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Autoxidation of Platinum(IV) Hydrocarbyl Hydride Complexes To Form Platinum(IV) Hydrocarbyl Hydroperoxide Complexes

Jennifer L. Look, Douglas D. Wick, James M. Mayer, and Karen I. Goldberg*

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

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The platinum(IV) hydride complexes $Tp^{Me_2}PtR_2H$ (Tp^{Me_2} = hydridotris(3,5-dimethylpyrazolyl)borate, R = Me (**1a**), Ph (**1b**)) react with molecular oxygen to form platinum(IV) hydroperoxide complexes $Tp^{Me_2}PtR_2OOH$ (R = Me (**2a**) and Ph (**2b**), respectively) in high yield. The results of kinetic and mechanistic studies of these reactions are consistent with the net insertion of molecular oxygen into the Pt(IV)−H bonds occurring via radical chain mechanisms. The radical chain pathways resemble, in many respects, those documented for autoxidations of organic substrates, but significant differences are also evident. The autoxidations of **1a** and **1b** both autoaccelerate, but the nature of the rate accelerations and the dependence of the rates on the hydroperoxide products are not the same. The different rate laws observed for the reactions of $Tp^{Me_2}PtR_2H$ complexes with molecular oxygen can be rationalized on the basis of similar initiation and propagation events with different chain termination steps.

Introduction

From economic and environmental standpoints, oxygen represents an ideal oxidant for use in large-scale chemical production. Molecular oxygen is abundantly available, inexpensive (particularly if it can be used without separation from air), and environmentally benign. The challenges and advantages of developing new catalytic processes that incorporate this oxidant for partial oxidation reactions are widely recognized, particularly for fine chemical and pharmaceutical syntheses.[1] Thus, while there have been remarkable recent advances in the development of new homogeneous catalysts for selective oxidations, more expensive and/or hazardous oxidants than O_2 are still often employed.[2] A key limiting factor in catalyst development utilizing O_2 as an oxidant is the current level of understanding of reactions between transition-metal complexes and O_2.[3] The discovery and investigation of well-defined reactions of molecular oxygen and organometallic compounds can provide the critical insight needed to effectively tap this abundant and environmentally benign oxidant in selective homogeneous catalysis.

One particular reaction that is of significant interest to understand is conversion of a metal hydride to a metal hydroperoxide species in the presence of molecular oxygen. Metal hydroperoxide species have been consistently proposed in an array of processes including olefin oxidations[4] and various biological oxidation reactions.[5] In addition, this mode of oxygen activation by a metal hydride species has been proposed in recent Pd- and Ir-catalyzed oxidations of organic substrates.[2a,6,7] Despite the importance of this insertion

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* To whom correspondence should be addressed. E-mail: goldberg@chem.washington.edu.

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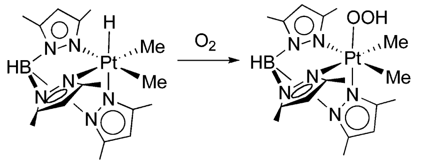
Scheme 1



1a **2a**

reaction, there are only a very few known well-defined models[8] and fewer still for which mechanistic studies have been carried out.[9,10]

Several years ago, we reported a high-yield reaction in which a platinum(IV) hydride undergoes a very clean insertion of molecular oxygen to form a stable platinum(IV) hydroperoxide.[11] As shown in Scheme 1, when a benzene solution of $Tp^{Me_2}PtMe_2H$ (**1a**) (Tp^{Me_2} = hydridotris(3,5-dimethylpyrazolyl)borate) was exposed to oxygen in ambient light, the Pt(IV) complex $Tp^{Me_2}PtMe_2OOH$ (**2a**) formed in quantitative yield. As discussed in the present contribution, related platinum(IV) hydrocarbyl hydride complexes have been found to share this unusual and clean reactivity with O_2. The phenyl derivative $Tp^{Me_2}PtPh_2H$ (**1b**) reacts with oxygen to quantitatively form the hydroperoxide complex $Tp^{Me_2}PtPh_2OOH$ (**2b**). In addition, the Tp complex $TpPtMe_2H$ (**1c**)[12] reacts to form $TpPtMe_2OOH$ (**2c**). The platinum(IV) hydroperoxide products of these reactions are stable, and **2a** has been structurally characterized.[11] In contrast to recent studies of oxygen insertion into palladium(II) hydrides to form palladium(II) hydroperoxide complexes which indicate non radical chain pathways,[9,10] extensive mechanistic data on these $Pt^{IV}H$ autoxidation reactions, as described below, are consistent with the operation of autoaccelerated radical chain pathways.

The results of preliminary experiments reported in 1999 led to the initial proposal that the reaction of **1a** with oxygen to form **2a** occurs via a radical chain process.[11] It was observed that the reaction accelerated upon irradiation with a photolysis lamp and occurred more slowly when carried out in the dark or in the presence of 1,4-cyclohexadiene. The oxidation of **1b** displays comparable behavior. For example, under ambient conditions, the reaction of **1b** with O_2 was complete after 6−8 days, while upon irradiation with a photolysis lamp, the reaction was complete after 2 h. In the presence of the radical initiator AIBN (azobisisobutyronitrile) at 343 K, the same reaction was complete within 30 min.

The radical chain pathways proposed for the oxidations of **1a** and **1b** with oxygen are reminiscent of the radical chain mechanisms involved in the oxidation of many organic substrates to form hydroperoxide products.[13] Such hydrocarbon oxidations have been studied for decades, and considerable information about the initiation, propagation, and termination steps involved in these systems is available.[14] Although the roles of metals as catalysts in organic autoxidations have been examined,[15,16] there are very few reports or studies of autoxidation with metal complexes as substrates.[8−11,17] Yet this insertion of oxygen into a metal hydride bond is clearly a key reaction to understand if the use of oxygen in metal-catalyzed reactions is to be developed for new types of chemical conversions. The mechanistic studies of the autoxidations of the platinum(IV) hydrides **1a** and **1b** described here reveal that there are striking similarities, but also important differences, with respect to the mechanism of autoxidations of organic substrates. This investigation represents an early step toward developing the critical understanding that may enable broader use of molecular oxygen as an oxidant in transition-metal-catalyzed reactions.

The specific platinum(IV) hydride to platinum(IV) hydroperoxide conversion depicted in Scheme 1 may also be important with respect to its particular relevance to platinum-catalyzed alkane oxidation reactions. Although platinum catalysts for alkane oxidation have been known for over 30 years, the search for an efficient process that incorporates a commercially viable oxidant continues.[18] Molecular oxygen

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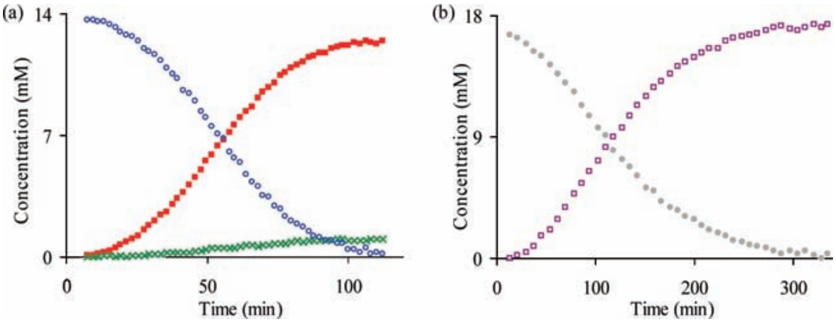

Figure 1. (a) Reaction profile for the oxidation of **1a** (blue open circles) to form **2a** (red filled squares) and **3a** (green times signs) in C_6D_6 at 323 K, with initial conditions of 11 atm of O_2 and 5 mM AIBN. (b) Reaction profile for the oxidation of **1b** (gray filled circles) to form **2b** (purple open squares) in C_6D_6 at 323 K with initial conditions of 11 atm of O_2 and 3 mM AIBN.

would be an ideal oxidant for such a process. Notably, reactant **1a**, a platinum(IV) dialkyl hydride complex, is directly analogous to compounds formed by intermolecular oxidative addition of the C−H bonds of alkanes to Pt(II).[19] The formal insertion of O_2 into the platinum−hydride bond thus represents an intriguing route to combining C−H bond activation and oxidation by O_2 to achieve selective alkane oxidation.

Results

To understand the reactions between molecular oxygen and the platinum(IV) hydride complexes **1a**−**c**, a series of kinetic studies were conducted to determine the effects of various reaction components. In addition to changing initial reactant and product concentrations, experiments with added radical initiators, inhibitors, and trapping agents were completed. Using this data, rate laws for each reaction were constructed providing insight into the mechanisms for these autoxidation reactions.

Shape of the Reaction Profiles. The autoxidation of **1a** at 323 K was monitored by ^{1}H NMR spectroscopy, with the tube remaining in the darkness of the NMR probe during the reaction. Figure 1a shows a typical reaction profile for the reaction of **1a** (blue open circles) with O_2 to form $Tp^{Me_2}PtMe_2OOH$, **2a** (red filled squares), in the presence of radical initiator AIBN. A minor product, $Tp^{Me_2}PtMe_2OH$, **3a** (green times signs), also formed under the reaction conditions employed in the kinetic investigations. In an independent experiment, **3a** formed in small amounts from the exposure of isolated **2a** to identical reaction conditions. The mass balance of platinum-containing species (the sum of **1a**, **2a**, and **3a**) was consistently 100(5)% except as noted below.

The autoxidation of **1b** (gray filled circles) to form **2b** (purple open squares) was also monitored at 323 K, and the data are shown in Figure 1b. The corresponding hydroxide product $Tp^{Me_2}PtPh_2OH$ (**3b**) was not detected under reaction conditions of high O_2 pressures (5−11 atm), and the measured concentrations of **1b** and **2b** accounted for 100(5)% of the platinum throughout the reaction. For each of the platinum hydrides **1a** and **1b**, different samples in different batches of C_6D_6 on different days yielded identical autoxidation behavior under these conditions.

The reaction profiles, as shown in Figure 1, are clearly sigmoidal. These distinctive and reproducible shapes are characteristic of autoaccelerated reactions, wherein species formed during the reaction (intermediates, products, or side products) increase the rate of reaction. An interesting difference between the oxidation reactions of **1a** and **1b** is noted in the symmetries of the plots. The reaction profile for the autoxidation of **1a** is symmetric about the midpoint of the time of the reaction. In contrast, the profile for **1b** is not symmetric; the time required for the first 50% conversion is shorter than the time required for the second 50%. The fact that the reaction is faster at the start is consistent with a higher order dependence on substrate **1b** than on the accelerating species. The term autocatalysis is often used to refer to the special case of autoacceleration in which the rate is directly proportional to the concentrations of substrate and product.[20] The symmetric reaction profile for **1a** is consistent with this common definition of autocatalysis, while the reaction profile for **1b** indicates a different form of autoacceleration. While it may be tempting to attribute the initial slow part of the reaction profiles to induction periods during which a sufficient concentration of radical chain carriers is generated, the effects of added initiators and products (described below) are indicative of autoaccelerating reactions.[21] Although some organic autoxidations can be prone to autoacceleration, typically organic autoxidations have been studied at very low conversions, which minimizes autoacceleration.[22] In some cases where reactions are examined to higher conversions, complicated reaction mechanisms

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(21) Some organic reactions can appear to autoaccelerate because of the presence of trace antioxidant impurities which are slowly consumed prior to establishment of the normal radical chain. This issue is more prevalent in reactions examined only at low conversion. For these platinum reactions, the success of the kinetic fittings through high conversions and the reproducible reaction rate profiles using different samples of solvent and platinum hydride complexes (with sufficient O_2 and consistent AIBN concentrations) both argue against an impurity origin of the autoacceleration.

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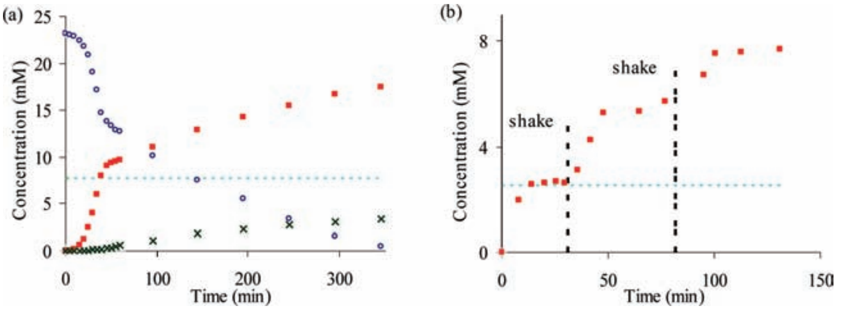

Figure 2. (a) Reaction profile showing that after the initially dissolved O_2 (sky blue dotted line) is depleted, the disappearance of **1a** (blue open circles) and formation of **2a** (red filled squares) slow, and the appearance of **3a** (green times signs) increases. Reaction conditions: 323 K in C_6D_6 with initially 23 mM **1a**, 1 atm of O_2, and no AIBN. (b) Reaction profile showing that after the initially dissolved O_2 (sky blue dotted line) is depleted the formation of **2a** (red filled squares) slows. Shaking the tube causes the rate of reaction to increase. Reaction conditions: 323 K, in C_6D_6 with initially 18 mM **1a**, 0.5 atm of O_2, and no AIBN.

involving dozens of elementary steps and degenerate chain branching have been required to computationally model autoxidations.[23]

Dependence on the O_2 Pressure. Autoxidation of many organic substrates has been shown to be independent of the O_2 pressure, provided sufficient O_2 is present (typically above 100−200 Torr).[24] Dioxygen diffuses into solution with continuous stirring of the reactions, ensuring an adequate supply for the reaction. In contrast, the platinum reactions were monitored in the NMR probe and thus were not stirred. Instead, the NMR tubes containing solutions of the Pt complexes under O_2 pressure were vigorously shaken to saturate the solution with O_2 prior to insertion into the probe. Using this procedure, it was found that the platinum oxidations also achieved O_2 independence but at higher pressure compared to the stirred organic oxidations. A high pressure of O_2 (several atmospheres) ensured that at least 1 molar equiv of O_2 to platinum was dissolved.[25]

When pressures of O_2 below this limit were employed, the O_2 concentration influenced the reaction. For example, with only 1 atm O_2 as shown in Figure 2a, when the initially dissolved O_2 was consumed, the disappearance of **1a** and the appearance of **2a** slowed dramatically, and the formation of **3a** significantly increased. Analogous behavior was noted when the same experiment was carried out in the presence of 10 mM AIBN. In a separate experiment (Figure 2b), it was shown that, after the reaction slowed, if the tube was removed from the NMR probe and briefly shaken, a faster rate of reaction resumed. This experiment clearly shows that the decreased rate of autoxidation noted in Figure 2a is caused by O_2 depletion in solution. Similar effects have been noted for organic autoxidations carried out under low O_2 conditions.[26]

As shown in Figure 3, when sufficient oxygen is present, the autoxidation rate of the platinum(IV) hydride is independent of O_2. Identical reaction profiles were obtained for the autoxidation of **1a** with 50 and 100 mM O_2 (3 and 6 molar equiv of dissolved O_2 to **1a**, 5.5 and 11 atm of O_2, respectively).[25] The autoxidation of **1b** was similarly found to be independent of the oxygen pressure (3 or 6 equiv of O_2 originally dissolved).

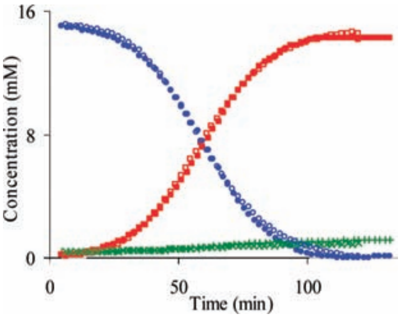

Figure 3. Reaction profiles showing that the autoxidation of **1a** is independent of the O_2 pressure: data exactly overlap with 5.5 atm of O_2, **1a** (blue open circles), **2a** (red open squares), **3a** (green times signs), and with 11 atm of O_2, **1a** (blue filled circles), **2a** (red filled squares), **3a** (green plus signs). Reaction conditions: 0.1 mM AIBN, 323 K, in C_6D_6.

Dependence on the Added Initiator. Attempts to study the autoxidation of **1a** in the absence of added initiator AIBN gave irreproducible results. Widely varying rates of reaction were observed: under identical reaction conditions, as much as 100% or as little as 4% conversion of starting material occurred after 2 h. Such behavior is common for a radical chain process since variable amounts of trace initiator are typically present.[27] To eliminate these difficulties and obtain reproducible rates of reaction, mechanistic studies of organic autoxidation reactions have typically been carried out in the presence of added initiator.

In the presence of 0.03−10.0 mM AIBN, the autoxidation of ca. 15 mM **1a** proceeds cleanly and with reproducible rates of reaction. The mass balance of known platinum complexes **1a**, **2a**, and **3a** remains at 100% throughout the reaction. Under the conditions of the reaction (323 K, benzene), the rate constant for the decay of AIBN is $2.2 \times 10^{-6}\ s^{-1}$,[28] so over the ca. 1 h reaction time with 10 mM

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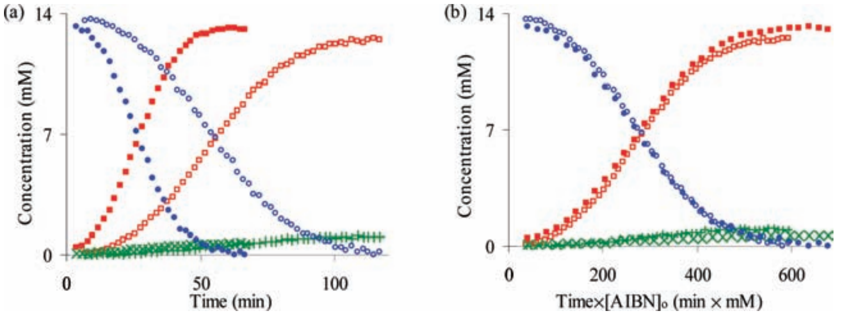

Figure 4. Reaction profiles of the autoxidation of **1a** show that (a) the rate of autoxidation increases as the concentration of AIBN is increased from 5 mM (**1a**, blue open circles; **2a**, red open squares; **3a**, green plus signs) to 10 mM (**1a**, blue filled circles; **2a**, red filled squares; **3a**, green times signs). (b) When the *x* axis is the product of the AIBN concentration and time, the curves overlap. Reaction conditions: 11 atm of O_2, 323 K, in C_6D_6.

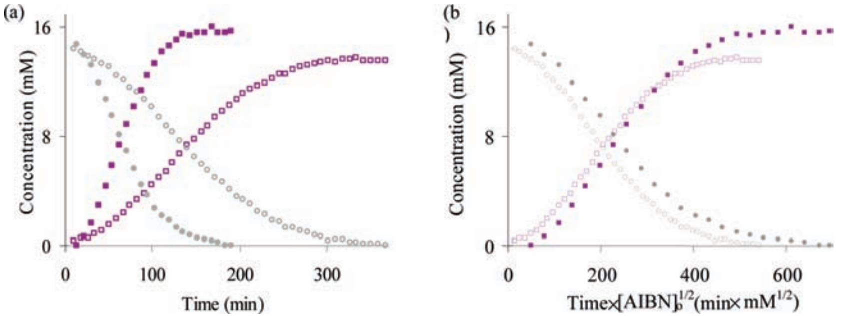

Figure 5. Reaction profiles of the autoxidation of **1b** show that (a) the rate of autoxidation increases as the concentration of AIBN is increased from 2 mM (**1b**, gray open circles; **2b**, purple open squares) to 13 mM (**1b**, gray filled circles; **2b**, purple filled squares). (b) When the *x* axis includes a half-order dependence on the AIBN concentration, the same curves overlap. A slight discrepancy in $[\mathbf{1b}]_o$ accounts for the small difference in the curves. Reaction conditions: 11 atm of O_2, 323 K, in C_6D_6.

AIBN, about 1% of the initiator decomposes and only ~0.2 mM radicals escape into solution. Notably, with higher concentrations of AIBN, small amounts of unidentified platinum products are also formed. When 91 mM AIBN was used, the combined yield of **2a** and **3a** was 95% at the end of the reaction. With 175 mM AIBN, only 83% of the material could be identified as **2a** or **3a** after all of **1a** was consumed. A variety of new signals were observed in the ^{1}H NMR spectra during the reactions conducted with high AIBN concentrations. In an independent experiment, **2a** was found to react with AIBN to form a mixture of unidentified platinum species. Perhaps related to the formation of additional products in the presence of high concentrations of AIBN, Wenzel has reported that the autoxidation of a platinum(II) hydride complex in the presence of excess AIBN formed a mixture of products, including proposed platinum complexes wherein fragments of AIBN act as ligands.[17e]

Despite the addition of even greater amounts of AIBN (up to 175 mM) to the autoxidation of **1a**, the reaction is consistently slower at the beginning compared to later reaction times. The persistence of the slower initial rate for the autoxidation of **1a**, together with the reproducible sigmoidal reaction profile, indicates that the slower initial period is not attributable to a radical chain induction period. Rather, this behavior is consistent with autoacceleration of the reaction.

With moderate AIBN concentrations (5−10 mM), doubling the amount of initiator doubles the instantaneous rates for the autoxidation of **1a** throughout the course of the reaction.[29] Two data sets from experiments which differ only in the initial AIBN concentration are shown in Figure 4a. The direct dependence of the rate on the AIBN concentration is best demonstrated by plotting the concentration versus the product of time × [AIBN] (eq 1). The resulting curves are identical (Figure 4b). Thus, the rate law for the autoxidation contains a first-order dependence on AIBN.

$$\begin{gathered}\frac{\Delta\,\text{concentration}}{\Delta\,\text{time}} = \text{rate} \propto [\text{AIBN}] \\ \underbrace{\text{concentration}}_{y} \propto \underbrace{\text{time}\times[\text{AIBN}]}_{x}\end{gathered} \tag{1}$$

For the autoxidation of **1b**, increasing the concentration of AIBN also increased the rate of autoxidation. However, increasing the concentration of AIBN by a factor of 6 caused the instantaneous rates to increase by a factor of 2.4 ($=6^{1/2}$), rather than a factor of 6. In analogy with Figure 4, plotting the concentration of platinum versus time × $[\text{AIBN}]^{1/2}$ gives almost identical curves (Figure 5, eq 2).

$$\begin{gathered}\frac{\Delta\,\text{concentration}}{\Delta\,\text{time}} = \text{rate} \propto [\text{AIBN}]^{1/2} \\ \underbrace{\text{concentration}}_{y} = \propto \underbrace{\text{time}\times[\text{AIBN}]^{1/2}}_{x}\end{gathered} \tag{2}$$

Dependence on the Added Inhibitor. In the presence of 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT), the rate of autoxidation of **1a** was significantly inhibited. Shown in Figure 6 are data from similar experiments with BHT (1.4 mM) and without BHT. In the presence

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[29] Reactions with low AIBN concentrations (0.03−0.1 mM) were more rapid than expected. See the Supporting Informationfor more details.

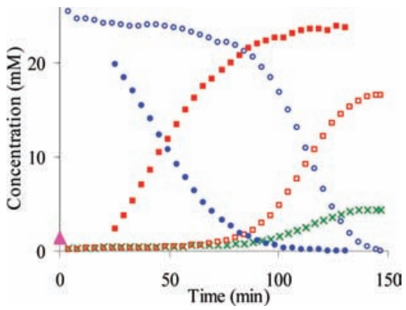

Figure 6. Reaction profile of autoxidation of **1a** with BHT (pink filled triangle, 1.4 mM) (**1a**, blue open circles; **2a**, red open squares; **3a**, green times signs) and without BHT (**1a**, blue filled circles; **2a**, red filled squares). Reaction conditions: 3 mM AIBN, 11 atm of O_2, 323 K, in C_6D_6.

of BHT, very little reaction occurred in the first 70 min. After the inhibitor was consumed, the rate of the reaction abruptly increased and the familiar sigmoidal profile was observed. Significant amounts of the hydroxide product **3a** formed as the reaction accelerated, and the rate ($-$d[**1a**]/d*t*) after inhibition is not the same as the rate of the reaction when no inhibitor was added. Thus, it appears that the product(s) of the inhibited reaction influence the autoxidation. This effect has been observed for some organic substrates and other inhibitors.[30]

It should be noted that, for a stoichiometric radical pathway, the disappearance of reactant would not be inhibited by BHT. The observed inhibition of the autoxidation is characteristic of radical chain mechanisms. However, since the autoxidation of **1a** autoaccelerates, the rate of initiation cannot be measured by conventional methods using inhibitors.[31] Without knowledge of the rate of initiation, standard parameters of autoxidation such as the chain length and oxidizability cannot be determined.[32]

Dependence on the Platinum(IV) Hydride Reactant. The instantaneous rates of reaction are directly proportional to the concentration of **1a** present (Figure 7a). Normalized concentration plots (plots of the extent of reaction versus time) exactly overlap for runs with 8, 16, and 32 mM $[\mathbf{1a}]_o$ (Figure 7b). The time to 50% completion (first half-life) is thus independent of the initial concentration. These are hallmarks for a reaction that is first-order in substrate, although autocatalytic systems are not typically first-order (see the Discussion).

The autoxidation of **1b** also generates sigmoidal reaction profiles, indicating autoacceleration. In this case, an apparent first-order dependence on the initial reactant concentration is not observed. Doubling the initial concentration of **1b** more than doubles the rate. Normalized plots (showing the extent of reaction versus time) do not overlap (Figure 8). This behavior is more typical of autoaccelerating systems.

Dependence on the Products. The sigmoidal shapes of the reaction profiles for the autoxidations of both **1a** and **1b** are characteristic of autoaccelerated reactions in which an intermediate, product, or side product acts to catalyze the reaction.[33] Thus, it is important to determine the effect of added products on the rates of these oxidation reactions. When isolated samples of the major product **2a** were added to the oxidation reaction of **1a**, the reaction (blue open circles) proceeded significantly faster than with no product added (blue filled circles) (Figure 9). In contrast, when the minor product **3a** (turquoise filled circles) was added to the autoxidation, the rate was only slightly different (a bit slower) from that with no product added. The initial concentration of **3a** (5 mM) in the reaction for which the data are shown in Figure 9 is significantly greater than the amount that forms during the autoxidation reaction (<1 mM).

Hydroperoxides are often effective radical initiators in their own right.[34] Indeed we found that experiments with added **2a** in the absence of AIBN yielded reproducible results. The reaction profiles for **2a**-initiated autoxidations retain the characteristic sigmoidal shape. Similar apparent first-order dependence on **1a** is observed for the product-initiated reactions; doubling the concentration of reactant doubles the rate of reaction, and normalized curves are identical (as in Figure 7). Increasing the amount of **2a** initially present increased the rate (Figure 10).

In contrast to the behavior observed when **2a** is added to solutions of **1a**, addition of **2b** to **1b** does *not* affect the rate of autoxidation. As shown in Figure 11, almost identical data are obtained for runs without and with added **1b** (0 and 14 mM). Note, however, that the sigmoidal shape of the reaction profile still indicates that the autoxidation of **1b** is autoaccelerated. Apparently an intermediate species or side product, rather than the major product, is accelerating the reaction.

Effect of Other Hydroperoxides. Because such different effects were observed with added **2a** and **2b,** experiments with crossed hydroperoxides were conducted. Addition of **2a** to the oxidation of **1b** accelerates the reaction (Figure 12a). However, addition of **2b** to the oxidation of **1a** does not affect the rate (Figure 12b). Thus, the addition of **2a** accelerates the autoxidation of both **1a** and **1b**, while addition of **2b** does not affect the oxidation of either **1a** or **1b**. Both the **1a** and **1b** autoxidations could involve the same type of intermediate if such a species is reversibly formed from isolated **2a**, while isolated **2b** cannot regenerate accelerating intermediates.

This behavior is consistent with the observed stability of the two hydroperoxide complexes under the reaction conditions employed. Small amounts of **3a** are always generated when the autoxidation of **1a** is carried out at 323 K. However, no **3b** is detected when the autoxidation of **1b** is carried out at the same temperature.

When isolated **2a** was heated in the presence of AIBN, a complicated mixture of unidentified products was obtained. Such reactivity does not occur to a significant extent during the autoxidation of **1a,** since the mass balance of identified platinum species is 100%. However, when the autoxidation of **1a** was heated at 323 K for 76 min beyond the end of the

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(30) (a) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1964**, *42*, 1044–1056. (b) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1964**, *42*, 1250–1253.

(31) Boozer, C. E.; Hammond, G. S.; Hamilton, C. E.; Sen, J. N. *J. Am. Chem. Soc.* **1955**, *77*, 3233–3237.

(32) Reference 14, pp 49−52.

(33) Perez-Benito, J. F.; Arias, C.; Brillas, E. *An. Quim.* **1991**, *87*, 849–862.

(34) *Organic Peroxides*; Ando, W., Ed.; Wiley: Chichester, U.K., 1992; pp 559−598.

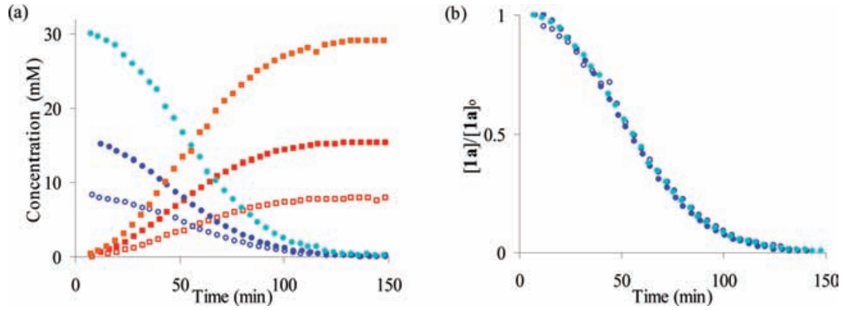

Figure 7. (a) Reaction profiles show that the rate doubles as [**1a**]$_o$ increases from 8 mM (**1a**, blue open circles; **2a**, red open squares) to 16 mM (**1a**, blue filled circles; **2a**, red filled squares) to 32 mM (**1a**, turquoise filled circles; **2a**, orange filled squares). (b) Normalized plots of conversion ([**1a**]/[**1a**]$_0$) vs time overlap. Reaction conditions: 11 atm of O_2, 3 mM AIBN, 323 K, in C_6D_6.

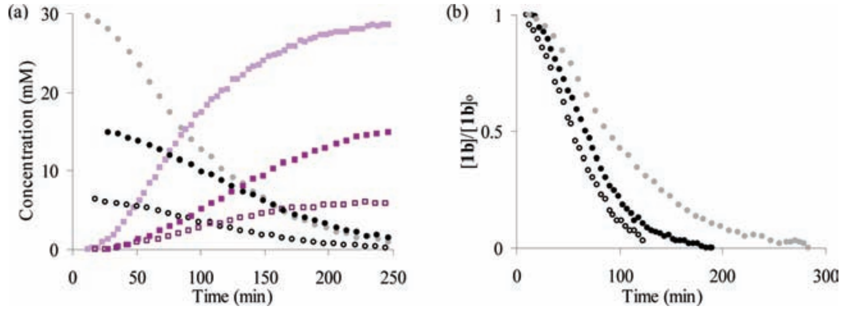

Figure 8. (a) Reaction profiles showing that the rate increases (but does not double) as [**1b**]$_o$ increases from 7 mM (**1b**, black open circles; **2b**, purple open squares), to 15 mM (**1b**, black filled circles; **2b**, purple filled squares) to 30 mM (**1b**, gray filled circles; **2b**, light purple filled squares). (b) Normalized plots of conversion ([**1b**]/[**1b**]$_o$) vs time do not overlap. Reaction conditions: 11 atm of O_2, 3 mM AIBN, 323 K, in C_6D_6.

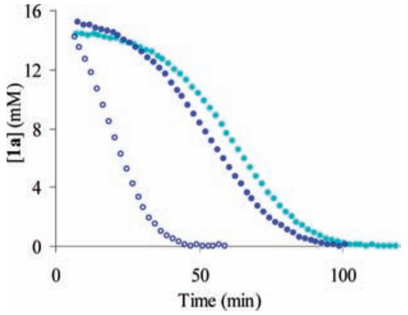

Figure 9. Reaction profiles show that the autoxidation of **1a** with no added product (blue filled circles) is slower than with 4 mM added **2a** (blue open circles), while 5 mM added **3a** (turquoise filled circles) has little effect. Reaction conditions: 11 atm of O_2 and 0.10 mM AIBN in C_6D_6 at 323 K.

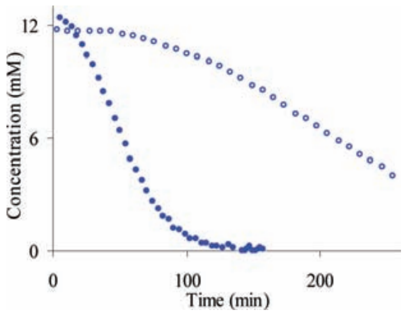

Figure 10. Reaction profiles show that the rate of autoxidation of **1a** increases as [**2a**]$_o$ increases from 0.8 mM (open circles) to 4.6 mM (filled circles). Reaction conditions: 11 atm of O_2, C_6D_6, 323 K.

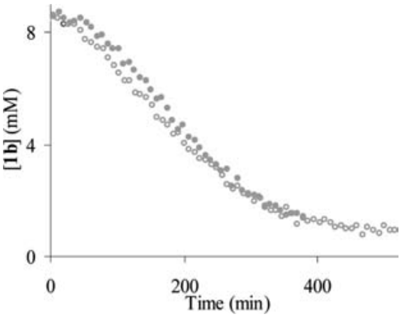

Figure 11. Reaction profiles for the autoxidation of **1b** are identical without added **2b** (filled circles) and with 14 mM added **2b** (open circles). Reaction conditions: 4 mM AIBN, 11 atm of O_2, C_6D_6, 323 K.

kinetics run (which required 53 min), decomposition of **2a** was observed. Disappearance of 6% of **2a** was accompanied by formation of an equivalent amount of **3a**. In contrast, when **2b** and AIBN were heated for 16 h past the time required for all the **1b** to be consumed, neither disappearance of **2b** nor appearance of **3b** was noted. After 4 days of heating, over 50% decomposition of **2b** to a variety of products was observed.

The effect of *tert*-butyl hydroperoxide (TBHP, added as a 5.5 M anhydrous solution in decane) on the autoxidation of **1a** was also examined. TBHP has been used to determine relative rates of propagation (k_p^r) for a variety of organic substrates.[35] It was found that the formation of **2a** was accelerated in the presence of TBHP (added as a 5.5 M anhydrous solution in decane) (Figure 13). However, unlike the previous autoxidation studies, no **3a** was detected. In addition, no ^{1}H NMR peak was observed for the Pt−OOH proton (δ 6.01), presumably due to exchange between **2a** and TBHP. The increase in rate can be attributed to chain transfer from a platinum peroxyl radical to TBHP. However, for the autoxidation of **1a** with excess TBHP, the shape of the reaction profile indicates that the reaction is still

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(35) Howard, J. A.; Ingold, K. U.; Symonds, M. *Can. J. Chem.* **1968**, *46*, 1017–1022.

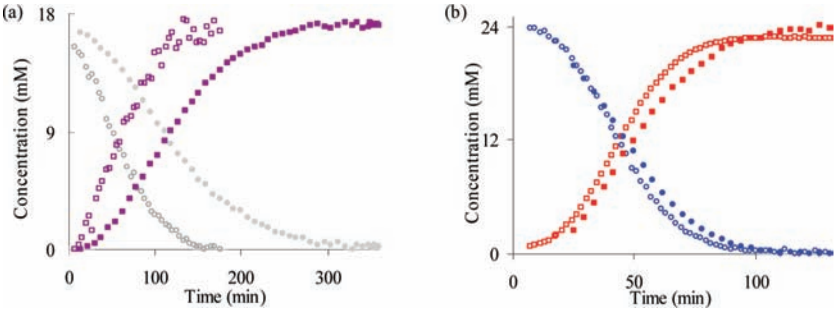


Figure 12. Reaction profiles show that (a) **2a** accelerates the autoxidation of **1b** (no **2a**: **1b**, gray filled circles; **2b**, purple filled squares; 5 mM **2a**: **1b**, gray open circles; **2b**, purple open squares) and (b) **2b** does not accelerate the autoxidation of **1a** (no **2b**: **1a**, blue filled circles; **2a**, red filled squares; 14 mM **2b**: **1a**, blue open circles; **2a**, red open squares). Reaction conditions: 3 mM AIBN, 11 atm of O_2, 323 K, in C_6D_6.

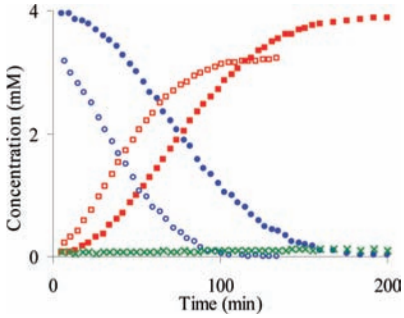
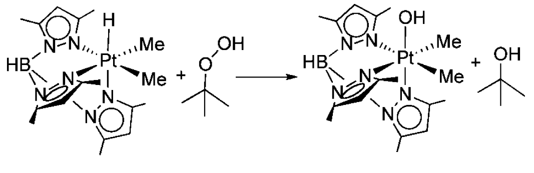


Figure 13. Reaction profiles show the autoxidation of **1a** with no added hydroperoxide (**1a**, blue filled circles; **2a**, red filled squares; **3a**, green times signs) is slower than the autoxidation with added TBHP (160 mM, 40 equiv) (**1a**, blue open circles; **2a**, red open squares). **3a** did not form in the presence of TBHP in the presence of O_2. Reaction conditions: 6 mM AIBN, 11 atm of O_2, 323 K, in C_6D_6.

Scheme 2



1a **3a**

autoaccelerating. There is also a slight inverse dependence on the AIBN concentration in the presence of TBHP: increasing the AIBN concentration from 3.5 to 7 mM causes the rate to decrease by 25%. The reaction is thus more complicated than the simple chain transfer case, and k_p^r values cannot be determined. In the absence of O_2, **1a** reacts with 1 equiv of TBHP to form **3a** and *t*-BuOH quantitatively (Scheme 2).

Alkyl hydroperoxides, such as TBHP, are well-known as initiators,[36] and the possibility that methyl hydroperoxide is produced in the reaction and acts as an accelerant should be considered. Notably, however, no evidence for reductive elimination of methyl hydroperoxide was noted during the formation or decomposition of **2a**. Furthermore, alkyl C−O reductive elimination is a relatively uncommon reaction,[37] and the analogous alkyl C−O reductive elimination to form methanol was not observed upon thermolysis of **3a**. Nevertheless, if MeOOH was formed even at trace levels, it could act as an initiator analogous to TBHP.

Oxidation of $TpPtMe_2H$. Autoxidation of the Tp complex (Tp = hydridotris(pyrazolyl)borate, with no substituents on the pyrazolyl) was also investigated. $TpPtMe_2H$ (**1c**) reacted with 1−11 atm of O_2 in C_6D_6 over several hours to cleanly generate a platinum product with C_s symmetry. A ^1H NMR signal that integrated to a single proton was observed at δ 6.61, consistent with a hydroperoxide product. Infrared absorption bands for the Tp ligand obscure that expected for ν_{O-O} (800−900 cm^{-1}).[38]

Chemical support for the characterization of this complex as a hydroperoxide was obtained by testing the reactivity with PMe_3. Platinum hydroperoxide compounds are known to oxidize phosphine compounds, while platinum hydroxide compounds do not.[8c,11] The proposed product $TpPtMe_2OOH$ (**2c**) was dissolved in C_6D_6 and allowed to react with excess PMe_3 (^{31}P, δ −62.0) in the absence of O_2 to form $OPMe_3$ (^{31}P, δ 36.2). The ^1H NMR signal corresponding to the hydroperoxide ligand (δ 6.61) was replaced by a signal corresponding to a metal hydroxide (δ −1.03). Other signals also shifted to values corresponding to the known platinum hydroxide product $TpPtMe_2OH$ (**3c**).[39]

The autoxidation of **1c** paralleled the autoxidation of **1a**. With added radical initiator AIBN, the reaction was reproducible. With 5.5 and 11 atm of O_2 (3 and 6 equiv dissolved in solution), identical reaction profiles were obtained. Similar to the autoxidation of **1a**, the reaction profiles for the autoxidation of **1c** show the symmetric sigmoidal shape characteristic of an autocatalytic reaction. Oxidation of **1c** was more rapid than that of **1a.** Under similar reaction conditions (323 K, 4 mM AIBN, 18 mM platinum hydride complex, 11 atm of O_2) the oxidation of **1c** was complete in 30 min, while the oxidation of **1a** required 153 min. The reaction was strongly inhibited by a radical trap: when the reaction was carried out in the presence of the radical inhibitor BHT (0.1 equiv), only 14% conversion of **1c** occurred after 4 h.

Halogenated Radical Traps. When **1a** was dissolved in CCl_4 and exposed to ambient light, very little reaction was

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(36) Reference 16 p 21.

(37) (a) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576–2587. (b) Khusnutdinova, J. R.; Newman, L. L.; Zavalij, P. Y.; Lam, Y.-F.; Vedernikov, A. N. *J. Am. Chem. Soc.* **2008**, *130*, 2174–2175.

(38) Guzhei, I. A.; Bakac, A. *Inorg. Chem.* **2001**, *40*, 2390–2393, and references therein.

(39) (a) Canty, A. J.; Fritsche, S. D.; Jin, H.; Patel, J.; Skelton, B. W.; White, A. H. *Organometallics* **1997**, *16*, 2175–2182. (b) Canty, A. J.; Fritsche, S. D.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *490*, C18–C19.

observed. Over the course of several weeks, low conversion (10%) to the products $CHCl_3$ and $Tp^{Me_2}PtMe_2Cl$ (**4**) occurred. In contrast, when a sample of **1a** in CCl_4 was irradiated with a Hg/Xe lamp, the reaction to form **4** and $CHCl_3$ was complete in 1 h. **4** was characterized by ^1H and ^{13}C NMR spectroscopy. A vibrational stretch was observed at 330 cm^{-1}, consistent with a Pt−Cl bond.[40]

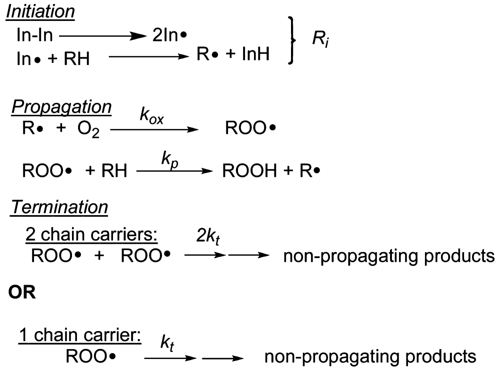
Metal hydride/chloride substitution reactions using CCl_4 are well-known[41] and often involve radical pathways,[42] although such reactions for platinum(IV) hydride complexes are rare.[43] The photochemical acceleration of the reaction of **1a** supports that it proceeds via a radical process. The quantitative formation of **4** is consistent with a platinum(III) intermediate having a singly occupied molecular orbital residing primarily on the metal center.

Discussion

The clean conversion of a metal hydride to a metal hydroperoxide via direct reaction with molecular oxygen provides a model for an oxygen activation pathway that may be of significant use in selective homogeneous oxidations. Understanding the mechanisms by which such activations occur can allow for the rational development of catalysts capable of activating and incorporating molecular oxygen as an oxidant. To date, there have been very few such studies due primarily to lack of systems wherein the reaction proceeds cleanly with both an isolable starting metal hydride and a stable metal hydroperoxide product. In this paper, we report several platinum(IV) hydrides that react cleanly with molecular oxygen to form platinum(IV) hydroperoxides and include detailed studies of these reactions.

The mechanistic evidence collected for these platinum(IV) hydride + O_2 reactions are most consistent with radical chain type mechanisms. In general, the reactions share many features of the well-established radical chain pathways found for the autoxidations of many organic substrates. However, despite the basic similarities between the radical chain reactions of **1a**−**c** and various organic substrates with molecular oxygen, the reactions of **1a**, **1b**, and the organics follow different rate laws. Remarkably, only slight differences in the basic radical chain mechanism proposed decades ago for organic substrates can readily account for these differences.

Scheme 3



The radical chain mechanism well accepted for organic autoxidations (Scheme 3) consists of initiation, propagation, and termination steps.[13] In the initiation steps, alkyl radicals ($R^\bullet$) are generated at a rate R_i. With sufficient O_2 present, the conversion of alkyl radicals into peroxyl radicals (k_{ox}) is rapid. The peroxyl radicals ($ROO^\bullet$) then abstract hydrogen atoms from the substrate (k_p), generating the product and re-forming alkyl radicals, which propagate the chain. Under these conditions, a first-order dependence on the substrate is observed with the rate determined by the propagation step such that $-d[O_2]/dt = k_p[RH][ROO^\bullet]$. The concentration of the peroxyl radicals, $[ROO^\bullet]$, and hence the rate of autoxidation (as this value appears in the rate expression), depends inextricably on both the rate of initiation and the rate of termination. With adequate O_2 present, chain termination for most substrates begins with the bimolecular reaction of two peroxyl radicals ($2k_t$ pathway). Termination pathways involving one peroxyl radical (k_t) have also been reported for some organic autoxidation reactions and include reaction at vessel walls, rearrangement of the chain carrier, and reaction with solvent or other species in solution.[44] When termination involves the bimolecular reaction of two radical chain carriers, the observed rate of autoxidation displays a half-order dependence on R_i (eq 3). If termination involves only one radical chain carrier, a first-order dependence of the rate of autoxidation on R_i is observed (eq 4).

$$-\frac{d[O_2]}{dt} = k_p[RH]\left(\frac{R_i}{2k_t}\right)^{1/2}$$

for termination involving two chain carriers ($2ROO^\bullet \xrightarrow{2k_t}$) (3)

$$-\frac{d[O_2]}{dt} = k_p[RH]\left(\frac{R_i}{k_t}\right)$$

for termination involving one chain carrier ($ROO^\bullet \xrightarrow{k_t}$) (4)

Empirical Rate Laws. The investigations described in the Results allow for the determination of empirical rate laws for the autoxidation of **1a** and **1b**. The rate laws are clearly different from those reported for typical organic autoxidations as the rate laws for the autoxidation of **1a** and **1b** must account for the observed autoacceleration. In addition, for all autoaccelerating processes, a separate, nonautoaccelerating path (k_1) must be present to allow initial formation of the accelerant.[33] Once some of the accelerant has been generated, the autoaccelerated pathway dominates, leading to the characteristic sigmoidal reaction profiles.

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(40) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley: New York, 1997; Part B, p 183.

(41) Schunn, R. A. Systematics of Transition Metal Hydride Chemistry. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; The Hydrogen Series, Vol. *1*; Marcel Dekker: New York, 1971; pp 203−270.

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(43) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219*, 157–185.

(44) (a) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1965**, *43*, 2729–2736. (b) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1965**, *43*, 2737–2743.

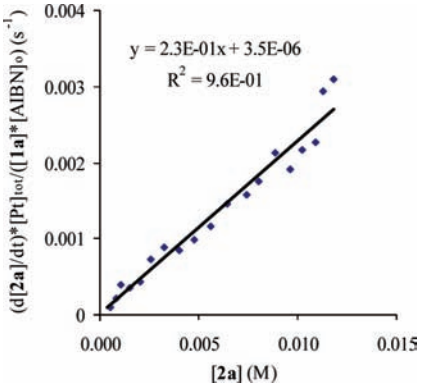

Figure 14. Linear fit of kinetic data to the rate expression given in eq 6. Reaction conditions: 11 atm of O_2, 14 mM $[\mathbf{1a}]_o$ and 10 mM AIBN in C_6D_6 at 323 K.

Under the conditions employed in the kinetics studies, the autoxidation of **1a** was found to be (a) independent of the O_2 concentration, (b) first-order in AIBN, and (c) apparently first-order in substrate and (d) accelerated by product **2a**. The symmetric sigmoidal reaction profiles for the autoxidation of **1a** and the effect of added **2a** are characteristic of an autocatalytic reaction in which the reaction rate is dependent on the concentration of the product **2a** as well as the substrate **1a**. The proportionality between the rate and concentration of substrate and the concentration-independent half-life seem to indicate a first-order dependence on **1a**. However, the reaction profiles do not show the exponential decay expected for a first-order process. The reaction appears to be both autocatalytic and first-order in **1a**, but these conditions are mutually exclusive; it cannot be both (eq 5). The amount of **2a** formed is approximately the amount of **1a** that has reacted, so increasing the concentration of the reactant also increases the concentration of the catalyst. To visualize this, one can imagine the effect on the rate if [**1a**] were doubled. Halfway through the reaction, [**2a**] would also be doubled so that, at 50% completion, the rate would quadruple, not double as expected for a first-order dependence. This is a general observation; for a typical autocatalytic rate law, a first-order dependence on the concentration of the starting material is not observed (eq 5).

$$\text{rate} \propto k[\mathbf{1a}][\mathbf{2a}] = k[\mathbf{1a}]([\mathbf{1a}]_o - [\mathbf{1a}]) \neq k'[\mathbf{1a}] \qquad (5)$$

However, an inverse dependence of the rate on the total platinum concentration ($[\text{Pt}]_{\text{tot}} = [\mathbf{1a}] + [\mathbf{2a}] + [\mathbf{3a}]$) could account for the observed behavior.[45] In fact, good agreement (Figure 14) is obtained between the data and just such an empirically derived rate law (eq 6).[46] Consistent values of k_2 are found throughout all experiments ($k_2 = (2.3 \pm 0.1) \times 10^{-1}\ \text{M}^{-1}\ \text{s}^{-1}$). The k_1 term in eq 6 is the nonautoaccelerating path that initially forms the accelerant **2a**.[47]

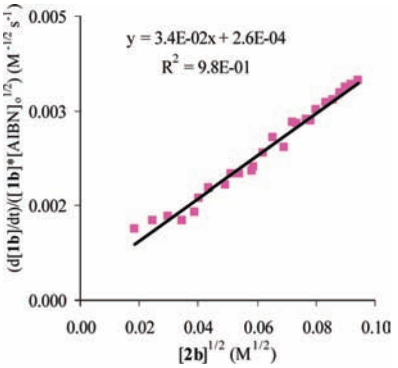

Figure 15. Linear fit of the kinetic data to the rate expression given in eq 7. Reaction conditions: 11 atm of O_2, 15 mM $[\mathbf{1b}]_o$ and 10 mM AIBN in C_6D_6 at 323 K.

$$\text{rate} = k_1[\mathbf{1a}][\text{AIBN}] + k_2\frac{[\mathbf{1a}][\mathbf{2a}][\text{AIBN}]}{[\mathbf{1a}] + [\mathbf{2a}] + [\mathbf{3a}]} \qquad (6)$$

For the autoxidation of **1b**, the reaction rate was also found to be independent of the O_2 concentration but only half-order in AIBN. The sigmoidal reaction profile for **1b** is also consistent with autoacceleration; however, the asymmetric shape of the profile with respect to time is indicative of a higher order dependence on the substrate than on the autoaccelerating species. As the addition of the product **2b** did not affect the rate of reaction, the acceleration in this case is attributed to an intermediate or side product that is present in concentrations proportional to the amount of product formed (or reactant consumed), rather than to the product itself. Since the concentration of **2b** formed (or **1b** consumed) is proportional to that of the accelerant **X**, [**2b**] can be substituted for [**X**] to plot eq 7. Reasonable linear fits are obtained between the data and a linear form of the empirically derived rate law shown as eq 7 (Figure 15).[48] Consistent values of k_2 are found throughout all experiments ($k_2 = (5 \pm 3) \times 10^{-2}\ \text{M}^{-1}\ \text{s}^{-1}$; this is a lower limit since the actual concentration of **X** is lower than [**2b**]).[47]

$$\text{rate} = k_1[\mathbf{1b}][\text{AIBN}] + k_2[\mathbf{1b}][\mathbf{X}]^{1/2}[\text{AIBN}]^{1/2} \qquad (7)$$

Explanation of Empirically Derived Rate Laws. Information about the radical chain mechanisms of these autoxidations can be deduced from a comparison of the empirical rate laws to rate expressions derived from radical chain mechanisms involving initiation, propagation, and termination steps. In such complicated reaction systems where all the elementary steps cannot be individually defined, pseudo-

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(45) Since only a small amount of **3a** is generated during the reaction, it is not clear whether there is an inverse dependence on this compound. However, experiments in which **3a** was added to the solution proceeded at a slightly slower rate (Figure 9), indicating that the inverse dependence is likely relative to the total platinum concentration, **1a** + **2a** + **3a**, rather than just **1a** + **2a**.

(46) At long reaction times, the data deviate from linearity because, as the concentration of **1a** approaches 0, the baseline noise in the NMR spectra becomes significant relative to the signal intensity. Only the linear portion (through 94−98% conversion) of the data was used for the regression analysis and figures.

(47) The initial process k_1 likely depends upon the initiator concentration, but the nature of the dependence could not be determined. The autocatalytic process dominates the reaction, and large uncertainties hampered interpretation of the k_1 calculated values. See the Supporting Information.

(48) Similar to the autoxidation of **1a** (see ref 46), the data deviate from linearity as the concentration of **1b** approaches 0. The problem is more pronounced for **1b** than **1a** since the baseline-resolved NMR signals which could be integrated corresponded to fewer protons. Only the linear portions of the data (through 50−75% conversion) were used for the regression analysis and figures.

elementary-step kinetic analysis has proven useful.[49] The overall rate of the reaction is determined by the rate of the propagation step in which the radical chain carrier (RCC) reacts with the substrate (see k_p step in Scheme 3). This expression is shown as eq 8 for the autoxidation of **1**.

$$\text{rate} = k_p[\mathbf{1}][\text{RCC}] \tag{8}$$

Under steady-state conditions, there is a small steady-state concentration of RCC such that the rate of initiation equals the rate of termination. The concentration of the RCC can then be expressed in terms of R_i and the termination rate constant, with the result that all three steps—initiation, propagation, and termination—contribute to the rate expression.[50] As observed for autoxidations of organic substrates, (Scheme 3), differences in termination steps lead to differing rate laws (eqs 3 and 4). Thus, if the termination process for **1a** involves one radical chain carrier and one platinum-containing molecule (**1a**, **2a**, or **3a**), then $R_i = R_t = k_t[\text{RCC}][\text{Pt}]_{\text{tot}}$ or $[\text{RCC}] = R_i/(k_t[\text{Pt}]_{\text{tot}})$ and the rate will have a first-order dependence on R_i and an inverse dependence on the total platinum concentration (eq 9). In this scenario, the rate of the termination step must be approximately the same for the reaction between the radical chain carrier and any of the platinum species **1a**, **2a**, and **3a**.[45] Alternatively, if termination involves two radical chain carriers for **1b**, then $R_i = R_t = k_t[\text{RCC}]^2$ or $[\text{RCC}] = (R_i/2k_t)^{1/2}$ and the predicted rate expression will have a half-order dependence on R_i (eq 10).

$$\text{rate} = k_p[\mathbf{1a}]\left(\frac{R_i}{k_t[\text{Pt}]_{\text{tot}}}\right) \tag{9}$$

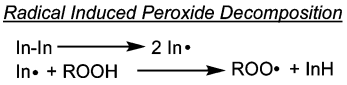
$$\text{rate} = k_p[\mathbf{1b}]\left(\frac{R_i}{2k_t}\right)^{1/2} \tag{10}$$

In comparing eqs 9 and 10 with the empirically derived rate laws shown in eqs 6 and 7, it can be seen that the equations are self-consistent for both reactions if R_i is proportional to the product of [AIBN] and [**2a**] or [**X**] (eq 11).

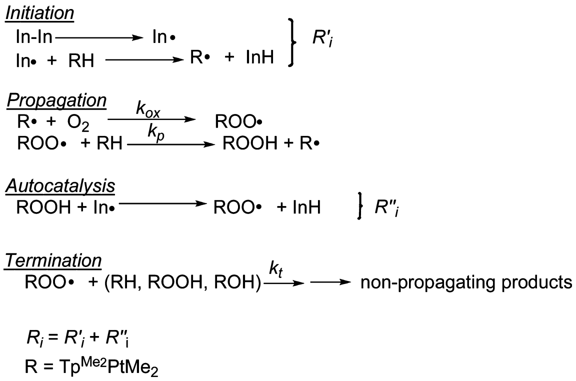
$$R_i = k[\text{AIBN}][\mathbf{2a} \text{ or } \mathbf{X}] \tag{11}$$

In our studies of the autoxidation of **1a**, it was observed that the rate of reaction was directly proportional to [AIBN] and [**2a**]. This is consistent with a first-order dependence on R_i as shown in eq 9. In contrast, the autoxidation of **1b** showed a half-order dependence on [AIBN] and [**X**]. This dependence of the rate on $[\text{AIBN}]^{1/2}$ and $[\mathbf{X}]^{1/2}$ is consistent with a half-order dependence on R_i, as shown in eq 10. The implication of this analysis of the initiation rate is that a similar process for the generation of the radical chain carriers may be operative in both systems, despite the difference in order of reaction with respect to the initiator.

Scheme 4



Scheme 5. Autoxidation Mechanism for **1a**



Since both AIBN and hydroperoxide compounds are known to act as initiators of radical reactions, a dependence of the rate on the sum of the [AIBN] and [**2a** or **X**] might be expected. However, the rate of initiation appears to instead be dependent on the product of the concentrations of these species. One explanation for this behavior may be that radical-induced decomposition of hydroperoxides, as shown in Scheme 4, generates the $\text{ROO}^\bullet$ radical chain carrier.[51]

Such an induced decomposition of **2a** by AIBN-derived radicals would be consistent with the observed rate law. The reaction of AIBN with the peroxide product **2a** would result in formation of the radical chain carrier. The RCC seems likely to be $\text{Tp}^{\text{Me}_2}(\text{Me})_2\text{PtOO}^\bullet$, which could be called, as a first approximation, a platinum(IV) superoxide complex. Bakac and co-workers have demonstrated that rhodium superoxide species catalyze the formation of hydroperoxides from the rhodium hydride $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{H}]^{2+}$ and related complexes.[17c] The autoaccelerative effect this would have on the reaction can be visualized as depicted in Scheme 5. The AIBN-initiated pathway (k_1) serves to generate a small amount of the platinum hydroperoxide species, similar to the initiating step in the traditional nonautoaccelerated radical chain mechanism. Once sufficient hydroperoxide is present, the second initiation step becomes important, listed as the autocatalytic initiation step in Scheme 5. Radical chain carriers are formed much more rapidly from the autoaccelerating species (presumed to be a hydroperoxide) than from the starting platinum hydride. This behavior can be explained if not all AIBN-derived radicals generate radical chain carriers. Rearrangement, coupling, and reaction with oxygen of AIBN-derived radicals have been noted.[52] These processes may compete with the generation of radical chain carriers at early reaction times. Once sufficient concentrations of the autoaccelerating species have formed, the autocatalytic process dominates these side reactions. To the best of our knowledge, autoaccelerating reactions of this type have not

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(49) (a) See, for example: Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382. (b) Noyes, R. M.; Field, R. J. *Nature* **1972**, 390–392.

(50) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 134−143.

(51) Koening, T. The Decomposition of Peroxides and Azoalkanes. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. *1*, pp 113−156.

(52) Hammond, G. S.; Trapp, O. D.; Keys, R. T.; Neff, D. L. *J. Am. Chem. Soc.* **1959**, *81*, 4878–4882.

been studied experimentally because of their complexity, although such steps have been included in computational models.[53]

The explanation of why the autoxidations of **1a** and **1b** follow somewhat different rate laws appears to lie within the termination step, although the details are not yet clear. The rate law for the autoxidation of **1a** can be rationalized on the basis of a termination sequence involving the reaction of platinum(IV) peroxyl radical with another Pt(IV) species (Scheme 5, termination for **1a**). Since **1a**, **2a**, and **3a** all share in common the $\mathrm{Tp^{Me_2}PtMe_2}$ fragment, it seems likely that the bimolecular reaction involves the $\mathrm{Tp^{Me_2}}$ ligand or Me groups.

The rate law for the autoxidation of **1b** can accommodate a radical chain mechanism very similar to that of **1a** except with a different termination step. The radical chain carrier from **1b** does not terminate by reaction with **1b** or **2b**. This could indicate that termination in the "**a**" series occurs by reaction at the platinum methyl groups, which are not present in the "**b**" complexes. The empirical rate law for the autoxidation of **2b** is consistent with a bimolecular radical termination process (Scheme 3). Such termination steps are common in organic autoxidations, for example, when two nontertiary peroxyl radicals react to form O_2 and nonradical ketone and alcohol products. A common difficulty in the study of radical chain mechanisms is that highly efficient chain processes involve few termination events, which results in termination product concentrations that are typically too low to detect. It is possible that **3a** is a termination product in the autoxidation of **1a**. In the autoxidation of **1b**, however, no other products were detected beyond **2b**, so further insight into possible termination product(s) in this system is unavailable. It is not yet clear why **2a** accelerates the autoxidation but an intermediate or side product rather than **2b** appears to be responsible for a similar autoacceleration in the case of **1b**. There are both steric and electronic differences between **1a** and **1b** (and **2a/2b**), and either of these factors may be important in determining the course of the radical chain.

Comparison with Hydrocarbon Autoxidation Reactions. Autoxidations of organic species have been studied for more than 175 years,[54] and through many elegant experiments, a great deal is known about these radical chain mechanisms. A comprehensive review of methane autoxidation, for instance, covered more than 75 individual reaction steps, and a similar analysis of isobutane autoxidation used these and hundreds more reactions.[55] This complexity results because all of the C−H bonds in the substrates are reactive when autoxidations proceed to completion. To simplify the analysis, solution mechanistic studies have examined organic autoxidations only to very low conversions, where the further oxidation of the products is not competitive. The platinum mechanistic studies reported here are, to our knowledge, unique in that the autoaccelerating autoxidations have been monitored to completion. This has been possible because the Pt−H bond is much more reactive in the radical chain than any of the other bonds in the reactant or products.

The mechanisms for the initial stages of hydrocarbon autoxidations are well established, as summarized in Scheme 3 above.[56] Under conditions of excess oxygen, termination occurs primarily via reversible combination of two peroxyl radicals to make a transient organic tetroxide, ROOOOR. When R is a primary or secondary alkyl group, this species predominantly decomposes to O_2, an alcohol, and a ketone or aldehyde. When R is a tertiary alkyl, the tetroxide decomposes to O_2 and two alkoxyl radicals $RO^\bullet$. Alkoxyl radicals are much more reactive than peroxyl radicals and can attack primary and secondary C−H bonds, again leading eventually to alcohol and carbonyl products. These secondary products are typically more reactive toward $ROO^\bullet$, necessitating studies at low conversion.

Other Platinum and Palladium Hydrides and Oxygen. Many features have been clarified about the radical chain mechanisms for autoxidation of these platinum hydrides. However, there also remain elements of the mechanisms that are not yet fully understood. The detailed nature of the termination steps, for example, are not well defined and are unlikely to be closely analogous to the organic analogues. Understanding these and other features of these complex processes will only be possible through the detailed study of the reaction of numerous metal hydrides and metal alkyls with oxygen. This detailed mechanistic understanding will be invaluable in the integration of autoxidations into new metal-mediated catalytic oxidation reactions.

For many years, organometallic chemists sought to protect their compounds from the air as rampant oxidation to decomposition products was often observed. The reactions reported here, along with other recent reports,[57] have clearly demonstrated that clean, selective aerobic oxidation reactions are possible with appropriate organometallic compounds. The $\mathrm{Tp^{Me_2}PtR_2H}$ autoxidation reactions occur by radical chain pathways. A radical chain has also been implicated in the reaction of the platinum(II) hydride complex $\mathrm{(dppen)Pt(CF_3)H}$ with oxygen to form the corresponding platinum(II) hydroperoxide (dppen = 1,2-bis(diphenylphospino)ethylene).[17e] However, radical chain autoxidation is but one pathway by which the activation of dioxygen can occur. Experimental and theoretical studies of palladium(II) hydrides and oxygen to form palladium hydroperoxide complexes have found evidence for two different non radical chain pathways.[9,10] The reactions of (tmeda)-$\mathrm{Pt^{II}Me_2}$ and $\mathrm{(Me_3tacn)Pt^{IV}Me_2H}$ with O_2 to form hydroperoxides also do not involve radical chains (tmeda = *N*,*N*,*N*′*N*′-tetramethylethylenediamine; $\mathrm{Me_3tacn}$ = 1,4,7-trimethyl-

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(53) Allara, D. L.; Edelson, D.; Irwin, K. C. *Int. J. Chem. Kinet.* **1972**, *4*, 345–362.

(54) Wöhler, F.; Liebig, J. *Liebigs Ann.* **1832**, *3*, 249–288.

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1,4,7-triazocyclononane).[8c,17a] Further work is clearly needed to develop a general understanding of reactions between metal hydrides and oxygen and the various mechanisms by which they can occur.

Conclusions

The work presented here, to our knowledge, provides the first detailed understanding of radical chain autoxidations of transition-metal hydride systems. In a number of key ways, the autoxidations of **1a** and **1b** are analogous to the well-studied autoxidations of organic substrates. First and foremost, a radical chain mechanism is operative. Initiation, propagation, and termination processes all contribute to the observed rate law. A mechanism involving hydrogen atom abstraction from substrate by a peroxyl chain carrier to propagate the reaction is consistent with the data. At sufficient pressures, the autoxidations were found to be independent of O_2, consistent with rapid reaction between the radicals and O_2.

However, there are important differences between the organic and organometallic substrates **1a** and **1b**. Although the autoxidation of organic substrates can be autocatalytic, such effects are typically minimized by monitoring only the initial portion of the reaction. Monitoring the entire course of the reaction revealed that the autoxidations of **1a** and **1b** both autoaccelerated. For **1a**, it was shown that the product **2a** catalyzed the reaction, while for **1b**, the data indicated autoacceleration by an intermediate or undetected side product. The rate laws determined for the autoxidation of **1a** and **1b** were different in terms of the dependence on the initiator, substrate, and product. However, these significant differences can be accommodated with very similar mechanisms by including different radical chain termination steps.

Although some questions remain concerning the intimate mechanisms of the radical chain pathways, significant progress has been made toward understanding the radical chain autoxidation of metal hydrocarbyl hydrides. The reactions between metal hydride complexes and O_2 constitute a rich and largely unexplored area of inorganic chemistry. Metal hydroperoxide complexes are key intermediates in many selective oxidation processes and may provide a route for utilizing O_2 that is far more selective than traditional organic radical chain processes. As the rules governing these reactions become better understood, the rational development of homogeneous catalysts that use O_2 as an oxidant should become a more realistic goal.

Experimental Section

General Considerations. Unless otherwise noted, all transformations were carried out under a N_2 atmosphere in a drybox, using standard Schlenk techniques, or under vacuum. Solvents were dried using standard techniques. AIBN (from Aldrich) was recrystallized from methanol and stored at −33 °C. PMe_3 (Strem) was dried over a sodium mirror. KH was purchased (Aldrich) as a suspension in mineral oil, isolated on a fritted glass funnel, washed repeatedly with hexanes, and dried under vacuum. Other reagents, unless specified, were used as received from commercial suppliers. $\mathrm{Tp^{Me_2}PtMe_2H}$,[58] $\mathrm{Tp^{Me_2}PtMe_2OOH}$,[11] $\mathrm{Tp^{Me_2}PtMe_2OH}$,[11] and $\mathrm{Tp^{Me_2}PtPh_2H}$[58] were prepared as previously reported.

NMR spectra were recorded on Bruker spectrometers. All coupling constants are reported in hertz. ^{1}H and ^{13}C spectra were referenced using residual solvent peaks and are reported in parts per million downfield of the tetramethylsilane signal. Photolysis experiments were carried out in NMR tubes or quartz reaction vessels placed 50 cm from the lamp. Light from an Oriel 200 W Hg/Xe arc lamp was passed through a 295 or 345 nm long-pass quartz filter.

General Treatment of Kinetic Samples. Appropriate amounts of the C_6D_6 solutions of platinum reagent, integration standard (THF), and AIBN were combined in Wilmad 504-PP medium walled Teflon-valve (J-Young) NMR tubes and subjected to three freeze−pump−thaw cycles. The NMR tubes were then connected to a custom-made high-pressure NMR tube manifold, charged with 80−160 psi of O_2, and quickly placed in the preheated NMR probe (time 0). A single scan (ns = 1, ds = 0) was acquired for each data point. Integrations were repeated in triplicate, and runs were checked for reproducibility. Concentrations were determined from NMR integrals.

Caution! *Radical chain reactions (particularly chain reactions in the presence of high pressures of oxygen and transition metals) have the potential to explode, so a number of safety precautions were employed. These included using blast shields, face shields, thick gloves, and steel jackets around tubes heated in an oil bath and testing the integrity of NMR tubes upon pressurization. Light bouncing of the tube in a polystyrene container tested for stress in the system. No explosions occurred in the course of these investigations.*

Synthesis of $\mathrm{Tp^{Me_2}PtPh_2OOH}$ (2b). This compound was prepared by a method analogous to that published for the preparation of $\mathrm{Tp^{Me_2}PtMe_2OOH}$ (**1b**).[11] A sample of $\mathrm{Tp^{Me_2}PtPh_2H}$ (20.5 mg, 0.032 mmol) was dissolved in 5 mL of benzene in a round-bottom flask. H_2O_2 (10.0 μL, 30% solution in H_2O) was added. The solution was stirred under air with exposure to ambient light for 10 days. Solvent was removed to give an off-white powder. Recrystallization from methylene chloride/pentane at −33 °C yielded small, well-formed crystals. Yield: 6.5 mg, 31%. Both this material and material that was prepared in the same manner as the kinetic runs (11 atm of O_2, no H_2O_2, in C_6D_6, at 323 K) was added to kinetic experiments to determine the effect of added **2b** on the rate of reaction. ^{1}H NMR (C_6D_6): δ 8.28 (d, 2H, *ortho*, $^3J_{PtH} = 30$, $^3J_{HH} = 8.4$), 7.29 (m, 2H, *meta*), 7.01 (dd, 2H, *para*, $^3J_{HH} = 6.9$), 6.70 (m, 2H, *meta′*), 6.60 (d, 2H, *ortho′*, $^3J_{PtH} = 39$, $^3J_{HH} = 7.6$), 6.27 (s, 1H, PtOOH), 5.53 (s, 2H, 4-pyrazolyls *trans* to PtPh), 5.48 (s, 1H, 4-pyrazolyl *trans* to PtOOH, $^4J_{PtH} = 13.0$), 1.18, 1.87, 2.10 (s, 3H, 6H, 9H, 3,5-CH_3 on pyrazolyls). ^{13}C{^{1}H} NMR (C_6D_6): δ 151.4, 143.2 (s, 2C, 2C, 3,5-CH_3 on pyrazolyl *trans* to PtPh), 150.6, 144.5 (s, 1C, 1C, 3,5-CH_3 on pyrazolyl *trans* to PtOOH), 136.0 (s, 2C, *ortho′*), 131.2 (s, 2C, *ortho*), 126.8 (s, 2C, *meta*), 126.7 (s, 2C, *meta′*), 126.4 (s, 2C, *ipso*), 125.1 (s, 2C, *para*), 108.8 (s, 1C, 4-pyrazolyl *trans* to PtOOH), 107.8 (s, 2C, 4-pyrazolyl *trans* to PtPh, $^3J_{PtC} = 11$), 13.1, 16.6 (s, 1C, 1C, 3,5-CH_3 on pyrazolyl *trans* to PtOOH) 12.5, 12.3 (s, 2C, 2C, 3,5-CH_3 on pyrazolyls *trans* to PtPh).

Synthesis of $\mathrm{Tp^{Me_2}PtPh_2OH}$ (3b). To a sample of $\mathrm{Tp^{Me_2}PtPh_2OOH}$ (3.1 mg, 4.6 μmol) dissolved in C_6D_6 was added 1.4 equiv of PMe_3 (6.93 Torr, 16.95 mL calibrated vessel, 6.3 μmol). The reaction vessel was then sealed and shaken vigorously. Conversion of **2b** to **3b** was complete as confirmed by ^{1}H NMR spectroscopy. ^{1}H

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(58) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684–5689.

NMR (C_6D_6): δ 8.51 (d, 2H, *ortho*, $^3J_{HH} = 7.1$), 7.30 (m, 2H), 7.02 (dd, 2H, *para*, $^3J_{HH} = 7.2$), 6.69 (m, 2H), 6.63 (br, 2H), 5.51 (s, 1H, 4-pyrazolyl *trans* to PtOH), 5.45 (s, 2H, 4-pyrazolyls *trans* to PtPh), 1.23, 1.78, 2.11, 2.13 (s, 3H, 6H, 6H, 3H, 3,5-CH_3 on pyrazolyls), 0.02 (s, 1H, PtOH, $^2J_{PtH} = 36$).

Synthesis of $Tp^{Me_2}PtMe_2Cl$. In a quartz reaction vessel, $Tp^{Me_2}PtMe_2H$ (51.5 mg, 98 μmol) was dissolved in 10 mL of CCl_4. The solution was stirred and irradiated with light passed through a 345 nm long-pass quartz filter for 150 min. The solvent was removed, and the resulting off-white powder was recrystallized from toluene layered with pentane at 249 K. Yield: 43.2 mg, 79.5%. ^1H NMR (C_6D_6): δ 5.58 (s, 2H, 4-pyrazolyl *trans* to $PtCH_3$), 5.29 (s, 1H, 4-pyrazolyl *trans* to PtCl, $^3J_{PtH} = 18$), 2.68, 2.07, 2.02, 1.94 (s, 6H, 6H, 3H, 3H, 3,5-CH_3 on pyrazolyls), 2.36 (s, 6H, $PtCH_3$, $^3J_{PtH} = 69.2$). ^{13}C(DEPT) NMR (C_6D_6): δ 109.3 (s, 1C, 4-pyrazolyl *trans* to PtCl), 108.3 (s, 2C, 4-pyrazolyls *trans* to $PtCH_3$), 13.4, 12.8, 12.1 (s, 3C, 1C, 2C, 3,5-CH_3 on pyrazolyls), −5.6 (s, 2C, $PtCH_3$, $^1J_{PtC} = 2190$). Raman: ν 330 cm^{-1} (PtCl).

Synthesis of $TpPtMe_2OOH$. In a typical experiment, $TpPtMe_2H$ (3.0 mg, 6.8 μmol) was placed in a J-Young valve NMR tube, and C_6D_6 was added by vacuum transfer. A 700 Torr pressure of O_2 was added, and the solution was shaken vigorously. After 20 h, complete consumption of the platinum hydride complex occurred, along with quantitative formation of $TpPtMe_2OOH$. ^1H NMR (C_6D_6): δ 7.81, 7.31 (s, 2H, 2H, 3,5-pyrazolyl-CH *trans* to $PtCH_3$), 7.11, 6.95 (s, 1H, 1H, 3,5-pyrazolyl-CH *trans* to PtOOH), 5.86 (s, 2H, 4-pyrazolyl-CH *trans* to $PtCH_3$), 5.59 (s, 1H, 4-pyrazolyl-CH *trans* to PtOOH), 1.85 (s, 6H, $PtCH_3$, $^2J_{PtH} = 70$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.2, 135.8 (s, 2C, 2C, 3,5-pyrazolyl *trans* to $PtCH_3$), 138.3, 134.7 (s, 1C, 1C, 3,5-pyrazolyl *trans* to PtOOH), 106.2 (s, 1C, 4-pyrazolyl *trans* to PtOOH), 106.0 (s, 2C, 4-pyrazolyls *trans* to $PtCH_3$), −1.7 (s, 2C, PtMe, satellites not resolved). IR (C_6D_6 solution): 2487 (ν(B−H)), 3500 (ν(O−H)) cm^{-1}.

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Supporting Information Available: Tables of rate constants and discussion of k_1 (preautocatalytic term) and the autoxidation of **1a** at low AIBN concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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