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Novel six-co-ordinate oxorhenium complexes with ligands containing PN_2 and PNO donor atom sets: syntheses and structural characterization

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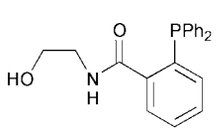
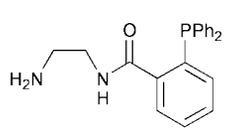
Reactions of [^{n}Bu$_4$N][Re(O)Cl$_4$] **1** with an excess of the recently described heterofunctionalized phosphane ligands 2-(diphenylphosphanyl)-*N*-(2-hydroxyethyl)benzamide (H_2PNO) and *N*-(2-aminoethyl)-2-(diphenylphosphanyl)-benzamide (HPN_2), in refluxing methanol, afforded the six-co-ordinated monooxorhenium(v) complexes [Re(O)(κ^3-PNO)(κ^2-H_2PNO)]Cl **5** and [Re(O)(κ^3-PN_2)(OMe)Cl] **6**, respectively. Ligand exchange between H_2PNO and [Re(O)Cl$_3$(PPh$_3$)$_2$] **2** in the presence of NaOAc has led to the six-co-ordinated monooxorhenium(v) complex [Re(O)(κ^3-PNO)(κ^2-DPPBA)] **7** (HDPPBA = 2-(diphenylphosphanyl)benzoic acid). The characterization of the compounds involved IR, ^{1}H and ^{31}P NMR spectroscopy and X-ray crystallographic analysis. The overall geometry around the metal is best described as a distorted octahedron: the co-ordination is defined by an oxo group, a tridentate dianionic PNO, and a bidentate co-ligand, which is the neutral H_2PNO in the first case **5**, and monoanionic DPPBA in the case of **7**. In both these complexes the equatorial plane is defined by the phosphorus, nitrogen and oxygen atoms of the dianionic PNO ligand and by a phosphorus atom of the co-ligand. The axial positions are occupied by the oxo group and by an oxygen atom of the co-ligand. In complex **6** the axial position is defined along the O=Re–OMe bond, three equatorial positions being occupied by the PN_2 ligand, whereas the fourth position is occupied by a chloride atom.

Introduction

In the past few years there has been a renewed interest in the chemistry of complexes of Re and Tc with phosphine ligands, in certain cases due to the potential usefulness of such compounds for the development of new radiopharmaceuticals.[1] Owing to the donor–acceptor properties of the phosphorus atom, phosphine ligands present enhanced co-ordination abilities leading to complexes with high stability, even under *in vivo* conditions.[2–4] Monodentate or bidentate phosphines as well as bidentate or tetradentate functionalized phosphines, with PN, PO, and PS or PN_2O, PN_2S, and P_2N_2 donor atom sets, have been the most studied towards the $[M{=}O]^{3+}$ (M = Re or Tc) core.[4–19] Recently, water-soluble phosphines revealed also a great potential for biomedical applications.[20–22] In our laboratory we have been synthesizing new heterofunctionalized phosphine ligands, potentially tridentate and dianionic,[23] with the H_2PNO (2-(diphenylphosphanyl)-*N*-(2-hydroxyethyl)benzamide) and HPN_2 (*N*-(2-aminoethyl)-2-(diphenylphosphanyl)-benzamide) donor atom sets. We have been exploring their co-ordination capabilities towards the core $[M{=}O]^{3+}$ (M = Re or Tc), by varying the reaction conditions, such as ligand-to-metal stoichiometric ratio, starting materials, solvents, and temperature.



H_2PNO

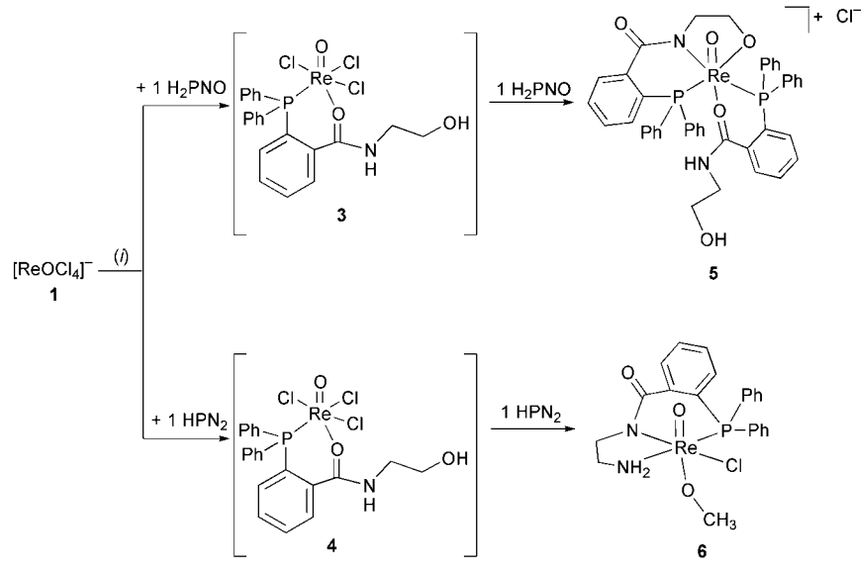


HPN_2

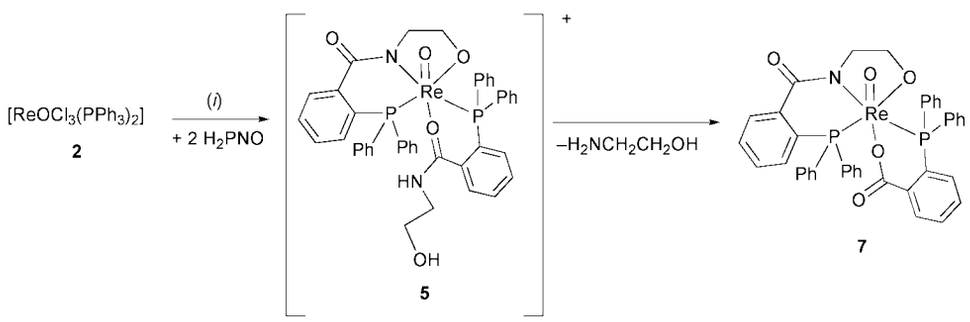
In this paper we report on the synthesis and characterization of the new complexes [Re(O)(κ^3-PNO)(κ^2-H_2PNO)]Cl, [Re(O)(κ^3-PN_2)(OMe)Cl], and [Re(O)(κ^3-PNO)(κ^2-DPPBA)] (HDPPBA = 2-(diphenylphosphanyl)benzoic acid), which were obtained by treating [^{n}Bu$_4$N][Re(O)Cl$_4$] **1** or [Re(O)Cl$_3$(PPh$_3$)$_2$] **2** with H_2PNO or HPN_2 under different reaction conditions.

Results and discussion

The oxo complex [^{n}Bu$_4$N][Re(O)Cl$_4$] **1** reacts with two or three equivalents of H_2PNO or HPN_2, in methanol under reflux, affording the cationic and the neutral complexes [Re(O)(κ^3-PNO)(κ^2-H_2PNO)]Cl **5** and [Re(O)(κ^3-PN_2)(OMe)Cl] **6**, respectively (Scheme 1). These complexes have been characterized by the usual analytical techniques, including X-ray diffraction analysis. In complex **5** one of the ligands is dianionic and tridentate, and the second one is neutral and bidentate. In **6** only one PN_2 ligand co-ordinates, acting as monoanionic and tridentate. The different basicity of the H_2PNO and HPN_2 ligands is responsible for the different type of complexes isolated. As we have previously described, [^{n}Bu$_4$N][Re(O)Cl$_4$] **1** reacts with one equivalent of H_2PNO or HPN_2, at room temperature, affording the neutral adducts [Re(O)Cl$_3$(κ^2-H_2PNO)] **3** and [Re(O)Cl$_3$(κ^2-HPN_2)] **4**, respectively.[23] Under these conditions, no deprotonation of the ligands was observed, and they co-ordinate as neutral and bidentate. In order to get a better insight into the mechanism of the reactions (Scheme 1), namely the role played by adducts **3** and **4** in the formation of **5** and **6**, these adducts were allowed to react with one or two equivalents of H_2PNO or HPN_2, in refluxing methanol. In both cases the complexes **5** and **6** were isolated, which clearly indicates that **3** and **4** are the intermediates involved in the direct synthesis of **5** and **6**, starting from $[Re(O)Cl_4]^-$ (Scheme 1). Indeed, the first equivalent of ligand reacts with $[Re(O)Cl_4]^-$ affording adducts **3** and **4**. Then, the enhanced labilization of the chlorides in adduct **3**, and the acidity of the amide and alcohol groups of the H_2PNO ligand, promote the replacement of the three chlorides by a dianionic κ^3-PNO ligand. The different



Scheme 1 (*i*) MeOH, reflux.



Scheme 2 (*i*) MeOH/NaOAc, reflux.

behaviour observed for the HPN_2 ligand is due to the higher basicity of the NH_2 group compared to the OH of the H_2PNO ligand. The use of an excess of HPN_2 merely promotes deprotonation of the amide group of the neutral bidentate HPN_2 ligand in adduct **4.** This mono-deprotonation is accompanied by a rearrangement of the initially neutral HPN_2 ligand, which becomes tridentate, through the phosphorus, amide and amine nitrogens. Further replacement of a chloride by a methoxide group is favoured by the *trans* effect of the oxo group in **6**.

We also studied reactions of [^{n}Bu$_4$N][Re(O)Cl$_4$] **1** or [Re(O)Cl$_3$(PPh$_3$)$_2$] **2** with the H_2PNO and HPN_2 ligands in the presence of the base NaOAc. Using the very reactive complex **1**, degradation of the ligands is observed and a mixture of uncharacterizable species is formed. Using the less reactive complex **2** we only succeeded with the H_2PNO ligand (Scheme 2). In this reaction, a deep brown solid was isolated and formulated as the neutral complex [Re(O)(κ^3-PNO)(κ^2-DPPBA)] **7** based on analytical data and X-ray diffraction analysis. This complex is obtained in relatively low yield (*ca.* 30%) because it is much likely a product resulting from the hydrolysis of **5**. However, complex **5**, as well as **6** and **7**, is relatively air and moisture stable in the solid state. They are very soluble in chlorinated solvents, moderately soluble in methanol and insoluble in water.

The IR spectra of complexes **5**–**7** exhibit the characteristic Re=O stretching vibrations at 980, 920, and 970 cm^{-1}, respectively. The values found for **5** and **7** are in the normal range for rhenium monooxo complexes (945–1067 cm^{-1}).[24] The significant bathochromic shift of this vibration in complex **6** is normal and compares well with the values found for other complexes containing alkoxide groups *trans* to the oxo moiety (915–940 cm^{-1}).[24] In the spectra of **5**–**7** also appear two strong absorption bands at *ca.* 750 and 690 cm^{-1}, which are characteristic of the phenylphosphine moiety of the heterofunctionalized ligands, and are associated with C–H and C–C out of plane bending vibrations in monosubstituted benzene rings.[25] Another common feature of all IR spectra is the presence of very strong bands in the range 1570–1640 cm^{-1}, which are associated with carbonyl stretching vibrations. By comparison of the IR spectra of complexes **5**–**7**, the bands at 1570 and 1580 cm^{-1} were assigned to the C=O stretching vibration of the carbonyl groups of the tridentate PNO and PN_2 ligands, which are co-ordinated as dianionic (**5** and **7**) or monoanionic (**6**). Relative to the corresponding "free" ligands, these values are lowered in energy (by *ca.* 50–60 cm^{-1}), confirming co-ordination. In complex **5** the presence of the bidentate and neutral H_2PNO ligand is confirmed by the existence of a strong band at 1600 cm^{-1}, which is due to the carbonyl co-ordinated to the metal centre *trans* to the oxo group. This value compares well with that found for the same stretching vibration in the adduct [Re(O)Cl$_3$(κ^2-H_2PNO)] **3** (1590 cm^{-1}), but is significantly lower than that value for the "free" ligand (by *ca.* 30 cm^{-1}).[23] In the IR spectrum of **7** appears also a strong band at 1640 cm^{-1}, which is assigned to the C=O carboxylate stretch of the DPPBA ligand. This value is shifted relative to that found for the "free" ligand (1690 cm^{-1} for free HDPPBA). The presence of chloride in complex **6** is confirmed by a weak band at 340 cm^{-1}, assigned to ν(Re–Cl).

The ^{31}P NMR spectra of complexes **5** and **7** show the presence of two magnetically different phosphorus atoms. In the spectrum of **5** two doublets appear at δ 2.9 and at −3.9, and in the spectrum of **7** two doublets appear at δ −4.7 and at −7.6. The associated J_{PP} coupling constants (**5**, 7.3; **7**, 8.3 Hz) are consistent with *cis*-positioned phosphorus atoms.[26] For complex **6** the ^{31}P NMR presents only one singlet at δ 3.9. These results indicate that the ^{31}P NMR signal of free H_2PNO and HPN_2 moves significantly downfield upon co-ordination, due to the strong acid character of the [Re=O]$^{3+}$ and [O=Re–OMe]$^{2+}$ cores.

The ^{1}H NMR spectra of complexes **5**–**7** show several sets of multiplets attributed to the protons of the aromatic rings. The spectrum of **5** presents also a broad triplet at δ 11.05 and two sets of four multiplets integrating for one proton each, which are assigned to the amide proton of the neutral ligand and to the ethylenic protons of the two PNO ligands, respectively. One of the sets (δ 4.66, 4.52, 3.99, 3.69) corresponds to the ethylenic protons of the tridentate ligand and the other (δ 3.38, 3.25, 2.07, 1.42) to the ethylenic protons of the neutral and bidentate ligand. This assignment was based on the multiplicity and intensity of the resonances, on selected homonuclear decoupling experiments (^{1}H) and by comparison of the ^{1}H NMR spectrum of **5** with that previously described for the adduct [Re(O)Cl$_3$(κ^2-H$_2$PNO)] **3**. It is worthwhile to note that the ethylenic protons of both the dianionic tridentate ligand and the neutral bidentate ligand are diastereotopic. While in the first case this fact arises from the co-ordination of the ligand through the phosphorus, amide and alkoxide groups, in the second case it can not be explained by the co-ordination mode since only the phosphorus atom and the carbonyl group are involved. The observed non-equivalence is much likely due to steric constraints. As we have described previously, in the adduct [Re(O)Cl$_3$(κ^2-H$_2$PNO)] **3** the same ligand is co-ordinated analogously and, for the ethylenic protons, only two resonances (integrating for two protons each) appear in the ^{1}H NMR. The ^{1}H NMR spectrum of complex **6** clearly indicates that the amino group is co-ordinated to the Re atom in solution as in the solid state. For this reason, the ethylenic and the amine protons are diastereotopic, appearing as one set of four multiplets of intensity one (δ 4.63, 3.68, 3.15, 3.06) and as two broad singlets (δ 5.17, 4.04), respectively. Relative to the "free" ligands these resonances are shifted down field upon co-ordination, whereas the methoxide group (δ 2.71), *trans* to the oxo moiety, is shielded. These effects are explained by the acidity of the [Re=O]$^{3+}$ moiety and by the electron density located along the Re=O axis, respectively.

Crystal structures

Purple single crystals of complexes **5** and **6** were obtained by recrystallization from ethanol–ethyl acetate (**5**) and by slow evaporation of a methanolic solution of **6**. A brownish red crystal was obtained by slow evaporation of a solution of **7** in CH_2Cl_2–MeOH. For **5** the X-ray crystallographic analysis on a poor quality crystal did not provide an adequate data set for an accurate determination of the structure of this complex. However, it was possible to define unambiguously the connectivities of the atoms around the Re and to conclude that the molecular structure is, in a certain way, comparable to the one found for **7**. The structure of **5** consists of monomeric octahedral rhenium(v) units, which are monocationic with a chloride atom counter ion. An ORTEP[27] drawing of [ReO(κ^3-PNO)(κ^2-H$_2$PNO)]Cl **5** is displayed in Fig. 1.

The structures of complexes **6** and **7** consist of neutral monomeric octahedral rhenium(v) units. ORTEP drawings are shown in Figs. 2 and 3. Selected bond distances and angles are presented in Tables 1 and 2. In **6** and **7** the Re^V is six-co-ordinated and the overall geometry around the metal is best described as a distorted octahedron. In **7** the equatorial plane is defined by the PNO atoms of the tridentate ligand and by a phosphorus atom of the co-ligand (monoanionic and bidentate, DPPBA). The axial position is defined by an oxo group and by an oxygen atom of the co-ligand. In [ReO(κ^3-PN$_2$)(OMe)Cl] **6** the axial position is defined along the O=Re–OMe bond, three equatorial positions being occupied by the tridentate PN$_2$ ligand, whereas the fourth equatorial position is occupied by a chloride. In complexes **6** and **7** the tridentate PN$_2$ or PNO ligands form around the metal a two (5, 6)-membered chelate ring system. The 6-membered rings in both structures are

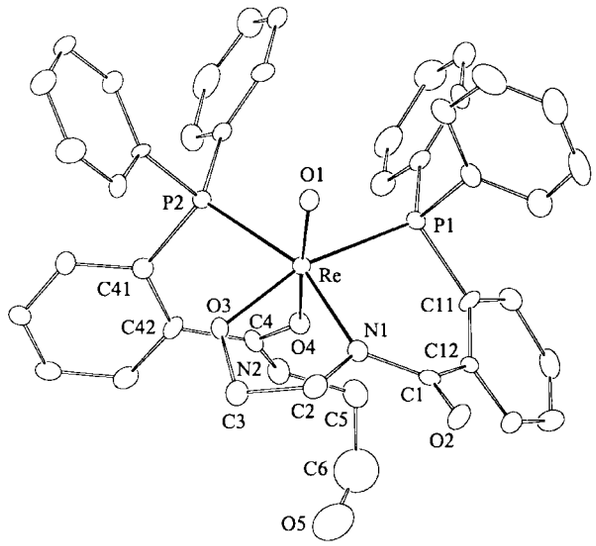


Fig. 1 An ORTEP drawing of one of two of the independent molecules of the cationic complex **5** with the atom numbering scheme.

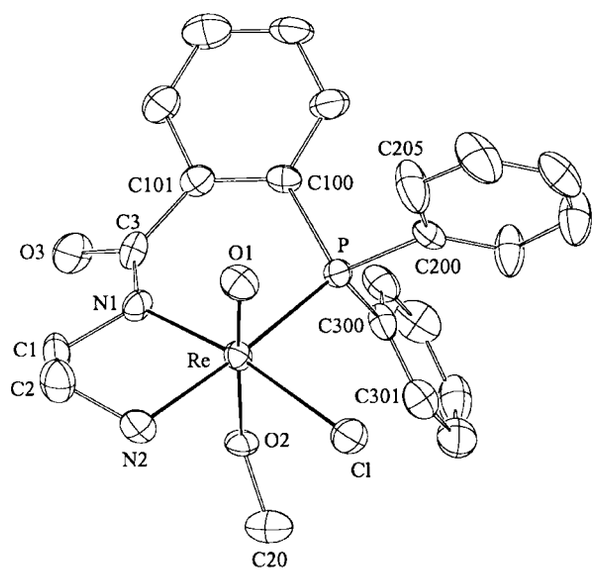


Fig. 2 An ORTEP drawing of complex **6** with the atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

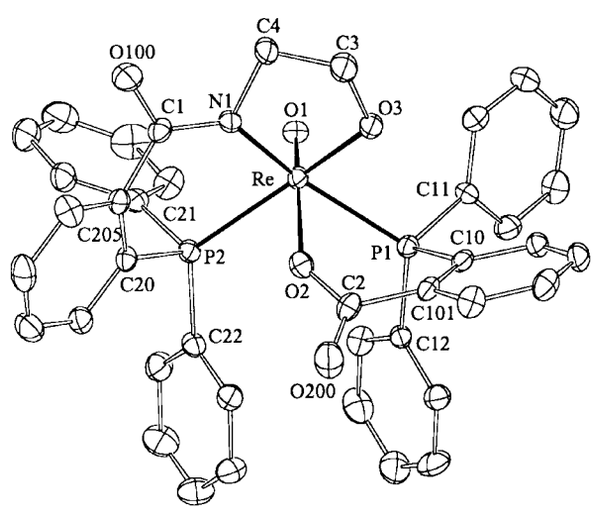


Fig. 3 An ORTEP drawing of complex **7** with the atom numbering scheme. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for [ReO(κ^3-PN_2)-(OMe)Cl] **6**

Re–O(1)	1.742(6)	C(3)–O(3)	1.236(11)
Re–O(2)	1.881(6)	N(1)–C(1)	1.497(12)
Re–N(1)	2.027(7)	N(1)–C(3)	1.355(12)
Re–N(2)	2.178(8)	N(2)–C(2)	1.483(12)
Re–Cl	2.453(3)	C(1)–C(2)	1.500(13)
Re–P	2.397(2)	C(3)–C(101)	1.496(13)
O(2)–C(20)	1.406(11)	Av. P–C	1.81(1)
O(1)–Re–O(2)	173.6(3)	N(1)–Re–P	93.0(2)
O(1)–Re–N(1)	95.6(3)	O(1)–Re–Cl	89.5(2)
O(2)–Re–N(1)	90.0(3)	O(2)–Re–Cl	84.5(2)
O(1)–Re–N(2)	90.7(3)	N(1)–Re–Cl	171.9(2)
O(2)–Re–N(2)	87.1(3)	N(2)–Re–P	174.9(2)
N(1)–Re–N(2)	82.0(3)	N(2)–Re–Cl	91.8(2)
O(1)–Re–P	90.5(2)	P–Re–Cl	93.18(9)
O(2)–Re–P	92.2(2)	Re–O(2)–C(20)	145.0(7)

Table 2 Selected bond lengths (Å) and angles (°) for [Re(O)(κ^3-PNO)-(κ^2-DPPBA)] **7**

Re–O(1)	1.668(4)	Re–P(2)	2.471(2)
Re–O(2)	2.100(4)	O(2)–C(2)	1.301(7)
Re–O(3)	1.951(4)	O(100)–C(1)	1.249(7)
Re–N(1)	2.025(5)	O(200)–C(2)	1.214(8)
Re–P(1)	2.459(2)		
O(1)–Re–O(3)	104.9(2)	O(2)–Re–P(1)	78.08(12)
O(1)–Re–N(1)	105.4(2)	O(3)–Re–P(1)	81.58(13)
O(3)–Re–N(1)	80.7(2)	N(1)–Re–P(2)	87.54(14)
O(1)–Re–O(2)	161.0(2)	O(2)–Re–P(2)	78.70(12)
O(3)–Re–O(2)	88.7(2)	P(1)–Re–P(2)	106.76(5)
N(1)–Re–O(2)	89.7(2)	O(1)–Re–P(2)	90.2(2)
O(1)–Re–P(1)	90.6(2)		

not planar [**6**, Re–N(1)–C(3)–C(101)–C(100)–P(1), RMSD = 0.2068 Å; **7**, N(1)–C(1)–C(205)–C(20)–P(2)–Re, RMSD = 0.2227 Å]. The 5-membered rings in both structures are also non-planar [**6**, Re–N(1)–C(1)–C(2)–N(2), RMSD = 0.1947 Å; **7**, Re–N(1)–C(4)–C(3)–O(3), RMSD = 0.179, but C(4)–C(3)–O(3)–Re, RMSD = 0.022 Å], and in **7** this ring presents an envelope conformation around the N(1) atom. Complex **7** still presents a second six-membered ring involving DPPBA and defined by the atoms Re–P(1)–C(10)–C(101)–C(2)–O(2), which is even more distorted (RMSD = 0.3412 Å).

The octahedral distortion is higher for complex **7** than for **6**, which can easily be seen by the displacement of the Re atom from the equatorial plane towards the multiply bonded oxygen (**6**, 0.06; **7**, 0.27 Å), by the non-linearity of the O_{oxo}=Re–OX bond angle (**6**, O_{oxo}–Re–O(2), 173.6(3)°; **7**, O(1)–Re–O(2), 161.0(2)°) and by the observed angles around the metal. The differences found are easily explained by the presence in **7** of a κ^2-coordinated co-ligand. As far as we are aware, the complexes reported herein are the first examples of oxo complexes of Re^V containing charged and tridentate heterofunctionalized phosphines. In a previous work we reported on the synthesis of complexes of this family but the ligands were co-ordinated as neutral and bidentate. For comparison there is only a limited number of compounds with bidentate and tetradentate functionalized phosphines.[9,10,13,18,19]

The Re–Cl bond length (2.453(3) Å) in complex **6** compares with the corresponding value found in the rhenium(V) complex [Re(O)$(PN)_2$Cl] (2.436(6) Å)[9] (HPN = (*o*-aminophenyl)-diphenylphosphine), but is larger and shorter than the corresponding values found in adduct **3** (av. Re–Cl, 2.366(5) Å)[23] and [Re(O)Cl(κ^4-L)] (2.494(6) Å)[18] (H_2L = *N*-{*N*-[3-(diphenylphosphino)propionyl]glycyl}-L-*S*-benzylcysteine methyl ester). These differences are due to the steric and electronic factors imposed by the nature of the atoms co-ordinated, by the denticity of the ligand, and by the position of the chloride ligand relative to the oxo group.

The Re–O(1) bond length (1.668(4) Å) in complex **7** is typical of this type of bond, being in the normal range for six-co-ordinated rhenium(V) complexes (*ca.* 1.67–1.70 Å).[24] The Re–O(1) bond length in **6** (1.742(6)Å) is comparable to the value found in [Re(O)(OMe)Cl_2(κ^2-PN(Me)$_2$)][10] (1.70(1) Å) ($PN(Me)_2$ = *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline), but is longer than the same bond in complex **7**. This difference is explained by the nature of the ligand which is *trans* to the oxo group. In complex **6** a methoxide is present, while in **7** a carboxylate is found. The competition of the methoxide with the oxo group in the interaction with the dπ orbitals of the metal is clearly shown by the short Re–O(2) bond distance found in **6** (1.881(6) Å), and by the unusually long Re–O(1) bond distance. In complex **7** the Re–O(2) bond distance found for the carboxylate is longer (2.100(4) Å), and this justifies a stronger interaction of the metal with the oxo group. The Re–P bond length in **6** (2.397(2) Å) is shorter than the values found for Re–P(1) (2.459(2) Å) and Re–P(2) (2.471(2) Å) in [Re(O)(κ^3-PNO)(κ^2-DPPBA)] **7**. This difference is certainly related with steric contraints imposed by the bidentate and anionic co-ligand (DPPBA) in complex **7**.

The Re–N(1) bond distance in complex **6** (2.027(7) Å) compares well with the value found for the same distance in **7** (2.025(5) Å). These are expected values when amide groups are involved. In **6** the larger Re–N(2) bond distance (2.178(8) Å) is consistent with non-deprotonation of the amine group, and is comparable to the average Re–N bond length in [ReO{$SC(CH_3)_2CH(CO_2CH_3)NH_2$}{$SC(CH_3)_2CH(CO_2)NH_2$}] (2.178(6) Å).[28] As discussed above, ^{1}H NMR spectroscopy shows two resonances for the diastereotopic NH protons.

Concluding remarks

The complexes [Re(O)(κ^3-PNO)(κ^2-H_2PNO)]Cl **5**, [Re(O)-(κ^3-PN_2)(OMe)Cl] **6** and [ReO(κ^3-PNO)(κ^2-DPPBA)] **7** are the first examples of rhenium(V) complexes stabilized by charged tridentate heterofunctionalized phosphines. The deprotonation of the ligands has been controlled by the reaction conditions, namely temperature, solvent and metal : ligand molar ratio. We have also shown that the previously described neutral adducts, [Re(O)Cl_3(κ^2-H_2PNO)] and [Re(O)Cl_3(κ^2-HPN_2)] are intermediates in the formation of the complexes **5**–**7**. The results reported herein show the flexibility of the H_2PNO and HPN_2 ligands, in terms of denticity and charge, and their adequacy to stabilize six-co-ordinated complexes. These results open the possibility of preparing complexes of Tc and Re at *non-carrier added level*, using the so-called [3+2] approach and, therefore, can potentially be useful for radiopharmaceutical development.

Experimental

General techniques

All chemicals were of reagent grade. 2-(Diphenylphosphanyl)-*N*-(2-hydroxyethyl)benzamide (H_2PNO), *N*-(2-aminoethyl)-2-(diphenylphosphanyl)benzamide (HPN_2), [Re(O)Cl_3(κ^2-H_2-PNO)] **3**, and [Re(O)Cl_3(κ^2-HPN_2)] **4** were prepared as previously described.[23] [^{n}Bu_4N][Re(O)Cl_4] **1** and [Re(O)Cl_3(PPh_3)$_2$] **2** were prepared as reported.[29,30] The reactions were run in air unless otherwise indicated. ^{1}H and ^{31}P NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; ^{1}H chemical shifts were referenced to the residual solvent resonance relative to tetramethylsilane and ^{31}P chemical shifts with external 85% H_3PO_4. The NMR samples were prepared in $CDCl_3$ or $(CD_3)_2SO$. Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 577 spectrometer using KBr pellets. Elemental analyses were performed on a Perkin-Elmer automatic analyser.

Table 3 Crystal data for complexes **6** and **7**

	6·CH_3OH	**7**·CH_3OH
Chemical formula	$C_{22}H_{23}ClN_2O_3PRe·CH_3OH$	$C_{40}H_{32}NO_5P_2Re·CH_3OH$
M	648.09	886.85
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
T/K	293(2)	293(2)
a/Å	9.1698(10)	9.496(1)
b/Å	24.026(3)	13.118(2)
c/Å	10.8833(11)	15.706(2)
α/°		83.86(1)
β/°	97.519(9)	83.55(1)
γ/°		69.17(1)
V/Å^3	2377.1(5)	1812.3(4)
Z	4	2
μ/mm^{-1}	5.324	3.490
No. of measured reflections	4911	7007
No. of independent reflections [R(int)]	4665 (0.1210)	6551 (0.0250)
No. of observed reflections [$F_o > 4\sigma(F_o)$]	3244	5456
$R1$	0.0500	0.0399
$wR2$	0.0830	0.0758

Preparations

[Re(O)(κ^3-PNO)(κ^2-H_2PNO)]Cl 5. Solid H_2PNO (0.10 g, 0.29 mmol) was added to a solution of [^{n}Bu$_4$N][Re(O)Cl$_4$] **1** (0.056 g, 0.095 mmol) in MeOH (10 mL). The mixture was allowed to reflux for 3 h after which the solution was brownish violet. The solvent was evaporated and the obtained viscous oil chromatographed on an appropriate column of silica gel with 2.5–10% MeOH–CH_2Cl_2 (gradient) to afford a purple oil, which gave a deep purple solid by washing with hexane (37 mg, 42% yield). Complex **5** could be recrystallized from a ethanol–ethyl acetate mixture providing deep purple crystals of suitable quality for structural analysis (Found: C, 49.4; H, 4.7; N, 2.8. $C_{42}H_{38}ClN_2O_5P_2Re·CH_2Cl_2$ requires C, 50.7; H, 4.0; N, 2.8%). $\tilde{\nu}_{max}$/cm^{-1} 1600vs (CO), 1580 (sh) (CO), 980s (Re=O), 690s and 750s (KBr); δ_H($CDCl_3$) 11.05 (1 H, br t, NH), 9.11 (1 H, m, aromatic), 8.32 (1 H, m, aromatic), 7.79–7.26 (17 H, m, aromatic), 7.12–7.08 (2 H, m, aromatic), 6.99–6.79 (5 H, m, aromatic), 6.39 (1 H, m, aromatic), 6.17 (1 H, m, aromatic), 4.66 (1 H, m, CH of tridentate ligand), 4.52 (1 H, m, CH of tridentate ligand), 3.99 (1 H, m, CH of tridentate ligand), 3.69 (1 H, m, CH of tridentate ligand), 3.38 (1H, m, CH of bidentate ligand), 3.25 (1 H, m, CH of bidentate ligand), 2.07 (1H, m, CH of bidentate ligand) and 1.42 (1H, m, CH of bidentate ligand); δ_P($CDCl_3$) 2.9 (d, J 7.3) and −3.9 (d, J 7.3 Hz).

[Re(O)(κ^3-PN_2)(OMe)Cl] 6. Solid HPN_2 (0.178 g, 0.51 mmol) was added to a solution of [^{n}Bu$_4$N][Re(O)Cl$_4$] **1** (0.10 g, 0.17 mmol) in methanol (10 mL). The mixture was allowed to reflux for 3 hours. After *ca.* 1.5 hours a light purple solid started to precipitate. The volume of solvent was then reduced to about one half of the initial amount and the solid isolated by centrifugation. The obtained purple solid was washed with methanol and dried under vacuum (0.055 g, 52%). Suitable purple crystals for X-ray diffraction analysis were obtained by recrystallization from boiling methanol (Found: C, 43.0; H, 4.2; N, 4.3. $C_{22}H_{23}ClN_2O_3PRe·CH_3OH$ requires C, 42.6; H, 4.2; N, 4.3%); $\tilde{\nu}_{max}$/cm^{-1} 1570vs (CO), 920vs (Re=O), 740s, 690s and 340w (Re–Cl) (KBr). δ_H($CDCl_3$) 8.55 (1 H, m, aromatic), 7.71–7.59 (4 H, m, aromatic), 7.52–7.35 (8 H, m, aromatic), 6.97 (1 H, m, aromatic), 5.17 (1 H, s br, NH), 4.63 (1 H, d, CH), 4.04 (1 H, s br, NH), 3.68 (1 H, m, CH), 3.15 (1 H, m, CH), 3.06 (1 H, m, CH) and 2.71 (3H, s, OMe); δ_P($CDCl_3$) 3.9.

[Re(O)(κ^3-PNO)(κ^2-DPPBA)] 7. To a stirred solution of ligand H_2PNO (0.10 g, 0.29 mmol) in MeOH (10 mL) was added 1 M NaOAc in MeOH (4.35 mL, 4.35 mmol) followed by solid [Re(O)Cl_3(PPh_3)$_2$] **2** (0.292 g, 0.37 mmol). The mixture was refluxed for 1 h, at which time it was brownish red. At room temperature it was diluted with ethyl acetate, washed with water (×2), and the organic phase dried over $MgSO_4$. Concentration in vacuum provided a brownish red residue which was washed with diethyl ether and vacuum dried (0.074 g, 30% yield). The solid obtained was recrystallized by slow evaporation of a CH_2Cl_2–MeOH solution to provide crystals of suitable quality for structural analysis (Found: C, 52.0; H, 4.0; N, 1.9. $C_{40}H_{32}NO_5P_2Re·CH_2Cl_2$ requires C, 52.4; H, 3.7; N, 1.5%); $\tilde{\nu}_{max}$/cm^{-1} 1640s (CO), 1580m (CO), 970s (Re=O), 690vs and 740s (KBr). δ_H($CDCl_3$) 8.42 (1 H, m, aromatic), 8.18 (1 H, m, aromatic), 7.79–7.34 (20 H, m, aromatic), 6.99–6.86 (4 H m, aromatic), 6.62 (1 H, m, aromatic), 6.44 (1H, m, aromatic), 4.86 (1 H, m, CH), 4.47 (1H, m, CH), 4.21 (1 H, m, CH), 3.92 (1H, m, CH); δ_P($CDCl_3$) −4.7 (d, J 8.3) and −7.6 (d, J 8.3 Hz).

X-Ray crystallographic analysis

Purple crystals of complexes **5** and **6**, and a brownish red crystal of **7**, were fixed inside thin-walled glass capillaries. Data were collected on a Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo-Kα radiation. For **5** it was not possible to refine the structure with acceptable R values and enough accuracy, worsened by the packing of two independent molecules in the asymmetric unit: triclinic, space group $P1$, $a = 14.300(3)$, $b = 16.977(2)$, $c = 18.752(4)$ Å, $\alpha = 92.570(14)$, $\beta = 109.78(2)$, $\gamma = 96.122(13)°$, $V = 4243.4(14)$ Å^3, $Z = 4$, $R1 = 0.0750$, $wR2 = 0.1853$ for 8367 reflections with $I > 2\sigma(I)$. For **6** and **7** a summary of the crystallographic data is given in Table 3. Data were corrected[31] for Lorentz-polarization effects, for linear decay (none observed for **7**, 2.1% for **6**) and for absorption by empirical corrections based on Ψ scans. The structures were solved by Patterson methods[32] and subsequent Fourier-difference techniques and refined by full-matrix least-squares procedures on F^2 using SHELXL 93.[33] For **6** and **7** a methanol solvent molecule of crystallisation was also located in the Fourier-difference map. All non-hydrogen atoms were refined with anisotropic thermal motion parameters except for the solvent atoms in **7**. The hydrogen atoms were introduced in calculated positions (except those of the solvent in **7**). Atomic scattering factors and anomalous dispersion terms were taken from ref. 33. The ORTEP drawings were made with ORTEP II[27] and all calculations were performed on a Decα 3000 computer.

CCDC reference number 186/2016.

See http://www.rsc.org/suppdata/dt/b0/b002798g/ for crystallographic files in .cif format.

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