



Oxygen-Atom Transfer

A Palladium(II) Peroxido Complex Supported by the Smallest Steric N-Heterocyclic Carbene, *I*Me = 1,3-Dimethylimidazole-2ylidene, and Its Reactivity by Oxygen-Atom Transfer

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Abstract: Stabilized with an N-heterocyclic carbene ligand of the smallest steric profile, $Pd^{II}(\eta^2-O_2)(IMe)_2$ (IMe = 1,3-dimethylimidazole-2-ylidene) was synthesized by the direct addition of dioxygen to $Pd^0(IMe)_2$. The peroxidopalladium complex with IMe, which was previously available only by computation, was

Introduction

Dioxygen is an ideal terminal oxidant for oxidation reactions of organic substrates with clear economic benefits and environmentally benign characteristics. For example, O₂ serves as a stoichiometric oxidant for the oxidation of alcohols and the oxidative heterocyclization of alkenes in the presence of the Pd(OAc)₂/DMSO system in addition to the recent discovery of oxygen-promoted C-H bond activation at Pd.^[1] The reaction scope was extended by introducing N-donor auxiliary ligands such as phenanthroline derivatives and N-heterocyclic carbenes (NHCs) that are resistant to oxidative conditions.^[2] To gain fundamental understanding of palladium-mediated oxygenation processes, several theoretical and experimental mechanistic studies have been conducted by the groups of Landis and Stahl, who studied the reaction between $Pd^{0}(IMe)_{2}$ (IMe = 1,3-dimethylimidazole-2-ylidene) and O2 with spin-unrestricted DFT methods to corroborate the solvent dependency in the thermodynamics of the process and to elucidate the stepwise mechanism that involves spin crossover.[3]

Although the $Pd^{II}(\eta^2-O_2)(/Me)_2$ complex has been utilized extensively in computational studies as a standard product of Pd^0

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oxygenation, the actual synthesis and characterization of this complex has not been reported to date. Herein, we report the synthesis and characterization of $Pd^{II}(\eta^2-O_2)(/Me)_2$ including its oxygen-atom-transfer reactivity, which involves thermolysis of the complex leading to the formation of the urea 1,3-dimethyl-imidazol-2-one (/MeO) and reaction of the complex with PPh₃ and (Me₃Si)₂ to give Ph₃PO and (Me₃Si)₂O, respectively.

Results and Discussion

The synthesis of the $Pd^{II}(\eta^2-O_2)$ complex by treating the Pd^0 precursor with O₂ in the solid state was previously demonstrated.^[2a,4] Storage of crystalline 1^[5] under an atmosphere of O₂ for 1 week produced surface coloration that was visible only under a microscope. However, exposure of a yellow homogeneous solution of 1 in THF to an atmosphere of O_2 resulted in quick discoloration and the formation of a bisque precipitate of peroxido complex 10₂, which slowly decomposed at 130 °C (Figure 1, a; see also Figure S1 in the Supporting Information). Featuring limited solubility, 102 was reasonably stable only in pyridine (py) and decomposed on the timescale of hours (DMF, CH₃CN and DMSO). However, the complex decomposed instantly in CH₂Cl₂ and acetone and was not soluble in C₆H₆, THF, or Et₂O (Figures S2–S4). These solubility and stability properties are unusual, because the most-known palladium peroxido complex, $Pd^{II}(\eta^2-O_2)(IMes)_2$, is soluble in aprotic nonpolar solvents such as C_6D_6 and $Pd^{II}(\eta^2-O_2)bc$ (bc = bathocuproine) is stable in CD_2CI_2 .^[2a,3a] After extensive efforts, crystals of $1O_2$ suitable for X-ray diffraction were obtained and analyzed, before losing crystallinity, in less than 12 h. The crystal structure of 1O₂ (Figure 1, b,c) confirmed its identity as the peroxide $Pd^{II}(\eta^2-O_2)$ -(IMe)₂, with structural parameters within the range of values observed for previously reported analogues.^[2a,3a,4,6] Each peroxide oxygen atom of 10_2 accepts four to five O···HC hydrogen bonds with distances of 2.14-2.71 Å. The O-O distances ob-



served in the two independent molecules, 1.475(3) and 1.476(5) Å, are the longest for various Pd^{II}(η^2 -O₂)(NHC)_n complexes^[2a,3a,4,6] among the palladium complexes containing IR spectroscopy data for v(O–O), possibly as a consequence of the extensive hydrogen bonding present and the strong donor character of the two /Me ligands. On the other hand, the weaker σ -donor character of the phosphine and nitrogen-based bc ligands in Pd^{II}(η^2 -O₂)[PPh(*t*Bu)₂]₂ and Pd^{III}(η^2 -O₂)bc causes the palladium(II) center to bind dioxygen weakly and to maintain shorter O–O bonds.^[2a] The observed bands for v(O–O) at 823 cm⁻¹ (¹⁸O₂: 782 cm⁻¹) in the solid state and at 837 cm⁻¹ in pyridine solution are consistent with the O–O distance/stretching frequency correlation established previously (Figures 2 and S15).^[7]



Figure 1. (a) Synthesis of $Pd^{II}(\eta^2-O_2)(/Me)_2$ (**1** O_2) and its reactivity. (b,c) ORTEP drawing of the crystal structure of **1** O_2 ·py-DMSO (50 % probability ellipsoids) showing the pattern of CH---O hydrogen bonds (orange dotted lines) to per-oxide oxygen atoms (red).



Figure 2. (a) IR spectra of $1O_2$ and $1O_2^{-18}O_2$ in Nujol showing the shift of v(O-O). (b) Correlation between O–O distance and stretching frequency in $Pd(\eta^2-O_2)L_2$ compounds. $Pd(\eta^2-O_2)[PPh(tBu)_2]_2$,^[2k] $Pd(\eta^2-O_2)(bc)$,^[2a] $Pd(\eta^2-O_2)(PPh_3)_2$,^[6b] $Pd(\eta^2-O_2)(Mes)_2$,^[3a] O_2^{-2} from Na_2O_2 .^[21]



In a previous computational study, the formation of $1O_2$ according to Figure 1 in the gas phase was characterized by a positive Gibbs free energy (ΔG°) value, however, solvation in common organic solvents was suggested to increase the stability of $1O_2$ to dissociation of O_2 considerably.^[3b] Heating solid $1O_2$ under 1 atm of N_2 for 8 h did not produce 1, as observed by ¹H NMR spectroscopy in solution, whereas thermolysis of the solid material at +130 °C for 8 h resulted in its decomposition to an insoluble brown tar still featuring a trace amount of residual $1O_2$. Thus, $1O_2$ appears to be relatively stable to the loss of O_2 in the solid state (Figure S1).

Computational studies adequately reproduce the key structural characteristics of 1 and 10₂ and suggest that CH···O hydrogen bonding indeed serves to elongate and weaken [v(O-O)] both the O-O and Pd-O bonds in the solid-state structure of $1O_2$ (Figures 3 and S10). The modest thermodynamic stability of 10₂ relative to that of 1 and ³O₂ computed in solvents (DMSO, py) in which $1O_2$ shows no signs of O_2 loss at room temperature, together with the low activation energy computed for the addition of ³O₂ to 1,^[3b] suggests that hydrogen-bonding interactions with solvent C-H bonds, such as those involving a DMSO molecule in the structure of $1O_{2}$, provides additional stabilization. We expected that the unique combination of low steric bulk and strong donor character of auxiliary ligands in 1 and 102 would enable their combination into $Pd^{II} \mu$ -oxo dimer $\mathbf{1}_2(\mu$ -O)₂, a rare type of compound that has not been structurally characterized without electrophilic stabilization of at least one µ-oxo ligand (Figure S10).^[8] Although the DFT calculations suggest that $1_2(\mu-O)_2$, featuring two very short CH····O (1.91 Å) hydrogen bonds to each μ-O, exhibits considerable stability with respect to constituents 1 and $1O_2$ (Figure S10), treatment of 1 with substoichiometric ${}^{3}O_2$ or 10₂ at room temperature in [D₆]DMSO did not produce a new compound, which suggests a kinetic barrier to such oxidative dimerization.



Figure 3. Free energies of 1, $1O_2$, and Pd/Me complexes that can be derived from 1 and O_2 in pyridine and DMSO computed at the B3PW91/BS I//BS II, SMD level.

Thermolysis of $1O_2$ in pyridine at +60 °C resulted in the formation of the cyclic urea *I*MeO^[9] and water, in addition to a brown solid not soluble in DMSO (Figures 4, S5, and S6). Complex $1O_2$ decomposed in under 24 h as well to form 1 (trace), *I*MeO (22 %), and H₂O (40 %) in thermolysis in [H₅]pyridine at +60 °C. Although 1 was not observed in the thermolysis of $1O_2$







Figure 4. ¹H NMR spectra of the thermolysis of **1**O₂ in [H₅]- and [D₅]pyridine and the ¹H NMR spectrum of *I*MeO isolated from these reactions.

in anhydrous $[D_5]$ pyridine, the presence of *I*MeO (22 %) and H₂O points to the *I*Me ligands as the source of reducing equivalents through the electrophilic or hydrogen-atom-abstraction reactivity of **1**O₂. Whereas mechanistic details of these reactions remain to be investigated, the DFT calculations in Figure 3 show the immediate products of *I*Me oxygenation, Pd⁰/Me and *I*MeO, to be strongly favored thermodynamically. Formation of *I*MeO from **1**O₂ is formally analogous to the well-known oxygenation of phosphines in related phosphine complexes^[10] and underscores the limits of the "oxidative stability" of NHC ligands, previously documented in the ready formation of saturated cyclic ureas from Cu^I(NHC)²⁺ complexes and O₂.^[11]

The typical oxygen-atom transfer (OAT) acceptors^[12] PPh₃ and (Me₃Si)₂ were converted into Ph₃PO (>90 %) and (Me₃Si)₂O (>90 %) with substoichiometric **1**O₂ in DMSO over 26 h; however, Pd⁰(*I*Me)₂ (**1**), which was expected as another product, was not observed among the complex mixture of Pd products formed concomitantly in this solvent, possibly as a consequence of the reactivity of **1** with DMSO.^[5] In [D₅]pyridine as the solvent, OAT from **1**O₂ to (Me₃Si)₂ resulted in 93 % of (Me₃Si)₂O, accompanied by **1**, which underwent slower conversion with the excess amount of (Me₃Si)₂ to *cis*-Pd(*I*Me)₂(SiMe₃)₂ (**2**) (Figures 5 and S7–S9).^[13] Observation of *I*MeO among the initial products of the **1**O₂/(Me₃Si)₂ reaction in [D₅]pyridine at room temperature is notable and speaks for the reactive character of partly deoxygenated **1**O₂. This OAT reactivity clearly supports the hypothesis that the current aerobic oxidation in palla-

dium catalysis with NHC proceeds by the formation of a palladium peroxido complex, and the previous examples demonstrate the formation of hydrogen peroxide with acid and peroxocarbonate palladium complex with CO_2 .^[3a,4]



Figure 5. (a) OAT reactivity of $1O_2$ to afford hexamethyldisilane and **2**. (b) Independent synthesis of **2** and (c) its X-ray crystal structure.

Conclusion

Described herein was the synthesis and characterization of the novel complex $Pd(\eta^2-O_2)(/Me)_2$ (1O₂) supported by /Me as an NHC ligand with one of the smallest steric profiles. Lack of auxiliary steric hindrance preserved the salient features of the struc-



Communication

ture and bonding in these complexes, yet facilitated oxygenatom-transfer reactivity with substrates, examples of which include the formation of /MeO upon thermolysis and quantitative OAT from 1O₂ to (Me₃Si)₂. The ready synthetic availability of 1 is expected to permit additional mechanistic studies of Pd^{0/II} reactivity uncoupled from large steric factors and also to provide insight into reactivity studies of Pd^{II}(η^2 -O₂) complexes supported by NHC ligands.

Experimental Section

Pd(η²-O₂)(*IM***e)₂ (1O₂): Compound 1** (400 mg, 1.34 mmol) was dissolved in THF (10 mL), and the yellow homogeneous solution was stirred vigorously at room temperature under O₂ pressure (1 atm) to yield a bisque precipitate. The solid was collected on a frit, washed, and dried in vacuo, yield 410 mg (1.24 mmol, 93 %). ¹H NMR (400 MHz, [D₅]pyridine, +22 °C): δ = 6.99 (s, 4 H), 3.59 ppm (s, 12 H). ¹³C NMR (126 MHz, [D₅]pyridine, +22 °C): δ = 180.4, 119.0, 37.9 ppm. IR (Nujol): $\tilde{\nu}$ = 1237 (s), 1127 (w), 1089 (w), 823 cm⁻¹ (s, η²-O₂). C₁₀H₁₆N₄O₂Pd (330.66): calcd. C 36.32, H 4.88, N 16.94; found C 36.13, H 4.49, N 16.58. Bisque-orange crystals suitable for X-ray were grown, over a total of 4 h, by layering DMSO (0.5 mL) containing **1**O₂ (15 mg) with pyridine (1.0 mL), followed by slow addition of THF (3 mL) to the homogeneous solution, storage at +4 °C for 1 h and at –15 °C for 3 h.

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