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Articles

Chemistry in Environmentally Benign Media. 3.[1] Synthesis and Characterization of Rhenium(V) Complexes Derived from Novel Water-Soluble (Hydroxymethyl)phosphines. Crystal Structures of $[Re(O)_2\{(HOH_2C)_2PC_6H_4P(CH_2OH)_2\}_2]I$ and $[Re(O)_2\{(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2\}_2]Cl$

V. Sreenivasa Reddy,[†] Douglas E. Berning,[†] Kattesh V. Katti,[*,†] Charles L. Barnes,[‡]
Wynn A. Volkert,[§] and A. R. Ketring[†]

Center for Radiological Research, Missouri University Research Reactor, and Department of Chemistry,
University of Missouri, Columbia, Missouri 65203, and H. S. Truman Memorial VA Hospital,
Columbia, Missouri 65203

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Water-soluble monophosphine $P(CH_2OH)_3$ (**1**) and bisphosphines $(HOH_2C)_2PC_6H_4P(CH_2OH)_2$ (**2**) and $(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2$ (**3**) were synthesized in near quantitative yields by the catalytic formylation of appropriate P−H bonded compounds in the presence of formaldehyde in aqueous media. The reactions of these mono- and bisphosphines **1**−**3** with $ReO_2I(PPh_3)_2$, in biphasic media (aqueous/organic), or $[ReO_2(NC_6H_5)_4]Cl$, in aqueous media, produced the water-soluble Re(V) complexes $[ReO_2\{P(CH_2OH)_3\}_4]^+$ (**4**), $[ReO_2\{(HOH_2C)_2PC_6H_4P(CH_2OH)_2\}_2]^+$ (**5**), and $[ReO_2\{(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2\}_2]^+$ (**6**) in near quantitative yields. The X-ray structures of **5** and **6**, reported in this paper, confirmed the dioxorhenium(V) structures of these new generation of water-soluble transition metal complexes. All the compounds were characterized by IR, ^1H, and ^{31}P NMR spectroscopy. X-ray data for **5**: monoclinic, $C2/c$, $a = 23.906(5)$ Å, $b = 7.049(1)$ Å, $c = 17.024(4)$ Å, $\beta = 105.93(1)°$, $Z = 4$, $R = 0.019$ ($R_w = 0.027$). For **6**: triclinic, $P\bar{1}$, $a = 6.493(1)$ Å, $b = 9.488(2)$ Å, $c = 10.577(2)$ Å, $\alpha = 104.4(1)°$, $\beta = 96.4(1)°$, $\gamma = 109.5(1)°$, $Z = 1$, $R = 0.045$ ($R_w = 0.060$).

Introduction

For transition metal-catalyzed organic transformations to be cost effective and performance efficient, the metal-based catalyst needs to be readily separated from the resulting products. In fact, recent studies demonstrate that the utility of water-soluble transition metal complexes enable catalytic reactions under biphasic conditions, wherein the organic-soluble products can be readily separated from the aqueous media after catalytic runs.[2−9] Commercial processes by Rhône-Poulenc,[10−12] Montedison,[13] and Kuraray,[14] for the production of olefins, telomers, fine chemicals, and pharmaceutical intermediates, exemplify the rich transition metal chemistry under biphasic conditions directed to specific catalytic transformations. The development of water-soluble transition metal complexes of specific metals and metallic radioisotopes is also important because of their potential utility in pharmaceutical (and radiopharmaceutical) applications. For example, the design and synthesis of ligands that can lead to water-soluble and *in vitro/in vivo* stable rhenium complexes may aid the development of the corresponding complexes of Re-188 at the tracer levels. Rhenium-188 is a β emitter ($\beta = 2.12$ MeV), and the conjugation of its complexes to specific biomolecules has been implicated as an important basis for the development of site-specific radiopharmaceuticals.[15−18] Therefore, the solution chemistry of water-soluble

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[*] Author to whom correspondence should be addressed.

[†] Center for Radiological Research and Missouri University Research Reactor, University of Missouri.

[‡] Department of Chemistry, University of Missouri.

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

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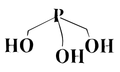
rhenium complexes is expected to function as a model for the subsequent labeling experiments with Re-188.

The utility of mono-, di-, or trisubstituted arylphosphines has become a common modality in the development of water-soluble transition metal complexes and catalysts.[19−21] While the sulfonated phosphines offer convenient access to water-soluble ligands in bulk quantities for the industrial-scale applications, the lack of their purity and, the often encountered, limited oxidative stability in aqueous media have become major barriers in the utility of this class of phosphines in specific catalytic transformations. New developments in the design of water-soluble phosphines will result in greater strides in the production of catalytically useful water-soluble transition metal complexes. In particular, the transition metal chemistry of water-soluble bisphosphines has remained relatively unexplored because of the lack of such functionalized bisphosphines and their precursors. As part of our ongoing research on the transition metal chemistry of functionalized phosphines,[22−29] we report, herein, the synthesis and characterization of water-soluble Re(V) complexes derived from the water-soluble monophosphine $P(CH_2OH)_3$ (**1**) and bisphosphines $(HOH_2C)_2PC_6H_4P(CH_2OH)_2$ (**2**), and $(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2$ (**3**). The X-ray structures of $[Re(O)_2\{(HOH_2C)_2PC_6H_4P(CH_2OH)_2\}_2]^+$ (**5**) and $[Re(O)_2\{(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2\}_2]^+$ (**6**), reported in this paper, confirmed the molecular constitution of this new generation of water-soluble phosphines.



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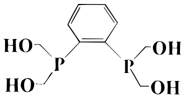

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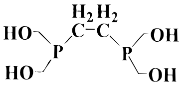

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Results and Discussion

The water-soluble hydroxymethyl bisphosphines **2** and **3** were prepared by the addition of formaldehyde to $H_2PC_6H_4PH_2$ and $H_2PCH_2CH_2PH_2$ in the presence of platinum catalyt, in ∼95% yield in aqueous media.[1,24] Tris(hydroxymethyl)phosphine was synthesized by using the reported procedure.[30] The water-soluble characteristics of these (hydroxymethyl)phosphines presented the prospect of investigating their coordination chemistry in water or under biphasic conditions. Tris(hydroxymethyl)phosphine (THP, **1**) in water upon interaction with $ReO_2I(PPh_3)_2$ in dichloromethane or with $[Re(O)_2(C_5H_6N)_4]Cl$, in water produced the cationic complex $[Re(O)_2(THP)_4]^+(X)^-$ ($X = Cl$ or I; **4**) in ∼80% yield (eq 1). The chemical constitution of **4** was confirmed by elemental analysis and ^1H and ^{31}P NMR spectroscopies. IR spectrum of **4** exhibits a band at 880 cm^{-1} and is assigned to the O=Re=O stretch. The ^{31}P NMR spectrum of **4** consisted of a single resonance at 27.7ppm, indicating significant downfield shift, compared to the free ligand (−24.3 ppm), upon coordination of the phosphine units to the dioxorhenium(V) center. The analytical data of **4** suggest that there are four ligands per metal center. The ^1H NMR spectrum of **4** shows multiplets centered at 4.30 ppm for methylene protons, suggesting that there is a slight downfield shift compared to the chemical shift of the free ligand (4.2 ppm).

$$ReO_2(PPh_3)_2I \text{ or } [ReO_2(NHC_5H_6)_4]Cl + 4P(CH_2OH)_3 \rightarrow [ReO_2\{P(CH_2OH)_3\}_4]^+ \quad (1)$$

1,2-Bis(bis(hydroxymethyl)phosphino)benzene (HMPB, **2**) in water, upon interaction with $ReO_2I(PPh_3)_2$ in dichloromethane, produced the cationic complex $[Re(O)_2(HMPB)_2]I$ (**5**) in 90% yield (Scheme 1). The chemical constitution of **5** was confirmed by elemental analysis and ^1H and ^{31}P NMR spectroscopies. The analytical data sugges that there are two ligands per metal center. The ^{31}P NMR spectrum of **5** consisted of a single resonance at 24.2 ppm, indicating significant downfield shift (∼55 ppm) upon coordination of the phosphine units to the Re(V) center. The ^1H NMR spectrum of **5** shows multiplets centered at 4.20 ppm for methylene protons. This cationic complex **5** can also be synthesized by the reaction of $[Re(O)_2(C_5H_6N)_4]Cl$ and ligand **2** (1:2 mmol) in an aqueous solution by refluxing for 2 h.

The molecular structure of **5** was further confirmed by X-ray crystallography. An ORTEP diagram of the molecule is shown in Figure 1, and the selected bond distances and bond angles are listed in Table 1. The unit cell consists of four molecules with no unusual inter- or intramolecular contracts. The geometry around the rhenium center is octahedral, and the Re lies on a center of symmetry. As revealed by the structure, two diphosphine units are coordinated to the metal center in a chelating fashion trans to each other. Two oxygens are trans to each other. The Re−P1 and Re−P2 distances are 2.461(1) and 2.456(1) Å, respectively. The P1−Re−P1 and P2−Re−P2 angles are 180.0° as required by symmetry. The P1−C5 and P2−C10 distances are 1.819(4) and 1.822(3) Å, respectively. The chelate angle of P1−Re−P2 (80.2(1)°) is less compared to the nonchelate angle of P1−Re−P2 (99.8(1)°).

The interaction of an aqueous solution of 1,2-bis(bis(hydroxymethyl)phosphino)ethane (HMPE) with $[Re(O)_2(C_5H_6N)_4]Cl$ (1:2 mole ratio), in water, produced the cationic complex of $[Re(O)_2(HMPE)_2]Cl$ in 85% yield (Scheme 2). The analytical data of **6** suggest that there are two ligands per metal center. The ^{31}P NMR spectrum of **6** shows a single resonance at 29.8 ppm, suggesting the presence of all the phosphorus nuclei in a similar chemical environment. The ^1H NMR spectrum is consistent with the proposed structure. The presence of a dioxorhenium unit was indicated in its IR spectrum, which shows a strong band at 876 cm^{-1}. The final confirmation of the structure was obtained by determining the X-ray crystal structure of **6**. An ORTEP diagram of the molecule is shown in Figure 2, and the selected bond distances and bond angles are listed in Table 2. The unit cell consists of a single molecule with no unusual inter- or intramolecular contacts. The geometry around the rhenium center is octahedral, and the Re lies on a center of symmetry. As revealed by the structure, two diphosphine units are coordinated to the metal center in a chelating fashion trans to each other. Two oxygens are bound to the rhenium center in a mutually trans fashion. The Re−P1 and Re−P2 distances are 2.480(2) and 2.474(2) Å, respectively, slightly longer compared to the analogous bond distances in **5**. The P1−Re−P1 and P2−Re−P2 angles are 180°, and the P1−

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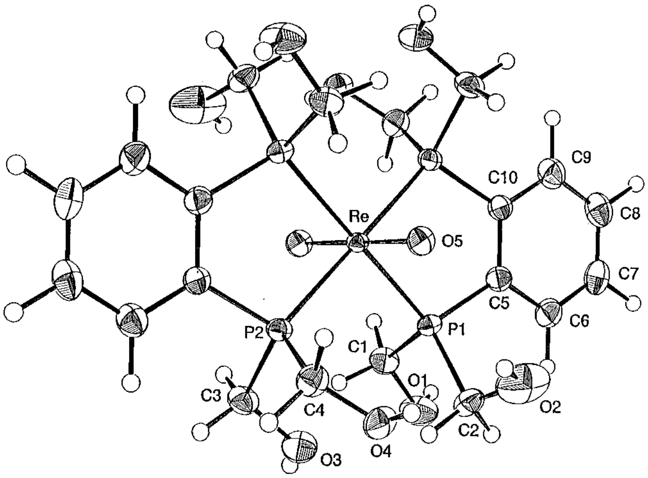
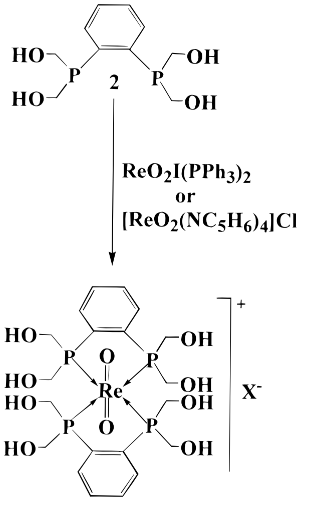


Figure 1. ORTEP drawing of **5** showing 50% probability ellipsoids.

Scheme 1



5 (X = Cl or I)

Table 1. Selected Bond Distances (Å) and Angles (deg) for **5**

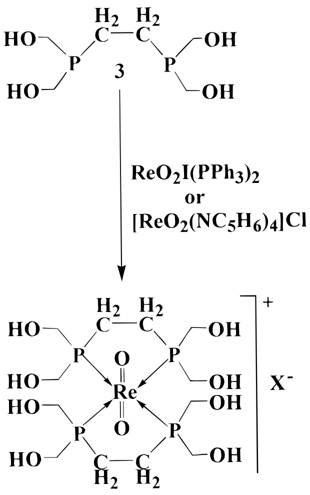
Re−P1	2.461(1)	P2−C4	1.844(3)
Re−P2	2.456(1)	P2−C10[a]	1.822(3)
Re−O5	1.779(2)	O1−C1	1.415(4)
P1−C1	1.844(3)	O2−C2	1.389(5)
P1−C2	1.837(3)	O3−C3	1.408(5)
P1−C5	1.819(4)	O4−C4	1.418(4)
P2−C3	1.834(3)		
P1−Re−P1[a]	180.0	P1−Re−P2[a]	80.2(1)
P1−Re−P2	99.8(1)	P2−Re−P2[a]	180.0
P1−C5−C10	119.0(2)	P2[a]−C10−C5	118.7(3)
P1−Re−O5	90.1(1)	P1−Re−O5[a]	89.9(1)

[a] Atom at 1.5 − *x*, 0.5 − *y*, −*z*.

C1 and P2−C2 distances are 1.832(9) and 1.825(8) Å. The chelate angle of P1−Re−P2 (80.5(1)°) is less compared to the nonchelate angle of P1−Re−P2 (99.5(1)°).

Stability Studies. The oxidative stability of HMPB and the corresponding rhenium complex **5** were analyzed by ^{31}P NMR spectroscopy. A 10 mg/mL solution of HMPB was prepared in non-degassed, distilled water. This solution was stirred in open air, and aliquots were monitored by ^{31}P NMR spectroscopy at various time intervals. The results indicate that even after 96 h only less than 10% of the phosphine was oxidized (Figure 3). A similar study performed on complex **5** showed no change in the spectrum over 96 h, demonstrating the kinetic inertness of this compound in aqueous media.

Scheme 2



6 (X = Cl or I)

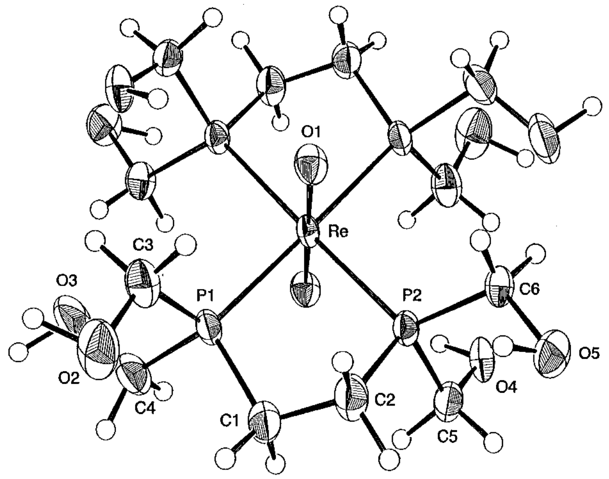


Figure 2. ORTEP drawing of **6** showing 50% probability ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **6**

Re−P1	2.480(2)	P2−C5	1.842(8)
Re−P2	2.474(2)	P2−C6	1.830(8)
Re−O1	1.774(5)	O2−C3	1.396(10)
P1−C1	1.832(9)	O3−C4	1.411(12)
P1−C3	1.860(9)	O4−C5	1.410(10)
P1−C4	1.835(9)	O5−C6	1.420(9)
P2−C2	1.825(8)	C1−C2	1.525(13)
P1−Re−P1[a]	180.0	P1−Re−P2	80.5(1)
P1−Re−P2[a]	99.5(1)	P2−Re−P2[a]	180.0
P2−C2−C1	111.3(6)	P1−C1−C2	111.4(6)
P1−Re−O1	90.7(2)	P1−Re−O1[a]	89.3(2)

[a] Atom at 1 − *x*, 1 − *y*, 1 − *z*.

Conclusions

It is important to recognize that in all of the reactions discussed above (eq 1; Schemes 1 and 2), typically, 95−98% of the metal precursor, $ReO_2I(PPh_3)_2$, from the organic phase was transferred into the phosphine-containing aqueous phase in ~5 min upon simple shaking of the respective solutions. Separation and evaporation of the aqueous phase produced the Re(V) complexes **4**−**6** in analytically pure forms. The preferential solubility of complexes **4**−**6** in aqueous media under biphasic conditions is remarkable in terms of the separation of pure complexes from these, deceptively complex, reactions. Pringle *et al.*[30] have recently demonstrated that the tris(hydroxymethyl)phosphine, $P(CH_2OH)_3$, upon reaction with *cis*-

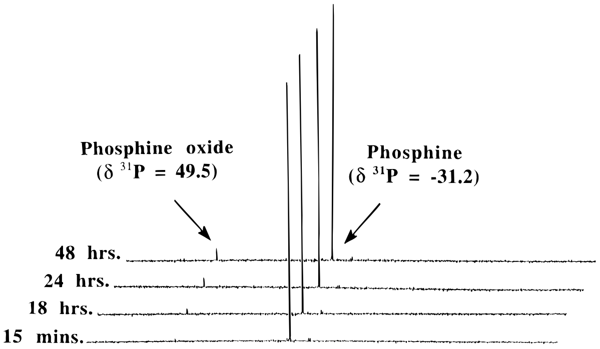


Figure 3. ^{31}P NMR spectra (121.5 MHz) of HMPB (**2**) at various time points.

[Pt(COD)Cl_2] or *cis*-[Pd$(PhCN)_2Cl_2$], produced PtL_2Cl_2 and PdL_2Cl_2 (L = $P(CH_2OH)_3$), respectively, *via* the simple loss of COD or PhCN functionalities. The coordination chemistry of bidentate hydroxymethyl phosphines **2** and **3** will add a new dimension to the chemistry of water-soluble transition metal complexes.

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. Reagents such as $ReO_2I(PPh_3)_2$ and $ReOCl_3(PPh_3)_2$ were purchased from Aldrich Chemical Co. and were used without further purification. The syntheses of (hydroxymethyl)phosphines $P(CH_2OH)_3$ (**1**),[30] $(HOH_2C)_2PC_6H_4P(CH_2OH)_2$ (**2**),[1] and $(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2$ (**3**)[24] are reported in the literature. Nuclear magnetic resonance spectra were recorded on a Bruker ARX-300 spectrometer using D_2O as a solvent. The ^{1}H NMR chemical shifts are reported in parts per million, downfield from external standard $SiMe_4$. The ^{31}P NMR (121.5 MHz) spectra were recorded with 85% H_3PO_4 as an external standard, and positive chemical shifts lie downfield of the standard. Elemental analyses were performed by Onieda Research Services, Inc., New York.

Synthesis of $[Re(O)_2\{P(CH_2OH)_3\}_4]^+$ (4). An aqueous solution (20 mL) of $P(CH_2OH)_3$, (4.0 mmol) was added dropwise to the rhenium precursor $Re(O)_2I(PPh_3)_2$ (1.0 mmol) in dichloromethane (20 mL) at 25 °C with constant stirring. The stirring was continued for 2 h, and the aqueous layer was separated from the organic layer. The aqueous solution was concentrated to ~5 mL *in vacuo* and evaporated slowly at room temperature to afford the yellow colored complex **4** in 90% yield. Anal. Calcd for $C_{12}H_{36}O_{14}P_4ReI$: C, 17.13; H, 4.31. Found: C, 17.43; H, 4.46. IR (Nujol): 880 (ν (O=Re=O)) cm^{-1}. ^{1}H NMR: δ 4.30 (m, P(CH_2OH)). ^{31}P NMR: δ 27.7(s).

Synthesis of $[Re(O)_2\{(HOH_2C)_2PC_6H_4P(CH_2OH)_2\}_2]^+$ (5). An aqueous solution (20 mL) of the ligand HMPB (**2**; 2.0 mmol) was added dropwise to the rhenium precursor $Re(O)_2I(PPh_3)_2$ (1.0 mmol) in dichloromethane (20 mL) at 25 °C with constant stirring. The stirring was continued for 30 min, and the aqueous layer was separated from the organic layer. The aqueous solution was concentrated to ~5 mL *in vacuo* and evaporated slowly at room temperature to give crystalline complex **2** in 85% yield. Anal. Calcd for $C_{29}H_{32}O_{10}P_4ReI$: C, 27.63; H, 3.71. Found: C, 27.73; H, 3.76. IR (Nujol): 878 (ν(O=Re=O)) cm^{-1}. ^{1}H NMR: δ 4.20 (m, 16H, P(CH_2OH)), 7.8 (m, 8H, C_6H_4). ^{31}P NMR: δ 24.2(s).

The above cationic complex can also be synthesized by the reaction of $[Re(O)_2(C_5H_6N)_4]Cl$ and ligand **2** (1:2 mmol) in aqueous solution by refluxing for 2 h.

Synthesis of $[Re(O)_2\{(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2\}_2]^+$ (6). An aqueous solution (20 mL) of the ligand HMPE (**3**; 2.0 mmol) was added dropwise to the rhenium precursor $[Re(O)_2(C_5H_6N)_4]Cl$ (1.0 mmol) also in water (20 mL) at 25 °C with constant stirring. The stirring was continued for 30 min, and the solution was concentrated to ~5 mL *in vacuo* and evaporated slowly at room temperature to give crystalline complex **6** in 85% yield. Anal. Calcd for $C_{12}H_{32}O_{10}P_4ReI$: C, 18.64; H, 4.17. Found: C, 18.68; H, 4.21. IR (Nujol): 876 (ν(O=Re=O)) cm^{-1}. ^{1}H NMR: δ 2.28 (m, 8H, CH_2CH_2), 4.40 (m, 16H, P(CH_2OH)). ^{31}P NMR: δ 29.8(s).

Table 3. Crystal Data for Complexes **5** and **6**

formula	$C_{20}H_{32}O_{10}P_4ReI$	$C_{12}H_{32}O_{10}P_4ReCl$
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
fw	869.47	717.38
a, Å	23.906(5)	6.493(1)
b, Å	7.049(1)	9.488(2)
c, Å	17.024(4)	10.577(2)
α, deg	90.0	104.4(1)
β, deg	105.93(1)	96.4(1)
γ, deg	90.0	109.5(1)
T, K	295(±1)	295(±1)
λ, Å	0.709 30	1.540 56
Z	4	1
F(000)	1680	353
V, Å^3	2758.7(9)	581.0(2)
ρ_{calc}, g/cm^3	2.093	2.050
ρ_{obsd}, g/cm^3	not measured	not measured
μ, mm^{-1}	4.74	13.99
R, R_w [a]	0.019, 0.027	0.045, 0.060

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

Table 4. Atomic Parameters *x*, *y*, *z*, and B_{eq}[a]

	x	*y*	*z*	B_{eq}
Re	$^3/_4$	$^1/_4$	0	1.319(9)
P1	0.841 58(3)	0.295 57(12)	0.107 71(5)	1.68(3)
P2	0.680 57(3)	0.364 59(10)	0.072 13(4)	1.64(3)
O1	0.899 97(11)	0.153 9(4)	0.256 53(14)	3.62(11)
O2	0.861 02(18)	0.670 3(4)	0.112 14(19)	6.28(21)
O3	0.741 16(11)	0.352 3(4)	0.225 77(15)	3.10(11)
O4	0.723 82(12)	0.715 4(4)	0.118 79(16)	2.79(11)
O5	0.742 84(8)	0.018 9(3)	0.038 17(12)	2.10(8)
C1	0.851 74(13)	0.115 1(5)	0.188 87(19)	2.48(13)
C2	0.853 77(13)	0.522 9(5)	0.162 62(20)	2.56(13)
C3	0.690 01(18)	0.270 8(5)	0.175 47(24)	2.48(15)
C4	0.670 86(14)	0.622 8(4)	0.079 53(20)	2.42(13)
C5	0.902 83(15)	0.273 1(4)	0.064 34(22)	2.04(12)
C6	0.959 19(13)	0.319 8(5)	0.109 13(20)	2.57(13)
C7	1.004 81(15)	0.302 8(6)	0.073 6(3)	3.09(15)
C8	0.505 14(20)	0.259 0(5)	0.005 9(3)	3.15(17)
C9	0.560 79(15)	0.308 4(5)	0.050 78(21)	2.63(14)
C10	0.607 22(13)	0.292 1(5)	0.016 61(19)	1.92(12)
1	0	0.802 00(6)	$^1/_4$	3.394(17)

[a] Estimated standard deviations refer to the last digit printed[b] for **5**. [b] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

The above cationic complex can also be synthesized by the reaction of $[Re(O)_2I(PPh_3)_2]$ in dichloromethane and ligand **3** (1:2 mmol) in aqueous media by stirring at room temperature for 30 min.

X-ray Data Collection and Processing. The crystal data and the details of data collection for both **5** and **6** are listed in Table 3. Yellow colored crystals of both **5** and **6** suitable for X-ray diffraction were obtained from slow evaporation of aqueous solution at 25 °C. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (**5**) and Cu Kα radiation (**6**) and a graphite monochromator at 22(1) °C. The cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections with $20 < 2\theta < 30°$ for **5** and $40 < 2\theta < 50°$ for **6**, respectively. The crystals exhibited no significant decay under X-ray irradiation.

The structures were solved by direct methods and were subsequently refined by the full-matrix least-squares method which minimizes $\Sigma w/(|F_o| - |F_c|)^2$, where $w^{-1} = [\sigma^2 F_o + 0.0005(F_o)^2]$. Atomic scattering factors including anomalous scattering contributions were from ref 31. Absorption corrections were made; the minimum and maximum transmission factors for **5** are 0.634 939 and 0.993 871 and for **6** are 0.061 060 and 0.215 886. All hydrogen atoms in both of the structures

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(31) *International Tables For X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.

Table 5. Atomic Parameters x, y, z, and B_{eq}[a]

	x	y	z	B_{eq}
Re	0	0	0	1.77(3)
P1	0.2163(3)	0.253(2)	0.1759(2)	2.33(9)
P2	−0.0885(3)	−0.0782(2)	0.1999(2)	2.17(9)
O1	0.2327(8)	−0.0577(6)	0.0140(5)	2.7(2)
O2	0.6400(12)	0.4249(9)	0.3233(7)	5.1(3)
O3	0.285(2)	0.4920(7)	0.0758(7)	5.7(5)
O4	−0.5360(9)	−0.1962(6)	0.1266(6)	3.1(3)
O5	−0.1000(12)	−0.2818(7)	0.3401(6)	3.9(3)
C1	0.148(4)	0.2374(10)	0.3364(8)	3.5(4)
C2	0.1079(14)	0.0733(10)	0.3470(8)	3.2(4)
C3	0.5247(14)	0.3108(10)	0.2010(9)	3.4(4)
C4	0.173(2)	0.4336(10)	0.1698(9)	3.7(4)
C5	−0.3637(13)	−0.0903(9)	0.2364(8)	2.9(4)
C6	−0.069(2)	−0.2620(9)	0.2139(8)	3.0(4)
Cl	0.3245(6)	−0.2504(5)	0.4893(4)	7.2(3)

[a] Estimated standard deviations refer to the last digit printed[b] for **6**. [b] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

were located in difference Fourier maps and refined with fixed isotropic thermal parameters. The final cycle of the least-squares refinement gave an agreement factor R of 0.019 ($R_w = 0.027$) for **5** and of 0.045 ($R_w = 0.060$) for **6**. Following convergence of the refinement of **6**, a residual peak of 3.47 e/Å^3 remained in the difference Fourier map, adjacent to the Re position, and probably due to absorption effects. The programs used for the crystallographic computations are reported in ref 32. Atomic coordinates and their equivalent isotropic displacement coefficients for both **5** and **6** are listed in Tables 4 and 5, respectively.

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Supporting Information Available: Tables giving complete crystallographic experimental details, distances and angles, positional parameters for all atoms, anisotropic thermal parameters, and hydrogen atom coordinates of **5** and **6** and a figure showing their thermal ellipsoid plot (5 pages). Ordering information is given on any current masthead page.

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(32) The following references are relevant to the NRCVAX system: (a) Gabe, E. J.; Page, Y. L.; Charland, J. L.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr*. **1989**, *22*, 384. (b) Flack, L. *Acta Crystallogr., Sect. A* **1983**, *39*, 876. (c) Johnson, C. K. *ORTEP-A Fortran Thermal Ellipsoid Plot Program*; Technical Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976. (d) Larson, A. C. *Crystallographic Computing*; Munksgaard: Copenhagen, 1970; p 293. (e) Page, Y. L. *J. Appl. Crystallogr*. **1988**, *21*, 983. (f) Page, Y. L.; Gabe, E. J. *J. Appl. Crystallogr*. **1979**, *12*, 464.