

## Theoretical Study on Cooperative Catalysis of Constrained Pincer-type Phosphorus Compound: Mechanism, Electronic Process, and Prediction

○Guixiang Zeng<sup>1</sup>, Satoshi Maeda<sup>1</sup>, Tetsuya Taketsugu<sup>1</sup>, Shigeyoshi Sakaki<sup>2</sup>

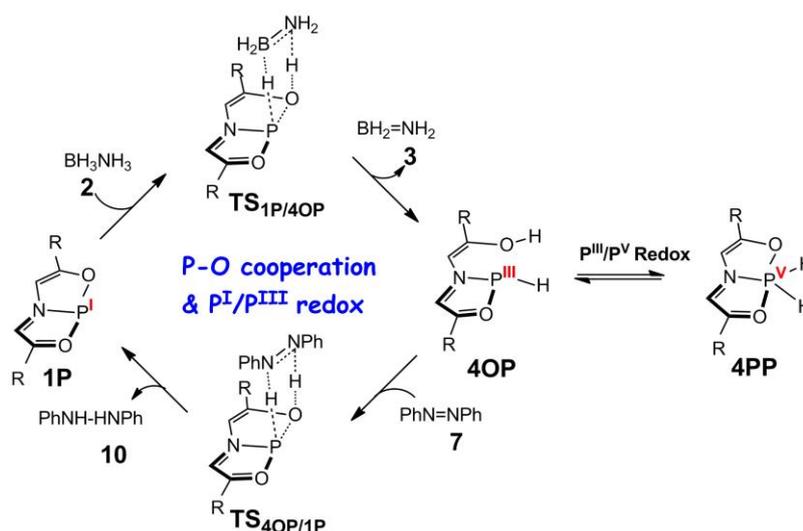
<sup>1</sup> 北大院理, <sup>2</sup> 京大福井センター

gxzeng@mail.sci.hokudai.ac.jp

Main-group element compounds are promising cheaper and green alternatives to transition-metal complexes in catalyses for their excellent reactivity similar to that of transition-metal complexes in typical elementary reaction steps [1]. However, the catalytic cycles by main-group element compounds are rare as compared with those by transition-metal complexes. Note that the metal-ligand cooperation catalytic cycle and the redox cycle are often found in the catalyses by transition-metal complexes. Therefore, constructing catalytic cycles is of crucial importance for the development of the catalyses of main-group element compounds, which would provide new possibilities for chemical syntheses.

Radosevich et al. reported a transfer hydrogenation reaction of azobenzene with  $\text{NH}_3\text{BH}_3$  mediated by a constrained phosphorus compound **1P** in 2012 [2]. We theoretically investigated this reaction to explore its mechanism with DFT method, where GRRM program was employed to search transition states [3]. The CCSD(T) and ONIOM(CCSD(T):MP2) methods were employed to elucidate the electronic processes of the reaction. Our computational results demonstrated that the reaction occurs through a phosphorus-ligand cooperation catalytic cycle (Scheme 1), in which the oxidation state of the phosphorus center changes between +I and +III. This electronic feature is different from that of the metal-ligand cooperation catalytic cycle, where the oxidation state of the metal center does not change.

We also investigated the substituent and framework effects on the activity of **1P**. More active pincer-type phosphorus catalyst was theoretically designed, which exhibits much wider applications than the experimentally reported one.



**Scheme 1.** Reaction mechanism of the transfer hydrogenation reaction mediated by **1P**.

[1] P. P. Power, *Nature* **463**, 171 (2010).

[2] N. L. Dunn, M. Ha, and A. T. Radosevich, *J. Am. Chem. Soc.* **134**, 11330 (2012).

[3] G. Zeng, S. Maeda, T. Taketsugu, and S. Sakaki, *Angew. Chem. Int. Ed.* **53**, 4633 (2014).