RICC Usage Report for Fiscal Year 2014

Project Title:

Computational Studies on Rare-Earth-Metal Polyhydride Clusters and Their Catalytic Activations of Organic Substrates

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1. Background and purpose of the project

Rare earth alkyl and hydride complexes are among the most reactive organometallic compounds due to its wide applications in stoichiometric and catalytic reactions. Their synthesis and reactivity has been received intensive attention in recent decades in the field of organometallic chemistry. Compare to mononuclear complexes, multinuclear complexes often show unique reactivity and high activity. Such superiority may benefits from their unique substrate activation and novel reaction patterns on basis of the possible cooperation effects between adjacent active metal centers. Additionally, high electronic density at the metal center makes the multinuclear polyhydride clusters be much more active than other metal clusters toward the activations of organic substrates. In recent years, Hou and coworkers have successfully synthesized series of rare-earth- and transition-metal polyhydride complexes which showed extremely high activity and selectivity in activation of small moleculars, such as CO, CO_2, H_2 and N_2. 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

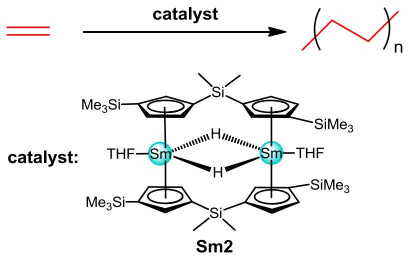
During the fiscal year 2014, large part of specified computational resources was used.

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 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

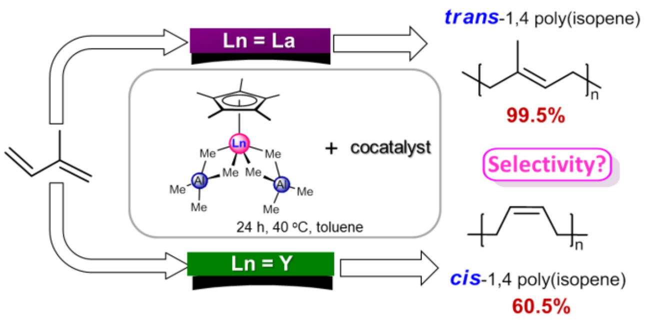
(a) Mechanism of Ethylene Polymerization by a Binuclear Samarium Hydride Complex. Polyolefins are very important chemical products in modern industry and a variety of high-performance polyolefin materials have been widely applied in our daily lives. Previously, numerous theoretical studies on the related olefin polymerization by mononuclear catalysts have successfully explained the experimental observations such as activity and selectivity, and effectively promoted the design and development of new catalysts. However, the related knowledge of olefin polymerization mechanism by multinuclear catalysts, which are of great current interest, is still in its infancy. We have carried out DFT calculations on the mechanism of ethylene polymerization by a dinuclear samarium hydride complex $[Me_2Si(C_5H_3\text{-}3\text{-}Me_3Si)_2SmH]_2$ (**Sm2**) (see Scheme 1).



Scheme 1. 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 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. (under preparation for publication)

(b) Isoprene Polymerization Catalyzed by a Cationic La-Al Binuclear Complex. Similar to dinuclear rare-earth hydride system, to have more information on olefin polymerization by bi- or multi-nuclear rare-earth catalysts, we choose a practical system of isoprene polymerization by Ln-Al (Ln = La and Y) binuclear cationic complexes. As we know, *cis*-1,4-polyisoprene (> 99% *cis* content), featuring low melting point, high solubility, and high elasticity, is a key component of natural rubber for tires and adhesives, whereas its isomer *trans*-1,4-polyisoprene called Gutta-percha is thermoplastic crystalline polymer with high hardness and high tensile strength, mainly used as the medical materials and a key component of tires-sides and tread rubbers. Thus far, the precise control on the microstructure of the isoprene polymers with specific properties has remained a very attractive and everlasting topic. Attracted by the strong correlation of the catalytic performance on the aluminum reagents, as well as the sophisticated mechanism of polymerization catalyzed by bimetallic systems, in this work, we focus on the mechanism of *trans*-1,4 (*cis*-1,4) polymerization of isoprene mediated by cationic rare earth and Al heterobimetallic half-sandwich complexes $[(C_5Me_5)Ln(AlMe4)]^+$ (Ln = La and Y) (see Scheme 2).

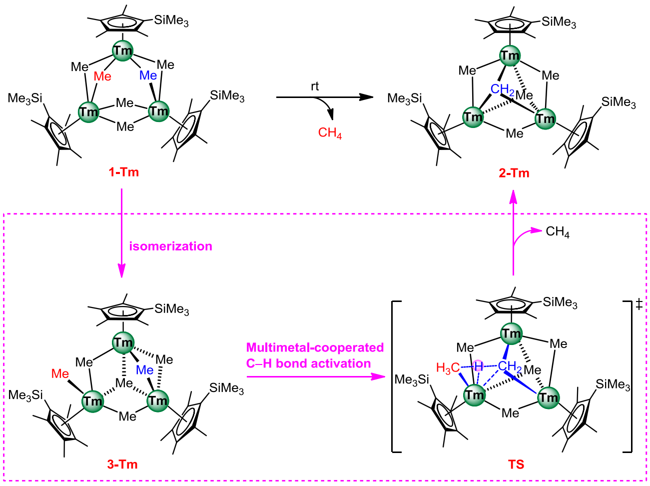


Scheme 2. Isoprene polymerization by Ln-Al (Ln = La and Y) binuclear complexes.

Three objectives are to be addressed in the current theoretical study. The first is to investigate the structure of the active species. The second is to explore the polymerization mechanism of isoprene in La–Al bimetallic systems. The third is to unveil the origin of dramatic difference in the polymerization selectivity between La and Y systems. We hope that the results reported here would give valuable information to the development of more efficient rare-earth metal polymerization systems.

We carefully examined the possible active species, the mechanism of chain initiation and propagation, and the selectivity and so on. The results show that the bare active species $[(C_5Me_5)La(\mu_2\text{-}Me)_3AlMe]^+$ (**A**) and $[(C_5Me_5)La(\mu_2\text{-}Me)_2AlMe_2]^+$ (**B**) is more stable than species $[(C_5Me_5)La(Me)(\mu_2\text{-}Me)AlMe_2]^+$ (**C**). The isoprene-coordinated complexes $\mathbf{Coo^{A}_{t}}$, $\mathbf{Coo^{B}_{t}}$, and $\mathbf{Coo^{C}_{t}}$ have also been located for bare species **A**, **B**, and **C**, respectively. Kinetically, the chain initiation promoted by $\mathbf{Coo^{B}_{t}}$ is less favorable than the transformation from $\mathbf{Coo^{B}_{t}}$ to $\mathbf{Coo^{C}_{t}}$, and the chain initiation promoted by $\mathbf{Coo^{A}_{t}}$ was failed because of big steric hindrance around La center. The chain initiation promoted by complex **Coo**$^{\mathrm{C}}_{\mathrm{t}}$ has relatively lower energy barrier and the **C** could be the true active species for chain initiation. During the chain propagation, the monomer insertion achieving *trans*-1,4 polymer occurs at La center of **Coo**$^{\mathrm{C}}_{\mathrm{t}}$ with $AlMe_3$ moiety as a ligand, whereas La/Al bimetal-cooperated monomer insertion pathways have been found to be unfavorable. The current calculation results indicate that the experimentally observed *trans*-1,4 stereoselectivity is under thermodynamic control. Interestingly, in the Y analogous system, the $AlMe_3$ ligand tends to go away from the Y center during the chain propagation, which results in a more favorable process producing *cis*-1,4 polyisoprene. This discrepancy could be ascribed to the larger ionic radius of La and less favorable dissociation of $AlMe_3$ moiety from the La center in comparison with the case of analogous Y system. Having achieved good agreement with experimental results, it is proposed that the $AlMe_3$ moiety serves as a ligand coordinating to La center via one of the three Me groups during the La-catalyzed *trans*-1,4 polymerization of isoprene but it dissociates from the rare earth metal center in the analogous Y system producing *cis*-1,4 polymer, suggesting a crucial role of the $AlMe_3$ moiety in the regulation of stereoselectivity in such polymerization systems. (Published in *Macromolecules* **2014**, *47*, 4596.)

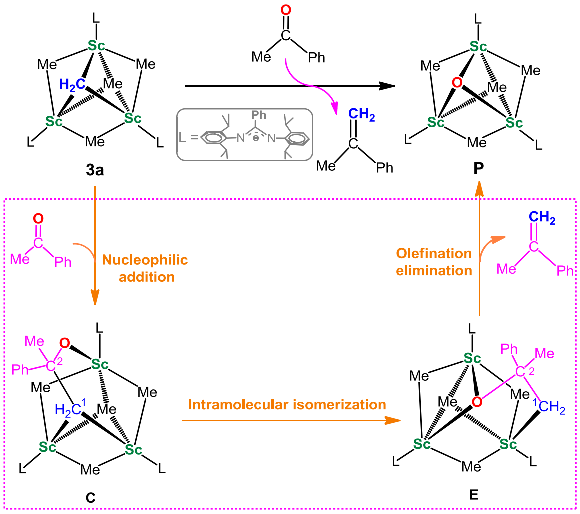
(c) C–H Bond Activation in a Trinuclear Rare-earth Polymethyl Complex. Like multinuclear polyhydride systems, multinuclear polyalkyl complexes have similar structural characteristics and also show high activity in chemical bond activations, such as C–H, P–H, N–H, C=O, C=S and so on. These bond activations often achieved by the intermetallic cooperation of multimetal sites. A better understanding of the behavior of the multimetal cooperation is also benefit to explore the rare-earth polyhydride complexes. However, the mechanism on such kind of reactions is far from fully understood. Based on the experimental fact reported by Hou's group, we performed DFT calculations on the process of methane elimination via an intramolecular C−H bond activation of a polymethyl trinuclear rare-earth metal complex (see Scheme 3).



Scheme 3. Intramolecular C–H bond activation of a trinuclear rare-earth polymethyl complex.

As shown in Scheme 3, the release of methane was achieved through rearrangement of Tm−CH_3 connections to form one terminal μ_1-CH_3 moiety and subsequent C−H activation to give the experimentally observed product. Interestingly, in the favorable C−H activation step, a μ_2-CH3 group changed its coordination manner from μ_2 to μ_3 mode prior to hydrogen transfer. This change in coordination manner process is a multimetal-cooperating σ-bond metathesis event, which enriches the known chemistry of σ-bond metathesis (σ-BM). It has been found that the cooperation of trimetallic centers makes the C−H bond activation kinetically easier in comparison with that of bimetallic centers. To the best of our knowledge, such a multimetal-cooperated σ-bond metathesis process for C−H bond activation is reported for the first time. The computed vertical dissociation energies of μ_n-C(H_3)−Tm and μ_n-C(H_2)−H (n = 1−3) bonds follow the order $\mu_3 < \mu_2 < \mu_1$ for the C−H bond and the reverse trend for the Tm−C bond. Such trends could result in a better understanding of the current finding that the coordination mode of a methyl group changed from μ_2 to terminal μ_1 fashion prior to accepting a hydrogen and releasing methane and that the hydrogen transfers from μ_3-CH_3 rather than μ_2-CH_3 to the terminal μ_1-CH_3. In addition, the 4f electrons do little effect on the geometry and reaction energy profile of such a trinuclear lanthanide cluster, which is similar to that of mononuclear lanthanide complexes reported previously. (Published in *Organometallics* **2014**, *33*, 1126.)

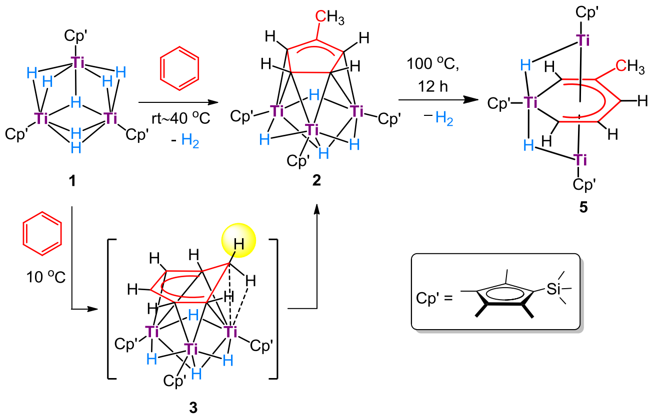
(d) C=O Bond Activation by a Trinuclear Rare-earth Polymethyl Complex. As mentioned above, multinuclear rare-earth polyalkyl complexes could show high activity to C=O double activation. Recently, a series of trinuclear methylidene complexes showed unique reactivity towards carbonyl complex, acting as methylidene transfer reagents, leading to terminal alkenes and rare-earth metal μ_3-oxygen complexes (a metal Wittig-type reaction). As we known, the mechanism of conventional Wittig reaction (metal-free reaction) or Wittig-type methylenation of ketones by Tebbe's reagent (monometal-mediated) and *gem*-dizinc reagent are generally considered to follow a two-step mechanism, viz., the initial addition and subsequent elimination. However, the mechanism of metal Wittig-type reaction mediated by multinuclear complexes has remained unclear to date. Here, the reaction of **3a** (as a metal Wittig reagent) with acetophenone to give α-methylstyrene and trinuclear 3-oxygen complex **P** (Scheme 4) was used as a model reaction to investigate the mechanism of carbonyl methylenation process (the CH_2^{2-}/O^{2-} group interchange) assisted by trinuclear rare-earth metal methylidene complexes and the behaviour of metal-connected μ_3-CH_2 group during the transfer process.



Scheme 4. C=O double bond activation by a trinuclear rare-earth polymethyl complex.

The result indicates that such an event assisted by cooperating multimetal sites is mechanistically different from carbonyl methylenation by conventional Wittig reaction or other methylidene reagents. The analysis of Wiberg bond indexes and the electron occupations clearly indicate that the reaction occurs via three stages, viz., (a) nucleophilic addition, (b) intramolecular isomerization, and (c) olefination elimination. The CH_2^{2-}/O^{2-} group interchange process (the bond-breaking and -forming of C=O and C=C bonds) mainly occurs at stage (a) and (c). During the stage (b), the complex undergoes intramolecular isomerization with the assistance of cooperating multimetal sites in preparation for further bond interchange. The frontier molecular orbital analysis of the two key transition states gives us a better understanding of bond-breaking and -forming processes. The natural charges clearly display that the electron transfer occurs at stages (a) and (c), and no electron transfer occurs in middle stage (b), in sharp contrast to other carbonyl olefination reactions. This study not only enriches the chemistry of metal Wittig-type reaction but also sheds light on the intermetallic cooperation for methylidene transfer leading to terminal olefin. (Published in *Organometallics* **2015**, *34*, 366.)

(e) **Benzene skeleton rearrangement at a molecular titanium polyhydride complex.** Like Group 3 (rare-earth-metal) polyhydride clusters, Group 4 multinuclear polyhydride complexes were also synthesized recently and a trinuclear titanium polyhydride complex $[(C_5Me_4SiMe_3)Ti]_3(\mu_3\text{-}H)(\mu_2\text{-}H)_6$ (**1**) exhibited unusual activity in activating the inert nitrogen N_2 and leading the N–N bond cleavage and N−H bond formation. We have performed DFT calculations to reveal its detailed mechanism, including the processes of N_2 coordination, the first and second H_2 elimination, N–N bond cleavage and N–H bond formation (see *Science* **2013**, *340*, 1549.). After that, Hou and coworkers examined carefully whether the hydride cluster could activate other chemically inactive molecules such as benzene. Fortunately, they found the reactions of the hydride cluster **1** with benzene involved various events, including C=C double-bond hydrometallation, H_2 release, and C–H and C–C bond cleavage and formation (see Scheme 5).



Scheme 5. Reaction of a trinuclear titanium polyhydride complex with benzene.

Unlike previous reports that benzene transform to methylcyclopentane and acyclic saturated hydrocarbons through C=C bond cleavage and rearrangement on the surfaces of solid catalysts, the current reaction occurs at the molecular titanium polyhydride. This work thus demonstrates that multimetallic titaniumhydrides such as **1** can serve as a unique platform for the activation of aromatic molecules, offering new opportunities for the transformation and functionalization of inactive aromatics. Due to its great significance with respect to the production of fuels and valued chemicals from natural resources such as petroleum and biomass, the experimental results were published in Nature (Nature, **2014**, *512*, 415). However, it's difficult to investigate the detailed mechanism experimentally. To get more information about such important transformations, we investigated the process of reactions shown in Scheme 5 by DFT calculations. The results indicate that the reaction of benzene with **1** starts with coordination activation of benzene via three-electron reduction, followed by ring-opening and hydride transfer to generate an intermediate with an acyclic C_5H_5Me moiety. The ring-contraction, -opening, and -rotation as well as H_2 release then sequentially occurs to give the final product with a six-membered metallacycle, as experimentally observed. The agostic interaction assisted oxidation addition and terminal hydrogen promoted H_2 elimination are the characters of such processes. It is certainly due to the cooperation of the multiple Ti–H sites that all of these different events could be accomplished at once. The current DFT result would be also benefit for us to understand the industrial processes of the transformation of benzene to methylcyclopentane. (been prepared for publication)

4. Conclusion

With the help of RICC system, the mechanisms of olefin polymerization by a binuclear samarium hydride complex and cationic Ln-Al (Ln = La and Y) binuclear complexes have been investigated. Additionally, we also focused on the mechanisms of C–H and C=O bond activation in multinuclear polyalkyl complexes. These studies effectively help us to recognize the behaviors of the multimetal cooperation during the chemical reactions. Finally, we give a detailed study on benzene skeleton rearrangement at a molecular titanium polyhydride cluster. The results show that the cooperation of the multiple Ti–H sites plays an important role during the transformation and would be also benefit for us to understand the industrial processes of the transformation of benzene to methylcyclopentane.

5. Schedule and prospect for the future

In the future, the mechanisms of a series of σ-bond and unsaturated bond, including P–H, N–H S–H, N≡N, C=C, C≡O and C=O, activated by multinuclear 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.

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 2014 List of Publications Resulting from the Use of RICC

[Publications]

(1) Xiaohui Kang, **Yi Luo***, Guangli Zhou, Xingbao Wang, Xuerong Yu, **Zhaomin Hou**, Jingping Qu. "Theoretical mechanistic studies on the *trans*-1,4-specific polymerization of isoprene catalyzed by a cationic La−Al binuclear complex" *Macromolecules*, **2014**, *47*, 4596–4606.

(2) Gen Luo, **Yi Luo***, Wen-Xiong Zhang, Jingping Qu, **Zhaomin Hou***. "DFT studies on the methane elimination reaction of a trinuclear rare-earth polymethyl complex: σ-bond metathesis assisted by cooperation of multimetal sites" *Organometallics*, **2014**, *33*, 1126–1134.

(3) Gen Luo, **Yi Luo***, Jingping Qu, **Zhaomin Hou***. "Mechanistic insights into the methylenation of ketone by a trinuclear rare-earth-metal methylidene complex" *Organometallics*, **2015**, *34*, 366−372.