

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

The cooperation of multiple metal centers can facilitate the activation of unreactive molecules which is difficult to achieve by just a single metal site. Metal hydrides are among the most reactive organometallic compounds and are fundamental components in a wide range of stoichiometric and catalytic reactions. The investigation of the reactivity of multi-metallic hydride complexes with inactive molecules is therefore of much interest and importance. Prof. Zhaomin Hou's group have found that multi-metallic titanium hydride complexes can show unique synergistic effects on the activation of small molecules such as N_2 (e.g., *Science*, **2013**, *340*, 1549; *ACIE*, **2016**, *55*, 12316; *JACS*, **2017**, *139*, 1818; *JACS* **2019**, *141*, 2713; *JACS* **2023**, *145*, 16906), CO (*JACS*, **2020**, *142*, 19889;), CO_2 (*JACS*, **2022**, *144*, 6972), benzene (*Nature*, **2014**, *512*, 413; *JACS* **2016**, *138*, 11550), pyridine (*Nat. Commun.* **2017**, *8*, 1866) and so on. To be noted, during the discovery of these reactions, computational chemistry plays an essential role in understanding reaction mechanisms and promoting reaction developments.

The direct use of abundant and easily accessible molecules such as dinitrogen (N_2) and alkenes as feedstocks for the synthesis of alkyl amines is of great interest and importance but remains unknown. Based on previous reactions, Hou's group has recently found that hydroamination of nonactivated alkenes with N_2 at a trititanium hydride framework, which can serve as an excellent platform for the

activation of both alkenes and N_2 and lead to selective C–N bond formation between these two substrates, efficiently affording the corresponding alkyl amines upon further hydrogenation and protonation (Fig. 1).

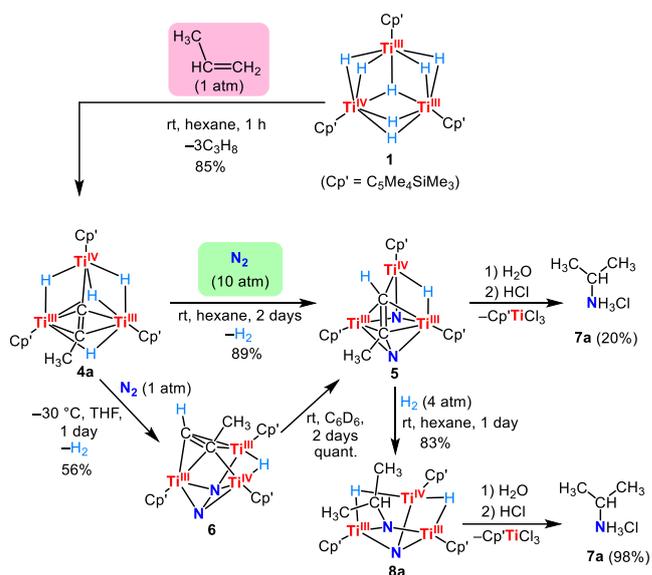


Fig. 1. Activation and transformation of propylene and N_2 in a trititanium hydride framework **1**.

To have a better understanding about N_2 activation and N–C bond formation reactions from **4a**, density functional theory (DFT) calculations were performed. Our computational results reveal the mechanistic details of N_2 activation and selective C–N bond formation.

2. Specific usage status of the system and calculation method

In the last FY2023, 1.4×10^6 core*hours were used for my Quick User project. All calculations were

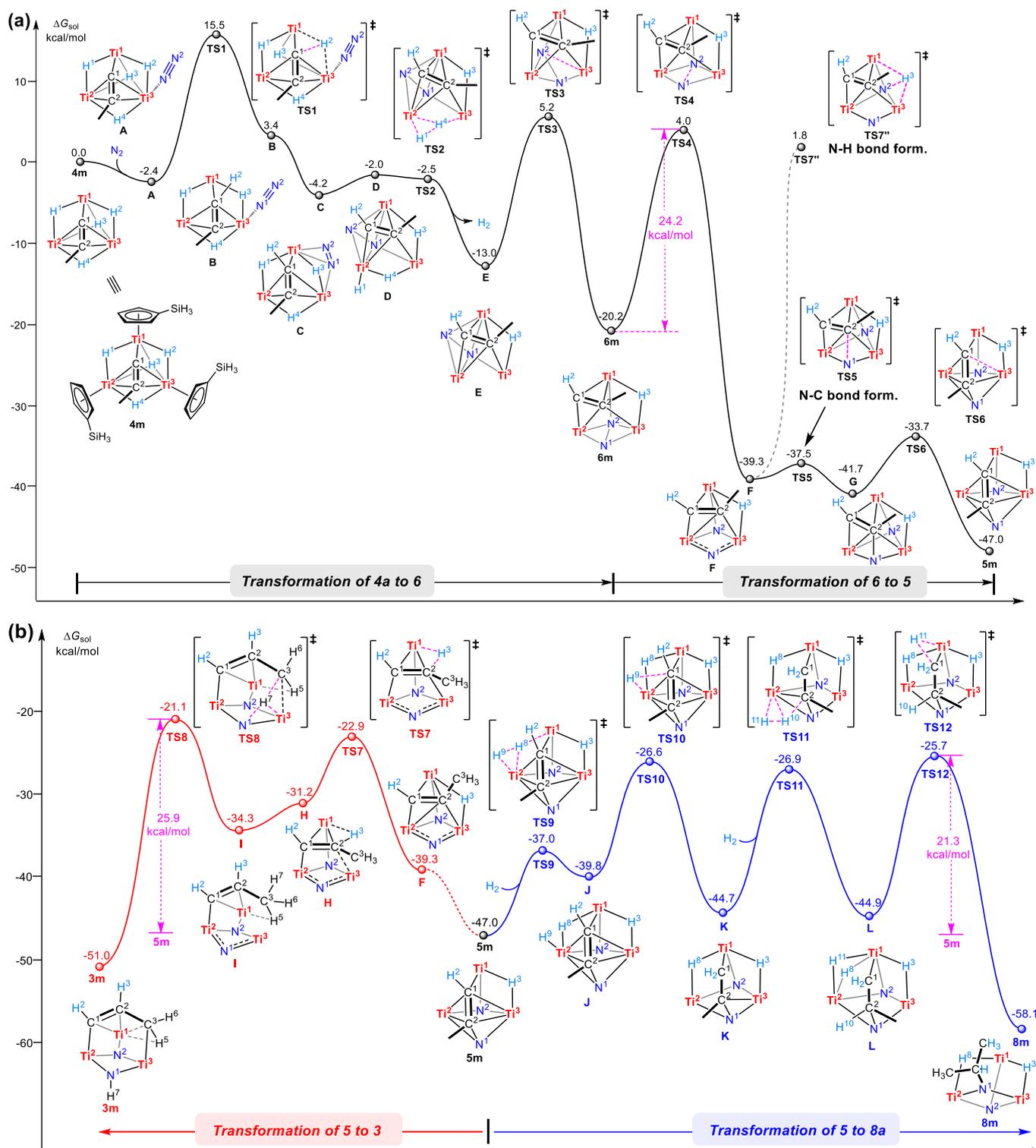


Fig. 2. Computational analysis for N_2 activation and N-C bond formation from **4m** (a model of **4a**) to **5m** and further reaction of **5m**.

performed by Gaussian 16 software together with DFT methods, such as B3LYP, B3LYP-D3, M06, M06L, M062X, B3PW91 and so on.

3. Result

In our DFT calculations, model complexes with simplified Cp-derived ligands were performed,

such as $[(C_5H_4SiH_3)_3Ti_3(\mu-\eta^1:\eta^2:\eta^2-C=CCH_3)(\mu-H)_4]$ (**4m**), in which the $C_5Me_4SiMe_3$ ligand in **4a** was replaced with $C_5H_4SiH_3$ for computational efficiency. The most favorable pathways of transformations are shown in Fig. 2. The coordination of N_2 to Ti_3 atom in **4m** gives $[(C_5H_4SiH_3)_3Ti_3(\eta^1-N_2)(\mu-\eta^1:\eta^2:\eta^2-C=CCH_3)(\mu-H)_4]$

(A). The reductive C1–H2 bond coupling in **A** via transition state **TS1** and the rearrangement of μ -H3 ligand could afford an intermediate **B**, which then induces reduction of the η^1 -N₂ ligand into an μ - η^1, η^2 -side-on-end-on dinitrogen species to afford **C**. The coordination rearrangement of the propenyl [C₃H₄] unit in **C** and further reduction of the dinitrogen unit would yield **D** with a terminal hydride ligand (H1). The reductive elimination of H1 and the adjacent μ_2 -H4 ligands via **TS2** leads to release one H₂ molecule to give **E**. Subsequently, rearrangement of the dinitrogen unit in **E** takes place to afford a more thermodynamically stable complex **6m**, which is equivalent to the dinitrogen complex **6** observed experimentally. The N1–N2 bond cleavage in **6m** then occurs via **TS4** to give the dinitride complex **F**. This process is significantly exergonic by 19.1 kcal/mol. Thereafter, facile N1–C2 bond formation in **F** and rearrangement of [C₃H₄] unit affords **5m**, which is equivalent to **5** obtained experimentally. The rate-determining step is the cleavage of N1–N2 bond with an energy barrier of 24.2 kcal/mol, which is in good agreement with the experimental result ($\Delta G_{(298.15\text{K})}^\ddagger = 23.7$ kcal/mol) obtained in the kinetic studie. Interestingly, N1–C2 bond formation from **F** needs to overcome much lower energy barriers (**TS5**: 1.8 kcal/mol) and is kinetically more favorable than another possible reaction processes such as C2–H3 bond formation (**TS7**: 16.4 kcal/mol) (Fig. 2b) and N2–H3 bond formation (**TS7'**: 41.1 kcal/mol) (Fig. 2a).

Further reaction processes for thermal conversion from **5** to **3** and hydrogenation reaction from **5** to **8a** were also investigated by DFT calculations. As shown in Fig. 2b (left), complex **5m** could easily undergo reversible processes to give **F**. When the C2–H3 bond formed from **F** via transition state **TS7**, **H** was obtained with a Ti1···H3–C2 agostic interaction. The complex **H** easily isomerizes to **I**, in which one C3–H5 bond of the terminal methyl group rather than the inner

methylene C2–H3 bond interacted with Ti1. The subsequent migration of a hydrogen (H7) on C3 atom to the μ -N1 nitride atom in **I** afforded the imide/nitride complex **3m**, which is equivalent to **3** observed experimentally. This reaction path requires overcoming an energy barrier of 25.9 kcal/mol (**5m** to **TS8**). In the whole process of the formation of **5m** from **4m** and N₂, the N–N bond cleavage from **6m** to yield **F** is the rate-determining step with an energy barrier of 24.2 kcal/mol, which is lower than that in the formation of **3m** from **5m** ($\Delta G^\ddagger = 25.9$ kcal/mol for H7 migration from C3 to N1 in **I**). These results are in agreement with the experimental observation that the kinetically favorable **5** was exclusively formed in the reaction of **4a** with N₂ at room temperature, while **5** was converted to the thermodynamically stable **3** at high temperature.

On the other hand, the reaction of **5m** with H₂ proceeds via H₂ addition on Ti2 center through **TS9** with an energy barrier of 10.0 kcal/mol, giving the intermediate **J** with two newly formed hydride ligands (μ_2 -H8 and H9). Then, the reductive C1–H9 bond coupling could take place to form **K**. Further hydrogenation takes place through σ -bond metathesis between H₂ (H10–H11) and a titanium–carbon (Ti2–C2) bond in **K** via transition state **TS11**, leading to concerted cleavage of H10–H11 and formation of C2–H10 and Ti2–H11 to give an intermediate **L**. The hydride ligand μ_2 -H11 in **L** could migrate to the C1 atom via **TS12** to give the isopropyl imide complex **8m**, which is equivalent to complex **8a** obtained experimentally. In the whole process of the formation of **8m** from **5m** and H₂, the transformation needs to overcome an energy barrier of 21.3 kcal/mol, which is lower than that in the conversion of **5m** to **3m** ($\Delta G^\ddagger = 25.9$ kcal/mol). These results are in well agreement with the experimental observation that **5** was selectively converted into **8a** under H₂ at room temperature.

4. Conclusion

Combined experimental and theoretical studies, we discovered that the trititanium hydride complex $[(C_5Me_4SiMe_3)Ti]_3(\mu_3-H)(\mu-H)_6$ (**1**) can serve as an excellent platform for the activation of both N_2 and alkenes and lead to selective C–N bond formation, efficiently affording the corresponding alkyl amines upon further hydrogenation and protonation. Computational studies reveal the mechanistic details of the hydroamination of alkenes with N_2 , in which the C–N bond formation process is kinetically more favorable than other processes such as C–H bond and N–H bond formation. Notably, the present synthetic strategy by activation of both nonactivated alkenes and N_2 and inducing selective C–N bond formation between activated carbon and nitrogen species at a trititanium hydride framework stands in good contrast with the precedent ones by reduction of N_2 , followed by addition of carbon electrophiles. It is also worth noting that the activated N_2 and alkene species at trititanium hydride framework selectively form C–N bond rather than N–H or C–H bonds, standing sharp contrast with previous observations that activations of N_2 and alkene by a ditantalum hydride complex induces C–H bond formation whereas C–N bond formation is not observed. This work offers a new strategy for N_2 functionalization with simple hydrocarbons such as nonactivated alkenes and would encourage further efforts in developing hydroamination of various hydrocarbons with N_2 at multinuclear hydride framework. ([This study has been submitted and is currently under review.](#))

5. Schedule and prospect for the future

In the following FY2024, I plan to continue collaboration with Prof. Zhaomin Hou (Organometallic Chemistry Laboratory & Advanced Catalysis Research Group, RIKEN) to investigate the related 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.

6. If no job was executed, specify the reason.

Usage Report for Fiscal Year 2022

Fiscal Year 2023 List of Publications Resulting from the Use of the supercomputer