Monohydride Complexes of Molybdenum(IV) and Tungsten(IV) containing Bulky Thiolate Ligands: X-Ray Crystal Structures of $[MH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$, M = Mo or W†

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The complexes $[MH(SC_6H_2R_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ **1** (M = Mo or W, R = Me or Pr^i) and their deuterio analogues have been prepared. The X-ray structures of **1** (M = Mo or W, R = Pr^i) have been determined, showing the overall geometry in both to be based on a distorted trigonal-bipyramidal arrangement of thiolates with the phosphines essentially *trans* to each other. The hydride ligand could not be located by X-ray diffraction in either structure, but its presence is established by spectroscopic studies. The preparation of $[MoBr(SPh)_3(PMe_2Ph)_2]$ is also described.

The study of molybdenum and tungsten compounds which have sulphur-donor ligands is currently of high interest because of their relevance to important catalytic processes, particularly nitrogen fixation[1] and hydrodesulphurisation.[2–6] In these processes, the key steps involve the transfer of hydrogen to the substrate, dinitrogen in nitrogenase and organosulphur compounds in hydrodesulphurisation. An important question is whether the transfer of hydrogen involves the metal, its sulphur-donor ligands, or both. We are studying the bonding of hydride ligands to metals in an environment of thiolate and other ligands in order to elucidate answers to this question. This paper describes the preparation, and structural and other physical properties of the series of formally 14-electron hydrides $[MH(SC_6H_2R_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ **1** (M = Mo or W, R = Me or Pr^i). A brief report on these compounds has already appeared.[7]

Results and Discussion

Preparation of the Complexes.—Previous to this work, examples of mononuclear hydride complexes of molybdenum and tungsten having thiolate or other sulphur-donor co-ligands were relatively rare, being confined to the series $[MoH(SR')(Ph_2PCH_2CH_2PPh_2)_2](SR' = SC_6H_2R_3\text{-}2,4,6,SPr^i$ or $SBu^t)$,[8,9] $[MoH_2(C_6H_4S_2)(PMePh_2)_3]$[10] and the trianion $[MoH(C_6H_4S_2)_3]^{3-}$.[11] The only tungsten hydride complexes of this class to be reported are dimeric, with bridging thioether ligands[12] or trimeric, with sulphide ligands.[13]

Two main routes have been adopted to prepare compounds **1**. The first, which is the best for molybdenum, uses hydrazido(2−) complexes as starting materials [reaction (1)].[14]

$$[MBr_2(NNH_2)(PMe_2Ph)_3] + 3HSC_6H_2R_3 + 2NEt_3 \longrightarrow [MH(SC_6H_2R_3)_3(PMe_2Ph)_2] + N_2 + H_2 + PMe_2Ph + 2[NHEt_3]Br \quad (1)$$

The second route uses metal hydrides as starting materials and is more effective for tungsten as in reaction (2). Related

$$[WH_6(PMe_2Ph)_3] + 3HSC_6H_2R_3 \longrightarrow [WH(SC_6H_2R_3)_3(PMe_2Ph)_2] + 4H_2 + PMe_2Ph \quad (2)$$

complexes not carrying hydride ligands have been prepared, *e.g.* the anion $[Mo(SC_6H_2R_3\text{-}2,4,6)_3(CO)_2]^-$ has been obtained from $[MoBr_2(CO)_4]$.[15]

Analytical data for these green, crystalline, diamagnetic compounds are shown in Table 1.

Structures of Compounds **1**.—A combination of X-ray crystallography and spectroscopy [NMR, IR and fast atom bombardment (FAB) mass spectrometry] has been used to prove the structure of these six-co-ordinate, formally 14-electron M^{IV} complexes.

X-Ray structures. X-Ray crystallography has established the overall geometry of **1** (M = Mo, R = Pr^i) (Fig. 1) and **1** (M = W, R = Pr^i) (Fig. 2) but the hydride ligand could not be located in either structure. This contrasts with the structure determination of the Mo^{II} complex $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)(Ph_2PCH_2CH_2PPh_2)_2]$ where the hydride was located.[9] Nevertheless, a comparison of these structures is useful in deciding upon the location of the hydride in complexes **1**, as discussed below.

The structure of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ (Fig. 1) shows that the molecule has a somewhat distorted trigonal-bipyramidal arrangement of ligands other than the hydride. The thiolates are arranged equatorially around the metal centre to minimise ligand–ligand repulsion, with two aryl rings pointing up and one pointing down. The two phosphines have a pseudo-axial arrangement. This equatorial arrangement of bulky thiolate ligands seems to be the preferred arrangement, *e.g.* as found in $[Mo(NNPh)(SC_6H_2Pr^i_3\text{-}2,4,6)_3(MeCN)]$[16] and $[Mo(SC_6H_2R_3\text{-}2,4,6)_3(CO)_2]^-$.[15] Thus inter-ligand repulsion is minimised and the distortion from octahedral symmetry gives a favourable, diamagnetic, d^2 electronic configuration at the metal.

The complex $[WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ has the same overall geometry and ligand arrangement. This is shown

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† Bis(dimethylphenylphosphine)hydridotris(2,4,6-triisopropylthiophenolato)-molybdenum(IV) and -tungsten(IV).

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

Table 1 Physical properties of compounds **1**

			Analysis[a]			
Complex	Yield (%)	Colour	C	H	M[b]	$E_{\frac{1}{2}}$(ox)[c]/V
$[MoH(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	70	Emerald green[d]	62.5 (62.5)	6.8 (6.7)	828 (828)	−0.18[e]
$[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	60	Emerald green	67.5 (67.9)	8.1 (8.6)	1080 (1080)	−0.26[e]
$[Mo^2H(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	60	Emerald green	67.4 (67.9)	8.4 (8.6)		
$[WH(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	45	Dark green[f]	56.4 (56.2)	6.2 (6.2)	914 (914)	−0.31
$[WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	50	Emerald green	62.7 (62.8)	7.9 (7.9)	1167 (1167)	
$[MoBr(SPh)_3(PMe_2Ph)_2]$	65	Brown	52.3 (52.4)	5.0 (4.6)		

[a] Calculated values in parentheses. [b] FAB mass spectrum, M^+, in nitrobenzyl alcohol or nitrophenyl octyl ether matrix. [c] Relative to ferrocene–ferrocenium. [d] λ_{max} = 658 nm (ε = 356 dm^3 mol^{-1} cm^{-1}) for ≈0.3 mmol dm^{-3} benzene solution. [e] E_p Value. [f] λ_{max} = 615 nm (ε = 4860 dm^3 mol^{-1} cm^{-1}) for ≈0.3 mmol dm^{-3} benzene solution.

Table 2 Comparison of bond distances (Å) and angles (°) for $[MH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ (M = Mo or W)*

	Mo	W
M–P(1)	2.418(6)	2.427(3)
M–P(2)	2.593(6)	2.586(3)
M–S(3)	2.312(6)	2.314(3)
M–S(4)	2.301(6)	2.311(3)
M–S(5)	2.339(6)	2.352(3)
P(1)–M–P(2)	168.1(2)	166.4(1)
P(1)–M–S(3)	93.8(2)	94.2(1)
P(1)–M–S(4)	79.4(2)	77.5(1)
P(1)–M–S(5)	114.2(2)	116.3(1)
P(2)–M–S(3)	78.7(2)	79.0(1)
P(2)–M–S(4)	97.3(2)	96.4(1)
P(2)–M–S(5)	77.7(2)	77.1(1)
S(3)–M–S(4)	125.7(2)	123.9(1)
S(3)–M–S(5)	121.5(2)	124.8(1)
S(4)–M–S(5)	109.9(2)	107.8(1)

* For the purpose of this comparison, the numbering scheme of the tungsten complex has been modified to conform with that of the molybdenum complex; see Figs. 1 and 2.

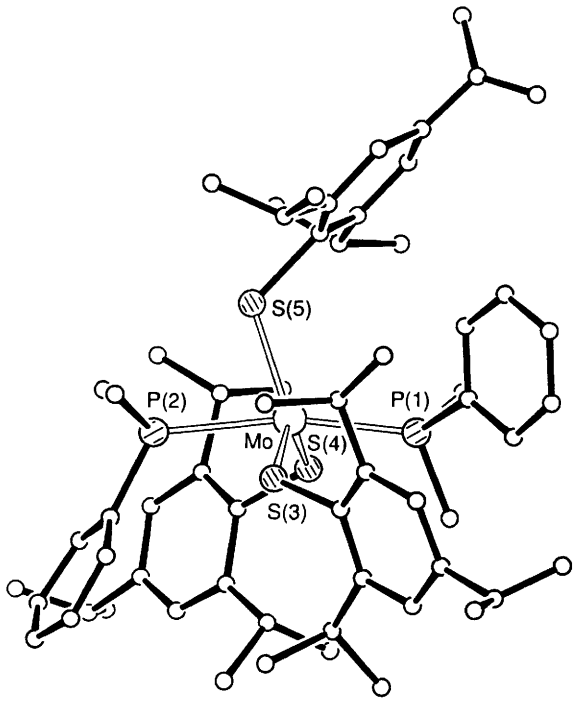

Fig. 1 View of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$

by comparing the corresponding bond distances and angles in Table 2. Atomic coordinates are given in Tables 3 and 4.

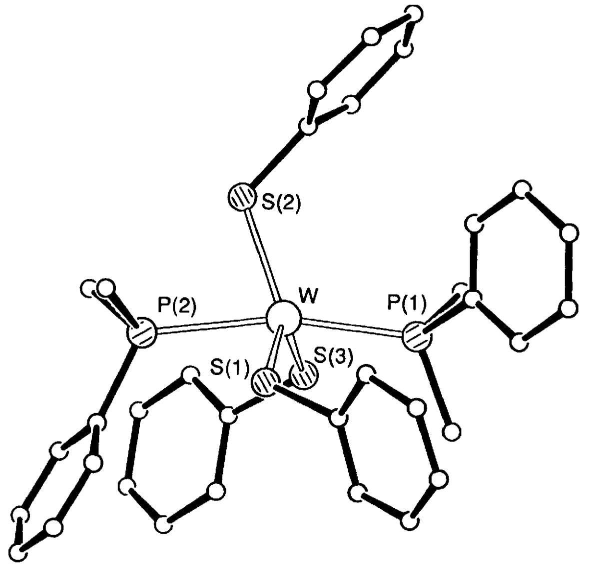

Fig. 2 View of the core of $[WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$; Pr^i groups omitted for clarity

The thiolate ligands are not symmetrically distributed around the metal centre, as shown by the S–M–S bond angles. Two of these angles are close to 120°, as expected for a trigonal arrangement of three ligands, but the third angle is smaller [109.9(2), M = Mo; 107.8(1)°, M = W]. This smaller angle can only be accommodated if the arene rings of each ligand point in opposite axial directions. Note that the corresponding angles in related five-co-ordinate complexes are larger, in the range 114–126° (Table 5).

In both structures, the P(1)–M–P(2) angle deviates from 180° by some 12–14°. This deviation is larger than is observed for corresponding axial angles in five-co-ordinate complexes (Table 5) and suggests an interaction in addition to the steric interactions between the phosphine and thiolate ligands. We therefore suggest that the hydride ligand is located on the P(1)–S(3)–S(5) face of the trigonal bipyramid indicated in Fig. 1 and the corresponding face in Fig. 2. This location is similar to that observed in $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)(Ph_2PCH_2CH_2PPh_2)_2]$ shown in Fig. 3 for comparison. The structure of these hydride complexes is thus essentially capped trigonal bipyramidal. Nevertheless, further proof of the presence of the hydride is necessary, as is detailed below.

Spectroscopic properties. That compounds **1** contain a hydride (or other undetected anionic ligand) is necessitated by their diamagnetism, and NMR and IR studies have confirmed the presence of the hydride ligand.

This is best illustrated for the tungsten complexes (Table 6), where the W–^{1}H resonance is observed as a doublet of doublets at δ 9.08 (R = Pr^i) and δ 8.86 (R = Me). The splitting pattern is primarily a consequence of the inequivalence of the two

Table 3 Final atomic coordinates (fractional × 10^4) for $[MoH_n(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	2276.6(7)	2616(1)	997(2)	C(36c)	2039(8)	7137(17)	3397(20)
P(1)	3116(2)	2918(5)	2370(6)	S(4)	1977(2)	2197(5)	2792(6)
C(11)	3751(7)	3232(16)	1791(18)	C(41)	1265(7)	2190(17)	3116(18)
C(12)	3904(7)	2396(18)	578(20)	C(42)	1063(8)	3221(18)	4091(19)
C(13)	4390(9)	2512(21)	72(25)	C(43)	555(7)	3134(16)	4360(19)
C(14)	4747(9)	3445(19)	707(26)	C(44)	221(7)	2133(16)	3941(20)
C(15)	4596(8)	4293(18)	1887(26)	C(45)	398(7)	1136(17)	3038(20)
C(16)	4119(7)	4203(19)	2437(24)	C(46)	941(8)	1155(17)	2639(21)
C(17)	3142(8)	3966(17)	4083(17)	C(42a)	1426(7)	4292(18)	4652(19)
C(18)	3286(8)	1708(17)	2796(21)	C(42b)	1118(9)	5336(20)	4845(23)
P(2)	1336(2)	2698(5)	−93(6)	C(42c)	1693(9)	4367(19)	5936(23)
C(21)	889(7)	3821(17)	775(19)	C(44a)	−350(9)	2070(18)	4388(21)
C(22)	979(9)	4952(18)	801(24)	C(44b)	−765(8)	1814(20)	3236(22)
C(23)	608(8)	5721(19)	1440(25)	C(44c)	−441(12)	1336(22)	5076(34)
C(24)	150(9)	5391(22)	1849(23)	C(46a)	1171(7)	−7(16))	1751(22)
C(25)	58(10)	4314(21)	1834(24)	C(46b)	1469(8)	−447(17)	2628(24)
C(26)	452(9)	3511(20)	1293(20)	C(46c)	723(8)	−877(16)	855(20)
C(27)	1376(8)	2919(16)	−1620(18)	S(5)	2200(2)	942(5)	−989(6)
C(28)	858(7)	1388(18)	−632(21)	C(51)	2803(7)	103(16)	−1417(17)
S(3)	2368(2)	4427(5)	913(6)	C(52)	2911(8)	−683(16)	−853(18)
C(31)	2940(7)	5476(16)	1538(18)	C(53)	3394(8)	−1201(18)	−1269(21)
C(32)	3355(8)	5556(16)	763(19)	C(54)	3739(9)	−1008(18)	−2128(22)
C(33)	3785(8)	6452(16)	1310(20)	C(55)	3576(9)	−231(18)	−2673(22)
C(34)	3791(8)	7204(18)	2619(22)	C(56)	3116(9)	387(23)	−2301(21)
C(35)	3363(8)	7187(17)	3353(19)	C(52a)	2518(7)	−1046(16)	−45(18)
C(36)	2931(7)	6303(16)	2857(20)	C(52b)	2784(9)	−1472(18)	937(22)
C(32a)	3347(8)	4717(16)	−678(17)	C(52c)	2058(8)	−1899(19)	−929(22)
C(32b)	2939(8)	5033(17)	−1578(19)	C(54a)	4230(9)	−1610(24)	−2450(30)
C(32c)	3892(8)	4693(19)	−1328(21)	C(54b)	4129(9)	−2802(20)	−3191(28)
C(34a)	4249(8)	8188(21)	3196(25)	C(54c)	4676(11)	−1075(25)	−1811(43)
C(34b)	4760(8)	7740(20)	3388(23)	C(56a)	2998(8)	1184(17)	−3066(20)
C(34c)	4289(12)	8980(24)	2668(32)	C(56b)	2549(9)	632(22)	−4182(22)
C(36a)	2463(8)	6455(17)	3782(20)	C(56c)	3455(9)	1643(21)	−3621(24)
C(36b)	2601(8)	6939(18)	5311(18)				

phosphines, expected regardless of the hydride location, because of the 'two up' 'one down' location of the aryl groups. The large value of one coupling constant is consistent with one phosphorus (P_A) being in a pseudo-*trans* position to the hydride and the other (P_B) pseudo-*cis*, as suggested above on the basis of the X-ray structure. Phosphorus P_A is considered to correspond to P(2) in Figs. 1 and 2.

The hydride resonances of **1** (M = Mo) were not so easily observed since they are to higher field of their tungsten analogues and overlap with thiolate resonances. However, the ^2H resonance of $[Mo^2H(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ occurs at δ 1.85 and therefore the Mo–^1H resonance should occur at about the same position, since ^2H shifts are essentially the same as ^1H shifts in analogous compounds.[19] The hydride resonance of **1** (M = Mo, R = Me) appears to be at about δ 2.5, but is partially obscured by the thiolate methyl resonance (Table 6).

The relatively low-field resonance for these complexes, and the shift to high field on passing from the 5d to 4d element of the group (W to Mo) is observed in other early transition-metal hydride systems (Table 7). Presumably the small d-orbital population of these relatively high-valent metals results in decreased shielding relative to compounds with higher d-orbital occupancy. Despite the low-field chemical shift, these hydride ligands are not acidic. This is demonstrated by the immediate reaction of **1** (M = W, R = Pr^i) with C^2HCl_3 to give C^2HHCl_2 and unidentified W-containing products. This experiment also rules out the possibility that this compound contains an S–H rather than a W–H bond since an S–H group would be expected to be acidic, not hydridic.

Additional evidence for the presence of the hydride ligands, especially needed for the molybdenum compounds, is provided by the ^{31}P NMR spectra. The two pseudo-*trans* phosphine ligands are inequivalent and thus give a resonance pattern of two doublets, which upon proton coupling become a triplet and a doublet, indicating large coupling to one phosphorus, which is therefore assigned as that pseudo-*trans* to the hydride (Table 6). The large value of $^2J(PP)$ is consistent with the essentially *trans* arrangement of the phosphines. A doublet of triplets and a doublet is seen for the deuteride as expected.

The NMR spectra of these compounds have been further studied by a combination of temperature variation, nuclear Overhauser effect and hetero-decoupling techniques to obtain structural information. These studies are most conveniently discussed according to the nature of the thiolate co-ligands.

Further NMR studies of complexes **1**. For all complexes **1** (R = Me or Pr^i, M = Mo or W) the ^{31}P NMR spectra show a doublet of doublets (Table 6) with a large $^2J(PP)$ value consistent with the inequivalent environment of the phosphine ligands as discussed above.

More information concerning the solution properties of **1** (M = Mo or W, R = Me) was obtained from the ^1H NMR spectra, in particular the dynamic behaviour of these complexes in solution. Reference will be made to the formalism shown in Fig. 4. A portion of the variable-temperature ^1H NMR spectrum of **1** (M = W, R = Me) is shown in Fig. 5. Not shown is the hydride region, where the hydride resonances show only slight broadening as the temperature is lowered. The PCH_3 resonances are also sharp until some broadening occurs below −50 °C in the P_ACH_3 resonance, although this may be linked to a broadening of the adjacent $Me_o{}'$ resonance (see below).

At 30 °C the thiolate ligands are fluxional and thus give only one sharp methyl resonance and a broad resonance. As the temperature is lowered, the sharp resonance does not change but the broad resonance splits, giving in total four resonances of approximate integration 6:6:9:6 (−20 °C), assigned to Me_o, $Me_o{}''$, Me_p and $Me_o{}'$, respectively as shown in Figs. 4 and 5. This splitting is a consequence of a mirror plane being present in the molecule and therefore the location of the hydride must be such

Table 4 Final atomic coordinates (fractional × 10^4) for $[WH_n(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]\cdot 0.5C_6H_6$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	268.4(4)	1532.8(3)	2793.9(2)	S(2)	−1608(3)	−132(2)	2916(1)
P(1)	1426(3)	1424(2)	1991(1)	C(211)	−2303(11)	−1143(9)	2349(4)
C(11)	626(11)	1420(9)	1357(4)	C(212)	−3355(11)	−1077(9)	2032(4)
C(12)	−574(13)	492(11)	1191(5)	C(213)	−3863(12)	−1871(10)	1590(5)
C(13)	−1170(18)	366(14)	686(7)	C(214)	−3422(13)	−2754(11)	1451(5)
C(14)	−576(16)	1149(13)	349(7)	C(215)	−2412(12)	−2839(10)	1762(5)
C(15)	624(16)	2092(14)	506(7)	C(216)	−1853(11)	−2056(9)	2214(4)
C(16)	1242(14)	2207(11)	1029(5)	C(217)	−3957(13)	−141(11)	2187(5)
C(17)	3128(13)	2497(11)	1959(5)	C(218)	−4651(17)	120(14)	1728(6)
C(18)	1714(13)	70(10)	1852(5)	C(219)	−4893(16)	−466(13)	2628(6)
P(2)	−467(3)	2090(2)	3711(1)	C(220)	−3995(16)	−3571(13)	958(6)
C(21)	514(12)	3422(10)	4139(5)	C(221)	−4435(19)	−4841(15)	1010(8)
C(22)	1220(14)	3366(12)	4596(6)	C(222)	−3227(26)	−3241(22)	500(9)
C(23)	1881(16)	4372(13)	4944(7)	C(223)	−825(11)	−2272(9)	2570(4)
C(24)	1867(17)	5426(15)	4831(7)	C(224)	16(14)	−2869(11)	2289(5)
C(25)	1179(18)	5498(15)	4371(7)	C(225)	−1600(16)	−2959(13)	3005(6)
C(26)	551(14)	4498(11)	4038(6)	S(3)	2179(3)	1273(2)	3088(1)
C(27)	−2057(13)	2285(11)	3637(5)	C(311)	2686(11)	1573(9)	3780(4)
C(28)	−874(13)	1047(10)	4182(5)	C(312)	3690(11)	2657(9)	3968(4)
S(1)	178(3)	3326(2)	2701(1)	C(313)	4225(12)	2834(10)	4482(5)
C(111)	711(10)	4092(8)	2139(4)	C(314)	3855(13)	1995(10)	4799(5)
C(112)	−251(10)	3948(8)	1724(4)	C(315)	2846(12)	913(10)	4615(5)
C(113)	178(12)	4646(10)	1314(5)	C(316)	2305(11)	691(9)	4099(4)
C(114)	1452(12)	5465(10)	1328(5)	C(317)	4235(12)	3632(9)	3628(5)
C(115)	2346(12)	5644(9)	1745(5)	C(318)	4513(15)	4832(12)	3919(6)
C(116)	2017(11)	4978(9)	2160(4)	C(319)	5429(16)	3542(14)	3347(7)
C(117)	−1684(12)	3114(10)	1716(5)	C(320)	4444(14)	2210(12)	5354(5)
C(118)	−2412(16)	2750(13)	1181(6)	C(321)	3350(18)	2169(16)	5771(7)
C(119)	−2514(14)	3631(12)	2098(6)	C(322)	5149(28)	1464(24)	5448(11)
C(120)	1902(14)	6226(11)	886(5)	C(323)	1318(11)	−540(8)	3886(4)
C(121)	950(19)	6850(16)	784(7)	C(324)	2107(14)	−1171(11)	3576(5)
C(122)	1972(17)	5477(14)	380(7)	C(325)	572(14)	−1240(11)	4307(5)
C(123)	2971(12)	5288(10)	2629(5)	C(1s)*	4470(30)	9074(25)	170(12)
C(124)	4471(14)	5736(12)	2510(6)	C(2s)*	3930(40)	9780(30)	351(13)
C(125)	2734(14)	6169(12)	3030(6)	C(3s)*	4590(70)	11030(60)	259(24)

* C(1s), C(2s) and C(3s) are associated with the benzene solvent molecule of crystallisation.

Table 5 Bond angles (°) from X-ray data for compounds containing three equatorial bulky thiolate ligands

Compound	L_{ax}–M–L_{ax}	S(1)–M–S(2)	S(1)–M–S(3)	S(2)–M–S(3)	Ref.
$[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_4(MeCN)]$	179.4	115.7	125.8	118.3	17
$[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(NO)]$		117.9			16
$[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NNPh)(MeCN)]$	179.4	118.1	118.1	121.6	16
$[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)_2]^-$	177.3	115.3	117.0	127.3	15
$[Tc(SC_6HMe_4\text{-}2,3,5,6)_3(MeCN)_2]$	178.8	118.7	121.4	119.7	18
$[Tc(SC_6HMe_4\text{-}2,3,5,6)_3(MeCN)(CO)]$	177.5	116.5	125.8	117.6	18
$[Tc(SC_6HMe_4\text{-}2,3,5,6)_3(C_5H_5N)(CO)]$	175.0	122.0	114.5	123.4	18
$[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	168.1(2)	125.7(2)	121.5(2)	109.9(2)	This work
$[WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	166.4(1)	123.9(1)	124.8(1)	107.8(1)	This work

Table 6 NMR and IR data for compounds **1**

	$^1H(^2H)$ hydride resonance[a]			^{31}P resonance[b]					
Complex	δ(M–^{1}H)	$^2J(HP_A)$	$^2J(HP_B)$	δ(P^A) (*cis*)	$^1J(P_AW)$	δ(P^B) (*trans*)	$^1J(P_BW)$	$^2J(P_AP_B)$	ν(MH)[c]/cm^{-1}
$[MoH(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	2.5	100.8[d]	8.7	−110.3	—	−147.8	—	109.0	1902
$[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	—	98.1[d]	n.o.[e]	−107.0	—	−146.5	—	106.6	1926
$[Mo^2H(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	1.85[f]	13.6	—	−107.3	—	−146.6	—	107.0	
$[WH(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	8.9	109.0	9	−129.2	140	−152.4	205	102.4	
$[W^2H(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2]$[g]	8.8[f]	16.8							
$[WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	9.1	105	8	−125.2	150	−150.5	208	100.7	
$[W^2H(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$	9.0[f]	15.7							
$[MoBr(SPh)_3(PMe_2Ph)_2]$				−106.2[h]		−106.2[h]			

[a] In $[^2H_6]$benzene or $[^2H_8]$toluene solution, δ relative to $SiMe_4$, *J*/Hz. [b] In $[^2H_6]$benzene, $[^2H_8]$toluene or thf solution, δ relative to $P(OMe)_3$, *J* in Hz. [c] In CsI discs [ν(MoH) and ν(WH) are not observed in Nujol mulls]. [d] From ^{1}H-coupled ^{31}P NMR spectrum. [e] n.o. = Not observed. [f] ^{2}H Resonance. [g] Prepared by reaction of $[WH(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ with $^2H_2$ gas.[7] [h] Equivalent phosphines, see text.

Table 7 Examples of other low-field hydrides

Compound	δ(H)	Ref.
$[(Me_3P)_2Cl_2Ta(\mu\text{-}H)_2TaCl_2(PMe_3)_2]$	8.52	20
$[\{Ta(\eta\text{-}C_5Me_5)Cl_2H\}_2]$	10.38	21
$[\{Ta(\eta\text{-}C_5Me_5)Br_2H\}_2]$	11.27	21
$[Hf(\eta\text{-}C_5Me_5)_2H(OMe)]$	9.92	22
$[Hf(\eta\text{-}C_5Me_5)_2H(Et)]$	12.41	22
$[Hf(\eta\text{-}C_5Me_5)_2H(CH_2CHMe_2)]$	13.64	22
$[Hf(\eta\text{-}C_5Me_5)_2H_2]$	15.57	22
$[Zr(\eta\text{-}C_5Me_5)_2H_2]$	7.47	22
$[Ti(\eta\text{-}C_5Me_5)_2H_2]$	0.28	22
$[Hf(\eta\text{-}C_5Me_5)_2H_2(CO)]$	2.67	22
$[W_4(\mu\text{-}H)_2(OPr^i)_{14}]$	7.87	23
$[WH(NNH_2)Cl_3(PMePh_2)_2]$	12.1	24

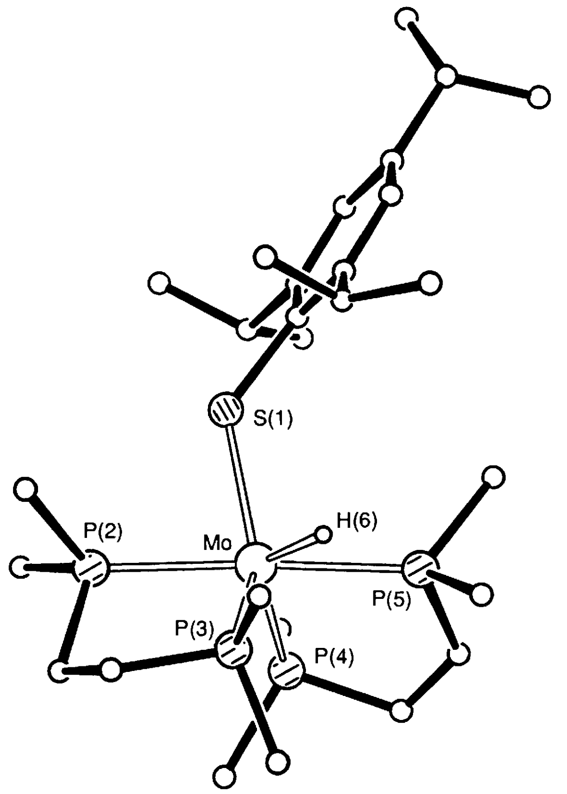

Fig. 3 View of the core of $[MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)(Ph_2PCH_2CH_2PPh_2)_2]$; phenyl groups omitted for clarity

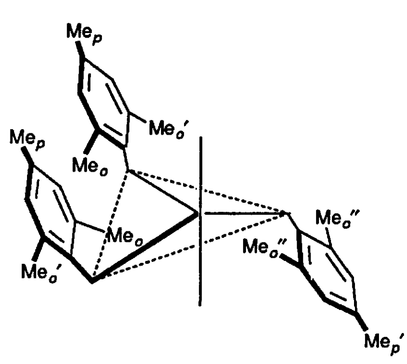

Fig. 4 Labelling scheme used for $[MH(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ in the NMR studies

as not to disturb that plane. The Me_p methyl protons on the up and down ligands are isochronous at this temperature.

At −70 °C the resonance due to Me_p splits into two, Me_p and Me_p' (Figs. 4 and 5), the Me_o' and Me_o'' resonances broaden and the phosphine methyls become inequivalent. There is general loss of resolution at this temperature, perhaps an effect of solvent viscosity.

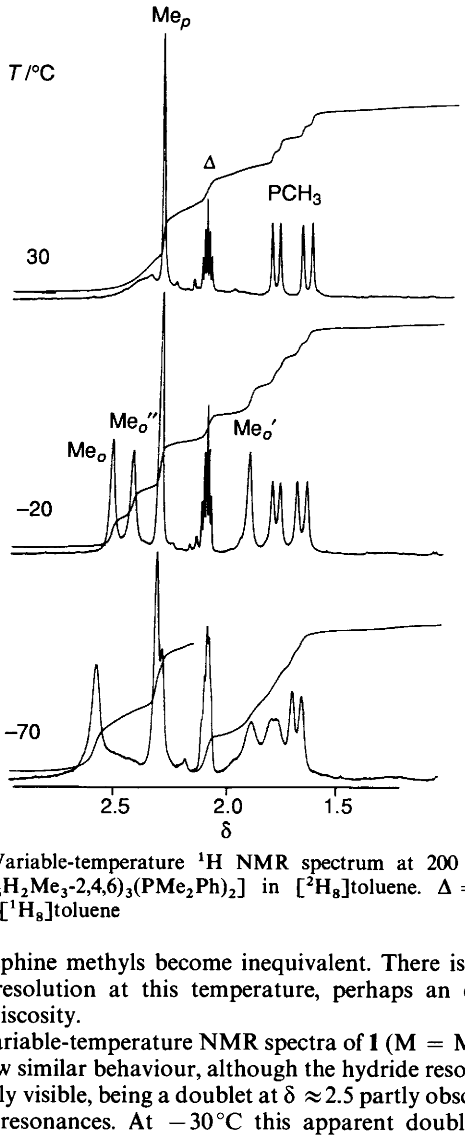

Fig. 5 Variable-temperature ^1H NMR spectrum at 200 MHz of $[WH(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ in $[^2H_8]$toluene. Δ = solvent impurity, $[^1H_8]$toluene

The variable-temperature NMR spectra of **1** (M = Mo, R = Me) show similar behaviour, although the hydride resonance is not clearly visible, being a doublet at δ ≈2.5 partly obscured by thiolate resonances. At −30 °C this apparent doublet shifts upfield to δ 2.16 and is not visible at lower temperatures. Further work on the fluxional process of this complex is in progress.

Clearly for both compounds **1** (M = Mo or W, R = Me) at 30 °C the thiolate ligands are exchanging rapidly on the NMR time-scale since the Me_o and Me_o' methyl protons give a broad resonance at this temperature. This can be explained by a rapid intramolecular process involving M–S bond rotation or inversion at sulphur and S–C bond rotation. As the temperature is lowered to −20 °C these processes slow so that the inequivalence of the inner (Me_o) and outer (Me_o') methyl protons becomes apparent while the Me_o'' and Me_p methyl protons remain isochronous. As the temperature is lowered further, splitting of the Me_p methyl protons begins and there is broadening of the Me_o resonance, as well as of the PCH_3 resonances of the phosphine *cis* to the hydride. The reason for this is not clear but possibly it is a consequence of the freezing of rotation about the M–P bond of the *cis* PMe_2Ph ligand so that the complex becomes chiral and these methyl groups become diastereotopic.

For the analogues **1** (M = Mo or W, R = Pr^i) the ^1H NMR resonances of the thiolate ligands are necessarily more complex than those above. Nevertheless the methine resonances show that at 20 °C these ligands are mobile, because only two resonances are seen for M = W (at δ 3.8 and 2.9, relative intensities 3:6), corresponding to the *para*- and *ortho*-isopropyl groups; three resonances are seen for M = Mo (at δ 3.4 and 2.8 with a broad resonance in the range δ 2.7–1.7, relative intensities

3:3:3) probably corresponding to the *para*- and *ortho*-isopropyl groups of two up $\mathrm{SC_6H_2Pr^i_3}$ ligands, with one broad resonance corresponding to both *ortho*- and *para*-isopropyl groups of the down ligand.

For the complex $[\mathrm{WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$ the nuclear Overhauser enhanced spectrum obtained by low-power selective excitation of the hydride resonance gave positive enhancement for the methyls on one phosphine, assigned to that phosphine *cis* to the hydride (see Experimental section).

Further information for $[\mathrm{WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2}]$ was provided by the ^{31}P heteronuclear correlation spectrum, which showed a long-range coupling between $\mathrm{P_A}$ and aromatic (presumed *ortho*) hydrogens on the phenyl groups of the phosphines. This technique demonstrated that a resonance at δ 6.5 was due to the phosphorus *cis* to the hydride ($\mathrm{P_B}$) and a resonance at δ 7.4, to the *trans* phosphorus ($\mathrm{P_A}$).

Electrochemical Studies.—The redox properties of complexes **1** have been examined by cyclic voltammetry (see Table 1). The molybdenum compounds both show an irreversible oxidation but the tungsten compounds both show a one-step reversible oxidation. It might be expected that loss of an electron from **1**, to give a formally 13-electron species, would result in instability; this is true in the case of the molybdenum complexes since no reversibility was seen in the cyclic voltammogram even at scan rates as high as 0.75 V $\mathrm{s^{-1}}$. The oxidation of the tungsten complexes is reversible and there is the possibility that the $\mathrm{W^V}$ hydride might be stable enough to isolate. Plots of i_p^ox *versus* $v^{\frac{1}{2}}$ for the tungsten complexes were linear, showing that the oxidation process is diffusion controlled.

Preparation of $[\mathrm{MoBr(SPh)_3(PMe_2Ph)_2}]$.—When PhSH was substituted for the much more bulky thiolates $\mathrm{HSC_6H_2R_3}$-2,4,6 in reaction (1), M = Mo, hydride was not retained at the metal centre, but instead was released as dihydrogen with the formation of the bromo complex $[\mathrm{MoBr(SPh)_3(PMe_2Ph)_2}]$. Its structure is assigned as octahedral with mutually *trans* phosphine ligands, on the basis of the singlet ^{31}P NMR resonance and the triplet pattern in the ^{1}H NMR spectrum (Table 6) due to virtually coupled *trans* $\mathrm{PCH_3}$ groups.[25] Thus it appears that large groups on the thiolates are required to stabilise hydride–thiolate complexes for molybdenum and tungsten as has been observed for the complexes $[\mathrm{MoH(SC_6H_2R_3\text{-}2,4,6)(Ph_2PCH_2CH_2PPh_2)_2}]$.[8,9]

Conclusion

We have prepared a new group of hydride–thiolate complexes which are notable for their low formal electronic configuration (14 electrons), distorted geometry and low-field hydride chemical shifts. From the data presented, particularly in the tungsten case, it seems clear that the hydride is bonded to the metal, although neutron diffraction studies are necessary to establish conclusively that there is no interaction of hydrogen with thiolate sulphur of the type suggested to occur in complexes $[\mathrm{Fe(SHPh)(CO)_3(PR_3)}]^-$.[26]

These compounds potentially are of interest in understanding processes where substrates are reduced at metal centres carrying thiolate ligands and we will report on their reactions in further papers.

Experimental

Thiols,[27] $[\mathrm{MBr_2(NNH_2)(PMe_2Ph)_3}]$ (M = Mo or W)[28] and $[\mathrm{WH_6(PMe_2Ph)_3}]$[29] were prepared by published methods. All other reagents and solvents were commercial products which were purified, dried and handled under dioxygen- and water-free conditions by standard techniques.[30]

Infrared spectra were recorded on Perkin-Elmer SP3-200 or Nicolet 5DXFTIR spectrometers and NMR spectra were obtained using Varian XL400, XL200 or JEOL FX270 instruments. Fast atom bombardment mass spectra were obtained using a VG70-250S spectrometer, using xenon flux, and UV/VIS spectra with Cary 2300 or Perkin-Elmer Lambda 5 spectrometers. Microanalyses were determined by Mr. C. Macdonald of the Nitrogen Fixation Laboratory or by Canadian Microanalytical Services, Delta, BC. A PAR model 273 potentiostat was used for cyclic voltammetry studies. The electrochemical cell contained a Pt working electrode, W secondary electrode and Ag wire reference electrode in a Luggin–Haber probe capillary; tetrahydrofuran (thf) solutions were 0.002 mol $\mathrm{dm^{-3}}$ in the complexes and 0.2 mol $\mathrm{dm^{-3}}$ in $[\mathrm{NBu_4}]\mathrm{BF_4}$. Reported potentials are referenced to ferrocene which was added to these solutions.

Preparations.—*Bis(dimethylphenylphosphine)hydridotris(*2,4,6-*trimethylthiophenolato)molybdenum*(IV). The complex $[\mathrm{MoBr_2(NNH_2)(PMe_2Ph)_3}]$ (5.97 g, 8.52 mmol) was suspended in MeOH (100 $\mathrm{cm^3}$) and $\mathrm{HSC_6H_2Me_3}$ (3.99 g, 3 equiv.) followed by $\mathrm{NEt_3}$ (3.56 $\mathrm{cm^3}$, 3 equiv.) was added. The suspension was heated to 60 °C and then allowed to cool slowly to room temperature (3 h). The green *microcrystalline solid* that formed was collected, washed with MeOH (2 × 20 $\mathrm{cm^3}$) and dried *in vacuo*. Yield 4.33 g. ^{1}H NMR ([$^2\mathrm{H_6}$]benzene): δ 7.7 (m, 2 H, *o*-H of *Ph*$\mathrm{PMe_2}$ *trans* to H); 7.15–6.64 (m, 2 H, *Ph*$\mathrm{PMe_2}$, $H_2\mathrm{C_6Me_3S}$); 6.40 (m, 2 H, *o*-H of *Ph*$\mathrm{PMe_2}$ *cis* to H); 2.69 (d, $^2J_\mathrm{PH}$ 8.74); 2.30 (s, 6 H, *o*-$Me_2\mathrm{C_6H_2MeS}$); 2.22 (br s, 9 H, *p*-$Me\mathrm{C_6H_2Me_2S}$); 2.15 (s, 6 H, *o*-$Me_2\mathrm{C_6H_2MeS}$); 2.05 (s, 6 H, *o*-$Me_2\mathrm{C_6H_2MeS}$); 1.71 (d, 6 H, Me_2PPh *cis* to H, $^2J_\mathrm{PH}$ 7.4); 1.54 (d, 6 H, Me_2PPh *trans* to H, $^2J_\mathrm{PH}$ 8.7 Hz).

*Bis(dimethylphenylphosphine)hydridotris(*2,4,6-*triisopropylthiophenolato)molybdenum*(IV). The complex $[\mathrm{MoBr_2(NNH_2)(PMe_2Ph)_3}]$ (4.73 g, 6.75 mmol) was suspended in MeOH (100 $\mathrm{cm^3}$) and $\mathrm{HSC_6H_2Pr^i_3}$ (4.76 g, 3 equiv.) followed by $\mathrm{NEt_3}$ (2.80 $\mathrm{cm^3}$, 3 equiv.) was added. The suspension was stirred under dinitrogen for 4 h and the resulting green precipitate was collected, washed with MeOH (3 × 20 $\mathrm{cm^3}$) and dried *in vacuo*. Yield 4.32 g. Recrystallisation from thf–MeOH gave green *plates*. ^{1}H NMR ([$^2\mathrm{H_2}$]dichloromethane): δ 7.65 (m, 2 H, *o*-H of *Ph*$\mathrm{PMe_2}$ *trans* to H); 7.33–6.76 (m, 8 H, *Ph*$\mathrm{PMe_2}$); 7.20 (s, 2 H), 7.08 (s, 2 H), 7.00 (s, 2 H) (6 H, $H_2\mathrm{C_6Pr^i_3S}$); 6.05 (m, 2 H, *o*-H of *Ph*$\mathrm{PMe_2}$ *cis* to H); 3.41 (m, 3 H), 2.83 (m, 3 H), 2.52–1.73 (m, 3 H) (9 H, $H\mathrm{CMe_2}$); 1.55 (d, 6 H, Me_2PPh *trans* to H, $^2J_\mathrm{PH}$ = 7.3); 1.36 (d, 6 H, Me_2PPh *cis* to H, $^2J_\mathrm{PH}$ 6.4); 1.32 (d, 12 H, $^3J_\mathrm{HH}$ 7.3); 1.30 (d, 12 H, $^3J_\mathrm{HH}$ 7.3); 1.21 (s, 6 H), 1.19 (s, 6 H), 1.17 (s, 6 H), 1.11 (d, 12 H, $^3J_\mathrm{HH}$ 7.3 Hz) (54 H, Me_2CH).

Bromobis(dimethylphenylphosphine)tris(thiophenolato)molybdenum(IV), $[\mathrm{MoBr(SPh)_3(PMe_2Ph)_2}]$. To $[\mathrm{MoBr_2(NNH_2)(PMe_2Ph)_3}]$ (0.42 g) suspended in MeOH (50 $\mathrm{cm^3}$) was added dropwise, PhSH (0.26 g, 4 equiv.), followed by $\mathrm{NEt_3}$ (0.2 $\mathrm{cm^3}$). The solution turned brown and was heated at reflux for 15 min, then cooled to 30 °C. Methanol (10 $\mathrm{cm^3}$) was removed *in vacuo* and the solution allowed to cool to 0 °C whereupon brown *microcrystals* deposited. These were filtered off, washed with MeOH and dried (0.30 g). NMR ([$^2\mathrm{H_6}$]benzene): ^{1}H, δ 2.20 (dt, 12 H, *trans*-PMe_2Ph); 6.1–7.5 (m, 25 H, $\mathrm{PC_6H_5}$ and $\mathrm{SC_6H_5}$). ^{31}P, δ 105.5 (s, *trans*-P).

*Bis(dimethylphenylphosphine)hydridotris(*2,4,6-*triisopropylthiophenolato)tungsten*(IV). The complex $[\mathrm{WH_6(PMe_2Ph)_3}]$ (0.40 g, 0.66 mmol) was dissolved in methanol (*ca.* 30 $\mathrm{cm^3}$). The solution was then warmed to 40 °C and $\mathrm{HSC_6H_2Pr^i_3}$ (0.5 $\mathrm{cm^3}$, 2.7 mmol, 4 equiv.) was added by syringe causing dihydrogen evolution. The solution was left stirring under argon for 16 h, during which time an emerald green *powder* precipitated which was filtered off and washed with methanol. Yield 0.39 g. ^{1}H NMR: δ 9.09 (WH, see Table 6); 7.84 (tm, 2 H, *o*-H of phenyl of P *trans* to hydride); 7.2–6.9 (m, 6 H, *Ph*$\mathrm{PMe_2}$); 6.32 (m, 2 H, *o*-H of phenyl of P *cis* to hydride); 7.30 (s, 2 H), 7.25 (s, 2 H), 7.02 (s, 2 H) (6 H, $H_2\mathrm{C_6Pr^i_3S}$); 3.8 (m, 3 H, $H\mathrm{CMe_2}$); 2.9 (m, 6 H, $H\mathrm{CMe_2}$); 1.69 (d, 6 H, Me_2PPh, *cis* to hydride, $^2J_\mathrm{PH}$ 7.9); 1.63 (d, 6 H, Me_2PPh, *trans* to hydride, $^2J_\mathrm{PH}$ 8.8); 1.39 (6 H), 1.37 (6 H), 1.35 (9 H), 1.34 (6 H), 1.32 (3 H), 1.00 (d, 6 H, $^3J_{HH}$ 6.4), 0.92 (d, 6 H, $^3J_{HH}$ 6.5 Hz) (54 H, Me_2CH).

*Bis(dimethylphenylphosphine)hydridotris(*2,4,6-*trimethylthiophenolato)tungsten*(IV). The procedure followed was as that for $[WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$. A turquoise green powder was isolated. Recrystallization from hot toluene gave shiny dark green *microcrystals*. ^{1}H NMR ($[^2H_8]$toluene): δ 8.86 (WH see Table 6); 7.7 (m, 2 H, *o*-H of *Ph*PMe$_2$ *trans* to hydride); 7.2–6.7 (m, *Ph*PMe$_2$, $H_2C_6Me_3S$); 6.44 (m, 2 H, *o*-H of *Ph*PMe$_2$ *cis* to hydride); 2.4 (br, *p*-$MeC_6H_2Me_2S$); 2.29 (s, *o*-$Me_2C_6H_2MeS$); 1.77 (d, 6 H, Me_2PPh, *cis* to H, $^2J_{PH}$ 7.6); 1.63 (d, 6 H, Me_2PPh, *trans* to H, $^2J_{PH}$ 8.6 Hz). The proton spectra at various temperatures are given in Fig. 5.

$^2HSC_6H_2Pr^i_3$-2,4,6. Sodium hydride (220 mg, 9.17 mmol) was suspended in thf (*ca.* 25 cm^3), and then $HSC_6H_2Pr^i_3$ (2 g, 8.5 mmol) was added. The solution effervesced, and turned less cloudy. After 10 min, the solution was clear and 37% ^{2}HCl in ^2H_2O (1.2 cm^3, 6 equiv.) was added very slowly with vigorous stirring. The solution turned red then yellow as the addition continued, and finally was colourless. When all the ^{2}HCl solution was added, the solution was almost clear. The solution was stripped, leaving behind a clear ^2H_2O layer and an organic layer. Hexanes were added to extract the organic layer; the hexane layer was removed and dried over $MgSO_4$. The hexane was removed to yield a clear colourless liquid which was distilled under vacuum (0.05 Torr, ≈6.65 Pa), collecting the *product* in the range 101.2–104 °C. Analysis by ^{1}H NMR showed that the product was 75% enriched in deuterium.

*Deuteridobis(dimethylphenylphosphine)tris(*2,4,6-*triisopropylthiophenolato)-molybdenum*(IV) *and -tungsten*(IV). These complexes were prepared in the same fashion as the hydrido complex $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ except that $^2HSC_6H_2Pr^i_3$ and MeO^{2}H were used; in the case of the tungsten complex, $[WBr_2(NNH_2)(PMe_2Ph)_3]$ was the starting material and the reaction proceeded for 16 h.

*Reaction of Bis(dimethylphenylphosphine)hydridotris(*2,4,6-*trimethylthiophenolato)tungsten*(IV) *with* $CDCl_3$.—The tungsten complex (10 mg) was dissolved in C^2HCl_3 (*ca.* 0.5 cm^3) under an N_2 atmosphere. A ^{1}H NMR spectrum of the turquoise-green solution was obtained soon thereafter. Two triplets of intensity 2:1 formed at δ 9.01 and 8.40, respectively. Upon standing overnight, the solution was clear yellow, and the hydride resonances had all but vanished. A 1:1:1 triplet at δ 5.55 had formed, corresponding to CH^2HCl_2. Other peaks in the final ^{1}H NMR spectrum (C^2HCl_3): δ 8.89 (tm, rel. int. 4), 8.37 (tm, rel. int. 2), 7.62 (s, rel. int. 3), 7.24 (s, rel. int. 4), 2.80 (s, rel. int. 18, *o*-$Me_2C_6H_2MeS$), 2.55 (s, rel. int. 9, *p*-$MeC_6H_2Me_2S$). The samples appeared to be paramagnetic judging by the abnormal ^{1}H NMR shifts.

X-Ray Crystallography.—For both compounds, despite repeated attempts using a variety of solvents, better-quality crystals could not be obtained.

X-Ray analysis of $[MoH_n(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$. Currently no hydride atoms have been located; it is assumed for the following data that $n = 1$.

Crystal data. $C_{61}H_{92}MoP_2S_3$, $M = 1079.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 24.853(17)$, $b = 12.593(12)$, $c = 10.626(6)$ Å, $\alpha = 112.30(6)$, $\beta = 92.30(5)$, $\gamma = 93.85(7)°$. $U = 3062$ Å^3, $Z = 2$, $D_c = 1.170$ g cm^{-3}, $F(000) = 1156$, μ(Mo-Kα) = 3.9 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å.

Preliminary photographic examination of several crystals showed the diffraction spots generally to be rather large and diffuse. Intensity measurements were made on a green plate-shaped crystal, size 0.07 × 0.24 × 0.52 mm, which was coated in epoxy resin, and mounted on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-Kα radiation. Of 5707 unique data with a θ range of 1–20°, 3582 reflections were considered 'observed' having $I > 2\sigma_I$.

The structure was solved (with the SHELX program system[31]) from a combination of direct methods and Patterson synthesis to locate the Mo, P and S atoms; the C atoms were then located in electron density and difference Fourier maps. Hydrogen atoms on the phosphine and thiolate ligands were included in idealised positions, and refinement, by block-diagonal-matrix least-squares methods,[32] was terminated with $R = 0.120$ and $R' = 0.097$ for the observed data, weighted $w = \sigma_F^{-2}$. These high R factors reflect the difficulties encountered in measuring the diffuse reflection intensities adequately.

No hydride atoms were visible in the final difference map; nor could the position of any be inferred from geometrical consideration of the molybdenum co-ordination sphere.

Scattering factors were taken from ref. 33. Computer programs used in this analysis include those noted above and in Table 4 of ref. 34, and were run on the VAX 11/750 and MicroVAX computers at the AFRC's Institute of Horticultural Research, Littlehampton (Glasshouse Crops Research Institute) and the Nitrogen Fixation Laboratory, respectively.

X-Ray analysis of $[WH_n(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)_2]$. Similarly no hydride atoms have been located for this complex; it is assumed that $n = 1$ for the following data. Recrystallisation of 300 mg of the complex in 0.5 cm^3 of hot benzene and 0.1 cm^3 methanol yielded turquoise crystals which were sealed in 0.2–0.3 mm Lindemann capillaries.

Crystal data. $C_{61}H_{92}P_2S_3W\cdot0.5C_6H_6$, $M = 1206.4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.667(7)$, $b = 12.473(8)$, $c = 25.661(7)$ Å, $\alpha = 96.67(4)$, $\beta = 90.47(4)$, $\gamma = 111.48(5)°$, $U = 3151(3)$ Å^3, $Z = 2$, $D_c = 1.27$ g cm^{-3}, $F(000) = 1262$, μ(Mo-Kα) = 20.5 cm^{-1}.

Accurate cell dimensions were determined on a CAD4 diffractometer (with monochromated radiation) from the setting angles of 25 reflections in the range $8 < \theta < 15°$. The crystal was 0.2 × 0.2 × 0.3 mm. Intensities of 9989 reflections for $1 < \theta < 22.5°$ were measured; 976 symmetry-related data with $\theta < 17.5°$ were also recorded; ω–2θ scans, ω scan width = (0.65 + 0.35 tan θ)°; intensities of two reflections measured every 8000 s used for scaling the data.[35] 651 Zero F_o data were rejected, 961 symmetry-equivalent reflections were merged ($R_{merge} = 0.044$), giving 9213 unique reflections; 7822 with $I > 3\sigma_I$ were 'observed' and used in the structure solution and refinement. Intensities were corrected for Lorentz and polarisation effects and for absorption;[36] minimum and maximum factors were 0.75 and 1.34.

The structure was solved by Patterson methods (for W) and successive Fourier and difference Fourier syntheses. Refinement was by full-matrix least-squares methods, initially with isotropic and then with anisotropic thermal parameters for W, P and S atoms. A difference map showed maxima in positions consistent with the expected locations of hydrogen atoms. These atoms were included in idealised positions (C–H 1.08 Å), riding on their bonded carbon atoms, with a common single thermal parameter U_{iso} which refined to 0.097 Å^2. The final cycles of refinement included 312 parameters, giving $R = 0.072$ and $R' = 0.077$, goodness of fit 1.251, with $w = (\sigma_F^2 + 0.005F_o^2)^{-1}$; max. shift/e.s.d. was 0.50 (for a positional parameter of a carbon atom in the disordered solvent molecule). In a final difference map, the highest peak (3.4 e Å^{-3}) was 1.12 Å from the W atom; there were no chemically significant features remaining. Scattering factors were embedded in the software.[31] All calculations were carried out on a 80-286 PC computer using NRCVAX[35] and an Apollo computer using SHELX[31] and SHELXS[37] at the University of Toronto.

The unit cell parameters for the two structures show close similarities; however, the crystal of the W complex contains molecules of solvent benzene, and the packing arrangements of the two complexes are rather different.

Neither structure determination has allowed the identification of the hydride ligands. The resolution of the two structures is reflected in their R factors, being particularly high for the Mo complex; indications of the reliability of the structures are found in the precision of the atomic coordinates (Tables 3 and 4) and in the molecular dimensions (Table 2).

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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