

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, relationship of the project with other projects

Chemical transformations by transition metal complexes has been received much attention in the past decades due to its important role in organic synthesis and organometallic chemistry. An understanding of the exact reaction mechanism is an essential aspect of chemistry in general, which would be helpful for improving the activity and selectivity of the reactions as well as for designing more efficient complexes and new reactions. As we know that it is difficult to isolate and detect intermediates during many chemical reactions experimentally. Density functional theory (DFT) calculation as a powerful tool play an important role in exploring chemical reaction mechanisms. In the past few years, I have made some efforts on mechanism investigation of metal-mediated homogeneous chemical reactions. In recent years, Prof. Zhaomin Hou (Chief Scientist, Organometallic Chemistry Laboratory) did lots of excellent works in metal-mediated chemical reactions, such as dinitrogen cleavage and hydrogenation, benzene cleavage and rearrangement. With the aid of the RIKEN Supercomputer system, we have successfully elucidated the detailed mechanism of N₂ and benzene activation by the trinuclear titanium polyhydride complex. Obviously, it is computationally found that the synergy of the dynamic rearrangement of the

hydride ligands, the facile redox of the titanium metal centres, and the cooperation of the multiple metal sites in the multimetallic hydride framework that has enabled those transformations of unsaturated substrates. Very recently, prof. Hou's group found some important new reactions experimentally. To have a better understanding of related reactions, I did some DFT calculations to explore the detailed mechanisms, which could be effective to develop new catalysts and new reactions. Some independent theoretical results or the combined experimental and theoretical results have been published in high level journals.

2. Specific usage status of the system and calculation method

In FY2017, about 515,000 core*hours were used for my Quick Use project. All calculations were performed by Gaussian 09/16 software together with DFT methods.

3. Result

(1) Heteroatom-assisted olefin polymerization

Heteroatom-functionalized polyolefins are of fundamental interest and practical importance. This has spurred investigations of the copolymerization of polar and nonpolar olefins. Recently, prof. Hou's group found that the interaction between a heteroatom in a functional α -olefin monomer and a rare-earth metal catalyst can significantly raise the olefin polymerization activity and thereby promote its copolymerization with ethylene. By using

the heteroatom-assisted olefin polymerization (HOP) strategy, a series of heteroatom (O, S, Se, N, and P)-functionalized polyolefins were successfully synthesized with high molecular weights and controllable functional monomer contents (Fig. 1).

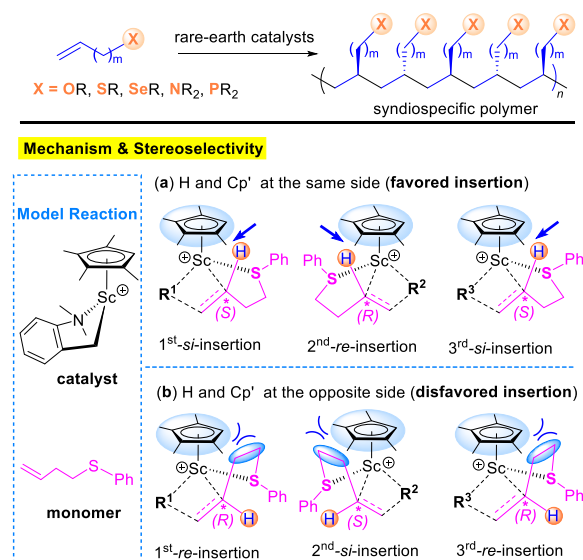


Fig. 1. Homopolymerization of heteroatom containing α -olefins and computational analysis.

To have a better understanding of the mechanistic aspect of the present HOP reaction, we performed the DFT calculations. It is computationally revealed an appropriate interaction between the heteroatom in an α -olefin and the catalyst metal center plays the critically important role in achieving the olefin polymerization and controlling the stereoselectivity. The combined experimental and theoretical results have been published in *Science Advances*, **2017**, *3*, e1701011.

(2) Cooperative trimerization of CO

The industrial Fischer–Tropsch (F–T) process for the reductive oligomerization of carbon monoxide (CO) to give hydrocarbons and oxygenates was developed more than several decades. The heterogeneously catalyzed F–T process is generally nonselective and complicated. It has been reported that addition of a main group metal component

such as an alkali metal compound to transition-metal-based catalysts could significantly improve the activity and selectivity. However, the cooperative effects of the heteromultimetallic components have not been fully understood at the molecular level. Recently, Hou et al. reported the cooperative trimerization (**4**) of CO by molecular lithium (**1**) and samarium boryl (**2**) complexes (Fig. 2). To have a better understanding of the mechanism and the selectivity of such new reaction, we performed DFT calculations. The results revealed that the CO trimerization reaction took place exclusively by coupling of a samarium boryl oxycarbene species with a lithium ketenolate species. These results offer unprecedented insight into CO oligomerization promoted by heteromultimetallic components and may help better understand the industrial F–T process and guide designing new catalysts. The combined experimental and theoretical results have been published in *J. Am. Chem. Soc.* **2017**, *139*, 16967.

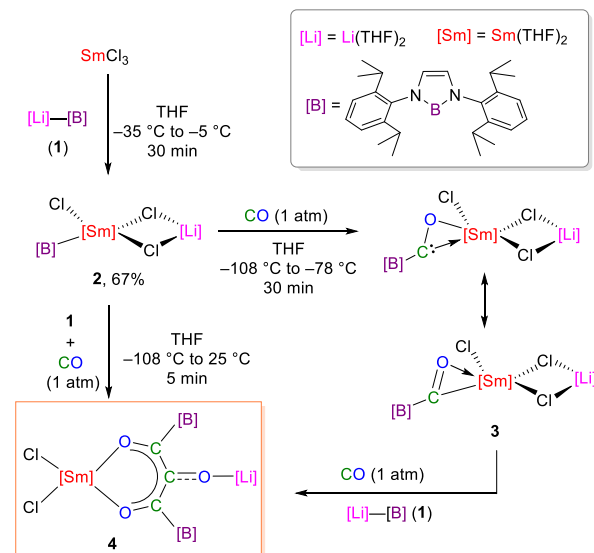


Fig. 2. The cooperative trimerization of CO by molecular lithium and samarium boryl complexes.

(3) Hydrodenitrogenation of pyridine

The hydrodenitrogenation (HDN) of aromatic *N*-heterocycles such as pyridines and

quinolines is an important process in the industrial petroleum refining to remove nitrogenous impurities from crude oil. This transformation is essential not only to suppress NO_x emissions upon combustion of the fuel but also to improve the performance of the hydrocracking and other downstream processes. To aid the design of new catalysts and achieve HDN under milder conditions, a better understanding of the reaction mechanism is of significant importance. Investigation of the reactions of aromatic N-heterocycles with molecular organometallic complexes has been expected to bring about a better understanding of the industrial HDN reaction mechanism and thereby lead to the development of more efficient transformations under milder conditions. The denitrogenation of a fused aromatic N-heterocycle such as quinoline by a molecular organometallic complex has not been reported previously. Very recently, prof. Hou's group reported the HDN of pyridines and quinolines by a molecular trinuclear titanium polyhydride complex (Fig. 3).

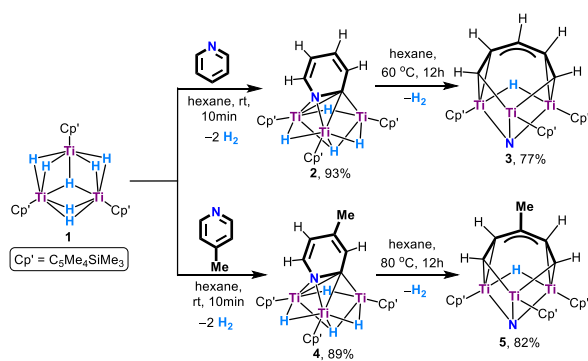


Fig. 3. Hydrodenitrogenation of pyridines by the titanium hydride complex.

The formation of **3** and **5** from the reactions of the titanium hydride cluster **1** with pyridines and quinolines represents a unique example of denitrogenation of an aromatic N-heterocycle by a well-defined molecular metal hydride complex (Fig. 3). To have a

better understanding about the denitrogenation of pyridine by **1**, we performed the densityfunctional theory (DFT) calculations on a model complex of **1**. The mechanism was well clarified and the result demonstrated that multimetallic hydrides play a critically important role. Besides, we found the first C–N bond cleavage is the rate-determining step and the second C–N bond cleavage has a low energy barrier. These results are in sharp contrast with those observed in the activation of pyridine by a titanium alkylidyne complex, where the energy barrier for ring opening (13.0 kcal/mol) was significantly lower than that for denitrogenation promoted by the addition of Me₃SiCl (27.0 kcal/mol). The results from this study may provide hints for designing new catalysts for the HDN of aromatic N-heterocycles under milder conditions as well as for other useful chemical transformations. The result was published in *Nature Communications*, **2017**, *8*, 1866.

(4) N–H and P–H bond activation

Transition-metal-mediated E–H (E = N and P) bond activation as a synthetic elementary step has received intense attention because of its great importance in the transformation of amines and phosphines to value-added compounds in the fields of medicine, agrochemicals, and materials. A deep understanding of the mechanisms of N–H/P–H bond activation by transition metal complexes is of great importance to establish an effective strategy for functionalization of amines and phosphines. In this field, several mechanisms mediated by mononuclear transition metal complexes were well-established based on both experimental and theoretical studies, *i.e.*, E–H bond cleavage by oxidative addition to low-valent

metal center, σ -bond metathesis with metal–alkyl/hydride bond, or metal–ligand cooperation. Most of these works focus on mononuclear systems, multinuclear complexes were also demonstrated that has a capable of activating N–H/P–H bonds. However, in contrast to mononuclear systems, the related mechanistic studies of N–H/P–H bond activation by multimetallic complexes still remain rather unexplored.

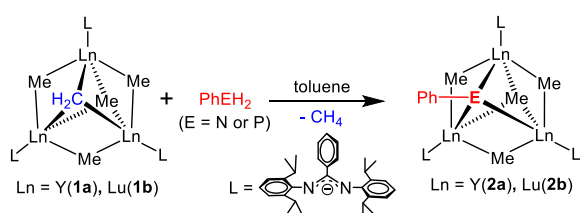


Fig. 4. E–H (E = N, P) bond activation by trinuclear rare-earth methylidene complexes.

Herein, the E–H (E = N, P) bond activation of PhEH_2 by a trinuclear yttrium methylidene complex were performed (Fig. 4). It has been revealed that the first E–H bond activation is a mono-metal-assisted σ -bond metathesis (σ -BM) process, while the second E–H bond activation is achieved by the cooperation of three metal sites. Based on the computational results, we also predict that the trinuclear yttrium methylidene complex should be also effective for activation of NH_3 and PH_3 . This work was published in *Organometallics*, **2017**, *36*, 4611.

(5) Hydroaminoalkylation of olefins with amines

Catalytic $\text{C}(\text{sp}^3)\text{--H}$ bond activation at the position α to a nitrogen atom has recently attracted much interest from synthetic organic chemists because this offers new and promising synthetic approaches for the functionalization of simple amines. The control of regioselectivity is highly important in organic synthesis and theoretical organic chemistry in general. In the hydroaminoalkylation of olefins, both linear and branched products could be formed. In

2016, Hou and co-workers reported that a rare-earth alkyl catalyst could promote the intermolecular hydroaminoalkylation of olefins with a variety of tertiary amines under relatively mild conditions and, in particular, with an exclusively substrate dependent regioselectivity. This reaction could offer an ideal model for mechanistic studies with the purpose of developing regioselective catalytic systems (Fig. 5). The mechanism of Sc-catalyzed hydroaminoalkylation of olefins with amines has been investigated by DFT calculations.

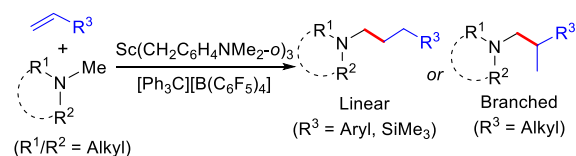


Fig. 5. Sc-Catalyzed hydroaminoalkylation of olefins with amines.

It has been computationally revealed that the true active species is an amine-coordinated η^2 -azametallacyclic complex, and electronic factors play a crucial role in achieving regioselectivity. The charge dispersion and charge alternation account well for the stability of the olefin insertion transition states and products. The charge distribution of 15 olefin substrates used previously in the experimental studies correlates well with the observed regioselectivity and could thus provide a potential model for regioselectivity prediction. These results would be helpful for designing more efficient reactions (*Organometallics*, **2017**, *36*, 1557).

4. Conclusion

In olefin polymerization system, we developed the heteroatom-assisted olefin polymerization (HOP) strategy used for synthesis heteroatom-functionalized polyolefins. DFT calculations revealed the mechanistic aspect of the HOP process in detail and the

special role in controlling stereoselectivity.

As to the reaction of cooperative trimerization of CO. The computational studies revealed that the reaction took place exclusively by coupling of a samarium boryl oxycarbene species with a lithium ketenolate species, which offers unprecedented insight into CO oligomerization promoted by hetero-multimetallic components.

In the reaction of hydrodenitrogenation of pyridine, we reported a unique example of denitrogenation of an aromatic N-heterocycle by a well-defined molecular metal hydride complex. DFT calculations revealed that multimetallic hydrides play a critically important role and the first C–N bond cleavage is the rate-determining step. These results may provide hints for designing new catalysts for the HDN of aromatic N-heterocycles under milder conditions as well as for other useful chemical transformations.

E–H (E = N, P) bond activation of PhEH₂ by a trinuclear yttrium methyldene complex were investigated by DFT calculations. It has been revealed that the first E–H bond activation is a mono-metal-assisted σ -bond metathesis (σ -BM) process, while the second E–H bond activation is achieved by the cooperation of three metal sites. We also predict that the trinuclear yttrium methyldene complex should be also effective for activation of NH₃ and PH₃.

Finally, the mechanism of scandium catalyzed hydroaminoalkylation of olefins with amines has been investigated. It has been revealed that the true active species is an amine-coordinated η^2 -azametallacyclic complex. DFT results give us a good explanation for experimental observations, such as activity and regioselectivity, which would be helpful for designing more efficient reactions.

5. Schedule and prospect for the future

In the future, I will collaborate with Prof. Zhaomin Hou's group (Organometallic Chemistry Laboratory) and continue to study the mechanisms of the metal-mediated homogeneous reactions. Actually, some collaborative projects are in progress at present. We will focus on mechanism studies of small molecules activation transition-metal complexes, including N₂, CO, thiophene, H₂ etc. The hydrolysis of trinuclear titanium nitride complex will also be investigated by DFT calculations. Therefore, I want to get the continuous support from RIKEN Supercomputer System in the FY2018.

Fiscal Year 2017 List of Publications Resulting from the Use of the supercomputer

[Publication]

1. Shaowei Hu[#], **Gen Luo**[#], Takanori Shima, Yi Luo*, **Zhaomin Hou***. Hydrodenitrogenation of pyridines and quinolines at a multinuclear titanium hydride framework, *Nature Communications*, **2017**, 8, 1866. (#contributed equally to this work)
RIKEN Press Releases: http://www.riken.jp/pr/press/2017/20171130_1/
2. Baoli Wang[#], **Gen Luo**[#], Masayoshi Nishiura, Yi Luo*, **Zhaomin Hou***. Cooperative trimerization of carbon monoxide by lithium and samarium boryls, *J. Am. Chem. Soc.*, **2017**, 139, 16967–16973. (#contributed equally to this work)
3. Chunxiang Wang[#], **Gen Luo**[#], Masayoshi Nishiura, Guoyong Song, Atsushi Yamamoto, Yi Luo*, **Zhaomin Hou***. Heteroatom-assisted olefin polymerization by rare-earth metal catalysts, *Science Advances*, **2017**, 3, e1701011 (#contributed equally to this work)
RIKEN Press Releases: http://www.riken.jp/pr/press/2017/20170722_1/
4. Baoli Wang[#], **Gen Luo**[#], Masayoshi Nishiura, Shaowei Hu, Takanori Shima, Yi Luo*, **Zhaomin Hou***. Dinitrogen activation by dihydrogen and a PNP-ligated titanium complex, *J. Am. Chem. Soc.*, **2017**, 139, 1818–1821. (#contributed equally to this work)
5. **Gen Luo**, Yi Luo*, **Zhaomin Hou***. E–H (E = N and P) bond activation of PhEH₂ by a trinuclear yttrium methylidene complex: theoretical insights into mechanism and multimetal cooperation behavior, *Organometallics*, **2017**, 36, 4611–4619. (Special Issue: Organometallic Actinide and Lanthanide Chemistry)
6. Fan Liu, **Gen Luo**, **Zhaomin Hou***, Yi Luo*. Mechanistic Insights into Scandium-Catalyzed Hydroaminoalkylation of Olefins with Amines: Origin of Regioselectivity and Charge-Based Prediction Model, *Organometallics*, **2017**, 36, 1557–1565. (Selected as ACS Editors' Choice)