Usage Report for Fiscal Year 2016

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 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 be clarified 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

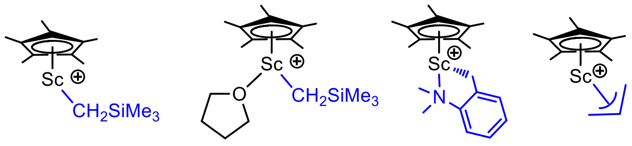
During the fiscal year 2016, most of specified computational resources was used. The geometry structures were optimized by DFT methods using Gaussian 09 software. Natural Bond Orbital (NBO) calculations were also carried out using some programs such as Gaussian 09, ADF and so on.

The B3PW91, M06-2X, 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 catalyzed reaction and the interaction between the counter-anion and cationic active species.

3. Results

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

Recently, numerous well-defined catalysts with high activity and high selectivity for polymerization based on group 4 and late transition metal complexes have been synthesized successfully, which effectively promoted the design and development of novel polymer materials. Hou et al. found that the THF-containing half-sandwich scandium complex [(η^5-$C_5Me_4SiMe_3$)Sc(CH_2SiMe_3)$_2$THF] as a precursor could give cyclopolymer of 1,6-heptadiene (HPD) with lower molecular weight and rather broad molecular weight distribution in comparison with the THF-free complex [(η^5-$C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-o)$_2$]. In addition, half-sandwich scandium complex such as [(η^5-$C_5Me_4SiMe_3$)Sc(CH_2SiMe_3)$_2$THF], in the presence of a proper activator, showed excellent activity and selectivity toward the (co)polymerization of a wide range of olefins, such as (co)polymerization of styrene with ethylene, 1,3-dienes, and other olefins. Aforementioned THF-free aminobenzyl complex in combination with an activator showed unprecedented activity for the copolymerization of 1-hexene with dicyclopentadiene. Although some effects of the alkyl and THF have been found in the aforementioned polymerization experiments, the molecular mechanism concerning with such alkyl effects on the induction period or chain-end microstructures at chain initiation stage has remained unclear. Therefore, 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 [(η^5-C_5Me_5)Sc(CH_2SiMe_3)(THF)$_n$]$^+$ (n = 0, **1**; n = 1, **1′**), [(η^5-C_5Me_5)Sc($CH_2C_6H_4NMe_2$-*o*)]$^+$ (**2**), and [(η^5-C_5Me_5)Sc(η^3-C_3H_5)]$^+$ (**3**). (see Scheme 1).



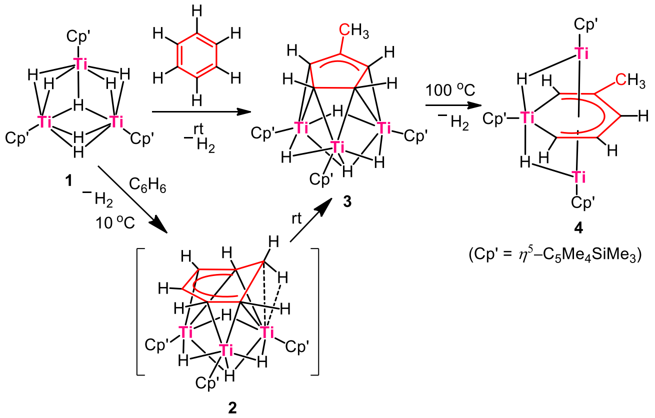
1 1′ 2 3

Scheme 1. Cationic Scandium Alkyl Species Initiating Polymerization.

It has been found that **2** with largest steric demanding aminobenzyl group results in the lowest initiation efficiency and thus longest induction period among the three catalysts investigated. In contrast, **1** with CH_2SiMe_3 displays the best chain initiation ability, and **3** with η^3-allyl gives moderate chain initiation activity mainly due to the most stable resulting coordination complex. Species **1** and **3** have better regioselectivity in the chain initiation of styrene polymerization than species **2**. In addition, species **1′** ([(η^5-C_5Me_5)Sc(CH_2SiMe_3)THF]$^+$) with THF ligand indicates better chain initiation efficiency in styrene and isoprene polymerizations than species **2** but reasonably worse than analogous **1** without THF ligand. (Published in *Organometallics* **2016**, *35*, 913−920)

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

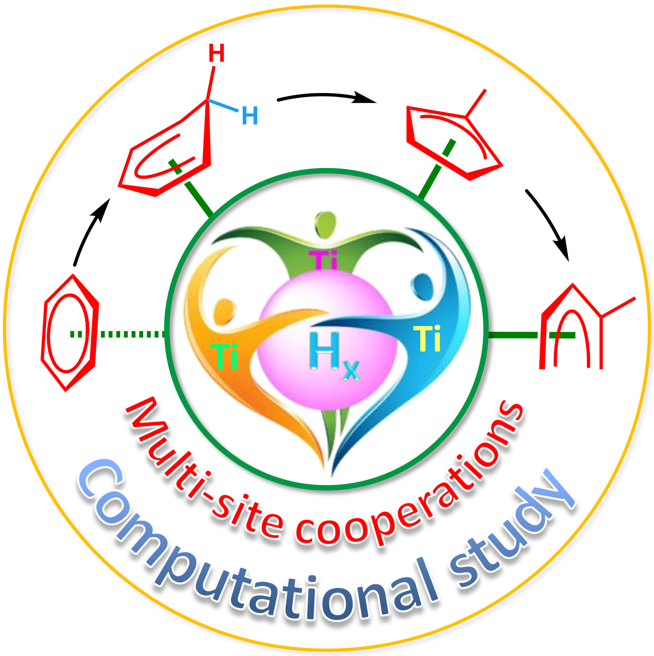
In contrast to a great number of examples of C–H bond cleavage and functionalization, studies on the C–C bond cleavage of a benzene skeleton which is the most fundamental aromatic hydrocarbon compound and one of the most elementary petrochemicals are scarce. In the industrial naphtha hydrocracking process, the cleavage of a benzene ring is performed on solid catalysts at high temperatures, which usually yields a mixture of several products, including the ring-contraction product methylcyclopentane and ring-opening acyclic saturated hydrocarbons. Because of the complexity of the catalyst system and difficulty in identifying the true active species in solid catalysts, little molecular-level information is available concerning the C–C bond cleavage and rearrangement. Microorganisms are known to degrade aromatic compounds under ambient conditions, but the mechanistic details are not clear and difficult to mimic. We recently found that a trinuclear titanium polyhydride complex [($C_5Me_4SiMe_3$)Ti]$_3$(μ_3-H)(μ_2-H)$_6$ (**1**) could act as a unique platform for the activation ofbenzene, which sequentially transformed benzene to a monohydrogenatedspecies [C_6H_7]$^{3-}$(**2**), a ring-contraction product [MeC_5H_4]$^{3-}$ (**3**), and a ring-opening species [CHC(Me)(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.

We found that dynamic rearrangement of the hydride ligands in the trimetallic framework could easily take place, thereby facilitating the activation of benzene through coordination of benzene to a titanium atom and the subsequent H_2 release, C=C double bond hydrometallation, and C–C (as well as C–H) bond cleavage and formation. These findings have provided unprecedented insights into the mechanistic details of the C−C bond activation and transformation of a benzene ring over a been reported, most of which concerned the reactions taking place in quite special circumstances such as relief of ring strain, formation of an aromatic system, chelation-assisted cyclometallation, and *β*-carbon elimination. Regarding ring multimetallic framework, and may also help design new catalysts for the activation and transformation of inactivated aromatics. (Published in *J. Am. Chem. Soc.* **2016**, *138*, 11550−11559)



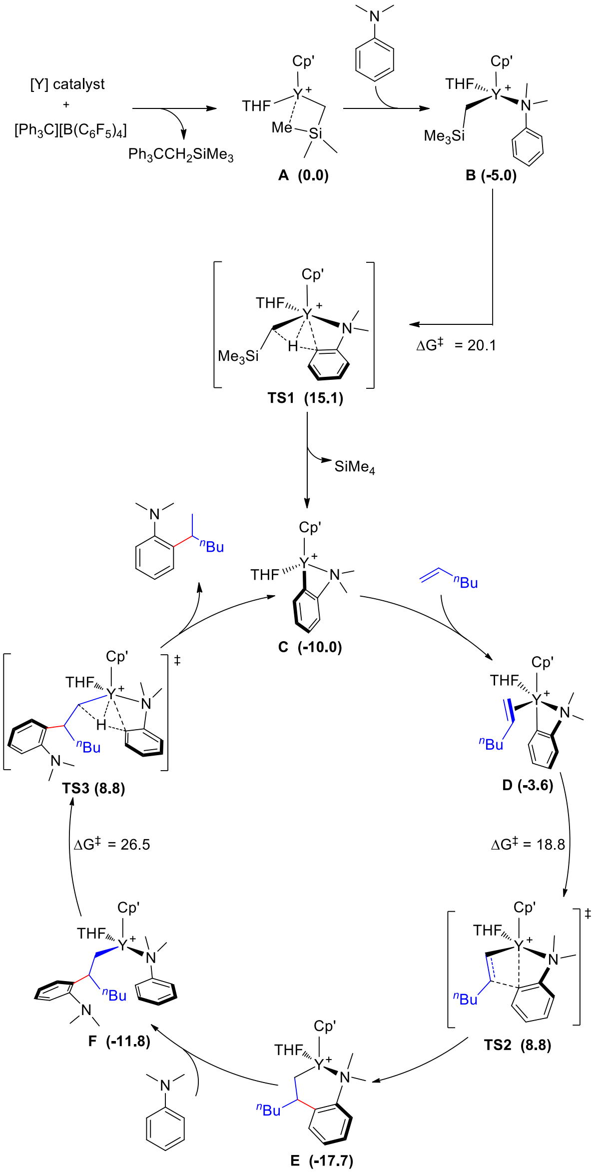
Scheme 3. Ring Cleavage and Contraction of Benzene over the Titanium Hydride Cluster.

(c) Computational 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. Catalytic C–H addition to alkenes is the most straightforward and atom-economical method for the preparation of alkylated aniline derivatives. However, direct C–H alkylation of tertiary anilines has met with limited success to date, mainly because of the low activity of a dialkylamino group to serve as a directing group (DG) for transition-metal catalysed C–H activation and easy *β*-H elimination of transition metal alkyl species. 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, because it is difficult for dialkylamino groups such as NMe$_2$ 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

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).

The coordination of *N,N*-dimethylaniline to a cationic yttrium alkyl species **A** generated from the reaction of yttrium catalyst with [Ph$_3$C][B(C$_6$F$_5$)$_4$] 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 C=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 metallacyle 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



Scheme 4. Catalytic Cycle by Yttrium Catalyst.

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, firstly, we have studied the alkyl effects on the chain initiation efficiency of olefin polymerization by cationic half-sandwich scandium catalysts; Secondly, the mechanism of ring cleavage and contraction of benzene over a titanium hydride cluster have been disclosed, 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 detail mechanism would be benefit for the design of new catalyst. These studies were successful in unveiling the key role of rare-earth and transition-metal complexes in these 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 studies. 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. At this stage, although some results have been obtained, more systematic results on the mechanism of newly discovered reactions mediated by rare-earth- and transition-metal complexes are expected.

Usage Report for Fiscal Year 2016

Fiscal Year 2016 List of Publications Resulting from the Use of the supercomputer

[Publication]

⑴ 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.

⑶ 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.

⑶ 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.

⑷ 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.

⑸ 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