O$_2$-Promoted C–H Activation

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Oxygen-Promoted C–H Bond Activation at Palladium**

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Abstract: *[Pd(P(Ar)(tBu)$_2$)$_2$] (**1**, Ar = naphthyl) reacts with molecular oxygen to form Pd^{II} hydroxide dimers in which the naphthyl ring is cyclometalated and one equivalent of phosphine per palladium atom is released. This reaction involves the cleavage of both C–H and O–O bonds, two transformations central to catalytic aerobic oxidizations of hydrocarbons. Observations at low temperature suggest the initial formation of a superoxo complex, which then generates a peroxo complex prior to the C–H activation step. A transition state for energetically viable C–H activation across a Pd–peroxo bond was located computationally.*

Transition-metal catalysis has emerged as a promising strategy for controlling the selectivity of oxidation reactions between molecular oxygen and organic molecules.[1–3] In particular, palladium-based, oxidase-type catalysts, which employ oxygen as an oxidant and proton acceptor, are widely used to oxidize functional groups in organic molecules.[4,5] Less common are oxygenase-type catalysts which incorporate oxygen atoms from molecular oxygen into the organic product. The functionalization of C–H bonds with such oxygenase catalysts is particularly desirable. While there are a few examples of oxygenase-type C–H functionalization reactions using O$_2$,[6–10] the majority of the palladium catalysts for C–H functionalization employ oxidants other than molecular oxygen.[11]

A better understanding of how O$_2$ and C–H bonds interact with palladium centers will be beneficial to the development of efficient metal-catalyzed oxygenase reactions that selectively functionalize C–H bonds.[12] Herein we report the stoichiometric reaction of a Pd^0 complex with O$_2$ that results in intramolecular cleavage of an aryl C–H bond and incorporation of oxygen to generate Pd^{II} hydroxide dimers. Most significantly, the intermediates observed indicate that Pd^0 reacts first with dioxygen and it is an oxygenated metal species that promotes C–H bond cleavage and O–H bond formation. Our studies of this previously unexplored pathway for oxygen-promoted C–H activation at palladium also provide insight into the initial interaction of O$_2$ with a Pd^0 center.

The Pd^0 complex [Pd(P(Ar)(*t*Bu)$_2$)$_2$] (**1**, Figure 1, Ar = naphthyl) was prepared by heating a solution of [(tmeda)PdMe$_2$][13] (tmeda = *N,N,N,N*-tetramethylethylenediamine) and two equivalents of (di-*tert*-butyl)naphthyl phosphine[14] in benzene at 60 °C for 18 h. The ^{31}P NMR spectrum of **1** in [D$_6$]benzene contains a singlet at δ = 43.5 ppm. Notably, one of the aromatic protons has a chemical shift in the ^{1}H NMR spectrum of δ = 12.2 ppm, significantly different from the others (δ = 7.25–8.06 ppm). The carbon atom attached to this unusual proton has a chemical shift of δ = 130.7 ppm, within the δ = 123.7–138.3 ppm range observed for the naphthyl carbon atoms in the ^{13}C NMR spectrum of **1**.

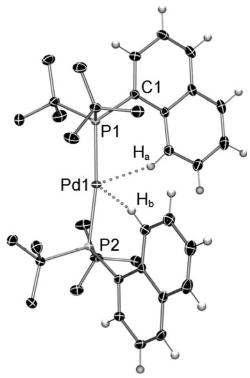

Figure 1. POV-Ray[15] rendition of the X-ray structure of **1** with thermal ellipsoids set at 50 % probability and hydrogen atoms on the *t*Bu groups omitted for clarity. Selected bond lengths [Å] and angles [°] for **1**: P1–Pd1 2.2973(3), P2–Pd1 2.2917(3), P2–Pd1–P1 172.615(11), C1–P1–Pd1 118.16(4).

An X-ray crystal structure of **1** (Figure 1),[16] with hydrogen atoms placed at idealized positions relative to the aromatic carbon atoms, revealed unusually short Pd···H distances of 2.30 and 2.33 Å for H$_a$ and H$_b$, respectively. A gas-phase structure of **1** was computed by DFT using the BP86[17] functional and a Slater-type triple zeta plus polarization (TZP) basis set.[18] The optimized structure had a Pd···H distance of 2.29 Å. The Pd···H–C angles were found to be 159.6°. In combination, the ^{1}H NMR shift, short Pd···H distances, and Pd···H–C angles are indicative of an anagostic interaction.[19]

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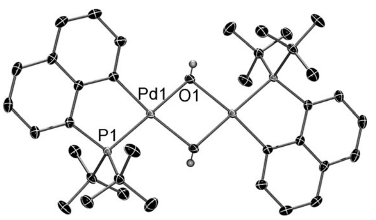

Figure 2. POV-Ray[15] rendition of the X-ray crystal structure of **2a** with thermal ellipsoids set at 50% probability. Hydrogen atoms (except on OH groups) and co-crystallized $[D_6]$benzene omitted for clarity.

Prolonged heating of **1** in $[D_6]$benzene, with or without added water, results in formation of a palladium "mirror" on the glass reaction vessel and generation of free phosphine. In contrast, exposure of a solution of **1** (ca. 10–15 mM) to 1–3 atm of air or oxygen at room temperature results in a rapid color change from yellow to orange/brown. In addition to this color change, the NMR resonances associated with **1** disappear.

When the reaction was repeated using a saturated suspension of **1** in $[D_6]$benzene (approx. 50–80 mM), crystals formed. These were crystallographically characterized as *trans*-$[\{(^{tBu2}PC)PdOH\}_2]$ (**2a**, $^{tBu2}PC^- = t Bu_2PC_{10}H_6^-$, Figure 2).[16] The product was isolated in 75% yield from the reaction in benzene and its purity was verified by elemental analysis (formula $C_{36}H_{50}O_2P_2Pd_2{\cdot}C_6H_6$).

Based on the crystal structure of **2a**, only one ^{31}P NMR resonance was expected. However when **2a** was dissolved in $[D_6]$benzene, two signals of unequal intensity were observed in the ^{31}P NMR spectrum, suggesting that in solution, two species are present. In addition, while only one resonance signal for hydroxide would be expected for **2a**, three resonance signals that all disappear on addition of D_2O were observed.[20] One of these, at $\delta = -0.86$ ppm (doublet, $^3J_{P-H} = 2.5$ Hz), integrates as one proton relative to an aryl signal of the major species, consistent with the C_{2h}-symmetric structure, **2a**. The other two resonances ($\delta = -2.70$ ppm, singlet, and $\delta = 0.49$ ppm, triplet, $^3J_{P-H} = 2.0$ Hz) are present in a 1:1 ratio. Each resonance signal integrates to half the intensity of an aromatic signal in the minor species, consistent with the minor species being the C_{2v}-symmetric dimer, *cis*-$[\{(^{tBu2}PC)PdOH\}_2]$ (**2b**).[21] Gas-phase DFT calculations on the optimized structures of **2a** and **2b** indicate an energy difference of less than 1 kcal mol^{-1} in the absence of solvent interactions. In $[D_6]$benzene the ratio of **2a** to **2b** is approximately 6:1 while in $[D_2]$dichloromethane, the ratio is approximately 3:1. The observation of different ratios upon dissolution of the same crystalline sample in different solvents suggests that **2a** and **2b** are in equilibrium. Efforts to independently synthesize **2a** yielded both **2a** and **2b** in the same ratio as observed in the reaction of **1** with oxygen.

There have been many studies of reactions of Pd^0 bis phosphine[22] and carbene[23] complexes with oxygen but products of C–H activation have not been reported. Typically, (η^2-peroxo)Pd^{II} complexes were observed when a product could be identified, with one notable exception; when the ancillary ligands were the bulky carbene 1,3-bis(diisopropyl)-phenylimidazol-2-yli-dene (IPr), a (bis-superoxo)Pd^{II} complex formed.[24]

In an effort to understand how the reaction of dioxygen with **1** leads to the formation of **2a** and **2b**, and in particular how oxygen might be involved in the promotion of C–H bond cleavage, we examined the reaction of **1** with dioxygen at low temperature.[25] Dioxygen was bubbled through a solution of **1** in $[D_8]$THF at −95 °C and the sample was then quickly inserted into an NMR probe pre-cooled to −100 °C. Under these conditions, a single major species, intermediate **A**, was present in greater than 80% yield (calculated by NMR integration vs. 1,3,5-trimethoxybenzene internal standard). The ^{31}P NMR spectrum of intermediate **A** consists of doublets at $\delta = 58$ and 55 ppm ($^2J_{P-P} = 15$ Hz) indicating inequivalent phosphine atoms. As observed for **1**, intermediate **A** has an aromatic proton with a chemical shift which is unusually far downfield, appearing at $\delta = 11.23$ ppm. In addition, there is an upfield signal at $\delta = 4.25$ ppm that was shown by COSY NMR experiments to correspond to another aromatic proton.[26] The resonance signals of intermediate **A** broaden substantially as the sample is warmed above −80 °C. We note that the ^{1}H NMR spectrum of the previously reported (bis-superoxo)Pd^{II} complex also showed broad resonances.[24] A UV/Vis absorption spectrum of intermediate **A** at −95 °C in THF revealed a feature centered at $\lambda = 403$ nm ($\varepsilon = 700$ M^{-1} cm^{-1}).

Resonance Raman (rR) spectroscopy ($\lambda_{ex} = 406.7$ nm, 77 K) was performed to further investigate the structure of intermediate **A**. The rR spectra of samples prepared with $^{16}O_2$ contained non-solvent features at 1363 and 1383 cm^{-1} (Figure 3a). When intermediate **A** was prepared with $^{18}O_2$, the intensity of these features decreased and a peak at 1290 cm^{-1} appeared (Figure 3b).

The peaks in the ^{16}O spectrum at 1363 and 1383 cm^{-1} likely constitute a Fermi doublet centered at 1373 cm^{-1}, as is often seen in rR spectra of metal–oxygen species.[27] These features are assigned as the ν_{O-O} band for a coordinated O_2^{n-} ligand. This assignment is based on the observed difference between the average position of the two peaks in the ^{16}O sample and the 1290 cm^{-1} peak in the ^{18}O sample ($\Delta^{18}O_{obs} = 83$ cm^{-1}; $\Delta^{18}O_{calcd} = 78$ cm^{-1}). The observed ν_{O-O} band is slightly higher than those reported for most other metal superoxide complexes (typically 1000–1300 cm^{-1}).[28] Using a previously described[29] correlation between ν_{O-O} and O–O

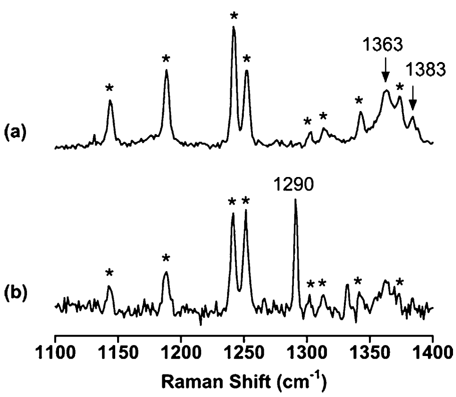

Figure 3. Resonance Raman spectra of **A** for samples prepared from a) $^{16}O_2$ or b) $^{18}O_2$ in THF at −80 °C ($\lambda_{ex} = 406.7$ nm, 77 K). Solvent peaks are marked with an asterisk.

bond lengths according to Badger's rule, the ν_{O-O} band at 1373 cm^{-1} corresponds to an O−O bond of 1.24 Å, which is only slightly longer than free O_2 (1.21 Å), suggesting that the coordinated O_2^{n-} moiety in intermediate **A** has only been reduced (at most) to the superoxide level.

Previous computational studies indicate that O_2 reacts with Pd^0 species by initial formation of an end-on superoxo species. As the distal oxygen atom approaches the palladium center, a second electron transfer then occurs to generate the observed (η^2-peroxo)Pd^{II} complex.[30] It has been suggested that rearrangement of ancillary ligands from a *trans* to *cis* configuration creates a barrier to the approach of the distal oxygen atom.[31] Thus a superoxo species can represent a local minimum on the reaction coordinate. Using spin-unrestricted DFT (TZP,[18] B3LYP[21,32]), we found a local minimum with a triplet ground state that may represent the structure for intermediate **A** (Figure 4a).[33] The O−O bond length of 1.27 Å, Pd−O bond lengths of 2.40 and 3.23 Å, and calculated ν_{O-O} band at 1258 cm^{-1} (BP86) are consistent with an η^1-superoxo complex in which the reduction of the O_2 moiety is minimal.[30] The P–Pd–P angle is 161.3°.[34]

Over a period of circa 80 min at −82 °C, the broad resonance signals in the ^{1}H NMR spectrum of intermediate **A** disappeared and resonance signals corresponding to a new species, intermediate **B**, appeared. This transformation was shown to be first order in [**A**] ($k = 5.05 \pm 0.06 \times 10^{-4}\ s^{-1}$at −82 °C).[21] The ^{1}H NMR spectrum of intermediate **B** was well-resolved and resonances for all 14 aromatic protons were identified. This result establishes that C−H activation and cyclometalation of the naphthyl group have not yet occurred.

The ^{31}P NMR spectrum of intermediate **B** consists of doublets at $\delta = 103$ and 55 ppm ($^2J_{P-P} = 21$ Hz), suggesting that there are two phosphine groups on the same palladium in a non-*trans* configuration.[35] The chemical shift of metal-bound phosphine groups strongly correlates with metal-phosphorus-R group angles.[36] Thus, the chemical shifts of the ^{31}P resonances could be explained by a structure in which the geometry around one phosphorus center is similar to that observed in **1**, while the other has bond angles around the phosphorus that more closely resemble those in **2a** and **2b**.

The addition of pentane to a solution of intermediate **B** at −78 °C formed a yellow precipitate. A thin-film IR spectrum of the precipitate revealed a peak at 924 cm^{-1}, similar to the ν_{O-O} value of 915 cm^{-1} reported for $[(tBu_2PhP)_2Pd(O_2)]$.[22c] Based on the measured ν_{O-O} value, Badger's rule predicts an O−O bond length of 1.41 Å. When intermediate **B** was prepared in the presence of $^{18}O_2$, a peak at 874 cm^{-1} was observed ($\Delta^{18}O_{obs} = 50\ cm^{-1}$; $\Delta^{18}O_{calcd} = 53\ cm^{-1}$).[21]

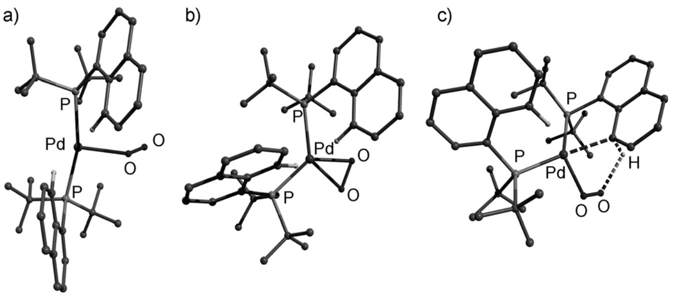

Figure 4. Proposed structures for a) Intermediate **A**. b) Intermediate **B**. c) TS1 (located by DFT).

The spectroscopic data suggest that intermediate **B** is a bis phosphine Pd^{II} peroxo complex. A plausible structure with a singlet ground state was found and optimized by DFT (TZP,[18] BP86,[17] Figure 4b). The two phosphine atoms have different Pd–P–$C_{naphthyl}$ angles (121.6 and 113.5°), consistent with their different ^{31}P NMR shifts. The O−O bond length of 1.39 Å, Pd−O bond lengths of 2.10 and 2.08 Å, and calculated ν_{O-O} value of 1012 cm^{-1} are consistent with a Pd^{II} peroxo complex.[22]

Above −40 °C, the resonance signals of intermediate **B** disappeared and approximately one equivalent of free phosphine (per equivalent of palladium starting material) was detected. No palladium species could be identified in the NMR spectra. However by EPR spectroscopy, signals at $g =$ 2.02 and 2.04 were observed, the signal at $g = 2.04$ appearing on approximately the timescale that intermediate **B** disappears. These EPR signals suggest that paramagnetic species may be involved in the transformation of **B** to the final products **2a** and **2b**.[21]

By ^{1}H NMR spectroscopy, the disappearance of intermediate **B** was found to be first order in [**B**]. Eyring analysis of the data between −40 °C and −20 °C found $\Delta H^{\neq}$ to be 16.3 ± 1.0 kcal mol^{-1} and $\Delta S^{\neq}$ to be −6 ± 4 e.u., indicating that at −20 °C $\Delta G^{\neq}$ equals 17.8 ± 2.0 kcal mol^{-1}. The first-order behavior for both the formation and disappearance of intermediate **B** are most consistent with the formulations of intermediates **A** and **B** as monometallic species.

From intermediate **B**, a plausible mechanism could be the addition of a C−H bond across a Pd−O bond with concurrent phosphine loss to generate a cyclometalated $[(^{tBu2}PC)Pd(OOH)]$ fragment. Subsequent dimerization with loss of oxygen would yield the product **2a**/**2b**. Addition of a C−H bond across a metal–oxygen bond has precedent[37] and there is an example of the phenol O−H bond adding across a Pt−O bond in a Pt−η^2−peroxo species.[38] Loss of an oxygen from M−OOH complexes to form the corresponding M−OH complexes has also been observed.[39]

The viability of intermediate **B** undergoing addition of an aryl C−H bond across a Pd−O bond with concurrent phosphine loss was examined computationally (Figure 5).[21] A transition state, TS1 (Figure 4c), was located and verified by its vibrational frequencies and by perturbing the structure prior to minimizing. The reaction is exothermic and the gas-phase $\Delta H^{\neq}$ was calculated to be 23 kcal mol^{-1}. When solvation (dielectric continuum) and entropy are taken into account, the $\Delta G^{\neq}$ of the reaction at −20 °C is calculated to be 21 kcal mol^{-1}.[40]

In summary, the reaction of the Pd^0 bis phosphine complex **1** with O_2 results in the formation of Pd^{II} hydroxide dimers **2a** and **2b**, a transformation that requires breaking both O−O and C−H bonds. Observation of low-temperature intermediates with all of the naphthyl C−H bonds intact suggests that this transformation proceeds by an initial O−O activation. This step involves the formation of a (superoxo)Pd^I complex that then rearranges to form a (η^2-peroxo)Pd^{II} species. The C−H bond cleavage occurs subsequently. The reaction of **1** with dioxygen represents a previously unex-

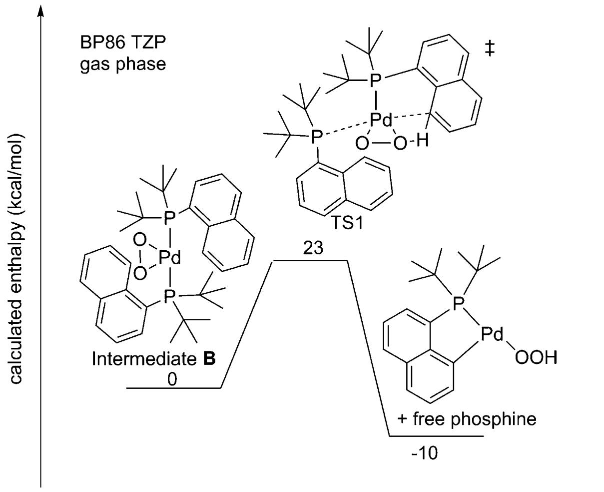

Figure 5. Addition of a C–H bond across a Pd–O bond concurrent with phosphine loss (DFT calculation).

plored pathway for the functionalization of C–H bonds by palladium complexes in which molecular oxygen is employed as the oxidant.

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[1] S. S. Stahl, *Science* **2005**, *309*, 1824.
[2] F. Cavani, J. H. Teles, *ChemSusChem* **2009**, *2*, 508.
[3] a) L. Boisvert, K. I. Goldberg, *Acc. Chem. Res.* **2012**, *45*, 899; b) A. N. Campbell, S. S. Stahl, *Acc. Chem. Res.* **2012**, *45*, 851; c) Z. Shi, C. Zhang, C. Tang, N. Jiao, *Chem. Soc. Rev.* **2012**, *41*, 3381; d) M. J. Schultz, M. S. Sigman, *Tetrahedron* **2006**, *62*, 8227; e) T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329.
[4] a) M. S. Sigman, D. R. Jensen, *Acc. Chem. Res.* **2006**, *39*, 221; b) K. M. Gligorich, M. S. Sigman, *Angew. Chem.* **2006**, *118*, 6764; *Angew. Chem. Int. Ed.* **2006**, *45*, 6612.
[5] a) W. Wu, H. Jiang, *Acc. Chem. Res.* **2012**, *45*, 1736; b) J. M. Takacs, X. T. Jiang, *Curr. Org. Chem.* **2003**, *7*, 369; c) J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier, A. Sabel, *Angew. Chem.* **1962**, *74*, 93; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 80.
[6] a) T. Jintoku, K. Nishimura, K. Takaki, Y. Fujiwara, *Chem. Lett.* **1991**, 193; b) T. Jintoku, K. Nishimura, K. Takaki, Y. Fujiwara, *Chem. Lett.* **1990**, 1687; c) T. Jintoku, K. Takaki, Y. Fujiwara, Y. Fuchita, K. Hiraki, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 438; d) T. Jintoku, H. Taniguchi, Y. Fujiwara, *Chem. Lett.* **1987**, 1865.
[7] S. Yamada, S. Sakaguchi, Y. Ishii, *J. Mol. Catal. A* **2007**, *262*, 48.
[8] Y.-H. Zhang, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 14654.
[9] G. J. Chuang, W. Wang, E. Lee, T. Ritter, *J. Am. Chem. Soc.* **2011**, *133*, 1760.
[10] Y. Yan, P. Feng, Q.-Z. Zheng, Y.-F. Liang, J.-F. Lu, Y. Cui, N. Jiao, *Angew. Chem.* **2013**, *125*, 5939; *Angew. Chem. Int. Ed.* **2013**, *52*, 5827.
[11] a) H. Li, B.-J. Li, Z.-J. Shi, *Catal. Sci. Technol.* **2011**, *1*, 191; b) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147.
[12] V. Durà-Vilà, D. M. P. Mingos, R. Vilar, A. J. P. White, D. J. Williams, *Chem. Commun.* **2000**, 1525.
[13] W. de Graaf, J. Boersma, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1989**, *8*, 2907.
[14] A. Karaçar, M. Freytag, H. Thönnessen, P. G. Jones, R. Bartsch, R. Schmutzler, *J. Organomet. Chem.* **2002**, *643–644*, 68.
[15] Persistence of Vision Ray-Tracer (POV-Ray), available at http://www.povray.org/.
[16] CCDC 983922 (**1**) and 983923 (**2a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[17] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.
[18] E. van Lenthe, E. J. Baerends, *J. Comput. Chem.* **2003**, *24*, 1142.
[19] M. Brookhart, M. L. H. Green, G. Parkin, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 6908.
[20] V. V. Grushin, H. Alper, *Organometallics* **1993**, *12*, 1890.
[21] See the Supporting Information for full details.
[22] For examples see: a) T. Yoshida, K. Tatsumi, M. Matsumoto, K. Nakatsu, A. Nakamura, T. Fueno, S. Otsuka, *Nouv. J. Chim.* **1979**, *3*, 761; b) S. Otsuka, T. Yoshida, M. Matsumoto, K. Nakatsu, *J. Am. Chem. Soc.* **1976**, *98*, 5850; c) M. Matsumoto, H. Yoshioka, K. Nakatsu, T. Yoshida, S. Otsuka, *J. Am. Chem. Soc.* **1974**, *96*, 3322.
[23] For example see: M. M. Konnick, I. A. Guzei, S. S. Stahl, *J. Am. Chem. Soc.* **2004**, *126*, 10212.
[24] X. Cai, S. Majumdar, G. C. Fortman, C. S. J. Cazin, A. M. Z. Slawin, C. Lhermitte, R. Prabhakar, M. E. Germain, T. Palluccio, S. P. Nolan, E. V. Rybak-Akimova, M. Temprado, B. Captain, C. D. Hoff, *J. Am. Chem. Soc.* **2011**, *133*, 1290.
[25] At room temperature, the best yields of **2a** and **2b** were obtained in benzene or toluene. At low temperatures, the same intermediates were observed in THF or toluene but the lower freezing point and position of the resonance signals of $[D_8]$THF proved advantageous for the characterization of intermediates at low temperatures.
[26] The unusual shift for this aromatic proton could perhaps be explained by an agostic interaction with the palladium center or a through-space interaction with the O_2 moiety.
[27] a) J. T. York, A. Llobet, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2007**, *129*, 7990; b) D. J. E. Spencer, A. M. Reynolds, P. L. Holland, B. A. Jazdzewski, C. Duboc-Toia, L. L. Pape, S. Yokota, Y. Tachi, S. Itoh, W. B. Tolman, *Inorg. Chem.* **2002**, *41*, 6307.
[28] J. S. Valentine, *Chem. Rev.* **1973**, *73*, 235.
[29] a) C. J. Cramer, W. B. Tolman, K. H. Theopold, A. L. Rheingold, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3635; b) C. Cramer, W. Tolman, *Acc. Chem. Res.* **2007**, *40*, 601.
[30] C. R. Landis, C. M. Morales, S. S. Stahl, *J. Am. Chem. Soc.* **2004**, *126*, 16302.
[31] B. V. Popp, J. E. Wendlandt, C. R. Landis, S. S. Stahl, *Angew. Chem.* **2007**, *119*, 607; *Angew. Chem. Int. Ed.* **2007**, *46*, 601.
[32] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[33] The open- and closed-shell singlets were higher in energy by 5 and 15 $kcal\,mol^{-1}$, respectively.
[34] Relatively short Pd–H distances (2.3–2.6 Å) were observed in both intermediates **A** and **B**.
[35] H. Fan, B. C. Fullmer, M. Pink, K. G. Caulton, *Angew. Chem.* **2008**, *120*, 9252; *Angew. Chem. Int. Ed.* **2008**, *47*, 9112.
[36] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229.
[37] W. J. Tenn, K. J. H. Young, G. Bhalla, J. Oxgaard, W. A. Goddard, R. A. Periana, *J. Am. Chem. Soc.* **2005**, *127*, 14172.
[38] S. Cenini, F. Porta, M. Pizzotti, *J. Organomet. Chem.* **1985**, *296*, 291.
[39] For example see: a) J. L. Look, D. D. Wick, J. M. Mayer, K. I. Goldberg, *Inorg. Chem.* **2009**, *48*, 1356; b) M. C. Denney, N. A. Smythe, K. L. Cetto, R. A. Kemp, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 2508; c) V. V. Rostovtsev, L. M. Henling, J. A. Labinger, J. E. Bercaw, *Inorg. Chem.* **2002**, *41*, 3608.
[40] J. Ho, A. Klamt, M. L. Coote, *J. Phys. Chem.A* **2010**, *114*, 13442.

