

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

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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.

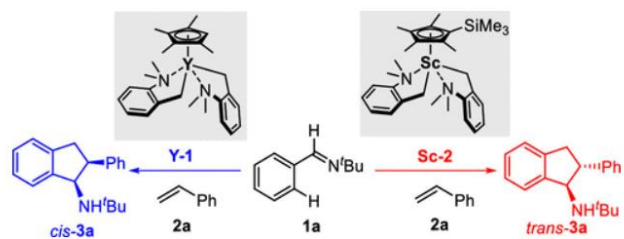
**2. Specific usage status of the system and calculation method**

During the FY2021, 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 09/16 software. The TPSS, B3LYP, B3PW91, 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. In addition, some ETS-NOCV (extended transition state-natural orbital for chemical valence) calculations were performed by Multiwfn 3.8 package

**3. Results****(a) Theoretical Studies of Rare-Earth-Catalyzed [3 + 2] Annulation of Aromatic Aldimine with Styrene**

Aminoindane moieties play an important role in organic chemistry and pharmaceutical chemistry research, especially for multisubstituted chiral 1-aminoindane frameworks. Among the possible approaches to the synthesis of 1-aminoindane, catalytic C(sp<sup>2</sup>)-H activation-triggered tandem [3 +

2] annulation of aromatic aldimines with olefins has been studied extensively due to its 100% atomic economy (Scheme 1).



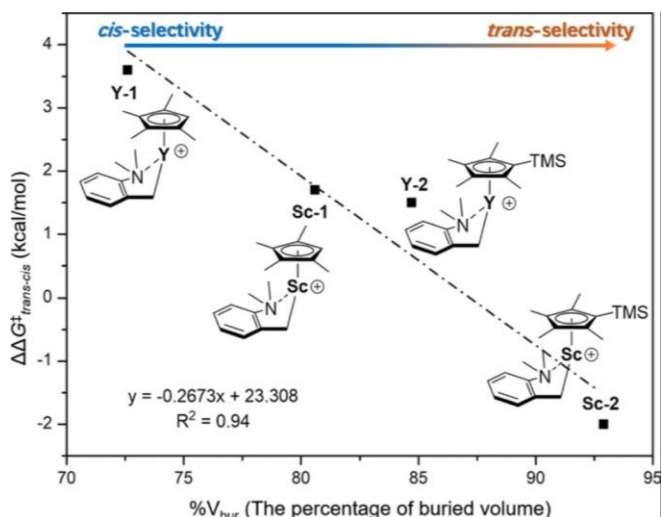
**Scheme 1** Rare-Earth-Catalyzed [3 + 2] Annulation of Benzaldimine with Styrene

An understanding of the exact reaction mechanism, especially for the origin of diastereoselectivity, is an essential aspect for further development of such reactions. In this study, density functional theory calculations have been carried out on the rare-earth-catalyzed diastereodivergent [3 + 2] annulation of benzaldimine with styrene. The results show that the reaction mainly involves generation of active species, olefin insertion, cyclization, and protonation steps. The noncovalent interactions, such as C–H $\cdots\pi$  and metal $\cdots\pi$  interactions, play an important role in stabilizing the key transition state or intermediate. Both steric and electronic factors account for the diastereoselectivity. The preferred cis-diastereoselectivity could be ascribed to more efficient orbital interaction, while the crowded space will induce the formation of a C–H $\cdots\pi$  interaction between the N<sup>t</sup>Bu group and benzene ring in a trans-diastereoselectivity manner, thus stabilizing the trans-selective transition state. Therefore, the stereospecific product could be obtained by fine-tuning the ligand/metal combination of the catalysts. The crowded space in the catalyst could change the interaction strength between the catalyst and styrene moieties, leading to the change in the energy barrier difference between the trans- and cis-insertion manners (Figure 1).

The results presented here could add better understanding to the mechanism and the origin of the diastereoselectivity of rare-earth-catalyzed [3 + 2]

annulation of aromatic aldimines with alkenes and would be helpful for further development of rare-earth-catalyzed diastereoselective reactions.

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**Figure 1** Linear relationship between the value of  $\Delta\Delta G^\ddagger$  trans-cis and the percentage of buried volume of the metal center in the cationic species of catalysts.

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

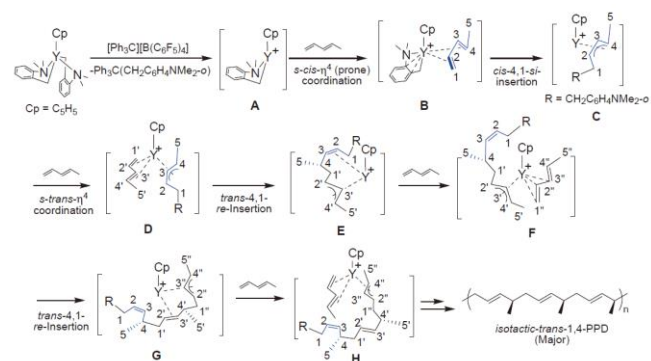
Dinitrogen ( $N_2$ ) is an abundant and easily accessible resource in the atmosphere. However, the activation of dinitrogen is a challenging chemical subject due to the inert chemical nature of the  $N\equiv N$  bond, lack of dipole moment, and large HOMO–LUMO gap.

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. 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.



*trans*-1,4-poly(pentadiene) showing good elastic properties without vulcanization (tensile strength up to 7.1 MPa with elongation at break of 2600%).

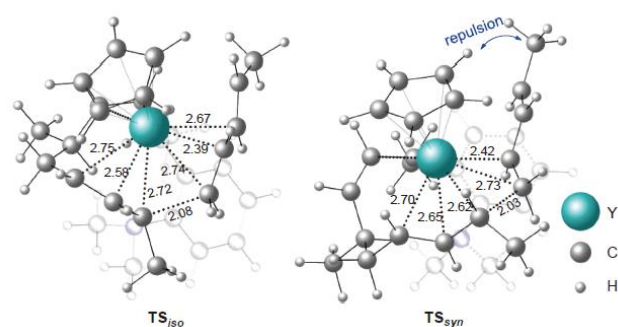
To gain insight into the origin of the observed isospecific *trans*-1,4-selectivity in the present polymerization of EPD, the DFT calculations were performed on the basis of cationic yttrium alkyl species  $[\text{CpY}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)]^+$  as the initial active species. On the basis of the computational studies, a possible reaction mechanism is proposed as shown in Scheme 4. In the case of the insertion of aminobenzyl unit, the coordination of EPD to the Y atom in the cationic yttrium aminobenzyl species **A** in an *s-cis*- $\eta^4$  fashion yields **B**. The subsequent insertion of the coordinated EPD unit into the Y–C  $\sigma$ -bond in **B** in a *cis*-4,1-*si* fashion is the most favorable among all possible insertion modes, affording **C** with a 4,1- $\eta^3$ - $\pi$ -anti-pentadienyl unit. In contrast, the coordination of an incoming monomer to **C** in an *s-trans* fashion is favored to give complex **D**, which could be enrolled in chain propagation. In the insertion of the second EPD monomer, the *trans*-4,1-*re* coordination to the metal center (**D**) to yield the corresponding *trans*-1,4-insertion product **E** is favored over the *cis*-4,1-*si* insertion that tends to give the *cis*-1,4 sequence.



**Scheme 4** Possible reaction mechanism of isospecific *trans*-1,4 polymerization of (*E*)-1,3-pentadiene

To investigate the origin of the observed stereo-selectivity, the insertion of the third monomer was further calculated. It was found that a critical factor for determining tacticity is the mutual

orientation of the pre-inserted dienyl unit and the subsequent coming olefin monomer part. Starting from the 4,1- $\eta^3$ - $\pi$ -syn-pentadienyl species **E** derived from the second monomer insertion, the isotactic-*trans*-1,4-PPD sequence formation process is more favorable than the syndiotactic-*trans*-1,4-PPD sequence formation process (Figure 2), in agreement with the observed high iso-selectivity. The distortion/interaction and geometry analyses of the insertion transition states suggest that an avoiding of steric repulsion between the Cp ligand and the methyl group of EPD could account for the iso-selectivity.



**Figure 2** Geometry structures of optimized *iso*-selective and *syndio*-selective polymerization transition states in EPD polymerization.

This work, together with those reported previously, demonstrates that fine-tuning the metal/ligand combination of halfsandwich rare-earth complexes can create unique catalysts for the efficient and selective polymerization of olefins and dienes. Further studies along this direction are in progress. (published in *Bulletin of the Chemical Society of Japan*, 2021, 94, 1285 - 1291, selected as BCSJ Award Article.)

#### 4. Conclusion

With the help of HOKUSAI system, (1) the model reaction of C(sp<sup>2</sup>)-H activation-triggered tandem [3 + 2] annulation of *N-tert*-butyl benzaldimine with styrene has been investigated by DFT calculations. The diastereoselectivity is controlled by both the steric and electronic factors, and the stereospecific

product could therefore be obtained by fine-tuning the ligand/metal combination of the catalysts. (2) 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<sub>2</sub> coordination and activation. Remarkably, the H<sub>2</sub> 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<sub>2</sub> elimination due to the similar polarity of the corresponding intermediates or transition states to THF molecule. (3) by using a C<sub>5</sub>H<sub>5</sub>-ligated yttrium catalyst we have successfully achieved the isospecific trans-1,4-selective living polymerization of (*E*)-1,3-pentadiene (EPD). The polymerization mechanism has been clarified by DFT calculations. The resulting well-defined polymers showed good elasticity without vulcanization probably due to the formation of network structures via physical crosslinks of highly stereoregular crystalline (hard) segments together with less stereoregular amorphous (soft) segments. 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 N<sub>2</sub>, CO<sub>2</sub>, benzene) 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.

We wish to continue to use HOKUSAI system for the current long-term project. 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.

**Fiscal Year 2021 List of Publications Resulting from the Use of the supercomputer**

**[Paper accepted by a journal]**

1. P. Wang, G. Luo, J. Yang, X. Cong, Z. Hou, and Y. Luo, "Theoretical Studies of Rare-Earth-Catalyzed [3 + 2] Annulation of Aromatic Aldimine with Styrene: Mechanism and Origin of Diastereoselectivity", *J. Org. Chem.*, **2021**, *86*, 4236-4244.
2. J. Yang, Q. Zhuo, Z. Mo, Z. Hou and Y. Luo, "Theoretical mechanistic insights into dinitrogen cleavage by a dititanium hydride complex bearing PNP-pincer ligands", *Dalton Trans.*, **2022**, *51*, 918-926.
3. K. Nishii, G. Zhou, Y. Saito, A. Yamamoto, M. Nishiura, Y. Luo, and Z. Hou, "Synthesis of Thermoplastic Elastomers by Yttrium-Catalyzed Isospecific Trans-1,4-Polymerization of (*E*)-1,3-Pentadiene", *Bull. Chem. Soc. Jpn.*, **2021**, *94*, 1285-1291. (Selected as BCSJ Award Article)