Formation of μ-peroxo–platinum complexes via attack of metallic and related electrophiles at η^2-dioxygen–platinum complexes

Hideo Kurosawa*, Toshio Achiha, Hiroshi Kajimaru and Isao Ikeda
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565 (Japan)

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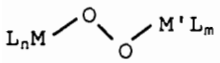
Abstract

Reactions of $PtO_2(PPh_3)_2$ with metallic chlorides or related chlorides L_nMCl in CD_2Cl_2 at -40 °C gave good yields of the corresponding μ-peroxo complexes $Pt(OOML_n)(Cl)(PPh_3)_2$ (2) ($L_nM = Me_3Si$, Ph_3Si, Ph_3Ge, $Ph_2P(O)$, $(PhO)_2P(O)$, $PhS(O)_2$) which were confirmed by ^{31}P NMR measurements. In ^{31}P NMR data of 2, the J(Pt–P) values for PPh_3 *trans* to $OOML_n$ increased as the electron-withdrawing ability of L_nM increased, whereas the J(Pt–P) values for PPh_3 *cis* to $OOML_n$ showed somewhat unusual inverse linear dependency on this ability. Treatment of $PtO_2(PR_3)_2$ with $[Pt_2(\mu\text{-}OH)_2(PR'_3)_4]^{2+}$ afforded μ-peroxo–diplatinum complexes $[(PR_3)_2Pt(\mu\text{-}OO)(\mu\text{-}OH)Pt(PR'_3)_2]^+$ ($R = R' =$ Ph, *p*-tolyl; $PR_3 = PPh_3$; $PR'_3 = PMe_2Ph$, $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$). Complexes 2 containing electron-withdrawing peroxo ligands ($L_nM = Ph_2P(O)$, $(PhO)_2P(O)$, $PhS(O)_2$) oxidized norbornene and cyclohexene to the corresponding epoxides.

Introduction

There is an increasing interest in μ-peroxo–transition metal complexes (A) [1]. However, complexes of the μ-peroxo ligand which bridges heterodimetallic moieties (A; $L_nM \neq L_mM'$) have not been studied as extensively as the homodinuclear μ-peroxo analogues (A; $L_nM = L_mM'$). As far as platinum complexes are concerned, even the latter type complexes received much less attention than



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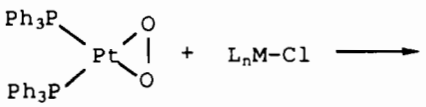
mononuclear dioxygen complexes. Here we describe conversion of the η^2-dioxygen–platinum complex into new dinuclear μ-peroxo complexes containing at least one platinum atom, and compare some of their reactivities with those of the parent dioxygen–platinum complex.

Results and discussion

It is known [2] that coordinated dioxygen of $PtO_2(PPh_3)_2$ (1) has some nucleophilicity; reactions of 1 with acids HX (X = OOCR, OPh, $N(COR)_2$) and alkyl or acyl chlorides gave hydroperoxo and alkyl- or acylperoxo complexes *cis*-$Pt(OOR)(X)(PPh_3)_2$ (R = H, CPh_3, C(O)Ph). We now generated complexes of the μ-peroxo ligand bridging platinum and other metallic or related moieties (2) by a reaction of 1 with the corresponding chlorides (eqn. (1); $L_nM = Me_3Si$, Ph_3Si, Ph_3Ge, $Ph_2P(O)$, $(PhO)_2P(O)$, $PhS(O)_2$). The reaction was performed in CD_2Cl_2 under argon at -40 °C in an NMR tube. The reaction of eqn. (1) was very clean at -40 °C. However, raising the temperature of the NMR solution caused gradual decomposition of 2 even at -10 °C, with the formation of triphenylphosphine oxide and $PtCl_2(PPh_3)_2$ having been confirmed by ^{31}P NMR measurements. Attempts to isolate any of the complexes 2 have so far been unsuccessful.



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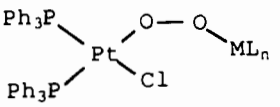

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*Author to whom correspondence should be addressed.

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TABLE 1. ^{31}P NMR spectral data of *cis*-$Pt(OOML_n)(Cl)(PPh_3)_2$ [a]

Complex	L_nM	PPh_3 *trans* to Cl			PPh_3 *trans* to $OOML_n$		
		δ	J(Pt–P)	J(P–P)	δ	J(Pt–P)	J(P–P)
2a	Me_3Si	−122.5	4089	19	−133.3	3189	19
2b	Ph_3Si	−120.8	4130	18	−135.2	3064	18
2c	Ph_3Ge	−120.8	4189	[b]	−134.4	3002	[b]
2d	$Ph_2P(O)$	−120.8	4029	18	−136.7	3236	18
2e	$(PhO)_2P(O)$	−120.2	4015	19	−136.3	3274	19
2f	$PhS(O)_2$	−122.4	3925	18	−136.1	3327	18
	Ph_3C	−120.6	4181	19	−134.6	3059	19
	PhC(O)	−122.1	4031	20	−136.6	3240	20

[a]In CD_2Cl_2. Chemical shifts in ppm, J in Hz. [b]Not observed.

The ^{31}P NMR data of each complex (Table 1) were assigned on the basis of the larger NMR *trans* influence of the oxygen donor ligands than the chloride ligand [3]. In Table 1 the data measured in this study for the isolable peroxo complexes *cis*-$Pt(OOR)(Cl)(PPh_3)_2$ (R = CPh_3, C(O)Ph) [2c, d] are also listed. Similarities of both chemical shifts and J(Pt–P) values between these known complexes and **2** are an additional credence to the above NMR assignments.

A correlation between two J(Pt–P) values for each complex is shown in Fig. 1. It is seen in this Figure that the J(Pt–P) value for PPh_3 which is *trans* to oxygen becomes larger as L_nM becomes more electron-withdrawing, in accord with the general *trans* influence concept in square-planar complexes. Of particular interest is the quite large variation of the J(Pt–P) values for PPh_3 *trans* to the chloride ligand in the reversed direction, a somewhat unusual *cis* influence trend. Usually, the *cis* influences of a series of ligands are not as regular as their *trans* influences or give rise to a change of NMR parameters in a parallel direction with, and, moreover, to a much smaller extent than the latter influences [4].

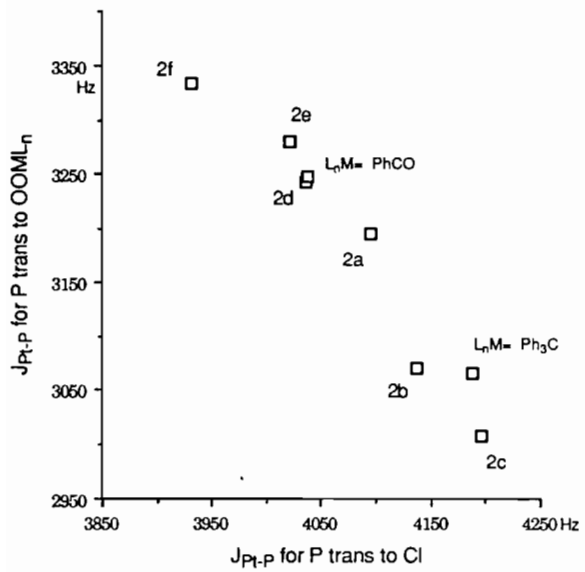
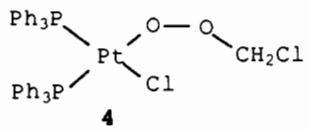


Fig. 1. Relation between two J(Pt–P) values for *cis*-$Pt(OOML_n)(Cl)(PPh_3)_2$; L_nM = Me_3Si (**2a**), Ph_3Si (**2b**), Ph_3Ge (**2c**), $Ph_2P(O)$ (**2d**), $(PhO)_2P(O)$ (**2e**), $PhS(O)_2$ (**2f**), PhCO and Ph_3C.

Analogous reactions of **1** with tin compounds R_3SnCl (R = Me, Et, Ph) gave much more complex spectral features where no ^{31}P NMR signals assignable to **2** (L_nM = R_3Sn) could be detected. Among several ^{31}P resonances were those due to *cis*-$PtCl_2(PPh_3)_2$ and a μ-peroxo–diplatinum cation $[Pt_2(\mu\text{-}OO)(\mu\text{-}OH)(PPh_3)_4]^+$ (**3a**) [5] in varying amounts depending on the nature of the tin compounds and the degree of purification of the solvent. This diplatinum cation was the major product (>80%) in the reaction of **1** with Me_3SnCl in moist CD_2Cl_2.

At this stage it seems appropriate to point out that the ^{31}P NMR data of **3a** (δ relative to *cis*-$PtCl_2(PPh_3)_2$: −7.8(d, J_{Pt} = 4497 Hz, J_P = 21 Hz) and −4.8(d, J_{Pt} = 3032 Hz)) are quite the same as the ^{31}P NMR data which Sherrer *et al.* previously assigned [6] as due to the complex **4** (δ relative to *cis*-$PtCl_2(PPh_3)_2$: −8.0(d, J_{Pt} = 4493 Hz, J_P = 20 Hz) and −4.8(d, J_{Pt} = 3017 Hz)), formed in up to 50% yield by allowing a CH_2Cl_2 solution of **1** to stand at room temperature for 3 days in the dark. However, their spectral data for the presumed complex **4** are very



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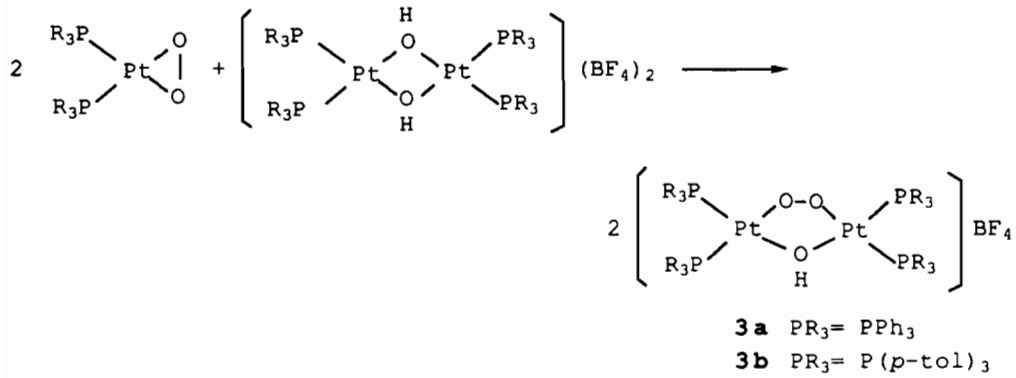
different from those for the complexes **2** and, in particular, *cis*-$Pt(OOCPh_3)(Cl)(PPh_3)_2$, these being similar in structure to **4**; in their data for '**4**' the higher field ^{31}P resonance exhibited the larger J_{Pt}



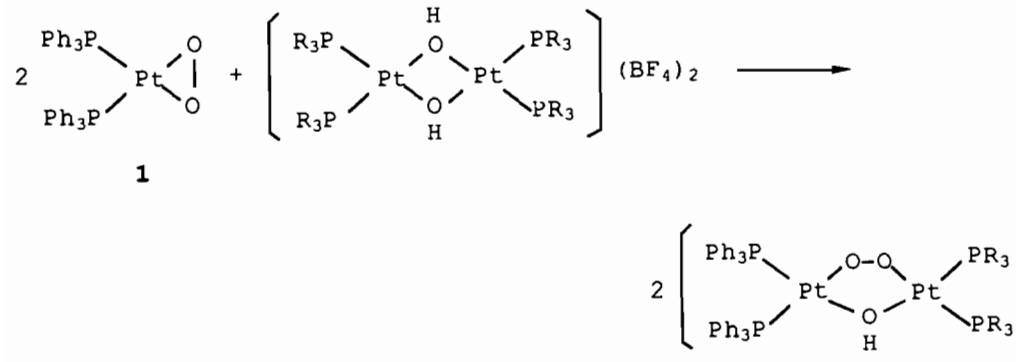
3a PR_3= PPh_3
3b PR_3= P(*p*-tol)$_3$

value, while in those shown in Table 1 it is the lower field ^{31}P resonances that show the larger J_{Pt} values. It then may well be that actually Scherrer *et al.* have obtained the cation **3a** by the reaction of **1** with H_2O (see below) contained in the CH_2Cl_2 solution.

It seems of interest to note that **1** reacted with another potentially strong electrophile $[Pt_2(\mu\text{-}OH)_2(PPh_3)_4](BF_4)_2$, giving rise to the above-mentioned μ-peroxo–diplatinum complex **3a** (eqn. (2); R = Ph). This reaction performed in CD_2Cl_2 at 25 °C was rather slow (*c.* 80% yield after 0.5 h), but almost quantitative after *c.* 2 h. The reaction was applied to a successful preparation of the *p*-tolylphosphine analogue $[Pt_2(\mu\text{-}OO)(\mu\text{-}OH)(P(p\text{-}tol)_3)_4]BF_4$ (**3b**). Previously, the salt of type **3a** was prepared by treatment of **1** with an acid in alcohol/CH_2Cl_2 or with $NaBPh_4$ in alcohol [5]. However, these methods applied to the *p*-tolylphosphine analogue, $PtO_2[P(p\text{-tol})_3]_2$, led to formation of only the μ-hydroxo dimer, $[Pt_2(\mu\text{-}OH)_2(P(p\text{-tol})_3)_4]^{2+}$ [5]. A possible origin of this difference in the efficiency of isolation of **3a** and **3b** from the reaction of **1** and its *p*-tolylphosphine analogue with H_2O would be related to the effect of the phosphine ligand in $[Pt_2(\mu\text{-}OH)_2(PR_3)_4]^{2+}$ upon the reaction of these with H_2O_2, as described later on.

We further found that unsymmetrical μ-peroxo–diplatinum complexes **3c** and **3d** can be generated by a reaction analogous to eqn. (2) in $CDCl_3$ (eqn. (3); both *c.* 80% yields), as confirmed by ^{31}P NMR measurements. In these reactions, however, concomitant formation of the corresponding symmetrical μ-peroxo complexes **3a** and $[Pt_2(\mu\text{-}OO)(\mu\text{-}OH)(PR_3)_4]^+$ (*c.* 10%) was inevitable.

We also found that treatment of $[Pt_2(\mu\text{-}OH)_2(PR_3)_4]^{2+}$ with excess H_2O_2 (in the form of $N(CH_2CH_2)_3N$ salt) in CD_2Cl_2, but not in $CDCl_3$, afforded complexes of the type **3** (eqn. (4)). Table 2 summarizes ^{31}P NMR data for some μ-peroxo–diplatinum complexes.



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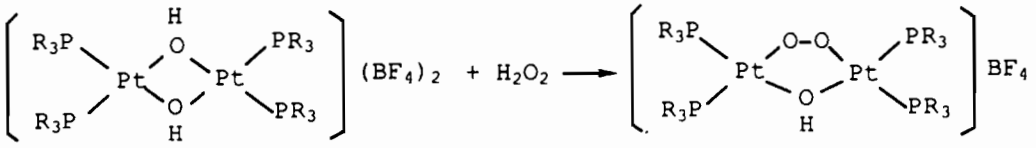
3c PR_3= PMe_2Ph

3d PR_3= 1/2 $Ph_2PCH_2CH_2PPh_2$



3a PR_3= PPh_3
3b PR_3= $P(p\text{-tol})_3$
3e PR_3= $P(p\text{-}C_6H_4Cl)_3$
3f PR_3= $1/2Ph_2PCH_2CH_2PPh_2$

(4)

TABLE 2. ^{31}P NMR spectral data of **3**[a]

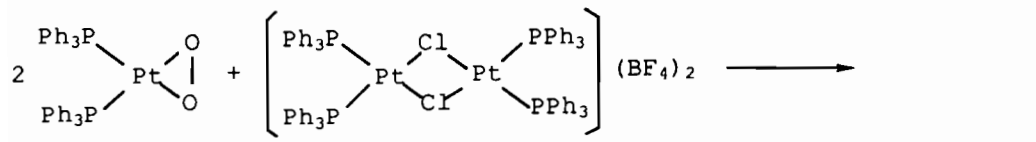
Complex	PR_3 *trans* to O–O			PR_3 *trans* to OH		
	δ	J(Pt–P)	J(P–P)	δ	J(Pt–P)	J(P–P)
3a	−134.3	3032	21	−137.3	4497	21
3b	−136.4	3010	21	−138.9	4482	21
3c[b]	−132.0	2998	21	−140.1	4383	21
	−165.2	2884	21	−164.1	4123	21
3d[b]	−132.0	3043	23	−138.2	4397	23
	−112.9	2873	9	−116.4	4230	9
3e	−135.9	3073	21	−139.5	4487	21
3f	−112.0	2875	7	−115.2	4212	7

[a]In CD_2Cl_2 except as noted. Chemical shifts in ppm, J in Hz. [b]In $CDCl_3$.

Interestingly, in the reaction of the μ-dihydroxo cations of the type $[Pt_2(\mu\text{-}OH)_2(L)_4]^{2+}$ with H_2O_2 the nature of the ligand L plays a crucial role in determining the course of the reaction. Thus, the yield of **3** in eqn. (4) was dependent on the nature of PR_3: $P(p\text{-}C_6H_4Cl)_3$ (100%) > PPh_3 (90%) > $P(p\text{-tol})_3$ (56%) > $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$ (16%) > PMe_2Ph (0%).

In the low yield cases the main product was R_3PO. On the other hand, analogous treatment of $[Pt_2(\mu\text{-}OH)_2(amine)_4]^{2+}$ with H_2O_2 was reported to result in oxidation of platinum to generate platinum (IV) complexes $[Pt_2(OH)_4(\mu\text{-}OH)_2(amine)_4]^{2+}$ [7]. Judging from the successful generation of the μ-peroxo–diplatinum cations containing the electron-donating phosphine ligands, **3c** and **3d**, according to eqn. (3), we suggest that the low efficiency of the reaction of eqn. (4) in the case of $PR_3 = PMe_2Ph$ and $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$ is not a thermodynamic consequence but a kinetic one. It is possible that the reaction of $[Pt_2(\mu\text{-}OH)_2(PR_3)_4]^{2+}$ containing the electron-donating phosphine ligands with H_2O_2 proceeded via initial oxidation of the platinum atom as in the amine complexes, followed by the phosphine oxidation.

Attempts were also made to generate μ-peroxo–μ-chloro–diplatinum complex **5** by reacting **1** with the μ-chloro dimer $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4](BF_4)_2$ in CD_2Cl_2 at room temperature (eqn. (5)). The ^{31}P NMR measurements showed disappearance of the resonances due to **1** and the chloride dimer and appearance of new peaks assignable to **5** (*c.* 40%), with the rest of the complexes existing as **3a** and the μ-hydroxo dimer $[Pt_2(\mu\text{-}OH)_2(PPh_3)_4]^{2+}$ in *c.* 50% total yields. ^{31}P NMR measurements also showed that **5** was formed in *c.* 40% yield when **3a** was treated with $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4](BF_4)_2$ (eqn. (6)).



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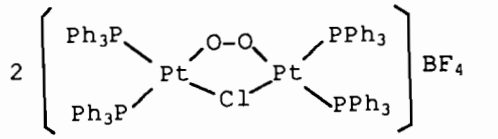

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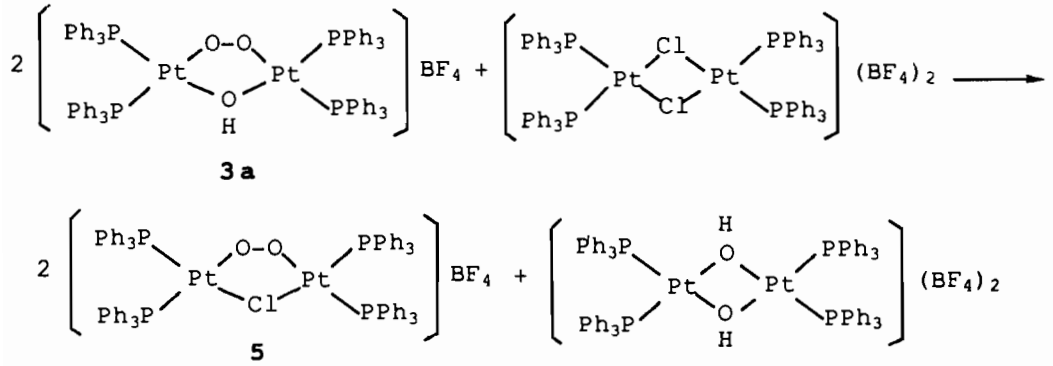

3a

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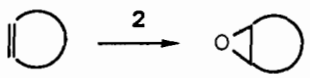
Complex **5** was also generated on treatment of the dimer $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4](BF_4)_2$ with H_2O_2 (*c.* 40% yield), with other products identified as $PtCl_2(PPh_3)_2$ (20%), $[Pt_2(\mu\text{-}OH)_2(PPh_3)_4]^{2+}$ (10%) and Ph_3PO (5%).

In contrast to the unreactive nature of **1** toward simple olefins, some of the μ-peroxo complexes **2** ($L_nM = Ph_2P(O)$, **2d**; $PhS(O)_2$, **2f**) oxidized cyclohexene and norbornene in CH_2Cl_2 at -80 to 25 °C to give the corresponding epoxides (eqn. (7); with **2d**, 15% and 47% yields, respectively; with **2f**, 2% and 5% yields, respectively). It is essential for this oxidation to be realized that the olefin be kept in contact with **2** at the moment of its generation at a low temperature (see 'Experimental'), for adding the olefin to a solution of **2** after this solution had been warmed to room temperature did not result in effective oxidation reaction. Species formed by decomposition of **2** at higher temperatures may not be effective in this respect.



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The complex **2e** ($L_nM = (PhO)_2P(O)$) also oxidized norbornene to the epoxide (6%), but no oxidation of cyclohexene with this complex occurred. The oxidizing ability of **2d** is comparable to that of $Pt(OOCOPh)(Cl)(PPh_3)_2$ reported previously [2d]. It seems of interest to note that all of these complexes that oxidized the olefin contain the electron-withdrawing group $OOML_n$, and consistently showed, in ^{31}P NMR spectra (Table 1), the J(Pt–P) values for the phosphine *trans* to the $OOML_n$ group larger than those of the other complexes (>3200 Hz). The complex **3a** was found inert to cyclohexene and *p*-benzoquinone, the latter having been reported to react with **1** to give a five-membered cycloadduct [8]. Attempts to activate the μ-peroxo ligand in **3a** for olefin oxidation by treating this complex with PhCOCl were unsuccessful.

Experimental

General information

^{31}P NMR spectra were obtained on a JEOL GSX-400 spectrometer, with chemical shifts being reported relative to external $P(OMe)_3$. GLC analyses were performed on a Hitachi 263-50 (TCD) chromatograph. Dichloromethane was dried over CaH_2. Commercially obtained starting materials were used without further purification. Complexes $PtO_2(PPh_3)_2$ (**1**) [9] $[Pt_2(OH)_2(PPh_3)_4][BF_4]_2$ [10], and $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ [11] were prepared by known methods.

General procedure for the generation of cis-$Pt(OOML_n)(Cl)(PPh_3)_2$ (2)

All manipulations and reactions were carried out under an argon atmosphere. To a solution of **1** (0.045 g; 0.06 mmol) in CD_2Cl_2 (3 ml) contained in an NMR tube fitted with a serum cap was added slowly a solution of metal chloride (1 equiv.) in CH_2Cl_2 (1 ml) at -80 °C by a hypodermic syringe. The reaction was monitored by measuring the ^{31}P NMR spectra at -40 °C. The formation of **2** was in most cases almost quantitative, with a small amount (up to 10%) of $PtCl_2(PPh_3)_2$ having been confirmed in some cases. The spectral data are shown in Table 1.

Preparation of $[Pt_2(OH)_2(P(p\text{-}tol)_3)_4][BF_4]_2$

A solution of silver tetrafluoroborate (0.10 g, 0.46 mmol) in acetone (3 ml) was added to a stirred solution of *cis*-$PtCl_2(P(p\text{-}tol)_3)_2$ (0.20 g, 0.23 mmol) in moist acetone (20 ml). White solids separated immediately. After 1 h, AgCl was filtered off. Addition of diethyl ether to the filtrate gave white precipitates. Yield 0.04 g (19%); m.p. 260–275 °C dec. ^{31}P NMR

($CDCl_3$): δ −135.6 (s, J(Pt–P) = 3741 Hz). *Anal.* Calc. for $C_{84}H_{86}B_2O_2F_8P_4Pt_2$: C, 55.58; H, 4.78. Found: C, 55.26; H, 4.48%.

Preparation of $[Pt_2(OH)_2(PMe_2Ph)_4][BF_4]_2$

The initial procedure was the same as that described above starting from 0.20 g (0.37 mmol) of *cis*-$PtCl_2(PMe_2Ph)_2$ and $AgBF_4$ (0.16 g; 0.74 mmol). After AgCl was filtered off and the filtrate was concentrated to dryness, the residual oil was dissolved in CH_2Cl_2. This solution was filtered again. After all the solvents were removed, the resulting white solids were dissolved in a small portion of methanol. A large portion of diethyl ether was added to the solution and it was allowed to stand for several hours in a refrigerator to give colorless crystals. Yield 0.15 g (71%); m.p. 193–202 °C dec. ^{31}P NMR ($CDCl_3$): δ −158.9 (s, J(Pt–P) = 3541 Hz). *Anal.* Calc. for $C_{32}H_{46}B_2O_2F_8P_4Pt_2$: C, 33.41; H, 4.03. Found: C, 33.11; H, 4.10%.

Preparation of $[Pt_2(OH)_2(dppe)_2][BF_4]_2$

The initial procedure was the same as that described above. Crude white solids were recrystallized from methanol and diethyl ether in a refrigerator to give colorless needles. Yield 62%; m.p. 216–225 °C dec. ^{31}P NMR ($CDCl_3$): δ −107.7 (s, J(Pt–P) = 3614 Hz). *Anal.* Calc. for $C_{52}H_{30}B_2O_2F_8P_4Pt_2$: C, 44.78; H, 3.61. Found: C, 44.04; H, 3.98%.

$[Pt_2(OH)_2(P(p\text{-}C_6H_4Cl)_3)_4][BF_4]_2$

This complex was prepared similarly. However, due to gradual decomposition in solution, it is advisable to cause precipitation of the product as quickly as possible by decreasing the volume of the filtrate from the reaction of $PtCl_2((P(p\text{-}C_6H_4Cl)_3)_2$ and $AgBF_4$ in moist acetone. Yield 15%; m.p. 257–265 °C. ^{31}P NMR ($CDCl_3$): δ −135.0 (s, J(Pt–P) = 3791 Hz). *Anal.* Calc. for $C_{72}H_{50}B_2O_2F_8P_4Cl_{12}Pt_2$: C, 41.97; H, 2.45. Found: C, 41.37; H, 2.49%.

Reaction of $[Pt_2(OH)_2(PPh_3)_4][BF_4]_2$ with 1

To an orange solution of **1** (0.0114 g, 0.0131 mmol) in CD_2Cl_2 (0.6 ml) in an NMR tube was added solid $[Pt_2(OH)_2(PPh_3)_4][BF_4]_2$ (0.0114 g, 0.0069 mmol). The reaction mixture changed into a light yellow solution. Then its ^{31}P NMR spectra were examined at appropriate intervals. An NMR yield (based on **1**) of $[Pt_2(O_2)(OH)(PPh_3)_4][BF_4]$ (**3a**) was almost 100% after *c.* 2 h. Reactions of **1** with $[Pt_2(OH)_2(PR_3)_4][BF_4]_2$ (PR_3 = PMe_2Ph, $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$) were carried out similarly.

Preparation of $[Pt_2(O_2)(OH)(P(p\text{-}tol)_3)_4][BF_4]$ (3b)

To a solution of $PtO_2(P(p\text{-tol})_3)_2$ (0.101 g, 0.121 mmol) in $CHCl_3$ (1.5 ml) was added solid $[Pt_2(OH)_2(P(p\text{-tol})_3)_4][BF_4]_2$ (0.110 g, 0.061 mmol). The reaction mixture became light yellow immediately, and the solution was stirred for 4 h. After filtration, the filtrate was concentrated to dryness to give oily yellow precipitates. Recrystallization from toluene–diethyl ether gave yellow crystals. Yield 0.039 g (18.5%); m.p. 182.5–187.5 °C dcc. ^{1}H NMR (CD_2Cl_2): δ 2.3 and 2.4 (br s, 36H, methyl), 6.9–7.3 (m, 48H, aromatic). *Anal.* Calc. for $C_{84}H_{85}B_1O_3F_4P_4Pt_2$: C, 57.87; H, 4.91. Found: C, 57.92; H, 4.95%.

General procedure for the reaction of $[Pt_2(OH)_2(PR_3)_4][BF_4]_2$ with $N(C_2H_4)_3N\cdot H_2O_2$

To a solution of $[Pt_2(OH)_2(PR_3)_4][BF_4]_2$ (0.003 mmol) in CD_2Cl_2 (0.6 ml) in an NMR tube was added solid $N(C_2H_4)_3N\cdot H_2O_2$ [12] (20 equiv.) at room temperature. The tube was shaken vigorously for a short period (*c.* 10 min). The color changed to light yellow. After 10 min the ^{31} P NMR spectra were measured.

Generation of $[Pt_2(\mu\text{-}OO)(\mu\text{-}Cl)(PPh_3)_4][BF_4]_2$

A mixture of **3a** (0.0097 g, 0.0061 mmol) and $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ (0.0051 g, 0.0030 mmol) was dissolved in CD_2Cl_2 (0.6 ml). The ^{31}P NMR spectra taken at 24 h after the dissolution showed the existence of $[Pt_2(OH)_2(PPh_3)_4]^{2+}$ (0.0026 mmol) and Ph_3PO (0.0025 mmol), together with the peaks assignable to **5** (0.0025 mmol; 41%): ^{31}P NMR: δ −140.0 (d, J_P = 18 Hz, J_{Pt} = 3705 Hz), −125.2 (d, J_P = 18 Hz, J_{Pt} = 3870 Hz). Alternatively, to a CD_2Cl_2 solution (1 ml) of $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ (0.007 g, 0.0042 mmol) was added under argon a CD_2Cl_2 solution (1 ml) of **1** (0.069 g; 0.0079 mmol) drop by drop. ^{31}P NMR measurements showed the formation of **5** (40%), together with **3a** (20%) and $[Pt_2(OH)_2(PPh_3)_4]^{2+}$ (30%). Complex **5** also formed (40%) when $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ (0.034 g, 0.020 mmol) in CD_2Cl_2 (3 ml) was treated with solid samples of $N(C_2H_4)_3N\cdot H_2O_2$ (0.003 g; 0.02 mmol). The color changed from pale-yellow to yellow. Other products identified included $[Pt_2(OH)_2(PPh_3)_4]^{2+}$ (10%), $PtCl_2(PPh_3)_2$ (20%) and Ph_3PO (5%).

Oxidation of olefins with 2

In a typical procedure, a mixture of **1** (0.084 g; 0.0966 mmol) and cyclohexene (1 mmol) together with toluene (5.3 μl) as the GLC internal standard was dissolved in CH_2Cl_2 (1 ml) under argon in a test tube fitted with a serum cap, and the solution cooled at −78 °C. To this solution was added $Ph_2P(O)Cl$ (0.097 mmol) dissolved in CH_2Cl_2 (1 ml) with a hypodermic syringe. The reaction mixture was kept at this temperature for *c.* 5 min. After the cold

bath was removed, the reaction mixture was allowed to stand until the solution temperature reached almost room temperature. The reaction mixture was examined by GLC (SE-30/uniport B-10%, 2 m stainless column). In the case of the oxidation of norbornene, *m*-xylene was used as the GLC standard.

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