

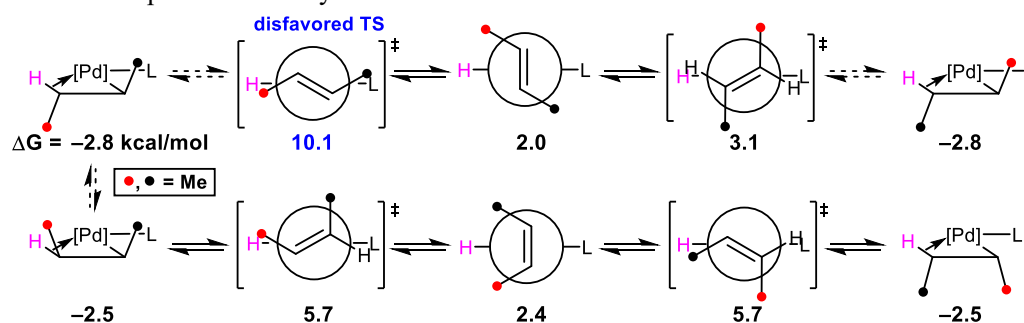
## Alkene Rotation as a Key Process in Chain Walking of a Palladium Catalyst and Its Effect on Selectivity of Reaction Pathways

(Faculty of Science and Technology, Keio University) ○Kazuma Muto, Miho Hatanaka, Fumitoshi Kakiuchi, Takuya Kochi

**Keywords:** Alkene Rotation, DFT Calculation, Palladium Catalyst, Chain Walking, Deuterium Labeling Study

Alkene rotation around the metal–alkene bond in complexes is one of the most fundamental elementary processes in organometallic chemistry, and the energy barrier of alkene rotation has been studied experimentally<sup>1</sup> and theoretically<sup>2</sup> for various alkene complexes. There have been numerous organometallic catalytic reactions involving the alkene rotation step, especially right before migratory insertion. However, it has rarely been recognized as key steps such as turnover-limiting or selectivity-determining steps in catalytic cycles. Chain walking is a process where alkylmetal species move along aliphatic carbon chains through repetitive  $\beta$ -hydride elimination, alkene rotation, and migratory insertion. During the course of our theoretical and experimental studies on the catalytic reactions proceeding via nondissociative chain walking of 1,10-phenanthroline palladium catalysts, we obtained some results indicating that the alkene rotation step mostly has the highest energy barrier in the chain walking process.

Explorations of nondissociative chain walking pathways of an *n*-propylpalladium species by DFT calculation suggested that the transition states on the alkene isomerization pathways only located during the alkene rotation. Alkene dissociation from the alkene hydrido complex and associative alkene exchange were also calculated and found to be less favorable than the nondissociative chain walking pathway. Theoretical calculation of palladium complexes with longer alkyl groups also provided similar results to the propylpalladium complex. In addition, it was suggested that chain walking of the palladium center between internal carbons proceeds via palladium hydride complexes ligated to cis alkene intermediates, although cis alkenes are thermodynamically less stable than trans alkenes. The preference of cis alkene intermediates was supported by a deuterium-labeling experiment of remote arylation substitution using a 1,10-phenanthroline palladium catalyst.<sup>3</sup>



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