Neutral Trichlorooxorhenium(V) Complexes Containing New Heterofunctionalized Phosphane Ligands of the Type PN_2 and PNO

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The new heterofunctionalized phosphane [(1*R*,2*R*)-*N*-(2-aminocyclohexyl)]-2-(diphenylphosphanyl)benzamide (**L¹**), *N*-(2-aminoethyl)-2-(diphenylphosphanyl)benzamide (**L²**) and 2-(diphenylphosphanyl)-*N*-(2-hydroxyethyl)benzamide (**L³**) were synthesized by reaction of *N*-[2-(diphenylphosphanyl)-benzoyloxy]succinimide (**3**) in dichloromethane with (1*R*,2*R*)-(–)-diaminocyclohexane, ethylenediamine and ethanolamine, respectively. Reactions of $[Re(O)Cl_4]^-$ with **L¹**, **L²** and **L³**, at a 1:1 metal/ligand molar ratio gave neutral trichlorooxorhenium(V) complexes of the type $[Re(O)Cl_3\{\kappa^2\text{-L}\}]$ [L = **L¹** (**4**), **L²** (**5**), **L³** (**6**)]. The characterization of the compounds involved IR, ^{1}H- and ^{31}P-NMR spectroscopy, and X-ray crystallographic analysis for **L¹**, **5** and **6**. The Re atom is six-coordinate in complexes **4**–**6**, with an oxo ligand, three chloride ligands and a neutral bidentate heterofunctionalized phosphane ligand.

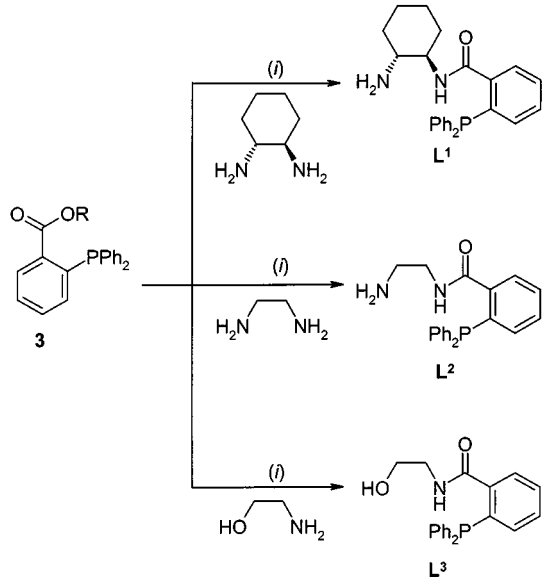
Introduction

The continuous demand for more sensitive and specific probes for targeting diseased organs or physiological functions in Nuclear Medicine, both in the diagnostic or therapeutic field, has led to an increasing interest in the development of receptor-binding radiopharmaceuticals.[1] Due to its physico-chemical properties and widespread availability, ^{99m}Tc is still the most used radionuclide for diagnosis, and both ^{186}Re and ^{188}Re appear as interesting radionuclides for the development of radiopharmaceuticals with therapeutic potential.[2] For the metal centre in the oxidation state (V) and an $[M{=}O]^{3+}$ core, the use of a bifunctional tetradentate or a tridentate ligand, and a bifunctional unidentate coligand ([3+1] approach) are among the most popular strategies for the design and preparation of new, more specific radiopharmaceuticals.[3] Due to its σ-donor and π-acceptor properties, phosphanes are known to stabilize complexes of rhenium and technetium with the metal centre in different oxidation states.[4,5] A number of heterofunctionalized phosphane-containing ligands have previously been described and used to stabilize the core $[M{=}O]^{3+}$ (M = Re, Tc).[6–8] However, they are all either bidentate, with PN, PO or PS donor sets [6–8] or tetradentate.[9] We have synthesized new tridentate PNO- and PN_2-type ligands, with potential tridentate character, with the aim of designing new radiopharmaceuticals using the [3+1] approach. Surprisingly, we observed that, depending on the reaction conditions, these ligands are very versatile in terms of coordination mode and charge. Indeed, they can act as neutral, mono- or dianionic bi/tridentate chelates.[10] In this paper we report on the synthesis and characterization of the new heterofunctionalized phosphane ligands as well as on the preparation of Re^V adducts where the ligands coordinate to the metal centre in a bidentate and neutral fashion.

Results and Discussion

Synthesis and Characterization of the Ligands

The heterofunctionalized phosphane ligands **L¹**, **L²** and **L³** were synthesized as depicted in Scheme 1. The activation of 2-(diphenylphosphanyl)benzoic acid with *N*-hydroxysuccinimide was achieved in good yield (94%) by a slight modification of a reported method.[11] Reaction of *N*-[2-(diphenylphosphanyl)benzoyloxy]succinimide (**3**) in CH_2Cl_2 at room temperature with (1*R*,2*R*)-(−)-diaminocyclohexane, ethylenediamine and ethanolamine afforded, after appropriate workup, **L¹** (89%), **L²** (74%) and **L³** (87%), respectively.



Scheme 1. Synthesis of the Ligands **L¹**, **L²**, and **L³**; R = *N*-succinimido; (*i*) dichloromethane, room temperature

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The IR spectra of $\mathbf{L^1}$ and $\mathbf{L^2}$ exhibit $\nu(NH_2)$ stretching bands at 3220 cm^{-1} and 3320 cm^{-1}, respectively, and for $\mathbf{L^3}$ the IR spectrum shows a strong band at 3310 cm^{-1} which is assigned to ν(OH). In all the spectra a strong band appears at 1630 cm^{-1} due to ν(C=O). In the ^{1}H-NMR spectra of $\mathbf{L^1}$ a doublet appears at $\delta = 5.71$ due to the NH of the amide group. For $\mathbf{L^2}$ and $\mathbf{L^3}$ the signals of these groups appear as broad singlets at $\delta = 6.23$ and 6.27, respectively.

Unlike $\mathbf{L^1}$, where a multiplet at $\delta = 1.89$, assigned to the protons of the amine group, is observed, the ^{1}H-NMR spectrum of $\mathbf{L^2}$ does not present any signal for this group. For $\mathbf{L^3}$, no resonance signal is observed for the hydroxy group. The ^{31}P-NMR spectra of $\mathbf{L^1}$, $\mathbf{L^2}$, and $\mathbf{L^3}$ show only one peak at $\delta = -10.5$, -9.3 and -9.9, respectively. $\mathbf{L^3}$ decomposed slightly in solution on standing, leading to the corresponding phosphane oxide, as indicated by the new ^{31}P-NMR signal which appears at $\delta = 36.6$.[12]

Single colorless crystals of $\mathbf{L^1}$, suitable for X-ray diffraction analysis, were obtained from a mixture of dichloromethane/hexane. $\mathbf{L^1}$ crystallizes in the monoclinic acentric space group $P2_1$ with three crystallographically independent molecules in the asymmetric unit. The three independent molecules are labelled similarly, being distinguished by the first digit of the atom label.

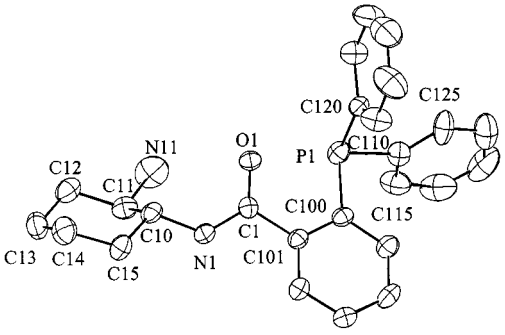
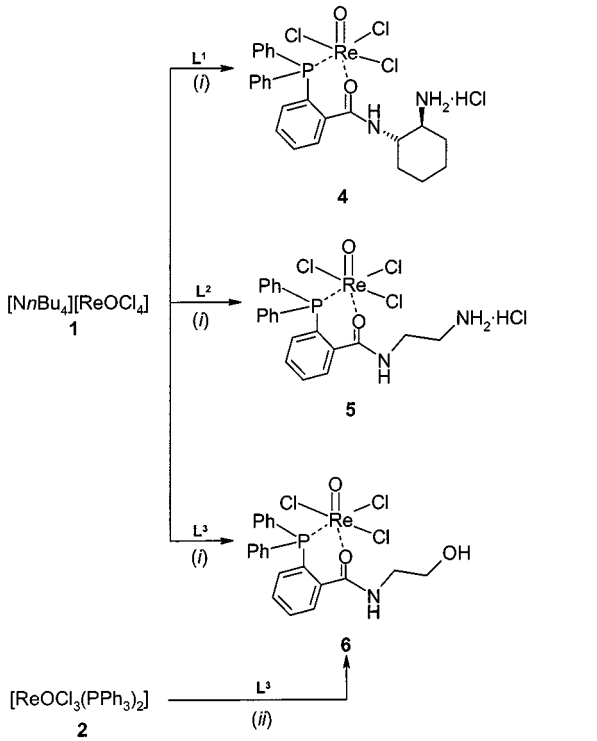


Figure 1. ORTEP drawing of ligand $\mathbf{L^1}$ with the atom numbering scheme; thermal ellipsoids are drawn at the 30% probability level; selected mean bond lengths [Å] and angles [°]: C(1)−O(1) 1.231(8), N(1)−C(1) 1.329(9), N(1)−C(10) 1.448(9), C(11)−N(11) 1.449(11), C(1)−C(101) 1.498(10), P(1)−C(100) 1.848(8), P(1)−C(110) 1.838(9), P(1)−C(120) 1.837(8), av. $(C-C)_{cyclohex}$ 1.51(1), av. $(C-C)_{Phenyl}$ 1.37(2); N(1)−C(1)−O(1) 123.3(7), O(1)−C(1)−C(101) 120.7(7), N(1)−C(1)−C(101) 116.1(7), C(10)−N(1)−C(1) 124.5(6)

Figure 1 shows an ORTEP view of one molecule with the atom numbering scheme as well as selected bond lengths and angles. Within two standard deviations the three molecules can be considered chemically equivalent, presenting similar molecular dimensions. The packing of the molecules forms a network of hydrogen bonds involving the amide N−H group and the carbonyl oxygen atoms. The shortest intermolecular distances are 2.887 Å for O(1) and N(2′) (x, y, $-1 + z$), 2.862 Å for O(2) and N(3′) ($1 - x$, $-0.5 + y$, $1 - z$) and 2.858 Å for O(3) and N(1′) ($2-x$, $y + 0.5$, $-z$) (the average N···O contact distance is 2.929 Å for the hydrogen bonds "C=O···H−N").[13] The cyclohexane ring shows the usual chain conformation.



Scheme 2. Synthesis of the complexes **4**−**6**; (*i*) MeOH, room temperature; (*ii*) dichloromethane, room temperature

Synthesis and Characterization of the Complexes

Reactions of $\mathbf{L^1}$, $\mathbf{L^2}$ and $\mathbf{L^3}$ with [nBu$_4$N][Re(O)Cl$_4$] (**1**) in methanol, at a 1:1 molar ratio, at room temperature, afforded the new unusual neutral trichlorooxorhenium(V) complexes **4**−**6** (Scheme 2). To the best of our knowledge, several compounds containing the "Re(O)Cl$_3$" moiety are known. However, this unit is stabilized either by diphosphanes or by neutral monodentate ligands.[14]−[16] When a heterofunctionalized phosphane ligand such as (2-hydroxyphenyl)diphenylphosphane (PO) is used, deprotonation occurs with formation of the monoanionic complex [Re(O)Cl$_3$(PO)]$^-$.[7c] Phosphane-containing peptides (PN$_2$O donor set) were studied, and deprotonation was also observed. In this case, the ligands coordinate in a dianionic and tetradentate fashion.[9b] Thus, the neutral behavior of our ligands and the observed coordination mode are not very common, probably as a result of the influence of the type of substituents attached to the amide nitrogen atom.

Complex **6** was also obtained by stoichiometric reaction of $\mathbf{L^3}$ with [Re(O)Cl$_3$(PPh$_3$)$_2$] (**2**) in CH$_2$Cl$_2$. After evaporation of the solvent, complexes **4** and **5** were obtained as light blue and pale green solids, respectively. Complex **6**, unlike **4** and **5**, precipitated from its reaction mixture and, upon appropriate workup, was obtained as a dark green solid in an almost quantitative yield. Complexes **4**−**6** are stable towards air and moisture and almost insoluble in most organic solvents and water. Complexes **5** and **6** are moderately soluble in acetonitrile, whereas **4** is insoluble in this solvent. Complex **4** is moderately soluble in tetrahydrofuran and dimethyl sulfoxide but tends to decompose in these solvents. The characterization of **4**−**6** has been done

by elemental analysis, IR, ^{1}H- and ^{31}P-NMR spectroscopy, and by X-ray crystallographic analysis in the case of **5** and **6**.

The IR spectra of complexes **4**–**6** exhibit Re=O stretching vibrations at 1000 cm^{-1}. These values are in the normal range as those found for monooxorhenium complexes (945–1067 cm^{-1}).[17] The C=O stretching vibration of the carbonyl group appears at 1570, 1590 and 1590 cm^{-1} for **4**, **5** and **6**, respectively. These values are lower in energy (by ca. 40–60 cm^{-1}) relative to the corresponding free ligands, confirming the coordination of the carbonyl group to the metal centre. In addition, all the complexes display IR absorptions typical of ν(Re–Cl) at 320 cm^{-1} and at 315 cm^{-1}; and absorptions of coordinated phosphane ligands, in particular two strong absorption bands at 750 cm^{-1} and at 697 cm^{-1}, associated with C–H and C–C out-of-plane bending vibrations in monosubstituted benzene rings.[18]

Due to the low solubility of all complexes their NMR spectra were run either in CD_3CN or in $(CD_3)_2SO$. The ^{31}P-NMR spectra of **5** and **6** in CD_3CN show only one resonance signal, which appears at δ = −15.4 and −16.5, respectively. These resonance signals are shifted slightly upfield in $(CD_3)_2SO$, and appear at δ = −18.1 for both complexes. When compared with those of the free ligands, the resonance signals found for **5** and **6** are shifted upfield (ca. 6 ppm). For complex **4**, it was only possible to run the ^{31}P-NMR spectrum in $(CD_3)_2SO$ and, in this solvent, the initial blue solution turned green within seconds. Two resonance signals are observed in the spectrum at δ = −17.2 and 32.9. The resonance signal at δ = −17.2 compares well with the value of δ = −18.1 found for complexes **5** and **6** in the same solvent, and led us to assign the signal to adduct **4**. An upfield shift (about 7.6 ppm) relative to the resonance signal of the free ligand [−9.6 ppm in $(CD_3)_2SO$], is observed for the resonance signal of **4**. This also compares well with the shift found for complexes **5** and **6**. The resonance at δ = 32.9 is assigned to the phosphane oxide of the ligand.[12] This result confirms that $(CH_3)_2SO$ is able to oxidise aromatic tertiary phosphanes coordinated to oxoRe complexes by oxygen transfer, as previously reported.[19] In order to confirm the presence of phosphane oxide signals in this region of the spectrum, **L^1** was oxidized with hydrogen peroxide in a parallel experiment. The ^{31}P-NMR spectrum of the resulting product in $(CD_3)_2SO$ reveals only one resonance signal at δ = 32.0.

The ^{1}H-NMR spectra of **5** and **6** present three sets of multiplets assigned to the protons of the aromatic rings. Two of the multiplets integrate for one proton each and the third for twelve protons. The chemical shifts are comparable in both complexes and the protons are slightly deshielded with respect to those of the free **L^2** and **L^3**. The remaining signals observed in the spectra are due to the amide and to the ethylene protons of the coordinated heterofunctionalized phosphane ligands. In both complexes the amide proton signal is significantly shifted downfield relative to those of the free ligands and this is certainly due to the more acidic character of this proton after the coordination of **L^2** and **L^3** to the rhenium atom through the carbonyl group.

As mentioned above, complex **4** decomposed in $(CD_3)_2SO$ yielding partially the oxidised form of the ligand. However, in the phenyl and amide region of the ^{1}H-NMR spectrum, we could easily identify some resonance signals that correspond to the remaining adduct **4**. In fact, we observe signals at δ = 11.16 (1 H, d, NH), 8.71 (1 H, t, aromatic), 8.11 (1 H, s, br., aromatic) and 7.19 (1 H, m, aromatic). The pattern, the chemical shifts and type of splitting compare very well with what is observed in the spectrum of complex **5**, in the same solvent. The region of the cyclohexyl protons is quite complicated and the assignment of the resonance signals of **4** is not possible.

Crystal Structures of Complexes 5 and 6

The X-ray crystallographic analysis on a poor-quality crystal of **5** did not provide an adequate data set for an accurate determination of the structure of this complex. It was not possible to refine the structure with acceptable *R* values (R_1 = 0.0925, wR_2 = 0.1946) and with sufficient accuracy. However, it was possible to unambiguously define the connectivities of the atoms around the Re atom (Figure 2), and to confirm that the molecular structure of complex **5** is analogous to that of **6**.

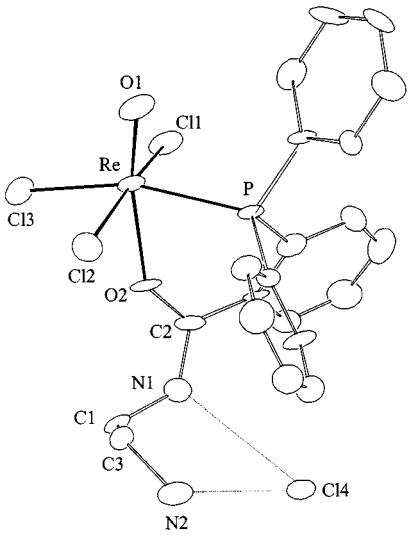


Figure 2. ORTEP drawing of complex **5** with the atom numbering scheme; thermal ellipsoids are drawn at the 30% probability level

Compound **5** crystallized from boiling acetonitrile as dark green crystals in the triclinic space group $P\bar{1}$ with cell parameters a = 9.840(2) Å, b = 12.000(3) Å, c = 13.604(3) Å, α = 66.12(2)°, β =86.01(2)°, γ = 68.30(1)°, V = 1358.7(5) Å^3, Z = 2, D_c = 1.788 gcm^{-3}. Besides a disordered acetonitrile molecule of solvent in the lattice, a residual peak of electron density of the order of 18 eÅ^{-3} was found which refined properly as a chloride ion. The chloride ion is hydrogen-bonded to the two nitrogen atoms of the molecule: to the amide N(1) atom [N(1)···Cl(4) 3.073 Å] and to the amine N(2) atom [N(2)···Cl(4) 3.273 Å]. The molecular structure of **6** as well as selected bond lengths and angles are shown in Figure 3.

The overall geometry around the six-coordinate rhenium atom is described as an highly distorted octahedron, as can

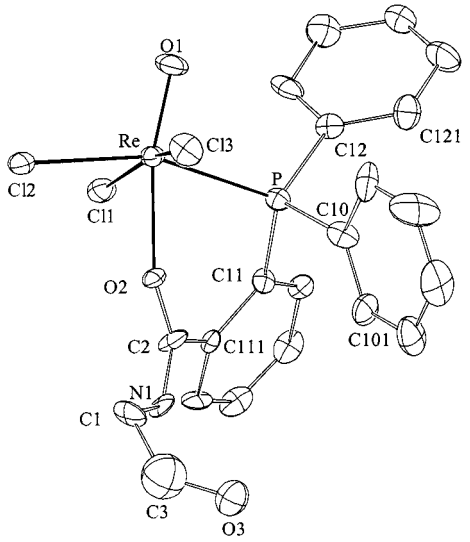


Figure 3. ORTEP drawing of complex **6** with the atom numbering scheme; thermal ellipsoids are drawn at the 30% probability level; selected mean bond lengths [Å] and angles [°]: Re−O(1) 1.659(10), Re−O(2) 2.133(10), Re−Cl(1) 2.367(5), Re−Cl(2) 2.377(4), Re−Cl(3) 2.355(4), Re−P 2.425(5), C(2)−O(2) 1.26(2), N(1)−C(2) 1.28(2), N(1)−C(1) 1.46(2), av. P−C 1.82(2); O(1)−Re−O(2) 167.2(5), O(1)−Re−Cl(1) 97.6(4), O(1)−Re−Cl(2) 107.5(4), O(1)−Re−Cl(3) 95.5(4), O(1)−Re−P 93.1(4), Cl(1)−Re−Cl(3) 166.1(2), Cl(2)−Re−Cl(3) 85.9(2), Cl(1)−Re−P 89.0(2), Cl(2)−Re−P 159.3(2), O(2)−Re−Cl(1) 85.3(4), Cl(3)−Re−P 94.9(2), Re−O(2)−C(2) 141.0(13), O(2)−C(2)−N(1) 121(2), O(2)−Re−P 74.5(3), C(2)−N(1)−C(1) 124.1(14), N(1)−C(2)−C(111) 118(2)

be seen by the bond angles around the Re atom. With the axial direction being defined along the Re=O bond, three equatorial positions are occupied by the chloride ions, whereas the fourth equatorial position is occupied by the phosphorous atom of the ligand. The equatorial plane deviates from planarity (atomic deviations from −0.091 to 0.087 Å), and the Re atom is displaced 0.34 Å towards the multiply bonded oxygen. The bidentate chelate forms a non-planar six-membered ring through the phosphorus and the carbonyl oxygen atoms bonded to the metal centre. The oxygen atom of the carbonyl group coordinates to the axial position *trans* to Re=O [O(1)−Re−O(2), 167.2(5)°].

As far as we are aware, this is the first structural characterization of an Re^V neutral adduct complex of the type $[Re(O)Cl_3(\kappa^2\text{-L})]$. For comparison, we have complexes with neutral monodentate ligands or with monoanionic bidentate ligands. The Re−O(1) bond length [1.659(10) Å] in **6** compares well with the values found in $[Re(O)Cl_3(Ph_3PO)(PPh_3)]$ [1.669(4)Å],[15] $[Re(O)Cl_3(PPh_3)(DMF)]$ [1.664(4) Å],[16] and in the anionic monooxorhenium(V) compound $[Re(O)Cl_3(PO)]^-$ [1.669(6) Å; PO = (2-hydroxyphenyl)diphenylphosphane].[7c] This distance in **6** is slightly shorter than the corresponding values 1.692(7) and 1.69(1) Å found in $[Re(O)(PN)_2(OEt)]$ and in the orthorhombic form of $[Re(O)(PN)_2Cl]$ [PN = (2-aminophenyl)diphenylphosphane], respectively.[6b]

The Re−P bond length [2.425(5) Å] compared well with the value found in the anionic monooxorhenium(V) compound $[Re(O)Cl_3(PO)]^-$ [2.422(2) Å] but is shorter than in $[Re(O)Cl_3(Ph_3PO)(PPh_3)]$ [2.506(2) Å], $[Re(O)(PN)_2(OEt)]$ [av. 2.494(3) Å] and in $[Re(O)(PN)_2Cl]$ [av. 2.450(5) Å].[7c,6b,15]

The Re−Cl bond length [av. Re−Cl, 2.366(5) Å] compares well with that found in $[Re(O)Cl_3(PO)]^-$ [av. 2.380(3) Å], but is shorter than in the Re^V complex containing two PN phosphane ligands $[Re(O)(PN)_2Cl]$ [2.422(6) Å].[6b,7c]

The shorter Re−P and Re−Cl bond lengths in complex **6**, relative to the corresponding bond lengths in the complexes mentioned above, are most likely due to steric factors, chelating mode of the ligands and nature of the atoms involved in the coordination with the rhenium centre. The *trans*-Re−O(2) (oxygen atom of the carbonyl group of the ligand) distance [2.133(10)Å] compares well with the value found in $[Re(O)Cl_3(PPh_3)(DMF)]$ [2.133(4)Å] for the bond between the oxygen atom of DMF and the metal centre.[16a] This bond length is considerably longer than that between the amide oxygen atom of MAG_1 (mercaptoacetyl glycine) and the rhenium atom in the complex $[Re(O)(MAG_1Et)_2]$ [2.051(5)Å].[16b] This difference is probably due to the different nature of the donor atoms of the ligands involved in the coordination sphere of the metal centre.

The severe problem of disorder in the terminal C(3)−O(3)H atoms prevents any discussion or comparison of bond lengths within the group, as can be seen by the large standard deviations. Nevertheless, we can say that there is no short intermolecular interaction involving the O(3) atom. An intermolecular interaction involving Cl(2)···N(1) atoms (distance of 3.272 Å) is observed in the packing of the molecules in the crystalline state.

Concluding Remarks

New tridentate heterofunctionalized phosphane ligands have been synthesised and fully characterized. No deprotonation of these ligands occurs under mild conditions when they react with $[n\text{Bu}_4\text{N}][Re(O)Cl_4]$. The new complexes formed are the neutral trichlorooxorhenium(V) adducts $[Re(O)Cl_3\{\kappa^2\text{-L}\}]$, which are rare examples of oxo complexes stabilized by neutral heterofunctionalized phosphane ligands. The rhenium atom is six-coordinate in an octahedral configuration with the oxo function *trans* to the oxygen atom of the carbonyl group and with the phosphorous atom in the equatorial position.

Experimental Section

General Procedures: All chemicals were of reagent grade. Ethylenediamine and ethanolamine were purchased from Aldrich and distilled prior to use. (1*R*,2*R*)-(−)-diaminocyclohexane was purchased from Aldrich and was used as received. The reactions were performed in air unless otherwise indicated. 2-(Diphenylphosphanyl)-benzoic acid and the complexes $[n\text{Bu}_4\text{N}][Re(O)Cl_4]$ (**1**) and $[Re(O)Cl_3(PPh_3)_2]$ (**2**) were prepared as reported in the literature.[20−22] ^{1}H- and ^{31}P-NMR spectra were recorded with a Varian Unity 300-MHz spectrometer; ^{1}H chemical shifts were referenced with the residual solvent resonance relative to tetramethylsilane and the ^{31}P chemical shifts were measured with an external H_3PO_4 solution

(85%) as a reference. Chemical shifts are given in ppm. The NMR samples were prepared in $CDCl_3$, CD_3CN or $(CD_3)_2SO$. Infrared spectra were recorded in the range 4000−200 cm^{-1} with a Perkin−Elmer 577 spectrometer using KBr pellets. Elemental analyses were performed with a Perkin−Elmer automatic analyser.

***N*-[2-(Diphenylphosphanyl)benzoyloxy]succinimide (3):** 2-(Diphenylphosphanyl)benzoic acid (1.00 g, 3.27 mmol) and *N*-hydroxysuccinimide (0.75 g, 6.54 mmol) were dissolved in dichloromethane (20 mL) at room temperature, and a solution of dicyclohexylcarbodiimide (1.35 g, 6.54 mmol) in dichloromethane was added dropwise. The reaction was complete after 3 h (TLC: ethyl acetate/hexane, 50:50). The formed urea was separated by filtration through a pad of Celite wetted with dichloromethane, and the filtrate concentrated to dryness. The resulting white residue was chromatographed on an appropriate column of silica gel with 20−35% ethyl acetate/hexane (gradient), to afford a white yellowish solid, which was further recrystallized from dichloromethane/hexane to give **3** in an analytical pure form. Yield 1.24 g (94%). − ^{1}H NMR ($CDCl_3$): δ = 2.81 (4 H, s, CH_2), 6.99 (1 H, m aromatic), 7.19−7.32 (9 H, m, aromatic), 7.45 (3 H, m, aromatic), 8.31 (1 H, m, aromatic). − ^{31}P NMR($CDCl_3$): δ = −4.4. − IR (KBr): $\tilde{\nu}$ = 1760 cm^{-1} (vs, C=O). − $C_{23}H_{18}NO_4P{\cdot}0.5CH_2Cl_2$ (445.8): calcd. C 63.31, H 4.30, N 3.14; found C 63.77, H 4.63, N 3.23.

[(1*R*,2*R*)-*N*-(2-Aminocyclohexyl)]-2-(diphenylphosphanyl)benzamide (L^1): *N*-[2-(Diphenylphosphanyl)benzoyloxy]succinimide (0.89 g, 2.20 mmol), dissolved in dichloromethane (10 mL), was added dropwise to a solution of (1*R*,2*R*)-(−)-diaminocyclohexane (0.50 g, 4.40 mmol) in the same solvent (25 mL). The reaction was complete after 3 h, as indicated by the TLC (ethyl acetate/hexane, 50:50). The mixture was washed with 25 mL of water and the organic phase was separated. The aqueous phase was extracted with dichloromethane (2 × 30 mL). The organic phases were collected, dried with $MgSO_4$, filtered and concentrated to dryness. The resulting viscous oil was recrystallized from dichloromethane/hexane, affording colourless crystals of $\mathbf{L^1}$. Yield 0.79 g (89%). − ^{1}H NMR ($CDCl_3$): δ = 0.85 (1 H, m, cyclohexyl), 1.17 (4 H, m, cyclohexyl), 1.65 (3 H, s, br., cyclohexyl), 1.89 (2 H, m, NH_2), 2.15 (1 H, m, C*H*NH_2), 3.60 (1 H, m, C*H*NH), 5.71 (1 H, d, NH), 6.92 (1 H, m, aromatic), 7.19−7.40 (12 H, m, aromatic), 7.62 (1 H, m, aromatic). − ^{31}P NMR($CDCl_3$): δ = −10.5. − ^{31}P NMR [$(CD_3)_2SO$]: δ = −9.6. − IR (KBr): $\tilde{\nu}$ = 3220 cm^{-1} (m, NH_2), 1630 cm^{-1} (vs, C=O). − $C_{25}H_{27}N_2OP$ (402.5): calcd. C 74.61, H 6.76, N, 6.96; found C 73.75, H 6.55, N 6.89.

***N*-(2-Aminoethyl)-2-(diphenylphosphanyl)benzamide (L^2):** *N*-[2-(Diphenylphosphanyl)benzoyloxy]succinimide (0.70 g, 1.74 mmol), dissolved in dichloromethane (10 mL), was added dropwise to a solution of ethylenediamine (0.25 mL, 3.70 mmol) in the same solvent. After 2 h (TLC: ethyl acetate/hexane, 50:50), the white precipitate was removed by filtration through a pad of Celite and the filtrate was concentrated to dryness. The resulting yellowish viscous oil was dissolved in the minimum amount of ethanol and water was added dropwise until no more white solid precipitated. The solid was recovered by filtration, washed twice with water and dried under vacuum, yielding $\mathbf{L^2}$ in an analytical pure form. Yield 0.45 g (74%). − ^{1}H NMR ($CDCl_3$): δ = 2.68 (2 H, t, CH_2), 3.30 (2 H, q, CH_2), 6.23 (1 H, s, br., NH), 6.92 (1 H, m, aromatic), 7.23−7.39 (12 H, m, aromatic), 7.59 (1 H, m, aromatic). − ^{31}P NMR ($CDCl_3$): δ = −9.3. − ^{31}P NMR (CD_3CN): δ = −8.6. − IR (KBr): $\tilde{\nu}$ = 3320 cm^{-1} (m, NH_2), 1630 cm^{-1} (vs, C=O). − $C_{21}H_{21}N_2OP{\cdot}H_2O$ (366.4): calcd. C 68.84, H 6.33, N 7.65; found C 69.61, H 6.08, N 8.17.

2-(Diphenylphosphanyl)-*N*-(2-hydroxyethyl)benzamide (L^3): *N*-[2-(Diphenylphosphanyl)benzoyloxy]succinimide (3.30 g, 8.20 mmol), dissolved in dichloromethane (20 mL), was added dropwise to a solution of ethanolamine (1.08 mL, 19.60 mmol) in the same solvent (45 mL). After 3 h (TLC: ethyl acetate/hexane, 50:50), the white solid, which precipitated, was eliminated by filtration through a pad of Celite and the filtrate was concentrated to dryness. The resulting yellowish viscous oil afforded a white solid after drying for several hours under vacuum. The compound was washed with water and recovered by filtration. After drying, $\mathbf{L^3}$ was obtained in an analytical pure form. Yield 2.50 g (87%). − ^{1}H NMR ($CDCl_3$): δ = 3.39 (2 H, q, CH_2), 3.59 (2 H, t, CH_2), 6.27 (1 H, s, br., NH), 6.94 (1 H, m, aromatic), 7.24−7.39 (12 H, m, aromatic), 7.59 (1 H, m, aromatic). − ^{31}P NMR ($CDCl_3$): δ = − 9.9. − ^{31}P NMR (CD_3CN): δ = − 8.4. − IR (KBr): $\tilde{\nu}$ = 3310 cm^{-1} (m, OH), 1630 cm^{-1} (vs, C=O). − $C_{21}H_{20}NO_2P$ (349.1): calcd. C 72.18, H 5.77, N 4.01; found C 71.74, H 6.56, N 4.25.

[{(1*R*,2*R*)-*N*-(2-Aminocyclohexyl)}-2-(diphenylphosphanyl)benzamide]trichlorooxorhenium(V), $[Re(O)(\kappa^2\text{-}L^1)Cl_3]{\cdot}HCl$ (4): L^1 (0.068 g, 0.17 mmol), dissolved in MeOH (5 mL), was added dropwise to a solution of **1** (0.10 mg, 0.17 mmol) in MeOH (10 mL). The reaction turned brown immediately and within a few minutes turned green. After 3 h at room temperature, the solution was concentrated to dryness giving an highly viscous oil. After washing several times with dichloromethane, a light blue solid precipitated, which was vacuum-dried. Yield 0.066 g (52%). − ^{31}P NMR: [$(CD_3)_2SO$]: δ = −17.2, 32.9. − IR (KBr): $\tilde{\nu}$ = 1570 cm^{-1} (vs, C=O), 1000 cm^{-1} (vs, Re=O), 320 cm^{-1} (m, Re−Cl). − $C_{25}H_{28}Cl_4N_2O_2PRe$ (747.5): calcd. C 40.17, H 3.78, N 3.75; found C 40.18, H 3.68, N 3.81.

[*N*-(2-Aminoethyl)-2-(diphenylphosphanyl)benzamide]trichlorooxorhenium(V), $[Re(O)(\kappa^2\text{-}L^2)Cl_3]{\cdot}HCl$ (5): Compound **5** was prepared in a similar manner to **4**. $\mathbf{L^2}$ (0.20 g, 0.58 mmol) and **1** (0.34 g, 0.58 mmol) were allowed to react to form a light green solid, **5**. Yield 0.23 g (58%). Single crystals of poor quality for X-ray crystallographic analysis were obtained by recrystallization of **5** from boiling acetonitrile. − ^{1}H NMR (CD_3CN): δ = 2.98 (2 H, s, br., CH_2), 3.45 (2 H, s, br, CH_2), 7.16 (1 H, m, aromatic), 7.52−7.80 (12 H, m, aromatic), 8.68 (1 H, t, br., aromatic), 11.48 (1 H, s, br., NH). − ^{1}H NMR [$(CD_3)_2SO$]: δ = 2.82 (2 H, m, CH_2), 3.26 (2 H, m, CH_2), 7.09 (1 H, m, aromatic), 7.48−7.66 (8 H, m, aromatic), 7.84 (2 H, m, aromatic), 8.08 (2 H, s, br., aromatic), 8.54 (1 H, m, aromatic), 11.42 (1 H, s, br., NH). − ^{31}P NMR (CD_3CN): δ = −15.4. − ^{31}P NMR [$(CD_3)_2SO$]: δ = −18.1. − IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1} (vs, C=O), 1000 cm^{-1} (vs, Re=O), 320 cm^{-1} (s, Re−Cl). − $C_{21}H_{22}Cl_4N_2O_2PRe$ (691.9): calcd. C 36.42, H 3.20, N 4.05; found C 36.02, H 2.60, N 3.74.

Trichloro[2-(diphenylphosphanyl)-*N*-(2-hydroxyethyl)benzamide]-oxorhenium(V), $[Re(O)(\kappa^2\text{-}L^3)Cl_3]$ (6). − Method a: L^3 (0.10 g, 0.29 mmol), dissolved in MeOH (5 mL), was added dropwise to a solution of **1** (0.17 g, 0.29 mmol) in MeOH (10 mL). The reaction turned dark green immediately, then violet-blue and finally bright green. A dark green solid precipitated which was then isolated by filtration, washed 3 times with MeOH and vacuum-dried. Complex **6** was obtained in an almost quantitative yield. − **Method b:** A suspension of complex **2** (0.092 g, 0.11 mmol) in dry dichloromethane (25 mL) was treated with $\mathbf{L^3}$ (0.040 g, 0.11 mmol) under an inert atmosphere. Within a few minutes a green reaction mixture was obtained. After 1 h, a dark green solid started to precipitate. The reaction was allowed to proceed for 18 h. The solid was then isolated by filtration and washed 3 times with dry dichloromethane. Single crystals, suitable for X-ray crystallographic analysis, were

Table 1. Crystal data and structure refinement of **L[1]** and **6**

	L[1]	**6**
Empirical formula	$C_{25}H_{27}N_2OP$	$C_{21}H_{20}Cl_3NO_3PRe{\cdot}CH_3CN$
M	402.46	698.95
Crystal size [mm]	0.70 × 0.54 × 0.18	0.34 × 0.12 × 0.11
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a [Å]	12.808(2)	8.0460(8)
b [Å]	15.193(2)	10.7286(10)
c [Å]	18.105(3)	30.116(3)
β [°]	106.544(14)	
V [Å^3]	3377.2(9)	2599.7(4)
Z	6	4
T [K]	293(2)	293(2)
D_c [g cm^{-3}]	1.187	1.786
μ(Mo-K_α) [mm^{-1}]	0.140	5.071
F(000)	1284	1360
No. reflections measured	6386	4566
No. unique reflections	6180 (0.0325)[a]	4311 (0.0972[a])
$R1$[b]	0.0670	0.0702
wR_2[b]	0.1085	0.0836

[a] Value of *R*(int). – [b] The values were calculated for data with $I > 2\sigma(I)$ only.

obtained by recrystallization from boiling CH_3CN. Yield 0.040 g (55%). – ^{1}H NMR (CD_3CN): δ = 3.16 (2 H, m, CH_2), 3.38 (2 H, t, CH_2), 7.14 (1 H, m, aromatic), 7.51–7.81 (12 H, m, aromatic), 8.03 (1 H, t, br., aromatic), 9.08 (1 H, s, br., NH). – ^{1}H NMR [$(CD_3)_2SO$]: δ = 3.09 (2 H, m, CH_2), 3.26 (2 H, m, CH_2), 7.06 (1 H, m, aromatic), 7.46–7.88 (12 H, m, aromatic), 8.23 (1 H, m, aromatic), 10.92 (1 H, s, br., NH). – ^{31}P NMR (CD_3CN): δ = −16.5. – ^{31}P NMR: [$(CD_3)_2SO$]: δ = – 18.1. – IR (KBr): $\tilde{\nu}$ = 3250 cm^{-1} (w, OH), 1590 cm^{-1} (vs, C=O), 1000 cm^{-1} (vs, Re=O), 315 cm^{-1} (s, Re–Cl). – $C_{21}H_{20}Cl_3NO_3PRe$ (657.9): calcd. C 38.34, H 3.06, N 2.13; found C 37.97, H 2.90, N 1.97.

X-ray Crystallographic Analysis: A colourless crystal of **L[1]** and a dark green crystal of **6** were fixed inside thin-walled glass capillaries. Data were collected at room temperature with an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo-K_α radiation, using an ω-2θ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with 16.6° < 2θ < 24.0° for **L[1]**, and 16.2° <2θ< 29.7° for **6**. A summary of the crystallographic data is given in Table 1. Data were corrected[23] for Lorentz polarization effects, for linear decay (no decay was observed for **L[1]**, and a decay of 16.7% was observed for **6**) and for absorption by empirical corrections based on ψ scans. The structures were solved by Patterson methods[24] and subsequent difference Fourier techniques and refined by full-matrix least-squares procedures on F^2 using SHELXL93[25]. For **6**, an acetonitrile solvent molecule of crystallization was also located in the Fourier difference map. During the isotropic refinement of **6** the terminal C(3)–O(3) atoms showed rather large thermal parameters and were found to be disordered over two different positions with 0.52 and 0.48 occupancies. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters, with isor restraints being applied to the disordered atoms. The contributions of the hydrogen atoms were included in calculated positions [except that of the disordered O(3)H atom]. The absolute configuration of both crystals studied were determined by refinement of the Flack parameters, and the refined models proved to be the correct enantiomorphs. A final Fourier difference synthesis was featureless for **L[1]**, and revealed residual electron densities of +1.11 and −1.27 e.Å^{-3} for **6** without any chemical meaning. Atomic scattering factors and anomalous dispersion terms were taken as in ref.[25] The ORTEP drawings were made with ORTEP II[26] and all calculations were performed with a Decα 3000 computer. A summary of the crystal data and of the refinement procedures is given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137148 (**L[1]**) and -137149 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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