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Oxygen Binding to [Pd(L)(L′)] (L= NHC, L′ = NHC or PR_3, NHC = *N*-Heterocyclic Carbene). Synthesis and Structure of a Paramagnetic *trans*-$[Pd(NHC)_2(\eta^1\text{-}O_2)_2]$ Complex

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S *Supporting Information*

ABSTRACT: The reactivity of a number of two-coordinate [Pd(L)(L′)] (L = *N*-heterocyclic carbene (NHC) and L′ = NHC or PR_3) complexes with O_2 has been examined. Stopped-flow kinetic studies show that O_2 binding to $[Pd(IPr)(P(p\text{-tolyl})_3)]$ to form *cis*-$[Pd(IPr)(P(p\text{-tolyl})_3)(\eta^2\text{-}O_2)]$ occurs in a rapid, second-order process. The enthalpy of O_2 binding to the Pd(0) center has been determined by solution calorimetry to be −26.2(1.9) kcal/mol. Extension of this work to the bis-NHC complex $[Pd(IPr)_2]$, however, did not lead to the formation of the expected diamagnetic complex *cis*-$[Pd(IPr)_2(\eta^2\text{-}O_2)]$ but to paramagnetic *trans*-$[(Pd(IPr)_2(\eta^1\text{-}O_2)_2]$, which has been fully characterized. Computational studies addressing the energetics of O_2 binding have been performed and provide insight into reactivity changes as steric pressure is increased.

Homogeneous catalytic oxidation is of fundamental importance, especially in its incarnation where molecular oxygen is used as oxidant.[1] In this context, catalytic oxidation utilizing 14-electron Pd(0) complexes bearing *N*-heterocyclic carbene (NHC) and/or PR_3 ligands is an area of growing interest.[2] In spite of the research activity in this domain, a limited number of studies have dealt with the kinetics and thermodynamics of O_2 binding to $[Pd(L_1)(L_2)]$ systems.[3,4] Due to our long-standing interests in oxygen activation at metal centers[5] and organometallic thermochemistry,[6] physical studies on these complexes were initiated. A good starting point was deemed to be the two-coordinate $[Pd(IPr)(PR_3)]$ (IPr = 1,3-bis(diisopropyl)phenylimidazol-2-ylidene) since the structures of both the parent complex and its O_2 adduct $[Pd(IPr)(PR_3)(\eta^2\text{-}O_2)]$ have been reported.[7,8] The oxygen adduct is best viewed as a distorted square planar Pd(II) complex of the peroxide ligand, which is typical of all O_2 binding modes to $[PdL_2]$ reported to date.[9]

Stopped-flow kinetic studies confirmed that O_2 binding to $[Pd(IPr)(P(p\text{-}CH_3C_6H_4)_3)]$ (**1**) was first-order in metal complex and oxygen and that it was rapid in THF, even at −90 °C. As spectroscopically observed (see Supporting Information), rapid bleaching occurs, and no intermediate complexes are detected on the way to forming the $\eta^2\text{-}O_2$ adduct. Activation parameters for O_2 binding, $\Delta H^\ddagger$ = 2.2 kcal/mol and $\Delta S^\ddagger$ = −28 cal/mol·K, are in keeping with a very small enthalpic barrier to O_2 addition. The net enthalpy of O_2 addition to this complex was measured by solution calorimetry in toluene solution as ΔH = −26.2(1.9) kcal/mol and permits construction of a simple experimental reaction profile for O_2 binding in this system (see Supporting Information). In view of the low enthalpy of activation and high negative entropy of activation, the transition state for O_2 binding in the mixed NHC/phosphine system is ascribed to simple formation of the initial $L_2Pd{-}O_2$ contact interaction. The nature of initial binding of O_2 to $[Pd(IPr)(P(p\text{-tolyl})_3)]$ (**1**), namely whether it occurs through an initial end-on η^1-adduct or side-on η^2-adduct, probably cannot be determined on the basis of experimental data. Even at −90 °C, the enthalpy of activation is so low that trapping or observation of an intermediate could not be achieved.

Extension of these physical studies from $[Pd(IPr)(PR_3)]$ to $[Pd(IPr)_2]$ (**2**) led to unexpected complexities. Qualitative visual studies showed that, at −78 °C, binding of O_2 was much slower (see Supporting Information) than the rapid reaction of **1** described above. Stahl and co-workers have reported that binding of O_2 to $[Pd(IMes)_2]$, yielding *cis*-$[Pd(IMes)_2(\eta^2\text{-}O_2)]$, is rapid, even at −78 °C (IMes = *N*,*N*′-bis(2,4,6- trimethyl)phenylimidazol-2-ylidene).[9a,12] In addition, at room temperature, binding of O_2 to **2** did not result in bleaching of its red-orange color but in development of a yellow-orange color instead (see Supporting Information). The NMR spectrum of the bound adduct was clearly in keeping with a paramagnetic and not a diamagnetic complex (see Supporting Information). Magnetic susceptibility studies on the isolated solid showed it to have 1.8 unpaired electrons. Elemental analysis was in agreement with the $[Pd(IPr)_2(O_2)_2]$ (**3**) formulation.

The crystal structure[10,11] of the complex (Figure 1) unambiguously shows oxygen binding consistent with a *trans*-$[Pd(IPr)_2(\eta^1\text{-}O_2)_2]$ (**3**) composition with an average O−O bond length of 1.327(18) Å, in keeping with formulation of this

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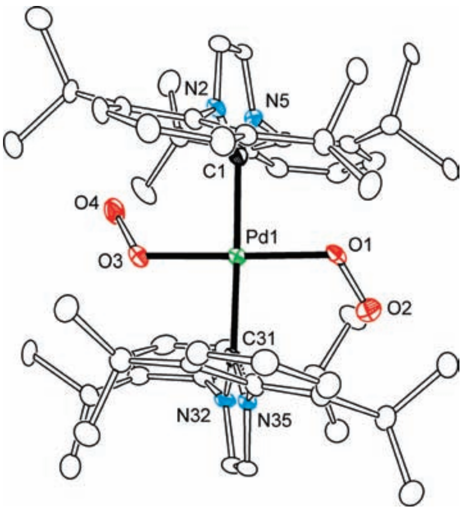


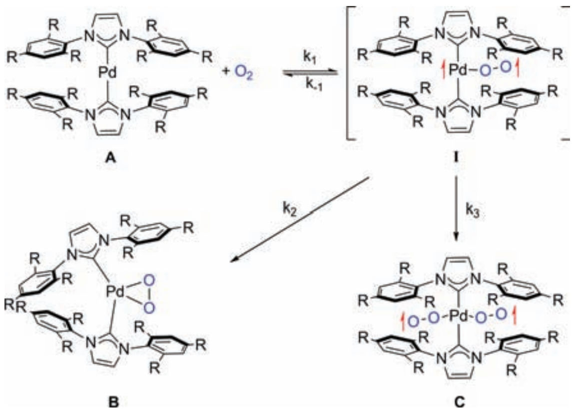
Figure 1. ORTEP diagram of *trans*-[Pd(IPr)$_2$(η^1-O$_2$)$_2$] (**3**), showing 30% thermal ellipsoid probability. Selected interatomic distances (Å) and angles (deg) are as follows: Pd−O1 = 2.010(8), Pd−O3 = 2.012(8), Pd−C1 = 2.059(11), Pd−C31 = 2.065(11), O1−O2 = 1.314(11), O3−O4 = 1.340(11), O3−Pd−O1 = 178.8(3), O3−Pd−C31 = 88.7(4), O1−Pd−C31 = 92.3(4), O3−Pd−C1 = 90.1(4), O1−Pd−C1 = 88.9(4), C31−Pd−C1 = 178.2(4).

complex as a bis-superoxo in which two paramagnetic O_2^- ligands are bound to Pd(II). This result was surprising since binding of O_2 to [Pd(L$_1$)(L$_2$)] complexes studied to date had yielded exclusively *cis*-[Pd(L$_1$)(L$_2$)(η^2-O$_2$)] structures. The complex is square planar, with trans O_2 ligands formulated as superoxides on the basis of the average O−O distance of 1.327(18) Å (Figure 1).[12] The sensitivity of bonding geometry has recently been demonstrated[13] for *cis*-[Pt(NHC)$_2$(CH$_3$)$_2$], where changing the steric parameters[14] of the NHC ligand was shown to lead to differing reactivity channels. The sensitivity of reaction product to the sterics of the NHC is highlighted in the present work, where the change from IMes to IPr results in quite different reactivities with respect to O_2 binding.

A plausible mechanism for stepwise binding of O_2 is shown in Scheme 1. This is proposed to involve, as originally delineated by Stahl,[15,16] initial formation of a reactive intermediate η^1-O$_2$ complex. Complex **I** is a branching point and can presumably undergo O_2 loss to regenerate **A**, rearrange to form the expected diamagnetic η^2-O$_2$ complex **B**, or add a second O_2 to form paramagnetic **C**. Once formed, applying vacuum does not regenerate **A** from either **B** (NHC = IMes) or **C** (NHC = IPr), and these steps are effectively irreversible at room temperature and below.

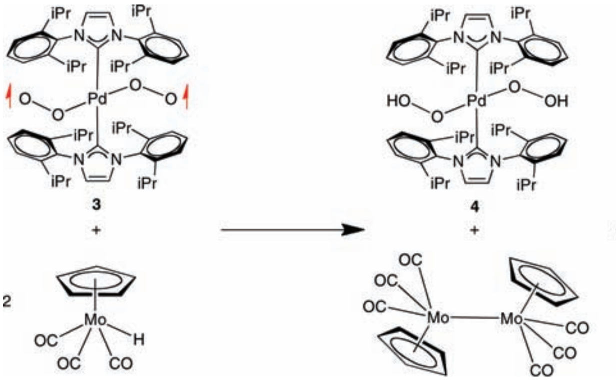
Stahl, Landis, and co-workers[16] have performed calculations for O_2 binding to [Pd(IMe)$_2$] using the truncated ligand "IMe" (IMe = 1,3-dimethylimidazol-2-ylidene) to allow faster computation. In view of the observed differing reactivities as a function of ligand sterics, computational studies were begun on the minimum energy structures for presumed initial end-on binding of one O_2 molecule. As determined previously for [Pd(IMe)$_2$], the lowest energy structure proved to be a paramagnetic T-shaped intermediate with one O_2 bound end-on as superoxide. The optimized structures at the B3LYP/Lanl2dz level of theory are shown in Figure 2 for [Pd(IPr)$_2$(η^1-O$_2$)] (**Ia**), [Pd(IMes)$_2$(η^1-O$_2$)] (**Ib**), and [Pd (IPr)(PPh$_3$)(η^1-O$_2$)] (**Ic**). These structures have been oriented to show, for each complex, the maximum amount of free space available as "wiggle room" for O_2. It is clear from these views that the aperture available for O_2 binding and subsequent rearrangement increases on going from **Ia** to **Ib** to **Ic**.

Scheme 1. Proposed Mechanism for the Reaction Involving [Pd(NHC)$_2$] and O$_2$



The product distribution in Scheme 1 is determined by the relative magnitudes of k_2 and k_3, which may depend critically on the specific ligand system involved. Examination of Figure 2 presents a qualitative picture of how the rate of the intramolecular cyclization step k_2 may be retarded for [Pd(IPr)$_2$(η^1-O$_2$)] (**Ia**), thus allowing trapping by additional O_2 in step k_3.[17] Full computational study of these systems as well as additional stopped-flow and calorimetric measurements on these systems are in progress and may allow more quantitative understanding.

The paramagnetic nature of a *trans*-[Pd(IPr)$_2$(η^1-O$_2$)$_2$] and its formulation as a bis-superoxide complex with spin density on the terminal O_2 atoms suggested that it might readily undergo H atom transfer reactions, as shown in eq 1. Since the H−Mo bond in HMo(Cp)(CO)$_3$ (Cp = η^5-C$_5$H$_5$) (65 kcal/mol) is weaker than the ROO−H bond (85 kcal/mol for H_2O_2), reaction 1 should be thermodynamically favorable.[18]



(1)

The reaction is, in fact, rapid and quantitative at room temperature. Attempts to grow X-ray-quality crystals of *trans*-[Pd(IPr)$_2$(OOH)$_2$] (**4**) proved unsuccessful in spite of spectroscopic evidence for its formation. However, for the saturated NHC analogue SIPr (SIPr = 1,3-bis(diisopropyl)phenylimidazolin-2-ylidene), this proved possible, and the crystal structure of the obtained *trans*-[Pd(SIPr)$_2$(OOH)$_2$] (**5**) complex is shown in Figure 3.[10,19] Only a few structures of the [L$_n$Pd(OOH)] type have been reported,[20] and we are unaware of any [Pd(L)$_n$(OOH)$_2$] of Pd(II).

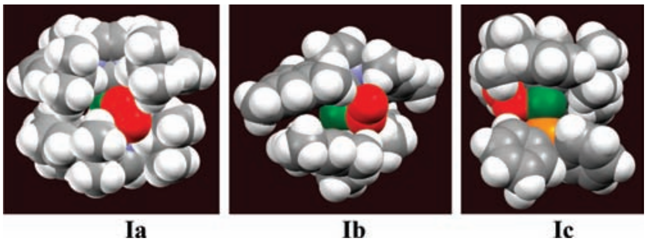

Ia Ib Ic

Figure 2. Space-filling models of the computed most stable form of the T-shaped end-on adducts of $[Pd(IPr)_2(\eta^1\text{-}O_2)]$ (**Ia**), $[Pd(IMes)_2(\eta^1\text{-}O_2)]$ (**Ib**), and $[Pd(IPr)(PPh_3)(\eta^1\text{-}O_2)]$ (**Ic**). Atomic dimensions are the atomic van der Waals radii. Pd, green; O, red; N, blue; C, gray; H, white; P, orange.

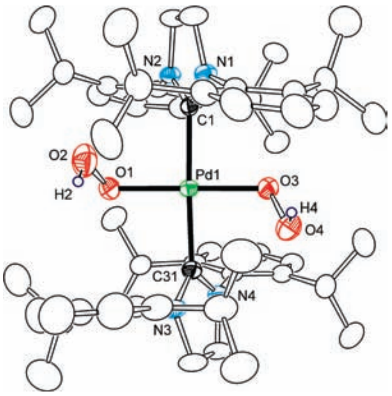


Figure 3. ORTEP diagram of *trans*-$[Pd(SIPr)_2(OOH)_2]$ (**5**), showing 30% thermal ellipsoid probability. Selected interatomic distances (Å) and angles (deg) are as follows: Pd−O1 = 2.0172(16), Pd−O3 = 1.9925(16), Pd−C1 = 2.065(2), Pd−C31 = 2.064(2), O1−O2 = 1.392(3), O3−O4 = 1.452(2), O3−Pd−O1 = 177.38(7), O3−Pd−C31 = 87.98(8), O1−Pd−C31 = 91.67(8), O3−Pd−C1 = 89.72(7), O1−Pd−C1= 90.62(7), C31−Pd−C1 = 177.68(8).

Discovery of the novel O_2 binding modes reported here was fortuitous since it occurred as part of a systematic study of the factors influencing the rate and energetics of O_2 binding as a function of changing the ligand environment. To our surprise, that effect proved larger than expected and led to discovery of new bis-O_2 complexes of Pd. This provides additional impetus to continue both experimental and computational study of O_2 binding in these and related systems.

■ ASSOCIATED CONTENT

S Supporting Information. Synthetic, kinetic, computational, and structural data (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Sheldon, R. A.; Arends, I.; Hanfeld, U. *Green Chemistry and Catalysis*; Wiley-VCH:Weinheim, Germany, 2007; Chapter 4, pp18−23. (b) van Leeuwen, P. V. N. M. *Homogeneous Catalysis: Understanding the Art*; Kluwer: Dordrecht, The Netherlands, 2004; Chapter 15. (c) Stahl, S. S. *Science* **2005,** *309*, 1824–1826.

(2) For reviews, see: (a) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004,** *43*, 3400–3420. (b) Nishimura, T.; Uemura, S. *Synlett* **2004,** 201–216. (c) Sigman, M. S.; Jensen, D. R. *Acc. Chem. Res.* **2006,** *39*, 221–229. (d) Gligorich, K. M.; Sigman, M. S. *Chem. Commun.* **2009,** 3854–3867. (e) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009,** *48*, 5094–5115. (f) Konnick, M. M.; Decharin, N.; Popp, B. V.; Stahl, S. S. *Chem. Sci.* **2011,** doi: 10.1039/C0SC00392A. (g) For a review on the role of NHC in late transition metal catalysis, see: Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009,** *109*, 3612–3676.

(3) For one example of kinetic investigation of the involvement of $[Pd(PPh_3)_2(\eta^2\text{-}O_2)]$ in homocoupling of boronic acids, see: Adamo, C.; Amatore, C.; Ciofini, I.; Jutand, A.; Lakmini, H. *J. Am. Chem. Soc.* **2006,** *128*, 6829–6836.

(4) For seminal work on transition metal−peroxo complexes, see: Vaska, L. *Acc. Chem. Res.* **1976,** *9*, 175–183 and references cited therein.

(5) Korendovych, I. V.; Kryatov, S. V.; Rybak-Akimova, E. V. *Acc. Chem. Res.* **2007,** *40*, 510–521.

(6) (a) McDonough, J. E.; Mendiratta, A.; Fortman, G. C.; Isrow, D. M.; Fantasia, S.; Cummins, C. C.; Rybak-Akimova, E. V.; Nolan, S. P.; Hoff, C. D. *Inorg. Chem.* **2008,** *47*, 2133–2141. (b) Scott, N. M.; Clavier, H.; Mahjoor, P.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2008,** *27*, 3181–3186. (c) Fortman, G. C.; Nolan, S. P. *Organometallics* **2010,** *29*, 4579–4583. (d) Hoff, C. D. *Coord. Chem. Rev.* **2000,** *206*, 451.

(7) Fantasia, S.; Nolan, S. P. *Chem.—Eur. J.* **2008,** *14*, 6987–6993.

(8) For other examples of mixed NHC/PR_3 supported M−(η^2-O_2) species, see: (a) Yu, X.-Y.; Patrick, B. O.; James, B. R. *Organometallics* **2006,** *25*, 4870–4877. (b) Praetorius, J. M.; Allen, D. P.; Wang, R.; Webb, J. D.; Grein, F.; Kennepohl, P.; Crudden, C. M. *J. Am. Chem. Soc.* **2008,** *130*, 3724–3725.

(9) (a) Konnick, M. M.; Guzei, I. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2004,** *126*, 10212–10213. (b) Yamashita, M.; Goto, K.; Kawashima, T. *J. Am. Chem. Soc.* **2005,** *127*, 7294–7295.

(10) CCDC-800882 (**3**) and CCDC-800883 (**5**) contain the supplementary crystallographic data for this contribution. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

(11) Crystal data for **3**: PdO_4N_4 $C_{54}H_{72}\cdot 1/2C_6H_{14}$, $M_r = 990.64$, monoclinic, space group $P2_1/c$, a = 13.766(4) Å, b = 15.624(4) Å, c = 25.915(8) Å, β = 103.647(7)°, V = 5416(3) Å^3, Z = 4, T = 93 K, Mo Kα = 0.71073 Å. GOF = 1.138, no. parameters = 595, $2\Theta_{max} = 50°$. The final $R1(F^2)$ was 0.1261 for 6664 reflections, $I > 2\sigma(I)$.

(12) This is close to the O−O bond distance value of 1.280(3) Å reported for the only other related superoxide structure the authors could locate, that for a Cu complex: Würtele, C.; Gaoutchenova, E.; Harms, K.; Holthausen, M. C.; Sundermeyer, J.; Schindler, S. *Angew. Chem., Int. Ed.* **2006,** *45*, 3867–3869.

(13) Fortman, G. C.; Scott, N. M.; Linden, A.; Stevens, E. D.; Dorta, R.; Nolan, S. P. *Chem. Commun.* **2010,** *46*, 1050–1052.

(14) For NHC ligand steric parameters, see: (a) Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010,** *46*, 841–861. (b) de Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009,** *253*, 862–892. (c) Kelly, R. A., III; Clavier, H.; Guidice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.;

Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202–210.

(15) Popp, B. V.; Stahl, S. S. *J. Am. Chem. Soc.* **2007**, *129*, 4410–4422.

(16) Popp, B. V.; Wendlandt, J. E.; Landis, C. R.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 601–604.

(17) Preliminary stopped-flow studies at −20 °C show a biphasic process.

(18) Data for H−O$_2$H BDE in the gas phase were computed from data available at http://webbook.nist.gov. Data for H−Mo(CO)$_3$Cp were taken from Landrum, J. T.; Hoff, C. D.; *J. Organomet. Chem.* **1985**, *282* 215.

(19) Crystal data for **5**: PdO$_4$N$_4$ C$_{54}$H$_{78}$, M_r = 953.60, triclinic, space group $P\bar{1}$, a = 12.2884(5) Å, b = 12.3340(5) Å, c = 17.2479(7) Å, α = 82.982(1)°, β = 87.966(1)°, γ = 89.015(1)°, V = 2592.74(18) Å^3, Z = 2, T = 296 K, Mo Kα = 0.71073 Å. GOF = 1.021, no. parameters = 586, $2\Theta_{max}$ = 57°. The final $R1(F^2)$ was 0.0375 for 10 468 reflections, $I > 2\sigma(I)$.

(20) For a selection of monohydroperoxide structurally characterized complexes, see the following. (a) For Pd−NHC: Konnick, M. M.; Gandhi, B. A.; Guzei, I. A.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2904–2907. (b) For Pd: Denney, M. C.; Smythe, N. A.; Cetto, K. L.; Kemp, R. A.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 2508–2509. (c) For Pt: Look, J. L.; Wick, D. D.; Mayer, J. M.; Goldberg, K. I. *Inorg. Chem.* **2009**, *48*, 1356–1369.

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