Compound B has NMR parameters (^{31}P, ^{119}Sn, ^{195}Pt) very similar to those of compounds of the type *cis*-$(PPh_3)_2Pt(Ph)(SnPh_3Cl)$[2] and hence is identified as *cis*-$(PPh_3)_2Pt(Ph)(Ph_2SnC(S)pyrr$ (Scheme I). Compound B was isolated by mixing $(PPh_3)_2PtC_2H_4$ and $Ph_3SnC(S)Spyrr$ in benzene and allowing the reaction to proceed for 24 h. Its analysis confirmed the identification (Table I).

The two classes of platinum(0) complexes described above represent the first examples of η^2-CS bonded compounds where the ligand contains a large heteroatom, in this case tin. The inclusion of such a large heteroatom leads to quite different properties of the complexes compared to those of smaller η^2-CS bonded ligands.

Platinum(0) complexes containing small η^2 ligands (e.g. CS_2, COS, RNCS) react readily with excess ligand, and the η^2-CS bond to platinum is replaced by two σ-bonds during intermolecular processes involving the central carbon atom. In contrast, the compounds containing η^2-CS bonded $Ph_2SnC(S)N'$ ligands undergo intramolecular rearrangement involving bond cleavage at the tin. An even greater contrast is given by the derivatives containing η^2-CS bonded $Ph_3SnC(S)SR$, which are quite stable, and no further reactions are observed on addition of excess ligand or CS_2.

The differences between the behavior of these Ph_3Sn ligands and those of the type Ph_3SnX (X = Ph, Cl, Br), which oxidatively add to platinum(0) with immediate cleavage of the Sn–Ph bond,[1] are also noteworthy.

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Registry No. I (R = Me), 87451-03-4; I (R = CH_2Ph), 87451-04-5; I (R = C_3H_5), 87451-02-3; $(PPh_3)_2Pt(Ph)(Ph_2SnC(S)NMeH)$, 87451-00-1; $(PPh_3)_2Pt(Ph)(Ph_2SnC(S)pyrr)$, 87451-01-2; $(PPh_3)_2Pt(Ph_3SnC(S)NMeH)$, 87451-05-6; $(PPh_3)_2Pt(Ph_3SnC(S)pyrr)$, 87451-06-7; $(PPh_3)_2PtC_2H_4$, 12120-15-9; $(PPh_3)_2PtCS_2$, 15308-68-6; Pt, 7440-06-4; Sn, 7440-31-5; $Ph_3SnC(S)SCH_2Ph$, 87451-07-8; $Ph_3SnC(S)NMeH$, 87451-08-9; $Ph_3SnC(S)pyrr$, 87451-09-0; $PhCH_2Cl$, 100-44-7; Ph_3SnCS_2Li, 84448-52-2; $Ph_3SnC(S)SMe$, 73137-42-5; pyrr, 109-97-7; dimethylamine, 124-40-3.

Supplementary Material Available: Tables S-I–S-V, listing bond lengths, bond angles, and equations of least-squares planes of the phenyl rings, anisotropic thermal parameters, and structure factors (17 pages). Ordering information is given on any current masthead page.

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tert-Butylperoxo Complexes of Platinum(II): Synthetic, Spectroscopic, and Structural Investigations. Oxygenation of 1-Octene by Trans Species

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Stable monomeric *tert*-butylperoxo complexes of Pt(II) of the type *trans*-$P_2Pt(Rx)(OO\text{-}t\text{-}Bu)$ (P = tertiary phosphine; Rx = CF_3, Ph-*o*-CN, Ph) have been prepared by condensation reactions of the corresponding hydroxo complexes with *t*-BuOOH. These have been characterized with conventional spectroscopic techniques: IR and ^{1}H, ^{19}F, and ^{31}P NMR. The X-ray crystal structure of *trans*-$(PPh_3)_2Pt(Ph)(OO\text{-}t\text{-}Bu)$ is also reported, which confirms the end-bonded peroxidic nature of these complexes. The crystals are triclinic, space group $P\bar{1}$ with 2 molecular units in a cell and lattice parameters a = 20.11 (1) Å, b = 10.114 (7) Å, c = 12.024 (8) Å, α = 103.4 (1)°, β = 118.5 (1)°, and γ = 98.5 (1)°. The structure was refined to an R value of 0.045 (R_w = 0.055) for 3335 independent reflections. Spectroscopic investigations with ^{31}P and ^{19}F NMR suggest a considerable covalent character for the Pt–O bond in both *tert*-butylperoxo and hydroperoxo species. All trans *tert*-butylperoxo derivatives except one (P = PBz_3) proved effective in the selective oxygenation of 1-octene to 2-octanone. The influence on the yield of the oxygenation reaction due to the ancillary phosphines and Rx ligand, along with conductivity and spectroscopic studies, constitutes the basis for a discussion of the possible oxygen-transfer pathways occurring in this system.

Introduction

Within the framework of our interest in the synthesis and reactivity of group 8 metal complexes containing "activated" oxygen, we have reported some stable hydroperoxo[2,3] and *tert*-butylperoxo[3] complexes of Pd(II) and Pt(II) of the type $P_2M(Rx)(OOR)$ (P_2 = 1,2-bis(diphenylphosphino)ethane (diphos) or -ethylene (diphoe), 2 PPh_3, 2 PPh_2Me; M = Pd, Pt; Rx = CF_3, Me, CH_2CN, CH_2CF_3; R = H, *t*-Bu). These compounds have been employed in oxygen-transfer reactions using a variety of substrates, namely PPh_3, CO, NO, benzaldehyde, and olefins. With the latter substrates oxygenation to the corresponding methyl ketones could be accomplished only with *trans*-$(PPh_2Me)_2Pt(CF_3)(OO\text{-}t\text{-}Bu)$, which was the only *tert*-butylperoxo complex with a trans geometry available in the prepared series. It seemed desirable to determine what factors controlled the ease of olefin oxidation: first, whether a trans geometry was essential; second, some observations by Bennett[4] on the behavior of closely related trans hydroxo complexes of platinum (which dissociate strongly as bases in protic media) seemed to suggest a possible role for an ionic intermediate of the type $[(PPh_2Me)_2Pt(CF_3)]^+(t\text{-}BuOO)^-$ in our observed olefin oxidation. In this paper we report the synthesis and characterization of a new series of trans-*tert*-butylperoxo complexes of platinum(II) along with their behavior in the oxygenation of 1-octene. In addition, we report the X-ray crystal structure of *trans*-$(PPh_3)_2Pt(Ph)(OO\text{-}t\text{-}Bu)$, which represents the first structural characterization of a d^8 metal complex containing a nonbridging, end-bonded alkylperoxo moiety.

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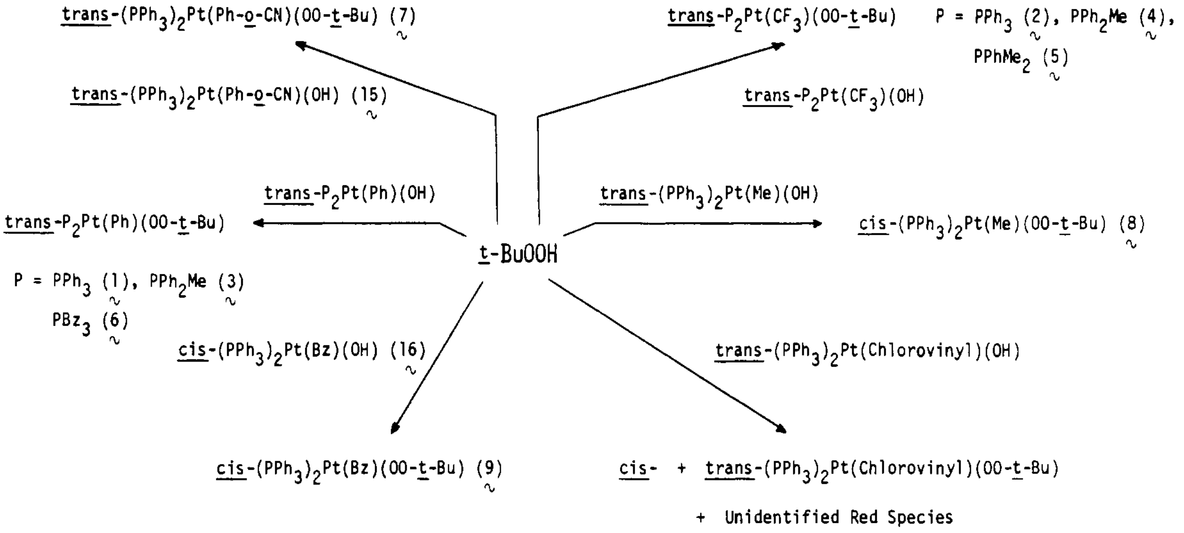
Scheme I. Summary of Reactions of *t*-BuOOH with Pt(II) Hydroxo Complexes



Results and Discussion

Synthesis. Since our goal was to synthesize a homologous series of trans peroxo complexes of a wide variety, we tried to change systematically both the Rx group and the phosphines although this did not always prove feasible. The basic synthetic route to $P_2Pt(Rx)(OOR)$ complexes has already been described[3] and involves, as the crucial step, the condensation reaction (1). The preparation of the trans complexes reported

$$P_2Pt(Rx)(OH) + ROOH \rightarrow P_2Pt(Rx)(OOR) + H_2O \quad (1)$$

here (Scheme I and Tables I and II) has been accomplished according to the same general method, although slight modifications have been necessary in a few cases. As we have already observed,[3] complexes **2** and **12** could not be obtained by simple addition of *t*-BuOOH or 30% H_2O_2 to a suspension of the parent hydroxo species, probably because of unfavorable equilibrium constants. Analogously, addition of 30% H_2O_2 to *trans*-$(PPh_3)_2Pt(Ph)(OH)$ results only in the formation of an equilibrium mixture containing no more than 50% of **10** (IR evidence from O–H stretches). These problems can be easily overcome by carrying out the reaction in either benzene or dichloroethane (DCE) solutions in the presence of anhydrous sodium sulfate. Although this procedure may sound hazardous, we never experienced any safety problems. In certain cases we experienced other problems. For example, when *trans*-$(PPh_3)_2Pt(Me)(OH)$ is reacted with *t*-BuOOH, reaction 1 proceeds with inversion of configuration and only *cis*-$(PPh_3)_2Pt(Me)(OO$-*t*-Bu) can be isolated as the final product. With the known[5] chlorovinyl complexes *trans*-$(PPh_3)_2Pt(CCl{=}CCl_2)(OH)$ and *trans*-$(PPh_3)_2Pt(CH{=}CCl_2)(OH)$, reaction 1, which must be carried out in the presence of anhydrous sodium sulfate, results in the formation of a mixture of compounds including the starting hydroxo complex, *cis*- and *trans*-$(PPh_3)_2Pt$(chlorovinyl)(OO-*t*-Bu), and some unidentified red species. Undesired isomerization also occurs in the reaction of *trans*-$(PPh_3)_2Pt(Bz)Cl$ to give the corresponding cis hydroxo complex, from which *cis*-$(PPh_3)_2Pt(Bz)(OO$-*t*-Bu) can be prepared.

It is worth noticing that the preparation of these trans *tert*-butylperoxo derivatives required the synthesis of new hydroxo complexes for which two different methods have been employed. The first method, as outlined by Bennett and coworkers,[4,7] involves the use of cyclooctadiene–platinum derivatives. The second method, developed in our laboratory,[6] involves oxidative addition of an appropriate alkyl halide to $Pt(PPh_3)_4$, followed, if necessary, by phosphine exchange, halide abstraction with Ag^+, and finally treatment with KOH.

The preparation of *tert*-butylperoxo complexes of group 8 transition metals reported so far has been accomplished successfully with palladium acetates,[8] with platinum hydroxides,[3] and more recently, following an early report[9] by Booth et al., with *trans*-$(PPh_3)_2Ir(CO)X$ type complexes (X = halide).[10] In the first two cases the preparation reaction is formally an acid–base process that proceeds without a change in the oxidation state of the metal. In the case of iridium, however, the *tert*-butylperoxo complexes are minor products arising from oxidative addition reactions. The main product of the reaction reported by Booth et al. is a poorly characterized blue-green solid, probably arising from a 1-electron redox process involving the general Haber–Weiss mechanism. We attempted to apply our mild condensation method to *trans*-$(PPh_3)_2Ir(CO)(OH)$[11] by reacting this complex with either H_2O_2 or *t*-BuOOH. In both cases deep blue-green materials are produced, giving no evidence of coordinated carbon monoxide, and are probably similar to those reported by Booth et al. This result suggests that, even in comparison with the facile condensation reaction, the tendency of hydroperoxides to give Haber–Weiss products is overwhelming for those metals for which 1-electron oxidation steps are relatively easily accessible, as in the case of Ir(I)/Ir(II)/Ir(III).[12]

Characterization. All the compounds reported here are diamagnetic; they give satisfactory C and H elemental analyses, and they have been characterized by IR and ^1H, ^{31}P, and ^{19}F NMR spectroscopies. In Table I, a selected list of their most significant spectroscopic features is reported. The *tert*-butylperoxo complexes show typical peroxidic stretchings at ~890 cm^{-1} analogous to those of the corresponding cis complexes.[3] In the ^1H NMR spectra the *t*-Bu signal is a sharp singlet that is generally shifted to higher fields with respect to free *t*-BuOOH (δ 1.24). The extent of this shielding effect appears to be dependent on the number of aryl substituents present on the phosphines, as shown in the two sequences **1**, **3**, **6** and **2**, **4**, **5**. Although this behavior has already been

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Table I. Spectroscopic Features of *tert*-Butylperoxo Complexes[a]

no.	complex	IR	^{1}H NMR	^{31}P NMR	^{19}F NMR
1	*trans*-(PPh$_3$)$_2$Pt(Ph)(OO-*t*-Bu)	1198 s (ν_{C-C}, *t*-Bu); 890 m (ν_{O-O})	0.35 s (*t*-Bu)	24.34 s, $^1J_{P-Pt}$ 3361	
2	*trans*-(PPh$_3$)$_2$Pt(CF$_3$)(OO-*t*-Bu)	1196 s (ν_{C-C}, *t*-Bu); 883 m (ν_{O-O})	0.16 s (*t*-Bu)	25.12 q, $^1J_{P-Pt}$ 3345, $^3J_{P-F}$ 15.7	−10.2 t, $^2J_{F-Pt}$ 555, $^3J_{F-P}$ 15.7
3	*trans*-(PPh$_2$Me)$_2$Pt(Ph)(OO-*t*-Bu)	1198 s (ν_{C-C}, *t*-Bu); 888 s (ν_{O-O}) (liquid film)	0.76 s (*t*-Bu); 1.74 t (Me), $^2J_{H-P}$ + $^4J_{H-P}$ 7.3, $^3J_{H-Pt}$ 33.3	9.78 s, $^1J_{P-Pt}$ 3242	
4	*trans*-(PPh$_2$Me)$_2$Pt(CF$_3$)(OO-*t*-Bu)	1195 m (ν_{C-C}, *t*-Bu); 890 m (ν_{O-O})	0.61 s (*t*-Bu); 2.13 t (Me), $^2J_{H-P}$ + $^4J_{H-P}$ 7.6, $^3J_{H-Pt}$ 30.7	13.66 q, $^1J_{P-Pt}$ 3211, $^3J_{P-F}$ 16.1	−10.0 t, $^2J_{F-Pt}$ 594, $^3J_{F-P}$ 16.1
5	*trans*-(PPhMe$_2$)$_2$Pt(CF$_3$)(OO-*t*-Bu)	1198 s (ν_{C-C}, *t*-Bu); *b*	0.82 s (*t*-Bu); 1.78 t (Me), $^2J_{H-P}$ + $^4J_{H-P}$ 7.5, $^3J_{H-Pt}$ 30.0	1.76 q, $^1J_{P-Pt}$ 3101, $^3J_{P-F}$ 16.3	−10.3 t, $^2J_{F-Pt}$ 623, $^3J_{F-P}$ 16.3
6	*trans*-(PBz$_3$)$_2$Pt(Ph)(OO-*t*-Bu)	1195 m (ν_{C-C}, *t*-Bu); 895 w (ν_{O-O})	1.27 s (*t*-Bu); 3.13 t (CH$_2$), $^2J_{H-P}$ + $^4J_{H-P}$ 7.6, $^3J_{H-Pt}$ 26.4	11.81 s, $^1J_{P-Pt}$ 3097	
7	*trans*-(PPh$_3$)$_2$Pt(Ph-*o*-CN)(OO-*t*-Bu)	2205 m ($\nu_{C\equiv N}$); 1198 m (ν_{C-C}, *t*-Bu); 890 w (ν_{O-O})	0.27 s (*t*-Bu)	23.59 s, $^1J_{P-Pt}$ 3235	
8	*cis*-(PPh$_3$)$_2$Pt(Me)(OO-*t*-Bu)	1201 m (ν_{C-C}, *t*-Bu); *b* 555 s (*c*)	0.82 s (*t*-Bu); 0.56 dd (Me), $^2J_{H-Pt}$ 64, $^3J_{H-P}$ 4.2 (cis) and 7.5 (trans)	31.25 d (trans Me), $^2J_{P-P}$ 9.5, $^1J_{P-Pt}$ 1817 and 16.21 d (cis Me), $^2J_{P-P}$ 9.5, $^1J_{P-Pt}$ 3592	
9	*cis*-(PPh$_3$)$_2$Pt(Bz)(OO-*t*-Bu)	1198 s (ν_{C-C}, *t*-Bu); 890 m (ν_{O-O}); 555 s[c]	0.82 s (*t*-Bu); 2.97 dd (CH$_2$), $^2J_{H-Pt}$ 82, $^3J_{H-P}$ 4.4 (cis) and 9.3 (trans)	26.68 d (trans Bz), $^2J_{P-P}$ 10.0, $^1J_{P-Pt}$ 1709 and 13.98 d (cis Bz), $^2J_{P-P}$ 10.0, $^1J_{P-Pt}$ 3847	

[a] IR: cm^{-1}; as Nujol mulls. NMR: in ppm, *J* in Hz; CD$_2$Cl$_2$ as solvent; references Me$_4$Si, H$_3$PO$_4$, CFCl$_3$; s = singlet, d = doublet, t = triplet, q = quartet. [b] ν_{O-O} covered by phosphine absorptions. [c] The presence of this band around 550 cm^{-1} is indicative of a cis geometry according to Mastin's identification method for isomers (PPh$_3$)$_2$PtXY.[31]

Table II. Spectroscopic Features of Other Platinum-Oxygen Complexes[a]

no.	complex	IR	^{1}H NMR	^{31}P NMR	^{19}F NMR
10	*trans*-(PPh$_3$)$_2$Pt(Ph)(OOH)	3530 w (ν_{O-H});[e] 815 w (ν_{O-O})	*d*	24.64 s, $^1J_{P-Pt}$ 3158	
11	*trans*-(PPh$_2$Me)$_2$Pt(Ph)(OOH)	3530 w (ν_{O-H});[e] *b*	1.57 t (Me), $^2J_{H-P}$ + $^4J_{H-P}$ 7.1, $^3J_{H-Pt}$ 34.6; *d*	9.48 s, $^1J_{P-Pt}$ 3195	
12	*trans*-(PPh$_3$)$_2$Pt(CF$_3$)(OOH)	3508 m (ν_{O-H}); *b*	4.43 s (OOH), $^3J_{H-Pt}$ 5–6	25.61 q, $^1J_{P-Pt}$ 3300, $^3J_{P-F}$ 15.0	−10.8 t, $^2J_{F-Pt}$ 585, $^3J_{F-P}$ 15.0
13	*trans*-(PPhMe$_2$)Pt(CF$_3$)(OH)	3630 w (ν_{O-H})	1.78 t (Me), $^2J_{H-P}$ + $^4J_{H-P}$ 3.5, $^3J_{H-Pt}$ 30.8; *d*	3.16 q, $^1J_{P-Pt}$ 3028, $^3J_{P-F}$ 16.1	−9.89 t, $^2J_{F-Pt}$ 638, $^3J_{F-P}$ 16.1
14	*trans*-(PBz$_3$)$_2$Pt(Ph)(OH)	3605 w (ν_{O-H})	2.97 t (CH$_2$), $^3J_{H-P}$ + $^4J_{H-P}$ 7.2, $^3J_{H-Pt}$ 27.1; *d*	9.77 s, $^1J_{H-Pt}$ 2975	
15	*trans*-(PPh$_3$)$_2$Pt(Ph-*o*-CN)(OH)	3620 w (ν_{O-H}); 2205 m ($\nu_{C\equiv N}$)	1.75 s (OH)	23.80 s, $^1J_{P-Pt}$ 3099	
16	*cis*-(PPh$_3$)$_2$Pt(Bz)(OH)	3605 w (ν_{O-H}); 555 s[c]	2.28 s (OH); 2.58 dd (CH$_2$), $^2J_{H-Pt}$ 81, $^3J_{H-P}$ 9.7 (trans and 5.8 (cis)	25.00 d (trans Bz), $^2J_{P-P}$ 11.9, $^1J_{P-Pt}$ 1758 and 16.30 d (cis Bz), $^2J_{P-P}$ 11.9, $^1J_{P-Pt}$ 3809	

[a] IR: cm^{-1}; as Nujol mulls. NMR: in ppm, *J* in Hz; CD$_2$Cl$_2$ as solvent; references Me$_4$Si, H$_3$PO$_4$, CFCl$_3$; s = singlet, d = doublet, t = triplet, q = quartet. [b] ν_{O-O} covered by phosphine absorptions. [c] The presence of this band around 550 cm^{-1} is indicative of a cis geometry for isomers (PPh$_3$)$_2$PtXY according to Mastin's identification method.[31] [d] OOH or OH resonance not located. [e] DCE solution.

Table III. Coupling Constants Involving ^{195}Pt for Some Substituted Alkyl Platinum(II) Complexes

complex	$^1J_{P-Pt}$,[a] Hz	$^2J_{F-Pt}$, Hz	ref
cis-$(PPh_3)_2Pt(CH_2CN)(OH)$	3458		17
cis-$(PPh_3)_2Pt(CH_2CN)$(OO-*t*-Bu)	3362		3
(diphoe)$Pt(CF_3)(OH)$	3263		6
(diphoe)$Pt(CF_3)(OOH)$[b]	3139		this work
(diphoe)$Pt(CF_3)$(OO-*t*-Bu)[c]	3075		this work
trans-$(PPh_3)_2Pt(CF_3)(OH)$		578	6
trans-$(PPh_3)_2Pt(CF_3)(OOH)$		585	this work
trans-$(PPh_3)_2Pt(CF_3)$(OO-*t*-Bu)		555	this work
trans-$(PPh_3)_2Pt(CF_3)H$		448	14
trans-$[(PPh_3)_2Pt(CF_3)(CH_2Cl_2)]BF_4$[d]		775	this work
trans-$(PPh_2Me)_2Pt(CF_3)(OH)$		629	6
trans-$(PPh_2Me)_2Pt(CF_3)(OOH)$		620	3
trans-$(PPh_2Me)_2Pt(CF_3)$(OO-*t*-Bu)		594	3
trans-$(PPhMe_2)_2Pt(CF_3)(OH)$		638	this work
trans-$(PPhMe_2)_2Pt(CF_3)$(OO-*t*-Bu)		623	this work
trans-$(PPhMe_2)_2Pt(CF_3)H$		462	18
trans-$(PPhMe_2)_2Pt(CF_3)(ONO_2)$		795	13
trans-$[(PPhMe_2)_2Pt(CF_3)(acetone)]PF_6$		858	19

[a] Phosphorus trans to oxygen. [b] $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 85% H_3PO_4 as external reference): P(trans to OOH) 32.9 (quintet, such a multiplicity arises from the similarity of $^2J_{P-P}$ with $^3J_{P-F}$), $^1J_{P-Pt} = 3139$, $^2J_{P-P} = {}^3J_{P-F} = 13.6$; P(trans to CF_3) 52.53 (doublet of quartets), $^1J_{P-Pt} = 2223$, $^2J_{P-P} = 13.6$, $^3J_{P-F} = 62.8$. [c] $^{31}P\{^1H\}$ NMR (CD_2Cl_2): P(trans to OO-*t*-Bu) 35.8 (quintet, the same as for *b*), $^1J_{P-Pt} = 3075$, $^2J_{P-P} = {}^3J_{P-F} = 13.6$; P(trans to CF_3) 50.3 (doublet of quartets), $^1J_{P-Pt} = 2213$, $^2J_{P-P} = 13.6$, $^3J_{P-F} = 61.2$. [d] ^{19}F NMR (CD_2Cl_2, $CFCl_3$ as internal reference): −8.73 (triplet), $^3J_{F-P} = 20.4$; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 24.97 (quartet), $^1J_{P-Pt} = 3015$, $^3J_{P-F} = 20.4$.

noticed in the case of cis complexes, in the present case where the two phosphines are trans to each other and both cis to the *t*-Bu moiety, it appears to be more evident. Finally, $^{31}P\{^1H\}$ and, where appropriate, ^{19}F NMR spectra provide unambiguous determination of the proposed geometries.

In Table II, three hydroperoxo complexes are spectroscopically characterized. In addition to the expected spectroscopic features of these compounds, a hitherto unobserved broad signal was detected in the ^1H NMR spectrum of complex **12**. We attribute this signal to the hydroperoxidic proton. Significantly, a $^3J_{H-Pt}$ (5–6 Hz) can be detected which is appreciably smaller than that of the parent hydroxo species ($^2J_{H-Pt} = 21.0$ Hz).[6]

The OOH and OO-*t*-Bu ligands appear to exert a trans influence similar to that of the OH ligand, as can be seen by inspection of $^1J_{P-Pt}$ data for *cis*-$P_2Pt(Rx)(Y)$ type complexes (P_2 = 2 PPh_3, diphoe; Rx = CH_2CN, CF_3; Y = OH, OOH, OO-*t*-Bu) listed in Table III. The values ranging between 3200 and 3500 Hz confirm that the Pt–Y bonds in these complexes have considerable covalent character as suggested by Appleton and Bennett for the (diphos)$Pt(C_6H_9)(OH)$ complex[7] ($^1J_{P-Pt} = 3401$ Hz). Similar arguments from $^2J_{F-Pt}$ data, which lead to the same conclusions, apply to a series of *trans*-$P_2Pt(CF_3)(Y)$ complexes (Table III). Within this context the reliability of parameters relating indirectly bound nuclei has been discussed and confirmed for a series of *trans*-$(PPhMe_2)_2Pt(CF_3)(Z)$ and *trans*-$[(PPhMe_2)_2Pt(CF_3)(L)]^+$ complexes (Z = anionic ligand; L = neutral ligand) by Clark and co-workers.[13] The values observed for hydroxo, hydroperoxo, and *tert*-butylperoxo complexes fall between those reported for opposite homologues, such as strongly covalently bound hydrides and ionic species. It is worth noting that in these complexes, at variance with the previous cis derivatives, the oxygen-bound ligands are trans to CF_3 for which a high trans influence could be expected.[7,13-16] Nevertheless, both the spectroscopic and conductivity data (vide infra) seem to indicate a considerable covalent character for the platinum–oxygen bond.

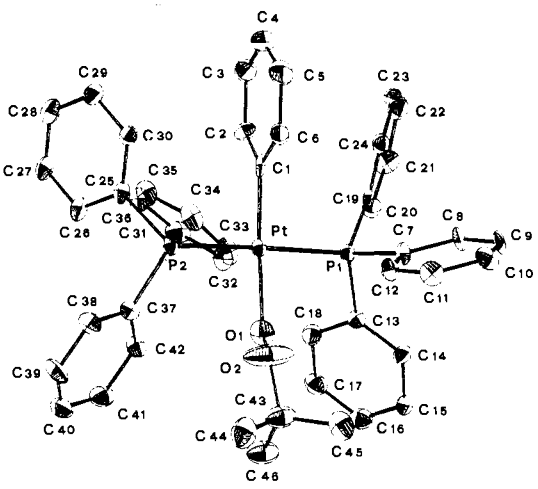

Figure 1. ORTEP drawing of the *trans*-$(PPh_3)_2Pt(Ph)$(OO-*t*-Bu) molecule (thermal ellipsoids of 33% probability).

Table IV. Relevant Bond Lengths (Å) and Angles (deg), with Estimated Standard Deviation in Parentheses[a]

Distances			
Pt-P(1)	2.304 (5)	C(1)-C(2)	1.40 (2)
Pt-P(2)	2.312 (5)	C(2)-C(3)	1.40 (2)
Pt-O(1)	1.99 (1)	C(3)-C(4)	1.34 (3)
Pt-C(1)	1.93 (1)	C(4)-C(5)	1.39 (4)
O(1)-O(2)	1.22 (3)	C(5)-C(6)	1.42 (3)
O(2)-C(43)	1.47 (2)	C(6)-C(1)	1.41 (2)
C(43)-C(44)	1.56 (4)	C-C (phenyls)	1.38 (3)
C(43)-C(45)	1.47 (4)	P-C (av)	1.82 (2)
C(43)-C(46)	1.52 (4)		
Angles			
P(1)-Pt-C(1)	92.0 (5)	C-C(43)-C (av)	110 (2)
P(1)-Pt-O(1)	85.0 (5)	Pt-C(1)-C(6)	122 (1)
P(2)-Pt-C(1)	89.4 (5)	Pt-C(1)-C(2)	126 (1)
P(2)-Pt-O(1)	93.6 (5)	C(2)-C(1)-C(6)	112 (1)
P(1)-Pt-P(2)	178.2 (2)	C(1)-C(2)-C(3)	125 (2)
O(1)-Pt-C(1)	177.0 (8)	C(2)-C(3)-C(4)	122 (2)
Pt-O(1)-O(2)	116 (1)	C(3)-C(4)-C(5)	118 (2)
O(1)-O(2)-C(43)	125 (2)	C(4)-C(5)-C(6)	120 (2)
O(2)-C(43)-C (av)	109 (2)	C(5)-C(6)-C(1)	124 (2)

[a] Esd's of the mean values refer to a single observation.

Description of the Structure of 1. A view of the *trans*-$(PPh_3)_2Pt(Ph)$(OO-*t*-Bu) (**1**) monomer, normal to the coordination plane, together with its atom-numbering scheme is given in Figure 1. Bond lengths and angles are listed in Table IV. The coordination geometry about the Pt(II) center is typically square planar with a negligible displacement (0.017 (2) Å) of the platinum atom from the best plane defined by two trans-coordinated phosphorus atoms, a carbon atom of

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Table V. Oxygenation of 1-Octene with $P_2Pt(Rx)(OOR)$ Complexes[a]

complex	% yield	solvent
trans-$(PPh_3)_2Pt(Ph)(OO$-*t*-Bu)	46	DCE
trans-$(PPh_2Me)_2Pt(Ph)(OO$-*t*-Bu)	38	DCE
trans-$(PBz_3)_2Pt(Ph)(OO$-*t*-Bu)		DCE
trans-$(PPh_3)_2Pt(CF_3)(OO$-*t*-Bu)	80	DCE
trans-$(PPh_2Me)_2Pt(CF_3)(OO$-*t*-Bu)	78	DCE
trans-$(PPhMe_2)_2Pt(CF_3)(OO$-*t*-Bu)	75	DCE
trans-$(PPh_3)_2Pt$(Ph-*o*-CN)(OO-*t*-Bu)	55	DCE
trans-$(PPh_3)_2Pt(Ph)(OO$-*t*-Bu)	16	toluene
trans-$(PPh_3)_2Pt(Ph)(OO$-*t*-Bu)	30	dioxane
trans-$(PPh_3)_2Pt(Ph)(OO$-*t*-Bu)	12	DMF
cis-$(PPh_3)_2Pt(Me)(OO$-*t*-Bu)		DCE
cis-$(PPh_3)_2Pt(Bz)(OO$-*t*-Bu)		DCE
trans-$(PPh_3)_2Pt(Ph)(OOH)$		DCE
trans-$(PPh_3)_2Pt(CF_3)(OOH)$		DCE
trans-$(PPh_2Me)_2Pt(Ph)(OOH)$		DCE
trans-$(PPh_3)_2Pt(Ph)(OO$-*t*-Bu)		DCE[b]

[a] Reaction conditions: $[Pt] = 4.6 \times 10^{-2}$ M; [olefin] = 1.6 M; $T = 80$ °C; time 16 h. [b] $[PPh_3] = 4.6 \times 10^{-2}$ M added.

the coordinated phenyl group, and the terminal oxygen atom of the *tert*-butylperoxo moiety. The trans triphenylphosphine ligands are mutually eclipsed with two trans-opposing phenyl moieties projecting almost perpendicular to the coordination plane. With this configuration the OO-*t*-Bu ligand can be sterically accommodated and may even be allowed a certain conformational flexibility. Indeed, the peroxo moiety is not symmetrically disposed between the trans phosphines, the dihedral angle between the coordination plane and the plane defined by the atoms O(1), O(2), and C(43) being 67.6° and the torsion angle about the O(1)–O(2) bond being 170.4°. As expected, the phenyl ligand is nearly perpendicular to the coordination plane (dihedral angle 85.8°).

The two Pt–P bond lengths of 2.304 (5) and 2.312 (5) Å are equivalent and normal. Unfortunately, the poor quality of the data due to crystal decomposition and the librational disorder of the peroxo group precludes any confident comparison of the more interesting bond lengths and angles in this structure with those reported elsewhere.[8,20,21] However, it is noted that, at this level of accuracy, there does not appear to be a significant trans influence of the phenyl carbon on the Pt–O(peroxo) bond. In view of the poor accuracy of the *t*-BuOO structural parameters, the O–O bond length of 1.22 (3) Å cannot give any reliable information on the peroxidic character of the O–O bond otherwise suggested by the corresponding stretching frequency (890 cm^{-1}).

Having demonstrated in this case that the peroxo moiety is coordinated to the platinum in an end-on, nonbridging manner, we are now attempting to prepare crystals of analogous complexes where the peroxo moiety is more constrained by bulkier flanking groups, with the aim of obtaining an accurate determination of the O–O bond distance.

Oxygenation of 1-Octene. As already reported for complex **4**,[3] all the trans *tert*-butylperoxo complexes of Table I are found to be active in stoichiometric oxygen transfer to 1-octene to give 2-octanone as the only product. This reaction has been already observed by Bregeault and Mimoun[22] for *μ*-*tert*-butylperoxo dinuclear platinum species. Reactions were carried out in a sealed tube at 80 °C, and the yields obtained after 16 h in the individual cases are reported in Table V. Analogous to previous observations,[3] these results provide clear-cut evidence that only *tert*-butylperoxo complexes with a trans geometry are active, whereas cis complexes (**8** and **9**) or hydroperoxo complexes (**10**–**12**) are not. However, it is important to note that hydroperoxo complexes of platinum metals have been recognized to be the reactive intermediates in catalytic oxygenation of olefins in at least a couple of examples involving Ir(III)[23] and Pd(II).[24]

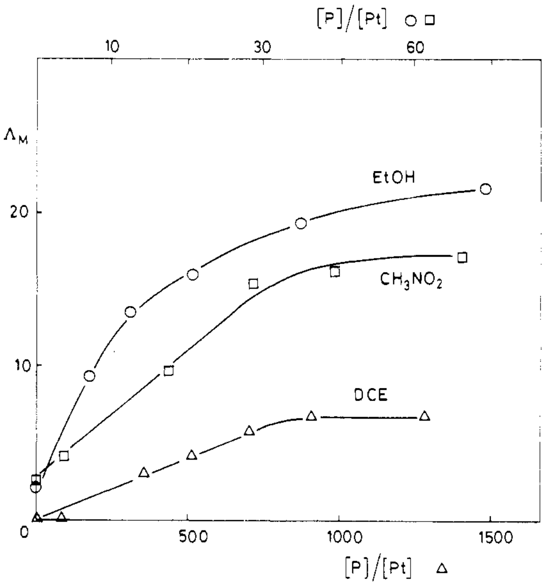

Figure 2. Effect on the molar conductivity of complex **1** in various solvents due to increasing amounts of free PPh_3.

In an attempt to evaluate the factors affecting this oxygen-transfer process, we considered initially the hypothesis of an ionic mechanism (reaction 2), based on the observations

$$trans\text{-}P_2Pt(Rx)(OO\text{-}t\text{-}Bu) \overset{ol}{\rightleftharpoons} [P_2Pt(Rx)(ol)]^+(t\text{-}BuOO)^- \quad (2)$$

made by Arnold and Bennett[4] that *trans*-$P_2Pt(Rx)(OH)$ complexes (P = tertiary phosphine; Rx = Ph, Me) are strong bases in $MeOH/H_2O$ mixtures. These authors also report that an increase in the electron density on the metal due to coordinated alkylphosphines enhances the dissociation capacity of these complexes. Actually, the molar conductivities (10^{-3} M) of *trans*-$(PPh_3)_2Pt(Ph)(OH)$ and *trans*-$(PPh_2Me)_2Pt(CF_3)(OH)$, which are precursors to complexes **1** and **4**, respectively, measured in $MeOH/H_2O$ mixture (9/1 v/v), are 15.0 and 11.2 Ω^{-1} mol^{-1} cm^2, respectively, which correspond roughly to 20% and 13% dissociation.[25] In nitromethane the values observed for all the parent hydroxo complexes are negligible, ranging between 0.5 and 1.1 Ω^{-1} mol^{-1} cm^2. These data are in agreement with previous spectroscopic correlations and indicate that in the $MeOH/H_2O$ mixture solvolytic effects must play a significant role in promoting ionic dissociation.[25] *tert*-Butylperoxo complexes behave similarly in nitromethane, with Λ_M ranging between 0.3 and 2.1 Ω^{-1} mol^{-1} cm^2. Taken as a whole these data suggest that for both hydroxo and *tert*-butylperoxo complexes ionic dissociation at room temperature is negligible from a macroscopic point of view, even in strong donating solvents such as nitromethane.

However, since oxygen-transfer reactions are carried out in the presence of a large excess of olefin (~30/1 = [olefin]/[Pt]), we must consider also the possibility of an ionic dissociation effect, promoted by the presence of an excess of ligand. When free PPh_3 is added to a solution of **1** in various solvents, the increase in conductivity shown in Figure 2 can

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be observed. The leveling effect occurs at Λ_M values corresponding to roughly 20% dissociation in all solvents.[25] It is interesting to note that in solvents like EtOH or nitromethane leveling off is reached at about 40–50 = [P]/[Pt], while in DCE, which is the solvent used in most oxygen-transfer experiments, the same effect requires [P]/[Pt] $\simeq$ 1000. This effect is completely absent in the same solvents when 1-octene is used instead of PPh_3. Moreover, the presence of basic phosphines, a factor that should be expected to increase the ionic dissociation ability of these complexes,[4] has a negligible effect on the yield of the reaction, with the exception of complex **6**, where it is completely suppressed probably because of steric effects.[26] Further evidence against a reaction pathway involving ionic dissociation is provided from solvent effects. As shown in Table V for complex **1**, maximum yield is obtained in DCE, i.e. a low-polarity nondonor solvent, and minimum in DMF. This observation is consistent with metal–olefin bond formation as being the critical step of the process.

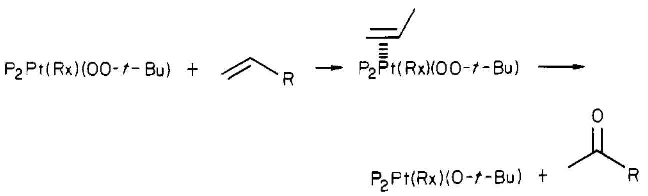
Interaction between the peroxidic moiety and the olefin at the platinum center will require prior coordination of the olefin. This can be achieved with or without phosphine exchange (reaction 3). Attempts to detect the process outlined in

$$trans\text{-}P_2Pt(Rx)(OO\text{-}t\text{-}Bu) \overset{\text{ol}}{\rightleftharpoons} P(ol)Pt(Rx)(OO\text{-}t\text{-}Bu) + P \qquad (3)$$

reaction 3 were always unsuccessful. ^{31}P NMR experiments carried out with complex **1** in the presence of an excess of 1-octene (up to 50/1) in a temperature range between 34 and 75 °C gave no evidence of any exchange process, with no signals corresponding to new species and with P–Pt coupling preserved throughout the experiment.

A simple metal–olefin interaction leading to a five-coordinate intermediate remains to be considered as a plausible mechanism. This interaction has long been recognized to be an important feature also in neutral-ligand exchange on square-planar complexes of platinum(II).[27] Molecular models indicate that, provided the cone angle of the mutually trans phosphines is not too large (as it is the case of PBz_3 cone angle 165° [26]), there is sufficient room along the axis of the plane of the complex to allow olefin coordination. Significantly, the system proved rather sensitive to steric requirements as shown by the inactivity of the PBz_3 derivative (**6**) and by the already noticed[3] olefin-size effect on the yield of the oxygen-transfer reaction with complex **4**. However, electronic effects due to the Rx ligand appear to be equally important (Table V) in that they are responsible for the extent of activation of the O_2 moiety. This is generally considered to be strictly related to the nature of the O–O bond and the electrophilic character of the peroxidic oxygen.[28] From this standpoint the influence of the ligand trans to it becomes very important. In fact, as the electron-withdrawing character of the Rx ligand increases (Ph < Ph-*o*-CN < CF_3), the efficiency of the oxygen-transfer reaction increases (**1** < **7** < **2**). This is in agreement with the benzoyl chloride activation of $(PPh_3)_2PtO_2$ found by Kochi[29] and parallels the reactivity of Mimoun's Pd(II) *tert*-butylperoxo carboxylates.[8]

The oxygenation of organic substrates by group 8 metal peroxo species has been suggested to occur in different manners for different systems by several authors.[8,28,30] For our platinum system all the above experimental results seem to suggest the following reaction pathway as the most plausible for the oxygenation of 1-octene:



Evolution of the five-coordinate intermediate into the final products is likely to occur via a quasi-peroxometallocycle as proposed by Mimoun and co-workers for related systems.[8,22,24] Evidence for the presence of a *tert*-butoxo complex arises from NMR experiments carried out on complex **5** in C_6D_6 in the presence of a large excess (30/1) of 1-octene. After standing for 8 h at 80 °C, the NMR tube (flame sealed) was analyzed. ^{19}F and $^{31}P\{^1H\}$ NMR spectra showed the presence, along with the starting complex (δ_{CF_3} −9.88 (t), $^3J_{F-P}$ = 16.1 Hz, $^2J_{F-Pt}$ = 621 Hz; δ_P 1.05 (q), $^3J_{P-F}$ = 16.1 Hz, $^1J_{P-Pt}$ = 3125 Hz), of a new species of identical phosphorus and fluorine array (δ_{CF_3} −9.77 (t), $^3J_{F-P}$ = 19.0 Hz, $^2J_{F-Pt}$ = 701 Hz; δ_P 0.42 (q), $^3J_{P-F}$ = 19.0 Hz, $^1J_{P-Pt}$ = 3068 Hz). These signals were parallelled in the ^1H NMR spectrum by the growing of a singlet at 1.18 ppm (starting complex 0.95 ppm) and might well be attributed to *trans*-$(PPhMe_2)_2Pt(CF_3)(O\text{-}t\text{-}Bu)$.

Conclusion. The reactivity of these complexes and the reported crystal structure seem to point to their relative inertness toward oxygen-transfer reactions as their most distinctive and somehow unexpected character. On the other hand, we believe that this is also the key for the success of the synthesis of such a wide variety of homologous peroxo species. While more insight into the detailed mechanism with which oxygen transfer occurs is expected from kinetic studies with free phosphines or activated olefins, which are currently under way, synthetic effort must be directed toward the preparation of more coordinatively unsaturated species or derivatives containing different types of peroxidic functional groups (for example organometallic peracids), for which development into novel catalytic oxidations may be more easily predictable.

Experimental Section

Apparatus. IR spectra in Nujol mulls were taken on a Perkin-Elmer 597 spectrophotometer. ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian FT80A spectrometer operating in FT mode, using as references internal Me_4Si or $CFCl_3$ or external 85% H_3PO_4, respectively. Negative chemical shifts are upfield from the reference. GLC measurements were taken on a Hewlett-Packard 5730A gas chromatograph equipped with a 3380A automatic integrator. Identification of products was made with GLC by comparison with authentic samples. Conductivity measurements were made with a Philips PR9500 instrument using 10^{-3} M solutions throughout.

Materials. Solvents were dried and purified according to standard methods. 1-Octene (Aldrich) was purified by passing through neutral alumina, distilled, and stored under N_2 in the dark. Hydrogen peroxide (30%, Hoechst) and *tert*-butyl hydroperoxide (80%, Fluka) were commercial products and were used without purification.

The preparation of new complexes was performed under dry N_2 by using conventional Schlenk and syringe techniques, although all of them were found to be air stable once isolated.

The following compounds were prepared by literature methods: *trans*-$(PPh_3)_2Pt(Ph)(OH)$,[32] *trans*-$(PPh_3)_2Pt(CF_3)(OH)$,[6] *trans*-$(PPh_2Me)_2Pt(Ph)(OH)$,[4] *trans*-$(PPh_3)_2Pt(CF_3)Cl$,[6] (COD)Pt(Ph)Cl,[33] *trans*-$(PPh_3)_2Pt(Me)(OH)$,[32] $(PPh_3)_4Pt$.[34]

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Preparation of *tert*-Butylperoxo Complexes. The general procedures followed have been outlined in ref 3, although a few variations have been necessary in some cases. Numbers in parentheses refer to Tables I and II.

***trans*-[(PPh$_3$)$_2$Pt(Ph)(OO-*t*-Bu)] (1).** *trans*-(PPh$_3$)$_2$Pt(Ph)(OH) (0.25 g, 0.31 mmol) was suspended in a THF/Et$_2$O (1/1, 20 mL) mixture, with stirring, under N$_2$. *t*-BuOOH (0.1 mL, ~1 mmol) was then added. The solid rapidly dissolved, and the solution was stirred for 30 min. The solvent was evaporated in vacuo, and the residue was treated with a Et$_2$O/heptane (1/1) mixture under vigorous stirring. The pale yellow solid was filtered off, washed with heptane, dried in vacuo, and recrystallized from benzene/heptane (yield 78%).

***trans*-[(PPh$_3$)$_2$Pt(CF$_3$)(OO-*t*-Bu)] (2).** *trans*-(PPh$_3$)$_2$Pt(CF$_3$)(OH) (0.50 g, 0.62 mmol) was dissolved in DCE (25 mL) and stirred under N$_2$. *t*-BuOOH (0.2 mL, ~2 mmol) was added and the solution stirred for 30 min. Anhydrous sodium sulfate was then added, and stirring was continued for a further 30 min. The slurry was filtered, and the resultant solution was washed with DCE and concentrated to dryness in vacuo. The solid residue was extracted with Et$_2$O, and the solution was concentrated in vacuo followed by addition of heptane to give a fine pale yellow powder. This was filtered off, washed with heptane, dried in vacuo, and recrystallized from benzene/heptane (yield 60%).

***trans*-[(PPh$_2$Me)$_2$Pt(Ph)(OO-*t*-Bu)] (3).** *trans*-(PPh$_2$Me)$_2$Pt(Ph)(OH) (0.50 g, 0.73 mmol) was suspended in Et$_2$O (15 mL) and stirred under N$_2$. After the addition of *t*-BuOOH (0.15 mL, ~1.5 mmol), the solid dissolved and stirring was continued for 30 min. The solution was concentrated to dryness in vacuo to give a yellow oil. Pentane was added, and the resulting solution was chilled at −78 °C. A white solid precipitated, which was rapidly filtered off and stored at −78 °C (yield 75%).

***trans*-[(PPhMe$_2$)$_2$Pt(CF$_3$)Cl].** This was prepared by ligand exchange in pentane from *trans*-(PPh$_3$)$_2$Pt(CF$_3$)Cl following the procedure outlined in ref 6 and was recrystallized from CH$_2$Cl$_2$/hexane (yield 52%). IR: 280 cm^{-1} ($\nu_{\mathrm{Pt-Cl}}$).

***trans*-[(PPhMe$_2$)$_2$Pt(CF$_3$)(OH)] (13).** This was prepared from *trans*-(PPhMe$_2$)$_2$Pt(CF$_3$)Cl by following the procedure outlined in ref 6 and was recrystallized from benzene/hexane (yield 70%).

***trans*-[(PPhMe$_2$)$_2$Pt(CF$_3$)(OO-*t*-Bu)] (5).** This was prepared in the same manner as **1** in Et$_2$O suspension. Recrystallization from Et$_2$O/pentane was carried out at −10 °C (yield 75%).

***trans*-[(PBz$_3$)$_2$Pt(Ph)Cl].** This was prepared according to the general method outlined by Eaborn et al.[35] and was recrystallized from CH$_2$Cl$_2$/Et$_2$O (yield 92%). IR: 265 cm^{-1} ($\nu_{\mathrm{Pt-Cl}}$).

***trans*-[(PBz$_3$)$_2$Pt(Ph)(OH)] (14).** *trans*-(PBz$_3$)$_2$Pt(Ph)Cl (2.45 g, 2.68 mmol) was suspended in acetone (120 mL). A solution of AgClO$_4$ in acetone (2.8 mL, 1.0 M) was added with stirring. After 2 h AgCl was filtered off, and to the filtrate was added dropwise KOH (0.18 g, 3.2 mmol) dissolved in 10 mL of H$_2$O. The resulting dark mixture was stirred for 2 h and brought to dryness in vacuo. The solid residue was extracted with benzene (150 mL) with vigorous stirring. The slurry was filtered and the pale yellow solution brought to dryness in vacuo, leaving a yellow oil. This was vigorously stirred with a hexane/Et$_2$O (9/1) mixture to yield a white solid, which was filtered, washed with hexane, dried, and recrystallized from benzene/hexane (yield 75%).

***trans*-[(PBz$_3$)$_2$Pt(Ph)(OO-*t*-Bu)] (6).** This was prepared as **5** (yield 60%).

***trans*-[(PPh$_3$)$_2$Pt(Ph-*o*-CN)Br].** (PPh$_3$)$_4$Pt (22.4 g, 18 mmol) and *o*-cyanobromobenzene (7.28 g, 40 mmol) were dissolved in toluene (150 mL) and heated at 100 °C for 100 h with stirring. The yellow-orange solution was cooled to room temperature and dropped into a Et$_2$O/hexane mixture (1/1, 600 mL) with vigorous stirring. The resulting yellow solid was repeatedly recrystallized from CH$_2$Cl$_2$/MeOH and benzene/MeOH to yield a white solid (yield 35%).

***trans*-[(PPh$_3$)$_2$Pt(Ph-*o*-CN)(OH)] (15).** This was prepared as **14** (yield 62%).

***trans*-[(PPh$_3$)$_2$Pt(Ph-*o*-CN)(OO-*t*-Bu)] (7).** This was prepared as **2** but by using benzene in place of DCE (yield 55%).

***cis*-[(PPh$_3$)$_2$Pt(Me)(OO-*t*-Bu)] (8).** This was prepared as **1** from *trans*-(PPh$_3$)$_2$Pt(Me)(OH) (yield 78%).

***trans*-[(PPh$_3$)$_2$Pt(Bz)Cl].** This was prepared from (PPh$_3$)$_4$Pt and benzyl chloride in benzene under reflux (yield 63%). IR: 268 cm^{-1} ($\nu_{\mathrm{Pt-Cl}}$).

Table VI. Crystal Data for *trans*-(PPh$_3$)$_2$Pt(Ph)(OO-*t*-Bu)

a = 20.11 (1) Å
V = 1993.6 Å^3
b = 10.114 (7) Å
space group $P\bar{1}$
c = 12.024 (8) Å
$C_{46}H_{44}O_2P_2Pt$
α = 103.4 (1)°
M_r = 885.8
β = 118.5 (1)°
D_{calcd} = 1.48 g cm^{-3}
γ = 98.5 (1)°
Z = 2
$F(000)$ = 888
μ(Mo Kα, λ = 0.71069 Å) = 38.2 cm^{-1}

Table VII. Final Non-Hydrogen Atom Coordinates (×10^4) for *trans*-(PPh$_3$)$_2$Pt(Ph)(OO-*t*-Bu)

	x	y	z
Pt	2402 (0)	524 (1)	729 (1)
P(1)	2465 (2)	7 (4)	−1182 (4)
P(2)	2336 (2)	969 (5)	2642 (4)
O(1)	1601 (8)	−1392 (14)	−192 (13)
O(2)	1811 (10)	−2314 (18)	261 (24)
C(1)	3193 (8)	2360 (16)	1551 (13)
C(2)	3054 (10)	3625 (15)	1351 (17)
C(3)	3644 (11)	4942 (19)	1959 (19)
C(4)	4407 (13)	5084 (22)	2789 (22)
C(5)	4607 (10)	3873 (24)	3022 (20)
C(6)	4005 (10)	2549 (19)	2407 (17)
C(7)	3206 (9)	−885 (16)	−1043 (14)
C(8)	3533 (11)	−913 (19)	−1843 (18)
C(9)	4080 (12)	−1663 (21)	−1699 (21)
C(10)	4319 (10)	−2335 (20)	−803 (20)
C(11)	3994 (11)	−2325 (21)	−3 (19)
C(12)	3457 (9)	−1570 (18)	−94 (16)
C(13)	1528 (8)	−1216 (15)	−2653 (14)
C(14)	1470 (10)	−2423 (16)	−3540 (15)
C(15)	722 (11)	−3315 (18)	−4621 (16)
C(16)	47 (10)	−2952 (19)	−4808 (17)
C(17)	102 (10)	−1787 (20)	−3928 (18)
C(18)	837 (9)	−912 (18)	−2816 (16)
C(19)	2679 (8)	1466 (15)	−1723 (13)
C(20)	2101 (10)	1683 (17)	−2838 (16)
C(21)	2301 (11)	2857 (19)	−3175 (18)
C(22)	3039 (11)	3824 (18)	−2454 (18)
C(23)	3616 (11)	3592 (19)	−1325 (18)
C(24)	3434 (10)	2407 (18)	−996 (16)
C(25)	2354 (9)	2758 (17)	3382 (14)
C(26)	1650 (10)	3042 (19)	3161 (15)
C(27)	1653 (11)	4430 (21)	3622 (18)
C(28)	2336 (12)	5553 (19)	4342 (18)
C(29)	3048 (11)	5282 (18)	4577 (17)
C(30)	3043 (9)	3912 (16)	4091 (16)
C(31)	3160 (9)	603 (17)	3964 (14)
C(32)	3375 (10)	−571 (19)	3550 (16)
C(33)	3980 (11)	−920 (21)	4553 (20)
C(34)	4373 (11)	−96 (23)	5864 (19)
C(35)	4144 (10)	1018 (21)	6279 (16)
C(36)	3534 (10)	1395 (19)	5328 (16)
C(37)	1460 (9)	−109 (16)	2453 (16)
C(38)	1492 (11)	−403 (21)	3551 (18)
C(39)	814 (11)	−1170 (23)	3419 (20)
C(40)	114 (11)	−1677 (19)	2247 (21)
C(41)	76 (10)	−1417 (20)	1133 (21)
C(42)	757 (9)	−626 (18)	1241 (16)
C(43)	1358 (11)	−3841 (21)	−387 (23)
C(44)	1468 (14)	−4314 (27)	821 (23)
C(45)	1693 (13)	−4620 (26)	−1088 (21)
C(46)	482 (12)	−4068 (24)	−1365 (23)

***cis*-[(PPh$_3$)$_2$Pt(Bz)(OH)] (16).** This was prepared from *trans*-(PPh$_3$)$_2$Pt(Bz)Cl according to the general method outlined in ref 6 (yield 65%).

***cis*-[(PPh$_3$)$_2$Pt(Bz)(OO-*t*-Bu)] (9).** This was prepared as **1** (yield 84%).

***trans*-[(PPh$_3$)$_2$Pt(Ph)(OOH)] (10).** *trans*-(PPh$_3$)$_2$Pt(Ph)(OH) (1.0 g, 1.2 mmol) was suspended in Et$_2$O (30 mL), and a large excess of anhydrous sodium sulfate was added. To the stirring mixture was added dropwise 30% H$_2$O$_2$ (0.3 mL). Stirring was continued for 30 min, pentane was then added, and the solid filtered off. This was extracted several times with DCE (80 mL total) to give a pale yellow solution, from which, after concentration to small volume, a white product was precipitated with Et$_2$O. This was filtered off, washed

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[35] Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1978**, 357.

with Et_2O, dried, and recrystallized from DCE/Et_2O (yield 70%).

***trans*-[$(PPh_2Me)_2Pt(Ph)(OOH)$] (11).** This was prepared according to the general method outlined in ref 3 (yield 75%).

***trans*-[$(PPh_3)_2Pt(CF_3)(OOH)$] (12).** This was prepared as **10** (yield 60%).

X-ray Diffraction Analysis. Crystals of **1**, suitable for X-ray structure determination, were isolated by slowly cooling to −50 °C a solution of the complex in toluene. Cell parameters were determined from Weissenberg and precession photographs and refined with an on-line automatic Siemens diffractometer. Pertinent crystallographic data are given in Table VI.

Three-dimensional intensity data were collected by the $\theta-2\theta$ scan technique using Mo Kα radiation for a maximum 2θ angle of 56°. A gradual decrease in the intensity of one check reflection during the collection of data (to 30% of the original value) indicated a gradual loss of crystallinity with irradiation, and this was also reflected in a change of the physical appearance of the crystal from transparent to opaque. For 3335 independent reflections having $I_o > 3\sigma(I_o)$, the intensities were scaled appropriately and corrected for Lorentz and polarization effects; these were used in subsequent calculations. Absorption corrections were not considered justified in view of the above decomposition and the approximately cubic shape of the used crystal (0.3 × 0.3 × 0.2 mm).

The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares methods.

The final refinement cycles were carried out with anisotropic thermal parameters specified for all non-hydrogen atoms (located by calculation; C–H = 0.98 Å, B = 5 $Å^2$ assumed) included in the least-squares totals. All hydrogen atoms were located on positive regions of the Fourier difference map. The refinement converged at an R value of 0.045. The final thermal parameters for all the atoms were higher than normally encountered, and this probably reflects the instability of the crystal structure to the X-rays. Over and above this, the peroxo group shows signs of limited librational disorder; this is especially evident for the O(2) atom, which has a highly exaggerated thermal motion in the c direction.

The final weighting scheme was $w = 1/(A + F_o + B\,F_o^2)$, where A = 30.2 and B = 0.01 were chosen so as to maintain $w(F_o - F_c)^2$ essentially constant over all ranges of F_o and $(\sin\theta)/\lambda$. All the calculations were done by using the computer programs for X-ray systems.[36] Final atomic parameters are listed in Table VII together with their estimated standard deviations. Hydrogen atom parameters, anisotropic thermal parameters, calculated and observed structure factors, and least-squares planes have been deposited as supplementary material. Atomic scattering factors used were those given in ref 37.

Oxygenation of 1-Octene. In a typical experiment the complex (0.23 mmol), 1-octene (1 mL), and solvent (4 mL) were placed in a thick-walled Carius tube. The system was degassed by several freeze and thaw cycles, saturated with N_2, and flame sealed. The reaction was carried out at 80 °C in an oil bath for 16 h. The tube was cooled, opened, and analyzed with GLC (6-ft UCC on Chromosorb W). Quantitative data were obtained by adding a calibrated amount of 2-octanone.

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Registry No. **1**, 87249-42-1; **2**, 87249-43-2; **3**, 87249-44-3; **5**, 87249-45-4; **6**, 87249-46-5; **7**, 87249-47-6; **8**, 87249-48-7; **9**, 87249-49-8; **10**, 87249-50-1; **11**, 87261-31-2; **12**, 87249-51-2; **13**, 87249-52-3; **14**, 87249-53-4; **15**, 87249-54-5; **16**, 87249-55-6; *trans*-[$(PPhMe_2)_2Pt(CF_3)Cl$], 38438-26-5; *trans*-[$(PBz_3)_2Pt(Ph)Cl$], 87249-56-7; *trans*-[$(PPh_3)_2Pt$(Ph-*o*-CN)Br], 87249-57-8; *trans*-[$(PPh_3)_2Pt(Bz)Cl$], 35569-77-6; *trans*-[$(PPh_3)_2Pt(Ph)(OH)$], 60399-83-9; *t*-BuOOH, 110-05-4; *trans*-$(PPh_3)_2Pt(CF_3)(OH)$, 71588-93-7; *trans*-$(PPh_2Me)_2Pt(Ph)(OH)$, 76316-23-9; *trans*-$(PPh_3)_2Pt(CF_3)Cl$, 71581-10-7; $(PPh_3)_4Pt$, 14221-02-4; *trans*-[$(PPh_3)_2Pt(Me)OH$], 60399-82-8; (COD)Pt(Ph)Cl, 51177-65-2; *trans*-$(PPh_2Me)_2Pt(CF_3)$(OO-*t*-Bu), 79273-02-2; (diphoe)Pt(CF_3)(OOH), 72953-62-9; (diphoe)Pt(CF_3)(OO-*t*-Bu), 79273-00-0; *trans*-[$(PPh_3)_2Pt(CF_3)(CH_2Cl_2)]BF_4$, 87249-59-0; *o*-cyanobromobenzene, 2042-37-7; benzyl chloride, 100-44-7; 1-octene, 111-66-0; 2-octenone, 25512-72-5.

Supplementary Material Available: Listings of H atom coordinates, anisotropic thermal parameters, calculated and observed structure factors, and least-squares planes (16 pages). Ordering information is given on any current masthead page.

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(37) Moore, F. H. *Acta Crystallogr.* **1963**, *16*, 1169.