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# PREPARATION OF NEW HYDROPEROXO COMPLEX OF RHODIUM

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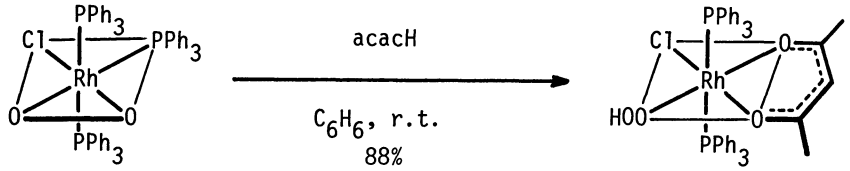
Novel hydroperoxo complex of rhodium, $(Ph_3P)_2(acac)ClRhOOH$, is prepared by the reaction of rhodium peroxo complex, $(Ph_3P)_3ClRhO_2$, with acetylacetone. This new complex is characterized by means of IR, NMR, elemental analysis, and $^{18}O_2$ labeling experiment. $(Ph_3P)_2(acac)ClRhOOH$ decomposes in chloroform solution to $(Ph_3P)_2(acac)RhCl_2$ by way of the corresponding hydroxo complex.

Transition metal hydroperoxo species have recently attracted an increasing interest since they are thought to be involved in the oxygenation of olefins catalyzed by group VIII transition metals.[1] However, to date, only a few reports for the isolation and characterization of them have been made except the "*bio*" systems containing porphyrins or Schiff bases as ligands.[2] Michelin *et al.* shortly reported that a series of hydroperoxo complexes were prepared and isolated by the anion exchange reaction of hydroxo or hydrido complexes with hydrogen peroxide only for the Pd(II) and Pt(II) complexes having both phosphine and particular alkyl ($-CF_3$, $-CH_2CN$, $-CH_2CF_3$) ligands,[3] but the corresponding Rh(III) hydroperoxo complexes were not isolated because of their instability. On the other hand, basicity of the coordinated dioxygen was confirmed for both mononuclear and dinuclear peroxo complexes by the reaction with acids, alcohols, or active methylene compound.[4] We report herein a preparation of new hydroperoxo complex of rhodium(III) by the reaction of chloroperoxotris(triphenylphosphine)rhodium, $(Ph_3P)_3ClRhO_2$, with acetylacetone as well as some chemical reactivity of the complex isolated.

Treatment of chloroperoxotris(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 gave a reddish orange solution. Concentration of the resulting solution under reduced pressure followed by the addition of dry diethyl ether afforded chlorohydroperoxo(2,4-pentanedionato)bis(triphenylphosphine)rhodium(III) (2) as yellowish orange powder in 88% yield.[5] 2: mp 135°C (dec); IR (KBr) $\nu$(O-H) 3470, $\nu$(C=O) 1582, 1568, $\nu$(O-O) 813 $cm^{-1}$; $^1$H-NMR ($CDCl_3$-TMS) $\delta$1.14 (3H, s, methyl), 1.27 (3H, s, methyl), 4.82 (1H, s, methine), 6.43 (1H, s, OH), 6.9-8.1 (30H, m, phenyl); $^{13}C\{^1H\}$-NMR ($CDCl_3$-TMS) $\delta$26.9 (methyl), 27.1 (methyl),

100.2 (methine), 127-137 (phenyl), 185.1 (carbonyl), 187.9 (carbonyl); $^{31}P\{^{1}H\}$-NMR ($CDCl_3$-$Ph_3P$) δ24.7 (d, $J_{^{103}Rh-P}$=99.6 Hz); mol wt (cryoscopy in benzene) calcd 795.1, found 736. Anal. Calcd for $C_{41}H_{38}O_4ClP_2Rh$: C, 61.94; H, 4.82; Cl, 4.46. Found: C, 61.30; H, 4.94; Cl, 4.88.



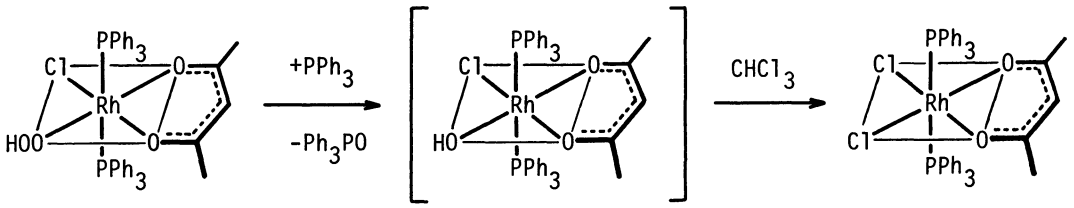

1 2 (1)

The Rh-OOH complex (2) derived from $^{18}O_2$ (>95% $^{18}O_2$) showed no absorption at 813 $cm^{-1}$, which was tentatively assigned as ν(O-O), with no new absorption observed. However, increase in the intensity of the absorption at 766 $cm^{-1}$ was observed. Simple harmonic oscillator calculations indicate ν($^{18}O$-$^{18}O$) will overlap the absorption band at 766 $cm^{-1}$, which inherently appears in the spectrum of the unlabeled complex 2. The $^{31}P\{^{1}H\}$-NMR spectrum of 2 is well consistent with the structure depicted in Eq. 1, in which two phosphine ligands are aligned *trans*.[6]

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

$$\underset{(0.240\ \text{mmol})}{(Ph_3P)_2(acac)ClRh^{18}O_2H} + \underset{(1.01\ \text{mmol})}{\text{excess } Ph_3P} \xrightarrow[C_6H_6,\ \text{under Ar}]{250°C,\ 150\ h} \underset{(0.386\ \text{mmol})}{Ph_3P^{18}O} \qquad (2)$$

The 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 phosphine ligand, 2 decomposed to a dichloro complex 4 by way of an intermediary rhodium hydroxo species 3 accompanied by the formation of triphenylphosphine oxide. (Eq. 3)




2 3 4 (3)

The decomposition of 2 to 4 was followed by taking $^{31}P$-NMR (Fig. 1) and IR spectra at different times.

(1) In the presence of 2.5 equiv of $Ph_3P$, decomposition of 2 was retarded. After standing for 10 min at room temperature, formation of new species, B, and $Ph_3PO$ was

observed. (Fig. 1 (b))

(2) On further standing of above solution for 1 h at room temperature, intensities of the resonance peaks of B and $Ph_3PO$ increased, and at the same time, a newer species, C, appeared. (Fig. 1 (c)) Furthermore, progressive increase in the intensity of a new shoulder peak at 3550 $cm^{-1}$ and simultaneous decrease in the intensity of that at 813 $cm^{-1}$ were observed in IR spectra of the reaction mixture measured at intervals of 10 min, paralleled with the growth of the $^{31}P$-NMR absorption peak of B.

(3) Warming the solution at 80°C for 10 h resulted in the quantitative conversion to C. (Fig. 1 (d)) Final product C was isolated and identified as dichloro(2,4-pentanedionato)bis(triphenylphosphine)-rhodium(III) (4). 4: mp 205-210°C (dec); IR (KBr) ν(C=O) 1560, ν(Rh-Cl) 330 $cm^{-1}$; $^1H$-NMR ($CDCl_3$-TMS) δ1.16 (6H, s, methyl), 4.60 (1H, s, methine), 6.9-8.1 (30H, m, phenyl); $^{13}C\{^1H\}$-NMR ($CDCl_3$-TMS) δ26.2 (methyl), 99.0 (methine), 127-137 (phenyl), 186.0 (carbonyl); $^{31}P\{^1H\}$-NMR ($CDCl_3$-$Ph_3P$) δ23.0 (d, $J_{^{103}Rh-P}$=90.8 Hz). Anal. Calcd for $C_{41}H_{37}O_2Cl_2P_2Rh$: C, 61.75; H, 4.68; Cl, 8.89. Found: C, 62.37; H, 4.65; Cl, 9.18.

(4) When no $Ph_3P$ was added to the $CHCl_3$ solution of 2, complex 2 immediately dissociated $Ph_3P$ as $Ph_3PO$ and was converted to $(Ph_3P)(C_5H_7O_2)ClRhOH$ species.[7] We tentatively identified this complex as the mixture of geometrical isomers, because four pairs of doublet peak appeared in the region of 39-46 ppm in the $^{31}P\{^1H\}$-NMR measured in $CDCl_3$ at -30°C.

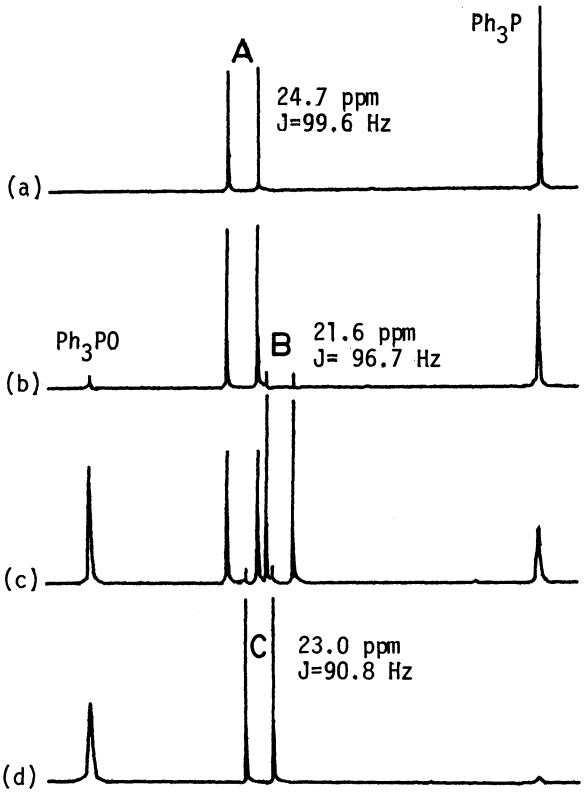



Fig. 1 $^{31}P$ $^1H$ -NMR spectra in $CDCl_3$ at -30°C under Ar atmosphere
(a) Freshly prepared $(Ph_3P)_2(acac)ClRhOOH$ + $Ph_3P$ (2.5 equiv)
(b) After standing for 10 min at r.t.
(c) After standing for 1 h at r.t.
(d) After standing for an additional 10 h at 80°C.
A, $(Ph_3P)_2(acac)ClRhOOH$ (2)
B, $(Ph_3P)_2(acac)ClRhOH$ (3)
C, $(Ph_3P)_2(acac)RhCl_2$ (4)

These results indicate that the intermediate B is the six-coordinate hydroxo complex 3 in which two phosphine ligands occupy the axial position.

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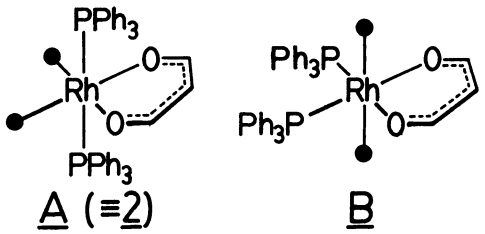
5. An attempt to recrystallize 2 was failed because of its instability in solution. Therefore, 2 was purified by washing with the mixed solvent of diethyl ether and n-pentane.
6. The fact that only one doublet peak was observed in the $^{31}P\{^{1}H\}$-NMR spectrum of 2 indicates that two phosphine ligands are magnetically equivalent. Following two structures, A and B, would satisfy such a requirment. On the other hand, in the $^{31}P\{^{1}H\}$-NMR spectrum of the peroxo complex 1, two kinds of doublet peak appear at 20.2 (2P, dd, $J_{Rh-P}$=98.6 and $J_{P-P}$=25.4 Hz) and 35.3 ppm (1P, dt, $J_{Rh-P}$=153.3 and $J_{P-P}$=25.4 Hz) downfield from the internal triphenylphosphine. In comparison with these results, the chemical shift of 24.7 ppm and the coupling constant of 99.6 Hz for the phosphine in the complex 2 suggest that two phosphine ligands are aligned *trans* as depicted in Eq. 1.



A (≡2) B

7. Anal. Calcd for $C_{23}H_{23}O_3ClPRh$: C, 53.46; H, 4.49; Cl, 6.86. Found: C, 52.60; H, 4.68; Cl, 6.58. IR (KBr) ν(OH) 3502, ν(C=O) 1570 $cm^{-1}$.

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