Usage Report for Fiscal Year 2019

Project Title:

Density functional theory studies on the mechanisms of transition metal mediated chemical transformations

Name:

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Advanced Catalysis Research Group

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

Chemical transformation catalyzed by transition metal complex has been received much attention in the past decades due to its important role in organic synthesis and organometallic chemistry. Prof. Zhaomin Hou's group (Organometallic Chemistry Laboratory & Advanced Catalysis Research Group, RIKEN) has achieved large amounts of excellent work in this field in the last two decades. As is well known, 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. However, it is often 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, with the collaboration with Prof. Hou's group, I have achieved many efforts on mechanism investigation of homogeneous chemical reactions, which effectively promoted the development of catalytic reactions. Nowadays, Prof. Hou and co-workers continue to develop new reactions experimentally, and the good understanding of such new reactions at the molecular level are urgently required. Obviously, DFT calculation is an effective approach to reveal the detailed mechanism, which could be effective to develop new catalysts and new reactions. In the last FY2019, with the aid of RIKEN's supercomputer system, some important results have been published in SCI level journals.

2. Specific usage status of the system and calculation method

In the last FY2019, about 1018 kilo core*hours were used for my Quick Use project. All calculations were performed by Gaussian 09 or Gaussian 16 software together with DFT methods.

3. Result

(a) Computational investigation of scandium-based catalysts for olefin hydroaminoalkylation and C–H addition

Great progress has been achieved in the olefin hydroaminoalkylation by using amines, which is an atom-efficient route for the synthesis of alkylated amine derivatives. However, success in the catalytic olefin hydroaminoalkylation with a simple tertiary amine is hitherto very limited. Hou et al. recently reported that a homoleptic tris(benzyl) scandium complex was an excellent catalyst working for the addition of C–H bond of various aliphatic tertiary amines into olefins.

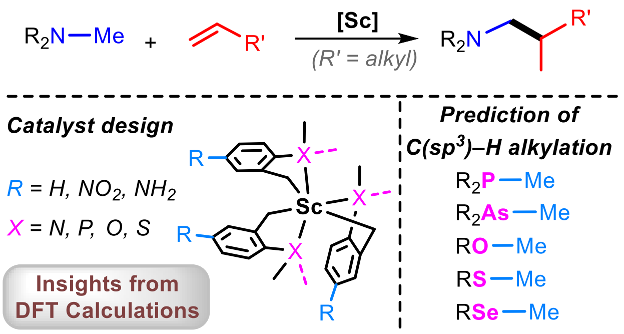

Fig. 1 DFT calculation on Sc-catalyzed olefin hydroaminoalkylation and C–H addition.

To have a better understanding of this reaction, we performd DFT calculations to investigate the hydroaminoalkylation of olefins with tertiary amines, catalyzed by a series of homoleptic tris(benzyl) scandium complexes (Fig. 1). It is found that the catalytic performance can be improved via substitution of electron-withdrawing groups and modifying ligand frameworks to reduce their steric hindrance. In addition, the potential applications of scandium catalysts in the *α*-C(sp^3)–H alkylation of various heteroatom-containing (P, As, O, S, and Se) substrates were explored. The results suggest that alkyl sulfides and selenides are promising substrates to undergo *α*-C(sp^3)–H addition to olefins. Importantly, the effects of ligand-backbone and substituent on catalytic performance and the different reactivities of the heteroatom-containing substrates were elucidated by frontier orbital, natural charge, topographic steric map, and distortion-interaction analyses, which give considerable insight into catalytic systems. This work provides useful information for developing new olefin hydroaminoalkylation reactions by using simple tertiary amines and for the addition of *α*-C(sp^3)–H bond of heteroatom-containing substrates to alkenes. This work has been published in *Organometallics* (2019, *38*, 1887–1896).

(b) CO_2 activation by Lewis pairs generated under copper catalysis enables difunctionalization of imines: Experimental and computational studies

The utilization of simple and easily accessible feedstocks for the synthesis of structurally complex and high value molecules is among the long-standing challenges to chemists. The last decades have witnessed significant progresses in the use of carbon dioxide (CO_2) as an attractive one-carbon source for the preparation of various useful chemicals. Recently, we describe a highly selective difunctionalization of imines through incorporation of activation of CO_2 by intramolecular N/B Lewis pairs into a copper catalytic cycle (Fig. 2).

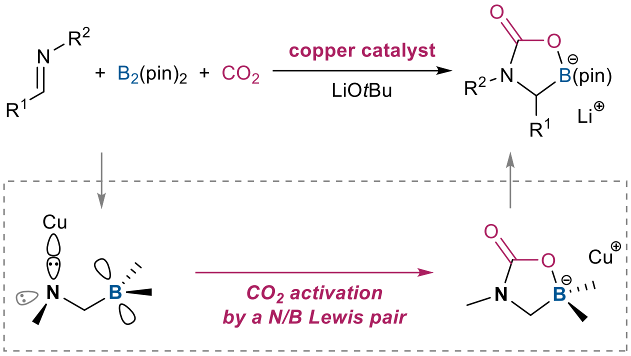

Fig. 2 Incorporation of CO_2 activation by Lewis pair into copper catalysis.

Computational and experimental studies on mechanistic aspect revealed an *α*-borylalkylamido intermediate, a metal amide-based Lewis pair formed by borylation of C−N double bond, enabled an unprecedented CO_2 fixation pattern which is in sharp contrast to the traditional CO_2 insertion into transition metal-element bonds. A possible mechanism for the current catalytic difunctionalization reaction is proposed (Fig. 3). The initial reaction of $B_2(pin)_2$ with [(SIMes)Cu(O*t*Bu)], which was formed from metathesis reaction between [(SIMes)CuCl] and LiO*t*Bu, would generate the boryl copper complex [(SIMes)CuB(pin)] **A**. The subsequent insertion of an imine **1** into the Cu−B bond of **A** would afford the active copper amide complex **B**. In the following transition state **TS**, the activation of CO_2 was enabled by its facile bonding to α-borylalkylamido unit, which represents a Lewis pair featuring a strong copper amide Lewis base moiety and a relatively weaker Lewis acidic borane moiety. The traditional CO_2 insertion into the Cu−N bond of **B** is less favorable in the current catalytic reaction. The connection of CO_2 with N atom and B atom together with migration of the (SIMes)Cu unit to a pinacolate oxygen atom lead to the generation of cyclic boracarbamate derivative **C**. Transmetalation between copper complex **C** and LiO*t*Bu would regenerate active species [(SIMes)Cu(O*t*Bu)] and release final product **3**.

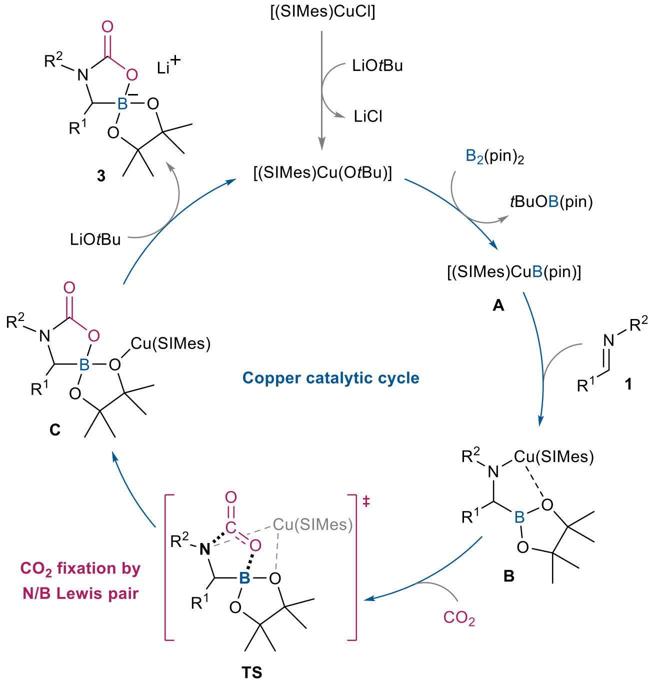

Fig. 3 A possible catalytic cycle for the formation of **3** based on computational and experimental results.

We hope that our findings may inspire further development of selective multicomponent reactions by incorporation of Lewis pair chemistry into transition-metal catalysis. This work has been published in *Journal of the American Chemical Society* (**2020**, *142*, 1966–1974.)

(c) Theoretical investigation on ε-Caprolactone/ Olefin polymerization

In addition to the C-H addition and CO_2 activation, some effects on catalytic polymerization were also investigated by DFT calculations. We has revealed the redox-switchable ROP mechanism of ε-caprolactone catalyzed by group 4 metal complexes bearing [OSSO]-type ferrocene ligands. (*Inorganic Chemistry Frontiers*, **2020**, DOI: 10.1039/c9qi01466g.). Besides, the polymerization of some polar monomer by rare-earth metal complexes were also studied, which provides useful information on the development of new polymerization systems (*Journal of the American Chemical Society*, **2019**, *141*, 12624–12633; *Catalysis Science & Technology*, **2019**, *9*, 6227–6233; *Chemical Communications* **2019**, *55*, 6689–6692.).

4. Conclusion

(1) In hydroaminoalkylation system: (a) Introduction of electron-withdrawing groups or with less steric hindrance surrounding the metal atom could improve catalyst performance; (b) It is found that P-, As-, and O-containing substrates are inert due to steric factors in the transition state of C–H activation. In contrast, alkyl sulfides and selenides are calculated to be promising candidates for *α*-C(sp^3)–H alkylation. These results provide valuable information on catalyst design and the application of these catalysts in the alkylation of *α*-C(sp^3)–H of heteroatom-containing compounds.

(2) In CO2 activation system, we have developed an efficient catalytic difunctionalization of imines via CO_2 activation by Lewis pairs as a key step in a copper-mediated catalytic cycle. This method enabled highly selective *C*-borylation with $B_2(pin)_2$ and *N*-carboxylation with CO_2 of the imine substrate, leading to the simultaneous introduction of two synthetically important functional groups, i.e. pinacolato boryl group and carboxylate group, across C–N double bonds. In particular, computational investigations identified an unusual activation mode of CO_2 by an *α*-borylalkylamido-based Lewis pair without direct intervention of copper metal center. The current method highlights the great significance of efficient construction of complex molecules via merger of Lewis pair CO_2 activation and copper catalysis. We anticipate this protocol will provoked further development of new catalytic processes of unsaturated bonds and small molecules toward the selective synthesis of valuable chemicals.

5. Schedule and prospect for the future

In the following FY2020, I will continue to collaborate with Prof. Zhaomin Hou (Organometallic Chemistry Laboratory & Advanced Catalysis Research Group, RIKEN) and investigated 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.

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Usage Report for Fiscal Year 2019

Fiscal Year 2019 List of Publications Resulting from the Use of the supercomputer

1. Gen Luo, Fan Liu, Yi Luo,* Guangli Zhou, Xiaohui Kang, **Zhaomin Hou***, and Lun Luo*. "Computational Investigation of Scandium-Based Catalysts for Olefin Hydroaminoalkylation and C–H Addition" *Organometallics* **2019**, *38*, 1887−1896. (SCI, Impact Factor: 4.100)

2. Zhenghua Li, Liang Zhang, Masayoshi Nishiura, **Gen Luo***, Yi Luo, **Zhaomin, Hou*.** "CO_2 Activation by Lewis Pairs Generated Under Copper Catalysis Enables Difunctionalization of Imines" *Journal of the American Chemical Society*, **2020**, *142*, 1966−1974. (SCI, Impact Factor:14.695)

3. Xiaowei Xu, **Gen Luo*, Zhaomin Hou**, Paula L. Diaconescu*, and Yi Luo* "Theoretical Insight into the Redox-switchable Activity of Group 4 Metal Complexes for the Ring-Opening Polymerization of ε-Caprolactone" *Inorganic Chemistry Frontiers*, **2020**, DOI: 10.1039/c9qi01466g. (SCI, Impact Factor: 5.934)

4. Haobing Wang, Yanan Zhao, Masayoshi Nishiura, Yang Yang, Gen Luo, Yi Luo*, **Zhaomin Hou***. "Scandium-Catalyzed Regio- and Stereoselective Cyclopolymerization of Functionalized α,ω-Dienes and Copolymerization with Ethylene" *Journal of the American Chemical Society*, **2019**, *141*, 12624–12633. (SCI, Impact Factor: 14.695)

5. Yanan Zhao, Han Lu, Gen Luo*, Xiaohui Kang*, **Zhaomin Hou**, and Yi Luo*. " Origin of Stereoselectivity and Multidimensional Quantitative Analysis of Ligand Effects on Yttrium-Catalysed Polymerization of 2-Vinylpyridine" *Catalysis Science & Technology*, **2019**, *9*, 6227−6233. (SCI, Impact Factor: 5.726.)

6. Yanan Zhao, **Gen Luo*,** Xiaohui Kang, Fang Guo, Xuefeng Zhu, Rencheng Zheng, **Zhaomin Hou** and Yi Luo*. "C−H···π Interaction Regulates Stereoselectivity in Olefin Polymerization" *Chemical Communications* **2019**, *55*, 6689–6692. (SCI, Impact Factor: 6.164)

[Poster presentation]

1. Gen Luo*, Yi Luo, **Zhaomin Hou**. Theoretical Insights into Nitrogen Activation by Multinuclear Titanium Hydride Complexes, *7th Asian Conference on Coordination Chemistry 2019 (ACCC7 2019)*, 15th–18th Oct 2019, Kuala Lumpur, Malaysia.

2. **Gen Luo*,** Yi Luo, Yuanhong Ma, **Zhaomin Hou***. Theoretical Mechanistic Studies on B(C6F5)3/Amine-Catalyzed C(sp)–H Silylation of Terminal Alkynes with Hydrosilanes, *1st International Conferences on Noncovalent Interactions (ICNI-2019)*, 2nd-6th Sept. 2019, Lisbon, Portugal.