Mechanism of molecular oxygen insertion in a Pd(II)-H Bond

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Sandia National Labs and U. Washington

234th ACS National Meeting, Boston

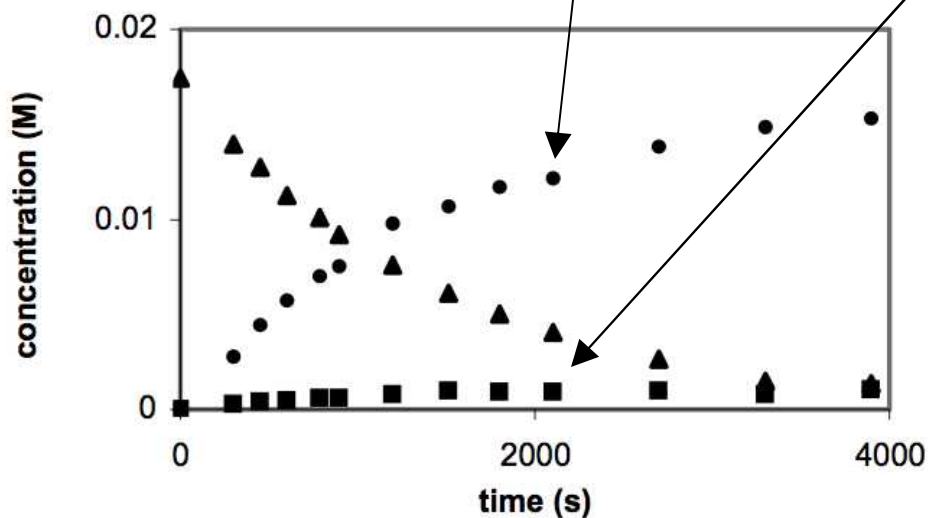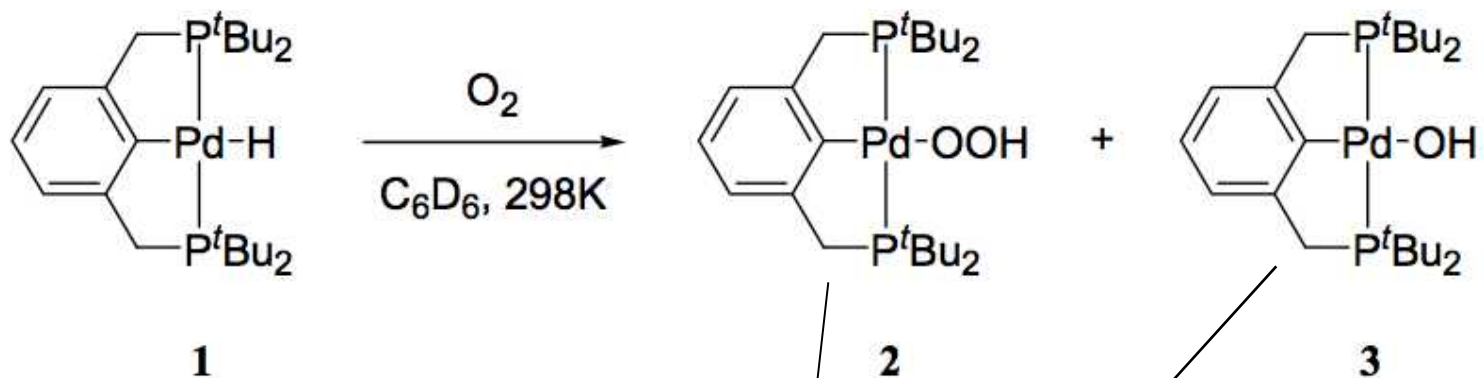August 19, 2007

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Why Is O_2 Activation Important?
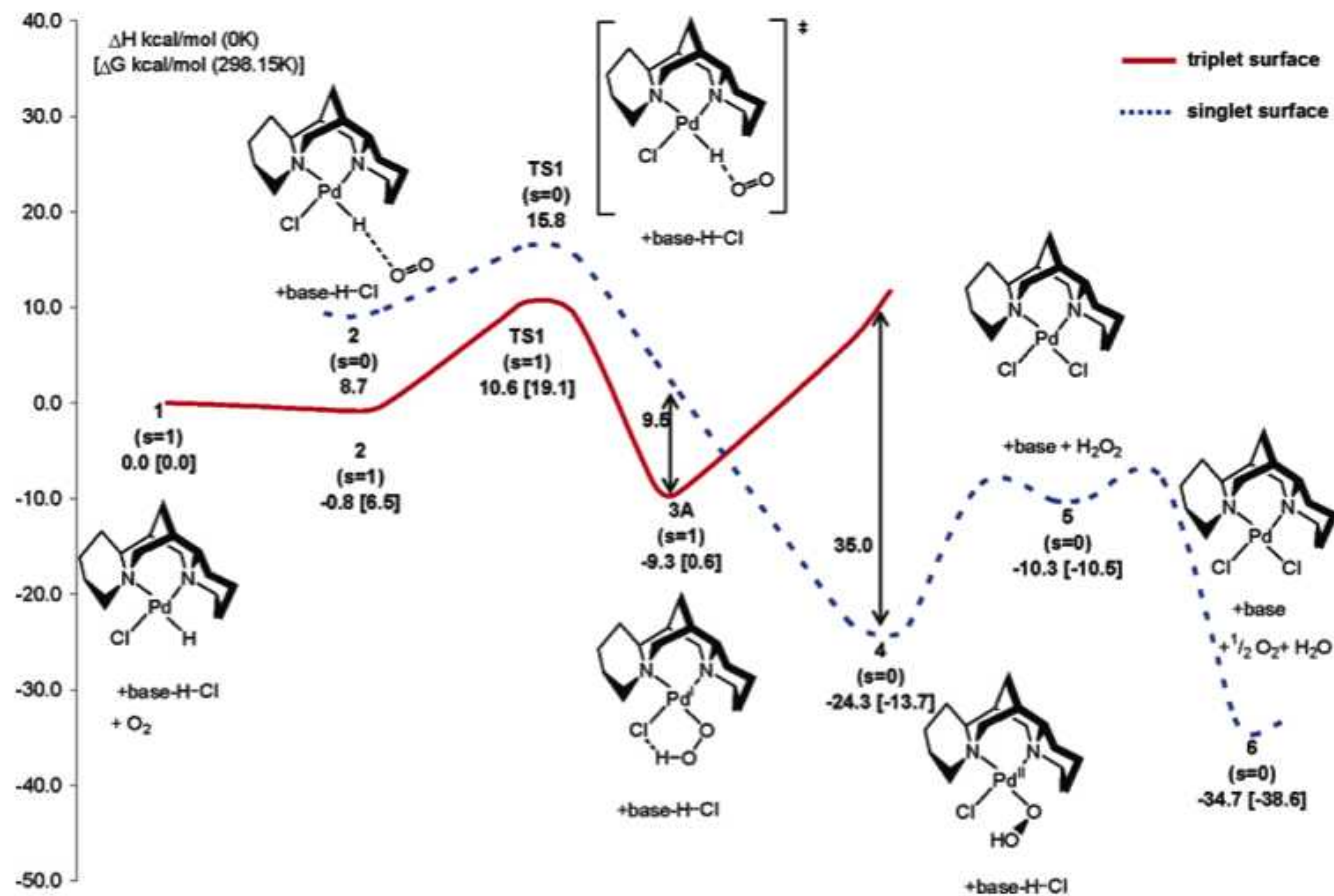
- Wacker
- Periana CH_4 Activation

Starting Points

- Kemp, Goldberg Pd-H Catalyst

Denney, Smythe, Cetto, Kemp, Goldberg, JACS, 128, 2508 (2006)
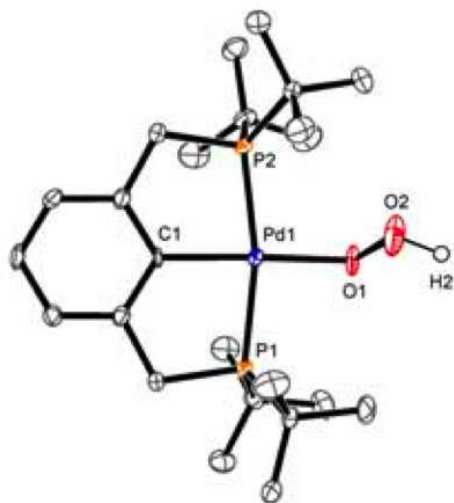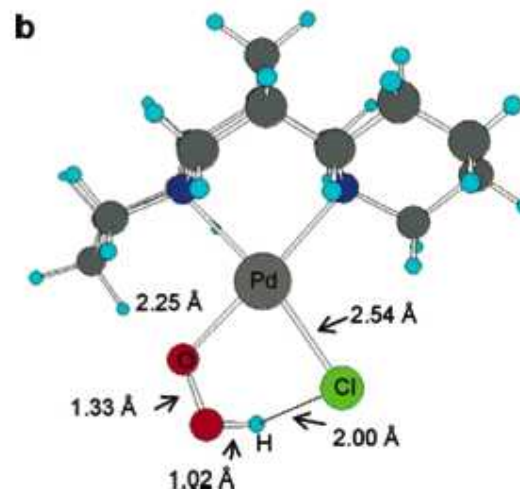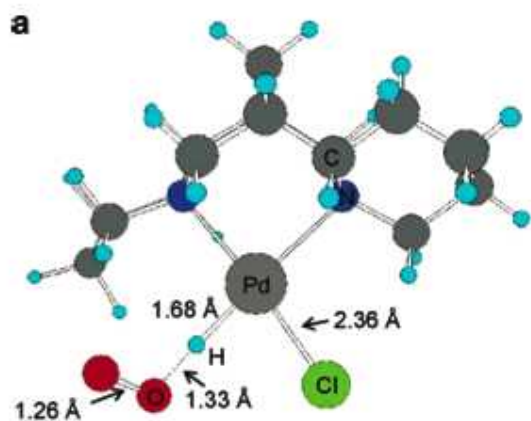
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Starting Points

- Goddard PdOOH Mechanism

Keith, Nielsen, Oxgaard, Goddard, JACS, 127, 13172 (2005)

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Mechanism Questions

- Goddard *et al* found a critical role for the Cl in stabilizing the intermediates for the insertion. Kemp/Goldberg's structure doesn't have any appropriate H-bond acceptor. How does it work?

Spin Forbidden MECP Calculations

Singlet

Oxygen Triplet-Singlet Gap

Triplet

????
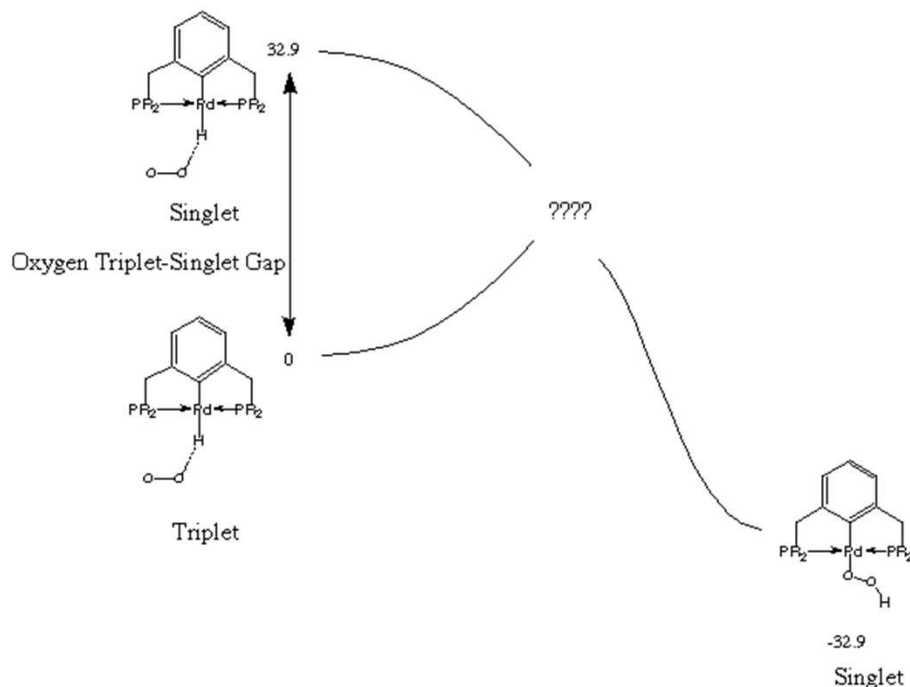
Singlet

- This is a spin-forbidden reaction
- In addition to the singlet, triplet PES, we need to find the MECP.
- Use the method of Harvey et al.
- Harvey, Aschi, Schwarz, Koch, TCA, 99, 95 (1998).
- Thanks to Harvey for providing software
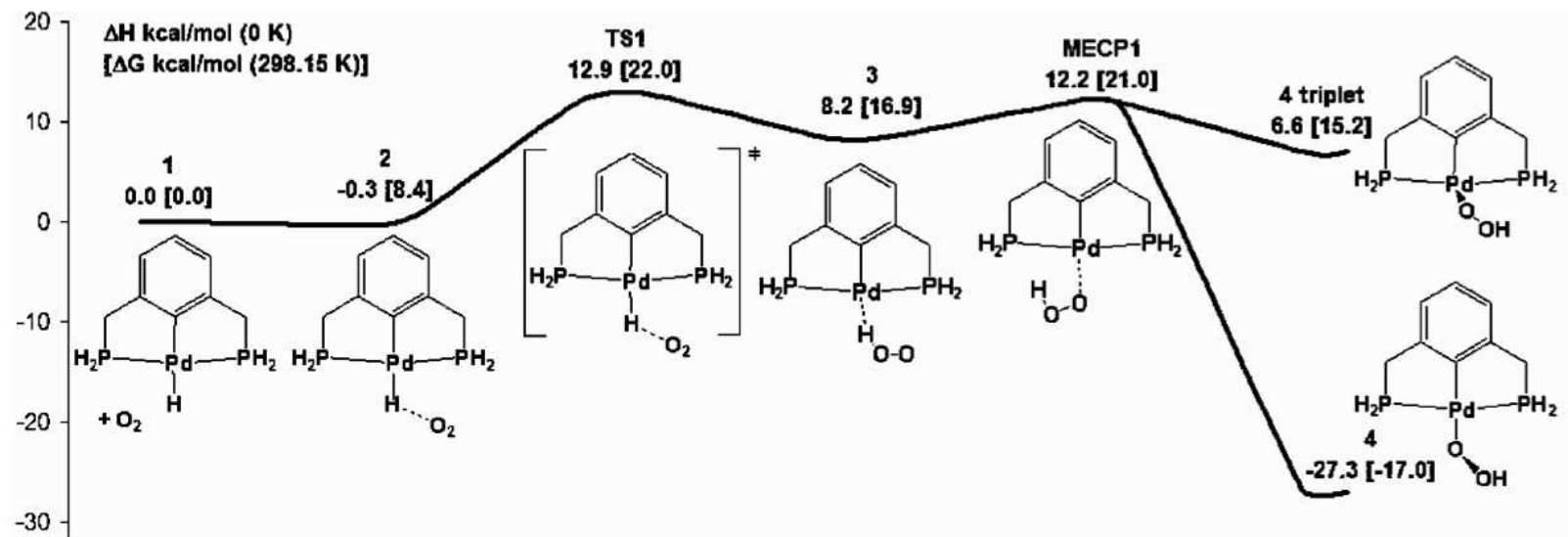
Mechanism Calculation
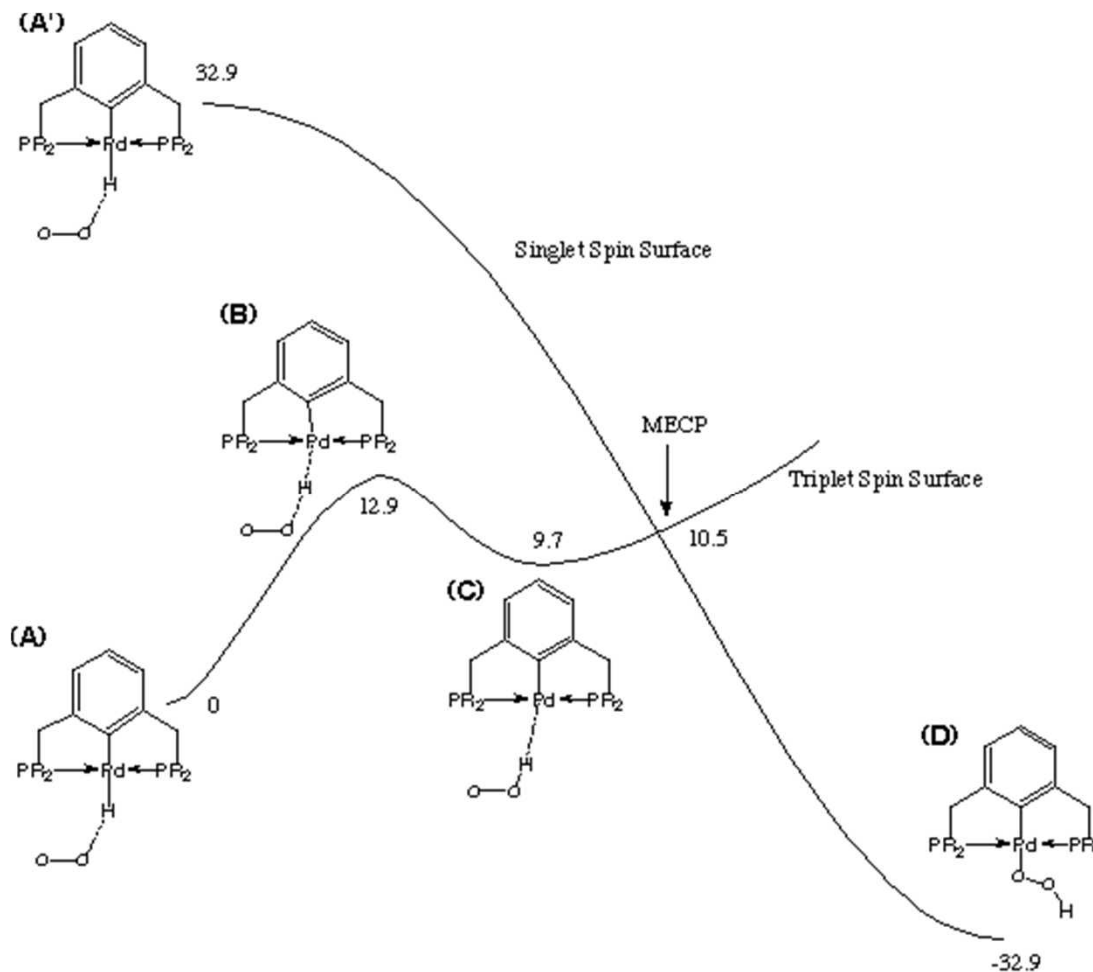
Structure of the MECP

Final Collaboration

Mechanism of Direct Molecular Oxygen Insertion in a Palladium(II)–Hydride Bond

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Future Directions

- Can we use the PdOOH to deliver an O to an appropriate species?