JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Reactivity of a Pd(I)−Pd(I) Dimer with O_2: Monohapto Pd Superoxide and Dipalladium Peroxide in Equilibrium

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Supporting Information

ABSTRACT: The Pd(I)−Pd(I) dimer $[(^F\text{PNP})\text{Pd}-]_2$ reacts with O_2 upon exposure to light to produce either the superoxide $(^F\text{PNP})\text{PdO}_2$ or the peroxide $[(^F\text{PNP})\text{PdO}-]_2$, which exist in equilibrium with free O_2. Both complexes contain square-planar Pd(II) centers. The unpaired electron density in $(^F\text{PNP})\text{PdO}_2$ is localized on the superoxide ligand.

The interest in transition-metal adducts with dioxygen has traditionally been spurred by their importance in biological and synthetic aerobic oxidations.[1] In recent years, the renewed focus on alternative energy schemes involving water oxidation has put the chemistry of transition-metal−O_x complexes into a new light.[2] Palladium is one of the most commonly used transition metals in catalysis, and it has been employed in innovative aerobic oxidation protocols.[3] Oxygenous complexes of Pd derived from reactions with O_2 are thus of special interest.[4] While the η^2-O_2−Pd complexes (cyclic peroxides) have previously been structurally characterized,[5] reports on η^1-O_2 complexes of Pd (superoxides) are limited to in situ spectroscopic characterization of Pd^{II} superoxides prepared by salt metathesis with KO_2[6] and a very recent report of $(\text{NHC})_2\text{Pd}(\eta^1\text{-}O_2)_2$ (NHC = N-heterocyclic carbene).[7] Pd^{I} superoxide has been proposed as an intermediate in the reaction of Pd^0 complexes with O_2.[8] Bridging Pd peroxides (with a Pd−O−O−Pd substructure) have been reported previously, but only from metathesis reactions with organic hydroperoxides.[9] In 2007, we reported that the dimeric complex $[(^F\text{PNP})\text{Pd}-]_2$ can easily be formed via photolysis of $(^F\text{PNP})\text{PdEt}$ (Scheme 1A) and that it is capable of cleaving H_2, H_2O, and NH_3.[10] Here we present our studies of the chemistry of $[(^F\text{PNP})\text{Pd}-]_2$ with O_2, which produces a Pd^{II} superoxide and a Pd^{II} bridging peroxide that exist in equilibrium.

Exposure of a solution of $[(^F\text{PNP})\text{Pd}-]_2$ in C_6D_6 or THF to excess O_2 (1 atm, >10 equiv; Scheme 1B) in direct sunlight resulted in a rapid color change (complete in <1 min) from the green of $[(^F\text{PNP})\text{Pd}-]_2$ to the orange of a new compound, $(^F\text{PNP})\text{PdO}_2$ (Scheme 1B), which was produced in >95% yield as determined by NMR spectroscopy. When smaller amounts of O_2 were used, a more oxygen-poor peroxide, $[(^F\text{PNP})\text{PdO}-]_2$, was observed. The rate of the reaction was clearly dependent on the exposure to light. Even fluorescent room lights effected it, albeit much more slowly, whereas in the absence of light, no reaction between a solution of $[(^F\text{PNP})\text{Pd}-]_2$ and O_2 took place.

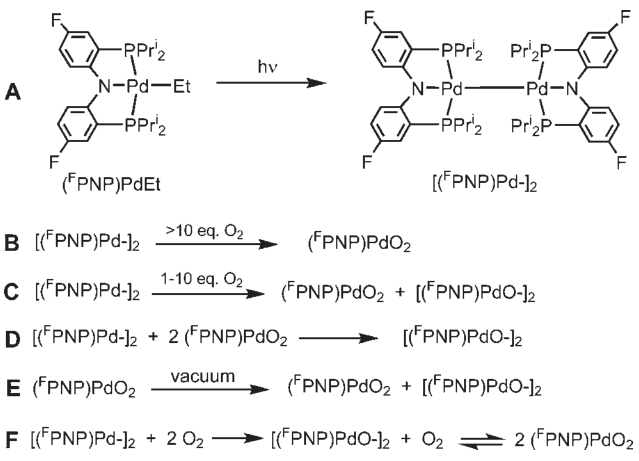
Although $(^F\text{PNP})\text{PdO}_2$ is paramagnetic (see below) and shows no detectable ^{31}P NMR signal and only broad resonances in its ^{1}H NMR spectrum,[11] it gave rise to a resonance of unremarkable width at δ −128.7 in the ^{19}F NMR spectrum; this is within the range observed for various diamagnetic (PNP)PdX complexes [e.g., δ −129.3 for $(^F\text{PNP})\text{PdOH}$].[12] $[(^F\text{PNP})\text{PdO}-]_2$ displayed NMR spectra typical for a diamagnetic $(^F\text{PNP})\text{PdX}$ complex, with a ^{19}F NMR resonance at δ −129.4. $[(^F\text{PNP})\text{PdO}-]_2$ rapidly reacted with excess Me_3SiBr to produce $(^F\text{PNP})\text{PdBr}$ quantitatively along with ~60% $Me_3SiOOSiMe_3$,[13] consistent with the proposed peroxide formulation.

Figure 1 demonstrates the outcome of the reactions of $[(^F\text{PNP})\text{Pd}-]_2$ with different partial pressures of O_2 (under sunlight). When substoichiometric amounts of O_2 were used, some unreacted $[(^F\text{PNP})\text{Pd}-]_2$ remained and no $(^F\text{PNP})\text{PdO}_2$ was formed. Instead, a compound assigned as $[(^F\text{PNP})\text{PdO}-]_2$ was observed. As the amount of O_2 was increased, $[(^F\text{PNP})\text{Pd}-]_2$ was completely consumed, and a mixture of $[(^F\text{PNP})\text{PdO}-]_2$ and $(^F\text{PNP})\text{PdO}_2$ resulted (Scheme 1C). At high enough concentrations of O_2, $(^F\text{PNP})\text{PdO}_2$ dominated. Preparation of relatively pure $[(^F\text{PNP})\text{PdO}-]_2$ was more conveniently accomplished by irradiation of an approximately 1:2 mixture of $[(^F\text{PNP})\text{Pd}-]_2$ and $(^F\text{PNP})\text{PdO}_2$ (Scheme 1D) than by attempting to dose exactly 1 equiv of O_2 with $[(^F\text{PNP})\text{Pd}-]_2$. When a solution of $(^F\text{PNP})\text{PdO}_2$ generated under 1 atm O_2 was subjected to removal of volatiles in vacuo, redissolution, and brief irradiation, the re-emergence of $[(^F\text{PNP})\text{PdO}-]_2$ was detected (Scheme 1E). These findings are summarized in Scheme 1F: the reaction of O_2 with $[(^F\text{PNP})\text{Pd}-]_2$ is irreversible, but $[(^F\text{PNP})\text{PdO}-]_2$ and $(^F\text{PNP})\text{PdO}_2$ exist in equilibrium with free O_2 (under irradiation). The more oxygen-rich superoxide is favored at higher concentrations of O_2.

Interestingly, the presently reported reactivity of the $(^F\text{PNP})\text{Pd}$ fragment with O_2 parallels the reactivity of O_2 with Wayland's (porphyrin)Rh species.[14] We previously pointed out the isolobality of $(\text{PNP})\text{Pd}^{\text{I}}$ and $(\text{porphyrin})\text{Rh}^{\text{II}}$ in the context of their analogous reactivity with H_2O.[15]

Received: January 13, 2011
Published: February 25, 2011

Scheme 1



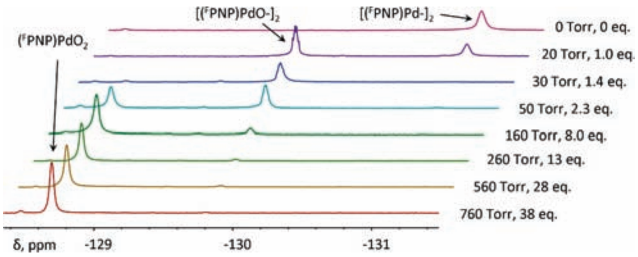


Figure 1. ^{19}F NMR spectra of the reactions of $[(^{F}PNP)Pd]_2$ with different amounts of O_2 in C_6D_6 collected after 5 min in direct sunlight.

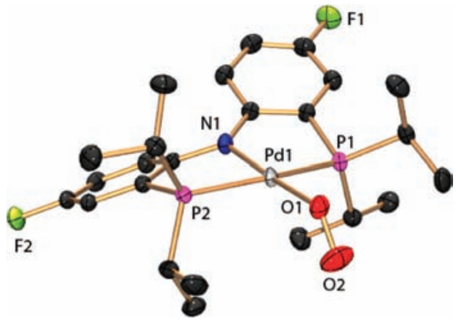


Figure 2. POV-Ray[17] rendition of the ORTEP[18] drawing (50% thermal ellipsoids) of $(^{F}PNP)PdO_2$ showing selected atom labeling. Hydrogen atoms and the THF solvent molecule have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−P1, 2.2886(5); Pd1−P2, 2.2981(4); Pd1−O1, 2.0096(13); Pd1−N1, 2.0263(14); O1−O2, 1.293(2); P1−Pd1−P2, 165.129(17); O1−Pd1−N1, 176.49(6); Pd1−O1−O2, 113.79(12).

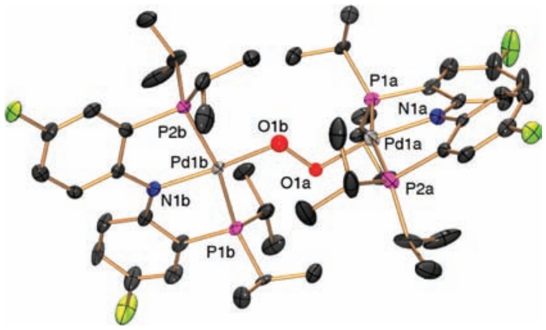


Figure 3. POV-Ray[17] rendition of the ORTEP[18] drawing (50% thermal ellipsoids) of $[(^{F}PNP)PdO-]_2$ showing selected atom labeling. Hydrogen atoms and the isopropyl Me groups have been omitted for clarity. Selected bond distances (Å) and angles (deg): O1a−O1b, 1.47(2); N1a−Pd1a, 2.032(8); O1a−Pd1a,1.985(13); O1b−Pd1b, 2.046(14); P1a−Pd1a, 2.290(3); P2a−Pd1a, 2.288(3); O1a−Pd1a−N1a, 163.7(5); P2a−Pd1a−P1a, 166.51(11); O1b−Pd1b−N1b, 167.3(5).

Both $[(^{F}PNP)PdO-]_2$ and $(^{F}PNP)PdO_2$ were stable in solution for hours in the dark at room temperature but decomposed readily upon thermolysis and/or exposure to fluorescent laboratory lighting and especially sunlight. The decomposition led to $(^{F}PNP)PdOH$[16] and a number of unknown products. It is not clear whether the decomposition of $(^{F}PNP)PdO_2$ proceeded by initial reversion to $[(^{F}PNP)PdO-]_2$; however, $(^{F}PNP)PdO_2$ decomposed even under 1 atm O_2.

Nonetheless, we successfully obtained X-ray-quality single crystals of both $(^{F}PNP)PdO_2$ and $[(^{F}PNP)PdO-]_2$. X-ray diffractometry (Figures 2 and 3) revealed that the Pd centers in both molecules exist in an approximately square-planar environment, with deviations arising mostly from the constraint of the ^{F}PNP ligand. The Pd−O−O angles are similar (102−114°) in the two complexes, and the distances to the more distal O are too long for bonding (>2.7 Å), indicating that both the peroxo and superoxo ligands function as monohapto ligands toward each Pd. The four Pd−element distances in $(^{F}PNP)PdO_2$ are very similar (differences of less than 0.02 Å) to the analogous Pd−element distances found in the structure of $(^{F}PNP)PdOAc$.[19] This suggests a single Pd−O bond character in $(^{F}PNP)PdO_2$ and a trans influence for the η^1-O_2 ligand that is comparable to that of acetate. The corresponding distances in $[(^{F}PNP)PdO-]_2$ are also similar, although the higher estimated standard deviation values prevented more precise analysis. The O−O distance of 1.293(2) Å in $(^{F}PNP)PdO_2$ is substantially longer than the O−O distance in free O_2 (1.20 Å)[20] and much shorter than the single-bond O−O distances typical for peroxides and hydroperoxides (1.41−1.49 Å).[9,20−22] Some recently reported η^2-O_2 complexes that formulaically are probably best described as cyclic peroxides have O−O distances of ∼1.36 Å,[23] but that is still considerably longer than the O−O distance in $(^{F}PNP)PdO_2$. On the other hand, the value of 1.293(2) Å falls squarely into the narrow range of O−O bonds typical for the superoxo (O_2^-) moiety.[24−27] The O−O distance of 1.47(2) Å in $[(^{F}PNP)PdO-]_2$ is within the typical range of O−O distances recorded for μ-κ^1:κ^1-peroxo moieties.[9,22]

A single one-line resonance at $g = 2.06$ was observed by EPR spectroscopy for $(^{F}PNP)PdO_2$. This suggested that the unpaired electron density is localized on the oxygen atoms of the superoxo moiety. The structural and spectroscopic information is thus consistent with the description of $(^{F}PNP)PdO_2$ as a Pd^{II} complex bearing a closed-shell anionic PNP pincer ligand and a monohapto ("end-on") superoxo ligand. To further probe this assignment, we performed density functional theory (DFT) calculations and found agreement as well.[28] Figure 4 presents a plot of the spin density (as obtained from the DFT calculations), showing its localization on the superoxide ligand. This localization is in line with the rather modest effect the unpaired electron exerts on the observed ^{19}F and ^{1}H NMR chemical shifts of the ^{F}PNP ligand in $(^{F}PNP)PdO_2$.

To illustrate in principle the capacity of this Pd system for catalytic O_2 activation, we found that $(^{F}PNP)PdO_2$ behaves as a catalyst for the oxidation of Ph_3P with O_2. In the presence of 2%

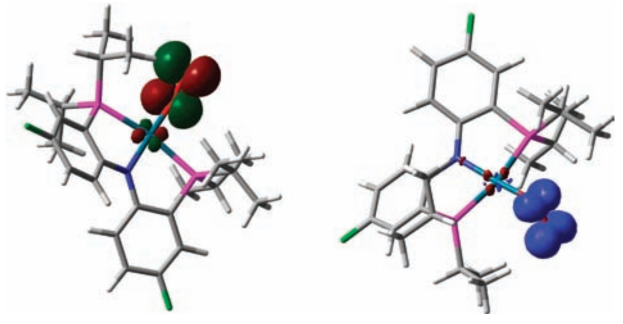


Figure 4. Calculated representation of (left) the singly occupied molecular orbital and (right) the spin density distribution in (^{F}PNP)PdO$_2$.

(^{F}PNP)PdO$_2$, we observed 95% conversion of Ph$_3$P to Ph$_3$PO after 3 days at ambient temperature in C$_6$D$_6$.[29] A control reaction in the absence of (^{F}PNP)PdO$_2$ led to only 5% conversion after 5 days. (^{F}PNP)PdO$_2$ remained the dominant species observed by NMR spectroscopy during the Ph$_3$P oxidation, but this does not exclude the possibility that [(^{F}PNP)PdO−]$_2$ or one of the decomposition products is the active catalyst.

In summary, we have reported the first structurally characterized Pd superoxide complex and the dipalladium peroxo complex that exists in equilibrium with it. (^{F}PNP)PdO$_2$ is easily obtained by photolysis of the Pd^I−Pd^I dimer [(^{F}PNP)Pd−]$_2$ in the presence of excess of O$_2$, while [(^{F}PNP)PdO−]$_2$ can be prepared under conditions of O$_2$ deficiency. Both molecules contain a Pd^{II} center bound to a monohapto oxygenous ligand. The unpaired electron in (^{F}PNP)PdO$_2$ is mostly localized on the superoxide moiety.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, crystallographic data (CIF), and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We are thankful for the support of this work by the U.S. National Science Foundation through the “Powering the Planet” Center for Chemical Innovation Grant (CHE-0802907) and a grant (CHE-0521047) for the acquisition of an X-ray diffractometer at Brandeis University. D.J.G. gratefully acknowledges the support of the Schiff Fellowship. R.H. gratefully acknowledges the support of the LSAMP BTD Fellowship. We are grateful to Dr. Joseph H. Reibenspies for assistance with X-ray structure solution.

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