Coordination Chemistry of Molybdenum with Novel Thiolate Ligands. The Crystal and Molecular Structures of a Binuclear Complex with a Mo–Mo Triple Bond $[Mo_2(SC_6H_4\text{-}o\text{-}PPh_2)_3Cl_3]$ and of $[Mo(SC_6H_3\text{-}2\text{-}SiMe_3\text{-}6\text{-}P(O)Ph_2)_2Cl_2]$, a Species Exhibiting $[MoO_2S_2Cl_2]$ Coordination

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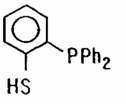
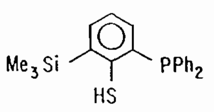
The demonstration by extended X-ray absorption fine structure spectroscopy [1, 2] of a predominantly sulfur coordination environment for molybdenum in nitrogenase has stimulated extensive studies of molybdenum–sulfur chemistry [3–6]. However, sulfur-ligated molybdenum complexes do not react with dinitrogen or, in general, with other nitrogenase substrates or inhibitors such as CO, hydrazine and isonitriles; on the other hand, low-valent tertiary phosphine complexes of molybdenum exhibit an extensive dinitrogen chemistry [7]. In an attempt to combine the synthetic advantages of phosphine ligands with the biological and structural relevance of thiolate donors, we have developed a novel class of phosphinothiolate ligands [8] of which $HSC_6H_4\text{-}o\text{-}PPh_2$ (**I**) is the prototype and compounds **II**–**IV** represent readily prepared analogues.



I



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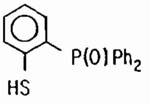

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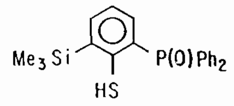

IV

Although there have been several investigations of the coordination chemistry of phosphinothiolate ligands [9–12], the chemistry remains comparatively undeveloped, particularly with respect to molybdenum. One of us has previously described the Mo(IV) complexes $[MoO(SCH_2CH_2PPh_2)_2]$ [13], $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ [14] and $[Mo(NNMe_2)\{PhP(CH_2CH_2S)_2\}_2]$ [14], which proved generally difficult to prepare as pure crystalline materials and unsuitable as precursors for reactions with small substrate molecules. In contrast, Mo(IV) and Mo(V) precursors react readily with **I** to give in good yield $[Mo_2(SC_6H_4\text{-}o\text{-}PPh_2)_3Cl_3]$ (**V**) and $[Mo(SC_6H_4\text{-}o\text{-}PPh_2)_2Cl_2]$ (**VI**), complexes which in turn serve as precursors for ligand substitution.

Reaction of $MoCl_5$ with **I** gives a mixture of $[Mo_2(SC_6H_4\text{-}o\text{-}PPh_2)_3Cl_3]$ (**V**) and $[Mo(SC_6H_4\text{-}o\text{-}PPh_2)_2Cl_2]$ (**VI**) in yields of 25–35% and 50%, respectively. Under argon atmosphere, $MoCl_5$ (0.35 g, 1.28 mmol) dissolved in CH_2Cl_2 (5 ml) was added to 2-(diphenylphosphino)benzenethiol (1.13 g, 3.84 mmol) in CH_2Cl_2 (20 ml). After 6 h of stirring at room temperature, the dark purple solution was evaporated to dryness, and the resultant dark powder was dissolved in CH_2Cl_2 (15 ml) and diluted with CH_3OH/CH_3CH_2OH (1:1, 10 ml). After 3 days at 0 °C, extremely air- and moisture-sensitive diamagnetic crystals of $[Mo_2(SC_6H_4\text{-}o\text{-}PPh_2)_3Cl_3]\cdot CH_2Cl_2\cdot EtOH$ (**V**) formed as a purple deposit. After an additional week at 0 °C, dark green crystals of (**VI**) were isolated in 50% yield. *Anal.* Calc. for $C_{57}H_{49}Cl_5Mo_2OP_3S_3$ (**V**): C, 52.3; H, 3.75. Found: C, 52.0; H, 3.86%. *Anal.* Calc. for $C_{36}H_{28}Cl_2MoP_2S_2$ (**VI**): C, 57.4; H, 3.72. Found: C, 57.1; H, 3.51%. **V** is electrochemically active and exhibits a reversible one-electron reduction at −1.54 V in CH_2Cl_2, relative to the ferrocene/ferrocenium couple. The thiolate acts both as ligand and reducing agent, as evidenced by the reduction of Mo from the 5+ state in $MoCl_5$ to 3+ in **V** and 4+ in **VI**. We were unable to isolate the ligand disulfide presumably formed as the by-product of this reaction. Complex **V** was isolated as dark purple crystals which are extremely air and moisture sensitive, while the bright green crystals of **VI** are indefinitely stable in air as solids. The infrared spectra of **V** and **VI** show only bands assignable to the coordinated ligand at 685–742 cm^{-1} and 525–545 cm^{-1} and to ν(Mo–Cl) at 300 cm^{-1}.

Crystal data for $C_{57}H_{49}Cl_5Mo_2OP_3S_3$ (**V**) are: monoclinic space group $C2/c$ with $a = 24.356(4)$, $b = 15.108(2)$, $c = 33.290(5)$ Å; $\beta = 109.83(2)°$, $V = 11523.6(11)$ Å^3, $Z = 8$, $D_{calc} = 1.51$ g cm^{-3}. Structure solution and refinement were based on 5805 reflections with $F_o \geqslant 4\sigma(F_o)$ (7556 collected; Mo Kα, $\lambda = 0.71073$ Å) and converged at a conventional discrepancy factor of 0.0454.

The structure of (**V**), illustrated in Fig. 1, consists of discrete binuclear units presenting the confacial bioctahedral geometry common to the $[Mo_2Cl_9]^{3-}$ class of complexes [15]. However, in contrast to the fundamental $[M_2X_9]^{n-}$ structural type, **V** exhibits three bidentate phosphinothiolate ligands bridging through the thiolate donor groups and consequently producing non-equivalent metal coordination geometries, $[MoS_3P_2Cl]$ and $[MoS_3PCl_2]$.

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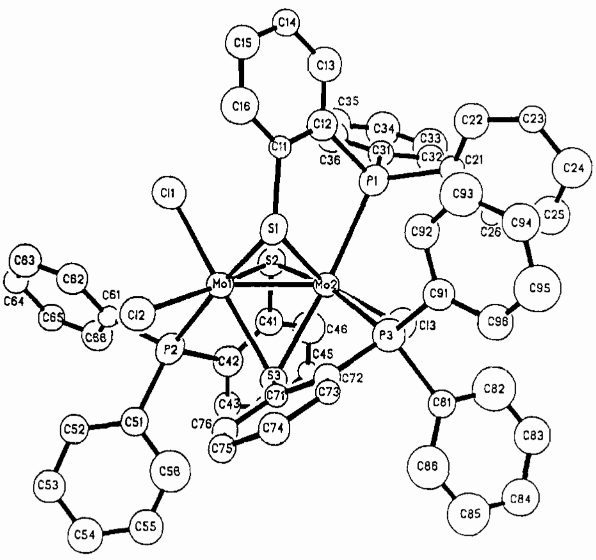

Fig. 1. ORTEP view of the structure of [Mo$_2$(SC$_6$H$_4$-*o*-PPh$_2$)$_3$Cl$_3$] (V), showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2), 2.404(1); Mo(1)–Cl(1), 2.437(2); Mo(1)–Cl(2), 2.460(2); Mo(1)–S(1), 2.469(2); Mo(1)–S(2), 2.413(2); Mo(1)–S(3), 2.505(2); Mo(1)–P(2), 2.578(2); Mo(2)–Cl(3), 2.428(2); Mo(2)–S(1), 2.450(2); Mo(2)–S(2), 2.470(2); Mo(2)–S(3), 2.473(2); Mo(2)–P(1), 2.578(2); Mo(2)–P(3), 2.675(2); Cl(1)–Mo(1)–S(3), 179.3(1); Cl(2)–Mo(1)–S(2), 163.6(1); P(2)–Mo(1)–S(1), 172.6(11); Cl(3)–Mo(2)–S(1), 162.6(1); P(3)–Mo(2)–S(2), 168.4(1); P(1)–Mo(2)–S(3), 173.5(1).

Although non-equivalent metal sites are not uncommon in triply metal–metal bonded binuclear systems [16, 17], the involvement of thiolate donors is unusual and limited to the ‘ethane’-type structures of (RS)$_3$MoMo(SR)$_3$ species [18, 19]. Although triple thiolate bridges are common in the chemistry of Mo(V) and have been reported for W(III)/W(IV) dimers [20], V represents the first structurally confirmed example of a binuclear Mo(III) species.

The isolation of V represents a convenient one-step synthesis from a commercially available molybdenum precursor of a metal–metal multiple-bonded complex with thiolate ligands, which may be employed as a precursor in substitution reactions at the easily displaced chloride sites. Reactions of V with appropriate pseudo-halides ($X = N_3^-$, NCS$^-$) yield complexes of the type [Mo$_2$(SC$_6$H$_4$-*o*-PPh$_2$)$_3$Cl$_{3-n}$X$_n$]. In a typical reaction V was reacted with an equimolar amount of TlSCN in acetonitrile. After addition of ether, a dark air-sensitive powder analyzing for [Mo$_2$(SC$_6$H$_4$-*o*-PPh$_2$)$_3$Cl$_2$(SCN)] was isolated in 25% yield.

The reaction of MoCl$_5$ with **II** yielded the phosphine oxide complex [Mo(SC$_6$H$_3$-2-SiMe$_3$-6-P(O)-Ph$_2$)$_2$Cl$_2$] (**VII**), presumably through the uptake of adventitious oxygen in the solvent. The yield of **VII** was considerably improved by reaction of MoCl$_5$ directly with **IV**. Addition of **IV**, (2.40 g, 6.57 mmol) in 20 ml of CH$_2$Cl$_2$ to MoCl$_5$ (0.06 g, 2.19 mmol) in 10 ml of CH$_2$Cl$_2$ resulted in a dark purple solution. After stirring for 2 h at room temperature, the solution was filtered and diethyl ether (60 ml) was layered carefully over the purple solution. After 2 weeks, green–purple crystals of **VII** were collected in 30% yield. *Anal.* Calc. for C$_{42}$H$_{44}$O$_2$P$_2$S$_2$Si$_2$Cl$_2$Mo (**VII**): C, 54.3; H, 4.77. Found: C, 55.3; H, 4.85%. IR (KBr, cm^{-1}): 1440(m), 1360(s), 1250(m), 1120(s, broad), 1052(s), 845(s, broad), 750(m), 730(m), 690(m), 550(vs), 320(m), 305(m). UV–Vis [CH$_3$CN; λ_{max}, nm (ϵ, cm^{-1} M^{-1}): 475 (3.5×10^2), 250 (4.0×10^3).

As shown in Fig. 2, the structure of **VII** consists of discrete mononuclear species with a pseudo-octahedrally coordinated Mo center displaying [MoO$_2$S$_2$Cl$_2$] coordination geometry. Crystal data for **VII** are: triclinic space group $P\bar{1}$, $a = 10.413(3)$, $b = 13.352(3)$, $c = 19.501(5)$ Å; $\alpha = 84.19(2)°$, $\beta = 86.32(2)°$, $\gamma = 82.06(1)°$, $V = 2668.3(11)$ Å^3, $Z = 2$, $D_{calc} = 1.37$ g cm^{-3}. Structure solution and refinement were based on 5226 reflections with $F_o \geqslant 6\sigma(F_o)$ (7235 collected) to give $R = 0.0570$. As with V, the chloride ligands of **VII** are readily displaced by appropriate pseudo-halides ($X = N_3^-$, NCS$^-$) and organohydrazines to yield complexes now under investigation.

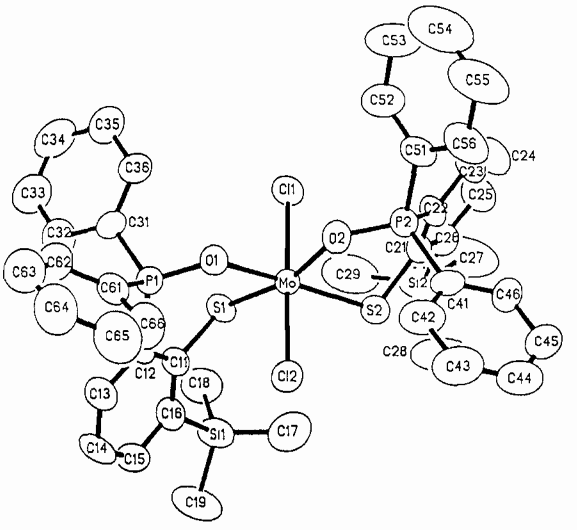

Fig. 2. ORTEP view of the structure of [Mo{SC$_6$H$_3$(SiMe$_3$)-PO(C$_6$H$_5$)$_2$}$_2$Cl$_2$] (VII), showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo–Cl(1), 2.395(2); Mo–Cl(2), 2.393(2); Mo–S(1), 2.347(2); Mo–S(2), 2.333(2); Mo–O(1), 2.107(5); Mo–O(2), 2.107(5); Cl(2)–Mo–Cl(1), 178.7(1); O(1)–Mo–S(2), 166.5(1); O(2)–Mo–S(1), 165.0(2).

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