Reactions of the Hydridethiolate Complexes [MH($SC_6H_2R_3$-2,4,6)$_3$(PMe_2Ph)$_2$] (M = Mo or W, R = Me or Pr^i): X-Ray Crystal Structures of [M($SC_6H_2Pr^i_3$-2,4,6)$_2$(CO)$_2$(PMe_2Ph)$_2$] (M = Mo or W) *

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Reaction of the complexes [MH($SC_6H_2R_3$-2,4,6)$_3$(PMe_2Ph)$_2$] **1** (M = Mo or W, R = Me or Pr^i) with neutral ligands L causes phosphine displacement to give the series [MH($SC_6H_2R_3$-2,4,6)$_3$(PMe_2Ph)L] **2** [L = $R'C_5H_4N$, P(OR″)$_3$ or MeCN; R′ = H, 2-, 3- or 4-Me, R″ = Me or Et]. Deuterido-analogues were also prepared. Reaction with CO caused hydride and thiolate displacement to give the compounds [M($SC_6H_2R_3$-2,4,6)$_2$(CO)$_2$(PMe_2Ph)$_2$] which have different geometries depending upon R. The X-ray crystal structure analyses of [M($SC_6H_2Pr^i_3$-2,4,6)$_2$(CO)$_2$(PMe_2Ph)$_2$] **3** (M = Mo or W) show them to have essentially trigonal prismatic structures with trigonal faces made from C(O), P and S atoms. The structures and fluxional properties of the carbonyl derivatives and of compounds **2** in solution have been studied by NMR spectroscopy. On treatment with $^2H_2$ at 1 atm, compounds **1** in solution undergo H/^{2}H exchange of the hydride ligand; the reaction is more effective for M = W than for M = Mo.

We have recently described three series of hydridethiolate complexes, one of Mo^{II}, [MoH($SC_6H_2R_3$-2,4,6)(dppe)$_2$] (R = Me or Pr^i, dppe = $Ph_2PCH_2CH_2PPh_2$),[1] and two of M^{IV} (M = Mo or W), [MH($SC_6H_2R_3$-2,4,6)$_3$(PMe_2Ph)$_2$] **1** and [MoH($SC_6H_2R_3$-2,4,6)$_3$($PR'Ph_2$)] (R′ = Me or Et).[2] These compounds are of high interest because they relate to sulphur-ligated metal centres which may be involved in catalytic processes such as nitrogen fixation[3] and hydrodesulphurisation.[4]

We have described the structural properties of these series and some reactions of the molybdenum(II) compounds, which are dominated by the ease of reductive elimination of thiol.[1,2] This property is the reason for the use of bulky thiolate substituents in the preparation of these hydrides, since they confer kinetic stability upon the complexes.[1]

The metal(IV) series, in contrast, can undergo a variety of reactions, many of which do not include thiolate elimination. We have described briefly some of these properties[2] and here describe in detail the substitution reactions of compounds **1** and the properties of the products. Three types of reaction have been defined: displacement of a phosphine with retention of hydride, elimination of thiol, and reaction of the hydride ligands.

Results and Discussion

Phosphine-displacement Reactions.—The aim of this study was to find routes to replace the phosphine co-ligands of hydride and thiolate by ligands having donor nitrogen (or oxygen) atoms. Thus the co-ordination environment of molybdenum (or tungsten) would move towards the S_3(N or O)$_3$ combination postulated to pertain to molybdenum in nitrogenase.[5]

Treatment of compounds **1** with pyridines, $R'C_5H_4N$ (R′ = H, 2-, 3- or 4-Me) causes the replacement of only one phosphine to give the series [MH($SC_6H_2R_3$-2,4,6)$_3$($R'C_5H_4N$)(PMe_2Ph)] **2** [reaction (1)]. These monomeric, green, diamagnetic compounds have been characterised by the analytical data shown in Table 1 and their structures are assigned on the basis of the following spectroscopic properties (see Table 2).

$$\underset{\mathbf{1}}{[MH(SC_6H_2R_3\text{-}2,4,6)_3(PMe_2Ph)_2]} + R'C_5H_4N \longrightarrow \underset{\mathbf{2}}{[MH(SC_6H_2R_3\text{-}2,4,6)_3(R'C_5H_4N)(PMe_2Ph)]} + PMe_2Ph \quad (1)$$

The infrared spectra of **2** (L = $R'C_5H_4N$) show hydride absorptions in the 1900–1960 cm^{-1} region. Their ^{1}H NMR hydride resonances occur at about δ 1.9–2.0 for M = Mo and about δ 8.9–9.6 for M = W (Table 2). These regions are close to those observed for the parent compounds **1**.[2] The large ^2J(HP) coupling implies that the hydride is in an essentially *trans* position to the remaining phosphine and this is also seen in the ^{31}P NMR spectra, which consist of the expected doublet. This doublet changes to the expected 1 : 1 : 1 triplet with the deuteride [Mo^{2}H($SC_6H_2Pr^i_3$-2,4,6)$_3$(C_5H_5N)(PMe_2Ph)] (Table 2). Thus the likely structure of these adducts is as in Fig. 1(*a*), analogous to those of compounds **1** (R = Pr^i),[2] but as yet we have no crystals suitable for an X-ray structure to confirm this suggestion.

The ^{1}H NMR spectra of **2** (R = Pr^i, L = $R'C_5H_4N$, R′ = H or 2-Me) show a pattern of five septets arising from the methyne C*H* of the Pr^i groups. This pattern is consistent with the arrangement of thiolate ligands shown in Fig. 1, *i.e.* two thiolate groups in the 'up' position and one thiolate 'down', together with hindered rotation in the molecule. If S–C rotation and M–S rotation/inversion is slow, the two thiolate groups 'up' will give different resonance positions from that of the thiolate in the

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* Dicarbonylbis(dimethylphenylphosphine)bis(2,4,6-triisopropylthiophenolato)-molybdenum(II) and tungsten(II)

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: atm = 101 325 Pa.

Table 1 Physical properties of the molybdenum and tungsten complexes

			Analysis (%)[a]			
Complex	Yield (%)	Colour	C	H	N	$M^{a,b}$
$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$	80	Olive green	69.0 (68.3)	8.3 (8.4)	1.1 (1.4)	
$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(2\text{-}MeC_5H_4N)(PMe_2Ph)}]$	56	Olive green	68.7 (68.5)	8.2 (8.5)	1.1 (1.4)	1034 (1035)
$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(3\text{-}MeC_5H_4N)(PMe_2Ph)}]$	70	Olive green	68.3 (68.5)	8.0 (8.5)	1.1 (1.4)	
$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(4\text{-}MeC_5H_4N)(PMe_2Ph)}]$	70	Olive green	68.4 (68.5)	8.1 (8.5)	1.1 (1.4)	1034 (1035)
$[\mathrm{Mo^2H(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$	80	Olive green	68.9 (68.3)	8.5 (8.4)	1.1 (1.4)	
$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3\{P(OMe)_3\}(PMe_2Ph)}]^c$	80	Dark blue				
$[\mathrm{Mo(SC_6H_2Me_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2}]$	56	Green	58.9 (59.2)	6.0 (6.0)		
$[\mathrm{Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2}]$	64	Red	63.8 (64.1)	7.7 (7.6)		
$[\mathrm{Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2(^{13}CO)_2(PMe_2Ph)_2}]^c$	50	Red				
$[\mathrm{WH(SC_6H_2Me_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$	90	Green				855 (855)
$[\mathrm{WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$	90	Green	62.1 (62.9)	7.7 (7.8)	1.3 (1.3)	1107 (1107)
$[\mathrm{WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(mim)(PMe_2Ph)}]$	95	Green	57.2 (61.6)	7.4 (7.9)	2.4 (2.5)	1111 (1110)
$[\mathrm{WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(MeCN)(PMe_2Ph)}]^c$	50	Light green				1069 (1069)
$[\mathrm{WH(SC_6H_2Me_3\text{-}2,4,6)_3\{P(OMe)_3\}(PMe_2Ph)}]^c$		Blue				900 (900)
$[\mathrm{WH(SC_6H_2Me_3\text{-}2,4,6)_3\{P(OEt)_3\}(PMe_2Ph)}]^c$		Blue-purple				943 (942)
$[\mathrm{WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3\{P(OMe)_3\}(PMe_2Ph)}]^c$		Blue				1152 (1152)
$[\mathrm{WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3\{P(OEt)_3\}(PMe_2Ph)}]^c$	45	Blue				
$[\mathrm{W(SC_6H_2Me_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2}]$		Green				818 (818)
$[\mathrm{W(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2}]$	95	Red	58.0 (58.4)	7.1 (6.9)	7.1 (6.6)[d]	986 (986)

[a] Calculated values in parenthesis. [b] By FAB mass spectrometry. [c] Not purified, see text. [d] S analysis.

Table 2 Selected ^{1}H and ^{31}P NMR and IR data for the complexes

	^{1}H (hydride) NMR[a]			^{31}P NMR[b]					
Complex	M^1H	$^2J(HP_A)$	$^2J(HP_B)$	P_A	$^1J(P_AW)$	P_B	$^1J(P_BW)$	$^2J(P_AP_B)$	IR (cm^{-1})[c]
$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$	2.0	84.3		−101.8					1903
$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(2\text{-}MeC_5H_4N)(PMe_2Ph)}]$	1.92	87.2		−102.0					1927
$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(3\text{-}MeC_5H_4N)(PMe_2Ph)}]$		85.0		−98.6					1904
$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(4\text{-}MeC_5H_4N)(PMe_2Ph)}]$		89.9		−101.0					1920
$[\mathrm{Mo^2H(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$		14.0[d]		−101.0					—
$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3\{P(OMe)_3\}(PMe_2Ph)}]$	2.6	90.0	8.0			−134.0		8.8	1920
$[\mathrm{Mo(SC_6H_2Me_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2}]$				−128.1		−147.6		10.9	1956,[e] 1869[e]
$[\mathrm{Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2}]$				−107.9		−107.9		0	1935,[e] 1850[e]
$[\mathrm{Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2(^{13}CO)_2(PMe_2Ph)_2}]^f$				−107.9					1900,[g] 1810[g]
$\{\mathrm{Mo^2H(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$	1.85[d]	13.6[d]		−107.3		−146.6			
$[\mathrm{WH(SC_6H_2Me_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$	8.9	102		−113.6	166				1955
$[\mathrm{WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$	9.6	102		−118.6	172				1939
$[\mathrm{WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(mim)(PMe_2Ph)}]^h$	9.0	102.8		−120.0	180				1926
$[\mathrm{WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(MeCN)(PMe_2Ph)}]$	9.8	105		−116.7	180				
$[\mathrm{WH(SC_6H_2Me_3\text{-}2,4,6)_3\{P(OMe)_3\}(PMe_2Ph)}]^{h,i}$	5.1	95	2.0	−3.0	316	−142.8	209	131	
				−6.5		−151.3		146	
$[\mathrm{WH(SC_6H_2Me_3\text{-}2,4,6)_3\{P(OEt)_3\}(PMe_2Ph)}]^{h,j}$	5.4	91		−7.9		−142.8		134	
				−9.5		−151.3		140	
$[\mathrm{WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3\{P(OMe)_3\}(PMe_2Ph)}]^{h,k}$	5.6	92	2.0	−7.8		−150.1		146	
				−2.2		−143.3		136	
$[\mathrm{WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3\{P(OEt)_3\}(PMe_2Ph)}]$	5.8	93	2.0	−9.1	292	−149.9	192	148	
$[\mathrm{W(SC_6H_2Me_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2}]^{h,l}$				−157.5	205	−162.4	142	7.5	1940,[e] 1810[e]
				−137.5	175	−137.5	175		
$[\mathrm{W(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2}]$				−137.4	190	−137.4	190		1921,[e] 1830[e]
$[\mathrm{W^2H(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$	8.8[d]	16.8[d]		−129.0		−152.0			

[a] In [$^2H_8$]toluene or $C^2H_2Cl_2$ solution; δ relative to $SiMe_4$, J in Hz. [b] P_A *trans* to hydride, P_B *cis* to hydride in [$^2H_8$]toluene, [$^2H_6$]benzene or thf solution; δ relative to $P(OMe)_3$; J in Hz. [c] Nujol mulls or CsI discs, ν(MH) unless otherwise stated. [d] $M–^2H$ or $J(^2HP)$. [e] ν(CO). [f] Isotopomers present, see text. ^{13}C NMR of $SC_6H_2Me_3$ analogue. $\delta(C_A)$ 224.7, $\delta(C_B)$ 240.9 relative to $SiMe_4$; $^2J_A(C_AP_A)$ 12.84, $^2J(C_AP_B)$ 57.41, $^2J(C_BP_A)$ 12.8 Hz. [g] ν(^{13}CO). [h] Two isomers, see text; major isomer first. [i] Major isomer 90% [j] Major isomer 60%. [k] Major isomer 95%. [l] Major isomer *ca.* 95%.

'down' position. Moreover, the Pr^i groups adjacent to the metal in the 'up' thiolates will differ from those on the outside of the molecule, and the 4-Pr^i groups will differ from the 2,6-Pr^i groups. If the 2,6-Pr^i groups of the 'down' thiolate are assumed to be equivalent, *i.e.* there is a plane of symmetry bisecting this thiolate group, then the five-septet pattern of 2:2:2:1:2 relative intensities is explained. A similar pattern of singlets of 2:2:2:1:2 relative intensities is seen for the CH_3 resonances of **2** (R = Me, L = $R'C_5H_4N$, R′ = H or 2-Me) and can be explained by the same arguments.

Treatment of compound **2** with $P(OR'')_3$ (R″ = Me or Et) leads to replacement of one phosphine to give a series of dark blue, monomeric, diamagnetic complexes $[\mathrm{MH(SC_6H_2R_3\text{-}2,4,6)_3\{P(OR'')_3\}(PMe_2Ph)}]$ which were very difficult to isolate because they form oils. Their structures are assigned, using the spectroscopic properties shown in Table 2, as analogous to **2** (L = $R'C_5H_4N$) but with the $P(OR'')_3$ ligands in the position pseudo-*trans* to the hydride [Fig. 1(*b*) and Table 2] to account for the large ^2J(HP) coupling between hydride and phosphite of 90–95 Hz. Relative to **2** (L = $R'C_5H_4N$) the ^{1}H NMR hydride

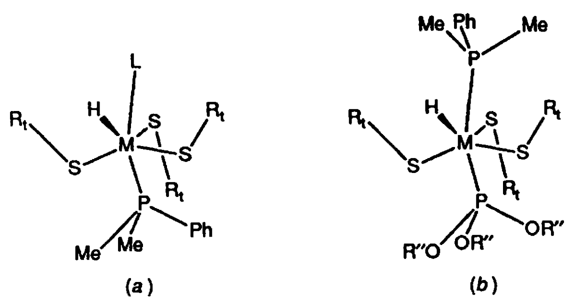

Fig. 1 Proposed structures for (*a*) **2** (L = $R'C_5H_4N$ or MeCN), (*b*) **2** [L = $P(OR'')_3$]; R_t = $C_6H_2R_3$-2,4,6

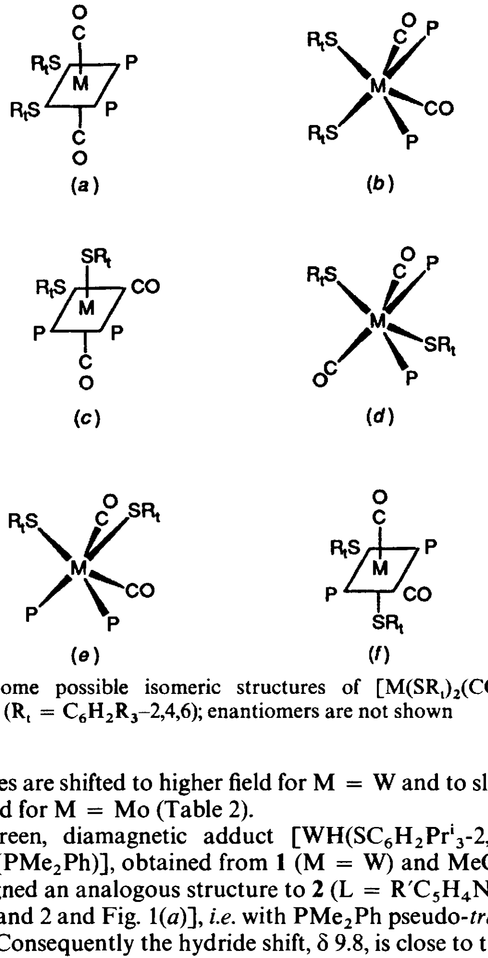

Fig. 2 Some possible isomeric structures of $[M(SR_t)_2(CO)_2(PMe_2Ph)_2]$ (R_t = $C_6H_2R_3$-2,4,6); enantiomers are not shown

resonances are shifted to higher field for M = W and to slightly lower field for M = Mo (Table 2).

The green, diamagnetic adduct $[WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(MeCN)(PMe_2Ph)]$, obtained from **1** (M = W) and MeCN, is also assigned an analogous structure to **2** (L = $R'C_5H_4N$) [see Tables 1 and 2 and Fig. 1(*a*)], *i.e.* with PMe_2Ph pseudo-*trans* to hydride. Consequently the hydride shift, δ 9.8, is close to that of the parent complex $[WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ (δ 9.1) and of **2** (L = $R'C_5H_4N$). The CH_3CN resonance occurs at δ 0.93, to high field of free CH_3CN (δ 1.93).

Thiol Displacement by Carbon Monoxide.—Treatment of compounds **1** with carbon monoxide leads to loss of thiol and formation of dicarbonyl complexes **3** as in reaction (2). A similar

$$[MH(SC_6H_2R_3\text{-}2,4,6)_3(PMe_2Ph)_2] + 2CO \longrightarrow \underset{\mathbf{3}}{[M(SC_6H_2R_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2]} + HSC_6H_2R_3\text{-}2,4,6 \quad (2)$$

displacement of thiol by CO occurs in $[MoH(SC_6H_2R_3\text{-}2,4,6)(dppe)_2]$.[1]

Properties of the Compounds $[M(SC_6H_2R_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2]$ **3**.—The diamagnetic compounds **3** are obtained in two isomeric forms, a red one when R is isopropyl, denoted **3** (red) and a green one when R is methyl, **3** (green). Analytical data are in Table 1. The complex **3** (M = W, R = Me) was isolated as a mixture of 90% **3** (green) and 10% **3** (red) on the basis of the ^{31}P NMR data (Table 2 and see below). The ^{13}C NMR spectra of crude samples obtained from reaction (2) showed that other isomers were present in solution but these could not be purified.

The X-ray structure determinations of **3** (red, M = Mo or W), described below, show these compounds to have in the solid an unusual, distorted trigonal prismatic (*TPR*) geometry with one SR, one PR_3 and one CO ligand in each triangular face. If this structure were to persist in solution the molecule would have C_2 symmetry with the C_2 axis running from the midpoint between the two sulphur atoms to the metal and this axis would make the two phosphorus atoms equivalent. As expected on this basis, the ^{31}P NMR resonance in solution is a singlet. Two C–O stretching frequencies in the IR spectrum are produced by pseudo-*cis* carbonyls. The ^{31}P NMR spectrum of ^{13}CO-labelled **3** (red), $[M(SC_6H_2R_3\text{-}2,4,6)_2(^{13}CO)_2(PMe_2Ph)_2]$, should consist of an AA′ pattern as part of an AA′XX′ spin system (A = ^{31}P, X = ^{13}C) if the complex retains the *TPR* geometry in solution. Instead a triplet is observed for **3** (red, ^{13}C NMR) at δ −107.6 with a coupling $^2J(^{31}P-^{13}C)$ of 31 Hz. [The spectra were complicated by the fact that the carbon monoxide used was only *ca.* 80% ^{13}C, so that a doublet with $^2J(^{31}P-^{13}C)$ of 31 Hz due to the $Mo(CO)(^{13}CO)$ isomer was also centred at δ −107.9.] These data therefore suggest that the structure of **3** (red) in solution is closer to octahedral [*i.e.* structure (*a*) of Fig. 2] than to the *TPR* solid-state structure shown as (*b*) in Fig. 2.

Compounds **3** (R = Pr^i, M = Mo or W) have been studied at low temperatures by ^1H NMR spectroscopy. At 20 °C both compounds show two broad resonances with integrals of ratio approximately 2:1 in the methyne-CH region ($[^2H_8]$toluene solution). As the temperature is lowered these resonances sharpen, then split into at least four overlapping complex multiplets at −60 °C. The ^{31}P NMR spectra, on the other hand, remain as singlets, showing some broadening at lower temperatures. Thus, judging by the relative invariance of the ^{31}P NMR spectra, the core geometry of these molecules appears to remain constant at lower temperature, but the mobility of the thiolate groups is restricted.

Complexes **3** (green) are likely to have C_1 symmetry because the two PMe_2Ph groups are inequivalent in solution as is revealed by the pattern of two doublets in the ^{31}P NMR spectrum. The ^{13}C NMR spectrum of a ^{13}C-enriched sample of **3** (green, M = Mo) shows that the two carbonyls are also inequivalent. One carbonyl gives rise to a doublet of doublets at δ 224.7 with a large coupling $^2J(^{13}C-^{31}P)$ to one PMe_2Ph (perhaps pseudo-*trans*) and a small coupling to the other (see footnote of Table 2). The other CO resonance is a doublet at δ 240.9 with a small coupling to a pseudo-*cis* PMe_2Ph. As for **3** (red), the structure of this compound can also be discussed in terms of octahedral or *TPR* geometry.

Of the five different isomers for octahedral $MA_2B_2C_2$ complexes, only isomer (*c*) of Fig. 2 has C_1 symmetry (only one entantiomer is shown). This structure is unlikely because the four bulky ligands are on one side of the octahedron. Moreover the ^{13}C NMR spectrum is not consistent with this structure. There is a doublet of doublets as expected for the CO *trans* to one P and *cis* to the other, but the second CO should have given a triplet from two *cis* P couplings, whereas only a doublet is observed.

There are 11 possible isomers for trigonal-prismatic $MA_2B_2C_2$ complexes (three of C_2 symmetry, four of C_s symmetry and four of C_1 symmetry), and seven of these (the C_2 and C_1 isomers) have enantiomers. However, the C_s and C_2 isomers are ruled out for **3** (green) because these would have magnetically equivalent P atoms. Of the C_1 isomers, those with three large groups in one triangle, *e.g.* $(SR)_2(PR_3)$ or $(SR)(PR_3)_2$, are probably unlikely on steric grounds. Similarly, isomers with four large ligands on one rectangular face of the prisms are unlikely, but these would have C_s or C_2 symmetry in any case. Only two pairs of enantiomers of C_1 symmetry remain and one enantiomer of each is shown in Fig. 2 as structures (*d*) and (*e*).

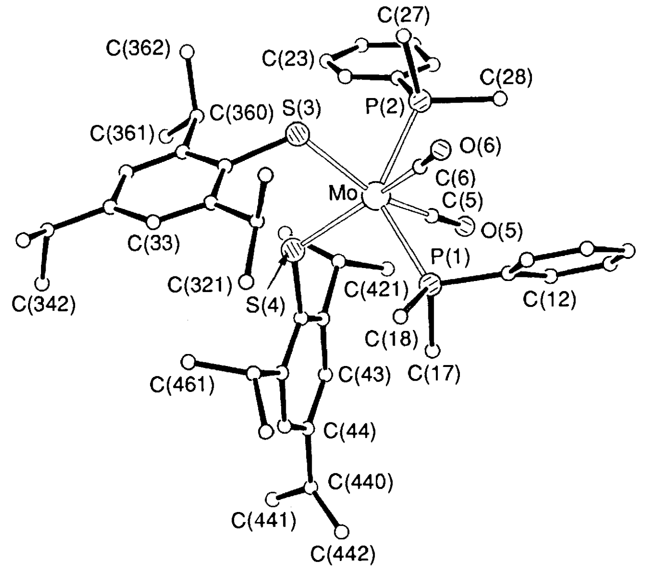

Fig. 3 Molecular structure of [Mo(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$]; the tungsten analogue is essentially isostructural

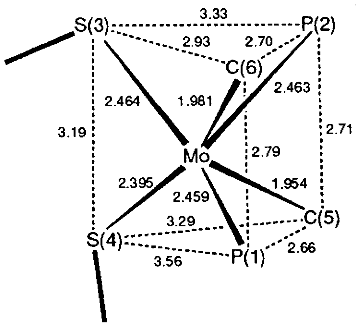

Fig. 4 Detail of the co-ordination (distances in Å) in the trigonal-prismatic structure of [Mo(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$]

Table 3 Selected bond lengths (Å) and angles (°) in [M(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$], (M = Mo or W). Estimated standard deviations (e.s.d.s) are in parentheses; those shown as (*) are less than 0.05°

	M = Mo	W
(*a*) About the metal atom		
M–P(1)	2.459(2)	2.472(2)
M–P(2)	2.463(2)	2.470(2)
M–S(3)	2.464(1)	2.460(2)
M–S(4)	2.395(1)	2.395(2)
M–C(5)	1.954(5)	1.967(7)
M–C(6)	1.981(5)	1.974(7)
P(1)–M–P(2)	125.7(*)	125.7(1)
P(1)–M–S(3)	134.3(*)	134.8(1)
P(1)–M–S(4)	94.4(*)	94.7(1)
P(1)–M–C(5)	73.2(2)	72.4(2)
P(1)–M–C(6)	77.2(2)	76.5(2)
P(2)–M–S(3)	85.1(*)	84.9(1)
P(2)–M–S(4)	132.6(*)	132.5(1)
P(2)–M–C(5)	74.8(2)	75.3(2)
P(2)–M–C(6)	74.0(2)	74.5(2)
S(3)–M–S(4)	82.1(*)	81.5(1)
S(3)–M–C(5)	152.6(2)	152.8(2)
S(3)–M–C(6)	81.6(2)	82.5(2)
S(4)–M–C(5)	97.7(2)	98.2(2)
S(4)–M–C(6)	147.1(2)	146.6(2)
C(5)–M–C(6)	109.8(2)	109.2(3)
(*b*) In the ligands		
P(1)–C(11)	1.824(6)	1.828(7)
P(1)–C(17)	1.812(5)	1.803(7)
P(1)–C(18)	1.807(6)	1.822(8)
P(2)–C(21)	1.815(6)	1.837(10), 1.819(7)[a]
P(2)–C(27)	1.799(6)	1.816(8)
P(2)–C(28)	1.801(7)	1.838(9)
M–P(1)–C(11)	115.5(2)	115.0(3)
M–P(1)–C(17)	118.7(2)	118.8(2)
M–P(1)–C(18)	112.4(2)	111.4(3)
C(11)–P(1)–C(17)	102.3(3)	102.4(3)
C(11)–P(1)–C(18)	104.1(3)	104.1(3)
C(17)–P(1)–C(18)	102.0(3)	103.4(4)
M–P(2)–C(21)	112.1(2)	113.8(3), 112.8(2)[a]
M–P(2)–C(27)	118.3(2)	117.6(3)
M–P(2)–C(28)	115.7(2)	114.5(3)
C(21)–P(2)–C(27)	102.0(3)	101.6(4), 102.5(4)[a]
C(21)–P(2)–C(28)	105.9(3)	105.6(4), 105.8(4)[a]
C(27)–P(2)–C(28)	101.2(3)	102.0(4)
S(3)–C(31)	1.790(5)	179.2(7)
S(4)–C(41)	1.784(5)	179.6(6)
M–S(3)–C(31)	116.8(2)	117.0(2)
M–S(4)–C(41)	122.6(2)	121.3(2)
C(5)–O(5)	1.161(6)	1.164(8)
C(6)–O(6)	1.150(7)	1.150(9)
M–C(5)–O(5)	178.5(4)	176.2(6)
M–C(6)–O(6)	174.5(5)	175.0(7)

[a] The two values for the tungsten complex refer to the two disordered phenyl rings, of C(21a) and C(21b)

Either of these structures could produce the observed NMR spectra and either one keeps the bulky groups quite far from each other. An X-ray diffraction study is required to resolve the question of the structure of the green isomers.

X-Ray Crystal Structures of [M(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] 3 (*red*, M = Mo *or* W).—These compounds are virtually isostructural and have essentially trigonal-prismatic geometry (Fig. 3) with C(6), P(2) and S(3) making up one triangular face and C(5), P(1) and S(4) the other. In this co-ordination sphere there is a pseudo-two-fold symmetry axis which bisects the S(3)–S(4) prism edge. The symmetry beyond this core, however, is spoiled by the varied orientations of the thiolate and phosphine groups. The S(3)–C(31) bond and the ring of C(31)–C(36) lie not far removed from the plane of the triangular face of S(3), P(2) and C(6), whereas the S(4)–C(41) bond is almost normal to the corresponding plane of S(4), P(1) and C(5). The orientations of the methyl and phenyl groups of the two phosphine ligands are also quite different when viewed in relation to the pseudo-symmetry axis.

These differences in orientations presumably result from the bulkiness of the thiolate ligands and to some extent from packing arrangements in the crystal; they will also account for the inequalities in dimensions about the metal atom, particularly in the M–S bond distances (Table 3) and in the dimensions of the S–P–C triangular faces, shown for the molybdenum complex in Fig. 4.

The trigonal-prismatic geometry is rare, but our structure may be regarded as derived from the octahedral isomers (*a*) or (*f*) in Fig. 2: the severe distortions arise from the steric demands of the bulky thiolate ligands. Other examples of six-co-ordinate thiolatecarbonyls, although with somewhat less bulky groups, exhibit essentially regular octahedral geometry.[6,7] For our complexes, deviations from the angles expected in the octahedral forms (*ca.* 90 or 180°) may be noted in the angles about the metal atom, listed in Table 3(*a*)

The principal differences between the two structures arise from disorder in the tungsten complex where the phenyl group of one phosphine ligand takes one of two possible orientations; disorder of an isopropyl group of a thiolate ligand is also suspected but has not been resolved. No disorder was observed in crystals of the molybdenum complex.

Reactions of the Hydride Ligand.—Under certain conditions, complexes **1** undergo $^1\mathrm{H}/^2\mathrm{H}$ exchange with deuterium gas. Complexes **1** (M = Mo) undergo only partial exchange when irradiated with tungsten-filament light in benzene under slightly more than one atmosphere pressure of $^2\mathrm{H}_2$ [reaction (3)]. The

$$[\mathrm{MH(SC_6H_2R_3\text{-}2,4,6)_3(PMe_2Ph)_2}] + {}^2\mathrm{H}_2 \longrightarrow [\mathrm{M}^2\mathrm{H(SC_6H_2R_3\text{-}2,4,6)_3(PMe_2Ph)_2}] + {}^2\mathrm{HH} \quad (3)$$

extent of exchange, demonstrated by $^2\mathrm{H}$ splitting of the $^{31}\mathrm{P}$ NMR spectrum, was usually less than 50% after exposure for 16 h, when the complex began to decompose. Complexes **1** (M = W), on the other hand, undergo exchange with deuterium much more readily, giving complete exchange, with no necessity for irradiation, in less than 16 h in benzene.

The reason for this difference may lie in the mechanism of formation and the structure of the intermediates in the reaction. The mechanism of the exchange must include the breaking of the $^2\mathrm{H}$–$^2\mathrm{H}$ bond, but the site at which this occurs is unknown. Most likely it is at the metal, forming a $\mathrm{MH(^2H)_2}$ or related intermediate, but it could also involve the sulphur atom(s) of the thiolates. Tungsten is likely to form a more strongly bonded $\mathrm{M{-}H_2}$ intermediate than is molybdenum since it forms stronger σ bonds and is more electron-releasing; this could account for the difference in reactivity observed.

The deuteriated products of these reactions were identified by their $^{31}\mathrm{P}$ and $^2\mathrm{H}$ NMR spectra (Table 2). The $^{31}\mathrm{P}$ spectra consist of a doublet and a doublet of 1:1:1 triplets. The magnitude of $^2J(\mathrm{P{-}^2H})$ is 13.6 Hz for **1** (M = Mo, R = $\mathrm{Pr^i}$) and 16.8 Hz for **1** (M = W, R = Me). These values are in the expected 1:6 ratio to the corresponding $^2J(\mathrm{P{-}^1H})$ couplings. The compound $[\mathrm{Mo^2H(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$ has also been synthesised separately by treatment of $[\mathrm{MoBr_2(NNH_2)(PMe_2Ph)_2}]$ with $\mathrm{^2HSC_6H_2Pr^i_3\text{-}2,4,6}$ in $\mathrm{MeO^2H}$. Its $^2\mathrm{H}$ NMR spectrum shows $\delta(\mathrm{Mo{-}^2H})$ 1.85, $^2J(\mathrm{P{-}^2H})$ 13.6 Hz.

Conclusion

Three reaction modes have been demonstrated for hydride-thiolate complexes. In the first, substitution of $\mathrm{PMe_2Ph}$ in the six-co-ordinate hydrides **1** can result in the incoming ligand occupying a position either pseudo-*trans* or pseudo-*cis* to the hydride. It might be considered that a dissociative mechanism, with subsequent rearrangement, is followed in these reactions, the phosphine *trans* to hydride being lost in the first step. Nevertheless, although steric factors appear to disfavour an associative mechanism, it cannot be ruled out in view of the low electron count for these metal(IV) species. Of particular note, however, is the stability of the metal–hydride–thiolate system, which is not disrupted until a strongly π-accepting co-ligand, CO, is used. In these reactions an associative process may occur. This is the second reaction mode. The third is the interesting $^1\mathrm{H}/^2\mathrm{H}$ exchange process involving complexes **1**.

The potentially rich chemistry of this class of hydride has been demonstrated and further reaction chemistry, including that shown by the even more electron-deficient, five-co-ordinate series $[\mathrm{MH(SC_6H_2R_3\text{-}2,4,6)_3(PR'Ph_2)}]^2$ will be described in later papers.

Experimental

The compounds $\mathrm{R'C_5H_4N}$, $\mathrm{P(OR'')_3}$, CO, $^2\mathrm{H}_2$ and $\mathrm{NEt_3}$ were used as supplied commercially. Complexes **1**[2,8] and thiols[9] were prepared by published methods. The NMR spectra were measured using JEOL FX270, Varian XL-400 or XL-200 instruments, infrared spectra on Perkin-Elmer SP3-200 or Nicolet 5DXFTIR spectrometers and fast atom bombardment (FAB) mass spectra with a VG70-250S spectrometer, using xenon flux. Microanalyses were determined by Mr. C. J. Macdonald of the Nitrogen Fixation Laboratory or by Canadian Microanalytical Services.

Preparations.—*(Dimethylphenylphosphine)hydrido(pyridine)tris*(2,4,6-*triisopropylthiophenolato)molybdenum*(IV). The compound $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$ (3.10 g, 2.87 mmol) was dissolved in neat pyridine (35 $\mathrm{cm^3}$). The resulting green solution was stirred at 60 °C for 15 min, and then left to stir under argon for 16 h. The pyridine was removed *in vacuo* and the resulting green-brown oil dissolved in benzene (30 $\mathrm{cm^3}$). The green solution was filtered through Celite to remove an oily, brown residue which was washed with more benzene (10 $\mathrm{cm^3}$). The volume of the solution was reduced *in vacuo* to 20 $\mathrm{cm^3}$, MeOH (50 $\mathrm{cm^3}$) was added and the resulting bright green microcrystalline *precipitate* was collected, washed with MeOH (1 × 10 $\mathrm{cm^3}$) and dried *in vacuo* (2.35 g). $^1\mathrm{H}$ NMR (in $[^2\mathrm{H}_6]$benzene): δ 7.75 (m, 2 H, *o*-H of $\mathit{Ph}\mathrm{PMe_2}$), 7.30–7.10 (m, 3 H, $\mathit{Ph}\mathrm{PMe_2}$), 7.30 (s, 2 H), 7.14 (s, 2 H), 7.05 (s, 2 H) (6 H, $\mathit{H}_2\mathrm{C_6Pr^i_3S}$), 6.76 (d, 2 H, py, J_{HH} = 2.01), 6.49 (d, 2 H, py, J_{HH} = 1.68), 6.43 (m, 1 H, py), 3.96 (spt, 2 H, $^3J_{\mathrm{HH}}$ = 6.72), 3.63 (spt, 2 H, $^3J_{\mathrm{HH}}$ = 6.72), 3.11 (spt, 2 H, $^3J_{\mathrm{HH}}$ = 6.72), 2.96 (spt, 1 H, $^3J_{\mathrm{HH}}$ = 7.06), 2.60 (spt, 2 H, $^3J_{\mathrm{HH}}$ = 7.06), ($\mathit{H}\mathrm{CMe_2}$), 2.0 (d, Mo*H*, see Table 2), 1.87 (d, 6 H, $\mathit{Me}_2\mathrm{PPh}$, $^2J_{\mathrm{PH}}$ = 9.32), 1.50 (d, 6 H, $^3J_{\mathrm{HH}}$ = 6.72), 1.44 (d, 6 H, $^3J_{\mathrm{HH}}$ = 6.72), 1.36 (d, 6 H, $^3J_{\mathrm{HH}}$ = 7.06), 1.32 (d, 6 H, $^3J_{\mathrm{HH}}$ = 6.72), 1.19 (d, 6 H, $^3J_{\mathrm{HH}}$ = 6.72), 1.18 (d, 6 H, $^3J_{\mathrm{HH}}$ = 7.06), 1.14 (d, 6 H, $^3J_{\mathrm{HH}}$ = 6.72) and 1.09 (d, 12 H, $^3J_{\mathrm{HH}}$ = 7.06 Hz), ($\mathit{Me}_2\mathrm{CH}$).

(Dimethylphenylphosphine)hydrido(2-*methylpyridine)tris*-(2,4,6-*triisopropylthiophenolato)molybdenum*(IV). The compound $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$ (0.26 g, 0.24 mmol) was dissolved in 2-methylpyridine (20 $\mathrm{cm^3}$). The green solution was stirred at 60 °C for 15 min, and then left to stir under argon for 3 h. The 2-methylpyridine was removed *in vacuo* and the resulting mixture of brown and green oils was filtered through Celite to remove an oily, brown residue which was washed with more benzene (10 $\mathrm{cm^3}$). The volume of the resulting brown solution was reduced to 4 $\mathrm{cm^3}$ *in vacuo* and MeOH (20 $\mathrm{cm^3}$) was added. This solution was left to stand under argon for 16 h. A mixture of green and brown crystalline material was collected, washed with MeOH (2 × 10 $\mathrm{cm^3}$) and dried *in vacuo*. On standing under argon all of the product became *green* crystals and all data presented are for this product. (0.14 g). $^1\mathrm{H}$ NMR (in $[^2\mathrm{H}_6]$benzene): δ 7.75 (m, 2 H, *o*-H, $\mathit{Ph}\mathrm{PMe_2}$), 7.30–7.10 (m, 3 H, $\mathit{Ph}\mathrm{PMe_2}$), 7.30 (s, 2 H), 7.18 (s, 2 H), 7.05 (s, 2 H) ($\mathit{H}_2\mathrm{C_6Pr^i_3S}$), 6.97 (d, 2 H, $\mathrm{MeC_5}\mathit{H}_4\mathrm{N}$, J_{HH} = 2.02), 6.94 (d, 2 H, $\mathrm{MeC_5}\mathit{H}_4\mathrm{N}$, J_{HH} = 1.69), 3.88 (spt, 2 H, $^3J_{\mathrm{HH}}$ = 7.06), 3.54 (spt, 2 H, $^3J_{\mathrm{HH}}$ = 6.72), 3.50 (spt, 2 H, $^3J_{\mathrm{HH}}$ = 6.72), 2.72 (spt, 1 H, $^3J_{\mathrm{HH}}$ = 6.72), 2.60 (spt, 2 H, $^3J_{\mathrm{HH}}$ = 6.72) ($\mathit{H}\mathrm{CMe_2}$), 2.90 (s, 3 H, $\mathit{Me}\mathrm{C_5H_4N}$), 1.92 (d, Mo*H*, see Table 2), 1.87 (d, 6 H, $\mathit{Me}_2\mathrm{PPh}$, $^2J_{\mathrm{PH}}$ = 9.41), 1.49 (d, 6 H, $^3J_{\mathrm{HH}}$ = 7.06), 1.44 (d, 6 H, $^3J_{\mathrm{HH}}$ = 7.06), 1.36 (d, 6 H, $^3J_{\mathrm{HH}}$ = 7.06), 1.24 (d, 6 H, $^3J_{\mathrm{HH}}$ = 6.73), 1.19 (d, 6 H, J_{HH} = 6.73), 1.18 (d, 6 H, $^3J_{\mathrm{HH}}$ = 6.72), 1.15 (d, 6 H, $^3J_{\mathrm{HH}}$ = 7.06) and 1.09 (d, 6 H, $^3J_{\mathrm{HH}}$ = 7.05 Hz) ($\mathit{Me}_2\mathrm{CH}$).

(Dimethylphenylphosphine)hydridotris(2,4,6-*triisopropylthiophenolato)(trimethyl phosphite)molybdenum*(IV). The compound $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$ (0.2 g, 0.18 mmol) was dissolved in benzene (10 $\mathrm{cm^3}$), $\mathrm{P(OMe)_3}$ (0.9 g 4 equivalents) was added and the solution was left to stir under dinitrogen for 70 h. The volume of the resulting blue-black solution was reduced slightly *in vacuo* and this solution was used for the $^{31}\mathrm{P}$ and $^1\mathrm{H}$ NMR studies. Removal of all solvent gave a blue-black *oil* which could not be crystallised.

Dicarbonylbis(dimethylphenylphosphine)bis(2,4,6-*triisopropylthiophenolato)molybdenum*(II). The compound $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$ (0.30 g, 0.27 mmol) was dissolved in hexane (25 $\mathrm{cm^3}$) and CO was bubbled through the green solution for 3 h. The resulting yellow-brown solution was left to stir under an atmosphere of CO for 18 h. The volume was reduced *in vacuo* to 10 $\mathrm{cm^3}$, MeOH (20 $\mathrm{cm^3}$) was layered on top and the solution cooled to −20 °C for 3 d. The red-brown *crystals* that formed were collected, washed with MeOH (2 × 10 $\mathrm{cm^3}$) and dried *in vacuo* (0.16 g). $^1\mathrm{H}$ NMR (in $[^2\mathrm{H}_8]$toluene): the compound is fluxional, see text; at 20 °C δ

7.04 (m, 2 H, *p*-H of *Ph*PMe$_2$), 7.0–6.9 (m, 14 H, *Ph*PMe$_2$ and *H*$_2$C$_6$Pr$^i{}_3$S), 1.27 (d, 12 H, *Me*$_2$PPh, $^2J_{PH}$ = 9.28), 1.25 (d, 12 H, $^3J_{HH}$ = 6.83), 1.14 (d, 12 H, $^3J_{HH}$ = 6.82) and 1.13 (d, 12 H, $^3J_{HH}$ = 6.83 Hz), (*Me*$_2$CH).

Dicarbonylbis(dimethylphenylphosphine)bis(2,4,6-*trimethylthiophenolato)molybdenum*(II). The compound [MoH(SC$_6$H$_2$Me$_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] (0.37 g, 0.44 mmol) was dissolved in hexane (25 cm^3) and CO was bubbled through the green solution for 3 h. The resulting green solution was left to stir under an atmosphere of CO for 18 h. The volume was reduced to 15 cm^3 *in vacuo*, MeOH (30 cm^3) was added and the resulting solution cooled at -20 °C for 24 h. The dark green *crystals* which had formed were collected, washed with MeOH (2 × 10 cm^3) and dried *in vacuo* (0.14 g). ^{1}H NMR (in [^{2}H$_6$]benzene): δ 7.80 (m, 2 H, *p*-H of *Ph*PMe$_2$), 7.42–7.25 (m, 8 H, *Ph*PMe$_2$), 7.08 (s, 4 H, *H*$_2$C$_6$Me$_3$S), 2.69 (s, 6 H), 2.64 (s, 6 H), 2.37 (s, 6 H) (*Me*$_3$C$_6$H$_2$S), 1.96 (d, 3 H, $^2J_{HP}$ = 6.06), 1.76 (d, 3 H, $^2J_{HP}$ = 5.56), 1.45 (d, 3 H, $^2J_{HP}$ = 7.07) and 1.34 (d, 3 H, $^2J_{HP}$ = 8.08 Hz) (*Me*$_2$PPh).

^{13}CO-*Labelled Dicarbonylbis(dimethylphenylphosphine)bis*(2,4,6-*triisopropylthiophenolato)molybdenum*(II). A Schlenk flask (50 cm^3) was charged with [MoH(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] (0.19 g, 0.17 mmol) and toluene (10 cm^3) was distilled in under vacuum at liquid-nitrogen temperature. Carbon-13 monoxide gas (80% ^{13}CO) was pumped into the flask *via* a Toëpler pump up to 0.5 atm. The green solution was warmed to ambient temperature and stirred for 16 h. The resulting dirty brown solution was frozen in liquid N$_2$ and the excess of ^{13}CO removed *via* a Toëpler pump. After warming to ambient temperature, MeOH (20 cm^3) was added and the solution cooled at -20 °C for 24 h. The red-brown precipitate which had formed was filtered off, washed with MeOH (2 × 10 cm^3) and dried *in vacuo* (0.08 g).

Deuteridobis(dimethylphenylphosphine)tris(2,4,6-*triisopropylthiophenolato)molybdenum*(IV). *Method* 1. The compound [MoH(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] (0.0721 g, 6.68 × 10^{-5} mol) was dissolved in benzene (3.5 cm^3) and left to stir under deuterium with continuous irradiation from a tungsten filament lamp for 21 h. Phosphorus-31 NMR spectroscopy showed that a small amount of exchange (approximately 25%) had taken place.

Method 2. The compound [MoH(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] (0.10 g, 9.26 × 10^{-5} mol) was dissolved in benzene (6.0 cm^3) and stirred vigorously with tungsten irradiation under deuterium gas (1 atm) for 16 h. Half of this solution was used for ^{31}P and ^{2}H NMR studies, and the remaining 3 cm^3 were left to stir under deuterium with irradiation for 28 h. After this time the percentage exchange had increased from 20 to 50% but the complex was beginning to decompose, evident by the presence of free phosphine in the ^{31}P NMR spectrum.

Method 3. The compound [MoBr$_2$(NNH$_2$)(PMe$_2$Ph)$_3$] (0.32 g, 0.45 mmol) was suspended in MeO^{2}H (20 cm^3) and ^{2}HSC$_6$H$_2$Pr$^i{}_3$-2,4,6 (0.42 g, 4 equivalents) then NEt$_3$, (0.23 cm^3, 3 equivalents) were added. The suspension was stirred under dinitrogen for 72 h and the resulting green *precipitate* was collected, washed quickly with MeOH (2 × 10 cm^3) and dried *in vacuo* (0.11 g).

(*Dimethylphenylphosphine)hydrido(pyridine)tris*(2,4,6-*triisopropylthiophenolato)tungsten*(IV). Under argon [WH(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] (0.92 g, 0.79 mmol) was dissolved in pyridine (10 cm^3) to give a green solution. The solution was warmed to 60 °C, left stirring overnight, then allowed to cool slowly to ambient temperature. The pyridine was stripped off, the resulting green oil dissolved in benzene and the product precipitated with methanol yielding a green *powder*. On occasions when the reaction did not go to completion the product was contaminated with the starting material. There was little or no contamination by side products according to ^{31}P NMR spectroscopy. ^{1}H NMR: δ 9.55 (d, WH, see Table 2), 7.76 (tm, 2 H, *o*-H of *Ph*PMe$_2$), 7.4–7.0 (m, 3 H, *Ph*PMe$_2$), 7.33 (s, 2 H), 7.23 (s, 2 H), 7.08 (s, 2 H), (*H*$_2$C$_6$Pr$^i{}_3$S), 6.80 (d, 2 H, py, J_{HH} = 1.7), 6.56 (d, 2 H, py, J_{HH} = 1.7), 6.22 (tm, 1 H, py), 4.0 (spt, 2 H, $^3J_{HH}$ = 6.7), 3.7 (spt, 2 H, $^3J_{HH}$ = 6.7), 3.21 (spt, 2 H, $^3J_{HH}$ = 6.7), 2.96 (spt, 1 H, $^3J_{HH}$ = 7.0), 2.66 (m, 2 H, $^3J_{HH}$ = 7.0) (*H*CMe$_2$), 2.06 (d, 6 H, *Me*$_2$PPh, $^2J_{PH}$ = 9.5), 1.52 (d, 6 H, $^3J_{HH}$ = 6.6), 1.44 (d, 6 H, $^3J_{HH}$ = 6.8), 1.38 (d, 6 H, $^3J_{HH}$ = 6.9), 1.33 (d, 6 H, $^3J_{HH}$ = 6.8), 1.21 (d, 6 H, $^3J_{HH}$ = 6.8), 1.19 (d, 6 H, $^3J_{HH}$ = 6.8), 1.14 (d, 6 H) and 1.10 (d, 12 H, $^3J_{HH}$ = 7.02 Hz) (*Me*$_2$CH of Pr^i).

(*Dimethylphenylphosphine)hydrido(pyridine)tris*(2,4,6-*trimethylthiophenolato)tungsten*(IV). The procedure was the same as that for [WH(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_3$(py)(PMe$_2$Ph)] A near-quantitative yield of the desired product of good purity (as indicated by ^{31}P NMR spectroscopy) was obtained. ^{1}H NMR: 8.85 (d, WH, see Table 2), 7.50 (tm, 2 H, *o*-H of *Ph*PMe$_2$), 7.2–6.9 (m, 9 H, *Ph*PMe$_2$, *H*$_2$C$_6$Me$_3$S), 6.55 (s, 2 H, py), 6.26 (s, 2 H, py), 6.11 (tm, 1 H, py), 2.16 (d, 6 H, *Me*$_2$PPh, $^2J_{PH}$ = 10 Hz), 2.62 (s, 6 H), 2.33 (s, 3 H), 2.28 (s, 6 H), 2.19 (s, 6 H) and 1.97 (s, 6 H) (*Me*$_3$C$_6$H$_2$S).

(*Dimethylphenylphosphine)hydrido*(N-*methylimidazole)tris*(2,4,6-*triisopropylthiophenolato)tungsten*(IV). The compound [WH(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] (0.09 g) was suspended in dry, degassed *N*-methylimidazole (mim) (10 cm^3) under argon. Benzene (20 cm^3) was added to dissolve the complex. This solution was stirred for 2 d at 40 °C. The solvent was evaporated under vacuum until a bright green *precipitate* formed. The product was filtered off and recrystallised from benzene–MeOH. ^{1}H NMR: δ 8.96 (d, WH, see Table 2), 7.70 (t, 2 H, *o*-H of *Ph*PMe$_2$), 7.4–6.8 (m, 10 H, *Ph*PMe$_2$, SC$_6$*H*$_2$Pr$^i{}_3$, mim), 5.96 (s, 1 H, mim), 5.39 (s, 1 H, mim), 4.07 (spt, 2 H, $^3J_{HH}$ = 7.0), 3.83 (spt, 2 H, $^3J_{HH}$ = 7.0), 3.28 (spt, 2 H, $^3J_{HH}$ = 6.8), 3.01 (spt, 1 H, $^3J_{HH}$ = 7.0), 2.70 (spt, 1 H, $^3J_{HH}$ = 6.9) (*H*CMe$_2$), 2.22 (s, 3 H, mim), 2.10 (d, 6 H, $^2J_{PH}$ = 9.4, PMe$_2$Ph), 1.53 (d, 6 H, $^3J_{HH}$ = 6.8), 1.45 (d, 6 H, $^3J_{HH}$ = 6.6), 1.39 (d, 12 H, $^3J_{HH}$ = 7), 1.27 (d, 6 H, $^3J_{HH}$ = 6.8), 1.22 (d, 6 H, $^3J_{HH}$ = 5), 1.18 (d, 6 H, $^3J_{HH}$ = 5) and 1.15 (d, 12 H, $^3J_{HH}$ = 6.7 Hz) (*Me*$_2$CH).

Acetonitrile(dimethylphenylphosphine)hydridotris(2,4,6-*triisopropylthiophenolato)tungsten*(IV). The compound [WH(SC$_6$H$_2$Me$_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] (0.1 g) was suspended in MeCN (15 cm^3) and sufficient benzene (*ca.* 15 cm^3) was added to dissolve the tungsten complex. The solution was left stirring overnight and then the solvent was removed. Benzene (21 cm^3) was added followed by acetonitrile (5 cm^3). After a few minutes methanol (20 cm^3) was added, and light green *crystals* of product precipitated. ^{1}H NMR: 9.78 (d, WH, see Table 2), 7.72 (tm, 2 H, *o*-H of *Ph*PMe$_2$), 7.5–7.0 (m, 3 H, *Ph*PMe$_2$), 7.36 (s, 2 H), 7.24 (s, 2 H), 7.05 (s, 2 H) (*H*$_2$C$_6$Pr$^i{}_3$S), 4.40 (spt, 2 H, $^3J_{HH}$ = 6.7), 4.13 (spt, 2 H, $^3J_{HH}$ = 6.8), 3.25 (spt, 2 H, $^3J_{HH}$ = 6.8), 3.07 (spt, 1 H, $^3J_{HH}$ = 7.0), 2.81 (m, 2 H, $^3J_{HH}$ = 7.0) (*H*CMe$_2$ of thiolate), 2.13 (d, 6 H, *Me*$_2$PPh, $^2J_{HP}$ = 9.5), 1.67 (d, 6 H, $^3J_{HH}$ = 6.8), 1.45 (d, 12 H, $^3J_{HH}$ = 7.0), 1.41 (d, 12 H, $^3J_{HH}$ = 6.9), 1.37 (d, 6 H, $^3J_{HH}$ = 7.1), 1.23 (d, 12 H, $^3J_{HH}$ = 6.8) and 1.13 (d, 6 H, $^3J_{HH}$ = 6.8 Hz) (*Me*$_2$CH).

Dicarbonylbis(dimethylphenylphosphine)bis(2,4,6-*triisopropylthiophenolato)tungsten*(II). The compound [WH(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] (0.1 g) was dissolved in hexane (20 cm^3), the solution was degassed then flushed with CO three times. The bright green solution was left stirring. The colour changed to a dirtier green after 15 min then, after 2 h, to brown, and overnight to a rust red. The solvent was stripped, the residues taken up in benzene and the product was precipitated using methanol to yield a microcrystalline brick red *powder*. The product is stable in air both as a solid and as a benzene solution for extended periods. ^{1}H NMR: the compound is fluxional, see text; at 22 °C δ 7.48 (tm, 2 H, *o*-H of *Ph*PMe$_2$), 7.3–6.9 (m, *ca.* 6 H, *Ph*PMe$_2$, *H*$_2$CPr$^i{}_3$S), 3.65 (br m, 2 H, *o*-*Me*$_2$CH), 2.9 (m, 1 H, *p*-Me$_2$C*H* of Pr^i), 1.6 (br s, 6 H, P*Me*$_2$Ph), 1.32 (d, 12 H, *o*-*Me*$_2$CH) and 0.9 (br, 6 H, *p*-*Me*$_2$CH of Pr^i).

Dicarbonylbis(dimethylphenylphosphine)bis(2,4,6-*trimethylthiophenolato)tungsten*(II). The compound [WH(SC$_6$H$_2$Me$_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] was dissolved in benzene and placed under a CO atmosphere. After stirring for 16 h the bright green solution turned red-green and addition of methanol yielded a green

Table 4 Final atomic coordinates (fractional × 10^4) for $[Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo	2367.7(4)	1871.4(3)	3641.3(2)
P(1)	3719(1)	1225.3(9)	4313.9(6)
C(11)	4423(5)	336(3)	4096(2)
C(12)	3844(6)	−367(3)	4122(2)
C(13)	4363(6)	−1038(4)	3926(3)
C(14)	5448(6)	−1008(4)	3723(2)
C(15)	6031(6)	−323(4)	3701(2)
C(16)	5535(5)	355(4)	3885(2)
C(17)	3133(5)	926(3)	4934(2)
C(18)	4959(5)	1836(3)	4543(2)
P(2)	1617(1)	1308(1)	2784.1(6)
C(21)	−2(5)	1313(3)	2702(2)
C(22)	−630(7)	1892(6)	2778(5)
C(23)	−1875(8)	1910(6)	2733(5)
C(24)	−2438(8)	1346(5)	2596(3)
C(25)	−1875(9)	757(7)	2508(6)
C(26)	−630(7)	725(7)	2591(5)
C(27)	2016(7)	1774(4)	2183(2)
C(28)	2064(6)	321(4)	2667(3)
S(3)	2439(1)	3102.6(8)	3145.0(5)
C(31)	2267(4)	3978(3)	3515(2)
C(32)	3264(4)	4316(3)	3793(2)
C(320)	4451(5)	3911(4)	3846(2)
C(321)	5186(5)	4081(4)	4356(2)
C(322)	5176(6)	4049(5)	3371(3)
C(33)	3107(5)	5043(3)	4029(2)
C(34)	2020(5)	5429(3)	4004(2)
C(340)	1814(6)	6199(4)	4284(3)
C(341)	2842(6)	6740(3)	4336(3)
C(342)	1299(7)	6039(4)	4811(3)
C(35)	1068(5)	5067(3)	3737(2)
C(36)	1156(5)	4351(3)	3495(2)
C(360)	39(4)	3994(4)	3224(2)
C(361)	−1080(5)	4132(4)	3510(3)
C(362)	−134(6)	4235(5)	2662(2)
S(4)	1464(1)	2686.7(8)	4270.6(5)
C(41)	1064(4)	2340(3)	4901(2)
C(42)	96(5)	1826(3)	4951(2)
C(420)	−681(4)	1556(3)	4470(2)
C(421)	−1239(6)	754(4)	4532(3)
C(422)	−1658(5)	2149(4)	4327(3)
C(43)	−178(5)	1607(3)	5460(2)
C(44)	435(6)	1874(4)	5915(2)
C(440)	127(7)	1625(5)	6461(3)
C(441)	−755(11)	1923(8)	6661(4)
C(442)	1036(9)	1301(7)	6780(3)
C(45)	1347(5)	2397(3)	5853(2)
C(46)	1692(4)	2632(3)	5363(2)
C(460)	2677(5)	3230(3)	5331(2)
C(461)	2174(6)	4038(3)	5318(3)
C(462)	3668(6)	3152(4)	5771(2)
C(5)	1602(5)	896(3)	3823(2)
O(5)	1139(3)	315(2)	3920(2)
C(6)	3796(5)	1651(3)	3247(2)
O(6)	4645(3)	1586(3)	3020(2)

powder. Phosphorus-31 NMR spectroscopy indicated that the product consisted of a major (*ca.* 80%) and a minor isomer. ^1H NMR: 7.59 (tm, 2 H, *o*-H of *Ph*PMe$_2$), 7.3–7.0 (m, 8 H, *Ph*PMe$_2$), 6.67 (s, 1 H, PMe$_2$*Ph*), 6.94 (s, 2 H, $H_2C_6Me_2S$), 6.83 (s, 2 H, $H_2C_6Me_3S$), 1.85 (d, 3 H, $^2J_{PH}$ = 7.3), 1.64 (d, 3 H, $^2J_{PH}$ = 7.52), 2.16 (d, 3 H, $^2J_{PH}$ = 8.6), 1.40 (d, 3 H, $^2J_{PH}$ = 9.0 Hz) (*Me*$_2$PPh), 2.51 (s, 6 H), 2.42 (s, 6 H), 2.16 (s, 6 H) and 1.97 (s, 6 H) ($C_6H_2Me_3S$).

(*Dimethylphenylphosphine*)*hydridotris*(2,4,6-*triisopropylthiophenolato*)(*trimethyl phosphite*)*tungsten*(IV). The compound $[WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ (0.1 g, 0.085 mmol) was dissolved in benzene (20 cm^3) under N_2. Trimethyl phosphite (15 mg, 0.12 mmol) was added and stirred for about 16 h. The solution turned more blue as time progressed, the final solution being dark blue. Analysis by ^{31}P NMR spectroscopy showed that the final product was an equimolar mixture of the desired product and starting materials. Using 2 equivalents of phosphite gave the same product, but with a higher conversion over the same time. Two isomers were detected by ^{31}P NMR spectroscopy; however, one was approximately twice as abundant as the other (see Tables 1 and 2). ^1H NMR (400 MHz): (major isomer) δ 5.61 (dd, WH, see Table 2) and 3.03 [d, 9 H, P(OMe)$_3$, $^2J_{PH}$ = 10.7]; (minor isomer) δ 3.06 [d, 9 H, P(OMe)$_3$, $^2J_{PH}$ = 10.7 Hz].

(*Dimethylphenylphosphine*)*hydrido*(*trimethyl phosphite*)*tris*(2,4,6-*trimethylthiophenolato*)*tungsten*(IV). The compound $[WH(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ (0.09 g) was treated with P(OMe)$_3$ (0.0369 g, 3 equivalents) in benzene (10 cm^3). The resulting solution turned purple-blue as it was stirred for 48 h. Analysis by ^{31}P NMR spectroscopy of the reaction mixture showed only two isomers in the product, one of which was of low abundance. The multiplet due to the hydride of only one isomer was seen in the ^1H NMR spectrum. ^1H NMR: 8.28 (tm, *ca.* 1.5 H, *o*-H of phenyl of PMe$_2$*Ph*), 7.9–7.0 (m, 4 H, *Ph*PMe$_2$), 6.82 (s, 6 H, $H_2C_6Me_3S$), 5.11 (dd, WH, see Table 2), 2.58 (d, 6 H, *Me*$_2$PPh, $^2J_{PH}$ = 10.7 Hz) and 2.44 (s, 18 H, *o*-$C_6H_2Me_3S$).

(*Dimethylphenylphosphine*)*hydrido*(*triethyl phosphite*)*tris*(2,4,6-*triisopropylthiophenolato*)*tungsten*(IV). Triethyl phosphite (0.065 g, 0.391 mmol) in benzene (5 cm^3) was added to $[WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ (0.115 g) under a nitrogen atmosphere. The solution turned darker blue-green from the original bright emerald green over the course of 48 h. Analysis of the reaction mixture by ^{31}P NMR spectroscopy showed approximately 50% completion of reaction in this time period. Extended reaction periods over 72 h resulted in a deeper blue solution, all starting material having reacted. The blue product was isolated with methanol, followed by recrystallisation from benzene–methanol as blue *crystals*. ^1H NMR: δ 5.81 (dd, WH, Table 2).

(*Dimethylphenylphosphine*)*hydrido*(*triethyl phosphite*)*tris*(2,4,6-*trimethylthiophenolato*)*tungsten*(IV). The procedure was similar to that of the preparation of $[WH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3\{P(OEt)_3\}(PMe_2Ph)]$. After 48 h the analysis of the reaction mixture by ^{31}P and ^1H NMR spectroscopy showed the reaction to be quantitative but the oily product was not purified.

Crystal Structure Analysis of $[Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2]$.—*Crystal data*. $C_{48}H_{68}MoO_2P_2S_2$, *M* = 899.1, monoclinic, space group $P2_1/n$ (equivalent to no. 14), *a* = 11.222(1), *b* = 17.207(2), *c* = 25.204(2) Å, β = 94.005(7)°, *U* = 4854.8 Å^3, *Z* = 4, D_c = 1.230 g cm^{-3}, *F*(000) = 1904, μ(Mo-Kα) = 4.4 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å.

The crystals are translucent red, rectangular plates. One, *ca.* 0.71 × 0.36 × 0.01 mm, was mounted on a glass fibre and coated with epoxy resin. After preliminary photographic investigation it was mounted on an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) where accurate cell dimensions were refined from the goniometer settings of 25 strong reflections with θ *ca.* 10.5°, each centred in four orientations. Diffraction intensities were then measured to θ_{max} = 20°.

During processing, these data were corrected for Lorentz and polarisation effects, slight deterioration, and to ensure no negative net intensities (using Bayesian statistical methods).

4519 Unique data were entered into the SHELX program system[10] where the position of the molybdenum atom was determined by the Patterson method. Subsequent electron-density and Fourier-difference syntheses yielded the positions of all non-hydrogen atoms. Refinement by block-diagonal, least-squares methods[11] was completed with $R = 0.057$, $R' = 0.048$[10] for all data, weighted $w = 0.614/\sigma^2(F)$.

In the final cycles of refinement, all non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms were placed in ideal positions (methyl groups staggered) with isotropic thermal parameters set to ride on those of their bonded carbon atoms. There were no peaks of significance in the final difference map. Final atom coordinates are in Table 4.

Scattering factors for neutral atoms were used and taken from ref. 12. All computer programs used in this analysis have been noted above and in ref. 13 and were run on a MicroVAX II machine in the Nitrogen Fixation Laboratory.

Crystal Structure Analysis of $[W(SC_6H_2Pr^i_3\text{-}2,4,6)(CO)_2(PMe_2Ph)_2]$.—*Crystal data.* $C_{48}H_{68}O_2P_2S_2W$, $M = 987.0$, monoclinic, space group $P2_1/n$ (equivalent to no. 14), $a = 11.255(3)$, $b = 17.273(2)$, $c = 25.258(3)$ Å, $\beta = 93.81(1)^\circ$, $U = 4899.0$ Å^3, $Z = 4$, $D_c = 1.338$ g cm^{-3}, $F(000) = 2032$, μ(Mo-Kα) = 24.6 cm^{-1}.

In an analysis similar to that above, accurate cell dimensions of a crystal, size 0.13 × 0.30 × 0.25 mm, were refined from the goniometer settings of 25 reflections having $10 < \theta < 15^\circ$ on a CAD4 diffractometer. Diffraction intensities were measured to $\theta_{max} = 27^\circ$. Corrections for Lorentz polarisation effects and absorption[14] were applied; no deterioration correction was necessary. Of 9035 unique reflections, the 6094 'observed' data having $I > 3\sigma_I$ were used in the analysis.

Structure solution was by standard heavy-atom methods, and refinement by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms. The analysis shows the complex to be virtually isostructural with the molybdenum complex, except in two regions of disorder; large thermal parameters indicated disorder in one phenyl group, where idealised phenyl rings were included in two orientations with occupation factors refining to 0.405(2) and 0.595(2), and in one isopropyl group disorder was identified but not resolved. Hydrogen atoms were included in idealised positions. Refinement was concluded with $R = 0.035$ and $R' = 0.041$[10] for the observed data, weighted $w = (\sigma_F^2 + 0.005F^2)^{-1}$. The highest peak in the final difference map was 0.57e Å^{-3}, close to the W atom.

Computations used the SDP package[15] on a PDP11/23 machine, and the SHELX[10] and SHELXS[16] programs on an Apollo computer at the University of Toronto.

Additional material for both structures available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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