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Oxorhenium(V) complexes with bis-phosphinite chelating coligands. The crystal structure of [$ReOCl_2(OMe)L^1$], [$ReOCl_3L^2$], [$ReOCl_2(OEt)L^2$] and [$ReOCl_2\{Ph_2PO(CH_2)_2O\}\{PPh_2(OEt)\}$] [$L^1 = Cy_2PO(CH_2)_2OPCy_2$, $L^2 = Ph_2PO(CH_2)_2OPPh_2$]

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Abstract

The new ligand 1,2-bis(dicyclohexylphosphinite)ethane (**L^1**) was prepared by reaction of ethylenglycol with dicyclohexylphosphine in the presence of triethylamine. By treating this ligand with the arsine complex [$ReOCl_3(AsPh_3)_2$] and triturating the formed oil with methanol, the complex [$ReOCl_2(OMe)L^1$] (**1**) was isolated and its crystal structure was studied by X-ray diffractometry. The coordination sphere around the Re atom is a pseudo-octahedron. The crystal structure of the previously reported complex [$ReOCl_3L^2$] (**2**) (L^2 = 1,2-bis[diphenylphosphinite]ethane) was solved by X-ray diffractometry. When Complex **2** was refluxed in EtOH, the oxo-alkoxide complex [$ReOCl_2(EtO)L^2$] (**3**) was formed by a metathesis reaction. X-ray diffraction studies of Complex **3** show a pseudo-octahedral geometry around the Re atom with the oxo and ethoxy groups mutually *trans*. Finally, reaction of **2** with the monodentate phosphinite $PPh_2(OEt)$ ligand yielded the paramagnetic Re(III) compound [$ReCl_3L^2\{PPh_2(OEt)\}$] (previously reported) and the new unexpected Re(V) by-product [$ReOCl_2(Ph_2POCH_2CH_2O)\{PPh_2(OEt)\}$] (**4**). On the contrary, compounds **1** and **3** did not react with $PPh_2(OEt)$ under the same conditions.

Keywords: Rhenium(V); Phosphinite ligands; Oxo-complexes; Alkoxo-complexes; Crystal structures

1. Introduction

The coordination chemistry of rhenium is a matter of considerable interest. In particular, the use of ^{186}Re and ^{188}Re as radionuclides for the development of radiopharmaceuticals with therapeutic potential is being increased due to the continuous demand for more specific probes for targeting diseased organs in nuclear medicine. Thus many Re compounds have been recently synthesized and studied for radiopharmaceutical and therapeutic purposes [1–7]. Moreover, oxorhenium(V) compounds containing halogen and phosphine ligands are of current interest [8–10], and there is an increasing demand for a fundamental knowledge about the structural properties and redox and substitution ligand reactivities to develop new, more sensitive Re pharmaceuticals.

Following previous work on rhenium phosphinite complexes [11,12], and with the aim of analyzing the influence of the nature of this ligands on the reactivity of the complex, we describe in this report the synthesis and characterization of the new ligand $Cy_2POCH_2CH_2OPCy_2$ (**L^1**) as well as the synthesis, characterization and crystal structure of the new complexes [$ReOCl_2(OMe)L^1$], [$ReOCl_2(OEt)L^2$] (L^2 = 1,2-bis[diphenylphosphinite]ethane), and [$ReOCl_2(Ph_2POCH_2CH_2O)\{PPh_2(OEt)\}$]. The crystal structure of the complex [$ReOCl_3L^2$], the synthesis of which has been previously described [11], is also reported.

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2. Experimental

2.1. Materials and instrumentation

All synthetic operations were performed under dry argon. A standard vacuum system and Schlenk type glassware were used in handling metal complexes. Solvents were pre-dried over sodium wire or calcium chloride before reflux and subsequent distillation, under argon, from a suitable drying agent [13]. Deuterated solvents for NMR measurements (Aldrich) were dried over molecular sieves. The complex $[ReOCl_3(AsPh_3)_2]$ was prepared after Michos et al. [14]. All other commercially available reagents were used as purchased.

The IR spectra of samples in KBr pellets were recorded on a Bruker Vector IFS28 FT spectrophotometer, and NMR spectra on a Bruker AMX 400 spectrometer. ^1H and $^{13}C\{^1H\}$ signals are referred to internal TMS, and $^{31}P\{^1H\}$ chemical shifts to 85% H_3PO_4, with downfield shifts considered positive. Mass spectra were recorded in the LSIMS, Cs^+ mode on a Micromass Autospec M instrument. Elemental analyses were carried out on a Fisons EA-1108 apparatus.

2.2. Synthesis of the ligand $Cy_2POCH_2CH_2OPCy_2$ ($\mathbf{L^1}$)

The ligand was synthesized by the method previously reported [12]: Cy_2PCl (5 g, 21 mmol) was slowly added dropwise (ca. 30 min) to a cooled (−80 °C) solution of freshly distilled Et_3N (2.93 ml, 21 mmol) and ethylene glycol (0.59 ml, 10 mmol) in 56 ml of toluene. The solution was stirred for 2 h and the formation of the ligand was established by the presence of a unique signal at 150.1 ppm in the $^{31}P\{^1H\}$ spectrum. The formed solid, $[Et_3NH]Cl$, was filtered off.

Attempts to isolate this product (by distillation and column chromatography) were unsuccessful due to its unstability, as shown by the disappearance of the characteristic signal in the $^{31}P\{^1H\}$ spectrum. So that, a ligand solution in toluene was used for the synthesis of the complexes, this solution being stable at room temperature for 1 week when stored under argon.

2.3. Synthesis of $[ReOCl_2(OMe)L^1]$ (**1**)

A 0.12 M solution of $\mathbf{L}^1$ in toluene (9.2 ml) was added to a solution of $[ReOCl_3(AsPh_3)_2]$ (1 g, 1 mmol) in tetrahydrofuran (40 ml). The resulting mixture was refluxed under argon for 1 h. After stirring for 3 h at room temperature and concentrating in vacuo a dark oil was formed. This oil was triturated with methanol, resulting in a violet precipitate that was filtered off, washed with methanol and dried under vacuum (0.46 g, 56% yield). IR (KBr pellets, cm^{-1}): 945s, ν(Re=O). ^1H NMR ($CHCl_3$-*d*, 400 MHz): $\delta = 1.14–2.89$ (m, 44H, Cy), 3.48 (s, 3H, OCH_3), 4.22 (m, 2H, CH_2), 4.37 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CHCl_3$-*d*, 100 MHz): $\delta =$ 67.4 (s, $-(CH_2)_2-$), 59.0 (s, OCH_3), 40.2–41.0 (m, Cy), 26.3–27.8 (m, Cy). $^{31}P\{^1H\}$ NMR ($CHCl_3$-*d*, 161 MHz): $\delta = 126.1$ (s). *Anal.* Found: C, 42.73; H, 6.78. Calc. for $C_{27}H_{51}Cl_2O_4P_2Re$ (758.22): C, 42.74; H, 6.77%. MS: *m/z* (referred to the most abundant isotopes): 758, [M]; 727, [M−OCH_3]; 723, [M−Cl]; 707, [M−O−Cl]; 692, [M−Cl−OCH_3]. The isotope patterns match those simulated. Single crystals were obtained by slow evaporation of an $MeOH/CH_2Cl_2$ (10:2, v/v) solution.

2.4. Crystallization of $[ReOCl_3L^2]$ (**2**)

This complex was synthesized as previously reported [11]: $[ReOCl_3(AsPh_3)_2]$ was reacted with $\mathbf{L}^2$ in THF. The addition of methanol to the formed oil produced a violet precipitate. After dissolving the solid in a Cl_2CH_2/EtOH (10:2, v/v) mixture, X-ray suitable crystals were isolated.

2.5. Preparation of $[ReOCl_2(OEt)L^2]$ (**3**)

Hundred milligram of $[ReOCl_3L^2]$ suspended in ethanol (20 ml) were refluxed under Ar. After 2–3 h a change of colour (from violet to pink) was observed. From this suspension a pink solid was filtered off and dried in vacuo (80% yield). The same complex was obtained as follows: a suspension of $[ReCl_3L^2\{PPh_2(OEt)\}]$ (100 mg) in ethanol (15 ml) was stirred and air-ventilated for 4 h. The solid formed was filtered off and dried under vacuum (70% yield). IR (KBr pellets, cm^{-1}): 910s, ν(Re=O). ^1H NMR ($CHCl_3$-*d*, 400 MHz): δ (ppm) = −0.16 (t, 3H, CH_3 $J = 7.0$ Hz), 2.13 (q, 2H, CH_2 $J = 7.0$ Hz), 4.24–4.46 (m, $-(CH_2)_2-$) 7.57–8.42 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CHCl_3$-*d*, 100 MHz): δ (ppm) = 135.3 (t, $C_{o,m}$ Ph, $J = 6.0$ Hz), 133.2 (s, C_p Ph), 131.9 (t, $C_{o,m}$ Ph, $J = 4.8$ Hz), 131.8 (s, C_p Ph), 129.2 (t, $C_{o,m}$ Ph, $J = 5.2$ Hz), 128.3 (t, $C_{o,m}$ Ph, $J = 5.6$ Hz), 66.7 (s, CH_2CH_2), 64.6 (s, OCH_2), 14.4 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CHCl_3$-*d*, 161 MHz): $\delta = 104.7$ (s). *Anal.* Found: C, 45.02; H, 3.80. Calc. for $C_{28}H_{29}Cl_2O_4P_2Re$ (748.04): C, 44.92; H, 3.88%. Single crystals were obtained by slow evaporation of an EtOH/CH_2Cl_2 (10:2, v/v) solution.

2.6. X-ray crystallography

Crystallographic data were collected on a Bruker Smart CCD diffractometer at 293 K using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) and were corrected for Lorentz and polarization effects. The frames were integrated with the Bruker SAINT [15] software package and the data were corrected for absorption using the program SADABS. The structures were solved by direct methods using the program

SHELXS-97 [16]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program SHELXL-97 [17]. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. Complex **1** crystallizes in the chiral space $P2_1$, and the analysis established its absolute stereochemistry [Flack parameter 0.004(18)]. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [18]. Drawings were produced with PLATON [19]. Crystallographic data and structure refinement parameters are listed in Table 1.

3. Results and discussion

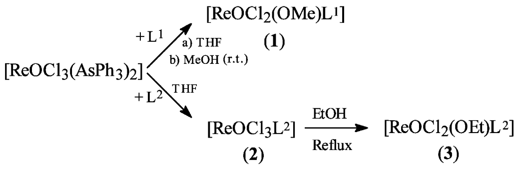
3.1. Synthesis and general properties

A new bidentate ligand, 1,2-bis(dicyclohexylphosphinite)ethane ($\mathbf{L}^1$), was synthesized by reacting ethylenglycol with dicyclohexylphosphine chloride in the presence of triethylamine following a previously reported method [11]. This reaction (see Section 2) yielded a toluene solution of the ligand that was used for ulterior reactions since any attempt to isolate the compound resulted in its decomposition. The solution remains unaltered for a week when stored under Ar.

The reaction of $\mathbf{L}^1$ with the arsine complex [ReOCl$_3$(AsPh$_3$)$_2$] afforded the oxo-alkoxide complex [ReOCl$_2$(OMe)L^1] (**1**) as a result of the replacement of two arsine ligands with the bidentate $\mathbf{L}^1$ ligand and of one Cl atom with the methoxy group coming from the methanol used in the breaking of the oil produced in the reaction. This behaviour is markedly different from that observed in a previously reported reaction [11], in which the similar ligand 1,2-bis(diphenylphosphinite)ethane ($\mathbf{L}^2$) had been used instead of $\mathbf{L}^1$. There, the reaction of that ligand with the arsine complex had yielded the oxo complex [ReOCl$_3$L^2] (**2**), the conversion of which into the corresponding oxo-alkoxy complex [ReOCl$_2$(OEt)L^2] (**3**) (see Scheme 1) required much more

Table 1
Crystal data and structure refinement parameters for the complexes **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{27}H_{51}Cl_2O_4P_2Re$	$C_{52}H_{48}Cl_6O_6P_4Re_2$	$C_{28}H_{29}Cl_2O_4P_2Re$	$C_{28}H_{29}Cl_2O_4P_2Re$
Formula weight	758.72	1477.88	748.55	748.55
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1$	$P2_1/a$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions				
a (Å)	9.25(7)	16.9015(2)	9.650	9.724(2)
b (Å)	14.25(11)	15.559	14.0477(3)	11.962(3)
c (Å)	11.36(9)	22.24090(10)	21.8875(4)	13.452(4)
α (°)	90	90.1564(6)	90.0450(10)	96.85(2)
β (°)	90.00(17)	110.9851(6)	91.8875(11)	108.268(18)
γ (°)	90	89.8356(4)	90.0124(9)	98.19(2)
V (Å^3)	1497(21)	5460.67(7)	2965.40(8)	1448.1(7)
Z	2	4	4	2
D_{calc} (Mg m^{-3})	1.683	1.798	1.677	1.717
Absorption coefficient (mm^{-1})	4.374	4.888	4.417	4.523
$F(0\,0\,0)$	768	2880	1472	736
Crystal size (mm)	0.03 × 0.05 × 0.09	0.40 × 0.20 × 0.15	0.35 × 0.20 × 0.10	0.30 × 0.10 × 0.05
θ Range for data collection (°)	1.79–30.88	0.98–28.31	1.72–28.27	1.62–28.28
Index ranges	$-12 \le h \le 12$, $-19 \le k \le 17$, $-12 \le l \le 14$	$-21 \le h \le 22$, $-20 \le k \le 18$, $-29 \le l \le 28$	$-6 \le h \le 12$, $-18 \le k \le 18$, $-29 \le l \le 29$	$-12 \le h \le 12$, $-15 \le k \le 15$, $-17 \le l \le 11$
Reflections collected	9831	37 097	19 878	9738
Independent reflections	5997 [$R_{int} = 0.0824$]	13 459 [$R_{int} = 0.0509$]	7326 [$R_{int} = 0.0376$]	6935 [$R_{int} = 0.0350$]
Absorption correction	SADABS	SADABS	SADABS	SADABS
Max. and min. transmission	1.0000 and 0.6741	1.0000 and 0.4057	1.0000 and 0.6317	1.0000 and 0.5809
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5997/1/326	13 459/0/631	7326/0/334	6935/0/334
Goodness-of-fit on F^2	0.847	0.976	1.041	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0723$, $wR_2 = 0.1360$	$R_1 = 0.0361$, $wR_2 = 0.0744$	$R_1 = 0.0332$, $wR_2 = 0.0595$	$R_1 = 0.0497$, $wR_2 = 0.1046$
R indices (all data)	$R_1 = 0.1282$, $wR_2 = 0.1538$	$R_1 = 0.0632$, $wR_2 = 0.0849$	$R_1 = 0.0566$, $wR_2 = 0.0667$	$R_1 = 0.0754$, $wR_2 = 0.1164$
Largest difference peak and hole (e Å^{-3})	2.098 and −1.706	1.242 and −1.816	0.884 and −0.702	1.862 and −3.137



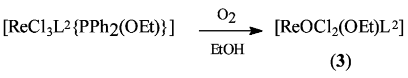
Scheme 1.

drastic conditions (i.e. reflux in the alcohol for several hours).

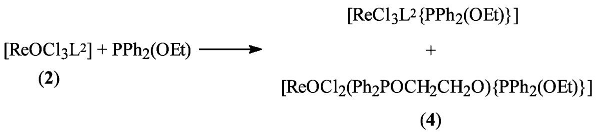
The same Complex **3** was obtained when a suspension of $[ReCl_3L^2\{PPh_2(OEt)\}]$ in ethanol was air-stirred at room temperature (Scheme 2). The pink solid was filtered off and vacuum dried. If the suspension is stirred under inert atmosphere no reaction is observed.

Finally, it is noteworthy to point out the serendipitous isolation of the new oxo–alkoxo complex $[ReOCl_2(Ph_2POCH_2CH_2O)\{PPh_2(OEt)\}]$ (**4**). After reducting $[ReOCl_3L^2]$ (Complex **2**) with $PPh_2(OEt)$ to yield $[ReCl_3L^2\{PPh_2(OEt)\}]$ as reported in a previous paper [11], from the mother liquor the unexpected Re(V) complex was obtained as a crystal solid suitable for X-ray diffraction (see Scheme 3). In the new P,O-donor ligand resulted from the breakage of a P–O bond in $\mathbf{L}^2$, a 'pseudo-alkoxy' character could be regarded.

This fact denotes a remarkable difference in the reactivity of the oxo Complex **2** when compared with the oxo–alkoxo complexes **1** and **3**. In effect, whereas the reduction of Re(V) oxo-chloride complexes by an excess of phosphonite or phosphinite $PPh_n(OR)_{(3-n)}$ ($n=1$, 2) ligands to form the corresponding Re(III) paramagnetic complexes is well documented [11,20], compounds **1** and **3** do not seem to react with $PPh_2(OEt)$ under the same conditions. (All attempts lead to the starting material.)



Scheme 2.



Scheme 3.

Table 2
Selected bond lengths (Å) and angles (°) for the prepared complexes

	1	2	3	4
Bond lengths				
Re(1)–O(1)	1.569(14)	1.686(3)	1.717(3)	1.700(5)
Re(1)–Cl(1)	2.459(16)	2.3793(12)	2.4458(10)	2.416(2)
Re(1)–Cl(2)	2.518(13)	2.3872(12)	2.4619(10)	2.4455(18)
Re(1)–Cl(3)		2.3835(11)		
Re(1)–P(1)	2.495(17)	2.4353(11)	2.4214(10)	2.438(2)
Re(1)–P(2)	2.504(14)	2.4586(11)	2.4319(10)	2.4100(18)
Re(1)–O(2)	1.722(14)		1.853(3)	1.894(4)
Re(2)–O(11)		1.696(3)		
Re(2)–Cl(12)		2.3703(12)		
Re(2)–Cl(13)		2.3739(12)		
Re(2)–Cl(11)		2.3984(12)		
Re(2)–P(12)		2.4411(12)		
Re(2)–P(11)		2.4593(11)		
Bond angles				
O(1)–Re(1)–Cl(1)	96.3(6)	101.67(11)	93.53(9)	99.5(2)
O(1)–Re(1)–Cl(2)	95.2(7)	102.70(11)	94.38(9)	97.57(18)
Cl(1)–Re(1)–Cl(2)	94.6(5)	86.83(5)	87.63(4)	86.50(8)
O(1)–Re(1)–Cl(3)		163.08(11)		
Cl(1)–Re(1)–Cl(3)		90.46(5)		
Cl(2)–Re(1)–Cl(3)		89.58(5)		
O(1)–Re(1)–P(1)	86.6(6)	87.98(10)	87.49(9)	85.07(19)
Cl(1)–Re(1)–P(1)	171.22(17)	169.54(5)	178.18(4)	174.89(6)
Cl(2)–Re(1)–P(1)	76.9(4)	87.10(4)	90.79(4)	90.59(7)
Cl(3)–Re(1)–P(1)		80.98(4)		
O(1)–Re(1)–P(2)	88.2(7)	88.60(11)	95.33(9)	93.30(18)
Cl(1)–Re(1)–P(2)	83.0(4)	86.90(4)	86.33(4)	87.78(7)
Cl(2)–Re(1)–P(2)	176.02(17)	167.99(5)	168.86(4)	168.42(7)
Cl(3)–Re(1)–P(2)		80.24(4)		
P(1)–Re(1)–P(2)	105.4(4)	97.48(4)	95.08(3)	94.34(7)
O(1)–Re–O(2)	176.9(6)		175.62(12)	167.3(2)
O(2)–Re–Cl(2)	87.4(7)		85.25(9)	88.19(14)
O(2)–Re–P(2)	89.1(7)		85.49(9)	81.96(14)
O(2)–Re–P(1)	95.6(6)		88.16(9)	83.59(16)
O(2)–Re–Cl(1)	81.9(6)		90.81(9)	92.12(16)

3.2. *Crystal structures*

3.2.1. *$[ReOCl_3L^2]$ (**2**)*

Table 2 lists selected bond distances and angles for the four complexes, and Fig. 1 shows a PLATON drawing of Complex **2** with the atom numbering scheme. The asymmetric unit consists of two $[ReOCl_3L^2]$ pseudo-octahedral entities with small structural differences between them. The bond lengths around both metal atoms are very similar: Re–Cl (avg.) = 2.3833 Å, 2.3809 Å; Re–O = 1.686(3), 1.696(3) Å; Re(1)–P = 2.4353(11), 2.4586(11) Å; Re(2)–P = 2.4593(11), 2.4411(12) Å for Re(1) and Re(2), respectively. The Re–Cl distances lie in the ranges reported by several authors for similar systems (ca. 2.31–2.39 Å [21–23], 2.37–2.44 Å [9,24]), and it is noteworthy that in both cases there is no difference among the Re–Cl bond lengths despite the *trans* influence of the oxo ligand. In fact, the Re–Cl bonds *trans* to Re–O [2.3835(11), 2.3739(12) Å] are roughly equal to $Re–Cl_{cis}$ [2.3793(12), 2.3872(12); 2.3703(12), 2.3984(12) Å], even though the oxo group has been reported to lengthen the opposite Re–Cl bond in related compounds [24]. The Re–O distances, on the other hand, are in keeping with that expected for Re(V) monooxo complexes showing a triple bond character, since attempts to rationalize the bond orders [25,26] assign to Re–O single, double and triple bonds the theoretical values of 2.04, 1.86 and 1.75 (or less) Å,

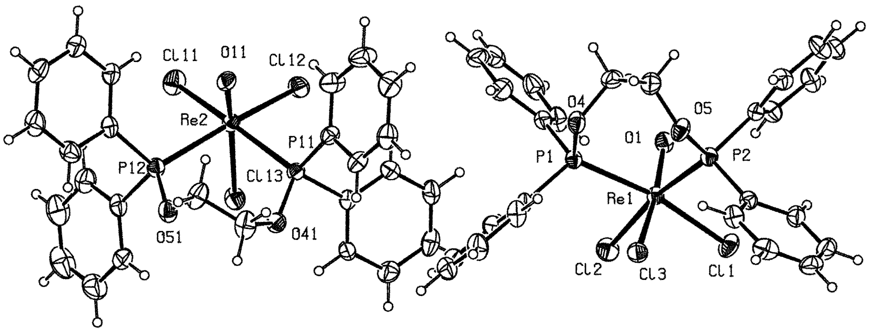


Fig. 1. A PLATON drawing of Complex **2** with the atom numbering scheme. Ellipsoids at 30% probability.

respectively [22,27–32]. This Re-oxide bond lengths are comparable to that observed in many other Re mono-oxo compounds, whereas in dioxide species they are usually longer (close to the double bond values) which has been regarded as a consequence of a competition in the Re–O π-bonding [33]. On the contrary, the Re–P bond lengths are in our case slightly shorter than found in other six-co-ordinated oxorhenium(V) complexes, usually in the range 2.46–2.52 Å [33–35]. Nevertheless, this small difference can be related with steric constraints imposed by the bidentate ligand rather than with electronic factors.

Regarding the bond angles, the major deviation from a regular geometry lies in the value of the O(1)–Re(1)–Cl(3) angle [163.08(11)°], as well as in that of both O(1)–Re(1)–P angles [87.98(10)° and 88.60(11)° for P(1) and P(2), respectively], which confirm that the oxo ligand (in both units) is bent towards the bidentate ligand as occurs in other diphosphine oxocomplexes of Re(V) [29].

3.2.2. $[ReOCl_2(OEt)L^2]$ (**3**)

The PLATON representation of the structure of Complex **3** is shown in Fig. 2. The substitution of one Cl atom in Complex **2** by an ethoxy group results in this new compound, which also shows a pseudo-octahedral arrangement around the Re atom but with some significant irregularities (see Table 2), the most remarkable of which affecting the two Re–O bond lengths, markedly different as a consequence of their bond character. In fact, the rhenium–oxide distance [1.717(3) Å] denotes a certain triple bond character, and is longer than in Complex **2** due to the competition for the Re–O π-bonding established between the oxo and the alkoxy groups, whereas the Re–O(ethoxy) distance, 1.853(3) Å, corresponds to a double bond. On the other hand, the values of O(1)–Re–O(2) [175.62(12)°], O(1)–Re–P(1) [87.49(9)°] and O(1)–Re–P(2) [95.33(9)°] angles indicate that the oxo ligand [O(1)] is bent towards P(1), making Cl(2) come near the ethoxy group [O(2)–Re–Cl(2) = 85.25(9)°]. Finally, this EtO ligand approaches the plane containing the P(1), P(2) and Re atoms: O(2)–Re–P(1): 88.16(9)°, O(2)–Re–P(2): 85.49(9)°.

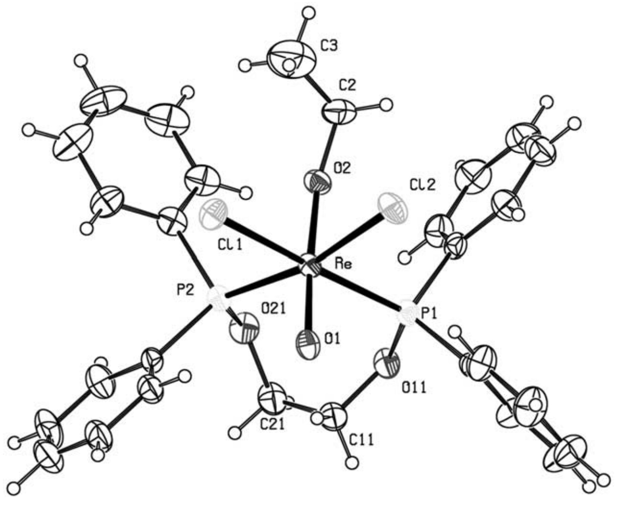


Fig. 2. Structure of Complex **3**, showing the atom-labeling scheme. Ellipsoids at 30% probability.

3.2.3. $[ReOCl_2(OMe)L^1]$ (**1**)

Fig. 3 shows the PLATON representation of the molecular structure of Complex **1**. The structural parameters of this compound, when compared with those discussed above, provide some suggestions about the reasons why any attempt to synthesize an $\mathbf{L}^1$ adduct similar to Complex **2** was unsuccessful. In fact, the presence of Cy instead of Ph makes this phosphinite ligand less π-acceptor and lowers the multiple character in the Re–P bond. This causes an increase in the metal–ligand bond lengths [2.495(17), 2.504(14) vs. 2.4214(10), 2.4319(10) Å] and, therefore, a strengthening of the internal (P-substituent) bonds in the ligand [i.e. (P–O) = 1.558(14), 1.552(15) vs. 1.609(3), 1.613(3) Å]. Consequently, the Re atom in Complex **1** bears electronic charge enough to result in a shortening of Re–O distances and a weakening of the rhenium–chloride bonds, so that one of the Cl is easily exchanged by an alkoxy group, being the remaining chloro ligands more distant from Re than in Complex **2** [2.459(16), 2.518(13) vs. 2.4458(10), 2.4619(10) Å]. Finally, the trans influence

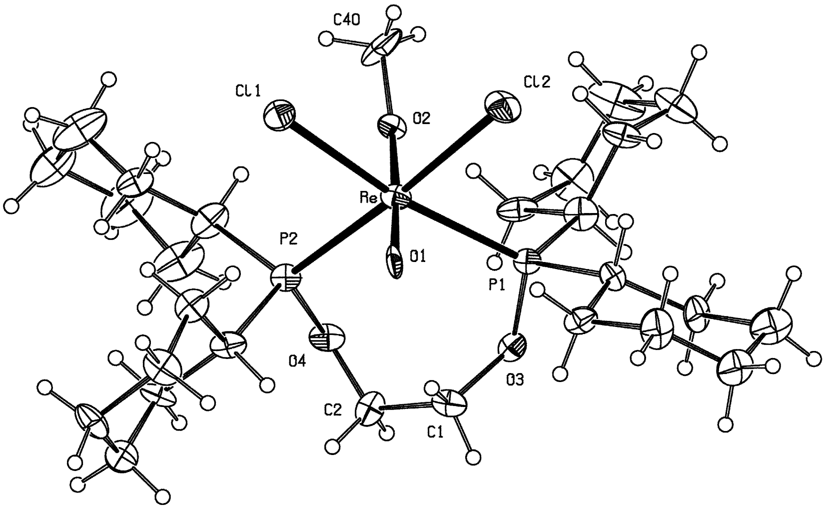


Fig. 3. Structure of Complex **1** with the atom numbering scheme. Ellipsoids at 30% probability.

caused by the oxo ligand decides which one of the three Cl atoms is the leaving ligand.

3.2.4. [ReOCl$_2$(Ph$_2$POCH$_2$CH$_2$O){PPh$_2$(OEt)}] (4)

Reaction of **2** with the monodentate PPh$_2$(OEt) ligand yielded the paramagnetic Re(III) compound [ReCl$_3$L^1{PPh$_2$(OEt)}] (previously reported) and the new unexpected Re(V) complex [ReOCl$_2$(Ph$_2$POCH$_2$CH$_2$O){PPh$_2$(OEt)}] (Complex **4**), which molecular structure is shown in Fig. 4. In this complex, around the Re atom coexist (besides one oxo and two Cl ligands) the monodentate PPh$_2$(OEt) ligand and a bidentate P,O-donor ligand arised from the breakage of a P–O bond in **L**^{2}. The Re atom is six-co-ordinated, with the two O atoms mutually in *trans* in competition for the π-interaction with the metal. Consequently, the Re–O(1) bond is weaker than in **2** [1.700(5) vs. 1.686(3) Å] but considerably stronger than the Re–O(2) bond [1.894(4) Å]. As commented above, the oxo group is thought to play some role in the losing of the *trans*-chloro ligand; and the new compound could be considered as arisen from Complex **3** by replacing one P atom of the bidentate ligand and the ethoxy group by the monodentate PPh$_2$(OEt) ligand and the O terminal (regarded as a 'pseudo-alkoxy' group) of the new P,O-donor ligand, respectively. The major differences between both pseudo-octahedral co-ordination spheres lie in the O(1)–Re–O(2) [167.3(2)°], O(2)–Re–Cl(1) [92.12(16)°] and O(2)–Re–Cl(2) [88.19(14)°] bond angles as a result of the bite of the bidentate ligand [O(2)–Re–P(1), 83.59(16)°].

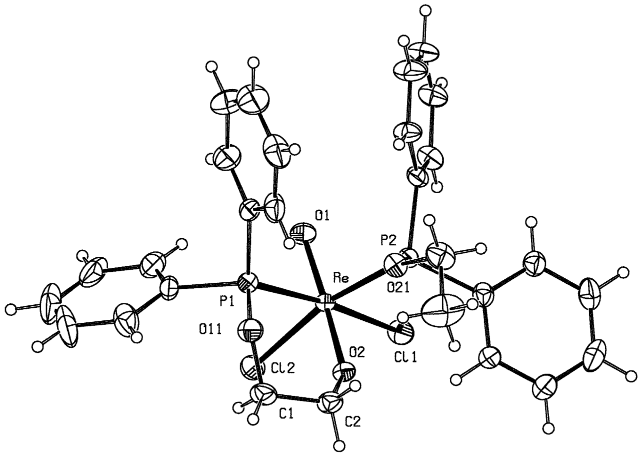


Fig. 4. PLATON view of Complex **4** with the atom-labeling scheme. Ellipsoids at 30% probability.

3.3. Spectroscopic studies

The IR spectra of the complexes show the Re≡O stretching band at frequencies similar to other oxorhenium(V) compounds, that is, in the range 1000–900 cm^{-1} [10,33]. This band lies at higher wave number for Complex **1** (945 cm^{-1}) than for Complex **3** (910 cm^{-1}), in keeping with the different Re–O bond lengths in both compounds showed by the X-ray diffractometric studies.

Regarding the ^{1}H NMR spectra, the signals of the ethyl and methyl hydrogens of the alkoxo groups are found at high field as occurs in other similar systems [33], whereas the signals of the other hydrogens are unremarkable. The ^{13}C{^{1}H} NMR spectra are similar to that found previously in other rhenium(V) alkoxo complexes. The ^{31}P{^{1}H} NMR spectrum of Complex **3** shows a singlet at higher field (104.7 ppm) than that of **1** (126.1 ppm). This fact is a consequence of the greater electronic density on the P atom in the first case, as a result of the more intense back-donor behaviour of the Re atom (due to the Ph substituents on the **L**^{2} ligand), that causes a stronger Re–P bond as confirmed by the difference in the bond lengths.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 201163 (**1**), 201164 (**2**), 201165 (**3**) and 201166 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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