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Synthesis and Characterization of Rhenium Phosphinothiolate Complexes. Crystal and Molecular Structures of $[HNEt_3][Re\{P(C_6H_4S)_3\}_2]$, $[ReOCl\{OP(C_6H_5)_2(C_6H_4S)\}\{(P(C_6H_5)_2(C_6H_4S)\}]$, $[Re_2O_5\{P(C_6H_5)_2(C_6H_4S)\}_2]$, and $[ReOCl\{OP(C_6H_5)_2(2\text{-}SC_6H_3\text{-}3\text{-}SiMe_3)\}_2]$

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The reactions of ammonium perrhenate, HCl(aq), and the phosphinothiol ligands $(2\text{-}HSC_6H_4)P(C_6H_4X)_2$, where X = H or SH [abbreviated $P{-}(SH)_x$ ($x = 1, 3$)], in alcohol have led to the isolation of a series of rhenium complexes containing the $\{M(P{-}S_x)_2\}$ core, represented by $[Re\{P(C_6H_4S)_3\}\{P(C_6H_4S)_2(C_6H_4SH)\}]$ (**1**), $[ReOCl\{OP(C_6H_5)_2(C_6H_4S)\}\{P(C_6H_5)_2(C_6H_4S)\}]$ (**3**), and $[ReOCl\{OP(C_6H_5)_2(2\text{-}SC_6H_3\text{-}3\text{-}SiMe_3)\}_2]$ (**5**). The reaction of **1** with NEt_3 results in the formation of $[HNEt_3][Re\{P(C_6H_4S)_3\}_2]$ (**2**) by deprotonation of a thiol ligand. The reaction of ammonium perrhenate with P−(SH) also led to the isolation of the binuclear species $[ReOCl\{OP(C_6H_5)_2(2\text{-}SC_6H_3\text{-}3\text{-}SiMe_3)\}_2]$ (**4**). Crystal data: **2**, $C_{43}H_{42}NP_2S_6Cl_2Re$, monoclinic, $P2_1/c$, $a = 14.2484(2)$ Å, $b = 15.3108(1)$ Å, $c = 19.5121(2)$ Å, $\beta = 90.366(1)°$, $V = 4256.56(8)$ Å^3, $Z = 2$, 26 410 reflections, $R = 0.0605$; **3**, $C_{36}H_{28}O_2P_2S_2ClRe$,triclinic, $P\bar{1}$, $a = 9.3427(1)$ Å, $b = 11.9075(1)$ Å, $c = 16.8504(1)$ Å, $\alpha = 98.177(1)°$, $\beta = 104.132(1)°$, $\gamma = 109.000(1)°$, $V = 1667.79(2)$ Å^3, $Z = 2$, 7567 reflections, $R = 0.0333$; **4**, $C_{36}H_{28}O_5P_2S_2Re_2$, monoclinic, $P2_1/n$, $a = 10.6714(1)$ Å, $b = 24.0076(2)$ Å, $c = 13.3610(1)$ Å, $\beta = 93.65(1)°$, $V = 3416.51(4)$ Å^3, $Z = 4$, 8073 reflections, $R = 0.0469$; **5**, $C_{44}H_{47}NO_3Si_2P_2S_2ClRe$, triclinic, $P\bar{1}$, $a = 10.1616(2)$ Å, $b = 14.7095(3)$ Å, $c = 17.0744(3)$ Å, $\alpha = 89.108(1)°$, $\beta = 83.634(1)°$, $\gamma = 70.901(1)°$, $V = 2396.21(8)$ Å^3, $Z = 2$, 6175 reflections, $R = 0.0837$.

Introduction

The widespread contempory interest in the coordination chemistry of the group VII elements technetium and rhenium reflects the applications of their radionuclides to the development of radiopharmaceuticals.[1−5] The nuclear properties of ^{99m}Tc ($t_{1/2} = 6$ h, $\gamma = 140$ keV) are ideal for diagnostic imaging, while the β-emitting ^{186}Re and ^{188}Re (respectively: $t_{1/2} = 90.64$ h, $E_{max} = 1.1$ MeV; $t_{1/2} = 17$ h, $E_{max} = 2.1$ MeV) are promising candidates for therapeutic applications.[6] Thiolate ligands have been routinely explored in the development of both Tc and Re coordination chemistry with radiopharmaceutical implications.[7−10] In the specific case of Re coordination chemistry,[11−18] the focus has been on polydentate ligands with sulfur and nitrogen donors, often paralleling the chemistry of the molybdenum−thiolate−amine system.[19−24] More recently, this chemistry was expanded to include phosphinothiolate groups as potentially polydentate ligands. While there are examples of complexes containing both thiolate and tertiary phosphine donors, those of Tc and Re have

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not been extensively studied.[25−34] Furthermore, unusual coordination chemistry of rhenium may be accessible by using sterically hindered multidentate phosphinothiolate ligands. Another advantage of using phosphine reagents is their ability to reduce the perrhenate ion and stabilize the lower oxidation states of the metal.

An important property of Re is the accessibility of multiple oxidation states, −3 to +7,[35] which, coupled with the ability to form aggregates, makes it a suitable candidate for accommodating polydentate, multianionic ligands. The high affinity of rhenium for sulfur and phosphorus has been established in numerous studies.[36−39] Moreover, the affinity of both Tc and Re for thiolate ligands[40−43] has allowed the development of reagents for the facile, rapid, and clean complexing of appropriate radionuclides.

In this paper, we continue our explorations of the coordination chemistry of the group VII metal rhenium with aromatic phosphinothiol ligands with the aim of developing a new class of coligands for radiolabeled chemotactic peptides.[44] We report the structures and characterization of a series of rhenium complexes with the tetradentate ligand tris(2-mercaptophenyl)phosphine and the bidentate ligands 2-(diphenylphosphino)benzenethiol and the sterically enhanced 2-(diphenylphosphinyl)-6-(trimethylsilyl)benzenethiol, namely, $[Re\{P(C_6H_4S)_3\}\{P(C_6H_4S)_2(C_6H_4SH)\}]$ (**1**), $[HNEt_3][Re\{P(C_6H_4S)_3\}_2]$ (**2**), $[ReOCl\{OP(C_6H_5)_2(C_6H_4S)\}\{P(C_6H_5)_2(C_6H_4S)\}]$ (**3**), $[Re_2O_5\{P(C_6H_5)_2(C_6H_4S)\}_2]$ (**4**), and $[ReOCl\{OP(C_6H_5)_2(2\text{-}SC_6H_3\text{-}3\text{-}SiMe_3)\}_2]$ (**5**).

Experimental Section

General Considerations. NMR spectra were recorded on a Bruker DPX 300 (^{1}H 300.10 MHz) spectrometer in CD_2Cl_2 (δ 5.32) or $CDCl_3$ (δ 7.34). IR spectra were recorded as KBr pellets with a Perkin-Elmer Series 1600 FTIR. Elemental analyses for carbon, hydrogen, and nitrogen for compound **1** were carried out by Oneida Research Services, Whitesboro, NY, while those for compounds **3**−**5** were carried out on a CHN Carlo Erba 1108 elemental analyzer by the Departmento de Quimica Inorganica, Universidad de Santiago de Compostela. Ammonium perrhenate (Aldrich) and triethylamine (Aldrich) were used as received without further purification. The phosphinothiolate ligands were synthesized by published procedures.[45]

Syntheses. (a) Preparation of $[Re\{P(C_6H_4S)_3\}\{P(C_6H_4S)_2(C_6H_4SH)\}]\cdot CH_3CH_2OH$ (1). To a refluxing solution of $P(C_6H_4SH)_3$ (0.660 g, 1.859 mmol) in 20 mL of ethanol was added a solution of NH_4ReO_4 (0.200 g, 0.746 mmol) in 0.5 mL of 37% HCl. The mixture was allowed to reflux for 0.5 h, after which it was cooled to room temperature and filtered. The resultant blue precipitate was air-dried (0.240 g, 0.268 mmol, 36%). Anal. Calcd for $C_{40}H_{36}OP_2S_6Re$ (mol wt 941.2): C, 48.4; H, 3.19. Found: C, 48.8; H, 3.22. IR (KBr, cm^{-1}): 1566 (m), 1444 (m), 1426 (s), 1254 (m), 1134 (w), 1108 (w), 1044 (m), 743 (s), 526 (m), 477 (m). ^{1}H NMR (CD_2Cl_2, ppm): 4.20 (s), 6.1−8.1 (m).

(b) Preparation of $[HNEt_3][Re\{P(C_6H_4S)_3\}_2]\cdot CH_2Cl_2$ (2). To a refluxing solution of **1** (0.100 g, 0.111 mmol) in 20 mL of ethanol was added a portion of triethlyamine (0.034 g, 0.333 mmol). The reaction mixture was refluxed for 12 h, whereupon the solvent was stripped on a rotoevaporator to give a dark blue residue. Crystals were grown by slow diffusion of pentane into the solution of **2** in CH_2Cl_2 (0.008 g, 0.008 mmol, 7.4%). IR (KBr, cm^{-1}): 3050 (m), 2950 (m), 1569 (m), 1446 (m), 1428 (s), 1252 (m), 1131 (w), 1100 (w), 1049 (m), 736 (s), 530 (m), 489 (m). ^{1}H NMR (CD_2Cl_2, ppm): 1.45 (m), 3.22 (m), 3.65 (s), 6.5−7.9 (m).

(c) Preparation of $[ReOCl\{OP(C_6H_5)_2(C_6H_4S)\}\{P(C_6H_5)_2(C_6H_4S)\}]$ (3). A solution of NH_4ReO_4 (0.046 g, 0.172 mmol), $[P(C_6H_5)_2(2\text{-}C_6H_4\text{-}SH)]$ (0.150 g, 0.510 mmol), and 0.5 mL of 37% HCl in 25 mL of methanol was refluxed for 12 h. The reaction mixture was cooled to room temperature and filtered. The orange-brown precipitate was air-dried (0.061 g, 0.0726 mmol, 67%). X-ray-quality crystals of **3** were grown by slow diffusion of pentane into the solution of **3** in CH_2Cl_2. Anal. Calcd for $C_{36}H_{28}O_2P_2S_2ClRe$ (mol wt 840.3): C, 51.5; H, 3.33. Found: C, 51.1; H, 3.75. IR (KBr, cm^{-1}): 1571 (w), 1437 (m), 1262 (s), 1094 (s), 1024 (s), 958 (m), 800 (s), 743 (m), 692 (m), 538 (m). ^{1}H NMR (CD_2Cl_2, ppm): 7.1−8.1 (m).

(d) Preparation of $[Re_2O_5\{P(C_6H_5)_2(C_6H_4S)\}_2]$ (4). A solution of NH_4ReO_4 (0.046 g, 0.172 mmol), $[P(C_6H_5)_2(2\text{-}C_6H_4SH)]$ (0.150 g, 0.510 mmol), and 0.5 mL of 37% HCl in 25 mL of methanol was refluxed for 12 h. The reaction mixture was cooled to room temperature and filtered, whereupon the dark red filtrate was evaporated to dryness. X-ray-quality red crystals of **4** were grown by slow diffusion of pentane into a solution of the residue of **4** in CH_2Cl_2. Anal. Calcd for $C_{36}H_{28}O_5Si_2P_2S_2Re$ (mol wt 1038.4): C, 41.6; H, 2.69. Found: C, 41.1; H, 2.32. IR (KBr, cm^{-1}): 1637 (m), 1438 (m), 1361 (m), 1262 (s), 1094 (s), 854 (s), 805 (s), 754 (w), 693 (m). ^{1}H NMR (CD_2Cl_2, ppm): 6.7−7.9 (m), 7.95 (d), 8.0 (m), 8.21 (m), 8.32 (m).

(e) Preparation of $[ReOCl\{OP(C_6H_5)_2(2\text{-}SC_6H_3\text{-}3\text{-}SiMe_3)\}_2]\cdot CH_3CN$ (5). A solution of NH_4ReO_4 (0.023 g, 0.086 mmol), $[P(C_6H_5)_2\text{-}(2\text{-}SC_6H_3\text{-}3\text{-}SiMe_3)]$ (0.100 g, 0.262 mmol), 0.5 mL of 37% HCl, and triphenylphospine (0.023 g, 0.086 mmol) in 25 mL of methanol was refluxed for 12 h. The reaction mixture was cooled to room temperature and filtered, and the resultant light green precipitate was air-dried (0.059 g, 0.0568 mmol, 74%). Anal. Calcd for $C_{42}H_{44}O_3Si_2P_2S_2ClRe$ (mol wt 999.7): C, 50.4; H, 4.40. Found: C, 49.9; H, 4.20. IR (KBr, cm^{-1}): 1560 (w), 1438 (m), 1359 (s), 1246 (s), 1120 (s), 1021 (m), 973 (m), 855 (s), 750 (w), 691 (m), 554 (m). ^{1}H NMR (CD_2Cl_2, ppm): 0.4 (s), 7.1−8.1 (m). X-ray-quality crystals of **5** were grown by slow diffusion of diethyl ether into the mixture of $C_{42}H_{44}O_3Si_2P_2S_2ClRe$ in CH_3CN, whereupon a molecule of CH_3CN cocrystallized.

X-ray Crystallography. All compounds were studied on a Siemens SMART system using graphite-monochromated Mo Kα radiation (λ(Mo Kα) = 0.710 73 Å). Data collections for **2**, **3**, and **5** were carried out at low temperature, while that of **4** was carried out under ambient conditions. The crystal parameters and other experimental details of the data collections are summarized in Table 1. A complete description of the details of the crystallographic methods is given in the Supporting Information. The structures were solved by direct methods.[46] Neutral-

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Table 1. Summary of Crystallographic Data for the Compounds $[HNEt_3][Re\{P(C_6H_4S)_3\}_2]\cdot CH_2Cl_2$ (**2**), $[ReOCl\{OP(C_6H_5)_2(C_6H_4S)\}\{P(C_6H_5)_2(C_6H_4S)\}]$ (**3**), $[Re_2O_5\{P(C_6H_5)_2(C_6H_4S)\}_2]$ (**4**), and $[ReOCl\{OP(C_6H_5)_2(C_6H_3SSiMe_3)\}_2]\cdot CH_3CN$ (**5**)

	2	**3**	**4**	**5**
empirical formula	$C_{43}H_{42}NP_2S_6Cl_2Re$	$C_{36}H_{28}O_2P_2S_2ClRe$	$C_{36}H_{28}O_5P_2S_2Re_2$	$C_{44}H_{47}NO_3Si_2P_2S_2ClRe$
a, Å	14.2484(2)	9.3427(1)	10.6714(1)	10.1616(2)
b, Å	15.3108(1)	11.9075(1)	24.0076(2)	14.7095(3)
c, Å	19.5121(2)	16.8504(1)	13.3610(1)	17.0744(3)
α, deg		98.177(1)		89.108(1)
β, deg	90.366(1)	104.132(1)	93.65	83.634(1)
γ, deg		109.000(1)		70.901(1)
V, Å^3	4256.56(8)	1667.79(2)	3416.51(4)	2396.21(8)
Z	4	2	4	2
fw	1084.18	840.29	1039.04	1041.72
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
T, K	150(1)	150(1)	293(2)	150(1)
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
D_{calc}, g cm^{-3}	1.692	1.673	2.020	1.444
μ, mm^{-1}	3.384	3.976	7.338	2.832
R^a	0.0605	0.0333	0.0469	0.0837
wR_2^b	0.1337	0.0711	0.1181	0.2021

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[HNEt_3][Re\{P(C_6H_4S)_3\}_2]$ (**2**)

Re(1)−P(1)	2.404(2)	Re(1)−P(2)	2.411(2)
Re(1)−S(3)	2.459(2)	Re(1)−S(5)	2.468(2)
Re(1)−S(4)	2.518(2)	Re(1)−S(1)	2.529(2)
Re(1)−S(6)	2.535(2)	Re(1)−S(2)	2.549(2)
P(1)−Re(1)−P(2)	123.02(6)	P(1)−Re(1)−S(3)	77.48(6)
P(2)−Re(1)−S(3)	147.89(6)	P(1)−Re(1)−S(5)	148.33(6)
P(2)−Re(1)−S(5)	78.12(6)	S(3)−Re(1)−S(5)	96.08(6)
P(1)−Re(1)−S(4)	76.01(6)	P(2)−Re(1)−S(4)	69.13(6)
S(3)−Re(1)−S(4)	142.98(6)	S(5)−Re(1)−S(4)	93.13(6)
P(1)−Re(1)−S(1)	68.26(6)	P(2)−Re(1)−S(1)	75.39(6)
S(3)−Re(1)−S(1)	93.17(6)	S(5)−Re(1)−S(1)	143.40(6)
S(4)−Re(1)−S(1)	100.44(6)	P(1)−Re(1)−S(6)	124.72(6)
P(2)−Re(1)−S(6)	78.44(6)	S(3)−Re(1)−S(6)	69.45(6)
S(5)−Re(1)−S(6)	79.63(6)	S(4)−Re(1)−S(6)	147.57(6)
S(1)−Re(1)−S(6)	70.71(6)	P(1)−Re(1)−S(2)	78.04(6)
P(2)−Re(1)−S(2)	126.09(6)	S(3)−Re(1)−S(2)	79.36(6)
S(5)−Re(1)−S(2)	70.30(6)	S(4)−Re(1)−S(2)	70.23(6)
S(1)−Re(1)−S(2)	146.30(6)	S(6)−Re(1)−S(2)	133.63(6)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[ReOCl\{OP(C_6H_5)_2(C_6H_4S)\}\{P(C_6H_5)_2(C_6H_4S)\}]$ (**3**)

Re(1)−O(1)	1.683(3)	Re(1)−O(2)	2.184(3)
Re(1)−S(1)	2.3018(12)	Re(1)−S(2)	2.3777(11)
Re(1)−P(1)	2.4388(11)	Re(1)−Cl(1)	2.4642(11)
O(1)−Re(1)−O(2)	163.46(14)	O(1)−Re(1)−S(1)	103.48(13)
O(2)−Re(1)−S(1)	89.12(9)	O(1)−Re(1)−S(2)	106.75(11)
O(2)−Re(1)−S(2)	85.44(8)	S(1)−Re(1)−S(2)	81.61(4)
O(1)−Re(1)−P(1)	93.91(11)	O(2)−Re(1)−P(1)	76.40(8)
S(1)−Re(1)−P(1)	84.58(4)	S(2)−Re(1)−P(1)	157.31(4)
O(1)−Re(1)−Cl(1)	88.80(12)	O(2)−Re(1)−Cl(1)	79.03(8)
S(1)−Re(1)−Cl(1)	167.68(4)	S(2)−Re(1)−Cl(1)	93.98(4)

atom scattering factors were taken from Cromer and Waber,[47] and anomalous dispersion corrections were taken from Creagh and McAuley.[48] All calculation were performed using SHELXTL.[49] Non-hydrogen atoms were refined anisotropically. No anomalies were encountered in the refinements of any of the structures. Atomic positional parameters and isotropic temperature factors for the structures are presented in the Supporting Information. Selected bond lengths and angles are given in Tables 2−5.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Re_2O_5\{P(C_6H_5)_2(C_6H_4S)\}_2]$ (**4**)

Re(1)−O(1)	1.678(5)	Re(1)−O(2)	2.190(5)
Re(1)−S(1)	2.338(2)	Re(1)−S(2)	2.343(2)
Re(1)−P(1)	2.483(2)	Re(1)−P(2)	2.492(2)
Re(2)−O(5)	1.695(9)	Re(2)−O(3)	1.703(9)
Re(2)−O(4)	1.718(6)	Re(2)−O(2)	1.735(5)
O(1)−Re(1)−O(2)	164.1(2)	O(1)−Re(1)−S(1)	104.3(2)
O(2)−Re(1)−S(1)	85.5(2)	O(1)−Re(1)−S(2)	104.2(2)
O(2)−Re(1)−S(2)	89.00(14)	S(1)−Re(1)−S(2)	85.02(7)
O(1)−Re(1)−P(1)	90.5(2)	O(2)−Re(1)−P(1)	77.92(14)
S(1)−Re(1)−P(1)	83.90(6)	S(2)−Re(1)−P(1)	163.45(7)
O(1)−Re(1)−P(2)	89.4(2)	O(2)−Re(1)−P(2)	83.17(14)
S(1)−Re(1)−P(2)	163.82(7)	S(2)−Re(1)−P(2)	83.30(6)
P(1)−Re(1)−P(2)	104.83(6)	O(5)−Re(2)−O(3)	106.8(5)
O(5)−Re(2)−O(4)	110.6(4)	O(3)−Re(2)−O(4)	108.2(4)
O(5)−Re(2)−O(2)	107.7(4)	O(3)−Re(2)−O(2)	110.7(4)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[ReOCl\{OP(C_6H_5)_2(C_6H_3SSiCH_3)\}_2]$ (**5**)

Re(1)−O(1)	1.714(10)	Re(1)−O(2)	2.084(10)
Re(1)−O(3)	2.187(9)	Re(1)−Cl(1)	2.340(4)
Re(1)−S(2)	2.372(4)	Re(1)−S(1)	2.379(4)
O(1)−Re(1)−O(2)	91.0(4)	O(1)−Re(1)−O(3)	170.3(4)
O(2)−Re(1)−O(3)	79.4(3)	O(1)−Re(1)−Cl(1)	98.1(3)
O(2)−Re(1)−Cl(1)	170.6(3)	O(3)−Re(1)−Cl(1)	91.5(3)
O(1)−Re(1)−S(2)	98.8(3)	O(2)−Re(1)−S(2)	91.2(3)
O(3)−Re(1)−S(2)	83.3(3)	Cl(1)−Re(1)−S(2)	85.48(14)
O(1)−Re(1)−S(1)	99.0(3)	O(2)−Re(1)−S(1)	93.6(3)
O(3)−Re(1)−S(1)	80.1(3)	Cl(1)−Re(1)−S(1)	86.96(14)
S(2)−Re(1)−S(1)	161.52(12)		

Results and Discussion

The rhenium−phosphinothiolate complexes **1**, **3**, and **5** were all obtained in reasonable yields by reacting NH_4ReO_4 with HCl(aq) in alcohol, adding the ligand, and allowing the solution to reflux for 12 h. The addition of base to facilitate deprotonation of the thiolates was found unnecessary. Recrystallization was effected by slow diffusion of pentane into a CH_2Cl_2 solution of the precipitated products. In general, the syntheses exploit the properties of the phosphinothiol reagents as effective reducing agents and chelators which stabilize the lower oxidation state of the rhenium site by π-back-bonding.

The reduction of the Re(VII) of the NH_4ReO_4 starting material by excess tris(2-mercaptophenyl)phosphine in ethanol in the presence of excess HCl yields $[Re\{P(C_6H_4S)_3\}\{P(C_6H_4S)_2(C_6H_4SH)\}]$ (**1**), as a blue solid. The infrared spectrum of **1** reveals

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(46) *teXan: Texray Structural Analysis Package*, revised; Molecular Structure Corp.: The Woodlands, TX, 1992.

(47) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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(49) *SHELXTL PC*; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1990.

a feature at 743 cm^{-1} attributed to ν(Re−P) and bands in the aromatic region characteristic of coordinated phosphinothiol ligands. The room-temperature ^{1}H NMR spectrum of **1** exhibits multiple peaks in the aromatic region associated with coordinated ligands, as well as a sharp peak at 4.20 ppm attributed to the S−H proton. This peak position is consistent with observations for other complexes containing pendant S−H groups.[50,51] This assignment is confirmed by the reaction of **1** with base which results in deprotonation of the S−H site and isolation of the eight-coordinate complex $[HNEt_3][Re\{P(C_6H_4S)_3\}_2]$ (**2**), according to eq 1.

$$\underset{\mathbf{1}}{[Re\{P(C_6H_4S)_3\}\{P(C_6H_4S)_2(C_6H_4SH)\}]} + NEt_3 \rightarrow \underset{\mathbf{2}}{[HNEt_3]\,[Re\{P(C_6H_4S)_3\}_2]} \quad (1)$$

The crude product of **2** was recrystallized from CH_2Cl_2/pentane, giving a dark blue crystalline product in moderate yield. The infrared spectrum of **2** is similar to that of **1** with additional peaks appearing at 2950 and 3050 cm^{-1}, attributed to the cation $[HNEt_3]^+$. The room-temperature ^{1}H NMR exhibits peaks in the aromatic region attributed to the protons of the phosphorus ligands. It also displays the peaks associated with the aliphatic protons of the cation, while the singlet in the 4 ppm region is no longer observed.

The chemistry of the related bidentate ligand 2-(diphenylphosphino)benzenethiol was also investigated in order to evaluate the effects of ligand geometry and denticity on reaction chemistry and product identity. Since the $(C_6H_5)_2P(C_6H_4SH)$ ligand may be viewed as a thiol-derivatized analogue of triphenylphosphine, reaction conditions similar to those employed in the synthesis of $[ReOCl_3(PPh_3)_2]$ from NH_4ReO_4 were employed, thus providing a facile route to Re(V)−thiolate complexes.

The reaction of NH_4ReO_4 with 2-(diphenylphosphino)benzenethiol in acidified methanol solution resulted in an orange-brown solid identified as $[ReOCl\{OP(C_6H_5)_2(C_6H_4S)\}\{P(C_6H_5)_2(C_6H_4S)\}]$ (**3**). The crude product was recrystallized by diffusing pentane into a mixture of **3** in CH_2Cl_2. The presence of both the bidentate phosphinothiolate and the bidentate oxophosphinothiolate forms of the ligand was confirmed by X-ray crystallography (vide infra). The oxygen incorporated into the oxophosphinothiolate moiety may originate either from the perrhenate or from adventitious oxygen in the solvent. Such facile oxidations of phosphines to phosphine oxides are not uncommon; for example, the reaction of $MoCl_5$ with $[P(C_6H_5)_2(2\text{-}SC_6H_3\text{-}3\text{-}SiMe_3)]$ yields $[Mo(SC_6H_3\text{-}2\text{-}SiMe_3\text{-}6\text{-}P(O)Ph_2)_2Cl_2]$.[52] The infrared spectrum of **3** exhibits medium-intensity bands at 958 and 800 cm^{-1}, attributed to ν(Re═O) and ν(P═O), respectively. The bands at 1437, 1262, and 743 cm^{-1} are characteristic of the ligand. The ^{1}H NMR spectrum exhibits multiple peaks between 7.1 and 8.1 ppm, attributed to the aromatic protons.

The binuclear rhenium species $[Re_2O_5\{P(C_6H_5)_2(C_6H_4S)\}_2]$ (**4**) was isolated as a minor product in the reaction filtrate from the synthesis of **3**. One rhenium site in **4** is coordinated to two chelating phosphinothiolate ligands, a terminal oxo, and by a bridging oxo group to a $[ReO_4]^-$ group. The $[ReO_4]^-$ unit can act as a weak ligand,[53] and structurally characterized binuclear species are documented.[54−56] The formation of **4** is a consequence of partial reduction of the Re(VII) by addition of the phosphinothiol in stiochiometry sufficient to reduce and ligate only 50% of the rhenium present in the reaction mixture. In the presence of excess phosphinothiol, compound **4** is not formed. The proton NMR exhibits multiple peaks in the 6.7−8.4 ppm region attributed to the ligand. The infrared spectrum displays a strong band at 854 cm^{-1}, assignable to ν(Re═O).

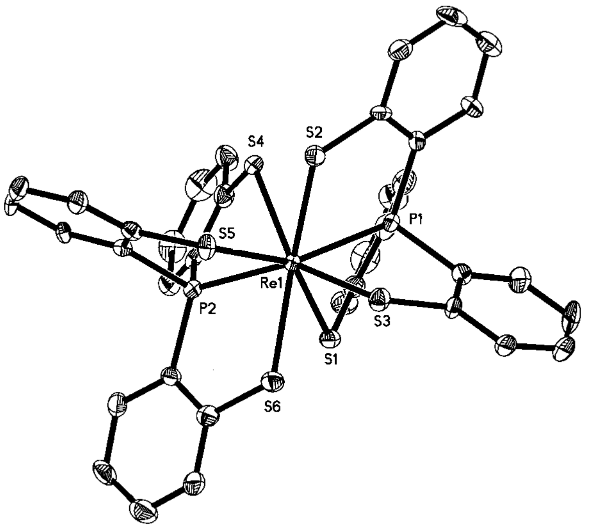

Figure 1. Structure of **2**, showing the atom-labeling scheme and 50% thermal ellipsoids.

To evaluate the results of steric constraints upon the rhenium−phosphinothiolate system, the reaction of NH_4ReO_4, with 2-(diphenylphosphinyl)-6-(trimethlysilyl)benzenethiol in ethanol in the presence of HCl was studied. However, the reaction did not proceed under conditions similar to those previuosly described for **1** and **3**. Thus, the synthesis of $[ReOCl\{OP(C_6H_5)_2(2\text{-}SC_6H_3\text{-}3\text{-}SiMe_3)\}_2]$ (**5**) required the addition of PPh_3 to induce the formation of a light green precipitate; in the absence of the PPh_3, the solution remains clear with a light yellow tint associated with the unreacted starting materials. Presumably, PPh_3 acts as a reducing agent, forming $OPPh_3$ and facilitating the Re(VII) to Re(V) redox process. The infrared spectrum of the light green crystals of **5** exhibits a sharp band at 1120 cm^{-1} attributed to ν(P−O), an intense band at 850 cm^{-1} characteristic of ν(Si−C), and a band at 750 cm^{-1} attributed to ν(Re−P). The ^{1}H NMR spectrum displays multiple peaks in the aromatic region between 7 and 8.1 ppm and a sharp singlet at 0.4 ppm assigned to the methyl protons of the silyl groups.

Description of the Structures. As shown in Figure 1, the anion of compound **2** adopts eight-coordination by bonding to two tetradentate (2-mercaptophenyl)phosphine ligands. The geometry around the metal is intermediate between the idealized square antiprismatic and dodecahedral geometries.[57] Although eight-coordinate molybdenum(IV)−thiolate species are quite common,[58,59] expansion of rhenium coordination above six is

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Table 6. Selected Bond Distances (Å) for Representative M−Phosphinothiolate Complexes[a]

complex	M−P	X[b]	M−S	Y[c]	ref
$[Tc(PS)_3]$	2.477(1)	S	2.489(2)	S	37
	2.406(1)	P	2.258(1)	S	
	2.424(1)	P	2.297(1)	P	
$[Mo_2(SC_6H_4\text{-}o\text{-}PPh_2)_3Cl_3]$	2.578(2)	S	2.469(2)		38
	2.578(2)	S	2.413(2)		
	2.675(2)	S	2.505(2)		
$[Tc(PS_3)(CN\text{-}i\text{-}Pr)_2]$	2.273(2)	C	2.233(2)	S	29
			2.245(3)	C	
			2.231(2)	S	
$[Tc(PS_3)(CN\text{-}i\text{-}Pr)]$	2.290(2)	C	2.390(2)	S	29
			2.310(2)		
			2.328(2)	S	
$[Re(2\text{-}Ph_2PC_6H_4S)_3]$	2.391(5)	P	2.269(5)	S	36
	2.411(5)	P	2.303(5)	P	
	2.473(5)	S	2.477(5)	S	
$[Tc(2\text{-}Ph_2PC_6H_4S)_3]$	2.399(2)	P	2.256(2)	S	36
	2.423(2)	P	2.293(2)	P	
	2.472(2)	S	2.486(3)	S	
$[HNEt_3][Re\{P(C_6H_4S)_3\}_2]$ (**2**)	2.397(6)		2.564(7)		this work
	2.409(6)		2.464(6)		
			2.564(6)		
			2.482(6)		
			2.536(6)		
			2.547(6)		
$[ReOCl\{OP(C_6H_5)_2(C_6H_4S)\}\{P(C_6H_5)_2(C_6H_4S)\}]$ (**3**)	2.439(1)	S	2.302(1)	Cl	this work
			2.378(1)	P	
$[Re_2O_5\{P(C_6H_5)_2(C_6H_4S)\}_2]$ (**4**)	2.482(2)	S	2.338(2)	P	this work
	2.492(2)	S	2.343(2)	P	
$[ReOCl\{OP(C_6H_5)_2(2\text{-}SC_6H_3\text{-}3\text{-}SiMe_3)\}_2]$ (**5**)			2.380(4)	S	this work
			2.373(4)	S	

[a] Esd's in parentheses. [b] X ≡ donor group trans to P. [c] Y ≡ donor group trans to S.

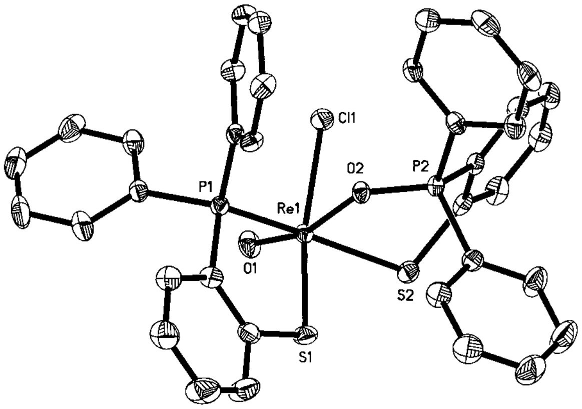

Figure 2. The structure of **3**, showing the atom-labeling scheme and 50% thermal ellipsoids.

relatively unusual.[60] While the average Re−S distance in **2** is 2.51 Å, well within the range of Re−S distances compiled in Table 6, there are in fact two distinct sulfur sites with the average bond lengths of 2.533(1) Å for S1, S2, S4, and S6 and 2.464(1) Å for S3 and S5.

The structure of $[ReOCl\{OP(C_6H_5)_2(C_6H_4S)\}\{P(C_6H_5)_2(C_6H_4S)\}]$ **3**, shown in Figure 2, consists of a rhenium(V) center in a distorted octahedral environment defined by an oxo ligand, a chloride ligand, the phosphorus and sulfur donors of the phosphinothiolate ligand, and the oxygen and sulfur donors of the oxophosphinothiolate ligand. The absence of a third phosphinothiolate ligand may reflect both steric constraints associated with accommodating the additional phenyl substituents and the relative inaccessibility of the Re(III) oxidation state required for the production of the $[Re\{Ph_2P(C_6H_4S)\}_3]$ complex. The stability of the oxorhenium(V) core in rhenium−thiolate chemistry is well documented.[61,62] The oxidation of the phosphine allows for the direct comparison of the Re−O bond with the Re═O bond. The Re═O1(terminal oxo) has a distance of 1.683(3) Å, while the Re−O2 distance of 2.184(3) Å represents a lengthened single-bond distance, demonstrating the trans influence of the terminal oxo ligand. The Re−S bond lengths of 2.301(1) and 2.377(1) Å are within the range observed for Re(V)−sulfur coordinated complexes.[63−65]

The binuclear rhenium species $[Re_2O_5\{P(C_6H_5)_2(C_6H_4S)\}_2]$ (**4**) possesses two unique metal environments, as shown in Figure 3. The structure may be descibed as a mixed-valence species constructed from a distorted octahedral Re(V) site corner-sharing with a tetrahedral Re(VII) site. The $\{ReO_2P_2S_2\}$ coordination geometry about Re1 is defined by a terminal oxo, a bridging oxo, and the phosphorus and sulfur donors of two phosphinothiolate ligands. The Re2 site consists of one bridging and three terminal oxo ligands. Valence sum calculations[66] confirm that Re2 is formally in the +7 oxidation state. The O2 atom adopts an unsymmetrical bridging geometry with Re2−O1 and Re1−O1 distances of 1.736(5) and 2.188(6) Å, respectively. The latter is relatively long for a Re−O single bond,[67−69] while the Re2−O1 bond exhibits significant double-

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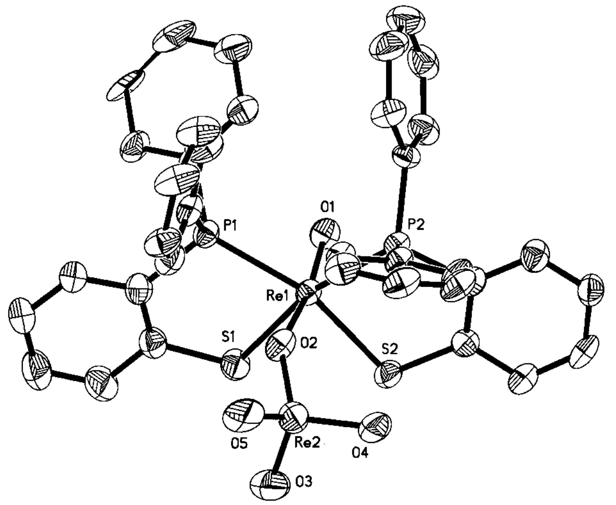

Figure 3. The rhenium dimer **4**, showing the atom-labeling scheme and 50% thermal ellipsoids.

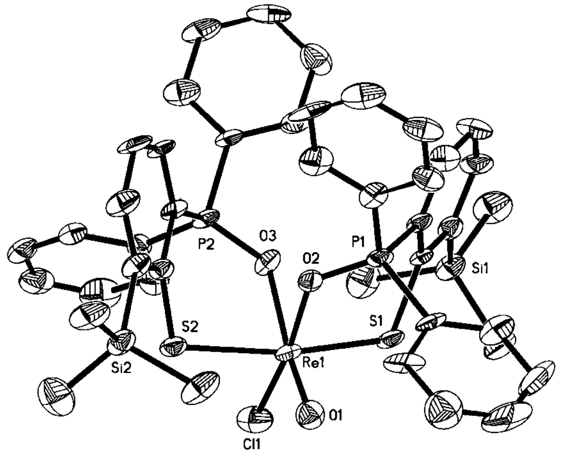

Figure 4. Structure of **5,** showing the atom-labeling scheme and 50% thermal ellipsoids.

bond character. Consequently, the binuclear structure may be described in terms of a contact pair, constructed from a rhenium(V) cation $[ReO\{P(C_6H_5)_2(C_6H_4S)_2\}]^+$ and a rhenium(VII) anion $[ReO_4]^-$.

The lengthening of the Re1−O1 bond may also be attributed to the trans influence of the terminal oxo. The 143.4(3)° valence angle at O1 may arise from the steric constraints of the phosphinothiol ligand and the requirements of the Re(VII) site. The average Re−S and Re−P distances of 2.335 and 2.485 Å, respectively, are similar to those reported previously.

The structure of $[ReOCl\{OP(C_6H_5)_2(2\text{-}SC_6H_3\text{-}3\text{-}SiMe_3)\}_2]$ (**5**), shown in Figure 4, consists of a six-coordinate rhenium(V) center with distorted octahedral geometry. The rhenium geometry is defined by a terminal oxo ligand, one chlorine donor, and the oxygen and sulfur donors of two bidentate 2-(diphenylphosphinyl)-6-(trimethlysilyl)benzenethiol ligands. As for compound **3**, a combination of steric and electronic constraints appears to restrict the coordination to two phosphinothiolate ligands. The Re−oxygen distances to the phosphine oxide units are significantly different, reflecting the trans influence of the terminal oxo ligand; thus, Re−O3 is 2.18(1) Å, while Re−O2 is 2.08(1) Å. As anticipated, the Re−S distances are similar to those of compound **3**, while all other metrical parameters are unexceptional.

Conclusion

Compounds **1**−**5** were readily prepared in good yields directly from NH_4ReO_4 by adopting the synthetic procedures long established for the preparation of $[ReOCl_3(PPh_3)_2]$. The rhenium phosphinothiolate chemistry is characterized by a variety of structural types, reflecting the multiple oxidation states available to rhenium, the denticity of the ligand, and the presence of steric constraints. The versatility of the phosphinothiolate chelates is illustrated by the oxo−chloro species $[ReOCl\{OP(C_6H_5)_2(C_6H_4S)\}\{P(C_6H_5)_2(C_6H_4S)\}]$ (**3**) and the binuclear $[Re_2O_5\{P(C_6H_5)_2(C_6H_4S)\}_2]$ (**4**), which originate from the same reaction mixture.

By employment of the potentially tetradentate ligand $P(C_6H_4SH)_3$, the seven-coordinate $[Re\{P(C_6H_4S)_3\}\{P(C_6H_4S)_2(C_6H_4SH)\}]$ (**1**) and eight-coordinate $[HNEt_3][Re\{P(C_6H_4S)_3\}_2]$ (**2**) were isolated. Compounds **1** and **2** demonstrate the preference for the Re(V) oxidation state and illustrate that the nearly ubiquitous oxo ligand may be displaced when appropriate ligand charge is provided and when steric congestion is minimized. The importance of steric influences is supported by the isolation of a species analogous to **3**, $[ReOCl\{OP(C_6H_5)_2(C_6H_3SSiCH_3)\}_2]$ (**5**), upon introducing the sterically demanding group $-SiMe_3$.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **2**−**5** are available on the Internet only. Access information is given on any current masthead page.

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