Molybdenum, Rhenium, and Tungsten Complexes with Bi- and Tri-dentate Phosphinothiolato-ligands; Structures of $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ and $[Mo(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2]$‡

Philip J. Blower, Jonathan R. Dilworth,*† **G. Jeffery Leigh, Bryan D. Neaves, and Fred B. Normanton**
A.F.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ
John Hutchinson and Jon A. Zubieta
Chemistry Department, State University of New York at Albany, Albany, New York 12222, U.S.A.

$[ReOCl_3(PPh_3)_2]$ reacts with two equivalents of $Ph_2PCH_2CH_2SH$ in tetrahydrofuran to give $[ReOCl(Ph_2PCH_2CH_2S)_2]$. An excess of tridentate $PhP(CH_2CH_2SH)_2$ reacts with $[ReOCl_3(PPh_3)_2]$ to yield $[Re\{PhP(CH_2CH_2S)_2\}\{PhP(CH_2CH_2S)(CH_2CH_2SH)\}]$ containing a pendant unco-ordinated SH group. This complex reacts reversibly with CO to form $[Re\{PhP(CH_2CH_2S)_2\}\{PhP(CH_2CH_2S)(CH_2CH_2SH)\}(CO)]$ [ν(CO) at 1 980 cm^{-1}]. The M^{IV} complexes $[MCl_4L_2]$ [M = Mo or W, L = PPh_3 or MeCN) react with $PhP(CH_2CH_2SH)_2$ in MeOH to give $[M\{PhP(CH_2CH_2S)_2\}_2]$. An *X*-ray crystal-structure determination for the complex with M = Mo showed a distorted octahedral structure with an average Mo–S distance of 2.44 Å. The complex crystallises in the triclinic space group $P\bar{1}$, with $a = 10.601(7)$, $b = 10.867(4)$, $c = 12.347(1)$ Å, $\alpha = 66.98(3)$, $\beta = 85.60(4)$, $\gamma = 63.70(4)°$, and $Z = 2$. 1 337 Unique reflections with $I_o \geqslant 3\sigma(I_o)$ used in the solution converged at $R = 0.0979$. The hydrazido(2−) complexes $[MCl(NNMe_2)_2(PPh_3)_2]Cl$ react with $PhP(CH_2CH_2SH)_2$ in MeOH to give $[M(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2]$ (M = Mo or W). An *X*-ray crystal-structure determination of the complex with M = Mo revealed a distorted pentagonal-bipyramidal structure with a linear apical $NNMe_2$ ligand. The complex crystallises in the monoclinic space group $P2_1/n$, with $a = 11.349(2)$, $b = 12.403(3)$, $c = 19.302(4)$ Å, $\beta = 104.28(2)°$, and $Z = 4$. 2 796 Unique reflections with $I_o > 3\sigma(I_o)$ used in the solution converged at $R = 0.605$.

The co-ordination environment of molybdenum in nitrogenase has been suggested by extended *X*-ray absorption fine structure spectroscopy[1] to be predominantly sulphur and this has stimulated much recent research into molybdenum–sulphur chemistry. However none of these sulphur-ligated species reacts with dinitrogen, whereas there is an extensive reported chemistry of dinitrogen bound to low-valent tertiary phosphine complexes. We have attempted to combine these two facets of model chemistry by studying complexes of phosphinothiolate ligands. We have previously described molybdenum(IV) complexes of the bidentate ligand $Ph_2PCH_2CH_2SH$[2] and we now report the extension of these studies to rhenium and tungsten and the tridentate ligand $PhP(CH_2CH_2SH)_2$.

The chemistry of phosphinothiolate ligands has been comparatively little studied. There was an early report[3] of nickel and platinum complexes of $PhP(CH_2CH_2SH)_2$ and $P(CH_2CH_2SH)_3$ of the type $[M_2L_2]$, with one sulphur bridging, one co-ordinated, and in the case of $P(CH_2CH_2SH)_3$ the third remains unco-ordinated. The structure of $[Ni_2\{P(CH_2CH_2S)_2(CH_2CH_2SH)\}_2]$ was confirmed by an *X*-ray crystal-structure determination.[3] There have also been several papers dealing with polydentate primary phosphinothiol ligands such as $H_2PCH_2CH_2SH$, $HP(CH_2CH_2SH)_2$, and $HSCH_2CH_2PHCH_2CH_2PHCH_2CH_2SH$ and their complexes with cobalt, rhodium, nickel, and platinum.[4–6] However no *X*-ray crystal structures were reported. More recently the preparations of $Ph_2PCH_2CH_2SH$ cyclopentadienyl complexes of iron, manganese, and molybdenum[7] have been published, but again without *X*-ray crystal-structure determinations. There has been a recent report of the *X*-ray structural characterisation of the iridium complex $[IrH(Ph_2PCH_2CH_2S)(Ph_2PCH_2CH_2SH)(CO)]Cl$ containing a co-ordinated SH group.[8]

Results and Discussion

Molybdenum and Tungsten Complexes.—(i) *Preparation and properties.* The tetrachloro-complexes $[MCl_4L_2]$ (M = Mo or W, L = MeCN or PPh_3) react with two equivalents of $PhP(CH_2CH_2SH)_2$ in methanol in the presence of triethylamine to give the complexes $[M\{PhP(CH_2CH_2S)_2\}_2]$ in 70—80% yield. Analogous reaction with $S(CH_2CH_2SH)_2$ gives the related Mo^{IV} complex $[Mo\{S(CH_2CH_2S)_2\}_2]$ in a similar yield. This preparative method is much more convenient and produces higher yields than the previously reported route[9] starting from $MoCl_5$.

The complex $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ is orange-brown and the tungsten derivative greenish yellow in the solid state; both dissolve to give brownish yellow solutions. The ^{31}P n.m.r. spectra in CH_2Cl_2 solutions of $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ and $[W\{PhP(CH_2CH_2S)_2\}_2]$ show singlets at −134.2 and −136.6 p.p.m. respectively, indicating that the phosphorus atoms are equivalent. The ^1H n.m.r. spectra are generally uninformative with broad multiplets for the aryl and methylene protons.

The hydrazido(2−) complexes $[MCl(NNR_2)_2(PPh_3)_2]Cl$ (M = Mo or W, R_2 = Me_2 or MePh) react with two equivalents of $PhP(CH_2CH_2SH)_2$ in methanol in the presence of triethyl-

---

† *Present address:* Department of Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ.

‡ Bis[3-phenyl-3-phosphapentane-1,5-dithiolato(2−)-*S*,*S*′,*P*]molybdenum(IV) and [*N*,*N*-dimethylhydrazido(2−)]bis[3-phenyl-3-phosphapentane-1,5-dithiolato(2−)-*S*,*S*′,*P*]molybdenum(VI) respectively.

Supplementary data available (No. SUP 56332, 10 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Phosphinothiolato-complexes of rhenium, molybdenum, and tungsten

Complex	Colour	Analysis[a] C	H	N	P	$\delta(^1H)$/p.p.m.[b]	$\delta(^{31}P)$/p.p.m.[c]
$[\mathrm{ReOCl(Ph_2PCH_2CH_2S)_2}]$	Orange	45.9 (46.2)	3.8 (3.9)	0.0 (0.0)	— —	2.6—3.7 (m, CH_2) 7.0—7.7 (m, Ph)	−114 (s)
$[\mathrm{Re\{PhP(CH_2CH_2S)_2\}\{PhP(CH_2CH_2S)(CH_2CH_2SH)\}}]$	Brown	37.4 (37.3)	4.1 (4.2)	0.0 (0.0)	9.0 (9.6)	1.62 (s, S–H) 1.8—2.2 (m, CH_2) 2.4—3.1 (m, CH_2) 7.3—7.8 (m, Ph)	−25.3 (d), −83.3 (d) (J|P–P| = 262 Hz)
$[\mathrm{Mo\{PhP(CH_2CH_2S)_2\}_2}]$	Orange-brown	42.7 (43.2)	4.5 (5.4)	0.0 (0.0)	—	2.6—3.7 (m, CH_2) 7.0—7.6 (m, Ph)	−18.3 (s), −134.2 (s)
$[\mathrm{Mo(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2}]\cdot\mathrm{CH_2Cl_2}$	Orange	39.8 (39.7)	5.0 (4.6)	4.4 (4.5)	— —	1.62 (s, $NNMe_2$) 2.51 (s, $NNMe_2$) 2.8—3.2 (m, CH_2) 7.0—7.7 (m, Ph)	−36.9 (d), −52.8 (d) (J|P–P| = 59 Hz)
$[\mathrm{Mo(NNMePh)\{PhP(CH_2CH_2S)_2\}_2}]$	Orange	46.5 (47.9)	5.4 (5.0)	4.3 (4.1)	— —	3.26 (s, NN*Me*Ph) 2.8—3.3 (m, CH_2) 7.0—7.7 (m, Ph)	−33.2 (d), −51.1 (d) (J|P–P| = 63 Hz)
$[\mathrm{W\{PhP(CH_2CH_2S)_2\}_2}]$	Green	37.6 (37.5)	3.9 (4.1)	0.0 (0.0)	— —	2.5—3.2 (m, CH_2) 7.1—7.8 (m, Ph)	−136.6 (s)
$[\mathrm{W(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2}]$	Yellow	38.5 (38.8)	4.4 (5.0)	4.3 (4.5)	— —	1.73 (s, $NNMe_2$) 2.7 (s, $NNMe_2$) 2.8—3.3 (m, CH_2) 7.0—7.7 (m, Ph)	−67.8 (d), −54.7 (d) (J|P–P| = 54 Hz)

[a] Calculated values in parentheses. [b] In $CDCl_3$ solution. [c] In CH_2Cl_2 solution.

Table 2. Electrochemical data[a] for polydentate thiolate complexes

Complex	Redox process	$E_p^{ox.}$/V	$E_p^{red.}$/V	ΔE_p/V
$[\mathrm{Mo\{S(CH_2CH_2S)_2\}}]$	1 e reversible red.	−0.42	−0.56	0.14
	1 e reversible ox.	+0.49	+0.38	0.11
$[\mathrm{W\{PhP(CH_2CH_2S)_2\}_2}]$	1 e reversible red.	−0.51	−0.57	0.06
	1 e reversible ox.	+0.24	+0.50	0.06
$[\mathrm{Mo\{PhP(CH_2CH_2S)_2\}_2}]$	1 e reversible red.	−0.38	−0.50	0.12
	1 e reversible ox.	+0.34	+0.22	0.12

[a] In CH_2Cl_2 solution, 0.2 mol dm^{-3} $[\mathrm{NBu^n_4}][\mathrm{BF_4}]$, Pt electrode, Ag reference electrode, calibrated *vs.* ferrocene–ferrocenium couple at +0.39 V in CH_2Cl_2.

amine to give the orange-yellow crystalline complexes $[\mathrm{M(NNR_2)\{PhP(CH_2CH_2S)_2\}_2}]$. These are air-stable, diamagnetic, crystalline solids which are non-electrolytes in dichloromethane solution. The ^{31}P n.m.r. spectra of $[\mathrm{M(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2}]$ in CH_2Cl_2 solution show a pair of doublets indicating that the phosphorus atoms are now inequivalent. The ^1H n.m.r. spectra in CD_2Cl_2 solution show two singlets for the hydrazido-methyls indicating that they are structurally inequivalent. The complexes prepared are detailed in Table 1 together with analytical and selected spectroscopic data.

The isolation of the seven-co-ordinate hydrazido-complexes suggested that the complexes $[\mathrm{M\{PhP(CH_2CH_2S)_2\}_2}]$ should be capable of adding additional ligands. However there is no evidence of reaction with CO or H_2 or other small molecules at ambient pressures. Attempts to open a co-ordination position by protonation of a thiol group (see Re complexes below), by addition of one equivalent of anhydrous HBF_4, led to extensive decomposition.

The electrochemical behaviour of the complexes $[\mathrm{M\{PhP(CH_2CH_2S)_2\}_2}]$ was studied by cyclic voltammetry and compared with that of the closely related complex $[\mathrm{Mo\{S(CH_2CH_2S)_2\}_2}]$. The relevant data and experimental conditions are summarised in Table 2. The complexes $[\mathrm{Mo\{PhP(CH_2CH_2S)_2\}_2}]$ and $[\mathrm{W\{PhP(CH_2CH_2S)_2\}_2}]$ both undergo reversible diffusion-controlled one-electron oxidation and reduction processes. In accord with previous observations that tungsten complexes are generally more electron-rich than their molybdenum analogues, $[\mathrm{W\{PhP(CH_2CH_2S)_2\}_2}]$ is easier to oxidise and harder to reduce than $[\mathrm{Mo\{PhP(CH_2CH_2S)_2\}_2}]$. The redox potentials of $[\mathrm{Mo\{PhP(CH_2CH_2S)_2\}_2}]$ are surprisingly similar to those of $[\mathrm{Mo\{S(CH_2CH_2S)_2\}_2}]$ in view of the differences in both co-ordination sphere and structure. Further irreversible processes were observed at more negative and more positive potentials and these give rise to redox-active products; these processes were not further studied. The redox chemistry of $[\mathrm{M\{PhP(CH_2CH_2S)_2\}_2}]$ was unchanged under 1 atm of CO indicating that the redox products were as unreactive to this substrate as their precursor. The complexes $[\mathrm{M(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2}]$ showed complex irreversible electrochemical behaviour which was not investigated further.

(ii) *Structures.* (*a*) $[\mathrm{Mo\{PhP(CH_2CH_2S)_2\}_2}]$. Suitable

Table 3. Summary of crystal and experimental data for structure determinations of $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ and $[Mo(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2]$

	$[Mo\{PhP(CH_2CH_2S)_2\}_2]$	$[Mo(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2]$
(*a*) Crystal parameters[a] at 23 °C		
a/Å	10.601(7)	11.349(2)
b/Å	10.867(4)	12.403(3)
c/Å	12.347(1)	19.302(4)
α/°	66.98(3)	104.28
β/°	85.60(4)	
γ/°	63.70(4)	
U/Å^3	1 165.6(9)	2 632.6(10)
Space group	$P\bar{1}$	$P2_1/n$
Z	2	4
D_c/g cm^{-3}	1.574	1.541
(*b*) Measurement of intensity data		
Crystal dimensions/mm	0.17 × 0.20 × 0.25	0.17 × 0.25 × 0.35
No. of independent reflections collected	3 043	4 328
No. of independent reflections used	1 337 with $I_o \geqslant 3\sigma(I_o)$	2 796 with $I_o \geqslant 3\sigma(I_o)$
(*c*) Reduction of intensity data and summary of structure solution and refinement[b]		
Absorption coefficient/cm^{-1}	10.34	9.10
Final discrepancy R	0.0979	0.0605
factors[c] R'	0.0975	0.0581
Goodness of fit[d]	2.056	1.669

Details common to both complexes: diffractometer, Nicolet *R*3*m*; radiation, Mo-K_α ($\bar{\lambda}$ = 0.710 69 Å); scan mode, coupled θ(crystal)—2θ(counter); scan rate, variable 3—30° min^{-1}; scan range, $0 < 2\theta < 45°$; scan length, $[2\theta(K_{\alpha1}) - 1.0]°$ to $[2\theta(K_{\alpha2}) + 1.0]°$; background measurement, stationary crystal, stationary counter at beginning and end of each 2θ scan, each for half the time taken for 2θ scan; standards, 3 collected every 197, no significant deviations; data corrected for background, attenuators, Lorentz and polarisation factors in the usual fashion; absorption correction, not applied; atom scattering factors from D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, 1968, **24**, 321; anomalous dispersion correction applied to all non-hydrogen atoms ('International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3); structure solution: Mo position located by Patterson synthesis; all other non-hydrogen atoms located on successive difference Fourier syntheses followed by least-squares refinement.

[a] From a least-squares fitting of the setting angles of 25 reflections. [b] All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using local versions of the Nicolet SHELXTL interactive crystallographic software package as described by G. M. Sheldrick, 'Nicolet SHELXTL Operations Manual', Nicolet XRD Corp., Cupertino, 1979. [c] The relatively high R values for $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ are a consequence of poor crystal quality; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Delta w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o) + g^*(F_o)^2]$; $g = 0.001$. [d] $\langle\Sigma w(|F_o| - |F_c|)^2/(N_o—N_v)\rangle^{\frac{1}{2}}$, where N_o is the number of observations and N_v the number of variables.

crystals of $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ were grown from dichloromethane–methanol. Details of the crystal structure determination are summarised in Table 3. An ORTEP view of the molecule is presented in Figure 1 which also shows the atom-labelling scheme. Atomic co-ordinates are given in Table 4 and selected bond lengths and angles in Table 5.

The complex displays pseudo-octahedral geometry, the significant distortions arising from the steric requirements of the five-membered P–S chelate rings. The overall geometry makes an interesting contrast to that of $[Mo\{S(CH_2CH_2S)_2\}_2]$ which is essentially trigonal prismatic.[9] The reasons for the difference in geometry are not yet entirely clear, but interligand S ··· S interactions are undoubtedly important in the stabilisation of the trigonal prism. The presence of two P atoms in $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ reduces the number of such S ··· S interactions from 6 to 4, and this may favour the octahedron *versus* the trigonal prism. Trigonal prismatic geometry is also observed for $[Re\{CH_3C(CH_2S)_3\}_2]$ and the influence of S ··· S interactions on geometry will be discussed in detail in the full paper dealing with this complex.[10] It is interesting to note that the overall sulphur geometry of $[Mo\{S(CH_2CH_2S)_2\}_2]$ is extremely similar to that found in MoS_2. This suggests that the sulphur atoms dominate the metal co-ordination and that the hydrocarbon backbone has relatively little effect. The average MoS distance in $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ is unexceptional at 2.348 Å and very close to that found in $[Mo\{S(CH_2CH_2S)_2\}_2]$ (2.361 Å).

(*b*) $[Mo(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2]$. Orange crystals suitable for an *X*-ray structure determination were grown from dichloromethane–methanol. A general ORTEP view of the molecule is shown in Figure 2 together with the atom-labelling scheme. Figure 3 presents an abbreviated view of the molecule showing the orientation of the hydrazido-methyl groups. Details of the *X*-ray crystal-structure determination are summarised in Table 3. Table 6 gives the atomic co-ordinates and selected bond lengths and angles are summarised in Table 7.

The geometry about the molybdenum atom is essentially pentagonal bipyramidal with apical $NNMe_2$ and thiolate groups. The equatorial plane is defined by atoms S(1), S(2), S(4), P(1), and P(2). One phosphinothiolate ligand occupies both equatorial sites exclusively while the other spans both equatorial and axial sites. The average Mo–S distance of 2.513 Å is somewhat longer than for $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ (2.348 Å) reflecting the higher co-ordination number and greater steric crowding in the former. The axial Mo–S(3) distance [2.498(3) Å] shows no sign of lengthening with respect to the average Mo–S equatorial distance due to the *trans* influence of the hydrazido-ligand. The chelate effect may well be responsible for preventing the axial thiolate sulphur moving away from the metal as conventional axial lengthening is not observed.

The Mo–N(1)–N(2) moiety is linear with N–N and Mo–N distances of 1.265(9) and 1.775(6) Å respectively. These parameters are similar to those found in other hydrazido(2 –)

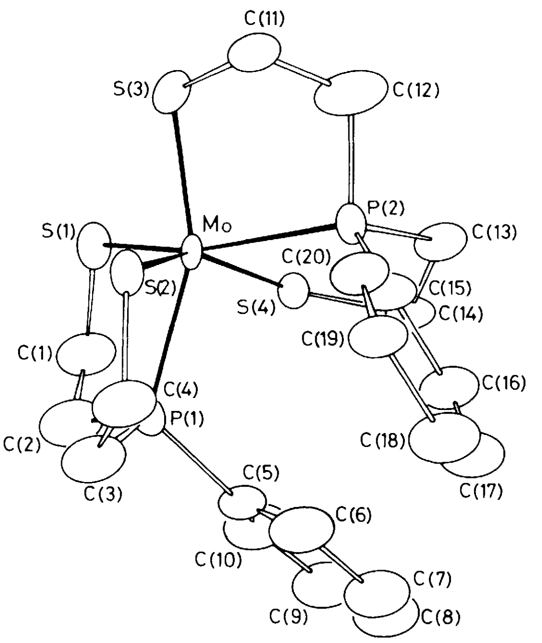

Figure 1. ORTEP view of the structure of $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ showing the atom-labelling scheme

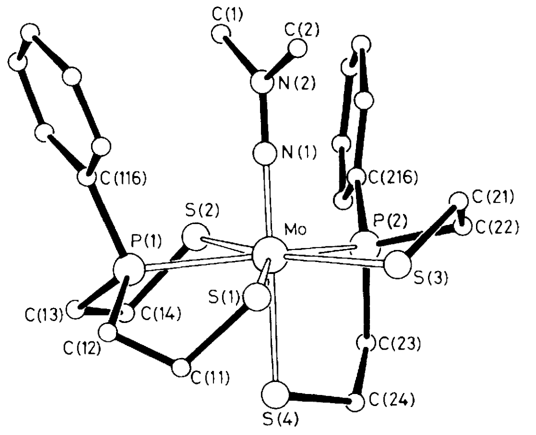

Figure 2. ORTEP view of the structure of $[Mo(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2]$ showing a partial atom-labelling scheme

Table 4. Atom co-ordinates (× 10^4) for $[Mo\{PhP(CH_2CH_2S)_2\}_2]$

Atom	*x*	*y*	*z*
Mo	9 321(3)	−551(3)	7 708(2)
S(1)	10 365(10)	947(10)	7 712(8)
S(2)	9 173(9)	−2 238(9)	9 551(6)
S(3)	11 470(9)	−2 519(10)	7 867(7)
S(4)	8 310(9)	1 310(9)	5 797(6)
P(1)	7 333(10)	1 158(9)	8 389(7)
P(2)	8 560(9)	−1 881(9)	6 870(7)
C(1)	8 875(38)	2 763(36)	7 666(30)
C(2)	7 851(42)	2 489(39)	8 465(31)
C(3)	7 024(38)	108(35)	9 842(27)
C(4)	7 407(34)	−1 432(32)	10 018(27)
C(5)	5 555(31)	2 295(29)	7 487(23)
C(6)	4 799(35)	1 544(34)	7 567(26)
C(7)	3 479(41)	2 383(39)	6 837(30)
C(8)	3 062(42)	3 754(40)	6 087(31)
C(9)	3 789(42)	4 517(42)	6 014(32)
C(10)	5 122(42)	3 731(38)	6 739(30)
C(11)	11 322(39)	−4 156(35)	7 998(29)
C(12)	10 129(36)	−3 521(35)	6 896(28)
C(13)	7 868(33)	−721(28)	5 314(23)
C(14)	7 184(34)	907(30)	5 103(25)
C(15)	7 295(31)	−2 535(29)	7 547(23)
C(16)	5 790(34)	−1 567(33)	7 110(26)
C(17)	4 824(36)	−2 029(33)	7 730(26)
C(18)	5 251(34)	−3 291(31)	8 738(26)
C(19)	7 597(34)	−3 769(31)	8 537(24)

Table 5. Selected bond lengths (Å) and angles (°) for $[Mo\{PhP(CH_2CH_2S)_2\}_2]$

Mo–S(1)	2.340(14)	Mo–S(2)	2.345(8)
Mo–S(3)	2.350(8)	Mo–S(4)	2.355(7)
Mo–P(1)	2.466(8)	Mo–P(2)	2.478(12)
S(1)–C(1)	1.885(34)	S(2)–C(4)	1.839(33)
S(3)–C(11)	1.856(47)	S(4)–C(14)	1.807(43)
P(1)–C(2)	1.794(54)	P12)–C(3)	1.807(43)
P(1)–C(5)	1.871(29)	P(2)–C(12)	1.811(31)
S(1)–Mo–S(2)	117.4(4)	S(1)–Mo–S(3)	90.3(4)
S(2)–Mo–S(3)	84.0(3)	S(1)–Mo–S(4)	83.6(4)
S(2)–Mo–S(4)	151.4(4)	S(3)–Mo–S(4)	117.0(3)
S(1)–Mo–P(1)	83.1(4)	S(2)–Mo–P(1)	79.1(3)
S(3)–Mo–P(1)	156.5(3)	S(4)–Mo–P(1)	84.8(3)
S(1)–Mo–P(2)	155.8(3)	S(2)–Mo–P(2)	85.0(3)
S(3)–Mo–P(2)	82.5(4)	S(4)–Mo–P(2)	79.2(3)
S(1)–Mo–P(2)	111.9(4)		

complexes of Mo^{VI}.[11] The β-nitrogen N(2) is planar, and the C(1),N(1),N(2),C(2) plane eclipses the Mo–S(2) bond vector. This implies that the methyl groups of the hydrazido-ligand should be inequivalent as is observed in the ^1H n.m.r. spectrum.

A feature of the structure is the relatively short S(1) ··· S(4) distance of 2.86 Å. This is accompanied by a slight contraction of the S(1)–Mo–S(4) angle to 69.7(1)° compared to S(1)–Mo–P(1) [72.3(1)°] and S(4)–Mo–P(2) [74.4(1)°]. The S–S interaction is interligand in nature and appears to have little effect on the overall observed geometry.

Rhenium Complexes.—The rhenium(V) oxo-complex $[ReOCl_3(PPh_3)_2]$ reacts with two equivalents of the bidentate ligand $Ph_2PCH_2CH_2SH$ in tetrahydrofuran to give the orange complex $[ReOCl(Ph_2PCH_2CH_2S)_2]$. This complex is moderately air-stable as a solid and its solutions in dichloromethane are non-conducting. A strong i.r. band at 931 cm^{-1} is assigned to ν(Re=O) and lies in the region normally found for Re^V oxo-complexes. The ^{31}P n.m.r. spectrum shows a singlet showing that the phosphorus atoms are equivalent and therefore *trans*. The proposed structure of the complex is shown in Figure 4(*a*), and analytical data are summarised in Table 1.

By contrast reaction of $[ReOCl_3(PPh_3)_2]$ with $PhP(CH_2CH_2SH)_2$ in methanol in the presence of triethylamine gives a brown-yellow product with no i.r. bands assignable to ν(Re=O) or ν(P=O). Microanalysis is consistent with the formulation $[Re\{PhP(CH_2CH_2S)_2\}_2]$. However the ^1H and ^{31}P n.m.r. spectra showed no evidence of the paramagnetism expected for a Re^{IV} complex; and a cryoscopic molecular weight determination in benzene showed that the complex is a monomer. Conductivity measurements showed no appreciable ionisation in acetonitrile and there was no evidence for any counter ions. These data suggest the formulation $[Re\{PhP(CH_2CH_2S)_2\}\{PhP(CH_2CH_2S)(CH_2CH_2SH)\}]$ with an SH group, either free or co-ordinated. Further evidence for the SH group comes from a broad singlet of integrated intensity 1 H at

Table 6. Atom co-ordinates (× 10^4) for [Mo(NNMe$_2$){PhP(CH$_2$CH$_2$S)$_2$}$_2$]

Atom	*x*	*y*	*z*
Mo	206(1)	1 490(1)	2 419(1)
S(1)	1 221(2)	66(2)	3 282(1)
P(1)	−1 167(2)	1 075(2)	3 229(1)
S(2)	−1 793(2)	2 501(2)	1 976(1)
S(3)	−763(2)	−13(2)	1 617(1)
P(2)	246(2)	2 351(2)	1 245(1)
S(4)	2 227(2)	1 051(2)	2 205(1)
N(1)	812(5)	2 631(5)	2 942(3)
N(2)	1 231(7)	3 461(6)	3 300(3)
C(1)	2 474(10)	3 447(9)	3 726(5)
C(2)	480(10)	4 380(7)	3 316(5)
C(11)	23(9)	−839(7)	3 376(5)
C(12)	−896(9)	−252(7)	3 661(5)
C(13)	−2 783(8)	1 088(9)	2 769(5)
C(14)	−2 954(7)	1 540(8)	2 031(4)
C(111)	111(7)	1 920(7)	4 523(4)
C(112)	347(9)	2 644(8)	4 088(4)
C(113)	−412(10)	3 476(8)	5 107(5)
C(114)	−1 417(10)	3 604(8)	4 553(5)
C(115)	−1 684(8)	2 884(7)	3 997(4)
C(116)	−932(7)	2 035(6)	3 965(4)
C(21)	−547(11)	350(10)	762(5)
C(22)	−661(11)	1 455(8)	557(4)
C(23)	1 777(9)	2 415(9)	1 089(5)
C(24)	2 694(8)	2 615(7)	1 777(5)
C(211)	350(8)	4 562(8)	1 386(4)
C(212)	22(8)	5 611(8)	1 219(5)
C(213)	−968(10)	5 822(8)	658(5)
C(214)	−1 624(9)	4 990(10)	284(5)
C(215)	−1 315(8)	3 930(9)	454(4)
C(216)	−294(7)	3 710(7)	1 011(4)

Table 7. Selected bond lengths (Å) and angles (°) for [Mo(NNMe$_2$){PhP(CH$_2$CH$_2$S)$_2$}$_2$]

Mo–S(1)	2.505(3)	Mo–P(1)	2.519(3)
Mo–S(2)	2.548(2)	Mo–S(3)	2.498(3)
Mo–P(2)	2.515(2)	Mo–S(4)	2.499(3)
Mo–N(1)	1.775(6)	S(1)–C(11)	1.806(10)
P(1)–C(12)	1.836(9)	P(1)–C(13)	1.830(8)
P(1)–C(116)	1.821(8)	S(2)–C(14)	1.798(9)
S(3)–C(21)	1.784(11)	P(2)–C(22)	1.840(9)
P(2)–C(23)	1.837(11)	P(2)–C(216)	1.812(9)
S(4)–C(24)	1.793(10)	N(1)–N(2)	1.265(9)
N(2)–C(1)	1.447(12)	N(2)–C(2)	1.428(12)
S(1)–Mo–P(1)	72.3(1)	S(1)–Mo–S(2)	142.6(1)
P(1)–Mo–S(2)	70.9(1)	S(1)–Mo–S(3)	86.9(1)
P(1)–Mo–S(3)	89.2(1)	S(2)–Mo–S(3)	86.5(1)
S(1)–Mo–P(2)	142.3(1)	P(1)–Mo–P(2)	142.9(1)
S(2)–Mo–P(2)	72.6(1)	S(3)–Mo–P(2)	82.0(1)
S(1)–Mo–S(4)	69.7(1)	P(1)–Mo–S(4)	142.0(1)
S(2)–Mo–S(4)	147.0(1)	S(3)–Mo–S(4)	90.2(1)
P(2)–Mo–S(4)	74.4(1)		
P(1)–Mo–N(1)	91.2(2)	S(1)–Mo–N(1)	97.7(2)
S(3)–Mo–N(1)	175.3(2)	S(2)–Mo–N(1)	89.2(2)
S(4)–Mo–N(1)	92.3(2)	P(2)–Mo–N(1)	94.8(2)

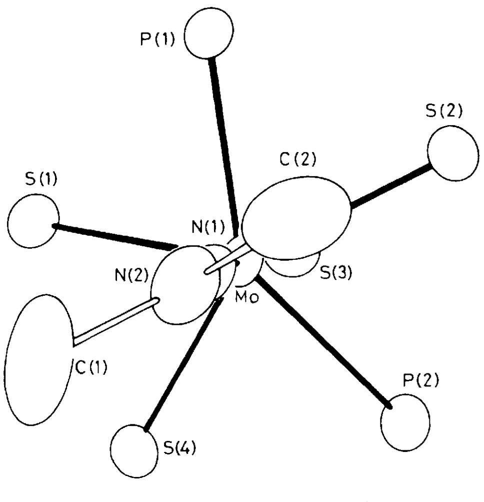

Figure 3. Partial ORTEP view of [Mo(NNMe$_2$){PhP(CH$_2$CH$_2$S)$_2$}$_2$] showing the orientation of the NNMe$_2$ group

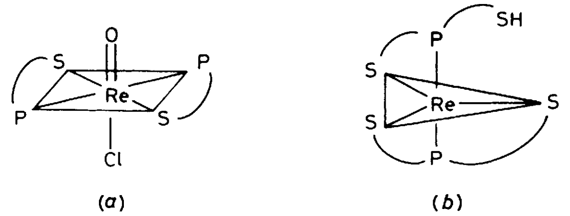

Figure 4. Proposed structures of (*a*) [ReOCl(Ph$_2$PCH$_2$CH$_2$S)$_2$] and (*b*) [Re{PhP(CH$_2$CH$_2$S)$_2$}{PhP(CH$_2$CH$_2$S)(CH$_2$CH$_2$SH)}]

1.62 p.p.m. in the ^{1}H n.m.r. spectrum which disappears after treatment with D$_2$O. The ^{31}P n.m.r. spectrum shows two doublets centred at −25.3 and −83.3 p.p.m. ($|J$P–P$|$ = 262 Hz) suggesting two inequivalent *trans* phosphorus atoms. The difference in shift may be due to one ligand having an unco-ordinated SH group. This shift difference is maintained on reaction with carbon monoxide (see below) suggesting that a co-ordinated SH is not displaced by CO. Two other pieces of evidence are in favour of a five-co-ordinate pseudo-trigonal pyramidal structure with apical phosphorus atoms and a pendant SH group [Figure 4(*b*)]. First, the complexes are very soluble in ether whereas [Mo{PhP(CH$_2$CH$_2$S)$_2$}$_2$] is much less soluble. Secondly, thiolato-complexes of Re^{III} show a preference for 14-electron trigonal-bipyramidal geometry as in [Re(SPh)$_3$(MeCN)(PPh$_3$)].[12]

Reactions of [Re{PhP(CH$_2$CH$_2$S)$_2$}{PhP(CH$_2$CH$_2$S)(CH$_2$CH$_2$SH)}] *with* CO. Treatment of a dichloromethane solution of [Re{PhP(CH$_2$CH$_2$S)$_2$}{PhP(CH$_2$CH$_2$S)(CH$_2$CH$_2$SH)}] with a stream of CO for 30 s causes a darkening of the solution and the appearance of a single strong i.r. band in the solution at 1 980 cm^{-1} assignable to ν(CO). This is accompanied by a shift in $\lambda_{max.}$ in the solution u.v. spectrum from 443 to 456 nm.

Although only one ν(C=O) band appears in the i.r. spectrum, the ^{31}P n.m.r. of the same solutions shows the presence of three species (Figure 5). There are three independent pairs of doublets and two of these, A and B, have a large P–P coupling constant (218 and 221 Hz) characteristic of *trans* phosphorus ligands. The third species, C, has resonances further upfield with $|J$(P–P)$|$ = 18 Hz suggesting *cis* phosphines.

There are five possible isomeric forms (Figure 6), assuming an octahedral geometry and excluding enantiomers. Three have CO *trans* to S [(a), (b), (c)] and two CO *trans* to P [(d), (e)]. Since only one ν(CO) bond is observed it is unlikely that CO is *trans* to both P and S. All the spectroscopic data are therefore consistent with the presence of the isomers (a), (b), and (c).

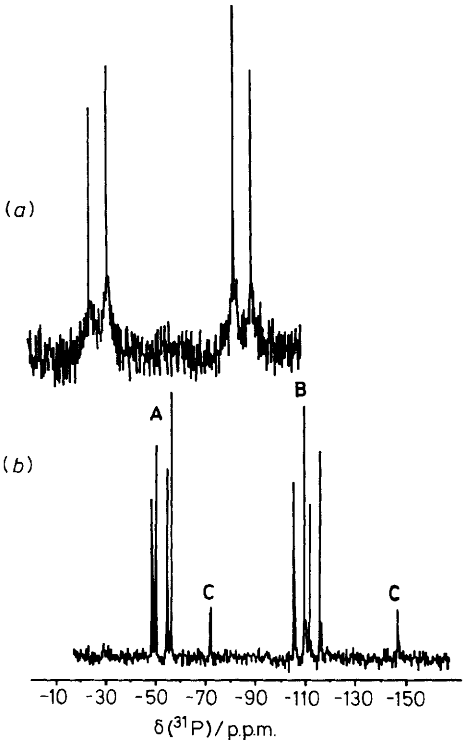

Figure 5. ^{31}P N.m.r. spectra of $[\mathrm{Re}\{\mathrm{PhP(CH_2CH_2S)_2}\}\{\mathrm{PhP(CH_2CH_2S)(CH_2CH_2SH)}\}]$: (*a*) alone, (*b*) after treatment with CO

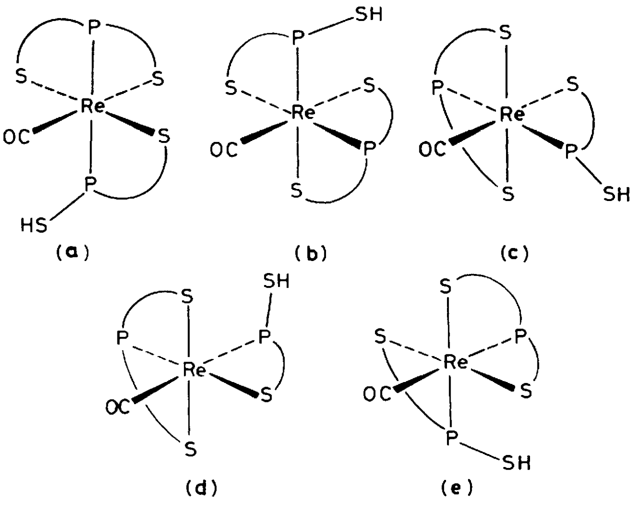

Figure 6. Possible isomers for the product of reaction of $[\mathrm{Re}\{\mathrm{PhP(CH_2CH_2S)_2}\}\{\mathrm{PhP(CH_2CH_2S)(CH_2CH_2SH)}\}]$ with CO

Experimental

All reactions were carried out under dinitrogen using conventional Schlenk techniques with solvents freshly distilled from drying agents under dinitrogen. Spectroscopic measurements and elemental analyses were performed as described previously.

The phosphinothiol $\mathrm{Ph_2PCH_2CH_2SH}$ was prepared as described previously.[2] $\mathrm{PhP(CH_2CH_2SH)_2}$ was prepared by a modification of a patent method[13] as described below. $[\mathrm{ReOCl_3(PPh_3)_2}]$,[14] $[\mathrm{MoCl_4(PPh_3)_2}]$,[15] $[\mathrm{WCl_4(PPh_3)_2}]$,[16] $[\mathrm{MoCl(NNMe_2)_2(PPh_3)_2}]\mathrm{Cl}$,[11] and $[\mathrm{WCl(NNMe_2)_2(PPh_3)_2}]\mathrm{Cl}$[11] were prepared by literature methods.

*3-Phenyl-3-phosphapentane-*1,5*-dithiol*, $\mathrm{PhP(CH_2CH_2SH)_2}$.—Phenylphosphine (30 g, 0.27 mol) was treated with sodium (6.2 g, 0.27 mol) in liquid ammonia (250 cm^3) at −60 °C to give an orange solution. Stirring was maintained for 25 min. A freshly prepared solution of ethylene sulphide (16.5 g, 0.41 mol) in diethyl ether (100 cm^3) was added dropwise with stirring at −60 °C to give a yellow solid. A further 6.2 g (0.27 mol) of sodium were then added as above at −60 °C in small pieces to give a dark brown solution after 30 min. A further 16.5 g of freshly prepared ethylene sulphide in diethyl ether (100 cm^3) were then added dropwise over 30 min. The liquid ammonia was then allowed to evaporate overnight at room temperature under a gentle stream of dinitrogen. The resulting yellow solid was hydrolysed by adding sequentially dropwise methanol (150 cm^3), diethyl ether (100 cm^3), and saturated ammonium chloride solution (150 cm^3). This generated a white solid phase and a colourless ethereal liquid phase. The ethereal layer was siphoned off under dinitrogen and dried over anhydrous sodium sulphate. The diethyl ether was then distilled off at atmospheric pressure and the residue fractionally distilled at 10^{-2} mmHg. The fraction boiling at *ca.* 60 °C was discarded and the fraction boiling at 144—149 °C collected. Yield 33 g, 53%. A product of sufficient purity for the preparation of the complexes described was obtained by pumping the residue at 10^{-2} mmHg for 2 h, after removal of the diethyl ether.

Chlorobis[2-(*diphenylphosphino*)*ethane-*1*-thiolato-*S,P]*oxorhenium*(V), $[\mathrm{ReOCl(Ph_2PCH_2CH_2S)_2}]$.—$[\mathrm{ReOCl_3(PPh_3)_2}]$ (0.5 g, 0.6 mmol) and $\mathrm{Ph_2PCH_2CH_2SH}$ (0.29 g, 1.2 mmol) were stirred in tetrahydrofuran (25 cm^3) for 1 h at room temperature. The resulting orange solution was evaporated to low volume under reduced pressure and the *complex* precipitated as an orange solid by the addition of methanol (30 cm^3). It was recrystallised as orange prisms from dichloromethane–methanol. Yield 0.4 g, 93%.

[3-*Phenyl-*3*-phosphapentane-*1,5*-dithiolato*(2−)-S,S′,P]-[3*-phenyl-*3*-phosphapentane-*1,5*-dithiolato*(1−)-S,P]*rhenium*(III), $[\mathrm{Re}\{\mathrm{PhP(CH_2CH_2S)_2}\}\{\mathrm{PhP(CH_2CH_2S)(CH_2CH_2SH)}\}]$.—$\mathrm{PhP(CH_2CH_2SH)_2}$ (0.5 cm^3, 2.4 mmol) was added dropwise to a stirred suspension of $[\mathrm{ReOCl_3(PPh_3)_2}]$ (0.84 g, 1.0 mmol) in methanol (40 cm^3) in the presence of triethylamine (0.7 cm^3, 5 mmol). After 3 h at room temperature the *complex* precipitated as a pale brown solid.

Bis[3*-phenyl-*3*-phosphapentane-*1,5*-dithiolato*(2−)-S,S′,P]*molybdenum*(IV), $[\mathrm{Mo}\{\mathrm{PhP(CH_2CH_2S)_2}\}_2]$.—$[\mathrm{MoCl_4(PPh_3)_2}]$ (2.0 g, 2.6 mmol) suspended in methanol (40 cm^3) was treated with $\mathrm{PhP(CH_2CH_2SH)_2}$ (1.2 cm^3, 5.3 mmol) and triethylamine (0.54 g, 5.3 mmol) and stirred at room temperature for 3 h. The *complex* precipitated from the solution as an orange solid which was recrystallised from dichloromethane–methanol as yellow-brown prisms.

The tungsten analogue, $[\mathrm{W}\{\mathrm{PhP(CH_2CH_2S)_2}\}_2]$, was prepared similarly from $[\mathrm{WCl_4(PPh_3)_2}]$.

[N,N-*Dimethylhydrazido*(2−)]*bis*[3*-phenyl-*3*-phosphapentane-*1,5*-dithiolato*(2−)-S,S′,P]*molybdenum*(VI), $[\mathrm{Mo(NNMe_2)}\{\mathrm{PhP(CH_2CH_2S)_2}\}_2]$.—$[\mathrm{MoCl(NNMe_2)_2(PPh_3)_2}]\mathrm{Cl}$ (0.5 g) was dissolved in methanol (40 cm^3) and $\mathrm{PhP(CH_2CH_2SH)_2}$ (0.5 cm^3) and triethylamine (0.5 cm^3) added. The solution was stirred at room temperature for 3 h, depositing the *complex* as an orange solid, which was recrystallised from dichloromethane–methanol. Yield 45—60%.

The tungsten analogue, $[\mathrm{W(NNMe_2)}\{\mathrm{PhP(CH_2CH_2S)_2}\}_2]$, was prepared similarly from $[\mathrm{WCl(NNMe_2)_2(PPh_3)_2}]\mathrm{Cl}$.

Chlorobis[N-*methyl*-N-*phenylhydrazido*(2 –)]*bis*(*triphenylphosphine*)*molybdenum*(VI) *Chloride*, [$MoCl(NNMePh)_2(PPh_3)_2$]Cl.—[$MoCl_4(PPh_3)_2$] (2.0 g, 2.6 mmol) was suspended in dry acetonitrile (40 cm^3) and *N*-methyl-*N*-phenylhydrazine (0.63 cm^3, 5.2 mmol) added dropwise. The solution was stirred at room temperature for 2 h and the solvent volume reduced to 10 cm^3 under reduced pressure causing the *complex* to precipitate as a bright yellow microcrystalline powder. Yield 55%.

[N-*Methyl*-N-*phenylhydrazido*(2 –)]*bis*[3-*phenyl*-3-*phospha pentane*-1,5-*dithiolato*(2 –)-S,S′,P]*molybdenum*(VI), [$Mo(NNMePh)\{PhP(CH_2CH_2S)_2\}_2$].—This complex was prepared analogously to [$Mo(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2$] above using [$MoCl(NNMePh)_2(PPh_3)_2$]Cl.

Acknowledgements

One of us (J. Z) thanks the National Institute of Health for financial support and J. R. D. and J. Z. thank N.A.T.O. for the award of a travel grant.

References

1 S. P. Kramer, H. O. Hodgson, W. O. Gillum, and L. E. Mortenson, *J. Am. Chem. Soc.*, 1978, **100**, 3398.
2 J. Chatt, J. R. Dilworth, J. A. Schmutz, and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1979, 1595.
3 G. Schwarzenbach, *Chem. Zvesti*, 1965, **19**, 200.
4 K. Issleib and W. Gans, *Z. Anorg. Chem.*, 1981, **475**, 116.
5 K. Issleib and D. Wienbeck, *Z. Anorg. Chem.*, 1978, **440**, 5.
6 K. Issleib and W. Gans, *Z. Anorg. Chem.*, 1982, **491**, 163.
7 M. Savignac, P. Cadiot, and E. Mathey, *Inorg. Chim. Acta*, 1980, **45**, L43.
8 D. W. Stephen, *Inorg. Chem.*, 1984, **23**, 2207.
9 J. Hyde, L. Magin, and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1980, 204.
10 P. J. Blower, J. R. Dilworth, J. P. Hutchinson, T. Nicholson, and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.*, in the press.
11 J. Chatt, B. A. L. Crichton, J. R. Dilworth, P. Dahlstrom, R. Gutkoska, and J. Zubieta, *Inorg. Chem.*, 1982, **21**, 2383.
12 J. R. Dilworth, B. D. Neaves, J. P. Hutchinson, and J. Zubieta, *Inorg. Chim. Acta*, 1982, **65**, L223.
13 J. R. Geigy, F.P. 1,401,930/1965.
14 N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1964, 1054.
15 A. V. Butcher and J. Chatt, *J. Chem. Soc. A*, 1970, 2652.
16 A. V. Butcher, J. Chatt, G. J. Leigh, and P. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1972, 1064.

Received 31*st January* 1985; *Paper* 5/172