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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1252). Services for accessing these data are described at the back of the journal.

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## Trichlorooxo(triphenylphosphine)(triphenylphosphine oxide)rhenium(V)

JEFFREY C. BRYAN,<sup>a</sup> MARC C. PERRY<sup>b</sup> AND JEFFREY B. ARTERBURN<sup>b</sup>

<sup>a</sup>Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6119, USA, and  
<sup>b</sup>Department of Chemistry, New Mexico State University, Box 30001, Department 3C, Las Cruces, NM 88003, USA.  
 E-mail: bryanjc@ornl.gov

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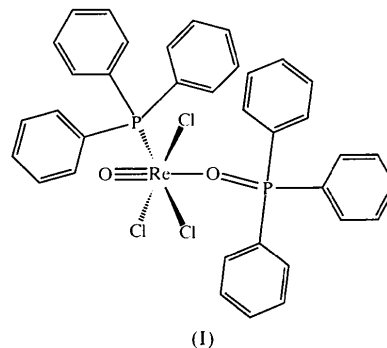
## Abstract

The title complex,  $[\text{ReCl}_3\text{O}(\text{C}_{18}\text{H}_{15}\text{OP})(\text{C}_{18}\text{H}_{15}\text{P})]$ , is produced in a reaction between  $[\text{Re}(\text{O})\text{Cl}_3(\text{PPh}_3)_2]$  and ethyl 2-hydroxymethyl sulfoxide. The structure is compared to that of  $[\text{Re}(\text{O})\text{Cl}_3(\text{PPhEt}_2)(\text{OPPhEt}_2)]$ . The Re—Cl distances are shorter [2.361 (2)–2.384 (2) Å] and the Re—P distance is longer [2.506 (2) Å] in the title complex.

## Comment

A variety of interesting and synthetically useful O-atom transfer reactions from sulfoxide substrates catalyzed by the precursor complex  $[\text{Re}(\text{O})\text{Cl}_3(\text{PPh}_3)_2]$  have recently been reported (Bryan *et al.*, 1987; Arterburn &

Perry, 1996; Arterburn & Nelson, 1996; Arterburn *et al.*, 1997). This compound was known to react with dimethyl sulfoxide in the presence of hydrochloric acid to form the mixed dimethylsulfide–triphenylphosphine oxide complex  $[\text{Re}(\text{O})\text{Cl}_3(\text{SMe}_2)(\text{OPPh}_3)]$ . However, no intermediate complexes from the catalytic reactions in organic solvents have yet been structurally identified. The precursor complex was found to react with one equivalent of ethyl 2-hydroxyethyl sulfoxide,  $\text{CH}_3\text{CH}_2\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{OH}$ , at ambient temperature to give a purple solution. The title complex, (I), and amorphous purple solids were obtained following precipitation with diethyl ether. These results are consistent with catalytic pathways involving coordinated  $\text{Re}^{\text{V}}\text{-oxo}$  complexes as intermediates.



A distorted octahedral coordination geometry is observed around Re (Fig. 1). The major distortion is an increase in the O1—Re—Cl angles, which is commonly observed in octahedral complexes containing a

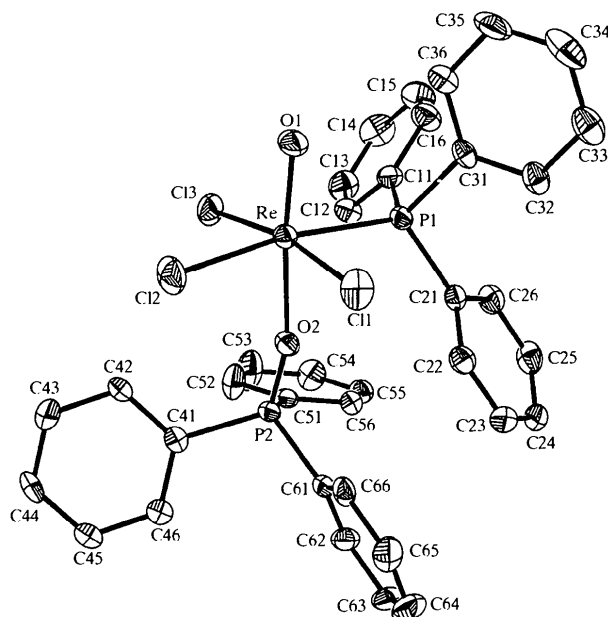


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

multiply bonding ligand (Nugent & Mayer, 1988; Bryan *et al.*, 1987). The location of softer ligands *cis* to the oxo ligand is also often observed (Bryan *et al.*, 1987). The short Re—oxo (O1) bond length of 1.669 (4) Å is consistent with a strong multiple bond (Nugent & Mayer, 1988). The structure of (I) is very similar to the closely related [Re(O)Cl<sub>3</sub>(PPhEt<sub>2</sub>)(OPPhEt<sub>2</sub>)] (Sergienko, 1994; Sergienko *et al.*, 1982). The Re—Cl distances are shorter [2.361 (2)–2.384 (2) Å] in (I) than in [Re(O)Cl<sub>3</sub>(PPhEt<sub>2</sub>)(OPPhEt<sub>2</sub>)] [2.394 (4)–2.407 (4) Å], while the Re—P distance is longer [2.506 (2) *versus* 2.464 (4) Å]. These differences can be understood by the fact that PPh<sub>3</sub> is a weaker donor ligand than OPPhEt<sub>2</sub>.

### Experimental

The preparation of (I) has been previously reported (Grove & Wilkinson, 1966; Bryan *et al.*, 1987). Green crystals suitable for X-ray diffraction were prepared by slow diffusion of methyl *tert*-butyl ether into an acetone solution of the complex.

#### Crystal data

[ReCl<sub>3</sub>O(C<sub>18</sub>H<sub>15</sub>OP)-  
(C<sub>18</sub>H<sub>15</sub>P)]  
M<sub>r</sub> = 849.14  
Monoclinic  
P2<sub>1</sub>/c  
a = 18.797 (2) Å  
b = 9.5553 (6) Å  
c = 19.4819 (13) Å  
β = 109.574 (6)°  
V = 3296.9 (5) Å<sup>3</sup>  
Z = 4  
D<sub>x</sub> = 1.711 Mg m<sup>-3</sup>  
D<sub>m</sub> not measured

Mo Kα radiation  
λ = 0.71073 Å  
Cell parameters from 25 reflections  
θ = 10.4–13.0°  
μ = 4.06 mm<sup>-1</sup>  
T = 173 K  
Prism  
0.46 × 0.27 × 0.23 mm  
Green

#### Data collection

Nonius CAD-4 diffractometer  
ω scans  
Absorption correction:  
ψ scan (Siemens, 1997)  
T<sub>min</sub> = 0.274, T<sub>max</sub> = 0.393  
8509 measured reflections  
7561 independent reflections  
5690 reflections with  
I > 2σ(I)

R<sub>int</sub> = 0.039  
θ<sub>max</sub> = 27.5°  
h = 0 → 24  
k = -12 → 5  
l = -25 → 23  
3 standard reflections  
frequency: 120 min  
intensity decay: 3%

#### Refinement

Refinement on F<sup>2</sup>  
R(F) = 0.040  
wR(F<sup>2</sup>) = 0.099  
S = 1.074  
7561 reflections  
397 parameters  
H atoms not refined  
w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0502P)<sup>2</sup>  
+ 4.6318P]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = -0.001  
Δρ<sub>max</sub> = 2.40 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -1.47 e Å<sup>-3</sup>  
Extinction correction: none  
Scattering factors from  
International Tables for  
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Re—C11	2.373 (2)	Re—O1	1.669 (4)
Re—C12	2.361 (2)	Re—O2	2.082 (4)
Re—C13	2.384 (2)	P2—O2	1.508 (4)
Re—P1	2.506 (2)		
C11—Re—C12	86.53 (6)	C12—Re—O2	87.33 (11)
C11—Re—C13	169.74 (6)	C13—Re—P1	95.09 (5)
C11—Re—P1	89.69 (5)	C13—Re—O1	94.07 (19)
C11—Re—O1	95.25 (19)	C13—Re—O2	84.17 (12)
C11—Re—O2	87.23 (12)	P1—Re—O1	86.82 (16)
C12—Re—C13	87.50 (6)	P1—Re—O2	84.90 (11)
C12—Re—P1	171.52 (6)	O1—Re—O2	171.35 (18)
C12—Re—O1	101.07 (16)	Re—O2—P2	165.1 (3)

Anisotropic displacement parameters were used for all non-H atoms. All H atoms were placed in calculated positions (C—H = 0.95 Å), refined using a riding model, and given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which they are attached. The highest eight peaks in the final difference map (electron density greater than 0.8 e Å<sup>-3</sup>) are located approximately 1 Å from Re.

Data collection: CAD-4-PC (Enraf-Nonius, 1993). Cell refinement: CAD-4-PC. Data reduction: XCAD4 (Harms, 1995). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL (Siemens, 1997). Software used to prepare material for publication: PLATON (Spek, 1998).

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