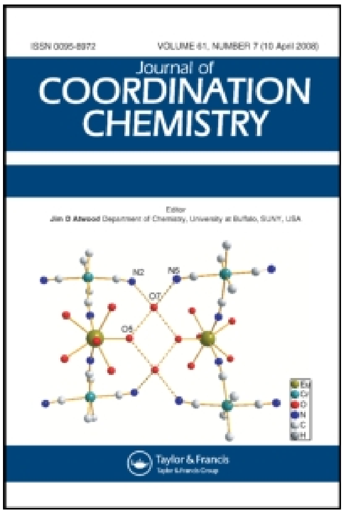

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# Synthesis and structure of *bis*(triphenylphosphino)dichlorohydroxooxorhenium(V)

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*Notes*

# Synthesis and structure of *bis*(triphenylphosphino)dichlorohydroxooxorhenium(V)

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The reaction of equimolar amounts of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] and 2-aminobenzimidazole in acetone containing 1% water led to the isolation of *trans*-[ReO(OH)Cl$_2$(PPh$_3$)$_2$]. The product has been characterized by infrared spectroscopy and X-ray crystallography. The hydroxo group is coordinated *trans* to the oxo group, with the respective bond lengths Re–OH = 1.911(3) and Re=O = 1.815(3) Å.

*Keywords*: Rhenium(V); Oxo-hydroxo; Crystal structure

## 1. Introduction

The ease of its preparation from perrhenate, its stability and the ready substitution of its chloride and phosphine ligands have made *trans*-[ReOCl$_3$(PPh$_3$)$_2$] one of the most convenient starting materials to synthesize new oxorhenium(V) coordination complexes [1–3]. The chloride *trans* to the oxo group is the most readily substituted, and compounds of the type [ReOCl$_2$(OR)(PPh$_3$)$_2$] (R = Me, Et, *etc.*) are well known [4]. However, the substitution of the *trans* chloride by hydroxide to form *trans*-[ReO(OH)Cl$_2$(PPh$_3$)$_2$] (**1**) has not been observed, and a search of the literature revealed that its crystal structure has not been reported.

## 2. Experimental

*trans*-[ReOCl$_3$(PPh$_3$)$_2$] was prepared by a literature procedure [5], and 2-aminobenzimidazole was obtained commercially. Scientific instrumentation and procedures used

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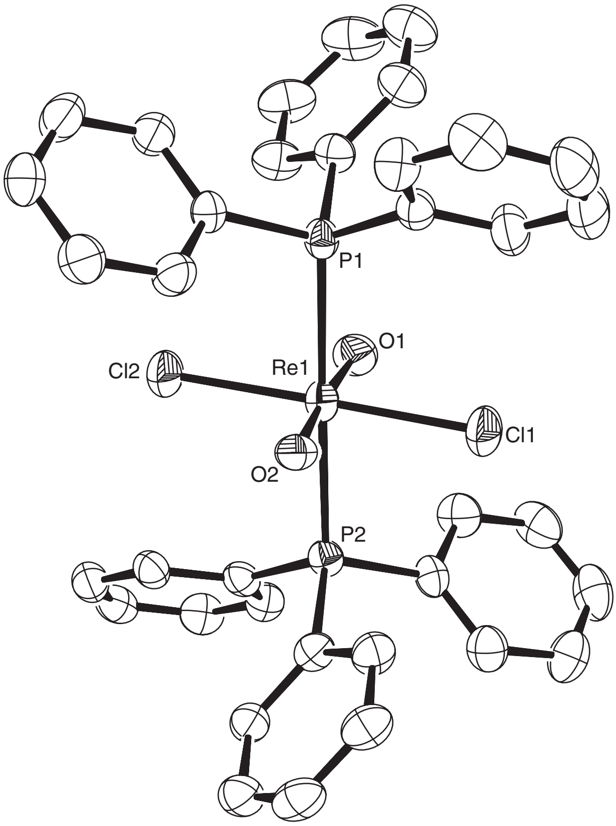

Figure 1. Structure of $[ReO(OH)Cl_2(PPh_3)_2]$ (**1**) with the atom numbering scheme and thermal ellipsoids drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

are the same as reported elsewhere [3]. Infrared spectra were obtained using KBr discs and $^1H$ NMR spectra were run in $d_6$-DMSO.

### 2.1. trans-*[ReO(OH)Cl$_2$(PPh$_3$)$_2$] (1)*

A mixture of 100 mg (120 µmol) of *trans*-$[ReOCl_3(PPh_3)_2]$ and 16 mg (120 µmol) of 2-aminobenzimidazole in 20 cm$^3$ of acetone containing 1% water was heated under reflux for 3 h. After heating was stopped and the green solution cooled to room temperature, the solution was filtered and left to evaporate slowly at ambient temperatures. After 2 days, lime-green crystals were collected. They were washed with ethanol and diethylether, and dried under vacuum. Yield = 66 mg (68%), m.p. 231°C. Anal. Calcd (%): C, 53.07; H, 3.84. Found: C, 53.21; H, 3.67. IR (cm$^{-1}$): $\nu$(Re=O) 937, $\nu$(Re–OH) 455, $\nu$(Re–Cl) 324. $^1H$ NMR (ppm): 7.51–7.67 (m, 30H, P*Ph*$_3$).

### 2.2. *Crystallography*

Data collection was performed at 200(2) K on a Nonius Kappa CCD using Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix

Table 1. Crystallographic data for **1**.

| | |
|---|---|
| Chemical formula | $C_{36}H_{31}O_2Cl_2P_2Re$ |
| Formula weight | 814.69 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions (Å, °) | |
| $a$ | 11.4622(2) |
| $b$ | 14.6781(4) |
| $c$ | 16.0647(4) |
| $\alpha$ | 115.992(1) |
| $\beta$ | 90.876(1) |
| $\gamma$ | 90.5716(9) |
| Volume (Å$^3$) | 2428.7(1) |
| $Z$ | 3 |
| Density (Calcd) (Mg m$^{-3}$) | 1.669 |
| Absorption coefficient (mm$^{-1}$) | 4.048 |
| $F$(000) | 1203 |
| Crystal size (mm$^3$) | $0.03 \times 0.06 \times 0.08$ |
| $\theta$ range for data collection (°) | 3.1–27.5 |
| Index ranges | $-14 \le h \le 14$; $-19 \le k \le 19$; $-20 \le l \le 20$ |
| Reflections measured | 35384 |
| Independent/observed reflections | 10914/8679 |
| Data/parameters | 10914/583 |
| Goodness-of-fit on $F^2$ | 1.03 |
| Final $R$ indices [$I > 2\sigma(I)$] | 0.0354, $wR_2 = 0.0916$ |
| Largest diff. peak and hole (e Å$^{-3}$) | 2.44, −1.47 |

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

| | | | |
|---|---|---|---|
| Re–O(1) | 1.815(3) | Re–O(2) | 1.911(3) |
| Re–P(1) | 2.529(1) | Re–P(2) | 2.535(1) |
| Re–Cl(1) | 2.4013(9) | Re–Cl(2) | 2.3724(9) |
| O(1)–Re–O(2) | 175.0(1) | P(1)–Re–P(2) | 178.38(3) |
| Cl(1)–Re–Cl(2) | 178.94(4) | O(1)–Re–Cl(1) | 88.0(1) |
| O(1)–Re–P(1) | 91.5(1) | O(1)–Re–Cl(2) | 91.5(1) |
| O(1)–Re–P(2) | 89.4(1) | P(1)–Re–Cl(1) | 95.18(3) |

least-squares procedures using SHELXL-97 [6]. All non-hydrogen atoms were refined anisotropically. An ORTEP view of **1**, along with the atom numbering scheme, is given in figure 1. Relevant crystallographic data are given in table 1, with selected bond lengths and angles in table 2.

## 3. Results and discussion

Reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with an equimolar quantity of 2-aminobenzimidazole (abi) in wet acetone led to the isolation of the unexpected product *trans*-[$ReO(OH)Cl_2(PPh_3)_2$] (**1**). In the infrared spectrum of **1** the stretching frequency of the rhenium(V)-oxo multiple bond occurs at 937 cm$^{-1}$, with $\nu$(Re–OH) and $\nu$(Re–Cl) at 455 and 324 cm$^{-1}$ respectively. The $^1$H NMR spectrum only establishes the presence of the two PPh$_3$ ligands, with the 30 protons giving rise to a multiplet of signals in the range 7.51–7.67 ppm.

The crystal structure of **1** (figure 1) shows that the complex is monomeric and neutral, and that the rhenium atom lies at the centre of a pseudo-octahedral environment. The basal plane is defined by the two chlorides Cl(1) and Cl(2) and by the two phosphorus atoms P(1) and P(2). The oxo group O(1) and the hydroxyl O(2) atoms are in *trans* axial positions. Selected bond distances and angles are given in table 2. Distortion from an ideal rhenium-centred octahedron mainly results in a nonlinear O(1) = Re–O(2) axis of 175.0(1)°, with Cl(1)–Re–Cl(2) and P(1)–Re–P(2) angles of 178.94(4)° and 178.38(3)°, respectively. The rhenium atom is lifted slightly out of the mean equatorial Cl$_2$P$_2$ plane by 0.0053(1) Å towards O(1), as the result of the nonorthogonal angles O(1)–Re–P(1) = 91.5(1)°, O(1)–Re–P(2) = 89.4(1)°, O(1)–Re–Cl(1) = 88.0(1)° and O(1)–Re–Cl(2) = 91.5(1)°. The Re atom is 1.23(1) Å from the P(1)Cl(1)O(1) plane and 1.21(1) Å from the P(2)Cl(2)O(2) plane, with the dihedral angle between these two planes being 0.78°.

The Re–O(1) bond length of 1.815(3) Å is considerably longer than is normally observed in monooxorhenium(V) complexes [1.65(1)–1.70(1) Å], and is also longer than the range [1.74(1)−1.79(1) Å] found in *trans*-dioxo complexes [7, 8]. However, it is shorter than bridging Re–O$_{oxo}$ bond lengths [1.92(2) Å average] found in complexes containing the $\mu$-oxo-bridged $[Re_2O_3]^{4+}$ moiety [2, 9]. Distances of 2.04, 1.86 and 1.75 Å have been proposed for typical rhenium-oxygen single, double and triple bonds respectively [8, 9]. The Re=O bond length in [ReO(OEt)Cl$_2$(PPh$_3$)$_2$] equals 1.76(1) Å [10]. The Re–O(2)H length of 1.911(3) Å intimates that this bond has significant double-bond character, and it is very similar to the Re–OEt bond length in [ReO(OEt)Cl$_2$(PPh$_3$)$_2$] of 1.89(1) Å [10]. Re–Cl and Re–P bond lengths are normal and similar to those in oxorhenium(V) complexes containing *trans* chlorides and phosphines [11, 13].

## Supplementary material

CCDC-299047 contains crystallographic data for complex **1**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1 EZ, UK; Fax: + 44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk).

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