Five-co-ordinate Complexes $[MoH(SC_6H_2R_3\text{-}2,4,6)_3(PR'Ph_2)]$ (R = Me or Pr^i, R′ = Me or Et) and their Reactions with Nitrogen Donors. Crystal Structures of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)]$, $[MoH(NC_5H_4S\text{-}2)_2(SC_6H_2Pr^i_3\text{-}2,4,6)(PEtPh_2)]$ and $[PPh_4][MoO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$†

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The complexes $[MoH(SC_6H_2R_3\text{-}2,4,6)_3(PR'Ph_2)]$ **1** (R = Me or Pr^i, R′ = Me or Et) have been prepared by reaction of $HSC_6H_2R_3\text{-}2,4,6$ with $[MoH_4(PR'Ph_2)_4]$ or *trans*-$[Mo(N_2)_2(PR'Ph_2)_4]$. Compound **1** (R = Pr^i, R′ = Me) reacted with N-donor ligands L (C_5H_5N, $3\text{-}MeC_5H_4N$, $3,5\text{-}Me_2C_5H_3N$ or C_3H_3NS) to give the adducts **2**, $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3L(PMePh_2)]$. The crystal structure of the analogue $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)]$ showed the compound to have a trigonal girdle of thiolate ligands with the pyridine and PMe_2Ph ligands in essentially apical positions. Reaction of **1** (R = Pr^i, R′ = Et) with $NC_5H_4SH\text{-}2$ gave the seven-co-ordinate complex $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)(NC_5H_4S\text{-}2)_2(PEtPh_2)]$, shown by X-ray crystallography to have an essentially pentagonal-pyramidal geometry with the hydride located in the equatorial plane. Spectroscopic data for the compounds are discussed in terms of their structures. Complex **1** (R = Pr^i, R′ = Et) exchanges hydride for deuteride on treatment with deuterium gas in benzene at 20 °C. Treatment of **1** (R = Pr^i, R′ = Me) in MeOH with $LiBEt_3H$, followed by $[PPh_4]Cl$, gave $[PPh_4][MoO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$, shown by X-ray crystallography to have an anion with square-pyramidal geometry and an apical oxide-ligand.

Compounds of molybdenum with hydride and sulfur-donor ligands are of importance in understanding the mechanism of such catalytic processes as nitrogen fixation[1] and hydrodesulfurisation.[2] In earlier papers we have described three series of molybdenum complexes containing hydride and thiolate ligands, $[MoH(SC_6H_2R_3\text{-}2,4,6)(Ph_2PCH_2CH_2PPh_2)_2]$ (R = Me or Pr^i),[3] $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PR'_2Ph)_2]$[4,5] and $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PR'Ph_2)]$ **1** (R′ = Me or Et).[6] We have described the structure and chemical reactions of $[MoH(SC_6H_2R_3\text{-}2,4,6)(Ph_2PCH_2CH_2PPh_2)_2]$ and $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PR'_2Ph)_2]$ in detail,[3–5] and some of those of compounds **1** in outline.[7] Here we give full details of the preparation of compounds **1**, their physical properties and addition reactions in which the hydride ligand is retained at the metal, or exchanged for deuterium, in the products. The adventitious formation of the anion $[MoO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]^-$ is also described.

Results and Discussion

Preparation of Complexes **1**.—The co-ordinatively unsaturated thiolatohydride complexes of molybdenum(IV) $[MoH(SC_6H_2R_3\text{-}2,4,6)_3(PR'Ph_2)]$ **1** (R = Me or Pr^i, R′ = Me or Et), which are the focus of this paper, have been obtained by reaction, at 0 °C, of the thiols $HSC_6H_2R_3\text{-}2,4,6$ (R = Me or Pr^i) with the hydrides $[MoH_4(PR'Ph_2)_4]$ or their dinitrogen analogues *trans*-$[Mo(N_2)_2(PR'Ph_2)_4]$, as illustrated in Scheme 1. Our earlier work has shown that fine control of the steric bulk around the metal centre determines the geometry and stoichiometry of the product formed by the above type of reaction.[3,4] Sterically hindered ligands are required to produce monomeric complexes and to help stabilise hydrides. The nature of the phosphine also has a marked effect on the product outcome. Thus with less bulky phosphines such as PMe_2Ph the products in Scheme 1 are six-co-ordinate complexes such as $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$.[4] The combined steric bulk of the thiol and phosphine limits the co-ordination number at the metal and this effect, presumably together with π-electron release from the sulfur-donor atoms, also stabilises the formally 12-electron hydrides **1**.

$$trans\text{-}[Mo(N_2)_2(PMePh_2)_4] + 3R''SH \longrightarrow [MoH(SR'')_3(PMePh_2)] + 2N_2 + 3PMePh_2 + H_2$$

$$[MoH_4(PEtPh_2)_4] + 3R''SH \longrightarrow [MoH(SR'')_3(PEtPh_2)] + 3H_2 + 3PEtPh_2$$

Scheme 1 Reactions to form five-co-ordinate hydride complexes. $R'' = C_6H_2Me_3\text{-}2,4,6$ or $C_6H_2Pr^i_3\text{-}2,4,6$

Scheme 1 shows examples of the technique of oxidative addition to low-valent molybdenum complexes (with concomitant loss of H_2 or N_2) which we have used to prepare the range of thiolatehydrides mentioned above. We have investigated the mechanism of the reaction used to produce $[MoH(SC_6H_2R_3\text{-}2,4,6)(Ph_2PCH_2CH_2PPh_2)_2]$ from $[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$ and thiol in detail,[3] and the reactions of Scheme 1 presumably have closely related mechanisms. When a deuteriated thiol is used in these reactions the product is the deuteride complex (Table 1 and Experimental section). If two equivalents of $HSC_6H_2Pr^i_3\text{-}2,4,6$ are added instead of three and toluene is used as the solvent in the reaction of $[MoH_4(PEt$-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

$\mathrm{Ph_2)_4}$] then an unidentified complex is detected by ^{31}P-{^{1}H} NMR spectroscopy by its singlet ^{31}P resonance at δ −59.4 *vs.* P(OMe)$_3$; on addition of a third equivalent of the thiol the product **1** can be isolated.

Complexes **1** are green, monomeric, diamagnetic crystalline solids which are air-sensitive and thermally unstable, as might be expected from their unsaturation. The thermal instability is a result of the tendency of these complexes to undergo S–C bond cleavage,[6] which will be discussed in other publications. The $\mathrm{SC_6H_2Me_3}$-2,4,6 complexes are more difficult to isolate and are more air-sensitive than their analogues with the larger $\mathrm{SC_6H_2Pr^i_3}$-2,4,6 ligand. This is presumably a steric effect. The observation of the intense ion corresponding to [$^{98}\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)$_3$(PEtPh$_2$) − H]$^+$ by FAB mass spectrometry of **1** (R = Pr^i, R′ = Et) in 3-nitrobenzyl alcohol helps to confirm the mononuclear formulation. The spectrum of this complex in 3-nitrophenyl octyl ether shows only the S–C bond cleavage product[6] [$^{98}\mathrm{Mo(SC_6H_2Pr^i_3}$-2,4,6)$_2$(PEtPh$_2$)-S]$^+$. Selected spectroscopic properties of complexes **1** are shown in Table 1. The hydride ligand gives rise to a doublet in the ^{1}H NMR spectrum which is seen at δ 3.3 (relative to SiMe$_4$) for [$\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)$_3$(PEtPh$_2$)] (Fig. 1), but which is obscured by organic ligand resonances in the spectra of other complexes of the series. The ^{2}H resonance of [$\mathrm{Mo^2H(SC_6H_2Pr^i_3}$-2,4,6)$_3$(PEtPh$_2$)] is observed as a doublet at δ 3.4 [^2J(PMo^{2}H) = 14 Hz]. The undecoupled ^{31}P NMR spectra of **1** show the expected coupling to the hydride or deuteride as appropriate and hydride stretching frequencies occur in the range 1858–1940 cm^{-1} in their IR spectra (Table 1).

The ^{1}H NMR spectra of the compounds [$\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)$_3$(PR′Ph$_2$)] show characteristic resonances due to the methine protons in the isopropyl groups of the thiophenolate ligands as five septets, two to low field of the other three, in a ratio 2 : 2 : 1 : 2 : 2. For example, these septets occur at δ 4.27, 4.06,

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

Complex	^{1}H NMR[a]	^{31}P NMR[b]	IR[c]/cm^{-1}
[$\mathrm{MoH(SC_6H_2Me_3}$-2,4,6)$_3$(PMePh$_2$)]	—	−78.7(d, 87.2)	1940
[$\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)$_3$(PMePh$_2$)]	—	−78.1(d, 87.2)	1880
[$\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)$_3$(PEtPh$_2$)]	3.28(d, 87.0)	−69.0(d, 87.0)	1858
[$\mathrm{Mo^2H(SC_6H_2Pr^i_3}$-2,4,6)$_3$(PEtPh$_2$)]	3.4(d, 14.0)[d]	−69.7(t, 14.0)[e]	—
[$\mathrm{MoH(SC_6H_2Me_3}$-2,4,6)$_3$($\mathrm{C_5H_5N}$)(PMePh$_2$)]	—	−82.8(br)	1900
[$\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)$_3$($\mathrm{C_5H_5N}$)(PMePh$_2$)]	3.0(d, 84)	−87.1(d, 87.0)	1890
[$\mathrm{Mo^2H(SC_6H_2Pr^i_3}$-2,4,6)$_3$($\mathrm{C_5H_5N}$)(PMePh$_2$)]	3.0(d, 13.6)[d]	−87.0(t, 13.6)[e]	—
[$\mathrm{Mo^2H(SC_6H_2Pr^i_3}$-2,4,6)$_3$($\mathrm{C_5H_5N}$)(PEtPh$_2$)]	2.9(d, 11)[d]	—	—
[$\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)$_3$(3-$\mathrm{MeC_5H_4N}$)(PMePh$_2$)]	—	−87.4(d, 87.2)	1900
[$\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)$_3$($\mathrm{C_3H_3NS}$)(PMePh$_2$)]	—	−86.9(d, 76.3)	1880
[$\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)($\mathrm{NC_5H_4S}$-2)$_2$(PEtPh$_2$)]	—	−92.4(d, 103.5)	1815
[$\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)$_3$(3,5-$\mathrm{Me_2C_5H_3N}$)(PMePh$_2$)]	—	−88.8(d, 92.7)	—

[a] Hydride resonance where observable, see text; δ in ppm relative to SiMe$_4$ (d = doublet, br = broad), ^2J(PMoH)/Hz. [b] δ in ppm relative to P(OMe)$_3$, ^2J(PMoH)/Hz [P(OMe)$_3$ has δ − 140.4 relative to 85% H$_3$PO$_4$ (aq)]. [c] ν(Mo–H), KBr disc spectra. [d] ^{2}H resonance. [e] t = 1 : 1 : 1 triplet; ^2J(PMo^{2}H).

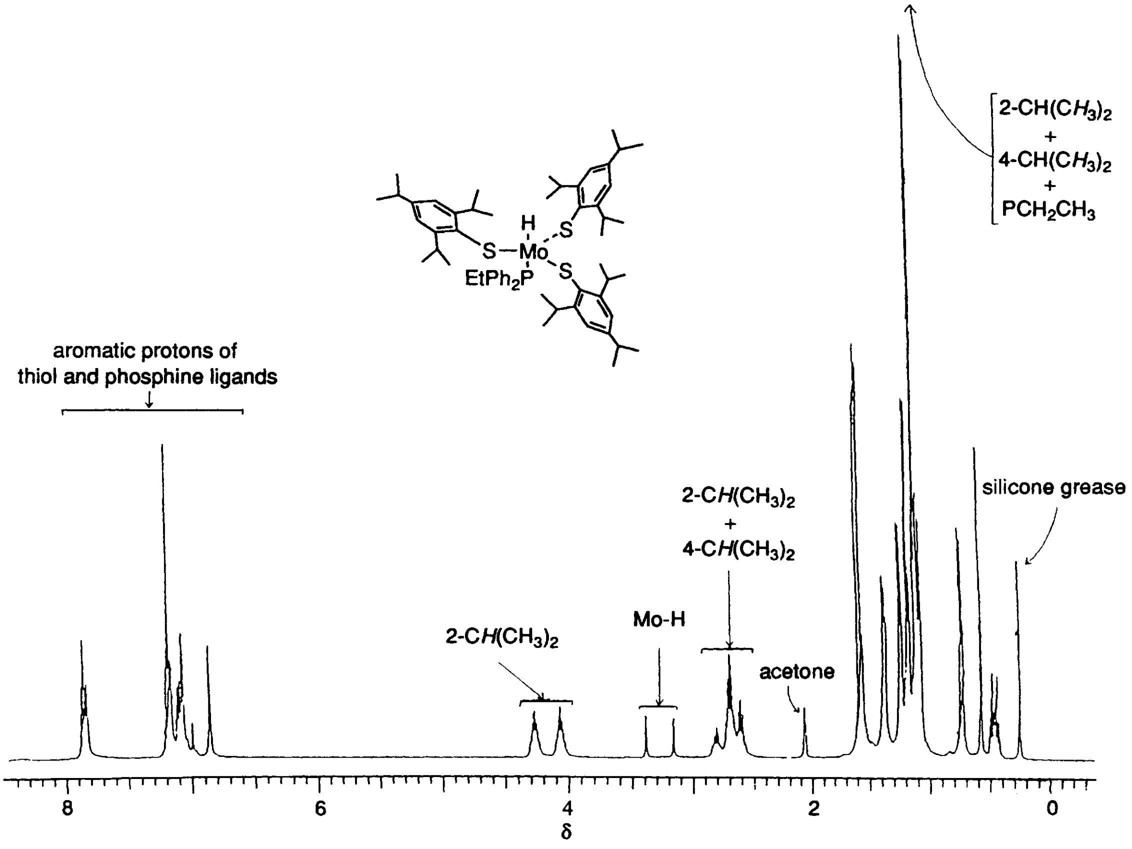


Fig. 1 Proton NMR spectrum of [$\mathrm{MoH(SC_6H_2Pr^i_3}$-2,4,6)$_3$(PEtPh$_2$)] in C$_6D_6$ (400 MHz)

2.82, 2.72 and 2.62 with $^3J_{HH}$ 6.8 Hz for **1** (R = $\mathrm{Pr^i}$, R' = Et) (see Fig. 1). This pattern indicates that one of the three equatorial thiolate ligands is inequivalent to the others. This 'two-up one-down' arrangement, *i.e.* the staggering of three equatorial thiolates, has already been described for the hydride complex $[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$[4,5] and is well documented in molybdenum thiolate complexes generally.[8] This configuration minimises the ligand–ligand repulsions of the bulky thiolates.

In view of these observations and the general tendency of five-co-ordinate tris(thiolate) complexes to favour a girdle of three thiolate ligands,[4–8] the most likely structure for complexes **1** is as shown in Fig. 2. Unfortunately the sensitivity of these compounds has precluded growth of crystals suitable for X-ray structural determination to confirm this suggestion.

Exchange with Deuterium.—A notable reaction of $[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PEtPh_2)}]$ is its ability to catalyse the exchange of hydrogen and deuterium.[7] It reacts in benzene at 20 °C with deuterium gas (1 atm, *ca.* 10^5 Pa) to produce the deuteride complex [doublet, δ 3.4, $^2J(\mathrm{P^2H})$ = 14 Hz] and $\mathrm{H^2H}$ gas [reaction (1)]. Exchange is essentially complete in 4 h

$$[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PEtPh_2)}] + {}^2\mathrm{H_2} \longrightarrow [\mathrm{Mo^2H(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PEtPh_2)}] + \mathrm{H^2H} \quad (1)$$

with a half-life of 1.5 h, as indicated by a ^{2}H NMR study. There is no reaction in the solid state over 12 h. The product of reaction (1) does not have an Mo–H stretch but the presence of an Mo–^{2}H stretch, expected at about 1313 cm^{-1}, could not be verified because ligand vibrations mask this region of the IR spectrum. Attempts to induce exchange in the complex $[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PMePh_2)}]$ have not been successful under 1 atm $^2\mathrm{H_2}$.

Hydrogen-2 NMR spectroscopy shows that the deuteride ligand is the only site of deuterium enrichment in the product. We have demonstrated that the mechanism for the reaction does not involve reductive elimination of the thiol and consequent oxidative addition of $^2\mathrm{HSC_6H_2Pr^i{}_3\text{-}2,4,6}$, by addition of an excess of the latter to a solution of the hydride, which does not result in deuterium enrichment of the complex.

Reaction (1) might involve an intermediate containing a dideuteridehydride **A**, a (dideuterium)hydride **B**, or dideuteridethiol **C**; the final step in the process is reductive elimination of hydrogendeuteride from the metal centre.

We attempted to detect the all-hydrogen analogue of intermediate **B**, $[\mathrm{MoH(H_2)(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PEtPh_2)}]$, by means of measurement of the NMR relaxation time (T_1) of the hydride in the complex $[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PEtPh_2)}]$ in $\mathrm{C_6D_6}$ under $\mathrm{N_2(g)}$ and then under $\mathrm{H_2(g)}$. Formation of even traces of the dihydrogen complex would cause a significant change in the T_1 value as demonstrated by Gusev *et al.*[9] for the complexes $[\mathrm{RuH(Cl)(CO)(PPr^i{}_3)_2}]$ and $[\mathrm{RuH(H_2)Cl(CO)(PPr^i{}_3)_2}]$. However, the T_1 values of the two peaks of the doublet for the hydride at δ 3.3 maintained the same values (0.5 s at 400 MHz, 20 °C) under the two gases and so there was no evidence for intermediate **B**. Similarly there was no change for a $[^2\mathrm{H_8}]$toluene solution of the complex under $\mathrm{H_2}$ at −69 °C ($T_1 \approx 0.9$ s).

Although no intermediate has been observed in this reaction examples of this type of exchange and of species which resemble **A**–**C** can be found in the literature. Many dihydrogen complexes have been seen to undergo exchange with deuterium,[10] as demonstrated by $[\mathrm{Cr(H_2)(CO)_5}]$ for example.[11] There are examples of stable, metal-bound thiol complexes such as $[\mathrm{Ru(C_5H_5)(HSBu^t)(Ph_2PCH_2PPh_2)}]^+$,[12] $[\mathrm{Ru(NH_3)_5(HSEt)}]^{2+}$ [13] and $[\mathrm{Cr(CO)_5(HSBu)}]$.[14] Darensbourg *et al.*[15] published evidence for a three-centre, metal–thiol interaction in $[\mathrm{Fe(CO)_3(\eta^2\text{-}HSMe)(PEt_3)}]^+$ which can be considered as an arrested intermediate in the production of thiolatohydride complexes. Examples of complexes losing dihydrogen from a metal–dithiol complex[16] or from thiolhydride complexes are known,[17,18] and loss of $\mathrm{H_2}$ has been observed in the reaction between a thiolatohydride complex and a small thiol to produce a dithiolate complex.[3]

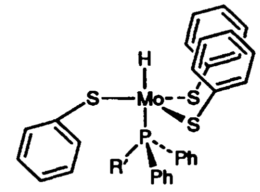
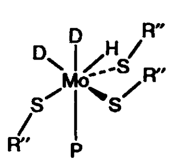
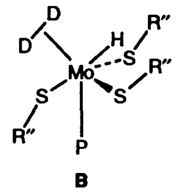


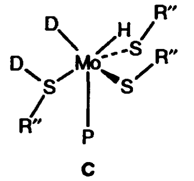
Fig. 2 Proposed structure of compounds **1**. Aryl substituents omitted for clarity



A



B



C

Reaction of Thiolatohydride Complexes with Nitrogen Donors.—Complexes **1** were treated with nitrogen donors in order to produce molybdenum centres containing co-ordinated sulfur and nitrogen, and also retaining their hydride. These centres would then have a ligand environment more closely resembling that of the molybdenum centre in nitrogenase ($\mathrm{NS_3O_2}$ ligation),[19] assuming that this centre is able to react to give hydrides during the nitrogenase function.[20] Pyridines and thiazole were found to add to **1**; the product with pyridine itself has been the most thoroughly studied. The reaction proceeds in tetrahydrofuran (thf) solution with a slight colour change from green to brown-green and typically is complete in under 5 min. Precipitation of the products with methanol produces bright green, microcrystalline, air-stable solids **2**, $[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3L(PMePh_2)}]$ (L = $\mathrm{C_5H_5N}$, 3-$\mathrm{MeC_5H_4N}$ or 3,5-$\mathrm{Me_2C_5H_3N}$). The thiazole complex has very similar physical properties to the pyridine adducts and it is therefore assumed that the thiazole is N-bound. The physical and spectroscopic properties of these complexes are detailed in Table 1.

Fast atom bombardment (FAB) mass spectrometry of complexes **2** reveals them to be monomeric and infrared spectroscopy shows them to have weak metal–hydride stretching absorptions in the range 1874–1940 cm^{-1}. The ν(Mo–H) values are to slightly higher wavenumber for the N-donor adducts than for their five-co-ordinate parent complexes (Table 1). The presence of a metal hydride is confirmed by NMR spectroscopy. For example, the hydride resonance of $[\mathrm{MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)}]$ occurs at δ 3 [doublet, ^2J(PMoH) = 84 Hz], the two lines in the signal coinciding with two of the multiplets assigned to the 2-methine protons of the thiolate isopropyl groups. Selective homonuclear decoupling of the methyl resonances in the isopropyl groups collapses the methine septets into singlets. This allows the hydride signal to be resolved as a doublet. Fig. 3 shows the ^{1}H NMR spectrum of the methine region before and after homonuclear decoupling. This complex shows a doublet at δ −87.1 [relative to $\mathrm{P(OMe)_3}$), ^2J(PMoH) = 87 Hz] in its proton-coupled ^{31}P NMR spectrum.

The ^{2}H NMR spectrum of the complex $[\mathrm{Mo^2H(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PEtPh_2)}]$ contains only one resonance, a doublet at δ 3 [$^2J(\mathrm{PMo^2H})$ = 13.6 Hz], arising from the deuteride ligand. As expected,[21] this resonance has a similar chemical shift, but smaller coupling constant (by $\gamma_{^2\mathrm{H}}/\gamma_{\mathrm{H}}$), than the hydride resonance of the undeuteriated analogue.

As in the case of the five-co-ordinate parent species, the ^{1}H NMR resonances of complexes **2** in the methine region reveal information on the geometry of the thiolate ligands. For example, $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)}]$ shows five incompletely resolved septets in the region δ 2–4. These correspond to five inequivalent methine protons in the isopropyl groups of the thiolate ligands. As for the five-co-ordinate hydride complexes, this is interpreted as a set of two 4-methine resonances (centred at δ 3.68 and 4.08, respectively) and three resonances due to the 2-methine groups in the complex (centred at δ 2.66, 2.88 and 3.77, respectively), consistent with three equatorial thiolate ligands adopting a 'two-up one-down' conformation.[4]

Compounds **2** (L = $\mathrm{1\text{-}MeC_3H_3N_2}$ or $\mathrm{C_3H_3NS}$), the spectral properties of which are very similar to those of the pyridine adducts (Table 1), are assigned the same geometry as their analogues (see below). Other analogues of complexes **2** have been made with the smaller phosphine ($\mathrm{PMe_2Ph}$) by a different route. For example treatment of the six-co-ordinate complex $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$ with neat pyridine at 60 °C leads to the formation of $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$ by phosphine displacement.[5] The structure of this complex has been determined in order to confirm the general structural features of this family of complexes, as deduced spectroscopically above and elsewhere.[5,7]

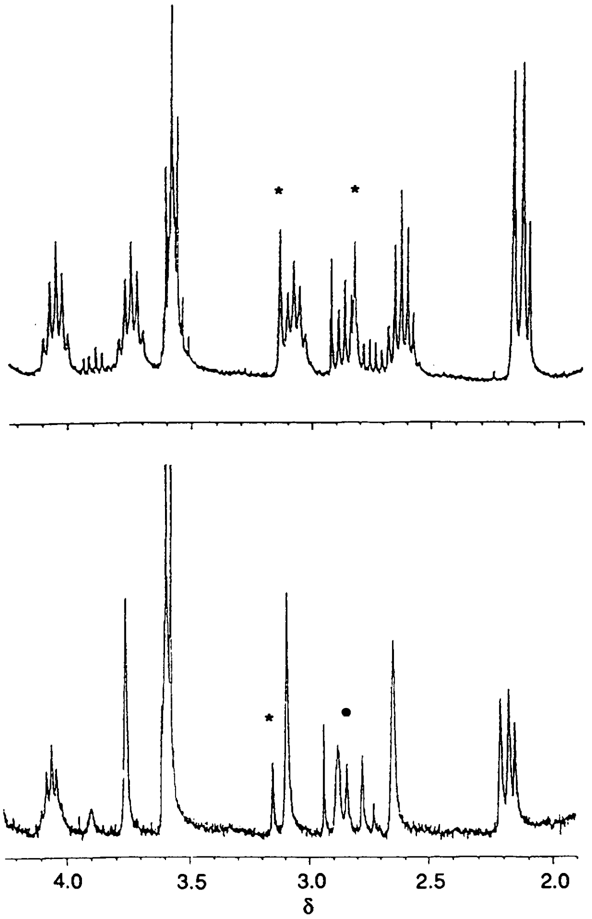


Fig. 3 Proton NMR spectrum of $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)}]$, showing the effect of selective homonuclear decoupling (lower spectrum). Hydride resonances are marked by asterisks

Crystal Structure of $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$.—The single-crystal structure of $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$ is shown in Fig. 4; atomic coordinates and bond dimensions are in Tables 2 and 3. The Mo atom lies on a mirror plane of symmetry; the thiophenolate ligand of S(1) lies astride this plane, and the pyridine ligand lies in it. In the phosphine ligand the phenyl group is disordered, tilted one way or the other out of the symmetry plane, with the two methyl groups related (approximately, perhaps with slight disorder) by the plane. The ligand of S(2) is out of the plane, related to the ligand of S(2′) by the mirror symmetry. The three thiophenolate ligands form the equatorial plane of the molybdenum co-ordination sphere and adopt the 'two-up one-down' conformation as proposed above. The pyridine and phosphine ligands occupy apical co-ordination sites, but subtend an N–Mo–P angle of 158.4(2)°.

The hydride was not located in this determination but its presence has been demonstrated spectroscopically. We estimate that it should lie on the mirror plane and roughly in the equatorial plane between the S(2) and S(2′) atoms; the angle subtended at the Mo atom by these S atoms is 129.5(1)°, considerably larger than the other S–Mo–S angles [115.2(1)°], and sufficiently wide to accommodate the hydride ligand. [See structure of complex **3** below, in which a P–Mo–S angle of 123.9(1)° accommodates a hydride.]

The large ^2J(P–M–H) coupling constant could be taken to indicate that the hydride ligand is located above the equatorial plane, with an obtuse angle to the phosphine and *cis* to the pyridine, as we have suggested in an earlier publication.[5] However, later NMR studies and a low-temperature crystal structure determination of the complex $[\mathrm{WH(SeC_6H_3Pr^i_2\text{-}2,6)_3(PMe_2Ph_2)}]$[22] have demonstrated that the most likely position of the hydride in these compounds is essentially *cis* to the phosphine ligand[22] but with an H–Mo–P angle of less than 90° (see discussion of complex **3**). The 'large coupling constant' criterion[5] of hydride location *trans* to phosphine is further demonstrated to be unreliable in the study which now follows.

Reaction with Pyridine-2-thiol.—In order to further vary the co-ordination of sulfur and nitrogen around the molybdenum

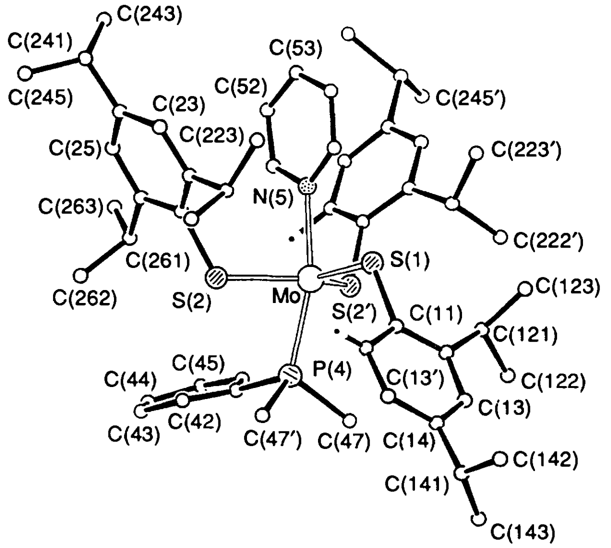


Fig. 4 Molecular structure of $[\mathrm{MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)}]$, indicating the atom numbering scheme. For clarity, the alternative sites for disordered groups are not shown, nor are two of the isopropyl groups in the S(1) and S(2′) thiolate ligands

Table 2 Final atomic coordinates (fractional ×10⁴) for [$MoH(SC_6H_2Pr^i_3$-2,4,6$)_3(C_5H_5N)(PMe_2Ph)$] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	s.o.f.*
Mo	4894.7(5)	2500	5452.7(6)	
S(1)	3789(2)	2500	4628(2)	
C(11)	3980(6)	2500	3532(6)	
C(12)	4050(4)	1905(4)	3107(5)	
C(121)	3951(5)	1256(4)	3525(5)	
C(122)	4463(8)	735(6)	3166(7)	
C(123)	3125(7)	1061(6)	3525(9)	
C(13)	4169(5)	1937(6)	2244(5)	
C(14)	4236(8)	2500	1797(9)	
C(141)	4306(10)	2500	845(8)	
C(142)	3602(13)	2500	408(16)	0.6
C(143)	4878(22)	2066(17)	529(23)	0.3
C(144)	3565(21)	2082(19)	512(26)	0.2
C(145)	4990(28)	2500	485(29)	0.4
C(146)	4379(55)	1794(47)	423(62)	0.2
S(2)	5331(1)	3519(1)	5844(1)	
C(21)	4922(5)	3889(4)	6765(5)	
C(22)	4201(5)	4176(4)	6733(5)	
C(221)	3735(4)	4209(4)	5936(5)	
C(222)	3919(7)	4834(6)	5483(8)	
C(223)	2880(5)	4150(6)	6084(7)	
C(23)	3925(6)	4485(5)	7422(6)	
C(24)	4329(8)	4540(5)	8156(7)	
C(241)	4041(12)	4892(8)	8926(8)	
C(242)	4129(28)	5671(17)	8771(24)	0.5
C(244)	3749(23)	4641(18)	9569(24)	0.5
C(243)	3943(16)	4346(15)	9662(18)	0.5
C(245)	4502(13)	5506(13)	9044(16)	0.5
C(247)	3831(87)	5391(67)	9135(80)	0.2
C(248)	3327(47)	4907(45)	9137(64)	0.2
C(25)	5031(8)	4256(5)	8169(6)	
C(26)	5361(5)	3938(5)	7505(6)	
C(261)	6155(6)	3659(6)	7521(8)	
C(262)	6734(7)	4170(7)	7301(11)	
C(263)	6360(9)	3398(10)	8387(11)	
P(4)	6054(2)	2500	4673(2)	
C(41)	6929(9)	2582(19)	5267(13)	0.5
C(42)	7237(14)	3207(20)	5330(21)	0.5
C(43)	7904(14)	3257(17)	5802(15)	0.5
C(44)	8191(17)	2774(23)	6330(31)	0.5
C(45)	7835(13)	2168(23)	6336(24)	0.5
C(46)	7199(16)	2107(21)	5815(18)	0.5
C(47)	6184(7)	1835(6)	3927(8)	
N(5)	4129(5)	2500	6571(6)	
C(51)	4459(7)	2500	7328(7)	
C(52)	4068(8)	2500	8061(8)	
C(53)	3297(8)	2500	8036(7)	
C(54)	2930(7)	2500	7279(7)	
C(55)	3370(6)	2500	6577(7)	

* Site occupancy factor, if different from 1.0.

Table 3 Selected molecular dimensions (lengths in Å, angles in °) in [$MoH(SC_6H_2Pr^i_3$-2,4,6$)_3(C_5H_5N)(PMe_2Ph)$] with e.s.d.s in parentheses

(*a*) About the Mo atom			
Mo–S(1)	2.356(3)	Mo–P(4)	2.396(3)
Mo–S(2)	2.326(2)	Mo–N(5)	2.244(9)
S(1)–Mo–S(2)	115.2(1)	S(1)–Mo–N(5)	87.2(2)
S(1)–Mo–P(4)	114.4(1)	S(2)–Mo–N(5)	89.0(1)
S(2)–Mo–P(4)	81.9(1)	P(4)–Mo–N(5)	158.4(2)
S(2)–Mo–S(2′)	129.5(1)		
(*b*) In the thiolate ligands			
S(1)–C(11)	1.789(11)	S(2)–C(21)	1.810(8)
Mo–S(1)–C(11)	113.3(3)	Mo–S(2)–C(21)	118.0(3)
(*c*) In the phosphine ligand			
P(4)–C(41)	1.821(18)	P(4)–C(47)	1.835(13)
Mo–P(4)–C(41)	116.7(7)	C(41)–P(4)–C(47)	107.7(4)
Mo–P(4)–C(47)	116.5(5)	C(47)–P(4)–C(47′)	96.9(6)
(*d*) In the pyridine ligand			
N(5)–C(51)	1.345(15)	N(5)–C(55)	1.339(14)
Mo–N(5)–C(51)	117.5(7)	C(51)–N(5)–C(55)	115.2(10)
Mo–N(5)–C(55)	127.3(7)		

Primed atoms are of the opposite half of the molecule, with coordinates $x, \frac{1}{2} - y, z$.

centre in compounds **1**, **1** (R = Prⁱ, R′ = Et) was treated with NC_5H_4SH-2. The reaction in thf solution at 0 °C produced a blood-red solution. Slow crystallisation after addition of cold methanol produced large red crystals having a pronounced (Mo–H) stretching absorption at 1815 cm^{-1}. The ^{31}P NMR spectrum of the product revealed a doublet at δ −92.4 with a large hydride–phosphorus coupling [^2J(PMoH) = 103.5 Hz] which collapsed to a singlet with proton decoupling. Elemental microanalysis and mass spectrometry are consistent with the formulation of the product as [$MoH(SC_6H_2Pr^i_3$-2,4,6)(NC_5H_4S-2$)_2(PEtPh_2)$] **3**. The reaction to form this product presumably proceeds *via* two oxidative additions of pyridinethiol and the reductive elimination of two molecules of $HSC_6H_2Pr^i_3$-2,4,6 (or one molecule of dihydrogen and the aryl disulfide) [reaction (2)]. The ^1H NMR spectrum of **3** consists

$$[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PEtPh_2)] + 2\,NC_5H_4SH\text{-}2 \longrightarrow$$
$$[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)(NC_5H_4S\text{-}2)_2(PEtPh_2)] +$$
$$2HSC_6H_2Pr^i_3\text{-}2,4,6\ [\text{or } H_2 + (2,4,6\text{-}Pr^i_3C_6H_2S)_2] \quad (2)$$

of a complex set of signals, from which the hydride resonance was not resolved.

Crystal Structure of Compound **3**.—A single-crystal structure determination of complex **3** showed it to have a distorted pentagonal-bipyramidal co-ordination geometry. We have briefly reported this[23] and here present the full details. The structure is shown in Fig. 5 with atomic coordinates and bond dimensions in Tables 4 and 5.

From the low-angle diffraction data it was possible to locate the hydride ligand in the structure; it lies in the equatorial plane between the phosphorus P(3) and the pyridinethiolate sulfur S(42) atoms. The hydride and phosphine ligands are thus adjacent [H–Mo–P angle of 65(1)°]; this is not the configuration expected from the ^{31}P NMR spectrum of the complex which shows a large ^2J(PMoH) value (103.5 Hz), thought to be more consistent with a *trans* arrangement of ligands (as discussed above). This confirms the unreliability of ^2J(PMoH) values as a criterion of hydride/phosphine configurations.[5] The proximity of the hydride and P(3) nuclei might allow considerable through-space coupling. The large *J*(PMoH) value of [$MoH(SC_6H_2Pr^i_3$-2,4,6$)_3(C_5H_5N)(PMe_2Ph)$] (see above) and its analogues[5] could also be accounted for by the close approach of the hydride and phosphorus nuclei allowing through-space coupling, *i.e.* the hydride ligand lies off the trigonal MoS_3 plane, towards the phosphorus. This is the hydride position observed in [$WH(SeC_6H_3Pr^i_2$-2,6$)_3$-$(PMe_2Ph)_2$].[22]

Table 4 Final atomic coordinates (fractional × 10^4) for $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)(NC_5H_4S\text{-}2)_2(PEtPh_2)]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	7 401.8(2)	114.8(1)	8 540.8(2)	P(3)	7 322.2(5)	310.3(4)	6 551.6(6)
N(11)	6 966(2)	−872(1)	8 136(2)	C(31a)	7 301(2)	−426(1)	5 757(2)
C(12)	6 053(2)	−829(2)	7 741(3)	C(32a)	8 104(3)	−739(2)	5 882(3)
S(12)	5 702.8(6)	−52.7(4)	7 714.9(9)	C(33a)	8 109(3)	−1 329(2)	5 402(3)
C(13)	5 511(3)	−1 360(2)	7 374(3)	C(34a)	7 326(4)	−1 614(2)	4 806(3)
C(14)	5 935(4)	−1 930(2)	7 436(4)	C(35a)	6 531(3)	−1 302(2)	4 652(4)
C(15)	6 850(4)	−1 972(2)	7 828(4)	C(36a)	6 513(3)	−717(2)	5 129(3)
C(16)	7 362(3)	−1 433(2)	8 176(3)	C(31b)	8 277(2)	738(1)	6 295(3)
S(2)	7 443.9(5)	1 191.0(4)	8 763.6(6)	C(32b)	8 954(2)	998(2)	7 192(3)
C(21)	7 426(2)	1 483(1)	10 141(2)	C(33b)	9 674(3)	1 312(2)	7 005(4)
C(22)	6 611(2)	1 657(1)	10 319(2)	C(34b)	9 721(3)	1 382(2)	5 929(5)
C(23)	6 641(2)	1 950(1)	11 350(3)	C(35b)	9 052(4)	1 137(3)	5 010(4)
C(24)	7 446(2)	2 080(1)	12 208(3)	C(36b)	8 315(3)	815(2)	5 189(3)
C(25)	8 243(2)	1 883(1)	12 009(2)	C(37)	6 332(3)	724(2)	5 576(3)
C(26)	8 259(2)	1 590(1)	11 000(2)	C(38)	6 159(3)	1 375(2)	5 941(3)
C(221)	5 704(2)	1 552(2)	9 393(3)	N(41)	7 215(2)	−21(1)	10 245(2)
C(222)	4 922(3)	1 414(2)	9 875(4)	C(42)	8 048(3)	−194(1)	10 898(3)
C(223)	5 477(3)	2 108(2)	8 583(3)	S(42)	8 742.8(6)	−262.2(4)	9 996.7(7)
C(241)	7 492(3)	2 439(2)	13 298(3)	C(43)	8 257(3)	−300(2)	12 061(3)
C(242)	7 444(4)	3 138(2)	13 078(4)	C(44)	7 588(4)	−239(2)	12 563(3)
C(243)	6 797(5)	2 247(3)	13 819(5)	C(45)	6 726(4)	−65(2)	11 909(4)
C(261)	9 156(2)	1 418(2)	10 821(3)	C(46)	6 565(3)	43(2)	10 741(3)
C(262)	9 861(3)	1 164(2)	11 911(3)	H(5)	8 387(28)	−118(16)	8 177(34)
C(263)	9 533(3)	1 964(2)	10 318(4)				

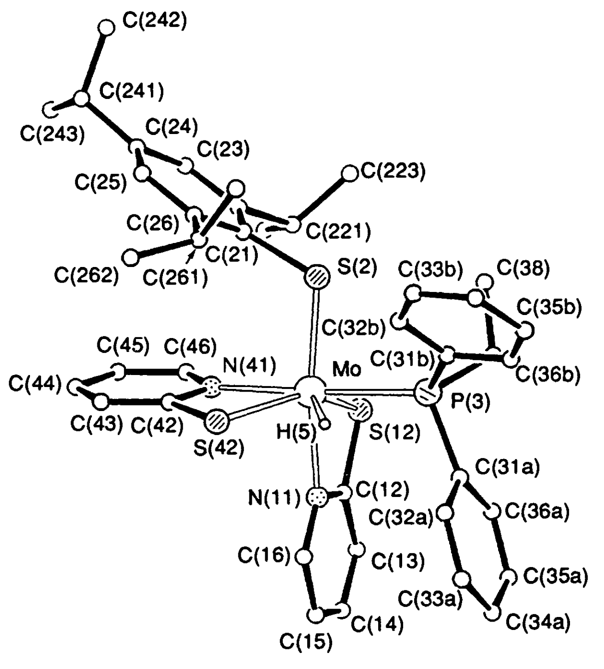


Fig. 5 Molecular structure of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)(NC_5H_4S\text{-}2)_2(PEtPh_2)]$ **3**, indicating the atom numbering scheme

Completing the equatorial pentagonal arrangement are N(41) of the same pyridinethiolate ligand as S(42), and S(12) of the second such ligand. The last atom is displaced considerably from the equatorial plane since the pyridine nitrogen N(11) of that ligand occupies an apical site. This pattern of pairs of chelating ligands (one in the equatorial plane, the other spanning equatorial/apical sites) has been noted in other metal complexes.[24,25] The Mo–S distances to these pyridinethiolate ligands are quite different. That to S(42), 2.415(1) Å, is typical of such bonds in molybdenum(IV) complexes,[26] whereas that to S(12) is much longer, 2.537(1) Å, resulting, principally, from the strong influence of the hydride ligand roughly *trans* to that atom.

The $SC_6H_2Pr^i_3\text{-}2,4,6$ ligand occupies the second apical site on the Mo, with an Mo–S distance of 2.297(1) Å. This is rather short and in the order of those observed for the six-co-ordinate fourteen-electron complexes $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$. This distance, together with the *ipso* Mo–S–C angle in the $SC_6H_2Pr^i_3\text{-}2,4,6$ ligand of 116.4(1)°, is consistent with a d_π–p_π interaction between the thiolate sulfur and the formally sixteen-electron molybdenum to allow electronic saturation at the metal.

The arrangement of the ligands around the metal in $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)(NC_5H_4S\text{-}2)_2(PEtPh_2)]$ can be compared to that in the complex $[W(CO)_2(NC_5H_4S\text{-}2)_2(PMePh_2)]$[27] in which the two pyridinethiolate ligands chelate the metal in a similar pattern; the nitrogen atoms are *cis* at 82.1(2)° and the sulfur atoms subtend an angle of 139.9(1)° at the W which has seven-fold co-ordination described as either distorted capped octahedral or '4:3 piano-stool'. The corresponding angles in **3** are 88.1(1) for N–Mo–N and 142.9(1) for S–Mo–S.

Preparation and Crystal Structure of $[PPh_4][MoO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$ **4**.—This complex was prepared adventitiously whilst attempting to add more hydrogen to the molybdenum in $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ by treating it with $LiBEt_3H$ in methanol. This produced a reddish solid which was filtered off, leaving a blue solution. Addition of $[PPh_4]Br$ to this solution, followed by storing it at 0 °C, gave purple crystals of $[PPh_4][MoO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$ **4**, the molecular structure of which, determined by X-ray analysis, is shown in Fig. 6. Atom coordinates and bond dimensions are in Tables 6 and 7. This complex anion has been reported in a communication but not fully characterised.[28] A number of analogous anions $[MoO(SR'')_4]^{n-}$ and $[MoO(SR'''S)_2]^{n-}$ [R'' = Ph, C_6F_5, $C_6H_4(NHCOMe)\text{-}2$ or $C_6HMe_4\text{-}2,3,5,6$; R''' = C_6H_4, CH_2CH_2, $(CH_2)_3$, or $C_2(CO_2Me)_2$; n = 0, 1 and/or 2] have also been prepared and, in some cases, structurally characterised; their structures have been discussed principally in relation to the environment of the molybdenum atom in molybdooxidases such as xanthine oxidase.[29]

The molybdenum in complex **4** has essentially square-pyramidal geometry with an apical oxide ligand, as found also in the analogous anions. In all the monodentate thiolate complexes of this type the ligand conformations show roughly four-fold symmetry about the Mo–O axis, with the S–C bonds aligned not far from the S_4 base plane; in our structure the

Table 5 Selected molecular dimensions (lengths in Å, angles in °) for $[MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)(NC_5H_4S\text{-}2)_2(PEtPh_2)]$ with e.s.d.s in parentheses

(*a*) About the Mo atom			
Mo–N(11)	2.207(2)	Mo–N(41)	2.202(3)
Mo–S(12)	2.537(1)	Mo–S(42)	2.415(1)
Mo–S(2)	2.297(1)	Mo–H(5)	1.79(5)
Mo–P(3)	2.424(1)		
N(11)–Mo–S(12)	64.5(1)	S(12)–Mo–S(42)	142.9*
N(11)–Mo–S(2)	164.5(1)	S(2)–Mo–S(42)	104.8*
S(12)–Mo–S(2)	100.0*	P(3)–Mo–S(42)	123.9*
N(11)–Mo–P(3)	91.2(1)	N(41)–Mo–S(42)	66.2(1)
S(12)–Mo–P(3)	84.3*	N(11)–Mo–H(5)	84.8(11)
S(2)–Mo–P(3)	86.5*	S(12)–Mo–H(5)	136.4(11)
N(11)–Mo–N(41)	88.1(1)	S(2)–Mo–H(5)	108.0(11)
S(12)–Mo–N(41)	86.2(1)	P(3)–Mo–H(5)	65.4(12)
S(2)–Mo–N(41)	91.5(1)	N(41)–Mo–H(5)	124.7(12)
P(3)–Mo–N(41)	169.8(1)	S(42)–Mo–H(5)	58.9(12)
N(11)–Mo–S(42)	89.2(1)		
(*b*) In the pyridinethiolate ligands			
N(11)–C(12)	1.349(4)	N(41)–C(42)	1.342(4)
N(11)–C(16)	1.334(4)	N(41)–C(46)	1.331(6)
C(12)–S(12)	1.731(4)	C(42)–S(42)	1.764(4)
Mo–N(11)–C(12)	103.4(2)	Mo–N(41)–C(42)	102.3(2)
Mo–N(11)–C(16)	137.1(2)	Mo–N(41)–C(46)	138.8(2)
C(12)–N(11)–C(16)	119.5(3)	C(42)–N(41)–C(46)	118.8(3)
N(11)–C(12)–S(12)	110.9(2)	N(41)–C(42)–S(42)	108.2(3)
N(11)–C(12)–C(13)	121.5(3)	N(41)–C(42)–C(43)	122.3(4)
S(12)–C(12)–C(13)	127.5(3)	S(42)–C(42)–C(43)	129.4(3)
Mo–S(12)–C(12)	81.1(1)	Mo–S(42)–C(42)	83.0(1)
(*c*) In the $SC_6H_2Pr^i{}_3$-2,4,6 ligand			
S(2)–C(21)	1.796(3)	Mo–S(2)–C(21)	116.4(1)
(*d*) In the phosphine ligand			
P(3)–C(31a)	1.833(3)	P(3)–C(37)	1.847(3)
P(3)–C(31b)	1.842(4)		
Mo–P(3)–C(31a)	111.7(1)	Mo–P(3)–C(37)	120.1(1)
Mo–P(3)–C(31b)	117.2(1)	C(31a)–P(3)–C(37)	100.8(1)
C(31a)–P(3)–C(31b)	102.4(2)	C(31b)–P(3)–C(37)	102.0(2)

* The e.s.d. is less than 0.05°.

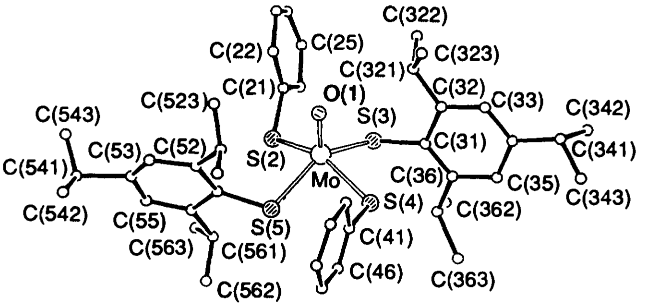


Fig. 6 Molecular structure of the anion in $[PPh_4][MoO(SC_6H_2Pr^i{}_3\text{-}2,4,6)_4]$ **4**, indicating the atom numbering scheme. For clarity, the isopropyl groups of the thiolate ligands of S(2) and S(4) have been omitted

O–Mo–S–C torsion angles are in the range 55.5(8)–70.7(8)°, and the phenyl ring planes are inclined similarly from the molybdenum axis as four propeller blades. Our dimensions are very similar to those found in previous studies of molybdenum(V) anions:[29] the apical Mo=O distance is within the normal range, and the small differences in Mo–S distances [those involving S(2) and S(4), mean 2.405(9) Å, being slightly longer than those of S(3) and S(5), mean 2.378(1) Å] and in the '*trans*'-S–Mo–S angles [146.9(2) *vs.* 138.9(2)°] are very similar to those described previously. It has been suggested that these variations in dimensions relate to a structural conformation intermediate between square pyramidal and trigonal bipyramidal.[29]

Conclusion

We have extended our knowledge of the reaction chemistry of the highly unsaturated, five-co-ordinate, hydride complexes **1**, to demonstrate that they can increase their co-ordination number to six or seven whilst retaining the hydride ligand. The co-ordination environment of hydride at molybdenum has been shown to be versatile, spanning the PS_3, NPS_3 and N_2S_3P donor sets, our future aim being to achieve the NO_2S_3 set found in nitrogenase.[1] The hydride ligand appears to be located in the position *cis* to the phosphine group in these complexes despite the large ^2J(PMoH) observed. The formal electron count of 12 electrons for these compounds might be relieved by the SR″ groups acting as four-electron donors, nevertheless compounds **1** are highly reactive and can lose the hydride under mild conditions, giving an oxide as reported here, or undergo S–C bond cleavage,[6] which will be the subject of other publications.

Experimental

All operations were performed under an atmosphere of dinitrogen. All solvents were dried and degassed before use. The molybdenum–phosphine starting materials[30] and the thiols[31] were prepared by literature methods. Pyridine, 3-methylpyridine, 3,5-dimethylpyridine, thiazole, and pyridine-2-thiol were used as supplied (Aldrich). Spectroscopic measurements were made with JEOL GX270 (NMR), Varian XL400 (NMR, for T_1 measurements), Perkin-Elmer SP3-200 (IR), Nicolet 5DX (FTIR) and VG70-250S (FAB mass spectra) instruments. Microanalyses were determined by Mr. C. J. Macdonald of the Nitrogen Fixation Laboratory or by Canadian Microanalytical Services, Delta, B.C.

S-*Deuteriated* 2,4,6-*Triisopropylbenzenethiol*.—2,4,6-Triisopropylbenzenethiol (8 g, 0.035 mmol) was added to a stirred suspension of sodium hydride (0.9 g, 0.038 mmol) in tetrahydrofuran (50 cm^3) to produce a cloudy white solution which became clear over 30 min with evolution of hydrogen gas. Deuterium chloride (37% in ^2H_2O, 4.8 cm^3, 6 mol equivalents) was added dropwise, causing the precipitation of sodium chloride. The reaction mixture was filtered and the organic layer separated off. The aqueous layer was extracted with hexane (2 × 10 cm^3) and the combined organic phases dried over sodium sulfate. The solvent was then removed under vacuum and the resulting liquid distilled under reduced pressure. Deuteriated 2,4,6-triisopropyl-benzenethiol ($^2HSC_6H_2Pr^i{}_3$-2,4,6) was collected as a colourless *liquid* b.p. 108 °C, 3 mmHg (*ca.* 399 Pa), 5.6 g, 68%).

Hydrido(methyldiphenylphosphine)tris(2,4,6-*trimethylbenzenethiolato)molybdenum*(IV), $[MoH(SC_6H_2Me_3\text{-}2,4,6)_3(PMePh_2)]$.—The complex *cis*-$[Mo(N_2)_2(PMePh_2)_4]$ (0.26 g, 0.27 mmol) was dissolved in thf (20 cm^3) and $HSC_6H_2Me_3$-2,4,6 (0.13 g, 3 equivalents) was added to the stirred solution. An immediate change from orange to green occurred. The green solution was stirred for 15 min and then solvent was removed *in vacuo* to half volume. Methanol (20 cm^3) was added and the solution cooled to −20 °C for 30 min. The resulting green *precipitate* was collected, washed with MeOH (1 × 5 cm^3) and dried *in vacuo* (0.5 g, 25%) (Found: C, 63.2; H, 6.5. $C_{40}H_{47}MoPS_3$ requires C, 64.0; H, 6.4%).

Hydrido(methyldiphenylphosphine)tris(2,4,6-*triisopropylbenzenethiolato)molybdenum*(IV), $[MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PMePh_2)]$. *Method A*. To a stirred solution of *cis*-$[Mo(N_2)_2(PMePh_2)_4]$ (0.25 g, 0.26 mmol) in thf (20 cm^3) at 0 °C was

Table 6 Final atomic coordinates (fractional × 10^4) for [PPh$_4$] [MoO(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_4$]·thf·C$_6$H$_5$Me·MeOH with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo	5 599(1)	5 365.4(6)	3 001.8(6)
O(1)	4 961(10)	4 837(5)	3 202(5)
S(2)	4 521(3)	6 106(2)	2 952(2)
C(21)	3 914(14)	6 222(8)	3 551(7)
C(22)	3 153(20)	5 902(10)	3 709(10)
C(23)	2 626(21)	6 054(11)	4 149(10)
C(24)	2 768(18)	6 486(10)	4 399(9)
C(25)	3 505(16)	6 792(9)	4 279(8)
C(26)	4 126(16)	6 656(8)	3 860(8)
C(221)	2 885(18)	5 409(10)	3 433(9)
C(222)	2 001(29)	5 468(15)	3 086(14)
C(223)	2 946(27)	4 951(13)	3 752(12)
C(241)	2 004(26)	6 669(13)	4 810(13)
C(242)	1 309(39)	6 946(20)	4 585(17)
C(243)	1 653(35)	6 254(18)	5 158(17)
C(261)	4 971(17)	7 038(9)	3 707(9)
C(262)	4 593(24)	7 495(12)	3 375(11)
C(263)	5 486(22)	7 254(11)	4 211(11)
S(3)	6 213(4)	5 813(2)	3 751(2)
C(31)	7 124(13)	5 458(7)	4 079(6)
C(32)	6 832(14)	5 002(8)	4 419(7)
C(33)	7 560(17)	4 766(9)	4 703(8)
C(34)	8 451(18)	4 903(10)	4 697(9)
C(35)	8 761(15)	5 324(8)	4 355(7)
C(36)	8 081(14)	5 610(7)	4 055(7)
C(321)	5 821(17)	4 861(8)	4 502(8)
C(322)	5 367(21)	5 136(11)	4 917(10)
C(323)	5 782(27)	4 255(13)	4 506(12)
C(341)	9 244(21)	4 642(12)	5 055(10)
C(342)*	9 547(32)	4 986(16)	5 499(15)
C(343)*	10 087(66)	4 563(39)	4 822(32)
C(344)*	9 796(48)	4 201(27)	4 840(24)
C(361)	8 332(15)	6 054(8)	3 739(8)
C(362)	8 267(21)	6 586(10)	4 029(11)
C(363)	9 356(21)	6 017(11)	3 465(10)
S(4)	7 197(3)	5 056(2)	2 898(2)
C(41)	7 281(13)	4 612(8)	2 335(7)
C(42)	6 928(17)	4 086(9)	2 374(8)
C(43)	6 986(21)	3 784(11)	1 932(11)
C(44)	7 358(17)	3 939(9)	1 465(9)
C(45)	7 783(19)	4 451(10)	1 490(9)
C(46)	7 686(13)	4 773(7)	1 894(7)
C(421)	6 389(20)	3 889(11)	2 856(10)
C(422)	7 021(35)	3 552(16)	3 167(16)
C(423)	5 391(23)	3 555(12)	2 797(12)
C(441)	7 347(22)	3 530(12)	1 011(12)
C(442)	8 159(26)	3 562(13)	667(13)
C(443)	6 515(27)	3 646(14)	698(14)
C(461)	8 100(19)	5 340(10)	1 840(9)
C(462)	9 144(25)	5 321(14)	2 003(13)
C(463)	7 939(22)	5 605(11)	1 283(9)
S(5)	5 637(3)	5 438(2)	2 069(2)
C(51)	4 502(14)	5 583(7)	1 796(7)
C(52)	3 800(18)	5 176(9)	1 733(9)
C(53)	2 970(20)	5 296(12)	1 394(9)
C(54)	2 864(23)	5 752(13)	1 244(11)
C(55)	3 465(18)	6 157(11)	1 294(9)
C(56)	4 327(17)	6 084(8)	1 586(7)
C(521)	3 993(18)	4 651(10)	1 936(10)
C(522)	4 421(28)	4 300(13)	1 576(12)
C(523)	3 154(26)	4 385(13)	2 202(13)
C(541)	1 989(33)	5 859(17)	835(16)
C(542)	2 020(44)	5 536(22)	450(19)
C(543)	1 177(34)	5 859(19)	1 110(18)
C(561)	5 045(16)	6 518(8)	1 625(8)
C(562)	5 611(23)	6 523(12)	1 144(11)
C(563)	4 631(20)	7 083(9)	1 729(10)
The phosphonium cation			
P(6)	4 684(5)	7 006(3)	7 224(3)
C(61a)	5 697(20)	7 425(10)	7 285(10)
C(62a)	6 238(24)	7 603(12)	6 801(13)
C(63a)	6 946(29)	7 975(15)	6 935(16)
C(64a)	7 141(25)	8 048(13)	7 363(12)
C(65a)	6 712(28)	7 893(14)	7 874(15)
C(66a)	5 936(21)	7 557(11)	7 787(12)
C(61b)	4 767(17)	6 487(9)	7 703(9)
C(62b)	5 543(24)	6 174(12)	7 724(12)
C(63b)	5 606(23)	5 754(11)	8 088(10)
C(64b)	4 886(22)	5 709(11)	8 353(11)
C(65b)	4 119(23)	5 995(12)	8 391(11)
C(66b)	3 994(20)	6 403(10)	8 037(10)
C(61c)	3 679(22)	7 422(12)	7 363(11)
C(62c)	2 683(39)	7 197(23)	7 337(18)
C(63c)	1 933(49)	7 486(25)	7 264(20)
C(64c)	2 030(30)	8 001(16)	7 433(13)
C(65c)	2 763(23)	8 224(12)	7 553(10)
C(66c)	3 656(24)	7 918(13)	7 536(12)
C(61d)	4 545(19)	6 732(9)	6 579(9)
C(62d)	4 619(20)	6 159(11)	6 519(10)
C(63d)	4 460(36)	5 964(20)	5 942(19)
C(64d)	4 319(34)	6 305(17)	5 544(17)
C(65d)	4 191(29)	6 885(16)	5 645(15)
C(66d)	4 439(22)	7 052(12)	6 159(11)
The disordered solvent molecules			
C(69)*	4 545(20)	7 339(10)	8 039(11)
C(71)*	8 384(47)	1 548(27)	6 104(25)
C(72)*	7 822(53)	1 433(27)	5 689(27)
C(73)*	7 090(48)	1 732(24)	5 472(22)
C(74)*	6 748(56)	2 273(29)	5 836(30)
C(75)*	7 478(61)	2 221(30)	6 213(29)
C(76)*	8 361(65)	2 029(37)	6 192(33)
C(81)*	5 893(26)	2 727(14)	5 874(16)
C(82)*	6 176(53)	2 797(31)	5 506(31)
C(83)*	5 033(100)	2 513(47)	5 261(50)
C(84)*	4 602(65)	2 259(33)	5 808(32)
C(85)*	5 483(75)	2 549(39)	6 192(42)
C(86)*	5 266(96)	2 475(46)	5 550(53)
C(91)*	6 020(114)	2 749(59)	5 062(60)
C(92)*	6 207(128)	3 070(67)	5 351(64)
C(93)*	4 160(64)	1 845(35)	5 841(31)
C(94)*	2 918(83)	1 958(44)	5 401(38)
C(95)*	3 147(162)	2 551(85)	5 620(80)
C(96)*	4 089(161)	2 649(73)	5 243(71)

* Site occupancy factor 0.5.

added HSC$_6$H$_2$Pr$^i_3$-2,4,6 (0.186 g, 0.78 mmol). The solution immediately changed from orange to black, becoming deep green over 2 h. The volume was reduced to a minimum under vacuum and cold methanol (20 cm^3) added. The sticky green solid which formed was filtered off and washed repeatedly with cold methanol. The complex [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(PMePh$_2$)] was collected as an olive-green *powder* (0.63 g, 25%) (Found: C, 69.1; H, 8.3. C$_{59}$H$_{83}$MoPS$_3$ requires C, 69.4; H, 8.3%). FAB mass spectrum: m/z = 1003 (M^+).

Method B. To a stirred solution of [MoH$_4$(PMePh$_2$)$_4$] (0.15 g, 0.16 mmol) in thf (20 cm^3) at 0 °C was added HSC$_6$H$_2$Pr$^i_3$-2,4,6 (0.12 g). The solution gradually changed from yellow to green over 5 h. Evaporation followed by addition of methanol yielded the product as an olive-green *powder* (0.31 g, 24%).

*(Ethyldiphenylphosphine)hydridotris(*2,4,6-*triisopropylbenzenethiolato)molybdenum(*IV*)*, [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(PEtPh$_2$)].—The complex [MoH$_4$(PEtPh$_2$)$_4$] was treated with 3 equivalents of HSC$_6$H$_2$Pr$^i_3$-2,4,6, following the experimental procedure outlined in method B above, to produce [MoH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(PEtPh$_2$)] as a green *solid* in 30% yield (Found: C, 67.0; H, 8.1. C$_{60}$H$_{85}$MoPS$_3$ requires C, 67.1;

Table 7 Selected molecular dimensions (lengths in Å, angles in °) in $[PPh_4][MoO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]\cdot thf\cdot C_6H_5Me\cdot MeOH$ with e.s.d.s in parentheses

(*a*) About the Mo atom			
Mo–O(1)	1.689(12)	Mo–S(4)	2.396(5)
Mo–S(2)	2.413(5)	Mo–S(5)	2.379(4)
Mo–S(3)	2.377(5)		
O(1)–Mo–S(2)	107.1(5)	S(3)–Mo–S(4)	84.3(2)
O(1)–Mo–S(3)	109.1(5)	O(1)–Mo–S(5)	111.9(5)
S(2)–Mo–S(3)	84.4(2)	S(2)–Mo–S(5)	84.3(2)
O(1)–Mo–S(4)	106.0(5)	S(3)–Mo–S(5)	138.9(2)
S(2)–Mo–S(4)	146.9(2)	S(4)–Mo–S(5)	84.0(2)
(*b*) In the thiolate ligands			
S(2)–C(21)	1.770(19)	S(3)–C(31)	1.772(18)
S(4)–C(41)	1.823(18)	S(5)–C(51)	1.780(20)
Mo–S(2)–C(21)	112.7(7)	Mo–S(3)–C(31)	113.6(6)
Mo–S(4)–C(41)	110.3(6)	Mo–S(5)–C(51)	112.6(6)
(*c*) In the phosphonium cation			
P(6)–C(61a)	1.783(28)	P(6)–C(61b)	1.791(23)
P(6)–C(61c)	1.80(3)	P(6)–C(61d)	1.792(23)

H, 8.4%); this sample contained some silicone stopcock grease according to the ^1H NMR spectrum (see Fig. 1). FAB mass spectrum: m/z = 1017 ($M^+ - H$).

(*Butyldiphenylphosphine*)*hydridotris*(2,4,6-*triisopropylbenzenethiolato*)*molybdenum*(IV), $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PBuPh_2)]$.—The complex $[MoH_4(PBuPh_2)_4]$ was treated with 3 equivalents of $HSC_6H_2Pr^i_3\text{-}2,4,6$ by method B to produce a green solution. A solid product was not isolated; the product was studied in solution.

Deuterido(*methyldiphenylphosphine*)*tris*(2,4,6-*triisopropylbenzenethiolato*)*molybdenum*(IV), $[Mo^2H(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$.—To a stirred solution of $[MoH_4(PMePh_2)_4]$ (0.05 g) in thf (10 cm^3) at 0 °C was added $^2HSC_6H_2Pr^i_3\text{-}2,4,6$ (0.04 g). The solution gradually changed from yellow to deep green over 2 h. The product was not isolated as a solid but was spectroscopically characterised and utilised in solution.

(*Dimethylphenylphosphine*)*hydrido*(*pyridine*)*tris*(*2,4,6-triisopropylbenzenethiolato*)*molybdenum*(IV), $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)]$.—The procedure used was taken from ref. 5. The compound $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ (3.0 g) was dissolved in neat pyridine (35 cm^3) and the resulting green solution stirred at 60 °C for 15 min. The pyridine was removed *in vacuo*, the resulting oil dissolved in toluene (25 cm^3) and MeOH (40 cm^3) added. On standing at -2 °C the solution deposited green *needles* which were suitable for a structure determination.

Hydrido(*methyldiphenylphosphine*)(*pyridine*)*tris*(2,4,6-*triisopropylbenzenethiolato*)*molybdenum*(IV), $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)]$.—To a stirred solution of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ (0.1 g, 0.1 mmol) in thf (20 cm^3) at 0 °C was added an excess of pyridine (1 cm^3). The solution was stirred at 0 °C for 30 min with a change from green to brown-green. The volume of the solvent was then reduced to a minimum (2 cm^3) under vacuum and the product precipitated by addition of cold methanol. The bright green solid was filtered off and washed with methanol. Crystallisation of the product, by slow diffusion of layered methanol over the reaction solution at 0 °C for 24 h, produced bright green *crystals* (0.07 g, 70%) (Found: C, 70.1; H, 8.2; N, 1.6. $C_{64}H_{88}MoNPS_3$ requires C, 70.2; H, 8.1; N, 1.3%). FAB mass spectrum: m/z = 1082 (M^+).

Hydrido(*methyldiphenylphosphine*)(3-*methylpyridine*)*tris*-(2,4,6-*triisopropylbenzenethiolato*)*molybdenum*(IV).—Using the same technique as above for $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)]$, $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ (0.1 g) and 3-methylpyridine (1 cm^3) were allowed to react to produce $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(3\text{-}MeC_5H_4N)(PMePh_2)]$, collected as a dark green *solid* in 60% yield (Found: C, 70.0; H, 8.5; N, 1.2. $C_{65}H_{91}MoNPS_3$ requires C, 70.0; H, 8.3; N, 1.3%). FAB mass spectrum: m/z = 1097 (M^+).

(3,5-*Dimethylpyridine*)*hydrido*(*methyldiphenylphosphine*)*tris*-(2,4,6-*triisopropylbenzenethiolato*)*molybdenum*(IV).—Using the same technique as above for $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)]$, $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ (0.1 g) and an excess of 3,5-dimethylpyridine were allowed to react to produce $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(3,5\text{-}Me_2C_5H_3N)(PMePh_2)]$ which was not isolated, but characterised in solution by ^{31}P NMR spectroscopy (Table 1).

Hydrido(*methyldiphenylphosphine*)(*pyridine*)*tris*(2,4,6-*trimethylbenzenethiolato*)*molybdenum*(IV).—Using the same technique as above for $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)]$, $[MoH(SC_6H_2Me_3\text{-}2,4,6)_3(PMePh_2)]$ (0.1 g) and an excess of pyridine (1 cm^3) were allowed to react to produce $[MoH(SC_6H_2Me_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)]$ as a green *solid*. The low yield of the reaction and the sensitivity of the product made it difficult to get reliable analyses for this product, which was characterised by spectroscopy (Table 1). The deuterido analogue was prepared similarly from $[Mo^2H(SC_6H_2Me_3\text{-}2,4,6)_3(C_5H_5N)(PMePh_2)]$ (see Table 1).

Deuterido(*ethyldiphenylphosphine*)(*pyridine*)*tris*(2,4,6-*triisopropylbenzenethiolato*)*molybdenum*(IV).—To a stirred solution of $[Mo^2H(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PEtPh_2)]$ (*ca.* 1 mmol), produced by the action of $^2HSC_6H_2Pr^i_3\text{-}2,4,6$ on $[MoH_4(PEtPh_2)_4]$, was added an excess of pyridine. Stirring at 0 °C for 1 h produced a brown-green solution from which green *microcrystals* of $[Mo^2H(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PEtPh_2)]$ were precipitated by the addition of cold methanol in 50% yield (Found: C, 70.4; H, 8.2; N, 1.5. $C_{65}H_{90}MoNPS_3$ requires C, 70.4; H, 8.2; N, 1.3%).

Hydrido(*methyldiphenylphosphine*)(1,3-*thiazole*)*tris*(2,4,6-*triisopropylbenzenethiolato*)*molybdenum*(IV).—To a stirred solution of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ (0.16 g, 0.18 mmol) in thf (15 cm^3) at 0 °C was added an excess of 1,3-thiazole (0.018 cm^3). The solution was stirred at 0 °C for 6 h with no observed colour change of the green solution. The volume was reduced to a minimum under vacuum and the product precipitated by addition of cold methanol. Crystallisation of the product by slow diffusion of methanol (30 cm^3) layered over the reaction solution at 0 °C produced bright green *microcrystals* in 1 week (Found: C, 68.0; H, 7.9; N, 1.1; S, 11.0. $C_{61}H_{86}MoNPS_4$ requires C, 67.3; H, 7.9; N, 1.3; S, 11.8%). FAB mass spectrum: m/z = 1088 (M^+).

(*Ethyldiphenylphosphine*)*hydridobis*(*pyridine*-2-*thiolato*)-(2,4,6-*triisopropylbenzenethiolato*)*molybdenum*(IV) **3**.—To a stirred solution of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PEtPh_2)]$ (0.26 g) in thf (20 cm^3) at 0 °C was added a solution of pyridine-2-thiol (0.03 g) in thf (4 cm^3). The solution was stirred at 0 °C for 1 h, changing from green to red. The volume was then reduced to a minimum under vacuum. Slow crystallisation of the product with methanol at 0 °C over 3 weeks produced large red *prisms* which were filtered off, washed with methanol and dried under vacuum (0.03 g, 18%) (Found: C, 61.5; H, 6.7; N, 3.8; S, 12.1. $C_{39}H_{47}MoN_2PS_3$ requires C, 61.1; H, 6.2; N, 3.7; S, 12.6%). FAB mass spectrum: m/z = 767 ($M^+ - H$).

Crystal Structure Analyses of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)]$, $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)(NC_5H_4S\text{-}2)_2(PEtPh_2)]$ **3** *and* $[PPh_4][MoO(SC_6H_2Pr^i_3\text{-}2,4,6)_4]\cdot x(thf/$

Table 8 Crystal data and crystallographic experimental details

Compound	[MoH($SC_6H_2Pr^i_3$-2,4,6)$_3$(C_5H_5N)(PMe_2Ph)]	[MoH($SC_6H_2Pr^i_3$-2,4,6)(NC_5H_4S-2)($PEtPh_2$)]	[PPh_4][MoO($SC_6H_2Pr^i_3$-2,4,6)$_4$]·*x*(thf/C_6H_5Me/MeOH)
Formula	$C_{58}H_{86}MoNPS_3$	$C_{39}H_{47}MoN_2PS_3$	$C_{84}H_{112}MoOPS_4$ *ca.* C_9H_{10}
M	1020.4	766.9	*ca.* 1511.1
Crystal			
Colour	Dark green	Deep red-brown	Very dark
Shape	Square-prismatic needles	*ca.* Square prisms	Well formed prisms
Size/mm	0.11 × 0.11 × 0.41	0.14 × 0.31 × 1.24	0.36 × 0.36 × 0.64
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group (no.)	*Pnma* (62)	$P2_1/n$ (equiv. to no. 14)	$P2_12_12_1$ (19)
a/Å	17.624(2)	15.494(2)	14.083(3)
b/Å	20.628(2)	21.208(2)	25.247(15)
c/Å	16.020(1)	12.183(1)	25.425(6)
β/°	—	107.936(9)	—
U/Å^3	5824.0	3808.6	9040.0
Z	4	4	4
D_c/g cm^{-3}	1.164	1.337	1.110
F(000)	2184	1600	3236
μ(Mo-Kα)/cm^{-1}	3.8	5.6	2.9
θ_{max}/°	22.5	23	20
Total unique reflections	3917	5277	4694
Reflections with $I > 2\sigma_I$	1895	4634	3489
Corrections applied for			
Crystal deterioration	No	No	No
Absorption	Yes	No	Yes
Negative intensities	Yes	Yes	Yes
Structure determination method	Heavy atom	Heavy atom	Automated Patterson[32]
Refinement			
Anisotropic atoms	All Mo, S, P, N, C (except C atoms in disordered thiolato ligands)	All Mo, S, P, N and C atoms	Mo, S, P and O atoms only
Hydrogen atoms	See text	Me groups: constrained Hydride: located, free Others: idealised positions U_{iso} of all: freely refined	All parameters riding on those of parent C atoms
R	0.099	0.040	0.095*
R'[33]	0.077	0.049	0.103
R_g[33]	0.071	0.061	0.132
No. of reflections (*n* in $I > n\sigma_I$)	2913 (1)	5277 (0)	3489 (2)
g in $w = (\sigma_F^2 + gF^2)^{-1}$	0.00041	0.002 28	0.0211
Final difference map peak/e Å^{-3}	0.6 (near Mo)	0.85 (close to Mo atom)	0.95 (near Mo)

* Refinement of the opposite enantiomer of this complex gave virtually identical results.

$C_6H_5Me/MeOH$) **4**.—The analysis of the first complex is described here in outline; the procedures for the others were very similar. Crystal data and crystallographic experimental data for the three complexes are in Table 8.

Crystals of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(C_5H_5N)(PMe_2Ph)]$ are small, dark green, square-prismatic needles. One was mounted, in air, on a glass fibre and, after photographic examination, was transferred to an Enraf-Nonius CAD4 diffractometer [with monochromated radiation, λ(Mo-Kα) = 0.710 69 Å] for determination of accurate cell parameters (by refinement from the settings of 25 reflections, θ *ca.* 10.5°, each centred in four orientations) and for measurement of diffraction intensities (to θ_{max} 22.5°). Of the 3917 unique reflections recorded, 1895 were 'observed', having $I > 2\sigma_I$. The intensities were corrected for Lorentz-polarisation effects, for absorption (by semi empirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). No correction for crystal deterioration was necessary.

The structure was determined by the heavy-atom method in the SHELX 76 system,[33] and the molecule was found to lie about a mirror plane of symmetry. Some of the isopropyl groups of the thiolate ligands were disordered, and the phosphine phenyl group was tilted one way or the other out of the symmetry plane. All the non-hydrogen atoms (except those of the disordered Pr^i groups) were allowed anisotropic thermal parameters. The hydride ligand was not located. Hydrogen atoms in the ordered methyl groups of the thiolate ligands were refined with geometrical constraints; the methine and phenyl H atoms in the thiolate and pyridine ligands were included in idealised positions. No hydrogen atoms were included in the phosphine ligand.

Refinement, by large-block-matrix least-squares methods, was concluded with $R = 0.099$ and $R' = 0.077$[33] for the 2913 reflections with $I > \sigma_I$. In a final difference map the largest peaks were *ca.* 0.6 e Å^{-3}, close to the Mo atom.

Scattering-factor curves for neutral atoms were taken from ref. 34. Computer programs used in this analysis have been noted above and in Table 4 of ref. 35, and were run on the DEC Micro VAX II machine in the Nitrogen Fixation Laboratory.

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

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