**Synthesis of the Metal Complexes.** All cobalt complexes were prepared under a nitrogen atmosphere. The yields of the complexes were in the 70–90% range.

**M[β-[18]aneP$_4$O$_2$][BF$_4$]$_2$ (M = Co, Ni).** A solution of the β ligand (0.2 mmol) in 20 mL of THF was added to a hot solution of M(BF$_4$)$_2$·6H$_2$O in 10 mL of EtOH. With the cobalt complex, a pink solid soon separated which was filtered off, washed with THF, and dried. With the nickel complex the solution was evaporated to about 8 mL. Crystals separated which were recrystallized from Me$_2$CO–EtOH. Anal. Calcd for $C_{36}H_{44}P_4O_2B_2F_8Co$: C, 49.97; H, 5.12. Found: C, 49.8; H, 5.4. Calcd for $C_{36}H_{44}P_4O_2B_2F_8Ni$: C, 49.99; H, 5.12. Found: C, 50.0; H, 5.3.

**Co[β-[18]aneP$_4$O$_2$][BPh$_4$]$_2$·2DMF and Ni[β-[18]aneP$_4$O$_2$][BPh$_4$]$_2$.** A solution of CoBr$_2$ (0.2 mmol) in 20 mL of Me$_2$CO was added to a solution of the β ligand (0.2 mmol) in 30 mL of THF. A solution of Na(BPh$_4$) (0.2 mmol) in 10 mL of Me$_2$CO was then added. The resulting suspension was evaporated to about 20 mL, and a 20 mL sample of EtOH was added in order to complete the precipitation. The crystals were filtered off and recrystallized from hot DMF. The nickel complex was prepared in a similar way, but it was recrystallized from Me$_2$CO. Anal. Calcd for $C_{90}H_{98}P_4N_2O_4B_2Co$: C, 73.22; H, 6.69; N, 1.90. Found: C, 72.9; H, 6.8; N, 1.8. Calcd for $C_{84}H_{84}P_4O_2B_2Ni$: C, 75.80; H, 6.37. Found: C, 75.7; H, 6.4.

**M[α-[18]aneP$_4$O$_2$][BPh$_4$]$_2$ (M = Co, Ni).** A solution of M(BF$_4$)$_2$·6H$_2$O (0.2 mmol) in 5 mL of EtOH was added to a hot solution of the α ligand (0.2 mmol) in 100 mL of Me$_2$CO. A solution of Na(BPh$_4$) (0.4 mmol) in 10 mL of Me$_2$CO was added dropwise. The resulting solution was evaporated to about 30 mL, and a 20-mL sample of EtOH was slowly added. Crystals of the complex separated, which were filtered, washed with EtOH, and recrystallized from Me$_2$CO–EtOH. Anal. Calcd for $C_{84}H_{84}P_4O_2B_2Co$: C, 75.80; H, 6.37. Found: C, 75.6; H, 6.3. Calcd for $C_{84}H_{84}P_4O_2B_2Ni$: C, 75.82; H, 6.36. Found: C, 75.6; H, 6.5.

**Technique.** IR spectra, electronic spectra, and magnetic susceptibilities were measured with standard methods. $^{31}$P NMR spectra were recorded at 20 °C on a VARIAN CFT 20 spectrometer operating at 31.19 MHz with proton-noise decoupling and a deuterium lock. The solvent was CDCl$_3$ (Merck, 99.8%) unless otherwise stated. The deuterium frequency of the solvent was used for internal heteronuclear stabilization of the magnetic field. Shifts were referenced against external H$_3$PO$_4$ (85%), upfield shifts being positive. Q-Band powder EPR spectra were recorded with a VARIAN E-9 spectrometer equipped with a VARIAN E-66 cavity.

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**Registry No.** α-[18]aneP$_4$O$_2$, 74783-07-6; β-[18]aneP$_4$O$_2$, 74807-53-7; γ-[18]aneP$_4$O$_2$, 79731-36-5; δ-[18]aneP$_4$O$_2$, 79731-37-6; ϵ-[18]aneP$_4$O$_2$, 79732-81-3; Co[β-[18]aneP$_4$O$_2$][BF$_4$]$_2$, 79733-78-1; Ni[β-[18]aneP$_4$O$_2$][BF$_4$]$_2$, 79682-22-7; Co[β-[18]aneP$_4$O$_2$][BPh$_4$]$_2$, 74776-04-8; Ni[β-[18]aneP$_4$O$_2$][BPh$_4$]$_2$, 79732-94-8; Co[α-[18]aneP$_4$O$_2$][BPh$_4$]$_2$, 74776-02-6; Ni[α-[18]aneP$_4$O$_2$][BPh$_4$]$_2$, 79682-24-9.

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# Preparation and Oxygen-Transfer Properties of Novel Palladium(II) and Platinum(II) Hydroperoxo and Alkylperoxo Complexes

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A series of mononuclear hydroperoxo and *tert*-butylperoxo complexes L$_2$M(Rx)(OOR) (L = $^1/_2$ diphosphine or monophosphine; M = Pd or Pt; Rx = activated alkyl; R = H or *t*-Bu) have been prepared by condensation reactions of L$_2$M(Rx)(OH) with ROOH (R = H or *t*-Bu). While *t*-BuOOH reacts in all the cases tested, with H$_2$O$_2$ the preparation reaction is sensitive to the nature of the alkyl ligand Rx. These compounds behave as typical oxygen-transfer agents, reacting with PPh$_3$, CO, NO, and benzaldehyde. In one case it is possible to oxidize terminal olefins to the corresponding methyl ketones.

## Introduction

The current interest in the synthesis of group 8 transition-metal complexes containing "activated" oxygen is still high, in particular with the aim of achieving cleaner, more convenient routes to oxygenated organic compounds.[2]

A useful concept elucidated recently by Sheldon and Kochi[2a] in reactions of oxygen transfer to olefins is that the principal role of a catalyst is to withdraw electrons from peroxidic oxygens in order to make them more susceptible to attack by nucleophiles such as olefins. Consequently by adding an electrophile such as benzoyl chloride to (PPh$_3$)$_2$PtO$_2$, Chen and Kochi[3] prepared a compound, (PPh$_3$)$_2$Pt(OOCOPh)Cl, stable only at very low temperatures, capable of successfully epoxidizing olefins. On the other hand the presence of an ancillary electron-withdrawing ligand has been found[4] to stabilize the platinum–oxygen σ bond and allowed us the synthesis of stable hydroxo and methoxo complexes of platinum(II).

However, not very much is known about stable hydroperoxo and alkylperoxo species of platinum metals. Except for compounds containing "bio" type ligands like porphyrins or Schiff bases, which have been extensively studied in the last decade, reports on these kinds of compounds include only a few Rh(III) and Co(III) hydroperoxo species[5-7] and Ir(III) alkylperoxo species.[8]

In a preliminary account of this paper,[9] we have reported the synthesis and reactivity of novel hydroperoxoplatinum(II) complexes starting from the corresponding hydroxo species via a route that appears to be of fairly general applicability. More recently Mimoun et al. have prepared[10] tetranuclear

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*t*-BuOOPd(II)-type compounds, which are capable of oxidizing terminal olefins to methyl ketones with selectivities close to 100%.

All these results seem to disclose new aspects in this area of chemistry coupling the existence as stable species of these complexes with the exploitation of the potential oxygen-transfer properties of the –OOR ligand. With the aim of investigating the stability and reactivity of the M–OOR bond we have been prompted to prepare a series of square-planar complexes of general formula *cis*- and *trans*-$L_2M(Rx)(OOR)$ ($L_2$ = 1,2-bis(diphenylphosphino)ethane (diphos) or -ethylene (diphoe), 2 $PPh_3$, 2 $PPh_2Me$; M = Pd, Pt; Rx = $CF_3$, $CH_3$, $CH_2CN$, $CH_2CF_3$; R = H, *t*-Bu) that we describe in this paper.

## Results and Discussion

The general route to the title compounds involves the reaction sequence given by eq 1–5. Reactions 1–4 to the key

$$(PPh_3)_4M + RxX \rightarrow (PPh_3)_2M(Rx)X + 2PPh_3 \quad (1)$$

$$(PPh_3)_2M(Rx)X + L_2 \rightarrow L_2M(Rx)X + 2PPh_3 \quad (2)$$

$$L_2M(Rx)X + Ag^+ \rightarrow [L_2M(Rx)(solv)]^+ + AgX \quad (3)$$

$$[L_2M(Rx)(solv)]^+ + KOH \rightarrow L_2M(Rx)(OH) + K^+ \quad (4)$$

$$L_2M(Rx)(OH) + ROOH \rightarrow L_2M(Rx)(OOR) + H_2O \quad (5)$$

$L_2$ = diphos, diphoe, 2 $PPh_3$, 2 $PPh_2Me$; M = Pd, Pt; Rx = $CF_3$, $CH_2CN$, $CH_2CF_3$; R = H, *t*-Bu; X = halogen

metal hydroxo intermediate are known and have been developed in our laboratory.[4,11] When Rx = $CH_3$, the hydroxo complexes can be prepared according to the method of Appleton and Bennett.[12]

Reaction 5 is generally carried out in THF solution at room temperature and is completed in less than 1 h; the yields of the peroxo complexes of platinum(II) are generally better than those for the corresponding palladium(II) complexes.

*t*-BuOOH was found to react according to reaction 5 in all the cases tested but one. On the other hand for platinum complexes the same reaction when $H_2O_2$ is used seems to be fairly sensitive to the nature of the alkyl ligand bound to the metal. So, for example, in the case of $CF_3$ (reaction 6)

$$(diphoe)Pt(CF_3)(OH) + H_2O_2 \rightarrow (diphoe)Pt(CF_3)(OOH) + H_2O \quad (6)$$

$$(diphoe)Pt(CH_2CN)(OH) + H_2O_2 \nrightarrow \quad (7)$$

$$cis\text{-}(PPh_3)_2Pt(CH_2CF_3)(OH) + H_2O_2 \nrightarrow \quad (8)$$

$$(diphoe)Pt(CH_3)(OH) + H_2O_2 \rightleftharpoons (diphoe)Pt(CH_3)(OOH) + H_2O \quad (9)$$

quantitative amount of the final product can be obtained, whereas for $CH_2CN$ or $CH_2CF_3$ (reactions 7 and 8) the system is unreactive toward $H_2O_2$ and the starting hydroxo complexes can be recovered unaltered. In the case of $CH_3$ (reaction 9) we found an intermediate situation, since an infrared spectrum of the final solid in 1,2-dichloroethane shows two O–H stretchings of roughly equal intensity: one at 3660 $cm^{-1}$ typical[12] of the starting compound and the other at 3530 $cm^{-1}$ attributable to the metal hydroperoxide. These observations suggest that with $H_2O_2$, reaction 5 might be looked at as an acid–base reaction and better described in terms of an equilibrium. This standpoint provides a partial explanation for the observed different behavior of reaction 5, when *t*-BuOOH or $H_2O_2$ is used. In fact while the former is available pure, the latter is always a 30% solution in water.

*trans*-$(PPh_3)_2Pt(CF_3)(OH)$ does not react with either *t*-BuOOH or $H_2O_2$. If an obvious explanation for the former could be the steric incompatibility between a *trans*-bis(triphenylphosphine) derivative and the very bulky *tert*-butyl moiety, the lack of reactivity toward $H_2O_2$ can hardly rely on the same argument.

The (hydroperoxo)platinum complexes $L_2Pt(CF_3)(OOH)$ can be prepared also by a different route starting from the corresponding hydrido derivatives[11] (reaction 10). Reaction

$$L_2Pt(CF_3)H + H_2O_2 \rightarrow L_2Pt(CF_3)(OOH) + H_2 \qquad L_2 = \text{diphos, diphoe, 2 } PPh_2Me \quad (10)$$

10 is slow (see the Experimental Section) and not viable when *t*-BuOOH is used. The presence of $H_2$ was detected by GLC; gas evolution measurements with standard techniques were found not reliable because of the spontaneous decomposition of the excess $H_2O_2$ on standing over long periods at room temperature.

All the MOOR compounds isolated are diamagnetic and air stable in the solid state and can be stored at room temperature for months without any change. They analyze well for the proposed structure, and a selected list of their IR and $^1H$ NMR features is reported in Table I.

Compounds **1–4** show typical O–H stretchings in the 3517–3585-$cm^{-1}$ region, which correspond to a 70–100-$cm^{-1}$ decrease as compared to the parent metal hydroxo complexes. In all of them except **2**, $\nu_{O-O}$ is covered by phosphine absorptions. Analogously with most of the corresponding hydroxo derivatives,[4,11,12] the hydroperoxidic proton in the $^1H$ NMR spectra could not be located in the range $\delta$ +7 to –5, probably because of hydrogen-bonding association.

The *tert*-butylperoxo derivatives (**5–12**) exhibit in the infrared spectra the characteristic peroxidic vibrations $\nu_{O-O}$ as a moderately intense absorption around 890 $cm^{-1}$. Other bands attributable to the *tert*-butyl moiety are observed at 2965–2975 ($\nu_{C-H}$) and 1195–1201 $cm^{-1}$ ($\nu_{C-C}$). In the $^1H$ NMR spectra the signal for the *tert*-butyl group is a sharp singlet at $\delta$ 0.73–0.92. This signal is shifted to higher fields of about 0.3–0.7 ppm as compared to free *t*-BuOOH (1.25 ppm) and the already reported (*tert*-butylperoxo)palladium carboxylates (1.33–1.45 ppm). This shielding effect could be due to the presence of the phenyl rings on the phosphorus cis to the *tert*-butylperoxo moiety. This argument seems to be supported by the further shift to 0.61 ppm in the case of **8**, which is the only compound of this group with a trans geometry, and is in agreement with a similar trend found for the corresponding methoxo complexes.[4]

Other signals characteristic of the phosphines and the individual alkyl group can be detected in $^1H$ NMR spectra (Table I).

To establish unambiguously the geometry of those complexes containing monodentate phosphines (i.e., **4**, **8**, **11**, and **12**) we report also the $^{31}P\{^1H\}$ and $^{19}F$ NMR spectra, which are fully consistent with the proposed geometries (Table II).

Additional evidence for the cis configuration of **11** and **12** is based on the strong infrared band at 555 $cm^{-1}$, assigned to the first overtone of the asymmetric $PC_3$ deformation mode in bis(triphenylphosphine)platinum(II) complexes, as proposed by Mastin.[13]

All these complexes are very easily hydrolyzed in the presence of strong acids:

$$MOOR + HX \xrightarrow{H_2O} ROOH(aq)$$

$$X = p\text{-toluenesulfonate, sulfate, chloride}$$

The liberated ROOH in a metal-free aqueous solution can be titrated by either permanganate or iodometric methods (see Experimental Section).

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**Table I.** Selected IR and $^1$H NMR Features of $L_2M(Rx)(OOR)$ Complexes

| no. | compd | IR, cm$^{-1}$ [a] | $^1$H NMR, δ (*J* in Hz)[b] |
|---|---|---|---|
| 1 | (diphos)Pd($CF_3$)(OOH) | 3585 w ($\nu_{O-H}$) | *c* |
| 2 | (diphoe)Pt($CF_3$)(OOH)[d] | 3517 w ($\nu_{O-H}$), 825 m ($\nu_{O-O}$), 517 w ($\nu_{Pt-O}$) | *c* |
| 3 | (diphos)Pt($CF_3$)(OOH)[d] | 3555 w ($\nu_{O-H}$) | *c* |
| 4 | *trans*-($PPh_2Me)_2Pt(CF_3$)(OOH)[d] | 3520 m ($\nu_{O-H}$)[e] | 2.13 t (Me); $^3J_{H-Pt} = 31.5$, $^2J_{H-P} + {}^4J_{H-P} = 6.7$[c] |
| 5 | (diphos)Pd($CF_3$)(OO-*t*-Bu) | 2970 s ($\nu_{C-H}$, *t*-Bu), 1201 s ($\nu_{C-C}$, *t*-Bu), 892 m ($\nu_{O-O}$)[f] | 0.81 s (*t*-Bu) |
| 6 | (diphoe)Pt($CF_3$)(OO-*t*-Bu) | 2975 s ($\nu_{C-H}$, *t*-Bu), 1201 s ($\nu_{C-C}$, *t*-Bu), 890 m ($\nu_{O-O}$), 520 w ($\nu_{Pt-O}$) | 0.80 s (*t*-Bu) |
| 7 | (diphos)Pt($CF_3$)(OO-*t*-Bu) | 2965 s ($\nu_{C-H}$, *t*-Bu), 1200 s ($\nu_{C-C}$, *t*-Bu), 887 m ($\nu_{O-O}$) | 0.73 s (*t*-Bu) |
| 8 | *trans*-($PPh_2Me)_2Pt(CF_3$)(OO-*t*-Bu) | 2970 s ($\nu_{C-H}$, *t*-Bu), 1195 s ($\nu_{C-C}$, *t*-Bu), 890 m ($\nu_{O-O}$) | 0.61 s (*t*-Bu), 2.13 t (Me); $^3J_{H-Pt} = 30.7$, $^2J_{H-P} + {}^4J_{H-P} = 7.6$ |
| 9 | (diphoe)Pt($CH_2CN$)(OO-*t*-Bu) | 2970 s ($\nu_{C-H}$, *t*-Bu), 1200 s ($\nu_{C-C}$, *t*-Bu), 891 m ($\nu_{O-O}$); 519 w ($\nu_{Pt-O}$), 2210 vs ($\nu_{C-N}$) | 0.92 s (*t*-Bu), 1.36 dd ($CH_2$); $^3J_{H-P} =$ 3.1 (cis), 10.0 (trans), $^2J_{H-Pt} = 79.0$ |
| 10 | (diphoe)Pt($CH_3$)(OO-*t*-Bu) | 2965 s ($\nu_{C-H}$, *t*-Bu), 1198 s ($\nu_{C-C}$, *t*-Bu), 890 m ($\nu_{O-O}$); 521 w ($\nu_{Pt-O}$) | 0.88 s (*t*-Bu), 0.32 dd ($CH_3$); $^3J_{H-P} =$ 2.9 (cis), 7.6 (trans), $^2J_{H-Pt} = 58.5$ |
| 11 | *cis*-($PPh_3)_2Pt(CH_2CF_3$)(OO-*t*-Bu) | 2975 s ($\nu_{C-H}$, *t*-Bu), 1198 s ($\nu_{C-C}$, *t*-Bu), 892 m ($\nu_{O-O}$), 555 m[g] | 0.75 s (*t*-Bu), 1.86 qdd ($CH_2$); $^3J_{H-F} =$ 15.6, $^3J_{H-P} =$ 5.3 (cis), 8.4 (trans), $^2J_{H-Pt} = 75$[h] |
| 12 | *cis*-($PPh_3)_2Pt(CH_2CN$)(OO-*t*-Bu) | 1200 s ($\nu_{C-C}$, *t*-Bu), 890 m ($\nu_{O-O}$), 555 m[g], 2200 vs ($\nu_{C-N}$) | 0.80 s (*t*-Bu), 1.60 dd ($CH_2$); $^3J_{H-P} =$ 4.8 (cis), 9.5 (trans), $^2J_{H-Pt} = 82$ |

[a] IR spectra measured as Nujol mulls. In the 3200–2600-cm$^{-1}$ region hexachlorobutadiene mulls were also tested for the OO-*t*-Bu derivatives. All trifluoromethyl complexes show strong bands due to the $CF_3$ moiety in the 1115–1085 and 1030–975-cm$^{-1}$ regions, partly overlapped with phosphine absorptions. Abbreviations: vs, very strong; s, strong, m, medium; w, weak. [b] Measured at room temperature in $CD_2Cl_2$ with use of $CH_2Cl_2$ as internal reference. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet. [c] OOH resonance could not be located. [d] IR and NMR data from ref 9. [e] 1,2-Dichloroethane solution. [f] Shoulder on phosphine absorption. [g] The presence of this band around 550 cm$^{-1}$ is indicative of a cis geometry for isomers $Pt(PPh_3)_2XY$ according to Mastin's identification method.[13] [h] Partly overlapped with the central signal.

**Table II.** $^{31}P\{^1H\}$ and $^{19}F$ NMR Data[a] for Monophosphine PtOOR Derivatives

| no. | compd | $^{31}P\{^1H\}$[b] | $^{19}F$[c] |
|---|---|---|---|
| 4 | *trans*-($PPh_2Me)_2Pt(CF_3$)(OOH) | 14.20 q; $^1J_{P-Pt} = 3162$, $^3J_{P-F} = 15.0$ | −11.07 t; $^2J_{F-Pt} = 620$, $^3J_{F-P} = 15.0$ |
| 8 | *trans*-($PPh_2Me)_2Pt(CF_3$)(OO-*t*-Bu) | 13.66 q; $^1J_{P-Pt} = 3211$, $^3J_{P-F} = 16.1$ | −10.00 t; $^2J_{F-Pt} = 594$, $^3J_{F-P} = 16.1$ |
| 11 | *cis*-($PPh_3)_2Pt(CH_2CF_3$)(OO-*t*-Bu) | 25.09 Q[d] (trans $CH_2CF_3$); $^1J_{P-Pt} = 2032$, $^2J_{P-P}$, $^4J_{P-F} = 15.9$<br>13.61 d (cis $CH_2CF_3$), $^1J_{P-Pt} = 3470$, $^2J_{P-P} = 15.9$ | −49.10 q[e]; $^3J_{F-Pt} = 153$, $^3J_{F-H} = 15.9$, $^4J_{F-P(trans)} = 15.9$ |
| 12 | *cis*-($PPh_3)_2Pt(CH_2CN$)(OO-*t*-Bu) | 25.92 d (trans $CH_2CN$); $^1J_{P-Pt} = 2284$, $^2J_{P-P} = 14.5$<br>11.60 d (cis $CH_2CN$), $^1J_{P-Pt} = 3362$, $^2J_{P-P} = 14.5$ | |

[a] In ppm, *J* in Hz; solvent $CD_2Cl_2$. Negative chemical shifts are upfield from the reference. Abbreviations: d, doublet; t, triplet; q, quartet; Q, quintet. [b] $H_3PO_4$ (85%) as external reference. [c] $CFCl_3$ as internal reference. [d] The accidental equality of $^2J_{P-P}$ and $^4J_{P-F}$ accounts for the observed quintet instead of the theoretical doublet of quartets. [e] The equality of $^2J_{P-P}$ and $^4J_{F-P}$ gives rise to a quartet instead of a doublet of triplets.

The general preparation method outlined in reaction 5 could in principle be extended to the preparation of *m*-chloroperbenzoate derivatives. However when (diphoe)Pt($CF_3$)(OH) is reacted with *m*-chloroperbenzoic acid, the new product that can be isolated from solution displays carbonyl stretchings (Nujol mull) at 1630 (antisym) and 1348 (sym) cm$^{-1}$, i.e., about 90 cm$^{-1}$ shifted with respect to free *m*-chloroperbenzoic acid (1739, 1710, 1258 cm$^{-1}$).[14] A safe assignment of the peroxidic stretching vibration, $\nu_{O-O}$, was not possible because of the many absorptions of the diphosphine in the 800–900-cm$^{-1}$ region. Compared to a similar compound $(PPh_3)_2Pt(OOCOPh)Cl$ ($\nu_{C-O}$ 1730, 1335 cm$^{-1}$) reported by Chen and Kochi[3] our product differs significantly in the antisymmetric carbonyl stretching. Since decomposition of organic hydroperoxides is a common feature to many transition-metal complexes, in order to establish unambiguously the nature of the isolated compound, we prepared from (diphoe)Pt($CF_3$)(OH) and *m*-chlorobenzoic acid a benzoate derivative, which was found identical (IR) with the product obtained from *m*-chloroperbenzoic acid. It is interesting to notice that, at variance with previously reported platinum alkyls,[15,16] in the present case the peroxy acid does not lead to cleavage of the platinum–carbon σ bond, probably because of the greater stability in the case of fluoroalkyls.[17]

With the aim of preparing more coordinatively unsaturated peroxo species, we attempted also to isolate hydroperoxo and *tert*-butylperoxo derivatives from the known[18] μ-hydroxo complex $[(PPh_3)_2Pt(OH)]_2(BF_4)_2$. However upon reaction with either $H_2O_2$ or *tert*-BuOOH, the starting platinum complex can be recovered unchanged.

A second attempt was made following our previous observation[19] that *trans*-$P_2PtHCl$-type complexes (P = tertiary phosphines) are reactive toward molecular oxygen to give a

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Table III. Oxidation of Olefins with *trans*-$(PPh_2Me)_2Pt(CF_3)(OO\text{-}t\text{-}Bu)$

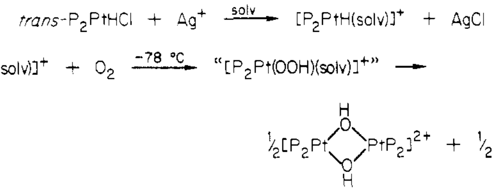
| olefin | product | % yield[a] | reacn time, h |
|---|---|---|---|
| propene | acetone | 72 | 5 |
| 1-hexene | 2-hexanone | 66 | 5 |
| 1-octene | 2-octanone | 37 | 9 |
| cyclohexene | | | 18 |
| allylbenzene | phenylacetone | 11 | 9 |
| cyclooctene | | | 18 |

[a] Based on platinum. For experimental conditions see Experimental Section.

mixture of products containing *cis*-$P_2PtCl_2$, phosphine oxide, water, and unidentified platinum(0) species (reaction 11).

$$trans\text{-}P_2PtHCl \xrightarrow{O_2} cis\text{-}P_2PtCl_2 + O{=}P + H_2O + Pt(0)\text{ species} \quad (11)$$

*trans*-$P_2PtHCl$ complexes can be made coordinatively unsaturated by removing the chloride ligand with silver salts, and from the solvato species stable hydrido olefin complexes have been prepared.[20] We found that when $[P_2PtH(solv)]^+$ compounds ($P = PPh_3$, $PPhMe_2$, $PEt_3$) are reacted with molecular oxygen at −78 °C in THF and the solution is allowed to warm up slowly to room temperature, a clean, quantitative formation of $\mu$-hydroxo $[P_2Pt(OH)]_2{}^{2+}$ complexes can be obtained (reaction 12). These have been identified from their infrared



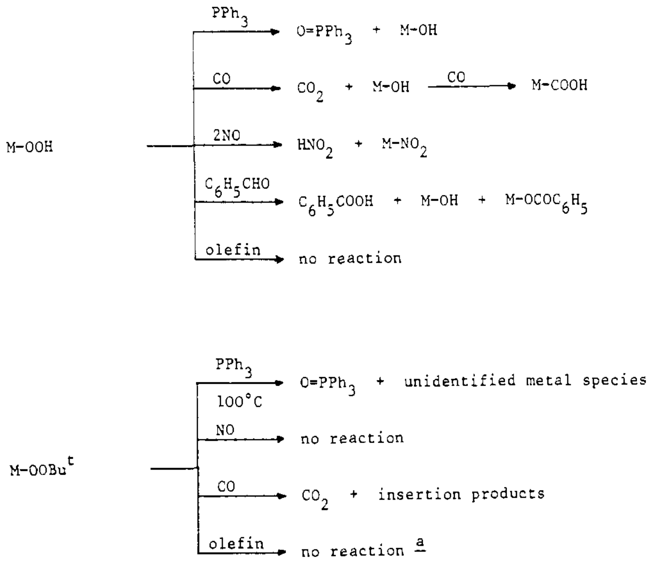
$$trans\text{-}P_2PtHCl + Ag^+ \xrightarrow{solv} [P_2PtH(solv)]^+ + AgCl$$

$$[P_2PtH(solv)]^+ + O_2 \xrightarrow{-78\ ^\circ C} \text{“}[P_2Pt(OOH)(solv)]^+\text{”} \longrightarrow \tfrac{1}{2}[P_2Pt(\mu\text{-}OH)_2PtP_2]^{2+} + \tfrac{1}{2}O_2 \quad (12)$$

spectra by comparison with authentic samples.[18,21,22] The isolation of hydroxo species accounts for the insertion of $O_2$ into the Pt–H bond, producing very reactive hydroperoxo species, which rapidly dimerize probably with elimination of $O_2$. A precedent to this reaction can be found in the catalytic oxidation of 1,5-cyclooctadiene (COD) with $[Ir(COD)HCl_2]_2$ using hydrogen/oxygen mixtures.[23] However when olefins (ethylene, propylene) are added to our system at −78 °C, no organic oxygenation products can be detected in solution after several hours or even after warming up to room temperature. Independently of the presence of olefins $[P_2Pt(OH)]_2{}^{2+}$ complexes are isolated from the reaction mixture.

The main goal for which the above reported hydroperoxo and *tert*-butylperoxo complexes were prepared was to test their oxygen-transfer properties toward olefins. All these compounds, with but only one significant exception (vide infra), were found inactive toward olefins, both linear (1-octene) and cyclic (cyclohexene), in a temperature range varying between 25 and 100 °C. In most cases the starting compound can be recovered unaltered. However when *trans*-$(PPh_2Me)_2Pt(CF_3)(OO\text{-}t\text{-}Bu)$ (**8**) is used, which is the only *tert*-butylperoxo complex prepared with a trans geometry, oxidation of a variety of olefins can be accomplished in toluene solution at 90 °C. Results reported in Table III. As shown, linear terminal olefins are oxidized to the corresponding methyl ketones, which were the only oxidation products found in the reaction mixtures. The reactivity decreases as the olefin size increases, while cyclic olefins are not oxidized at all.

Scheme I



M = Pd, Pt

[a] Except complex 8.

The fact that at 90 °C none of the other complexes used are active for transferring oxygen to terminal olefins seems to point to the trans geometry of complex **8** as the critical factor affecting the process. This fact could be merely incidental; however, *trans*-$P_2PtR(OH)$-type complexes (P = tertiary phosphines; R = Ph, Me) have been found to be strong bases in protic media,[24] owing to the strong trans-labilizing effect of the R ligand, which is enhanced as the phosphine basicity increases. Hence in our system under these experimental conditions, one must consider also the possibility of creating a vacant coordination site via dissociation of the *tert*-butylperoxo moiety to form very tight ion pairs in analogy to what was suggested for the catalytic hydration of nitriles.[24,25] From this standpoint the lack of reactivity of all the other complexes could be accounted either in terms of lack of dissociation or, in the case of *trans*-$(PPh_2Me)Pt(CF_3)(OOH)$, for the known inability of free $HOO^-$ to oxidize olefins. Obviously at this stage this is mostly speculative, and further effort for the synthesis of other *tert*-butylperoxo complexes with a trans geometry will be necessary to corroborate the mechanistic aspects of this process.

The further reactivity of the hydroperoxo and *tert*-butylperoxo compounds prepared is summarized in Scheme I. All reactions were carried out at room temperature under nitrogen atmosphere in THF solution. As it appears, MOOH complexes are more versatile oxygen-transfer agents than the corresponding MOO-*t*-Bu species, the latter being reactive only toward CO at room temperature. However the yield in $CO_2$ is not quantitative with respect to the metal, and from solution a material can be recovered showing carbonyl stretching vibrations around 1540 and 1610 cm$^{-1}$, probably a mixture of insertion products. At variance, with MOOH, complete oxidation to $CO_2$ occurs and further addition of CO to the liberated metal hydroxo species will give the corresponding insertion carboxylates.[4] Analogously nitric oxide is oxidized to coordinated nitrite[26] (IR (Nujol), $NO_2$: 1380–1400 ($\nu_{as}$), 1330–1350 ($\nu_s$), ca. 820 cm$^{-1}$ ($\delta$)), as we already reported for

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Table IV. Analytical Data for New Complexes

| complex | anal. (calcd) found |  | mp, °C dec |
|---|---|---|---|
|  | % C | % H |  |
| (diphos)Pd($CF_3$)(OOH) | (53.43) 52.19 | (4.15) 4.11 | 143–147 |
| (diphoe)Pt($CF_3$)(OOH) | (46.76) 46.73 | (3.34) 3.43 | 167–169 |
| (diphos)Pt($CF_3$)(OOH) | (46.62) 47.05 | (3.62) 3.92 | 164–166 |
| *trans*-($PPh_2Me$)$_2$Pt($CF_3$)-(OOH) | (46.49) 46.23 | (3.90) 3.84 | 106 |
| (diphos)Pd($CF_3$)(OO-*t*-Bu) | (56.16) 55.64 | (5.01) 4.80 | 136–137 |
| (diphoe)Pt($CF_3$)(OO-*t*-Bu) | (49.67) 49.71 | (4.17) 4.10 | 189–190 |
| (diphos)Pt($CF_3$)(OO-*t*-Bu) | (49.54) 49.71 | (4.43) 4.14 | 186–187 |
| *trans*-($PPh_2Me$)$_2$Pt($CF_3$)-(OO-*t*-Bu) | (49.40) 49.30 | (4.68) 4.57 | 124–126 |
| (diphoe)Pt($CH_2CN$)-(OO-*t*-Bu) | (53.33) 52.59 | (4.62) 4.32 | 165–168 |
| (diphoe)Pt($CH_3$)(OO-*t*-Bu) | (54.31) 53.16 | (4.84) 4.69 | 145–153 |
| *cis*-($PPh_3$)$_2$Pt($CH_2CF_3$)-(OO-*t*-Bu) | (56.56) 55.80 | (4.63) 4.80 | 159 |
| *cis*-($PPh_3$)$_2$Pt($CH_2CN$)-(OO-*t*-Bu) | (59.43) 58.01 | (4.87) 4.66 | 162–163 |
| (diphoe)Pt($CF_3$)(MCB)[a] | (50.04) 48.70 | (3.21) 3.37 | 188–190 |
| (diphos)Pt($CF_3$)(MCB)[a] | (49.92) 48.41 | (3.45) 3.54 | 156–157 |
| (diphos)Pd($CF_3$)(MCB)[a] | (55.99) 55.33 | (3.87) 3.72 | 179–181 |
| (diphos)Pd($CF_3$)(OH) | (54.88) 55.16 | (4.26) 4.35 | 144–148 |

[a] MCB = *m*-chlorobenzoate.

platinum,[9] and benzaldehyde to benzoic acid (see Experimental Section).

A direct comparison of the oxidizing ability of these two types of complexes, i.e., MOOH and MOO-*t*-Bu, is provided by the oxidation of $PPh_3$. While the former are active at 25 °C in THF solution, the latter require heating up to 100 °C in pure phosphine.

In conclusion peroxo species of palladium(II) and platinum(II) appear to be stabilized by the presence of a M–C bond in particular by those alkyls that bear in the alkyl chain electronegative substituents. Such a trend has been observed also for the parent hydroxo and alkoxo derivatives.[4] If such a stabilization can be invoked to explain partially the lack of a facile oxygen-transfer ability, however, it does not explain the difference in this effect between hydroperoxo and *tert*-butylperoxo derivatives. This cannot be simply related to the different bulkiness of the two ligands; in fact other factors such as the geometry of the complexes, the nature of the alkyl group, and the type of phosphine used appear to influence the general chemical behavior of these species. If a general conclusion cannot be drawn for the above considerations, it is conceivable that kinetic experiments and X-ray analysis, which are under investigation, may shed some light on this subject.

## Experimental Section

**Apparatus.** IR spectra in Nujol or hexachlorobutadiene mulls were taken on a Perkin-Elmer 597 spectrophotometer. $^1H$ NMR spectra at 90 MHz were recorded on a Varian EM 390 spectrometer with $CH_2Cl_2$ as internal reference; chemical shifts were calculated with the assumption of δ 5.32 as the chemical shift of the reference. $^{31}P\{^1H\}$ and $^{19}F$ NMR spectra at 80 MHz were recorded on a Varian FT 80A spectrometer operating in the FT mode, using external $H_3PO_4$ 85% or internal $CFCl_3$ references, 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. Melting points were taken on a hot-plate apparatus and are uncorrected. Elemental analyses were performed in the Institute of Organic Chemistry of the University of Padua (Table IV).

**Materials.** Solvents were dried and purified according to standard methods. Liquid olefins were purified by passing through neutral alumina and distilled and stored under nitrogen. 30% hydrogen peroxide and *tert*-butyl hydroperoxide were commercial products and were used without purification.

The preparation of new compounds was performed under dry nitrogen with use of conventional Schlenk and syringe techniques, although all of them were found air stable once isolated.

The following compounds were prepared by literature methods: $L_2Pt(Rx)(OH)$ ($L_2$ = diphos, Rx = $CF_3$; $L_2$ = diphoe, Rx = $CF_3$, $CH_2CN$; L = $PPh_3$, Rx = $CH_2CN$, $CH_2CF_3$; L = $PPh_2Me$, Rx = $CF_3$),[4] (diphoe)Pt($CH_3$)(OH),[12] Pd($PPh_3$)$_4$,[27] [($PPh_3$)$_2$Pt($\mu$-OH)]$_2$($BF_4$)$_2$,[22] [($PEt_3$)$_2$Pt($\mu$-OH)]$_2$($BF_4$)$_2$,[21] ($PPh_3$)$_2$PtHCl,[28] ($PPhMe_2$)$_2$PtHCl,[29] ($PEt_3$)$_2$PtHCl.[30]

**Preparation of Hydroperoxo Complexes.** The following general procedure (with a few variations in the individual cases) was followed by starting from $L_2M(Rx)(OH)$. Numbers in parentheses refer to Table I.

**[(diphoe)Pt($CF_3$)(OOH)] (2).** (diphoe)Pt($CF_3$)(OH) (0.5 g, 0.7 mmol) is suspended in $Et_2O$ (100 mL) under $N_2$. 0.25 mL of a 30% solution of $H_2O_2$ is added and the mixture stirred overnight. The white solid is filtered, washed several times with $Et_2O$, dried, and recrystallized from $CH_2Cl_2$/$Et_2O$ (yield 92%).

Alternatively (diphoe)Pt($CF_3$)(OH) (0.5 g, 0.7 mmol) is dissolved in THF (100 mL). 30% $H_2O_2$ (0.25 mL) is added, and the solution is stirred for 1 h, concentrated in vacuo to small volume, and added with $Et_2O$. However the quality of the product is worse and the yield lower (70%).

**[(diphos)Pt($CF_3$)(OOH)] (3).** This compound was prepared in the same manner as **2** and can be recrystallized from $CH_2Cl_2$/$Et_2O$ (yield 87%).

***trans*-[($PPh_2Me$)$_2$Pt($CF_3$)(OOH)] (4).** This compound was prepared in the same manner as **2**. However since it is slightly soluble in $Et_2O$, the reaction is carried out for 4 h and an equal volume of heptane is added before filtering. Recrystallization is from $CH_2Cl_2$/heptane (yield 67%).

An alternative route to the above complexes can be accomplished by starting from the corresponding hydrido complexes[31] and using the same procedure as for **2**. Stirring is prolonged for 5 days.

**[(diphos)Pd($CF_3$)(OOH)] (1).** This compound was prepared in the same manner as **2**. Recrystallization from $CH_2Cl_2$/$Et_2O$ must be done with rigorously purified solvents since the compound hydrolyzes rapidly back to the starting material in the presence of traces of acids (yield 85%).

**Preparation of *tert*-Butylperoxo Complexes.** The general procedure is given for (**6**).

**[(diphoe)Pt($CF_3$)(OO-*t*-Bu)] (6).** (diphoe)Pt($CF_3$)(OH) (0.5 g, 0.7 mmol) is suspended in THF (20 mL) under $N_2$ with stirring. *t*-BuOOH (0.1 mL, 1.0 mmol) is added, and the solid dissolves in a few minutes. Stirring is continued for 30 min. Solvent is evaporated in vacuo, leaving an oily residue, which upon addition of $Et_2O$ precipitates, after vigorous stirring, a white microcrystalline solid. This is filtered, thoroughly washed with $Et_2O$, and dried. Recrystallization is from $CH_2Cl_2$/benzene (yield 90%).

**[(diphos)Pd($CF_3$)(OO-*t*-Bu)] (5), [(diphos)Pt($CF_3$)(OO-*t*-Bu)] (7), [(diphoe)Pt($CH_2CN$)(OO-*t*-Bu)] (9), and [(diphoe)Pt($CH_3$)(OO-*t*-Bu)] (10).** These complexes were prepared with a procedure identical with that used for **6** (yields > 85%).

***trans*-[($PPh_2Me$)$_2$Pt($CF_3$)(OO-*t*-Bu)] (8).** *trans*-($PPh_2Me$)Pt($CF_3$)(OH) (0.5 g, 0.7 mmol) is suspended in $Et_2O$ (20 mL) under $N_2$ with stirring. *t*-BuOOH (0.1 mL, 0.1 mmol) is added, and the solid dissolves in ca. 15 min while stirring is continued for 1 h. Solvent is evaporated in vacuo, and from the oily residue on addition of heptane a white solid precipitates after vigorous stirring. This is filtered, washed with heptane, and dried in vacuo. Care must be taken since the final product is soluble in pentane and hexane (yield 65%).

***cis*-[($PPh_3$)$_2$Pt($CH_2CF_3$)(OO-*t*-Bu)] (11).** This compound was prepared in the same manner as **6**, except that the oily residue must be treated with $Et_2O$/heptane (1/1 v/v) mixtures, since the final product is moderately soluble in $Et_2O$ alone (yield 77%).

***cis*-[($PPh_3$)$_2$Pt($CH_2CN$)(OO-*t*-Bu)] (12).** This compound was prepared in the same manner as **11** (yield 75%).

**Preparation of [(diphos)Pd($CF_3$)(OH)].** This compound was prepared analogously to the corresponding platinum complexes,[4] according to the following route. All the compounds here reported are new.

**[($PPh_3$)$_2$Pd($CF_3$)Br].** Pd($PPh_3$)$_4$ (20 g, 17 mmol) is partially

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dissolved in 400 mL of benzene under $N_2$. The system is evacuated and saturated with $CF_3Br$. After stirring for 2 months at room temperature, the yellow precipitate obtained is filtered, washed with benzene and $Et_2O$, and dried. Recrystallization is from $CH_2Cl_2$/benzene (yield 67%).

**[(diphos)Pd($CF_3$)Br].** $(PPh_3)_2Pd(CF_3)Br$ (9.0 g, 12 mmol) is suspended in a heptane/benzene mixture (10/1 v/v). diphos (4.6 g, 12 mmol) is added solid and the slurry stirred for 3 h. Solvent is then decanted and fresh solvent containing 1.0 g of diphos added. Stirring is continued overnight. The pale yellow solid is filtered, washed several times with heptane, and dried. Recrystallization is from $CH_2Cl_2$/MeOH (yield 95%).

**[(diphos)Pd($CF_3$)Cl].** (diphos)Pd($CF_3$)Br (7.5 g, 12 mmol) is dissolved in $CH_2Cl_2$ (300 mL), and $AgClO_4$ (2.4 g, 12 mmol) is added. The mixture is stirred at room temperature for 3 h. AgBr is filtered off and the filtrate concentrated to dryness. MeOH (150 mL) is added to give a pale yellow solution. On addition of LiCl (0.6 g, 14 mmol) a white solid precipitates, which is filtered, washed several times with $H_2O$ and then small amounts of MeOH and $Et_2O$, and dried. Recrystallization is from $CH_2Cl_2$/MeOH (yield 75%). IR: $\nu_{Pd-Cl}$ 328 $cm^{-1}$.

**[(diphos)Pd($CF_3$)(OH)].** (diphos)Pd($CF_3$)Cl (5.2 g, 8.5 mmol) is dissolved in $CH_2Cl_2$ (300 mL), and $AgClO_4$ (1.8 g, 8.5 mmol) is added. The mixture is stirred at room temperature for 3 h. AgCl is filtered off and the filtrate concentrated to dryness. MeOH (150 mL) is added to give a pale yellow solution. KOH (1.0 g, 18 mmol), dissolved in 4 mL of $H_2O$, is added dropwise with vigorous stirring. The resulting slurry is filtered and the filtrate concentrated to dryness. This is extracted with $CH_2Cl_2$, and traces of silver or palladium metals are filtered off. The solution is concentrated to small volume, and on addition of benzene fine white crystals are obtained. These are filtered, washed with benzene, and dried. Recrystallization is from $CH_2Cl_2$/benzene (yield 60%). IR: $\nu_{O-H}$ 3615 $cm^{-1}$.

**Attempted Preparation of *m*-Chloroperbenzoato Complexes. [(diphoe)Pt($CF_3$)($OCO-C_6H_4$-*m*-Cl)].** (diphoe)Pt($CF_3$)(OH) (0.2 g, 0.3 mmol) is suspended in THF (10 mL) under $N_2$ with stirring. *m*-Chloroperbenzoic acid (0.07 g, 0.4 mmol) is added, giving immediately a clear solution. Stirring is continued for 1 h, solvent is evaporated in vacuo, and the residue is stirred vigorously with $Et_2O$. A white powder is obtained, which is filtered, washed with $Et_2O$, and dried (yield 78%). IR: $\nu_{C-O}$ 1640 (antisym), 1348 (sym) $cm^{-1}$.

When connected with a standard gas-uptake apparatus, the above system evolves 10.4 mL of $O_2$ at 25 °C and 760 mmHg corresponding to 105% of the *m*-chloroperbenzoic acid introduced.

**(diphos)Pt($CF_3$)($OCO-C_6H_4$-*m*-Cl).** This compound was prepared with a procedure identical with that above (yield 82%). IR: $\nu_{C-O}$ 1632 (antisym), 1348 (sym) $cm^{-1}$.

Identical compounds can be obtained from *m*-chlorobenzoic acid.

**Insertion of $O_2$ into the Pt-H Bond.** In a typical experiment $(PEt_3)_2PtHCl$ (0.20 g, 0.42 mmol) and $AgBF_4$ (0.084 g, 0.43 mmol) are placed solid in a Schlenk tube, which is evacuated, filled with $N_2$, and placed in an ice bath. Dry, $N_2$ saturated, cold THF is added (5 mL) and the mixture stirred for 3 h. AgCl is filtered off under $N_2$ and the clear solution placed at −78 °C, degassed, and saturated with $O_2$. The mixture is kept chilled for 30 min and then slowly warmed to room temperature. From the pale yellow solution a white solid precipitates which is filtered, washed with $Et_2O$, dried, and recognized[21] as $[(PEt_3)_2Pt(\mu\text{-}OH)]_2(BF_4)_2$. From the mother liquor a further crop of product can be obtained upon concentration.

Alternatively before addition of $O_2$, the solution can be saturated with ethylene or propylene, kept at −78 °C for 1 day, and then evacuated and saturated with a 1/1 ethylene or propylene/$O_2$ mixture. No organic oxidation product is revealed with GLC, and when the mixture is warmed, $[(PEt_3)_2Pt(\mu\text{-}OH)]_2(BF_4)_2$ precipitates.

Both these procedures can be repeated with both $(PPh_3)_2PtHCl$ and $(PPhMe_2)_2PtHCl$ giving the same results.

**Titration of the Peroxidic Moiety.** A 0.10-g sample of the complex (any) is dissolved in 5 mL of dichloromethane and shaken with 5 mL of a 1 N aqueous solution of HCl for 30 min. To the aqueous layer containing the liberated hydroperoxide is added ca. 0.10 g of KI, and the liberated iodine is titrated with a standard solution of sodium thiosulfate.

Alternatively, only for $H_2O_2$, the acidic aqueous layer is titrated with a standard solution of potassium permanganate.

**Oxygen-Transfer Reactions. With Olefins.** As reported above only *trans*-$(PPh_2Me)_2Pt(CF_3)$(OO-*t*-Bu) was found reactive at 90 °C. In a typical experiment the complex (0.20 g, 0.27 mmol), toluene (4 mL), and the required olefin (1 mL) are placed in a thick-walled Carius tube. The system is degassed by several freeze and thaw cycles, saturated with $N_2$, and flame sealed. The reaction is carried out at 90 °C in an oil bath for the required time according to Table II. The tube is cooled and opened, and the solution is analyzed with GLC.

**With $PPh_3$.** In a typical experiment (diphos)Pt($CF_3$)(OOH) (0.20 g, 0.29 mmol) is dissolved in THF (20 mL). $PPh_3$ (0.075 g, 0.29 mmol) is added and the solution stirred at room temperature under $N_2$ for 3 h. Solvent is removed in vacuo, and the resulting solid is extracted with $Et_2O$ and stirred vigorously. After filtration the white solid is recognized as (diphoe)Pt($CF_3$)(OH)[4] (IR), while the filtrate is brought to dryness yielding $Ph_3P{=}O$ (IR).

The same reaction can be accomplished under identical conditions with all the hydroperoxo complexes here reported.

When *tert*-butylperoxo derivatives are used, the complex and $PPh_3$ are placed without solvent in a Carius tube, which is evacuated and flame sealed. This is heated at 100 °C in an oil bath for 1 h. The tube is cooled and opened, and the solid mixture is extracted with $Et_2O$. From the filtrate $Ph_3P{=}O$ can be recovered. The nature of the metal species was not identified.

**With CO.** In a typical experiment (diphoe)Pt($CF_3$)(OOH) (0.20 g, 0.29 mmol) is dissolved in THF (30 mL). The system is evacuated and saturated with CO. The mixture is stirred at room temperature for 3 h. Bubbling of the gas phase through an aqueous solution of $Ba(OH)_2$ precipitates $BaCO_3$. From the THF solution precipitation of the known[4] (diphoe)Pt($CF_3$)(COOH) complex occurs. Weighing of $BaCO_3$ indicates a yield of >85%.

The same reaction can be accomplished under identical conditions with all the platinum hydroperoxo complexes here reported.

With *tert*-butylperoxo derivatives under the same experimental conditions $CO_2$ is produced in ~10% yields, while from THF precipitation of a white material occurs, probably a mixture of different insertion products, showing IR bands centered around 3650 (w), 2680 (w), 1610 (vs), 1540 (m), and 890 (m) $cm^{-1}$.

**With NO.** In a typical experiment (diphoe)Pt($CF_3$)(OOH) (0.20 g, 0.29 mmol) was suspended in a THF/$Et_2O$ mixture (1/4 v/v, 15 mL). The system is evacuated and saturated with NO. The mixture is stirred at room temperature for 1.5 h. $N_2$ is bubbled through the suspension to remove excess NO. The white solid is filtered, washed with $Et_2O$, dried, recrystallized from $CH_2Cl_2$/MeOH, and recognized[26] as (diphoe)Pt($CF_3$)($NO_2$). IR: $\nu_{NO_2}$ 1395 (antisym), 1337 (sym) $cm^{-1}$; $\delta_{NO_2}$ 820 $cm^{-1}$.

**With Benzaldehyde.** In a typical experiment to (diphoe)Pt($CF_3$)(OOH) (0.24 g, 0.35 mmol) in THF is added benzaldehyde (0.050 mL, 0.50 mmol). The mixture is degassed and kept under $N_2$ with stirring for 3 days. GLC reveals the presence of benzoic acid corresponding to 15% yield. The solution is concentrated in vacuo and $Et_2O$ added; precipitation of a small amount of (diphoe)Pt($CF_3$)(OH) occurs. The filtrate is concentrated to dryness, giving a white solid, which is identified as (diphoe)Pt($CF_3$)(OCOPh), by comparison with an authentic sample obtained from (diphoe)Pt($CF_3$)(OH) and benzoic acid. IR: $\nu_{C-O}$ 1638 (antisym), 1345 (sym) $cm^{-1}$.

The same reaction can be accomplished under identical conditions with all the hydroperoxo complexes here reported.

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**Registry No. 1**, 79272-99-4; **2**, 72953-62-9; **3**, 72953-61-8; **4**, 79355-45-6; **5**, 79299-92-6; **6**, 79273-00-0; **7**, 79273-01-1; **8**, 79273-02-2; **9**, 79255-66-6; **10**, 79255-67-7; **11**, 79255-68-8; **12**, 79255-69-9; (diphoe)Pt($CF_3$)(MCB), 79272-95-0; (diphos)Pt($CF_3$)(MCB), 79272-96-1; (diphos)Pd($CF_3$)(MCB), 79272-97-2; (diphos)Pd($CF_3$)(OH), 79272-98-3; (diphoe)Pt($CF_3$)(OH), 70504-87-9; (diphos)Pt($CF_3$)(OH), 72953-78-7; *trans*-$(PPh_2Me)Pt(CF_3)(OH)$, 71588-94-8; *cis*-$(PPh_3)_2Pt(CH_2CF_3)(OH)$, 71588-95-9; *cis*-$(PPh_3)_2Pt(CH_2CN)(OH)$, 69073-99-0; $(PPh_3)_2Pd(CF_3)Br$, 79272-92-7; (diphos)Pd($CF_3$)Br, 79272-93-8; (diphos)Pd($CF_3$)Cl, 79272-94-9; $Pd(PPh_3)_4$, 14221-01-3; $(PEt_3)_2PtHCl$, 16842-17-4; $(PPh_3)_2PtHCl$, 16841-99-9; $(PPhMe_2)_2PtHCl$, 12112-64-0; $PPh_3$, 603-35-0; CO, 630-08-0; NO, 10102-43-9; benzaldehyde, 100-52-7; (diphoe)Pt($CF_3$)($NO_2$), 79299-90-4; (diphoe)Pt($CF_3$)(OCOPh), 79299-91-5; propene, 115-07-1; 1-hexene, 592-41-6; 1-octene, 111-66-0; cyclohexene, 110-83-8; allylbenzene, 300-57-2; cyclooctene, 931-88-4.