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Bidentate phosphinophenol ligands. Preparation and electrochemistry of the Re(III) complexes of 2-(diphenylphosphinomethyl)-4-methylphenol (P_1 -OH) and 2-diphenylphosphinophenol (P_2 -OH). Crystal and molecular structure of *mer*-Re[P_1 -O]₃

Frédérique Loiseau ^a, Fabienne Connac ^a, Yolande Lucchese ^a, Michèle Dartiguenave ^{a,*}, Sébastien Fortin ^b, André L. Beauchamp ^b, Yvon Coulais ^c

^a Laboratoire de Chimie Inorganique, Université Paul Sabatier, 118 Route de Narbonne, F-31062 Toulouse Cedex, France

^b Département de Chimie, Université de Montréal, C.P. 6128, Succ. Centre-Ville, Montréal, Oue., Canada, H3C 3J7

^c Laboratoire d'Imagerie Médicale, Morphologique et Fonctionnelle, Hôpital Purpan, Université Paul Sabatier, Place du Dr. Baylac, F-31059 Toulouse, France

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Abstract

The reaction of 2-(diphenylphosphinomethyl)-4-methylphenol (P_1 -OH) and 2-diphenylphosphinophenol (P_2 -OH) on ReCl₃(MeCN)(PPh₃)₂ in a 3:1 ratio leads to the formation of the homoleptic Re(III) complexes Re(P_1 -O)₃ (1) and Re(P_2 -O)₃ (2) in high yield. 1 is reasonably stable in air in the solid state and in solution, which is not the case for 2. Orange-red crystals of 1 contain distorted octahedral Re entities in which the metal is coordinated to three bidentate phosphinophenolato ligands in the *mer* configuration. Cyclic voltammetry of 1 and 2 shows two well defined monoelectronic quasi-reversible redox waves, one reductive attributed to the Re(III)/Re(II) couple and one oxidative due to the Re(III)/Re(IV) one. A second oxidative wave, attributed to the Re(IV)/Re(V) couple, is reversible only for 1, indicating the lower stability of 2 toward oxidation. In agreement with this, 2 gives, in air, the Re(V)-oxo species ReO(O-P₂=O)(P₂-O)₂ (3) quantitatively, whose structure is confirmed by X-ray diffraction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhenium complexes; Phosphinophenol complexes; Crystal structures; Electrochemistry

1. Introduction

The reaction of mono- and polydentate phosphinophenol ligands on rhenium and technetium centers has been investigated thoroughly in relation with their applications as radiopharmaceuticals. There are several examples of rhenium(V) oxo, imido and nitrido complexes with $Ph_2PC_6H_4OH$ (P₂–OH) [1–4] and $Ph_2PCH_2C_6H_3(CH_3)OH$ (P₁–OH) [5]. However, although the technetium(III) complex, $Tc(P_2-O)_3$ [2] has

been known for a while, the related Re(III) species, $Re(P_2-O)_3$ has not been synthesized yet. This is not the case for the phosphinothiophenol ligand, for which both the Tc(III) and Re(III) complexes are known [3,6].

We wish to report here the synthesis of the two homoleptic $\text{Re}(P_1-O)_3$ (1) and $\text{Re}(P_2-O)_3$ (2) complexes. Surprisingly, we observed that using $\text{Ph}_2\text{PCH}_2\text{C}_6\text{H}_3$ -(CH₃)OH (P₁-OH), which introduces more flexibility in the bonding because of the presence of an sp³ carbon atom in the metallacycle, increases the stability of the complex. Complex 1 was characterized by X-ray diffraction. The air sensitive $\text{Re}(P_2-O)_3$ complex (2) gives the Re(V) complex $\text{ReO}(O-P_2=O)(P_2-O)_2$ (3) as an oxidation product, quantitatively in air, which was characterized by X-ray diffraction. These differ-

^{*} Corresponding author. Tel.: + 33-5-6155 6121; fax: + 33-5-6155 6118.

E-mail address: dartigue@iris.ups-tlse.fr (M. Dartiguenave).

ences are also apparent on the cyclic voltammograms of these two complexes.

2. Experimental

2.1. Reactants and physical measurements

 $\operatorname{ReCl}_3(\operatorname{MeCN})(\operatorname{PPh}_3)_2$ [7], 2-(diphenylphosphinomethyl)-4-methylphenol (P1-OH) [8] and diphenylphosphinophenol (P₂-OH) [9] were synthesized by the procedures described in the literature. The reactions were carried out in an atmosphere of nitrogen using standard Schlenk techniques. Ether was dried over sodium benzophenone ketyl and distilled prior to use. CH₂Cl₂ and ethanol were distilled freshly over molecular sieves (3 Å). Infrared spectra $(400-4000 \text{ cm}^{-1})$ were recorded as CsI pellets on a Bruker VICTOR spectrophotometer. The ${}^{31}P{}^{1}H$ NMR spectrum of **3** was recorded in CD₂Cl₂ at room temperature (r.t.) on a Bruker ARX 400 instrument. Magnetic moments were determined in the solid state at 25°C by the Faraday method, using a Cahn microbalance coupled with a Drusch electromagnet. HgCo(NCS)₄ was used as standard $(X_g =$ 16.44.10⁻⁶ cgs emu) and corrections were applied for the diamagnetism of the ligands [10]. Mass determinations were made with a NERMAG-R 1010 spectrometer (FAB⁺). Electrochemical measurements were carried out at room temperature with a locally made potentiostat controlled by a personal computer. A conventional three-electrode electrochemical cell (10 ml) was used: Pt working electrode (disk of 2 mm diameter, EDI Tacussel 1 mm diameter for cyclic voltammetry experiments); platinum wire counter electrode; doublejunction saturated calomel reference electrode. The experiments were run in 0.1 M NBu₄ClO₄-DMF or NBu₄PF₆-CH₂Cl₂ (Aldrich Electrochemical Grade), which were used without further purification. Elemental analyses were carried out at the Laboratoire de Chimie de Coordination du CNRS, Toulouse.

2.2. Synthetic work

2.2.1. Synthesis of $Re(P_1-O)_3$ (1)

A solution of 0.31 g (0.35 mmol) of ReCl₃(MeCN)(PPh₃)₂, 0.32 g (1.1 mmol) of P₁–OH and 0.11 g (1.1 mmol) of NEt₃ in ethanol (40 ml) was refluxed for 17 h under stirring. An orange–red solid deposited on cooling, which was filtered, washed with alcohol and dried in vacuo. Yield: 70%. Recrystallization from CH₂Cl₂–ether (1/1) at 4°C gave orange–red crystals suitable for X-ray work. *Anal.* Calc. (Found) for C₆₀H₅₄O₃P₃Re: C, 65.38 (65.07); H, 4.94 (4.93%). MS (FAB⁺): $m/z = 1102 [M]^+$. μ_{eff} (r.t., solid state): 0.7 BM.

2.2.2. Synthesis of $Re(P_2-O)_3$ (2)

Same method as 1, using 0.308 g (0.36 mmol) of ReCl₃(MeCN)(PPh₃)₂, 0.30 g (1.08 mmol) of P₂–OH and 0.109 g (1.08 mmol) of NEt₃ in 25 ml of ethanol. The dark red precipitate was filtered off, washed with cold ethanol and diethyl ether, and dried in vacuo. Yield: 65%. The product was soluble in common organic solvents. *Anal.* Calc. (Found) for C₅₄H₄₂O₃P₃Re: C, 63.71 (63.47); H, 4.16 (4.13); O, 4.71 (4.90%). MS (FAB⁺): $m/z = 1018 [M]^+$. μ_{eff} (r.t., solid state): 1.5 BM.

2.2.3. Synthesis of $ReO(O-P_2=O)(P_2-O)_2$ (3)

A red solution of Re(P₂–O)₃ (2) (0.20 g, 0.20 mmol) in 15 ml of diethyl ether was stirred in air for 2 h, during which time it turned green. Slow concentration of the solution precipitated a green crystalline compound, which was filtered off, washed with cold diethyl ether, and dried in vacuo. Yield: 80%. *Anal.* Calc. (Found) for C₅₄H₄₂O₅P₃Re: C, 61.77 (60.21); H, 4.03 (4.33%). IR (CsI, cm⁻¹): 957, ν (Re=O); 1175, ν (P=O). MS (FAB⁺): m/z = 1050 [M]⁺. ³¹P{¹H} NMR (CD₂Cl₂, 161.98 MHz, ppm): 3.6, 7.7 (dd, ²J_{PP} = 6.7 Hz), 28.5 (s). Recrystallization in acetonitrile gave crystals suitable for X-ray work.

2.3. X-ray diffraction studies

In both cases, the crystal was mounted on a glass fiber and transferred to an Enraf–Nonius CAD-4 diffractometer, where the data were collected at room temperature with the graphite-monochromatized Cu K α radiation. The reduced cells were obtained from rotation photographs [11]. Space group was determined from the Laue symmetry and systematic absences checked in the final data set. Intensity data were corrected for absorption (Gaussian integration based on crystal faces, NRCVAX package [12]) and averaged. Crystal data and conditions for data collection are summarized in Table 1.

2.3.1. Structure resolution for $Re(P_1-O)_3$ (1)

Suitable crystals were obtained by recrystallization from CH₂Cl₂-ether at 4°C. The structure was solved by the direct-methods of SHELXS-86 [13] and ΔF syntheses using SHELXL-93 [14]. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed initially at idealized positions and moved after each run using a riding model, the fixed C-H distances being 0.93 (CH), 0.97 (CH₂) or 0.96 Å (CH₃). The isotropic displacement factors U_{iso} were adjusted to 50 (CH₃) or 20% (others) higher than that of the bonded carbon atom. The CH₂Cl₂ solvent molecule was found to be disordered over two positions with populations of 0.45 and 0.55, respectively. Constraints were imposed for the refinement of the two sets of individual positions, as explained in the supplementary material. Refinement converged normally to R = 0.039.

2.3.2. Structure resolution for $ReO(O-P_2=O)(P_2-O)_2$ (3)

Single crystals were obtained by recrystallization from acetonitrile. The Re atom located from a Patterson map was used as the starting model. All other non-hydrogen atoms in the complex were found from successive ΔF maps. The non-hydrogen atoms were handled as above. Refinement converged to a conventional R factor of 0.041. The ΔF map phased on the complex showed a series of weak residuals around (0, 0, 0)0) and (1/2, 1/2, 1/2), likely due to acetonitrile solvent molecules. However, because of severe disorder, these residuals could not be assembled into discrete orientations. Therefore, this part of the structure was modeled by using the SQUEEZE procedure of the PLATON software [15], which indicated that each of the two symmetry-equivalent pockets had a void volume of 245 Å³ and contained ~ 26 electrons. Thus, each pocket included one acetonitrile molecule, which corresponds to onehalf acetonitrile per complex. This composition was used to calculate the derived quantities in Table 1. The contribution of the disordered solvent was calculated with the Bypass procedure of van der Sluis and Spek [16], and a new hkl/F_{o}^{2} list bypassing the solvent contribution was generated. The final model consisting of the ordered part only, without the disordered solvent contribution, was refined against this new data list, which is the one provided in the CIF file. Refinement con-

Table 1

Crystal data and details of the structure determination for $Re(P_1-O)_3$ (1) and ReO(O-P₂=O)(P₂-O)₂ (3)

Formula	C ₆₀ H ₅₄ O ₃ P ₃ Re,	C ₅₃ H ₄₂ O ₅ P ₃ Re,
	CH_2Cl_2	1/2CH ₃ CN
Formula weight	1187.08	1070.6
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	13.466(5)	14.756(5)
$b(\mathbf{A})$	22.390(9)	18.691(5)
c (Å)	18.314(6)	17.840(5)
β (°)	103.56(3)	102.18(2)
$V(Å^3)$	5368(3)	4810(2)
Z	4	4
$D_{\rm calc} \ ({\rm g} \ {\rm cm}^{-3})$	1.469	1.478
$\mu ({\rm mm^{-1}})$	6.41	6.10
Radiation $(\lambda, \text{ Å})$	Cu Ka	Cu Ka
<i>T</i> (K)	293(2)	293(2)
Reflections measured	37 936	33 354
Unique reflections	10 160	9096
Reflections with	6727	7639
$[I_{\rm net} > 2.0\sigma(I_{\rm net})]$		
$R_{\rm f}$ (significant reflections) ^a	0.0391	0.0373
$R_{\rm w}$ (significant reflections) ^b	0.0782	0.1009

^a $R_{\rm f} = \Sigma ||F_{\rm o}| - |F_{\rm c}|| / \Sigma |F_{\rm o}|.$ ^b $R_{\rm w} = [\Sigma [w(F_{\rm o}^2 - F_{\rm c}^2)^2] / \Sigma [w(F_{\rm o}^2)^2]]^{1/2}.$

verged to R = 0.037. The highest residuals were +1.15and -1.41 e Å⁻³ (near Re) and the general background was below ± 0.8 e Å⁻³.

Final atomic coordinates and complete crystallographic results for 1 and 3 are available as supplementary material.

3. Results and discussion

The reaction of 3 equiv. of (P-OH) ligand on ReCl₃(MeCN)(PPh₃)₂ for 17 h in refluxing ethanol, in presence of 3 equiv. of NEt₃ as a proton quencher, leads to the formation of $Re(P-O)_3$ (1 and 2), which precipitate as orange-red powders in good yield.

1 was recrystallized from CH_2Cl_2 -ether (1/1) at 4°C giving orange-red crystals suitable for X-ray work. They can be handled in air and in solution without noticeable decomposition. This is in contrast with the behavior of $Re(P_2-O)_3$ (2), which in air leads irreversibly to the Re(V)-oxo complex ReO(P₂-O)₂- $(O-P_2=O)$ (3) (vide infra).

The elemental analysis and mass spectrometry (FAB⁺ technique), which shows the molecular peaks at $[M]^+ = 1102$ (1) and 1018 (2), confirm the molecular structure. The magnetic moment of the solids, $\mu_{\rm eff} = 0.7$ B.M for 1 and 1.5 B.M for 2, is temperature independent between 300 and 90 K. This value lies in the wide range reported for d⁴ low-spin octahedral Re(III) complexes (³T_{1g} ground state) [17-24]. This paramagnetism precludes the obtention of a ³¹P NMR spectrum, but the ¹H NMR spectrum gives many sharp signals in the 0-20 ppm range, that we have not been able to interpret yet.

3.1. Crystal structure of 1

An ORTEP view is shown in Fig. 1. Selected bond distances and angles are given in Table 2.

The structure consists of a discrete distorted octahedral Re(III) monomer, the rhenium atom being bonded to three P-O anionic ligands in a mer configuration, with two trans P and two trans O atoms. If electronic effects were predominant, a *fac* configuration would be generated, that is, three σ -donor oxygen atoms would be located *trans* to the π -acceptor phosphorus atoms. This is not the case and the *mer* configuration results probably from the important steric effect due to the presence of nine phenyl rings in the molecule. It must be noticed that the *mer* arrangement is the only one reported so far for homoleptic Re(III) and Tc(III) complexes of this type, namely $M(Ph_2PC_6H_4S)_3$ (M = Tc, Re) [6], Tc(2-Ph₂PCH₂CH₂CO₂)₃, 2Me₂SO [25] and even ReCl₃(PEt₂Ph)₃ [26].

The distortion of the octahedron is illustrated in the bond distance and angle values. One P1-O1 ligand



Fig. 1. ORTEP drawing of $\text{Re}(P_1-O)_3$ (1). Ring atoms are assigned symbols C_{ij} , where *j* corresponds to the position around the ring starting with *j* = 1 for the *ipso* carbon, and *i* is the (one- or two-digit) ring number. Hydrogens are omitted for clarity. Ellipsoids correspond to 50% probability.

Table 2

Selected interatomic distances (Å) and bond angles (°) in $Re(P_1-O)_3$ (1)

Re-P1	2.462(2)	Re–O1	2.080(3)	
Re–P2	2.412(2)	Re–O2	1.993(3)	
Re–P3	2.405(2)	Re–O3	1.992(4)	
P1–Re–P2	96.72(5)	P2–Re–P3	96.27(5)	
P1-Re-P3	166.71(5)	P2-Re-O1	177.41(10)	
P1-Re-O1	85.51(10)	P2–Re–O2	87.51(11)	
P1–Re–O2	82.71(11)	P2-Re-O3	91.21(11)	
P1–Re–O3	91.88(11)	P3-Re-O1	81.58(10)	
O1–Re–O2	94.11(14)	P3–Re–O2	95.05(11)	
O1–Re–O3	87.39(15)	P3–Re–O3	90.66(11)	
O2–Re–O3	174.24(14)			



Fig. 2. Cyclic voltammogram of $Re(P_1-O)_3$ (1) 10^{-3} M in NBu_4ClO_4-DMF at a platinum electrode, scan rate: 0.1 V s⁻¹.

shows Re–P and Re–O bond distances significantly longer (by 0.05 and 0.08 Å, respectively) than the other two. As a consequence, the corresponding O1–Re–P1 bite angle value ($85.5(1)^\circ$) is smaller. The importance of steric effects is also emphasized by the large angular distortions observed at the phosphorus atoms, methylene carbons and phenolic oxygens. In the case of phosphorus, the angle values range from 96.9(2)° for C211-P2-C221 to 126.2(2)° for C111-P1-Re, while those at the carbon atoms are 106.1(3)° for P1-C10-C11, 116.6(4)° for P2-C20-C21 and 117.1(4)° for P3-C30-C31. The increase of the Re-O-C angle from 120.6(3)° (Re-O1-C12) to 128.9(3)° (Re-O2-C22) and 135.3(3)° (Re-O3-C32) could result from a modification of the original sp³ hybridization of the phenolic oxygen atom due to an increasing contribution of the oxygen π electrons to the bonding. However, since short Re–O bond distances (~ 1.95 Å) have also been reported for monodentate phenolate ligands coordinated with Re–O–C angles of ~126° [27], change in hybridization is probably not the only factor involved, intramolecular inter-ligand non-bonded contacts and distortion in the coordination polyhedron undoubtedly making contributions as well.

The structure of **1** is quite similar to that of the phosphinothiol complex $\text{Re}(\text{P}_2-\text{S})_3$, for which a distorted octahedral geometry with a *mer* configuration was also observed [6]. Although in this case the ligand generates three planar five-membered metallacycles, distortion of the octahedron is less severe than in **1**, because of the presence of Re–S bonds (2.349(5) Å av.) that are significantly longer than Re–O bonds (2.022(4) Å av.).

3.2. Voltammetric study

The redox properties of 1 and 2 were studied by cyclic voltammetry at a platinum wire electrode in DMF solution containing Bu_4NClO_4 under an atmosphere of nitrogen. The cyclic voltammograms are shown in Figs. 2 and 3, and the data in Table 3. Both complexes display two well-defined monoelectronic quasi-reversible redox waves, one reductive and one oxidative, by comparison of the anodic and cathodic currents with the ferrocenium/ferrocene couple as the internal standard. They conform to the conventional criteria for Nernstian diffusion-controlled one-electron reversible electron transfer. The reductive waves are consistent with the Re(III)/Re(II) couple and the oxidation wave with the Re(III)/Re(IV) one. The second oxidative couple corresponds to the Re(IV)/Re(V) pro-



Fig. 3. Cyclic voltammogram of $\text{Re}(\text{P}_2-\text{O})_3$ (2) 10^{-3} M in $\text{NBu}_4\text{ClO}_4-\text{DMF}$ at a platinum electrode, scan rate: 0.1 V s⁻¹.



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	voltammetry	data	18 * 1	TOT	The	nnoer	nnnnn	nnenoi	rneniiim	compleyes
Cycne	vonammeny	uata	L 1/21	101	unc	phose	Juno	phenor	monum	complexes
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Compound	$E^{\circ}_{1/2}$ (V)						
	Re(II)/Re(III)	Re(III)/Re(IV)	Re(IV)/Re(V)	Re(V)/Re(VI)			
$Re(P_1-O)_3$ (1)	-1.231	-0.043	0.885				
$Re(P_2-O)_3$ (2) ^a	-1.078	0.151	0.972				
$ReO(O-P_2=O)(P_2-O)_2(3)^{a}$			-1.196	1.100			
ReOCl(P ₂ –O) ₂ ^b			-1.053				
Re(Ph ₂ PC ₆ H ₄ S) ₃ °	-1.025	0.201	0.976				

^a In 0.1 M NBu₄ClO₄–DMF, platinum disk electrode, v = 0.1 V s⁻¹.

^b In NBu₄PF₆–CH₂Cl₂, platinum disk electrode; v = 81.3 V s⁻¹.

^c From [6]. $E_{1/2}^{\circ} = 1/2(E_{pa} + E_{pr}).$

cess that is a quasi-reversible monoelectronic process for 1 only. In 2, it is not associated with an anodic response, indicating that the Re(V) homoleptic complex is unstable on the cyclic-voltammetry time scale.

Such a variety of available oxidation states was observed for the related $M(P-S)_3$ (M = Tc, Re) complexes [6] (Table 3). It appears that 1 is slightly harder to reduce and easier to oxidize than 2, which could result from the presence in 1 of non-planar six-membered metallacycles less favorable to electron delocalization from the metal than the planar five-membered metallacycles present in the other complex. Differences in the flexibility of the metallacycles is probably also the factor responsible for the different reversibilities of the Re(IV)/Re(V) couples, the P₁–O ligand being more able to accommodate the shortening of the bond distances in the Re(V) species.

Compound 1 is stable in the solid state and in solution. In contrast, when the red diethylether solution of 2 is exposed to air, it turns green. By reducing the volume, a green powder precipitates, and green single crystals of $\text{ReO}(O-P_2=O)(P_2-O)_2$ (3) are obtained by crystallization from acetonitrile.

Besides the main absorptions of the P₂–O ligand, the IR spectrum of **3** includes two strong absorptions at 1157 and 957 cm⁻¹, characteristic of the v(P=O) [27] and v(Re=O) [28] vibrations, respectively. These results, together with the microanalysis and the FAB⁺ mass spectrum (parent peak $[M^+] = 1050$), confirm the formation of an oxo-rhenium(V) species. The ³¹P{¹H} NMR spectrum exhibits a singlet at 28.5 ppm, consistent with a phosphine oxide [29], as well as an AX spin system (doublets at 3.6 and 7.7 ppm, ²J_{PP} = 6.7 Hz), typical of a *cis*-P,P twisted octahedral structure. An





X-ray analysis (vide infra) confirms the structure of this green compound formed according to Scheme 1. This diamagnetic complex contains a Re(V) center. This agrees with its cyclic voltammogram, that shows a reversible Re(V)/Re(IV) reduction wave at -1.196 V, a value that compares well with that of the related ReOCl(P₂–O)₂, complex. Thus, comparing the Re(V)/Re(IV) redox couples for 1 (0.967 V) and 3 (-1.196 V) confirms that the Re=O core stabilizes considerably the +5 oxidation state. The irreversible oxidation peak, observed for 3 at 1.1 V, should probably correspond to the Re(V)/Re(VI) process, the Re(VI) species being chemically unstable [30]. It was checked that no redox reaction involving the ligand lies in this potential range.

Re(III) complex $Re(PPh_2(CH_2)_2S)_2(S(CH_2)_2-$ А Ph₂P=O) with a pendant P=O unit was described previously [31]. It did not result from air oxidation of the five-coordinate $\operatorname{Re}(P-S)_2(S-P)$ molecule, where S-P is a S-bonded monodentate phosphinethiolate ligand, but from the reaction of a mixture of P-SH and O=P-SH ligands on $\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2$. It was noticed that exposure of the $Re(P-S)_2(S-P)$ solution to air during the synthesis generated no oxidation of the pendant phosphine, but that oxidation took place at the rhenium center giving ReOCl(P-S)₂. In the present system, oxidation does not occur under strictly anaerobic conditions, but conversion of 2 is complete in air at room temperature. A concerted oxidation mechanism is tentatively proposed (Scheme 2), involving simultaneous oxidation of the Re center and the phosphine, in a transition state where a Re-P bond is broken and the molecule adopts the five-coordinate, trigonal-bipyramidal, structure observed for Re(P-S)₂(S-P) [16]. The stereo-non-rigidity of this coordination could explain the formation of the cis-P,P twisted structure of 3, via O_2/P_2 interchange by a twist mechanism [32] (Scheme 2).

3.3. Crystal structure of $ReO(O-P_2=O)(P_2-O)_2$ (3)

Crystals of **3** contain the neutral, six-coordinate, rhenium(V) monomer shown in Fig. 4. Selected bond lengths and angles are listed in Table 4.



Scheme 2.

The compound presents two bidentate P–O ligands and adopts the *cis*-P,P twisted arrangement with the *trans* O=Re–O linkage reported for ReOCl(P₂–O)₂ [4]. The sixth site is occupied by the phenolate group of a monodentate phosphinophenol ligand whose P atom has oxidized to phosphine oxide.

The octahedron is severely distorted, as evidenced from the *trans* angles varying from 161 to 163° (Table 4). Geometry is controlled to a large extent by the bite of the P-O ligand, which imposes intra-ring P-Re-O angles of $78-80^\circ$, and by the size of the *cis* PPh₂ units, which opens the P-Re-P angles to 101.27(4)°. The ligands do not experience the repulsive effect of the oxo group to the same extent. The Re atom lies at 0.275(2)Å from the O–P–P–O plane and the O=Re–L angles are large for the negatively O donors (101.0(1) and $112.0(1)^{\circ}$), but close to 90° for the phosphines (92.2(1)) and 86.6(1)°). Steric crowding is also indicated by the significant departures of the Re atom from the O-C-C-P plane in the chelate rings (0.269 and 0.120 Å), which may reflect the greater steric demand of the phosphine oxide ligand.

The Re=O distance of 1.679(3) Å is typical of monooxo compounds [33]. The Re–O12 bond (2.027(3) Å), *trans* to Re=O, is longer than the *cis* Re–O42 bond (1.990(3) Å). This difference cannot be safely related to the *trans* influence of Re=O, because of the presence of an highly distorted octahedron and bulky substituents on phosphorus.

Table 4								
Selected	interatomic	distances	(Å)	and	bond	angles	(°)	in
ReO(O-H	$P_{2}=O)-(P_{2}-O)_{2}$, (3)						

Re–P1	2.434(1)	Re–O12	2.027(3)
Re–P4	2.460(1)	Re–O42	1.990(3)
Re–O1	1.679(3)	Re–O72	2.020(3)
P1-Re-O42	161.35(10)	P4–Re–O1	92.19(10)
P4-Re-072	161.87(9)	P4-Re-O12	83.80(9)
O12–Re–O1	163.01(13)	P4-Re-O42	80.42(9)
P1–Re–O1	86.56(11)	O12-Re-O42	83.67(12)
P1–Re–P4	101.27(4)	O12-Re-O72	86.96(13)
P1–Re–O12	78.09(9)	O42-Re-O1	112.02(14)
P1-Re-072	92.00(9)	O42-Re-O72	83.09(12)
O1–Re–O72	100.97(13)		



Fig. 4. ORTEP drawing of ReO $(P_2-O)_2(O-P_2=O)$ (3). Ellipsoids correspond to 50% probability. Hydrogens are omitted for clarity.

The monodentate phenolate group is part of a phosphine oxide molecule. It behaves as a simple phenolate unit [34] by coordinating with a Re–O72–C72 angle of 123.2(3)°. However, the Re–O72 bond (2.020(3) Å) remains similar to those in the chelate rings and much longer than observed for a simple phenolate (~ 1.95 Å). The P=O bond points away from the metal and does not participate in particular interactions with the rest of the structure. The P=O distance (1.496(3) Å) is normal [35]. There is a small, but significant, difference between the mean values of the O7–P7–C (111.0°) and C–P7–C angles (108.0°), and those of free OPPh₃ (112.5 and 106.4°, respectively), which reflects greater crowding in the complex.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC142218 (1) and CCDC142219 (3). Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:hhttp://www.ccdc.cam.ac.uk).

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