

Project Title:

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

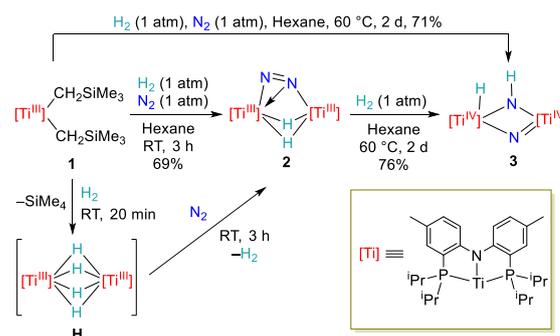
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1. Background and purpose of the project

The activation of inert substrates by transition metal complexes is significant and filled with challenges in organic synthesis and organometallic chemistry. After many effects on this topic, our lab has found that multinuclear transition metal polyhydrides have high reactivity to many inert substrates. For instance, the trinuclear titanium polyhydride can induce dinitrogen cleavage and partial hydrogenation at ambient temperature and pressure (*Science*, **2013**, *340*, 1549.) and carbon-carbon bond cleavage and rearrangement of benzene (*Nature*, **2014**, *512*, 413; *J. Am. Chem. Soc.*, **2016**, *138*, 11550). This unusually high reactivity of the multinuclear polyhydride complex motivated us to examine carefully other hydride clusters toward to activate inert small molecules.

Very recently, after carefully check the different ligands, we found that the reaction of H₂ with a PNP-ligated titanium dialkyl complex $\{(\text{PNP})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\}$ (**1**, PNP = N(C₆H₃-2-PⁱPr-4-CH₃)₂) could afford a binuclear titanium tetrahydride complex $\{[(\text{PNP})\text{Ti}]_2\text{H}_4\}$, which could further react with N₂ to give a imido/nitrido/hydrido complex $\{[(\text{PNP})\text{Ti}]_2(\mu\text{-NH})(\mu\text{-N})(\text{H})\}$ (**3**) in the presence of H₂ (Scheme 1). However, the important processes of N₂ cleavage and hydrogenation (the transformation **2** to **3**) are difficult to be clarified due to the limitation of experimental technique. To clarify the detailed mechanism, density functional theory calculations are performed.

Scheme 1. Activation and Hydrogenation of N₂ by H₂ at a PNP-Ti Platform

2. Specific usage status of the system and calculation method

In the past 6 months, about 555,800 core*hours were used. The “GWACSL” resources were used up and more than 70% were used for the “GWACSG” resources.

All calculations were performed with Gaussian 09 software.

3. Result

The computed energy profile of the most favorable pathway is shown in Figure 1. Addition of H₂ across to a Ti–N bond in **2m** (a model of **2**) could take place via a transition state **TS1** with an energy barrier of 20.2 kcal/mol to give intermediate **A**. The isomerization of the μ_2, η^1, η^2 -(HN=N) unit in **A** to a μ_2, η^2, η^2 -(HN=N) unit accompanied by the reduction of the HN=N double bond to a HN–N single bond and the oxidation of the two Ti(III) sites to Ti(IV) could give intermediate **B**. Release of one molecule of H₂ from **B** by the reductive elimination of two hydride (H⁻) ligands from the Ti(IV) sites then takes place via **TS3** to give intermediate

C, in which the two titanium sites are formally reduced to Ti(III). Finally, cleavage of the N–N bond accompanied by the oxidation of Ti(III) to Ti(IV) affords the thermodynamically stable imide/nitride product **3m**, which is equivalent to **3** observed experimentally. The whole transformation of **2m** to **3m** is exergonic by 39.8 kcal/mol. The overall energy barrier is 26.5 kcal/mol, which is reasonable in view of the experimental conditions.

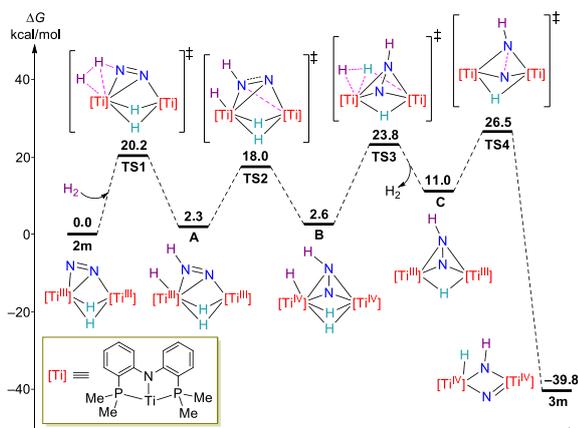


Fig. 1. Computed energy profile for the transformation of **2m** (a model of **2**) to **3m** (a model of **3**) in the presence of H₂.

To see if the transformation of **2** to **3** could take place without the aid of external H₂, the intramolecular hydrogen migration from titanium to the dinitrogen unit in **2m** was also computed. It was found that this process requires overcoming an energy barrier of more than 32 kcal/mol, suggesting that an intramolecular hydrogen migration would be difficult under the current experimental conditions (60 °C). This is in contrast with what was observed in the N₂ activation by the trinuclear titanium polyhydride complex $\{[(C_5Me_4SiMe_3)Ti]_3(\mu_3-H)(\mu_2-H)_6\}$, in which N–N bond cleavage and N–H bond formation occurred in an intramolecular fashion without need for external H₂.

4. Conclusion

The DFT calculations revealed that the important transformation of the dinitrogen unit in **2** to the imido/nitrido species in **3** is initiated by the hydrogenation of the dinitrogen unit with an external H₂, followed by release of another molecule of H₂ from the titanium framework and the subsequent cleavage of the N–N bond. The mechanistic aspect on the special role of H₂ found in this study probably offer new insights for understanding the mechanistic aspects of the heterogeneous Haber-Bosch process.

5. Schedule and prospect for the future

Actually, I also do some preliminary studies of other chemical reactions at this moment. I hope that I can accomplish these studies and continue to explore new reactions with the aid of ACCC. At present, some new experimental results have been found in our group and their mechanisms need to be further clarified by DFT calculations, such as the activation of H₂, CO, pyridine, and olefin polymerization *etc.* Therefore, I want to get the continuous support from RICC in the new FY.

Usage Report for Fiscal Year 2016

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

[Publication]

Baoli Wang[†], **Gen Luo**[†], Masayoshi Nishiura, Shaowei Hu, Takanori Shima, Yi Luo*, and Zhaomin Hou* “*Dinitrogen Activation by Dihydrogen and a PNP-Ligated Titanium Complex*” *J. Am. Chem. Soc.*, **2017**, *139*, 1818–1821. (†equal contribution. January 30, 2017)