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

**Jason M. Keith,[†] Richard P. Muller,[‡] Richard A. Kemp,[§,∥] Karen I. Goldberg,[⊥]**
**William A. Goddard, III,[*,†] and Jonas Oxgaard[*,†]**

*Materials Process and Simulations Center, Beckman Institute (139-74),*
*California Institute of Technology, Pasadena, California 91125,*
*Multiscale Computational Materials Methods, Sandia National Laboratories,*
*Albuquerque, New Mexico 87185-1322, Department of Chemistry, University of New Mexico,*
*Albuquerque, New Mexico 87131, Advanced Materials Laboratory, Sandia National Laboratories,*
*Albuquerque, New Mexico 87106, and Department of Chemistry, University of Washington,*
*Box 351700, Seattle, Washington 98195-1700*

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The mechanism of the direct insertion of molecular oxygen into a palladium hydride bond has been elucidated using quantum mechanics (B3LYP/LACVP** with the PBF continuum solvent model). The key step is found to be the abstraction of the hydrogen atom resulting in the formation of a $Pd^I/HO_2$ (triplet) radical pair, which then proceeds to form a singlet palladium hydroperoxo species. Potential palladium(0) pathways were explored and were found to be inaccessible. The results are in agreement with recent experimental results and are consistent with our previously predicted mechanism for an analogue system.

The activation of molecular oxygen by transition metals, especially palladium, has been widely discussed in recent years. However, there are still numerous questions regarding the mechanism or mechanisms at play. The two current schools of thought focus on either a direct insertion of oxygen into a palladium−hydride bond or the interaction of oxygen with a palladium(0) complex. There is some indication that both mechanisms are feasible under varying conditions,[1−3] although support for the former mechanism was previously found only in our theoretical work.[2]

Recently, however, Goldberg and co-workers experimentally isolated a palladium−hydride species, $[1,3\text{-}(CH_2P^tBu_2)_2\text{-}C_6H_3]PdH$, and tracked the progress of a reaction between this species and oxygen.[3] The results suggested that the reaction proceeds by the aforementioned palladium−hydride insertion mechanism and should thus be a direct counterpart to our earlier theoretical work.[2] Consequently, we performed a detailed theoretical examination of the mechanism involved. We demonstrate that an insertion mechanism not only is possible but also is the only plausible solution. We discuss differences and similarities between this system and our previously studied Pd(sparteine)(Cl)(H) system.[2]

All calculations were performed using B3LYP/LACVP** as implemented by the *Jaguar 6.5* program package.[4] Implicit solvent effects for benzene were calculated with the Poisson−Boltzmann (PBF) continuum approximation,[5] using the parameter $\epsilon = 2.284$ and solvent radius = 2.60 Å. $1,3\text{-}(CH_2PH_2)_2C_6H_3$ (PCP) was also substituted for the $1,3\text{-}(CH_2P^tBu_2)_2C_6H_3$ ligand. This methodology was found to be an adequate level of theory in our previous, more exhaustive, study of Pd(sparteine)(Cl)(H).[2]

As the starting point for the study, we chose $[1,3\text{-}(CH_2PH_2)_2C_6H_3]PdH$ (**1**; Figure 1), also abbreviated (PCP)PdH. Introduction of (triplet) molecular oxygen leads immediately to the formation of a weakly bound van der Waals complex $[(PCP)PdH]\cdot O_2$ (**2**), with $\Delta H = -0.3$ kcal/mol, where the $O_2$ is coordinating to the hydride in the plane (forming pseudo-$C_s$ symmetry) and not to the metal. All attempts at finding a starting point where the $O_2$ coordinates directly to the metal failed, instead collapsing to **1** and free $O_2$ or to complex **2**. This is similar to our findings for Pd(sparteine)-

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* To whom correspondence should be addressed. E-mail: oxgaard@wag.caltech.edu.

[†] California Institute of Technology.

[‡] Multiscale Computational Materials Methods, Sandia National Laboratories.

[§] University of New Mexico.

[∥] Advanced Materials Laboratory, Sandia National Laboratories.

[⊥] University of Washington.

(1) (a) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400 and references cited therein. (b) Konnick, M. M.; Guzei, I. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 10212. (c) Stahl, S. S.; Thorman, J. L.; Nelson, R. C.; Kozee, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 7188.

(2) Keith, J. M.; Nielsen, R. J.; Oxgaard, J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **2005**, *127*, 13172.

(3) (a) Denny, M. C.; Smythe, N. A.; Cetto, K. L.; Kemp, R. A.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 2508. (b) A second paper appearing shortly after that also reports insertion of molecular oxygen into a $Pd^{II}-H$ bond: Konnick, M. M.; Gandhi, B. A.; Guzei, I. A.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2904.

(4) *Jaguar 6.5*; Schrodinger, Inc.: Portland, OR, 2005.

(5) (a) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W. A., III; Honig, B. *J. Am. Chem. Soc.* **1994**, *116*, 11875. (b) Marten, B.; Kim, K.; Cortis, C.; Friesner, R. A.; Murphy, R. B.; Ringnalda, M. N.; Sitkoff, D.; Honig, B. *J. Phys. Chem.* **1996**, *100*, 11775.

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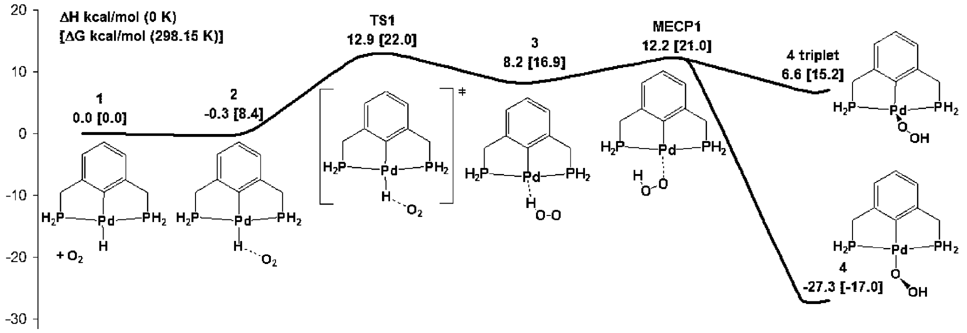

**Figure 1.** Calculated mechanism for oxygen insertion in (PCP)PdH in benzene. Energies are in kilocalories per mole (Δ*H* [Δ*G*]).

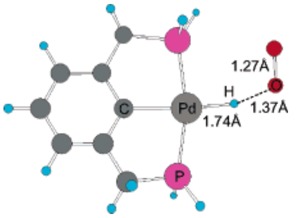

**Figure 2.** Transition-state structure for the hydrogen abstraction/oxygen insertion mechanism.

(Cl)(H)[2] and is most likely due to repulsion between the electron-rich oxygens and the filled d orbitals on the metal.

Electron transfer in **2** is negligible between the oxygen and the palladium complex (Mulliken charges on the two oxygens change from 0 and 0 to 0.02 and 0.01 electrons, while the palladium gains 0.03 electrons). Spin analysis demonstrates that all unpaired spins reside on the oxygen (one $\pi^*$ orbital parallel to the plane and one $\pi^*$ orbital perpendicular to the plane).

From **2**, we explored the transition state for the oxygen insertion mechanism. The transition state, **TS1** (Figure 2), has triplet oxygen positioned to abstract the hydrogen from the palladium center with $\Delta H^{\ddagger} = 12.9$ kcal/mol. This results in a stretching of the Pd−H bond distance from 1.62 to 1.74 Å, while the O−O bond distance increases from 1.21 to 1.27 Å. The O−H distance of 1.37 Å (compared to 0.96 Å in $HO_2$) indicates that the O−H bond has not yet formed. The spin population for the oxygen moiety is ~0.75 electrons on each oxygen atom, while that for palladium and the adjacent carbon are 0.19 and 0.26 electrons, respectively.

The reaction proceeds from the transition state to form the triplet species **3**, which can be best described as a Pd$^{I}$ T-complex with a closely associated $HO_2$ radical, with an overall $\Delta H = 8.2$ kcal/mol. The O−H bond length of 1.01 Å is similar to that of free $HO_2$, and the elongated Pd−H bond distance of 2.36 Å demonstrates the complete breaking of the Pd−H bond. Further analysis shows that one of the unpaired spins resides on the palladium in the orbital formerly bonded to hydrogen while the $HO_2$ fragment coordinates to the same orbital in an agostic fashion. **TS1** and **3** are almost planar; in both cases, the O−O moiety angles out of the (PCP)Pd plane by ~5°. Calculations using bulkier substituents on the phosphorus ligand show more deviation from planarity, but we do not expect this to significantly alter the overall mechanism.

From species **3**, the reaction proceeds to the singlet ($\eta^1$-hydroperoxo)palladium(II) product [**4**; (PCP)Pd−OOH] by rotation of the $HO_2$ fragment. Δ*H* for the formation of product = −27.3 kcal/mol. A triplet version of **4** is also possible, although higher in energy, and is thus expected to be short-lived. **4** is clearly a Pd$^{II}$OOH complex: the Pd−O bond distance of 2.04 Å is consistent with those of similar species,[2] while the O−O bond distance of 1.47 Å is what would be expected for a normal O−O single bond. The O−H bond distance of 0.97 Å is comparable to that in $H_2O_2$. It should also be noted that the calculated bond lengths are in close agreement with the bond lengths in the crystal structure from ref 3a [Pd−O = 2.074(3) Å and O−O = 1.470(4) Å].

We used the method of Harvey and co-workers[6] to compute the minimum energy crossing point structure (**MECP1**) between the singlet and triplet potential energy surfaces close to structure **3**. This structure has an energy $\Delta H = 12.2$ kcal/mol, and its structure is quite similar to that of triplet **4**, although with a slight rotation out of the plane around the Pd−O axis. The fact that the energy of **MECP1** is only marginally higher than the energy of **3** suggests that **3** will repeatedly explore the parts of the potential energy surface that contain the MECP and make a spin-forbidden transition possible.

We also considered a dissociative process, where the (PCP)Pd and OOH moieties separate in the solution to isolated radical species. Reassociation with a radical of the appropriate spin could then generate the singlet **4** without a formally forbidden spin crossing. Our calculations show that this dissociative process is less favorable than the concerted process on the Δ*H* surface, with a calculated Δ*H* of 13.1 kcal/mol, but more favorable on the Δ*G* surface, with a calculated Δ*G* of 11.1 kcal/mol. However, the accuracy of these solution-phase Δ*G* calculations is uncertain, and we thus cannot for sure state which mechanism is preferred.

While the above results show the viability of the direct insertion, various possible palladium(0) pathways should also be excluded. The tridentate ligand employed in this process excludes the commonly proposed square-planar $\eta^2$-$O_2$ complex without manipulation of the PCP backbone. However, two viable candidates were considered, assuming various possible ligand deformations (**5** and **6**; Figure 3). **5** is simply the product of an intramolecular reductive elimination of the hydride with the adjacent phosphorus moiety. This species

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(6) (a) Harvey, J. N.; Aschi, M.; Schwarz, H.; Koch, W. *Theor. Chem. Acc.* **1998**, *99*, 95. (b) Smith, K. M.; Poli, R.; Harvey, J. N. *Chem.—Eur. J.* **2001**, *7*, 1679. (c) Poli, R.; Harvey, J. N. *Chem. Soc. Rev.* **2003**, *32*, 1.

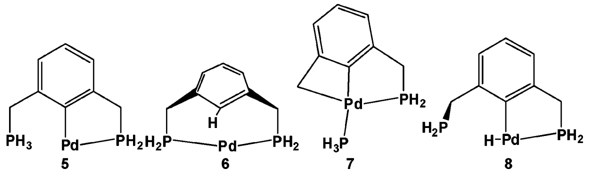

**Figure 3.** Possible candidates examined along the hypothetical palladium(0) pathway.

was not found despite numerous attempts, all of which instead collapsed to either species **1**, **7**, or **8**. No mechanisms through **7** and **8** were pursued because both are too high in energy (19.6 and 17.5 kcal/mol greater than **1**).

**6**, on the other hand, is a stable linear palladium(0) species with $\Delta H = -14.7$ kcal/mol. Despite the favorable energetics, **6** has two main problems: (1) The linear nature of the bonding does not allow for bonding of $O_2$ in an $\eta^2$ fashion. (2) Examination of the surrounding surface did not demonstrate a feasible barrier from **1** to **6**. Furthermore, because **6** is so much lower in energy than **1**, this should be the resting state of the catalyst if a low-energy mechanism for interconversion exists. Because the resting state of this (PCP)PdH complex is experimentally known to be species **1**, this indicates that no such mechanism exists, and **6** is thus not considered to be a viable intermediate.

These results are in contrast to our previous study of Pd(sparteine)(Cl)(H), where the possibility of palladium(0) pathways are not yet excluded. Indeed, preliminary studies suggest that palladium(0) pathways are competitive for the same system in coordinating solvents. Nevertheless, these palladium(0) pathways are not viable for the current system because the PCP ligand seemingly prevents the formation of palladium(0).

The current direct insertion mechanism is, however, in the initial aspects similar to the insertion mechanism we previously described for an analogue Pd(sparteine) system without a hydrogen-bonding X-type ligand.[2] Indeed, **TS1** is almost identical with the corresponding transition state in the Pd(sparteine)$CH_3$ system, both energetically (12.9 and 13.2 kcal/mol, respectively) and geometrically (Pd−H 1.74 and 1.72 Å, O−H 1.37 and 1.27 Å, and O−O 1.27 and 1.28 Å, respectively). Conversely, while the hydrogen-abstraction transition states are similar, the resulting intermediate in the present case is lower with $\Delta H = 8.2$ kcal/mol, compared to 12.5 kcal/mol for the previous case. Similarly, the dissociation energy of the $HO_2$ radical (which we believed to be energetically prohibitive to the process in the previous study) is lowered from 19.0 to 13.0 kcal/mol, allowing the reaction to proceed without excessive barriers.

In addition to the correlation between the Pd(sparteine) and the Goldberg system, we also examined the kinetic isotope effect (KIE) present when the hydrogen atom attached to palladium is switched to a deuterium atom. For **TS1**, we calculate a classical KIE value of 2.49. To correct for tunneling, this should be multiplied by an additional transmission coefficient, which we estimate as 5.2, based on a one-dimensional parabolic approximation of the potential barrier outlined by Skodje and Truhlar.[7] The total KIE (12.9), while off by a factor of 2 if we assume our classical KIE is correct, is still in fair agreement with Goldberg's reported KIE of 5.8. Indeed, our results thus validate the suggestion by Goldberg and co-workers that tunneling makes an important contribution to the total KIE (they postulate that the classical part of the measured KIE should be $<3.3$).[3a]

We also explored the possibility of **MECP1** being the rate-determining step. The corresponding KIE should be[8]

$$\kappa = \frac{\kappa(\mathbf{TS1})\,\kappa(\mathrm{MECP})}{\kappa(-\mathbf{TS1})}$$

While we cannot at this point calculate the tunneling contribution from **MECP1**, the calculated classical KIE values are $\kappa(\mathbf{TS1}) = 2.49$, $\kappa(\mathbf{MECP1}) = 0.75$ (as both singlet and triplet), and $\kappa(-\mathbf{TS1}) = 7.46$. The calculated $\kappa$ for this case is 0.25, i.e., an inverse effect. While it is technically possible that the tunneling contribution could alter this value to the observed KIE of 5.8, it would require a tunneling coefficient for the **MECP1** of 23.2, which is unrealistic. Also, calculations of the equilibrium isotope effect of the isolated radicals described above show a similar ratio (0.38). Consequently, we believe the possibility of the spin crossing being the rate-determining step can be ruled out.

In conclusion, a direct insertion of triplet $O_2$ into a specific Pd−H bond to form a ($\eta^1$-hydroperoxo)palladium(II) species has been established. The mechanism starts with abstraction of a hydrogen atom by molecular oxygen, which then forms a $Pd^I/HO_2$ radical pair. The $HO_2$ moiety rotates and flips the spins, resulting in the product hydroperoxo species. It is not clear whether this occurs through a concerted or dissociative mechanism. The calculated mechanism presented here agrees with the experimental evidence put forward by Goldberg and co-workers and supports our previous hypothesis that this type of insertion mechanism is both possible and in some cases the only viable process.

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**Supporting Information Available:** Tables of geometries, zero-point-energy corrections, absolute energies, and frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Skodje, R. T.; Truhlar, D. G. *J. Phys. Chem.* **1981**, *85*, 624.

(8) For a more in-depth discussion of this, see, for example: Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403.