

PRF# 56090-UNI3

Title: Towards Transition Metal Catalyzed Oxidative Functionalization of Alkanes by Molecular Oxygen Progress Report

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Recent results:

As outlined previously the Keith group is examining insertion of molecular oxygen into M-R bonds ($R = H, CH_3$) in an effort to understand mechanistic pathways for selective alkane oxidation by transition metal catalysts. The group examines these mechanistic pathways computationally with Density Functional Theory. Towards this goal the group has focused on the reaction of the following two compounds with O_2 to form the corresponding peroxy methyl species (MOOMe) (Figure 1).

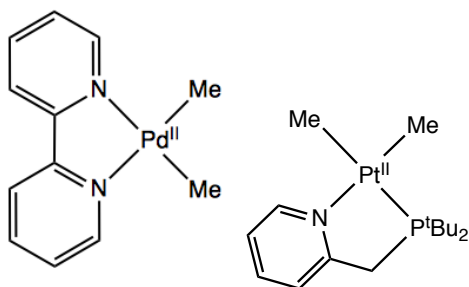


Figure 1. Square planar complexes reported by Goldberg et al.^{1,2} to insert O_2 through a radical mechanism.

Two general pathways are possible proceeding through either the +1 or +3 oxidation state (Figure 2).

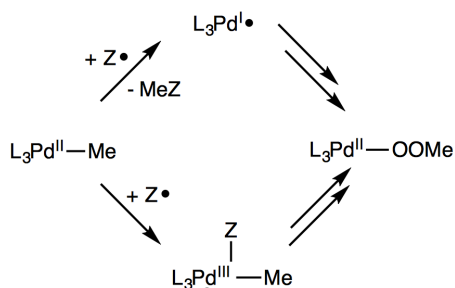
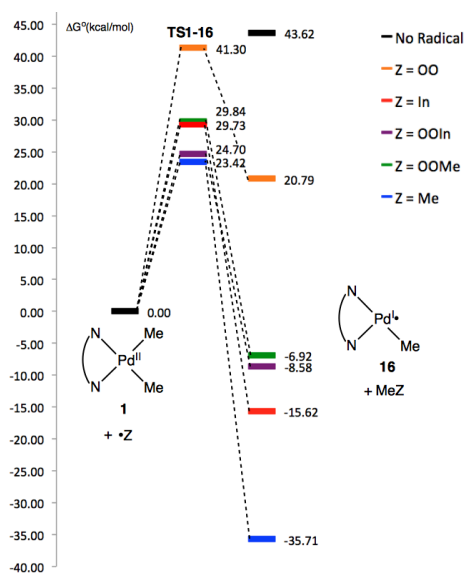


Figure 2 (above). Scheme for radical (i.e. 1 electron) pathways for insertion of O_2 into Pd-Me bond.

Figure 3 (right). PES for PdI Me radical abstraction pathways



M^I pathways involving Me radical abstraction were deemed too high in energy suggesting that M^{III} pathways were predominate (Figure 3). Investigation into possible M^{III} pathways involved 5-coordinate pseudo square pyramidal structures resulting from radical addition to the open axial position on the metal center. This addition leads to facile ligand substitution and formation of product (Figure 4).

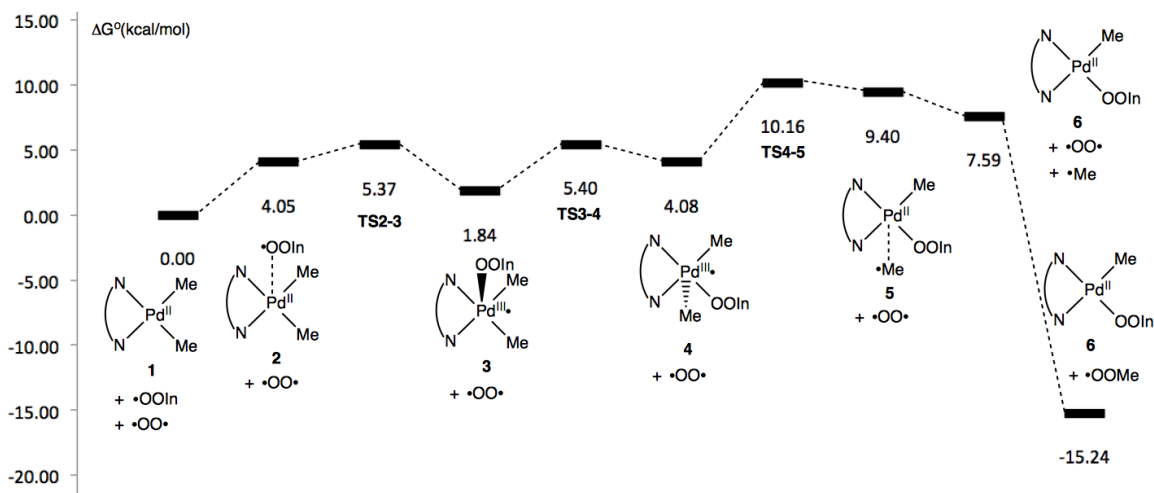


Figure 4. PES for Addition of activated O₂ species to Pd^{II}.

Similar results were found for In = Me in both the Pt and Pd systems fully explaining the observed reactivity in those systems.

This work is currently being compiled for publication.

- 1) Boisvert, L.; Denney, M. C.; Hanson, S. K.; Goldberg, K. I. *J. Am. Chem. Soc.* **2009**, *131*, 15802-158814.
- 2) Grice, K. A.; Goldberg, K. I.; *Organometallics* **2009**, *28*, 953-955.