

**Project Title:**

**Computational Studies on the Electronic Structures and the Reaction Mechanisms of Rare-Earth- and Transition-Metal Complexes**

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

The rare-earth- and transition-metal complexes catalyzed chemical transformations are important procedures in both industrial and academia fields, thus, the development of more efficient and reactive rare-earth- and transition-metal catalysts is one of the important topics in modern chemistry. To date, a diverse of rare-earth- and transition-metal catalysts have been successfully developed, and numerous valuable chemical products have been produced by using these organometallic complexes. The reactivity and selectivity of organometallic catalysts could be mainly ascribed to its unique physical and chemical properties, which could be modulated by the cooperation effect between metal center and auxiliary ligand. Although much effort has been made to intensively develop the new catalyst by modification of the ligand sphere, the rational design of new catalyst, especially the computational guided catalyst design, is the state-of-the-art approach.

To develop new catalysts more efficiently, the fully understanding of the catalytic mechanism is of fundamental importance, in which the key factors controlling the catalytic reactivity and selectivity could be found. However, it is difficult for traditional experimental to investigate the detailed reaction mechanism, because the intermediates and transition states during reaction are highly reactive and rarely detected, which hinders the rational catalyst design. Instead, the computational chemistry, as a powerful tool for studying chemical process at the molecular and atomic level, could help to elucidate the detailed reaction mechanisms, the

electronic structures of catalysts, the key factors controlling the reactivity and selectivity, and *etc.* These mechanistic insights would help improve the performance of existing catalysts and further provide instructive information for rational catalyst design. Therefore, based on the experiment results, a series of computational jobs were carried out for better understanding of the related mechanisms which could contribute to the development of new catalysts and reactions.

**2. Specific usage status of the system and calculation method**

During the FY2022, a large number of specified computational resources were used for the theoretical calculations. In general, the geometry structures were optimized by DFT method using Gaussian 09 and Gaussian 16 software. The electronic structures of key active species and transition states were characterized by utilizing the ADF software. Natural Bond Orbital (NBO) analyses were also performed using some programs such as Gaussian 09, Gaussian 16 and so on.

The B3LYP, B3PW91, TPSS and M06 functionals were utilized for DFT calculations. Dispersion corrections were treated with the D3 version of Grimme's dispersion with Becke-Johnson damping (GD3BJ) as well. For calculation of the relatively large catalytic system, such as multinuclear clusters, large polymerization systems, and the bioactive systems, the QM/MM method (ONIOM) was also adopted for accelerating the calculations and analyses.

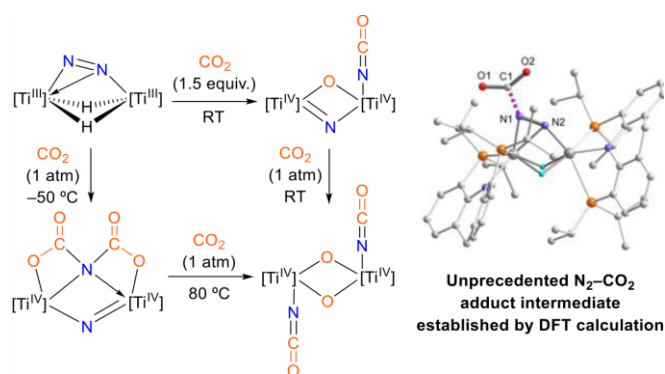
**3. Results**

**(a) DFT study on dinitrogen cleavage and**

### functionalization with carbon dioxide in a dititanium dihydride framework.

The activation and functionalization of dinitrogen ( $N_2$ ) with carbon dioxide ( $CO_2$ ) are of great interest and importance but highly challenging. We report here for the first time the reaction of  $N_2$  with  $CO_2$  in a dititanium dihydride framework, which leads to N–C bond formation and N–N and C–O bond cleavage.

The mechanistic details were clarified by the  $^{15}N$ - and  $^{13}C$ -labeled experiments and density functional theory (DFT) calculations, providing unprecedented insights into the reaction of  $N_2$  with  $CO_2$ . A titanium-mediated cycle for the synthesis of trimethylsilyl isocyanate  $Me_3SiNCO$  from  $N_2$ ,  $CO_2$ , and  $Me_3SiCl$  using  $H_2$  as a reducing agent was also established.



Scheme 1.  $N_2$  cleavage and functionalization with  $CO_2$  in a dititanium dihydride framework.

(published in *Journal of the American Chemical Society* **2022**, *144*, 6972–6980.)

### (b) Theoretical mechanistic insights into dinitrogen cleavage by a dititanium hydride complex bearing PNP-pincer ligands.

Dinitrogen ( $N_2$ ) is an abundant and easily accessible resource in the atmosphere. However, the activation of dinitrogen is a challenging chemical subject due to the inert chemical nature of the  $N\equiv N$  bond, lack of dipole moment, and large HOMO–LUMO gap. For industrial catalytic  $N_2$  transformation, the only successful example is the well-known Haber–Bosch process, in which ammonia is produced from  $N_2$  and  $H_2$  by heterogeneous catalysis under harsh conditions (350–550 °C,

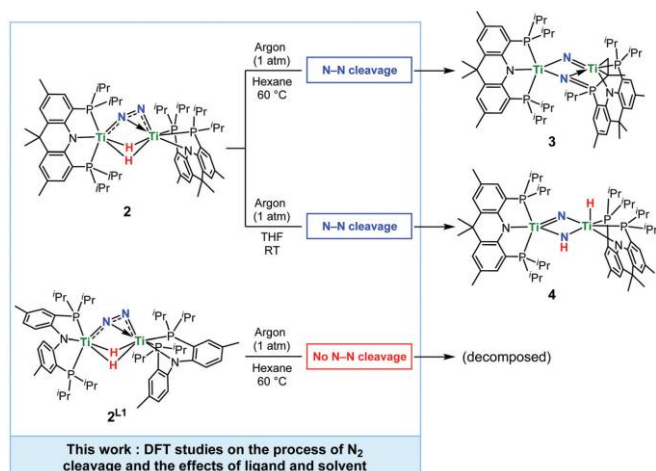
150–350 atm).

Therefore, an enormous amount of energy is required for industrial nitrogen fixation, which is equivalent to about 1% of global energy consumption. On the other hand, nitrogenase could accomplish  $N_2$  transformation under ambient conditions. Nevertheless, the mechanism of such biochemical systems is relatively complicated, making it difficult to mimic artificially. In view of this fact, dinitrogen activation by molecular multinuclear metal complexes is an alternative strategy to develop efficient nitrogen fixation systems owing to flexible  $N_2$  coordination modes, high reactivity under milder conditions, intermetallic cooperation, and relative ease in mechanism investigation. In the field of molecular metal complexes for dinitrogen transformation, exploring multinuclear transition metal polyhydride complexes is attractive because no extra reductant and proton sources are needed. Numerous well-defined multinuclear transition metal hydride complexes towards  $N_2$  activation have been established, such as Ti, Zr, Nb, Ta, and Cr, and even an example of titanium/ruthenium heteromultimetallic hydride complex was also reported to cleave dinitrogen.

In the mechanistic aspect, numerous hydride- and nitride-intermediates are involved in multinuclear hydride systems, which could help us understand the mechanism on the Haber–Bosch process. According to previous mechanistic studies,  $N_2$  activation by multinuclear metal hydrides is generally accomplished by the oxidation of hydrides, generating free  $H_2$  molecule or proton in imido species. However, further mechanistic studies are limited but required, in particular, for the case of different ligands and different transformation manner. Recently, a dinitrogen dititanium hydride complex **2** (Scheme 2) bearing the rigid acridane-based  $acri$ PNP-pincer ligands was reported, where the dinitrogen could be cleaved under inert atmosphere, nonpolar solvent, and mild conditions. In addition, the dinitrogen cleavage in complex **2**

could even take place under room temperature in the THF solvent, yielding complex 4. In contrast, the analogues complex  $2^{L1}$  bearing the diphenylamine-based PNP-pincer ligand showed no such reactivity, indicating that the structure of the pincer ligand could affect the activity towards the  $N_2$  cleavage. The effects of ancillary ligands on catalytic  $N_2$  fixation in a series of mononuclear Fe-PNP or Co-PNP systems were investigated, it was found that the structure of the PNP-pincer ligand has a great influence on the catalytic activity and selectivity. However, studies on the effects of ancillary ligands in  $N_2$  activation by multinuclear hydride complexes are still lacking.

In this study, the mechanism of dinitrogen cleavage by a PNP-coordinated dititanium polyhydride complex has been computationally investigated. A “multi-state reactivity” scenario has been disclosed for the whole process of  $N_2$  coordination and activation. Remarkably, the  $H_2$  elimination prior to the N–N cleavage is accomplished by the coupling of two terminal hydrides, and planar PNP-pincer ligand could stabilize the corresponding transition state. Besides, the tetrahydrofuran (THF) solvent could also promote the  $H_2$  elimination due to the similar polarity of the corresponding intermediates or transition states to THF molecule.



Scheme 2.  $N_2$  activation by dititanium hydride complexes bearing PNP-pincer ligands.

(published in *Dalton Transactions* 2022, 51, 918–926.)

#### 4. Conclusion

With the help of HOKUSAI system, (1) The mechanistic details of dinitrogen cleavage and functionalization with carbon dioxide in a dititanium dihydride framework were investigated. (2) the mechanism of  $N_2$  coordination and cleavage were investigated. (3) The effects of ligands and solvent on the reactivity towards  $N_2$  activation were revealed.

These studies were successful in unveiling the key role of rare-earth- and transition-metal complexes in chemical reactions.

#### 5. Schedule and prospect for the future

In the future, the reaction mechanism of inert molecule activation (such as  $H_2$ ,  $N_2$ ,  $NH_3$ ) catalyzed by multinuclear cluster will be studied continuously. Besides, we will focus on the copolymerization of ethylene and polar monomer mediated by rare-earth- and transition-metal complexes. Furthermore, data analysis of the polymerization will be carried out, the multiple linear regression and machine learning methods will be also performed. Although some primary results have been obtained, more systematic studies on the mechanism of newly discovered reactions mediated by rare-earth- and transition-metal complexes are obviously necessary

Usage Report for Fiscal Year 2022

**Fiscal Year 2022 List of Publications Resulting from the Use of the supercomputer**

**[Paper accepted by a journal]**

- (1) Qingde Zhuo, Jimin Yang, Zhenbo Mo, Xiaoxi Zhou, Takanori Shima, **Yi Luo\***, **Zhaomin Hou\*** “Dinitrogen Cleavage and Functionalization by Carbon Dioxide at a Ditungsten Dihydride Framework” *Journal of the American Chemical Society* **2022**, *144*, 6972–6980. (SCI, Impact Factor: 16.383)
- (2) Jimin Yang, Qingde Zhuo, Zhenbo Mo, **Zhaomin Hou\***, **Yi Luo\***, “Theoretical mechanistic insights into dinitrogen cleavage by a ditungsten hydride complex bearing PNP-pincer ligands” *Dalton Transactions* **2022**, *51*, 918–926. (SCI, Impact Factor: 4.569)