

Solid State Study on Rhenium Dimethylphosphinoethane Complexes: X-ray Crystal Structures of *trans*-[ReO₂ (dmpe)₂]PF₆·2H₂O, *trans*-[ReO(OH)(dmpe)₂](CF₃SO₃)₂, *trans*-[ReN(Cl)(dmpe)₂]CF₃SO₃ and *trans*-[ReCl₂(dmpe)₂]ReO₄

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The reaction of trans-[ReO2(en)2]Cl with dimethylphosphinoethane (dmpe) yielded the yellow complex trans-[ReO2 (dmpe)₂]Cl (1), which, upon reaction with CF₃SO₃H, yields orange crystals of the oxo-hydroxo complex trans-[ReO (OH)(dmpe)₂](CF₃SO₃)₂ (2). Reaction of trans-[ReNCl₂(PPh₃)₂] with dmpe resulted in orange crystals of trans-[ReN(Cl)(dmpe)₂]-CF₃SO₃ (3). Adjustment of the pH of a solution of *trans*-[ReN(Cl)(dmpe)₂]CF₃SO₃ to 11.7 with NaOH resulted in the formation of yellow crystals of trans-[ReCl2(dmpe)2]ReO4 (4). A shortening of the Re-P bond distances were observed as the axial ligands (i.e., core: O=Re^V-OH < O=Re^V=O < N=Re^V-Cl < Cl-Re^{III}-Cl) increased the electron density on the metal center, allowing for better Re-P n back bonding. The preliminary pK_a determination for the protonation of $[ReO_2(dmpe)_2]^+$ to form [ReO(OH)(dmpe)₂]²⁺ showed the pK_{a2} to be <1. Crystallographic data: trans-[ReO₂(dmpe)₂]⁺: monoclinic space group P2₁/c with a = 11.5299(7) Å, b = 15.2397(9) Å, c = 15.0230(9) Å, $\beta = 97.7260(10)^{\circ}$, Z = 4; trans-[ReO(OH)(dmpe)₂]²⁺: monoclinic space group $P2_1/c$ with a = 8.0426(4) Å, b = 11.5472(6) Å, c = 16.0303(8) Å, $\beta = 101.9360(10)^{\circ}$, Z = 2; trans-[ReN(Cl) (dmpe)₂]⁺: orthorhombic space group Pmc2 with

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a = 11.5068(10) Å, b = 9.6656(8) Å, c = 12.1772(11) Å, Z = 2; trans-[Re(Cl)₂(dmpe)₂]⁺: monoclinic space group P2₁/c with a = 19.375(3) Å, b = 8.6840(12) Å, c = 15.910(2) Å, β = 111.270(3) °, Z = 4. The conformation of the two dmpe ligands in all of the complexes described were $\lambda\delta$ (eclipsed).

Keywords Rhenium, Dimethylphosphinoethane (dmpe), pKa, back bonding

INTRODUCTION

Technetium-99m is used in over 90% of all diagnostic nuclear medicine scans (Clarke and Podbielski, 1987; Deutsch et al., 1983; Deutsch and Libson, 1984; Dilworth and Parrott, 1998; Steigman and Eckelman, 1992) due to its favorable nuclear properties ($t_{1/2}$; = 6.02 hr, γ = 140 keV) and availability from a generator. Tc-99m is used routinely for brain, heart, liver, kidney and bone imaging. Technetium's third row congener rhenium also has applications to nuclear medicine because its two radioactive isotopes, Re-186 and Re-188, have nuclear properties suitable for radiotherapeutic applications (Deutsch et al., 1986).

Mono-cationic complexes of Tc are of interest because of their extensive use as ^{99m}Tc myocardial imaging agents (Deutsch et al., 1981a; Jurisson et al., 1993) with examples including (Cardiolite) or $[^{99m}Tc(MIBI)_6]^+$ (MIBI = 2-methoxy-2-methylpropylisocyanide) (Holman et al., 1984; Prats et al., 1999) and Myoview ($[^{99m}TcO_2(\text{Tetrofosmin})_2]^+$). While the mono-cationic complexes are traditionally based on the $[O=Tc^V=O]^+$, $[Cl-Tc^{III}-Cl]^+$ and Tc^I cores, a new class of myocardial imaging agents feature the $[^{99m}Tc^V=N]^{2+}$

core, an example being the Tc-N-NOET complex (bis(N-ethoxy-N-ethyldithiocarbamato)nitrido-technetium(V)).

The "lanthanide contraction" results in similar physical characteristics for analogous Re and Tc complexes (i.e., size, lipophilicity, etc.) (Deutsch et al., 1986; Dilworth and Parrott, 1998). Rhenium is often used as the non-radioactive surrogate for the development of radioactive Tc chemistry. Their similar physical characteristics make it very difficult for biological systems to distinguish between analogous Tc and Re (Deutsch et al., 1986) complexes based on properties such as size, shape and charge. However, they do differ in their redox properties, which can result in different in vivo handling of analogous complexes. Rhenium complexes are more stable in higher oxidation states and thus are more difficult to reduce (by ca. 200 mV) than their Tc analogs (Vanderheyden et al., 1985). Thus, Re is more readily re-oxidized to perrhenate (ReO_4^-) than Tc is to pertechnetate (TcO_4^-) in vivo, and perrhenate requires the use of stronger reducing agents for the synthesis of Re radiopharmaceuticals. A second difference is the larger ligand field splitting for Re complexes, which results in slower ligand substitution onto Re than Tc.

Both Tc and Re complexes are known with oxidation states between -1 and +7, with the lower states (*i.e.*, -1, 0, +1) generally containing strong π -acceptors ligands such as a carbonyl group (Treichel, 1982). The higher oxidation states are stabilized by metal-oxo formation (Pipes and Meyer, 1986). Perrhenate and pertechnetate (MO_4) (M = Tc, Re)with M in the +7 oxidation state are reduced to the +5 state via a two electron reduction. The exact mechanism is not known, but it is believed to proceed via the abstraction of an oxygen atom. Common reducing agents include phosphine, arsine and tin(II), amongst others. The most common oxygen atom acceptors are tertiary phosphines, whose nucleophilicities or basicities usually increase with the number of alkyl groups, with the most widely used being triphenylphosphine (PPh₃) (Holm, 1987). Johnson et al. (Johnson et al., 1984) reported the reduction of Re^{VII} to Re^V by an oxygen atom transfer to triethylphosphine to form triethylphosphine oxide. In pyridine (py), ReO_4^- is inert to reduction by phosphine, while in a hydrochloric acid solution, the perrhenic acid is completely reduced by triphenylphosphine to the Re^V compound, [ReOCl₃(PPh₃)₂]. Numerous examples of crystal structures in which the PPh₃ ligand, acting as a Lewis acid, is coordinated to the axial O as if "caught in the act" of oxygen abstraction

are known (Bhattacharyya et al., 2000; Göldner et al., 2001; Seymore and Brown, 2000).

The development of technetium myocardial imaging agents began with work by Deutsch (Deutsch et al., 1981; Deutsch et al., 1989; Gerson et al., 1983; Vanderheyden et al., 1984, 1985) on the investigation of the [99mTcCl2 $(dmpe)_2$ ⁺ [dmpe = bis(1,2-dimethylphosphino)ethane] and $[^{99m}TcX_2(diars)_2]^+$ complexes (diars = o-phenylenebis(dimethylarsine), X = Cl, Br) (Deutsch et al., 1981b). Animal studies indicated that the reduction of Tc^{III} to Tc^{II} is biologically accessible for the cationic [^{99m}Tc^{III}Cl₂(dmpe)₂]⁺ complex and it is reduced to the neutral [99mTc^{II}Cl₂(dmpe)₂] complex, which then washes out of the heart and becomes trapped in the liver. The reduction of Re^{III} to Re^{II} $[^{186}\text{Re}^{III}\text{Cl}_2 (dmpe)_2]^+$ is 0.2 V more negative than for the Tc analog complex is thus retained in the heart (Vanderheyden et al., 1984). The kinetic, electrochemical, and structural work on the $[\text{Re}/\text{Tc}^{II}\text{Cl}_2(\text{DMPE})_2]$ complexes that has been published illustrates its importance (Bakir et al., 1987; Eglin et al., 1998; Esjornson et al., 1990; Lewis et al., 1993; Libson et al., 1988; Roodt et al., 1991).

Two technetium phosphine complexes are currently used in nuclear medicine for myocardial imaging, namely Myoview ($[^{99m}TcO_2(Tetrofosmin)_2]^+$) and TechneScan Q12/ TechneCard ($[^{99m}TcO_2(Tetrofosmin)_2]^+$) (Figure 1) (Smith et al., 1997). [$^{99m}TcO_2(Tetrofosmin)_2]^+$ is a Tc(V) complex that shows substantial myocardial uptake (Kelly et al., 1993). It is interesting to note that [$^{99m}TcO_2(dmpe)_2]^+$, which has methyl groups on the phosphine rather than the ether groups in Tetrofosmin, is not retained in the myocardium (Kelly et al., 1991). In order to determine how the phosphine ligand affects the biological behavior of the myocardial imaging agent [$^{99m}TcO_2(Tetrofosmin)_2]^+$, similar bidentate P-donor ligands have been investigated (*i.e.*, dmpe, dppe, etc.) The structural similarities between Tetrofosmin and dmpe, used in this study are illustrated in Figure 1.

Deutsch reported that the Re-P and Re-Cl bond lengths in $[\text{Re}^{\text{III}}\text{Cl}_2(\text{dmpe})_2]^+$ were dependent on (1) the steric crowding with respect to the coordination number and to multiply bonded ligands, (2) structural *trans* effects of strongly bonded ligands, (3) oxidation state of the metal center, and (4) the π -acceptor ability of the ligand which is important in the lower oxidation states (Vanderheyden et al., 1985). In this article, the structural effects induced by different



FIG. 1. Structures of the Tetrofosmin and dmpe ligands.

Re-cores are discussed. The equatorial ligand (dmpe) was held constant and the axial core varied to investigate the impact this change induces on the solid state structure of the co-ordinated polyhedron and on the bidentate tertiary phosphine ligand. With the ongoing development of new Tc and Re agents, it is essential that their basic coordination chemistry be understood. This study investigated the effect(s) of ligand modification on the metal core of Tc and Re cationic complexes to aid in the development of future complexes. The structural influence of the Re core was investigated by keeping the equa-

torial ligand (dmpe) the same and varying the axial ligands as

well as the Re oxidation state.

The dioxo ($[O=Re=O]^+$), oxo-hydroxo ($[O=Re-OH]^{2+}$) and nitrido-chloro ($[N=Re-Cl]^+$) Re(V) and the dichloro ($[Cl-Re-Cl]^+$) Re(III) cores with equatorial phosphine ligands were investigated. The rationale was to determine what effects the electron density on the Re center (dependent on the particular core) had on the Re-P bond distances, as phosphine donor atoms in the equatorial plane are potential π -back bonding ligands.

The structure of the Tc analogs of three of the complexes to be discussed below, *i.e.*, $[ReO(OH)(dmpe)_2](CF_3SO_3)_2$ (2), $[ReN(Cl)(dmpe)_2]CF_3SO_3$ (3) and $[Re(Cl)_2(dmpe)_2]ReO_4$ (4) have been reported (Archer et al., 1992; Vanderheyden et al.,



SCH. 1. Synthesis of trans- $[ReO_2(dmpe)_2]PF_6 \cdot 2H_2O(1)$, trans- $[ReO(OH)(dmpe)_2](CF_3SO_3)_2(2)$, trans- $[ReN(Cl)(dmpe)_2]CF_3SO_3(3)$ and trans- $[Re(Cl)_2(dmpe)_2]ReO_4(4)$.

1984, 1985) and will be used for correlation with the current structures.

EXPERIMENTAL SECTION

Materials

All experiments were carried out in air and doubly distilled water was used in all the preparations unless otherwise noted. Potassium perrhenate (KReO₄) and dmpe were purchased from Strem Chemicals. Ethylenediamine (en) was purchased from the Sigma-Aldrich Chemical Company. All reagents were used as received without further purification.

Preparation of Complexes. (Bu₄ⁿN)ReO₄

KReO₄ (0.5 g, 1.73 mmol) and (Buⁿ₄N)Cl (0.625 g, 2.25 mmol) were dissolved individually in a minimum amount of warm water (*ca.* 5 – 10 mL, 70 °C) with the latter being slowly added to the ReO₄ solution while stirring. The solution was then cooled in an ice bath and the resultant white precipitate vacuum filtered and dried overnight in a vacuum desiccator over P₂O₅. Quantitative yield was achieved. IR: $\nu_{(Re=O)} = 909 \text{ cm}^{-1}$.

trans-[ReOCl₃(PPh₃)₂]

trans-[ReOCl₃(PPh₃)₂] was synthesised by a slight variation on the method of Johnson et al. (Johnson et al., 1967) Triphenylphosphine (5.4 g, 20.6 mmol) was dissolved in glacial acetic acid (80 mL). (Buⁿ₄N)ReO₄ (0.6 g, 1.22 mmol) was dissolved in concentrated hydrochloric acid (6 mL) and added to the triphenylphosphine solution over a period of *ca*. 45 min while stirring. Once the addition of the (Buⁿ₄N)ReO₄ was complete the dropping funnel was rinsed with glacial acetic acid (10 mL) and was added to the reaction mixture. Stirring was continued for 5 h. The light green precipitate was filtered and washed with glacial acetic acid (10 mL), diethyl ether (3 × 10 mL) and dried overnight in a vacuum desiccator over P₂O₅. (Yield: 0.91 g, 90%). The IR spectrum of this material was identical to that reported previously (Johnson et al., 1967) with IR: $\nu_{(Re=O)} = 969 \text{ cm}^{-1}$.

trans-[ReO2(en)2]Cl

This complex was synthesized via a slight variation of the procedure reported by Ram et al. (Ram and Hupp, 1991) using en instead of py. trans-[ReOCl₃(PPh₃)₂] (250 mg, 0.3 mmol) was suspended in acetone (20 mL), and water (0.6 mL) and the en (0.721 g, 12.0 mmol), {Re:en, 1: \sim 40} was added while stirring. The mixture was refluxed for 90 min and then allowed to cool. The precipitate was filtered and washed with toluene (2 × 5 mL) ether (2 × 5 mL) and dried overnight in a vacuum desiccator over P₂O₅. The complex was recrystallized by dissolution in a minimum amount of water (ca. 5 mL) followed by slow addition of ethanol (ca. 30 mL) to give orange-brown crystals. The UV/Vis and IR spectra of the complex was identical to that reported previously (Ram and Hupp, 1991). (Yield: 79 mg, 70%).

Spectral data: IR: $\nu_{(\mathbf{Re}=\mathbf{O})} = 820 \text{ cm}^{-1}$; ¹H NMR: 2.43 ppm (singlet, 2 × CH₂, 4H, C₁ and C₂).

trans-[ReNCl₂(PPh₃)₂]

KReO₄ (0.5 g, 1.73 mmol) and HCl (3 mL, 10 M) were refluxed for 30 min., and then NaN₃ (0.4 g, 6.2 mmol), dissolved in water (4 mL), was added. The resultant mixture was refluxed until the solution became clear (*ca.* 30 min). The solution was left to cool for *ca.* 2 min and triphenylphosphine (2.5 g, 9.5 mmol) dissolved in acetone (50 mL) was carefully added and the resulting solution refluxed for 30 min. (Care should be taken not to reflux the solution for too long as this leads to the formation of *trans*-[ReOCl₃(PPh₃)₂]). The red-brown precipitate was collected by vacuum filtration and washed with warm water (3 × 10 mL), ethanol (2 × 10 mL) and acetone (1 × 10 mL). (Yield: 1.17 g, 85%) (Damoense et al., 1994).

trans-[ReO2(dmpe)2]PF6 · 2H2O

trans-[ReO₂(en)₂]Cl (50 mg, 0.134 mmol) was dissolved under an inert N2 atmosphere in deoxygenated methanol and dmpe (0.9 mL, 5.4 mmol) was added. The mixture was refluxed while stirring under N2 until all the trans- $[\text{ReO}_2(\text{en})_2]$ Cl had disappeared (ca. 5 hr) to yield a yellow solution. This solution was evaporated to dryness, redissolved in a minimum amount of water (ca. 5 mL) and filtered. X-ray quality crystals were obtained by dissolving the crude trans- $[\text{ReO}_2(\text{dmpe})_2]$ Cl (50 mg, 0.09 mmol) in water (ca. 2 mL) and adding NH₄PF₆ (100 mg, 0.6 mmol). The solution was filtered, allowed to evaporate slowly at room temperature and after four days, yellow crystals were harvested. (Yield: 38 mg, 60%). Spectral data: IR: $\nu_{(\mathbf{Re}=\mathbf{O})} = 777 \text{ cm}^{-1}$; ¹H NMR: 0.71 ppm (singlet, $2 \times CH_2$, 4H, C_1 and C_2) and 1.86 ppm (singlet, $4 \times CH_3$, 12H, R_1-R_4). ³¹P NMR: 6.3 (singlet); UV/Vis: λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 340 (214).

trans-[ReO(OH)(dmpe)₂](CF₃SO₃)₂

trans-[ReO₂(dmpe)₂]Cl (15 mg, 0.027 mmol) was dissolved in water (*ca.* 3 mL) and conc. CF₃SO₃H (5 drops) added. Orange crystals were obtained after 4 days of evaporation of the solvent at ambient temperature. (Yield: 17 mg, 75%). Spectral data: IR: $\nu_{(Re=O)} = 954 \text{ cm}^{-1}$; UV/Vis: λ_{max} , nm (ε , M⁻¹ cm⁻¹): 384 (175).

trans-[ReN(Cl)(dmpe)₂]CF₃SO₃

trans-[ReNCl₂(PPh₃)₂] (0.1 g, 0.13 mmol) was dissolved under an inert N₂ atmosphere in deoxygenated CHCl₃ and dmpe (90 μ L, 0.54 mmol) was added. The resulting solution was refluxed while stirring under N₂ until a yellow precipitate formed (*ca*. 6 h). The solution was completely evaporated and the solid redissolved in a minimum amount of water (*ca*. 10 mL) and filtered to remove the liberated triphenylphosphine. After standing for 2 days, a white precipitate formed that was filtered (presumably the excess phosphine that oxidized) and yielded a crystalline product after another 4 days of evaporation at ambient temperature. X-ray quality crystals were obtained by dissolving the crude *trans*-[ReN(Cl) (dmpe)₂]Cl (110 mg, 0.19 mmol) in water (*ca.* 2 mL) and adjusting the pH to *ca.* 1.4 with conc. CF₃SO₃H. The yellow crystals were harvested after 2 days of evaporation of the solvent at ambient temperature. (Yield: 96 mg, 73%). Spectral data: IR: $\nu_{(Re=N)} = 1056 \text{ cm}^{-1}$; ³¹P NMR: 16.3 (singlet); UV/Vis: λ_{max} , nm (ε , M⁻¹ cm⁻¹): 405 (241).

trans-[ReCl2(dmpe)2]ReO4

trans-[ReN(Cl)(dmpe)₂]Cl (110 mg, 0.19 mmol) was dissolved in water (*ca.* 2 mL) and the pH adjusted to *ca.* 11.7 with conc. NaOH. Yellow crystals were obtained after 5 days of evaporation of the solvent at ambient temperature. (Yield: 64 mg, 41%). Spectral data: IR: $\nu_{(\text{Re}=\text{O})} = 945 \text{ cm}^{-1}$ for ReO₄⁻; UV/Vis: λ_{max} , nm (ε , M⁻¹ cm⁻¹): 405 (458) and 440 (397) (shoulder).

Techniques, Apparatus, and Methods

¹H NMR spectra were recorded in D₂O on a Bruker 300 MHz spectrometer; ¹H chemical shifts are reported relative to H₂O (4.60 ppm). IR spectra were recorded as KBr pellets on a Hitachi 270–50 spectrometer and the UV/Vis spectral changes and absorbance spectra on Hitachi 150–20 and Varian Cary 50 Conc spectrophotometers in a 1.000 \pm 0.001 cm quartz cell.

X-ray structure determinations were performed on the complexes trans-[ReO₂(dmpe)₂]PF₆·2H₂O (1), trans-[ReO(OH) (dmpe)₂](CF₃SO₃)₂ (2), trans-[ReN(Cl)(dmpe)₂]CF₃SO₃ (3) and trans-[Re(Cl)₂(dmpe)₂]ReO₄ (4), and are described below.

The reflection data were collected on a 1K SMART Siemens diffractometer equipped with a CCD area detector, using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at ambient temperature (293 K). All the structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares on F² by using SHELX-97 (Sheldrick, 1997), while the graphic display was done with Diamond (Brandenburg et al., 1999).

The positions of the hydrogen atoms were calculated as riding on the adjacent carbon and nitrogen atoms with the bond distances as: methylene C-H as 0.97 Å and methyl C-H = 0.96 Å. The densities of the crystals were determined by flotation in iodomethane/benzene.

Special refinement techniques were used to obtain complete convergence in certain structures. These included the use of the ISOR command to restrain the anisotropic vibrations of certain atoms to isotropic level (*trans*-[ReN(Cl)(dmpe)₂]⁺). The DFIX command was employed to restrain certain bond lengths (*trans*-[ReO(OH)(dmpe)₂]²⁺ and *trans*-[ReN(Cl)(dmpe)₂]⁺) to obtain more reliable Re=O, Re-OH, Re=N and Re-Cl bond lengths. The BASF and TWIN commands were used in conjunction to solve twinned structures (*trans*-[ReN(Cl) (dmpe)₂]⁺). The EADP command was employed so that the same anisotropic displacement parameters would be used for different atoms $(trans-[Re(Cl)_2(dmpe)_2]^+)$. The EXTI command was used to refine additional extinction not accounted for by the atoms placed. More specific constraints are discussed separately at the relevant structures below.

The general crystal data and refinement parameters for the above mentioned complexes are reported in Table 1, while a complete list of atomic coordinates, equivalent isotropic parameters, bond distances and angles, anisotropic displacement parameters and hydrogen coordinates is available as supplementary data. CCDC 253892–253895 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/ data_request/cif.

RESULTS

Figure 1 shows the structural similarities between the dmpe and Tetrofosmin ligands. It is obvious that the dmpe ligand has two phosphine donor atoms, which are functionalized with two pendant methyl groups each.

trans-[ReO2(dmpe)2]PF6 · 2H2O

Yellow crystals of the title compound were isolated as mentioned above. The numbering scheme in the *trans*- $[\text{ReO}_2(\text{dmpe})_2]^+$ cation is presented in Figure 2, with the most important interatomic bond distances and angles given in Table 2.

trans-[ReO₂(dmpe)₂]PF₆· 2H₂O crystallizes with one formula unit in the asymmetric unit in the monoclinic space group $P2_1/c$, each asymmetric unit consisting of one Re(V) complex, one PF₆ anion, and two water molecules. The Re(V)-cation shows a distorted octahedral geometry with a six coordinate Re(V) atom, four phosphorus atoms in the equatorial plane and the two oxo ligands occupying the axial positions. The Re complex and the PF₆ anion both occupy general positions. All hydrogen atom positions were calculated, as mentioned previously. After full-matrix least-square anisotropic refinement of the crystal parameters, a final R-value of 4.61% [I > 2sigma(I)] was obtained. Comparisons with analogous structures are discussed below.

trans-[ReO(OH)(dmpe)₂](CF₃SO₃)₂

The numbering scheme in the *trans*- $[ReO(OH)(dmpe)_2]^{2+}$ cation is presented in Figure 3, with the most important interatomic bond distances and angles given in Table 3.

trans-[ReO(OH)(dmpe)₂](CF₃SO₃)₂ crystallizes with one formula unit per asymmetric unit in the monoclinic space group $P2_1/c$, each asymmetric unit consisting of one Re complex and two CF₃SO₃ anions. The Re(V) cation shows a distorted octahedral geometry with a six coordinate Re(V) atom and four phosphorus atoms in the equatorial plane and the oxo and hydroxo ligands occupying the axial positions. The complex is 50% statistically disordered around a center

TABLE 1 Crystal data and refinement parameters for the bis(phosphine) complexes investigated in this study

Crystal data	$[\text{ReO}_2(\text{dmpe})_2]^{+a}$	$[\text{ReO(OH)}(\text{dmpe})_2]^{2+b}$	$[\text{ReN}(\text{Cl})(\text{dmpe})_2]^{+c}$	$[\operatorname{Re}(\operatorname{Cl})_2(\operatorname{dmpe})_2]^{+d}$
Empirical formula Formula weight	C ₁₂ H ₃₆ F ₆ O ₄ P ₅ Re 699.46	C ₁₄ H ₃₃ F ₆ O ₈ P ₄ S ₂ Re 817.60	C ₁₃ H ₃₂ ClF ₃ NO ₃ P ₄ SRe 684.99	C ₁₂ H ₃₂ Cl ₂ O ₄ P ₄ Re ₂ 807.56
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	Pmc2	$P2_1/c$
a (Å)	11.5299(7)	8.0426(4)	11.5068(10)	19.375(3)
b (Å)	15.2397(9)	11.5472(6)	9.6656(8)	8.6840(12)
c (Å)	15.0230(9)	16.0303(8)	12.1772(11)	15.910(2)
α (°)	90	90	90	90
β (°)	97.7260(10)	101.9360(10)	90	111.270(3)
γ (°)	90	90	90	90
Volume (Å ³)	2615.8(3)	1456.54(13)	1354.3(2)	2494.6(6)
Z	4	2	2	4
$\rho_{\rm exp} ({\rm g \ cm^{-3}})$	1.72	1.86	1.72	2.18
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.776	1.864	1.680	2.150
Crystal size (mm)	$0.40 \times 0.10 \times 0.09$	$0.46 \times 0.40 \times 0.24$	$0.60 \times 0.30 \times 0.14$	$0.23 \times 0.15 \times 0.07$
Absorption coefficient (mm ⁻¹)	5.008	4.607	4.931	10.180
F(000)	1376	804	672	1520
θ range (°)	1.78 to 28.30	5.90 to 28.31	1.77 to 26.38	4.12 to 28.28
Index ranges	$-15 \le h \le 15$	$-10 \le h \le 10$	$-14 \le h \le 14$	$-25 \le h \le 17$
	$-15 \le k \le 20$	$-15 \le k \le 15$	$-12 \le k \le 12$	$-11 \le k \le 11$
	$-20 \le 1 \le 20$	$-21 \le 1 \le 20$	$-15 \le 1 \le 15$	$-21 \le 1 \le 20$
Refl collected/unique	18129/6475	15679/3577	7921/7921	17013/6165
R(int)	0.0575	0.0268	0.0430	0.0406
Completeness to theta $(^{\circ}; \%)$	28.30; 95.9	28.31; 94.1	26.38; 99.6	28.28; 93.4
$T_{max} - T_{min}$	0.6614 and 0.2393	0.6614 and 0.2393	0.5452 and 0.1559	0.5360 and 0.2030
Data/restraints/ parameters	6475/0/262	3577/4/173	7921/41/144	6165/0/242
Goodness-of-fit on F ²	1.006	1.139	1.053	0.972
Final R indices [I > 2sigma(I)]	$R_1 = 0.0461$	$R_1 = 0.0253$	$R_1 = 0.0426$	$R_1 = 0.0350$
	$wR_2 = 0.0885$	$wR_2 = 0.0593$	$wR_2 = 0.1134$	$wR_2 = 0.0852$
R indices (all data)	$R_1 = 0.1060$	$R_1 = 0.0311$	$R_1 = 0.0449$	$R_1 = 0.0702$
	$wR_2 = 0.1060$	$wR_2 = 0.0629$	$wR_2 = 0.1144$	$wR_2 = 0.0970$
Batch scale factor	_		0.544(11)	
Largest diff. peak and hole $(e.Å^{-3})$	0.803 and -0.923	0.496 and -1.260	4.674 and -1.982	1.188 and -1.075

^{*a*}[ReO₂(dmpe)₂]⁺ = [ReO₂(dmpe)₂]PF₆ · 2H₂O.

 ${}^{b}[\text{ReO(OH)(dmpe)}_{2}]^{2+} = [\text{ReO(OH)(dmpe)}_{2}](\text{CF}_{3}\text{SO}_{3})_{2}.$

 c [ReN(Cl)(dmpe)₂]⁺ = [ReN(Cl)(dmpe)₂]CF₃SO₃.

 d [Re(Cl)₂(dmpe)₂]⁺ = [Re(Cl)₂(dmpe)₂]ReO₄.

of symmetry, situated between the two Re atoms. The $CF_3SO_3^-$ anions occupy general positions.

In order to elucidate the disorder in the Re atom, the DFIX command was used to restrain the Re-P bonds to average lengths, which resulted in the Re=O and Re-OH bonds

being obtained. All hydrogen atom positions were calculated as mentioned previously, except for the OH⁻ group where the hydrogen atom position could be determined from a difference Fourier map. After full-matrix least-square anisotropic refinement of the crystal parameters, a final R-value of 2.53%

C22 C32 02 C42 C12 1.788(5) C2 C3 P2 P3 Re1 2.461(2) P1 P4 1.789(4) C1 C31 C21 01 C41

FIG. 2. Diamond drawing of the cation in [ReO2(dmpe)2]PF6 · 2H2O. The PF6 anion, water molecules, and hydrogen atoms are omitted for clarity.

[I > 2sigma(I)] was obtained. Comparisons with analogous structures are discussed later.

trans-[ReN(Cl)(dmpe)₂]CF₃SO₃

The development of new generation myocardial imaging agents features the Tc \equiv N core (Dilworth and Parrott, 1998). The excellent electron donating capabilities of the nitrido ligand further motivated this structure determination, since the nitrido ligand has an even larger *trans* influence than an oxo (Leipoldt et al., 1994) and an N³⁻ in the apical position is expected to induce a rather pronounced distortion from the

TABLE 2 Selected bond lengths (Å) and angles ($^{\circ}$) for [ReO₂(dmpe)₂]PF₆ · 2H₂O

Re(1)-O(2)	1.788(5)	P(1)-C(12)	1.803(9)
Re(1)-O(1)	1.789(4)	P(1)-C(11)	1.819(7)
Re(1)-P(2)	2.458(2)	P(1)-C(1)	1.834(10)
Re(1)-P(3)	2.4587(19)	P(2)-C(21)	1.782(10)
Re(1)-P(1)	2.4605(19)	P(2)-C(22)	1.813(8)
Re(1)-P(4)	2.468(2)	P(2)-C(2)	1.820(9)
O(2)-Re(1)-O(1)	178.8(2)	C(21)-P(2)-C(22)	105.6(5)
P(2)-Re(1)-P(1)	81.11(7)	C(21)-P(2)-C(2)	104.7(6)
P(3)-Re(1)-P(4)	81.93(7)	C(22)-P(2)-C(2)	103.6(4)
C(12)-P(1)-C(11)	105.5(4)	C(21)-P(2)-Re(1)	115.7(4)
C(12)-P(1)-C(1)	104.5(5)	C(22)-P(2)-Re(1)	118.3(3)
C(11)-P(1)-C(1)	104.1(4)	C(2)-P(2)-Re(1)	107.5(3)
C(12)-P(1)-Re(1)	115.5(3)	C(2)-C(1)-P(1)	110.2(6)
C(11)-P(1)-Re(1)	119.4(3)	C(1)-C(2)-P(2)	110.5(6)
C(1)-P(1)-Re(1)	106.2(3)	P(3)-Re(1)-P(1)	178.62(7)
P(2)-Re(1)-P(4)	179.43(7)		

equatorial plane. Thus, consequent significant variations in bond lengths are also expected.

The numbering scheme in the *trans*- $[ReN(Cl)(dmpe)_2]^+$ cation is presented in Figure 4, with the most important interatomic bond distances and angles given in Table 4.

trans-[ReN(Cl)(dmpe)₂]CF₃SO₃ crystallizes with one formula unit per asymmetric unit in the orthorhombic space group $Pmc2_1$, each asymmetric unit consisting of one Re(V) complex and one CF₃SO₃⁻ anion. The Re(V) cation shows a distorted octahedral geometry with a six coordinate Re(V) atom and four phosphorus atoms in the equatorial plane and the nitrido and chloro ligands occupying the axial positions. The Re atom lies on a general position with a twofold screw axis running along the N \equiv Re-Cl core as well as through the rather severely disordered CF₃SO₃⁻ anion.

All hydrogen atom positions were calculated as mentioned previously. After full-matrix least-square anisotropic refinement of the crystal parameters, a final R-value of 4.26%[I > 2sigma(I)] was obtained. The residual electron density representing 4 electrons (at 0.0000; 0.2271; 0.4397) could not be satisfactory accounted for but is still low enough to be due to effects induced by the quite heavy Re center.

The BASF and TWIN commands were used to solve the twinned structure and a final batch scale factor of 0.544(11) was obtained. The DFIX and ISOR commands were used to restrain the bond lengths and anisotropic vibrations in the anion and resulted in the successful elucidation of the CF₃SO₃⁻ anion structure.

The analogous Tc complex crystallizes in the monoclinic space group $P2_1/n$ and the unit cell dimensions are: a = 19.862(4) Å, b = 12.983(3) Å, c = 15.919(3) Å, $\beta = 107.11(2)^{\circ}$ and Z = 4 and therefore the Re and Tc structures are not isomorphous (Table 1). Comparisons with analogous structures are discussed later.



FIG. 3. Diamond drawing of the cation in $[ReO(OH)(dmpe)_2](CF_3SO_3)_2$ illustrating the 50% statistical disorder (fragmented bonds). The $CF_3SO_3^-$ anions and hydrogen atoms are omitted for clarity. Primed atoms denote those generated by the symmetry.

trans-[Re(Cl)₂(dmpe)₂]ReO₄

Both the Tc and Re analogs of the title compound have been determined previously (Vanderheyden et al., 1985; Vanderheyden et al., 1984). This structure, however, represents another polymorph, which was obtained as a decomposition product in an effort to synthesize a cation containing the $[N \equiv Re-OH]^+$ core. The ReO₄ counter anion is most probably obtained *via* the oxidation of the parent *trans*-[ReN(Cl)(dmpe)₂]⁺ complex. The reducing capabilities of phosphines are well known and it is assumed that the nitrido ligand is removed in a Wittig type reaction (Wittig, 1980) by the dmpe (Lewis acid), liberated in the Re(V) oxidation to ReO₄. Another possibility could be the substitution of the

coordinated Cl by an OH and the resulting *trans*- $[ReN(OH)(dmpe)_2]^+$ and consequent disproportionation to Re^{III} and Re^{VII}.

The numbering scheme in the *trans*- $[Re(Cl)_2(dmpe)_2]^+$ cation is presented in Figure 5, with the most important interatomic bond distances and angles given in Table 5.

trans-[Re(Cl)₂(dmpe)₂]ReO₄ crystallizes with two independent formula units per asymmetric unit in the monoclinic space group $P2_1/c$, each asymmetric unit consisting of two Re(III) cations and two ReO₄⁻ anions, with both the complexes on inversion centers and the 50% statistically disordered ReO₄⁻ in a general position. The complex shows a distorted octahedral geometry with a six coordinate Re(III) atom and four

TABLE 3
Selected bond lengths (Å) and angles (°) for [ReO(OH)(dmpe) ₂] (CF ₃ SO ₃)

Re(1)-O(1)#1	1.652(3)	P(1)-C(11)	1.809(4)
Re(1)-O(1)	1.935(3)	P(1)-C(13)	1.827(3)
Re(1)-P(2)	2.467(2)	P(2)-C(21)	1.801(4)
Re(1)-P(1)	2.483(2)	P(2)-C(22)	1.802(4)
P(1)-C(12)	1.799(4)	P(2)-C(23)	1.833(3)
O(1)#1-Re(1)-O(1)	179.22(13)	O(1)#1-Re(1)-P(1)	93.93(12)
O(1)#1-Re(1)-P(2)	94.25(13)	O(1)-Re(1)-P(1)	86.13(10)
O(1)-Re(1)-P(2)	86.50(12)	P(2)-Re(1)-P(1)	99.03(7)
O(1)#1-Re(1)-P(1)#1	92.60(12)	P(1)#1-Re(1)-P(1)	173.44(9)
O(1)-Re(1)-P(1)#1	87.34(11)	O(1)#1-Re(1)-P(2)#1	92.30(13)
P(2)-Re(1)-P(1)#1	81.07(6)	O(1)-Re(1)-P(2)#1	86.94(11)
P(1)#1-Re(1)-P(2)#1	98.51(7)	P(2)-Re(1)-P(2)#1	173.45(10)
P(1)-Re(1)-P(2)#1	80.64(6)		

Symmetry transformations used to generate equivalent atoms: #1 (-x, -y+1, -z+1).



FIG. 4. Diamond drawing of the cation in $[ReN(Cl)(dmpe)_2]CF_3SO_3$. The $CF_3SO_3^-$ anion and hydrogen atoms are omitted for clarity. Primed atoms denote those generated by the symmetry.

phosphorus atoms in the equatorial plane and the two chloride ligands occupying the axial positions.

The ReO₄⁻ anion is statistically disordered around the center of symmetry, situated between the two Re atoms. The EADP command was employed assuring similar anisotropic displacement for two of the oxo ligands coordinated to the Re center in ReO₄⁻. All hydrogen atom positions were calculated as mentioned previously. After full-matrix least-square anisotropic refinement, a final R-value of 3.50% [I > 2sigma(I)] was obtained.

Both the previously characterised Tc (Vanderheyden et al., 1984) and Re (Vanderheyden et al., 1985) structures crystallized in the monoclinic space group $P2_1/c$ and the unit cell dimensions are: a = 8.076(2) Å, b = 24.40(1) Å,

TABLE 4 Selected bond lengths (Å) and angles (°) for [ReN(Cl)(dmpe)₂]CF₃SO₃

Re(1)-N(1)	1.817(7)	P(1)-C(11)	1.807(6)
Re(1)-P(1)	2.4446(15)	P(1)-C(1)	1.833(7)
Re(1)-P(2)	2.4435(16)	P(2)-C(22)	1.790(6)
Re(1)-Cl(1)	2.5741(19)	P(2)-C(21)	1.793(8)
P(1)-C(12)	1.794(7)	P(2)-C(2)	1.827(7)
P(2)-Re(1)-P(1)	81.27(5)	C(11)-P(1)-C(1)	104.4(4)
N(1)-Re(1)-Cl(1)	178.1(2)	C(22)-P(2)-C(21)	103.1(4)
P(1)-Re(1)-Cl(1)	82.92(5)	C(22)-P(2)-C(2)	105.6(4)
C(12)-P(1)-C(11)	103.0(4)	C(21)-P(2)-C(2)	103.9(4)
C(12)-P(1)-C(1)	105.3(4)	P(2)#1-Re(1)-P(1)	169.90(6)

Symmetry transformations used to generate equivalent atoms: #1 (-x, y, z).

c = 13.435(4) Å, β = 96.61(2) ° and Z = 2 for the Tc structure and a = 10.661(5) Å, b = 10.214(6) Å, c = 12.835(6) Å, β = 115.43(4) ° and Z = 2 for the Re analog. It is evident from Table 1 that these structures are not isomorphous to the structure reported in the current study. Comparisons with analogous structures are discussed later.

DISCUSSION

trans-[ReO₂(dmpe)₂]PF₆ \cdot 2H₂O

The average Re=O bond of 1.789(5) Å is slightly longer than the average reported for Re dioxo complexes (1.761(15)) Å) (Mayer, 1988) with different equatorial ligands. The Re-P bond length has an average of 2.461(2) Å and compares favorably with the Re-P distances reported previously (see below). The Re-P bonds are much longer than the amine bond distances, as is to be expected with the larger atom radius of the phosphorus atoms.

An extensive hydrogen bonding network is observed between the F atoms of the PF_6^- anions and the different hydrogen atoms present, with the interactions ranging from 2.37-2.86 Å.

Similar to the dioxo complexes reported below, the title compound has hydrogen interactions between adjacent complexes with molecular water molecules forming the corners of the zigzag line along the $[O=Re=O]^+$ cores. The bond lengths for these interactions are 2.79 and 2.87 Å, respectively.

The carbon backbones exhibit the $\lambda\delta$ (eclipsed) conformation (see Figure 2). Apart from thermodynamic considerations, it has to be considered that this structure is very symmetrical and that the crystal packing might be influenced by such phenomena, as pointed out by Bernal et al. (1993).



FIG. 5. Diamond drawing of one of the cations in $[Re(Cl)_2(dmpe)_2]ReO_4$. The other cation, ReO_4^- anion and hydrogen atoms are omitted for clarity. Primed atoms denote those generated by the symmetry.

trans-[ReO(OH)(dmpe)₂](CF₃SO₃)₂

As mentioned previously, the analogous Tc(V) structure has been determined (Vanderheyden et al., 1984) and the two structures are isomorphous. The tendency of shortening in the Re=O bond, as generally reported, is observed when changing from the dioxo ($[O=Re=O]^+$) to oxo hydroxo $([O=Re-OH]^{2+})$ core. Due to the change in orbital overlap, the oxo bonds shortens (1.652(3) Å) and the hydroxo bond lengthens (1.935(3) Å). The Tc analog is also disordered but was resolved using EXAFS (extended X-ray absorption fine structure), and the values of 1.66 Å (Tc=O) and 1.96 Å (Tc-OH) (Vanderheyden et al., 1984) are in good agreement

Selected bond lengths (A) and angles (⁶) for $[Re(Cl)_2(dmpe)_2]ReO_4$							
Re(1)-Cl(1)	2.3369(14)	Re(2)-Cl(2)	2.3313(15)				
Re(1)-P(11)	2.4342(17)	Re(2)-P(22)	2.4262(16)				
Re(1)-P(12)	2.4311(15)	Re(2)-P(21)	2.4342(18)				
P(11)-C(111)	1.782(7)	P(21)-C(211)	1.799(9)				
P(11)-C(112)	1.809(7)	P(21)-C(212)	1.814(7)				
P(11)-C(11)	1.834(9)	P(21)-C(21)	1.822(8)				
P(12)-C(122)	1.803(7)	P(22)-C(222)	1.768(9)				
P(12)-C(12)#1	1.819(9)	P(22)-C(221)	1.821(7)				
P(12)-C(121)	1.821(7)	P(22)-C(22)	1.852(8)				
Cl(1)-Re(1)-Cl(1)#1	180.0	Cl(2)-Re(2)-Cl(2)#2	180.0				
P(12)-Re(1)-P(11)#1	81.42(6)	P(22)-Re(2)-P(21)#2	81.95(6)				
P(12)#1-Re(1)-P(11)	81.42(6)	P(22)#2-Re(2)-P(21)	81.95(6)				
C(111)-P(11)-C(112)	104.1(4)	C(211)-P(21)-C(212)	102.8(5)				
C(111)-P(11)-C(11)	105.9(5)	C(211)-P(21)-C(21)	102.8(5)				
C(112)-P(11)-C(11)	102.2(4)	C(212)-P(21)-C(21)	105.4(4)				
C(111)-P(11)-Re(1)	116.1(3)	C(211)-P(21)-Re(2)	116.4(3)				
C(112)-P(11)-Re(1)	119.8(3)	C(212)-P(21)-Re(2)	119.5(3)				
C(11)-P(11)-Re(1)	107.0(3)	C(21)-P(21)-Re(2)	108.3(3)				

TABLE 5 Selected bond lengths (Å) and angles ($^{\circ}$) for [Re(Cl)₂(dmpe)₂]ReO₄

Symmetry transformations used to generate equivalent atoms: #1 (-x + 1, -y, -z + 1) #2 (-x, -y + 1, -z + 1).

with those obtained for the rhenium analog reported here. The shortened Re=O bond is confirmed by the increase in the $v_{(Re=O)}$ IR stretching frequency from 777 cm⁻¹ for the dioxo complex to 954 cm⁻¹ for the title compound.

A rather surprising observation for this structure is that the average Re-P bond lengthens (2.480(2) Å) when compared to the dioxo analog (2.461(2) Å) (Tables 2 and 3)—considering that the complex is changed from a classic 18 electron complex to a 16 electron one. This might be attributed to the decrease in π back-bonding between the Re center and the phosphine with the lowering of the electron density on the Re center when a dioxo core is changed to a less electron donating oxo hydroxo moiety. The bite angle (80.86(6)°) shows a slight decrease when compared to the dioxo complex (81.52(7)°), most probably due to the increase in the Re-P bond length.

The carbon backbone is again orientated in the $\lambda\delta$ (eclipsed) conformation, as was observed in the above mentioned dioxo complex. Of particular interest is that the $\lambda\delta$ (eclipsed) conformation was not observed in the analogous *trans*-[ReO(OH)(4Meen)₂]²⁺ complex (4Meen = N,N,N',N'-Tetramethylethylenediamine) (Engelbrecht, 2001). Thermodynamic factors, and not symmetry considerations, are thought to dominate the crystallization pathway.

The packing interactions are dominated by one hydrogen bond (2.51 Å) observed between a hydrogen atom on one of the pendant methyl groups, and an F atom on one of the CF₃SO₃⁻ anions. As was the case in the *trans*-[ReO(OH)(DiEten)₂](ClO₄)₂ (DiEten = N,N-Diethylethylenediamine) (Engelbrecht et al.) complex, the CF₃SO₃⁻ anion has a hydrogen interaction (2.2 Å) with the OH⁻ group.

The Re atom is similarly displaced by 0.142(2) Å out of the equatorial plane defined by the four phosphorus atoms towards the apical oxo as observed in other oxo hydroxo complexes (see further discussion below).

trans-[ReN(Cl)(dmpe)₂]CF₃SO₃

The Re \equiv N bond length of 1.817(7) Å is in line with the values reported for other phosphine complexes with a Re \equiv N core (see below) and is also slightly shorter than the distance reported for Tc \equiv N (1.853(6) Å).

The Re-Cl bond distance (2.574(2) Å) also compares well with the analogous distances reported for related complexes with the $[N \equiv \text{Re-Cl}]^+$ core. As previously mentioned, the N^{3-} has a larger *trans* influence and the relatively long Re-Cl bond can be attributed to the influence that the chloride experiences from the apical N^{3-} . Just as was observed in the $\text{Re} \equiv N$ bond length, the Re-Cl bond distance is shorter than the analog Tc-Cl length (2.608(3 Å). The differences in both the nitrido and chloro bond lengths are attributed to the disorder observed in the Tc complex.

The Re-P bond of 2.444(2) Å is shorter than the 2.461(2) and 2.480(2) Å for the dioxo and oxo hydroxo complexes as reported above, and could be due to the better

 π back-bonding between the bidentate phosphine ligand and the more electron rich Re center (due to the strong π -donating N³⁻ group in the apical position). The analogous Tc-P bond distance of 2.448(2) Å compares very favorably with that of the title compound. The bite angle of 81.27(5)° compares well with the 81.52(7)° and 80.86(6)° reported for the dioxo and oxo hydroxo complexes (see above), respectively.

The carbon backbone again has the same $\lambda\delta$ (eclipsed) conformation as was observed in the dioxo and oxo hydroxo complexes (see above). Even with such severe distortions as observed in this structure, the $\lambda\delta$ conformation still persists and it is concluded that the crystallization pathway does not consider internal symmetry in the dmpe structures and that thermodynamic considerations predominate (Bernal et al., 1993).

The Re is displaced by 0.214(1) Å out of the plane defined by the four equatorial phosphorous atoms towards the nitrido ligand. This displacement is much more than that of the oxo hydroxo complex (0.142(2) Å) and is consistent with the general trend observed, as illustrated in Table 6. It is evident that the stronger the apical ligand binds (N³⁻ vs. O²⁻) to the metal center, the larger the distortion is out of the equatorial plane; this might be an important criteria for the uptake of certain radiopharmaceuticals as is observed, for example, in the crystals structure of HMPAO where only the *d*,*l* isomer is retained in the brain (Jurisson et al., 1986).

The hydrogen bonding observed involves the coordinated chloride and the hydrogens on the methyl groups within the same molecule as well as those on a neighboring complex, as illustrated in Figure 7 (see supplementary data). The intramolecular interactions are 2.74 Å, while the intermolecular interactions are 2.82 Å. The hydrogen bonding with the F atoms on the CF₃SO₃⁻ anions range from 2.83–2.87 Å.

trans-[Re(Cl)2(dmpe)2]ReO4

The two cations in the asymmetric unit are virtually identical when comparing the Re-Cl and R-P bond lengths, the Re-Cl bond distances being 2.337(1) and 2.331(2) Å for the Re1 and Re2 complexes, respectively. The average Re-P bond lengths in both complexes are also very similar (2.433(2) and 2.430(2) Å for the Re1 and Re2, respectively).

The average Re-Cl bond of 2.334(2) Å is in good agreement with the Re^{III}-Cl and Tc^{III}-Cl bond lengths of *ca.* 2.32 Å reported below. The Re^{III}-P bond of 2.432(2) Å is even shorter than for the previous Re(V) structures (see above) and seem to serve as conformation that the better π backbonding with the more electron rich Re^{III} center is responsible for the shorter Re-P bond lengths. This same tendency was observed for the analogous Tc complexes (Vanderheyden et al., 1984). The Re-P bond distance of the title compound (2.432(2) Å) is in good agreement with that of the previously reported Re structure (2.438(2) Å) (Table 6).

Two rather weak hydrogen interactions are observed in this structure. The one is an intramolecular interaction of 2.86 Å

			annie/pric	sprine com	plexes				
Complex	M≡O (Å)	M-OH (Å)	M-N/P (Å)	Bite angle (Å)	δM^a (Å)	pKa2 ^b	$\nu(cm^{-1})$ M=O	Conf ^c	Ref.
Dioxo complexes									
$[\operatorname{ReO}_2(4\operatorname{Meen})_2]^+$	1.756(7)	_	2.229(9)	80.9(4)	—	_	813	$\lambda\delta$	(Engelbrecht, 2001)
$[\text{ReO}_2(\text{dmpe})_2]^+$	1.789(5)		2.461(2)	81.52(7)	_		777	$\lambda\delta$	(Engelbrecht, 2001)
$[TcO_2(dmpe)_2]^+$	d	_			_	_	775		(Vanderheyden et al., 1984)
Oxo hydroxo complexes							1		
$[\text{ReO(OH)}(4\text{Meen})_2]^{2+}$	1.710(6)	1.818(5)	2.221(10)	82.4(6) ^e	0.01 ^e	0.33	840	δδ	(Engelbrecht, 2001)
$[\text{ReO(OH)}(\text{dmpe})_2]^{2+}$	1.652(3)	1.935(3)	2.475(2)	80.86(6)	0.142	<1	954	λδ	(Engelbrecht, 2001)
$[TcO(OH)(dmpe)_2]^{2+}$	1.66 ^f	1.96 ^f	2.477(1)	81.2(1)		0.80	965	$\lambda\delta$	(Vanderheyden et al., 1984)

 TABLE 6

 Average bond lengths, bite angles, distortion-from-plane-distances and (M=O) IR stretching frequencies for the analogous amine/phosphine complexes

^aDisplacement of metal out of the equatorial plane.

 ${}^{b}[O = Re - OH]^{2+} \rightleftharpoons [O = Re = O]^{+}.$

^cConformation of the ethylene carbon backbones.

^dStructure not determined.

^eResults of only one molecule reported.

¹Disordered (determined with EXAFS).

between the chloride and a hydrogen atom on one of the pendant methyl groups. There is also another intermolecular interaction of 2.86 Å between the coordinated chloride ligand of one molecule and a hydrogen atom on the methyl group of an adjacent molecule. The ReO_4^- anion is also involved in some hydrogen interactions with the complexes that range from 2.38 to 2.75 Å.

The bite angle of $81.69(6)^{\circ}$ is in good agreement with the angles of the previously reported Tc $(81.4(1)^{\circ})$ and Re $(81.5(1)^{\circ})$ structures (see Table 6) and will be discussed in more detail below.

The difference in the calculated and experimental density imply that there is electron density unaccounted for, but this is assumed to be due to some molecular water molecules not being located because of the general thermal vibrations and the large number of electrons present in the structure.

Comparative bond lengths, bite angles, displacement-fromplane-distances and $\nu_{(M=O, M=N, M-Cl)}$ IR stretching frequencies for different analogous amine/phosphine complexes are compared in Table 6, while in Table 7, a more complete summary of structures containing [O=Re=O]⁺, [O=Re-OH]²⁺, [N=Re-Cl]⁺ and [Cl-Re-Cl]⁺ cores is given.

The Re=O bonds for the dioxo and oxo hydroxo compounds are in good agreement with the other values reported and the Re-OH bonds are within experimental error. The Re=N and Re-Cl bonds are also comparable with the other structures reported and the large *trans* influence of the N³⁻ ligand being evident in the relatively long M-Cl bonds. The nitrido ligand also induces more distortion of the metal out of the equatorial plane (δ M, Table 6) than the analogous oxo complexes. This distortion is also manifested in the *trans* P-Re-P bond angles, which decrease from ca. 179 to 173 to 169° for the [O=Re=O]⁺, [O=Re-OH]²⁺, [N=Re-Cl]⁺, respectively (Tables 2, 3 and 4).

It seems as if the Re-P bonds shortens with the increase of electron density on the metal center, *i.e.*, when changing the cores from $[O=Re-OH]^{2+}$ to $[O=Re=O]^+$ to $[Re=N]^{3+}$ as well as the reduction in the formal oxidation state. This shortening in Re-P bond lengths could be due to better π back-bonding between the metal and the equatorial phosphine ligands as mentioned above. The increase in the axial ligand bond strength (*i.e.*, more electron density) is also reflected by the increase in the $\nu_{(M=O, M=N)}$ IR stretching frequency when moving from the dioxo ($[O=Re=O]^+$) to the oxo hydroxo ($[O=Re-OH]^{2+}$) to the nitrido ($[Re=N]^{3+}$) core (see Table 6).

Preliminary ³¹P NMR studies showed that the pK_{a2} value of the *trans*-[ReO₂(dmpe)₂]⁺ complex (<1) is comparable to that of the *trans*-[ReO₂(4Meen)₂]⁺ (0.33) and [TcO₂(dmpe)₂]⁺ (0.80) complexes. All three of the complexes reported in Table 7 have low pK_a values. It is surprising that the Tc analog also has such a low pK_a value after the research done

TABLE 7 Average bond lengths, bite angles, displacement-from-plane-distances and $\nu_{(M=O, M=N, M-CI)}$ IR stretching frequencies for rhenium and technetium phosphine complexes

Complex	M≡O/N (Å)	M-T ^{a} (Å)	M-P/As (Å)	Bite angle (Å)	$\delta M^{h}(A)$	$\frac{\nu_{(M-X)}}{(cm^{-1})}^c$	Ref.
M(V) complexes							(Kremer et al., 1999)
[ReO ₂ (dppp) ₂] ⁺	1.761(6)	_	2,536(2)	85 51(7)		785	(Kremer et al. 1999)
$[\text{ReO}_2(\text{dppp})_2]^+$	1.765(5)		2.544(2)	85.34(6)		785	(Kremer et al. 1999)
$[\text{ReO}_2(\text{dppp})_2]^+$	1.770(6)		2 549(3)	85 27(7)			(Suescun et al. 1999)
$[\text{ReO}_2(\text{dppp})_2]^+$	1.775(6)		2 531(3)	85 48(9)			(Suescun et al. 1999)
$[\text{ReO}_2(\text{dppp})_2]^+$	1 778(8)		2 531(3)	85 48(9)			(Suescun et al. 1000)
$[\text{ReO}_2(\text{dppp})_2]^+$	1.772(4)		2.485(3)	79.4(1)		786	(Kramar at al., 1999)
$[ReO_2(HMPE)_2]^+$	1.772(4)		2.403(3)	80.5(1)		276	(Richer et al., 1999) (Paddy at al., 1006)
$[ReO_2(HMPB)_2]^+$	1.779(2)		2.459(1)	80.2(1)		870	(Reddy et al., 1990) (Reddy et al., 1996)
$[\text{ReO}_2(\text{Invit} D)_2]$	1.779(2) 1.780(4)	_	2.459(1)	80.2(1)		706	(Keduy et al., 1996) (Keamor et al., 1996)
$[\text{ReO}_2(\text{dppe})_2]$	1.781(6)		2.300(2)	80.30(8)	2.2	786	(Kremer et al., 1999)
$[\text{ReO}_2(\text{uppe})_2]$	1.781(0)		2.491(3)	79.7(1)		780	(Weyer et al., 1992)
[ReO ₂ (uppee) ₂]	1.700(0)	Conception of the Institute of the Insti	2.475(2)	81.2(1)			(Konii et al., 1994)
$[\text{ReO}_2(\text{dmpe})_2]^+$	1.789(5)		2.461(2)	81.52(7)		777	J
$[\operatorname{ReO}_2(\operatorname{PMe}_3)_4]^+$	1.79(2)		2.485(8)	_		770	(Edwards et al., 1984)
$[\text{ReO}_2(\text{dmppe})_2]^+$	1.790(4)		2.509(2)	81.00(6)		781	(Yam et al., 2000)
$[TcO_2(Tetrofosmin)_2]^+$	1.738(17)		2.473(7)	81.4(2)			(Kelly et al., 1993)
$[TcO_2(dmpe)_2]^+$	d					775	(Vanderheyden et al., 1984)
ReO(OH)(dmpe) ₂] ²⁺	1.652(3)	1.935(3)	2.475(2)	80.86(6)	0.142	954	f
$TcO(OH)(dmpe)_2]^{2+}$	1.66	1.96 ^e	2.477(1)	81.2(1)	—	965	(Vanderheyden et al., 1984)
$[ReN(Cl)(dppa)_2]^+$	1.711(8)	2.496(3)	2.450(3)	66.9(1)	0.195	_	(Rossi et al., 1993)
ReN(Cl)(dmppe) ₂] ⁺	1.762(7)	2,485(2)	2.446(2)	81,76(3)	0.09^{g}	1.045	(Yam et al. 2000)
ReN(Cl)(dmpe) ₂] ⁺	1.817(7)	2.574(2)	2.444(2)	81.27(5)	0.214	1.056	f
ReN(Cl)(dpae)-1+	1.839(8)	2.451(3)	2 543(1)	80.95(4)	0.1828	1.046	(Yam et al. 1992)
$TcN(Cl)(dmpe)_2l^+$	$1.853(6)^d$	2.608(3)	2.448(2)	81.5(1)	0.1858	1,010	(Archer et al. 1992)
$TcN(Cl)(dmpe)_2l^+$	1.613(9)	2 643(3)	2.454(3)	81.15(10)	0.269		(Rochon et al. 1996)
$[TcN(Cl)(dppe)_2]^+$	$1.794(7)^{e}$	$2.412(2)^{e}$	2.482(1)	80.34(5)			(Rochon et al., 1996)
M(III) complexes							
$Re(Cl)_2(dpcp)_2]^+$		2.317(6)	2.508(7)	82.6(2)		1000	(Cotton et al., 1991)
$[Re(Cl)_2(dmpe)_2]^+$	_	2.337(1)	2.438(2)	81.5(1)	-	315	(Vanderheyden et al., 1985)
$[Re(Cl)_2(dmpe)_2]^+$	_	2.334(2)	2.432(2)	81.69(6)	_	-	ſ
$Re(Cl)_2(dppe)_2]^+$		2.323(1)	2,496(6)	80.43(1)		342 + 375	(Salih et al. 1993)
$Re(Cl)_2(dppe)_2]^+$		2.314(6)	2,483(11)	80.9(2)		320	(Salih et al. 1993)
$Tc(Cl)_2(dppe)_2]^+$		2,319(1)	2 501(1)	80.57(3)			(Libson et al. 1988)
$[Tc(Cl)_2(dtpe)_2]^+$		2.310(3)	2.489(4)	81.00(7)		-	(Cotton and Daniels,
(Te(Cl) (dere) 1+		2 225/21	2 450-22	01.5(2)			1988)
$rc(Cl)_2(depe)_2$]	_	2.335(3)	2.450(3)	81.5(2)			(Cotton and Daniels, 1988)
$[Tc(Cl)_2(PMe_2Ph)_4]^+$		2.328(1)	2.512(1)			345	(Rochon et al., 2000)
$[Tc(Cl)_2(PMe_3)_4]^+$		2.344(2)	2.469(2)			330	(Rochon et al., 2000)
$[Tc(Cl)_2(PMe_3)_4]^+$		2.344(3)	2.477(3)			330	(Rochon et al., 2000)
$[Tc(Cl)_2(diars)_2]^+$		2.329(1)	2.509(1)	82.4(1)			(Elder et al., 1980)

(continued)

Table 7. Commed								
Complex	M=O/N (Å)	M-T ^{a} (Å)	M-P/As (Å)	Bite angle (Å)	$\delta \mathbf{M}^{b}(\mathbf{\mathring{A}})$	$\frac{\nu_{(M-X)}}{(cm^{-1})}^c$	Ref.	
$[Tc(Cl)_2(diars)_2]^+$	_	2.318(8)	2.515(2)	83.50(4)		_	(Glavan et al., 1980)	
$[Tc(Cl)_2(dmpe)_2]^+$	_	2.323(2)	2.436(2)	81.4(1)	—	345	(Vanderheyden et al., 1984)	

Table 7. Continued

"Ligand trans to oxo/nitrido in apical position.

^bDisplacement of metal out of the equatorial plane.

 ${}^{c}\nu_{(M-X)} = \nu_{(M=O, M=N, M-CI)}$

^dStructure not determined.

^eDisorder (determined with EXAFS).

^fThis work.

^{*g*}Calculated using simple trigonometrical functions. dppp = 1,3-Bis(diphenylphosphino)propane. dmppe = 1,2-Bis(di-4-methoxyphenylphosphino)ethane. dppa = Bis(diphenylphosphino)amine. HMPE = 1,2-Bis(bis(hydroxymethyl)phosphino)ethane. dpae = 1,2-Bis(diphenylphosphino)ethane. HMPB = 1,2-Bis(bis(hydroxymethyl)phosphino)benzene. diars = *o*-phenylenebis(dimethylarsine). dppe = 1,2-Bis (diphenylphosphino)ethane. dpcp = (\pm)-*trans*-1,2-bis(diphenyl-phosphino)cyclopentane. dmppe = 1,2-Bis(di-4-methoxyphenylphosphino) ethane. dpcp = (\pm)-*trans*-1,2-bis(diphenyl-phosphino)cyclopentane. dmppe = 1,2-Bis(di-4-methoxyphenylphosphino) ethane. dpcp = Ph₂PCHCHPPh₂.

by Roodt et al. (Roodt et al., 1999) who found technetium to have a higher pK_a than the analogous Re in the $[MO_2 (CN)_4]^{3-}$ complexes. What is of great interest are the pK_a values of the *trans*- $[ReO(OH)(4Meen)_2]^{2+}$ and $[TcO(OH) (dmpe)_2]^{2+}$ complexes, which are very similar. This observation is in direct agreement with the decrease in bond distance found, as mentioned in the previous paragraph.

The $\nu_{(Re=O)}$ IR stretching frequencies in the dioxo dmpe complex (777 cm⁻¹) is lower than that of the amine complex (813 cm⁻¹)—indicating that the phosphine is probably a better electron donor to the Re. The Tc and Re dioxo complexes have near identical $\nu_{(M=O)}$ IR stretching frequencies. The $\nu_{(M=O)}$ stretching frequency increases for the phosphine complexes upon moving from the dioxo ([O=Re=O]⁺) to the oxo hydroxo ([O=Re-OH]²⁺) core, but the same amount of increase is not observed for the amine complex. This might be due to the fact that for the amine complex only small changes in the Re=O and Re-OH bond lengths were observed.

The Re=O bond length in the dioxo dmpe complex is longer than in the amine analog, as would be expected from the IR stretching frequencies—illustrating the better donor capabilities of phosphine. Dramatic shortening in the Re=O bond for the phosphine complex with an oxo hydroxo core is due to less electron density being obtained from the phosphine (Re-P bond lengthens in the *trans*-[ReO(OH)(dmpe)₂]²⁺ complex). This is again manifested in the relative pK_a value change observed.

The bite angles are well within range of each other, with only small differences that could be attributed to the differences in bond lengths and atom radii. Similarly, the displacement of the rhenium out of the equatorial plane in the $[O=Re-OH]^{2+}$ complexes is more pronounced for the

phosphine complex because of the rather significant shortening in the Re=O bond length.

As mentioned previously, π back-bonding is possible with the dmpe phosphine ligand but not for the analogous 4Meen amine ligand. The Re-P bonds are longer than the Re-N bonds, as is to be expected with the larger covalent radius of the phosphorus atom compared to that of nitrogen (1.06 Å vs. 0.75 Å) (Rodgers, 1994). When moving from the dioxo $([O=Re=O]^+)$ to the oxo hydroxo $([O=Re-OH]^{2+})$ core there is a shortening in the Re-N bonds while the Re-P bonds lengthen. For the N-donor ligands, this is in agreement with changing from classic 18 electron to 16 electron complexes. This lengthening in the case of the P-donor ligands is attributed to the π back-bonding with the phosphine that decreases when a more electron deficient $[O=Re-OH]^{2+}$ core is employed.

Both the Re-As bond distances reported (*trans*- $[\text{ReN}(\text{Cl})(\text{dpae})_2]^+$ and $[\text{Tc}(\text{Cl})_2(\text{diars})_2]^+$) are significantly longer than any of the corresponding phosphine distances, as is expected from the larger covalent radius of As *vs.* P (1.20 Å *vs.* 1.06 Å) (Rodgers, 1994).

The bite angles for all the five-membered phosphine chelating rings are in good agreement with each other and compare well with previously reported structures (see Table 7). The bite angles of the six-membered ring systems (85.43° of *trans*-[ReO₂(dppp)₂]⁺ in Table 7) are significantly larger by *ca.* 4°, as would be expected with the reduced steric strain in the carbon backbones. Surprisingly, the angle of 85.43° for sixmembered phosphine ring systems is significantly smaller than the *ca.* 90° reported for six-membered amine ring systems. This might be due to the functional groups incorporated on the P-donor.

The two *trans* chloro ligands quoted for the Re^{III}/Tc^{III} complexes have shorter bond distances than those in the N≡Re-Cl

complexes, and this is attributed to the large *trans* influence exerted by the nitrido ligand, as previously mentioned.

An interesting observation is that for all four structures reported in this study, the orientation of the two carbon backbones in the dmpe ligands relative to each other has the $\lambda\delta$ (eclipsed) conformation. This strongly suggests an energy minimum for these conformers, as was found in a previous study (Engelbrecht et al.). The $\lambda\delta$ (eclipsed) conformation is only observed for the *trans*-[ReO(OH)(4Meen)₂]²⁺ complex, where the relatively small chloride anion in addition to the PF₆ is present. Thus, the orientations of the carbon backbones might be sensitive to type or size (cavities available) of anions present. This effect, which has also been observed for the dioxo ethylenediamine and oxo hydroxo ethylenediamine type complexes, will be pursued further in the future, also with respect to theoretical work.

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