

Project Title:

DFT Studies on the Electronic Structures and the Reaction Mechanisms of Multinuclear Polyhydride Complexes

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Background and purpose of the project, relationship of the project with other projects

The chemical reaction of transition-metal polyhydride clusters have been of special interest in recent decades in the field of organometallic chemistry. Multi-metal sites' cooperative effect makes the metal polyhydride cluster to be much more active than other mononuclear clusters toward the activations of organic substrates. Group 4 transition metal hydride complexes have received much interest because of their importance in various chemical transformations. Group 4 metal hydride complexes of the half-sandwich type "[Cp)MH_n]", which bear one cyclopentadienyl ligand per metal, have hardly been studied, although such complexes are of much interest both structurally and chemically. In 2013 our lab (Organometallic Chemistry Laboratory, Chief Scientist: Zhaomin Hou) has successfully synthesized a series of Group 4 tri- and tetranuclear polyhydrides. Especially, the trinuclear titanium polyhydrides can induce dinitrogen cleavage and partial hydrogenation at ambient temperature and pressure (Science, 2013, 340, 1549). At present, a series of new polyhydride cluster and new reactions are in process.

Besides, multinuclear polyalkyl compounds have similar structural characteristics to multinuclear polyhydride complexes 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. For example, our lab reported that trinuclear rare-earth polymethyl complex can eliminate a methane molecule by intramolecular C-H bond activation to give a trinuclear methyldiene complex (*J. Am. Chem. Soc.* **2011**, *133*,

5712.). As for trinuclear rare-earth methyldiene complexes, they often show unique reactivity towards carbonyl complex, acting as methyldiene transfer reagents, leading to terminal alkenes and rare-earth metal μ_3 -oxygen complexes (a metal Wittig-type reaction). All these transformations are very interesting and useful, however, the related mechanisms are unclear and it's difficult to investigate experimentally. A better understanding of the behavior of the multimetal cooperation is also benefit to explore the multinuclear polyhydride complexes.

Computational chemistry plays a key role in uncovering the electronic structures of multi-metal clusters and exploring reaction mechanisms. In literatures, numerous theoretical studies on reaction processes have successfully explained the experimental observations (such as reactivity and selectivity) and effectively promoted the design and development of new catalysts. For example, our Lab has successfully elucidated the detailed mechanism of N₂ activation by trinuclear titanium polyhydride complex by DFT calculations. The result shows the multimetallic cooperation effect plays an important role during the reaction. To have a better understanding on the new reactions, numerous Gaussian jobs need to be carried out, which could be effective to develop new clusters and to fully explore other inert substrates activation.

Specific usage status of the system and calculation method

From Oct. 2014, more than 57,000 core*hours have been used.

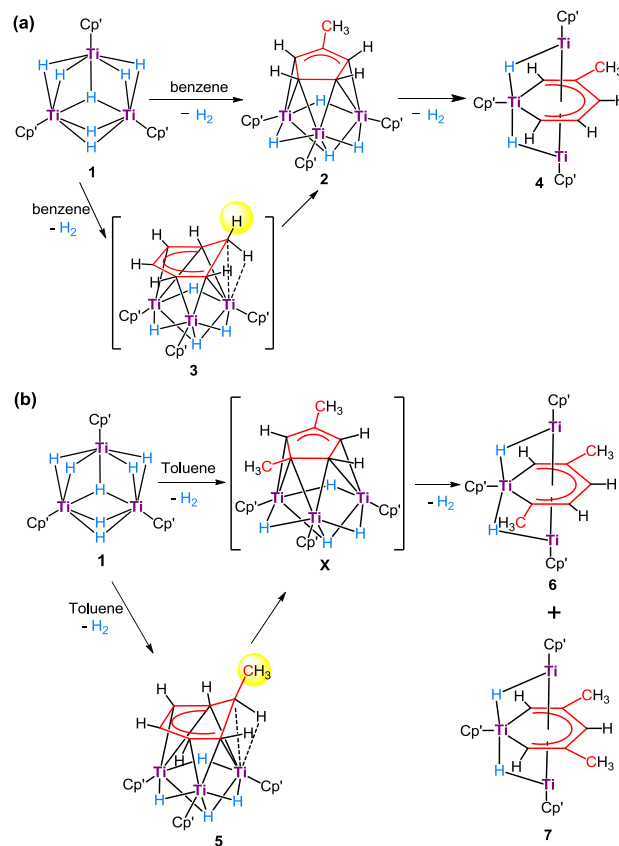
All the structures were optimized using Gaussian 09 software with DFT methods.

Result

After the study of N_2 activation, Hou and coworkers examined carefully whether the multinuclear hydride cluster could activate other chemically inactive molecules such as benzene. Fortunately, they found the reactions of the hydride cluster $[(C_5Me_4SiMe_3)Ti]_3(\mu_3-H)(\mu_2-H)_6$ (**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. These transformations also work for toluene. 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. 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 result was published in *Nature* (*Nature*, **2014**, *512*, 415). Particularly, the understanding of these processes would be also benefit for us to understand the industrial processes of the transformation of benzene to methylcyclopentane. However, the detailed mechanism is difficult to investigate by experiment approach. In this situation, we preformed DFT calculations to reveal the related processes of reactions of polyhydride complex **1** with benzene and toluene shown in Scheme 1.

DFT calculations suggest that the reaction is initiated by the approach of a benzene or toluene molecule to the Ti atoms in **1** with release of one molecule of H_2 , analogously to the reaction of **1** with N_2 reported previously. Then six-membered ring-opening and hydride transfer occur 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 structures along with the reaction pathway clearly indicate that the

cooperation of the multiple Ti-H sites and Ti-Ti play an important role in achieving the transformation. The agostic interaction assisted oxidation addition and terminal hydrogen promoted H_2 elimination are the characters of such processes.



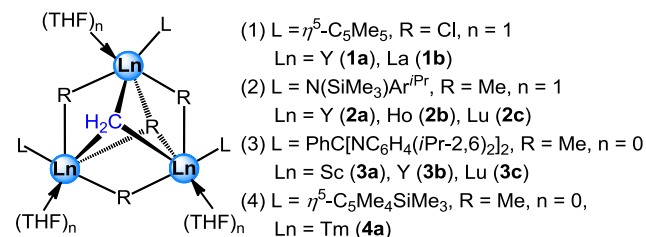
Scheme 1. Reactions of a trinuclear titanium polyhydride **1** with benzene (a) and toluene (b).

This work thus shows 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. (Prepare to submit)

Trinuclear rare-earth metal methylenide (CH_2^{2-}) complexes are an emerging class of compounds which have a striking structural feature with a " $Ln_3(\mu_3-CH_2)$ " (Ln = rare-earth metals) motif (See Chart 1). Due to highly reactive of methylenide motif, these compounds could activate many chemical bonds such as C-H, P-H, N-H and so on. Moreover, most of these trinuclear methylenide complexes have shown unique reactivity towards carbonyl complex, acting as methylenide transfer reagents, leading to terminal alkenes and rare-earth metal μ_3 -oxygen

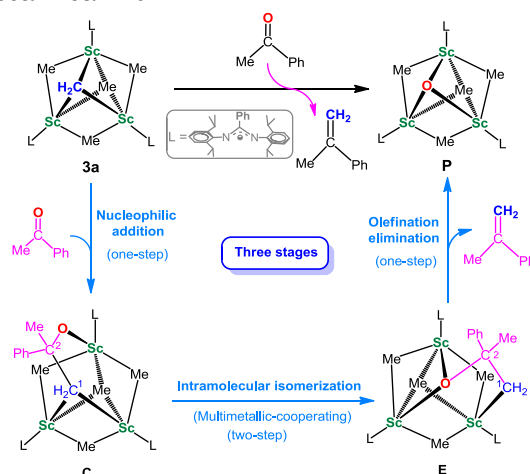
complexes (a metal Wittig-type reaction).

Chart 1. Homometallic Trinuclear Rare-earth Metal Methylidene Complexes



Although a series of homometallic trinuclear rare-earth metal methylidene complexes and their reactivity as methylidene transfer agents have been explored experimentally, the related theoretical study is still in its infancy possibly due to the huge computational consumption and complexities in the calculations of multinuclear systems. Herein, the reaction of **3a** (as a metal Wittig reagent) with acetophenone to give α -methylstyrene and trinuclear μ_3 -oxygen complex **P** (See Scheme 2) 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 $\mu_3\text{-CH}_2$ group during the transfer process.

As shown in Scheme 2, methylidene complex undergoes a nucleophilic addition reaction with acetophenone to an intermediate **C** having a bridging structure supported by three metal centers. With the aid of multimetallic-cooperating effect, complex **C** further isomerizes to complex **E**. Finally, the elimination occurs via a multimetal-assisted four-center transition state leading to the final product α -methylstyrene and trinuclear μ_3 -oxygen complex **P**, which was structurally identified experimentally.



Scheme 2. C=O double bond activation by a trinuclear rare-earth polymethyl complex.

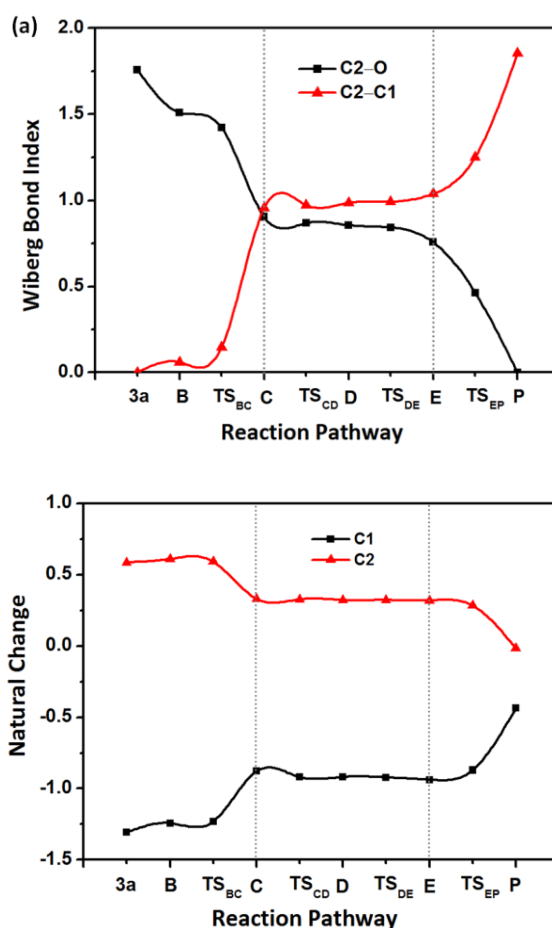


Fig. 1. The change of Wiberg bond indexes (WBIs) for C2–O and C2–C1 bond and natural charges for C1 and C2 atoms along with the reaction pathway.

Interestingly, the changes of WBIs in Fig. 1 obviously demonstrate that the whole reaction occurs via three stages. That is, (a) weakening C2=O to C2–O single bond and formation of C2–C1 single

bond (nucleophilic addition, from **3a** to **C**), (b) intramolecular isomerization retaining single bond characters of C2–O and C2–C1 bonds (from **C** to **E**), and (c) cleavage of C2–O single bond and formation of C2=C1 double bond (olefination elimination, from **E** to **P**). This result is markedly different from the cases of pervious carbonyl methylenation, which is generally considered as a two-step reaction, viz., the initial addition and subsequent elimination step. In current system, the CH₂²⁻/O²⁻ group interchange process (the bond-breaking and -forming of C2=O and C2=C1 bonds) mainly occurs in stage (a) and (c). During the stage (b), with the assistance of the cooperating multimetal sites, the complex undergoes intramolecular isomerization for further bond interchange. (See Fig. 1) The change of natural charges also indicates that the reaction includes three stages as demonstrated in Fig. 1. This is contrast to the case of carbonyl methylenation by *gem*-dizinc reagent, in which the charge changes monotonously from the reactant to the product.

This work is the first example of mechanistic study on multimetal-cooperating methyldene (CH₂) transfer leading to terminal olefin and does demonstrate new insights in Wittig-type chemistry. The results show that the mechanism of the CH₂²⁻/O²⁻ group interchange process in such trinuclear complexes goes through a three-step mechanism being in sharp contrast to known two-step mechanism. Additionally, the current result provide us a better understanding of the behaviour of intermetallic cooperation for methyldene (CH₂) transfer in such newly uprising trinuclear complexes. (Published in *Organometallics* **2015**, *34*, 366.)

Conclusion

During the last several months, we have performed DFT calculations on multinuclear polyhydride and polyalkyl complexes. Based on our group's experimental results, we carried out DFT

calculations on benzene and toluene skeleton rearrangement at a molecular titanium polyhydride. The structures along with the reaction pathway clearly indicate that the cooperation of the multiple Ti–H sites and Ti–Ti play an important role in achieving the transformation. This work thus shows 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.

As for multinuclear polyalkyl complexes, we focus on the newly uprising trinuclear methyldene compounds. The reaction of methyldene compound **3a** (as a metal Wittig reagent) with acetophenone was investigated. This work is the first example of mechanistic study on multimetal-cooperating methyldene transfer leading to terminal olefin and does demonstrate new insights in metal Wittig-type chemistry.

Schedule and prospect for the future

Firstly, I am very grateful that I can use RICC for calculations. I will continue to study the mechanisms of the multinuclear complexes. At present, some new experimental results have been found in our group and their mechanism need to be clarified with the help of DFT calculations, such as the activation of N₂, CO, CO₂ and pyridine. Therefore, I want to get the continuous support from RICC in the future.

RICC Usage Report for Fiscal Year 2014

Fiscal Year 2014 List of Publications Resulting from the Use of RICC

[Publication]

- (1) **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. (Dec 19, 2014)