

Project Title:**Computational Studies on Rare-Earth-Metal Polyhydride Clusters and Their Catalytic Activations of Organic Substrates****Name:** OYi LUO**Laboratory at RIKEN:** Organometallic Chemistry Laboratory**Background and purpose of the project**

The reaction chemistry of transition metal polyhydride clusters have been received intensive attention in recent decades in the field of organometallic chemistry. High electronic density at the metal center makes the metal polyhydride cluster to 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 polyhydrides which showed extremely high activity and selectivity in small molecular activation. Having a better understanding on these reaction processes could be instrumental to develop new clusters and to full utilization of challenging inert substrates activation. 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.

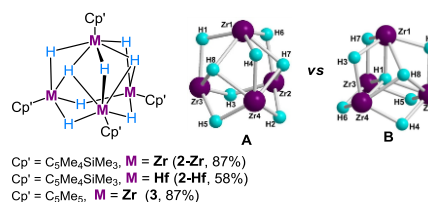
Specific usage status of the system and calculation method

70 percent of specified computational resources were used. The DFT method planted in Gaussian 09 and ADF programs were used.

Result

Group 4 transition metal hydride complexes have received much interest because of their importance in various chemical transformations. However, group 4 metal hydride complexes of the

half-sandwich type “[$(Cp)MH_n$]”, which bear one cyclopentadienyl ligand per metal have hardly been studied. Recently, Hou developed a series of tetranuclear group 4 transition metal octahydride complexes $[(C_5Me_4R)_4M_4(\mu-H)_8]$ ($M = Ti, Zr, Hf$) were synthesized. Interestingly, X-ray diffraction studies revealed that these hydride clusters possess two μ_3-H and six μ_2-H ligands, which is different from the previously reported Y complex contained μ_4-H ligand. The two kind of modes were compared (**A** and **B** in Chart 1) and their bonding manners are further clarified by DFT studies.

Chart 1. Tetranuclear Octahydride Complexes

Both the Haber-Bosch and biological ammonia syntheses are thought to rely on the cooperation of multiple metals in breaking the strong $N \equiv N$ triple bond and forming an $N-H$ bond. This has spurred investigations of the reactivity of molecular multimetallic hydrides with dinitrogen. Hou report here the reaction of a trinuclear titanium polyhydride complex with dinitrogen, which induces dinitrogen cleavage and partial hydrogenation at ambient temperature and pressure. For its mechanism, we performed DFT calculations. In the light of the computational results and experimental observation, we have determined that the dinitrogen reduction proceeds sequentially through scission of an N_2 molecule bonded to three Ti atoms in a

$\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-end-on-side-on}$ fashion to give a $\mu_2\text{-N}/\mu_3\text{-N}$ dinitrido species, followed by intramolecular hydrogen migration from Ti to the $\mu_2\text{-N}$ nitrido unit (see Fig. 1).

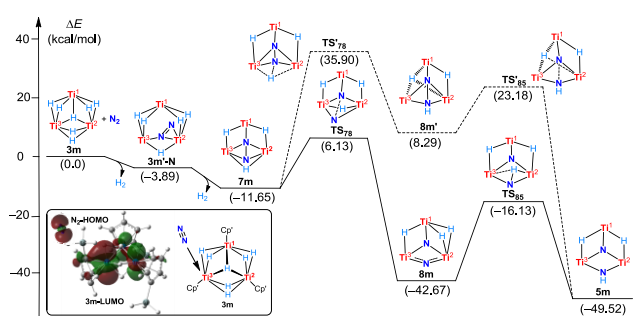


Fig. 1. Computational analysis of the reaction of trinuclear titanium polyhydride complex with N_2 .

Similar to polyhydride systems, in multinuclear polyalkyl systems, they also have high activity in chemical bond activations. The intermetallic cooperation always plays an important role in achieving chemical reactions. However, the mechanism of the reaction assisted by multimetal sites is far from fully understood. Based on the experimental fact, DFT studies have been performed for the process of methane elimination via an intramolecular C–H bond activation of the polymethyl trinuclear rare-earth-metal complex. 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 (see Fig. 2). The computed vertical dissociation energies of $\mu_n\text{-C}(\text{H}_3)\text{-Tm}$ and $\mu_n\text{-C}(\text{H}_2)\text{-H}$ ($n = 1\text{--}3$) 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 $\mu_3\text{-CH}_3$ rather than

$\mu_2\text{-CH}_3$ to the terminal $\mu_1\text{-CH}_3$.

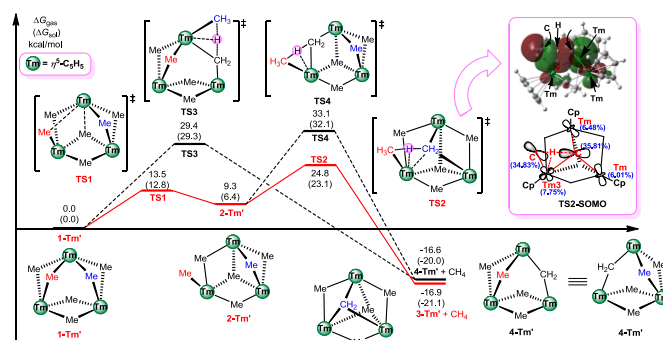


Fig. 2. Energy profile for the methane elimination reaction of $1\text{-Tm}'$.

Conclusion

With the help of RICC system, the electronic structures of $[(\text{C}_5\text{Me}_4\text{R})_4\text{M}_4(\mu\text{-H})_8]$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) were calculated and it confirms that the structures without an interstitial $\mu_4\text{-H}$ ligand, in contrast with the case for analogous rare-earth polyhydride complexes. Additionally, the detailed mechanism of N_2 activation by $[(\text{C}_5\text{Me}_4\text{SiMe}_3)_3\text{Ti}_3\text{H}_7]$ has been also elucidated. Finally, we give a detailed process of the methane elimination reaction, which was demonstrated to occur via multimetal-cooperated σ -bond metathesis.

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, $\text{N}=\text{N}$, $\text{C}=\text{C}$, and $\text{C}=\text{O}$, activated by multinuclear polyhydride /polyalkyl complexes will be studied.

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 multinuclear polyhydride /polyalkyl complexes are expected.

Fiscal Year 2013 List of Publications Resulting from the Use of RICC

[Publication]

- (1) Takanori Shima, Shaowei Hu, Gen Luo, Xiaohui Kang, **Yi Luo**, Zhaomin Hou* “Dinitrogen Cleavage and Hydrogenation by a Trinuclear Titanium Polyhydride Complex”, *Science* **2013**, *340*, 1549–1552.
- (2) Kei Nishii, Xiaohui Kang, Masayoshi Nishiura, **Yi Luo**, Zhaomin Hou* “Regio- and stereospecific living polymerization and copolymerization of (*E*)-1,3-pentadiene with 1,3-butadiene by half-sandwich scandium catalysts”, *Dalton Trans.* **2013**, *42*, 9030–9032
- (3) Shaowei Hu, Takanori Shima*, **Yi Luo***, Zhaomin Hou* “Tetranuclear zirconium and hafnium polyhydride complexes composed of the “CpMH₂” units”, *Organometallics* **2013**, *32*, 2145–2151.
- (4) 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**, dx.doi.org/10.1021/om400920x.