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Insertion of Molecular Oxygen into a Palladium(II) Hydride Bond

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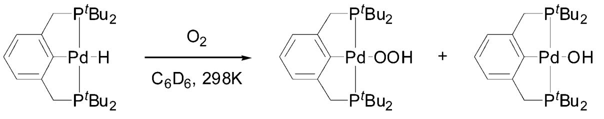
Molecular oxygen is a highly desirable oxidant from chemical, environmental, and economic standpoints. However, effective utilization of this reagent in selective oxidation reactions has been limited by an inadequate understanding of how transition metal complexes activate O_2. Significant recent progress in the use of palladium catalysts for selective aerobic oxidations has emphasized the importance of developing a thorough comprehension of reactions between palladium complexes and O_2.[1] One proposed pathway for oxygen activation in palladium-catalyzed oxidations is the reaction of palladium(0) with oxygen to form (η^2-peroxo)palladium species.[1] Experimental support, including the observation of the reaction in model systems, has recently been reported.[1b,c] Another pathway that has been proposed is the direct insertion of oxygen into a palladium(II) hydride intermediate to form a palladium hydroperoxide species.[1a,2] A limited number of such insertion reactions have been documented with other transition metal hydrides,[3] but similar reactions in model palladium systems have remained elusive. Reported here is the first direct observation of insertion of molecular oxygen into a palladium(II) hydride bond to form an (η^1-hydroperoxo)palladium(II) complex.

Upon exposure to O_2 (0.8−10 atm), solutions of ($^{t\mathrm{Bu}}$PCP)PdH[4] (**1**) ($^{t\mathrm{Bu}}$PCP = [1,3-($CH_2P^tBu_2)_2C_6H_3]^-$) in benzene-d_6 react cleanly to form ($^{t\mathrm{Bu}}$PCP)Pd(OOH) (**2**) and ($^{t\mathrm{Bu}}$PCP)Pd(OH) (**3**) in variable ratios (eq 1). While the initial ratio of **2**:**3** can be up to 25:1, over time **2** is observed to convert to **3**, and ultimately, **3** is obtained in high yield (90%).



(1)

1 **2** **3**

Complex **3** was also synthesized independently by the addition of KOH to ($^{t\mathrm{Bu}}$PCP)Pd(ONO_2), similar to the reported preparation of the closely related hydroxide complex, ($^{i\mathrm{Pr}}$PCP)Pd(OH).[5] The NMR data for **2** and **3** are, for the most part, very similar.[6] The $^{31}P\{^1H\}$ NMR signals for **2** and **3** appear as singlets at 72.3 and 70.8 ppm, respectively in benzene-d_6. The ^1H NMR resonances attributed to the $^{t\mathrm{Bu}}$PCP ligands of **2** and **3** are almost identical. The signals arising from the methylene protons are coincident, and those due to the *tert*-butyl protons nearly overlap. In contrast, the hydroxide and hydroperoxide proton signals appear in distinct regions of the ^1H NMR spectrum. The hydroxide proton of **3** is observed at −1.6 ppm (in benzene-d_6), while the hydroperoxide proton of **2** appears as a broad singlet between 5.4 and 6.3 ppm, depending on concentration. The chemical shift range observed corresponds to a concentration range of ca. 3−15 mM, the signal shifting downfield with increasing concentration. Chemical shifts of ca. 6 ppm are consistent with data reported for other late metal hydroperoxide protons.[1b,3b]

There are only a small number of structurally characterized transition metal η^1-hydroperoxide species.[3b,7] X-ray quality crystals of **2** were obtained from the reaction of **1** with O_2 (10 atm) in pentane at −10 °C. The ORTEP is shown in Figure 1.[8] The unit cell is comprised of two molecules of **2**. Hydrogen bonding occurs between neighboring hydroperoxyl moieties, forming a six-membered, radially symmetric ring (Figure S1). A similar arrangement was reported for the platinum(IV) hydroperoxo species, (Tp^{Me_2})$PtMe_2$(OOH) (Tp^{Me_2} = hydridotris(3,5-dimethylpyrazolyl)borate).[3b]

The reaction of **1** with O_2 to form **2** and **3** was conveniently monitored by $^1H\{^{31}P\}$ NMR spectroscopy. The reactions of **1** with O_2 were first order with respect to **1**, as shown by the exponential decay in Figure 2 and the linear fits for the first-order plots of ln[**1**] versus time in Figure 3. The doubling of the rate constant from $5.6(8) \times 10^{-4}$ s^{-1} under 5 atm O_2 to $1.13(3) \times 10^{-3}$ s^{-1} under 10 atm O_2 clearly indicates that there is also a first-order dependence on O_2.[9]

The reaction of the deuteride analogue **1-*d*$_1$** with O_2 (to form **2-*d*$_1$** and **3-*d*$_1$**) resulted in a significant retardation in the observed reaction rate (10 atm O_2; $k_{\mathrm{obs}} = 1.95(11) \times 10^{-4}$ s^{-1}). This corresponds to a kinetic isotope effect (k_H/k_D) of 5.8(5) for the insertion of O_2 into the Pd−H(D) bond. A similar KIE value was recorded when the measurement was repeated under 5 atm of oxygen. Based on the Pd−H(D) stretching frequencies for **1** (1717.8 cm^{-1}) and **1-*d*$_1$** (1227.5 cm^{-1}), a maximum theoretical kinetic isotope effect for direct homolytic cleavage of 3.3 can be calculated.[10] While it is not obvious why the observed KIE is significantly greater than this value, the large magnitude of the observed KIE strongly implicates the involvement of Pd−H bond cleavage in the rate-determining step.

The reaction of **1** with O_2 to form **2** is similar to the reported reaction of (Tp^{Me_2})$PtMe_2$(H) with O_2 to form the corresponding platinum(IV) hydroperoxide complex.[3b] The platinum reaction was proposed to proceed via a radical chain pathway. This mechanistic proposal was based on the dramatic difference in reaction rates between reactions carried out in the light and in the dark, and between reactions with added radical initiator or radical inhibitor. Involvement of radical mechanisms have also been implicated in other reported reactions of metal hydrides and oxygen.[3a,b,11] In contrast to these reactions, the insertion of molecular oxygen into the Pd−H bond of **1** was found to proceed at reproducible rates that were relatively insensitive to the presence of radical inhibitors or light. When the reaction of **1** with O_2 (10 atm) was carried out in the presence of radical inhibitors 2,6-di-*tert*-butyl-4-hydroxytoluene (BHT; k_{obs} = ca. 1.4 s^{-1}) and 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO; $k_{\mathrm{obs}} = 1.16$ s^{-1}), no significant effect on the reaction rate was observed.[12] Furthermore, parallel reactions carried out under ambient light and in the dark showed highly comparable rates for the consumption of **1**. These results

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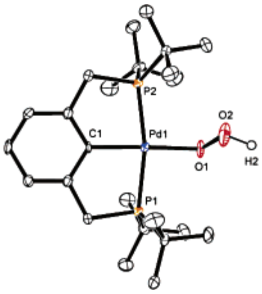

Figure 1. Molecular structure of **3**. Ellipsoids are shown at 50% probability and nonlocated hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−O(1) 2.074(3); Pd(1)−C(1) 2.022(3); O(1)−O(2) 1.470(4); O(2)−H(2) 1.10(4); C(1)−Pd(1)−P(2) 84.34(10); C(1)−Pd(1)−O(1) 175.27(11); P(1)−Pd(1)−P(2) 167.68(4); Pd(1)−O(1)−O(2) 108.53(19); O(1)−O(2)−H(2) 99(2).

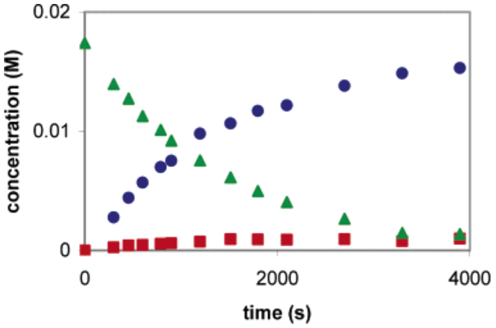

Figure 2. Reaction of **1** with O_2 (5 atm) over time. The concentrations of **1** (▲), **2** (●), and **3** (■) are shown.

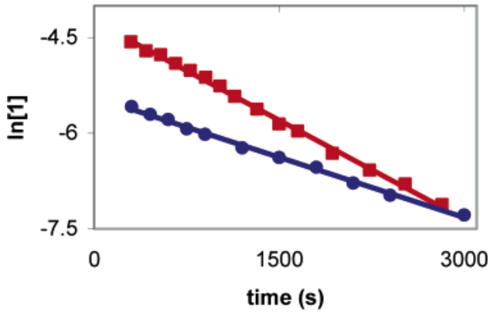

Figure 3. Linear relationship between ln[**1**] and time. Kinetic plots for reactions of **1** with 10 atm (■) and 5atm (●) O_2 are shown.

strongly suggest that the insertion of O_2 into the Pd−H bond of **1** to form **2** does not proceed via a radical chain mechanism.

The hydroperoxo species, **2**, is relatively stable as a solid at ambient temperature. However, solutions of **2** in benzene-d_6 were observed to form **3**. Other metal hydroperoxide complexes have been observed to disproportionate to form their corresponding hydroxide complexes and O_2.[13] In contrast to the reaction of **1** with O_2 to generate **2** and **3**, the rate of conversion of **2** to **3** was variable and appeared sensitive to light. For reactions of **1** and O_2 carried out in ambient light, **3** was present at higher concentrations than **2** throughout the reaction, while in the dark the ratio of **2** to **3** was substantially higher. This is suggestive of the involvement of a radical mechanism for the conversion of **2** to **3**, perhaps similar to the decomposition of organic analogues such as *tert*-butyl hydroperoxide, which decomposes to form *tert*-butyl alcohol and O_2.[14] Further investigations into the mechanism of the conversion reaction of **2** to **3** are underway.

In summary, the insertion of molecular oxygen into a palladium hydride bond has been directly observed, and the palladium hydroperoxide product has been structurally characterized. A second-order rate law (first-order in palladium and first-order in oxygen) was documented and evidence of significant Pd−H bond cleavage in the rate-determining step was provided. These observations are consistent with a mechanism involving the direct reaction of oxygen with the Pd−H bond or, alternatively, coordination of oxygen to the palladium(II) center followed by migratory insertion into the Pd−H bond. The reaction was unaffected by radical inhibitors and light, supporting that a radical chain mechanism is not involved. This finding is of particular interest since the selectivity of oxidation reactions can be compromised by the propensity of O_2 to participate in radical chain pathways. The identification of a clean, well-characterized activation of dioxygen by an isolable palladium(II) hydride complex should have significant impact on the development of palladium-catalyzed selective aerobic oxidation reactions.

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Supporting Information Available: Synthetic procedures and spectral characterization for **1**, **2**, and **3**, experimental details of kinetic experiments; X-ray crystallographic data files in CIF format for **2.** This information is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400 and references 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) (a) Takehira, K.; Hayakawa, T.; Orita, H.; Shimizu, M. *Stud. Org. Chem. (Amsterdam)* **1988**, *33*, 307. (b) Takehira, K.; Hayakawa, T.; Orita, H.; Shimizu, M. *J. Mol. Catal.* **1989**, *53*, 15. (c) Hosokawa, T.; Murahashi, S. *Acc. Chem. Res.* **1990**, *23*, 49. (d) Hosokawa, T.; Nakahira, T.; Takano, M.; Murahashi, S. *J. Mol. Catal.* **1992**, *74*, 489. (e) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 6750. (f) Nishimura, T.; Kakiuchi, N.; Onoue, T.; Ohe, K.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1915. (g) Keith, J. M.; Nielsen, R. J.; Oxgaard, J.; Goddard, W. A, III. *J. Am. Chem. Soc.* **2005**, *127*, 13172.
(3) (a) Wenzel, T. T. *Stud. Surf. Sci. Catal.* **1991**, *66*, 545. (b) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 11900. (c) Thyagarajan, S.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *Chem. Commun.* **2001**, 2198.
(4) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.
(5) Cámpora, J.; Palma, P.; Del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652.
(6) Characterization data for **2** and **3** are in the Supporting Information.
(7) (a) Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608. (b) Miyaji, T.; Kujime, M.; Hikichi, S.; Moro-oka, Y.; Akita, M. *Inorg. Chem.* **2002**, *41*, 5286 and references therein. (c) Ahijado, M.; Braun, T.; Noveski, D.; Kocher, N.; Neumann, B.; Stalke, D.; Stammler, H.-G. *Angew. Chem., Int. Ed.* **2005**, *44*, 6947.
(8) Farrugia, L. R. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(9) Using an Ostwald coefficient (*L*) of 0.22, the concentration of O_2 in benzene was calculated to be 0.045 M under 5 atm partial pressure of O_2 and 0.090 M under 10 atm partial pressure of O_2 (Battino, R. *Oxygen and Ozone*; Solubility Data Ser.; Pergamon Press: Oxford, 1981; Vol. 7).
(10) Atkins, P.; de Paula, J. *Physical Chemistry*, 7th ed.; W. H. Freeman & Company; New York, 2002; p 888.
(11) Endicott, J. F.; Wong, C.-L.; Inoue, T.; Natarajan, P. *Inorg. Chem.* **1979**, *18*, 450 and subsequent references.
(12) Several common radical inhibitors have been reported to react with palladium hydride species (Albénia, A. C.; Espinet, P.; López-Fernández, R.; Sen, A. *J. Am. Chem. Soc.* **2002**, *124*, 11278). Galvinoxyl was found to react directly with **1**. TEMPO and BHT did not react with **1**.
(13) (a) Pregalia, G.; Morelli, D.; Conti, F.; Gregorio, G.; Ugo, R. *Faraday Discuss. Chem. Soc.* **1968**, 110. (b) Karlin, K. D.; Ghosh, P.; Cruse, R. W.; Farooq, A.; Gultneh, Y.; Jacobson, R. R.; Blackburn, N. J.; Strange, R. W.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 6769.
(14) Hiatt, R.; Mill, T.; Mayo, F. R. *J. Org. Chem.* **1968**, *33*, 1416 and subsequent papers.

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