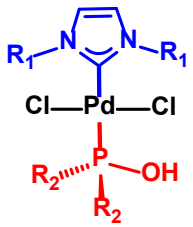
Computational Design of Heteroleptic Palladium Precatalysts in the Activation Process for Cross-coupling Reactions

Wei-Chih Chen*

Department of Applied Chemistry, Providence University, Taichung, Taiwan
wcchen94@gm.pu.edu.tw

N-heterocyclic carbene (NHC) And Phosphinous Acid (NAPA) heteroleptic palladium precatalysts have been applied in cross-coupling reactions with superb catalytic efficiency. However, the detailed activation mechanisms of such heteroleptic palladium precatalysts remain elusive. This study investigated the reduction process from NAPA-type palladium precatalysts to active catalyst species in the Suzuki-Miyaura cross-coupling reaction through computational and experimental approaches. We found that the deprotonation of the phosphinous acid (PA^-) ligand by the base is the first step in the activation process. Then, the NHC ligand is dissociated from the palladium center because of the stronger donating ability of the PA^- ligand. Moreover, the computational results reveal that this dissociation process is the rate-determining step in activating the precatalyst. Therefore, tuning the dissociation energy barrier of the NAPA-type precatalysts can be a key factor in improving catalytic performance. Eventually, this work also provides thousands of data on ligand dissociation energy in NAPA-type precatalyst candidates, which guide the rational design of potential precatalysts.



NAPA-type Palladium Precatalysts

References

1. Liang, S. W.; Guo, Y. J.; Lee, W. C.; Zeng, P. R.; Lin, T. H.; Xie, P. Z.; Kang, H. H; Lu, I. C.*; Chang, Y. C.* ChemCatChem, **2022**, *14*, e202200736.
2. Hong, L. H.; Feng, W. J.; Chen, W. C.; Chang, Y. C.* Dalton Trans., **2023**, 52, 5101-5109.