

Project Title:

Density functional theory studies on the mechanisms of transition metal mediated chemical transformations

Name:

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

Main group element or metal-assisted chemical transformation has been received much attention in the past decades due to its important role in organic synthesis and organometallic chemistry. An understanding of the exact reaction mechanism is an essential aspect of chemistry in general, which would be helpful for improving the activity and selectivity of the reactions as well as for designing more efficient complexes and new reactions. As we know that it is difficult to isolate and detect intermediates during many chemical reactions experimentally. Density functional theory (DFT) calculation as a powerful tool play an important role in exploring chemical reaction mechanisms. In the past few years, I have made some efforts on mechanism investigation of homogeneous chemical reactions. In recent years, Prof. Zhaomin Hou (Chief Scientist, Organometallic Chemistry Laboratory) did lots of excellent works in homogeneous chemical reactions, such as dinitrogen cleavage and hydrogenation, benzene cleavage and rearrangement. With the aid of the RIKEN Supercomputer system, we have successfully elucidated the detailed mechanism of N_2 and benzene activation by the trinuclear titanium polyhydride complex. Obviously, it is computationally found that the synergy of the dynamic rearrangement of the hydride ligands, the facile redox of the titanium metal centres, and the cooperation of the multiple metal sites in the multimetallic hydride framework that has enabled those transformations of unsaturated substrates.

Hou and co-workers continue to develop new reactions experimentally. To have a better understanding of related reactions at the molecular level, density functional theory (DFT) calculations are obviously required to explore the detailed mechanisms, which could be effective to develop new catalysts and new reactions. In FY2018, some important combined experimental and theoretical results have been published in high level journals.

2. Specific usage status of the system and calculation method

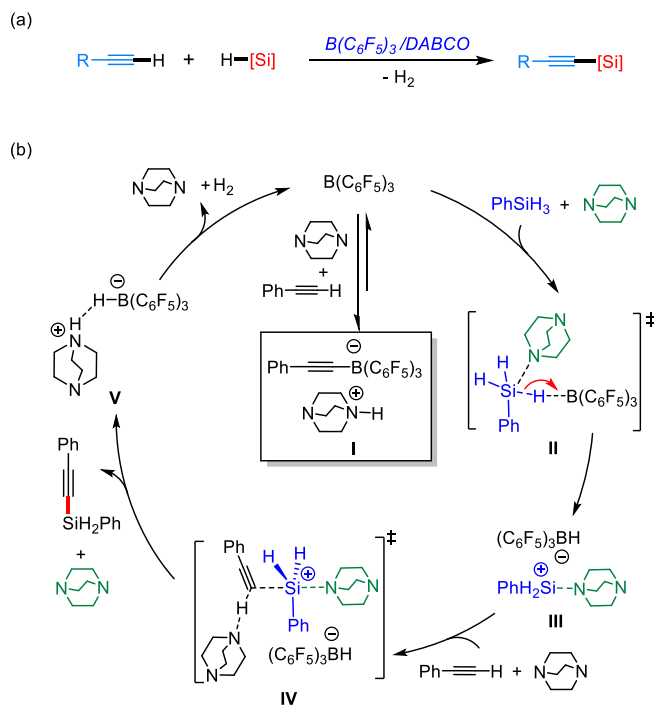
In FY2018, about 420 kilo core*hours were used for my General Use project. All calculations were performed by Gaussian 09 or Gaussian 16 software together with DFT methods.

3. Result

(1) $B(C_6F_5)_3$ /Amine-Catalyzed C(sp)-H Silylation of Terminal Alkynes with Hydrosilanes

Transition-metal-catalyzed C-H functionalization of organic compounds has proved to be a useful atom-efficient strategy in organic synthesis. In contrast, main-group-element-based catalytic processes for C-H functionalization have remained much underexplored to date. Very recently, Hou et al reported the catalytic C(sp)-H silylation of a wide range of terminal alkynes with hydrosilanes by a combination of $B(C_6F_5)_3$ and an organic base such as triethylenediamine (DABCO). This protocol constitutes the first example of boron-catalyzed C(sp)-H functionalization, offering a convenient route for the synthesis of a

variety of alkynylsilanes. To have a better understanding of such transformation, we performed DFT calculations on the mechanism based on the model reaction of phenylacetylene with phenylsilane (see Scheme 1). It is computationally found that the reaction works in a new base-assisted mechanism, in which DABCO plays critically important dual roles during the catalytic transformation (*i.e.*, One is acting as a Lewis base to stabilize the cationic PhSiH_2^+ species and the other is serving as a Brønsted base to deprotonate a terminal alkyne.), thus offering unprecedented insights into the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed C–H silylation reactions. This work was published in *Angew. Chem. Int. Ed.* **2018**, *57*, 15222–15226.

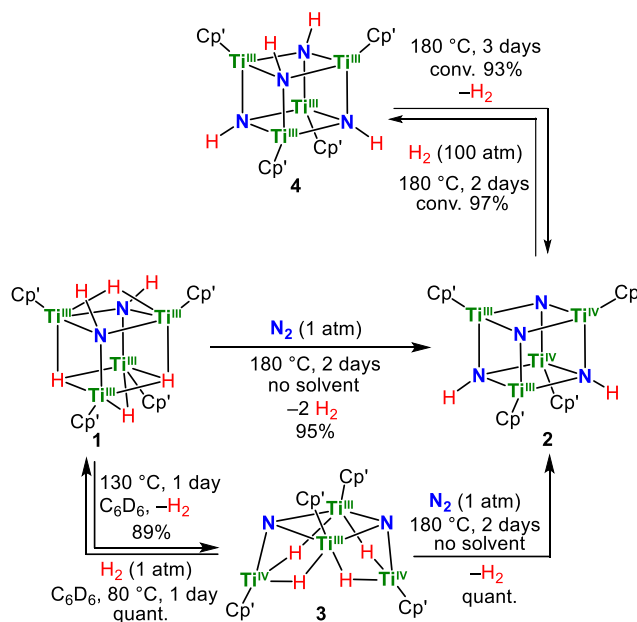


Scheme 1. Proposed catalytic cycle based on experimental and DFT studies.

(2) Dinitrogen Activation and Hydrogenation at a Tetranuclear Titanium Imide/Hydride Framework

The activation of N_2 by a tetranuclear titanium(III) diimide/tetrahydride complex $[(\text{Cp}'\text{Ti})_4(\mu_3\text{-NH})_2(\mu\text{-H})_4]$ (**1**) ($\text{Cp}' = \text{C}_5\text{Me}_4\text{SiMe}_3$), which was obtained by the reaction of the Cp' -ligated titanium trialkyl complex $\text{Cp}'\text{Ti}(\text{CH}_2\text{SiMe}_3)_3$ with H_2 and N_2 , was

investigated in detail by experimental and DFT studies. The reaction of **1** in solid state with N_2 (1 atm) at 180°C gave the dinitride/diimide complex $[(\text{Cp}'\text{Ti})_4(\mu_3\text{-N})_2(\mu_3\text{-NH})_2]$ (**2**) through the incorporation, cleavage, and partial hydrogenation of one molecule of N_2 and release of two molecules of H_2 . At 130°C , the formation of **2** was not observed, but instead, the dehydrogenation of **1** took place through cleavage of the N–H bond in an imide ligand followed by deprotonation of the other imide ligand with a hydride ligand, affording the dinitride/tetrahydride complex $[(\text{Cp}'\text{Ti})_4(\mu_3\text{-N})_2(\mu\text{-H})_4]$ (**3**). Upon heating under N_2 (1 atm) at 180°C , **3** was quantitatively converted to the dinitride/diimide complex **2** (see Scheme 2).



Scheme 2. Activation and transformation of N_2 at a tetranuclear titanium framework.

DFT calculations suggest that this transformation was initiated by migration of a hydride ligand to a nitride ligand to give one imide unit followed by N_2 coordination to a Ti atom and H_2 release through the reductive elimination of two hydride ligands. The other imide ligand in **2** was formed by hydride migration to one of the two nitride ligands generated through the cleavage of the newly incorporated N_2 unit. The hydrogenation of **2** with H_2 (100 atm) at 180°C

afforded the tetraimide complex $[(\text{Cp}^*\text{Ti})_4(\mu_3\text{-NH})_4]$ (**4**). This reaction was initiated by σ -bond metathesis between H_2 and a titanium–nitride bond followed by migration of the resulting hydride ligand to the remaining nitride ligand. It was also computationally found that the hydrogenation of **4** with H_2 to give an amide species needs to overcome an energy barrier of as high as 46.8 kcal/mol, which is kinetically inaccessible under the experimental conditions. In all of these transformations, the interplays among the hydride, imide, and nitride ligands, including the reversible dehydrogenation/hydrogenation of imide and nitride species, at the multimetallic titanium framework played a critically important role. This work was published in *J. Am. Chem. Soc.*, **2019**, DOI: 10.1021/jacs.8b13341.

4. Conclusion

In summary, with the aid of DFT calculations, the reaction process of $\text{B}(\text{C}_6\text{F}_5)_3/\text{DABCO}$ -catalyzed $\text{C}(\text{sp})\text{-H}$ silylation of terminal alkynes with hydrosilanes was carefully investigated. It is computationally found that the reaction works in a new base-assisted mechanism, in which DABCO plays critically important dual roles during the catalytic transformation (both acting as Lewis base and Brønsted base), thus offering unprecedented insights into the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed C-H silylation reactions.

Besides, the reaction of dinitrogen activation and hydrogenation at a tetranuclear titanium imide/hydride framework have been computationally revealed that the interplays among the hydride, imide, and nitride ligands, including the reversible dehydrogenation and hydrogenation of the imide and nitride species in the multimetallic titanium framework played a critically important role in the activation and transformation of N_2 . This work has provided unprecedented molecular-level details of N_2 activation at a multimetallic platform, and may

also help better understand the mechanistic aspects of the biological nitrogen fixation and the industrial Haber-Bosch process.

5. Schedule and prospect for the future

In FY2019, I will continue to collaborate with Prof. Zhaomin Hou (Organometallic Chemistry Laboratory) and study the mechanisms of the metal-mediated homogeneous chemical reactions, including small molecule activation, olefin polymerization, C-H alkylation and so on. The mechanism will also be investigated by DFT calculations. Therefore, I want to get the continuous support from RIKEN Supercomputer System in the future.

Fiscal Year 2018 List of Publications Resulting from the Use of the supercomputer

- (1) Takanori Shima[‡], **Gen Luo[‡]**, Shaowei Hu, Yi Luo*, **Zhaomin Hou***. Experimental and Computational Studies of Dinitrogen Activation and Hydrogenation at a Tetranuclear Titanium Imide/Hydride Framework. *J. Am. Chem. Soc.* **2019**, DOI: 10.1021/jacs.8b13341. (‡Contributed equally to this work, SCI, Impact Factor: 14.357.)
<https://pubs.acs.org/ccindex.cn/doi/10.1021/jacs.8b13341>

- (2) Yuanhong Ma, Shao-Jie Lou, **Gen Luo***, Yong Luo, Gu Zhan, Masayoshi Nishiura, Yi Luo, **Zhaomin Hou***. “B(C₆F₅)₃/Amine-Catalyzed C(sp)-H Silylation of Terminal Alkynes with Hydrosilanes: Experimental and Theoretical Studies” *Angew. Chem. Int. Ed.* **2018**, *57*, 15222–15226. (SCI, Impact Factor: 12.102)