

Project Title:**Density functional theory studies on the mechanisms of transition metal mediated chemical transformations****Name:** Gen Luo**Laboratory at RIKEN:** Organometallic Chemistry Laboratory**1. Background and purpose of the project**

Metal-assisted chemical transformation has been received much attention in the past decades due to its important role in organic synthesis and organometallic chemistry. The activation of inert substrates by transition metal complexes is significant and filled with challenges. After many efforts on this topic, our lab previously found that multinuclear polyhydrides have high reactivity to many inert substrates. For instance, the trinuclear titanium polyhydrides 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.

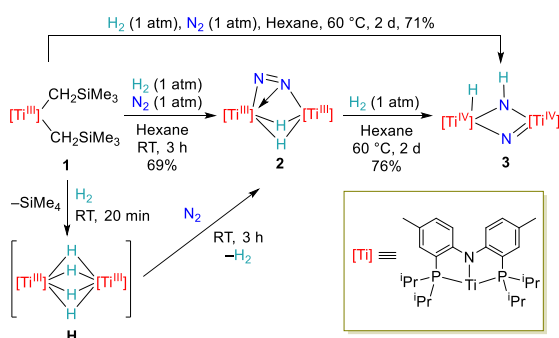
The activation and functionalization of dinitrogen (N_2) is a long-standing important research subject, because N_2 is an abundant and easily accessible resource, but it is highly inert under ordinary conditions. Industrially, the cleavage and hydrogenation of N_2 is achieved by reaction with H_2 at high temperatures (350–550 °C) and high pressures (150–350 atm) on solid catalysts to afford ammonia (NH_3) (the Haber-Bosch process). This is the only commercially successful process using N_2 gas as a feedstock. In order to have a better understanding of the

N_2 activation mechanism and thereby achieve ammonia synthesis under milder conditions, extensive studies on the activation of N_2 by molecular organometallic complexes have been carried out over the past decades. It has been reported that the reduction and cleavage of N_2 could be achieved at ambient temperature and pressure by using a combination of transition metal complexes and strongly reducing metal reagents such as KC_8 , Na/Hg, Mg, and Cp_2Co . In view of the fact that H_2 is the only source of both electrons and protons in the industrial Haber-Bosch ammonia synthesis, the activation of N_2 by H_2 in the presence of a transition metal complex is particularly of interest. However, studies on the activation and hydrogenation of N_2 by H_2 at the molecular level remained scarce. Our previous studies suggested that multimetallic transition metal polyhydrides generated by the reaction of H_2 and a half-sandwich titanium trialkyl complex could effectively achieve the cleavage and hydrogenation of N_2 (*Science*, **2013**, *340*, 1549.). This finding motivated us to investigate the reactivity of other hydride complexes with non-Cp (non-half-sandwich) ligands.

Fortunately, after carefully check the ligands, we found that the reaction of H_2 with a PNP-ligated titanium dialkyl complex $\{(PNP)Ti(CH_2SiMe_3)_2\}$ (**1**, PNP = $N(C_6H_3-2-P-Pr_2-4-CH_3)_2$) could afford a binuclear titanium tetrahydride complex $\{[(PNP)Ti]_2H_4\}$ (**H**), which could further react

with N₂ to produce a binuclear titanium dinitrogen side-on/end-on complex $\{[(\text{PNP})\text{Ti}]_2(\mu_2, \eta^1, \eta^2\text{-N}_2)(\mu_2\text{-H})_2\}$ (**2**) at room temperature. The complex **2** upon heating at 60 °C under H₂ (1 atm) led to formation of an imido/nitrido/hydrido complex $\{[(\text{PNP})\text{Ti}]_2(\mu\text{-NH})(\mu\text{-N})(\text{H})\}$ (**3**) through the cleavage and hydrogenation of the unit (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

Due to the relative large molecular size of multinuclear complexes, most of jobs need large memory capacity for frequency calculations and longer consuming time. “GWMPCC” resources often cannot meet the demand and the jobs often interrupted abnormally. Therefore, only “GWACSL” and “GWACSG” resources were applied for my General User account. In the past 5 months, more than 132,600 core*hours of “GWACSL” and “GWACSG” resources were used.

All calculations were performed by Gaussian 09 software together with DFT methods.

3. Result

As shown in Figs 1 and 2, the direct hydrogenation of $[\text{N}=\text{N}]^{2-}$ in **2m** by a hydride ligand via transition state **TS1''** needs to overcome a high energy barrier of 32.4 kcal/mol. By contrast, the hydrogenation of $[\text{N}=\text{N}]^{2-}$ in **2m** by a molecule of H₂ could easily occur via **TS1** with a lower energy barrier of 20.2 kcal/mol to give an intermediate **A**. An isomerization of $[\text{N}=\text{NH}]^-$ in **A** then easily takes place to give an intermediate **B**. The other pathway for isomerization of $[\text{N}=\text{N}]^{2-}$ unit prior to H₂ addition (viz., **2m**→**TS1'**→**A'**→**TS2'**→**B**) was also considered. The result suggests that such pathway is unfavorable due to the relatively high energy barrier of 28.7 kcal/mol for hydrogenation process. Besides, the possibility of direct hydrogenation in **A'** by a hydride ligand was excluded owing to the high energy barrier (40.5 kcal/mol for **TS2''**), which is energetically inaccessible under current experimental condition. Starting from **B**, there are two possible pathways for H₂ elimination. One is that the terminal hydride and a μ -hydride in **B** bind to each other to form a molecule of H₂ and **C**. The other is that the two μ -hydride ligands forms a molecule of H₂ and **C'**. Both pathways are endergonic. The further transformation suggests that the N–N cleavage in **C** via **TS4** (26.5 kcal/mol) is more favorable than that in **C'** via **TS4'** (37.0 kcal/mol). As for the transformation of **A** to **C**, another pathway via **A**→**TS2'''**→**B'**→**TS3'**→**C**, in which H₂ elimination followed by isomerization of $[\text{N}=\text{NH}]^-$, was also considered. The result suggests that isomerization prior to H₂ elimination, viz., **A**→**TS2**→**B**→**TS3**→**C**, is more favorable than the other one.

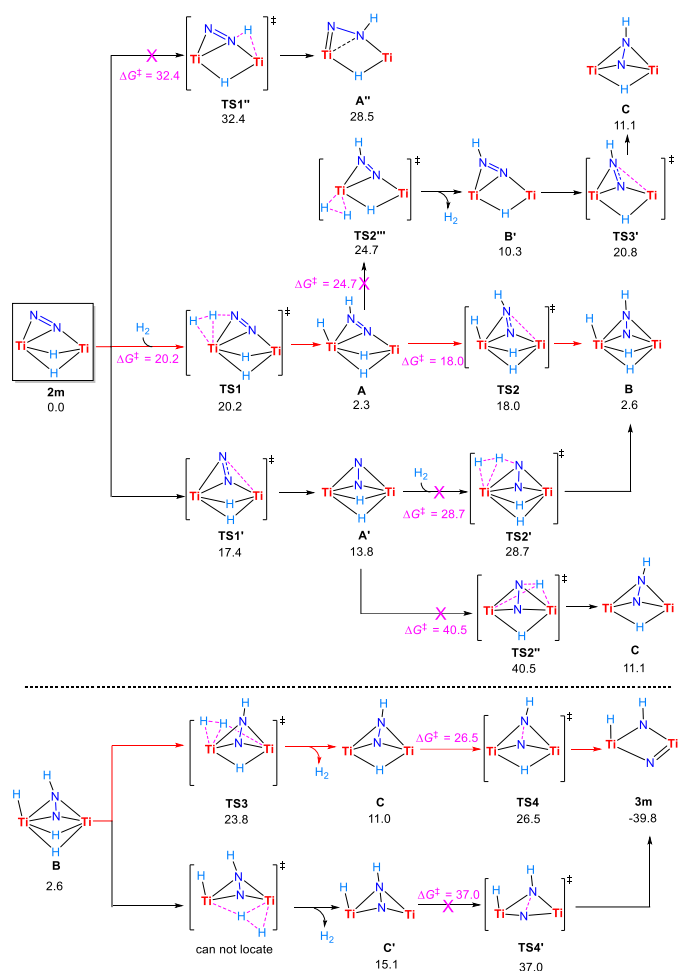


Fig. 1. Computed pathways for the transformation of **2m** (a model of **2**) to **3m** (a model of **3**). Relative free energies are given in kcal/mol. The PNP ligands were omitted for clarity. The pathway with red arrow is the most favorable one.

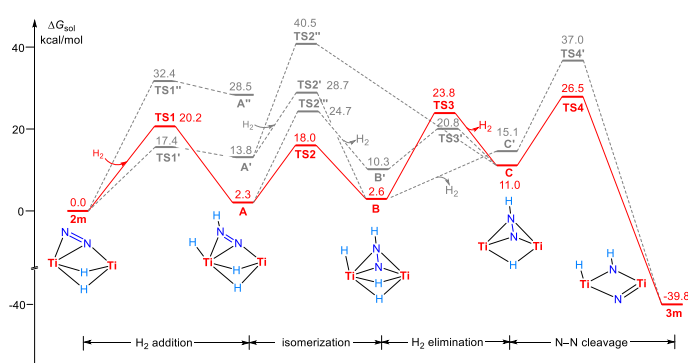


Fig. 2. Energy profiles for the pathways of the transformation of **2m** (a mode of **2**) to **3m** (a model of **3**) shown in Figure 1. Relative free energies are given in kcal/mol. The PNP ligands were omitted for clarity.

The most favorable pathway (red path) shows that addition of H₂ across to a Ti–N bond in **2m** 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 μ₂,η¹,η²-(HN=N) unit in **A** to a μ₂,η²,η²-(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 (60 °C, two days).

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 $\{[(C_5Me_4SiMe_3)Ti]_3(\mu_3-H)(\mu_2-H)_6\}$, in which N–N bond cleavage and N–H bond formation occurred in an intramolecular fashion without need for external H₂. Therefore, this new mechanistic information 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.

4. Conclusion

In summary, we have demonstrated that a PNP-ligated titanium complex can serve as a unique platform for dinitrogen activation. The hydrogenolysis of the dialkyl complex **1** with H₂ in the presence of N₂ easily yielded the dinitrogen complex **2** possibly via a tetrahydride species **H**. The reaction of **2** with H₂ at 60 °C or room temperature enabled the hydrogenation and cleavage of the dinitrogen unit, leading to formation of the mixed imido/nitrido/hydrido complex **3**. 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. This work constitutes the first example of dinitrogen cleavage and hydrogenation by H₂ in a well-defined molecular system without the pre-activation of N₂ by other reducing agents and 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.

CO₂ and pyridine. Therefore, I want to get the continuous support from RICC in the new FY.

5. Schedule and prospect for the future

Thanks very much for providing the computational resources from HOKUSAI GreatWave supercomputer system in the past few months. Actually, I also do some preliminary studies of other chemical reactions at this moment. I hope that I can finish these studies and 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 with the help of DFT calculations, such as the activation of H₂, CO,

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)