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A HYDROPEROXORHODIUM COMPLEX: OXIDATION OF THE COORDINATED TRIPHENYLPHOSPHINE

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Summary

A novel hydroperoxorhodium complex, $(Ph_3P)_2(acac)ClRhOOH$, has been prepared by treatment of the peroxorhodium complex $(Ph_3P)_3ClRh(O)_2$ with acetylacetone (acacH) in benzene. The stretching vibration of the O–O bond is proven to appear at 813 cm^{-1} by comparison with that of the $^{18}O_2$-labeled complex. The hydroperoxorhodium complex decomposes in chloroform in the presence of triphenylphosphine to $(Ph_3P)_2(acac)RhCl_2$ via the corresponding hydroxo complex, with oxidation of the coordinated triphenylphosphine.

Introduction

Transition-metal hydroperoxo species have recently attracted increasing interest since they are believed to be involved in the oxygenation of olefins catalyzed by Group VIII transition metals [1] and in several biochemical processes [2]. However,

$$L_2M(R)X + H_2O_2 \longrightarrow L_2M(R)(OOH) + HX \qquad (1)$$

M = Pd, Pt R = $-CF_3$, $-CH_2CF_3$, $-CH_2CN$
X = H, –OH L_2 = dppe, $2PMePh_2$

to date, there have been only a few reports on the isolation and characterization of these species, apart from the "bio" systems containing porphyrins or Schiff bases as ligands [3]. Strukul et al. isolated a series of hydroperoxo complexes by the anion exchange reaction of hydroxo and hydrido complexes with hydrogen peroxide only for palladium(II) and platinum(II) complexes having both phosphine and electron-withdrawing alkyl ligands such as CF_3, CH_2CN, and CH_2CF_3 [4], but the corresponding hydroperoxorhodium(III) complexes were not isolable because of their instability (eq. 1). It was reported that the metal–oxygen bonds in the peroxometal complexes were cleaved by the attack of electrophiles such as PhCOX, Ph_3CX, and

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$CClH_2COOH$ on the peroxo ligand to give peroxides, ROOR (R = PhCO, Ph_3C, and H), by way of M–OOR (R = PhCO, Ph_3C, and H) [5] (eqs. 2 and 3). Kochi et

$$(t\text{-BuNC})_2NiO_2 + 2PhCOX \longrightarrow (t\text{-BuNC})_2NiX_2 + (PhCOO)_2 \quad (2)$$

X = Cl, Br

$$(Ph_3P)_2MO_2 \xrightarrow{CH_2ClCOOH} [(Ph_3P)_2M(OCOCH_2Cl)(OOH)] \xrightarrow{CH_2ClCOOH} (Ph_3P)_2M(OCOCH_2Cl)_2 + H_2O_2 \quad (3)$$

M = Pd, Pt

al. confirmed the formation of peroxobenzoatoplatinum species in the reaction of $(Ph_3P)_2Pt(O_2)$ with benzoyl chloride by its characteristic IR bands [6] (eq. 4). The μ-peroxodirhodium complex (1,5-COD)Rh(μ-O_2)Rh(1,5-COD) liberated hydrogen peroxide on treatment with 2 mol of acetylacetone to yield (1,5-COD)Rh(acac) [7]

$$(Ph_3P)_2PtO_2 + PhCOCl \longrightarrow (Ph_3P)_2Pt(OOCOPh)Cl \quad (4)$$

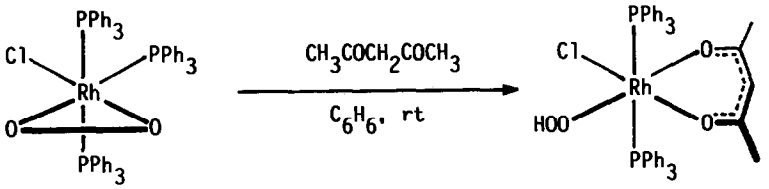
$$[(1,5\text{-COD})RhO]_2 + 2CH_3COCH_2COCH_3 \longrightarrow (1,5\text{-COD})Rh(acac) + H_2O_2 \quad (5)$$

(eq. 5). This reaction may be initiated by Rh–O cleavage, but intermediary hydroperoxorhodium species would immediately react with another mole of acetylacetone to afford hydrogen peroxide and (1,5-COD)Rh(acac). Although these works (eqs. 2–5) suggested the possibility of the formation of the hydroperoxorhodium complex, no hydroperoxorhodium complex was isolated. In 1982 we reported the first example of a hydroperoxorhodium complex [8]. The details of this work, along with additional information on the oxygenation of phosphine, are described here.

Results and discussion

Synthesis and characterizarion of $(Ph_3P)_2(acac)ClRhOOH$

Our experiments centered around the metal–oxygen bond cleavage of the peroxometal complexes by the attack of active methylene compounds. As shown in eq. 6, treatment of chloroperoxobis(triphenylphosphine)rhodium(III) (**1**) with 1.5 equiv. of acetylacetone in the presence of 2 equiv. of triphenylphosphine in dry benzene at room temperature for 0.5 h afforded chlorohydroperoxo(2,4-pentanedionato)bis(triphenylphosphine)rhodium(III) (**2**) as a yellowish-orange powder in 88% yield.



1 2 (6)

Treatment of the dimeric peroxorhodium complex $[(Ph_3P)_2ClRh(O_2)]_2$ (**3**) [9] with acetylacetone in benzene resulted in the recovery of the starting complex **3**, regardless of the presence or absence of added triphenylphosphine. Even with a prolonged reaction time at room temperature, treatment of chloroperoxocarbonylbis(triphenylphosphine)iridium(III), $(Ph_3P)_2(CO)ClIr(O_2)$ (**4**) [10], with acetylacetone also resulted in the recovery of **4**. The reactivity of the peroxometal complexes with acetylacetone could be elucidated on the basis of the basicity of the peroxo ligand. The presence of a strong π-acceptor ligand in **4** and the bridging coordination of the dioxygen ligands in **3** may suppress the electron density on the oxygen atoms. The stretching vibrations of the oxygen–oxygen bonds (889, 849, and 859 cm^{-1} for **1**, **3**, and **4**, respectively) correlate to some extent with the basicity of each dioxygen ligand. The structure of the complex obtained by the reaction of peroxo complex **1** with acetylacetone was confirmed as that of chlorohydroperoxo(2,4-pentanedionato)bis(triphenylphosphine)rhodium(III) (**2**) on the basis of elemental analysis, molecular weight measurement, and spectral data. The molecular weight measured by cryoscopy in benzene, MW (found) = 736, agreed well with that of the monomeric structure of **2**, MW (calcd.) = 795.1. The characteristic IR bands at 3470 and 813 cm^{-1} strongly suggested the presence of a hydroperoxo ligand. The hydroperoxorhodium complex **2** derived from $(Ph_3P)_3ClRh(^{18}O_2)$ (> 95% $^{18}O_2$) showed no absorption which could be tentatively assigned as ν(O–O). However, an increase in the intensity of the absorption at 766 cm^{-1} was observed (Fig. 1). Simple harmonic oscillator calculations indicate that $\nu(^{18}O–^{18}O)$ will overlap the absorption band at 766 cm^{-1}, which is inherent in the spectrum of the unlabeled complex **2**.

In the $^{31}P\{^1H\}$ NMR spectrum of complex **2**, a doublet peak coupled only with the rhodium nucleus (J(P–Rh) 99.6 Hz) was observed at 24.7 ppm downfield from the external triphenylphosphine. Equivalency of the two phosphine ligands in the ^{31}P NMR spectrum and non-equivalency of two methyl groups, 1.14 and 1.27 ppm, in the ^1H NMR spectrum of **2** indicated that the two phosphine ligands are aligned *trans*, as depicted in eq. 6. The chemical shift of 24.7 ppm and the coupling constant of 99.6 Hz for the phosphine in complex **2** agreed well with those of *trans*-phosphine ligands in the peroxo complex **1** (20.2 ppm downfield from the external triphenylphosphine, J(P–Rh) 98.6 Hz).

In the ^1H NMR spectrum of **2**, the singlet peaks observed at 4.82 and 6.43 ppm were assigned to the resonances of the methine and hydroperoxo protons, respectively. The ^1H NMR spectrum of the partially ^2H-labeled complex **2** derived from the reaction of peroxo complex **1** with partially deuterated acetylacetone, 3,3-dideutero-pentan-2,4-dione (isotopic purity 70%), also revealed singlet peaks at 4.82 and 6.43 ppm with integral intensities which had decreased by a factor of 0.3 (eq. 7). This

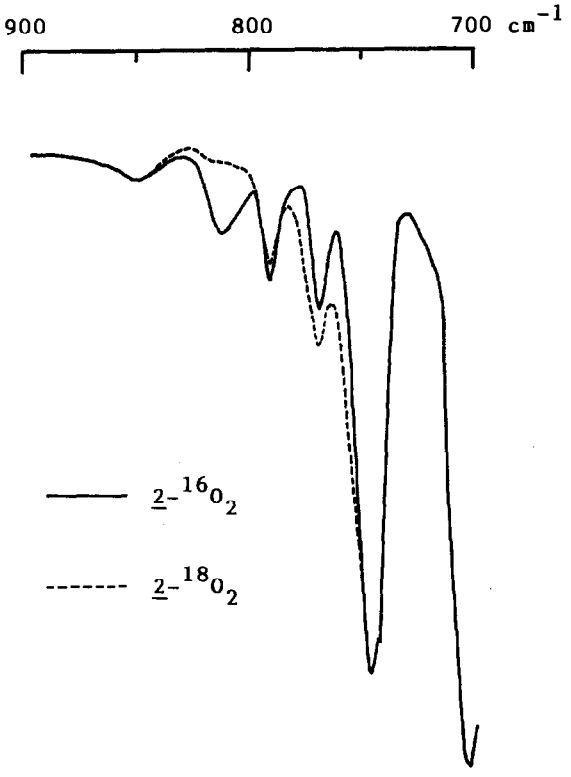
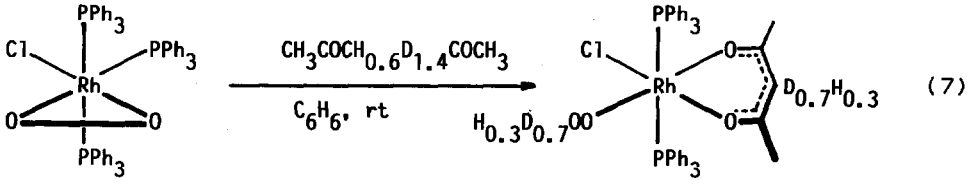


Fig. 1. Infrared spectra in the ν(O–O) region of 2-$^{16}O_2$ and 2-$^{18}O_2$.



(7)

observation proved the validity of the assignment of the reasonance peaks for the methine and hydroperoxo protons, and indicated that the proton in the hydroperoxo ligand arose from the methylene proton of acetylacetone.

The oxygen incorporated in complex **2** was quantified by means of GC-MS through the analysis of $Ph_3P^{18}O$ produced by the pyrolysis of ^{18}O-labeled hydroperoxo complex **2**. When ^{18}O-labeled hydroperoxo complex **2** was heated in degassed benzene at 250°C in a sealed tube with 4 equiv. of triphenylphosphine under an atmosphere of argon, incorporated oxygen-18 was recovered as $Ph_3P^{18}O$ in an 80.3% yield (eq. 8).

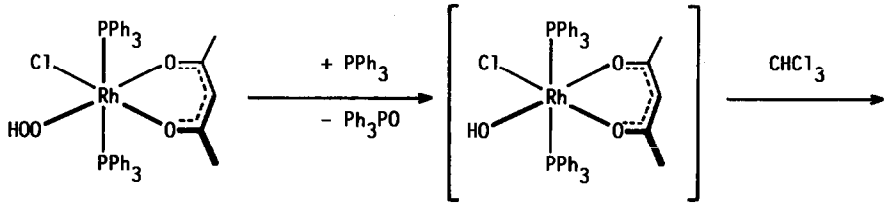
$$(Ph_3P)_2(acac)ClRh^{18}O^{18}OH + \text{excess } PPh_3 \xrightarrow[C_6H_6,\ \text{under Ar}]{250°C,\ 150\ h} Ph_3P^{18}O \qquad (8)$$

Attempts to allow peroxo complex **1** to react with various active methylene compounds such as methyl acetoacetate, diethyl malonate, cyclopentadiene, and acetone were unsuccessful, with the exception of the cyclopentadiene case.

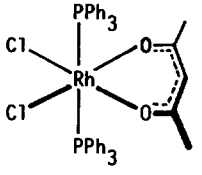
Treatment of **1** with excess cyclopentadiene in dimethoxyethane in the presence of triphenylphosphine afforded a reddish-brown complex with the empirical formula $C_{23}H_{21}O_2ClPRh$ in 43% yield. The IR spectrum of the complex in the solid state exhibited absorptions attributable to ν(O–H) and ν(O–O) at 3430 and 850 cm^{-1}, respectively. This strongly suggested the formation of the hydroperoxorhodium complex $(Ph_3P)(\eta\text{-}C_5H_5)ClRhOOH$ (**5**). However, we unfortunately could not obtain further information since the complex was extremely unstable in solution even at low temperature.

Reactivity of $[(Ph_3)_3P]_2(acac)ClRhOOH$ (2)

Complex **2** is sufficiently stable in the solid state but unstable in solution, even under an atmosphere of argon. Especially in CH_2Cl_2 or $CHCl_3$ in the presence of excess triphenylphosphine, **2** decomposed to a dichloro complex, **7**, via an intermediary hydroxorhodium species **6**, with formation of triphenylphosphine oxide (eq. 9).



2 6



(9)

7

The decomposition of **2** to **7** was followed by taking ^{31}P NMR (Fig. 2) and IR spectra at suitable intervals.

(1) After 10 min at room temperature in the presence of 2.5 equiv. of triphenylphosphine, the formation of a new species, **B**, and triphenylphosphine oxide was observed (Fig. 2(b)).

(2) After an additional 1 h at room temperature, the intensities of the resonance peaks of **B** and triphenylphosphine oxide increased, and at the same time, a new species, **C**, appeared (Fig. 2(c)). Furthermore, a progressive increase in the intensity of a new shoulder peak at 3550 cm^{-1} and a significant decrease in the intensity of that at 813 cm^{-1} were observed in the IR spectra of the reaction mixture measured at 10 min, paralleling the growth of the ^{31}P NMR absorption peak of **B**.

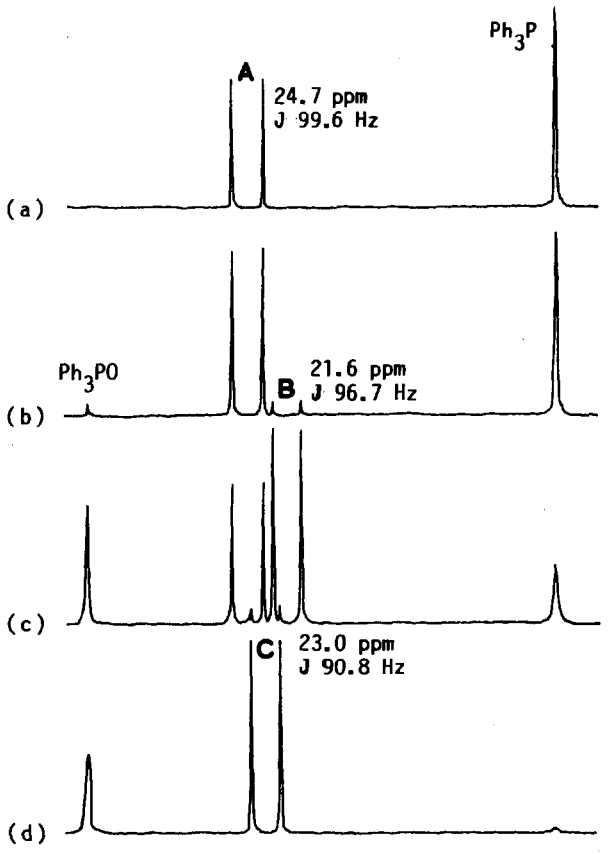


Fig. 2. $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ at $-30°C$ under an Ar atmosphere. (a) Freshly prepared **2** + Ph_3P (2.5 equiv.); (b) after standing for 10 min at room temperature; (c) after standing for 1 h at room temperature; (d) after standing for an additional 10 h at 80°C. A, $(Ph_3P)_2$(acac)ClRhOOH (**2**); B, $(Ph_3P)_2$(acac)ClRhOH (**6**); C, $(Ph_3P)_2$(acac)$RhCl_2$ (**7**).

(3) Warming the solution at 80°C for 10 h resulted in quantitative conversion to **C** (Fig. 2(d)). The final product **C** was isolated and identified as dichloro(2,4-pentanedionato)bis(triphenylphosphine)rhodium(III) (**7**) on the basis of elemental analysis and spectral data. These results indicate that the intermediate **B** is the six-coordinate hydroxo complex **6**. The phosphine ligands are concluded to be aligned *trans* in complexes **6** and **7** as well as in **2** on the basis of the chemical shifts and the coupling constants of the phosphine ligand recorded in the ^{31}P NMR spectra.

On the other hand, the triphenylphosphine ligand was immediately dissociated as triphenylphosphine oxide from complex **2** and **2** was converted to (Ph_3P)(acac)ClRhOH (**8**) when no triphenylphosphine was added to the solution of **2** in chloroform. The decomposition was also monitored by taking IR spectra (Fig. 3). A decrease in the intensity of the peak at 813 cm^{-1} paralleled the growth of a new peak at 3502 cm^{-1}. The final product **8** was tentatively identified as a mixture of geometrical isomers, because four pairs of doublet peaks appeared in the region of 39–46 ppm in the ^{31}P NMR spectrum measured in $CDCl_3$ at $-30°C$.

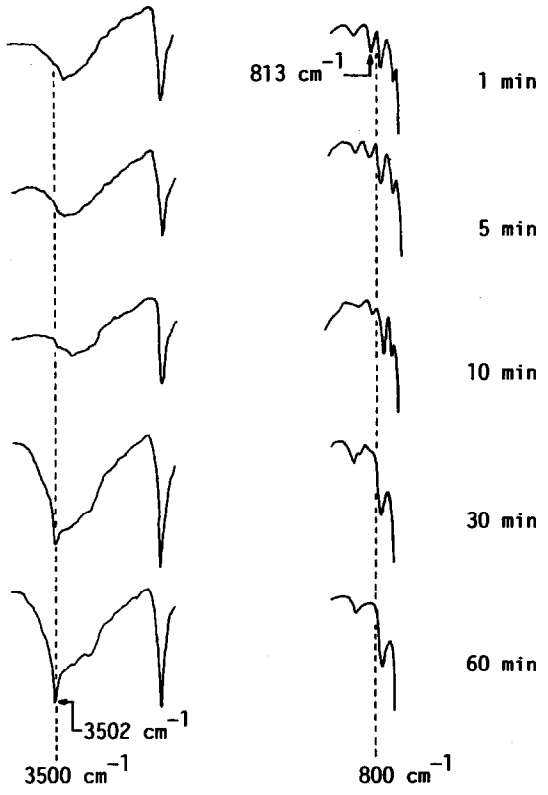
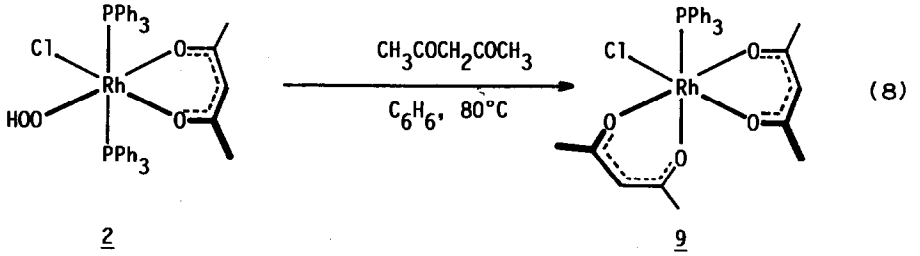


Fig. 3. Decomposition of **2** to **8** followed by IR.

The hydroperoxo complex **2** reacted with acetylacetone in refluxing benzene to give chlorobis(2,4-pentanedionato)(triphenylphosphine)rhodium(III) (**9**) in a 27% yield (eq. 10).

The ^{1}H NMR spectrum of complex **9** measured in $CDCl_3$ at 30°C revealed the peaks of four magnetically non-equivalent methyl groups (δ 1.57, 1.83, 1.92, and 2.18 ppm) and two methine protons (δ 4.95 and 5.42 ppm) of the 2,4-pentanedionato ligands. This observation agreed with that expected from the structure of complex **9** depicted in eq. 10 in which the chloro and triphenylphosphine ligands are aligned *cis*.



2 9 (8)

Stoichiometric oxidation of 1-octene, 2-octene, cyclohexene, and cyclohexanone to the corresponding ketones and lactone by the hydroperoxo complex **2** was

attempted; however, in no case were oxidation products detected, except for triphenylphosphine oxide.

Mechanism of oxidation of coordinated triphenylphosphine

As mentioned above, the hydroperoxo complex **2** decomposed in $CDCl_3$ to **7** with the formation of triphenylphosphine oxide. The most straightforward reaction path would be an intramolecular oxygen transfer to the coordinated triphenylphosphine; however, some care should be taken in ruling out the possibility of intermolecular oxygen transfer to uncoordinated triphenylphosphine. The reaction of ^{18}O-labeled hydroperoxo complex **2** with triphenylphosphine-d_5 in $CHCl_3$ was therefore carried out to elucidate the mechanism of the oxidation of triphenylphosphine.

Decomposition of the ^{18}O-labeled complex **2** in $CHCl_3$ in the presence of 4 equiv. of triphenylphosphine-d_5, $(C_6H_5)_2(C_6D_5)P$, was monitored by means of GC-MS (Fig. 4).

The molar ratio of $(C_6H_5)_3P^{18}O$ to $(C_6H_5)_2(C_6D_5)P^{18}O$ formed in the decomposition should be 0 if oxygen transfer is much faster than ligand exchange ($r_{ox} \gg r_{ex}$) in the intermolecular mechanism; the ratio should be 0.5 in the reverse case ($r_{ox} \ll r_{ex}$). On the other hand, the ratio should be ∞ and 0.5 in the case of $r_{ox} \gg r_{ex}$ and $r_{ox} \ll r_{ex}$, respectively, in the intramolecular mechanism. Consequently, a ratio greater than 0.5 indicates that intramolecular oxygen transfer predominates over intermolecular oxygen transfer, and vice versa. The results illustrated in Fig. 4 evidently show that oxidation of triphenylphosphine proceeds in the intramolecular fashion, as depicted in Scheme 1. Nucleophilic attack of the hydroperoxy group on the coordinated triphenylphosphine followed by liberation of triphenylphosphine oxide would form the six-coordinate hydroxorhodium species **6**.

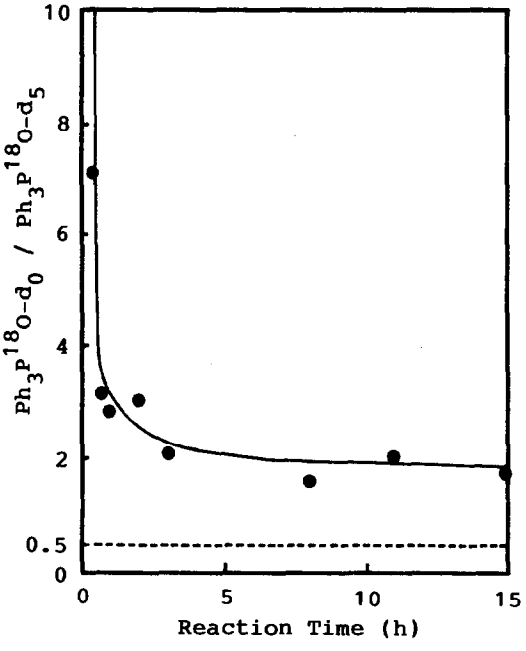
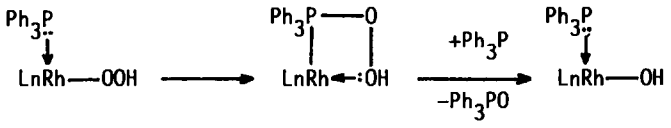


Fig. 4. Plots of $Ph_3P^{18}O$-d_0/$Ph_3P^{18}O$-d_5 as a function of the reaction time.

SCHEME 1



Experimental

All manipulations were conducted with the use of standard Schlenk or vacuum techniques. Nuclear magnetic resonance spectra were recorded on a Hitachi High Resolution NMR Spectrometer R24B or a JEOL FX-100 spectrometer. All ^{1}H and ^{13}C chemical shifts are reported relative to internal tetramethylsilane. Chemical shifts in the ^{31}P NMR spectra are expressed in parts per million downfield from external triphenylphosphine. Infrared spectra were recorded on a Hitachi 260-50 grating spectrophotometer. Melting points were determined on a Buchi Melting Point Determinator 510 in sealed capillaries and are uncorrected.

Gas–liquid chromatographic analyses were performed with a Hitachi Gas Chromatograph 163, using a 1 m × 3 mm stainless steel column packed with 20% PEG 20M on Celite 545 or 10% SE 30 on Chromosorb W. Mass spectroscopic analyses were conducted on a Hitachi Gas Chromatograph-Mass Spectrometer M-80. Elemental analyses were performed using the analytical facility in the Research Laboratory of Resources Utilization at the Tokyo Institute of Technology.

All solvents used were dried in the usual manner and were distilled under an atmosphere of dry argon prior to use. $P(C_6H_5)_3$ was recrystallized from ethanol. $P(C_6H_5)_2(C_6D_5)$ was prepared by the reaction of $P(C_6H_5)_2Cl$ and LiC_6D_5 derived from C_6D_5Br and was purified by recrystallization and column chromatography on silica gel. $[(C_6H_5)_3P]_3ClRh(O_2)$[9], $[((C_6H_5)_3P)_2ClRh(O_2)]_2$[9], and $[(C_6H_5)_3P]_2(CO)ClIr(O_2)$[10] were prepared by literature methods. $[(C_6H_5)_3P]_3ClRh(^{18}O_2)$ was prepared using $^{18}O_2$ (95%) obtained from Prochem Company (The British Oxygen Co. Ltd.).

$[(C_6H_5)_3P]_2(C_5H_7O_2)ClRh(OOH)$ (2)

To a solution of $[(C_6H_5)_3P]_3ClRh(O_2)$ (0.53 g, 0.54 mmol) and $(C_6H_5)_3P$ (0.36 g, 1.37 mmol) in dry benzene (5 ml) was added 2,4-pentanedione (0.1 ml, 1.0 mmol) dropwise under a static flow of dry argon. The solution was stirred for 20 min at room temperature. Concentration of the resulting reddish-orange solution under reduced pressure and the addition of diethyl ether (20 ml) followed by filtration gave yellowish-orange precipitates on the glass frit. The remaining crystalline solid was washed with diethyl ether (2 × 10 ml) and dried in vacuo; yield: 88% (0.38 g, 0.47 mmol). M.p. 135°C (dec); IR (KBr): 3470 (O–H), 1582 (C=O), 1568 (C=O), and 813 cm^{-1} (O–O); ^{1}H NMR ($CDCl_3$): δ 1.14 (3H, s, CH_3), 1.27 (3H, s, CH_3), 4.82 (1H, s, CH), 6.43 (1H, s, OOH), and 6.9–8.1 (30H, m, C_6H_5); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, −30°C): δ 26.9 (CH_3), 27.1 (CH_3), 100.2 (CH), 127–137 (C_6H_5), 185.1 (C=O), and 187.7 (C=O); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, −30°C): δ 24.7 (d, J(Rh–P) 99.6 Hz). Found: C, 61.30; H, 4.90; Cl, 4.88. $C_{41}H_{38}O_4ClP_2Rh$ calcd.: C, 61.94; H, 4.82; Cl, 4.46%. Mol. wt. (cryoscopy in C_6H_6). Found: 736. calcd.: 795.1.

^{18}O-Labeled hydroperoxo complex **2** was prepared in a similar manner using $[(C_6H_5)_3P]_3ClRh(^{18}O_2)$ as the starting material instead of $[(C_6H_5)_3P]_3ClRh(O_2)$. The disappearance of the characteristic band at 813 cm^{-1} and an increase in the intensity of the band at 766 cm^{-1} were observed in the IR spectra.

$[(C_6H_5)_3P](\eta\text{-}C_5H_5)ClRh(OOH)$ (5)

To a stirred solution of $[(C_6H_5)_3P]_3ClRh(O_2)$ (0.20 g, 0.21 mmol) and $(C_6H_5)_3P$ (0.07 g, 0.26 mmol) in dimethoxyethane (8 ml) was added cyclopentadiene (0.1 ml, 1.2 mmol) dropwise at room temperature under an atmosphere of dry argon. After stirring for 10 min at room temperature, the reaction mixture was immediately cooled to −78°C. Addition of diethyl ether (20 ml) gave reddish-brown precipitates, which were filtered and washed with diethyl ether (2 × 10 ml). Drying in vacuo gave **5** in a 43% (0.04 g, 0.09 mmol) yield. M.p. 176°C (dec); IR (KBr): 3430 (O–H) and 850 cm^{-1} (O–O). Found: C, 55.48; H, 4.13; Cl, 7.13. $C_{23}H_{21}O_2ClPRh$ calcd.: C, 55.39; H, 4.24; Cl, 7.11%.

Determination of oxygen incorporated in 2

$[(C_6H_5)_3P]_2(C_5H_7O_2)ClRh(^{18}O_2H)$ (**2**-$^{18}O_2$) (0.19 g, 0.24 mmol), $(C_6H_5)_3P$ (0.26 g, 1.01 mmol), and benzene (1 ml) were placed in a 10 mm Pyrex tube filled with dry argon. After the reaction vessel was sealed, the reaction mixture was heated at 250°C for 150 h. The triphenylphosphine oxide formed was separated from the reaction mixture by column chromatography on silica gel with benzene/chloroform (1/1). Triphenylphosphine oxide-^{18}O was quantified (0.11 g, 80.3% based on **2**) by means of GC-MS.

Decomposition of 2 in $CHCl_3$ in the presence of $(C_6H_5)_3P$

$[(C_6H_5)_3P]_2(C_5H_7O_2)ClRh(OOH)$ (**2**) (0.11 g, 0.14 mmol), $(C_6H_5)_3P$ (0.09 g, 0.34 mmol), and chloroform-d_1 (2 ml) were placed in a 10 mm NMR sample tube filled with argon. Just after the NMR sample tube was sealed, a $^{31}P\{^1H\}$ NMR spectrum was taken at −30°C (Fig. 2(a)). After standing at room temperature, $^{31}P\{^1H\}$ NMR spectra were taken at the prescribed time at −30°C (Fig. 2(b)–(d)). In parallel with the NMR experiment, decomposition of **2** was carried out in a Schlenk tube, and IR spectra of the solid precipitated from the reaction mixture were taken in the same time interval as the NMR experiment. After completion of the reaction, $[(C_6H_5)_3P]_2(C_5H_7O_2)Cl_2Rh$ (**7**) was isolated from the NMR sample in a 68% (0.07 g) yield. M.p. 205–210°C (dec); IR (KBr): 329 cm^{-1} (Rh–Cl); ^1H NMR ($CDCl_3$): δ 1.16 (6H, s, CH_3), 4.60 (1H, s, CH), and 6.9–8.1 ppm (30H, m, C_6H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$, −30°C): δ 26.2 (CH_3), 99.0 (CH), 127–137 (C_6H_5), and 186.0 ppm (C=O); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −30°C): δ 23.0 ppm (d, J(Rh–P) 90.8 Hz). Found: C, 61.75; H, 4.68; Cl, 8.89. $C_{41}H_{39}O_2Cl_2P_2Rh$ calcd.: C, 62.37; H, 4.65; Cl, 9.18%.

Decomposition of 2 in $CHCl_3$ in the absence of $(C_6H_5)_3P$

$[(C_6H_5)_3P]_2(C_5H_7O_2)ClRh(OOH)$ (**2**) (0.65 g, 0.82 mmol) and $CHCl_3$ (6 ml) were placed in a Schlenk tube filled with dry argon. The reaction mixture was stirred at room temperature, and aliquots (1 ml each) were removed with a syringe after 1, 5, 10, 30, and 60 min. Concentration of each solution under reduced pressure followed by the addition of diethyl ether (20 ml) gave orange precipitates, which

were filtered and washed with diethyl ether (2 × 10 ml). After drying in vacuo, IR spectra were taken (Fig. 3). After stirring for an additional 30 min at room temperature, the remaining reaction mixture was concentrated under reduced pressure. In a similar manner to that mentioned above, a mixture of geometrical isomers of $[(C_6H_5)_3P](C_5H_7O_2)ClRhOH$ (**8**) was isolated from the residue. M.p. 143–150°C (dec); IR (KBr): 3502 cm^{-1} (OH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −30°C): δ 39.2 (d, *J*(Rh–P) 125.0 Hz), 42.6 (d, *J*(Rh–P) 132.8 Hz), 43.9 (d, *J*(Rh–P) 129.9 Hz), and 45.9 (d, *J*(Rh–P) 136.7 Hz). Found: C, 52.60; H, 4.68; Cl, 6.58. $C_{23}H_{23}O_3ClPRh$ calcd.: C, 53.46; H, 4.49; Cl, 6.86%.

Decomposition of $[(C_6H_5)_3P]_2(C_5H_7O_2)ClRh(^{18}O^{18}OH)$ (2-$^{18}O_2$) in $CHCl_3$ in the presence of $(C_6H_5)_2(C_6D_5)P$

$[(C_6H_5)_3P]_2(C_5H_7O_2)ClRh(^{18}O^{18}OH)$ (**2**-$^{18}O_2$) (0.35 g, 0.44 mmol), $(C_6H_5)_2(C_6D_5)P$ (0.47 g, 1.76 mmol), and degassed $CHCl_3$ (30 ml) were placed in a Schlenk tube filled with dry argon. The reaction mixture was stirred at room temperature. Each 2.5 ml of the reaction mixture was removed with a syringe at the prescribed time and concentrated under reduced pressure. Solid precipitated by the addition of diethyl ether (20 ml) was collected on a glass frit and washed with diethyl ether (3 × 10 ml). The filtrate and washings were combined and concentrated under reduced pressure. Triphenylphosphine oxide was separated from the resulting oily liquid by means of column chromatography on silica gel with $C_6H_6/CHCl_3$ (1/1). $(C_6H_5)_3P^{18}O$ and $(C_6H_5)_2(C_6D_5)P^{18}O$ were quantified by means of GC-MS.

Time (h)	0.33	0.67	1	2	3	8	11	15
$(C_6H_5)_3P^{18}O$ (mg)	11.2	11.7	8.4	12.4	11.2	8.5	13.3	13.3
$(C_6H_5)_2(C_6D_5)P^{18}O$ (mg)	1.6	3.7	2.9	4.0	5.2	5.0	6.3	7.0

The ratios of $(C_6H_5)_3P^{18}O$ to $(C_6H_5)_2(C_6D_5)P^{18}O$ are shown in Fig. 4. The total amounts of recovered $(C_6H_5)_3P^{18}O$ and $(C_6H_5)_2(C_6D_5)P^{18}O$ were 139.3 mg (0.498 mmol) and 58.8 mg (0.206 mmol), respectively.

*$[(C_6H_5)_3P](C_5H_7O_2)_2ClRh$ (**9**)*

To a stirred solution of $[(C_6H_5)_3P]_2(C_5H_7O_2)_2ClRh(OOH)$ (**2**) (0.10 g, 0.13 mmol) in benzene (5 ml) was added 2,4-pentanedione (0.1 ml, 1.0 mmol) at room temperature. After stirring for 1 h at 80°C, the reaction mixture was concentrated under reduced pressure. The yellow, crystalline solid which precipitated from the resulting oily liquid on the addition of diethyl ether (20 ml) was filtered and washed with diethyl ether (2 × 8 ml). Drying in vacuo afforded **9** in a 27% (0.02 g) yield. M.p. 128°C (dec); IR (KBr); 328 cm^{-1} (Rh–Cl); ^1H NMR ($CDCl_3$): δ 1.57 (3H, s, CH_3), 1.83 (3H, s, CH_3), 1.92 (3H, s, CH_3), 2.18 (3H, s, CH_3), 4.95 (1H, s, CH), 5.42 (1H, s, CH), and 7.2–8.0 (15H, m, C_6H_5) ppm. Found: C, 55.69; H, 4.66; Cl, 6.07. $C_{28}H_{29}O_4ClPRh$ calcd.: C, 56.13; H, 4.88; Cl, 5.92%.

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