Project Title:

Computational Study on Rare Earth Metal Complexes and Their Catalytic Reactions

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Background and purpose of the project

Chemical conversions driven by catalysts are essential to modern society. The ability to predict and modify the reaction route and rate-determining steps in chemical reactions would be a boon in designing better catalysts. Technical innovations in computer simulations bring that goal closer. Our research is focused on the fundamental study of molecular design for rare earth metal catalysts. As a powerful tool, quantum chemical theory planted into available programs was used to investigate the relationship between electronic structure and properties and hence predict and design new molecules. Since it is hard for experiment to do the same, static quantum chemical calculation and molecular dynamics simulation play an important role in this field.

Specific usage status of the system and calculation method

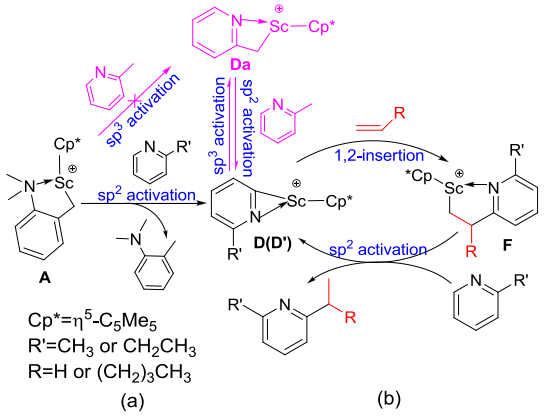
Part of specified computational resources was used. The DFT method planted in Gaussian and ADF programs were used.

Result

To gain details for the reaction of Sc-catalyzed addition of the *ortho*-C–H bond of pyridine derivatives to olefins, such as the accessibility and the geometric and energetic aspects of pathways, as well as the factors governing the activity and regioselectivity, density functional theory (DFT) computations were performed. The computational results show that mechanism mainly involves two processes: (a) the formation of active intermediates and (b) the process of catalyzing C–H addition of pyridines to olefins (Scheme 1). The later includes two steps: coordination and insertion of olefin, and the metal-mediated C–H activation of pyridines. In addition, it has been also computationally found that the methyl sp^3 C–H activation product of α-picoline is mainly resulted from the conversion of sp^2 C–H activation product of α-picoline rather than from the direct reaction of cationic species $Cp^*Sc(CH_2C_6H_4NMe_2\text{-}o)^+$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with pyridine, and such a conversion is reversible. The scandium-catalyzed C–H bond addition of 2-ethyl pyridine to 1-hexene preferably yields the 1,2-insertion product. Both steric and electronic factors control the regioselectivity in the current system. Interestingly, the energy analyses of the 1,2- and 2,1-insertion transition states of 1-hexene indicate that the interaction energy between 1-hexene moiety and active species rather than their deformations plays an important role in the stabilization of such transition states. The competition between olefin polymerization and pyridine C–H activation were also investigated in this study. It has been found that the coordination of α-picoline to the metal center is significantly favorable in comparison with that of ethylene, which could suppress ethylene

polymerization in the presence of *α*-picoline. Additionally, it is predicted that the cationic species $Cp^*Sc(MeC_5H_3N)^+$ has shorter induction period than $Cp^*Sc(CH_2C_6H_4NMe_2\text{-}o)^+$ for the chain-initiation stage of ethylene polymerization.

Scheme 1 The Whole Reaction Process of Sc-catalyzed C–H Addition of Pyridines to Olefins.



In the olefin polymerization, 1-hexene polymerization catalyzed by dicationic rare earth metal alkyl species $[Ln(^i\text{Pr-trisox})(CH_2SiMe_3)]^{2+}$ (Ln = Sc and Y, trisox = trisoxazoline) has been computationally studied by using QM/MM approach. It has been found that the initiation of 1-hexene polymerization kinetically prefers 1,2-insertion (free energy barrier of 17.23 kcal/mol) to 2,1-insertion (free energy barrier of 20.05 kcal/mol). Such a preference of 1,2-insertion has been also found for chain propagation stage. The isotactic polymerization was computed to be more kinetically preferable in comparison with syndiotactic manner, and the dicationic system resulted in lower insertion free energy barrier and more stable insertion product in comparison with the monocationic system. The stereoselectivity was found to follow chain-end mechanism, and the isospecific insertion of 1-hexene is mainly controlled by kinetics. In addition, the current computational results, for the first time, indicate that the higher activity of Sc species toward 1-hexene polymerization in comparison with the Y analogue could be ascribed to lower insertion barrier, easier generation of the active species, and its larger chemical hardness.

More investigations on the mechanism of olefin polymerization catalyzed by dinuclear rare earth metal complexes are in process and some positive results have been obtained.

Conclusion

The usage of RICC has provided details to the mechanism of Sc-catalyzed addition of the *ortho*-C–H bond of pyridine derivatives to olefins. The mechanism of olefin polymerization catalyzed by mononuclear rare earth complex has been also elucidated with the help of RICC system.

In the future, the mechanisms of C–H bond activated by mononuclear and multinuclear rare earth metal complexes and olefin polymerization catalyzed binuclear metal complex will be studied.

We wish to continue to use RICC system for the current long-term project. At this stage, only primary results were obtained. More systematic results on the mechanism of newly discovered reactions catalyzed by rare earth metal complexes are expected.

Fiscal Year 2012 List of Publications Resulting from the Use of RICC

[Publication]

1. Gen Luo, **Yi Luo**,* Jingping Qu, Zhaomin Hou* "Mechanistic Investigation on Scandium-Catalyzed C-H Addition of Pyridines to Olefins", *Organometallics* **2012**, *31*, 3930–3937.
2. **Yi Luo***, Yang Li, Hang Yu, Jinfeng Zhao, Yanhui Chen, Zhaomin Hou, Jingping Qu* "DFT Studies on Reduction of Dinitrogen to Ammonia by a Thiolate-bridged Diiron Complex as Nitrogenase Mimic" *Organometallics* **2012**, *31*, 335–344.
3. Xiaohui Kang, Yuming Song, **Yi Luo**,* Gang Li, Zhaomin Hou,* Jingping Qu* "Computational Studies on Isospecific Polymerization of 1-Hexene Catalyzed by Cationic Rare Earth Metal Alkyl Complex Bearing a C_3 *i*Pr-trisox Ligand" *Macromolecules* **2012**, *45*, 640–651.