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Article

Structural and Mechanistic Investigations of the Oxidation of Dimethylplatinum(II) Complexes by Dioxygen

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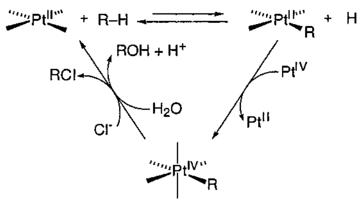
The oxidation of (tmeda)$Pt^{II}(CH_3)_2$ (**1**, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) to (tmeda)$Pt^{IV}(OH)(OCH_3)(CH_3)_2$ (**3**) by dioxygen in methanol proceeds via a two-step mechanism. The initial reaction between (tmeda)$Pt(CH_3)_2$ and dioxygen yields a hydroperoxoplatinum(IV) intermediate, (tmeda)$Pt(OOH)(OCH_3)(CH_3)_2$ (**2**), which reacts with a second equivalent of (tmeda)$Pt(CH_3)_2$ to afford the final product **3**. Both **2** and **3** have been fully characterized, including X-ray crystallographic structure determinations. The effect of ligand variation on the oxidation of several dimethylplatinum(II) complexes by **2** as well as by dioxygen has been examined.

Introduction

The selective oxidation of alkanes by aqueous platinum salts was originally reported by Shilov in 1972 (eq 1).[1] The mechanism of this catalytic cycle, a topic of extensive mechanistic studies in a number of research groups, consists of three steps as shown in eq 2.[2] Alkane activation results in the formation of a platinum(II) alkyl complex, which is then oxidized by $[PtCl_6]^{2-}$. The resulting platinum(IV) alkyl then undergoes an S_N2-type displacement to afford the alcohol (or alkyl chloride) and regenerate the active platinum(II) species. The oxidation is typically carried out in water or aqueous acetic acid at 100−120 °C. A wide range of hydrocarbons can be converted to the corresponding alcohols or alkyl chlorides.

One of the main drawbacks of the Shilov system is the use of stoichiometric platinum(IV). The oxidation step has been shown to proceed by electron transfer rather than alkyl transfer, thus potentially allowing the use of common, inexpensive oxidants instead of hexachloroplatinate.[3] However, the oxidant must not be too strong, or all platinum(II) will be converted to platinum(IV), destroying the catalytic species. Ideally one would like the redox potential to lie in a window such that the alkylplatinum(II) intermediate would be oxidized while the remaining inorganic platinum(II) salts would not. Unfortunately it is difficult to use electrochemical measurements to predict the desired redox potential, because of the irreversibility of most Pt^{II}/Pt^{IV} potentials.[4] Several oxidants have been examined, including chlorine,[5] peroxydisulfate,[6] hydrogen peroxide,[7] and an electrochemical cell,[8] with limited success (low turnovers and rates).

$$RCH_3 + PtCl_6^{2-} + H_2O\ (Cl^-) \xrightarrow[H_2O,\ 120\ ^\circ C]{PtCl_4^{2-}} RCH_2OH\ (RCH_2Cl) + PtCl_4^{2-} + 2\ HCl \qquad (1)$$



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From a practical standpoint, dioxygen is undoubtedly the most attractive reagent for catalytic alkane oxidation. Shilov and co-workers reported that combinations of cupric or

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[1] Gol'dshleger, N. F.; Es'kova, V. V.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim. (Engl. Transl.)* **1972**, *46*, 785.

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[4] Based on irreversible one electron oxidation potentials, dimethylplatinum(II) compounds are almost 0.5 V easier to oxidize than chloromethylplatinum(II) complexes, which in turn are about 0.5 V easier to oxidize than dichloroplatinum(II) complexes. J. D. Scollard, J. A. Labinger, J. E. Bercaw, unpublished results.

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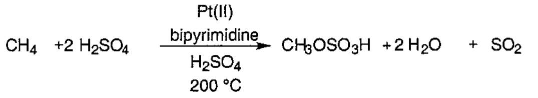
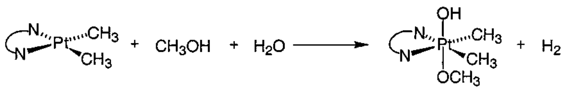
10.1021/ic0112903 CCC: $22.00

cuprous chloride, quinones, or polyoxometalates with air can be used instead of platinum(IV) salts.[9] In a recent publication, Sen and co-workers applied the $Na_2PtCl_4/CuCl_2/O_2$ system to the oxidation of a number of alkylsulfonic acids.[10] Again, turnovers are only modest, and conditions are relatively harsh (160−200 °C). A much more efficient platinum(II)-catalyzed oxidation can be achieved under still more stringent conditions (200 °C, oleum), utilizing bipyrimidine as a stabilizing ligand (eq 3);[11] unfortunately the product obtained, methyl bisulfate, has little direct use, and the cost of its conversion to a desirable product such as methanol along with that of recycling sulfuric acid apparently precludes practical application.



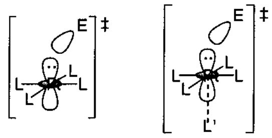
$$CH_4 + 2\,H_2SO_4 \xrightarrow[\substack{H_2SO_4 \\ 200\ ^\circ C}]{\substack{Pt(II) \\ bipyrimidine}} CH_3OSO_3H + 2\,H_2O + SO_2 \qquad (3)$$

The possibility of achieving a mild and facile O_2-oxidation of Pt(II) to Pt(IV), perhaps by means of auxiliary ligands, offers an intriguing route toward more efficient catalytic systems. In 1984, Puddephatt and Monaghan reported that several dimethylplatinum(II) complexes with diimine ligands, such as bipyridyl, can be oxidized to dimethylplatinum(IV) compounds by alcohols and/or water (eq 4).[12] Since this seemed at odds with the proposed last step in the Shilov cycle, in which water *reduces* platinum(IV) to platinum(II), we (and, simultaneously and independently, the group led by Karen Goldberg) decided to reinvestigate this chemistry, and determined that oxidation by O_2 is involved; a preliminary report of those findings has been published.[13]

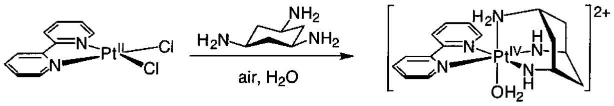


(4)

The oxidation of platinum(II) complexes has been extensively studied.[14] Halogens,[15] peroxides,[16] platinum(IV) complexes,[17] and a number of other oxidizing agents[18] can be used in this reaction. The generally accepted mechanism involves an axial electrophilic attack of the oxidizing agent on the square-planar platinum(II) complex. In some cases, precoordination of a fifth ligand prior to the oxidation step is indicated.[14b]

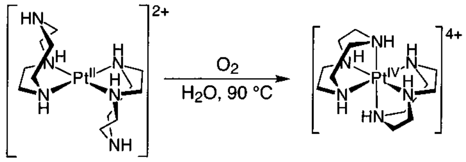


There are only a few examples of the oxidation of platinum(II) complexes with dioxygen. In 1977, Sarneski and co-workers reported that $[(bipy)Pt(\kappa^2\text{-tach})]^{2+}$, generated in situ, was converted to $[(bipy)Pt(\kappa^3\text{-tach})(OH_2)]^{2+}$ in water under air (eq 5).[19]



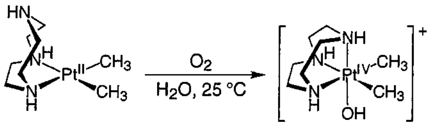
(5)

Six years later, Wieghardt and co-workers described the aerobic oxidation of $[(\kappa^2\text{-tacn})_2Pt]^{2+}$ to $[(\kappa^3\text{-tacn})_2Pt]^{4+}$ in water at 90 °C (eq 6).[20]



(6)

Most recently, Puddephatt and co-workers found that $(\kappa^2\text{-tacn})Pt(CH_3)_2$ is oxidized to $[(\kappa^3\text{-tacn})Pt(CH_3)_2(OH)]^+$ with dioxygen (eq 7).[21] It is noteworthy that all cases involve a potentially tridentate ligand that initially is κ^2-coordinated to platinum(II).



(7)

We report here our further mechanistic and structural studies on the oxidation of dimethylplatinum(II) complexes with dioxygen.

Results and Discussion

Oxidation of (tmeda)Pt(CH$_3$)$_2$. The dimethylplatinum(II) complexes $(bipy)Pt(CH_3)_2$ (bipy = 2,2′-bipyridyl), $(phen)Pt(CH_3)_2$ (phen = 1,10-phenanthroline), and $(tmeda)Pt(CH_3)_2$ (**1**) exhibit no sign of oxidation to Pt(IV) in methanol-d_4 under an argon atmosphere. ^1H NMR spectroscopy reveals only slow deuterium incorporation into Pt−CH_3 groups, followed by the formation of methane isotopomers (CH_3D, CH_2D_2, and CHD_3) along with the protonolysis

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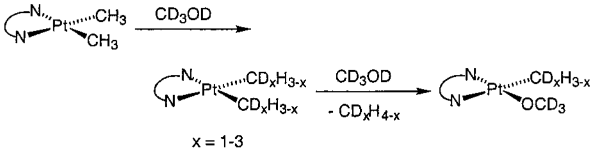
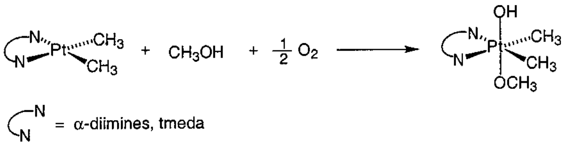
product (N-N)Pt(OCH_3)(CH_3) (eq 8). This reaction probably proceeds via dimethylhydridoplatinum(IV) intermediates, formed by protonation of dimethylplatinum(II) complexes with methanol, which undergo competing H/D exchange and reductive elimination of methane, as previously observed in related systems.[22]



(8)

In contrast, in the presence of dioxygen, (tmeda)Pt(CH_3)$_2$, (phen)Pt(CH_3)$_2$, and (bipy)Pt(CH_3)$_2$ undergo more rapid conversions in methanol solution. In the latter two cases, the products exhibit ^{1}H NMR spectra identical to those reported by Puddephatt and Monaghan for the hydroxo(methoxo)platinum(IV) complexes (N-N)Pt(OH)(OCH_3)(CH_3)$_2$ (N-N = phen, bipy).[12] Exposure of a solution of (tmeda)Pt(CH_3)$_2$ in methanol to air leads to the formation of several intermediates, which can observed by ^{1}H NMR and UV−vis spectroscopies, depending upon conditions (see below); but ultimately a single product is formed, which can be isolated and fully characterized by ^{1}H NMR spectroscopy, elemental analysis, and X-ray crystallography (see below) as the hydroxy−methoxy−platinum(IV) complex (tmeda)Pt(OH)(OCH_3)(CH_3)$_2$ (**3**). In all three cases the overall transformation is that of eq 9.



(9)

When exposed to air, a solution of (tmeda)Pt(CH_3)$_2$ (**1**) in methanol turns initially pale yellow (λ_{max} = 480 nm) and then blue (λ_{max} = 640 nm) as the yellow color fades away. The blue color is most intense at low dioxygen pressures and high concentrations of **1**. Addition of radical scavengers, such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) or *p*-methoxyphenol, immediately bleaches the blue color. If the radical scavenger is added to the reaction mixture before addition of dioxygen, the colored species are not observed, but there is no effect on the rate or the outcome of the overall oxidation to Pt(IV).

In aprotic solvents (THF, CH_2Cl_2, toluene) **1** reacts with dioxygen to give intensely blue-colored solutions. Only a small fraction (<10%) converts to the colored species, as ^{1}H NMR spectroscopy shows most of **1** remains unreacted, although the peaks are quite broad. These solutions are EPR active as well (Figure 1), suggesting that the blue color is due to a paramagnetic species, which probably consists of several platinum atoms linked together to form a “stacked” mixed-valent oligomer.[23] Again, the formation of the colored species is prevented by addition of radical scavengers (BHT, *p*-methoxyphenol). The blue solutions can also be quenched with methanol; the resulting ^{1}H NMR spectrum indicates a complex mixture of platinum(IV)-containing products.

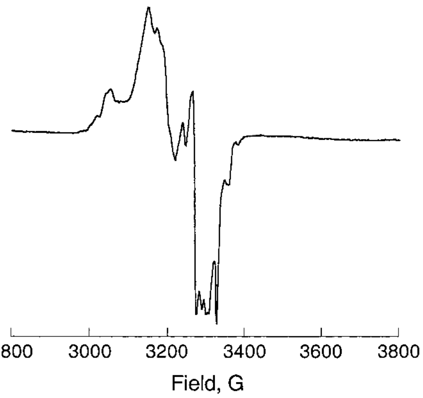
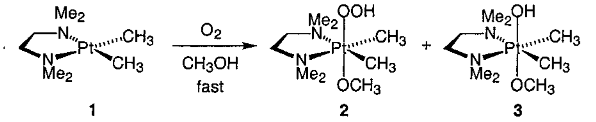


Figure 1. EPR spectrum of the frozen blue-colored benzene solution formed after (tmeda)Pt(CH_3)$_2$ was exposed to 1 atm of O_2.

At high dioxygen pressures (0.6−1 atm) in methanol, (tmeda)Pt(CH_3)$_2$ cleanly reacts within minutes at room temperature, to form a mixture of **3** and an additional dimethylplatinum(IV) species, characterized (see below) as hydroperoxy−methoxy complex (tmeda)Pt(OOH)(OCH_3)(CH_3)$_2$ (**2**, eq 10). Subsequent conversion of **2** to **3** occurs more slowly, over hours or days (eq 11). Eventually, all starting (tmeda)Pt(CH_3)$_2$ ends up as (tmeda)Pt(OH)(OCH_3)(CH_3)$_2$. The dioxygen uptake was measured, using a Toepler pump, under conditions of high (tmeda)Pt(CH_3)$_2$ and low O_2 concentrations: 1 equiv of dioxygen is consumed per 2 equiv of (tmeda)Pt(CH_3)$_2$ (eq 12).



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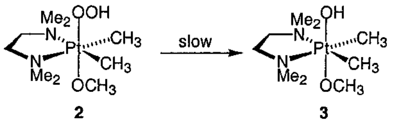

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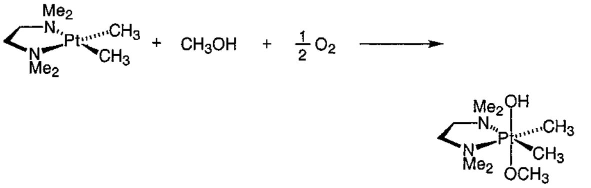

(12)

The relative ratio of **2** to **3** (measured by ^{1}H NMR spectroscopy shortly after all **1** is consumed) is strongly dependent on the concentrations of both **1** and O_2. A high concentration of O_2 (4−8.1 mM) and a low concentration of (tmeda)Pt(CH_3)$_2$ (0.5 mM) favor the formation of **2**, while **3** is favored by low [O_2] (0.7−4 mM) and high [**1**] (50−190 mM), as shown in Figure 2.

Isolation, Characterization, and Reactivity of (tmeda)-Pt(OOH)(OCH_3)(CH_3)$_2$ (2). The dependence of the ratio of **2**/**3** on O_2 and (tmeda)Pt(CH_3)$_2$ concentrations can be exploited: stirring a dilute solution of (tmeda)Pt(CH_3)$_2$ in

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(22) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961−5976.
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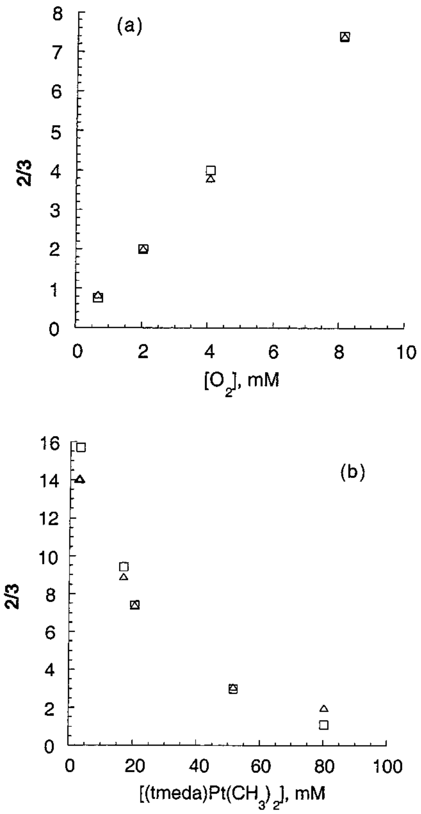
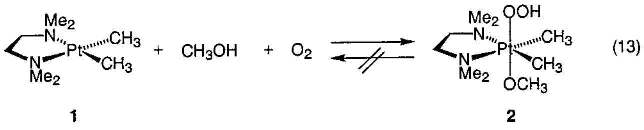


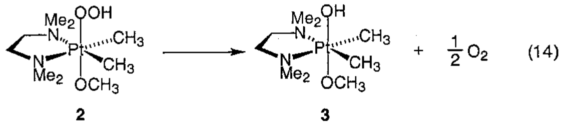
Figure 2. Dependence of **2**/**3** ratio (△) on concentrations of (tmeda)Pt-$(CH_3)_2$ and O_2: (a) [(tmeda)Pt$(CH_3)_2$] = 21 mM; (b) [O_2] = 8.1 mM. Theoretical values (□) are calculated for a consecutive mechanism as described in the text (see Results and Discussion).

methanol (ca. 5 mM) under 1 atm of dioxygen results in clean formation of (tmeda)Pt(OOH)$(OCH_3)(CH_3)_2$ (eq 13), isolated and characterized as hydroperoxy complex **2** by elemental analysis, ^1H and ^{195}Pt NMR spectroscopy, and X-ray crystallography (see below). The ^1H and ^{195}Pt NMR data for **2** and **3** are very similar, except for the hydroperoxy and hydroxy protons. The former resonates at δ 6.48 ppm while the latter shifts to δ −2.5 ppm. **2** is not stable in the solid state for long periods of time and decomposes to an unidentified mixture of platinum(IV)-containing compounds.

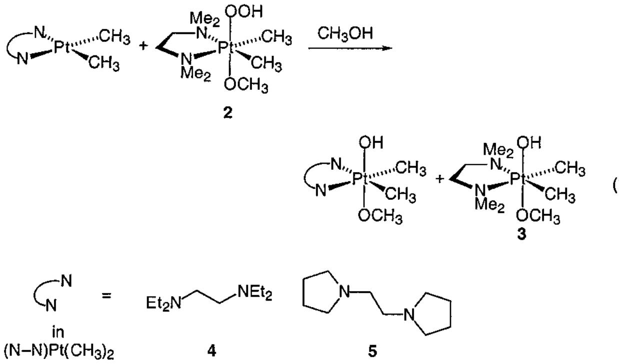


A degassed solution of (tmeda)Pt$(^{18}O_2H)(OCH_3)(CH_3)_2$ in methanol (prepared by treating (tmeda)Pt$(CH_3)_2$ with $^{18}O_2$) was stirred under air for 30 min at room temperature. Mass-spectroscopic analysis of a sample of gas from the reaction headspace revealed that ^{18}O was present only at the natural abundance level, indicating that the formation of **2** by eq 13 is irreversible.

In methanol, **2** disproportionates to **3** and O_2 over several days at room temperature, with evolution of $^1/_2$ equiv of dioxygen, as measured by Toepler pump; the identity of the gas was confirmed by mass spectroscopy (eq 14). Attempts to follow the kinetics of the disproportionation reaction by ^1H NMR spectroscopy at 50−60 °C gave only irreproducible rates and apparent reaction order.



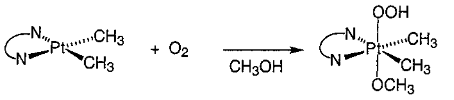
Several dimethylplatinum(II) complexes are oxidized to the corresponding Pt(IV) complexes by hydroperoxy complex **2** (eq 15). The reaction between (tmeda)Pt$(CH_3)_2$ and **2** in methanol cleanly affords 2 equiv of (tmeda)Pt(OH)(OCH_3)-$(CH_3)_2$. The rate of oxidation is too fast to follow conveniently (at −80 °C the half-life is about 5 min at normal NMR concentrations with a 10-fold excess of **1**). However, increasing steric crowding around platinum(II) slows this reaction, so that the oxidation of (teeda)Pt$(CH_3)_2$ (**4**, teeda = *N*,*N*,*N*′,*N*′-tetraethylethylenediamine) by **2** can be monitored by ^1H NMR spectroscopy around 0 °C. The reaction is first order in both platinum reagents with k_2 (−9 °C) = 7.6×10^{-3} $M^{-1}\cdot s^{-1}$. The temperature dependence of the rate constant was also examined, and the activation parameters were calculated from an Eyring plot: $\Delta H^\ddagger = 13.6$ kcal·mol^{-1}, $\Delta S^\ddagger = -16.5$ kcal·mol^{-1}·K^{-1}. Oxidation of (dpe)Pt$(CH_3)_2$ (**5**, dpe = 1,2-dipyrrolidinoethane) by **2** is slightly faster than that of **4**: at 0 °C and [**2**] = 41 mM, the pseudo-first-order rate constant $k_{obs} = 16.7(3) \times 10^{-4}$ s^{-1} and $9.3(3) \times 10^{-4}$ s^{-1} for **5** and **4**, respectively.



Mechanism of Oxidation of Pt(II) by O_2. The observation of paramagnetic blue-colored species during the course of the reaction initially led us to propose a radical-based mechanism for the oxidation.[13] However, since these can be inhibited by addition of radical scavengers without affecting the rate or outcome of the oxidation, formation of a mixture of (tmeda)Pt(OOH)$(OCH_3)(CH_3)_2$ and (tmeda)Pt(OH)(OCH_3)-$(CH_3)_2$, we believe that single-electron transfer pathways are minor side reactions.

We propose that the reduction of dioxygen occurs in two consecutive two-electron steps. In the first step (eq 16), (N-N)Pt$(CH_3)_2$ reacts with dioxygen to give (N-N)Pt(OOH)-$(OCH_3)(CH_3)_2$, which can be isolated from reaction mixtures and fully characterized for N-N = tmeda (**2**). In the second step, this hydroperoxo complex oxidizes a second equivalent of (N-N)PtMe$_2$ to form 2 equiv of (N-N)Pt(OH)(OCH_3)-$(CH_3)_2$ (eq 17). Disproportionation of (N-N)Pt(OOH)(OCH_3)-

$(CH_3)_2$ to (N-N)Pt(OH)$(OCH_3)(CH_3)_2$ and O_2 occurs at a slower rate (eq 18). Therefore, after conversion to the hydroxy complex is complete, the overall stoichiometry is 2 equiv of platinum(II) per 1 equiv of dioxygen, in agreement with experiment. An analogous mechanism was proposed for eq 17 by Puddephatt and co-workers.[21]



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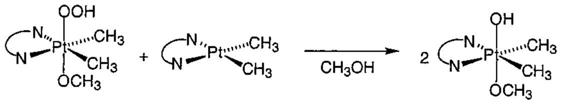

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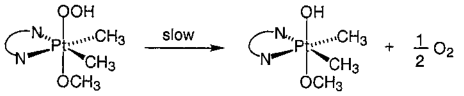
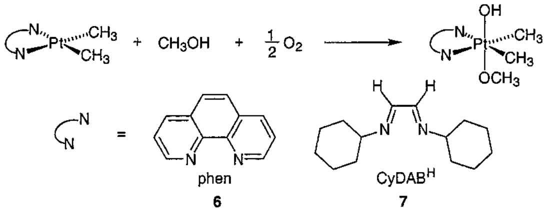


(18)

According to the proposed mechanism, the ratio of the platinum(IV) products (before eq 18 has proceeded significantly) should depend on the concentrations of Pt(II) and dioxygen, because the hydroperoxy complex and dioxygen will compete for unreacted Pt(II). This proposal was tested for (tmeda)Pt$(CH_3)_2$ (**1**). Figure 2 shows qualitative agreement: at high concentrations of O_2, **2** is the main product, whereas at higher concentrations of platinum or lower concentrations of O_2, **3** becomes predominant. That the **2**/**3** ratio depends at all on $[O_2]$ rules out an alternative mechanism in which **2** and **3** are formed in competing parallel reactions of **1** with O_2; in such a case the product ratio would be independent of dioxygen concentration.

The proposed mechanism can also be tested quantitatively, by kinetic simulation. Assuming the two-step sequence of eqs 16 and 17, the ratio of the peroxy:hydroxy products (**2**/**3**) can be predicted, from the initial concentrations and the ratio of second-order rate constants for eqs 16 and 17, by numerical integration of the appropriate differential equations. This calculation was performed for the conditions corresponding to the data point of plot a (Figure 2) with highest $[O_2]$ while the rate constant ratio k_{16}/k_{17} was varied until good agreement between the calculated and experimental values of **2**/**3** was achieved, yielding $k_{16}/k_{17} = 18$. This ratio was then used to predict **2**/**3** ratios at other concentrations of O_2 and **1**. As shown in Figure 2, the predictions are in good agreement with experiment, strongly supporting the sequential mechanism.

Reactions of Other Platinum(II) Complexes with O_2. The reactions of (phen)Pt$(CH_3)_2$ (**6**) and (CyDAB^H)Pt$(CH_3)_2$ (**7**) with dioxygen were studied by ^{1}H NMR spectroscopy (eq 19).



(19)

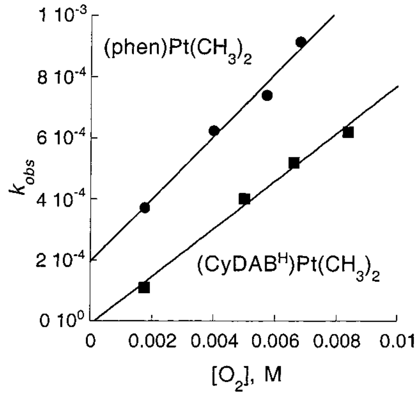


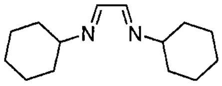
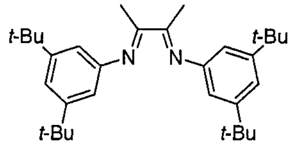
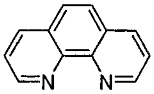
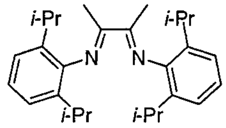
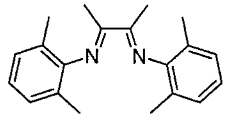
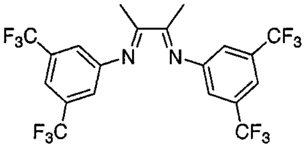
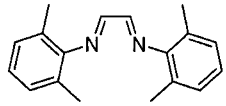
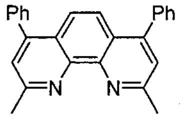
Figure 3. First-order dependence of the observed rate of oxidation of (phen)Pt$(CH_3)_2$ (●) and (CyDAB^H)Pt$(CH_3)_2$ (■) on $[O_2]$. $T = 23$ °C.

A red-orange solution of **6** in methanol-d_4 slowly fades to pale yellow under dioxygen, with formation of (phen)Pt(OH)$(OCH_3)(CH_3)_2$. At least one additional dimethylplatinum(IV) species can be observed in the reaction mixture. Unlike (tmeda)Pt$(CH_3)_2$, (phen)Pt$(CH_3)_2$ is unreactive under a dioxygen atmosphere in aprotic solvents (THF, benzene, toluene). Dioxygen also reacts with **7** in methanol-d_4 to give (CyDAB^H)Pt(OH)$(OCH_3)(CH_3)_2$. Although several intermediates were observed during the course of the oxidation by ^{1}H NMR spectroscopy, all of them eventually converted to the final product (CyDAB^H)Pt(OH)$(OCH_3)(CH_3)_2$.

The rates of oxidation of **6** and **7** can be monitored by UV−vis spectroscopy at 412 and 364 nm, respectively. The reactions are first-order in both platinum(II) and dioxygen (Figure 3); the nonzero intercept of the line for **6** is due to competing protonolysis to (phen)Pt$(CH_3)(OCH_3)$ (and presumably methane). The second-order rate constants are only slightly different: 0.11 and 0.08 $s^{-1}\cdot M^{-1}$ for (phen)Pt$(CH_3)_2$ and (CyDAB^H)Pt$(CH_3)_2$, respectively. Addition of a radical scavenger (BHT) or exclusion of light does not change the observed rate of oxidation, nor is the rate significantly different in 1.0 M $LiClO_4$ solution in methanol. At low dioxygen pressures the absorbance−time graphs have a distinct S-shape, indicating deviations from first-order behavior. This could conceivably result from one or more of the following causes: autocatalysis, slow approach to equilibrium distribution of dioxygen between gas and liquid phases, or a multistage reaction mechanism. Neither the addition of an aliquot of the starting material to the reaction mixture after the first half-life nor the use of solvents presaturated with dioxygen affects the observed rate, arguing against autocatalysis and gas solubility problems, respectively. On the basis of the results of ^{1}H NMR studies, it seems likely that non-first-order behavior at low O_2 pressure reflects the complex reaction mechanism.

Oxidation of a number of (α-diimine)Pt$(CH_3)_2$ complexes was monitored by UV−vis spectroscopy to assess the influence of steric and electronic factors on the observed rate of oxidation. Overall, α-diimine complexes of platinum(II) react more slowly with O_2 than do diamine complexes. This difference in rates may be correlated with the expected electron density at the metal center. α-Diimines, as weaker

Table 1. Relative Rates for Reaction of (α-Diimine)Pt$(CH_3)_2$ with Dioxygen in Acetonitrile/Methanol Solution

diimine ligand	ν(CO) (cm^{-1}) for $[(diimine)Pt(CO)CH_3]^+BF_4^-$	relative rate of reaction (23°C) of (diimine)Pt$(CH_3)_2$ with O_2 (1 atm) in 1:25 acetonitrile:methanol
	2104.7	1.0
	2104.6	6
	not det.	4
	2108.7	no reaction
	2109.6	very slow
	2113.5	1.4
	2114.9	no reaction
	not det.	2

σ-donors and better π-acceptors than diamines, should give less electron-rich platinum complexes. The electronic character of a ligand may be assessed by the stretching frequency of the corresponding carbonyl cation where lower frequency indicates a more electron-donating ligand. Using C−O stretching frequencies in [(N-N)Pt(CH_3)(CO)]BF_4 as a probe of electron density,[24] we find $\nu_{CO} = 2102.0$ cm^{-1} for N-N = tmeda compared to 2108.4 cm^{-1} for N-N = phen, and 2105−2115 cm^{-1} for diazabutadiene derivatives (Table 1). Within the group of α-diimines, observed pseudo first-order rate constants (1 atm O_2) do not vary greatly with electronic character, spanning only a small range of values from 2.7×10^{-4} to 14.5×10^{-4} s^{-1}. On the other hand, there is a pronounced steric effect: complexes of bulky ligands (*N,N′*-diaryldiazabutadienes with ortho substituents of the aryl groups) react with O_2 very slowly or not at all.

Replacement of methyl groups on Pt(II) has a more pronounced effect on reactivity. Whereas both (tmeda)Pt$(CH_3)_2$ and (CyDAB^H)Pt$(CH_3)_2$ are oxidized by dioxygen, no oxidation takes place with (tmeda)Pt(CH_3)Cl, (tmeda)$PtCl_2$, (tmeda)Pt$(C_6H_5)_2$, or (CyDAB^H)Pt$(C_6H_5)_2$. The mixed methyl−phenyl compounds (tmeda)Pt$(C_6H_5)(CH_3)$ and (CyDAB^H)Pt$(C_6H_5)(CH_3)$ do exhibit NMR changes consistent with oxidation to Pt(IV) on exposure to dioxygen in methanol, although the products were not isolated. Thus one methyl group may be replaced by phenyl and reaction still occurs, but replacing both leads to complete unreactivity toward O_2. This might be due to either steric or electronic effects.

Dimethylplatinum(II) complexes of α-diimines are also oxidized by **2**, but these oxidations are not as clean as those described above. With 1 equiv each of (N-N)Pt$(CH_3)_2$ (N-N = phen, **6**; CyDAB^H, **7**) and **2**, equimolar amounts of (N-N)Pt(OH)$(OCH_3)(CH_3)_2$ and **3** are formed (eq 20). However, if an excess of **2** is present, all of it is converted to **3**, even though only a stoichiometric amount of (N-N)Pt(OH)$(OCH_3)(CH_3)_2$ is formed. This implies that some species formed in these reactions must act as a catalyst for

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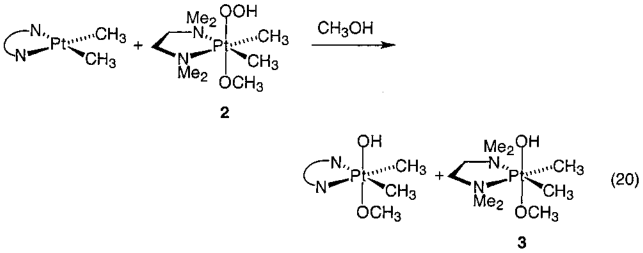
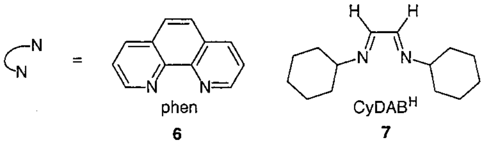
(24) Zhong, A. Z.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378−1399.

decomposition of **2** to **3** plus O_2, although this behavior has not been further investigated.



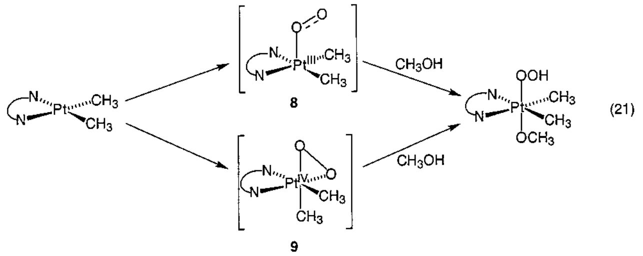
(20)



All dimethylplatinum(II) complexes can be oxidized by aqueous hydrogen peroxide as well as dioxygen; in methanol the same products, (N-N)Pt(OH)(OCH_3)$(CH_3)_2$, are obtained. In nonprotic solvents the analogous dihydroxy complexes (N-N)$Pt(OH)_2(CH_3)_2$ are formed.[16]

The oxidizing capability of (tmeda)Pt(OOH)(OCH_3)$(CH_3)_2$ (**2**) is of limited scope: besides the oxidation of dimethylplatinum(II) complexes, it converts triphenylphosphine to triphenylphosphine oxide, but does not react with Me_2S, Me_2SO, cyclohexene, or styrene. Moreover, addition of strong acid does not promote the oxidization of these same substrates by hydroperoxy complex **2**.

Interaction of Pt(II) with Dioxygen. There must be at least two reaction pathways accessible for the reaction of dimethylplatinum(II) complexes with dioxygen, but the radical pathway signaled by the appearance of deeply colored species appears to be a minor side reaction. The major detectable product from the reaction of platinum(II) with dioxygen is the hydroperoxy complex (N-N)Pt(OOH)(OCH_3)$(CH_3)_2$. Most probably that would arise via protonation of a dioxygen complex (eq 21). There are no precedents for formation of stable or metastable dioxygen complexes of platinum(II), with either η^1- (**8**) or η^2-structures (**9**). Platinum(0) reacts with dioxygen to form η^2-complexes,[25] as do square-planar iridium(I) complexes isoelectronic with (N-N)$Pt(CH_3)_2$.[26] Protonation of η^2-peroxo complexes of iridium(III) and platinum(II), to give binuclear μ_2,η^1-peroxo complexes or hydrogen peroxide, has been reported.[27] We were unable to detect hydrogen peroxide by electrochemical methods in any of our reactions.

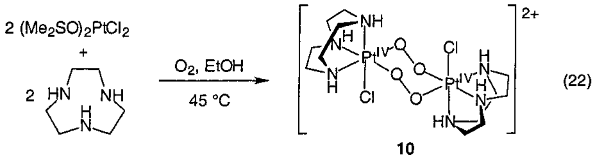


(21)

A plausible alternative mechanism might be suggested by the recent finding of a photochemical reaction of Tp*Pt$(CH_3)_2$H (Tp* = tris(*3,5*-dimethylpyrazolyl)borate), which reacts with dioxygen in benzene to afford Tp*Pt$(CH_3)_2$(OOH), apparently by a radical mechanism.[28] It is known that in protic solvents such as methanol, dimethylplatinum(II) complexes are in equilibrium with alkylhydridoplatinum(IV) species;[22] the latter could undergo insertion of O_2 into the Pt^{IV}−H bond to give the hydroperoxy complex. Arguing against this is the fact that none of our oxidations shows any effect whatsoever of exclusion of light, as well as the absence of any indicators of a radical pathway, except for the minor side reaction, which as discussed above may be inhibited without affecting formation of the Pt(IV) species.

Since formation of a hydroperoxy complex involves a proton transfer, one might expect some dependence on [H^+]. However, addition of sodium methoxide (0.5 M) does not change the rate of oxidation of (phen)$Pt(CH_3)_2$, nor is the rate sensitive to the concentration of methanol (18−24 M) in CH_3CN/CH_3OH mixed solvent. This suggests that the first step in eq 21, formation of **8** or **9**, is rate-limiting. Oxidation cannot be followed in acidic solutions because of competing protonolysis of the platinum−carbon bond (see above).

There are examples of oxidations that may well involve Pt(II)−O_2 intermediates. The bis(μ_2-peroxo)platinum(IV) dimer **10** is obtained in aerobic oxidation of Pt(II) in the presence of triazacyclononane (eq 22) and is thought to form via a complex between κ^2-tacn−Pt(II) and O_2 followed by dimerization.[29]



(22)

Formation of the alkylperoxoplatinum(II) complex in eq 23 was proposed to occur in a concerted manner through a six-membered transition state.[30] It is interesting that eq 23 proceeds for α-diimines with bulky aryl groups (Ar = 2,6-diisopropylphenyl, 2,6-dimethylphenyl); the corresponding dimethyl complexes do *not* react with dioxygen in methanol (see Table 1). The latter reaction is apparently more sensitive to steric crowding; possibly this indicates that both dioxygen and methanol must coordinate in the transition state.

In this context it is noteworthy that in our systems, involving strictly bidentate ligands, only neutral platinum(II) complexes with very strong σ-donors such as methyl

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(25) Nyman, C. J.; Wymore, C. E.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 561−563.

(26) Lawson, H. J.; Atwood, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 6223−6227.

(27) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F. *J. Am. Chem. Soc.* **1990**, *112*, 6726−6728. Bhaduri, S.; Casella, L.; Ugo, R.; Raithby, P. R.; Zuccaro, C.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1979**, 1624−1629. Hughes, G. R.; Mingos, D. M. P. *Transition Met. Chem.* **1978**, *3*, 381−382. Muto, S.; Kamiya, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2587−2589.

(28) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 11900−11901.

(29) Davies, M. S.; Hambley, T. W. *Inorg. Chem.* **1998**, *37*, 5408−5409.

(30) Tom Dieck, H.; Fendesak, G.; Munz, C. *Polyhedron* **1991**, *10*, 255−260.

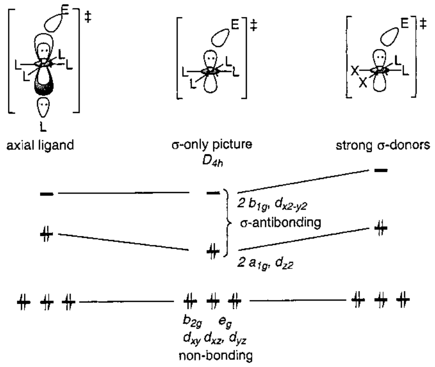
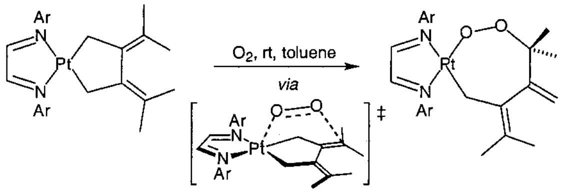


Figure 4. Qualitative MO diagram of a square-planar platinum(II) complex. Effects of axial ligands and strong σ-donors on HOMO energy.

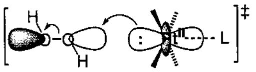
groups react with dioxygen. In contrast, with κ^2-bound but potentially tridentate ligands, even cationic platinum(II)



(23)

complexes with weaker nitrogen-based σ-donors (amines, imines) are converted to platinum(IV) products with air (eqs 5−7). Wieghardt and co-workers propose that coordination of the "dangling" arm brings about repulsion between the lone pair ligand and the filled d_{z^2} orbital (Figure 4, left side), raising the energy of HOMO of the platinum complex (σ-antibonding d_{z^2}-based orbital) and facilitating oxidation.[20] In dimethylplatinum(II) complexes, strong σ-bonds raise the energy of the HOMO, making it more susceptible to oxidation (Figure 4, right side); additional coordination of a nonchelating ligand (solvent methanol) may also be required, as suggested by the steric argument in the preceding paragraph.

Reactivity of (tmeda)Pt(OOH)(OCH$_3$)(CH$_3$)$_2$ (2). We interpret oxidation of dimethylplatinum(II) complexes by (tmeda)Pt(OOH)(OCH$_3$)(CH$_3$)$_2$ in the same mechanistic terms as reactions of alkyl or hydrogen peroxides with triphenylphosphine, dimethyl sulfide, or other oxidizable nucleophiles.[31] The lone pair of the nucleophile—in this case, a pair of electrons in the d_{z^2} orbital of platinum(II) complex—attacks the antibonding (σ*) molecular orbital, effecting heterolysis of the O−O bond (**11**).



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In the case of (N-N)Pt(OOH)(OCH$_3$)(CH$_3$)$_2$, attack most likely occurs at the β-oxygen of the hydroperoxy ligand (eq 24). The increased steric bulk of (teeda)Pt(CH$_3$)$_2$ vs (tmeda)-Pt(CH$_3$)$_2$ destabilizes the transition state and slows down the rate of the reaction. Oxidation of triphenylphosphines by **2** probably occurs through an analogous transition state. The slower reaction of **2** with (N-N)Pt(CH$_3$)$_2$ (N-N = phen, CyDAB^{H}) than with (tmeda)Pt(CH$_3$)$_2$ probably reflects the lower electron density at platinum in the former.

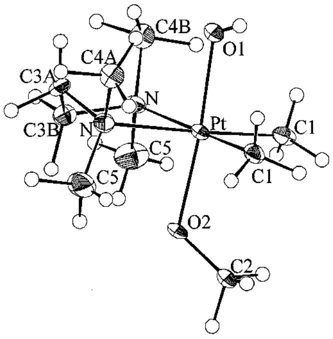
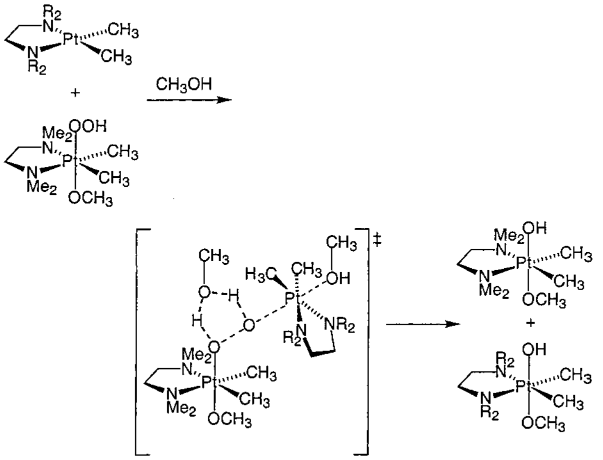


Figure 5. Labeled Diamond view of (tmeda)Pt(OH)(OCH$_3$)(CH$_3$)$_2$ (**3**) with 50% ellipsoids.



(24)

Disproportionation of (tmeda)Pt(OOH)(OCH$_3$)(CH$_3$)$_2$ to dioxygen and (tmeda)Pt(OH)(OCH$_3$)(CH$_3$)$_2$ has precedent in the chemistry of platinum(IV), Tp*Pt(CH$_3$)$_2$(OOH),[28] and cobalt(III), [(CN)$_5$CoOOH]$^{3-}$.[32] Taking into account the substitutional inertness of octahedral platinum(IV) complexes,[33] it seems likely that formation of O$_2$ is initiated by homolytic cleavage of the O−O bond. A similar mode of activation has been proposed for the disproportionation of *t*-BuOOH to *t*-BuOH and O$_2$.[34]

Molecular Structures of (tmeda)Pt(OH)(OCH$_3$)(CH$_3$)$_2$ (3) and (tmeda)Pt(OOH)(OCH$_3$)(CH$_3$)$_2$ (2). An X-ray structure determination for (tmeda)Pt(OH)(OCH$_3$)(CH$_3$)$_2$ (**3**) (Figure 5) confirmed that proposed for the bipy analogue by Puddephatt and Monaghan on the basis of spectroscopic features.[12] Bond lengths and angles around platinum are within the range expected for Pt−O, Pt−N, and Pt−C bonds. Selected bond lengths and angles are shown in Table 2. There is an intermolecular hydrogen bond between O1 and O2 (at *x*, *y*, *z* − 1) of 2.946(9) Å (the O1−H1A−O2 angle is

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(31) Conte, V.; Di Furia, F.; Modena, G. In *Organic Peroxides*; Ando, W., Ed.; John Wiley & Sons: Chichester, 1992; pp 559−598.

(32) Pregaglia, G.; Morelli, D.; Conti, F.; Gregorio, G.; Ugo, R. *Faraday Discuss. Chem. Soc.* **1968**, 110−121.

(33) No exchange was observed between (tmeda)Pt(OH)(OCH$_3$)(CH$_3$)$_2$ and H$_2$^{17}O after several days at room temperature. (phen)Pt(OH)(OCH$_3$)-(CH$_3$)$_2$ is stable in 1 M HCl for days (see ref 12).

(34) Hiatt, R.; Mill, T.; Mayo, F. R. *J. Org. Chem.* **1968**, *33*, 1416−1420.

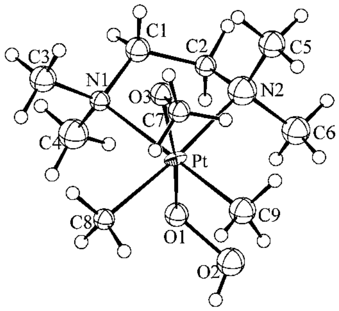

Figure 6. Labeled Diamond view of (tmeda)Pt(OOH)(OCH$_3$)(CH$_3$)$_2$ (**2**) with 50% ellipsoids.

Table 2. Selected Bond Lengths and Angles for (tmeda)Pt(OH)(OCH$_3$)(CH$_3$)$_2$ (**3**)

	length (Å)		angle (deg)
Pt−O1	1.995(7)	O1−Pt−C1	90.8(3)
Pt−C1	2.007(8)	C1^{i}-Pt−C1^{a}	89.6(5)
Pt−O2	2.028(6)	O1−Pt−O2	174.9(3)
Pt−N	2.229(6)	C1−Pt−O2	92.8(3)
O1−H0A	0.55(12)	O1−Pt−N	87.6(2)
O2−C2	1.362(13)	C1^{i}-Pt−N	176.1(3)
C4A···C4B	0.60(3)	C1−Pt−N	93.9(3)
C3A···C3B	0.74(2)	O2−Pt−N	88.6(2)
		N−Pt−N^{i}	82.5(3)
		Pt−O1−H0A	113(10)
		C2−O2−Pt	119.5(6)

^{a} Symmetry transformations used to generate equivalent atoms: (i) x, $-y + {}^{3}/_{2}$, z.

Table 3. Selected Bond Lengths and Angles for (tmeda)Pt(OOH)(OCH$_3$)(CH$_3$)$_2$ (**2**)

	length (Å)		angle (deg)
Pt−O1A	2.006(16)	O1A−Pt−O3A	170.5(6)
Pt−O3A	2.051(13)	C8A−Pt−N2A	174.1(7)
Pt−C8A	2.069(18)	C9A−Pt−N1A	179.2(8)
Pt−C9A	2.01(2)	O2A−O1A−Pt	112.7(10)
Pt−N1A	2.276(16)	C7A−O3A−Pt	120.0(12)
Pt−N2A	2.17(2)	O1B−Pt−O3B	170.8(5)
O1A−O2A	1.48(2)	C9B−Pt−N1B	173.9(7)
O3A−C7A	1.40(2)	C8B−Pt−N2B	177.0(8)
Pt−O1B	2.015(16)	O2B−O1B−Pt	116.0(11)
Pt−O3B	2.033(13)	C7B−O3B−Pt	121.9(15)
Pt−C8B	2.04(2)		
Pt−C9B	2.05(2)		
Pt−N1B	2.200(16)		
Pt−N2B	2.281(16)		
O1B−O2B	1.44(2)		
O3B−C7B	1.39(3)		

172(18)°), which forms a linear chain along the O2−Pt−O1 axis (c axis).

The determination of the X-ray structure for (tmeda)Pt(OOH)(OCH$_3$)(CH$_3$)$_2$ (**2**) was especially problematic, since this structure is both twinned and disordered. The asymmetric unit consists of one molecule of **2**, which is disordered ∼1:1 over two orientations. Its solution was possible, although the bond distances and angles are necessarily rather imprecise. Orientation A, shown in Figure 6, has a slightly more reasonable structure than orientation B, which has a carbon atom (C1B of the tmeda backbone) with distorted geometry. This distortion is most likely due to additional disorder of the tmeda ligand. The selected bond lengths and angles for both orientations are shown in Table 3. All dimensions around the central platinum atom are within the limits expected for Pt(IV)−O, Pt(IV)−N, and Pt(IV)−C bonds. The O−O bond lengths (1.44(2) and 1.48(2) Å) are close to values reported in the literature for Pt(IV)−peroxy species (cf. 1.481(5) Å in Tp*Pt(OOH)(CH$_3$)$_2$ (Tp* = tris(3,5-dimethylpyrazolyl)borate),[35] 1.465(3) Å in **10** (see above), and 1.394(6) Å in (phen)Pt(OOCHMe$_2$)(CH$_3$)$_2$Cl).[36] As shown in the hydrogen bond table (see Supporting Information), there is a hydrogen bond between the hydroperoxy group of one orientation and the methoxy oxygen of the other orientation. These close intermolecular contacts may explain the low stability of **2** in the solid.

Experimental Section

General Considerations. All air and moisture sensitive compounds were manipulated using standard high-vacuum line, Schlenk, or cannula techniques, or in a drybox under a nitrogen atmosphere. *N*,*N*,*N′*,*N′*-Tetramethylethylenediamine (tmeda) and 1,10-phenanthroline (phen) were purchased from Aldrich. (COD)Pt(CH$_3$)$_2$ was purchased from Strem Chemicals. Ultrahigh-purity oxygen was purchased from Liquid Air Products and used without further purification. Solvents were dried over sodium/benzophenone ketyl (Et$_2$O, THF, petroleum ether), 4 Å molecular seives (CH$_3$OH, CH$_3$NO$_2$), or CaH$_2$ (CH$_2$Cl$_2$). The following compounds were prepared according to literature procedures: (CH$_3$)$_2$Pt{μ_2-(CH$_3$)$_2$S}$_2$-Pt(CH$_3$)$_2$, {(CH$_3$)$_2$S}$_2$Pt(CH$_3$)Cl,[37] {(CH$_3$)$_2$S}$_2$PtPh$_2$,[38] (tmeda)Pt-(CH$_3$)$_2$, (phen)Pt(CH$_3$)$_2$,[39] and 1,2-dipyrrolidinoethane (dpe).[40] Dimethylplatinum(II) complexes of α-diimines were prepared from (CH$_3$)$_2$Pt{μ_2-(CH$_3$)$_2$S}$_2$Pt(CH$_3$)$_2$ by the method published by Bercaw and co-workers.[41] α-Diimines were prepared as described earlier.[42] NMR spectra were acquired on Varian $^{\mathrm{UNITY}}$INOVA 500 (499.853 MHz for ^{1}H), Varian Mercury-vx 300 (300.08 MHz for ^{1}H), General Electric QE300 (300 MHz for ^{1}H) ,and Bruker AM500 (500.13 MHz for ^{1}H) spectrometers. All ^{1}H NMR shifts are relative to the residual NMR solvent. ^{195}Pt NMR shifts were referenced with respect to a saturated aqueous solution of K$_2$PtCl$_4$. UV−vis spectra were recorded on a HP8452A diode array spectrophotometer. EPR spectra were acquired on a Bruker X-band EPR spectrometer. Elemental analyses were carried out either at the Caltech Elemental Analysis Facility by Mr. Fenton Harvey or by Midwest Microlab, Indianapolis, IN.

General Procedure for the Synthesis of (N-N)Pt(CH$_3$)$_2$. In a 50 mL Schlenk flask, (CH$_3$)$_2$Pt{μ_2-(CH$_3$)$_2$S}$_2$Pt(CH$_3$)$_2$ (0.5−0.8 mmol) was dissolved in 10 mL of dry THF. The desired diamine (2 equiv, 1.0−1.6 mmol) was added to the solution. The resulting mixture was stirred for 8 h at room temperature. The solution was occasionally purged with argon to remove the liberated dimethyl sulfide. Removal of volatiles under vacuum provided the desired compound. If necessary, the resulting complex was purified by recrystallization from THF/pentane or toluene/pentane mixtures.

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(teeda)Pt(CH$_3$)$_2$. The general procedure afforded the title compound as a white solid. Yield**:** 0.22 mg (55%) after recrystallization from THF. ^{1}H NMR (C$_6$D$_6$, δ): 0.97 (s, 6H, $^2J_{PtH}$ = 88.0 Hz, Pt−C*H*$_3$), 1.08 (t, 12H, $^3J_{HH}$ = 7 Hz, NCH$_2$C*H*$_3$), 1.96 (s, 4H, NC*H*$_2$C*H*$_2$N), 2.44 (dq, 4H, $^2J_{HH}$ = 13 Hz, $^3J_{HH}$ = 7 Hz, NC*H*$_2$-CH$_3$), 2.68 (dq, 4H, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7 Hz, N−C*H*$_2$−CH$_3$). Anal. Calcd for $C_{12}H_{30}N_2Pt$: C 36.26; H 7.61; N 7.05. Found: C 36.03; H 7.48; N 6.78.

(dpe)Pt(CH$_3$)$_2$. The general procedure afforded the title compound as a white solid in 72% yield. The product was recrystallized from toluene/PE. ^{1}H NMR (CD$_3$CN, δ): 0.07 (s, 6H, $^2J_{PtH}$ = 86.0 Hz, PtC*H*$_3$), 1.78 (m, 8H, N(c-C$_4$*H*$_8$)), 2.62 (s, 4H, $^3J_{PtH}$ = 12.4 Hz, NC*H*$_2$C*H*$_2$N), 2.86 (m, 4H, N(c-C$_4$*H*$_8$)), 3.21 (m, 4H, N(c-C$_4$*H*$_8$)). Anal. Calcd for $C_{12}H_{26}N_2Pt$: C 36.63; H 6.66; N 7.12. Found: C 36.40; H 6.99; N 6.87.

(tmeda)Pt(OH)(OCH$_3$)(CH$_3$)$_2$. A solution of (tmeda)Pt(CH$_3$)$_2$ (341 mg, 1 mmol) in methanol (10 mL) was stirred under air for 20 h and then concentrated in vacuo. The residual solid was taken up in CH$_2$Cl$_2$ (5 mL), treated with charcoal, and filtered. Addition of petroleum ether gave pale yellow (tmeda)Pt(OH)(OCH$_3$)(CH$_3$)$_2$ (370 mg, 95%). ^{1}H NMR (CD$_2$Cl$_2$, 200 K, δ): −2.5 (s, 1H, Pt−O*H*), 0.99 (s, 6H, $^2J_{PtH}$ = 74 Hz, PtC*H*$_3$), 2.39 (m, 4H, NC*H*$_2$C*H*$_2$N), 2.56 (overlapping s, 12H, NC*H*$_3$), 2.82 (s, 3H, $^3J_{PtH}$ = 42 Hz, PtOC*H*$_3$). ^{195}Pt NMR (CD$_3$OD, δ): −727.76. This preparation of **3** did not give satisfactory elemental analyses, but an analytically pure sample was obtained by oxidizing (tmeda)Pt(CH$_3$)$_2$ with a slight excess of 30% aqueous H$_2$O$_2$ and following a similar workup; the NMR spectrum was identical. Anal. Calcd for $C_9H_{28}N_2O_3Pt$ ((tmeda)Pt(OH)(OCH$_3$)(CH$_3$)$_2$·H$_2$O): C 26.56; H 6.93; N 6.88. Found: C 26.37; H 6.55; N 6.70.

(tmeda)Pt(OOH)(OCH$_3$)(CH$_3$)$_2$. In a drybox, (tmeda)Pt(CH$_3$)$_2$ (19 mg, 0.056 mmol) was placed in a 100 mL round bottom flask, which was then fitted with a 180° Kontes valve. The flask was removed from the box, and dry methanol (50 mL) was added by cannula. The resulting solution was degassed at −78 °C, and the flask was filled with dioxygen (1 atm). The reaction mixture was stirred for 2 h. Volatiles were removed in vacuo to give the title compound as a white solid. Yield: 21 mg (96%). ^{1}H NMR (toluene-*d*$_8$, δ): 1.64 (s, 6H, $^2J_{PtH}$ = 76 Hz, PtC*H*$_3$), 1.95 (broad s, 4H, NC*H*$_2$C*H*$_2$N), 2.18 (s, 6H, NC*H*$_3$), 2.24 (s, 6H, NC*H*$_3$), 3.27 (s, 3H, $^3J_{PtH}$ = 41.5 Hz, PtOC*H*$_3$), 6.48 (s, 1H, $^3J_{PtH}$ = 13 Hz, PtOO*H*). ^{195}Pt NMR (CD$_3$OD, δ): −716.89. Anal. Calcd for $C_9H_{26}N_2O_3Pt$: C 26.66; H 6.46; N 6.91. Found: C 26.67; H 6.52; N 6.90.

(tmeda)Pt(C$_6$H$_5$)$_2$. (Me$_2$S)$_2$PtPh$_2$ was prepared by slowly adding a toluene/Et$_2$O solution of PhLi (1.05 mL, 1.8 M) by syringe to a slurry of (Me$_2$S)$_2$PtCl$_2$ (0.3 g, 0.77 mmol) in Et$_2$O (15 mL) cooled to 0 °C. The reaction mixture, initially yellow, was stirred at 0 °C until a beige suspension was obtained. Excess tmeda (0.2 mL, 1.3 mmol) was added by syringe, and the reaction mixture was stirred for an additional 30 min at room temperature. The reaction mixture was quenched with a cold saturated aqueous solution of NH$_4$Cl (10 mL). The organic layer was separated, and the aqueous layer was washed with Et$_2$O (2 × 20 mL). The combined organic portions were dried over MgSO$_4$, treated with 0.1 g of charcoal, and filtered. Evaporation of Et$_2$O gave a white powder. Yield: 30 mg (9%). ^{1}H NMR (CD$_2$Cl$_2$/CD$_3$OD, δ): 2.46 (s, 12H, $^3J_{PtH}$ = 22.2 Hz, NC*H*$_3$), 2.69 (s, 4H, $^3J_{PtH}$ = 11.1 Hz, NC*H*$_2$C*H*$_2$N), 6.61 (m, 2H, *p*-H in Pt−C$_6$*H*$_5$), 6.75 (m, 4H, *m*-H in Pt−C$_6$*H*$_5$), 7.38 (m, 4H, $^3J_{PtH}$ = 75.0 Hz, *o*-H in Pt−C$_6$*H*$_5$).

(CyDAB^H)Pt(C$_6$H$_5$)$_2$ was prepared from (Me$_2$S)$_2$PtPh$_2$ and CyDAB^H according to the above procedure. ^{1}H NMR (CD$_2$Cl$_2$/CD$_3$OD (1:1), δ): 0.9−2.2 (m, 10H, N−C$_6$*H*$_{11}$), 3.68 (m, 2H, N−C*H*), 6.79 (pseudo t, 2H, *p*-H in Pt−C$_6$*H*$_5$), 6.96 (pseudo t, 4H, *m*-H in Pt−C$_6$*H*$_5$), 7.22 (d, 4H, $^3J_{PtH}$ = 67.0 Hz, *o*-H in PtC$_6$*H*$_5$), 8.81 (s, 2H, $^3J_{PtH}$ = 36.8 Hz, Pt−N═C*H*).

(tmeda)Pt(C$_6$H$_5$)(CH$_3$). Phenyllithium (0.25 mL, 1.8 M ether solution, 0.45 mmol) was added by syringe to a slurry of (Me$_2$S)$_2$-Pt(CH$_3$)Cl (150 mg, 0.41 mmol) in 20 mL of dry Et$_2$O at −78 °C. The reaction mixture was stirred for 15 min, then warmed to 0 °C, and stirred for an additional 25 min. Tmeda (0.5 mL) was added via syringe, and the resulting suspension was kept at room temperature for another 15 min and then quenched with a cold saturated aqueous solution of NH$_4$Cl (10 mL). The organic layer was separated, and the aqueous layer was washed with Et$_2$O (2 × 20 mL). The combined organic portions were dried over MgSO$_4$, treated with charcoal (0.1 g), and filtered. Evaporation of Et$_2$O gave a white powder. Yield: 30 mg (18%). ^{1}H NMR (CDCl$_3$, δ): 0.45 (s, 3H, $^2J_{PtH}$ = 88.5 Hz, PtC*H*$_3$), 2.54 (s, 6H, NC*H*$_3$), 2.72 (s, 6H, NC*H*$_3$), 6.83 (pseudo d, 1H, *p*-H in PtC$_6$*H*$_5$), 6.93 (pseudo dd, 2H, *m*-H in PtC$_6$*H*$_5$), 7.38 (d, 2H, $^3J_{PtH}$ = 73 Hz, *o*-H in PtC$_6$*H*$_5$).

(CyDAB^H)Pt(C$_6$H$_5$)(CH$_3$). Substituting CyDAB^H for tmeda in the above procedure gave the title compound as an approximately 1:1 mixture with (CyDAB^H)Pt(C$_6$H$_5$)$_2$. ^{1}H NMR signals assigned to (CyDAB^H)Pt(C$_6$H$_5$)(CH$_3$) (CD$_2$Cl$_2$/CD$_3$OD (1:1), δ): 0.9−2.2 (m, 10H, N−C$_6$*H*$_{11}$), 1.23 (s, 3H, $^2J_{PtH}$ = 85.4 Hz, PtC*H*$_3$), 3.79 (m, 2H, N−C*H*), 6.72 (pseudo t, 2H, *p*-H in Pt−C$_6$*H*$_5$), 6.90 (pseudo t, 4H, *m*-H in Pt−C$_6$*H*$_5$), 7.32 (d, 4H, $^3J_{PtH}$ = 72.5 Hz, *o*-H in PtC$_6$*H*$_5$), 8.85 (s, 1H, $^3J_{PtH}$ = 30.1 Hz, Pt−N═C*H*, trans to the methyl group), 8.94 (s, 1H, $^3J_{PtH}$ = 37.9 Hz, Pt−N═C*H*, trans to the phenyl group).

Determination of Stoichiometry in Dioxygen. A solution of (tmeda)Pt(CH$_3$)$_2$ (341 mg, 1 mmol) in methanol (20 mL) was stirred under 2 equiv of dioxygen for 2.5 days. The leftover gas (1.5 equiv) was quantified by a Toepler pump.

Conversion of 2 to 3. A freshly prepared solution of **2** in methanol was placed into a medium-walled glass bomb. The solution was degassed and placed into a 65 °C oil bath for 20 h. The evolved gas was quantified by a Toepler pump.

General Procedure for the NMR Tube Reaction of (N-N)-Pt(CH$_3$)$_2$ with Dioxygen. The appropriate platinum complex (∼5 mg, 0.015 mmol) was placed into an NMR tube equipped with a J Young valve. Methanol-*d*$_4$ (0.6 mL) was added by vacuum transfer. The NMR tube was filled with dioxygen (1 atm) at −78 °C. The sample was vigorously shaken as it was warmed to room temperature. The reaction was usually complete within several minutes. In some cases (see main text), the solution turned pale pink or pale blue.

General Procedure for Monitoring the Oxidation of Dimethylplatinum(II) Complexes with Dioxygen by UV/Vis Spectroscopy. In a drybox, a stock solution of a platinum complex in acetonitrile or toluene (50 μL, 2−5 mM) was placed in a 1 cm UV cell equipped with a magnetic stir bar, a 14/20 ground glass adapter at 120° to the UV cell axis, and a side arm with a magnetic stir bar (5 mL round bottom flask at 90° to the UV cell axis). The cell was capped, taken out of the drybox, and attached to a vacuum line through a 128.2 mL gas bulb. Dry methanol (2.5 mL) was added via syringe into the side arm. The entire cell was cooled to −78 °C and degassed. The gas bulb was filled with the appropriate amount of dioxygen (100−630 Torr). After dioxygen was admitted into the UV cell at −78 °C, both the solution of platinum complex and the methanol were stirred for 3 min as they warmed to room temperature, to ensure that a sufficient amount of dioxygen dissolved in the liquid phase. The methanol was then added to the UV cell by tipping the cell. The reaction mixture was vigorously stirred in the cell holder. Reactions were monitored for at least 3 half-lives.

Table 4. X-ray Experimental Data

	2	**3**
formula	$C_9H_{26}N_2O_3Pt$	$C_9H_{26}N_2O_2Pt$
fw	405.41	389.41
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	*Pnma* (No. 62)
a, Å	6.5985(8)	16.101(5)
b, Å	13.5019(16)	13.245(4)
c, Å	14.9187(18)	6.134(2)
α, deg	90	90
β, deg	93.408(2)	90
γ, deg	90	90
vol, Å^3	1326.8(3)	1308.1(7)
Z	4	4
ρ_{calc}, g/cm^3	2.030	1.977
μ, mm^{-1}	10.57	10.71
$T_{max,min}$	1.000, 0.471	1.10, 0.89
F_{000}	784	752
cryst shape	irregular thin wedge	prismatic
cryst color	colorless	colorless
cryst size, mm	0.07 × 0.21 × 0.22	0.11 × 0.13 × 0.15
T, K	98	84
type of diffractometer	Bruker SMART 1000 ccd	Nonius CAD-4
wavelength	0.71073 Å Mo Kα	0.71073 Å Mo Kα
θ range, deg	2.0, 25.0	1.5, 25
h,k,l limits	−7, 7; −16, 16; −17, 17	−19, 19; −15, 0; −7, 7
data measd	16295	5701
unique data	2335	1203
R_{int}	0.074	0.013
data, $F_o > 4\sigma(F_o)$	2096	1026
params/restraints	123/0	133/0
R1, wR2; all data	0.052, 0.100	0.046, 0.059
R1, wR2; $F_o > 4\sigma(F_o)$	0.046, 0.099	0.030, 0.053
GOF on F^2	2.20	1.83
$\Delta\rho_{max,min}$, e Å^{-3}	2.98, −2.73	1.62, −2.31

Standard numerical integration (Euler method) using Chipmunk BASIC software (http://www.rahul.net/rhn/basic/) was employed for simulation of kinetics as a function of concentrations.

General Procedure for Monitoring the Oxidation of (teeda)Pt(CH_3)$_2$ with (tmeda)Pt(OOH)(OCH_3)(CH_3)$_2$ by ^{1}H NMR Spectroscopy. In a drybox, a stock solution of (tmeda)Pt(OOH)(OCH_3)(CH_3)$_2$ (0.6−0.7 mL, 40−120 mM) in CD_3OD was placed into a Wilmad NMR tube equipped with a screw cap with Teflon insert. An aliquot of (teeda)Pt(CH_3)$_2$ solution in methanol (50 mL) was added by syringe to the cold NMR tube (−78 °C). The NMR tube was vigorously shaken, placed into the spectrometer, and allowed to equilibrate to the probe temperature while the sample was shimmed. Arrayed spectra were scaled to the first spectrum in the series, and kinetic fits were done using *kini* and *kind* functions built into VNMR software (version 6.1B, Varian Associates, Inc.).

Structure Determination of (tmeda)Pt(OH)(OCH_3)(CH_3)$_2$ (3). The title complex was crystallized from methanol at −78 °C. Four crystals were examined on the diffractometer, but only one was eventually used (Table 4). The first three crystals were discarded due to broad diffraction peaks and severe indexing problems. The crystals were mounted on a glass fiber with Paratone-N oil. Data were collected with 1.5° ω-scans because of the poor crystal quality. The individual backgrounds were replaced by a background function of 2θ derived from weak reflections with $I < 3\sigma(I)$. The GOF$_{merge}$ was 1.08 (1203 multiples); R_{int} was 0.013 for 94 duplicates (there are a small number of duplicates since four equivalent sets of reflections were collected). Ψ-Scan data were used for the absorption correction. There was no decay. No outlying reflections were omitted from the refinement. Weights were calculated as $1/s^2(F_o{}^2)$; variances ($s^2(F_o{}^2)$) were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\langle I\rangle)^2$. No reflections were specifically omitted from the final processed data set; 2095 reflections were rejected, with 33 space group absence violations and 32 inconsistent equivalents. Refinement of F^2 was against all reflections. The weighted R-factor (R_w) and goodness of fit (S) are based on F^2, and conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) and is not relevant to the choice of reflections for refinement. The coordinates of all hydrogen atoms including the half-populated sites were refined with U_{iso}'s fixed at 120% of the U_{eq} of the attached atom. There are 17 peaks in the final difference map with intensities ≥|1| e·Å^{-3}; the two largest are −2.31 e·Å^{-3} (0.92 Å from Pt) and 1.62 e·Å^{-3} (0.89 Å from Pt). Nine of these peaks, with intensities up to 1.45 e·Å^{-3} and −1.53 e·Å^{-3}, are in the vicinity of the disordered region. The largest shift/esd of 0.155 is for the x coordinate of the half-hydrogen H3AA which oscillates approximately 0.05 Å.

Structure Determinations for (tmeda)Pt(OOH)(OCH_3)(CH_3)$_2$ (2). A semi-opaque, rounded thin wedge was selected from a batch of crystals, which were freshly grown from acetone at −35 °C, and mounted on a glass fiber with Paratone-N oil. This sample was the best of many chosen from a number of crystallizations; data collected at room temperature were no better than low-temperature data (Table 4). Five runs of data were collected with 15 s long, −0.3° wide ω-scans at five values of φ (0°, 120°, 240°, 180°, and 300°) with the detector 5 cm (nominal) distant at a θ of −28°. The spots were broad and sometimes split. The initial cell for data reduction was calculated from 999 centered reflections chosen from throughout the data frames. A total of 41 reflections were discarded in the triclinic least-squares with a reciprocal lattice vector tolerance of 0.008 (0.005 is customary). Of the rejects, 20 had substantially nonintegral indices and presumably are from a small fragment with a different orientation. There was no evidence of a larger cell. For data processing with SAINT v6.02, all defaults were used, except that a fixed box size of 2.0 × 2.0 × 1.2 was used, periodic orientation matrix updating was disabled, the instrument error was set to zero, no Laue class integration restraints were used, and, for the postintegration global least squares refinement, no constraints were applied. The profiles exhibited an apparently considerable truncation of many reflections, especially in the z-direction. A number of both larger and smaller box sizes were tried but gave worse refinements of the structure. Both the initial cell refinement and the global cell refinement gave an ω zero ∼0.4° too negative. No decay correction was needed. The crystal boundaries were rudely indexed as faces; these were not good enough for a face-indexed absorption correction. A SADABS v2.03 β correction was applied (relative correction factors: 1.000−0.471) with $g = 0.113$, 100 refinement cycles, and defaults for the remaining parameters. Again, a number of other options such as discarding portions of the data and using different orders of Bessel functions did not lead to a better model refinement.

No reflections were specifically omitted from the final processed data set, but the data were truncated at a 2θ of 50° as the high-angle spots seemed fuzzier; 3469 reflections were rejected, with 20 space group absence violations, 0 inconsistent equivalents, and no reflections suppressed. Refinement of F^2 was against all reflections. The weighted R-factor (R_w) and goodness of fit (S) are based on F^2, and conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt), and is not relevant to the choice of reflections for refinement.

The platinum atom was refined anisotropically, and all other non-hydrogen atoms were refined isotropically. The solvents form layers perpendicular to the c-axis at $z \sim 0$, $^1/_2$, and 1, but do not appear to interact. All hydrogen atoms were placed at calculated positions with U_{iso}'s fixed at 120% of the U_{iso}'s of the attached atoms. No restraints or constraints were used. Of the 20 largest peaks in the final difference map, 6 are greater than |2| e•Å^{-3} and another 12 are greater than |1| e•Å^{-3}. Seven of these 18 peaks are near the platinum atom, including the largest positive peak of 2.98 e•Å^{-3} at a distance of 0.89 Å. The largest negative peak of −2.73 e•Å^{-3} is 0.75 Å from N2B (anomalously small U_{iso}); the other big excursions not near the platinum are 2.29 e•Å^{-3} at 0.88 Å from C8B, 1.79 e•Å^{-3} at 0.67 Å from C6B, −1.66 e•Å^{-3} at 1.45 Å from O2B, 1.63 e•Å^{-3} at 0.68 Å from N2B, −1.23 e•Å^{-3} at 0.99 Å from H8BC, −1.21 e•Å^{-3} at 1.07 Å from O2A, 1.13 e•Å^{-3} at 0.76 Å from C4B, and 1.06 e•Å^{-3} at 0.80 Å from O1B.

The 6 most disagreeable reflections all have $k = 5$ with F_{calc} weak and less than F_{obs}, suggesting twinning. The 20 reflections discarded in the initial unit cell determination could not be indexed by themselves. No other effort was made to investigate this fairly minor problem.

An analysis of intermolecular contacts suggests two potential hydrogen bonds, each between a donor hydroperoxy group and an acceptor methoxy group. One bond is between two molecules of orientation A translated one unit along the *a*-axis; the other between two molecules of orientation B, which are similarly related. However, the intermolecular distances also reveal some impossibly short contacts, such as 2.08 Å between O2A (x, y, z) and C5A ($x + 1$, y, z). Therefore, two molecules of orientation A cannot be adjacent along the *a*-axis and thus molecules of orientation A must comprise no more than 50% of the total molecules in the crystal. The population parameter for orientation A refined to 0.508(9), or essentially 1:1. Thus, orientations A and B must alternate along the *a*-axis. This alternation must be occasionally broken as there is no evidence for a larger cell. There are no appreciable intermolecular platinum−hydroperoxy or hydroperoxy−hydroperoxy interactions. As shown in the hydrogen bond table (Supporting Information), there is a hydrogen bond between the hydroperoxy group of one orientation and the methoxy oxygen of the other orientation. These close intermolecular contacts may explain the low stability of **2** in the solid.

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Supporting Information Available: Details of the structure determinations of (tmeda)Pt(OH)(OCH$_3$)(CH$_3$)$_2$ (**3**) and (tmeda)Pt(OOH)(OCH$_3$)(CH$_3$)$_2$ (**2**), including atomic coordinates, bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for compounds **2** (CDC 163314) and **3** (CDC 160706) can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax, +44 1223 336033; or deposit@ccdc.cam.ac.uk). Structure factors are available from the authors via e-mail: xray@caltech.edu.

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