Complexes of Multifunctional Phosphorus Ligands. Rhenium(V) Complexes of the Multidentate Phenoxyphosphine Ligands Bis(*o*-trimethylsilyloxyphenyl)phenylphosphine and Tris(*o*-trimethylsilyloxyphenyl)phosphine. Stepwise Elimination of Me_3SiX (X = Cl, OEt) from the Metal−Ligand System

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The silylated aryloxo ligands bis(*o*-silyloxyphenyl)phenylphosphine (abbreviated $PhP\{OT\}_2$) and tris(*o*-trimethylsilyloxyphenyl)phosphine (abbreviated $P\{OT\}_3$, where T = Me_3Si) were prepared. Complexation reactions with $O{=}ReCl_2(OEt)(PPh_3)_2$ and $O{=}ReCl_3(PPh_3)_2$ proceed by displacement of one PPh_3 and the subsequent stepwise replacement of the OEt and/or Cl substituents. The new complex $Re(O)Cl_2[\kappa^2\text{-}(P,O)\text{-}(PhP\{O\}\{OT\})](PPh_3)$, formed by elimination of Me_3SiOEt, exists in diastereomeric cis and trans forms. Elimination of a second equivalent of Me_3SiCl gives $Re(O)Cl[\kappa^3\text{-}(P,O,O)\text{-}(PhP\{O\}_2)](PPh_3)$. Similarly $P\{OT\}_3$ converts $Re(O)Cl_2(OEt)(PPh_3)_2$ to $ReOCl_2[\kappa^2\text{-}(P,O)\text{-}(P\{O\}\{OT\}_2)](PPh_3)$ (**5**) (structurally characterized as **5**·$0.875CH_2Cl_2$): crystal data; triclinic $P\bar{1}$, a = 14.302(4) Å, b = 18.734(2) Å, c = 17.639(4) Å, α = 80.950(12)°, β = 80.12(2)°, γ = 81.76(2)°, Z = 4. Final R_1 and wR_2 values are 0.0852 and 0.1525, respectively on $F_o^2 > 2\sigma(F_o^2)$ data (or 0.1948 and 0.2019 on all data). The phenoxy phosphine ligand in **5** is bound via P and one O to Re. The P atoms are mutually cis to each other and to the terminal oxygen on Re. Two *ortho*-trimethylsiloxy substituted phenyl rings dangle from the coordinated phosphorus atom. Complex **5** can be converted to $Re(O)Cl[\kappa^3\text{-}(P,O,O)\text{-}(P\{O\}_2\{OT\})](PPh_3)$ (**6**) by treatment with $PPN^+\,Cl^-$ and **6** was also obtained by direct reaction of $Re(O)Cl_3(PPh_3)_2$ with $P\{OT\}_3$ at higher temperatures. The complex **6** has been structurally characterized: crystal data triclinic, $P\bar{1}$, a = 10.1509(6) Å, b = 12.1123(8) Å, c = 16.2142(14) Å, α = 97.851(7)°, β = 94.852(7)°, γ = 96.889(6)°, Z = 2. Final R_1 and wR_2 values were 0.0303 and 0.0721 on $F_o^2 > 2\sigma(F_o^2)$ data (or 0.0348 and 0.0742 on all data). The phenoxyphosphine ligand in **6** is bound *facially* to Re through P and two of the phenoxy oxygens. The Ph_3P group and terminal oxygen atoms are cis to the oxygen atoms of the phenoxy ligands and the Cl lies trans to P. One trimethylsiloxyphenol group dangles. Careful hydrolysis of **6** gave $Re(O)Cl[\kappa^3\text{-}(P,O,O)\text{-}(P\{O\}_2\{OH\})](PPh_3)$ which was also formed during complexation reactions in moist solvent. Solution $^{31}P\{^1H\}$ NMR demonstrated *cis*- or *trans*-(P,P) geometry for the complexes, which was confirmed in the two aforementioned cases by structure determinations.

Introduction

Multidentate chelate ligands which can offer a selection of hard−soft donor atoms that are capable of adapting to the character of the metal center continue to excite interest. Recent interest in the chemistry of heteromultifunctional phosphine complexes of rhenium has been stimulated by the potential for use of such complexes as radiopharmaceutical agents.[1] Multidentate PO ligands have also been effectively used in certain homogeneous catalytic processes.[2] We have a continuing broad interest in phosphine ligand systems containing pendant functionalities that can potentially form additional bonds in order to establish multidentate chelation. Previous work with main group centers such as Si and P wherein bound multifunctional sulfur, phosphine or amine ligands may, or may not, exhibit further coordination to the "central" atom depending on the electronic environment of this atom has been recently reviewed.[3] The "atranes" described by Verkade and co-workers[4] also exemplify this kind of behavior. Recent exploitations of systems such as the amidoamine complexes of a variety of metals[5] illustrate that metal complexes may also adopt similar internal coordination. The potentially tetradentate ligand tris(*o*-thiophenol)phosphine [abbreviated $P\{SH\}_3$] offers a set of up to four soft ligating atoms of different character (P and S) to a metal and so should stabilize soft transition metal centers (i.e. metals in their lower oxidation states and those on the right-hand side of the transition-metal block). Within the context of the present study we note recent applications of this particular ligand to the chemistry of rhenium in intermediate and high oxidation states[6,7] and the tetradentate "umbrella" chelation

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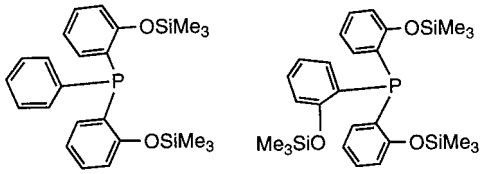

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Figure 1. The ligands PhP{OT}$_2$ (**1**) and P{OT}$_3$ (**2**).

demonstrated by P{SH}$_3$ toward Tc(III).[7] Tris(ethylenethiol)-amine, N{S}$_3$, offers the reverse ligating combination with a hard principal donor atom and up to three additional soft ligating centers. This amine ligand gave tetradentate complexes of Tc-(III) or Re(III) when reacted with the respective MO_4- anions using triphenylphosphine as the metal reductant.[8,9]

The *ortho*-phenolatophosphine ligands, $R_{3-x}P\{O\}_x^{-x}$ ($x = 1$ to 3) provide a soft−hard element combination with one soft "central" atom. These ligands have more rigid backbones than the ethylene bridged thiols mentioned above and the "bite" distance is reduced relative to that of the P{S}$_3$ chelate. Already these ligands have yielded a wide range of complexes encompassing a variety of oxidation states for group 7 metal centers. Thus (*ortho*-phenol)diphenylphosphine, [abbreviated $Ph_2P\{OH\}$] was used to form Tc(III)[10] and Tc(V)/Re(V)[11,12] complexes. Some Tc(V) and Re(V) complex chemistry with bis(*ortho*-phenol)phenylphosphine [abbreviated PhP{OH}$_2$] has been described earlier.[11] The Fe or Co coordination chemistry of the trianionic tris(phenolato)phosphine P{O}$_3$ ligand has been briefly described but no synthetic details were given.[13] As part of our continuing study[14−17] of the interaction of heterobifunctional, hemilabile, phosphorus based, hard−soft, ligands with both transition-metal and main group[18,19] elements, we were interested in extending the chemistry of the potentially tridentate PhP{OH}$_2$ and the potentially tetradentate P{OH}$_3$ ligands to Re(V) precursors. Recently alternate routes to ligands of this type have been described.[20] For this study we have converted the known ligand, PhP{OH}$_2$, into the silylated form, abbreviated PhP{OT}$_2$, **1** (Figure 1) (where T = Me_3Si). We also describe the synthesis of the hydrochloride salt form of tris-(*ortho*-phenolato)phosphine (P{OH}$_3$·HCl) which we convert to the trimethylsilylated derivative tris(*o*-(trimethylsilyloxy)-phenyl)phosphine, P{OT}$_3$, **2** (Figure 1). These silylated ligands were reacted with selected Re(V) precursors focusing on situations wherein we expected to form metal−oxygen covalent bonds through the elimination or possible migration of the labile $SiMe_3$ substituent on the ligand in addition to the coordination of the phosphine.

Experimental Section

Materials. All manipulations were performed under an atmosphere of prepurified Ar using Schlenk techniques. Solvents were dried, freshly distilled, and thoroughly deoxygenated immediately before use by purging the solvent for 15 min with Ar. Phenol, PPh_3, PCl_3, dimethoxymethane, *n*-butyllithium (1.6 M), TMEDA, PPN^+Cl^-, $AgBF_4$, and $HN(SiMe_3)_2$ were reagent grade chemicals purchased from Aldrich and used as received. Anhydrous HCl(g) was obtained from Matheson. The NH_4ReO_4 was supplied by Strem Chemicals Inc. The mom-protected starting material, $PhOCH_2OCH_3$ (mom = methyloxymethyl), was prepared from phenol and dimethoxymethane as described in the literature.[21] PhP(*o*-$C_6H_4OH)_2$·HCl,[11] [ReO(OEt)$Cl_2(PPh_3)_2$],[22] and [Re-$OCl_3(PPh_3)_2$][23] were prepared as previously described.

Instrumentation. Infrared spectra were recorded on either a Nicolet 7199 infrared spectrometer (as dichloromethane casts on KBr plates) or a NICPLAN microscope (as solid crystalline samples). Electrospray mass spectra were obtained with a Micromass Autospec TOF/MS/MS instrument. Elemental analyses were carried out by the Microanalytical Services laboratory at the University of Alberta. Phosphorus-31 NMR spectra (in ppm referenced to external 85% H_3PO_4) were recorded on either a Bruker WH-400 spectrometer operating at 161.978 MHz or a Bruker WH-200 instrument operating at 80.989 MHz. Both spectrometers were locked to the solvent deuterium resonance and positive chemical shifts are deshielded relative to the reference. Proton spectra (in ppm relative to external $SiMe_4$) were recorded on the Bruker WH-400 instrument at 400.135 MHz. Accurate relative chemical shifts and coupling constants for the phosphorus nuclei for the second-order spectra of the two diastereomers of *trans*-[$ReOCl_2(PPh_3)(\kappa^2$-PhP(*o*-$C_6H_4O)$(*o*-$C_6H_4OSiMe_3)$)] (**3a**) were obtained via the simulation program gNMR.[24] The spectroscopic abbreviations used are s (singlet), om (overlapping multiplets), d (doublet), t (triplet), tt (triplet of triplets), dd (doublet of doublets), ddt (doublet of doublets of triplets), ddd (doublet of doublets of doublets), mu (multiplet), b (broad), st (strong), m (medium), and sh (sharp). Crystal structure determinations were carried out in the Structure Determination Laboratory, Department of Chemistry, University of Alberta.

Ligand Preparation. PhP(*o*-$C_6H_4OSiMe_3)_2$. PhP(*o*-$C_6H_4OSiMe_3)_2$ (**1**) was prepared from the hydrochloride salt, PhP(*o*-$C_6H_4OH)_2$·HCl,[11] following a procedure similar to that described by Wong *et al.*[18] A slurry of PhP(*o*-$C_6H_4OH)_2$·HCl (1.97 g, 5.96 mmol) in 40 mL of HN-$(SiMe_3)_2$ was heated under reflux conditions (∼140 °C) for 8 h. During this time, the hydrochloride salt dissolved, giving way to a clear colorless solution. The volatile materials were removed under vacuum. The resulting buff solid was then kept under a dynamic vacuum for 12 h. This buff solid proved to be an analytically pure sample of PhP(*o*-$C_6H_4OSiMe_3)_2$ (**1**). The yield was 2.14 g (4.88 mmol, 82% (based on the starting hydrochloride salt)). Anal. Calcd for $C_{24}H_{31}O_2Si_2P$: C, 65.72; H, 7.12. Found: C, 65.54; H, 7.03. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −25.5 (s). ^1H NMR (CD_2Cl_2): 6.63−7.37 (om, 13H, $-C_6H_5$/-C_6H_4-$OSiMe_3$); 0.12 (s, $-OSi(CH_3)_3$, 18H).

P(*o*-$C_6H_4OSiMe_3)_3$. A. Preparation of P(*o*-$C_6H_4OCH_2OCH_3)_3$. A pale yellow mixture composed of 45.4 mL of 1.60 M n-BuLi (72.6 mmol) in hexanes and 10.3 mL of freshly distilled TMEDA (68.2 mmol) in 30 mL of hexane was slowly (15 min) added dropwise by means of a cannula to a rapidly stirred, ice-cold solution of 10.05 g of

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methoxymethylphenyl ether (72.7 mmol)[21] dissolved in 80 mL of hexane. The ice-bath was then removed and the mixture was allowed to reach ambient temperature unaided. Stirring was continued at room temperature for 2 h. The mixture was then re-cooled to 0 °C, and a solution of 2.08 mL of PCl_3 (23.8 mmol) dissolved in 10 mL of diethyl ether was added dropwise over a 10 min period. The resulting cloudy yellow solution was then warmed to room temperature and stirred overnight (16 h). The solvents and volatile products were removed in vacuo to yield a viscous oil which then was extracted with diethyl ether (150 mL) and chloroform (150 mL). The two organic extracts were combined and washed with 150 mL of deoxygenated 0.10 M Na_2HPO_4(aq). The aqueous layer was discarded and the organic solvents were removed under vacuum to leave a mixture of an off-white solid and a sticky orange oil. This mixture was then washed with 30 mL of cold, deoxygenated methanol and 30 mL of freshly distilled hexane to afford a pure white solid identified as $P(o\text{-}C_6H_4OCH_2OCH_3)_3 \cdot 0.25\ CH_3OH$ (yield, 3.28 g (7.28 mmol), 31% (based on PCl_3)). Anal. Calcd for $C_{24}H_{27}O_6P \cdot 0.25\ CH_3OH$: C, 64.66 H, 5.94. Found: C, 64.30; H, 6.27. FAB MS: *m*/*z* 443 ($[P(o\text{-}C_6H_4OCH_2OCH_3)_3 + H]^+$). ^1H NMR (CD_2Cl_2): 7.30 (ddt, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.7$ Hz, $^4J_{PH} = 0.6$ Hz, 3H, *m*′-*H*); 7.10 (ddd, $^3J_{HH} = 8.3$ Hz, $^3J_{PH} = 4.6$ Hz, $^4J_{HH} = 1.0$ Hz, 3H, *o*′-*H*); 6.90 (dt, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.0$ Hz, 3H, *p*-*H*); 6.75 (ddd, $^3J_{HH} = 7.5$ Hz, $^4J_{PH} = 4.3$ Hz, $^4J_{HH} = 1.7$ Hz, 3H, *m*-*H*); 5.10 (s, 6H, $-OCH_2OCH_3$); 3.25 (s, 9H, $-OCH_2OCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −37.4 (s).

B. Preparation of $P(o\text{-}C_6H_4OH)_3 \cdot HCl$. Anhydrous HCl gas was bubbled into a suspension of 3.20 g of $P(o\text{-}C_6H_4OCH_2OCH_3) \cdot 0.25CH_3OH$ (7.10 mmol) in 150 mL of deoxygenated methanol at 60 °C for 1 h. Approximately 5 s after the initial contact of HCl gas with the solution, all of the solid had dissolved and a clear, colorless solution formed. The solvent volume was reduced to 40 mL in vacuo, and the concentrated solution was stored in the freezer (−20 °C) overnight, whereupon a white crystalline solid formed. The supernatant liquid was removed by cannula and the remaining white crystalline solid was washed with hexane (2 × 20 mL) and then dried under dynamic vacuum at 40 °C for 2 h. A total of 1.59 g (4.60 mmol) of analytically pure crystals of $[P(o\text{-}C_6H_4OH)_3 \cdot HCl]$ were obtained. (Yield 63% based on the starting mom-protected phosphine). Anal. Calcd for $C_{18}H_{16}O_3ClP$: C, 62.35; H, 4.65; Cl, 10.22. Found: C, 61.98; H, 4.60; Cl, 10.18%. FAB MS: *m*/*z* 311 ($[P(o\text{-}C_6H_4OH)_3H]^+$). $^{31}P\{^1H\}$ NMR (CD_3OD): −19.4 (s). ^1H NMR (CD_3OD): 7.65 (mu, $^3J_{HH} = 7.8$ Hz, 3H, p-*H*); 7.22 (ddd, $^3J_{PH} = 15.4$ Hz, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 1.5$ Hz, 3H, *o*′-*H*), 7.06 (om, 6H, *m*′-*H*/*m*-H); 5.18 (d, $^1J_{PH} = 1108$ Hz, 1H, P-*H*);-C_6H_4OH (not observed).

C. Preparation of $P(o\text{-}C_6H_4OSiMe_3)_3$ (2) from $[P(o\text{-}C_6H_4OH)_3 \cdot HCl]$. A procedure similar to that described above for the synthesis of $[PhP(o\text{-}C_6H_4OSiMe_3)_2]$[18] was used. A slurry of 1.54 g of $P(o\text{-}C_6H_4OH)_3 \cdot HCl$ (4.44 mmol) in 45 mL of dried, deoxygenated, $HN(SiMe_3)_2$ was heated under reflux conditions (ca. 140 °C) for 6 h, during which time the solid dissolved. The solvent and other volatile materials were removed in vacuo to leave a pink crystalline solid which was dried under a dynamic vacuum at 40 °C for 2 h to yield an analytically pure sample of $P(o\text{-}C_6H_4OSiMe_3)_3$ (**2**) (yield 2.09 g (89%), based on the starting hydroxyphenyl phosphine). Anal. Calcd for $C_{27}H_{39}O_3PSi_3$: C, 61.56; H, 7.46. Found: C, 61.33; H, 7.38%. ^1H NMR (CD_2Cl_2): 7.22 (dt, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.8$ Hz, $^4J_{PH} = 0.5$ Hz, 2H, *m*′-*H*); 6.88, (m, 1H), 6.84 (t, $^3J_{HH} = 7.7$ Hz, 3H, *p*-*H*); 6.81 (dd, $^3J_{HH} = 7.7$ Hz, $^3J_{PH} = 4.8$ Hz, 3H, *o*′-*H*); 6.72 (ddd, $^3J_{HH} = 7.7$ Hz, $^4J_{PH} = 4$ Hz, $^4J_{HH} = 1.7$ Hz, 3H, *m*-*H*); 0.15 (s, 27H, $-OSi(CH_3)_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −36.1 (s).

Preparation of the Metal Complexes. Reaction of $PhP(o\text{-}C_6H_4OSiMe_3)_2$ with $ReOCl_2(OEt)(PPh_3)_2$ in THF-d_8. Dried, deoxygenated THF-d_8 (5 mL) was added by means of a syringe to a Schlenk vessel containing a solid, homogeneous mixture of $PhP(o\text{-}C_6H_4OSiMe_3)_2$ (**1**) (0.139 g, 0.317 mmol) and $[ReO(OEt)Cl_2(PPh_3)_2]$ (0.265 g, 0.314 mmol). The resulting brown-green slurry was heated at 45 °C for 3 h during which time a clear green-brown solution formed. The solution was allowed to cool to room temperature and a 1 mL portion of the sample was analyzed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum for the reaction mixture showed free triphenylphosphine (−5.33 ppm) along with eight doublets consistent with four new Re complexes: two diastereomers of the trans complex, *trans*-$[ReOCl_2(PPh_3)(\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)]$ (**3a**). Diastereomer **A**, AB quartet, 7.27 (d), 2.67 (d), $^2J_{(PP)} = 295$ Hz; diastereomer **B**, AB quartet, 6.11 (d), 3.82 (d), $^2J_{(PP)} = 292$ Hz, representing 27.5% and 0.88%, respectively, of the total phosphorus intensity (excluding the PPh_3 resonance) *and* two diastereomers of the cis complex, *cis*-$[ReOCl_2(PPh_3)(\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)]$ (**3b**). Diastereomer **A**, AX doublets, −10.0 (d), −1.36 (d), $^2J_{PP} = 12$ Hz, *and* diastereomer **B**, AX doublets, −10.82 (d), −2.88 (d), $^2J_{PP} = 12$ Hz, respectively, that comprise 67.7% and 3.88% of the total phosphorus intensity. A stoichiometric quantity of the expected intramolecular elimination product, trimethylsilylethyl ether (Me_3SiOEt), was also clearly identifiable in the proton spectrum of the reaction mixture, appearing as a set of singlet (0.086 (9H)), triplet (1.14 (3H, $^2J_{HH} = 7.0$ Hz)), and quartet (3.64 ppm (2H, $^3J_{HH} = 7.0$ Hz)) resonances with the appropriate intensity ratios. (Phosphorus NMR shifts are higher by ca. 0.7−1.5 ppm in THF-d_8 than in CD_2Cl_2. The CD_2Cl_2 NMR shift values obtained by reference to separated samples are quoted above.)

Preparation of a Mixture of *trans*-$ReOCl_2(PPh_3)(\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)]$ (3a) and *cis*-$[ReOCl_2(PPh_3)(\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)]$ (3b) and the Subsequent Separation of the Two Isomers by Crystallization. A colorless solution of $PhP(o\text{-}C_6H_4OSiMe_3)_2$ (**1**) (0.208 g, 0.474 mmol) in 10 mL of freshly distilled THF was transferred by cannula to a rapidly stirred, brown-green slurry of $ReO(OEt)Cl_2(PPh_3)_2$ (0.400 g, 0.475 mmol) in 10 mL of THF. The mixture was then heated to 40 °C and kept at this temperature for 4 h. The solid gradually dissolved to give a green-brown solution which was then cooled to 23 °C. The solvent was then removed in vacuo, to afford a yellow-green solid, which was then washed with 12 mL of diethyl ether. The residue was then dissolved in dichloromethane (3 mL) to produce a clear yellow-green solution. Diethyl ether was gently layered on top of this solution. Small tawny-green crystals (0.038 g) grew just below the interface of the two solvent layers over a five-day period. The supernatant layer was then transferred to a second vessel, whereupon green-yellow crystals (0.141 g) grew out of this homogeneous Et_2O/CH_2Cl_2 solution. After recovery, both groups of crystals were dried overnight under vacuum. The green-yellow crystals were identified as one diastereomer (**A**) of *trans*-$[ReOCl_2(PPh_3)(\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)]$ (**3a**). Likewise, the tawny-green crystals were identified as one diastereomer of *cis*-$[ReOCl_2(PPh_3)(\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)]$ (**3b**). The overall yield for both isomers formed in the reaction was 41.1%, based on the starting phosphine ligand. (We note that the phosphorus NMR chemical shift values found in THF are generally lie about 0.5−1.5 ppm to lower field relative to the halocarbon solvent values given in this section and Table 1, however the coupling constants do not vary.)

trans-$[ReOCl_2(PPh_3)\{\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)\}]$ (**3a**) (yellow-green crystals), 33% yield. Anal. Calcd for $C_{39}H_{37}O_3Cl_2P_2SiRe$: C, 52.00; H, 4.14; Cl, 7.87. Found: C, 52.07; H, 3.87; Cl, 8.29. $^{31}P\{^1H\}$ NMR (in CD_2Cl_2): AB quartet, 2.67 (d), 7.27 (d), $^2J_{PP} = 295$ Hz. ^1H NMR (CD_2Cl_2): 8.22 (dd, 2H, two *o*-H atoms, $^3J_{HH} = 7.7$ Hz, $^3J_{PH} = 5$ Hz), 7.83−7.55 (om, 25H, -C_6H_4/-C_6H_4ORe/-$C_6H_4OSiMe_3$), 6.05 (dd, 1H, 1′-H on -C_6H_4O ring, $^3J_{HH} = 7.7$ Hz, $^3J_{PH} = 5$ Hz), 0.04 (s, 9H, $-OSi(CH_3)_3$). Electrospray MS: *m*/*z* 865 ($[ReOCl_2(PPh_3)\{\kappa^2\text{-}(P,O)\text{-}P(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)] - Cl]^+$, 757 ($[ReOCl_2(PPh_3)\{\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)] - SiMe_3Cl - Cl]^+$.

cis-$[ReOCl_2(PPh_3)(\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)] \cdot CH_2Cl_2$ (**3b**) (tawny-green crystals), 8.1% yield. Anal. Calcd for $C_{40}H_{39}O_3Cl_4P_2SiRe$: C, 48.74; H, 3.99; Cl, 14.4. Found; C, 49.30; H, 3.81; Cl, 13.1. $^{31}P\{^1H\}$ NMR (in CD_2Cl_2): −8.21 (d), −0.66 (d), $^2J_{PP} = 12$ Hz. ^1H NMR (CD_2Cl_2): 7.62 (dt, 1H, *m*′-*H*, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.8$ Hz), 7.45−6.70 (om, 26H, -C_6H_5/-C_6H_4ORe/-$C_6H_4OSiMe_3$), 5.74 (ddd, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{PH} = 4.0$ Hz, $^4J_{HH} = 1.7$ Hz, *m*-*H*), 5.32 (s, 2H, cocrystallized CH_2Cl_2) −0.02 (s, 9H, $-OSi(CH_3)_3$. Electrospray MS: *m*/*z* 865 [($[ReOCl_2(PPh_3)\{\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)] - Cl]^+$, 757 [($[ReOCl_2(PPh_3)\{\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)] - SiMe_3Cl - Cl]^+$. IR ($CH_2Cl_2$ cast on a KBr Disk): 973 cm^{-1} (sh, m, $\nu_{Re=O}$).

Preparation and Isolation of a Single Diastereomer of *trans*-$[ReOCl_2(PPh_3)\{\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)]$ (3a). Tetrahydrofuran (40 mL) was transferred by means of a syringe to a 100

Table 1. Phosphorus-31 NMR Data for the New Ligands and Their Re(V) Complexes[a]

compound	no.	δ PPh_3 (ppm)	δ P[b] (ppm)	$^2J_{PP}$ (Hz)	$\Delta\delta P$[c] (ppm)
$PhP(o\text{-}C_6H_4OSiMe_3)_2$	**1**	−	−25.5	−	n.a.
$P(o\text{-}C_6H_4OSiMe_3)_3$	**2**	−	−36.1	−	n.a.
trans-$[ReOCl_2(PPh_3)(\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)]$	**3a**[d]	2.67	7.27	295	32.8
cis-$[ReOCl_2(PPh_3)(\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)]$	**3b**[d]	−8.21	−0.66	12	24.8
cis-$[ReOCl_2(PPh_3)(\kappa^3\text{-}(P,O,O)\text{-}PhP(o\text{-}C_6H_4O)_2)]$	**4**	−1.33	20.25	5.1	45.8
cis-$ReOCl_2(PPh_3)(\kappa^2\text{-}(P,O)\text{-}P(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)_2)]$	**5**	−9.45	−0.32	12.7	35.8
cis-$[ReOCl(PPh_3)(\kappa^3\text{-}(P,O,O)\text{-}P(o\text{-}C_6H_4O)_2(o\text{-}C_6H_4OSiMe_3))]$	**6**	−0.06	15.38	8.2	51.5
cis-$[ReOCl(PPh_3)(\kappa^3\text{-}(P,O,O)\text{-}P(o\text{-}C_6H_4O)_2(o\text{-}C_6H_4OH))]$	**7**	−1.47	16.35	7.8	52.5
cis-$[Re(OH)Cl(PPh_3)(\kappa^3\text{-}(P,O,O)\text{-}P(o\text{-}C_6H_4O)_2(o\text{-}C_6H_4OSiMe_3))]BF_4$	**8**	2.08	17.88	8	54.0

[a] Chemical shifts are measured in ppm relative to external 85% H_3PO_4 and determined in CD_2Cl_2 solution. [b] Phenoxyphenylphosphine shifts. [c] Defined as the phenoxyphenylphosphine coordination shift: (δ complex − δ free ligand). [d] Major component.

Table 2. Crystallographic Experimental Details

A. Crystal Data

	5·(0.875 CH_2Cl_2)	**6·(CH_2Cl_2)**
empirical formula	$C_{42.875}H_{46.75}Cl_{3.75}O_4P_2ReSi_2$	$C_{40}H_{38}Cl_3O_4P_2ReSi$
fw	1063.31	965.28
cryst dimens (mm)	0.34 × 0.09 × 0.02	0.22 × 0.12 × 0.08
cryst syst, space group	triclinic, $P\bar{1}$ (No. 2)	triclinic, $P\bar{1}$ (No. 2)
unit cell parameters:		
a (Å)	14.302 (4)	10.1509 (6)
b (Å)	18.734 (2)	12.1123 (8)
c (Å)	17.639 (4)	16.2142 (14)
α (deg)	80.950 (12)	97.851 (7)
β (deg)	80.12 (2)	94.852 (7)
γ (deg)	81.76 (2)	96.889 (6)
V (Å^3)	4565.3 (17)	1950.2 (2)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.547	1.644
μ (mm^{-1})	3.043	9.382

B. Data Collection and Refinement Conditions

	5	**6**
diffractometer	Enraf-Nonius CAD4	Siemens P4/RA[d]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.710 73)	graphite-monochromated Cu Kα (1.541 78)
temperature (°C)	−60	−60
scan type	$\theta-2\theta$	$\theta-2\theta$
data collection 2θlimit (deg)	50.0	113.5
total data collected	15987 ($0 \le h \le 17$, $-21 \le k \le 22$, $-20 \le l \le 20$)	5524 ($0 \le h \le 11$, $-12 \le k \le 12$, $-17 \le l \le 17$)
no. of indep reflcns	15 285	5168
no. of observns (*NO*)	7615 ($F_o^2 \ge 2\sigma(F_o^2)$)	4770 ($F_o^2 \ge 2\sigma(F_o^2)$)
structure solution method	direct methods (*SHELXS-86*[a])	direct methods (*SHELXS-86*[a])
refinement method	full-matrix least-squares on F^2 (*SHELXS-93*[b])	full-matrix least-squares on F^2 (*SHELXS-93*[b])
absorption correction method	Gaussian integration (face-indexed)	semiempirical (ψ scans)
range of transmission factors	0.9255−0.7573	0.7783−0.2073
data/restraints/parameters	15274 [$F_o^2 \ge 3\sigma(F_o^2)$]/6[c]/948	5168 [$F_o^2 \ge 3\sigma(F_o^2)$]/0/460
goodness-of-fit (S)[d]	1.021 [$F_o^2 \ge 3\sigma(F_o^2)$]	1.062 [$F_o^2 \ge 3\sigma(F_o^2)$]
final R indices[e]		
$F_o^2 \ge 3\sigma(F_o^2)$	$R_1 = 0.0852$, w$R_2 = 0.1525$	$R_1 = 0.0303$, w$R_2 = 0.0721$
all data	$R_1 = 0.1948$, w$R_2 = 0.2019$	$R_1 = 0.0348$, w$R_2 = 0.0742$

[a] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473. [b] Sheldrick, G. M. *SHELXL-93: Program for crystal structure determination;* University of Göttingen: Germany, 1993. Refinement on F_o^2 for all reflections (except in the case of **5** where 11 reflections having $F_o^2 \ge 3\sigma(F_o^2)$ were omitted). Weighted R factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional R factors R_1 are based F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 \ge 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. R factors based on F_o^2 are statistically about twice as large as those based on F_o, and R factors based on all data will be even larger. [c] Restraints were applied to the interatomic distances within the solvent CH_2Cl_2 molecules: d(C−Cl) = 1.80(1) Å and d(Cl···Cl) = 2.95 Å. [d] $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$). For **5**, $a = 0.0553$, $b = 12.1175$. For **6**, $a = 0.0418$, $b = 3.3953$. [e] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

mL Schlenk vessel containing a solid mixture of $ReO(OEt)Cl_2(PPh_3)_2$ (0.292 g, 0.346 mmol) and $PhP(o\text{-}C_6H_4OSiMe_3)_2$ (**1**) (0.151 g, 0.344 mmol) and the resulting green-brown slurry was heated under reflux conditions (67 °C) for 4 h. The solid slowly dissolved to form yellow-green solution. The solvent was then removed in vacuo, to leave a yellow-green solid, which was washed with two 5 mL aliquots of diethyl ether. Recrystallization of the washed product from mixed dichloromethane/diethyl ether (1/1) at 25 °C afforded yellow-green crystals (0.159 g, 0.176 mmol) of *one* diastereomer **A** of *trans*-$[ReOCl_2(PPh_3)\{\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)\}]$ (**3a**) (yield, 51% based on the phosphine ligand). Phosphorus NMR spectroscopy revealed that the only species present in the mother liquor above the yellow-green crystals was (**3a**)**A**.

Preparation of $[ReOCl(PPh_3)\{\kappa^3\text{-}(P,O,O')\text{-}PhP(o\text{-}C_6H_4O)_2\}]$ (4) from a mixture of *cis*/*trans*-$[ReOCl_2(PPh_3)\{\kappa^2\text{-}(P,O)\text{-}PhP(o\text{-}C_6HO)(o\text{-}C_6H_4OSiMe_3)\}]$ (3a/3b). A solid mixture of **3a** (0.061 g, 0.068 mmol) and **3b** (0.069 g, 0.077 mmol) was dissolved in 15 mL of freshly distilled toluene and the resulting green-brown solution was heated under reflux conditions (∼111 °C) for 3 h, during which time the solution became brown. The solvent was then removed in vacuo to

Table 3. Selected Interatomic Distances for **5** and **6** (Å)

Distances for **5**

		distance	
atom 1	atom 2	molecule **A**	molecule **B**
Re	Cl(1)	2.373(5)	2.384(4)
Re	Cl(2)	2.374(5)	2.389(5)
Re	P(1)	2.483(5)	2.472(4)
Re	P(2)	2.502(5)	2.506(5)
Re	O(1)	1.676(11)	1.678(11)
Re	O(10)	1.984(11)	1.996(11)
Si(1)	O(20)	1.681(13)	1.672(12)
Si(2)	O(30)	1.669(12)	1.659(13)
O(10)	C(12)	1.36(2)	1.35(2)
O(20)	C(22)	1.36(2)	1.35(2)
O(30)	C(32)	1.36(2)	1.37(2)

Distances for **6**

atom 1	atom 2	distance
Re	Cl(1)	2.3759(12)
Re	P(1)	2.4240(12)
Re	P(2)	2.4833(12)
Re	O(1)	1.670(3)
Re	O(10)	2.047(3)
Re	O(20)	2.019(3)
Si	O(30)	1.680(4)
O(10)	C(16)	1.346(6)
O(20)	C(26)	1.364(6)
O(30)	C(36)	1.355(6)

leave a brown solid, shown by ^{31}P NMR spectroscopy to be the known[11] compound [ReOCl(PPh$_3$){κ^3-(P,O,O′)-PhP(*o*-C$_6$H$_4$O)$_2$}] (**4**). Brown crystals of [ReOCl(PPh$_3$){κ^3-(P,O,O)-PhP(*o*-C$_6$H$_4$O)$_2$}]·0.25 CH$_2$Cl$_2$ (0.055 g) were grown over 18 h from mixed dichloromethane/diethyl ether (1/1) at 25 °C. The yield was 47% (based on the total mass of both isomers). Anal. Calcd for $C_{36.25}H_{28.5}O_3Cl_{1.5}P_2Re$: C, 53.52; H, 3.53; Cl, 6.53. Found: C, 53.70; H, 3.31; Cl, 6.61. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 20.25 (d), −1.33 (d), $^2J_{PP}$ = 5.1 Hz. ^{1}H NMR (CD$_2$Cl$_2$): 7.55−7.19 (om, 24H, -OC$_6$*H*$_4$/-C$_6$*H*$_5$), 6.92 (t, 1H), 6.80 (t, 1H), 6.69 (t, 1H, *p*-*H* on C$_6$H$_4$O- ring), 5.76 (dd, 1H, $^3J_{HH}$ = 7.7 Hz, $^3J_{PH}$ = 5 Hz, *o*′-*H* on C$_6$H$_4$O- ring). Electrospray MS: *m*/*z* 793 ([ReOCl(PPh$_3$){κ^3-(P,O,O)-PhP(*o*-C$_6$H$_4$O)$_2$}] + H)$^+$, 757 ([ReOCl(PPh$_3$){κ^3-(P,O,O)-PhP(*o*-C$_6$H$_4$O)$_2$}] − Cl)$^+$.

Preparation of *cis*-[ReOCl$_2$(PPh$_3$){κ^2-(P,O)-P(*o*-C$_6$H$_4$O)(*o*-C$_6$H$_4$OSiMe$_3$)$_2$}] (5). Tetrahydrofuran (50 mL) was added by means of a cannula to an intimate mixture of [ReO(OEt)Cl$_2$(PPh$_3$)$_2$] (0.960 g, 1.14 mmol) and P(*o*-C$_6$H$_4$OSiMe$_3$)$_3$ (**2**) (0.573 g, 1.09 mmol). The resulting brown-green solution was heated to 50 °C and kept at this temperature with stirring overnight (17 h). The solution was cooled to 23 °C, and the solvent was then removed under vacuum to give a green-brown solid. Recrystallization of this product from dichloromethane−diethyl ether (1:1) solution at 23 °C, afforded *cis*-[ReOCl$_2$(PPh$_3$){κ^2-(P,O)-P(*o*-C$_6$H$_4$O)(*o*-C$_6$H$_4$OSiMe$_3$)$_2$] (**5**·0.5CH$_2$Cl$_2$) (0.331 g, 0.321 mmol) as a green-brown crystalline solid (yield 29% based on the amount of phosphine used). Alternatively, compound **5** can be obtained by heating equimolar amounts of [ReO(OEt)Cl$_2$(PPh$_3$)$_2$] and [P(*o*-C$_6$H$_4$OSiMe$_3$)$_3$] (**5**) at 80 °C in acetonitrile for 2−3 h. Yields approaching 70% were achieved by using this procedure. Anal. (for a batch of crystals of **5**·0.5CH$_2$Cl$_2$). Calcd for $C_{42.5}H_{46}O_4Cl_3P_2Si_2Re$: C, 49.49; H, 4.50; Cl, 10.31. Found: C, 49.74; H, 4.37; Cl, 10.27. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): −9.45 (d), −0.32 (d), $^2J_{PP}$ = 12.7 Hz. ^{1}H NMR (CD$_2$Cl$_2$): 7.75 (m, 1H) 7.53−6.70 (om, 23H, -C$_6$*H*$_4$O/-C$_6$*H*$_4$OSiMe$_3$/-C$_6$*H*$_5$), 6.59 (ddd, 1H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, *J* = 14 Hz, -C$_6$*H*$_4$ORe *or* -C$_6$*H*$_4$OSiMe$_3$), 6.21 (dt, 1H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.7 Hz), 5.71 (dd, 1H, $^3J_{PH}$ = 5 Hz, $^3J_{HH}$ = 7.7 Hz, *o*′-*H* on the -C$_6$H$_4$ORe ring), 5.32 (s, 1H, cocrystallized C*H*$_2$Cl$_2$). Electrospray MS: *m*/*z* 845 ([ReOCl$_2$(PPh$_3$)(κ^2-(P,O)-P(*o*-C$_6$H$_4$O)(*o*-C$_6$H$_4$OSiMe$_3$)] − Cl − SiMe$_3$Cl)$^+$. When the above reaction was repeated in warm (50 °C) THF-d_8, a stoichiometric quantity of the expected intramolecular elimination product, EtOSiMe$_3$, was clearly visible in the proton NMR spectrum of the reaction mixture.

Synthesis of [ReOCl(PPh$_3$){κ^3-(P,O,O)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OSiMe$_3$)}] (6). A slurry of [ReOCl$_3$(PPh$_3$)$_2$] (0.210 g, 0.252 mmol) and P(*o*-C$_6$H$_4$OSiMe$_3$)$_3$ (**1**) (0.133 g, 0.252 mmol) in 20 mL of dry, deoxygenated acetonitrile was heated under reflux conditions (85 °C) for 14 h to yield a green-brown solution and a small amount of an insoluble brown solid. The reaction mixture was filtered, the brown solid discarded and the supernatant liquid evaporated to dryness under vacuum. The residue was then recrystallized from CH$_2$Cl$_2$−Et$_2$O (1/3) to give [ReOCl(PPh$_3$){κ^3-(P,O,O)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OSiMe$_3$)}] (**6**·CH$_2$Cl$_2$) (0.059 g, 0.061 mmol) as green-brown crystals (yield 24% based on starting phosphine. Anal. Calcd. for $C_{40}H_{38}O_4Cl_3P_2SiRe$: C, 49.77; H, 3.97; Cl, 11.02. Found; C, 50.06; H, 3.73; Cl, 11.78. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 15.38 (d), −0.06 (d), $^2J_{PP}$ = 8.2 Hz. ^{1}H NMR (CD$_2$Cl$_2$): 7.56−6.84 (om, 24H, -C$_6$*H*$_4$ORe/-C$_6$*H*$_4$OSiMe$_3$/-C$_6$*H*$_5$), 6.72 (dd, 1H, -C$_6$*H*$_4$ORe or -C$_6$*H*$_4$OSiMe$_3$), 6.63 (dd, 1H), 5.70 (dd, 1H, $^3J_{PH}$ = 5 Hz, $^3J_{HH}$ = 7.7 Hz, *o*′-*H* of a phenoxy ring), 5.32 (s, 2H, cocrystallized C*H*$_2$Cl$_2$), 0.02 (s, 9H, −OSi(C*H*$_3$)$_3$). Electrospray MS: *m*/*z* 903 ([ReOCl(PPh$_3$)$_2${κ^3-(P,O,O)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OSiMe$_3$)}] + Na)$^+$, 881 ([ReOCl(PPh$_3$)$_2${κ^3-(P,O,O)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OSiMe$_3$)}] + H)$^+$.

[ReOCl(PPh$_3$){κ^3-(P,O,O)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OSiMe$_3$)}] (**6**) was also prepared (in 30% yield) by treating [ReOCl$_2$(PPh$_3$){κ^2-(P,O)-P(*o*-C$_6$H$_4$O)(*o*-C$_6$H$_4$OSiMe$_3$)$_2$}] (**5**) with an equimolar amount of PPN$^+$Cl$^-$ in THF.

Heating (**5**) in boiling acetonitrile for 4 h gave (**6**) in high yield (∼90%).

Preparation of [ReOCl(PPh$_3$){κ^3-(P,O,O′)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OH)}] (7). Water (0.0025 g, 0.140 mmol) was added to a solution of [ReOCl(PPh$_3$){κ^3-(P,O,O)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OSiMe$_3$)}] (**6**) (0.120 g, 0.136 mmol) in ethanol (20 mL), and the solution was stirred for 5 days at 25 °C. The solution gradually changed color from green-brown to yellow. The solvent was removed in vacuo and the residue was recrystallized from mixed acetonitrile/diethyl ether (1/1) at 23 °C to give yellow-brown needles of [ReOCl(PPh$_3$){κ^3-P,O,O)-P(*o*-C$_6$H$_4$O)$_2$-(*o*-C$_6$H$_4$OH)}] (**7**) (0.093 g, 0.115 mmol, 85% yield). Anal. Calcd for $C_{36}H_{28}O_4ClP_2Re$: C, 53.50; H, 3.49; Cl, 4.39. Found: C, 54.62; H, 3.47; Cl, 5.19. ^{31}P{^{1}H} NMR (acetone-d_6): 16.35 (d), −1.47 (d), $^2J_{PP}$ = 7.8 Hz. ^{1}H NMR (DMF-d_7): 7.83 (t, 1H, *m*′-*H* on a phenoxy ring, $^3J_{HH}$ = 7.7 Hz), 7.69−6.84 (om, 24H, -C$_6$*H*$_5$/-C$_6$*H*$_4$OSiMe$_3$/-C$_6$*H*$_4$O), 6.78 (t, 1H), 6.61 (t, 1H), 5.76 (dd, 1H, $^3J_{HH}$ = 7.7 Hz, $^3J_{PH}$ = 5 Hz, *o*′-*H* on a phenoxy ring). FAB MS: *m*/*z* 773 ([ReOCl(PPh$_3$){κ^3-(P,O,O)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OH)] − Cl)$^+$, 511 ([ReOCl(PPh$_3$){κ^3-(P,O,O)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OH)}] − Cl − PPh$_3$)$^+$. IR (Nujol mull on KBr plates, cm^{-1}): 960 (st, sh, $\nu_{Re=O}$), 3430 (st, b, ν_{O-H}).

Preparation of [Re(OH)Cl(PPh$_3$)(κ^3-(P,O,O)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OSiMe$_3$)]BF$_4$ (8). A green-brown solution of [ReOCl$_2$(PPh$_3$)(κ^2-(P,O)-P(*o*-C$_6$H$_4$O)(*o*-C$_6$H$_4$OSiMe$_3$)$_2$] (**5**) (0.127 g, 0.128 mmol) dissolved in 20 mL of acetonitrile was transferred by cannula to a Schlenk vessel containing solid AgBF$_4$ (0.025 g, 0.128 mmol). The reaction vessel was wrapped in aluminum foil and the mixture was stirred in the dark for 2 h, during which time a gray solid precipitated from the solution. The solution was filtered to remove the solid precipitate (which analyzed satisfactorily for AgCl) and the filtrate was taken to dryness under vacuum, to afford a brown residue. Recrystallization from CH$_2$-Cl$_2$/Et$_2$O (1/1) at 23 °C (over 2 days) gave small brown crystals of [Re(OH)Cl(PPh$_3$)(κ^3-(P,O,O)-P(*o*-C$_6$H$_4$O)$_2$(*o*-C$_6$H$_4$OSiMe$_3$)]BF$_4$·CH$_2$-Cl$_2$ (**8**) (0.031 g, 0.029 mmol, 23% yield). Anal. Calcd for $C_{40}H_{39}O_4$-$Cl_3P_2SiBF_4Re$: C, 45.62; H, 3.73. Found: C, 46.36; H, 3.43. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 17.88 (d), 2.08 (d), $^2J_{PP}$ = 8 Hz. ^{1}H NMR (CD$_2$Cl$_2$): 7.61−6.69 (om, 26H, -C$_6$*H*$_4$ORe/-C$_6$*H*$_4$OSiMe$_3$/-C$_6$*H*$_5$) 5.67 (dd, 1H, $^3J_{HH}$ = 7.7 Hz, $^3J_{PH}$ = 5 Hz, *o*′-*H* on a phenoxy ring), 5.32 (s, 2H, cocrystallized C*H*$_2$Cl$_2$), −0.04 (s, 9H, −OSi(C*H*$_3$)$_3$), O-*H* (not observed). IR (μscope, cm^{-1}) 3417 (m, sh, ν_{O-H}), 1098 (st, b, νBF$_4^-$).

Results and Discussion

Syntheses and Characterization of Ligands. Previous work[11] described a refinement of the preparation of PhP{OH}$_2$·HCl[25] which was then used to prepare several Re(V) complexes. We have now converted this ligand to the silylated form by the straightforward reaction of the hydrochloride salt with hexamethyldisilazane and further explored the complexation chem-

(25) Rauchfuss, T. B. *Inorg. Chem.* **1977**, *16*, 2966−2968.

Table 4. Selected Interatomic Angles for **5** and **6** (deg)

Angles for **5**

atom 1	atom 2	atom 3	angle	
			molecule A	molecule B
Cl(1)	Re	Cl(2)	84.9(2)	85.2(2)
Cl(1)	Re	P(1)	164.3(2)	162.21(15)
Cl(1)	Re	P(2)	85.7(2)	85.0(15)
Cl(1)	Re	O(1)	103.8(4)	105.7(4)
Cl(1)	Re	O(10)	90.0(3)	87.5(3)
Cl(2)	Re	P(1)	87.9(2)	90.1(2)
Cl(2)	Re	P(2)	168.4(2)	169.9(2)
Cl(2)	Re	O(1)	100.5(4)	98.7(4)
Cl(2)	Re	O(10)	89.5(4)	90.7(4)
P(1)	Re	P(2)	99.5(2)	98.60(14)
P(1)	Re	O(1)	91.2(4)	92.0(4)
P(1)	Re	O(10)	75.9(3)	75.4(3)
P(2)	Re	O(1)	88.2(4)	86.3(4)
P(2)	Re	O(10)	83.8(4)	86.5(3)
O(1)	Re	O(10)	163.5(5)	164.3(5)
Re	P(1)	C(11)	99.6(6)	98.4(5)
Re	P(1)	C(21)	120.8(6)	121.7(6)
Re	P(1)	C(31)	112.6(6)	111.3(5)
Re	P(2)	C(41)	109.8(6)	116.4(6)
Re	P(2)	C(51)	117.4(6)	117.7(5)
Re	P(2)	C(61)	114.3(6)	108.8(6)
Re	O(10)	C(12)	126.4(10)	127.7(10)
Si(1)	O(20)	C(22)	128.6(12)	132.1(12)
Si(2)	O(30)	C(32)	130.8(12)	130.8(13)

Angles for **6** (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cl(1)	Re	P(1)	159.78(5)	O(1)	Re	O(10)	161.61(14)
Cl(1)	Re	P(2)	86.94(4)	O(1)	Re	O(20)	104.6(2)
Cl(1)	Re	O(1)	104.13(12)	O(10)	Re	O(20)	85.87(13)
Cl(1)	Re	O(10)	92.02(9)	Re	P(1)	C(11)	104.1(2)
Cl(1)	Re	O(20)	82.50(10)	Re	P(1)	C(21)	98.7(2)
P(1)	Re	P(2)	104.67(4)	Re	P(1)	C(31)	128.3(2)
P(1)	Re	O(1)	92.07(12)	Re	P(2)	C(41)	115.3(2)
P(1)	Re	O(10)	74.29(9)	Re	P(2)	C(51)	116.3(2)
P(1)	Re	O(20)	81.73(10)	Re	P(2)	C(61)	111.7(2)
P(2)	Re	O(1)	92.34(12)	Re	O(10)	C(16)	128.2(3)
P(2)	Re	O(10)	79.63(9)	Re	O(20)	C(26)	121.9(3)
P(2)	Re	O(20)	161.73(10)	Si	O(30)	C(36)	133.4(3)

istry of this form of the ligand. It has been our experience that elimination of Me_3SiCl in the reactions of metal halides with silylated ligands is a much cleaner preparative route to complexes than reactions which involve elimination of HCl because eliminated Me_3SiCl rarely reacts further with the desired product whereas, hydroxy ligands often frequently yield protonated complexes. Therefore, the additional preparative step of ligand silylation is generally worthwhile.[18] The preferred route to $PhP\{OH\}_2$·HCl involves the initial preparation of the protected derivative $PhP\{Omom\}_2$ (where mom is methoxymethyl ether protecting group). Unfortunately the protecting group cannot be directly removed by reaction with hexamethyldisilazane. Therefore, a two-stage procedure, deprotection and conversion to the hydrochloride followed by silylation, is required.

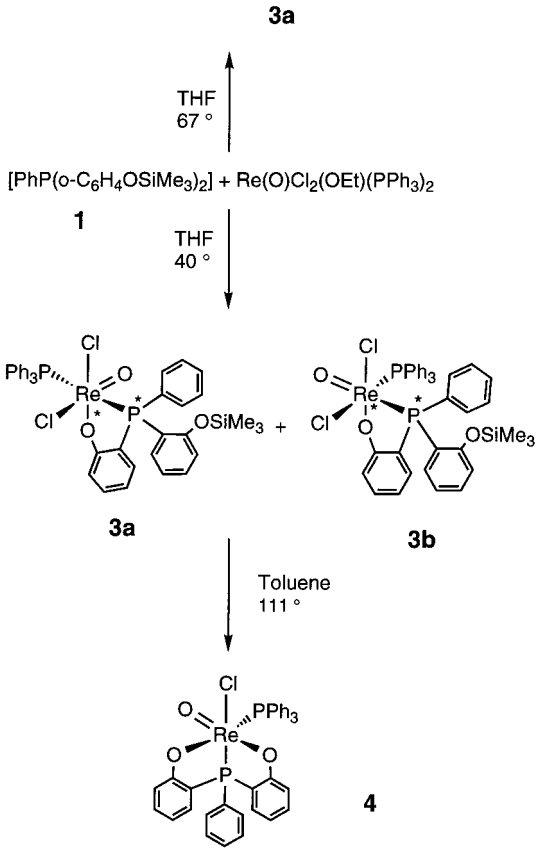
A few complexes of the related potentially tetradentate ligand tris(o-hydroxyphenyl)phosphine, abbreviated herein $P\{OH\}_3$, have been briefly described.[13] We prepared $P\{Omom\}_3$ and, from it, $P\{OH\}_3$·HCl, using procedures analogous to those used to prepare $PhP\{Omom\}_2$ and $PhP\{OH\}_2$·HCl, respectively.[11] The silylated form of the ligand, $P\{OT\}_3$, was then formed easily by reacting this $P\{OH\}_3$·HCl salt with refluxing hexamethyldisilazane in the same fashion.

The $^{31}P\{^1H\}$ NMR spectra for each of the three forms of the ligand, $P\{Omom\}_3$, $P\{OH\}_3$·HCl, and $P\{OT\}_3$ in solvents such as CD_2Cl_2 appeared as a singlet, at −37.4, −19.4, and −36.1 ppm respectively, all upfield from triphenyl phosphine (∼−5 ppm). In DMSO-d_6 however, the chemical shift of $P\{OH\}_3$·HCl was positive. A similar behavior was noted previously for $PhP\{OH\}_2$·HCl which also gave a positive $^{31}P\{^1H\}$ NMR shift in DMSO-d_6 (+34.6 ppm) and a negative shift in py-d_5 (−30.6 ppm). These markedly different values were ascribed to the formation of different protonated forms in different solvents.[11] Since the preferred form of both ligands for our studies was the silylated version, the consequences of this different NMR behavior in different solvents was deemed irrelevant and not further pursued. Notably the phosphorus chemical shift for the silylated ligand $PhP\{OT\}_2$ prepared herein, −25.5 ppm is in line with the value for $P\{OT\}_3$.

The ^1H NMR spectrum of each ligand showed four types of aromatic hydrogen atoms to be present. The four signals, roughly two triplets and two doublet of doublets, were assignable from $^1H\{^{31}P\}$ NMR and $^1H-^1H$ COSY experiments. The P−H coupling decreased in the order $o' > m > m' > p$.[26] The $^4J_{PH}$ coupling displayed in both *m*-H and *m*′-H signals are very similar.

Formation of Re(V) Complexes. The new, potentially tridentate, bis(trimethylsilyoxyphenyl)phenylphosphine ligand, $[PhP(o\text{-}C_6H_4OSiMe_3)_2]$(**1**), reacted smoothly with $[ReO(OEt)Cl_2(PPh_3)_2]$ in THF at 40 °C to produce a mixture of the

Scheme 1



structural isomers *trans*- and *cis*-[$ReOCl_2(PPh_3)\{\kappa^2$-(P,O,O)-$PhP(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)\}$], compounds **3a** and **3b**, respectively (Scheme 1). The OEt group and one PPh_3 ligand are replaced, the former by the relatively rare elimination of Me_3SiOEt. The trans/cis designation of the products refers to the relationship of the two coordinated phosphines.[27] Analysis of the ^{31}P NMR spectrum for the reaction mixture revealed that each structural isomer, **3a** and **3b** in turn, exists as diastereomers because each contains two chiral elements, viz. a chiral Re center and a chiral phosphorus atom. The cis isomer is the dominant member of the reaction product obtained under these (the mildest) conditions and one trans diastereomer dominates the trans set.

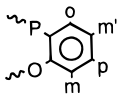
In a separate experiment, it was established that only one structural isomer (the trans form), **3a**, was obtained if the aforementioned reaction was performed in refluxing THF (~67 °C) suggesting that the trans isomer may be the thermodynamically preferred form. Surprisingly however, vide infra, the much higher temperature reaction in toluene (111 °C) yields the cis form of the κ^3-(P,O,O) complex which was also the product obtained from the reaction of $ReOCl_3(PPh_3)_2$ with $PhP\{OH\}_2$·HCl.[11] The cis forms of the complexes were also obtained exclusively in the reactions of **2** described below.

In an effort to detect intermediate compounds in the formation reaction of **3** and to verify that chelation of the phosphine ligand occurs with the concomitant release of both PPh_3 and $EtOSiMe_3$, the reaction between **1** and [$ReO(OEt)Cl_2(PPh_3)_2$] was monitored by proton and ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum showed the anticipated signal for free PPh_3, two AB quartets with large $^2J_{PP}$ coupling (7.27, 2.67 ppm, $^2J_{PP} = 295$ Hz; 6.11, 3.82 ppm, $^2J_{PP} = 292$ Hz) that are assigned to the diastereomers of **3a** and two pairs of AX doublets with significantly smaller $^{31}P-^{31}P$ coupling (−10.0, −1.36 ppm, $^2J_{PP} = 12$ Hz; −10.82, −2.88 ppm, $^2J_{PP} = 12$ Hz) which are assigned to the diastereomers of **3b**. We have used the magnitude of $^2J_{PP}$ as the basis for our stereochemical assignments. Thus, those resonances with relatively small $^2J_{PP}$ values (~12 Hz) are attributed to the cis complexes while the second-order distorted resonances with much larger $^2J_{PP}$ values(~292−295 Hz) are ascribed to the trans complexes. The ^1H NMR spectrum for the product mixture contained phenyl-type signals (**3a/3b** and PPh_3), $-C_6H_4OSiMe_3$ resonances (**3a/3b**) and a set of resonances for the other major product from the reaction, $EtOSiMe_3$ (details given in the Experimental Section). The spectroscopic evidence gathered for **3a/3b** along with data for previously reported analogous Re(V) chelate complexes,[11] suggests that compounds **3a** and **3b** have the structures shown in Scheme 1.

In each of the complexes **3a/3b**, the phenoxyphosphine ligand is coordinated in an κ^2-P,O fashion to the Re metal center, thereby forming a five-membered chelate ring. The phenoxyphosphine phosphorus atoms are shifted downfield by approximately 22−33 ppm (Table 1) which is consistent with the usual behavior of phosphine chelates.[28] (Note also that the values in THF-d_8 are larger by ca. 0.7−1.5 ppm. The numbers given refer to the referenced values in CD_2Cl_2.) The related compound [$ReOCl(PPh_3)\{\kappa^3$-(P,O,O)-$PhP(o\text{-}C_6H_4O)_2\}$] (**4**) (formed when both phenoxy groups are bound to Re (previously obtained[11,12] from the reaction of the $PhP\{OH\}_2$·HCl form of the ligand with $Re(O)Cl_3(PPh_3)_2$) was obtained upon heating toluene solutions of **3a/3b** under reflux conditions for ~3 h. The characterization data for compound (**4**) compares well with that previously published.[11] The conversion of **3a/3b** to **4** which transforms the ligand from the bidentate (κ^2-P,O) to the tridentate (κ^3-P,O,O′) bonding mode probably proceeds via an intramolecular elimination of Me_3SiCl. This, however, has not been unequivocally established. It is interesting to note that the analogous phenylphosphinebis(*ortho*-phenylthiol) ligand $PhP\{SH\}_2$ reduced Re(V) to Re(IV) to form paramagnetic complexes rather than form the analogous diamagnetic Re(V) complexes.[6]

The coordination chemistry of the potentially tetradentate ligand, [$P(o\text{-}C_6H_4OSiMe_3)_3$] (**2**), was explored initially through a reaction of the ligand with an equimolar ratio of [$ReO(OEt)Cl_2(PPh_3)_2$] in warm THF (50 °C) for 17 h. We had hoped to ascertain whether the "umbrella" mode of coordination, similar to that displayed by Tc(III),[7] could be accessed. The ^{31}P NMR spectrum of the resultant product mixture contained free PPh_3 and two doublets with $^2J_{PP} = 12.7$ Hz at −9.45 and −0.32 ppm which belong to a new Re complex **5**. The relatively small value of $^2J_{PP}$ implied a cis (P,P) geometry for **5**. In addition to signals for **5** and PPh_3, the presence of $EtOSiMe_3$ in the product mixture (identified by its proton NMR spectrum) confirmed that P,O-chelation had occurred via the displacement of PPh_3 *and* the elimination of $EtOSiMe_3$. Spectroscopic and analytical data for a crystalline sample of **5** indicated the formula [$ReOCl_2(PPh_3)\{\kappa^2$-$P(o\text{-}C_6H_4O)(o\text{-}C_6H_4OSiMe_3)_2\}$] (Scheme 2) which was subsequently confirmed by a crystallographic study (vide infra)

(26) The hydrogen atoms in the trimethylsilyloxyphenyl rings are labeled as ortho, meta, and para, with respect to the phosphorus position on the ring, thus the oxo substituent occupies one of the ortho positions:



(27) The trans isomers are those in which the phenoxyphenylphosphine ligand P lies trans to the Re−PPh_3 bond whereas cis complexes are those in which this ligand phosphorus lies cis to the PPh_3 ligand.

(28) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229−266.

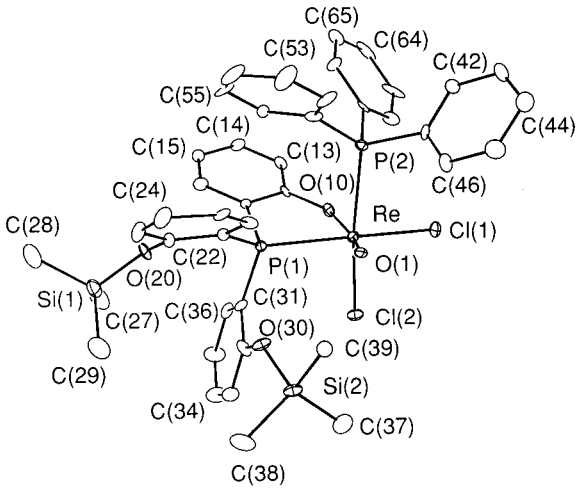
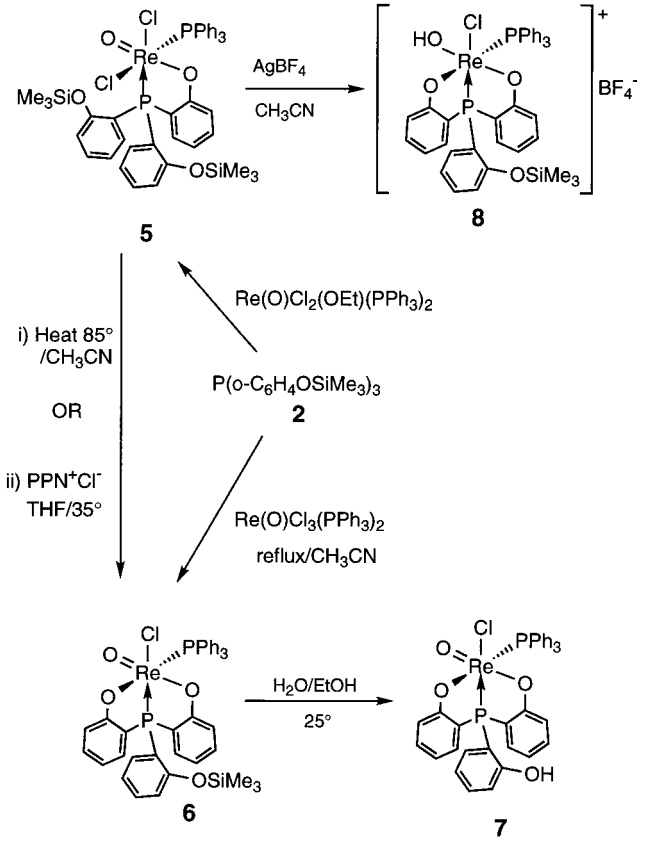


Figure 2. Perspective ORTEP[29] view of one of the two crystallographically independent molecules of $[ReCl_2(=O)(PPh_3)\{\kappa^2\text{-}P(C_6H_4O)(C_6H_4OSiMe_3)_2\}]$, **5**, (molecule **A**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. All hydrogen atoms are omitted for clarity.

Scheme 2



(Figure 2).[29] The results obtained herein with $P\{OT\}_3$ and Re(V) are thus similar to the results of the coordination of $P\{SH\}_3$ with Rh, Ru, and Ir[6] in that only two (at most) of the ortho substituted ligand components (and the phosphine) bind to the metal center.

It is also noteworthy that both of the aforementioned reaction pathways (preparations of **4** and **5**) yield *exclusively* the cis complex; the trans complex has not been observed at any time

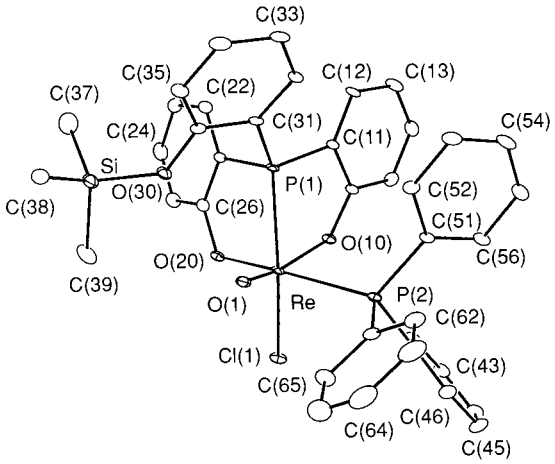


Figure 3. Perspective ORTEP[29] view of the $[ReCl(=O)(PPh_3)\{\kappa^3\text{-}P(C_6H_4O)_2(C_6H_4OSiMe_3)\}]$, **6**, molecule showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. All hydrogen atoms are omitted for clarity.

in any of the reaction mixtures produced by either synthetic pathway and yet trans could be accessed *exclusively* under one certain condition in the reactions of **1** with $ReOCl_2(OEt)(PPh_3)_2$. Clearly the mechanisms by which the various isomers are formed are complex.

The crystal and molecular structure of **5** (Figure 2)[29] (which crystallizes with two independent molecules in the unit cell) shows clearly in both cases that the phosphine centers lie in mutually cis positions, that the bound phenolate lies trans to the Re=O bond and that there are two dangling siloxy groups. One of the two free Me_3Si groups in each molecule is oriented so as to lie in reasonable proximity to the Cl which in turn is positioned trans to the PPh_3 unit. The Si(2)−Cl(2) separations in the two molecules (**A** and **B**, 4.308(7) and 4.481(7) Å respectively) suggest that facile elimination of Me_3SiCl could be accomplished if the process were intramolecular. Thermal elimination was demonstrated in this system (although this is not always the case) by heating **5** under reflux conditions in acetonitrile for 4 h to form **6**. The same product (**6**) was also obtained upon direct reaction of (**2**) with $[ReOCl_3(PPh_3)_2]$ in boiling acetonitrile.

It is notable that formation of **5** from $Re(O)(OEt)(PPh_3)_2Cl_2$, in which the Cl and the phosphines are mutually trans,[30] involves significant rearrangement. The final stereochemistry of **5** in which there are cis related Cl substituents can be derived from the following sequence of steps. A phenoxide first binds through elimination of Me_3SiOEt. This first bound phenoxo substituent replaces the unique ethoxide ligand (which lies trans to the Re=O bond). A subsequent trans nucleophilic displacement of one of the PPh_3 ligands by the phosphine of the newly bound ligand displaces this opposite phosphine and pushes the adjacent Cl into the position formerly occupied by the departed PPh_3 group. The fact that both $ReOCl_3(PPh_3)_2$ and $Re(O)(OEt)(PPh_3)_2Cl_2$ react with **5** to give products with the same stereochemistry suggests that the initially replaced Cl in the former case is that which lies opposite the Re=O unit so the subsequent stages of the reaction may follow the same path to provide the final cis dichloride structure.

The crystal and molecular structure of **6** (Figure 3)[29] showed a very similar stereochemistry to that of **5** clearly suggesting that the proximate trimethylsilyl group noted above had

(29) Johnson, C. K. *ORTEP*; Report ORNL No. 5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(30) Graziani, R.; Casellato, U.; Rossi, R.; Marchi, A. *J. Crystallogr. Spectrosc. Res.* **1985**, *15*, 573−579.

undergone Me_3SiCl elimination to form the second chelate ring. The result is that the two coordinated phosphine centers are mutually cis, one phenolate oxygen is trans to the Re═O unit as in **5** and the new phenolate link lies trans to the PPh_3 ligand.

Efforts to force further elimination of Me_3SiCl from **6** with a view to achieving the "umbrella" tetradentate chelation demonstrated for the sulfur ligand analogue with Tc(III)[7] were without success. In view of the structure of **6**, it seems unlikely that such an elimination would occur because substantial reorganization of ligands about the Re center would be required to bring the remaining Cl to a cis position to facilitate this elimination. Although it is possible that in such systems migration of Me_3Si to the terminal oxygen[31] could provide a pathway for the ultimate formation of the tetradentate binding of the ligand, this has not been observed in this case. Reduction of the Re center might lead to the full tetradentate complexation of Re(III) by this ligand in a fashion analogous to that observed with Tc(III). We did not pursue this avenue because our interest focuses on the chemistry of the higher oxidation states of Re.

To ascertain whether the elimination of Me_3SiCl could be promoted by a nucleophilic attack of free Cl^- on species such as **5** and **6**, wherein the components are "ready" for elimination, we treated **5** with PPN^+Cl^- as a source of Cl^-. Catalytic amounts were without effect. However, a stoichiometric amount of PPN^+Cl^- in THF at 35 °C gave **6** in ca. 30% yield. Presumably this reaction begins with Cl^- attack at the Si atom in one of the pendant $OSiMe_3$ groups. This leads to elimination of Me_3SiCl and concomitant formation of a phenolate anion which then replaces a chloride ligand on the Re center via a nucleophilic attack, thereby generating the κ^3-P,O,O′-bonded chelate complex.

Both **5** and **6** are moderately moisture sensitive in solution forming the corresponding *o*-hydroxy compounds. Treating **6** with water in ethanol at room temperature gave **7** in 85% (recrystallized) yield. The reaction took several days to reach completion. The direct reaction of $P\{OT\}_3$ with either of the Re(V) precursors in solvents which had not been dried also gave **7**, which is analogous to the complexes $Re(Z)Cl(PPh_3)(PhP\{O\}_2)$ (Z = O, NPh) obtained from $PhP\{OH\}_2$·HCl and $Re(Z)Cl_3(PPh_3)_2$.[11] Complex **7**, which is air stable in the solid state and in solution, was fully characterized by elemental analysis, infrared spectroscopy, mass (FABMS) spectrometry, $^1H-^{31}P\{^1H\}$ NMR spectroscopy. The fragment cations (loss of Cl and PPh_3) were present, along with the (strongest) $[ReO(PPh_3)\{PO_3\}H]^+$ ion. The IR spectrum showed a ν_{O-H} stretch at about 3430 cm^{-1}, while the Re═O bond stretching vibrations were found at 960 cm^{-1}, normal for the respective moieties.

The $^{31}P\{^1H\}$ NMR spectrum of **7** showed an AX system, with a small coupling constant of 7.8 Hz indicating a *cis*-(P,P) geometry. The peak at 16.4 ppm was assigned to the phosphorus of the $P\{O_2\}\{OH\}^{2-}$ ligand and that at −1.5 ppm to the PPh_3 ligand which is consistent with the analogous $[Re(O)Cl(PhP\{O\}_2)(PPh_3)]$ complex[11] and with similar complexes reported herein. It was also possible to fully assign the phenyl region of the ^1H NMR spectra of the phenoxy ligand as the signals for the 15 types of aromatic hydrogen atoms were reasonably well separated.

Finally, it was of interest to ascertain if the elimination of Me_3SiCl from the complexes having proximate $SiMe_3$ and Cl groups could be promoted by the initial abstraction of a bound Cl substituent. We therefore treated **5**, which has two dangling $OSiMe_3$ groups on a bidentate ligand, with $AgBF_4$, but the result was the formation of $[Re(OH)Cl(PPh_3)\{P(o\text{-}C_6H_4O)_2(o\text{-}C_6H_4OSiMe_3)\}]BF_4$ (**8**), which contains a κ^3-P,O,O′-bonded phenoxyphosphine ligand and, notably, one unchelated trimethylsilylphenoxy ligand. This pathway therefore does not result in the hydrolytic removal of the Me_3Si group. We infer from the IR evidence that the terminal oxygen has been protonated, which is in accord with the valence state and coordination of Re. We can speculate that removal of Cl^- opens a coordination site on the Re which is subsequently filled by the coordination of the oxygen of the trimethylsiloxy group, thereby making the ligand tridentate and placing this newly attached siloxy group in a cis position relative to the Re═O unit. The next step could be migration[31] of this $SiMe_3$ group to the terminal oxygen to form a second Re−O electrovalent bond between the Re and the ligand thereby converting the terminal Re═O unit to a single $Re-OSiMe_3$ unit in an intermediate such as $[Re(OSiMe_3)Cl(PPh_3)\{P(o\text{-}C_6H_4O)_2(o\text{-}C_6H_4OSiMe_3)\}]^+$. Subsequent hydrolysis of the $OSiMe_3$ group on Re by adventitious water or by the acetonitrile solvent would give the observed product. We observed above that the hydrolysis of the silyl groups on the phenoxy ligand was relatively slow (vide supra). The reaction of a siloxy group on a metal would likely be much more rapid.

Summary and Conclusions

The silylated, multidentate, phenoxyphosphine ligands bis(trimethylsilyoxyphenyl)phenylphosphine and tris(trimethylsilyoxyphenyl)phosphine readily react with $Re(O)(X)Cl_2(PPh_3)_2$ (X = Cl or OEt) by means of elimination of the chloro or ethoxy substituents and the replacement of one initially coordinated triphenylphosphine by the phosphorus center of the multidentate ligand. The former ligand produces chiral intermediate complexes in which the ligand is bidentate and one of the siloxy groups remains on the phosphine substituent. The latter ligand likewise demonstrates stepwise replacement of up to two anionic substituents via Me_3SiX elimination. In both cases the structures demonstrate cis P,P stereochemistry presumably as a result of the sequential replacement steps, a few of which are captured here as isolated intermediates.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada the University of Alberta and the Alberta Cancer Board for support of this work.

Supporting Information Available: Complete tables of atom coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

(31) Katti, K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 3033−3036.

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