

**DFT Investigation on the Mechanistic Study of Olefin Isomerization
Reaction by Dimeric Palladium (I) Catalyst**

Sriman De and Debasis Koley*

*Department of Chemical Sciences, Indian Institute of Science Education and Research
(IISER) Kolkata, Mohanpur - 741 246*

E-mail: koley@iiserkol.ac.in

Enol esters are considered as one of the most valuable precursors in a variety of organic transformations[1]. Due to their importance in organic transformations, several studies have been performed towards the development of enol ester synthesis[2]. Recently, Gooßen et. al.[3] have developed an olefin isomerization reaction for the formation of enol esters with the help of highly active dimeric $[\text{Pd}(\mu\text{-Br})(\text{PtBu}_3)]_2$ catalyst 1. Preliminary DFT calculations have been performed to address the actual catalyst responsible for the transformation with successive effort in understanding the detailed mechanistic profiles of the title reaction. We have considered the direct coordination of the substrate to the dimeric palladium complex as well as the monomeric Palladium(II)-hydride species $[\text{Pd}(\text{HBr})(\text{PtBu}_3)]$ generated after decomposition route. Unfortunately, both the pathways show unfavourable thermodynamics which is incompatible with the experimental conditions. In an alternative approach, activation of catalyst 1 via internal C-H activation will furnish dimeric Palladium(I)-hydride species. Our computational endeavour suggest that dimeric Palladium(I)-hydride species will act as a potential candidate for the facile conversion of allylic ester to enol ester. In addition, the active catalyst formation is found to be the rate-limiting step of the overall reaction.

References:

1. a) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029; b) Urabe, H.; Suzuki, D.; Sasaki, M.; Sato, F. *J. Am. Chem. Soc.* **2003**, *125*, 4036; c) Yanagisawa, A.; Matsumoto, Y.; Asakawa, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1999**, *121*, 892.
2. a) Smith, M. B.; March, J. *Advanced Organic Chemistry 5th ed.*; John Wiley & Sons, New York, **2001**, 486; b) DeBergh, J. R.; Spivey, K. M.; Ready, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 7828; c) Yoo, W. -J.; Li, C. -J. *J. Org. Chem.* **2006**, *71*, 6266.
3. Mamone, P.; Grünberg, M. F.; Fromm, A.; Khan, B. A.; Gooßen, L. *J. Org. Lett.* **2012**, *14*, 3716.