

Insertion of Molecular Oxygen into a Palladium(II) Methyl Bond: A Radical Chain Mechanism Involving Palladium(III) Intermediates

Luc Boisvert, Melanie C. Denney, Susan Kloek Hanson, and Karen I. Goldberg*

Department of Chemistry, University of Washington, Box 351700,
Seattle, Washington, 98195-1700

Received July 23, 2009; E-mail: goldberg@chem.washington.edu

Abstract: The reaction of (bipy)PdMe₂ (**1**) (bipy = 2,2'-bipyridine) with molecular oxygen results in the formation of the palladium(II) methylperoxide complex (bipy)PdMe(OOMe) (**2**). The identity of the product **2** has been confirmed by independent synthesis. Results of kinetic studies of this unprecedented oxygen insertion reaction into a palladium alkyl bond support the involvement of a radical chain mechanism. Reproducible rates, attained in the presence of the radical initiator 2,2'-azobis(2-methylpropionitrile) (AIBN), reveal that the reaction is overall first-order (one-half-order in both [**1**] and [AIBN], and zero-order in [O₂]). The unusual rate law (half-order in [**1**]) implies that the reaction proceeds by a mechanism that differs significantly from those for organic autoxidations and for the recently reported examples of insertion of O₂ into Pd(II) hydride bonds. The mechanism for the autoxidation of **1** is more closely related to that found for the autoxidation of main group and early transition metal alkyl complexes. Notably, the chain propagation is proposed to proceed via a stepwise associative homolytic substitution at the Pd center of **1** with formation of a pentacoordinate Pd(III) intermediate.

Introduction

The need to develop more efficient, cost-effective, and environmentally benign processes for the selective oxidation of organic compounds has led to a growing interest in the reactivity of organometallic compounds toward molecular oxygen.^{1,2} From both environmental and economic perspectives, oxygen represents an ideal oxidant. Particularly promising for the discovery of new processes is the wide variety of reactivity patterns that have been observed in reactions of O₂ with transition metals.³ However, the current understanding of the mechanisms by which organometallic complexes react with molecular oxygen is still limited, hindering the widespread use of this oxidant in homogeneous catalytic reactions.

Among the late transition metals, palladium has attracted particular attention for its ability to catalyze numerous homogeneous aerobic oxidation reactions.^{2,4} Efficient processes have been developed with "palladium oxidase"⁵ type systems, where molecular oxygen acts as an oxidant for the Pd center (or for a cocatalyst),⁶ as exemplified by the aerobic oxidation of alcohols^{2,4-7} and by the Wacker process.⁸

In contrast, palladium-catalyzed transformations where oxygen atoms from O₂ are incorporated into the substrate ("palladium

oxygenase"⁵ catalysis) remain scarce.⁹ One possible mechanism for the incorporation of molecular oxygen into an organic substrate involves the insertion of O₂ into a palladium alkyl bond. However, such reactivity involving oxygen has not been reported for palladium alkyl complexes and, in fact, there are few documented examples of O₂ insertions into late transition metal-alkyl bonds. The known examples are almost exclusively limited to Co(III) alkyl complexes of macrocyclic nitrogen ligands¹⁰ and to two recent reports involving Pt(II)-Me complexes.¹¹⁻¹³ In contrast, the reactions of alkyl complexes of main group and early transition metals with O₂ to yield metal alkyl peroxides or metal alkoxides are well known.¹⁴⁻¹⁶ The usefulness of this transformation can be illustrated by its involvement in the aluminum-based "Ziegler alcohol" processes for the industrial production of fatty alcohols¹⁷ as well as in a variety of synthetic contexts such as the synthesis

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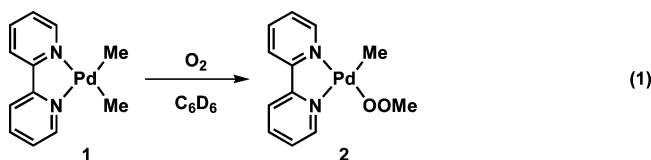
of alcohols and alkyl hydroperoxides from main group organo-metallics,¹⁸ the epoxidation of alkenes via in situ generated zinc alkylperoxides,¹⁹ and the use of alkylboranes as radical initiators.²⁰ Autoxidation reactions of this type involving late transition metal complexes could be particularly valuable due to the capacity of late transition metals to generate metal alkyls by activation of C–H bonds.²¹ The coupling of these two transformations could be a powerful combination for alkane functionalization.

Described herein is the first observation of the insertion of O₂ into a Pd(II)–Me bond, forming a Pd(II) alkylperoxide complex. The reaction of (bipy)PdMe₂ (**1**) with O₂ to form (bipy)PdMe(OOMe) (**2**) is a rare example of insertion of O₂ into a late transition metal–alkyl bond,²² and represents significant progress toward the development of a “palladium oxygenase” paradigm. The results of mechanistic studies suggest that the reaction proceeds by a radical chain process. Several possible radical chain mecha-

nisms have been evaluated in relation to the experimentally determined rate law and a viable mechanism for this reaction is proposed. Important implications for the development of catalysts for the functionalization of alkanes that could proceed via an oxygen insertion reaction are also discussed.

Results

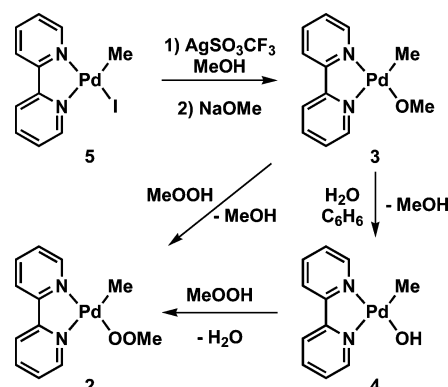
Reaction of (bipy)PdMe₂ (1**) with O₂.** When a solution of (bipy)PdMe₂ (**1**) in degassed C₆D₆ under reduced pressure was heated at 50 °C for 18 h, < 5% decomposition occurred (measured by integration of signals in ¹H NMR spectra against an internal standard), although traces of Pd black were visible. However, when a solution of **1** in C₆D₆ was exposed to oxygen (1–10 atm) at room temperature, the novel methylperoxide species (bipy)PdMe(OOMe) (**2**) was formed in yields of up to ca. 70% as determined by NMR spectroscopy (eq 1). Experiments in which independently prepared (bipy)PdMe(OOMe) (**2**) (see below) was added to solutions of the product formed in the reaction between **1** and O₂ unambiguously confirmed the identity of the product as the methylperoxide derivative **2**. It was also found that the ¹H NMR chemical shifts of **2** are very similar to those of the methoxide derivative (bipy)PdMe(OMe) (**3**). Notably, addition of **3** to the same product solutions clearly demonstrated that **3** was not formed in the oxygenation reaction.



Independent Synthesis of (bipy)PdMe(OOMe) (2**) and Confirmation of Structure.** The palladium(II) methylperoxide complex **2** can be independently prepared by the reaction of the palladium(II) methoxide complex **3** or of the hydroxide complex (bipy)PdMe(OH) (**4**) with MeOOH (Scheme 1). Complexes **3** and **4** were prepared from the known iodide derivative (bipy)PdMe(I) (**5**).²³ The reaction of **5** with silver trifluoromethanesulfonate and sodium methoxide in methanol cleanly generated the methoxide complex **3** (Scheme 1). The ¹H NMR data for **3** (in CD₃OD) matched that previously reported by van Koten and co-workers, who prepared **3-d₃** by dissolving (bipy)PdMe(OCH(CF₃)₂) in CD₃OD.²⁴ The new hydroxide complex **4** was obtained by addition of H₂O to solutions of **3** in benzene (Scheme 1).

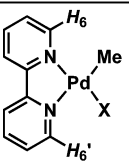
Complex **2** could be efficiently synthesized by a variety of routes involving the use of methyl hydroperoxide. Since MeOOH is not commercially available, it was obtained by methylation of hydrogen peroxide with dimethyl sulfate under

Scheme 1



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Table 1. Selected Values of ^1H and ^{13}C NMR Chemical Shifts for Complexes **1–4**^a

		H_6 (δ , ppm)	H_6' (δ , ppm)	Pd-CH ₃ (δ , ppm)		X (δ , ppm)	
Complex		¹ H	¹ H	¹ H	¹³ C	¹ H	¹³ C
	1 (X = Me)	8.71	-	0.18	-7.4	-	-
	2 (X = OOMe)	8.59	8.96	0.67	3.1	3.64	63.8
	3 (X = OMe)	8.63	8.85	0.69	1.4	3.45	57.4
	4 (X = OH)	8.57	8.87	0.53	-4.2	-1.39	-

^a Conditions: CD_2Cl_2 , 233 K, 500 MHz. ^{13}C NMR chemical shifts determined by HMQC analysis.

basic conditions²⁵ and used as a $\sim 1:2$ MeOOH/ Et_2O solution.²⁶ The identity of MeOOH was confirmed by addition of Ph_3P to a sample of MeOOH in CDCl_3 ; immediate formation of Ph_3PO and MeOH was observed by ^1H NMR spectroscopy.²⁷

Methylperoxide complex **2** was obtained and characterized in situ (by NMR spectroscopy), together with one molar equivalent of ROH (R = Me or H), when MeOOH in Et_2O was added to a C_6D_6 or CD_2Cl_2 solution of (bipy)PdMe(OMe) (**3**) or of (bipy)PdMe(OH) (**4**) (Scheme 1). Alternatively, when MeOOH was added to toluene solutions of either methoxide complex **3** or hydroxide complex **4** followed by cooling of the reaction mixture to -35°C , complex **2** precipitated from solution and was isolable as a yellow solid.

Even though complexes **2** and **3** have very similar structures, differing only by one oxygen atom, it was possible to clearly show that the product of the reaction between **1** and O_2 was the methylperoxide complex **2**. Initially, the analysis was complicated by the fact that the ^1H NMR chemical shifts recorded in C_6D_6 of complexes **2** and **3** vary with the presence of protic impurities. Thus, simple matching of the chemical shift data from the spectra of the reaction mixture recorded in C_6D_6 to that of the independently prepared complexes was ambiguous. These variations in

chemical shifts are likely due to hydrogen bonding between **2/3** and ROH. Notably, it has been reported that complexes of the type (bipy)PdMe(OR) (OR = $\text{OCH}(\text{CF}_3)_2$, OAr) form strong hydrogen bonds with ROH in solution and in the solid state.²⁸ In fact, in some preparations of complexes **2** and **3**, analysis by ^1H NMR spectroscopy showed the presence of some ROH (ROH = H_2O , MeOH, MeOOH), even after extensive washing of the solids. However, addition of independently prepared samples of **2** and **3** to solutions of the product of the reaction of **1** with oxygen in C_6D_6 conclusively identified **2** as the product.

It was also observed in the course of characterization of the products that the oxygenated Pd complexes **2**, **3**, and **4** decomposed in solution to Pd black over minutes to hours at room temperature and were only slightly soluble in aromatic solvents at low temperature. Therefore, although reactions between **1** and O_2 to form **2** were conducted in C_6D_6 at temperatures ranging from 298 to 323 K (see below), detailed analysis of the products by ^1H and ^{13}C NMR spectroscopies was better carried out in CD_2Cl_2 at low temperatures (ca. 233 K). Under these conditions (233 K in CD_2Cl_2), no decomposition was observed and the ^1H NMR chemical shifts of complexes **2** and **3** were only weakly affected by protic impurities.

The ^1H NMR spectra (CD_2Cl_2 , 233 K) of complexes **2**, **3**, and **4** exhibit an unsymmetrical bipyridine environment and a singlet at 0.5–0.7 ppm for the Pd–Me groups (Table 1). The proton of the hydroxide group of **4** can be seen as a broad singlet at around -1.4 ppm, as has been described for similar complexes.²⁹ This proton was shown by NOESY experiments to be in chemical exchange with traces of water in the sample. As seen in Table 1, complexes **2** and **3** can be readily differentiated by both ^1H and ^{13}C NMR spectroscopies in CD_2Cl_2 . Most significant is the large chemical shift difference observed by ^{13}C NMR spectroscopy for the $-\text{OOCH}_3$ and $-\text{OCH}_3$ groups of **2** and **3**, respectively. More importantly, when the C_6D_6 solvent was removed from the completed reaction between **1** and O_2 and replaced with CD_2Cl_2 , the spectra were indistinguishable from those of **2** obtained by reactions involving MeOOH.

Complex **2** is a rare example of a Pd(II) alkylperoxide complex,³⁰ and it appears to be the first reported Pd(II) methylperoxide complex. Notably, two Pt(II) methylperoxide complexes, formed by the overall insertion of O_2 into Pt(II)–Me bonds, were recently characterized by X-ray crystallography.^{11,12}

Effects of Light and AIBN on the Reaction between (bipy)PdMe₂ (1**) and O_2 .** The reaction between (bipy)PdMe₂ (**1**) and O_2 (1–10 atm) to form (bipy)PdMe(OOMe) (**2**) in C_6D_6

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- (25) See Experimental Section for details. The protocol for the synthesis of MeOOH was adapted from: (a) Rieche, A.; Hitz, F. *Ber.* **1929**, 62, 2458. (b) Vaghjiani, G. L.; Ravishankara, A. R. *J. Phys. Chem.* **1989**, 93, 1948. See also: (c) Davies, D. M.; Deary, M. E. *J. Chem. Soc., Perkin Trans. 2* **1992**, 559. (d) O'Sullivan, D. W.; Lee, M.; Noone, B. C.; Heikes, B. G. *J. Phys. Chem.* **1996**, 100, 3241.
- (26) Pure alkyl hydroperoxides are potentially explosive and should be avoided if possible. They can be violently decomposed by adventitious catalysts (acids, metals) with formation of, among others, oxygen gas. Distillation of alkylperoxides is not recommended. See: (a) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, 12, 63. (b) Hill, J. G.; Rossiter, B. E.; Sharpless, K. B. *J. Org. Chem.* **1983**, 48, 3607. It has been documented that explosions occurred when pure MeOOH was heated (ref 25a) and that the residue obtained after distillation of pure samples of MeOOH exploded violently (ref 25b).
- (27) MeOOH is easily distinguished from MeOH by both ^1H and ^{13}C NMR spectroscopies, as shown by HMQC analysis performed on a $\sim 1:2:2$ $\text{CH}_3\text{OOH}/\text{CH}_3\text{OH}/\text{Et}_2\text{O}$ mixture (CD_2Cl_2 , 500 MHz, 233 K): CH_3OOH (^1H NMR: 3.78 ppm, ^{13}C NMR: 65.3 ppm); CH_3OH (^1H NMR: 3.36 ppm, ^{13}C NMR: 50.4 ppm).

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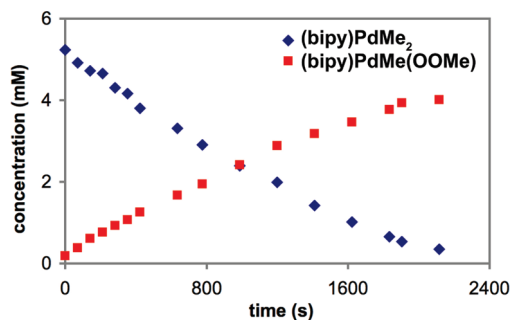


Figure 1. Concentrations of (bipy)PdMe₂ (**1**) and (bipy)PdMe(OOMe) (**2**) as a function of time as determined by ¹H NMR spectroscopy. Reaction conditions: [1]₀ = 5.2 mM, [AIBN] = 5.8(1) mM, p(O₂) = 10 atm, C₆D₆, 323 K.

was monitored by ¹H NMR spectroscopy. Initially, the rates were found to be highly irreproducible, which is often indicative of the involvement of radical intermediates. Notably, a majority of the known reactions of insertion of O₂ into M–R bonds have been found to proceed by radical chain pathways.^{10–16} For these reactions, the effects of radical initiators or inhibitors and light have been well documented. Similar effects were observed in the reactions between **1** and O₂. For example, in ambient light at room temperature, 42% of **1** reacted after ca. 6 h, compared with 7% for a sample kept in the dark (see Experimental Section). When reactions between **1** and O₂ were conducted in the presence of the radical initiator AIBN, higher rates and yields (up to ca. 85% of **2** as determined by ¹H NMR spectroscopy) relative to those for reactions with no added initiator were observed (see Experimental Section). Significantly, the presence of AIBN led to reproducible reaction rates, so that kinetic studies could be carried out (Figure 1).³¹

Determination of the Order in [(bipy)PdMe₂]. Since the rates of the reaction between **1** and O₂ were reproducible when AIBN was used as a radical initiator, investigations into the mechanism of the reaction were pursued via kinetic studies of the reaction in the presence of AIBN. Kinetic experiments were conducted at 323 K in C₆D₆ at pressures of oxygen of 5 and 10 atm,^{32,33} and ¹H NMR spectra were collected over at least three half-lives.³⁴ The disappearance of the bipyridine signal of **1** ([1]₀ = 3.8–5.2 mM) at 8.8 ppm could be easily monitored (and integrated against an internal standard)³⁵ and maximum yields of ca. 85% of **2** were observed after complete consumption of **1**.³⁶ Notably, no intermediates were detected during the reactions. The concentration of AIBN (2–32 mM), determined by integration of its CH₃ signal relative to the signal of the 1,4-

dioxane internal standard, remained approximately constant throughout the reactions and is reported as the average value determined over at least two half-lives.³⁷

Half-order and first-order kinetic plots with respect to (bipy)-PdMe₂ (**1**) for representative reactions at pressures of oxygen of 5 and 10 atm are presented in Figure 2. More examples of such comparisons can be found in the Supporting Information, Figures S2 and S3. In addition, kinetic plots for three-halves order and second-order dependences for the data shown in Figure 2b are also provided in Figure S1. It is clear from examination of these data that the rate of consumption of **1** exhibits a well-behaved half-order dependence on [1]. Furthermore, Figure 2 also shows that this behavior is observed both at high (Figure 2a) and low (Figure 2b) concentrations of AIBN.

Determination of the Order in [AIBN]. Values of the rate constant *k*_{obs}, calculated from the slope of the half-order plots according to [1]_t^{1/2} – [1]₀^{1/2} = –(*k*_{obs}/2)·*t*, were obtained for reactions at different concentrations of AIBN. As shown by the plots in Figure 3 for reactions at pressures of oxygen of 5 and 10 atm, a linear relationship is observed between the value of *k*_{obs} and [AIBN]^{1/2}.³⁸ Meanwhile, a linear fit to [AIBN]¹ is much less satisfying.

The half-order dependence on the concentration of AIBN was confirmed by treatment of the kinetic data as shown in Figure 4.^{31a} If the rate of the reaction is proportional to [AIBN]^{*n*} (eq 2), then the kinetic data can be plotted as indicated in eq 3.

$$\text{rate} = -\Delta[(\text{bipy})\text{PdMe}_2]/\Delta t \propto [\text{AIBN}]^n \quad (2)$$

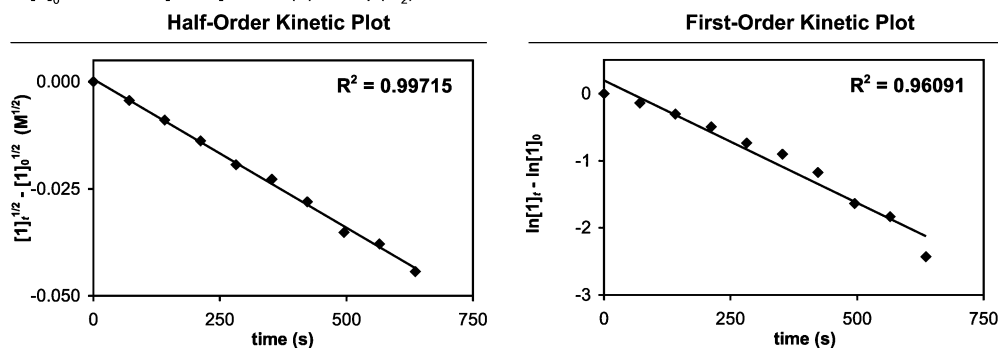
$$[(\text{bipy})\text{PdMe}_2] \propto [\text{AIBN}]^n \cdot t \quad (3)$$

Equation 3 shows that for reactions with similar initial concentrations of (bipy)PdMe₂ (**1**), plots of [1] versus [AIBN]^{*n*}·*t* should be superimposable. Figure 4 shows such an analysis for two reactions having similar initial concentrations of **1** but different concentrations of AIBN. The significantly better overlay found in Figure 4 for plots of [1] versus [AIBN]^{1/2}·*t* than for plots of [1] versus [AIBN]·*t* confirms a half-order dependence on [AIBN] for the reactions of autoxidation of **1**.

- (30) For other examples, see: (a) Kujime, M.; Hikichi, S.; Akita, M. *Chem. Lett.* **2003**, 32, 486. (b) Miyaji, T.; Kujime, M.; Hikichi, S.; Moro-oka, Y.; Akita, M. *Inorg. Chem.* **2002**, 41, 5286. (c) Oshima, N.; Hamatani, Y.; Fukui, H.; Suzuki, H.; Moro-oka, Y. *J. Organomet. Chem.* **1986**, 303, C21. (d) Strukul, G.; Ros, R.; Michelin, R. A. *Inorg. Chem.* **1982**, 21, 495. (e) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, 102, 1047.
- (31) The appearance of the curves in Figure 1 suggests that auto-acceleration or auto-catalysis effects, for which sigmoidal curves would be expected, are not involved in the present reactions. Effects of this type have been observed in the autoxidation of alkyl complexes of boron (see ref 15p) and cadmium (see ref 15m). For recent discussions concerning their involvement in autoxidation reactions, see: (a) Look, J. L.; Wick, D. D.; Mayer, J. M.; Goldberg, K. I. *Inorg. Chem.* **2009**, 48, 1356. (b) Hermans, I.; Jacobs, P. A.; Peeters, J. *Chem.—Eur. J.* **2006**, 12, 4229.
- (32) The use of high pressures (several atmospheres) ensures that the reaction will not be affected by inefficient mass transport of O₂ through the narrow gas/liquid interface of the NMR tubes used in the experiments. For recent discussions, see: ref 31a and Steinhoff, B. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2006**, 128, 4348.

- (33) The concentration of dissolved O₂ in C₆D₆ is expected to be similar to the concentration in C₆H₆. Assuming that the ideal gas law and Henry's law are applicable, a doubling of the pressure of O₂ is expected to lead to a doubling of the concentration of dissolved O₂. The concentration of O₂ in C₆H₆ at 323 K (using an Ostwald coefficient *L*^{323K} of 0.247 (ref a) and a density for C₆H₆ of *d*^{323K} = 0.8481 g/mL (ref b)) at partial pressures of O₂ of 5 and 10 atm is calculated to be of about 47 and 93 mM, respectively. (a) *Oxygen and Ozone*; Battino, R., Ed.; Solubility Data Series; Pergamon Press: Oxford, 1981; Vol. 7, p 250. (b) Lide, D. R. *Handbook of Chemistry and Physics*, 85th ed.; CRC Press: Boca Raton, FL, 2004–2005; p 15–28.
- (34) The determination of initial rates at low [AIBN] with (bipy)PdMe₂ or (4,4'-di-*tert*-butyl-2,2'-bipyridine)PdMe₂ proved unsatisfactory as too few data points could be acquired before reaching >10–20% conversions.
- (35) Similar results were obtained when the rates were determined by following the disappearance of the methyl signal of **1** but overlap with the signal for AIBN precluded a full analysis.
- (36) In all reactions, complete consumption of **1** was observed and extents of conversion reported in the different plots refer to the maximum conversion that could be reliably determined by integration of the signals in the ¹H NMR spectra.
- (37) The half-life of AIBN at 50 °C in C₆H₆ is calculated to be ca. 87.5 h (*k* = 2.2 × 10^{–6} s^{–1}). See: *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley & Sons: New York, 1999.
- (38) The negative intercepts of the plots of *k*_{obs} versus [AIBN]^{1/2} are most likely due to the presence of small amounts of adventitious inhibitors. This behavior is also consistent with the irreproducible kinetics observed at low concentrations of AIBN or when no AIBN was added.

a) $[I]_0 = 4.0$ mM, $[AIBN] = 25.6(1)$ mM, $p(O_2) = 5$ atm, conversion = 91%



b) $[I]_0 = 5.3$ mM, $[AIBN] = 2.2(1)$ mM, $p(O_2) = 10$ atm, conversion = 91%

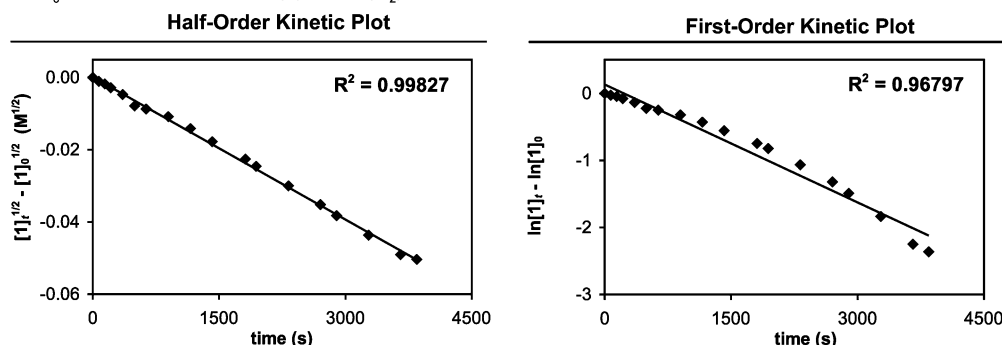
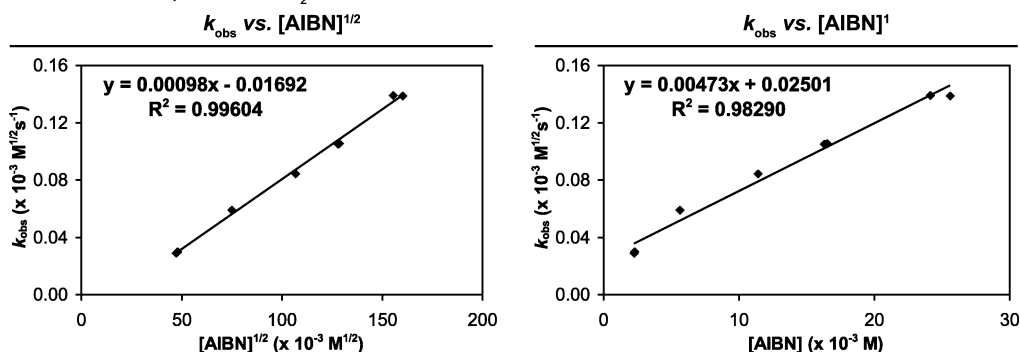


Figure 2. Representative half-order and first-order kinetic plots for reactions under (a) 5 and (b) 10 atm of O_2 in C_6D_6 at 323 K.

a) Reactions with pressure of $O_2 = 5$ atm



b) Reactions with pressure of $O_2 = 10$ atm

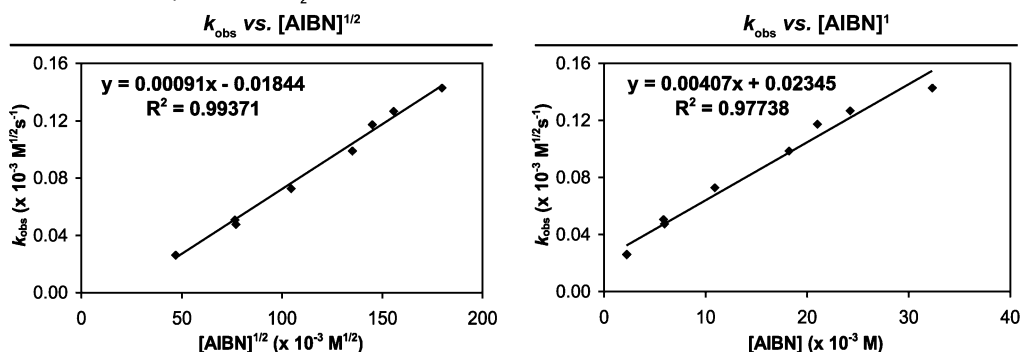


Figure 3. Dependence of the value of the observed rate constant on the concentration of AIBN showing a linear relationship between k_{obs} and $[AIBN]^{1/2}$ for reactions with pressures of O_2 of (a) 5 and (b) 10 atm. Reaction conditions: $[I]_0 = 3.8$ – 5.3 mM, C_6D_6 , 323 K.

Other similar examples showing much better agreement between half-order plots than between first-order plots can be found in the Supporting Information, Figure S4.

Determination of the Order in $[O_2]$. From the slope of a plot of k_{obs} versus $[AIBN]^{1/2}$ for the experiments with pressures of

O_2 of 5 atm (Figure 3a), a value of $k = 9.8(3) \times 10^{-4} s^{-1}$ is obtained, and for the experiments with pressures of O_2 of 10 atm (Figure 3b), a value of $k = 9.1(3) \times 10^{-4} s^{-1}$ is obtained. The very similar values of k at pressures of O_2 of 5 and 10 atm indicate that the rate of the reaction is independent of $[O_2]$.³³

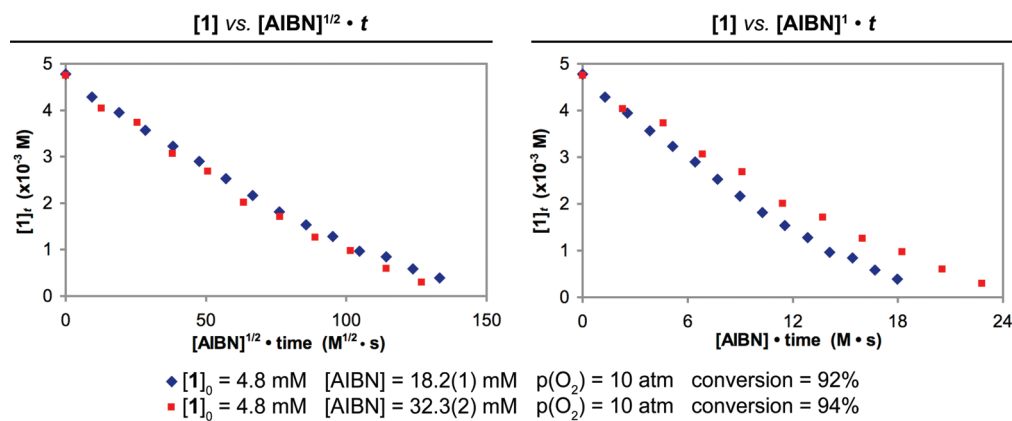


Figure 4. Overlay of plots according to eq 3 showing a better agreement between plots of [1] vs [AIBN]^{1/2}·t than between plots of [1] vs [AIBN]·t.

Empirical Rate Law for the Reaction between (bipy)PdMe₂ (1) and O₂. Overall, the insertion of O₂ (5–10 atm) into a palladium methyl bond of (bipy)PdMe₂ (1) in the presence of AIBN in C₆D₆ at 323 K is a first-order process, half-order with respect to 1 and half-order with respect to AIBN. There is a zero-order dependence on the concentration of oxygen. These results are summarized in the empirically derived rate expression shown in eq 4.

$$\text{rate} = -d[(\text{bipy})\text{PdMe}_2]/dt = k_{\text{obs}}[\mathbf{1}]^{1/2} = k[\mathbf{1}]^{1/2}[\text{AIBN}]^{1/2}[\text{O}_2]^0 \quad (4)$$

Discussion

The kinetic studies presented herein, together with the observed effect of radical initiators and light, strongly suggest the involvement of a radical chain mechanism for the reaction of (bipy)PdMe₂ (1) with O₂ to form (bipy)PdMe(OOMe) (2). Since 1 is a Pd(II) complex, the possibility that Pd(I) and/or Pd(III) complexes might be involved as chain carriers must be considered. Notably, while mononuclear complexes of Pd(I) and Pd(III) complexes are rare,^{39,40} their intermediacy has been proposed or verified in a variety of situations, most commonly during radical oxidative addition/reductive elimination processes and during electrochemical studies.^{41,42}

The reproducible rates of reaction in the presence of AIBN and the lack of a dependence on the oxygen pressure for the reactions between (bipy)PdMe₂ (1) and O₂ are reminiscent of the observations recorded for autoxidations of organic substrates. The general radical chain mechanism established for organic autoxidations is discussed below and compared to the results obtained for the experiments involving (bipy)PdMe₂ (1). In addition, important differences between the general radical chain mechanisms for autoxidation of organic compounds and that of main group and early transition metal alkyl complexes are highlighted and discussed in the context of the autoxidation of 1. A mechanism for the reaction between 1 and O₂ to form (bipy)PdMe(OOMe) (2) consistent with the experimental results

is proposed, and this mechanism is compared to ones that have been proposed for insertions of O₂ into late metal–hydride bonds.

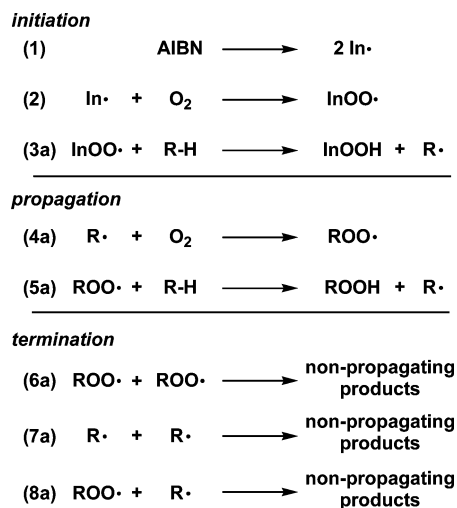
Autoxidation of Organic Compounds and Extension to the Autoxidation of 1. The autoxidation of organic compounds to form alkyl hydroperoxides is usually thought to occur by the general mechanism shown in Scheme 2.^{43,44} In this mechanism, the chain-propagating and product-forming step is a hydrogen atom abstraction (step 5a).

Kinetic studies on these reactions are usually conducted in the presence of a radical initiator like AIBN to provide reproducible reaction rates and avoid variable initiation periods. In addition, sufficient pressures of O₂ are typically used to ensure that the dominant termination process is the homocoupling of two alkylperoxy radicals (step 6a).^{43,44} Under these conditions,

- (39) Cauty, A. J. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E. I., Ed.; Wiley: New York, 2002; Vol. 1, p 189.
 (40) For binuclear Pd(I) complexes, see: (a) Murahashi, T.; Kurosawa, H. *Coord. Chem. Rev.* **2002**, 231, 207. For binuclear Pd(III) complexes, see: (b) Powers, D. C.; Ritter, T. *Nat. Chem.* **2009**, 1, 302. (c) Cotton, F. A.; Koshevoy, I. O.; Lahuerta, P.; Murillo, C. A.; Sanau, M.; Ubeda, M. A.; Zhao, Q. *J. Am. Chem. Soc.* **2006**, 128, 13674. (d) Ara, I.; Chaouche, N.; Fornies, J.; Fortuno, C.; Kribbi, A.; Tsipis, A. C. *Organometallics* **2006**, 25, 1084. (e) Bond, A. M.; Cauty, A. J.; Cooper, J. B.; Tedesco, V.; Traill, P. R.; Way, D. M. *Inorg. Chim. Acta* **1996**, 251, 185.

- (41) For representative examples of the involvement of mononuclear Pd(I) complexes, see: (a) Fafard, C. M.; Adhikari, D.; Foxman, B. M.; Mindiola, D. J.; Ozerov, O. V. *J. Am. Chem. Soc.* **2007**, 129, 10318. (b) Burns, C. T.; Shen, H.; Jordan, R. F. *J. Organomet. Chem.* **2003**, 683, 240. (c) Albéniz, A. C.; Espinet, P.; Lopez-Fernandez, R.; Sen, A. *J. Am. Chem. Soc.* **2002**, 124, 11278. (d) Stadtmüller, H.; Vaupel, A.; Tucker, C. E.; Stüdemann, T.; Knochel, P. *Chem.—Eur. J.* **1996**, 2, 1204. (e) Ishiyama, T.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1991**, 32, 6923. (f) Stille, J. K.; Lau, K. S. Y. *J. Am. Chem. Soc.* **1976**, 98, 5841. (g) Osborn, J. A. In *Organotransition-Metal Chemistry*; Ishii, Y., Tsutsui, M., Eds.; Plenum Press: New York, 1975; p 65. (h) Kramer, A. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, 96, 7832. (i) Kramer, A. V.; Labinger, J. A.; Bradley, J. S.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, 96, 7145. (j) Stille, J. K.; Hines, L. F.; Fries, R. W.; Wong, P. K.; James, D. E.; Lau, K. *Adv. Chem. Ser.* **1974**, 132, 90.
 (42) For representative examples of the involvement of mononuclear Pd(III) complexes, see: (a) Kraatz, H.-B.; van der Boom, M. E.; Ben-David, Y.; Milstein, D. *Isr. J. Chem.* **2001**, 41, 163. (b) Matsumoto, M.; Itoh, M.; Funahashi, S.; Takagi, H. D. *Can. J. Chem.* **1999**, 77, 1638. (c) Blake, A. J.; Crofts, R. D.; de Groot, B.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1993**, 485. (d) Pandey, K. K. *Coord. Chem. Rev.* **1992**, 121, 1. (e) Reid, G.; Schröder, M. *Chem. Soc. Rev.* **1990**, 19, 239. (f) McAuley, A.; Whitcombe, T. W. *Inorg. Chem.* **1988**, 27, 3090. (g) Lane, G. A.; Geiger, W. E.; Connelly, N. G. *J. Am. Chem. Soc.* **1987**, 109, 402. (h) van Leeuwen, P. W. N. M.; Roobeek, C. F.; Huis, R. J. *Organomet. Chem.* **1977**, 142, 233. (i) Manolikakes, G.; Knochel, P. *Angew. Chem., Int. Ed.* **2009**, 48, 205.
 (43) (a) Reich, L.; Stivala, S. S. *Autoxidation of Hydrocarbons and Polyolefins—Kinetics and Mechanisms*; Marcel Dekker: New York, 1969; Chapters 2 and 3. (b) Huyser, E. S. *Free-Radical Chain Reactions*; John Wiley & Sons: New York, 1970; Chapters 3 and 11. (c) Howard, J. A. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley & Sons: New York, 1973; Vol. II, Chapter 12. (d) Walling, C. In *Active Oxygen in Chemistry*; Foote, C. S., Valentine, J. S., Greenberg, A., Liebman, J. F., Eds.; Blackie Academic & Professional: London, 1995; Chapter 2.
 (44) (a) Porter, N. A. *Acc. Chem. Res.* **1986**, 19, 262. (b) Betts, J. Q. *Rev., Chem. Soc.* **1971**, 25, 265. (c) Mayo, F. R. *Acc. Chem. Res.* **1968**, 1, 193.

Scheme 2



the rate of a reaction proceeding by the mechanism shown in Scheme 2 will be independent of the pressure of oxygen and will show a first-order dependence on the concentration of the substrate and a half-order dependence on the concentration of AIBN (eq 5).^{43b,c}

$$\text{rate} \propto [\text{RH}]^1 [\text{AIBN}]^{1/2} [\text{O}_2]^0 \quad (5)$$

The reaction of insertion of O_2 into a Pd–Me bond of **1** in the presence of AIBN could potentially proceed by a mechanism analogous to the one found in Scheme 2 for the autoxidation of organic compounds. Such a mechanism would involve the abstraction by (bipy)PdMe(OO·) of a methyl group from (bipy)PdMe₂ (**1**) (steps 5b in Scheme 3) by homolytic displacement at the carbon of Pd–Me. In this mechanism, Pd(I) radicals would be involved as chain carriers.⁴¹

Analogously to what was presented in Scheme 2 for the autoxidation of organics, the third step of the initiation would then consist of a methyl group abstraction from **1** by InOO· and, under a sufficiently high pressure of oxygen, the termination step would involve the reaction of two (bipy)PdMe(OO·) species to generate non-chain propagating species.

The rate law derived for this series of steps (eq 6) would have the same form as the one found for the autoxidation of organics (eq 5).

$$\text{rate} \propto [\text{1}]^1 [\text{AIBN}]^{1/2} [\text{O}_2]^0 \quad (6)$$

For the reactions of autoxidation of (bipy)PdMe₂ (**1**), a half-order dependence on [AIBN] was indeed found (eq 4). Additionally, a zero-order dependence on $[\text{O}_2]$ was determined (for reactions at pressures of O_2 of 5 and 10 atm), suggesting that (1) the reaction is not limited by O_2 mass-transfer effects³² and (2) a sufficient excess concentration of O_2 is present to ensure termination by the coupling of two O_2 -derived radicals. As described above, a zero-order dependence on $[\text{O}_2]$ is common for radical chain autoxidations of organic compounds conducted under a sufficient excess of oxygen. This zero-order oxygen dependence has also been reported for the autoxidation of several main group and early transition metal alkyl complexes (see below).^{14,15i,g,n-p} However, while a first-order dependence on [**1**] is expected from eq 6, a well-behaved half-order dependence on [**1**] was found experimentally for the reaction between (bipy)PdMe₂ (**1**) and O_2 in the presence of AIBN. It is therefore

clear that the reaction does not proceed by the mechanism presented in Scheme 3 that involves radical substitutions at the carbon of the Pd–Me group of **1**.

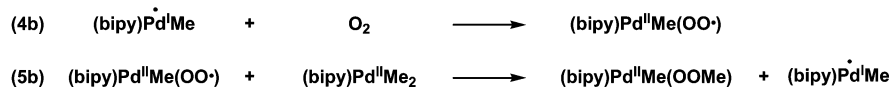
The methyl group abstraction reactions by radicals from Pd–Me could also be viewed as bimolecular homolytic substitutions at carbon ($\text{S}_{\text{H}}2$). Notably, very few examples of homolytic displacements at the carbon of transition metal alkyl complexes have been reported.⁴⁵ Homolytic substitutions at the carbon of transition metal alkyls that involve simple alkyl groups (e.g., M–R with R = Me, benzyl), for which a concerted displacement ($\text{S}_{\text{H}}2$) is expected, have thus far been limited to Co(III) complexes of macrocyclic nitrogen ligands.⁴⁶ This reactivity is likely related to the facility with which these types of complexes generate alkyl radicals by homolysis of $\text{Co}^{\text{III}}\text{--R}$ bonds.^{10,47} Rare examples of radical substitutions at the alkyl group of complexes of other metals like Fe,⁴⁸ Rh,⁴⁹ and Ir⁴⁹ involve unsaturated groups of the type M– $\text{CR}_2\text{--CR}=\text{CR}_2$ (e.g., M–(η^1 -allyl), M–(η^1 -cyclopentadienyl)). For these, and for many Co complexes,^{46a,c} mechanistic studies suggest that the homolytic displacement most likely does not involve direct attack at the carbon bound to the metal (α position) but rather an initial attack at the γ carbon of the allyl system, with an overall transposition of the allyl moiety. Considered together with the inconsistent rate law, this literature background concerning $\text{S}_{\text{H}}2$ reactions at metal alkyl species further supports the conclusion that a mechanism for the reaction of (bipy)PdMe₂ (**1**) with O_2 that involves radical substitution at a methyl group of **1** (i.e., methyl group abstraction from **1**) is unlikely.

Autoxidation of Main Group and Early Transition Metal Alkyl Complexes and Extension to the Autoxidation of **1.** The formation of metal alkylperoxides (or other oxygenated derivatives) by autoxidation reactions has been documented for a wide variety of main group and early transition metal alkyl complexes.^{14–16} Mechanistic studies have been reported on a relatively limited number of these reactions and radical chain mechanisms are usually involved.^{14a} In the absence of radical initiators, the initiation step generally proposed for these reactions consists of the generation of $\text{R}\cdot$ radicals by homolysis of M–R bonds.^{14a} For reactions conducted in the presence of a radical initiator like AIBN, a general mechanism can be described by the series of steps illustrated in Scheme 4. In such

- (45) The following two-step transformation has been documented: $\text{M}^n + \text{Me}\cdot \rightarrow \text{M}^{n+1}(\text{Me})$ followed by $\text{M}^{n+1}(\text{Me}) + \text{Me}\cdot \rightarrow \text{M}^n + \text{Me–Me}$. The second step may involve a homolytic displacement at the alkyl group (or attack at the metal center followed by reductive elimination) but mechanistic studies are lacking. For examples with Ni complexes, see: (a) Kurzion-Zilbermann, T.; Masarwa, A.; Maimon, E.; Cohen, H.; Meyerstein, D. *Dalton Trans.* **2007**, 3959. Radical oxidative addition and reductive elimination processes of transition metal complexes can involve steps related to homolytic substitutions at alkyl groups. For relevant discussions on these types of reactions, see: (b) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, NY, 1978. (c) Chanon, M. *Bull. Soc. Chim. Fr.* **1982**, II–197.
- (46) For a review, see: (a) Johnson, M. D. *Acc. Chem. Res.* **1983**, *16*, 343. For more recent examples, see: (b) Li, S.; de Bruin, B.; Peng, C.-H.; Fryd, M.; Wayland, B. B. *J. Am. Chem. Soc.* **2008**, *130*, 13373. (c) Gupta, B. D.; Vijaikanth, V. *J. Organomet. Chem.* **2004**, *689*, 1102. (d) Stolzenberg, A. M.; Cao, Y. *J. Am. Chem. Soc.* **2001**, *123*, 9078. (e) Huston, P.; Espenson, J. H.; Bakac, A. *J. Am. Chem. Soc.* **1992**, *114*, 9510.
- (47) (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238. (b) Peng, C.-H.; Li, S.; Wayland, B. B. *Inorg. Chem.* **2009**, *48*, 5039.
- (48) (a) Fabian, B. D.; Labinger, J. A. *Organometallics* **1983**, *2*, 659. (b) Rosenblum, M.; Waterman, P. J. *Organomet. Chem.* **1981**, *206*, 197.
- (49) Crease, A. E.; Gupta, B. D.; Johnson, M. D.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1978**, 1821.

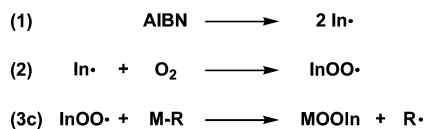
Scheme 3

propagation

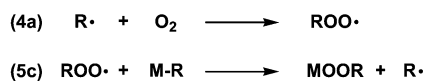


Scheme 4

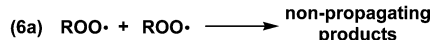
initiation



propagation



termination



a mechanism, the chain-propagating and product-forming step is a bimolecular homolytic substitution at the metal center (step 5c).⁵⁰

Under conditions of sufficient oxygen concentration such that step 4a is rapid, the rate law derived for this mechanism is given by eq 7. Accordingly, when radical initiators such as AIBN are used in these reactions, a first-order dependence on the concentration of the metal alkyl and a half-order dependence on the concentration of AIBN are often found.^{15o} Notably, this rate law is similar to that found for reactions involving organics (see eq 5).

$$\text{rate} \propto [\text{MR}]^1 [\text{AIBN}]^{1/2} [\text{O}_2]^0 \quad (7)$$

The observed reaction of autoxidation of (bipy)PdMe₂ (**1**) could potentially proceed by a mechanism analogous to the one found in Scheme 4 for the autoxidation of main group and early transition metal alkyl complexes. Such a mechanism would involve homolytic substitutions at the Pd center of **1** by MeOO• radicals (step 5d in Scheme 5). In analogous fashion to what was presented in Scheme 4 for the autoxidation of main group and early transition metal alkyl complexes, the third step of the initiation would then consist of a homolytic substitution of a Me• group of **1** by InOO• and, under a sufficiently high pressure of oxygen, the termination step would involve the homocoupling of two MeOO• radicals. However, the derived rate law for such a process would have the same form as eq 6 derived above for Scheme 3, so that a first-order dependence on [**1**] would be expected. Thus, if the reaction between (bipy)PdMe₂ (**1**) and O₂ were to proceed by concerted homolytic displacements at the carbon of Pd–Me (Scheme 3) or at the Pd center (Scheme 5), the rate of the reaction would be expected to show a half-order dependence on [AIBN] and a first-order dependence on [(bipy)PdMe₂] (eq 6). Experimentally, a half-order dependence on both [AIBN] and [(bipy)PdMe₂] is found (eq 4). Therefore a different mechanism must be operative.⁵¹

Mechanism of the Reaction between **1 and O₂.** Free radical substitution reactions can proceed by a variety of mechanisms.^{45b,50,52} For example, the formation of the new bond with

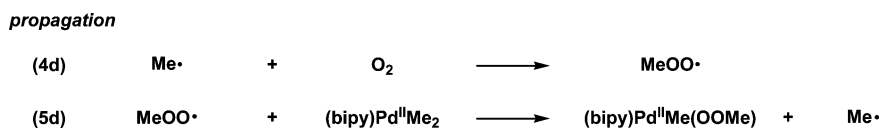
the incoming radical and the cleavage of the bond with the departing radical can be concerted (S_H2). This reactivity is expected for displacements that occur at centers that do not have the ability to form hypervalent intermediates, such as the carbon of simple alkyl groups (as in Scheme 3). Homolytic displacements can also be stepwise associative processes, involving an intermediate formed by expansion of the valency at the reacting center. A typical example of this behavior is encountered in the autoxidation of trivalent phosphorus compounds.⁵³ Because many transition metals can easily expand their valency, a variety of mechanisms are expected for homolytic displacements at transition metal centers, including concerted (as was presented in Scheme 5) and stepwise associative processes.

The reactivity patterns observed within the chemistry of Pt(II) complexes are often used as models for analogous Pd(II) complexes. In this context, it should be noted that there is substantial precedent for radical substitution reactions at Pt(II) centers. For example, non-chain radical substitutions by BuO• radicals at Pt(II) centers to release alkyl radicals have been documented (Scheme 6a).⁵⁴ The displaced R• radicals have been detected by electron spin resonance spectroscopy and characterized by spin-trapping experiments. In addition, radical chain substitution reactions of alkyl groups by RS• radicals at Pt(II) centers have been reported,^{54,55} and it has been shown that some of these reactions benefit from the addition of AIBN.⁵⁵ It has also been proposed that the photolysis of Pt(IV)–methyl complexes leads to the formation of five-coordinate Pt(III) complexes, and that Me• radicals can be eliminated from these species to form Pt(II) complexes (Scheme 6b).⁵⁶ Furthermore, the reactions of (diimine)PtMe₂ complexes such as **6** with PrI in the presence of air are proposed to proceed by a radical chain mechanism as shown in Scheme 6c.⁵⁷ In this mechanism, the addition of a peroxy radical, formed by the interception of an

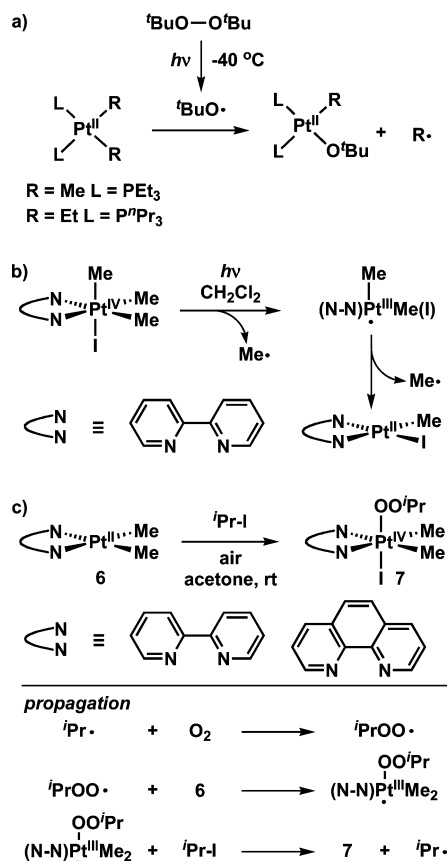
- (51) Related discussions about the distinction between radical substitution at the alkyl group and at the metal center for radical chain insertion reactions into M–R bonds have been previously presented. For example, based on the well-documented reactivity of Co(III) alkyl complexes, the radical chain insertion of SO₂ into Co^{III}–R bonds was proposed to proceed via homolytic displacements at carbon rather than via homolytic displacements at the metal center (refs a and b). In contrast, in ref 15g a mechanism involving radical substitutions at the metal center was favored for the reaction between a chromium alkyl complex and O₂. (a) Crease, A. E.; Johnson, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 8013. (b) Gupta, B. D.; Roy, M.; Oberoi, M.; Dixit, V. *J. Organomet. Chem.* **1992**, *430*, 197.
- (52) (a) Walton, J. C. *Acc. Chem. Res.* **1998**, *31*, 99. (b) Schiesser, C. H.; Wild, L. M. *Tetrahedron* **1996**, *52*, 13265. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 4.
- (53) (a) Ogata, Y.; Yamashita, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 730. (b) Hwang, W.-S.; Yoke, J. T. *J. Org. Chem.* **1980**, *45*, 2088. (c) Schwetlick, K. *Pure Appl. Chem.* **1983**, *55*, 1629. For reactions between BuOO• radicals and trivalent phosphorus compounds, see: (d) Furimsky, E.; Howard, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 369.
- (54) (a) Cardin, D. J.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Chem. Commun.* **1973**, 350. See also: (b) Kaptein, R.; van Leeuwen, P. W. N. M.; Huis, R. *J. Chem. Soc., Chem. Commun.* **1975**, 568.
- (55) Johnson, A.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1975**, 115.
- (56) Perkins, D. C. L.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1979**, *166*, 261 (see also ref 42h).

(50) Davies, A. G.; Roberts, B. P. *Acc. Chem. Res.* **1972**, *5*, 387.

Scheme 5



Scheme 6



alkyl radical by O_2 , to the $\text{Pt}(\text{II})$ center of **6** leads to the formation of a five-coordinate $\text{Pt}(\text{III})$ intermediate that abstracts iodine from iPrI . Other examples of oxidative additions involving $\text{Pt}(\text{II})$ complexes to form $\text{Pt}(\text{IV})$ derivatives have also been proposed to proceed through the intermediacy of five-coordinate $\text{Pt}(\text{III})$ radicals.⁵⁸

These reports indicate that radical substitution reactions at $\text{Pt}(\text{II})$ centers are viable pathways and that five-coordinate $\text{Pt}(\text{III})$ complexes can be reasonably proposed as intermediates. An extension of such reactivity to palladium leads to the proposed mechanism shown in Scheme 7 for the autoxidation of **1**. Rather than the concerted displacements presented in Scheme 5, the displacement of $\text{Me}\cdot$ by $\text{MeOO}\cdot$ could be a stepwise associative process with initial formation of a pentacoordinate

$\text{Pd}(\text{III})$ intermediate, $(\text{bipy})\text{Pd}^{\text{III}}(\text{Me})_2(\text{OOMe})\cdot$ (**8**) (Scheme 7, steps 5i and 5ii).^{42,59} The involvement of this intermediate could be key in differentiating the observed reactivity of **1** from reactions of autoxidation of organic compounds where the formation of an analogous hypervalent intermediate is not possible.

It is reasonable to propose that the reaction between **1** and $\text{MeOO}\cdot$ radicals to form **8** would be reversible (Scheme 7, steps 5i and -5i),⁶⁰ and that loss of either $\text{MeOO}\cdot$ or $\text{Me}\cdot$ should be possible from intermediate **8**. However, at the high pressures of oxygen used experimentally, the release of the $\text{Me}\cdot$ radicals (step 5ii) would be rendered irreversible by their fast trapping with O_2 to form $\text{MeOO}\cdot$ radicals.⁶¹

The rate law for such a mechanism, if the termination step were the coupling of two $\text{MeOO}\cdot$ radicals as proposed above in Scheme 5,⁶² is given by eq 6, so that a first-order dependence of the rate on $[\text{I}]$ would still be expected. However, under the reaction conditions, the concentration of **1** is expected to be much larger than that of $\text{MeOO}\cdot$.⁶³ Consequently, one might expect that the reaction of $\text{MeOO}\cdot$ radicals with **1** would yield a significant concentration of pentacoordinate $\text{Pd}(\text{III})$ species $(\text{bipy})\text{Pd}^{\text{III}}(\text{Me})_2(\text{OOMe})\cdot$ (**8**).⁶⁴ Under these conditions, it is quite reasonable to suggest that the coupling of **8** with $\text{MeOO}\cdot$ would then become the dominant termination step (Scheme 7, step 6e).⁶⁵ In fact, a very similar process (involving the reversible reaction of $\text{ROO}\cdot$ with an inhibitor followed by reaction of the resulting complex with a second $\text{ROO}\cdot$ radical) was originally proposed by Hammond

(57) (a) Ferguson, G.; Monaghan, P. K.; Parvez, M.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1669. (b) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 439. (c) Hill, R. H.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1218.

(58) See: ref 42d and (a) Thomas, S. W., III; Venkatesan, K.; Müller, P.; Swager, T. M. *J. Am. Chem. Soc.* **2006**, *128*, 16641. (b) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735. (c) von Zelewsky, A.; Suckling, A. P.; Stoekli-Evans, H. *Inorg. Chem.* **1993**, *32*, 4585. (d) Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; von Zelewsky, A. *J. Am. Chem. Soc.* **1987**, *109*, 7720. (e) Hall, T. L.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1980**, 1448. For relevant discussions on these types of reactions, see refs 45b, c.

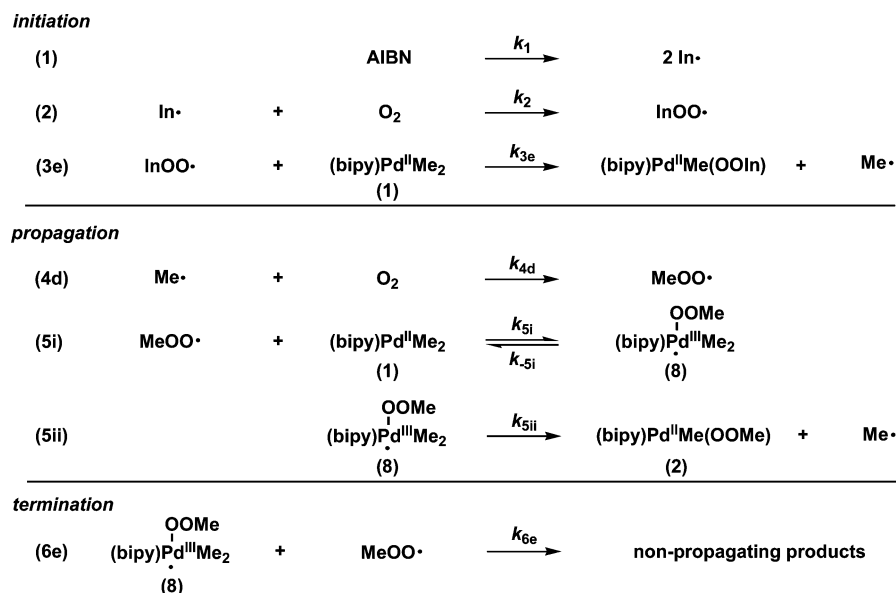
(59) Reactions of $\text{Pd}(\text{II})$ complexes with in situ generated $\text{ROO}\cdot$ radicals from H_2O_2 or tBuOOH have been proposed: (a) Kamaraj, K.; Bandyopadhyay, D. *Organometallics* **1999**, *18*, 438. (b) Wadhwani, P.; Bandyopadhyay, D. *Organometallics* **2000**, *19*, 4435.

(60) The following reaction between a first-row transition metal complex (often with $\text{L} = \text{macrocyclic nitrogen ligand}$; $\text{M} = \text{Cr, Mn, Fe, Co, Ni}$, and also Cu) and $\text{Me}\cdot$ or $\text{MeOO}\cdot$ radicals in aqueous medium is well documented: $(\text{L})\text{M}^n(\text{H}_2\text{O}) + \text{R}\cdot \leftrightarrow (\text{L})\text{M}^{n+1}(\text{R}) + \text{H}_2\text{O}$. For reactions involving $\text{MeOO}\cdot$, values of $K_{\text{eq}} = 10^2\text{--}10^3$ have been determined for Fe (ref d) and Cu (ref e) complexes, while the reaction seems to be essentially irreversible for some Co complexes (refs f and g). (a) Goldstein, S.; Czapski, G.; van Eldik, R.; Shaham, N.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **2001**, *40*, 4966. (b) van Eldik, R.; Meyerstein, D. *Acc. Chem. Res.* **2000**, *33*, 207. (c) van Eldik, R.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1994**, *33*, 1566. (d) Mansano-Weiss, C.; Cohen, H.; Meyerstein, D. *J. Inorg. Biochem.* **2002**, *91*, 199. (e) Mansano-Weiss, C.; Masarwa, A.; Cohen, H.; Meyerstein, D. *Inorg. Chim. Acta* **2005**, *358*, 2199. (f) Solomon-Rapaport, E.; Masarwa, A.; Cohen, H.; Valentine, J. S.; Meyerstein, D. *Eur. J. Inorg. Chem.* **2002**, 2427. (g) Solomon-Rapaport, E.; Masarwa, A.; Cohen, H.; Meyerstein, D. *Inorg. Chim. Acta* **2000**, 299, 41.

(61) The coupling of $\text{R}\cdot$ with O_2 to form $\text{ROO}\cdot$ is essentially diffusion-limited (for compilations of rate data see refs a and b). A value of $k = 4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ has been determined for the reaction of $\text{Me}\cdot$ with O_2 in H_2O at 296 K (ref c). (a) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1990**, *19*, 413. (b) Neta, P.; Grodkowski, J.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1996**, *25*, 709. (c) Thomas, J. K. *J. Phys. Chem.* **1967**, *71*, 1919.

(62) The homocoupling of two alkyl radicals ($\text{Me}\cdot$ in cyclohexane at 298 K: $k = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, ref a) is essentially diffusion-limited. The rate constant for the homocoupling of two $\text{MeOO}\cdot$ radicals in benzene at 295 K is $k = 1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (ref b). (a) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047. (b) Khursan, S. L.; Safiullin, R. L.; Martemianov, V. S.; Nikolayev, A. V.; Urozhai, I. A. *React. Kinet. Catal. Lett.* **1989**, *39*, 261. For a compilation of rate data, see ref 61b.

Scheme 7



and co-workers to explain the inverse half-order dependence of the rate on the concentration of the inhibitor in some radical chain autoxidation reactions.⁶⁶

The rate law describing the rate of disappearance of (bipy)-PdMe₂ (1) according to Scheme 7 is given by eq 8 (see Supporting Information for a derivation).

$$\text{rate} = -d[(\text{bipy})\text{PdMe}_2]/dt =$$

$$k_{\text{Scheme7}}[(\text{bipy})\text{PdMe}_2]^{1/2}[\text{AIBN}]^{1/2} \quad (8)$$

$$k_{\text{Scheme7}} = (2ek_1k_{5i}k_{5ii}^2/(k_{6e}(k_{-5i} + k_{5ii}))^{1/2} \quad (9)$$

Notably, eq 8 shows a half-order dependence of the rate on the concentration of both (bipy)PdMe₂ (1) and AIBN and is of the same form as the empirical rate law determined experimentally for the reaction of 1 with O₂ (eq 4). The involvement of the five-coordinate Pd(III) intermediate (bipy)Pd^{III}(Me)₂(OOMe)• (8), formed by attack of MeOO• on 1, thus provides a simple explanation to the unusual kinetics determined experimentally. This key intermediate 8 is involved both as a chain carrier to form the product (bipy)PdMe(OOMe) (2) by release of Me• radicals (Scheme 7, step 5ii), and as a trap for MeOO• radicals to terminate the chain process (Scheme 7, step 6e). The deviation from the usual kinetic behavior found for the autoxidation of organics, where a first-order dependence of the rate on the concentration of the substrate is typically found,^{43,44} can thus be easily explained by the formation of this hypervalent intermediate which is not available to organic compounds. In that respect, the radical chain mechanism determined for the autoxidation of (bipy)PdMe₂ (1) seems to be more closely related to the one found for the autoxidation of main group and early transition metal alkyl complexes for which stepwise homolytic substitutions at the main group or metal center have often been proposed.^{14–16}

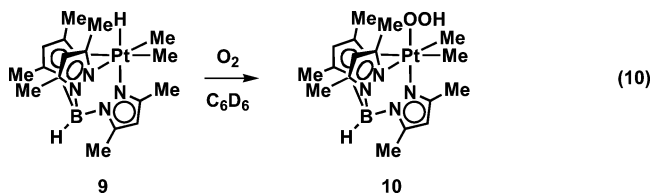
Comparison to Known Examples of Insertion of O₂ into Late Metal–Hydride Bonds and Implications for Catalysis. In sharp contrast to the radical chain nature of the reaction of insertion of O₂ into a Pd(II)–Me bond of (bipy)PdMe₂ (1), the known examples of insertion of O₂ into Pd(II)–H bonds to form Pd(II)–OOH complexes have been shown not to proceed by

radical chain mechanisms.^{67,68} Experimental and computational investigations on these reactions support a mechanism proceeding, depending on the complex, by either hydrogen atom abstraction by O₂ and recombination to form PdOOH⁶⁷ or by a pathway involving reductive elimination and reaction of Pd(0) with O₂ followed by reprotonation.⁶⁸

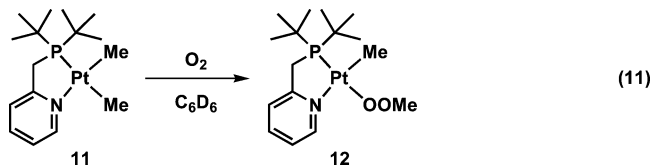
Significantly however, the insertion of molecular oxygen into the Pt(IV)–H bond of Tp^{Me2}PtMe₂H (Tp^{Me2} = hydridotris(3,5-dimethylpyrazolyl)borate) (9) has been shown to proceed by a radical chain mechanism.^{31a,69} It is notable that although the Pt(IV) complex 9 contains both methyl and hydride ligands,

- (63) No chemically induced dynamic nuclear polarization (CIDNP) effects were observed during the reactions between 1 and O₂. Weak CIDNP effects have been observed in some non-chain homolytic displacements at Pt(II) centers (see ref 54b, see also ref 42h) while no effects were detected for some radical chain reactions (see ref 55, also ref 57a). For the observation of strong CIDNP effects in the autoxidation of boranes, see ref 15q.
- (64) Apart from the processes described in note 60, rate constants for the addition of radicals to transition metal complexes have rarely been measured. (a) The rate constant for the addition of ¹Pr• radicals to (phen)PtMe₂ (ref 57b) and to *trans*-IrClCO(PMe₃)₂ was estimated to be $k \approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$; Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Inorg. Chem.* **1980**, *19*, 3236. (b) In ref 41g, the rate constant for the addition of the 5-hexenyl radical to Pt(PEt₃)₃ was estimated to be $k \approx 10^6 \text{ M}^{-1} \text{ s}^{-1}$. (c) In ref 45a, for the equilibrium [(L)Ni^{II}]²⁺ + Me• + H₂O $\leftrightarrow$ [(L)(H₂O)Ni^{III}(Me)]²⁺, values of the rate constant for the forward reaction with three different complexes were determined to be $k_{\text{forward}} = 1.6\text{--}6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and the equilibrium constant for five different complexes were found to be $K_{\text{eq}} = 450\text{--}12000 \text{ M}^{-1}$. (d) Both the forward and reverse reactions involving the Lewis acid-base adduct [(acetylacetonato)₂Pt^{II}•••I₂] for the equilibrium reaction I• + [(acetylacetonato)₂Pt^{II}•••I₂] $\leftrightarrow$ (acetylacetonato)₂Pt^{IV}(I)₂ + I• were found to be diffusion-controlled, with an equilibrium constant of $K_{\text{eq}} = 0.694$; Hopgood, D.; Jenkins, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 4461.
- (65) See note 45 for similar reactivity in nonchain radical reactions with transition metal complexes. The two-step transformation LCo^{II} + MeOO• $\rightarrow$ LCo^{III}(OOMe) followed by LCo^{III}(OOMe) + MeOO• $\rightarrow$ products has been studied, see refs 60f, g.
- (66) Hammond, G. S.; Boozer, C. E.; Hamilton, C. E.; Sen, J. N. *J. Am. Chem. Soc.* **1955**, *77*, 3238.
- (67) (a) Denney, M. C.; Smythe, N. A.; Cetto, K. L.; Kemp, R. A.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 2508. (b) Keith, J. M.; Muller, R. P.; Kemp, R. A.; Goldberg, K. I.; Goddard, W. A., III; Ongaard, J. *Inorg. Chem.* **2006**, *45*, 9631. (c) Chowdhury, S.; Rivalta, I.; Russo, N.; Sicilia, E. *Chem. Phys. Lett.* **2007**, *443*, 183.

only insertion into the Pt(IV)–H bond was observed (eq 10). The mechanism proposed for the autoxidation of **9** is reminiscent of the one usually encountered in the autoxidation of organic compounds, with the key chain carriers formed through H-atom abstraction reactions.^{31a,69}



The mechanism of the autoxidation of (bipy)PdMe₂ (**1**), which involves a radical chain process proceeding by stepwise homolytic substitutions at the metal center, stands in contrast to the documented mechanisms of autoxidation of late transition metal hydrides. Given that we are only now beginning to find well-characterized examples of the insertion of molecular oxygen into late transition metal–alkyl bonds,^{10–12} the generality of this type of radical chain mechanism remains to be determined.⁷⁰ However, the recognition that such a mechanism can be operative has some important implications. It will be particularly significant to establish whether autoxidation of late transition metal alkyl complexes can occur at saturated metal centers, such as in complex **9**, that are not able to expand their valency to accommodate a mechanism such as the one proposed in Scheme 7. Notably, another rare example of insertion of molecular oxygen into a late metal–alkyl bond was recently discovered in our laboratory.¹¹ The insertion of O₂ into a Pt(II)–Me bond of (PN)PtMe₂ (PN = 2-(di-*tert*-butylphosphino-methyl)pyridine) (**11**) to form (PN)PtMe(OOMe) was found to proceed readily at room temperature (eq 11).



Although the mechanism of this reaction has not been fully studied, preliminary observations suggest the involvement of a radical chain mechanism.¹¹ The fact that both (bipy)PdMe₂ (**1**) and (PN)PtMe₂ (**11**) are sixteen-electron d⁸ square planar complexes with the ability to expand their valency to five-coordinate seventeen-electron species may be an important feature that allows them to undergo this insertion reaction. Clearly, further studies of the reaction of molecular oxygen with both saturated and unsaturated metal alkyl complexes will deepen our understanding of the mechanisms and requirements for oxygen insertion into late metal–alkyl bonds and potentially

guide the successful design of transition metal catalysts for alkane oxidation using molecular oxygen.

Conclusions

A rare example of insertion of molecular oxygen into a late transition metal–alkyl bond has been described and the mechanism of the reaction investigated through detailed kinetic studies. The autoxidation of (bipy)PdMe₂ (**1**) results in the formation of the Pd(II) methylperoxide complex (bipy)PdMe(OOMe) (**2**). Although a variety of main group and early transition metal alkyl complexes are known to react with O₂ to form alkylperoxide complexes,^{14–16} this type of autoxidation reaction has not been well established for late transition metals.^{10–12} As numerous complexes of late transition metals have been shown to directly activate alkanes to form metal alkyls, this new mode of reactivity may constitute a promising lead for a selective alkane functionalization process.

Reproducible rates were achieved in the presence of AIBN, and the reaction was determined to be one-half-order in both [**1**] and [AIBN], and zero-order in [O₂]. The marked effects of light and AIBN on the rate of the reaction suggest the involvement of a radical chain mechanism. This result is particularly striking considering that the recently documented insertions of O₂ into Pd(II)–H bonds have been shown not to proceed by radical chain mechanisms.^{67,68} On the basis of the observed kinetic data and on literature precedents, stepwise homolytic substitution reactions at the metal center of (bipy)PdMe₂ (**1**) are proposed as key steps in the autoxidation of **1**. A salient feature of this scheme is the formation of a five-coordinate Pd(III) intermediate by expansion of the valency of the metal center. Overall, the mechanism for the autoxidation of **1** appears to be more closely related to the general mechanism proposed for the autoxidation of main group and early transition metal alkyl complexes than to the general mechanism usually involved in the autoxidation of organic compounds and recently proposed for the autoxidation of Pt(IV)–H complexes. Considering that a wide variety of useful processes based on the autoxidation of main group metal alkyl complexes have been developed,^{17–20} such behavior is particularly promising for the development of “palladium oxygenase” catalytic transformations.

Understanding the mechanisms by which O₂ reacts with transition metal complexes may facilitate the development of a variety of aerobic oxidation reactions. While associative homolytic substitutions such as those involved in the autoxidation of **1** have not been systematically studied with late transition metals, they could potentially be applicable to a wide variety of transformations. A greater awareness of the requirements for these types of reactions, such as the necessity to expand the valency at the metal center, may help in the rational design of catalysts for the functionalization of alkanes.

Experimental Section

Materials and Methods. Unless otherwise noted, all manipulations were carried out using high-vacuum line techniques, under an atmosphere of dry dinitrogen using standard Schlenk techniques or in an inert atmosphere glovebox. Glassware was dried for a minimum of eight hours at >150 °C. Benzene, dichloromethane, diethyl ether, tetrahydrofuran and pentane were dried by passage through activated alumina and molecular sieves columns under a stream of argon. Methanol was freshly distilled from magnesium turnings and iodine. Benzene-*d*₆ and 1,4-dioxane were vacuum-transferred from sodium benzophenone ketyl. Dichloromethane-*d*₂ and chloroform-*d* were vacuum-transferred from calcium hydride. All other reagents were used as received from commercial suppliers.

- (68) (a) Konnick, M. M.; Gandhi, B. A.; Guzei, I. A.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2904. (b) Popp, B. V.; Stahl, S. S. *J. Am. Chem. Soc.* **2007**, *129*, 4410. (c) Konnick, M. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 5753. (d) Chowdhury, S.; Rivalta, I.; Russo, N.; Sicilia, E. *J. Chem. Theory Comput.* **2008**, *4*, 1283. (e) Keith, J. M.; Goddard, W. A., III *J. Am. Chem. Soc.* **2009**, *131*, 1416.
- (69) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 11900.
- (70) For example, singlet oxygen generated by photosensitization was implicated in a recently reported example of oxygen insertion into a Pt(II)–Me bond to form a Pt(II)–OOMe complex. See ref 12.

(bipy)PdMe₂ (**1**) was prepared according to a literature procedure.^{23b} NMR experiments were performed on Bruker AV300, AV301, DRX499 and AV500 spectrometers using, unless otherwise noted, 5 mm medium-walled Wilmad 504-PP NMR tubes fitted with a J. Young Teflon valve. ¹H NMR spectra are referenced to residual protiated solvent signals (CDCl₃: 7.26 ppm, C₆D₆: 7.16 ppm, CD₂Cl₂: 5.32 ppm). ¹³C NMR spectra are referenced to deuterated solvent signals (CD₂Cl₂: 54.0 ppm). Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (0.00 ppm) and coupling constants are reported in hertz (Hz). The following abbreviations are used: s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), m (multiplet), br (broad). Assignments of the ¹H NMR resonances were made from COSY, NOESY and HMQC spectra of the complexes. The numbering scheme for the protons on the bipy ligand is illustrated in Table 1.

Safety Note on the Handling of Alkylperoxides. *Pure alkylperoxides are potentially explosive and should be avoided if possible.*²⁶ They can be violently decomposed by adventitious catalysts (acids, metals) with formation of, among others, oxygen gas. Distillation of alkylperoxides is not recommended. It has been documented that explosions occurred when pure MeOOH was heated^{25a} and that the residue obtained after distillation of pure samples of MeOOH exploded violently.^{25b}

Synthesis of MeOOH. By modification of literature protocols:²⁵ To avoid metal-catalyzed decomposition of the peroxides, all manipulations were carried out in carefully washed glassware. In a well-ventilated fume hood, Me₂SO₄ (15 mL, 159 mmol) was added to a mixture of H₂O (50 mL) and H₂O₂ (30 wt % in H₂O, 30 mL) at 0 °C. A solution of KOH (16.8 g, 299 mmol) in H₂O (25 mL) was then added dropwise with vigorous stirring to the biphasic reaction mixture over 30–40 min at 0 °C. On addition of the KOH solution, the formation of the byproduct MeOOME was immediately apparent from the liberation of a gas. At the end of the addition, bubbling was still intense and a single phase was visible. After stirring a further 40 min at 0 °C (at which point the bubbling was much less intense), the mixture was warmed to room temperature (bubbling intensified) and stirred at room temperature until the liberation of gas was much less intense (ca. 4.5 h). After stirring at 60 °C for 45 min, the bubbling had essentially stopped and the mixture was cooled to room temperature and stirred for ca. 10 h. The mixture was cooled to 0 °C and neutralized to pH ≈ 7 with 50% H₂SO₄. A final volume of ca. 120 mL was obtained. This solution was then continually extracted for 7 h with ca. 25 mL of Et₂O. Analysis of the Et₂O solution by ¹H NMR spectroscopy (CDCl₃, 298 K) revealed a ratio of ~1:9 MeOOH/Et₂O. A second continuous extraction (ca. 25 mL of Et₂O, 12 h) yielded a similar result. The Et₂O solution was dried overnight over Na₂SO₄ at 4 °C then filtered through glass wool in a wide-bore vial containing a magnetic stir bar. A thermometer was placed above the opening of the vial, and the solution was concentrated by heating with an oil bath with stirring at 40–45 °C until the temperature above the opening of the vial decreased from 33–37 °C to ca. 30 °C (the boiling point of pure MeOOH is 38–40 °C at 65 mmHg).^{25a} Analysis of the residue by ¹H NMR spectroscopy (CDCl₃, 298 K) revealed a ratio of ~1:2 MeOOH/Et₂O. This mixture was dried for 1 h over CuSO₄ at 4 °C then filtered through glass wool in a vial. It was kept in the freezer of the inert atmosphere glovebox at –35 °C and used as such for the subsequent reactions. ¹H NMR analysis of the ~1: 2 MeOOH/Et₂O mixture (CDCl₃, 300 MHz, 298 K): δ (ppm) 8.72 (s, 1H, CH₃OOH), 3.88 (s, 3H, CH₃OOH), 3.48 (q, 4H, *J* = 7.0 Hz, (CH₃CH₂)₂O), 1.20 (t, 6H, *J* = 7.0 Hz, (CH₃CH₂)₂O); lit.,^{25a} (pure MeOOH in CDCl₃) δ (ppm) 8.86 (br s, 1H, CH₃OOH), 3.87 (s, 3H, CH₃OOH). Apart from a trace amount of water, only MeOOH and Et₂O were detectable by ¹H NMR spectroscopy; no MeOH or H₂O₂ could be detected even after storing the sample for several months at –35 °C. The identity of MeOOH was confirmed by addition of Ph₃P to a sample of MeOOH

in CDCl₃: immediate formation of Ph₃PO and MeOH was observed by ¹H NMR spectroscopy.²⁷

Synthesis of (bipy)PdMe(OOME) (2**).** Methylperoxide complex **2** could be efficiently generated from either methoxide complex **3** or hydroxide complex **4**; the protocol outlined below is illustrated for a reaction involving **3**.

Under an atmosphere of dinitrogen, (bipy)PdMe(OMe) **3** (1.3 mg, 4.2 μmol) was weighed into a vial and toluene (0.5 mL) was added. A solution of ~1:2 MeOOH/Et₂O (1.0 μL; as prepared above) was added by syringe at room temperature and the yellow-orange solution immediately became yellow. The vial was capped, shaken for <30 s and stored in the freezer at –35 °C for ca. 11 h. Pentane (0.5 mL) was added and the sample was allowed to stand at –35 °C for 2 min. The colorless supernatant was removed at –35 °C, the yellow solid was washed with pentane (4 × 0.5 mL), and traces of solvent were quickly removed under vacuum. Complex **2** was unstable in solution at room temperature and was stored as a solid under an atmosphere of dinitrogen at –35 °C. ¹H NMR (CD₂Cl₂, 500 MHz, 233 K) δ (ppm) 8.96 (d, 1H, *J* = 4.4 Hz, H₆), 8.59 (d, 1H, *J* = 5.2 Hz, H₆), 8.09–7.98 (m, 4H, H₃, H₃, H₄, H₄), 7.57 (ddd, 1H, *J* = 7.3, 5.2, and 1.2 Hz, H₅), 7.47 (ddd, 1H, *J* = 7.5, 5.6, and 1.3 Hz, H₅), 3.64 (s, 3H, Pd–OCH₃), 0.67 (s, 3H, Pd–CH₃). HMQC analysis (CD₂Cl₂, 500 MHz, 233 K): PdOCH₃ (¹H NMR: 3.64 ppm, ¹³C NMR: 63.8 ppm), PdCH₃ (¹H NMR: 0.65 ppm, ¹³C NMR: 3.1 ppm). Alternatively, complex **2** was formed quantitatively, together with one molar equivalent of ROH (R = Me or H), when MeOOH was added to a C₆D₆ or CD₂Cl₂ solution of (bipy)PdMe(OMe) (**3**) or (bipy)PdMe(OH) (**4**), as observed by ¹H NMR spectroscopy.

Synthesis of (bipy)PdMe(OMe) (3**).** Under an atmosphere of dinitrogen, (bipy)PdMe(I) (35.6 mg, 0.0880 mmol) and AgSO₃CF₃ (23.7 mg, 0.0924 mmol) were combined in CH₃OH (4 mL). The reaction mixture was stirred for 1–2 min to allow the formation of a pale gray precipitate, then NaOMe (9.5 mg, 0.18 mmol) was added. The mixture was filtered through a PTFE syringe filter, and the solvent immediately removed under vacuum. The yellow residue was extracted with CH₂Cl₂ (2 × 1 mL) and filtered through glass wool/Celite. Addition of pentane (6 mL) resulted in precipitation of a pale yellow solid. The solid was washed with pentane (2 × 3 mL) and dried under vacuum. Yield: 20.5 mg (75%). Complex **3** was unstable in solution at room temperature and was stored as a solid under an atmosphere of dinitrogen at –35 °C. ¹H NMR (CD₂Cl₂, 300 MHz, 298 K) δ (ppm) 8.95 (d, 1H, *J* = 4.8 Hz, H₆), 8.68 (d, 1H, *J* = 5.7 Hz, H₆), 8.11–7.94 (m, 4H, H₃, H₃, H₄, H₄), 7.60 (ddd, 1H, *J* = 5.7, 4.8, and 2.5 Hz, H₅), 7.43 (ddd, 1H, *J* = 7.5, 5.7, and 3.0 Hz, H₅), 3.55 (s, 3H, Pd–OCH₃), 0.77 (s, 3H, Pd–CH₃). ¹H NMR (CD₂Cl₂, 500 MHz, 233 K) δ (ppm) 8.85 (d, 1H, *J* = 4.8 Hz, H₆), 8.63 (d, 1H, *J* = 5.3 Hz, H₆), 8.11–7.94 (m, 4H, H₃, H₃, H₄, H₄), 7.59 (t, 1H, *J* = 5.7 Hz, H₅), 7.45 (t, 1H, *J* = 6.3 Hz, H₅), 3.45 (s, 3H, Pd–OCH₃), 0.69 (s, 3H, Pd–CH₃). ¹H NMR data in CD₃OD matched that previously reported by van Koten and co-workers.²⁴ HMQC analysis of a 1: 1 (bipy)PdMe(OMe) (**3**)/(bipy)PdMe(OH) (**4**) mixture (CD₂Cl₂, 500 MHz, 233 K): (bipy)PdMe(OCH₃) (¹H NMR: 3.45 ppm, ¹³C NMR: 57.4 ppm), (bipy)PdCH₃(OMe) (¹H NMR: 0.68 ppm, ¹³C NMR: 1.4 ppm); (bipy)PdCH₃(OH) (¹H NMR: 0.53 ppm, ¹³C NMR: –4.2 ppm).

Synthesis of (bipy)PdMe(OH) (4**).** Under an atmosphere of dinitrogen, (bipy)PdMe(OMe) **3** (1.3 mg, 4.2 μmol) was weighed into a medium-walled NMR tube fitted with a J. Young Teflon valve. A small amount of hexamethylbenzene (as an internal standard) and benzene (0.4 mL) was added, and the tube was shaken to obtain a yellow-orange solution. H₂O (0.4 μL, 22 μmol) was added, and the tube was shaken for ca. 2 min until a colorless supernatant and a beige solid were obtained. The solvent was removed under vacuum, CD₂Cl₂ was added by vacuum-transfer, and the sample was kept at –78 °C. Analysis by ¹H NMR spectroscopy showed complete conversion to **4** with >90% purity. Complex **4** was unstable in solution at room temperature but solutions kept at temperatures lower than ca. –35 °C showed no

sign of decomposition. ^1H NMR (CD_2Cl_2 , 300 MHz, 298 K) δ (ppm) 8.96 (d, 1H, $J = 5.6$ Hz, H_6'), 8.65 (d, 1H, $J = 5.7$ Hz, H_6), 8.09–7.96 (m, 4H, H_3 , H_3' , H_4 , H_4'), 7.60 (ddd, 1H, $J = 6.7$, 5.6, and 2.2 Hz, H_5'), 7.43 (ddd, 1H, $J = 7.4$, 5.7, and 1.7 Hz, H_5), 0.59 (s, 3H, Pd– CH_3), –1.50 (br s, 1H, Pd–OH). ^1H NMR (CD_2Cl_2 , 500 MHz, 233 K) δ (ppm) 8.87 (d, 1H, $J = 5.6$ Hz, H_6'), 8.57 (d, 1H, $J = 5.7$ Hz, H_6), 8.08–7.96 (m, 4H, H_3 , H_3' , H_4 , H_4'), 7.59 (m, H_5'), 7.45 (m, H_5), 0.53 (s, 3H, Pd– CH_3), –1.39 (s, 1H, Pd–OH). NOESY analysis (CD_2Cl_2 , 500 MHz, 233 K) showed chemical exchange between Pd–OH and trace H_2O (~ 3 ppm) (see *Synthesis of (bipy)PdMe(OMe)* for HMQC data of the methyl group of (bipy)PdMe(OH) **4**).

Synthesis of (bipy)PdMe(I) (5). Under an atmosphere of dinitrogen, (bipy)PdMe₂ **1** (84.0 mg, 0.287 mmol) was dissolved in acetone (20 mL). Upon addition of iodomethane (19 μL , 0.30 mmol), the solution turned a lighter yellow color and the reaction was stirred for 30 min at room temperature. The volume was then reduced under vacuum to ca. 5 mL, resulting in the precipitation of a pale yellow solid. After addition of hexanes (10 mL), the yellow solid was collected on filter paper, washed with hexanes (2×3 mL), and dried under vacuum. Yield: 100 mg (86%). ^1H NMR data for (bipy)PdMe(I) (acetone- d_6) matched that previously reported by Byers and Canty.^{23a}

SAFETY NOTE on the Handling of Pressurized NMR Tubes. Extreme caution should be used while handling J. Young Teflon tubes under pressure. While under pressure, NMR tubes were stored in a protective jacket.

Control Experiment: (bipy)PdMe₂ in C₆D₆ in the Absence of Oxygen. Under an atmosphere of dinitrogen, (bipy)PdMe₂ **1** (ca. 0.1 mg) was weighed into a medium-walled NMR tube fitted with a ground glass joint and 1,3,5-tri-*tert*-butylbenzene was added as an internal standard. C₆D₆ was added by vacuum transfer and the sample was kept frozen in a liquid nitrogen bath. The tube was flame-sealed under vacuum. The sample was thawed, shaken, and allowed to react at room temperature. No reaction was observed by ^1H NMR spectroscopy over 24 h. The sample was heated at 50 °C in a temperature-controlled oil bath for over 18 h. Although traces of palladium black were visible on the sides of the NMR tube, only **1** was observed by ^1H NMR spectroscopy in >95% of its initial concentration.

Verification of the Effect of Light. A stock solution of (bipy)PdMe₂ **1** and 1,4-dioxane (as internal standard) in C₆D₆ was added to two medium-walled NMR tubes fitted with J. Young Teflon valves. Both tubes were degassed (three freeze–pump–thaw cycles) and kept frozen in an ice/methanol bath. The tubes were pressurized with oxygen (5 atm) using a high-pressure manifold. The samples were thawed, shaken and allowed to react at room temperature. One tube was kept under room light and the other kept in the dark. The extent of reaction was monitored by ^1H NMR spectroscopy over three days. For the reaction kept under light, 80%, 58% and 0% of **1** remained after 3, 6, and 72 h, respectively. For the reaction kept in the dark, 97%, 93% and 74% of **1** remained after 3, 6, and 72 h, respectively.

Verification of the Effect of AIBN. (1) In a typical experiment, (bipy)PdMe₂ **1** (ca. 0.1 mg) was weighed into a medium-walled NMR tube fitted with a J. Young Teflon valve under an atmosphere of dinitrogen. C₆D₆ and hexamethylbenzene (1–2 crystals) or 1,4-dioxane (ca. 0.2 μL) (as internal standard) were added. The sample was degassed (three freeze–pump–thaw cycles) and the tube was pressurized with O₂ (1–10 atm) using a high-pressure manifold. The sample was thawed, shaken and allowed to react at room temperature or at 50 °C in a temperature-controlled oil bath and the reaction was monitored by ^1H NMR spectroscopy. Under these conditions, the rate of consumption of **1** was found to be highly variable and maximum yields of ca. 70% of **2** were obtained. When AIBN was present and the reaction was conducted at 50 °C in a temperature-controlled oil bath, complete conversion of **1** was achieved and up to ca. 85% of **2** could be obtained.

(2) A stock solution of (bipy)PdMe₂ **1** and 1,4-dioxane (as internal standard) in C₆D₆ was added to two medium-walled NMR tubes fitted with J. Young Teflon valves. To one of the tubes was added AIBN. Reference ^1H NMR spectra were then recorded at 298 K. Both tubes were degassed (two freeze–pump–thaw cycles) and kept frozen in an ice/methanol bath. The tubes were pressurized with oxygen (5 atm) using a high-pressure manifold. The samples were thawed, shaken, and heated at 50 °C in a temperature-controlled oil bath. The extent of reaction was monitored by ^1H NMR spectroscopy. For the reaction with no added AIBN, 80% of **1** was still present after 40 min, 31% after 160 min. All of **1** was consumed after 40 min for the reaction with added AIBN.

Kinetic Studies. In a typical experiment, AIBN (0–1.5 mg, 0–9.1 μmol) was weighed into a medium-walled NMR tube fitted with a J. Young Teflon valve. A stock solution of (bipy)PdMe₂ **1** (5.3 mM), AIBN (2.2–8.2 mM) and 1,4-dioxane (as internal standard) (3.5–7.0 mM) in C₆D₆ (0.3 mL) was added. A reference ^1H NMR spectrum was then recorded in a NMR probe preheated to 323 K. The sample was degassed (three freeze–pump–thaw cycles) and kept frozen in an ice/methanol bath. The tube was pressurized with oxygen (5–10 atm) using a high-pressure manifold. The sample was thawed, shaken, and placed into a NMR probe preheated to 323 K. ^1H NMR spectra were acquired using single scans separated by at least 60 s in order to ensure accurate integration. Spectra were collected over at least three half-lives. The total concentration of AIBN, determined by integration of its CH₃ signal relative to the 1,4-dioxane signal, remained approximately constant throughout the reaction and is reported as the average value determined over at least two half-lives.³⁷ Rates (defined as rate = $-\text{d}[(\text{bipy})\text{PdMe}_2]/\text{d}t$) were determined by following the disappearance of the bipyridine signal of **1** at 8.8 ppm compared with the 1,4-dioxane signal. Similar results were obtained when the rates were determined by following the disappearance of the methyl signal of **1**. Concentrations of **2** found in Figure 1 were determined by following the appearance of the OOMe signal of **2** compared with the 1,4-dioxane signal.

Under these conditions, maximum yields of ca. 85% of **2** were observed after complete consumption of **1**. In all reactions, complete consumption of **1** was observed and extents of conversion reported in the different plots refer to the maximum conversion that could be reliably determined by integration of the signals in the ^1H NMR spectra. ^1H NMR (signals for **2** in crude reaction mixture, C₆D₆, 500 MHz, 298 K) δ (ppm) 9.37 (d, 1H, $J = 3.8$ Hz, bipy), 8.36 (d, 1H, $J = 4.7$ Hz, bipy), 7.00–6.84 (m, 4H, bipy), 6.61 (m, 1H, bipy), 6.32 (m, 1H, bipy) 4.26 (s, 3H, Pd–OOCCH₃), 1.48 (s, 3H, Pd–CH₃). The ^1H NMR chemical shifts of complexes **2** and **3** in C₆D₆ varied with the presence of protic impurities. However, the addition of independently synthesized methylperoxide complex **2** and methoxide complex **3** to the crude reaction mixture obtained above showed that the product of the reaction between **1** and oxygen was complex **2**. To fully characterize the product of the reaction of **1** with oxygen by NMR spectroscopy at low temperature, it was preferable to remove the volatiles under vacuum and add CD₂Cl₂ by vacuum-transfer. ^1H NMR and HMQC analyses of the resulting mixture at 233 K showed the signals for **2** (see *Synthesis of (bipy)PdMe(OOMe)* (**2**) above), the identity of which could be further confirmed by the addition of independently synthesized **2** and **3**.

Acknowledgment. This work was supported by the National Science Foundation (Grants CHE-0137394 and CHE-0719372). L.B. is the recipient of a postdoctoral fellowship from Fonds québécois de la recherche sur la nature et les technologies.

Supporting Information Available: Additional kinetic plots and derivation of eq 8. This information is available free of charge via the Internet at <http://pubs.acs.org>.

JA9061932