that the less steric hindrance of species **3** provides the most stable coordination complexes, which could also be ascribed to the biggest chemical hardness and the closest frontier molecular orbital energy between **3** and monomers. All species-**1**-mediated processes are the most

kinetically favorable. Because of the larger hindrance of the aminobenzyl group in **2**, the coordination and insertion of olefin is the most difficult, thus leading to a longer induction period in comparison with other two species. The alkyls play no effect on the regioselectivity at the chain initiation stage of monoolefin polymerization. However, species **3** with allyl group prefers cis-fashion of dienes for insertion reaction, and species **2** results in bad regioselectivity in the chain initiation of styrene polymerization, which could be rooted in the steric hindrance of $-\text{NMe}_2$ group. In addition, it is found that the coordination of Lewis base THF decreases the activity of chain initiation, and species **1'** still shows higher chain initiation efficiency than species **2** in ethylene, styrene, and isoprene polymerizations. (Published in *Organometallics* **2016**, *35*, 913–920)

(b) Mechanism of Ring Cleavage and Contraction of Benzene catalyzed by a Titanium Hydride Cluster

Benzene is the most fundamental aromatic hydrocarbon compound and one of the most elementary petrochemicals. The hexagonal aromatic benzene ring is a ubiquitous structure motif, widely existing in natural resources such as petroleum and biomass. Cleavage of a benzene ring by transition metals is therefore of great interest and importance. However, the carbon skeleton of benzene is among the most robust chemical bonds because of its high aromaticity and non-polarity. We recently found that a trinuclear titanium polyhydride complex $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}]_3(\mu_3\text{-H})(\mu_2\text{-H})_6$ (**1**) could act as a unique platform for the activation of benzene, which sequentially transformed benzene to a monohydrogenated species $[\text{C}_6\text{H}_7]^{3-}$ (**2**), a ring-contraction product $[\text{MeC}_5\text{H}_4]^{3-}$ (**3**), and a ring-opening species $[\text{CHC}(\text{Me})(\text{CH})_3]^{5-}$ (a titanium insertion product) (**4**) under mild conditions (see Scheme 2). This is the first example of C–C bond cleavage and rearrangement of benzene by a metal complex at room temperature. However, the

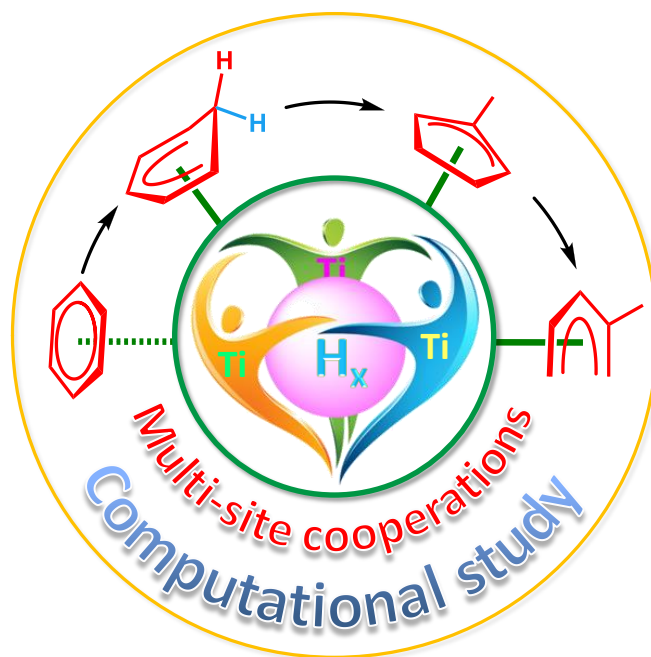
mechanistic details of this transformation are still unclear. Several fundamental questions arose from this intriguing discovery, such as, (1) how the reaction of benzene with the metal hydride is initiated, (2) how a six-membered ring is contracted (broken and rearranged) to a methyl-substituted five-membered ring, (3) how a titanium atom is inserted into the five-membered ring in **3** to give **4**, and (4) what possible roles the multiple metal hydrides can play. To answer these questions, we carried out theoretical calculations.



Scheme 2. Hydrogenation and ring cleavage and contraction of benzene by a molecular titanium hydride cluster.

By computationally modelling the reaction of benzene with the trinuclear titanium heptahydride complex **1**, we have elucidated the mechanistic details of the carbon-carbon bond cleavage and skeleton rearrangement of an aromatic compound over a multimetallic polyhydride framework. Coordination of benzene to **1**, could induce release of one molecule of H_2 . Subsequently, hydrometallation of the coordinated C_6H_6 unit can take place to afford a C_6H_7 species. Repeated C-C and C-H bond cleavage and formation in the C_6H_7 moiety, accompanied by rearrangement of the hydride ligands in **2**, would yield the ring contraction product MeC_5H_4 . The analogous C-C bond cleavage and C-H bond formation in the MeC_5H_4 unit in **3**, followed by metal framework rearrangement and H_2 release, could afford the metallacycle product **4**. (see Scheme

3). The mechanism elucidated for the ring cleavage and contraction of benzene can also be generally applied to the transformation of toluene, though structural isomerization of some reaction intermediates is needed to induce a C-C bond cleavage (ring-opening) because of the presence of a methyl substituent.



Scheme 3. Ring Cleavage and Contraction of Benzene over the Titanium Hydride Cluster.

Obviously, the dynamic rearrangements of the multiple hydride ligands and redox-active metal centers, and the cooperation of the multiple metal sites in the trimetallic hydride framework of **1** have played a critically important role throughout the whole transformation. The dearomatization (or three electron reduction) of a benzene ring via H_2 release and hydrometallation seems essential to induce the C-C bond cleavage (ring-opening). Oxidative addition and reductive elimination at the multimetallic framework are key elemental steps for the C-C (as well as C-H) bond cleavage and formation involved in the benzene ring cleavage and rearrangement. These findings should be of help for design of molecular metal catalysts for the activation and transformation of inactive aromatics. In particular, a multimetallic polyhydride framework

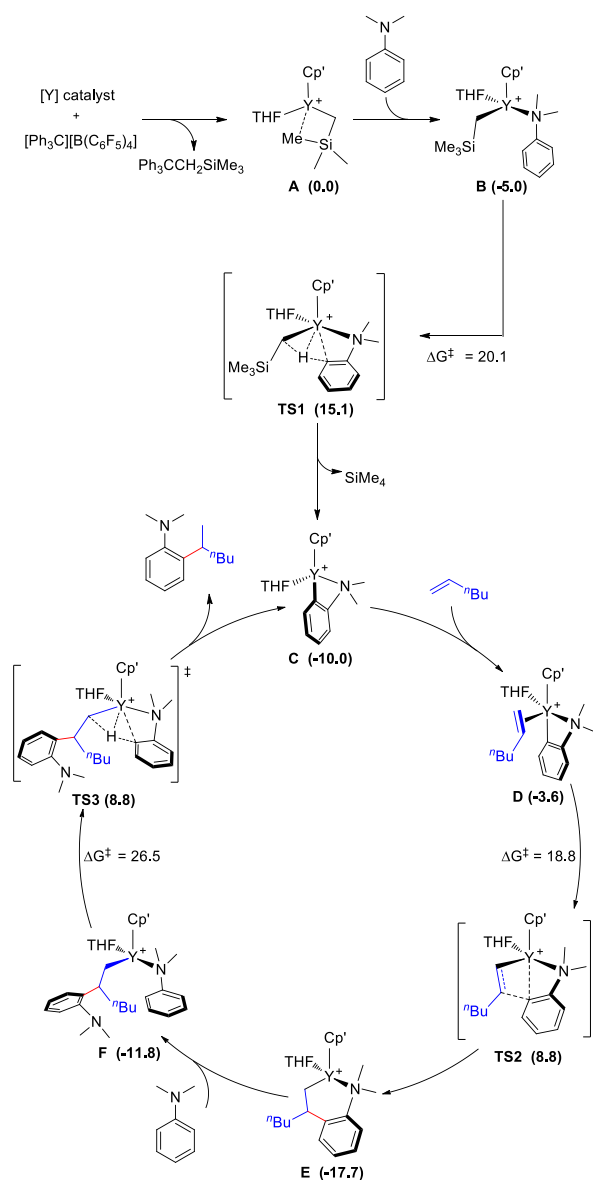
that possesses redox active metal centers and that can facilitate release of H₂ to provide electrons and alter charge population on the metal centers should be among the most desirable features or requisites for an active catalyst, as demonstrated by the complex **1**. (Published in *J. Am. Chem. Soc.* **2016**, *138*, 11550–11559)

(c) DFT Studies on *Ortho*-Selective C–H Addition of *N,N*-Dimethyl Anilines to Alkenes by a Yttrium Catalyst

Tertiary aniline is among the most important aromatic structural motifs in pharmaceuticals, fluorescent dyes, natural products and organic functional materials. Therefore, the development of efficient, atom-economical processes for the synthesis of aniline-containing compounds through direct C–H functionalization of aniline has received intensive attention. Among possible approaches, catalytic C–H addition to alkenes is the most straightforward and atom-economical method for the preparation of alkylated aniline derivatives. It is well known that the use of a directing group (DG) could lead to *ortho*-selective C–H alkylation of arenes with alkenes in the presence of transition metal catalysts through cyclometalation. However, it is difficult for dialkylamino groups such as NMe₂ directly bonded to an aromatic ring to act as a DG for the activation of an *ortho* C–H bond by a late transition metal catalyst, because the reaction would require the formation of an unfavourable four-membered, cyclometallated intermediate. To the best of our knowledge, catalytic *ortho*-selective C–H functionalization (either alkylation or alkenylation) of a tertiary aniline has not been reported previously.

Recently, we found the highly efficient, *ortho*-selective C–H addition of a wide range of *N,N*-dimethyl anilines to alkenes catalyzed by a cationic half-sandwich yttrium alkyl complex. This transformation represents the first example of *ortho*-specific C–H alkylation of *N,N*-dialkyl anilines with alkenes, efficiently affording a new family of

alkylated tertiary aniline derivatives which are otherwise difficult to prepare. However, the exact mechanism of this unprecedented transformation remains unknown, we performed DFT calculations on the reaction of *N,N*-dimethylaniline with 1-hexene to gain more insight into the mechanism of this transformation. (see Scheme 4).



Scheme 4. Catalytic Cycle by Yttrium Catalyst.

The coordination of *N,N*-dimethylaniline to a cationic yttrium alkyl species **A** generated from the reaction of yttrium catalyst with [Ph₃C][B(C₆F₅)₄] gives **B**, which then undergoes proton transfer via a four-centre transition state **TS1** to afford an *o*-dimethylaminophenyl yttrium species **C** with

release of SiMe_4 . Then, the coordination of the $\text{C}=\text{C}$ double bond of 1-hexene to the Y atom in **C** can take place to form **D**. Furthermore, the 1,2-insertion of 1-hexene into yttrium–phenyl bond generates a six-membered metallacycle complex **E** through a four-centre transition state **TS2**. Finally, the coordination of *N,N*-dimethylaniline to **E** affords **F**, which then undergoes intramolecular C–H activation through **TS3** to give the species **C**, with release of the final branched alkylation product. The DFT studies have revealed that the interaction between the amino group in the aniline substrate and the yttrium atom in the catalyst plays an important role in the *ortho* selective C–H activation of the aniline moiety. The intramolecular σ -bond metathesis reaction between an yttrium alkyl species and an *ortho* C–H bond of the aniline moiety is the rate-determining step, in agreement with the experimental KIE observations. (Published in *Chem. Sci.*, **2016**, *7*, 5265–5270)

4. Conclusion

With the help of RICC system, the alkyl effects on the chain initiation efficiency of olefin polymerization by cationic half-sandwich scandium catalysts have been investigated firstly. In this work, we studied the relationship between the alkyl of the cationic catalysts and the reactivity; Secondly, we have disclosed the mechanism of ring cleavage and contraction of benzene over a titanium hydride cluster, providing the theoretical information for further investigation on the benzene transformation; Finally, the mechanism on *ortho*-selective C–H addition of *N,N*-dimethyl anilines to alkenes by a yttrium catalyst has been analyzed, the disclosed mechanism would be beneficial for the design of new catalyst. 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 σ -bond and unsaturated bond mediated by

rare-earth and transition-metal complexes will continue to be studied. We will focus on the multimetallic cooperation effect as well as that between metal center and ligand. Besides, we will concentrate on the nonpolar monomer polymerization catalyzed by rare-earth metal complexes.

We wish to continue to use RICC 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 2016 List of Publications Resulting from the Use of the supercomputer

[Publication]

(1) Xiaohui Kang, Gen Luo, Lun Luo, Shaowei Hu, Yi Luo,* Zhaomin Hou* “Mechanistic Insights into Ring Cleavage and Contraction of Benzene over a Titanium Hydride Cluster” *Journal of the American Chemical Society* **2016**, *138*, 11550–11559.

(2) Xiaohui Kang, Guangli Zhou, Xingbao Wang, Jingping Qu, Zhaomin Hou,* Yi Luo*, “Alkyl Effects on the Chain Initiation Efficiency of Olefin Polymerization by Cationic Half-sandwich Scandium Catalysts: A DFT Study” *Organometallics* **2016**, *35*, 913–920.

(3) Guoyong Song, Gen Luo, Juzo Oyamada, Yi Luo,* Zhaomin Hou* “*Ortho*-Selective C–H Addition of N,N-Dimethyl Anilines to Alkenes by a Yttrium Catalyst” *Chemical Science* **2016**, *7*, 5265–5270.

(4) Gen Luo, Yi Luo*, Zhaomin Hou*, and Jingping Qu, “Intermetallic Cooperation in Olefin Polymerization Catalyzed by a Binuclear Samarocene Hydride: A Theoretical Study” *Organometallics* **2016**, *35*, 778–784.

(5) Xingbao Wang, Fei Lin, Jingping Qu, Zhaomin Hou, Yi Luo* “DFT Studies on Styrene Polymerization Catalyzed by Cationic Rare-earth Metal Complexes: Origin of Ligand-dependent Activities” *Organometallics* **2016**, *35*, 3205–3214.