# Mechanism of Formation of Peroxocarbonates $\overline{\text{RhOOC(O)O}}\text{(Cl)(P)}_3$ and Their Reactivity as Oxygen Transfer Agents Mimicking Monooxygenases. The First Evidence of $CO_2$ Insertion into the O−O Bond of Rh($\eta^2$-$O_2$) Complexes

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*Received August 29, 1995*⊗

Extended labeling experiments have shown that formation of rhodium peroxocarbonate from $CO_2$ and [RhCl($\eta^2$-$O_2$)(P)$_3$] (P is $PEt_2Ph$ or $PEtPh_2$) proceeds through O−O bond cleavage and $CO_2$ insertion. O-transfer to ancillary phosphine ligand to give $R_3P{=}O$ selectively (>85%) involves the Rh-linked O atom of the peroxo group of $RhCl(CO_4)(P)_3$.

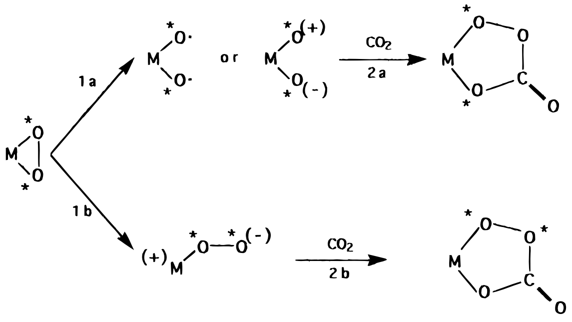
## Introduction

Transition-metal peroxocarbonates of formula $L_nM(CO_4)X_m$ (L = ancillary ligand; $n = 2, 3$; X = halogen; $m = 0, 1$), known for a long time, have been usually prepared by reaction of dioxygen complexes of transition metals $L_nM(O_2)X_m$ (M = Pd, Pt, Rh, Ir) with carbon dioxide.[1ab] More recently, we have shown that they can be synthesized by reaction of carbon dioxide complexes of formula $L_nM(CO_2)X_m$ (M = Ni, Rh) with dioxygen.[2ab] They are interesting compounds not only for their structural properties but also because they behave as oxidants. Indeed, we have ascertained that they are good oxygen transfer agents to oxophiles (phosphines, olefins, active methylene groups),[3,4] being, thus, candidates for a practical application. Very interestingly, in this reaction they transfer only one oxygen atom, mimicking, thus, monooxygenases.

Despite the cospicuous synthetic work available in the literature, very little was reported about the mechanism of formation of peroxocarbonates from dioxygen complexes and $CO_2$. In principle, two ways (routes **1a**, **1b**, Scheme 1) are possible that imply the O−O (route **1a**, Scheme 1) or M−O (route **1b**, Scheme 1) bond opening with subsequent $CO_2$ insertion and ring closure (routes **2a**, **2b**, Scheme 1) to afford the peroxocarbonate structure.

We have undertaken a detailed study in order to ascertain which mechanism is operating, making an extensive use of labeled compounds ($^{16}O_2$, $^{18}O_2$, $C^{16}O_2$, $C^{18}O_2$) in order to gain correct information on the mechanism of the interaction of coordinated dioxygen with $CO_2$. The availability of such labeled compounds has also permitted elucidatation of the oxygen transfer process and ascertainment of which of the peroxo O-atoms is transferred to a substrate.

**Scheme 1**



In these studies, infrared and Raman techniques (solid state and solution) were very informative. NMR studies, using $^{17}O$ isotope, gave only qualitative indications as the quality of the $^{17}O$ signals was poor for a quantitative use in the reaction mechanism assessment.

## Results and Discussion

**Synthesis of Peroxocarbonates of Formula $RhCl(CO_4)(P)_3$ and Their Behavior in Solution.** Complex $RhCl(CO_4)(PEt_2Ph)_3$ was obtained by reacting $CO_2$ with RhCl($\eta^2$-$O_2$)($PEt_2Ph$)$_3$ [2b] at 253 K in toluene. In a similar way, RhCl($\eta^2$-$O_2$)($PEtPh_2$)$_3$ and $CO_2$ afford $RhCl(CO_4)(PEtPh_2)_3$. Structural data are not available for these complexes as they decompose under X-ray irradiation. However, low-temperature NMR spectra have demonstrated that they have an octahedral geometry with two axial phosphines. The $^{31}P$ spectrum of $RhCl(CO_4)(PEt_2Ph)_3$ at 213 K in $CD_2Cl_2$ shows a doublet of doublets (+11.4 ppm, $J_{P-Rh} = 91$ Hz, $J_{PP} = 26$ Hz), assigned to the axial phosphines, and a doublet of triplets (+20.4 ppm, $J_{P-Rh} = 119.9$ Hz), due to the equatorial P ligand (Figure 1). When the solution was warmed to 273 K and left at this temperature for a few minutes, a reaction took place, as demonstrated by the change of the $^{31}P$ NMR spectrum. The original compound converts into several new ones. By comparison with authentic samples, it was possible to locate the following resonances: $\delta$ 42.9 (s), $O{=}PEt_2Ph$; 26.0 (d, $J_{P-Rh} = 128.7$ Hz), *trans*-$RhCl(CO)(PEt_2Ph)_2$; 3.7 (dd, $J_{P-Rh} = 84$ Hz, $J_{PP} = 23.1$ Hz) and 16.9 (dt, $J_{P-Rh} = 111.3$ Hz), *mer*-$RhCl_3(PEt_2Ph)_3$; 14.2 (dd, $J_{P-Rh} = 89$ Hz, $J_{PP} = 23.8$ Hz) and 22.7 (dt, $J_{P-Rh} = 125$ Hz),

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⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1996.

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S0020-1669(95)01154-2 CCC: $12.00

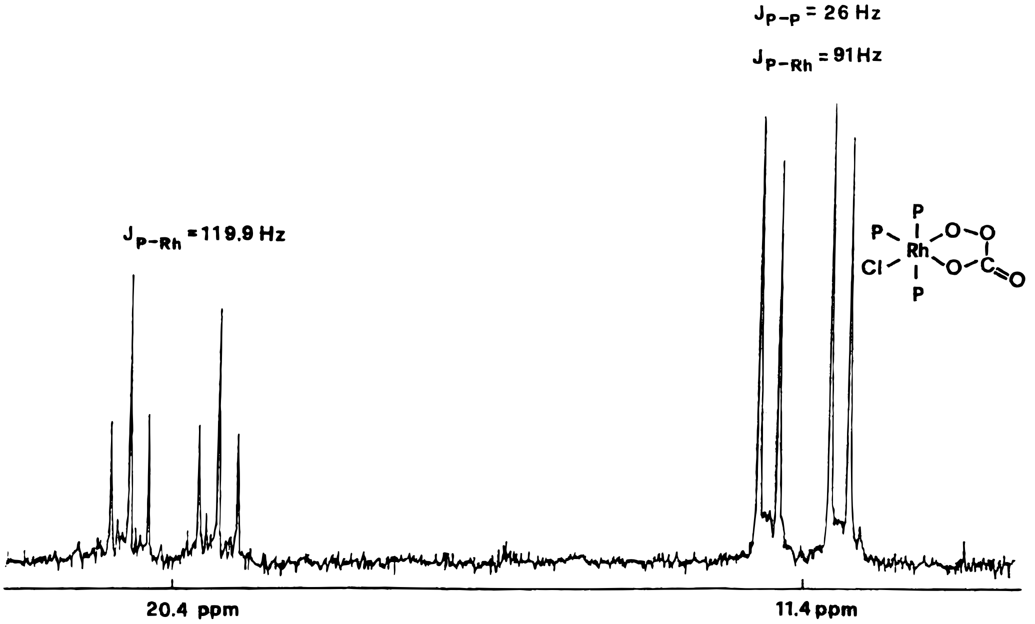
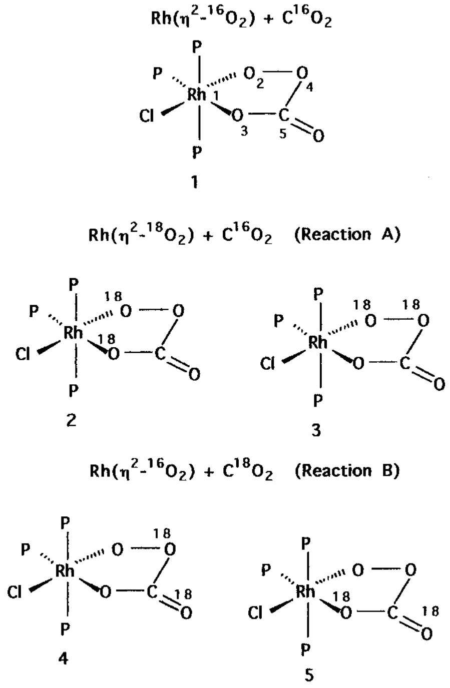


**Figure 1.** $^{31}$P NMR spectrum (213 K, $CD_2Cl_2$) of $RhCl(CO_4)(PEt_2Ph)_3$.

**Chart 1**



*mer*-$RhCl(CO_3)(PEt_2Ph)_3$. Also, the new complexes formed according to Scheme 2.

**Scheme 2**

$$RhCl(CO_4)(PEt_2Ph)_3 \xrightarrow{\Delta} \begin{cases} \textit{trans}\text{-}RhCl(CO)(PEt_2Ph)_2 \\ \textit{mer}\text{-}RhCl_3(PEt_2Ph)_3 \\ \textit{mer}\text{-}RhCl(CO_3)(PEt_2Ph)_3 \\ RhCl(PEt_2Ph)_3 \\ O{=}PEt_2Ph \end{cases}$$

The identified compounds suggest the following basic considerations.

(i) The reaction of formation of peroxocarbonates from RhCl(P)$_3$, $O_2$, and $CO_2$, is reversible (see also below).

(ii) The peroxocarbonate is an oxygen transfer agent that generates a carbonate.

(iii) $RhCl_3(P)_3$ is formed upon reaction of RhCl(P)$_3$ with the chlorinated solvent, as previously demonstrated.[5]

(iv) RhCl(CO)(P)$_2$ is formed *via* reduction of $CO_2$ to CO by the phosphane.[6]

We have investigated in detail the mechanism of formation of the peroxocarbonate using labeled $CO_2$ ($^{13}C^{16}O_2$, $^{12}C^{18}O_2$, $^{12}C^{16}O_2$) and $O_2$ ($^{16}O_2$, $^{18}O_2$) and have shown which of the oxygen atoms of the peroxo group O−O is transferred to the oxophile during the oxidation reaction.

**Mechanism of Formation of Peroxocarbonate from "Rh−($\eta^2$-$O_2$)" and $CO_2$.** The mechanism of formation of $RhCl(CO_4)(PEt_2Ph)_3$ from $CO_2$ and RhCl($\eta^2$-$O_2$)$(PEt_2Ph)_3$ was ascertained through a normal coordinate analysis for the fragment $[RhCl(CO_4)(PC)_3]$ (molecule **1**, Chart 1) and all its derivatives obtainable from isotopic labeling with $^{18}O_2$ (molecules **2** and **3**, Chart 1) and $C^{18}O_2$ (molecules **4** and **5**, Chart 1). Scheme 1 clearly shows that, according to the bond cleavage mechanism (Rh−O or O−O cleavage) and using labeled $O_2$ and $CO_2$, different species are obtained. Namely, the Rh−O cleavage affords molecules **3** and **5** in Chart 1, while the O−O splitting affords molecules **2** and **4**. This generates different O−O isotope coupling and makes the vibration of the *O−*O (or *O−O) bond and that of Rh−*O and C−*O diagnostic of the reaction mechanism.

In order to locate the O−O, Rh−O, and C−O bands, we have performed a theoretical calculation of the frequencies for the $RhCl(CO_4)(PC)_3$ fragment. As reported above, the solid state structure of these peroxocarbonates is not known as they decompose under X-ray irradiation, but the low-temperature solution NMR spectroscopy is informative about their octahedral structure.

**(A) FTIR Spectra of Solid $RhCl(CO_4)(PEt_2Ph)_3$ and Its $^{18}$O Labeled Derivatives.** The FTIR spectra of solid $RhCl(CO_4)(PEt_2Ph)_3$ and its $^{18}$O labeled derivatives, obtained by the following coupling reactions,

$$RhCl(^{18}O_2)(PEt_2Ph)_3 + CO_2 \tag{A}$$

$$RhCl(O_2)(PEt_2Ph)_3 + C^{18}O_2 \tag{B}$$

are presented in Figures 2 and 3.

**(1) Vibrational Spectrum of the Ligand.** As the vibrational spectrum of coordinated $PEt_2Ph$ is quite similar to that of the

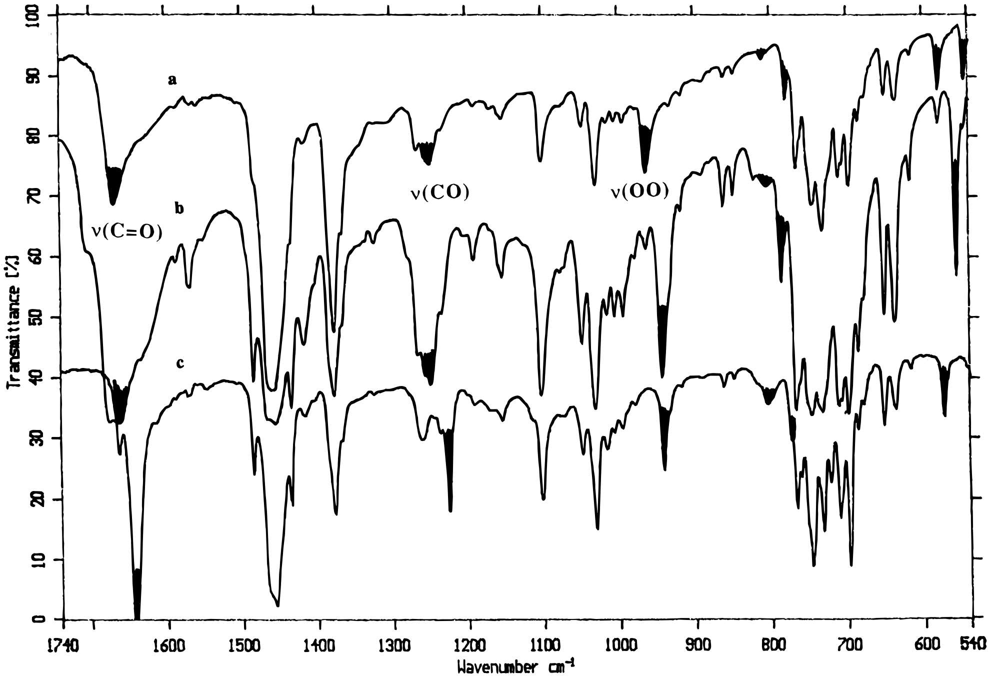


**Figure 2.** FTIR spectra in the region 540−1740 cm$^{-1}$ for RhCl(CO$_4$)(PEt$_2$Ph)$_3$ (a) and its labeled derivatives with $^{18}$O$_2$ (b) and C$^{18}$O$_2$ (c) (bands sensitive to isotopic labeling are indicated in black).

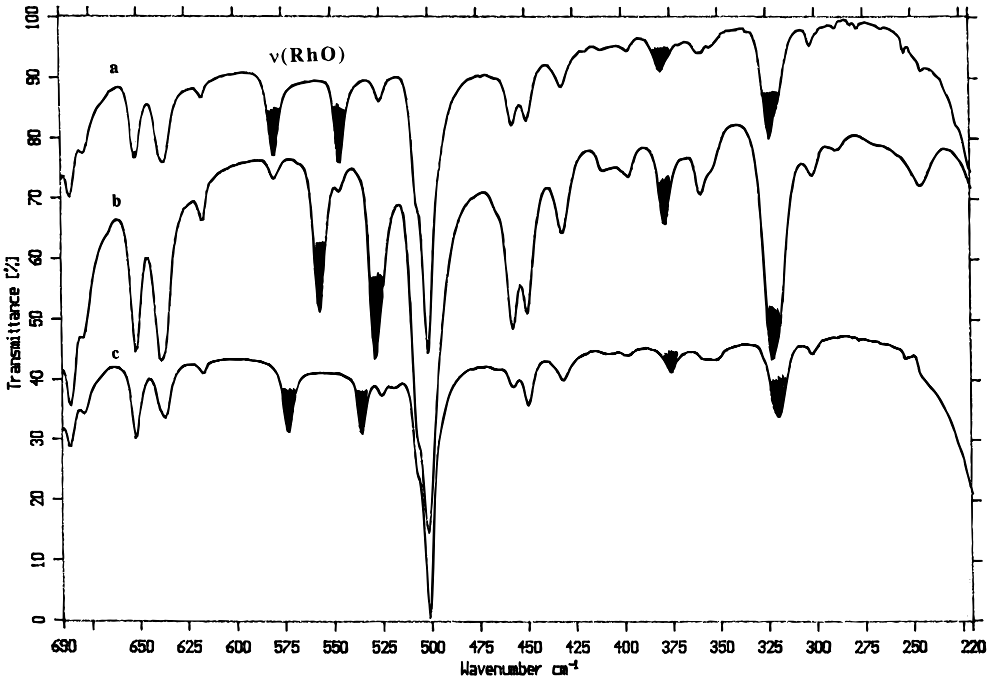


**Figure 3.** FTIR spectra in the region 220−690 cm$^{-1}$ for RhCl(CO$_4$)(PEt$_2$Ph)$_3$ (a) and its labeled derivatives with $^{18}$O$_2$ (b) and C$^{18}$O$_2$ (c) (bands sensitive to isotopic labeling are indicated in black).

free molecule, except in the low-frequency region,[7] and is not shifted by isotopic $^{18}$O labeling, it is easily recognizable and described separately only in the region of interest, below 2000 cm$^{-1}$.

The deformations $\delta$(CH$_3$) and $\delta$(CH$_2$) of the ethyl groups together with the stretching modes $\nu$(C=C) of phenyl moieties are observed in the region 1262−1483 cm$^{-1}$ and are partially obscured by Nujol absorptions at 1461 and 1377 cm$^{-1}$. Phenyl deformations $\beta$(=CH) are located between 1151 and 1030 cm$^{-1}$, whereas rocking motions of ethyl moieties are assigned to weak bands at 994, 970 cm$^{-1}$ for $r_{\|}$(CH$_3$) and at 860, 846 cm$^{-1}$ for $r_{\perp}$(CH$_3$). In the congested region between 766 (s) and 636 (m) cm$^{-1}$, we observe the stretching modes of phosphines $\nu_a$(PC$_3$), $\nu'_s$(PC$_3$), and $\nu_s$(PC$_3$), the bending motions $\delta$(C=C), and the out-of-plane deformations $\gamma$(=CH) of the phenyl groups, together with a weak contribution of Nujol at 723 cm$^{-1}$.

The deformations $\delta$(PC$_3$) are expected in the low-frequency region, below 540 cm$^{-1}$, and probably located between 525 (w) and 396 (vw) cm$^{-1}$ together with $\nu$(Rh−P) and $\nu$(Rh−Cl) (vibrations commonly observed around 320 cm$^{-1}$). Full as-

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signments in the far-infrared region will be discussed further, with results of normal coordinate analysis.

**(2) Vibrations Due to the Peroxocarbonate Moiety.** In addition to the Rh−$PEt_2Ph$ and Rh−Cl absorptions, bands that are shifted by isotopic labeling experiments can be observed. The strong absorption present in the IR spectrum of **1** at 1665 $cm^{-1}$, shifted to 1643 $cm^{-1}$ by $C^{18}O_2$ labeling, is assigned to the carbonyl stretching $\nu$(C=O). The medium band at 1249 $cm^{-1}$ has an isotopic effect of 25 $cm^{-1}$ by $C^{18}O_2$ labeling and is therefore associated with one of the CO stretching modes. The stretching vibration $\nu$(O—O) is expected in the 900−1000 $cm^{-1}$ region: we can easily observe in the spectrum of **1** a medium strong sharp absorption at 963 $cm^{-1}$, which is shifted to 943 $cm^{-1}$ upon $^{18}O_2$ labeling. Two sharp bands at 579 and 545 $cm^{-1}$ have isotopic effects of 23 and 17 $cm^{-1}$ by $^{18}O_2$ labeling and 6 and 10 $cm^{-1}$ by $C^{18}O_2$ enrichment, respectively. We assign them to the two stretching modes $\nu$(Rh—O). Bands at 808, 779, 380, and 322 $cm^{-1}$ also show weak isotopic effects by $C^{18}O_2$ and/or $^{18}O_2$ labeling and are therefore associated with vibrations of the $\overline{\text{RhOOC(O)O}}$ moiety. Full assignments will be made with the help of normal mode analysis; see below.

**(B) Structure of $RhCl(CO_4)(PEt_2Ph)_3$: A Normal Mode Analysis.** There are no structural data for this complex, but NMR spectra have shown that it has an octahedral geometry, with two axial phosphines. The chlorine atom, one phosphine, and the peroxocarbonato metallacycle lay in the equatorial plane. It is not possible to locate the chlorine atom, *trans* or *cis* to the peroxo bond, on the basis of the NMR spectrum of **1** only.

So, in order to (i) elucidate the mechanism of the $CO_2$ insertion reaction in the $\eta^2$-$O_2$ compound, (ii) assign all of the observed frequencies, and (iii) know the chlorine position, we have performed normal coordinate analysis for the fragment $RhCl(PC_3)(O_2CO_2)$ (molecule **1**) and all of its derivatives obtainable from isotopic labeling with $^{18}O_2$ (molecules **2** and **3**) and $C^{18}O_2$ (molecules **4** and **5**). We only consider the vibrations of the equatorial plane, neglecting ethyl and phenyl groups for simplification.

The structural parameters used (see Chart 1 and Table 1) were those of (glycolato)peroxomolydenum complex $K_2(MoO(O_2)_2(glyc))\cdot 2H_2O$,[8] various chlorine phosphine rhodium complexes such as *trans*-$RhCl(PMe_3)_2(PPh_3)$,[9] $RhCl(PMe_3)_3$,[10] and $RhCl(PPh_3)_3$ [11] and the (peroxocarbonato)rhodium complex $Rh(S_2CNMe_2)(CO_4)(PPh_3)_2$.[12]

The initial force field was taken from values calculated by Fouassier *et al.* for acetone,[13] Nakamura *et al.* for dioxygen−transition metal complexes,[14] and Forel and co-workers for maleic anhydride,[15] together with our previous results obtained for different transition metal complexes with coordinated $CO_2$.[16] The program used to calculate the generalized valence force field was similar to Schachtschneider's one.[17] Because of the limited vibrational data in the low-frequency region, the fitting was limited to 300 $cm^{-1}$, but all modes were calculated, the total number of nonzero interaction force constants being 5 for 26 calculated frequencies (22 observed). In the refinement procedure, the adjustment of the isotopic shifts had priority to that of frequencies themselves, because the former are more sensitive to the geometry of the molecule.

**Table 1.** Structure[a] and Valence Force Field[b] for $RhCl(CO_4)(PC_3)$

| geometrical values[a] | | force constants | initial values[b] | final values[b] |
|---|---|---|---|---|
| $d(RhO_2)$ | 2.077 | $\nu(RhO_2)$ | 3.2 | 2.75 |
| $d(RhO_3)$ | 2.240 | $\nu(RhO_3)$ | 3.2 | 2.70 |
| $d(O_2O_4)$ | 1.470 | $\nu(O_2O_4)$ | 3.3 | 3.90 |
| $d(C_5O_3)$ | 1.325 | $\nu(C_5O_3)$ | 5.3 | 3.21 |
| $d(C_5O_4)$ | 1.321 | $\nu(C_5O_4)$ | 5.3 | 4.83 |
| $d(C_5O_6)$ | 1.220 | $\nu(C_5O_6)$ | 9.6 | 9.41 |
| $d(RhCl)$ | 2.410 | $\nu(RhCl)$ | 1.7 | 1.56 |
| $d(RhP)$ | 2.308 | $\nu(RhP)$ | 1.6 | 1.725 |
| $d(PC)$ | 1.83 | $\nu_s(PC_3)$ | 2.75 | 2.75 |
| | | $\nu'_s(PC_3)$ | 2.42 | 2.42 |
| | | $\nu_a(PC_3)$ | 2.42 | 2.42 |
| $\alpha(O_2RhO_3)$ | 72 | $\delta(O_2RhO_3)$ | 0.25 | 0.25 |
| $\alpha(RhO_2O_4)$ | 120.3 | $\delta(RhO_2O_4)$ | 0.35 | 0.35 |
| $\alpha(O_2O_4C_5)$ | 111.7 | $\delta(O_2O_4C_5)$ | 0.35 | 0.35 |
| $\alpha(O_4C_5O_3)$ | 120.2 | $\delta(O_4C_5O_3)$ | 0.35 | 0.46 |
| $\alpha(C_5O_3Rh)$ | 115.8 | $\delta(C_5O_3Rh)$ | 0.35 | 0.45 |
| $\alpha(O_3C_5O_6)$ | 124.9 | $\delta(C_5O_6)$ | 1.09 | 0.79 |
| $\alpha(O_4C_5O_6)$ | 114.9 | $\gamma(C_5O_6)$ | 0.68 | 0.66 |
| $\alpha(PRhCl)$ | 85 | $\delta(PRhCl)$ | 0.16 | 0.16 |
| $\alpha(O_2RhP)$ | 101.5 | $\delta(O_2RhP)$ | 0.24 | 0.24 |
| $\alpha(O_3RhCl)$ | 101.5 | $\delta(O_3RhCl)$ | 0.24 | 0.24 |
| $\alpha(CPC)$ | 120 | $\delta_s(PC_3)$ | 0.46 | 0.46 |
| | | $\delta'_s(PC_3)$ | 0.64 | 0.64 |
| | | $\delta_a(PC_3)$ | 0.64 | 0.64 |
| | | $r_{\parallel}(PC_3)$ | 0.46 | 0.46 |
| | | $r(PC_3)$ | 0.46 | 0.46 |
| | | $\tau(PRh)$ | 0.0005 | 0.0 |
| | | $\tau(RhO_2)$ | 0.0005 | 0.0 |
| | | $\tau(RhO_3)$ | 0.0005 | 0.0 |
| | | $\tau(O_2O_4)$ | 0.0005 | 0.0 |
| | | $\tau(C_5O_4)$ | 0.05 | 0.0 |
| | | $\tau(C_5O_3)$ | 0.05 | 0.0 |
| | | $f(C_5O_4,\delta(C_5O_6))$ | −0.4 | −0.8 |
| | | $f(C_5O_3,\delta(C_5O_6))$ | −0.4 | −0.8 |
| | | $f(C_5O_4,C_5O_3)$ | 0 | 0.57 |
| | | $f(RhP,\delta_s(PC_3))$ | −0.09 | −0.09 |
| | | $f(RhO_2,RhO_3)$ | 0 | 0.3 |

[a] Bond lengths in Å; angles in deg. [b] Force constants are given in mdyn $Å^{-1}$ for bonds, mdyn Å $rad^{-2}$ for angles, and mdyn $rad^{-1}$ for bond−angle interactions.

Tables 1 and 2 summarize the final results for the valence force field of the complex and the assignment of the vibrational modes with the chlorine atom placed in a *trans* position with regard to the peroxo moiety.

The excellent agreement of calculated and observed values for the unlabeled $[RhCl(CO_4)(PC)_3]$ fragment (columns 1 and 2 in Table 2) confirms that the used parameters are correct.

Considering the spectrum, we can see that if $\nu$(C=O), $\nu$(O—O), and the two $\nu$(Rh—O) modes are relatively pure (see PED on Table 2) and located at usual wavenumbers (1665, 963, 579, and 545 $cm^{-1}$, respectively), normal coordinate analysis is necessary for assigning all other vibrations.

It is generally assumed that interaction force constants must be lower than one-tenth of the main corresponding force constants. The values calculated can then be considered as accurate. The good agreement between observed and calculated wavenumbers and isotopic shifts allow us to propose a relevant force field for this compound.

While the final force constant values calculated for both RhO bonds (RhO and Rh—OO) are identical (2.7 mdyn $Å^{-1}$), a

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**Table 2.** Assignments of IR Observed Wavenumbers (cm$^{-1}$) of $RhCl(CO_4)(PEt_2Ph)_3$ and Its $^{18}O$ Labeled Derivatives Compared with Calculated Values for Molecules **1**−**5**[a]

| wavenumbers, cm$^{-1}$ molecule **1** | | | $\Delta^{18}O$ frequency shifts, cm$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $Rh^{18}O_2 + {}^{12}C^{16}O_2$ molecules **2** and **3** | | | $Rh^{16}O_2 + {}^{12}C1^{8}O_2$ molecules **4** and **5** | | |
| obsd | calcd (1) | assgnts (PED)[b] | obsd *$O_2$ (A) | calcd for **2** | calcd for **3** | obsd C*$O_2$ (B) | calcd for **4** | calcd for **5** |
| **1665** (vs) | 1663 | $\nu(C{=}O)$ (76) | 0 | 1.1 | 2.5 | 22 | 23.3 | 26.7 |
| 1483 (m) | | | | | | | | |
| 1433 (m) | | $\nu(C{=}C)$, $\delta(CH)$ | | | | | | |
| 1415 (w) | | | | | | | | |
| 1262 (sh) | | | | | | | | |
| **1255** (sh) | | | 0 | | | 25 | | |
| **1249** (s) | 1250 | $\nu(C_5O_4)$ (53) + $\nu(C_5O_3)$ (17) + $\delta(C{=}O)$ (16) | 1 | 0.9 | 19 | 25 | 25.1 | 7.4 |
| 1151 (w) | | | | | | | | |
| 1101 (m) | | $\beta({=}CH)$ | | | | | | |
| 1046 (w) | | | | | | | | |
| 1030 (m) | | | | | | | | |
| 994 (w) | | $r_{\parallel}(CH_3)$ | | | | | | |
| 970 (w) | | | | | | | | |
| **963** (m) | 962 | $\nu(O_2O_4)$ (83) | 20 | 28 | 53 | 22 | 24.4 | 0.5 |
| 860 (w) | | $r(CH_3)$ | | | | | | |
| 846 (w) | | | | | | | | |
| **808** (w) | 796 | $\gamma(C{=}O)$ (100) | 0 | 2.9 | 2.3 | 5 | 6 | 6.5 |
| **779** (m) | 777 | $\nu(C_5O_3)$ (54) + $\nu(RhO_3)$ (32) | n.o. | 34.2 | 0.7 | 9 | 6.7 | 40.2 |
| 766 (s) | | | | | | | | |
| 746 (s) | | | | | | | | |
| 732 (s) | | | | | | | | |
| 711 (s) | | $\nu_a$, $\nu'_s$, $\nu_s(PC_3)$ | | | | | | |
| 705 (sh) | | $\gamma({=}CH)$ | | | | | | |
| 697 (s) | | $\delta(C{=}C)$ | | | | | | |
| 685 (m) | | | | | | | | |
| 650 (m) | | | | | | | | |
| 636 (m) | | | | | | | | |
| **579** (m) | 575 | $\nu(RhO_2)$ (62) | 23 | 23.4 | 18.2 | 6 | 4.4 | 4.2 |
| **545** (m) | 543 | $\nu(RhO_3)$ (28) + $\nu(C_5O_3)$ (34) + $\delta(C{=}O)$ (14) | 17 | 21.9 | 13.2 | 8 | 5.4 | 19.2 |
| 525 (w) | | | | | | | | |
| 501 (s) | | | | | | | | |
| 457 (m) | | $\delta_a$, $\delta'_s$, $\delta s(PC_3)$ | | | | | | |
| 449 (m) | | | | | | | | |
| 431 (w) | | | | | | | | |
| 396 (vw) | | | | | | | | |
| **380** (m) | 379 *(376)* | $\delta(C{=}O)$ (33) + $\nu(RhP)$ (19) + $\delta(O_2O_4C_5)$ (14) | 2 | 3.5 *(5)* | 5 | 5 | 7.5 *(11)* | 5.9 |
| **360** (w) | 358 *(360)* | $\nu(RhP)$ (45) + $\delta_s(PC_3)$ (24) + $\delta(C{=}O)$ (21) | 0 | 3.3 *(1)* | 3.4 | 0 | 4 *(0.2)* | 3.9 |
| 352 (w) | | ? | | | | | | |
| **322** (ms) | 323 *(331)* | $\nu(RhCl)$ (67) + $\delta(C{=}O)$ (26) | 1 | 1 *(8)* | 2.4 | 4 | 3 *(4.6)* | 2 |
| **303** (w) | 302 *(296)* | $\delta(C{=}O)$ (63) + $\nu(C_5O_4)$ (24) + $\nu(RhCl)$ (24) | n.o. | 2 *(2)* | 5.5 | n.o. | 10.3 *(5.7)* | 6.5 |

[a] n.o. = not observed. The Cl atom is assumed *trans* to the peroxo group. Values in *italics* are given for the same molecules with the chlorine atom in a *cis* position with regard to the peroxo bond. [b] PED = potential energy distribution.

different situation is found for the C—O bonds, for which the value obtained for the bond relevant to the peroxo group is 50% higher (4.8 instead of 3.2 mdyn Å$^{-1}$) than the oxo. Anyway, all of these values are lower than those habitually encountered for similar bonds (see initial values in Table 1). Values calculated for the O—O and C=O bonds, as well as those found for the in-plane and out-of-plane deformation motions of the $O_3O_4CO_6$ moiety fall within normal values.

Only five interaction force constants were necessary to fit the calculation of normal modes. Among them, interactions between RhP stretching and $PC_3$ symmetric deformation, and CO stretchings and in-plane C=O bending, respectively, have the usual values. Interactions between both RhO (0.3 mdyn rad$^{-1}$) and CO (0.57 mdyn rad$^{-1}$) stretching modes depend on the cyclic structure of the compound. Table 2 shows the results of coupling on the frequencies and potential energy distribution of the motions.

The high-frequency $\nu$(CO) mode at 1250 cm$^{-1}$ can be considered as the asymmetric stretching motion of the $O_3O_4C$ moiety, whereas the symmetic counterpart is lowered to 777 cm$^{-1}$. As already observed in similar compounds (see for example maleic anhydride[15]), the out-of-plane motion $\gamma$(CO) is found at a higher frequency (796 cm$^{-1}$) than in $CO_2$ complexes, where this mode is observed around 550 cm$^{-1}$ [16] and is higher than the corresponding in-plane bending $\delta$(CO). This vibration is, in fact, highly mixed with several other modes ($\nu$(C—O), $\nu$(Rh—O), $\nu$(Rh—Cl), and bending motions of the cycle) at different wavenumbers (1250, 543, 379, 358, 323, and mainly 303 cm$^{-1}$). This explains why small isotopic shifts are observed for Rh—P and Rh—Cl stretching modes in $^{18}O$ labeled species.

One question which the NMR spectra of **1** could not answer is if the Cl atom is in a *trans* or *cis* position with regard to the peroxo bond. We have performed other calculations with the same valence force field. Only the position of Cl has been changed, leaving all other structural parameters identical. Calculated frequencies and isotopic shifts are the same for all modes, except for 380, 360, 322, and 303 cm$^{-1}$, in the low-frequency region. Table 2 shows in italics calculated frequencies and isotopic shifts for molecules **2** and **4** with Cl *cis* to the peroxo group. Available experimental data strongly support the "*trans*" structure (see isotopic shifts obtained for modes at 380, 322, and 303 cm$^{-1}$). However, we have not observed values for the $\delta$(CO) + $\nu$(Rh—Cl) motion in isotopically labeled species that would have allowed an unambiguous conclusion in favor of the *trans* position of Cl with regard to the peroxo bond.

**(C) Studies with $^{18}O_2$.** Calculated frequencies reported in Table 2 show that molecules **2** and **3** are easily recognizable when the isotopic shifts obtained on the $\nu$(O—O) mode are considered. Indeed, molecule **3** obtained by opening of the Rh—O bond in reaction A has the maximum frequency shift (53 cm$^{-1}$) on this stretching mode because of the presence of the $^{18}$O—$^{18}$O bond, whereas molecule **2**, where only one oxygen atom of the peroxo bond is isotopically labeled, presents a shift almost reduced by half (28 cm$^{-1}$). The experimental value (20 cm$^{-1}$) is quite close to the latter, indicating molecule **2** as the most likely to be formed. Further support in favor of molecule **2** comes from the good agreement between calculated and observed values relevant to $\nu(Rh—O_2)$, $\nu(Rh—O_3) + \nu(C_5O_3) + \delta(C{=}O)$ and $\delta(O_2O_4C_5) + \delta(C{=}O) + \nu(Rh—P)$ (see Table 2).

Therefore, comparison of observed and calculated values on the peroxocarbonate, obtained by reacting Rh—$^{18}O_2$ and $^{12}C^{16}O_2$, clearly shows that reaction A leads to molecule **2**. This result is also confirmed by the isotopic shift obtained on the high-frequency stretching mode $\nu$(CO) located at 1249 cm$^{-1}$ in the unlabeled compound.

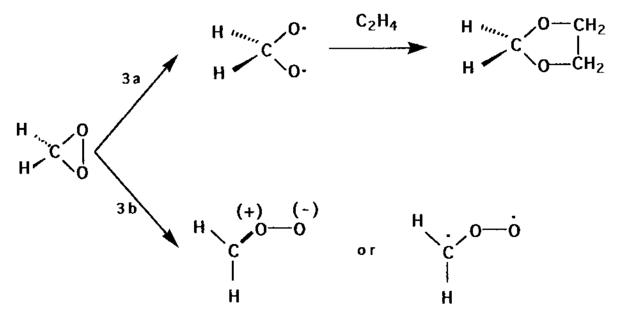
**(D) Studies with $^{12}C^{18}O_2$.** Reaction B uses $^{16}O_2$ and $^{12}C^{18}O_2$. The opening of one Rh—O bond should leave unchanged the $\nu(O_2—O_4)$ frequency, whereas opening of the O—O bond leads to a "half-labeled" $^{16}$O—$^{18}$O bond and to a frequency shift of about 25 cm$^{-1}$. The experimental (22 cm$^{-1}$) and calculated values ($\Delta_{calcd}$ is 24.4 cm$^{-1}$ for O—O splitting and 0.5 for Rh—O splitting) permit us to conclude that reaction B proceeds through the opening of the O—O bond. This result is also supported by other stretching modes such as the following: (a) $\nu(C_5O_4) + \nu(C_5O_3) + \delta(C{=}O)$ ($\Delta_{obs} = 25$ cm$^{-1}$; $\Delta_{calcd} = 25.1$ cm$^{-1}$); (b) $\nu(C_5O_3) + \nu(RhO_3)$ which is located at 779 cm$^{-1}$ in the unlabeled compound **1** for which $\Delta_{obs}$ is 9 cm$^{-1}$ (for this mode the calculated isotopic shift is very important (40 cm$^{-1}$) in molecule **5** and weak (7 cm$^{-1}$) in molecule **4**); (c) $\nu(RhO_3) + \nu(C_5O_3) + \delta(C{=}O)$ ($\Delta_{obs} = 8$ cm$^{-1}$; $\Delta_{calcd}$ for **4** = 5.4 cm$^{-1}$; $\Delta_{calcd}$ for **5** = 19.2 cm$^{-1}$).

In conclusion, Table 2 clearly shows that the agreement between the calculated and found values for the O—O, O—C, and O—Rh stretching is very good when species **2** and **4** of Chart 1 are considered, while no agreement is found for species **3** and **5**. This finding clearly supports the O—O bond splitting as the reaction mechanism for the formation of peroxocarbonate from Rh—$O_2$ and $CO_2$.

This reaction pathway finds a rationale in the value of the bond energy of Rh—O (≅60 kcal/mol)[18] and O—O (28−48 kcal/mol for most inorganic and organic peroxides).[19]

Such a mechanism and situation are reminiscent of that of organic dioxiranes (Scheme 3)[20] for which the splitting of the O—O bond is assumed to operate when, for example, ethylene reacts with dioxirane to give an insertion reaction (route **3a**, Scheme 3).

**Scheme 3**



**(E) Synthesis of Asymmetrically Labeled $^{16}$O−$^{18}$O Moieties.** The reaction we have observed of rhodium−dioxygen complexes with labeled $CO_2$ brings to the synthesis an asymmetrically labeled *O—O peroxo bond. In fact, depending on the procedure used for the synthesis of the peroxocarbonate, either a Rh—$^{16}$O—$^{18}$O or a Rh—$^{18}$O—$^{16}$O peroxo bond is formed. Such asymmetric peroxo groups were never observed before. They constitute an opportunity of studying the reaction mechanism of oxygen transfer to oxophiles from the peroxocarbonate moiety (see paragraph below).

**(F) Reversibility of the Peroxocarbonate Moiety Formation.** Interestingly, the reaction of dioxygen−rhodium complexes $[RhCl(O_2)(P)_3]$ (P is $PPh_2Et$ or $PEt_2Ph$) with $CO_2$ is reversible. In fact, $^{31}$P NMR spectroscopy shows that $[RhCl(CO_4)(P)_3]$ heated above 270 K can either convert into $[RhCl(CO_3)(P)_3]$ with oxygen transfer to the ancillary phosphine ligand or revert to the starting $RhCl(P)_3$ complex. The latter is the only Rh compound formed when $[RhCl(CO_4)(P)_3]$ is irradiated also at 213 K in the solid state with Raman radiations. Such behavior is not documented in the literature for other peroxocarbonates.

**Oxygen Transfer from Peroxocarbonate to Oxophiles.** As reported above, in general the peroxocarbonate complexes are potential oxidants. $RhCl(CO_4)(PEt_2Ph)_3$ and $RhCl(CO_4)(PEtPh_2)_3$ behave as oxidants toward phosphines,[2a,b] olefines,[4] and ethers.[4] We have also observed that $CO_2$ is able to modulate the oxidative ability of $O_2$ in the presence of a rhodium−phosphine catalyst. This is clearly due to the formation of peroxocarbonates.

When styrene is reacted with $O_2$ in the presence of $RhCl(PEt_2Ph)_3$, the major product is benzaldehyde, with minor amounts of epoxide and phenyl methyl ketone. These products were formed according to a molecular ratio of 5:3:1, respectively.

The addition of $CO_2$ produces an inversion in the abundance of the oxidized species formed from styrene. Indeed, the most abundant species is now phenylacetaldehyde followed by styrene epoxide, phenyl methyl ketone, and benzaldehyde in the molar ratio 5:5:3:1. Benzaldehyde, in this case, is formed only in a minor amount.

Analogously, when $RhCl(CO_4)(PEt_2Ph)_3$ was dissolved in tetrahydrofuran (THF) at 273 K the formation of butyrolactone was evident, although the main process was the oxygen transfer to the P ligand. When diphos or bipy (2,2′-bipyridyl) were used as ligands, the O-transfer to the ligand was avoided, and only the organic substrate was implied in the oxidation process. $Rh(bipy)(C_2H_4)Cl$ alone in THF afforded, thus, 2-hydroxytetrahydrofuran and butyrolactone (turnover 30 and 50 *per* hour) as the only oxidation products in the presence of $CO_2$−$O_2$ mixtures (1:1 (v/v), 0.103 MPa total pressure) with an induction time of roughly 2 h.

These results are quite interesting as they show that with passage from $O_2$ to peroxocarbonate it is possible to find effects similar to those observed when dioxygenases or monooxygenase are considered.

Peroxocarbonates are prone to transfer one single oxygen atom to an oxophile or an olefin, while $O_2$ causes essentially

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the splitting of the olefinic double bond, using two oxygen atoms. This tendency is explained by the fact that peroxocarbonates convert into carbonates according to reaction 1.

$$\text{“}Rh(CO_4)\text{”} + XY \rightarrow \text{“}Rh(CO_3)\text{”} + XYO \qquad (1)$$

It is of interest at this point to investigate the reaction mechanism of oxygen transfer.

This was made possible by the availability of an asymmetrically labeled peroxo group bonded to rhodium ($Rh-^{16}O-^{18}O-C$ or a $Rh-^{18}O-^{16}O-C$). Therefore, we have studied the oxygen transfer reaction using phosphine as acceptor, which makes simple the reaction as only one product (phosphine oxide) is possible.

When $Cl\overline{Rh(^{18}O^{16}OC(O)O})(PEt_2Ph)_3$ was dissolved in $CH_2Cl_2$ at room temperature, the O-transfer reaction to phosphine took place according to eq 2. The GC-MS analysis of the solution has allowed to determine that the phosphine oxide formed contained more than 85−90% $^{18}O$. This suggests that the oxygen atom of the peroxo group transferred is that linked to Rh, more than that linked to carbon. This result is confirmed also by the reaction of $Cl\overline{Rh(^{16}O^{18}OC(^{18}O)^{16}O})(PEt_2Ph)_3$ that affords $RhCl(CO_3)(P)_2$ and $P{=}^{16}O$ when dissolved in $CH_2Cl_2$ at room temperature with a similar selectivity (85−90% $^{16}O$ on phosphine oxide).

$$Cl\overline{Rh(^{18}O^{16}OC(O)^{18}O})(P)_3 \rightarrow RhCl(CO_3)(P)_2 + P{=}^{18}O \qquad P = PEt_2Ph \quad (2)$$

More detailed studies are in progress in order to elucidate if this specific step of the oxidative reaction takes place *via* an O−O bond splitting followed by the reaction with the entering oxophile or *via* an intramolecular reaction.

## Experimental Section

**General Procedure.** Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen or $CO_2$ atmosphere by using vacuum-line techniques. All solvents were dried as described in the literature[21] and stored under dinitrogen. $CO_2$ (≥99.95%) and $O_2$ (≥99.998%) were from SIO SpA, $C^{18}O_2$ (97.7% $^{18}O$) was from CEA-ORIS and $^{18}O_2$ (99% $^{18}O$) from SIC. $RhCl(P)_3$ complexes were prepared from $[RhCl(C_2H_4)]_2$ (Aldrich) and the corresponding phosphines (Aldrich) according to previously reported experimental procedures.[22] The synthesis of $RhCl(\eta^2\text{-}O_2)(P)_3$ ($P = PEt_2Ph$, $PEtPh_2$) has been described elsewhere.[2b] The same procedure, using $^{18}O_2$, was followed in this work for the preparation of $RhCl(\eta^2\text{-}^{18}O_2)(PEt_2Ph)_3$.

$^{31}P$ NMR spectra were obtained at 81 MHz with a Varian XL-200 instrument. $^{31}P$ chemical shifts are referred to 85% $H_3PO_4$ using the high-frequency-positive convention.

FTIR spectra were recorded using a Bruker 113V Fourier transform interferometer. Frequencies are accurate to $\pm 1\ cm^{-1}$. Solid samples were studied as Nujol mulls (Nujol was previously dried on sodium wire and bubbled with argon). The extreme sensitivity of $RhCl(CO_4)(PEt_2Ph)_3$ under laser irradiation prevented us from obtaining Raman spectra (even with weak red exciting lines at low temperature).

GC analysis were performed with a Dani HR 3800 gas chromatograph equipped with a 2 m SE-30 or a 2 m OV-17 packed column.

GC-MS analysis was carried out with a HP 5890 gas chromatograph linked to a HP 5970 mass detector (capillary column: SE-30, 30 m × 0.00032 m, 0.25 $\mu$m film thickness).

**Synthesis of $Cl\overline{Rh(^{16}O^{18}OC(^{18}O)^{16}O})(PEt_2Ph)_3$ and $Cl\overline{Rh(^{18}O^{16}OC(^{16}O)^{18}O})(PEt_2Ph)_3$.** We report in detail the synthesis of $Cl\overline{Rh(^{18}O^{16}OC(^{16}O)^{18}O})(PEt_2Ph)_3$ from $RhCl(\eta^2\text{-}^{18}O_2)(PEt_2Ph)_3$ and $C^{16}O_2$. A similar procedure was followed for the synthesis of $Cl\overline{Rh(^{16}O^{18}OC(^{18}O)^{16}O})(PEt_2Ph)_3$ starting from $RhCl(\eta^2\text{-}^{16}O_2)(PEt_2Ph)_3$ and $C^{18}O_2$.

A solid sample of $RhCl(\eta^2\text{-}^{18}O_2)(PEt_2Ph)_3$ (0.300 g, 0.45 mmol) was dissolved in toluene (30 mL) saturated with $C^{16}O_2$ at 243 K. The solution was then added with pentane (50 mL) and stored overnight at 243 K. The yellow solid that separated was filtered under Ar, washed with pentane, and dried *in vacuo*. Anal. Calcd for $C_{31}H_{45}Cl^{18}O_2{}^{16}O_2P_3Rh$: C, 51.93; H, 6.32; P, 12.97; Cl, 4.94. Found: C, 51.83; H, 6.42; P, 12.87; Cl, 4.84.

The same procedure affords the $PEtPh_2$ complexes $Cl\overline{Rh(^{16}O^{18}OC(^{18}O)^{16}O})(PEtPh_2)_3$ and $Cl\overline{Rh(^{18}O^{16}OC(^{16}O)^{18}O})(PEtPh_2)_3$.

**Styrene Oxidation by $O_2$ in the Presence of $RhCl(PEt_2Ph)_3$.** A 0.100 mg (0.16 mmol) amount of $RhCl(PEt_2Ph)_3$ was dissolved in 20 mL of toluene, and 2 mL of styrene was added. The reaction mixture was stirred at 278 K under 0.1 MPa of $O_2$ pressure. Samples were withdrawn each hour and analyzed by GC. The reaction was stopped when no further conversion of styrene was observed.

**Styrene Oxidation by $O_2/CO_2$ in the Presence of $RhCl(PEt_2Ph)_3$.** A 0.100 mg (0.16 mmol) amount of $RhCl(PEt_2Ph)_3$ was dissolved in 20 mL of toluene, and 2 mL of styrene was added. The reaction mixture was reacted with a $O_2/CO_2$ mixture (1:1 molar ratio; total pressure = 0.1 MPa) at 278 K. Samples were withdrawn each hour and analyzed by GC. The reaction was stopped when no further conversion of styrene was observed.

**THF Oxidation to Butyrolactone by $ClRh(CO_4)(PEt_2Ph)_3$.** A 0.150 g (0.21 mmol) amount of $ClRh(CO_4)(PEt_2Ph)_3$ was dissolved in 5 mL of THF at 273 K. The GC analysis of the reaction mixture shows the formation of butyrolactone, the main process being in these conditions the oxidation of the P ligand.

**O-Transfer to Phosphine Ligand.** A 0.150 g (0.21 mmol) amount of $ClRh(^{18}O^{16}OC(^{16}O)^{18}O)(PEt_2Ph)_3$ was dissolved in 5 mL of $CH_2Cl_2$. The solution was stirred at 313 K for 1 h and analyzed by GC-MS. The GC-MS analysis showed the formation of $^{18}O{=}P(Et_2Ph)_3$ and $^{16}O{=}P(Et_2Ph)_3$ in molar ratio 85:15. The experiment was repeated in the same conditions using $ClRh(^{16}O^{18}OC(^{18}O)^{16}O)(PEt_2Ph)_3$. In this case, $^{18}O{=}P(Et_2Ph)_3$ and $^{16}O{=}P(Et_2Ph)_3$ were formed in 15:85 molar ratio.

**Acknowledgment.** We thank Italian MURST (40%, 60%) and the EU COST Program (D3/007/94) for financial support. M.A. wishes to thank Prof. J. Ibers for having inspired the idea of this work.

IC951154W

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