Uncommon Anionic Dioxorhenium(V) and Neutral Monooxorhenium(V) Mixed-Ligand Complexes Containing Heterofunctionalized Phosphine Ligands: Syntheses and Structural Characterization

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The potentially bidentate hybrid ligand (*o*-hydroxyphenyl)diphenylphosphine, abbreviated POH, reacted *via* ligand-exchange with pentavalent rhenium precursors to give a series of six-coordinate mono- and dioxo complexes. Accurate control of the metal:ligand stoichiometric ratio allowed for the isolation of the mono-substituted $[ReOCl_3(PO)]^-$ (**1**) and $[ReOCl_2(PO)(PPh_3)]$ (**2**) derivatives. **1** was found to be the key intermediate for the syntheses of three more types of bis-substituted compounds: anionic dioxo $[ReO_2(PO)_2][A]$ (A = NBu_4 (**3**), $AsPh_4$ (**4**)), neutral monooxo $[ReOX(PO)_2]$ (X = Cl (**5**), Br (**6**), I (**7**)), and neutral monooxo mixed-ligand [ReOX(PO)(PNH)] [PNH = (*o*-amidophenyl)diphenylphosphine; X = Cl (**8**), Br (**9**), I (**10**)] complexes. In the mono-substituted complexes, the P,O-donors of the bidentate ligand spanned an equatorial (P) and the apical position (O) *trans* to the Re═O linkage in a distorted octahedral arrangement. In all of the bis-substituted monooxo compounds, the second chelate ligated on the equatorial plane almost orthogonally positioned with respect to the first one, the two phosphorus donors showing a mutual *cis*-(P,P) orientation. Dioxo complexes retained the *cis*-(P,P) configuration with the bidentate ligands symmetrically coordinated on the equatorial plane normal to the *trans*-ReO_2 core. All the complexes were characterized by various physical techniques, including IR, MS, and $^1H/^{31}P\{^1H\}$ NMR. The X-ray structure of a representative compound for each category, namely $[ReOCl_3(PO)][NBu_4]$ (**1**), $[ReO_2(PO)_2][AsPh_4]$ (**4**), $[ReOCl(PO)_2]$ (**5**), and [ReOCl(PO)(PNH)] (**8**), were determined. Crystals of **1** were monoclinic, $P2_1/n$, $a = 10.840(3)$ Å, $b = 22.167(6)$ Å, $c = 15.210(4)$ Å, $\beta = 95.91(2)°$, and $Z = 4$; those of **4** were triclinic, $P\bar{1}$, $a = 12.679(7)$ Å, $b = 13.082(7)$ Å, $c = 19.649(8)$ Å, $\alpha = 82.64(4)°$, $\beta = 81.16(4)°$, $\gamma = 62.27(3)°$, and $Z = 2$; those of **5** were orthorhombic, $a = 10.225(4)$ Å, $b = 14.208(6)$ Å, $c = 21.771(9)$ Å, $P2_12_12_1$, and $Z = 4$; and those of **8** were orthorhombic, $a = 10.199(2)$ Å, $b = 14.147(4)$ Å, $c = 21.772(6)$ Å, $P2_12_12_1$, and $Z = 4$. The four structures were solved by the Patterson method and refined by full-matrix least-squares procedures to $R = 0.050$, 0.063, 0.043, and 0.039 for **1**, **4**, **5** and **8**, respectively. Both solution state ($^{31}P\{^1H\}$ NMR) and solid state (X-ray) demonstrated a *cis*-(P,P) arrangement for each bis-substituted complex, with the Re atom at the center of a highly distorted octahedron. Detailed analyses of the IR spectra of this series of Re(V) compounds in the region 900−580 cm^{-1} allowed us the possibility to distinguish between symmetrical and asymmetrical bis-substituted complexes.

Introduction

In the framework of our ongoing interest in Tc and Re coordination chemistry,[1] we have synthesized a number of functionalized phosphine ligands which combine a soft phosphorus donor with a hard nitrogen or oxygen donor. These heterofunctionalized ligands act as reducing agents toward the permetalate salts $[MO_4]^-$ (M = Tc, Re) and also as chelate agents, thereby generally stabilizing the metal in intermediate oxidation states (III−V).[2] (*o*-Hydroxyphenyl)diphenylphosphine, abbreviated POH, and (*o*-aminophenyl)diphenylphosphine, abbreviated PNH_2, represent two prototypical examples of fully aromatic bidentate hybrid ligands in which the presence of an anchoring anionic oxygen or nitrogen atom enhances the coordination ability of tertiary phosphines. These are spontaneously able to form stable complexes with Tc and Re in various oxidation states,[3] mainly in conjunction with halide co-ligands. In the recent past, the reactivity of PNH_2 with Tc and Re has been thoroughly investigated by our research group: a number of oxo−M(V) complexes of the type $[MO(PNH)_2(X)]$ (M = Tc, Re; X = monodentate nucleophile such as halide or alkoxo)[4] and homoleptic $[M^{III}(PNH)_3]$ complexes[5] have been fully characterized.

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The coordination of at least two anionic phosphinoamido ligands, either in a symmetrical (*i.e.* two chelates ligated on the equatorial plane of a distorted octahedron in $[MO(PNH)_2(X)]$ species termed "equatorial") or asymmetrical (*i.e.* two chelates orthogonally positioned each other in the isomeric form $[MO(PNH)_2(X)]$ termed "twisted") fashion, appeared to be the common feature in all oxo−M(V) compounds. The twisted geometry has been also suggested by other authors[6] in solution for bis-substituted P,O-derivatives in $[MOCl(PO)_2]$ species, according to ^{31}P NMR spectroscopy, and confirmed in the solid state *via* structural characterization of the technetium complex.[7]

In this paper we report on a detailed study of the reactivity of POH with pentavalent oxo−rhenium precursors. A remarkable result was the obtainment of: (*i*) a stable anionic dioxo derivative, $[ReO_2(PO)_2]^-$, which represents, to our knowledge, one of the rare examples of an anionic dioxo−Re(V) compounds[8] and (*ii*) stable monooxo−Re(V) complexes containing a mixed-ligand coordination sphere as a combination of two bidentate heterofunctionalized phosphines. The isolation of a P,O mono-substituted species has revealed to be the key intermediate for the syntheses of different classes of bis-substituted species. The recent availability of large clinical-scale $^{188}W/^{188}Re$ generators,[9] functionally identical to the currently used $^{99}Mo/^{99m}Tc$, makes inorganic chemistry studies on stable Re(V) complexes very attractive for the potential application of these species as therapeutic radiopharmaceuticals based on the ^{188}Re isotope.[10]

Experimental Section

Materials. Unless otherwise noted, all chemicals were of reagent grade and were used as received. (*o*-Hydroxyphenyl)diphenylphosphine[11] (POH) and (*o*-aminophenyl)diphenylphosphine[12] (PNH_2) were prepared according to published procedures. $[(n\text{-}Bu)_4N][ReOCl_4]$ and $[ReOCl_3(PPh_3)_2]$ were prepared as previously reported[13] starting from metallic rhenium, which was obtained as a gift from H. C. Starck GmbH, Goslar, Germany.

Instrumentation. Elemental analyses (C, H, N) were performed on a Fisons EA 1108 elemental analyzer. IR spectra were recorded on a Mattson 3030 Fourier-transform spectrometer (4000−400 cm^{-1}) using KBr pellets. ^1H and ^{31}P NMR spectra were collected on a Bruker AC-200 instrument, using $SiMe_4$ as internal reference (^1H) and 85% aqueous H_3PO_4 as external reference (^{31}P). UV−vis spectra were recorded in CH_2Cl_2 using a Cary 17D spectrophotometer (700−220 nm). Conductivity measurements were made in MeCN or MeCN:CH_2Cl_2 (90:10) mixtures at 25 °C using a Metrohm Herison E518 conductimeter. Electron impact (EI) or fast atom bombardment in the positive mode (FAB^+) mass spectra were recorded on a VG ZAB-2F spectrometer.

Synthesis of the Complexes. $[(n\text{-}Bu)_4N][ReOCl_3(PO)]$, 1. Solid POH (0.050 g, 0.18 mmol) was added to a solution of $[(n\text{-}Bu)_4N][ReOCl_4]$ (0.104 g, 0.18 mmol) dissolved in acetonitrile (5 mL) under stirring. The solution immediately turned from yellow-green to emerald green. After 1 h of stirring at room temperature, addition of diethyl ether (20 mL) afforded an emerald-green solid which was filtered off and dried under vacuum. No recrystallization was necessary to obtain a pure sample (yield 95%). **1** is soluble in chlorinated solvents, acetonitrile, and acetone and insoluble in alcohols and diethyl ether. Anal. Calcd for $C_{34}H_{50}O_2NPCl_3Re$: C, 49.30; H, 6.08; N, 1.69. Found: C, 48.95; H, 5.91; N, 1.64. IR (KBr, cm^{-1}): 3054 (w), 2960 (m), 2872 (m), 1583 (m), 1440 (s), 1273 (s), 1099 (m), 964 (s) [ν(Re=O)], 855 (s), 775 (m), 749 (m), 710 (m), 693 (m), 607 (m), 518 (m). Λ_M (CH_3CN): 121.3 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). UV−vis [CH_2Cl_2, nm (ϵ)]: 640 (105), 370 (2350), 290 (sh). ^1H NMR ($CDCl_3$, ppm): δ 0.90 (t, 12H), 1.31 (quint, 8H), 1.53 (mult, 8H) 3.19 (mult, 8H), 6.45−7.90 (14H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ −8.57 (s). FAB^+ (*m/z*, %): 551 (M + 2H − Cl, 100), 516 (M + 2H − 2Cl, 76). Crystals suitable for X-ray analysis were grown from an acetonitrile/diisopropyl ether solution.

$[ReOCl_2(PO)(PPh_3)]$, 2. Solid POH (0.042 g, 0.15 mmol) was added to a suspension of $[ReOCl_3(PPh_3)_2]$ (0.124 g, 0.15 mmol) in benzene (10 mL) under stirring. The mixture was then refluxed for 1 h under a nitrogen atmosphere. After cooling, the clear green solution deposited a green solid, which was filtered off, washed with ethanol and diethyl ether, and dried under vacuum (yield 92%). **2** is soluble in chlorinated solvents, partially soluble in benzene, and insoluble in alcohols, acetonitrile, acetone, and diethyl ether. Anal. Calcd for $C_{36}H_{29}O_2P_2Cl_2Re$: C, 53.21; H, 3.60. Found: C, 53.49; H, 3.53. IR (KBr, cm^{-1}): 3056 (w), 1583 (m), 1442 (s), 1268 (s), 1095 (s), 961 (s) [ν(Re=O)], 859 (s), 753 (s), 691 (s), 622 (m), 520 (s). Λ_M (CH_2Cl_2/CH_3CN): 7.3 Ω^{-1} cm^2 mol^{-1} (neutral). UV−vis [CH_2Cl_2, nm (ϵ)]: 490 (130), 375 (3170), 300 (sh), 260 (sh). ^1H NMR ($CDCl_3$, ppm): δ 6.00 (dd, 1H), 6.75−7.60 (mult, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ −5.20 (d), 1.67 (d) $^2J_{PP}$ = 12 Hz. EI (*m/z*, %): 480 (M − 2Cl − PPh_3, 100), 464 (M − 2Cl − PPh_3 − O, 14).

$[(n\text{-}Bu)_4N][ReO_2(PO)_2]$, 3. **1** (0.084 g, 0.10 mmol) was dissolved in acetonitrile (5 mL). To this emerald green solution were added solid POH (0.028 g, 0.10 mmol) and 0.2 M sodium ethoxide (2 mL) under stirring, and the reaction mixture was left to react at room temperature overnight. The solvent was removed from the yellow mixture by a gentle stream of dinitrogen and the residue treated with dichloromethane (10 mL) and water (10 mL). The two-phase mixture was transferred into a dropping funnel and the organic phase collected and reduced to dryness. The resulting yellow solid was dissolved in ethanol (2 mL) and treated with *n*-hexane (20 mL), affording a pure pale yellow solid, which was separated by filtration and washed twice with *n*-hexane (yield 82%). **3** is soluble in the most common organic solvents, slightly soluble in diethyl ether, and insoluble in alkanes. Anal. Calcd for $C_{52}H_{64}O_4NP_2Re$: C, 61.51; H, 6.35. Found: C, 60.98; H, 6.50. IR (KBr, cm^{-1}): 3050 (w), 2959 (m), 2872 (m), 1584 (m), 1438 (s), 1303 (s), 1101 (m), 907 (m), 847 (m), 776 (s) [ν(O=Re=O)], 749 (m), 690 (m), 601 (m), 497 (m). Λ_M (CH_3CN): 116.0 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). UV−vis [CH_2Cl_2, nm (ϵ)]: 310 (7060). ^1H NMR ($CDCl_3$, ppm): δ 0.72 (t, 12H), 1.05 (mult, 8H), 1.31 (mult, 8H) 3.07 (mult, 8H), 6.50−7.60 (28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 4.50 (s). FAB^+ (*m/z*, %): 774 (M + 2H, 32), 758 (M + 2H − O, 100), 497 (M + 2H − PO, 92).

$[AsPh_4][ReO_2(PO)_2]$, 4. This complex can be prepared as described for the tetrabutylammonium derivative **3** starting from $[AsPh_4][ReOCl_4]$ through the isolation of the intermediate complex $[AsPh_4][ReOCl_3(PO)]$ (yield 70%). Anal. Calcd for $C_{60}H_{48}O_4P_2AsRe$: C, 62.33; H, 4.18. Found: C, 61.23; H, 4.48. IR (KBr, cm^{-1}): 3053 (w), 1583 (m), 1436 (s), 1304 (s), 1100 (m), 847 (m), 781 (s) [ν(O=Re=O)], 745 (m), 690 (m), 601 (m), 500 (m). Λ_M (CH_3CN): 105.1 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). UV−vis [CH_2Cl_2, nm (ϵ)]: 310 (7060). ^1H NMR ($CDCl_3$, ppm): δ 6.40−7.70. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 4.89 (s). Crystals suitable for X-ray analysis were grown from an ethanol/diisopropyl ether solution.

$[ReOCl(PO)_2]$, 5. Solid POH (0.095 g, 0.34 mmol) was added to a solution of $[(n\text{-}Bu)_4N][ReOCl_4]$ (0.099 g, 0.17 mmol) dissolved in ethanol (5 mL) under stirring. The reaction mixture was refluxed for

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Table 1. Crystallographic Data for the Structure Determinations of $[ReOCl_3(PO)][NBu_4]$ (**1**), $[ReO_2(PO)_2][AsPh_4]\cdot{}^1/_2EtOH\cdot{}^1/_2Me_2CO$ (**4**), $[ReOCl(PO)_2]$ (**5**), and [ReOCl(PO)(PNH)] (**8**)

	1	4	5	8
empirical formula	$C_{34}H_{50}Cl_3NO_2PRe$	$C_{60}H_{48}AsO_4P_2Re\cdot{}^1/_2EtOH\cdot{}^1/_2Me_2CO$	$C_{36}H_{28}ClO_3P_2Re$	$C_{36}H_{29}ClNO_2P_2Re$
a, Å	10.840(3)	12.679(7)	10.225(4)	10.199(2)
b, Å	22.167(6)	13.082(7)	14.208(6)	14.147(4)
c, Å	15.210(4)	19.649(8)	21.771(9)	21.772(6)
α, deg		82.64(4)		
β, deg	95.91(2)	81.16(4)		
γ, deg		62.27(3)		
V, Å^3	3635(2)	2845(2)	3163(2)	3141(1)
Z	4	2	4	4
space group	$P2_1/n$, No. 14	$P\bar{1}$, No. 2	$P2_12_12_1$, No. 19	$P2_12_12_1$, No. 19
D_{calc}, g/cm^3	1.513	1.409	1.664	1.673
μ, cm^{-1}	36.4	28.2	40.6	40.9
λ(MoKα), Å	0.710 73	0.710 73	0.710 73	0.710 73
T, K	294	294	294	294
no. obsd reflns	4134	2598	2101	2060
R^a	0.050	0.063	0.043	0.039
w$R2^b$	0.129	0.153	0.084	0.104
GOF^c	0.994	1.077	0.949	0.858

^{a} $R = \sum||F_c| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum(w(|F_o|^2 - |F_c|^2)^2)/\sum(w|F_o^2)]^{1/2}$. ^{c} $GOF = [\sum(w(|F_o|^2 - |F_c|^2)^2]/(n - p)]^{1/2}$.

30 min during which a bottle-green solid was deposited. It was then isolated by filtration, washed with ethanol and diethyl ether, and dried under vacuum. (yield 90%). **5** is soluble in chlorinated solvents and insoluble in acetonitrile, alcohols, and diethyl ether. Anal. Calcd for $C_{36}H_{28}O_3P_2ClRe$: C, 54.63; H, 3.56. Found: C, 54.23; H, 3.70. IR (KBr, cm^{-1}): 3056 (w), 1583 (m), 1439 (s), 1261 (s), 1097 (m), 959 (s) [ν(Re═O)], 854 (s), 766 (m), 745 (m), 709 (m), 692 (m), 645 (m), 610 (m), 495 (m). Λ_M (CH_2Cl_2/CH_3CN): 6.4 $\Omega^{-1}m^2$ mol^{-1} (neutral). UV−vis [CH_2Cl_2, nm (ϵ)]: 610(175), 390 (3390), 290 (sh), 270 (sh). ^{1}H NMR ($CDCl_3$, ppm): δ 5.95−7.70. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 13.83 (d), 0.64 (d) $^2J_{PP}$ = 10 Hz. EI (*m/z*, %): 790 (M, 100), 755 (M − Cl, 21), 513 (M − PO, 42), 478 (M − Cl − PO, 13). Crystals suitable for X-ray analysis were grown from a dichloromethane/acetonitrile solution.

[ReOBr(PO)$_2$], 6. **3** (0.030 g, 0.03 mmol) was dissolved in acetonitrile (3 mL) at room temperature producing a clear yellow solution. Addition of two drops of 48% HBr afforded dark-brown microcrystals of the desired product within 1 h. They were filtered off, washed with two portions of diethyl ether (2 mL), and dried under vacuum (yield 85%). **6** is soluble in chlorinated solvents only. Anal. Calcd for $C_{36}H_{28}O_3P_2BrRe$: C, 51.68; H, 3.37. Found: C, 52.06; H, 3.41. IR (KBr, cm^{-1}): 3053 (w), 1582 (m), 1439 (s), 1260 (s), 1097 (m), 957 (s) [ν(Re═O)], 852 (s), 766 (m), 741 (m), 709 (m), 693 (m), 642 (m), 610 (m), 494 (m). Λ_M (CH_2Cl_2/CH_3CN): 9.8 Ω^{-1} cm^2 mol^{-1} (neutral). UV−vis [CH_2Cl_2, nm (ϵ)]: 620(200), 400 (3690), 300 (sh), 270 (sh). ^{1}H NMR ($CDCl_3$, ppm): δ 5.95−7.75. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 14.29 (d), −0.02 (d) $^2J_{PP}$ = 10 Hz. EI (*m/z*, %): 835 (M, 56), 755 (M − Br, 100), 478 (M − Br − PO, 6).

[ReOI(PO)$_2$], 7. This complex was prepared as **6** except for the use of 57% HI (yield 80%). **7** is soluble in chlorinated solvents only. Anal. Calcd for $C_{36}H_{28}O_3P_2IRe$: C, 48.93; H, 3.19. Found: C, 47.99; H, 3.43. IR (KBr, cm^{-1}): 3052 (w), 1582 (m), 1439 (s), 1259 (s), 1099 (m), 956 (s) [ν(Re═O)], 852 (s), 765 (m), 744 (m), 709 (m), 692 (m), 640 (m), 610 (m), 493 (m). Λ_M (CH_2Cl_2/CH_3CN): 8.7 Ω^{-1} cm^2 mol^{-1} (neutral). UV−vis [CH_2Cl_2, nm (ϵ)]: 640(130), 420 (3160), 355 (5300), 275 (sh). ^{1}H NMR ($CDCl_3$, ppm): δ 5.90−7.80. $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 13.38 (d), −1.04 (d) $^2J_{PP}$ = 10 Hz. EI (*m/z*, %): 882 (M, 4), 755 (M − I, 100), 478 (M − I − PO, 27).

[ReOCl(PO)(PNH)], 8. Solid POH (0.063 g, 0.22 mmol) was added to a solution of [(n-Bu)$_4$N][$ReOCl_4$] (0.132 g, 0.22 mmol) dissolved in acetonitrile (10 mL) under stirring. To this solution, which immediately turned from yellow-green to emerald green, additional PNH_2 (0.062 g, 0.22 mmol) was added and the mixture was left to stir overnight at room temperature. A brown precipitate was collected by filtration, washed with acetonitrile, ethanol, and diethyl ether, and dried under vacuum. No recrystallization was necessary to obtain a pure sample (yield 82%). **8** is soluble in chlorinated solvents, insoluble in acetonitrile, alcohols and diethyl ether. Anal. Calcd for $C_{36}H_{29}O_2NP_2ClRe$: C, 54.77; H, 3.57; N, 1.77. Found: C, 54.10; H, 3.70; N, 2.09. IR (KBr, cm^{-1}): 3355(w) [ν(N−H)], 3055 (w), 1583 (m), 1441 (s), 1302 (m), 1097 (m), 941 (s) [ν(Re═O)], 853 (m), 760 (m), 745 (s), 691 (s), 640 (m), 611 (m), 490 (m). Λ_M (CH_3CN): 8.9 Ω^{-1} cm^2 mol^{-1} (neutral). UV−vis [CH_2Cl_2, nm (ϵ)]: 590 (350), 395 (8920), 320 (9770), 270 (sh). ^{1}H NMR ($CDCl_3$, ppm): δ 5.85−7.75 (28H), 10.68 (s, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 20.93 (d), −2.77 (d) $^2J_{PP}$ = 10 Hz. EI (*m/z*, %): 789 (M, 75), 754 (M − Cl, 100), 512 (M − PO, 35). Crystals suitable for X-ray analysis were grown from a dichloromethane/acetonitrile mixture.

[ReOX(PO)(PNH)], (X = Br, 9; I, 10). Neat ethylene glycol (0.5 mL) and three drops of neat triethylamine were added to a solution of [(n-Bu)$_4$N][$ReOCl_4$] (0.169 g, 0.29 mmol), dissolved in ethanol (10 mL) under stirring at room temperature. To this violet mixture were added solid POH (0.081 g, 0.29 mmol) followed by solid PNH_2 (0.077 g, 0.28 mmol). The mixture was left to stir at room temperature for 2 h until an orange solid was deposited. It was filtered off and washed with a few drops of ethanol and diethyl ether. The orange powder[14] was then redissolved in ethanol (4 mL) and treated with 3 drops of 1 M HBr (or 1 M HI). A brown microcrystalline solid formed within 30 min. It was filtered off and washed with ethanol and diethyl ether, and dried under vacuum (yield 55%).

[ReOBr(PO)(PNH)] 9 (Yield 51%). **9** is soluble in chlorinated solvents, insoluble in acetonitrile, alcohols and diethyl ether. Anal. Calcd for $C_{36}H_{29}O_2NP_2BrRe$: C, 51.85; H, 3.38; N, 1.67. Found: C, 51.07; H, 3.28; N, 1.74. IR (KBr, cm^{-1}): 3350(w) [ν(N−H)], 3056 (w), 1583 (m), 1441 (s), 1302 (m), 1096 (m), 940 (s) [ν(Re═O)], 853 (m), 760 (m), 744 (s), 691 (s), 638 (m), 611 (m), 491 (m). Λ_M (CH_3CN): 10.1 Ω^{-1} cm^2 mol^{-1} (neutral). UV−vis [CH_2Cl_2, nm (ϵ)]: 590 (515), 395 (9620), 320 (11090), 270 (sh). ^{1}H NMR ($CDCl_3$, ppm): δ 5.85−7.75 (28H), 10.88 (s, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 21.08 (d), −3.69 (d) $^2J_{PP}$ = 10 Hz. EI (*m/z*, %): 833 (M, 32), 754 (M − Br, 100), 556 (M − PO, 12).

[ReOI(PO)(PNH)], 10 (Yield 44%). **10** is soluble in chlorinated solvents only. Anal. Calcd for $C_{36}H_{29}O_2NP_2IRe$: C, 49.08; H, 3.20; N, 1.59. Found: C, 48.60; H, 2.95; N, 1.42. IR (KBr, cm^{-1}): 3347(w) [ν(N−H)], 3054 (w), 1583 (m), 1441 (s), 1303 (m), 1096 (m), 940 (s) [ν(Re═O)], 853 (m), 758 (m), 744 (s), 692 (s), 635 (m), 612 (m), 491 (m). Λ_M (CH_3CN): 10.5 Ω^{-1} cm^2 mol^{-1} (neutral). UV−vis [CH_2Cl_2, nm (ϵ)]: 600 (550), 400 (12390), 320 (13050), 270 (sh). ^{1}H NMR ($CDCl_3$, ppm): δ 5.80−7.75 (28H), 11.12 (s, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 20.10 (d), −5.40 (d) $^2J_{PP}$ = 10 Hz. EI (*m/z*, %): 881 (M, 9), 754 (M − I, 100), 477 (M − I − PO, 21).

X-ray Crystallographic Studies. The experimental X-ray data for **1**, **4**, **5**, and **8** are summarized in Table 1, and some selected bond

(14) This orange powder contains a mixture of monooxo mixed ligand complexes (^{1}H and ^{31}P NMR) with both bidentate chelates equatorially coordinated on the plane orthogonal to the Re═O moiety. The sixth site (*trans* to the Re═O linkage) is labile and can accommodate various monodentate nucleophiles (see ref 1d).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[ReOCl_3(PO)][NBu_4]$ (**1**)

Re−Cl(1)	2.398(3)	Re−O(2)	2.016(6)
Re−Cl(2)	2.374(3)	P(1)−C(1)	1.780(8)
Re−Cl(3)	2.369(2)	P(1)−C(1a)	1.794(8)
Re−P(1)	2.422(2)	P(1)−C(1b)	1.818(8)
Re−O(1)	1.669(6)	O(2)−C(6)	1.32(1)
Cl(1)−Re−Cl(2)	168.7(1)	Cl(3)−Re−P(1)	165.7(1)
Cl(1)−Re−Cl(3)	87.4(1)	Cl(3)−Re−O(1)	106.4(2)
Cl(1)−Re−P(1)	92.2(1)	Cl(3)−Re−O(2)	89.6(2)
Cl(1)−Re−O(1)	94.1(3)	P(1)−Re−O(1)	87.9(2)
Cl(1)−Re−O(2)	82.9(2)	P(1)−Re−O(2)	76.1(2)
Cl(2)−Re−Cl(3)	85.9(1)	O(1)−Re−O(2)	163.6(3)
Cl(2)−Re−P(1)	92.0(1)	Re−P(1)−C(1)	101.0(3)
Cl(2)−Re−O(1)	96.6(3)	Re−O(2)−C(6)	126.5(5)
Cl(2)−Re−O(2)	87.9(2)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[ReO_2(PO)_2][AsPh_4]\cdot{}^1/_2EtOH\cdot{}^1/_2Me_2CO$ (**4**)

Re−P(1)	2.394(5)	Re−O(4)	2.13(1)
Re−P(2)	2.409(6)	P(1)−C(1)	1.80(2)
Re−O(1)	1.75(1)	P(2)−C(7)	1.81(2)
Re−O(2)	1.73(1)	O(3)−C(6)	1.31(2)
Re−O(3)	2.12(1)	O(4)−C(12)	1.35(2)
P(1)−Re−P(2)	109.6(2)	O(1)−Re−O(3)	92.2(5)
P(1)−Re−O(1)	88.4(4)	O(1)−Re−O(4)	89.5(5)
P(1)−Re−O(2)	89.4(4)	O(2)−Re−O(3)	91.5(5)
P(1)−Re−O(3)	79.5(4)	O(2)−Re−O(4)	93.3(5)
P(1)−Re−O(4)	169.8(4)	O(3)−Re−O(4)	90.6(5)
P(2)−Re−O(1)	87.9(4)	Re−P(1)−C(1)	99.3(7)
P(2)−Re−O(2)	88.9(4)	Re−P(2)−C(7)	100.6(7)
P(2)−Re−O(3)	171.0(4)	Re−O(3)−C(6)	122(1)
P(2)−Re−O(4)	80.4(4)	Re−O(4)−C(12)	119(1)
O(1)−Re−O(2)	175.3(6)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[ReOCl(PO)_2]$ (**5**)

Re−Cl(1)	2.403(4)	Re−O(3)	1.69(1)
Re−P(1)	2.447(4)	P(1)−C(1)	1.82(1)
Re−P(2)	2.488(4)	P(2)−C(7)	1.80(1)
Re−O(1)	2.013(9)	O(1)−C(6)	1.39(2)
Re−O(2)	2.032(9)	O(2)−C(12)	1.35(2)
Cl(1)−Re−P(1)	162.9(2)	P(2)−Re−O(2)	77.3(3)
Cl(1)−Re−P(2)	90.3(1)	P(2)−Re−O(3)	89.5(3)
Cl(1)−Re−O(1)	85.0(3)	O(1)−Re−O(2)	86.0(4)
Cl(1)−Re−O(2)	89.0(3)	O(1)−Re−O(3)	107.7(4)
Cl(1)−Re−O(3)	100.7(3)	O(2)−Re−O(3)	163.7(4)
P(1)−Re−P(2)	100.2(1)	Re−P(1)−C(1)	99.2(5)
P(1)−Re−O(1)	80.9(3)	Re−P(2)−C(7)	100.7(5)
P(1)−Re−O(2)	80.3(3)	Re−O(1)−C(6)	123.7(8)
P(1)−Re−O(3)	92.9(3)	Re−O(2)−C(12)	127.0(8)
P(2)−Re−O(1)	162.7(3)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[ReOCl(PO)(PNH)]$ (**8**)

Re−Cl	2.401(4)	Re−N(1)	1.99(1)
Re−P(1)	2.438(3)	P(1)−C(1)	1.80(1)
Re−P(2)	2.485(4)	P(2)−C(7)	1.81(1)
Re−O(1)	1.70(1)	N(1)−C(6)	1.35(2)
Re−O(2)	2.04(1)	O(2)−C(12)	1.34(2)
Cl−Re−P(1)	162.6(1)	P(2)−Re−O(1)	90.0(3)
Cl−Re−P(2)	90.6(1)	P(2)−Re−O(2)	76.7(3)
Cl−Re−N(1)	86.6(3)	N(1)−Re−O(1)	106.7(5)
Cl−Re−O(1)	100.0(3)	N(1)−Re−O(2)	86.7(4)
Cl−Re−O(2)	89.1(3)	O(1)−Re−O(2)	164.1(4)
P(1)−Re−P(2)	100.3(1)	Re−P(1)−C(1)	100.2(5)
P(1)−Re−N(1)	79.0(3)	Re−N(1)−C(6)	128(1)
P(1)−Re−O(1)	93.5(3)	Re−P(2)−C(7)	100.2(5)
P(1)−Re−O(2)	80.4(3)	Re−O(2)−C(12)	128.6(8)
P(2)−Re−N(1)	163.3(3)		

lengths and angles are reported in Tables 2−5. Further details are provided in the Supporting Information. The crystals proved of sufficient size and quality to collect data on a Nicolet R3m/V diffractometer. In no case was significant crystal decomposition observed during the course of data collection. The final unit-cell parameters were obtained by least-squares on the setting angles for 50 reflections with $2\theta > 18°$. For each of the four studies, data were corrected for Lorentz, polarization, and absorption (empirical, based on azimuthal scans for four reflections) effects in the usual fashion. In addition, the structures were solved by Patterson techniques and refined by full-matrix least-squares methods using the SHELXS-86 and SHELXL-93 program packages.[15] Scattering factors were those provided with the SHELXL program system. In all cases, refinement proceeded routinely and no anomalies in temperature factors or excursions of electron density in the final Fourier maps were observed. In **1** the atoms of the anionic complex were refined using anisotropic thermal parameters; in **4**, **5**, and **8** only the heavy atoms were refined this way. In the case of compound **4**, the solvent molecules were found to be disordered, but no disorder model was found to be adequate, and consequently, the atomic parameters for EtOH and Me_2CO were fixed at the different Fourier positions. In addition, the phenyl rings of $[AsPh_4]^+$ were treated as rigid bodies.

Results

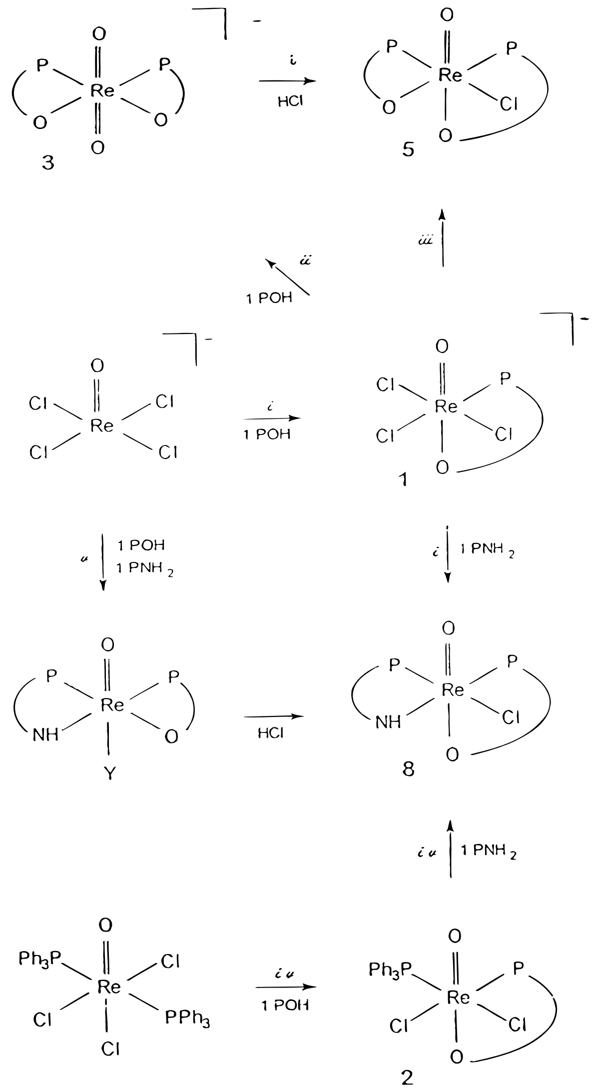
Synthesis of the Complexes. As summarized in Scheme 1, monooxo Re(V) phosphino−phenolato complexes can be prepared in high yield *via* ligand-exchange reactions of POH onto labile pentavalent rhenium precursors such as $[ReOCl_4]^-$ and $[ReOCl_3(PPh_3)_2]$ at autogenous pH in acetonitrile or benzene solutions. Accurate control of the 1:1 metal/ligand stoichiometric ratio allows for the collection of mono-substituted P,O-derivatives $[ReOCl_3(PO)]^-$ (**1**) and $[ReOCl_2(PO)(PPh_3)]$ (**2**).

Further reaction of **1** with 1 mol of POH or PNH_2 in acetonitrile, still under autogenous pH conditions, yields the bis-substituted "twisted" complexes $[ReOCl(PO)_2]$ (**5**) and [ReOCl(PO)(PNH)] (**8**), respectively. On the contrary, treatment of **1** with 1 mol of POH in basic media (by sodium ethoxide) affords the light yellow anionic *trans*-dioxo $[ReO_2(PO)_2]^-$ species **3**−**4**, which can be isolated from the organic phase of a dichloromethane/water mixture. Dioxo complexes readily rearrange into green-brown $[ReOX(PO)_2]$ "twisted" derivatives **5**−**7** by addition of the appropriate hydrohalogenic acid HX (X = Cl, Br, I) in acetonitrile solutions. While the acid provides a means for extracting one oxide ligand, the substitution of chloride for oxide appears to be the primary (thermodynamic) factor determining the "equatorial-to-twisted" isomerization. Addition of PNH_2 to a basic solution of **1** produces instead an orange-red mixture.[14] From this, mixed bis-substituted [ReOX(PO)(PNH)] compounds **8**−**10** can be isolated as pure products by addition of the appropriate hydrohalogenic acid HX (X = Cl, Br, I). The mixed bis-substituted [ReOCl(PO)(PNH)] complex can be prepared also by mixing equimolar amounts of $[ReOCl_4]^-$, POH, and PHN_2 reagents in ethanol solutions. In this case, the mixed-ligand complex is contaminated by trace amounts of bis-substituted $[ReO(PO)_2Cl]$ derivative, as evidenced by ^{31}P NMR. Doubling the amount of one of the two hybrid ligands does not cause a change in the reaction pathway, and the mixed-ligand [ReOCl(PO)(PNH)] complex is always recovered in high yield.

Characterization. Elemental analyses, as given in the Experimental Section, are in good agreement with the proposed formulations. The compositional assignments are also accomplished with EI and positive-ion FAB mass spectrometry. The related spectra show the molecular parent peaks along with several fragment ions, corresponding to losses of halide and PO^- ligands. The IR spectra of monooxo−Re(V) complexes exhibit the characteristic Re═O stretching vibration in the range

(15) Sheldrick, G. M. SHELXS-86. A program for crystal structure solution. University of Gottingen, 1990; SHELXL-93, Crystal structure refinement. University of Gottingen, 1993.

Scheme 1



963−940 cm^{-1}, whereas in the dioxo species, the O═Re═O vibration moves to lower energies[16] at 776 and 781 cm^{-1} for the tetrabutylammonium and the tetraphenylarsonium salts, respectively. In addition, all complexes possess IR absorptions typical of the coordinated phosphine ligands. In particular, the 900−580 cm^{-1} range is diagnostic for both ligand coordination and geometry of the resulting complex. In this region, uncoordinated POH exhibits two strong absorptions at 751 and 697 cm^{-1}, as depicted in Figure 1; these bands are associated with C−H and C−C out-of-plane bending vibrations in mono-substituted benzene rings.[17] Upon ligand coordination, the pertinent region becomes more complicated: the wagging vibrations mentioned above are slightly red-shifted in the symmetric dioxo complexes, and the related bands split into two components in both mono-substituted and bis-substituted monooxo compounds that had a "twisted" configuration. In addition, in all complexes two more absorptions appear around 850 and 610 cm^{-1}. This latter band is again split into two

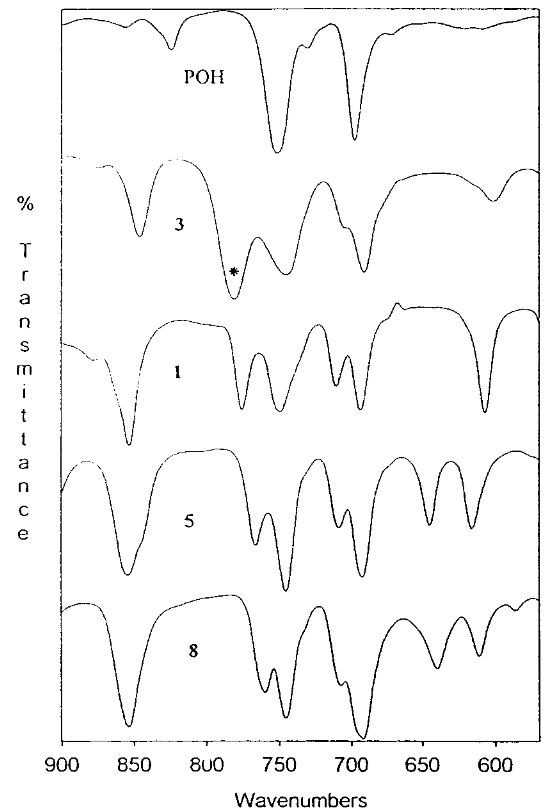


Figure 1. Infrared spectra in the region 900−580 cm^{-1} of selected rhenium complexes synthesized in this work. An asterisk denotes the [O═Re═O] stretching vibration.

components in asymmetric bis-substituted complexes, whereas it remains unique in mono-substituted and symmetric bis-substituted complexes. Finally, mixed P,O−P,N complexes lack the ν(N−H) vibration characteristic of free PNH_2. Electronic spectra of dioxo complexes exhibit a unique distinguishable absorption centered at 315 nm, attributable to the oxo to rhenium charge transfer transition.[18,19] On the contrary, a more complicated four-band pattern is observed in all monooxo compounds. Such a system is only slightly affected by halide variation in both series of bis-substituted $[ReOX(PO)_2]$ and mixed [ReOX(PNH)(PO)] compounds.

The ^{31}P NMR signal of free POH moves significantly downfield upon coordination (see Table 6) as the $[ReO]^{3+}$ and $[ReO_2]^{+}$ cores are strong acid centers. The characteristic singlet shown by the mono-substituted complex $[ReOCl_3(PO)]^-$ (**1**) becomes a doublet of doublets in all "twisted" bis-substituted complexes **5**−**10** and in $[ReOCl_2(PO)(PPh_3)]$ (**2**) owing to the magnetic unequivalence of the *cis*-positioned phosphorus atoms ($^2J_{PP}$ *ca.* 10 Hz).[20] Dioxo derivatives give again a pure singlet due to the symmetrical coordination of both P,O-ligands. Proton NMR spectra of all "twisted" complexes exhibit the aromatic signals spread in a range of about 2 ppm centered at δ 6.80 ppm. Such a range is halved in symmetric dioxo complexes **3** and **4**. In addition, mixed P,O−P,N complexes show a sharp singlet beyond 10 ppm attributable to the *N*-amido proton, which is only slightly affected by the presence of a different halide co-ligand.

Structural Description. The identification of the atoms and the four molecular structures are depicted in Figures 2−5. All

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Table 6. Selected Spectroscopic Data of Some Oxo−Re(V) Complexes

compound	ν(Re═O), cm^{-1}	^{31}P NMR, ppm	Δ_{PP}, ppm	Re═O$_{oxo}$, Å	Re−X$_{trans}$,[a] Å	Re−X$_{cis}$,[a] Å	Re−P$_{tw}$,[b] Å	Re−P$_{equat}$,[b] Å
[ReOCl$_3$(PO)][Nbu$_4$] (**1**)	963	−8.57 (s)		1.669(6)	2.016(6)		2.422(2)	
[ReO$_2$(PO)$_2$][AsPh$_4$] (**4**)	781	4.89 (s)		1.75(1) 1.73(1)		2.13(1) 2.12(1)		2.394(5) 2.409(6)
[ReOCl(PO)$_2$] (**5**)	959	0.64 (d) 13.83 (d)	13.19	1.69(1)	2.032(9)	2.013(9)	2.488(4)	2.447(4)
[ReOBr(PO)$_2$] (**6**)	957	0.06 (d) 14.34 (d)	14.28					
[ReOI(PO)$_2$] (**7**)	956	−1.04 (d) 13.38 (d)	14.42					
[ReOCl(PO)(PNH)] (**8**)	941	−2.77 (d) 20.93 (d)	23.70	1.70(1)	2.04(1)	1.99(1)	2.485(4)	2.438(3)
[ReOBr(PO)(PNH)] (**9**)	940	−3.69 (d) 21.08 (d)	24.77					
[ReOI(PO)$_2$] (**10**)	940	−5.40 (d) 20.10 (d)	25.50					
[ReOCl(PNH)$_2$][c]	907	1.79 (d) 12.36 (d)	10.57	1.69(1)	2.04(1)	2.01(1)	2.476(5)	2.434(5)
[ReOBr(PNH)$_2$][c]	906	1.13 (d) 12.57 (d)	11.44					
[ReOI(PNH)$_2$][c]	905	−0.96 (d) 12.04 (d)	13.00					

[a] X = O or N; the positions *cis* and *trans* are relative to the Re═O moiety. [b] P$_{tw}$ and P$_{equat}$ belong to the "twisted" and "equatorially" coordinated phosphorus donors, respectively. [c] Data taken from ref 4.

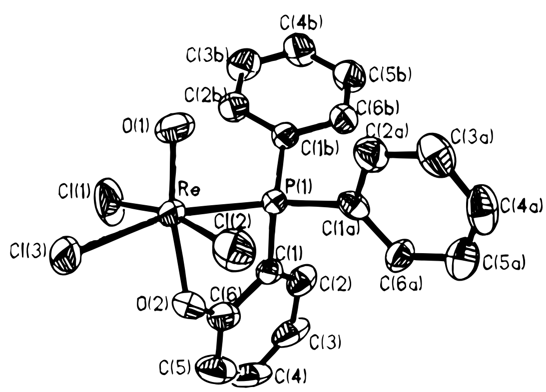


Figure 2. ORTEP view of the anionic portion of complex **1**, showing the atom labeling scheme. The thermal ellipsoids are drawn at 40% probability, and the [NBu$_4$]$^+$ group is omitted for clarity.

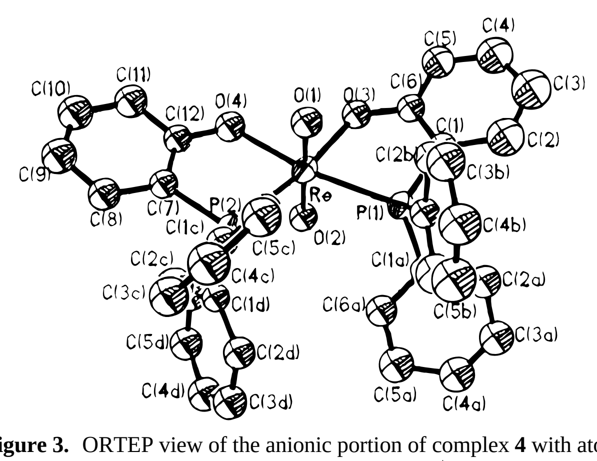


Figure 3. ORTEP view of the anionic portion of complex **4** with atom contours shown at 40% probability. The [AsPh$_4$]$^+$ group, EtOH, and Me$_2$CO molecules have been omitted for clarity.

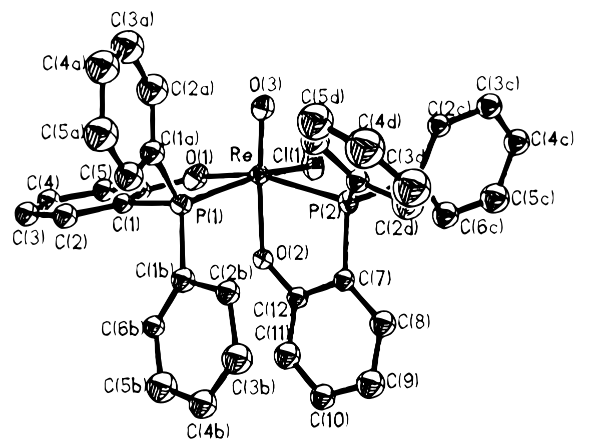


Figure 4. ORTEP view of complex **5**, showing the atom labeling scheme. The thermal ellipsoids are drawn at 40% probability.

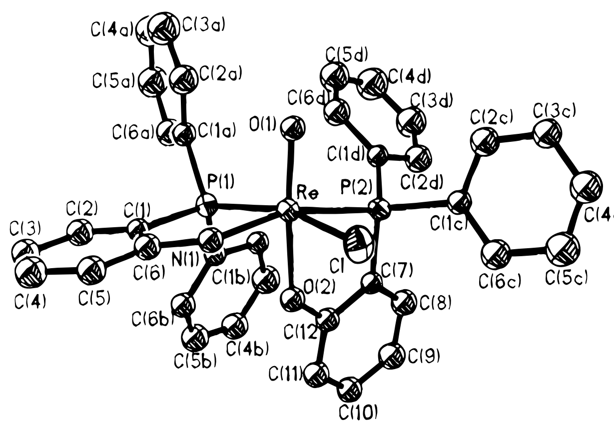
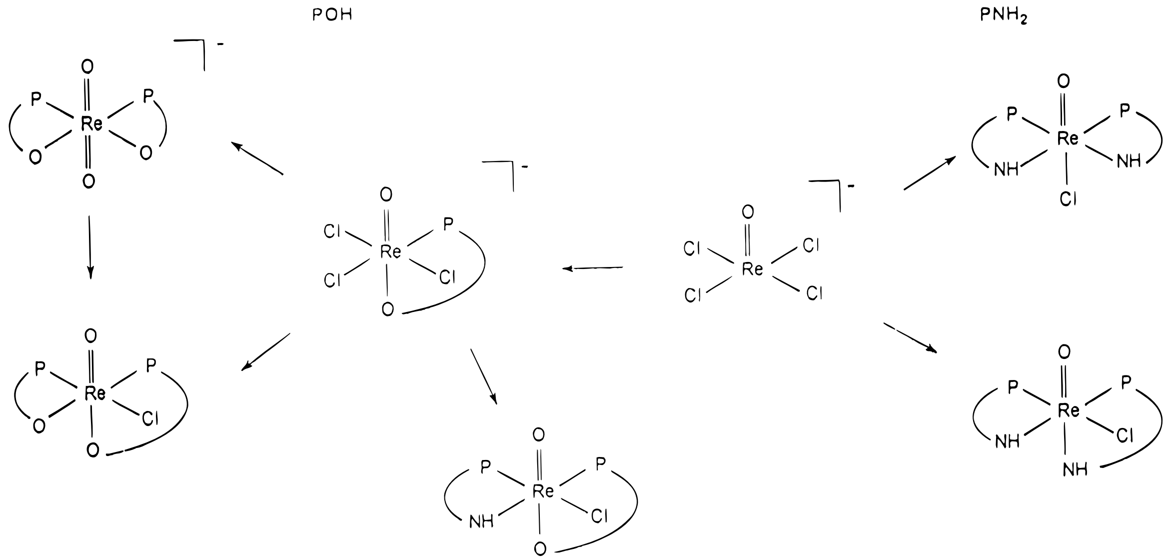


Figure 5. ORTEP view of complex **8**, showing the atom labeling scheme. The thermal ellipsoids are drawn at 40% probability.

of the structures consist of discrete, monomeric octahedral rhenium(V) complexes, which in **1** and **4** are monoanionic and in **5** and **8** are neutral. Apart from **4**, which shows the linear *trans*-[ReO$_2$]$^+$ group, they contain the [ReO]$^{3+}$ moiety and are packed with no intermolecular contacts shorter than van der Waals radii sum. As a common feature the organic P,O-ligand acts as a bidentate uninegative chelate in all four structures, and the resulting donor set is Cl$_3$O$_2$P in **1**, O$_4$P$_2$ in **4**, ClO$_3$P$_2$ in **5**, and ClNO$_2$P$_2$ in **8**. The equatorial mean plane (formed by the three chloride and the phosphorus atoms in **1**, by the donor atoms of the two P,O-ligands in **4**, by the chloride, the two donors of a P,O-ligand, and the phosphorus of the second chelate in **5**, and finally by the chloride, the phosphorus atom of the P,O-ligand, and the two donors of the P,N-ligand in **8**) is puckered by ±0.04 Å in **1**, **5**, and **8** and by 0.02 Å in **4**, while the Re−O$_{oxo}$ axis is inclined at 85.4, 86.5, and 85.9° in **1**, **5**,

Scheme 2



and **8**, respectively, with respect to the equatorial mean plane; conversely, the O(1)---O(2) axis is virtually normal to this plane in the *trans*-dioxo complex **4**. In the coordination sphere, the five-membered Re−P−C−C−O chelate ring displays an envelope configuration (C_s) in **1** (with Re 0.59 Å out of the plane formed by the remaining four atoms) and in **4** (the Re displacement from the two rings are 0.40 and 0.26 Å, respectively), as well as in **5** (the pertinent value is 0.15 Å) and in **8** (the value of displacement is 0.24 Å) for the ligand which is virtually perpendicular to the mean equatorial plane, *i.e.* that coordinating in the "twisted" fashion. On the contrary, the chelate ring has a planar configuration for the ligand substantially coplanar with the equatorial plane, *i.e.* that ligating in the "equatorial" manner, in **5**. The same feature is shown by the five-membered Re−P−C−C−N ring of **8**. In the three monooxorhenium complexes the phenolate donor coordinates *trans* to the Re═O linkage and in bis-substituted species **4**, **5**, and **8** the bidentate ligands exhibit an equatorial *cis*-phosphorus orientation with a "bite" P--O separation in the range 2.75−2.85 Å, and the corresponding "bite" angle is between 76.1 and 78.0°. When both ligands chelate equatorially, as in **4**, the "bite" distance lengthens to a mean value of 2.92 Å and the angle enlarges to 80.0°. The dihedral angles between the five-membered Re−P−C−C−O rings and the equatorial planes are 100.9° in **1**, 7.2° and 5.5° in **4**, 10.0 and 98.4° in **5**, and 81.9° in **8**.

The internal geometrical parameters (Tables 2−5) indicate a distorted octahedral geometry about the metal, especially for the monooxo complexes. Distortions from the ideal Re-centered octahedron result in the following: (*i*) the metal lying out of the mean equatorial plane toward the oxo-atom (0.25 Å in **1**, 0.29 Å in **5** and **8**, whereas in **4** the Re atom practically resides in the equatorial plane); (*ii*) a nonlinear O_{oxo}−Re-O axis of 163.6(3), 163.7(4), and 164.1(4)° in **1**, **5**, and **8**, respectively, while the corresponding value (175.3(6)°) for **4** approaches 180°; (*iii*) in the Cl_3O_2P polyhedron of **1** the Re atom being +1.44 Å away from the P(1)O(2)Cl(1) plane and −1.02 Å from the Cl(2)O(1)Cl(3) plane, with the angle between the two triangles being 7.6°. The corresponding values are +1.09 Å, −1.12 Å, and 5.1° for **4**, +1.41 Å, −0.95 Å, and 10.9° for **5**, and +1.42 Å, −0.95 Å, and 12.4° for **8**.

Discussion. POH and PNH_2 ligands are solid and air stable tertiary phosphines which are obtained by functionalizing with an hydroxyl (or an amine) group the ortho position of one phenyl ring on triphenylphosphine.[11,12] These ligands match one soft phosphine phosphorus donor with an anchoring hard phenolate (or anilide) donor: such a combination allows the enhancement of the bonding of the phosphorus atom to the metal center while the presence of oxygen (or nitrogen) in the chelate contributes to the stabilization of Re centers in intermediate oxidation states. The syntheses and full characterization of new series of mono-substituted and bis-substituted oxo−Re(V) complexes containing the phosphino−phenolato (PO^-) chelate has allowed for the comparison of its reactivity toward the rhenium metal with respect to that exhibited by the related phosphinoamine ligand PNH_2. Scheme 2 depicts the reaction pathways arising from the mixing of the labile $[ReOCl_4]^-$ precursor with POH and PNH_2, respectively.

Two differences can be pointed out: (*i)* PNH_2 affords only bis-substituted derivatives, whereas POH gives either mono- and bis-substituted compounds; (*ii)* PNH_2 stabilizes symmetric ("equatorial") monooxo neutral species in basic media, while POH stabilizes symmetric (still "equatorial") dioxo anionic ones. On the other hand, both POH and PNH_2 afford "twisted" bis-substituted $(PO)_2$, $(PNH)_2$, and mixed (PO)(PNH) neutral complexes in neutral or acid media. The cone angle (ϑ) of the free POH and PNH_2 ligands[21] is very similar, and consequently, steric factors cannot be invoked to explain their different reactivity. So, it appears that electronic factors arising from the peculiar derivatization of the tertiary phosphine play the major role in determining the final products. Upon coordination to the rhenium center, the mono-deprotonation of both chelates induces the initial sp^3 hybridization of the phenolic oxygen and the aniline nitrogen to rearrange to a more *p*-rich contribution. Such a rearrangement is marked in the case of the actual *N*-amido donor, being an additional electron donation from amido ligands to the metal a well-known phenomenon, particularly with early transition metals.[22] In accordance with this observation, structural data describe an almost pure sp^2 hybrid-

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(22) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bond: The Chemistry of Transition Metal Complexes Containing Oxo, Nitrido, Imido, Alkylidene, and Alkylidine Ligands*; Wiley: New York, 1988. (b) The amine nitrogen of the PNH_2 ligand may also doubly deprotonate to afford multiple metal−imido bonds. An example is represented by the complex $[Re(NP)(PNH)Cl_2]$, in which the nitrogen atoms of the two phosphinoamine ligands act as amido and imido donor, respectively. See: Refosco, F.; Tisato, F.; Moresco, A.; Bandoli, G. *J. Chem. Soc., Dalton Trans.* **1995**, 3475.

ization for the *N*-amido atom in **8**, and such hybridization is much less pronounced in the case of the phenolate donor. In other words, the phosphinoamide nitrogen is able to supply the metal center with an amount of electron density larger than that of the phenolate oxygen. In the dioxo derivatives the ReO_2^+ core is able to tolerate two "less donating" PO^- systems in a negatively charged species, but it has to rearrange to the neutral monooxo array to accommodate the two "more donating" PNH^- chelates. Similar electronic factors can be invoked to explain the obtainement of the mono-substituted monooxo complex $[ReOCl_3(PO)]^-$. It is worth noting that a *cis*-P,P orientation is always obtained both in solution and in the solid state. Steric factors alone would favor a *trans*-P,P configuration in order to minimize ligand constraints by placing on opposite sides the four phenyl groups attached to the phosphorus atoms and which are not directly involved in the coordination. Thus, it appears again that ligand electronic properties are the main factor responsible for the determination of the final *cis*-P,P arrangement *i.e.* by placing a phosphine phosphorus acceptor *trans* to a phenolate oxygen (or anilide nitrogen) donor.

A detailed analysis of the infrared spectra offers helpful suggestions to corroborate the assumption based on the different degree of nucleophilicity of PNH^- and PO^- ligands. In particular, the ν(Re═O) is a diagnostic probe that investigates the distribution of the overall electron density in these oxo−Re(V) complexes: in fact, it moves to higher or lower frequencies depending on the donor ability of the coordinated ligand set.[16] As summarized in Table 6, the comparison of the Re═O stretching vibrations in bis-substituted monooxo species reveals a bathochromic shift on going from $(PO)_2$ to (PO)(PNH) and to $(PNH)_2$ derivatives, in agreement with a decreasing Re═O strength caused by the increasing of the nucleophilic character of the coordinated phosphine. In addition, the infrared region 900−580 cm^{-1}, depicted in Figure 1 for the chloro compounds (a similar trend is observed for the bromo and iodo derivatives), gives useful information about the molecular configuration of these type-complexes. The bands at *ca.* 850 and 620 cm^{-1} appear only in the metal complexes and are therefore diagnostic for ligand coordination; moreover, the splitting into two components of the aromatic C−H and C−C wagging vibrations at around 850 and 700 cm^{-1} indicates the coordination of a phosphino−phenolate ligand orthogonally positioned with respect to the mean equatorial plane, with the phenolate oxygen *trans* to the Re═O linkage. On the contrary, a complete equatorially coordination of the two phosphines, as in **4**, does not induce this splitting. Mono-substituted and bis-substituted "twisted" species can then be distinguished on the basis of a further splitting of the band in the 640−600 cm^{-1} region. These hypotheses are fully confirmed by the analysis of the X-ray molecular structure of the four representatives **1**, **4**, **5**, and **8** Re(V) complexes. They all exhibit distorted octahedral arrangements. In particular, the structures of $[ReOCl(PO)_2]$ (**5**) and [ReOCl(PNH)(PO)] (**8**) are superimposable (Figure 6), the weighted root-mean-square (rms) deviation, derived by the BMFIT program,[23] being only 0.043 Å when the fitting is performed using the octahedron atoms. In addition, **5** is isostructural with $[TcOCl(PO)_2]$[7] (rms 0.024 Å) and **8** with $[ReOCl(PNH)_2]$ (β-form)[4] (rms 0.045 Å, Figure 6). In conclusion, the four structures, *i.e.* **5**, **8**, [ReOCl(PNH)(PO)], and $[TcOCl(PO)_2]$, are practically superimposable; their space group is $P2_12_12_1$ and their volume, for $Z = 4$, average 3106 $Å^3$. Bond lengths and angles do not differ significantly from the expected values,[6,24] even if, as a general feature, the presence of a phosphinoamido ligand lengthens the Re═O bond and the chelate coordinated in the "twisted" fashion exhibits slightly longer metal-donor distances. Only the *N*-amido to Re(V) bond in **8** (1.99(1) Å) deserves a comment. In fact, it is markedly shorter than the N-amino to Re(V) bond (2.28(1) Å) in $[ReOCl_2(PNMe_2)(OMe)]$[20] [$PNMe_2$ = *N,N′*-dimethyl(2-diphenylphosphino)benzeneamine] and parallels the averaged value (2.00 Å) found in $[ReO(PNH)_2(X)]$ (X = Cl, OMe).[4] Similar trends have been previously observed for $Pt-N_{amino}$ *vs* $Pt-N_{amido}$ distances in *cis/trans*-$[Pt(PNH_2)_2]^{2+}$ and $[Pt(PNH)_2]$ complexes,[26] but with a difference restricted to 0.08 Å, and for $Rh-N_{amino}$ *vs* $Rh-N_{amido}$ distances (2.14 and 2.02 Å, respectively) in $[RhCl_2(PNH)(PNH_2)]$.[27]

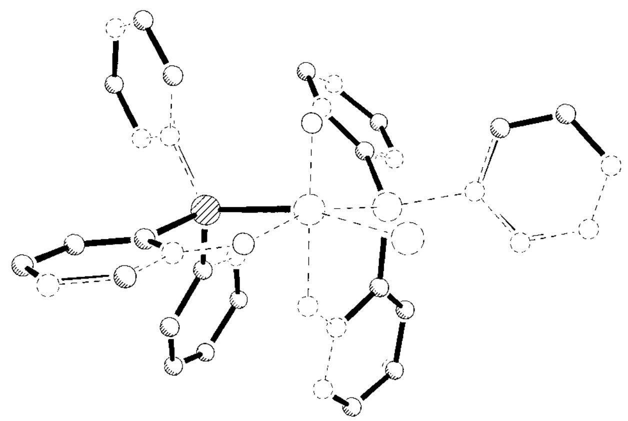

Figure 6. Superimposition of isostructural complexes $[TcOCl(PO)_2]$ (- - -) and $[ReOCl(PO)_2]$ (**5**).

The synthesis at millimolar level of stable anionic dioxo−Re(V) and stable monooxo−Re(V) mixed-ligand complexes obtained under controlled experimental conditions, offers the possibility to reproduce this chemistry at "carrier free" level (nanomolar concentrations) with the ^{186}Re and ^{188}Re isotopes for the development of a new class of potential radiotherapeutic agents. In our case, the phosphine ligands may work both as reducing agent toward the perrhenate ion eluted from commercially available ^{188}W/^{188}Re generators and as a coordinating agent to give the final product in a "one pot reaction": an improved procedure both from the radiation safety and synthetic points of view. In addition, negative (or positive) charges beared by rhenium (or technetium) species are known to be responsible for specific biodistribution pathways.[28] Lastly, mixed-ligand technetium monooxo(V) species are receiving increasing interest because the approach of incorporating two different ligands in the coordination sphere of the TcO^{3+} core[29] may be helpful to develop ^{99m}Tc-agents which bind biologically active moieties. Very recently, a mixed-ligand ^{99m}Tc−oxo complex as a potential dopamine transporter imaging agent has been proposed by Kung and co-workers.[30]

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Conclusions. The bidentate phosphinophenol ligand POH reacts as a mononegative chelate with Re(V) precursors through mono-substituted intermediates, namely $[ReOCl_3(PO)]^-$ and $[ReOCl_2(PO)(PPh_3)]$, to produce various bis-substituted complexes depending on the reaction conditions employed. Basic media afford a rare example of anionic dioxo species $[ReO_2(PO)_2]^-$, whereas acid media give the more common $[ReO(PO)_2X]$ complexes. Accurate mixing of two heterofunctionalized bidentate phosphines allows for the generation of a class of mixed ligand [ReO(PO)(PNH)X] compounds (X = halide). In the latter two series, the two ligands (bis-PO^- or PO^-/PNH^-) are asymmetrically coordinated around the metal center, with the plane described by the five-membered chelate rings including the P,X (X = O, N) donors and rhenium almost orthogonally positioned. Both solution state (^{31}P NMR) and solid state measurements (IR and X-ray determinations) confirm the mutual *cis*-P,P configuration.

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Supporting Information Available: A CIF file containing tables of crystal data and experimental conditions, atomic positional parameters, bond lengths, bond angles, and anisotropic temperature factors for **1**, **4**, **5**, and **8**. Ordering information is given on any current masthead page. Structure factors are available from the authors upon request.

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