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Synthesis, characterization and crystal structures of rhenium(V) complexes with diphosphines

Carlos Kremer [a], Mario Rivero [a], Eduardo Kremer [a], Leopoldo Suescun [b], Alvaro W. Mombrú [b], Raúl Mariezcurrena [b], Sixto Domínguez [c], Alfredo Mederos [c,*], Stefano Midollini [d], Alfonso Castiñeiras [e]

[a] *Cátedra de Química Inorgánica, Facultad de Química, CC 1157, Montevideo, Uruguay*
[b] *Laboratorio de Cristalografía, Cátedra de Física, Facultad de Química, CC 1157, Montevideo, Uruguay*
[c] *Departamento de Química Inorgánica, Universidad de La Laguna, 38200 La Laguna, Tenerife, Canary Islands, Spain*
[d] *Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, Via J. Nardi 39, 50132 Florence, Italy*
[e] *Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de Santiago de Compostela, Campus Sur, 15706 Santiago de Compostela, Galicia, Spain*

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Abstract

Two cationic complexes containing a $Re^V(O)_2{}^+$ core have been prepared by substitution on the precursor $[Re(O)_2(PPh_3)_2I]$. Careful control of reaction conditions allowed the synthesis of $[Re(O)_2L_2]I$ (L = bis(1,2-diphenylylphosphino)ethane (dppe), bis(1,3-diphenylphosphino)propane (dppp)) compounds in high yield. Complexes were characterized by UV–Vis and IR spectrophotometry, elemental analyses, FAB, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra and high-performance liquid chromatography. Four compounds have also been characterized by single-crystal X-ray analyses. Cations consist of a six-coordinated rhenium atom bonded to two *trans*-oxo groups. The phosphines lie on the equatorial plane, almost perpendicular to the $Re^V(O)_2{}^+$ core. The average value for the Re–O bond is 1.77 Å, similar to that in other Re(V) dioxo complexes. Diphosphine ligands form five- and six-membered rings in which λδ conformation is adopted. The unexpected $[Re(O)(OCH_3)(dppp)(Cl)_2]\cdot CH_3OH$ has been additionally characterized from X-ray data. It is also an octahedral complex with a methoxy ligand *trans* to an oxo group. Species are very stable towards redox processes and can be protonated in acidic media (70:30 dioxane:water, v/v) to yield $[Re(OH)_2L_2]^{3+}$. The protonation constants of the diphosphine ligands are also obtained for the first time.

Keywords: Crystal structures; Rhenium complexes; Oxo complexes; Diphosphine complexes

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1. Introduction

Rhenium(V) chemistry is of great interest, not only because of promising applications of *trans*-Re(V) dioxo complexes in photophysics [1–3]. Taking into account the strong resemblance between second- and third-row congeners, Re complexes permit non-radioactive model studies for ^{99m}Tc radiopharmaceuticals. Moreover, the recent development of $^{188}W/^{188}Re$ generators attracts attention in connection with the utilization of this radionuclide for therapeutic radiopharmaceuticals [4–6].

As far as the relevant chemistry is concerned, rhenium(V) and technetium(V) chemistry is governed by oxo species. It is supposed that the major factor of the formation of these complexes is the lowering of the high positive formal charge on metal(V) [7,8]. Hence, negatively charged ancillary ligands favor monooxospecies (with $[M(O)]^{3+}$ core) while neutral ligands, such as amines or phosphines, favor the formation of bisoxometal(V) species containing a $[M(O)_2]^+$ core. With this in mind, $[M(O)_2L_n]^+$ complexes (L = amine, phosphine, arsine; $n = 1, 2, 4$) have been extensively studied [2,9–17].

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* Corresponding author. Tel.: +34-922-318 458; fax: +34-922-318 461.
E-mail address: amederos@ull.es (A. Mederos)

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Recently, interest in Tc(V) with bidentate phosphine ligands has been renewed due to the development of the radiopharmaceutical ^{99m}Tc-tetrofosmin [18]. This is a Tc(V) dioxo complex with bis(2-ethyoxyethyl)-phosphinoethane. In this case also, the study of analogous diphosphine complexes of Re will provide very useful information for developing and predicting in vivo behavior of similar new Tc radiopharmaceuticals. For this study, we have chosen the simplest complexes of this group, i.e. $[Re(O)_2L_2]^+$ (L = 1,2-bis-(diphenylphosphino)ethane (dppe); 1,3-bis(diphenylphosphino)propane (dppp)). Preparation of these complexes has already been reported [2,19,20]. However, they have not been fully studied even though the structure of $[Re(O)_2(dppe)_2]ReO_4$ has been elucidated [21].

In this work we prepared and characterized $[Re(O)_2L_2]I$ (L = dppe, dppp) compounds. In addition, the related methoxo–oxo compound $[ReO(OCH_3)(dppp)Cl_2]$ was prepared for the first time. With these results, it is possible to compare the effect of changing chelate ring size on the stability of the molecule. Additionally, these structures provide useful information when compared with the similar $[Re(O)_2L_2]^+$ (L = 1,2-diaminoethane (en) and trimethylenediamine (tn)).

2. Experimental

2.1. Materials

All chemicals were of reagent grade and used as received. HPLC grade methanol and all other solvents (reagent grade) were used without further purification. Violet microcrystals of $[Re(O)_2(PPh_3)_2I]$ were obtained by using the reported method [22] except for $NH_4[ReO_4]$, which was used in place of $H[ReO_4]$. $[Re(O)Cl_3(PPh_3)_2]$ was obtained by using the reported method [23].

2.2. Physical measurements

Electronic absorption spectra were obtained using a Spectronic 3000 spectrophotometer. IR spectra were recorded as KBr pellets on a Bomen MB FT-IR spectrophotometer. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 spectrometer operating at 299.94 and 75.42 MHz, respectively, or on a Bruker AC200 operating at 200.13 and 50.32 MHz. Peak positions (in ppm) are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). $^{31}P\{^1H\}$ NMR spectra were recorded on the same instruments operating at 121.42 or 81.01 MHz, respectively. Chemical shifts (in ppm) were measured relative to external 85% H_3PO_4 with downfield values taken as positive. Elemental analysis was accomplished with an elemental analyzer Carlo Erba model 1108. Iodine was analyzed by titration with $AgNO_3$. Fast atom bombardment (FAB) was obtained from a 3-nitrobenzylalcohol matrix using a Kratos MS50TC spectrometer connected to a DS90 system.

2.3. HPLC analyses

Chromatograms were obtained with a HPLC system (E. Merck) equipped with a variable wavelength monitor and a PRP-X200 (10 μm) cation exchange column (4 × 250 mm). A 0.02 M solution of NaCl in methanol was used as mobile phase with 1.5 ml min^{-1} flow. Detection was accomplished at 255 nm.

2.4. Potentiometric measurements

The potentiometric titrations were carried out in mixed solvent 70:30 dioxane:water (v/v) solutions at 25°C and ionic strength $I = 0.1$ mol dm^{-3} in KCl. The sealed 100 cm^3 thermostated double-walled glass reaction vessel was fitted with a Radiometer G202B glass electrode, a Radiometer K711 calomel reference electrode, and inert argon atmosphere inlet and outlet tubes, a magnetic stirrer and a titrant (aqueous 0.05 mol dm^{-3} HCl) inlet. Readings of potentials were obtained with a Radiometer type PHM-85 potentiometer. The titrant was delivered through an immersed capillary tip from a Crison Microbur 2031 piston buret, and the temperature was maintained at 25.0 ± 0.1°C by circulating water from a refrigerated constant-temperature bath. The cell constants $E°$ and the liquid junction potentials J were determined according to the methods of Sillén [24] and Liberti and Light [25] by means of a least-squares program before each experiment. The autodissociation constant of the solvent pK_w was 16.3, in good agreement with reported data [26]. Measurements were taken of phosphine ligands alone (to compare basicity of the P atoms in the mixed solvent) at the concentrations $C_L = 1.0$ and 2.0 mol dm^{-3}, and the complexes at $C_C = 1.2$ and 2.1 mol dm^{-3}. The experimental potentiometric data were analyzed by means of the SUPERQUAD program [27] (Table 5).

2.5. Cyclic voltammetry

Cyclic voltammograms in methanol were obtained on a Metrohm glassy-carbon working electrode versus Ag/AgCl (methanol, saturated in LiCl). A Pt wire was used as the auxiliary electrode. The solutions were purged with nitrogen before recording the voltammograms. Ionic strength was kept constant at 0.5 M LiCl. Scans were carried out at rates between 50 and 500 mV min^{-1}. All experiments were performed at 25.0 ± 0.1°C. A PGP 201 potentiostat (Radiometer, Copenhagen) was employed as electrochemical controller.

Data were processed by Voltamaster 1 software. All potentials were later referred to the standard hydrogen electrode (SHE).

2.6. *Preparation of the complexes*

2.6.1. *[Re(O)$_2$(dppe)$_2$]I* (***1***)

[Re(O)$_2$(PPh$_3$)$_2$I] (0.30 g, 0.345 mmol) and 1,2-diphosphinoethane (1.5 g, 3.76 mmol) were stirred in dichloromethane (20 ml) for 10 min. A yellow solution was obtained and the solvent was completely evaporated by heating in a water bath (80°C). From this crude material, the complex was extracted with methanol (4 × 10 ml). The pale-yellow solution was filtered (through paper) and the solvent was evaporated again. The yellow solid was washed with ether (4 × 5 ml); yield 60–65%. Even when this solid presented a high purity (see below), it could be recrystallized from methanol; yield 70%. The complex is soluble in acetone, dichloromethane, chloroform, 2-propanol and acetonitrile and virtually insoluble in water and diethyl ether. Suitable crystals for X-ray diffraction were obtained by slow diffusion of a methanolic solution into diethyl ether. IR: 786.3 cm^{-1} ν_{as}(O=Re=O). UV–Vis (methanol; λ, nm (ε, M^{-1} cm^{-1})): 205 (174 600), 264 (65 300). Selected NMR data (CD$_2$Cl$_2$, 22°C). ^{1}H (299.94 MHz): δ 2.8 (m, 4H, CH$_2$); ^{13}C{^{1}H} (75.42 MHz): δ 32 (m, CH$_2$); ^{31}P{^{1}H} (121.42 MHz): δ 9.16 (s) ppm. *Anal.* Calc. for $C_{52}H_{48}IO_2P_4Re$: C, 54.69; H, 4.24; I, 11.11. Found: C, 54.27; H, 4.26; I, 11.0%.

2.6.2. *[Re(O)$_2$(dppe)$_2$]PF$_6$·2CH$_3$OH* (***2***)

To obtain crystals for X-ray diffraction, a large excess of NaPF$_6$ was added to a solution of **1** in 90:10 methanol–dichloromethane (v/v). The solvent was allowed to evaporate slowly in open air.

2.6.3. *[Re(O)$_2$(dppp)$_2$]I*

As above. Yield 55%. The complex is soluble in dichloromethane and chloroform, partially soluble in methanol and acetonitrile, slightly soluble in ethanol and 2-propanol and insoluble in water and diethyl ether. IR: 784.8 cm^{-1} ν_{as}(O=Re=O). UV–Vis (methanol; λ, nm (ε, M^{-1} cm^{-1})): 204 (164 300), 265 (55 600). Selected NMR data (CD$_2$Cl$_2$, 22°C). ^{1}H (299.94 MHz): δ 1.84 (m, 2H, CH$_2$*CH$_2$*CH$_2$), 2.78 (m, 4H, C*H$_2$*CH$_2$C*H$_2$*); ^{13}C{^{1}H} (75.42 MHz): δ 19.6 (m, CH$_2$*C*H$_2$CH$_2$), 27.2 (m, *C*H$_2$CH$_2$*C*H$_2$); ^{31}P{^{1}H} (121.42 MHz): δ −31.9 (s) ppm. *Anal.* Calc. for $C_{54}H_{52}IO_2P_4Re$: C, 55.43; H, 4.48; I, 10.75. Found: C, 55.97; H, 4.52; I, 10.9%.

2.6.4. *[Re(O)$_2$(dppp)$_2$]PF$_6$·CH$_3$OH* (***3***)

This compound was synthesized by the same procedure used for the preparation of complex **2** except that [Re(O)$_2$(dppp)$_2$]I was used in place of **1**.

2.6.5. *Perchlorate salts*

In order to avoid interference from the iodide in the voltammograms, the perchlorate salts were obtained by adding a large excess of LiClO$_4$ to a methanolic solution of the complexes. Yield 65–70%.

Caution! Perchlorate salts of [Re(O$_2$)(amine)$_2$]ClO$_4$ have been reported as hazardous materials [28]. During development of this work, no problems were detected with these perchlorates. Nevertheless, experiments with them were carried out with small amounts only and handled with care.

2.6.6. *[Re(O)$_2$(dppp)$_2$](ClO$_4$)$_x$(I)$_{1-x}$·H$_2$O·CH$_3$OH (x = 0.585(4))* (***4***)

Single crystals suitable for X-ray crystallography were grown by slow evaporation at room temperature (r.t.) of a methanolic solution of [Re(O)$_2$(dppp)$_2$]I with an excess of LiClO$_4$.

2.6.7. *[Re(O)(OCH$_3$)(dppp)(Cl)$_2$]·CH$_3$OH* (***5***)

Violet single crystals suitable for X-ray crystallography were obtained by slow evaporation at r.t. of a 50:50 methanol:ether (v/v) solution of [Re(O)$_2$(dppp)$_2$]I with an excess of LiClO$_4$. In order to obtain large amounts of this compound, [Re(O)Cl$_3$(PPh$_3$)$_2$] was assayed as starting material. [Re(O)Cl$_3$(PPh$_3$)$_2$] (0.30 g, 0.42 mmol) and 1,3-diphosphinopropane (0.175 g, 0.42 mmol) were refluxed in methanol (20 ml) for 1 h. A yellow solution was obtained and after 1 day at r.t., a violet solid appeared. The solid was collected by filtration and washed with ether (4 × 5 ml); yield 30–50%. The complex could be recrystallized from acetonitrile; yield 80–90%. The complex is soluble in hot acetonitrile and dichloromethane. IR: 909.1 cm^{-1} ν_{as}(Re(O). UV–Vis (acetonitrile; λ, nm (ε, M^{-1} cm^{-1})): 234 (46 600), 502 (35). Selected NMR data (CD$_2$Cl$_2$, 22°C). ^{1}H (200.13 MHz): δ 2.31 (t, 3H, $^4J_{P-H} = 1$ Hz, Re–O–*CH$_3$*), 3.50–2.60 (m, 4H, *CH$_2$*–CH$_2$–*CH$_2$*), 3.25–3.43 (m, 2H, CH$_2$–*CH$_2$*–CH$_2$); ^{13}C{^{1}H} (50.32 MHz): δ 21.6 (s, CH$_2$–*CH$_2$*–CH$_2$), 30.6 (m, *CH$_2$*–CH$_2$–*CH$_2$*), 57.85 (s, CH$_3$–O–Re); ^{31}P{^{1}H} (81.01 MHz): δ 15.22 (s). *Anal.* Calc. for $C_{28}H_{29}Cl_2O_2P_2Re$: C, 46.93; H, 4.08. Found: C, 47.05, H, 4.57%.

2.7. *Crystallographic measurements and structure determinations*

X-ray data collection for all compounds was performed at r.t. on a Rigaku AFC7S diffractometer using Mo Kα radiation. Important crystallographic data are collected in Table 1. The cell parameters were refined with 25 centered reflections. The intensity was monitored every 150 measurements with three standard reflections. Lorentz, polarization and absorption corrections were applied. Structure determination for compounds **1**–**3** was carried out by direct methods. The other two structures were solved by the heavy atom method, locating the Re atoms from a Patterson map. In all cases, the other non-hydrogen atoms were located by successive ΔF maps. Refinement was anisotropic for all non-hydrogen atoms, except for the methanol molecule in **3** and **5**. The hydrogen atoms belonging to phenyl and methylene groups were calculated at idealized positions (0.93 and 0.97 Å, respectively). The hydrogen atoms corresponding to methyl groups in the methanol molecules were also calculated (0.96 Å). The distances corresponding to other hydrogen atoms were left free to refine. Structure determination was achieved using SHELXS86 [29] and refinement was done using SHELXL97 [30]. Drawings were performed using ZORTEP [31]. Absorption correction was performed by Ψ-scan [32] and no extinction correction was applied for all five compounds. Other crystallographic data are summarized in the supplementary crystallographic data.

2.7.1. $[Re(O)_2(dppe)_2]I$ (**1**)

A yellow prismatic crystal with dimensions 0.2 × 0.1 × 0.1 mm was used. Intensities were measured for 6074 reflections up to a maximum value of $\theta = 27.50°$, $R_{int} = 0.0358$, and $0 \leq h \leq 15$, $-16 \leq k \leq 16$ and $-12 \leq l \leq 11$. The remanent electron density after refinement led to the values -2.441 and 2.461 e Å^{-3}, as minimum and maximum, respectively.

2.7.2. $[Re(O)_2(dppe)_2]PF_6 \cdot 2CH_3OH$ (**2**)

A yellow prismatic crystal with dimensions 0.4 × 0.35 × 0.2 mm was used. Intensities were measured for 6424 reflections up to a maximum value of $\theta = 27.62°$, $R_{int} = 0.0843$, and $0 \leq h \leq 12$, $0 \leq k \leq 21$ and $-22 \leq l \leq 21$. No disorder was observed in this structure. Residual peaks in the range 3.071 to -2.804 e Å^{-3} remained after the final refinement.

2.7.3. $[Re(O)_2(dppp)_2]PF_6 \cdot CH_3OH$ (**3**)

A yellow prismatic crystal with dimensions 0.35 × 0.20 × 0.20 mm was used. Intensities were measured for 12 534 reflections up to a maximum value of $\theta = 27.5°$, $R_{int} = 0.0300$, and $0 \leq h \leq 18$, $0 \leq k \leq 24$ and $-25 \leq l \leq 25$. After the final refinement residual peaks -3.226 and 1.024 e Å^{-3} remained unexplained.

2.7.4. $[Re(O)_2(dppp)_2](ClO_4)_x(I)_{1-x} \cdot H_2O \cdot CH_3OH$ ($x = 0.586(4)$) (**4**)

A yellow prismatic crystal with dimensions 0.4 × 0.2 × 0.2 mm was used. Intensities were measured for 12 324 reflections up to a maximum value of $\theta = 27.5°$, $R_{int} = 0.0211$, and $0 \leq h \leq 18$, $0 \leq k \leq 24$ and $-25 \leq$

Table 1
Crystal data and structural refinement parameters for structures $[Re(O)_2(dppe)_2]I$ (**1**), $[Re(O)_2(dppe)_2]PF_6 \cdot 2CH_3OH$ (**2**), $[Re(O)_2(dppp)_2]PF_6 \cdot CH_3OH$ (**3**), $[Re(O_2)(dppp)_2](ClO_4)_x(I)_{1-x} \cdot H_2O \cdot CH_3OH$ (**4**), and $[Re(O)(OCH_3)(dppp)Cl_2]CH_3OH$ (**5**) [a]

	1	2	3	4	5
Formula weight	1141.88	1224.04	1220.05	1202.11	762.62
Space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$	orthorhombic, $Pnma$
Unit cell dimensions					
a (Å)	11.950(4)	9.516(9)	13.904(4)	13.948(6)	17.113(5)
b (Å)	12.860(4)	16.552(7)	18.978(3)	18.813(4)	21.3461(12)
c (Å)	9.627(3)	17.251(9)	19.879(4)	19.659(5)	8.174(2)
α (°)	104.33(2)	90	90	90	90
β (°)	108.59(2)	104.21(6)	91.41(2)	90.91(3)	90
γ (°)	105.72(3)	90	90	90	90
V (Å^3)	1256.3(7)	2634(3)	5244(2)	5158(3)	2985.8(11)
Z	1	2	4	4	4
$D_{calc.}$ (g cm^{-3})	1.509	1.543	1.545	1.548	1.697
μ (mm^{-1})	3.20	2.52	2.53	2.81	4.39
$F(000)$	564	1232	2456	2415	1512
θ Range (°)	2.07–27.50	2.21–27.62	2.05–27.50	2.07–27.50	2.38–27.49
Data collected	6074	6424	12 534	12 324	4437
No. of observed data [$I \geq 2\sigma(I)$]	4988	4139	7854	7849	2944
R_1 [b]	0.0727	0.0518	0.0605	0.0483	0.0360
wR_2 [c]	0.2074	0.1336	0.1579	0.1191	0.0995
Transmission factors range	0.720–1.000	0.575–1.000	0.895–1.000	0.798–1.000	0.230–1.000
s_1 [d]	0.1238	0.1068	0.0713	0.0470	0.0595
s_2 [d]	6.8114	0	24.3259	26.9698	6.0381

[a] In all cases, temperature was 293(2) K and radiation Mo Kα, $\lambda = 0.71069$ Å.

[b] $R_1 = \Sigma|F_o - F_c|/\Sigma F_c$.

[c] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

[d] $w = 1/[\sigma^2(F_o)^2 + (s_1)^2 + s_2 P]$; $P = [\max(F_o)^2 + 2F_o^2]/3$.

$l \leq 25$. The iodide and perchlorate anions occupied the same crystallographic position in different asymmetric units producing a partial substitution. The refinement was performed balancing their occupancies. Residual peaks within $-3.576/3.257$ e Å^{-3} remained near the Re atom. This high residual electron density can be explained by the absorption correction performed by psi-scans for non-regular crystal shapes.

2.7.5. [Re(O)(OCH$_3$)(dppp)(Cl)$_2$]·CH$_3$OH (**5**)

A violet prismatic crystal with dimensions $0.4 \times 0.4 \times 0.1$ mm was used. Intensities were measured for 4437 reflections up to a maximum value of $\theta = 27.49°$, $R_{\text{int}} = 0.0156$, and $-10 \leq h \leq 22$, $-20 \leq k \leq 27$ and $-7 \leq l \leq 10$. From 3525 unique reflections, 2944 observed reflections ($I/\sigma(I) \geq 2$) were used for structure determination. Residual peaks within ± 2.30 e Å^{-3} remained in the final difference Fourier map near the Re atom. The atoms of CH$_3$OH were disordered and refined anisotropically with an occupancy factor of 0.5.

3. Results and discussion

Dioxo rhenium(V) complexes with general formula [Re(O)$_2$(diphosphine)$_2$]I can be readily prepared by using the strategy suggested by Brewer and Gray [33]. Yields are usually high (greater than 70%) and pure compounds are obtained. This fact can be easily checked by HPLC. Using a cation-exchange column (see Section 2), complexes appear as a two-peaks profile. One peak corresponds to the iodide counterion (retention time: 1.6 min), while the second corresponds to the cationic complex (retention times: 5.4 min (Re–dppe) or 6.7 min (Re–dppp)).

Compositions (by elemental analysis) of the solids fit with the expected formula. This is confirmed by the FAB MS spectrum, in which molecular ion peaks appear at $m/z = 1016$ (Re–dppe) and 1042 (Re–dppp). Doubly and triply charged ions, previously reported for en and tn analogous complexes [17] were not detected. The most prominent peaks were present at $m/z = 617$ (Re–dppe) and 629 (Re–dppp), corresponding to the loss of one ligand ($M^+ -$ dppe or $M^+ -$ dppp).

The structures of [Re(O)$_2$(dppe)$_2$]I (**1**), [Re(O)$_2$(dppe)$_2$]PF$_6$·2CH$_3$OH (**2**), [Re(O)$_2$(dppp)$_2$]PF$_6$·CH$_3$OH (**3**), [Re(O)$_2$(dppp)$_2$](ClO$_4$)$_x$(I)$_{1-x}$·H$_2$O·CH$_3$OH (**4**) and [Re(O)(OCH$_3$)(dppp)(Cl)$_2$]·CH$_3$OH (**5**) were determined. ORTEP drawings of the complexes are shown in Figs. 1–3, while selected distances and angles are listed in Tables 2–4.

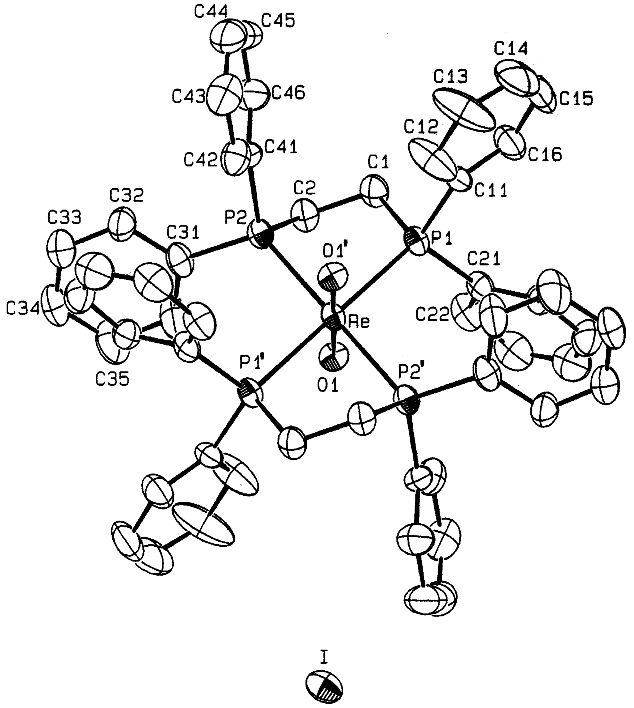

Fig. 1. ORTEP view of complex **1** with displacement ellipsoids drawn at 30% probability level. H atoms are omitted for clarity.

Cations **1**–**4** consist of squashed octahedrons around the Re(V) ion. Oxygen atoms occupy the *trans* position, almost linear with the Re atom. Re–O distances range from 1.768 to 1.782 Å, typical of such complexes [15,17,34–37]. Diphosphine ligands lie on the equatorial plane of the octahedron. Re–P distances (between 2.483 and 2.602 Å) are similar to those previously reported for other Re(V) complexes [2,16,38,39]. On the other hand, they are significantly longer than Re–N distances in the Re–en and Re–tn complexes that do not exceed 2.20 Å [40], as a consequence of changing N

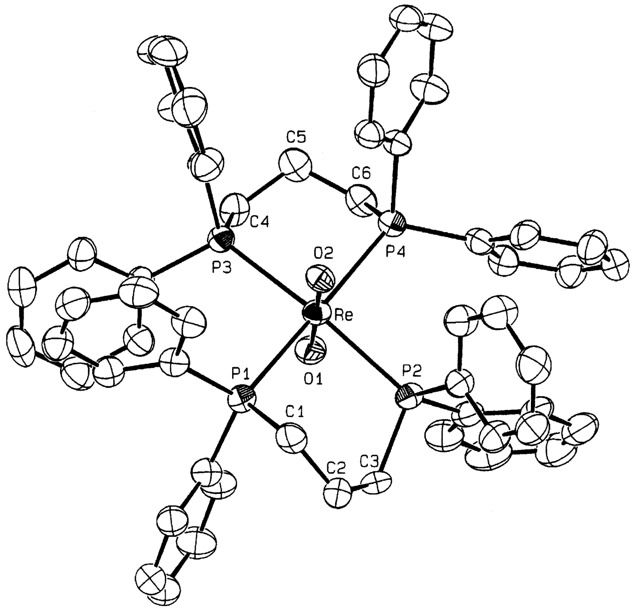

Fig. 2. ORTEP view of the [Re(O)$_2$(dppp)$_2$]$^+$ (**3**) cationic complex (50% probability ellipsoids; H atoms are omitted for clarity).

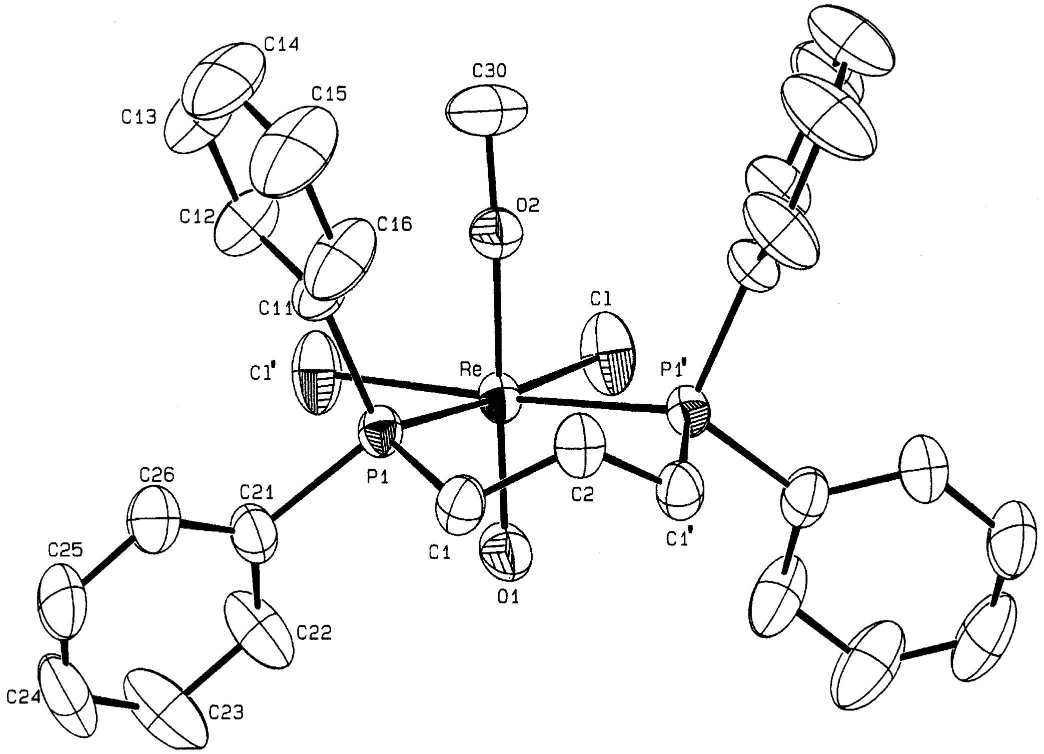

Fig. 3. ORTEP view of the complex [Re(O)(OCH_3)(dppp)$(Cl)_2$]·CH_3OH (**5**) (30% probability ellipsoids; H atoms are omitted for clarity).

to P with a larger covalent radius. Taking into account average Re–P bond lengths and P–Re–P angles, the distances between P atoms belonging to the same ring (bite size) can be calculated as 3.82 (dppe) and 3.72 Å (dppp). This represents a much more open ring than those of Re–en and Re–tn analogs [40]. Consequently, steric crowding in the complexes is greatly reduced, allowing the accommodation of eight phenyl groups per Re atom.

The five- and six-membered rings formed between Re, P and C atoms offer the possibility of having molecules in different conformations. In the four cations, a λδ conformation is adopted. As previously studied by molecular mechanics and semi-empirical calculations [40], this is the most stable conformation. The presence of the phenyl groups seems to stabilize the λδ conformation (with eclipsed substitutes on phosphorus atoms) in comparison with λλ or δδ conformations.

Together with crystals of compound **4**, violet crystals were observed. X-ray diffraction structure determination proved them to be [Re(O)(OCH_3)(dppp)$(Cl)_2$]·CH_3OH (**5**). The appearance of this compound seems to be the result of a redox process in which the perchlorate anion is reduced to chloride. Then, in a second step, one dppe ligand is substituted by two chlorides. One of the oxo groups is lost, a methoxy group arising from the crystallization solvent occupying the *trans* position. Compound **5** also shows an octahedral arrangement around the Re atom but with significant irregularities. The O(1)–Re–O(2′) angle is 175.5(2)°, i.e. O(1) is slightly bent towards the dppp ligand giving an O(1)–Re–P(1) angle of 87.58(13)°. Re–O distances are markedly different as a consequence of the bond character. The Re–O(1) distance is 1.702(5) Å, which is shorter than those for compounds **1**–**4**. This length is comparable with that expected for Re(V) monooxo complexes [37], showing a certain triple bond character.

Table 2
Comparison of selected bond lengths (Å) and bond angles (°) for the complexes [Re$(O)_2$$(dppe)_2$]I (**1**) and [Re$(O)_2$$(dppe)_2$]$PF_6$·2$CH_3OH$ (**2**) [a]

	1	**2**
Re–O(1)	1.772(4)	1.780(4)
Re–P(1)	2.487(3)	2.513(2)
Re–P(2)	2.483(3)	2.487(2)
O(1)–Re–O(1′)	180.0	180.0
O(1)–Re–P(1)	84.4(2)	94.50(14)
O(1)–Re–P(2)	84.8(2)	94.87(13)
O(1)–Re–P(1′)	95.6(2)	85.50(14)
O(1)–Re–P(2′)	95.2(2)	85.13(13)
P(1)–Re–P(2)	79.4(1)	80.50(6)
P(1)–Re–P(1′)	180.0	180.0
P(2)–Re–P(2′)	180.0	180.0
P(1)–C(1)–C(2)	113.5(7)	113.3(4)
P(2)–C(2)–C(1)	110.6(7)	110.8(4)

[a] The atoms labeled (′) are related by the symmetry operation $-x+1$, $-y$, $-z+1$ (in (**1**)) and $-x$, $-y+1$, $-z$ (in (**2**)).

Table 3
Comparison of selected bond lengths (Å) and bond angles (°) for the complexes $[Re(O)_2(dppp)_2]PF_6{\cdot}CH_3OH$ (**3**) and $[Re(O)_2(dppp)_2](ClO_4)_x(I)_{1-x}$ (**4**)

	3	**4**
Re–O(1)	1.768(6)	1.782(5)
Re–O(2)	1.754(5)	1.748(4)
Re–P(1)	2.568(2)	2.5209(18)
Re–P(2)	2.541(2)	2.519(2)
Re–P(4)	2.517(2)	2.5331(18)
Re–P(3)	2.517(2)	2.602(2)
O(1)–Re–O(2)	177.0(3)	177.5(2)
O(1)–Re–P(1)	95.9(2)	85.62(17)
O(1)–Re–P(2)	87.5(2)	88.8(2)
O(1)–Re–P(4)	89.1(2)	87.99(17)
O(1)–Re–P(3)	85.6(2)	96.1(2)
O(2)–Re–P(1)	81.09(17)	94.58(15)
O(2)–Re–P(2)	92.13(18)	93.69(15)
O(2)–Re–P(4)	93.91(17)	91.72(15)
O(2)–Re–P(3)	94.66(18)	81.41(15)
P(1)–Re–P(2)	84.53(7)	86.41(6)
P(4)–Re–P(3)	86.49(7)	84.27(6)
P(1)–Re–P(4)	174.99(7)	173.27(6)
P(2)–Re–P(3)	172.83(7)	175.09(6)
P(1)–C(1)–C(2)	113.4(7)	115.2(5)
P(2)–C(3)–C(2)	114.7(6)	114.7(5)
P(4)–C(6)–C(5)	114.7(6)	116.1(5)
P(3)–C(4)–C(5)	115.7(6)	113.7(6)
C(1)–C(2)–C(3)	119.4(8)	114.3(7)
C(4)–C(5)–C(6)	115.3(8)	116.9(6)

On the other hand, Re–O(2) is 1.856(4) Å. This is in line with the reported distance in $[Re(O)(acac)\{\eta^2\text{-}B(pz)_4\}(OMe)]$ (acac = acetylacetonate; pz = pyrazolyl) of 1.896 Å [41] in which the methoxy group is coordinated to the Re(V) *trans* to an oxo group. However, it is different from the distance reported for a methanol ligand coordinated to Re(V) center, 2.38 Å [42]. Re–Cl distances in compound **5** are 2.450(1) Å. They are similar to others reported for *cis* dichloro complexes of Re(V), ranging from 2.33 to 2.40 Å [43–46] and slightly shorter than the Re–Cl distance for a chlorine atom *trans* to an oxo group (2.44 Å) [46]. Based on the structure of this new compound, the synthesis from $[Re(O)(Cl)_3(PPh_3)_2]$ was performed.

Table 4
Selected bond lengths (Å) and bond angles (°) for the complex $[Re(O)(OCH_3)(dppp)(Cl)_2]{\cdot}CH_3OH$ (**5**) [a]

	5
Re–O(1)	1.702(5)
Re–O(2)	1.856(4)
Re–P(1)	2.4431(11)
O(1)–Re–O(2)	175.5(2)
O(1)–Re–P(1)	87.58(13)
O(2)–Re–P(1)	89.39(10)
P(1)–Re–P(1′)	94.49(5)
P(1)–C(1)–C(2)	113.8(4)
C(1)–C(2)–C(1′)	113.1(6)

[a] The atoms labeled (′) are related by the symmetry operation *x*, $-y+1/2$, *z*.

The methanol solvent molecules are connected to oxo groups in compounds **2**, **4** and **5** by hydrogen bonds of O···O mean length 2.77(2) Å. In compound **4** there is evidence of the formation of hydrogen bonding connections between the water molecule and the perchlorate anion with an O···O distance of 2.75(1) Å and the water molecule and the iodide anion with an I···O distance of 3.76(1) Å.

The IR spectra of the iodide salts show a very strong and sharp absorption at 786.3 cm^{-1} (Re–dppe) and 784.8 (Re–dppp) cm^{-1}, characteristic of the linear $[O{=}Re{=}O]^+$ core. These vibrations are in the expected range (775–835 cm^{-1}) for the asymmetric $Re(O)_2$ stretching [47]. However, the Re–O stretching frequency lies in the lower part of this range, showing a reduction in the bond order. This phenomenon should be interpreted in terms of the fact that phosphorus donor atoms are part of a conjugated system which could increase Re–P bond order. In addition, typical signals of the ligands are also found in the complexes [48,49]. For dppe: 3052.0 (CH stretching of the phenyl groups), 2905.3 (CH_2 stretching), 1484.9 (CH_2 bending), 1435.2 (P-phenyl group stretching), 1102.6 (C–C stretching), 743.7 and 693.0 cm^{-1} (out of plane CH bending). Analogously for dppp: 3052.1, 2922.8, 1484.3, 1436.1, 1099.4, 741.9 and 697.7 cm^{-1}. The IR spectrum of **5** shows characteristic absorption of the $[Re(O]^{3+}$ core at 909.9 cm^{-1}. The presence of Re–OCH_3 is detected by a weak vibration at 787.9 cm^{-1}. Both bands are similar to others previously reported [50,51]. Also, a strong $\nu(O–CH_3)$ vibration at 1109.5 cm^{-1} is detected.

Electronic absorption spectra of the cations are mainly determined by the strong absorptions of the ligands. Typical bands of the $[Re(O)_2]^+$ core seem to be shadowed by the aromatic system of phosphines.

The $^{31}P\{^1H\}$ spectra of the complexes $[Re(O)_2(dppe)_2]I$ and $[Re(O)_2(dppp)_2]I$, with a singlet resonance at 9.16 and -31.9 ppm, respectively, are consistent with an octahedral geometry in which the two chelate ligands are in *trans* position to each other on the equatorial plane of the coordination polyhedron. ^1H and $^{13}C\{^1H\}$ spectra (see Section 2) are in agreement. The values of the ^{31}P chemical shifts appear in line with those previously reported for other rhenium(V) octahedral diphosphine complexes [52]. The $^{31}P\{^1H\}$ spectrum of complex **5**, with a singlet resonance at -15.22 ppm, indicates that the two phosphorus atoms are equivalent and in *trans* position to the chlorine atoms. ^1H and $^{13}C\{^1H\}$ spectra are consistent with such a geometry, the ^1H absorption of Re–O–CH_3 being a triplet, due to the long-range coupling with the two phosphorus atoms.

Table 5
Protonation constants of dppe, dppp, $[Re(O)_2(dppe)_2]^+$ and $[Re(O)_2(dppp)_2]^+$ (70:30 dioxane:water (v/v), 25°C, $I = 0.1$ mol dm^{-3} KCl)

Compound	Number of experimental points/number of titrations	pH range	$\log \beta_{12}$	χ^2	$\sigma(E)$
Dppe	60/2	2.0–3.1	3.55 ± 0.05	16.0	0.28
Dppp	68/2	1.8–3.3	3.52 ± 0.03	25.2	0.30
$[Re(O)_2(dppe)_2]^+$	94/2	1.7–3.5	3.9 ± 0.1	14.1	0.94
$[Re(O)_2(dppp)_2]^+$	91/2	1.7–3.5	3.69 ± 0.07	14.6	1.31

Potentiometric titrations were performed in 70:30 dioxane:water (v/v) in order to reach sufficient solubility of the complexes. For $[Re(O)_2(amine)_2]^+$ species in aqueous solution, experiments previously reported showed successive protonation of the oxo groups [17,53]. Hence, $[Re(O)_2(amine)_2]^+$, $[Re(O)(OH)(amine)_2]^{2+}$ and $[Re(OH)_2(amine)_2]^{3+}$ species exist in solution. In this case the result is different. Both protonations are simultaneous, without a significant presence of the monoprotonated species. For both complexes, the processes involved in the titrations are:

$$[Re(O_2(phosphine)_2]^+ + 2H^+ \rightleftarrows [Re(OH)_2(phosphine)_2]^{3+}$$

The protonation constant β_{11} is rejected, but β_{12} is well defined 3.9(1) for Re–dppe and 3.69(7) for Re–dppp.

It is interesting to compare these values with those corresponding to the free ligands. Also, a simultaneous protonation of both phosphine groups is detected with β_{12} values near 3.5 (see Table 5). Assuming that P atom basicity is reduced if coordinated, it is reasonable to postulate protonation of the complexes on the oxo groups as in the case of amine analogues.

Cyclic voltammograms of the complexes in methanol do not show signals in the studied range of potentials (−1000 to 1400 mV versus SHE). Re(V) dioxo complexes with amines show electronic processes in this range [15,36,53–55]. Although it is difficult to compare the results because experiments were performed under different conditions, it seems clear that phosphine complexes are much more stable than amine analogs. This fact is also reflected in the good stability of solutions of the cations.

4. Conclusions

Dppe and dppp form stable *trans* Re(V) dioxo complexes. They can be easily obtained from $[Re(O)_2(PPh_3)_2I]$. It is interesting to compare these complexes with Tc(V) analogues. ^{99m}Tc(V)-tetrafosmin, a potential myocardial perfusion imaging agent, bases its biological behavior on the +1 formal charge and the redox stability of the cation [56,57]. With this in mind, Re analogs are expected to be more robust complexes. The solid state structure shows low strain of the five- and six-membered rings and protonation reactions and redox changes seem to be out of reach for biological systems. The stability of Re(V) dioxo complexes with P-containing ligands offers the possibility to develop new therapeutic radiopharmaceuticals with the $[Re^V(O)_2]^+$ core.

5. Supplementary material

Complete listings of atomic coordinates, anisotropic thermal parameters, complete bond distances and angles, hydrogen coordinates, as well as a listing of calculated and observed structure factors are available from the authors on request.

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