Development of Palladium-catalyzed Oxidative Amination of 1,3-Diene and Elucidation of Catalytic Species

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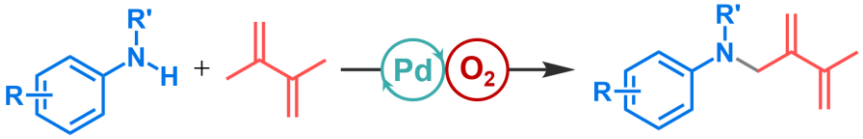
Palladium-catalyzed coupling reaction is a powerful tool in organic chemistry. Especially, oxidative coupling is one of the most straightforward coupling reactions.[1] This strategy is based on the oxidation of two hydrogen atoms where the coupling event occurs, succeeding in an atom- and step-economical reaction. It is well known that metal complexes are key intermediates including monometallic active sites in the proposed mechanism. However, the practical catalytic system involved a variety of catalytic species differing from a metal complex such as metal nanoparticles and metal nanoclusters, which exhibits a unique catalytic activity due to their reaction fields and dynamics.[2]

Here, we developed palladium-catalyzed aerobic oxidative amination of 1,3-diene. This reaction readily furnished nitrogen containing 1,3-dienes from commercially accessible feedstocks. The use of palladium complex with disilane allowed the reaction to proceeded with a high-chemo selectivity rather than electrophilic additions to 1,3-diene such as 1,4-hydroamination. Results of X-ray absorption spectroscopy (XAS) indicated our system involved unique palladium catalyst species contributing to the formation of products. Transmission electron microscopy and other X-ray techniques such as small angle X-ray scattering (SAXS) and X-ray diffraction (XRD) suggested the presence of palladium nanoparticles generated through the reduction by disilane. To obtain detailed understandings of the reaction, we evaluated both complex and nanoparticles catalyst reaction routes by computational studies and solution-phase XAS analysis.



- ✓ *Aerobic oxidative amination of 1,3-diene*
- ✓ *Characterization by XAS, SAXS, XRD…*
- ✓ *Computational studies*

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