Rhenium(V) and Technetium(V) Complexes of Bis(*o*-hydroxyphenyl)phenylphosphine (PO_2^{2-}) and (*o*-Hydroxyphenyl)diphenylphosphine (PO^-) Ligands

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A modified preparation of the hydrochloride adduct of the potentially tridentate ligand bis(*o*-hydroxyphenyl)-phenylphosphine (abbreviated H_2PO_2·HCl) is described. From this ligand and a potentially bidentate analog, (*o*-hydroxyphenyl)diphenylphosphine (HPO), PO_x^{x-} ($x = 1, 2$) complexes of rhenium(V) and technetium(V) were prepared by metathesis reactions with the appropriate metal(V) precursor and/or by reduction/ligand-exchange reactions with ammonium perrhenate or pertechnetate. The new complexes fall into four categories: bis(PO) complexes ($MOCl(PO)_2$, M = Re or Tc, and $ReN(PO)_2(PPh_3)$); mono(PO_2) complexes ($ReZCl(PPh_3)(PO_2)$, Z = O or NPh); mixed(PO/PO_2) complexes ($ReZ(PO)(PO_2)$, Z = O or NPh); and bis(PO_2) complexes ($MO(PO_2)$-(HPO_2), M = Re or Tc). For the mono(PO_2) phenylimido complexes, two facial isomers, *cis*- and *trans*-(P,P)-$Re(NPh)Cl(PPh_3)(PO_2)$, were isolated from different solvents. For the mixed(PO/PO_2) complexes, *fac-cis*-(P,P)-$ReO(PO)(PO_2)$ and *fac-trans*-(P,P)-$Re(NPh)(PO)(PO_2)$ were prepared. Two non-interconvertible diastereomers were present in $ReO(PO_2)(HPO_2)$ as evinced by $^{31}P\{^1H\}$ NMR. The isomerism was shown to be derived from the orientation of the unligated hydroxyphenyl group of the HPO_2^- ligand. All the complexes were characterized by various physical techniques, including IR, MS, and $^1H/^{31}P\{^1H\}$ NMR. The X-ray structures of *fac-cis*-(P,P)-$[Re(NPh)Cl(PPh_3)(PO_2)]$·$2CHCl_3$ (**1**, $C_{44}H_{35}Cl_7NO_2P_2Re$) and *fac-cis*-(P,P)-$[ReO(PO)(PO_2)]$ (**2**, $C_{36}H_{27}O_4P_2Re$) were determined. Crystals of **1** are triclinic, $P\bar{1}$, $a = 11.997(1)$ Å, $b = 20.637(2)$ Å, $c = 10.511(1)$ Å, $\alpha = 103.772(9)°$, $\beta = 113.504(8)°$, $\gamma = 76.072(9)°$, $Z = 2$; and those of **2** are monoclinic, $P2_1/n$, $a = 10.132(2)$ Å, $b = 14.026(3)$ Å, $c = 22.046(2)$ Å, $\beta = 102.38(1)°$, $Z = 4$. The two structures were solved by the Patterson method and were refined by full-matrix least-squares procedures to $R = 0.034$ and 0.030 ($R_w = 0.034$ and 0.026) for 8203 and 5957 reflections with $I \geq 3\sigma(I)$, respectively. The structures of **1** and **2** reveal that the anchoring *o*-oxyphenyl groups strengthen the Re–P bonds significantly. The solution $^{31}P\{^1H\}$ NMR spectra and the crystal structures both demonstrated *cis*-(P,P) geometry for each complex, with the Re atom being in the center of a highly distorted octahedron of *cis*-(chloro, phenylimido) atoms, two *cis*-(P,P) phosphine phosphorus atoms, and two phenolate oxygen atoms of the PO_2^{2-} ligands for **1** and of one oxo oxygen atom, two *cis*-(P,P) phosphine phosphorus atoms, and three phenolate oxygen atoms of the PO_2^{2-} and PO^- ligands for **2**.

Introduction

As part of a continuing investigation of new neutral or cationic technetium and rhenium complexes of intermediate oxidation states,[1-3] we recently synthesized bis(*o*-hydroxyphenyl)phenylphosphine for use as a ligand. We are interested in these ligands because the combination of one soft phosphine phosphorus donor and two hard phenolate oxygen donors in the chelate should stabilize Tc or Re centers in intermediate oxidation states. The phosphine phosphorus atom, a good σ-donor, is able to accept back-donation from the metal center, and the anchoring anionic oxygen atoms should enhance the bonding of the phosphorus atom to the metal center.

Triphenylphosphine itself is known to form complexes with Re and Tc in various oxidation states,[4-6] and neutral complexes are formed by incorporating halo and/or oxo ligands. These complexes are usually prepared from perrhenate or pertechnetate, by reaction with the phosphine in the presence of a hydrohalic acid, the phosphine functioning as both ligand and reductant. The ease of synthesis makes many of these complexes good starting materials (via ligand exchange); however there are no reports on their possible application in radiopharmaceutical studies, presumably due to the hydrolyzable monodentate ligands (e.g. Cl).[7]

Phosphines functionalized with anionic groups have appeared in Tc/Re chemistry. Functionalization at an ortho position of one or more phenyl groups on triphenylphosphine leads to potentially multidentate and, upon deprotonation, quite basic phosphine ligands, which may be good for the preparation of new hydrolytically stable Tc/Re complexes. Davison and coworkers synthesized three Tc(III) complexes with an umbrella tetradentate tribasic phosphinetrithiol (PS_3) ligand.[8,9] Refosco *et al.* have been studying Tc(III) complexes with bidentate monobasic (PX) ligands (X = N,[10] S, or O[11]) and Tc(V) and

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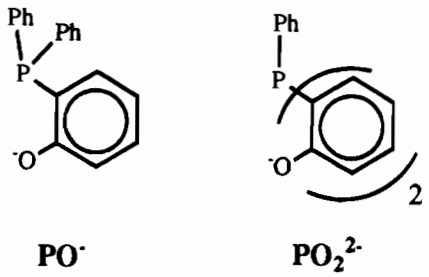
Re(V) complexes with the PN ligand.[12] In all the above cases, the anionic functional groups neutralized all or part of the charge at the metal centers while forming neutral Tc/Re complexes.



PO· **PO_2^{2-}**

There are, to our knowledge, no reports of Tc/Re complexes with potentially tridentate dibasic PX_2 phosphine ligands. To initiate these studies, we have focused on bis(*o*-hydroxyphenyl)-phenylphosphine (H_2PO_2). To the best of our knowledge, H_2PO_2 as a ligand has not been investigated; however, it has been used as an intermediate in the synthesis of macrocyclic ligands.[13] (Very recently, Fe and Co complexes of PO_2^{2-} and PO_3^{3-} ligands were reported.[14]) We have prepared this bis(hydroxyphenyl)phosphine ligand (H_2PO_2) by a convenient large-scale route and investigated its coordination chemistry as well as that of the monobasic (hydroxyphenyl)diphenylphosphine (HPO), with pentavalent Tc and Re.

Experimental Section

Materials. All chemicals were reagent grade and were used as received: phenol, PPh_3, Ph_2PCl, $PhPCl_2$, dimethoxymethane, *n*-butyllithium, and TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) were from Aldrich; NH_4ReO_4 was a gift of Johnson-Matthey, Inc.; HCl gas was from Matheson; $[NH_4][^{99}TcO_4]$ was a gift from the Du Pont Merck Pharmaceutical Co. $PhOCH_2OCH_3$ (mom-protected phenol),[15] $[(n\text{-}Bu)_4N][TcOCl_4]$,[16] $ReOCl_3(PPh_3)_2$, $ReNCl_2(PPh_3)_2$,[17,18] and (hydroxyphenyl)diphenylphosphine (HPO)[19] were prepared according to published procedures. $Re(NPh)Cl_3(PPh_3)_2$ was prepared by following a preparation for $Re(NPh)Cl_3(PPhEt_2)_2$.[18]

Caution! ^{99}Tc is a low-energy (0.292 MeV) β^- emitter with a half-life of 2.12×10^5 years. All manipulations of solutions and solids were performed in a laboratory approved for the handling of low-level radioisotopes, and normal safety procedures were followed at all times to prevent contamination.

Instrumentation. Mass spectra were obtained with either a Kratos MS 50 (electron impact ionization, EIMS) or a Kratos Concept II H32Q instrument (Cs^+-LSIMS with positive or negative ion detection). Only the most intense peaks are given where consistent isotopic patterns were observed. Infrared spectra were recorded as KBr pellets in the range 4000−400 cm^{-1} on a Perkin-Elmer PE 783 spectrophotometer and were referenced to polystyrene. Microanalyses were performed by Mr. P. Borda in this department or by Canadian Microanalytical Services Ltd. (Tc complexes). ^1H NMR spectra (200, 400, and 500 MHz) were recorded on Bruker AC-200E, Bruker WH-400 ($^1H-^1H$ COSY), and Bruker AMX-500 ($^1H\{^{31}P\}$) spectrometers with δ referenced to external TMS. The $^{31}P\{^1H\}$ NMR spectra (81 and 121 MHz) were recorded on Bruker AC-200E and Varian XL 300 spectrometers, respectively, with δ referenced to external phosphoric acid. The assignments were based on those for the unbound ligand and those for analogous complexes.

$PhP(o\text{-}C_6H_4OCH_2OCH_3)_2$ ($(mom)_2PO_2$, mom = CH_2OCH_3). This was prepared from the mom-protected phenol according to a procedure for $Ph_2P(o\text{-}C_6H_4OCH_2OCH_3)$ ((mom)PO) with some modifications.[20] To an ice-cooled solution of methoxymethyl phenyl ether (20.6 g, 149 mmol) in *ca.* 200 mL of petroleum ether (bp 35−65 °C, dried with anhydrous Na_2SO_4 overnight) was added a suspension of 100 mL of 1.6 M *n*-BuLi in hexanes and 17.5 g of TMEDA in 50 mL of petroleum ether under N_2. The mixture was stirred overnight at room temperature. A yellow precipitate formed from the orange solution, which was subsequently heated to about 40 °C under stirring. After the mixture was cooled to 0 °C, $PhPCl_2$ (21.7g, 121 mmol) was added via a syringe. The resultant mixture was stirred for another 10 h, during which time it warmed to room temperature. The solvents were removed by rotary evaporation, and to the residue was added Na_2HPO_4 (0.1 M, 100 mL). The reaction mixture was then extracted with Et_2O (2 × 200 mL) followed by $CHCl_3$ (2 × 100 mL). All the organic layers were combined, concentrated to a reddish oil under low pressure, diluted with Et_2O (*ca.* 20 mL), and stored at −4 °C overnight. A crystalline product was filtered out, washed with cold methanol (2 × 10 mL), and dried *in vacuo*. The yield was 15.6 g (55% based on mom-protected phenol). Anal. Calcd (found) for $C_{22}H_{23}O_4P$: C, 69.1 (68.8); H, 6.1 (6.1). EIMS: m/z = 382 ($[(mom)_2PO_2]^+$), 367 ($[(mom)_2PO_2 - CH_3]^+$). ^1H NMR ($CDCl_3$) δ: 7.35−7.25 (overlapped multiplets, 7H), 7.10−7.00 (multiplets, 2H), 6.84 (t, 2H), 6.75−6.65 (multiplets, 2H), 5.05 (d, 2H, CH_2, $^2J_{HH'}$ = 8 Hz), 5.00 (d, 2H, CH'_2, $^2J_{HH'}$ = 8 Hz), 3.1 (s, 6H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −26.1 (s). IR (cm^{-1}, KBr disk): 3020 (m, ν_{C-H}), 3000−2800 (m, methyl and methene ν_{C-H}).

Bis(*o*-hydroxyphenyl)phenylphosphine hydrochloride, $H_2PO_2{\cdot}HCl$. This was prepared from the mom-protected (hydroxyphenyl)phosphine ($(mom)_2PO_2$) according to a procedure for HPO, with some modifications.[20] Into a solution of $(mom)_2PO_2$ (10.1 g, 26.4 mmol) in 400 mL of anhydrous methanol (or ethanol) was bubbled anhydrous HCl gas via a dispersion tube for *ca.* 6 h with stirring. The mixture was further stirred overnight and then concentrated to off-white solids, which were washed with methanol (3 × 15 mL) and dried *in vacuo*. The yield was 5.8 g (67% based on phosphine); no recrystallization was necessary to obtain an analytically pure sample. Anal. Calcd (found) for $C_{18}H_{16}ClO_2P$: C, 65.4 (65.0); H, 4.9 (4.9); Cl, 10.7 (10.9). EIMS: m/z = 294 ($[H_2PO_2]^+$), 199 ($[H_2PO_2 - C_6H_7O]^+$). ^1H NMR (DMSO-d_6) δ: 10.2 (broad s, 2H), 7.8−7.3 (overlapped multiplets, 9H), 7.0−6.8 (multiplet, 4H). $^{31}P\{^1H\}$ NMR δ: 34.6 (s, DMSO-d_6), −30.6 (s, py-d_5). IR (cm^{-1}, KBr disk): 3020 (vs, b, ν_{C-H}).

***cis*-(P,P)-$ReOCl(PO)_2{\cdot}0.5H_2O$.** To a mixture of $ReOCl_3(PPh_3)_2$ (84 mg, 0.1 mmol) and HPO (60 mg, 0.22 mmol) was added 10 mL of ethanol. The mixture was brought to reflux for $^1/_2$ h, three drops of triethylamine were added, and the reaction mixture was refluxed for a further 1 h. After the mixture was cooled to room temperature, green solids were filtered out and recrystallized from CH_2Cl_2/Et_2O. The final product, yellowish green crystals, was washed with cold Et_2O and dried *in vacuo* overnight. The yield was 54 mg (67%). The product was soluble in acetone, acetonitrile, $CHCl_3$, and CH_2Cl_2 but insoluble in diethyl ether or cyclohexane. Anal. Calcd (found) for $C_{36}H_{28}ClO_3P_2Re{\cdot}0.5H_2O$: C, 54.0 (54.0); H, 3.7 (3.5); Cl, 4.4 (4.4). LSIMS: m/z = 792 ($[ReOCl(PO)_2]^+$), 757 ($[ReO(PO)_2]^+$). ^1H NMR ($CDCl_3$) δ: 7.70−7.28 (overlapped multiplets, 16H), 7.20−7.04 (overlapped multiplets, 4H), 6.9 (overlapped multiplets, 4H, including t, 1H, *p*-H on the equatorial PO-phenyl ring, t, 1H, *m′*-H on the axial PO-phenyl ring, dd, 2H, *m*-Ph-H), 6.64 (t, 1H, *p*-H on the axial PO-phenyl ring), 6.56 (dd, 2H, *o*-Ph-H), 6.01 (dd, 1H, *o′*-H on the axial PO-phenyl ring). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 15.4 (d), 2.2 (d); $^2J_{PP}$ = 10.1 Hz. IR (cm^{-1}, KBr disk): 3060 (m, ν_{C-H}), 965 (s, $\nu_{Re=O}$).

***cis*-(P,P)-$TcOCl(PO)_2{\cdot}^1/_6(CHCl_3)$.** A procedure similar to that for $[ReOCl(PO)_2]$ was followed using 51 mg of $[(n\text{-}Bu)_4N][TcOCl_4]$ (0.1 mmol) and 59 mg of HPO (0.21 mmol), except that no base was added and the brown precipitate was recrystallized from $CHCl_3/Et_2O$. The yield of the purple crystalline product was 26 mg (36%). The product was soluble in $CHCl_3$ and CH_2Cl_2 but insoluble in diethyl ether or

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cyclohexane. Anal. Calcd (found) for $C_{36}H_{28}ClO_3P_2Tc \cdot {}^1/_6(CHCl_3)$: C, 59.9 (59.9); H, 3.9 (4.2); Cl, 7.3 (7.5). LSIMS: m/z = 704 ([TcOCl-$(PO)_2]^+$), 669 ([$TcO(PO)_2]^+$). ^{1}H NMR ($CDCl_3$): 7.75−7.25 (overlapped multiplets, 16H), 7.18−7.04 (overlapped multiplets, 4H), 6.9 (overlapped multiplets, 4H, including *p*-H on the equatorial PO-phenyl ring, *m'*-H on the axial PO-phenyl ring, *m*-Ph-H as in Re analog), 6.64 (t, 1H, *p*-H on the axial PO-phenyl ring), 6.60 (dd, 2H, *o*-Ph-H), 6.0 (dd, 1H, *o'*-H on the axial PO-phenyl ring). IR (cm^{-1}, KBr disk): 3060 (m, ν_{C-H}), 940 (s, $\nu_{Tc=O}$).

***mer*-(P,P,P)-ReN(PO)$_2$(PPh$_3$)·H$_2$O.** To a mixture of $ReNCl_2(PPh_3)_2$ (87 mg, 0.11 mmol) and HPO (77 mg, 0.28 mmol) was added 50 mL of ethanol, and the mixture was brought to reflux overnight. To the orange-red solution was added 10 mL of cyclohexane; then the solution was clarified by filtration and stored at 5 °C for slow evaporation. Green-yellow crystals were filtered out, washed with cyclohexane, and dried *in vacuo* overnight. The yield was 42 mg (38%). The product was soluble in $CHCl_3$ and CH_2Cl_2, moderately soluble in ethanol, but insoluble in diethyl ether or cyclohexane. Anal. Calcd (found) for $C_{54}H_{43}NO_2P_3Re \cdot H_2O$: C, 62.7 (62.8); H, 4.4 (4.2); N, 1.4 (1.2). LSIMS: m/z = 1018 ([$ReN(PO)_2(PPh_3)$ + 1]$^+$), 755 ([$ReN(PO)_2]^+$). ^{1}H NMR (CD_2Cl_2) δ: 8.08 (dd, 2H), 7.98 (dd, 2H), 7.55−6.68 (overlapped multiplets, 33H), 6.53 (t, 1H), 6.31 (overlapped multiplets, 3H), 6.22 (t, 1H, *p*-H on the axial PO-phenyl ring), 5.87 (dd, 1H, *o'*-H on the axial PO-phenyl ring). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 34.7 (dd, P_A), 23.0 (dd, P_B), 13.9 (multiplet, P_X); $^2J_{AB}$ = 222.3, $^2J_{AX}$ = 11.5, $^2J_{BX}$ = 5.7 Hz. IR (cm^{-1}, KBr disk): 3060 (m, ν_{C-H}), 1045 (m, $\nu_{Re=N}$).

***fac-cis*-(P,P)-ReOCl(PPh$_3$)(PO$_2$).** To $ReOCl_3(PPh_3)_2$ (85 mg, 0.1 mmol) and $H_2PO_2 \cdot HCl$ (64 mg, 0.19 mmol) was added 10 mL of ethanol. The mixture was brought to reflux for 1.5 h and then cooled to room temperature, whereupon the solvent was removed from the green solution by rotary evaporation. A golden crystalline product was obtained after the residue was recrystallized from $CHCl_3/Et_2O$. The crystals were filtered out, washed with cyclohexane, and dried *in vacuo* overnight. The yield was 31 mg (39%). The product was soluble in $CHCl_3$ and CH_2Cl_2 but insoluble in diethyl ether or cyclohexane. Anal. Calcd (found) for $C_{36}H_{28}ClO_3P_2Re$: C, 54.6 (54.2); H, 3.6 (3.7); Cl, 4.5 (4.6). LSIMS: m/z = 793 ([$ReOCl(PPh_3)(PO_2)$ + 1]$^+$), 757 ([$ReO(PO_2)(PPh_3)]^+$), 530 ([$ReOCl(PO_2)]^+$), 495 ([$ReO(PO_2)]^+$). ^{1}H NMR ($CDCl_3$), δ: 7.48 (overlapped multiplets, 8H), 7.40−7.26 (overlapped multiplets, 9H), 7.17 (overlapped multiplets, 7H), 6.84 (t, 1H, *m'*-H on the axial PO-phenyl ring), 6.73 (t, 1H), 6.61 (t, 1H, *p*-H on the axial PO-phenyl ring), 5.76 (dd, 1H, *o'*-H on the axial PO-phenyl ring). ^{31}P{^{1}H} NMR (CD_2Cl_2), δ: 19.5 (d), −2.1 (d); $^2J_{PP}$ = 7.2 Hz. IR (cm^{-1}, KBr disk): 3060 (m, ν_{C-H}), 965 (s, $\nu_{Re=O}$).

***fac-cis*-(P,P)-Re(NPh)Cl(PPh$_3$)(PO$_2$)·2CHCl$_3$.** To $Re(NPh)Cl_3(PPh_3)_2$ (93 mg, 0.11 mmol) and $H_2PO_2 \cdot HCl$ (31 mg, 0.095 mmol) were added 10 mL of benzene and 3 mL of ethanol. The mixture was brought to reflux overnight and then cooled to room temperature. A dark green product was filtered out and recrystallized from $CHCl_3$/hexane. The crystals were washed with cyclohexane and dried *in vacuo* overnight. The yield was 54 mg (65%). The product was soluble in $CHCl_3$ and CH_2Cl_2, moderately soluble in benzene, methanol, ethanol, and acetone, but insoluble in diethyl ether, water, or cyclohexane. Anal. Calcd (found) for $C_{42}H_{33}ClNO_2P_2Re \cdot 2CHCl_3$: C, 47.8 (47.8); H, 3.2 (3.1); N, 1.3 (1.3). LSIMS: m/z = 867 ([$Re(NPh)Cl(PPh_3)(PO_2)]^+$), 832 ([$Re(NPh)(PPh_3)(PO_2)]^+$), 605 ([$Re(NPh)Cl(PO_2)]^+$), 570 ([$Re(NPh)(PO_2)]^+$). ^{1}H NMR ($CDCl_3$), δ: 7.50 (dd, 6H, *o*-H on PPh_3), 7.42−7.10 (overlapped multiplets, 18H), 7.01 (t, 1H), 6.87 (t, 1H, *m'*-H on the axial PO-phenyl ring), 6.79 (t, 2H, *m*-H on NPh), 6.58 (t, 1H), 6.55 (t, 1H, *p*-H on the axial PO-phenyl ring), 6.43 (d, 2H, *o*-H on NPh), 6.04 (dd, 1H, *o'*-H on the axial PO-phenyl ring). ^{31}P{^{1}H} NMR ($CDCl_3$), δ: 28.3 (s),[21] 15.4 (s). IR (cm^{-1}, KBr disk): 3060, 2990 (m, ν_{C-H}), 1030 (m, $\nu_{Re=NPh}$).

***fac-trans*-(P,P)-Re(NPh)Cl(PPh$_3$)(PO$_2$)·H$_2$O.** To a solution of $H_2PO_2 \cdot HCl$ (41.1 mg, 0.12 mmol) in 8 mL of methanol was added $Re(NPh)Cl_3(PPh_3)_2$ (90 mg, 0.10 mmol). The mixture was brought to reflux under N_2 for 1 h and then cooled to room temperature. A brown precipitate was filtered out, washed with cold methanol and diethyl ether, and dried *in vacuo* overnight. The yield was 54 mg (63%). The product was soluble in $CHCl_3$, CH_2Cl_2, and 1,2-dichloropropane, moderately soluble in acetonitrile, and insoluble in cold methanol, diethyl ether, or cyclohexane. Anal. Calcd (found) for $C_{42}H_{33}ClNO_2P_2Re \cdot H_2O$: C, 57.0 (56.8); H, 4.0 (3.7); N, 1.6 (1.7). LSIMS: m/z = 867 ([$Re(NPh)Cl(PPh_3)(PO_2)]^+$), 832 ([$Re(NPh)(PPh_3)(PO_2)]^+$), 605 ([$Re(NPh)Cl(PO_2)]^+$), 570 ([$Re(NPh)(PO_2)]^+$). ^{1}H NMR ($CDCl_3$), δ: 7.85 (dd, 6H, *o*-H on PPh_3), 7.70 (dd, 2H, *o*-H on PPh), 7.50 (t, 1H, *m*-H on the equatorial PO-phenyl ring), 7.46−7.18 (overlapped multiplets, 15H), 7.08 (t, 1H, *m'*-H on the axial PO-phenyl ring), 7.02 (dd, 1H, *o'*-H on the equatorial PO-phenyl ring), 6.78 (t, 2H, *m*-H on NPh), 6.68 (t, 1H, *p*-H on the equatorial PO-phenyl ring), 6.62 (d, 2H, *o*-H on NPh), 6.60 (t, 1H, *p*-H on the axial PO-phenyl ring), 6.32 (dd, 1H, *o'*-H on the axial PO-phenyl ring). ^{31}P{^{1}H} NMR ($CDCl_3$), δ: 34.5 (d), 2.9 (d); $^2J_{PP}$ = 241.2 Hz. IR (cm^{-1}, KBr disk): 3060 (m, ν_{C-H}), 1030 (m, $\nu_{Re=NPh}$).

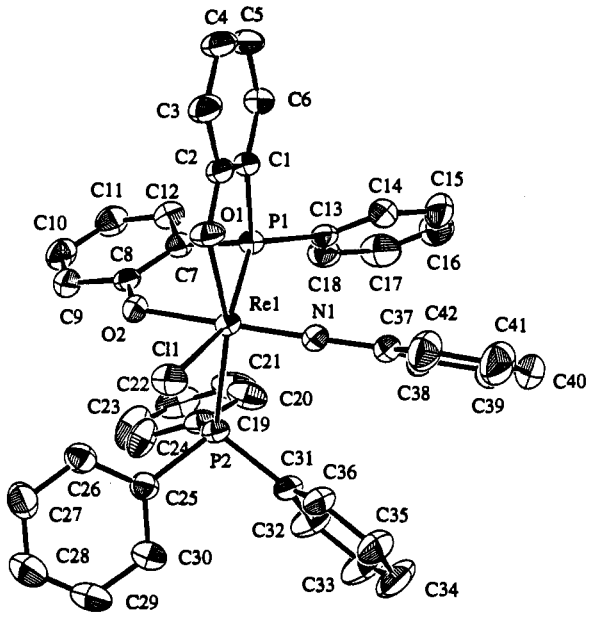
***fac-cis*-(P,P)-ReO(PO)(PO$_2$)·1.5H$_2$O.** To a solution of HPO (16 mg, 0.060 mmol) in 11 mL of ethanol was added *fac-cis*-(P,P)-ReOCl-$(PPh_3)(PO_2)$ (36 mg, 0.046 mmol). The mixture was brought to reflux under N_2 for 3.5 h, and to it was subsequently added NaOAc (4.1 mg, 0.050 mmol) in 2 mL ethanol. After an additional 1 h of refluxing, the solution was stored at 5 °C for slow evaporation. A brownish green crystalline product was filtered out, washed with cold ethanol and diethyl ether, and then dried *in vacuo* overnight. The yield was 24 mg (62%). The product was soluble in $CHCl_3$ but insoluble in ethanol or diethyl ether. Anal. Calcd (found) for $C_{36}H_{27}O_4P_2Re \cdot 1.5H_2O$: C, 54.1 (53.9); H, 3.8 (3.7). LSIMS: m/z = 773 ([$ReO(PO)(PO_2)$ + 1]$^+$), 495 ([$ReO(PO_2)]^+$). ^{1}H NMR ($CDCl_3$), δ: 7.85 (dd, 2H), 7.65−7.00 (overlapped multiplets, 21H), 6.77 (t, 1H), 6.62 (t, 1H, *m'*-H on the axial PO-phenyl ring), 6.42 (t, 1H, *p*-H on axial PO-phenyl ring), 5.68 (dd, 1H, *o'*-H on the axial PO-phenyl ring). ^{31}P{^{1}H} NMR ($CDCl_3$), δ: 20.6 (d), 16.0 (d); $^2J_{PP}$ = 4.0 Hz. IR (cm^{-1}, KBr disk): 3060 (m, ν_{C-H}), 965 (s, $\nu_{Re=O}$).

***trans*-(P,P)-Re(NPh)(PO)(PO$_2$).** To a solution of HPO (17 mg, 0.060 mmol) in 10 mL of methanol was added *trans*-(P,P)-Re(NPh)-$Cl(PPh_3)(PO_2) \cdot H_2O$ (42 mg, 0.048 mmol). The mixture was stirred for 10 min; then NaOAc (4.7 mg, 0.05 mmol) in 2 mL of methanol was added dropwise. The mixture was refluxed under N_2 for 4.5 h; then the solution was clarified by filtration and stored at 5 °C for slow evaporation. The supernatant was removed, and brownish green crystals were collected and dried *in vacuo* overnight. The yield was 15 mg (35%). The product was soluble in $CHCl_3$, CH_3CN, and acetone but insoluble in ethanol or diethyl ether. Anal. Calcd (found) for $C_{42}H_{32}NO_3P_2Re$: C, 59.6 (59.4); H, 3.8 (3.9); N, 1.7 (1.6). LSIMS: m/z = 848 ([$Re(NPh)(PO)(PO_2)$ + 1]$^+$), 570 ([$Re(NPh)(PO_2)]^+$). ^{1}H NMR ($CDCl_3$), δ: 7.95−6.40 (overlapped multiplets, 31H), 5.97 (dd, 1H, *o'*-H on axial PO-phenyl ring). ^{31}P{^{1}H} NMR ($CDCl_3$), δ: 35.7 (d), 15.4 (d); $^2J_{PP}$ = 229.6 Hz. IR (cm^{-1}, KBr disk): 3060 (m, ν_{C-H}), 1030 (m, $\nu_{Re=NPh}$).

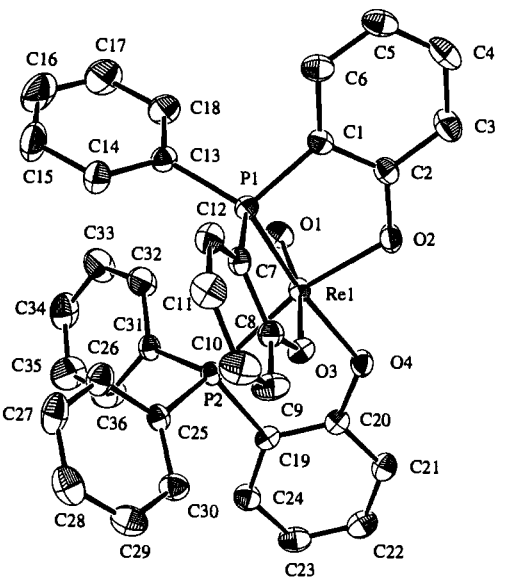
***cis*-(P,P)-ReO(PO$_2$)(HPO$_2$).** To NH_4ReO_4 (27 mg, 0.10 mmol) and $H_2PO_2 \cdot HCl$ (119 mg, 0.36 mmol) was added 40 mL of ethanol. The mixture was refluxed overnight. After cooling, a green crystalline product was filtered out, washed with methanol and diethyl ether, and then dried *in vacuo*. The yield was 66 mg (84%). The product was soluble in DMSO and DMF, slightly soluble in $CHCl_3$, CH_2Cl_2, ethanol, and methanol, but insoluble in benzene, diethyl ether, water, or cyclohexane. Anal. Calcd (found) for $C_{36}H_{27}O_5P_2Re$: C, 54.9 (54.7); H, 3.5 (3.5). LSIMS: m/z = 789 ([$ReO(PO_2)(HPO_2)$ + 1]$^+$), 771 ([$Re(PO_2)_2]^+$), 495 ([$ReO(PO_2)]^+$), 787 ([$ReO(PO_2)_2]^-$). ^{1}H NMR (DMSO-d_6), δ: 9.95 (br, s, O*H*), 8.0−6.30 (overlapped multiplets), 5.45 (dd, 1H of the minor isomer, *o'*-H on the axial PO-phenyl ring), 5.23 (dd, 1H of the major isomer, *o'*-H on the axial PO-phenyl ring). ^{31}P{^{1}H} NMR (DMSO-d_6), δ: 20.9 (d), 11.6 (d); $^2J_{PP}$ = 4.1 Hz; a minor set also observed at 22.8 (d) and 17.5 (br, s); $^2J_{PP}$ = 5.0 Hz). IR (cm^{-1}, KBr disk): 3060 (m, ν_{C-H}), 990, 970 (m, $\nu_{Re=O}$).

***cis*-(P,P)-TcO(PO$_2$)(HPO$_2$). Method A.** To NH_4TcO_4 (17.5 mg, 0.10 mmol) and $H_2PO_2 \cdot HCl$ (107 mg, 0.32 mmol) was added 20 mL of ethanol. The solution immediately became brownish red and then dark brown upon heating. The mixture was refluxed overnight. After cooling, a brown powder was filtered out, washed with cold ethanol and diethyl ether, and then dried *in vacuo*. The yield was 61 mg (87%). The product was soluble in DMSO and DMF, very slightly soluble in $CHCl_3$, CH_2Cl_2, methanol, and ethanol, but insoluble in diethyl ether or cyclohexane. Anal. Calcd (found) for $C_{36}H_{27}O_5P_2Tc$: C, 61.7

(21) This signal became a doublet at −20 °C or lower temperatures, with the coupling constant varying with temperature (5.2 Hz at −20 °C, 16.4 Hz at −70 °C).



(1)



(2)

Figure 1. ORTEP drawings of *fac-cis*-(P,P)-Re(NPh)Cl(PPh_3)(PO_2)·2$CHCl_3$ (**1**) (with the solvent molecules omitted) and *cis*-(P,P)-ReO(PO)(PO_2) (**2**). 33% probability thermal ellipsoids are shown.

Table 1. Selected Crystallographic Data

compound	Re(NPh)Cl(PPh_3)(PO_2)·2$CHCl_3$ (**1**)	ReO(PO)(PO_2) (**2**)
formula	$C_{44}H_{35}Cl_7NO_2P_2Re$	$C_{36}H_{27}O_4P_2Re$
fw	1106.09	771.76
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	11.997(1)	10.132(2)
b, Å	20.637(2)	14.026(3)
c, Å	10.511(1)	22.046(2)
α, deg	103.772(9)	
β, deg	113.504(8)	102.38(1)
γ, deg	76.072(9)	
V, Å^3	2286.6(5)	3060.2(9)
Z	2	4
ϱ_{calc}, g/cm^3	1.606	1.675
T, °C	21	21
radiation	Mo	Mo
λ, Å	0.710 69	0.710 69
μ, cm^{-1}	31.74	41.65
transm factors	0.59−1.00	0.58−1.00
no. of reflns $I \geq 3\sigma(I)$	8203	5957
no. of variables	541	388
R[a]	0.034	0.030
R_w[b]	0.034	0.026

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

(61.4); H, 3.9 (4.0). LSIMS (sample ground with KBr): m/z = 739 ([TcO(PO_2)(HPO_2) + K]$^+$), 701 ([TcO(PO_2)(HPO_2) + 1]$^+$). ^{1}H NMR (DMSO-d_6), δ: 10.15 (br, s, O*H*), 8.0−6.30 (overlapped multiplets), 5.45 (dd, 1H of the minor isomer, *o'*-H on the axial PO-phenyl ring), 5.23 (dd, 1H of the major isomer, *o'*-H on the axial PO-phenyl ring). IR (cm^{-1}, KBr disk): 3050 (m, ν_{C-H}), 965 (s, $\nu_{Tc=O}$).

Method B. To (n-Bu_4N)$TcOCl_4$ (52 mg, 0.10 mmol) and H_2PO_2·HCl (64 mg, 0.19 mmol) was added 10 mL of ethanol. The mixture was brought to reflux for 4 h; then it was cooled to −4 °C. A brown powder was filtered out, washed with methanol and diethyl ether, and dried in air. The yield was 44 mg (66%). This product is identical to that from method A, as supported by IR and microanalysis data.

X-ray Crystallographic Analyses of *fac-cis*-(P,P)-Re(NPh)Cl(PPh_3)(PO_2)·2$CHCl_3$ (1) and *cis*-(P,P)-ReO(PO)(PO_2) (2). Selected crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares procedures on the setting angles for 25 reflections with 2θ = 27.0−33.5° for **1** and 31.6−36.0° for **2**. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, decayed linearly by 3.8% for **1** and showed only small random fluctuations for **2**. The data were processed[22] and corrected for Lorentz and polarization effects, decay (for **1**), and absorption (empirical, based on azimuthal scans for three reflections).

The structure analysis of **1** was initiated in the centrosymmetric space group $P\bar{1}$ on the basis of the E-statistics and the Patterson function, this choice being verified by the successful solution and refinement of the structure. The structures were solved by conventional heavy atom methods, the coordinates of the Re and P atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. One of the two chloroform molecules in **1** was (7:3) disordered with respect to rotation about the C−H bond. A split-atom model was employed. The population parameters were adjusted as the refinement progressed to result in approximately equal average thermal parameters for the two sets of Cl atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in calculated positions with C−H = 0.98 Å and $B_H = 1.2B_{bonded\ atom}$. No secondary extinction corrections were necessary. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 23. The final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2. Selected bond lengths and bond angles for the two structures appear in Tables 3 and 4, respectively. Complete tables of crystallographic data, anisotropic thermal parameters, bond lengths and angles, torsion angles, and intermolecular contacts for both structures are included as supplementary material (see paragraph at end of paper).

Results and Discussion

HPO and H_2PO_2 Ligands. A few procedures for the synthesis of *o*-(diphenylphosphino)phenol (HPO) are known.[19,20] The preparation of H_2PO_2, starting from anisole, was reported by von Zon[13] as an intermediate in the synthesis of macrocyclic monophospha-crown ether ligands from phenyl methyl ether. On the basis of our experience in the synthesis of HPO, we realized that the methyl protection is difficult to undo, so we adapted a method used for HPO[20] to our preparation of the H_2-

(22) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985, 1992.
(23) (a) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99−102. (b) *International Tables for Crystallography*; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, pp 200−206.

Table 2. Final Atomic Coordinates (Fractional) and Equivalent Isotropic Thermal Parameters B_{eq} (Å^2)[a] for Re(NPh)Cl(PPh$_3$)(PO$_2$)·2CHCl$_3$ (**1**) and ReO(PO)(PO$_2$) (**2**)

atom	*x*	*y*	*z*	B_{eq}	occ[b]	atom	*x*	*y*	*z*	B_{eq}	occ[b]
				Re(NPh)Cl(PPh3)(PO$_2$)·2CHCl$_3$ (**1**)							
Re(1)	0.273264(15)	0.238598(9)	0.37528(2)	3.085(7)		C(15)	0.5053(5)	0.1131(4)	0.8532(8)	7.2(3)	
Cl(1)	0.22275(11)	0.24661(6)	0.13299(12)	4.64(5)		C(16)	0.5452(6)	0.1559(5)	0.9745(8)	8.0(4)	
Cl(2)	0.3020(2)	0.06498(12)	0.9596(2)	10.3(1)		C(17)	0.4948(6)	0.2236(4)	0.9825(6)	7.3(4)	
Cl(3)	0.2094(2)	0.01042(12)	1.1130(3)	13.0(2)		C(18)	0.3987(5)	0.2477(3)	0.8656(5)	5.2(2)	
Cl(4)	0.0432(2)	0.08172(15)	0.8919(2)	12.5(1)		C(19)	0.3807(4)	0.3930(2)	0.6000(5)	4.0(2)	
Cl(5)	−0.1117(6)	0.3680(3)	0.0601(8)	14.0(3)	0.70	C(20)	0.4360(6)	0.3713(3)	0.7293(6)	6.0(3)	
Cl(6)	−0.1795(3)	0.2925(2)	0.1940(4)	11.1(2)	0.70	C(21)	0.4287(7)	0.4153(4)	0.8510(6)	7.5(4)	
Cl(7)	−0.1731(6)	0.2386(3)	−0.0744(6)	20.0(4)	0.70	C(22)	0.3638(7)	0.4803(4)	0.8407(7)	7.3(4)	
Cl(8)	−0.0980(9)	0.2742(6)	−0.1170(9)	12.4(6)	0.30	C(23)	0.3110(6)	0.5015(3)	0.7151(7)	7.6(3)	
Cl(9)	−0.1963(9)	0.2331(7)	0.0443(14)	14.0(7)	0.30	C(24)	0.3179(5)	0.4587(3)	0.5939(5)	5.7(2)	
Cl(10)	−0.142(2)	0.3642(7)	0.096(2)	19(1)	0.30	C(25)	0.3313(4)	0.3912(2)	0.3131(4)	3.8(2)	
P(1)	0.24326(10)	0.22997(6)	0.58151(12)	3.33(4)		C(26)	0.2056(4)	0.4073(2)	0.2356(5)	4.4(2)	
P(2)	0.38550(10)	0.33377(6)	0.44240(11)	3.35(4)		C(27)	0.1638(5)	0.4535(3)	0.1435(6)	5.7(3)	
O(1)	0.1390(3)	0.1787(2)	0.2849(3)	4.2(1)		C(28)	0.2441(7)	0.4844(3)	0.1280(7)	7.4(4)	
O(2)	0.1350(2)	0.31780(14)	0.3876(3)	3.7(1)		C(29)	0.3666(7)	0.4700(3)	0.2039(8)	7.9(4)	
N(1)	0.4067(3)	0.1795(2)	0.4100(4)	3.5(1)		C(30)	0.4118(5)	0.4227(3)	0.2954(6)	5.8(3)	
C(1)	0.1419(4)	0.1680(2)	0.5089(5)	3.6(2)		C(31)	0.5486(4)	0.3086(2)	0.4680(5)	4.0(2)	
C(2)	0.0978(4)	0.1541(2)	0.3621(5)	3.9(2)		C(32)	0.6393(5)	0.3407(3)	0.5760(6)	6.7(3)	
C(3)	0.0061(4)	0.1125(2)	0.2933(5)	4.7(2)		C(33)	0.7607(6)	0.3199(5)	0.5844(9)	9.6(5)	
C(4)	−0.0364(5)	0.0861(3)	0.3707(7)	5.5(2)		C(34)	0.7920(5)	0.2713(5)	0.4907(9)	8.9(4)	
C(5)	0.0094(5)	0.0997(3)	0.5158(6)	5.4(3)		C(35)	0.7044(6)	0.2390(3)	0.3840(7)	6.8(3)	
C(6)	0.0972(4)	0.1408(2)	0.5858(5)	4.7(2)		C(36)	0.5819(4)	0.2583(3)	0.3717(6)	5.0(2)	
C(7)	0.1506(4)	0.3086(2)	0.6151(4)	3.6(2)		C(37)	0.5175(4)	0.1366(2)	0.4581(5)	4.0(2)	
C(8)	0.1036(4)	0.3438(2)	0.5005(5)	3.6(2)		C(38)	0.6005(4)	0.1499(3)	0.5926(6)	5.1(2)	
C(9)	0.0237(4)	0.4048(2)	0.5058(5)	4.6(2)		C(39)	0.7110(5)	0.1061(3)	0.6371(7)	6.6(3)	
C(10)	−0.0080(5)	0.4302(2)	0.6220(6)	5.4(2)		C(40)	0.7385(5)	0.0510(3)	0.5479(9)	7.5(3)	
C(11)	0.0371(5)	0.3958(3)	0.7354(6)	5.2(2)		C(41)	0.6578(6)	0.0392(3)	0.4107(9)	7.8(3)	
C(12)	0.1143(4)	0.3347(3)	0.7315(5)	4.6(2)		C(42)	0.5469(5)	0.0812(3)	0.3654(6)	6.2(3)	
C(13)	0.3593(4)	0.2034(2)	0.7419(5)	4.0(2)		C(43)	0.1866(5)	0.0749(3)	1.0246(6)	5.6(2)	
C(14)	0.4126(5)	0.1353(3)	0.7357(6)	5.3(2)		C(44)	−0.1041(6)	0.2856(4)	0.0691(8)	8.0(3)	
				ReO(PO)(PO$_2$) (**2**)							
Re(1)	0.02119(2)	0.235071(11)	0.379712(8)	2.290(5)		C(16)	0.3196(7)	0.6119(4)	0.4618(3)	6.5(3)	
P(1)	0.08785(11)	0.38014(7)	0.33784(5)	2.31(4)		C(17)	0.1860(7)	0.5951(4)	0.4619(3)	6.0(3)	
P(2)	0.22266(10)	0.16590(7)	0.44439(5)	2.26(4)		C(18)	0.1166(5)	0.5268(3)	0.4233(2)	4.1(2)	
O(1)	−0.0229(3)	0.2963(2)	0.43847(13)	3.3(1)		C(19)	0.1616(4)	0.0450(3)	0.4468(2)	2.5(2)	
O(2)	−0.1510(3)	0.2625(2)	0.31409(13)	3.3(1)		C(20)	0.0298(4)	0.0309(3)	0.4131(2)	2.5(2)	
O(3)	0.1101(3)	0.1876(2)	0.31139(12)	2.6(1)		C(21)	−0.0289(4)	−0.0599(3)	0.4113(2)	3.2(2)	
O(4)	−0.0459(3)	0.1017(2)	0.38152(13)	3.0(1)		C(22)	0.0445(5)	−0.1339(3)	0.4424(2)	3.8(2)	
C(1)	−0.0767(4)	0.4237(3)	0.3014(2)	2.6(2)		C(23)	0.1747(5)	−0.1207(3)	0.4762(2)	4.1(2)	
C(2)	−0.1773(4)	0.3522(3)	0.2944(2)	2.8(2)		C(24)	0.2335(5)	−0.0311(3)	0.4788(2)	3.5(2)	
C(3)	−0.3107(5)	0.3780(3)	0.2669(2)	4.0(2)		C(25)	0.3726(4)	0.1600(3)	0.4127(2)	2.6(2)	
C(4)	−0.3412(5)	0.4699(4)	0.2484(2)	4.2(2)		C(26)	0.4498(5)	0.2430(3)	0.4142(2)	3.8(2)	
C(5)	−0.2431(5)	0.5399(3)	0.2557(2)	3.8(2)		C(27)	0.5652(5)	0.2404(4)	0.3884(2)	4.7(2)	
C(6)	−0.1112(5)	0.5167(3)	0.2817(2)	3.3(2)		C(28)	0.6030(5)	0.1583(4)	0.3630(2)	4.6(2)	
C(7)	0.1766(4)	0.3401(3)	0.2809(2)	2.5(2)		C(29)	0.5260(5)	0.0793(4)	0.3613(2)	4.2(2)	
C(8)	0.1758(4)	0.2396(3)	0.2763(2)	2.7(2)		C(30)	0.4100(5)	0.0784(3)	0.3854(2)	3.5(2)	
C(9)	0.2406(5)	0.1980(3)	0.2333(2)	3.8(2)		C(31)	0.2834(4)	0.2116(3)	0.5229(2)	2.7(2)	
C(10)	0.3020(5)	0.2525(4)	0.1962(2)	4.4(2)		C(32)	0.2339(5)	0.2951(4)	0.5422(2)	5.0(2)	
C(11)	0.3008(5)	0.3518(4)	0.1990(2)	3.9(2)		C(33)	0.2775(6)	0.3282(5)	0.6019(3)	6.4(3)	
C(12)	0.2377(5)	0.3941(3)	0.2417(2)	3.2(2)		C(34)	0.3713(6)	0.2791(4)	0.6429(2)	5.4(3)	
C(13)	0.1790(4)	0.4749(3)	0.3839(2)	2.8(2)		C(35)	0.4235(7)	0.1989(4)	0.6246(3)	6.7(3)	
C(14)	0.3154(5)	0.4911(3)	0.3852(2)	3.8(2)		C(36)	0.3833(6)	0.1649(4)	0.5643(2)	5.6(3)	
C(15)	0.3845(6)	0.5610(4)	0.4249(3)	5.5(3)							

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$. [b] occ = occupancy.

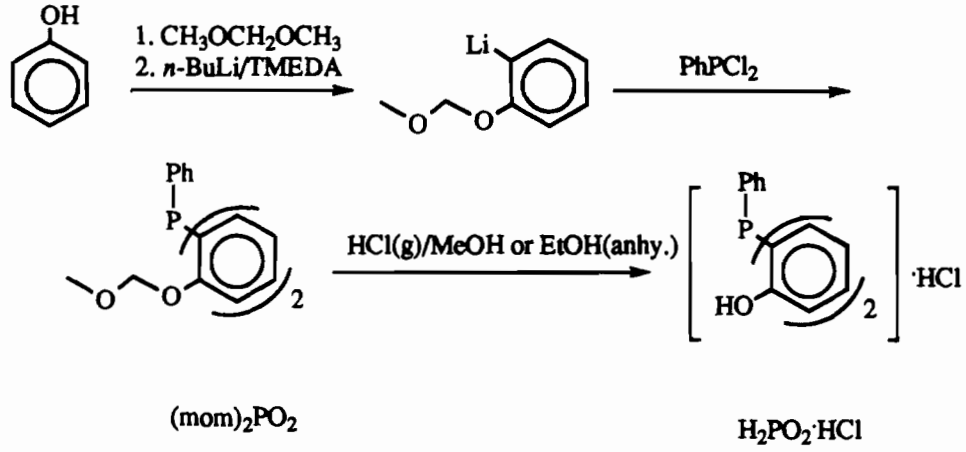
Table 3. Selected Bond Lengths (Å) for Re(NPh)Cl(PPh$_3$)(PO$_2$)·2CHCl$_3$ (**1**) and ReO(PO)(PO$_2$) (**2**)

	1	**2**		**1**	**2**
Re(1)−N(1)	1.728(3)		P(2)−C(19)	1.821(4)	1.810(4)
Re(1)−Cl(1)	2.409(1)		P(2)−C(25)	1.834(4)	1.805(4)
Re(1)−P(1)	2.387(1)	2.391(1)	P(2)−C(31)	1.824(4)	1.825(4)
Re(1)−P(2)	2.454(1)	2.428(1)	O(1)−C(2)	1.342(5)	
Re(1)−O(1)	2.050(3)	1.692(3)	O(2)−C(2)		1.339(5)
Re(1)−O(2)	2.050(3)	2.050(3)	O(2)−C(8)	1.340(5)	
Re(1)−O(3)		2.026(3)	O(3)−C(8)		1.339(5)
Re(1)−O(4)		1.994(3)	O(4)−C(20)		1.353(5)
P(1)−C(1)	1.800(4)	1.795(4)	C(1)−C(2)	1.398(6)	1.414(6)
P(1)−C(7)	1.780(4)	1.785(4)	C(7)−C(8)	1.406(6)	1.413(6)
P(1)−C(13)	1.811(4)	1.802(4)	C(19)−C(20)		1.396(5)

PO$_2$ ligand, in which the methoxymethyl, or mom, group was used to protect the phenol OH. It is known that the mom group is easy to cleave with mineral acids.[15] The mom-protected phenol was ortho-lithiated and then reacted with dichlorophenylphosphine to give the mom-protected intermediate, (mom)$_2$PO$_2$. Upon treatment with anhydrous HCl gas, the expected bis(hydroxyphenyl)phenylphosphine was obtained as the hydrochloride adduct (Scheme 1).

For the intermediate, (mom)$_2$PO$_2$, the mass spectrometric parent ion peak (m/z = 382, [(mom)$_2$PO$_2$]$^+$) was present, consistent with the elemental analysis. In the ^{31}P{^{1}H} NMR spectrum in CDCl$_3$, a singlet at −26 ppm was present and upfield from triphenylphosphine (at −5 ppm). The ^{1}H NMR spectrum showed that aromatic hydrogen atoms were present in the range 6.6−7.4 ppm; there were an AB quartet centered at 5.0 ppm and a singlet at 3.1 ppm. The 13 aromatic hydrogen atoms were easily subgrouped into four, with the integral ratio

Scheme 1



$(mom)_2PO_2$ $H_2PO_2{\cdot}HCl$

Table 4. Selected Bond Angles (deg) for $Re(NPh)Cl(PPh_3)(PO_2){\cdot}2CHCl_3$ (**1**) and $ReO(PO)(PO_2)$ (**2**)

	1	**2**
Re(1)−N(1)−C(37)	171.7(3)	
Cl(1)−Re(1)−N(1)	102.5(1)	
P(1)−Re(1)−N(1)	93.0(1)	
P(2)−Re(1)−N(1)	93.1(1)	
O(1)−Re(1)−N(1)	102.2(1)	
O(2)−Re(1)−N(1)	165.4(1)	
P(1)−Re(1)−O(1)	80.96(8)	90.4(1)
P(2)−Re(1)−O(1)		94.6(1)
O(1)−Re(1)−O(2)	86.6(1)	96.9(1)
O(1)−Re(1)−O(3)		165.5(1)
O(1)−Re(1)−O(4)		108.3(1)
O(2)−Re(1)−O(3)		89.1(1)
P(1)−Re(1)−P(2)	105.64(4)	107.18(4)
P(1)−Re(1)−O(2)	76.65(8)	80.54(8)
P(1)−Re(1)−O(3)		77.59(8)
Cl(1)−Re(1)−P(2)	88.25(4)	
P(2)−Re(1)−O(4)		81.99(8)

7:2:2:2. The last three subgroups were assigned to the hydrogen atoms on the two phenolic arms by the $^1H-^1H$ COSY spectrum. Peaks for the other hydrogen atoms on each phenolic arm were overlapped by the phenyl hydrogen atoms. The two doublets at 5.0 ppm (integrating for four hydrogen atoms) were assigned to the methylene hydrogen atoms (an AB quartet, indicating nonequivalence of the two methylene hydrogen atoms). Given the steric demands of the mom groups, the free rotation of P−C bonds and/or C−O bonds was restricted.

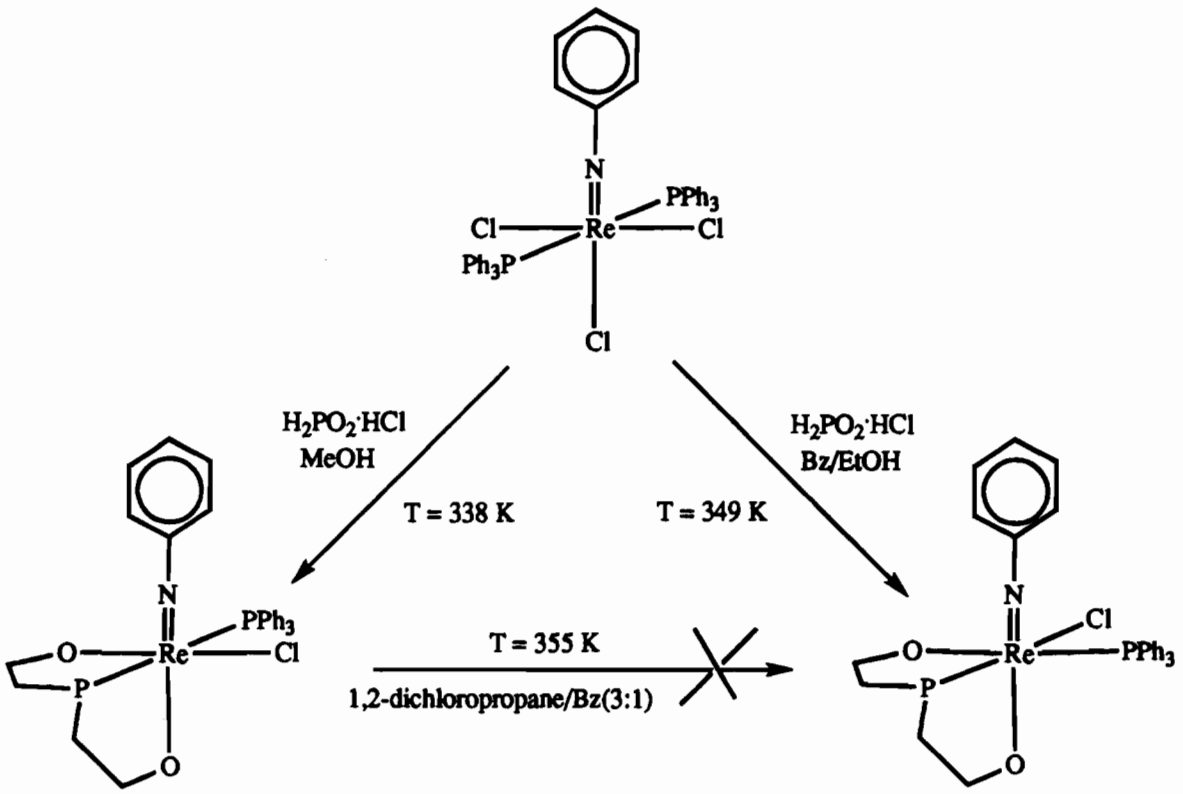
The formulation of $H_2PO_2{\cdot}HCl$ was supported by the elemental analysis and by the chemical shift characteristic[24] for phosphonium P at +34.6 ppm in DMSO-d_6, even though the EIMS showed only H_2PO_2. In the synthesis of HPO by this method, an analytically pure sample was obtained by sublimation.[20] (Given that the author did not neutralize his product with a base, a routine practice for free phosphines,[19,25] and that phosphine hydrochloride adducts dissociate at high temperature, it is quite possible that the crude HPO product cited[20] could have been HPO·HCl.) In our work, no attempt was made to convert the adduct $H_2PO_2{\cdot}HCl$ to the free phosphine, since the adduct dissociated in the ligand-exchange reactions with it (*vide infra*) and in basic solution, as was indicated by the chemical shift of −30.6 ppm in py-d_5.

Synthesis of the Complexes. The reaction of HPO with oxo- or nitridometal(V) starting materials in a 2:1 ratio gave the bis(PO) complexes $[MOCl(PO)_2]$ (M = Tc, Re) or $ReN(PO)_2(PPh_3)$. With the bidentate monoprotic HPO, the formation of bis(ligand)chlorooxometal complexes, upon ligand exchange, was not surprising since the formulation $MOXL_2$ is common for the substitution of ReO^{3+} and TcO^{3+} cores with other bidentate monobasic ligands. A Tc(III) $Tc(PO)_3$ complex was recently reported[11] suggesting that the combination of hard (O) and soft (P) donors in the chelate will be suitable for stabilizing various intermediate oxidation states of Tc or Re. The formation of $ReN(PO)_2(PPh_3)$ from $ReNCl_2(PPh_3)_2$ was, however, mildly surprising. It is a six-coordinate complex whereas a five-coordinate complex might have been expected because of the strongly *trans*-labilizing nitrido group[26a,b] and the sterically demanding ligand phenyl groups; however the latter effect may actually be small. To our knowledge, this is the first example of three triarylphosphine phosphorus donors coordinating the same Re(V) center, suggesting that the bonding of the phenolato oxygen atom of each PO^- ligand to the Re center may actually offset the steric repulsion among the bulky phenyl groups around the metal center. The other evidence for the reduced steric repulsion is that the anchored phosphines are found to bind the metal more tightly than the unanchored phosphine PPh_3 (*vide infra*).

The phosphine hydrochloride adduct, $H_2PO_2{\cdot}HCl$, reacted directly with $ReZCl_3(PPh_3)_2$, resulting in the mono(PO_2) complexes $ReZCl(PPh_3)(PO_2)$ (Z = O, NPh), suggesting the direct dissociation of the adduct to a potentially tridentate dibasic bis(hydroxyphenyl)phosphine ligand. The mono(PO_2) complex $ReOCl(PPh_3)(PO_2)$ formed even though a 2:1 L:M ratio was used in the ligand-exchange reaction with $ReOCl_3(PPh_3)_2$. In contrast, with $[(n\text{-}Bu)_4N]TcOCl_4$ as the starting material under the same conditions, the ligand-exchange reaction led to the formation of the bis(PO_2) complex $TcO(PO_2)(HPO_2)$ (*vide infra*). These observations, taken together, suggest that the chelation of a PO_2^{2-} is an easy first step and the bonding of the second PO_2^{2-} is hindered by the presence of PPh_3. With the phenylimido starting material, the isolated product was of either *cis*- or *trans*-(P,P) geometry depending on the reaction solvent (Scheme 2). The starting material, $Re(NPh)Cl_3(PPh_3)_2$, has the *trans*-(P,P) configuration.[27] In polar methanol, the *trans* configuration was retained after one PO_2 ligand replaced one PPh_3 and two adjacent Cl ligands in the starting material; however, in the less polar benzene/ethanol (10:3) mixture, the *cis*-(P,P) product was formed. There was no conversion from *trans*-(P,P)-Re(NPh)Cl(PPh_3)(PO_2) to *cis*-(P,P)-Re(NPh)Cl-

(24) Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; p 27.
(25) Senear, A. E.; Valient, W.; Wirth, J. *J. Org. Chem.* **1960**, *25*, 2001.
(26) Nugent, W. A.; Mayer, J. M. In *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988; (a) p 156. (b) p 179, (c) p116, (d) p 123, (e) p 154, (f) p 175.
(27) Forsellini, E.; Casellato, U.; Graziani, R.; Carletti, M. C.; Magon, L. *Acta Crystallogr.* **1984**, *C40*, 1795.

Scheme 2



$(PPh_3)(PO_2)$, after the former was heated at 80−85 °C in a 1,2-dichloropropane/benzene-d_6 (3:1) mixture for 40 min. Clearly, the product geometry is not determined by temperature only; with oxo starting materials, the *cis* product was obtained in ethanol while attempts to prepare the *trans* product in methanol led to a mixture.

The mixed(PO/PO_2) complexes $ReZ(PO)(PO_2)$, which incorporate both PO_2^{2-} and PO^- ligands, were synthesized via ligand-exchange reactions of $ReZCl(PPh_3)(PO_2)$ (Z = O, NPh) with HPO in the presence of NaOAc. Direct ligand exchange of $Re(NPh)Cl_3(PPh_3)_2$ with H_2PO_2·HCl and HPO (M:L:L′ = 1:1:1) yielded mostly $Re(NPh)Cl(PPh_3)(PO_2)$ with traces of *trans*-(P,P)-$Re(NPh)(PO)(PO_2)$, suggesting that the binding of the PO_2^{2-} was the first step, and that the substitution of the PO^- ligand for the remaining Cl and PPh_3 ligands was unfavorable, as one HPO was competing against the three Cl^- and one PPh_3 in the solution. An attempt with $[(n\text{-}Bu)_4N]ReOBr_4$ and H_2PO_2·HCl and HPO (M:L:L′ = 1:1:1) produced a mixture of $ReO(PO)(PO_2)$, $ReO(PO_2)(HPO_2)$, and $ReOBr(PO)_2$, as evinced by mass spectrometry (LSIMS) and $^{31}P\{^1H\}$ NMR spectroscopy. Recrystallization of this mixture in EtOH yielded a good crystal of $ReO(PO)(PO_2)$, which was suitable for X-ray analysis.

An alternative route for the incorporation of two PO_2 ligands into one metal center was explored, a reduction/ligand-exchange reaction with ammonium perrhenate or pertechnetate and an excess of H_2PO_2·HCl. The hydrochloride adduct dissociated to the corresponding phosphine which functioned as reducing agent as well as ligand. Most reductions of MO_4^- (M = Re, Tc) with phosphines have been done in acidic environments.[17,18,28] The HCl adduct, however, reacted with NH_4MO_4, at a molar ratio of L:M = ~3.5:1, without any extra acid required, leading to the bis(PO_2) complexes $MO(PO_2)(HPO_2)$ (M = Tc, Re) in high yields. Similar conditions applied to phosphinoaniline, *o*-phosphinothiophenol, and *o*-phosphinophenol (HPO) ligands formed $Tc(PX)_3$-type complexes (X = N, P, O) from NH_4TcO_4.[11,12] These ligands can both coordinate and reduce the metal center, a distinct advantage in the formulation of potential ^{99m}Tc-radiopharmaceuticals, where the only convenient source is $^{99m}TcO_4^-$ from a $^{99}Mo/^{99m}Tc$ generator. In an attempt to synthesize the binary complex $Tc(PO_2)_2$ through the reaction of $[TcO_4]^-$ and H_2PO_2·HCl, despite an excess of ligand (L:M = 6:1), the only product was $TcO(PO_2)(HPO_2)$, which was also synthesized via a ligand-exchange reaction with $[(n\text{-}Bu)_4N]TcOCl_4$. Reaction of $ReCl_4(PPh_3)_2$ with 2 equiv of H_2PO_2·HCl produced only $ReOCl(PPh_3)(PO_2)$ presumably by aerial oxidation of the metal center.

Characterization of the Complexes. All the complexes were air stable in the solid state and in solution. They were characterized by elemental analysis, infrared spectroscopy, mass spectrometry, $^1H/^{31}P\{^1H\}$ NMR spectroscopy, and X-ray crystallography in the cases of *fac-cis*-(P,P)-$Re(NPh)Cl(PPh_3)(PO_2)$ and *fac-cis*-(P,P)-$ReO(PO)(PO_2)$. Mass spectrometric data confirmed the formation of the complexes when the expected parent ions and/or their fragments were found, while microanalysis established the formulation of all the compounds. IR measurements confirmed the existence of metal−ligand multiple bonds and ensured that the multidentate ligands were coordinated as evidenced by the absorptions shifted in comparison with those of the free ligands and starting materials. Due to the overlapping of multiplets in the aromatic hydrogen region (5.0−8.5 ppm), full assignments of the ^1H NMR spectra were mostly impossible; nevertheless, the ^1H NMR spectra were still useful in verifying the similarities of the analogous Re and Tc complexes. On the other hand, $^{31}P\{^1H\}$ NMR played a crucial role in both identifying and determining the geometries of the Re complexes (*vide infra*).

Bis(PO) Complexes. In the mass spectra, the loss of one chloro ligand from a $[MOCl(PO)_2]$ unit or the loss of the triphenylphosphine ligand from the $[ReN(PO)_2(PPh_3)]$ unit produced $[MO(PO)_2]^+$ or $[ReN(PO)_2]^+$ base peaks, respectively,

(28) Mazzi, U.; de Paoli, G.; di Bernardo, P.; Magon, L. *J. Inorg. Nucl. Chem.* **1976**, *38*, 721.

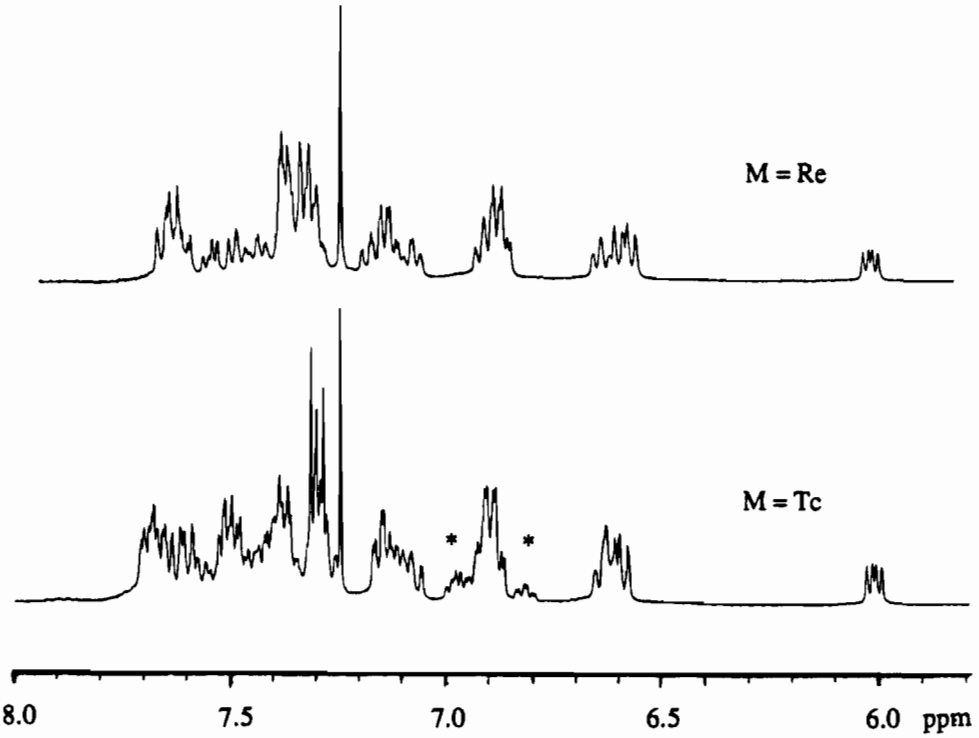
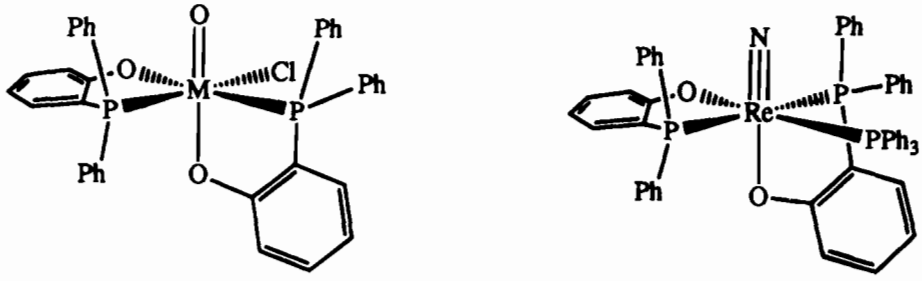


Figure 2. ^{1}H NMR of $MOCl(PO)_2$ (M = Re, Tc) in $CDCl_3$ (* = impurities).

Chart 1. Proposed Structures for $MOCl(PO)_2$ (Left) and $ReN(PO)_2(PPh_3)$ (Right)



indicating that the bidentate PO^- ligands were more strongly bound than the monodentate Cl or PPh_3. The parent ion peaks were all present but were weaker in intensity. The IR spectrum of $TcOCl(PO)_2$ was almost superimposible on that of its ReO congener ($\nu_{Tc=O}$ = 940 cm^{-1}, $\nu_{Re=O}$ = 975 cm^{-1}) but quite different from that of the nitrido complex ($\nu_{Re\equiv N}$ = 1045 cm^{-1}), reflecting the structures proposed (*vide infra*). All these absorption bands were in the normal range.[26c]

For the oxorhenium complex $ReOCl(PO)_2$, an "equatorial" structure[12] where two PO^- ligands were bound in the equatorial plane (relative to the axial Re=O) was ruled out by the ^{31}P-{^{1}H} NMR, which showed two doublets with a coupling constant of 10 Hz, consistent with two nonequivalent phosphorus donors being *cis* to one another. A *cis*-(P,P) "twisted" structure is thus proposed for this complex—each of the two PO^- moieties acts as a bidentate (P, O) monobasic ligand, with the phenolate oxygen donor of the axial PO^- ligand *trans* to the Re=O group (Chart 1). The exclusion of a P donor *trans* to the oxo is based on other reported bis(ligand)halooxometal(V) complexes of bidentate monobasic ligands, where the neutral donors are always *cis* to the oxo group.[2,12] Upon coordination of HPO, an increase in chemical shift was observed from that of −28.7 ppm for the free ligand, as is generally seen for most phosphines (except PX_3 and $P(OR)_3$), due to the resultant deshielding effect.[29] The upfield resonance at 2.2 ppm in the ^{31}P{^{1}H} NMR was assigned to the P donor of the axial ligand (*vide infra*), as it was more shielded since the neutral donor of the axial ligand usually donates less strongly than that of the equatorial one, consistent with the previously reported $ReOBr(ma)_2$ species (ma = maltolate anion) and as reflected by the bond distances.[2] For the *cis*-(P,P) "twisted" $ReOCl(PN)_2$, the Re−P bonds of the equatorial ligand were found to be significantly shorter than those of the axial ligand in each of two solved structures.[12] For a series of five- or six-coordinate Ru(II) complexes, a linear correlation of P−Ru distances with ^{31}P chemical shifts has been noted with the strongly bound phosphines giving downfield resonances.[30]

This *cis*-(P,P) "twisted" structure for $MOCl(PO)_2$ (M = Tc, Re) was consistent with the ^{1}H NMR spectra (Figure 2). The low symmetry produces rather complicated spectra since there are six different types of phenyl rings in each complex; however, the eight hydrogen atoms of the two phenolic arms are easily correlated in the ^{1}H−^{1}H COSY spectrum (not shown), the upfield set of four hydrogen atoms being those of the axial ring as in $ReOBr(ma)_2$[2] and analogous complexes of the $ReOCl(PN)_2$ formulation.[12] For the axial PO-phenyl ring set, the most upfield resonance at δ 6.01, a doublet of doublets resulting from coupling to the neighboring phosphorus and hydrogen nuclei, was assigned to the hydrogen atom on the other position ortho to P. This doublet of doublets became a simple doublet upon

(29) Parish, R. V. *NMR, NQR, EPR, and Mossbauer Spectroscopy in Inorganic Chemistry*, 1st ed.; Ellis Horwood: New York, 1990; p 64.

(30) Jessop, P. G.; Rettig, S. J.; Lee, C.-L.; James, B. R. *Inorg. Chem.* **1991**, *30*, 4617.

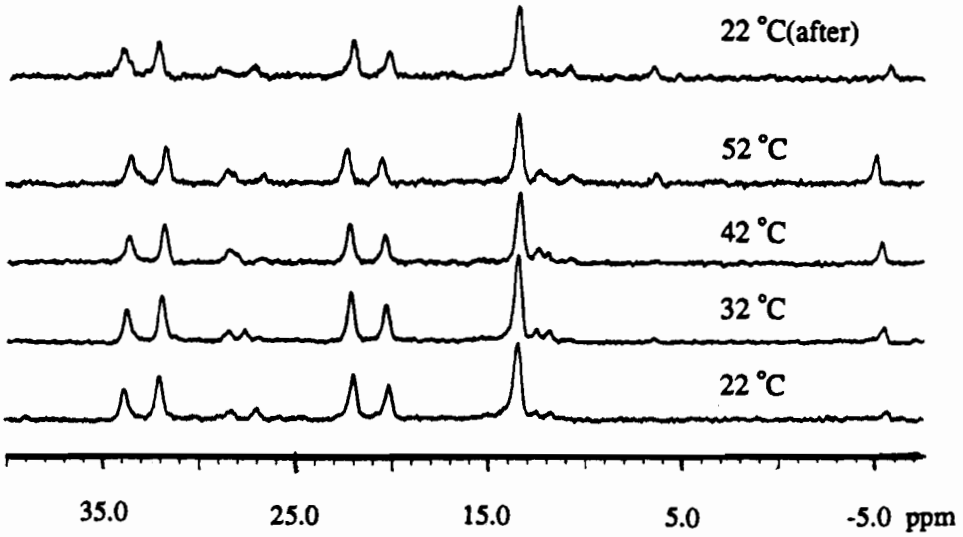


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $ReN(PO)_2(PPh_3)$ in $CDCl_3$ (heating to 52 °C and cooling back to 22 °C).

decoupling the upfield P at 2.2 ppm, indicating that the latter belongs to the axial PO phosphorus atom. The ^1H NMR spectrum of the Tc analog (Figure 2) is identical, indicating the same arrangement. Consistent with this, the Tc complex showed two broad "waves" in the range 10−50 ppm in its $^{31}P\{^1H\}$ NMR spectrum; these "waves" became broad peaks upon cooling to −35 °C, at about 27 and 40 ppm, respectively, suggesting that there two nonequivalent P atoms in the complex. This resonance broadening is not uncommon in Tc−phosphine complexes[12] and is probably caused by a scalar coupling of the ^{31}P nuclei with the quadrupolar ^{99}Tc nucleus.[31,32]

In the $^{31}P\{^1H\}$ NMR spectrum of the nitrido complex $ReN(PO)_2(PPh_3)$ in $CDCl_3$, an ABX system was observed (Figures 3 and 6A), indicating that there were three nonequivalent P atoms in a meridional arrangement. The downfield doublet of doublets (34.7 ppm), with coupling constants of 222 ($^2J_{AB}$) and 12 Hz ($^2J_{AX}$), corresponds to one of the two *trans* P atoms, while the upfield doublet of doublets (23.0 ppm), with coupling constants of 222 ($^2J_{BA}$) and 6 Hz ($^2J_{BX}$), corresponds to the other *trans* P atom. The unique P atom (resonance at 13.9 ppm) is *cis* to both of the above P atoms, giving a multiplet resulting from coupling to the two *cis* P nuclei. This unique phosphorus is assigned to the bound PPh_3 ligand on the basis of the replacement of the PPh_3 ligand with pyridine (*vide infra*); thus the two *trans* P nuclei belong to the PO^- ligands. As in $ReOCl(PO)_2$, the downfield resonance at 34.7 ppm is assigned to the P donor of the equatorial ligand and that at 23.0 ppm to the axial P. The crowded environment around the Re center, which includes three triarylphosphines, led to the detectable dissociation of the PPh_3 ligand in $CDCl_3$, as revealed by the presence of a small peak at about −5 ppm in the $^{31}P\{^1H\}$ NMR. This peak is free PPh_3; its intensity increased significantly upon addition of PPh_3 to the NMR sample in a separate test. The PPh_3 dissociation was enhanced at a higher temperature, as shown in Figure 3.

Mono(PO_2) Re Complexes. The parent ions $[ReOCl(PPh_3)(PO_2) + 1]^+$ or $[Re(NPh)Cl(PPh_3)(PO_2)]^+$ and three fragment cations (loss of PPh_3 and/or Cl) were present in about the same intensities in the positive ion detection LSIMS. In all the cases, the only Re-containing fragments incorporated PO_2^{2-}, showing that the $ReZ(PO_2)$ (Z = O, NPh) moiety was retained as a highly stable unit. The IR spectra of all the complexes showed one ν_{C-H} stretch at about 3050 cm^{-1}, while the *cis*-(P,P)-phenylimido complex showed an additional band at 2980 cm^{-1}. The Re=Z bond stretching vibrations were found at 970 cm^{-1} (Z = O) or 1030 cm^{-1} (Z = NPh), normal for the respective moieties.[26c,d]

No dissociation of PPh_3 in solution was observed for the three mono(PO_2) complexes at room temperature, presumably due to less steric repulsion than in $ReN(PO)_2(PPh_3)$. The oxo complex $ReOCl(PPh_3)(PO_2)$ showed an AX system in the $^{31}P\{^1H\}$ NMR spectrum, with the small coupling constant of 7.2 Hz indicating a *cis*-(P,P) geometry. The peak at 19.5 ppm was assigned to the PO_2^{2-} ligand and the one at −2.1 ppm to the PPh_3 ligand, as suggested by its displacement by pyridine (*vide infra*). This assignment was consistent with the crystal structure of the *cis*-(P,P)-phenylimido analog, where the PO_2^{2-} ligand Re−P distance was shorter than the PPh_3 Re−P distance (*vide infra*), indicating the P nucleus of the former ligand donates more electron density, thus is less shielded, than that of the latter. For the phenylimido complex $Re(NPh)Cl(PPh_3)(PO_2)$, the *cis*-(P,P) isomer distinguished itself effectively from the *trans*-(P,P) isomer in the $^{31}P\{^1H\}$ NMR spectrum. For the *trans* isomer, a typical AB quartet pattern demonstrated a *trans*-(P,P) structure where the coupling constant was large ($^2J_{PP}$ = 241 Hz). The $^{31}P\{^1H\}$ NMR spectrum of the *cis*-(P,P) isomer was consistent with two nonequivalent *cis* P nuclei. Again, the downfield peak (28.3 ppm for the *cis* or 34.5 ppm for the *trans* isomer) was assigned to the PO_2^{2-} phosphorus atom while the upfield peak (15.4 ppm for the *cis* or 2.9 ppm for the *trans* isomer) was assigned to bound PPh_3 phosphorus atom as was seen in $ReOCl(PPh_3)(PO_2)$.

Mixed(PO/PO_2) Complexes. In the LSIMS, the peaks for the parent ions $[ReZ(PO_2)(PO) + 1]^+$ were stronger than those for the ions $[ReZ(PO_2)]^+$, indicating that the parent ions were stabilized by replacement of monodentate ligands with the PO^- chelate. In the IR spectra of both the complexes, there was one ν_{C-H} at ~3050 cm^{-1} and Re=Z stretching vibrations were found at 965 cm^{-1} (Z = O) or 1030 cm^{-1} (Z = NPh), in the normal range for either type of linkage.[26c,d]

A *cis*-(P,P) structure for the oxo complex was revealed by a small coupling constant of about 4 Hz in an AX system in the $^{31}P\{^1H\}$ NMR spectrum. For the phenylimido complex, an AB quartet with a large $^2J_{PP}$ = 230 Hz coupling constant demonstrated a *trans*-(P,P) structure. These results were not surprising considering the geometry of the mono(PO_2) precursors for each mixed(PO/PO_2) complex. As discussed before, the downfield resonance was assigned to the PO_2^{2-}, while the other one was

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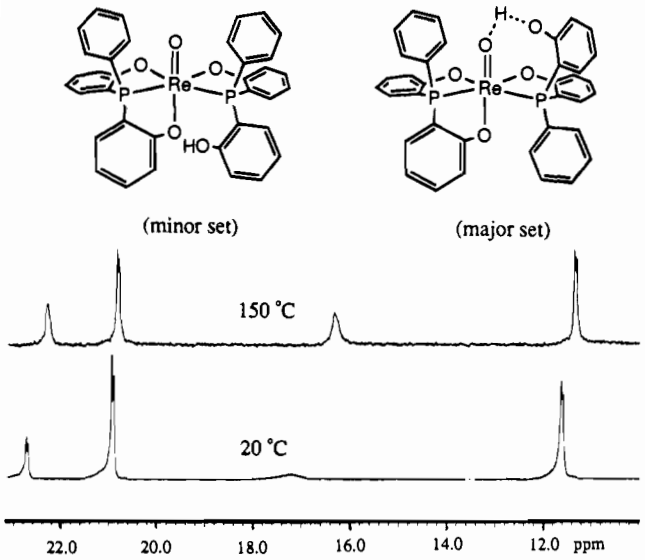

Figure 4. $^{31}P\{^1H\}$ NMR of $ReO(PO_2)(HPO_2)$ in DMSO-d_6 at room temperature and high temperature and the proposed structures for the two diastereomers.

assigned to the PO^- phosphorus atom in each case. This assignment was also consistent with the crystal structure of *fac-cis*-(P,P)-$ReO(PO)(PO_2)$, in which the Re−P distance for PO_2^{2-} was significantly shorter than that for PO^- (*vide infra*). Compared to that for the corresponding mono(PO_2) precursor, the chemical shift for the PO_2^{2-} phosphorus atom in each mixed-(PO/PO_2) complex did not change much, (19.5 and 34.5 ppm in the each precursor, 20.6 and 35.7 ppm in the mixed oxo and phenylimido complexes, respectively) while the PO^- phosphorus atom was further deshielded (16.0 and 15.4 ppm in the mixed oxo and phenylimido complexes, respectively) with respect to the bound PPh_3 phosphorus in the precursor (−2.1 and 2.9 ppm in the oxo and phenylimido complexes, respectively). This can be rationalized by stronger Re−P binding for PO^- than for PPh_3 due to increased anchoring, as illustrated by the structural data (Table 3).

Bis(PO_2) Complexes. The formulations $MO(PO_2)(HPO_2)$ (M = Re, Tc) were based on elemental analyses as well as on spectral data. In the +LSIMS for $ReO(PO_2)(HPO_2)$, the neat sample in DMSO gave peaks corresponding to molecular ion plus proton (M + 1), molecular ion losing one ligand (M − HPO_2), and molecular ion losing one oxygen and one hydrogen atom (M − O − H, or $Re(PO_2)_2$); the last was thought to be formed under the ionization conditions rather than coming from the original sample. When the samples were ground with KBr, prominent peaks were observed for $[MO(PO_2)(HPO_2) + K]^+$ and $[MO(PO_2)(HPO_2) + 1]^+$ (M = Re, Tc) in the +LSIMS; the −LSIMS of $ReO(PO_2)(HPO_2)$ revealed $[ReO(PO_2)_2]^-$.

The IR spectra showed medium ν_{C-H} stretches at about 3060 cm^{-1} for each compound. The spectrum of $TcO(PO_2)(HPO_2)$ was almost superimposable on that of $ReO(PO_2)(HPO_2)$ except for the M=O stretching vibrations; the Tc analog showed a strong $\nu_{Tc=O}$ stretch at 965 cm^{-1}, while the Re=O vibration was weaker, and a doublet at 970 and 975 cm^{-1} with a sharp absorption at 990 cm^{-1}, possibly a solid state effect.

Two sets of AX patterns of relative intensities 3:1, were observed in the $^{31}P\{^1H\}$ NMR spectrum of $ReO(PO_2)(HPO_2)$ (Figure 4), suggesting two isomers in the product. *cis*-(P,P) structures were proposed for each isomer, as the coupling constants involved were small. $^2J_{PP}$ for the major set of doublets (20.9, 11.6 ppm) was 4.1 Hz, while for the minor pair, one peak was a doublet of 5.0 Hz (22.8 ppm) and the other was broad (17.5 ppm). The isomerism was consistent with the two possible diastereomers, where the free phenol group was oriented up or down (Figure 4). As has already been discussed, the phosphorus on the fully bound (tridentate) PO_2^{2-} was more deshielded than the PO^- or PPh_3 phosphorus; thus the upfield peak was assigned to the bidentate HPO_2^- ligand, while the downfield peaks were assigned to the tridentate PO_2^{2-} ligands in each pair. The major set was assigned to the diastereomer with the up-orientation of the free phenol group, while the minor pair was assigned to the diastereomer with the down-orientation. Thus, the broadness of the HPO^- phosphorus peak in the minor pair was explained by intermolecular proton exchange between the free phenolic hydroxyl group and the solvent. For the major diastereomer, hydrogen-bonding to the oxo group would hinder such a proton exchange, ensuring a normal narrow ^{31}P resonance for the P atom in the bidentate HPO^- ligand. There was no evidence for the interconversion of these two diastereomers as shown in high-temperature $^{31}P\{^1H\}$ NMR (Figure 4). In the $^{31}P\{^1H\}$ NMR spectrum, the Tc analog showed two broad shouldered peaks at 34.5 and 45.0 ppm, indicating the presence of two diastereomers as in the Re complex. As monitored by the $^{31}P\{^1H\}$ NMR spectrum, the Tc complex started to decompose at about 80 °C, giving a yellow species and phosphine oxide in DMSO-d_6.

In the ^1H NMR spectrum of $ReO(PO_2)(HPO_2)$, the two isomers were consistent with two upfield aromatic hydrogen signals, one major and one minor at about a 3:1 ratio (Figure 5). These two signals, as doublets of doublets, were assigned to the hydrogen adjacent to the P atom in the axial phenolato ring of each isomer. The spectrum also showed the presence of a hydrogen-bonded[33] phenolic hydrogen atom at about 10 ppm. The Tc analog showed a similar ^1H NMR spectrum, indicating similar structures, at least in solution (Figure 5).

X-ray Structures of *fac-cis*-(P,P)-Re(NPh)Cl(PPh_3)-(PO_2)·2$CHCl_3$ (1) and *fac-cis*-(P,P)-ReO(PO)(PO_2) (2). Crystals of $ReOCl(PO)_2$, $TcOCl(PO)_2$, $ReN(PO)_2(PPh_3)$, and ReOCl-(PPh_3)(PO_2) were easily grown to suitable size, while ReO-(PO_2)(HPO_2) tended to form small crystals and $TcO(PO_2)(HPO_2)$ always precipitated as a powder. Single crystals of *fac-cis*-(P,P)-Re(NPh)Cl(PPh_3)(PO_2)·2$CHCl_3$ were obtained from chloroform/cyclohexane solvent mixtures, while those of *fac-cis*-(P,P)-ReO(PO)(PO_2) were obtained from ethanol, both by slow evaporation, and the structures of both complexes were solved. The ORTEP diagrams of the molecules are shown in Figure 1, while atomic coordinates, selected bond distances, and selected angles are listed in Tables 2−4, respectively.

The overall geometry around the rhenium atom in both cases is best described as a highly distorted facial octahedron ("pinched") with *cis* phosphine ligands. In both molecules, the PO_2^{2-} ligand is bound in a facial manner, the meridional mode being sterically unavailable. Each of the two phenolato moieties in the PO_2^{2-} ligand functions as an anchor for the phosphine, with one PO-phenyl ring sitting in an equatorial plane and the other axial to the Re=NPh (**1**) or Re=O (**2**) unit. The PPh_3 (**1**) or PO^- (**2**) ligand coordinates such that its P donor is *cis* to the PO_2^{2-} P atom. The "pinched" distortion from octahedral geometry is mainly caused by the acute bite angles between the phenolate O atom and the P atom of the PO_2^{2-} or PO^- ligands (P(1)−Re(1)−O(1) = 80.96(8)° and P(1)−Re(1)−O(2) = 79.98(8)° for **1**; (P(1)−Re(1)−O(2) = 80.54(8)°, P(1)−Re-(1)−O(2) = 79.98(8)°, and P(2)−Re(1)−O(4) = 81.99(8)° for **2**). The repulsions between the two bulky triarylphosphine P donors, and between the sterically demanding Re=Z (Z = NPh, **1**; Z = O, **2**) linkage and the negatively charged *cis* donors relative to Re=Z account for this distortion as well. The P(1)−Re(1)−P(2) angles are 105.64(4) and 107.18(4)° for **1** and **2**,

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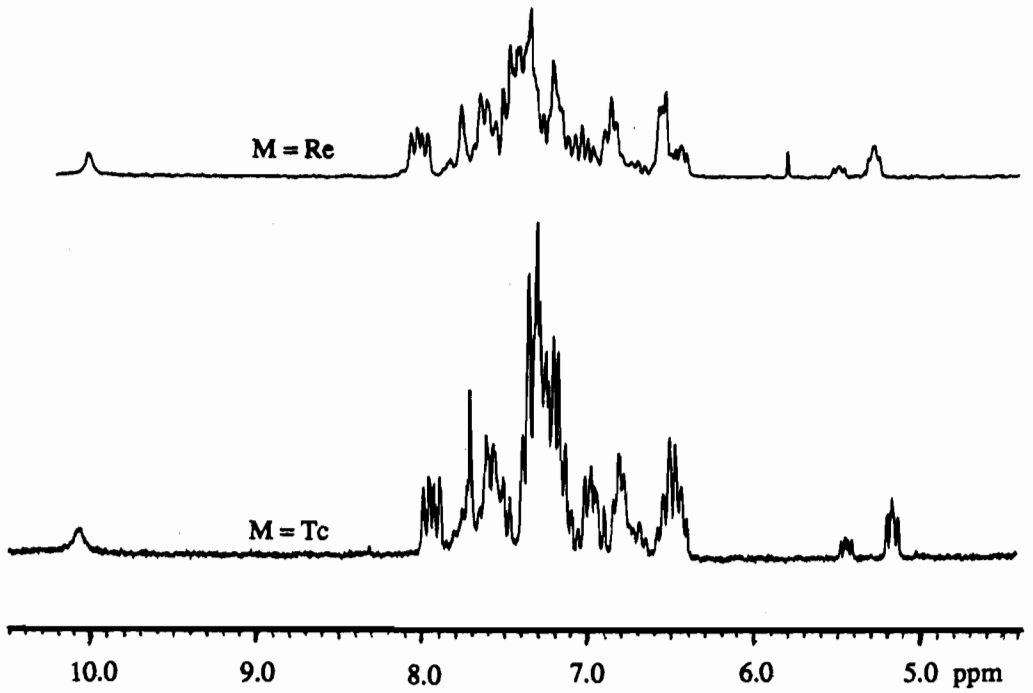

Figure 5. ^{1}H NMR of $MO(PO_2)(HPO_2)$ (M = Re, Tc) in DMSO-d_6.

respectively. The Cl(1)−Re(1)−N(1) and O(1)-Re-N(1) angles are 102.5(1) and 102.2(1)° (**1**), while the O(1)−Re(1)−O(2) and O(1)−Re−O(4) angles are 96.9(1) and 108.3(1)° (**2**), respectively. In contrast, P(1)−Re(1)−N(1) and P(2)−Re(1)−N(1) are 93.0(1) and 93.1(1)° (**1**), and P(1)−Re(1)−O(1) and P(2)−Re(1)−O(1) are 90.4(1) and 94.59(10)° (**2**), respectively, indicating less repulsion between the Re=Z group and the neutral *cis* donors. The Re atom is 0.296 (**1**) or 0.273 Å (**2**) out of the equatorial plane formed by the four *cis* donors. It has been suggested that the repulsion exerted by the oxo group on the ligands *cis* to it increases in the order of increasing hardness of the ligands.[34]

For **1**, the Re(1)−N(1) bond length of 1.728(3) Å, the same as that in the starting material $Re(NPh)Cl_3(PPh_3)_2$[27] and not significantly different from that in $[Re(ma)_2(NPh)(PPh_3)]^+$ (ma = maltolate anion) (1.709(8) Å),[35] indicates the retention of a multiple bond. The Re(1)−N(1)−C(37) angle is 171.7(3)°, equal to the analogous angles of 172.6(6)° in $Re(NPh)Cl_3(PPh_3)_2$[27] and 171.8(4)° in $Tc(NPh)Cl_3(PPh_3)_2$.[36] The small deviations from 180° in these cases suggest that the imido nitrogen is essentially sp-hybridized and that the M−N linkage is a real triple bond.[26e] In **2**, with the length of 1.692(3) Å, the Re(1)−O(1) bond is longer than that in $ReOCl_3(PPh_3)_2$ (1.663(5) Å)[37] but still in the range of values found in other oxo complexes of rhenium(V),[26f] indicating the retention of a multiple bond. The *trans* influence of these multiple bonds was insignificant in **1** and **2**, however; the *trans* Re(1)−O(2) bond (2.050(3) Å) was identical to the *cis* Re(1)−O(1) bond (**1**), while the *trans* Re(1)−O(3) bond (2.026(3) Å) is actually shorter than one *cis* bond Re(1)−O(2) (2.050(3) Å) but longer than the other Re(1)−O(4) bond (1.994(3) Å) (**2**). Similar observations were found in $[Re(ma)_2(NPh)(PPh_3)]^+$, where close values of 1.996(7) and 1.987(7) Å were found for Re−O bonds *trans* and *cis* to the Re=NPh group, respectively.[35] Furthermore, in $Re(NPh)Cl_3(PPh_3)_2$, the *trans* Re−Cl bond (2.402(2) Å) is shorter than any of the *cis* Re−Cl bonds (2.415(2) and 2.411(2) Å),[27] and in $(CH_3)_4N[ReO(O_2C_6H_4)(PPh_3)]$, the *trans* Re−O bond (2.041(7) Å) is shorter than the *cis* Re−O bond (2.062(9) Å,[38] indicating a nonexistent *trans* influence. In the Tc analog $Tc(NPh)Cl_3(PPh_3)_2$, the *trans* influence was not observed either.[36] All these factors suggest that the *trans* influence of multiple metal−ligand bonds is insignificant in these complexes. The *cis* ancillary ligands may play a role as well. The Re(1)−Cl(1) distance (2.409(1) Å) in **1** equals the average Re−Cl value in $Re(NPh)Cl_3(PPh_3)_2$.[27]

The double-phenolato-anchored P donor in tridentate PO_2^{2-} (**1** and **2**) was bound to the Re center significantly more closely than the single-phenolato anchored P atom in bidentate PO^- (**2**), which is in turn more closely bound than the nonanchored phosphorus atom in monodentate PPh_3 (**1**). The Re−PO_2^{2-} distance, Re(1)−P(1) = 2.387(1) Å in **1**, is the shortest Re(V)−P bond to our knowledge (contrast it with 2.454(1) Å for Re(1)−P(2) in **1**). On the other hand, Re(1)−P(1) and Re(1)−P(2) are found to be 2.391(1) and 2.428(1) Å, respectively, in **2**. The average Re−P distances are 2.496 Å in $Re(NPh)Cl_3(PPh_3)_2$[27] and 2.519(1) Å in $ReOCl_3(PPh_3)_2$.[37] Single aminophenylphosphine-anchored Re−P bonds are in the range 2.42−2.50 Å.[12] The strengthening of the Re−P bond with increased anchoring can be explained by the synergistic electronic effect ($\sigma + \pi$) as well as reduced steric effects[39] due to the reorientation and bonding of the anchoring arms (*vide infra*).

Whereas the phenyl groups in the bound PPh_3 (**1**) are found in a *syn* conformation, as in free PPh_3,[40] the anchoring *o*-oxyphenyl groups are reoriented by the rotation of the P−C bond to fit the required octahedral geometry while anchoring in both **1** and **2**. This reorientation makes it possible for the *o*-oxyphenyl groups to anchor on the metal, forming chelate rings. Upon anchoring, there is no repulsive contribution (i.e.

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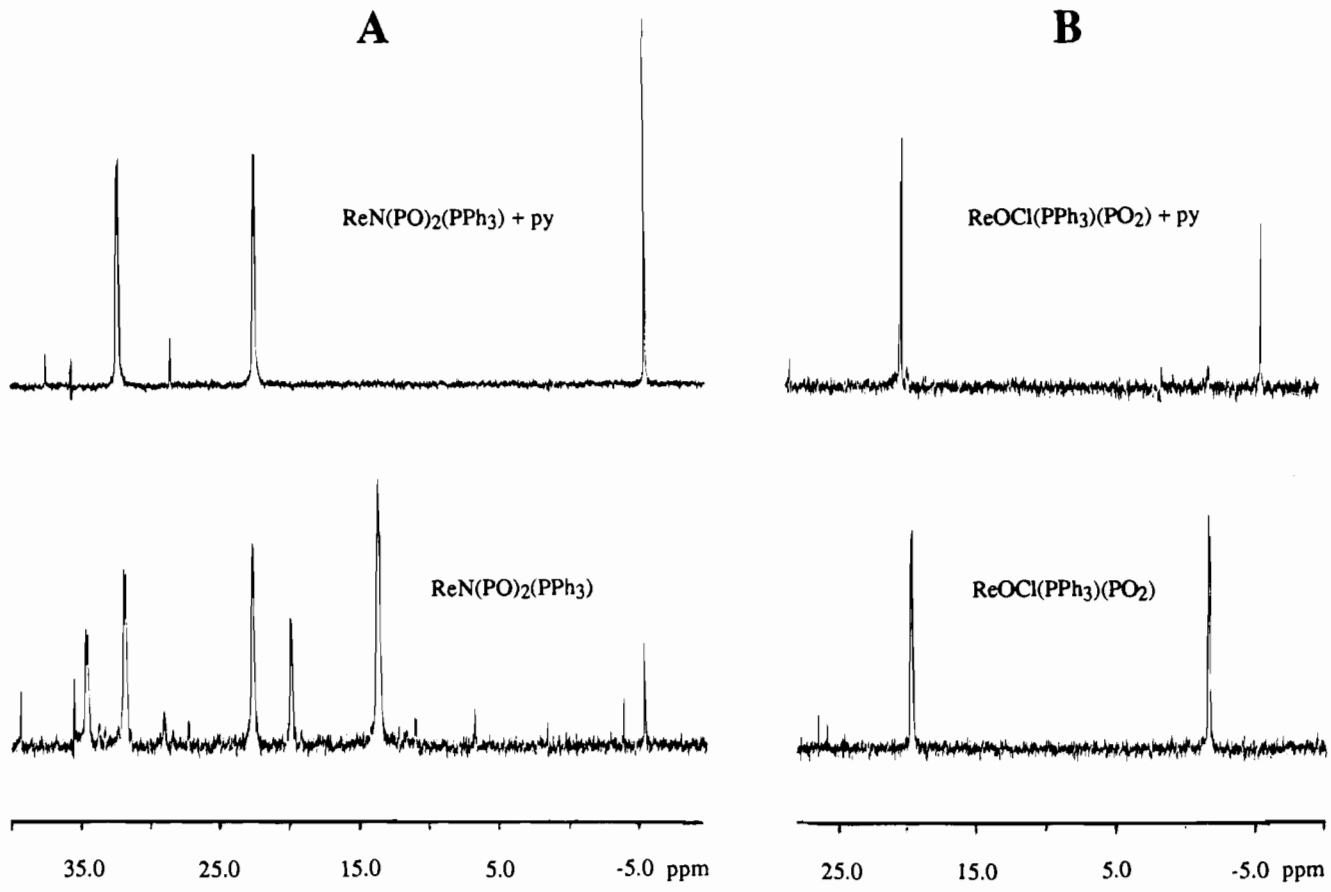

Figure 6. Reactivity of some complexes toward pyridine monitored by $^{31}P\{^1H\}$ NMR in $CDCl_3$: (A) $ReN(PO)_2(PPh_3)$; (B) $ReOCl(PPh_3)(PO_2)$.

large cone angle) from the *o*-oxyphenyl groups since these groups are not bulky phenyl rings which keep P away from the metal; in fact they are holding the metal. In addition, the orientation of the *o*-oxyphenyl rings is coplanar or perpendicular to the equatorial plane, possibly locating the P atom in a position that favors transferring π donation from the metal center to the *o*-oxyphenyl rings. Thus, the steric repulsion decreases, and the π back-bonding (and σ-donating) increases, in the order of PPh_3, PO^-, PO_2^{2-}, resulting in Re−P distances that decrease in the same order.

While the C−O and C−C bonds in the equatorial PO_2^{2-} chelate rings are the same as those in the axial rings, within experimental error, the extreme P−C bond lengths are significantly different ($\sigma(\Delta) = 0.006$ Å). The axial ring P−C bonds are shorter (P(1)−C(7) = 1.780(4) Å (**1**), 1.785(4) Å (**2**)) than their equatorial analogs (P(1)−C(1) = 1.800(4) Å (**1**), 1.795(4) Å (**2**)) (Table 3). The average corresponding distances are 1.826 Å in the bound PPh_3 moiety (**1**) and 1.831 Å in the free PPh_3. This may indicate that the $\pi-\pi$ interaction between P and C decreases in the following order: axial anchoring rings, equatorial anchoring rings, bound PPh_3, free PPh_3. All the anchoring phenyl rings of the PO_x^{x-} ligands in **1** and **2** were found to be quite planar, as are the other phenyl rings attached to either phosphine, indicating that upon coordination the aromaticity of the phenyl rings is retained.

Reactivity to Water/Pyridine. To the complex $ReO(PO_2)(HPO_2)$ or $TcO(PO_2)(HPO_2)$ in DMSO-d_6 was added 5 drops of D_2O. A fluffy greenish precipitate or a brownish cloudy material, respectively, formed between the two solution layers and disappeared upon shaking the tube. No detectable change was observed in the $^{31}P\{^1H\}$ NMR measurement in each test; however, in the ^1H NMR spectra the phenol hydrogen resonance at 10 ppm disappeared, consistent with an intermolecular H−D exchange. The addition of water to $ReO(PO_2)(HPO_2)$ led to no visible reaction after weeks. The bis(PO_2) complexes are stable in the presence of water.

The complexes *mer*-(P,P,P)-$ReN(PO)_2(PPh_3)$ and *cis*-(P,P)-$ReOCl(PPh_3)(PO_2)$, in chloroform-d_1 (NMR sample), were treated with about 5 drops of pyridine, and color changes from brownish green to green for the former and from brownish red to brown for the latter were observed. In each case, replacement of PPh_3 with pyridine was seen in the $^{31}P\{^1H\}$ NMR spectrum by the increase or appearance of a singlet at ~−5 ppm and the disappearance of the upfield P signal in the original spectrum (Figure 6). Clearly, the PPh_3 ligands are labile in the two complexes and the assignment of the bound PPh_3 in the original $^{31}P\{^1H\}$ NMR spectra can be made. Although dissociation of PPh_3 in *mer*-(P,P,P)-$ReN(PO)_2(PPh_3)$ was observed in $CDCl_3$ (*vide supra*), an associative interchange mechanism, as opposed to a dissociative interchange, is believed to be involved in the py-exchange reaction because of the large excess of py, leading to a *cis*-(P,P)-pyridino species (Figure 6). No such py exchange was found for the complex *trans*-(P,P)-Re(NPh)Cl(PPh_3)(PO_2) at room temperature, although the exchange with HPO was observed in the presence of a base and heat.

Conclusion. Neutral rhenium(V) and technetium(V) complexes of the forms $MOCl(PO)_2$, $ReN(PO)_2(PPh_3)$, *fac*-ReZCl-(PPh_3)(PO_2), *fac*-ReZ(PO)(PO_2), and $MO(PO_2)(HPO_2)$, where M is Tc or Re, Z is O or NPh, and PO_x^{x-} is the diphenyl-(hydroxyphenyl)phosphine ($x = 1$) anion or the phenylbis-(hydroxyphenyl)phosphine ($x = 2$) dianion, have been synthesized and characterized. The bidentate (P,O) monobasic ligands form oxometal(V) complexes which are structurally analogous to the complexes of the two metals with other bidentate monobasic ligands. The mono(PO_2) phenylimido complexes were isolated as *cis*- or *trans*-(P,P) geometrical isomers, depending on the reaction conditions, while only a *cis*-(P,P) product was prepared for the mono(PO_2) oxo analog. Mixed-

ligand complexes incorporating both PO_2^{2-} and PO^- ligands with *cis*- or *trans*-(P,P) geometry were synthesized from appropriate mono(PO_2) complexes. Bis(PO_2) complexes were obtained as mixtures of two diastereomers with one ligand protonated (HPO_2^-); these diastereomers were not interconvertible and showed good resistance to hydrolysis. They could also be prepared by reduction directly from perrhenate or pertechnetate. Mixed(PO/PO_2) complexes or bis(PO_2) complexes could not be prepared from triphenylphosphine-containing precursors via ligand-exchange reactions. The double-anchoring phenolate rings in PO_2^{2-} strengthen the Re−P bonds even more significantly than one phenolate does in PO^-. These compounds are important since they provide fully characterized models for the structures of intermediates in the synthesis of potential radiopharmaceuticals. Work on ^{99m}Tc complexes of these ligands and their radiopharmaceutical chemistry is underway.

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Supplementary Material Available: Complete tables of crystallographic data, hydrogen coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, and intermolecular contacts (37 pages). Ordering information is given on any current masthead page.

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