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Multifaceted Reactions of $P(CH_2OH)_3$ with Rhenium(V) Precursors. Synthesis, Characterization, and X-ray Structural Studies of *trans,trans,trans*-$[ReO_2\{P(CH_2OH)_3\}_2(py)_2]Cl$, *trans,cis,cis*-$[ReO_2\{P(CH_2OH)_3\}_2(py)_2]Cl$, and Novel Alkoxide $[Re(O)(\mu\text{-}O)(P\{CH_2OH\}_3)(\mu\text{-}\eta^2\text{-}P\{CH_2OH\}_2CH_2O)]_4$

Douglas E. Berning,[†,‡] **Kattesh V. Katti,***[†,§] **Leonard J. Barbour,**[‡] **and Wynn A. Volkert**[†,||]

Department of Radiology and Center for Radiology Research and Missouri University Research Reactor, 301 Business Loop 70 West, Allton Bldg., Room 106, Columbia, Missouri 65203, Department of Chemistry, University of Missouri−Columbia, Columbia, Missouri 65211, and H. S. Truman Memorial VA Hospital, Columbia, Missouri 65203

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The reaction of the water-soluble monophosphine tris(hydroxymethyl)phosphine (THP, **1**) with $[ReO_2(py)_4]Cl$ produced either *trans,trans,trans*-$[ReO_2(THP)_2(py)_2]Cl$ (**3,** referred to as *trans*-$[ReO_2(THP)_2(py)_2]Cl$ throughout the text) or *trans,cis,cis*-$[ReO_2(THP)_2(py)_2]Cl$ (**4,** referred to as *cis*-$[ReO_2(THP)_2(py)_2]Cl$ throughout the text) depending on the reaction conditions. In contrast, the reaction of THP with $ReO_2I(PPh_3)_2$ in biphasic media produced the novel, neutral, cyclic tetranuclear, rhenium(V) alkoxide **5** in low yields. A similar reaction of bis(hydroxymethyl)phenylphosphine (**2**) with $[ReO_2(py)_4]Cl$ produced the *trans,trans,trans*-$[ReO_2\{PPh(CH_2OH)_2\}_2(py)_2]Cl$ complex (**6**, referred to as *trans*-$[ReO_2\{PPh(CH_2OH)_2\}_2(py)_2]Cl$ throughout the text) in high yields. All compounds were characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy and mass spectroscopy. X-ray data for **3**: monoclinic, $C2/c$, $a = 17.7964(11)$ Å, $b = 8.8972(6)$ Å, $c = 15.3247(9)$ Å, $\beta = 97.683(1)°$, $Z = 4$, $R = 0.0179$ ($R_w = 0.0426$). X-ray data for **4**: monoclinic, $P2_1/n$, $a = 12.1025(7)$ Å, $b = 12.2670(7)$ Å, $c = 15.5230(9)$ Å, $\beta = 97.683(1)°$, $Z = 4$, $R = 0.0191$ ($R_w = 0.0483$). X-ray data for **5**: monoclinic, $P2/c$, $a = 12.3759(7)$ Å, $b = 9.8274(5)$ Å, $c = 22.4272(12)$ Å, $\beta = 96.807(1)°$, $Z = 2$, $R = 0.0437$ ($R_w = 0.0887$). X-ray data for **6**: monoclinic, $P2_1/n$, $a = 9.3654(5)$ Å, $b = 13.2578(7)$ Å, $c = 12.0257(7)$ Å, $b = 107.0480(10)°$, $Z = 2$, $R = 0.0218$ ($R_w = 0.0578$).

Introduction

Numerous investigations have revolved around the use of *trans*-tetrakis(pyridine)dioxorhenium(V) chloride due to its photophysical activity,[1−6] redox catalytic activity,[7,8] multielectron electrochemical behavior,[7,9] and use as a precursor in the development of rhenium(V) complexes bounded to a diverse range of ligand frameworks.[10−12] However, it is surprising to note that studies relating to the systematic and stepwise replacement of pyridines from $[ReO_2(py)_4]Cl$ by specific ligand(s) are relatively rare. An understanding of factors (kinetic versus thermodynamic) that would influence the formation of cis and trans substitution products such as $[ReO_2L(py)_3]^+$, $[ReO_2L_2(py)_2]^+$, $[ReO_2L_3(py)]^+$, and $[ReO_2L_4]^+$ (L = monodentate ligand) is important in gaining insight into the overall regio- and stereoselectivity involved in the nucleophilic substitution reactions at the rhenium(V) center. Pyridines are easily replaceable ligands with other stronger electron donors on rhenium(V). Therefore, the development of systematic strategies to obtain bis-substituted rhenium(V) complexes (e.g., $[ReO_2L_2(py)_2]^+$) with ligands disposed in trans positions becomes particularly important in the context of producing rhenium(V)-containing linear polymers via the replacement of trans pyridines with bifunctional electron donors.

As part of our ongoing studies on the development of water-soluble transition metal compounds for catalytic and biomedical applications,[13−15] we herein report the synthesis, isolation, and X-ray crystallographic investigations of *cis*- and *trans*-$[ReO_2(THP)_2(py)_2]Cl$ (THP = tris(hydroxymethyl)phosphine). The synthesis and X-ray structural analysis of a novel, tetranuclear rhenium(V) alkoxide $[Re(O)(\mu\text{-}O)(P\{CH_2OH\}_3)(\mu\text{-}\eta^2\text{-}P\{CH_2OH\}_2CH_2O)]_4$ obtained via the reaction of $ReO_2I(PPh_3)_2$ and

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[*] To whom correspondence should be addressed.

[†] Department of Radiology and Center for Radiology Research.

[‡] Department of Chemistry, University of Missouri.

[§] University of Missouri Research Reactor.

[||] H. S. Truman Memorial VA Hospital.

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Table 1. Crystal Data and Details of Data Collection for Complexes **3**−**6**

compd	**3**	**4**	**5**	**6**
formula	$C_{16}H_{28}ClN_2O_8P_2Re$	$C_{16}H_{28}ClN_2O_8P_2Re$	$C_{24}H_{68}O_{32}P_8Re_4$	$C_{26}H_{32}ClN_2O_6P_2Re$
space group	*C*2/*c*	*P*2$_1$/*n*	*P*2/*c*	*P*2$_1$/*n*
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
fw	659.99	659.99	1861.98	716.10
a, Å	17.7964(11)	12.1025(7)	12.3759(7)	9.3654(5)
b, Å	8.8972(6)	12.2670(7)	9.8274(5)	13.2578(7)
c, Å	15.3247(9)	15.5230(9)	22.4272(12)	12.0257(7)
ϖ, deg	109.433(1)	97.683(1)	96.807(1)	107.048(1)
T, °C	25(2)	25(2)	25(2)	−100(2)
λ, Å	0.710 70	0.710 70	0.710 70	0.710 70
Z	4	4	2	2
F(000)	1296	1296	1452	708
V, Å^3	2288.3(2)	2283.9(2)	2708.4	1427.56
ρ_{calc}, g/cm^3	1.916	1.919	1.878	1.666
ρ_{obs}, g/cm^3	not measd	not measd	not measd	not measd
μ, cm^{-1}	56.11	56.22	91.83	45.00
R_1	0.0179	0.0191	0.0437	0.0218
R_w[a]	0.0426	0.0483	0.0887	0.0578
gof	1.023	1.029	1.061	1.131

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$; $R_w = [[\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]]^{1/2}$.

THP under biphasic conditions is also described. Furthermore, the synthesis and X-ray structural analysis of *trans*-$[ReO_2\{PhP(CH_2OH)_2\}_2(py)_2]Cl$ is reported.

Experimental Section

All reactions were carried out under purified nitrogen by standard Schlenk techniques. Solvents were purified and dried by standard methods and distilled under nitrogen prior to use. Tetrakis(hydroxymethyl)phosphonium chloride was obtained from Fluka Chemical Co. Phenylphosphine and $ReO_2I(PPh_3)_2$ were obtained from Aldrich Chemical Co. and used without further purification. Waters Sep-Pak Vac C18 columns (35 cm^3, 10 g) were obtained from Fisher Scientific Co. Tris(hydroxymethyl)phosphine (**1**) was prepared by previously reported literature methods.[16−17] $PhP(CH_2OH)_2$ (**2**) was prepared by a modified literature procedure.[18] $[ReO_2(py)_4]Cl$ was prepared as described in the literature.[19] Nuclear magnetic resonance spectra were recorded on a Bruker ARX-300 spectrometer. The ^1H and ^{13}C chemical shifts are reported relative to an external standard of TMS, while ^{31}P NMR chemical shifts are reported to an external standard of 85% H_3PO_4. Mass spectral analyses were performed by the Washington University Resource for Biomedical and Bio-organic Mass Spectrometry, St. Louis, MO. Melting points were determined on a Mel-Temp II apparatus and are uncorrected.

Synthesis of *trans*-$[ReO_2(THP)_2(py)_2]Cl$ (3). Tris(hydroxymethyl)phosphine (**1**, 0.8771 mmol) in ethanol (5 mL) was added dropwise to $[ReO_2(py)_4]Cl$ (0.4385 mmol) also in ethanol (5 mL) and stirred at 25 °C for 12 h. The product was filtered off and dried in vacuo to give complex **3** in 80% yield. HRFAB: Calc for $C_{16}H_{28}N_2O_8P_2Re$, 625.0879; found ($[M]^+$), *m/z* = 625.0879. Mp = 123−125 °C (dec). ^1H NMR (D_2O): δ 4.02 (s, 12 H, $P(CH_2OH)_3$), 7.53 (m, 4 H, 3,5-C_5H_5), 7.89 (m, 2 H, 4-C_5H_5), 8.84 (m, 4 H, 2,6-C_5H_5). ^{13}C NMR (D_2O): δ 53.6 (virtual triplet, $P(CH_2OH)_3$, $^1J_{PC}$ = 31.7 Hz), 126.7 (s, 3,5-C_5H_5) 142.0 (s, 4-C_5H_5), 152.0 (s, 2,6-C_5H_5). ^{31}P NMR (D_2O): δ −17.1 (s).

The same complex can be synthesized by refluxing THP (**1**, 2.0 mmol) in methanol (10 mL) with $[ReO_2(py)_4]Cl$ (0.5 mmol) for 30 min followed by purification on a Waters Sep-Pak Vac C18 column. Extended refluxing leads to the cis isomer.

Synthesis of *cis*-$[ReO_2(THP)_2(py)_2]Cl$ (4). Tris(hydroxymethyl)phosphine (**1**, 1.798 mmol) in methanol (5 mL) was added dropwise to $[ReO_2(py)_4]Cl$ (0.4385 mmol) also in methanol (5 mL) and refluxed for 3 h. The solvent was concentrated to approximately 5 mL and stored at 5 °C. The crystals were filtered off and dried in vacuo to give complex **4** in 90% yield. HRFAB: Calc for $C_{16}H_{28}N_2O_8P_2Re$, 625.0879; found ($[M]^+$), *m/z* = 625.0891. Mp = 135−140 °C (dec). ^1H NMR (D_2O): δ 4.02 (s, 12 H, $P(CH_2OH)_3$), 7.39 (m, 4 H, 3,5-C_5H_5), 7.81 (m, 2 H, 4-C_5H_5), 8.68 (m, 4 H, 2,6-C_5H_5). ^{13}C NMR (D_2O): δ 56.8 (d, $P(CH_2OH)_3$, $^1J_{PC}$ = 38.2 Hz), 126.8 (s, 3,5-C_5H_5), 142.0 (s, 4-C_5H_5), 148.8 (s, 2,6-C_5H_5). ^{31}P NMR (D_2O): δ −2.7 (s).

Synthesis of $[Re(O)(\mu\text{-}O)(P\{CH_2OH\}_3)(\mu\text{-}\eta^2\text{-}P\{CH_2OH\}_2CH_2O)]_4$ (5). Tris(hydroxymethyl)phosphine (**1**, 4.6 mmol) in water (10 mL) was added dropwise to a dichloromethane (10 mL) solution of $ReO_2I(PPh_3)_2$ (1.1 mmol) and stirred at room temperature under dry nitrogen for 3 h. The reaction mixture was filtered, and the aqueous layer was separated and concentrated in vacuo before loading onto a Waters Sep-Pak Vac C18 column. The column was eluted with water followed by methanol. Removal of the solvent gave the analytically pure compound in low yields (5−10%). HRFAB: Calc for $C_{24}H_{68}O_{32}P_8Re_4$, 1861.9804; found ($[M]^+$), *m/z* = 1861.9800. ^1H NMR (D_2O): δ 4.30−4.57 (m). ^{13}C NMR (D_2O): d 57.0 (d, $^1J_{PC}$ = 25.3 Hz), 57.8 (d, $^1J_{PC}$ = 32.6 Hz) and 58.4 (d, $^1J_{PC}$ = 34.0 Hz), 58.7 ($^1J_{PC}$ = 45.3 Hz). ^{31}P NMR (D_2O): δ −19.7 (s), −4.0 (s).

Synthesis of *trans*-$[ReO_2\{PhP(CH_2OH)_2\}_2(py)_2]Cl$ (6). Bis(hydroxymethyl)phenylphosphine (**2**, 5.878 mmol) in ethanol (10 mL) was added dropwise to $[ReO_2(py)_4]Cl$ (1.176 mmol) also in ethanol (10 mL) and refluxed for 30 min. The product was filtered off and dried in vacuo to give complex **6** in 85% yield. HRFAB: Calc for $C_{26}H_{32}N_2O_6P_2Re$, 717.1294; found ($[M]^+$), *m/z* = 717.1290. Mp = 160−165 °C (dec). ^1H NMR (D_2O): δ 4.30−4.60 (m, 8H, $P(CH_2OH)_2$), 7.05−7.40 (m, 14H, aromatics), 7.65−7.75 (m, 2H, 4-C_5H_5), 8.4 (d, 4H, 2,6-C_5H_5). ^{13}C NMR (D_2O): δ 54.3 (virtual triplet, $P(CH_2OH)_2$, $^1J_{PC}$ = 32.6 Hz), 126.1, 129.0, 130.4, 130.8, 140.8, 148.0, 150.6. ^{31}P NMR (D_2O): δ −9.8 (s).

X-ray Data Collection and Processing. The crystal data and details of data collection for complexes **3**−**6** are given in Table 1. Clear, red crystals of **3** and **4** suitable for X-ray diffraction were obtained from methanol solutions at 5 °C. Dark, red crystals of **5** suitable for X-ray diffraction were obtained from a methanol solution at −20 °C. Yellow-orange crystals of **6** were obtained from water at 5 °C. Intensity data were collected on a Siemens SMART CDD system using the ω scan mode. Data were corrected for absorption using the program SADABS, which is based on the method of Blessing.[20] Crystal decay was negligible, and a correction was deemed unnecessary. The structures were solved by the Patterson method using SHELXS-86[21] and refined by the full-matrix least-squares method on F^2 using SHELXL-93.[22]

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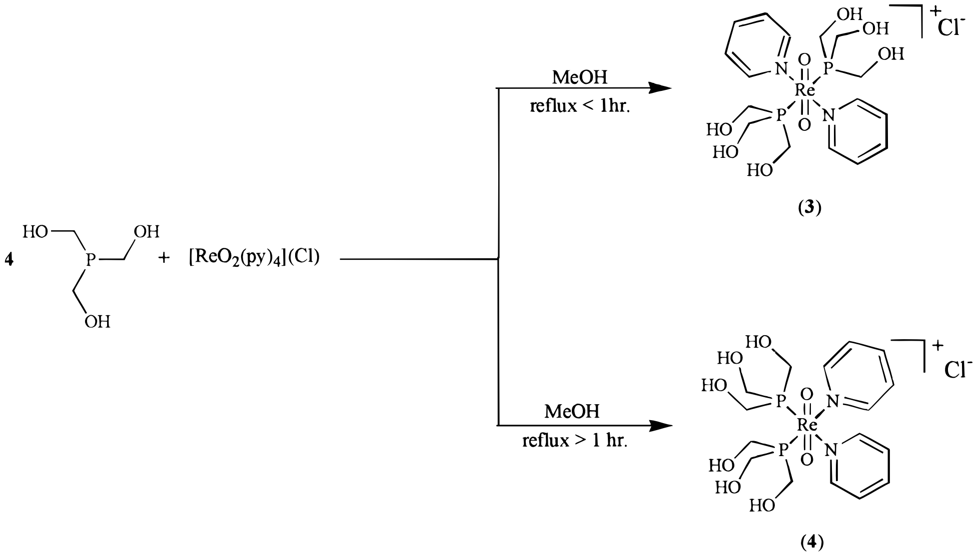
Scheme 1



For complexes **3**, **4**, and **6** all non-hydrogen atoms were refined anisotropically. Ethylenic hydrogen atoms were placed in calculated positions with their thermal parameters fixed at values of 1.2 those of their parent atoms. Hydroxyl hydrogen atoms were located in difference Fourier maps and refined isotropically with no restraints.

For complex **5**, all non-hydrogen atoms, with the exception of the lattice water oxygen atoms, were refined anisotropically. Ethylenic and hydroxyl hydrogen atoms were placed in calculated positions with their thermal parameters fixed at values of 1.2 those of their parent atoms. Two of the hydroxyl oxygen atoms were each disordered over two positions. In each case, the site occupancy factors of the disordered atoms were refined, the total value for each set being constrained to unity. Hydrogen atom positions were not generated for the disordered oxygen atoms, and the water hydrogen atoms were not located. The complex is situated about a 2-fold rotation axis as is one of the lattice water molecules.

Results and Discussion

Synthesis and Characterization of *trans*- and *cis*-[ReO$_2$(THP)$_2$(py)$_2$](Cl). Refluxing a methanolic solution of tris(hydroxymethyl)phosphine (**1**) with [ReO$_2$(py)$_4$](Cl) produces the complexes *trans*-[ReO$_2$(THP)$_2$(py)$_2$](Cl) (**3**) and *cis*-[ReO$_2$(THP)$_2$(py)$_2$](Cl) (**4**) (Scheme 1). Short refluxing times ($<$0.5 h) yield the trans isomer (**3**) while longer refluxing times ($>$1 h) yield the cis isomer (**4**) in near-quantitative yields. The isomers can be separated on a Waters Sep-Pak Vac C18 column; however we found that the most productive method of synthesizing the trans isomer (**3**) was to perform the reaction in ethanol at room temperature overnight. Filtration of the precipitate produces complex **3** in nearly quantitative yields. In contrast, the most productive method of synthesizing the cis isomer (**4**) is to reflux excess THP (**1**) in methanol with [ReO$_2$(py)$_4$](Cl) for 2−3 h. Monitoring the reaction by ^{31}P NMR spectroscopy illustrates the disappearance of the trans isomer (**3**) and the emergence of the cis isomer (**4**) as a function of time.

The molecular constitutions of **3** and **4** have been confirmed by fast atom bombardment mass spectra ([M]$^+$, $m/z = 625.0879$ for **3**; [M]$^+$, $m/z = 625.0891$ for **4**). The ^{31}P NMR spectra of **3** and **4** consist of singlets at −17.1 and −2.7 ppm, respectively, indicating downfield shifts compared to THP (**1**) ($\Delta\delta = 6.3$ for **3** and 20.7 for **4**). Furthermore, both the ^{1}H and ^{13}C NMR spectra are consistent with the proposed structures for complexes **3** and **4**. It is interesting to note that $^2J_{PH}$ coupling in both complexes **3** and **4** is not observable.

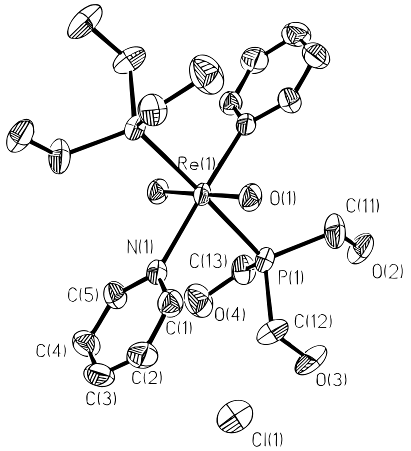


Figure 1. ORTEP diagram of **3**, showing 50% probability ellipsoids.

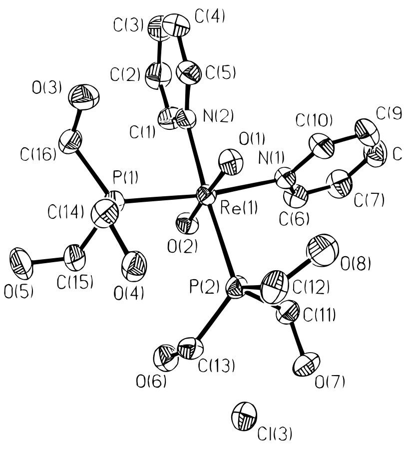


Figure 2. ORTEP diagram of **4**, showing 50% probability ellipsoids.

The molecular structures of **3** and **4** have been further confirmed by X-ray crystallography. The crystal data and details of data collection are listed in Table 1. The ORTEP diagrams of the cationic molecules **3** and **4** are shown in Figures 1 and 2, respectively. The selected bond distances and bond angles of complexes **3** and **4** are listed in Tables 2 and 3, respectively. Atomic coordinates and their equivalent isotropic displacement coefficients for complexes **3** and **4** are included in the Supporting Information. The asymmetric units of both complexes consist

Table 2. Selected Bond Distances (Å) and Angles (deg) for **3**[a]

Re(1)−O(1a)	1.768(2)	Re(1)−O(1)	1.768(2)
Re(1)−N(1a)	2.161(2)	Re(1)−N(1)	2.161(2)
Re(1)−P(1a)	2.491(1)	Re(1)−P(1)	2.491(1)
O(1)−Re(1)−N(1)q	89.7(1)	O(1a)−Re(1)−N(1)	90.3(1)
O(1)−Re(1)−P(1)	88.8(1)	O(1a)−Re(1)−P(1)	90.2(1)
N(1)−Re(1)−P(1)	88.7(1)	N(1a)−Re(1)−P(1)	91.3(1)
O(1a)−Re(1)−O(1)	180.0	N(1)−Re(1)−N(1a)	180.0
P(1)−Re(1)−P(1a)	180.0		

[a] The "a" atom is at equivalent position $-x + {}^1/_2, -y + 1, -z$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **4**

Re(1)−O(1)	1.762(2)	Re(1)−O(2)	1.774(2)
Re(1)−N(1)	2.252(2)	Re(1)−N(2)	2.225(2)
Re(1)−P(1)	2.418(1)	Re(1)−P(2)	2.429(1)
O(1)−Re(1)−N(2)	90.3(1)	O(1)−Re(1)−N(1)	87.3(1)
O(2)−Re(1)−N(2)	87.6(1)	O(2)−Re(1)−N(1)	88.7(1)
O(1)−Re(1)−P(1)	91.1(1)	O(1)−Re(1)−P(2)	92.0(1)
O(2)−Re(1)−P(1)	92.6(1)	O(2)−Re(1)−P(2)	89.7(1)
N(1)−Re(1)−P(2)	91.4(1)	N(2)−Re(1)−P(1)	89.8(1)
N(2)−Re(1)−N(1)	83.1(1)	P(1)−Re(1)−P(2)	95.8(1)
O(1)−Re(1)−O(2)	175.7(1)	N(1)−Re(1)−P(1)	172.8(1)
N(2)−Re(1)−P(2)	173.9(1)		

of the complex cation $[ReO_2(P(CH_2OH)_3)_2(C_5H_5N)_2]^+$ and one noncoordinating chloride counterion, respectively.

In complex **3**, the geometry around the rhenium(V) center is octahedral with two oxygens in the axial positions and two tris(hydroxymethyl)phosphines, and two pyridines in the equatorial positions. As revealed by the structure (Figure 1), the two phosphine units are coordinated to the metal center in a trans fashion to each other. The Re−P and Re−N bond lengths are 2.491(1) and 2.161(2) Å, respectively. The Re−O bond distances are 1.768(2) Å.

In complex **4**, the geometry around the rhenium(V) center is octahedral with two oxygens in the axial positions and two tris(hydroxymethyl)phosphines and two pyridines in the equatorial positions. As revealed by the structure (Figure 2), the two phosphine units are coordinated to the metal center in a cis fashion to each other. The Re−P bond distances are 2.418(1) and 2.429(1) Å yielding an average bond distance of 2.424 Å. The Re−N bond lengths are 2.252(2) and 2.225(2) Å with an average length of 2.238 Å. The Re−O bond distances are 1.762(2) and 1.774(2) Å corresponding to an average length of 1.768 Å.

A comparison of the cis and trans isomers reveals that the trans influence of the phosphine ligands is evident. In the trans isomer, the Re−P bonds are on the average 0.067 Å longer as compared to the cis isomer. In contrast, the Re−N bonds in the cis isomer are on the average 0.077 Å longer as compared to the trans isomer.

Synthesis and Characterization of $[Re(O)(\mu\text{-}O)(P\{CH_2OH\}_3)(\mu\text{-}\eta^2\text{-}P\{CH_2OH\}_2CH_2O)]_4$. The interaction of an aqueous solution of tris(hydroxymethyl)phosphine (**1**) with $ReO_2I(PPh_3)_2$, in dichloromethane, produces a dark red reaction mixture (Scheme 2). Examination of the organic and aqueous layers separately using ^{31}P NMR spectroscopy indicates the presence of triphenylphosphine in the dichloromethane layer and a mixture of products in the aqueous phase. Separation of the aqueous layer and elution through a Sep-Pak Vac C18 column using water followed by methanol as eluants gives, essentially, two major chemical species. The ^{31}P NMR spectrum of the fractions eluted in water consists of a singlet at 27 ppm, in addition to other minor products. The singlet at 27 ppm has been identified to be tetrakis(hydroxymethyl)phosphonium iodide by ^{1}H and ^{13}C NMR spectroscopy and high-resolution fast atom bombardment mass spectroscopy. The fractions that were eluted in methanol show a single spot by thin-layer chromatography although its ^{31}P NMR spectrum consists of two singlets. In addition, the high-resolution fast atom bombardment mass spectrum shows a molecular ion peak at $m/z = 1861.9800$. These observations indicate the presence of a single chemical species with multirhenium centers coordinated to phosphines in two chemical environments.

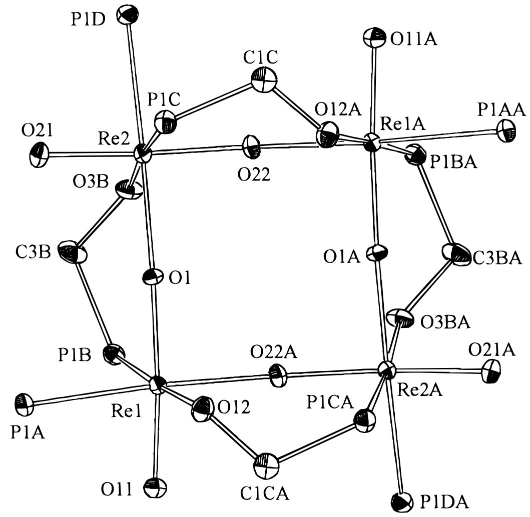
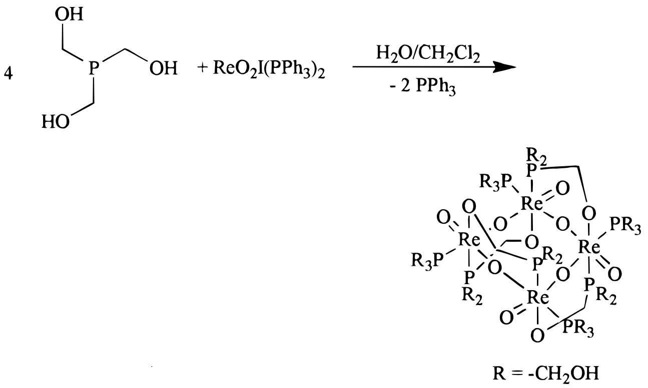


Figure 3. ORTEP diagram of **5**, showing 30% probability ellipsoids. Free $-CH_2OH$ groups have been removed for clarity.

Scheme 2



(**5**)

The two different types of (hydroxymethyl)phosphines (protonated and deprotonated) in **5** account for the two singlets at −19.7 and −4.0 ppm in the ^{31}P NMR spectrum. The ^{1}H NMR spectrum of **5** consists of multiplets from 4.30 to 4.75 ppm. The ^{13}C NMR spectrum of **5** consists of four doublets centered at 57.0 ($^1J_{PC} = 25.3$ Hz), 57.8 ($^1J_{PC} = 32.6$ Hz), 58.4 ($^1J_{PC} = 34.0$ Hz), and 58.7 ($^1J_{PC} = 45.3$ Hz), which is consistent with the proposed structure. The best yields of **5**, so far, are only 10% as may be anticipated because of the complex cyclizations and water-mediated acid−base reactions resulting in considerable amounts of uncharacterized side products.

The molecular constitution of this compound has come from an X-ray crystallographic analysis of a single crystal obtained from methanol at −20 °C. The crystal data and the details of data collection for **5** are listed in Table 1. The ORTEP diagram, as shown in Figure 3, depicts the molecular structure of a novel, neutral, cyclic, tetranuclear, rhenium(V) alkoxide (**5**). The selected bond distances and bond angles are shown in Table 4. Atomic coordinates and their equivalent isotropic displacement

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **5**

Re(1)−O(11)	1.746(6)	Re(2)−O(21)	1.751(6)
Re(1)−O(1)	1.818(5)	Re(2)−O(1)	2.080(5)
Re(1)−O(12)	2.085(6)	Re(2)−O(3B)	2.100(6)
Re(1)−O(22A)	2.090(5)	Re(2)−O(22)	1.813(5)
Re(1)−P(1B)	2.427(2)	Re(2)−P(1C)	2.410(2)
Re(1)−P(1A)	2.427(2)	Re(2)−P(1D)	2.431(3)
O(11)−Re(1)−O(1)	171.8(3)	O(21)−Re(2)−O(22)	173.5(3)
O(11)−Re(1)−O(12)	93.4(3)	O(21)−Re(2)−O(3B)	93.6(3)
O(1)−Re(1)−O(12)	94.6(3)	O(22)−Re(2)−O(3B)	92.8(3)
O(11)−Re(1)−O(22A)	91.3(3)	O(21)−Re(2)−O(1)	91.5(3)
O(1)−Re(1)−O(22A)	90.5(2)	O(22)−Re(2)−O(1)	90.0(2)
O(12)−Re(1)−O(22A)	86.2(2)	O(1)−Re(2)−O(3B)	86.1(2)
O(11)−Re(1)−P(1B)	87.7(2)	O(21)−Re(2)−P(1C)	89.0(2)
O(1)−Re(1)−P(1B)	84.3(2)	O(22)−Re(2)−P(1C)	84.7(2)
O(12)−Re(1)−P(1B)	176.3(2)	O(3B)−Re(2)−P(1C)	175.3(2)
O(22A)−Re(1)−P(1B)	90.2(2)	O(1)−Re(2)−P(1C)	89.8(2)
O(11)−Re(1)−P(1A)	86.9(2)	O(21)−Re(2)−P(1D)	88.0(2)
O(1)−Re(1)−P(1A)	92.3(2)	O(22)−Re(2)−P(1D)	91.1(2)
O(12)−Re(1)−P(1A)	87.1(2)	O(3B)−Re(2)−P(1D)	88.2(2)
(O22A)−Re(1)−P(1A)	173.0(2)	O(1)−Re(2)−P(1D)	174.2(2)
P(1B)−Re(1)−P(1A)	96.5(1)	P(1C)−Re(2)−P(1D)	95.9(1)
Re(1)−O(1)−Re(2)	160.0(3)	Re(2)−O(22)−Re(1A)	158.5(3)

coefficients for complex **5** are included in the Supporting Information. The tetrameric structure **5** contains an eight-membered ring composed of four rhenium(V) centers connected by four bridging oxygens. The octahedral geometry of the rhenium(V) centers is completed with an oxo group, two coordinated phosphines, and an alkoxide oxygen from a deprotonated hydroxymethylphosphine moiety of an adjacent rhenium(V) center. The entire unit is, therefore, composed of four six-membered rings that are each fused to the eight-membered ring through the four Re−O−Re′ bridges. The six-membered rings are completed with an alkoxide unit (Re−O−CH_2−P$(CH_2OH)_2$−Re′). A crystallographic 2-fold axis, perpendicular to the eight-membered ring, passes through the centroid of the four rhenium atoms. The deprotonated hydroxymethylphosphines are trans to alkoxide oxygens (generated from the deprotonation of a hydroxymethylphosphine from an adjacent rhenium center) of the rhenium octahedra. This establishes a unique tetranuclear rhenium(V) connectivity within **5**.

The six-membered rings are unique because this repeating unit possessing double (Re═O), single (Re−O), and bridging (Re−O−Re) rhenium−oxygen bonds allows for the direct comparison of distinctly different transition metal oxygen bonds within the same molecule. The average bond lengths for the rhenium−oxygen bonds in the oxo group and the alkoxides are 1.748 and 2.092 Å, respectively. The bridging oxygens trans to the oxo group have Re−O bond distances of 1.818(5) and 1.813(5) Å, while those trans to the tris(hydroxymethyl)phosphine are 2.090(5) and 2.080(5) Å. Presumably, these longer μ-O bond lengths are due to the repulsion of the filled dπ−pπ orbitals. A similar observation has been made by Shih et al., where $Re_2(\mu\text{-}O)_2(O)_2Cl_4(\mu\text{-dppm})_2$ shows the *trans* μ-oxo bond lengths are much shorter as compared to the *cis* μ-oxo bond lengths.[23] The Re−P bonds range from 2.410(2) to 2.431(3) Å with an average of 2.424 Å.

The remarkable feature of the reaction depicted in Scheme 2 is that the alkoxide is water soluble and kinetically inert (in aqueous media) due, in large measure, to the network of 20 hydroxymethyl functionalities spanning structure **5.** The simplicity of ligand **1** coupled with its potential reactions with other early transition metal precursors may provide new avenues for the development of phosphine-functionalized water-soluble transition metal alkoxides.

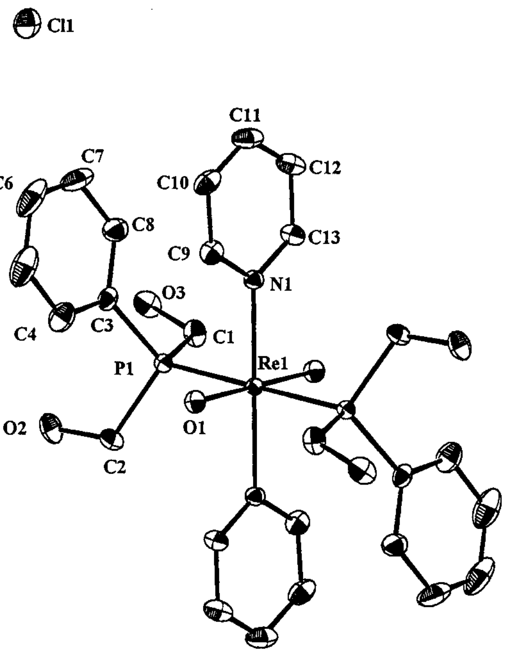
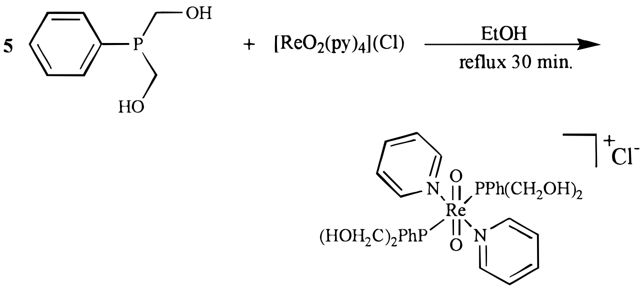


Figure 4. ORTEP diagram of **6**, showing 50% probability ellipsoids.

Scheme 3



(**6**)

Synthesis and Characterization of *trans*-[$ReO_2\{PhP(CH_2OH)_2\}_2(py)_2$](Cl). Refluxing a ethanolic solution of $PhP(CH_2OH)_2$ (**2**) with [$ReO_2(py)_4$]Cl produces the *trans*-[$ReO_2\{PhP(CH_2OH)_2\}_2(py)_2$]Cl (**6**) (Scheme 3). The molecular constitution of **6** has been confirmed by fast atom bombardment mass spectroscopy ($[M]^+$, $m/z = 717.1290$). The ^{31}P NMR spectra shows a singlet at −9.8 ppm corresponding to a downfield shift ($\Delta\delta = 9.8$) relative to the parent ligand (**2**). Both the ^1H and ^{13}C spectra are consistent with the proposed structure.

The molecular structure of **6** has been further confirmed by X-ray diffraction analysis. The crystal data and details of data collection are listed in Table 1. The ORTEP diagram of the cationic molecule is shown in Figure 4. The selected bond distances and bond angles are listed in Table 5. Atomic coordinates and their equivalent isotropic displacement coefficients for the complex are included in the Supporting Information. The asymmetric unit consist of the complex cation [$ReO_2\{PhP(CH_2OH)_2\}_2(py)_2$]Cl and one noncoordinating chloride counterion.

In complex **6**, the geometry around the rhenium(V) center is octahedral with two oxygens in the axial positions and two bis(hydroxymethy)phenylphosphines and two pyridines in the equatorial positions. As revealed by the structure (Figure 4),

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(23) Shih, K.-Y., Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **1993**, *213*, 247.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **6**[a]

Re(1)−O(1)	1.777(2)	Re(1)−P(1)	2.474(1)
Re(1)−N(1)	2.166(2)		
O(1)−Re(1)−N(1)	90.4(1)	O(1a)−Re(1)−N(1)	89.6(1)
O(1)−Re(1)−P(1)	89.6(1)	O(1a)−Re(1)−P(1)	90.4(1)
N(1)−Re(1)−P(1)	87.3(1)	N(1a)−Re(1)−P(1)	92.7(1)
O(1)−Re(1)−O(1a)	180.0	P(1)−Re(1)−P(1a)	180.0
N(1)−Re(1)−N(1a)	180.0		

[a] The “a” atom is at equivalent position $-x$, $-y + 1$, $-z$.

the two phosphine units are coordinated to the metal center in a trans fashion to each other. The Re−P and Re−N bond lengths are 2.474(1) and 2.166(2) Å, respectively. The Re−O bond lengths are 1.777(2) Å.

Refluxing a solution of $PhP(CH_2OH)_2$ with $[ReO_2(py)_4](Cl)$ in methanol for extended periods of time (>5 h) produced a dark red solution containing *trans*-$[ReO_2\{PhP(CH_2OH)_2\}_2(py)_2](Cl)$ and another product with a ^{31}P NMR chemical shift of −3.5 ppm. The yields of the new product (as determined by ^{31}P NMR spectroscopy) were relatively low (20−25%). Furthermore, the complete disappearance of the *trans*-$[ReO_2\{PhP(CH_2OH)_2\}_2(py)_2](Cl)$ product was never observed. Although this other product could not be isolated, we propose the structural identity of this compound to be *cis*-$[ReO_2\{PhP(CH_2OH)_2\}_2(py)_2](Cl)$ on the basis of ^{31}P NMR spectroscopy and the reaction conditions for the formation of *cis*- and *trans*-$[ReO_2(THP)_2(py)_2](Cl)$. Presumably inability to form the cis isomer in high yields is due to steric hindrance caused by the increased cone angle.

Conclusions

The use of $[ReO_2(py)_4](Cl)$ as a starting precursor for rhenium(V) complexes has been established.[10−12] The primary reason for the interest in this starting material is the lability of the pyridyl moieties in regard to substitution by other heteroatoms. To date, the addition of other ligands to $[ReO_2(py)_4](Cl)$ normally has resulted in the complete substitution of the pyridyl moieties.[10−12] Although various groups have been able to systematically vary the pyridyl ligand substitutents on the rhenium(V) complexes by starting with the labile five-coordinate rhenium(V) species $Re(O)(OEt)(py)_2(I)_2$,[19,24] the stepwise addition of phosphine ligands to $[ReO_2(py)_4](Cl)$ has not been reported to our knowledge. To that end, the cis and trans disubstituted THP products have been isolated. Yet, the emergence of mono-, tri-, or tetrasubstituted products has not been isolated or even detected (by ^{31}P NMR spectroscopy). Preliminary results indicate that the trans isomer is kinetically favored and the cis isomer is thermodynamically favored as shown by monitoring the reaction with ^{31}P NMR spectroscopy which is in agreement with the trans effect.

Most of the reactions of THP, to date, have been limited to its use as a phosphine donor to transition metals.[16,17,25−27] However, the presence of three hydroxymethyl groups on the backbone of P^{III} presents the prospect of using this ligand as an oxygen donor in the synthesis of novel transition metal alkoxides. In fact, Hoye and co-workers have proposed a dinuclear, platinum alkoxide intermediate derived from the deprotonation of tris(hydroxymethyl)phosphine.[28] The synthesis and structural characterization of the new rhenium(V) compound **5** represents a new dimension in the dual utility of $P(CH_2OH)_3$ as both a P^{III} donor and an oxygen donor to produce compounds with μ-O σ bonds via the deprotonation of the $-CH_2OH$ groups present in THP.

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Supporting Information Available: Tables giving complete crystallographic experimental details, bond distances and angles, positional parameters for all atoms, anisotropic thermal parameters, and hydrogen atom coordinates for all four complexes and figures showing their thermal ellipsoid plots (27 pages). Ordering information is given on any current masthead page.

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