Preparation and Crystal Structure of $[PHBu_3][MoHCl_4(PBu_3)_2]$†

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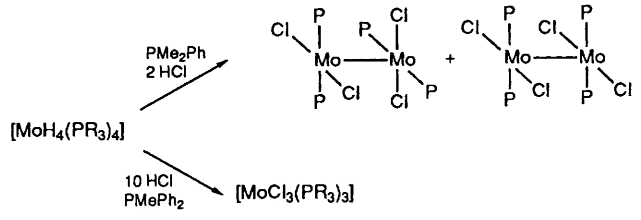
The preparation of the series of anionic, paramagnetic, hydrido complexes $[PHR_3][MoHCl_4(PR_3)_2]$ (R = Et, X = Cl or Br; R = Bu, X = Cl; R_3 = Me_2Ph, X = Br) from the reactions of anhydrous HX with $[MoH_4(PR_3)_4]$ in tetrahydrofuran is described. The structure of one example, $[PHBu_3][MoHCl_4(PBu_3)_2]$, has been determined by X-ray crystallography. The co-ordination geometry of the anion is best described as a distorted pentagonal bipyramid, with apical chloro-groups $[(Mo{-}Cl_{ax})_{av}$ 2.423(10) Å]. The hydride was located in the structure [Mo–H 1.83(4) Å] and is displaced 0.31 Å out of the equatorial plane towards one of the axial sites. The remaining ligands in the equatorial positions have bond lengths $(Mo{-}Cl_{eq})_{av}$ 2.485(1) and $(Mo{-}P)_{av}$ 2.511(5) Å.

Recently we have shown that protonation of $[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$ in tetrahydrofuran (thf) can be a facile and versatile method of binding and activating a variety of small molecules.[1] We are exploiting this strategy as a means of preparing new compounds, not attainable by other synthetic routes. In this paper we report the series of anionic, paramagnetic, hydrido complexes, $[MoHX_4(PR_3)_2]^-$ (R = Et, X = Cl or Br; R = Bu, X = Cl; R_3 = Me_2Ph, X = Br), prepared by the reactions of anhydrous HX with $[MoH_4(PR_3)_4]$, together with the X-ray crystal structure of $[PHBu_3][MoHCl_4(PBu_3)_2]$.

Results and Discussion

Previous studies[2] on the reactions of aqueous HCl with $[MoH_4(PR_3)_4]$ (R_3 = Me_2Ph or $MePh_2$) have shown that a variety of products is attainable as shown in Scheme 1. Clearly the nature of the phosphine influences the reaction direction. We have found that attempts to isolate clean products from the reaction of anhydrous HCl with $[MoH_4(PMePh_2)_4]$ in thf are complicated by the difficulty of separating the molybdenum-containing species from the side products, phosphonium chloride salts. To circumvent this problem we investigated the reactions of anhydrous acid with $[MoH_4(PR_3)_4]$ (R = Et or Bu). In particular, the use of the long-chain butyl substituents renders the molybdenum products (but not the corresponding phosphonium halide salts) soluble in diethyl ether or hexane, hence affording a separation of these two materials.

The complexes, $[MoH_4(PR_3)_4]$ (R_3 = Et_3, Bu_3 or $MePh_2$) were prepared by treating $[MoCl_4(thf)_2]$ with $Li[BHEt_3]$ (super hydride) in the presence of the necessary phosphine by a method analogous to that described in the literature.[3] The analytical and spectroscopic characterisation of these complexes is shown in Table 1. The previously unknown $[MoH_4(PBu_3)_4]$ has been obtained as waxy, off-white needles. Attempts to prepare $[MoD_4(PR_3)_4]$ by employing $Li[BDEt_3]$ (super deuteride) met with mixed success. The isolation of $[MoD_4(PBu_3)_4]$ was not accomplished, instead the major product was shown to be the tetrahydride by NMR spectroscopy. The source of the hydride ligands may be either inter- or intra-molecular C–H ligand exchange, or the solvent. The complex $[MoD_4(PEt_3)_4]$, however, has been isolated. The clearest indication of perdeuteriation is the ^{31}P NMR spectrum which, when resolution enhanced, shows a nine-line pattern characteristic of four equivalent spin-1 nuclei [^2J(PD) 5.0 Hz]. There are no signals attributable to 'hydrides' in the ^1H NMR spectrum of this material.



Scheme 1 Products from the reactions of aqueous HCl with $[MoH_4(PMe_2Ph)_4]$ or $[MoH_4(PMePh_2)_4]$

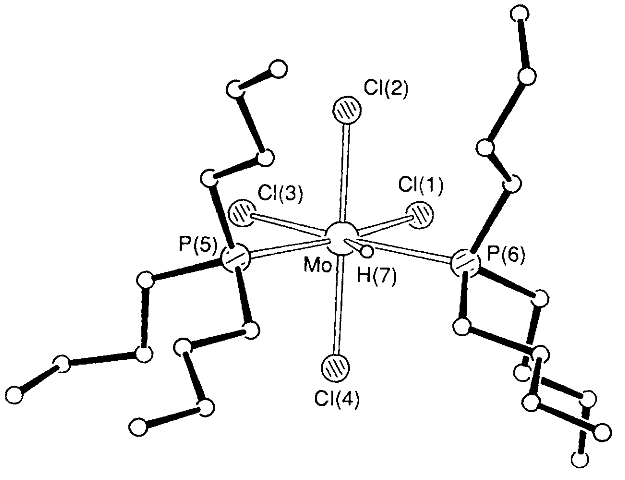


Fig. 1 View of the anion in $[PHBu_3][MoHCl_4(PBu_3)_2]$

Upon adding an excess of anhydrous HCl to a solution of $[MoH_4(PBu_3)_4]$ in thf there is a rapid reaction, which is complete within 5 min to produce an orange solid and evolve dihydrogen. The product can be isolated from the phosphonium chloride salts by dissolving the molybdenum complex in diethyl ether and slowly growing crystals at −20 °C. These crystals have been studied by X-ray crystallography and shown to be

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Analytical and spectroscopic characterisation of the complexes

Complex	Elemental analysis[a] (%) C	H	Λ_M[b]/Ω^{-1} $cm^2 mol^{-1}$	IR bands/cm^{-1}	δ[c] ^1H	$^{31}P-\{^1H\}$
$[MoH_4(PBu_3)_4]$	63.8 (63.4)	12.1 (12.3)		1710, ν(Mo–H)	−4.23(1)[d] [qnt, J(P–H) 34.8, Mo–H]	−96.7 (s) −96.7 [qnt, J(P–H) 34.0][e]
$[MoH_4(PEt_3)_4]$	50.4 (50.4)	11.1 (11.2)		1810s, 1710m, 1680vs, ν(Mo–H)	−5.60(1)[f] [qnt, J(P–H) 33.8, Mo–H]	−96.3 (s) −96.3 [qnt, J(P–H) 33.2][e]
$[MoD_4(PEt_3)_4]$				1300m, 1230m, 1210m, ν(Mo–D)		−96.3 [n, J(P–D) 5.0]
$[PHBu_3][MoHCl_4(PBu_3)_2]$	51.0 (51.1)	10.1 (9.8)	130	2420s, ν(P–H); 1845m, ν(Mo–H); 300s, 290s, 280s, ν(Mo–Cl)	3.0(7), 2.1(8), 1.5(27), 1.1–1.0(33), −22.4(6) (all broad)	+24.1 ($\Delta\nu_{\frac{1}{2}}$ = 2230 Hz)
$[PHEt_3][MoHCl_4(PEt_3)_2]$	36.0 (36.5)	8.0 (7.6)	137	2420s, ν(P–H); 1850w, ν(Mo–H); 305m, 290m, 280m, ν(Mo–Cl)	10.3(5), 1.8(23), 1.1(27)	
$[PHMe_2Ph][MoHBr_4(PMe_2Ph)_2]$[g]	46.1 (46.1)	4.2 (3.8)	93	2380m, ν(P–H); 1840vw, ν(Mo–H)		
$[PHEt_3][MoHBr_4(PEt_3)_2]$[h]	29.7 (29.8)	6.4 (6.2)	224	2400m, ν(P–H); 2350m, ν(P–H); 1860w, 1840w, ν(Mo–H)	19.1(1), 2.2(5), 1.4(9)	

[a] Calculated values in parentheses. [b] Measured in nitromethane. [c] Chemical shifts are relative to $SiMe_4$ (^1H) and $P(OMe)_3$ (^{31}P); coupling constants (*J*) are in Hz. [d] Peaks due to Bu^n residues also present: 1.64(12) [br, α-CH_2 and β-CH_2], 1.43(6) [q, J(HH) 6.7, γ-CH_2], 1.00(9) [t, J(HH) 7.4 Hz, Me]. [e] Proton undecoupled. [f] Peaks due to Et residues also present: 1.40(6) [q, J(HH) 6.5, α-CH_2], 1.05(9) [t, J(HH) 7.0 Hz, Me]. [g] No ^1H or $^{31}P-\{^1H\}$ spectra observed. [h] Contaminated with an equal amount of $[PHEt_3]Br$.

$[PHBu_3][MoHCl_4(PBu_3)_2]$ (see below). The stoichiometry of the protonation reaction is presumably as shown in equation (1).

$$[MoH_4(PR_3)_4] + 5HX \longrightarrow [PHR_3][MoHX_4(PR_3)_2] + [PHR_3]X + 3H_2 \quad (1)$$

Crystal Structure of $[PHBu_3][MoHCl_4(PBu_3)_2]$.—In the crystal the cation and anion are well separated and since our interest is primarily in the molybdenum component we shall discuss only the structural aspects of the anion. Atomic coordinates are listed in Table 2 and dimensions about the molybdenum atom are in Table 3.

The geometry of the anion is best described as a distorted pentagonal bipyramid, with the axial sites occupied by chloro-groups as shown in Fig. 1. The equatorial girdle contains two adjacent chloro ligands, which are both pseudo-*trans* to the hydride. Three other seven-co-ordinate, molybdenum monohydrido complexes, containing monotertiary phosphines, have been studied by X-ray crystallography, $[MoH(O_2CH)(PMe_3)_4]$,[4] $[MoH(BH_4)(PMe_3)_4]$[5] and $[MoH(O_2CCF_3)\{P(OMe)_3\}_4]$.[6] All these compounds adopt a distorted pentagonal bipyramid structure, with the axial positions occupied by phosphorus atoms, and in the equatorial girdle the hydride is *trans* to the chelating ligand. There is a significant difference in the mean bond lengths Mo–P_{ax} and Mo–P_{eq} (2.426 and 2.369 Å respectively in the formato-complex).[4] In our complex a similar difference is found between axial and equatorial Mo–Cl bond lengths [2.423(10) and 2.485(1) Å respectively]. In the equatorial plane the angles between the adjacent phosphorus and chlorine atoms, and also between the adjacent chloride ligands are all approximately the same (81.3 ± 1.3°). This is not observed in the other complexes since the chelate bite angles introduce distortion into the equatorial plane. The hydride ligand was identified but a Mo–H distance restraint had to be applied during refinement. This ligand does not appear to lie in the equatorial plane but is displaced 0.31(5) Å towards the side of Cl(2). This displacement appears to be a steric effect, resulting from the orientation of the P–C bonds in the adjacent phosphine ligands. A similar situation is found for the structure of $[MoH(O_2CCF_3)\{P(OMe)_3\}_4]$ where the hydride ligand is displaced 0.41 Å out of the equatorial plane towards one of the axial sites. In each phosphine ligand of our complex two of the butyl chains are well ordered and adopt all-*trans* conformations, the third, however, shows site-disorder, some of which is not well resolved; the major conformations shown in Fig. 1 have a *gauche* arrangement for the end methyl group.

The cation is disordered, occupying one of two overlapping sites, with the alternative phosphorus positions 0.33(2) Å apart; some of the butyl chains also show alternative conformations. In each orientation, the P–H bond is directed between three chloride ligands of the anion. In the major orientation, P(8a) is between 3.52(1) and 3.75(1) Å from Cl(1), Cl(2) and Cl(3) thus forming a trifurcated hydrogen bond. The corresponding bond of the other arrangement is slightly weaker and less regular, with P(8x) at distances 3.69(2) to 3.92(2) Å from the three Cl atoms.

Spectroscopic Properties of $[PHR_3][MoHX_4(PR_3)_2]$.—The analytical and spectroscopic characterisation of $[PHBu_3][MoHCl_4(PBu_3)_2]$ is shown in Table 1. Probably the most characteristic feature is the IR spectrum with the ν(P–H) and ν(Mo–H) at *ca.* 2400 and *ca.* 1850 cm^{-1} respectively. Both the $^{31}P-\{^1H\}$ and ^1H NMR spectra show broad signals and large chemical shifts characteristic of a paramagnetic species. However, no signal attributable to this molybdenum(IV) ($S = 1$) species was observed by EPR spectroscopy. The complexes $[MX_4(PMe_2Ph)_2]$ and $[MX_4(PMe_2Ph)_3]$ (M = Mo or W, X = Cl or Br) also exhibit signals with abnormal chemical shifts in the ^1H NMR spectrum.[7]

The products from the reactions of HCl or HBr with $[MoH_4(PEt_3)_4]$ or HBr with $[MoH_4(PMePh_2)_4]$ are also believed to be $[PHR_3][MoHX_4(PR_3)_2]$, on the basis of their paramagnetism, conductivity and IR spectra. However, we have been unable to separate $[PHEt_3]Br$ from $[PHEt_3][MoHBr_4(PEt_3)_2]$ in the reaction products from HBr with $[MoH_4(PEt_3)_4]$. This illustrates the recurring problem in protonation reactions of hydrido complexes containing monotertiary phosphines, namely the separation of phosphonium salts from the molybdenum product.

In conclusion we have shown that protonation of $[MoH_4$-

Table 2 Final atomic coordinates (fractional × 10⁴) for $[PHBu_3][MoHCl_4(PBu_3)_2]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	S.o.f.*
Mo	2791.5(5)	4024.4(4)	3793.9(3)	
Cl(1)	2653(2)	4217(2)	4795.1(8)	
Cl(2)	4591(2)	4056(2)	3889.1(9)	
Cl(3)	2817(2)	2420(1)	4042.8(9)	
Cl(4)	1023(1)	4037(2)	3630.4(9)	
P(5)	2889(2)	3378(1)	2855.7(8)	
C(511)	2188(6)	4014(6)	2350(3)	
C(521)	2185(9)	3604(7)	1762(3)	
C(531)	1606(10)	4237(9)	1376(4)	
C(541)	1543(14)	3814(12)	816(5)	
C(512)	2482(7)	2231(5)	2746(4)	
C(522)	1352(8)	2072(6)	2862(5)	
C(532)	1139(14)	1080(8)	2713(6)	
C(542)	991(15)	966(12)	2089(13)	0.7
C(552)	331(45)	818(39)	2774(28)	0.3
C(513)	4155(7)	3284(8)	2589(4)	
C(523)	4638(7)	4188(8)	2451(5)	
C(533)	5710(9)	4012(12)	2223(8)	
C(543)	6178(14)	4754(17)	2059(12)	
P(6)	2619(2)	5691(2)	3844(1)	
C(611)	2086(8)	6174(5)	3230(4)	
C(621)	1805(9)	7194(7)	3272(5)	
C(631)	1454(11)	7563(7)	2713(5)	
C(641)	1102(14)	8478(9)	2784(8)	
C(612)	1901(11)	6179(8)	4414(5)	
C(622)	829(12)	5934(8)	4399(6)	
C(632)	293(17)	6433(13)	4842(12)	
C(642)	−671(20)	6192(17)	4964(13)	
C(613)	3795(14)	6262(8)	3941(10)	
C(623)	4528(16)	6290(13)	3518(8)	0.55
C(633)	5523(32)	6728(28)	3691(18)	0.55
C(643)	6178(22)	6309(19)	4067(14)	0.8
C(653)	4508(29)	6304(24)	4197(15)	0.45
C(663)	5557(32)	6617(30)	4150(20)	0.3
C(673)	5959(45)	6302(40)	3657(27)	0.2
C(693)	5532(44)	7019(38)	3886(28)	0.2
H(7)	2978(39)	4851(31)	3257(20)	
P(8a)	4837(9)	2729(7)	5062(5)	0.55
P(8x)	4798(14)	2515(10)	5080(7)	0.45
C(81a)	5942(14)	3453(15)	5128(10)	0.55
C(82a)	5559(21)	4325(18)	5430(13)	0.55
C(83a)	6630(40)	4882(32)	5437(24)	0.55
C(84a)	6354(28)	5709(24)	5657(17)	0.55
C(81x)	5336(19)	3286(15)	5582(10)	0.45
C(82x)	5834(18)	3980(18)	5344(10)	0.45
C(83x)	6176(24)	4733(22)	5771(13)	0.45
C(84x)	6752(39)	5314(32)	5547(25)	0.45
C(81b)	5278(20)	1677(13)	4762(11)	0.55
C(82b)	5697(16)	1911(14)	4173(9)	0.55
C(83b)	5978(19)	1170(16)	3844(9)	
C(84b)	6686(31)	1375(30)	3445(18)	0.4
C(85b)	6151(28)	1325(24)	3262(15)	0.4
C(81y)	5788(15)	2236(15)	4590(9)	0.45
C(82y)	5355(29)	1418(25)	4375(17)	0.45
C(84y)	6174(51)	1820(43)	3313(32)	0.2
C(81c)	4352(16)	2554(14)	5753(6)	0.55
C(82c)	3518(12)	1784(10)	5708(7)	
C(83c)	3169(26)	1643(23)	6234(14)	0.55
C(84c)	2941(33)	455(30)	6143(18)	0.55
C(81z)	4199(20)	1510(14)	5357(11)	0.45
C(83z)	2995(38)	1103(36)	5960(22)	0.45
C(84z)	2450(25)	907(23)	6346(14)	0.45

* Site occupancy factor, if different from 1.0.

$(PR_3)_4]$ with anhydrous acids gives the anionic, paramagnetic hydrido complexes, $[MoHX_4(PR_3)_2]^-$, very different species from those formed by the reactions with aqueous acids.[2]

Experimental

All manipulations were routinely performed under an atmosphere of argon using standard Schlenk tube techniques. Predried solvents were further dried by distillation from appropriate drying agents immediately prior to use. Microanalyses were performed at the Nitrogen Fixation Laboratory by Mr. C. Macdonald. The following spectroscopic instruments were used: IR, Perkin-Elmer 883 spectrophotometer; NMR, JEOL G.S.X. 270 spectrometer.

The compounds $Li[BHEt_3]$, $Li[BDEt_3]$ (1.0 mol dm^3 in thf), MeOD, PBu_3, $SiMe_3Cl$ and $SiMe_3Br$ (Aldrich) were all used as received. The phosphines PEt_3[8] and $PMePh_2$[9] were synthesised in-house by published procedures. The complex, $[MoCl_4(thf)_2]$ was prepared by the literature method[10] and used within 24 h of its isolation.

Tetrahydridotetrakis(tributylphosphine)molybdenum.—To a suspension of $[MoCl_4(thf)_2]$ (1.0 g, 2.6 mmol) in thf (*ca.* 30 cm^3) was added PBu_3 (2.5 cm^3, 12.4 mmol) to give a maroon-coloured solution. This solution was stirred for 20 min, then $Li[BHEt_3]$ (15 cm^3 of 1.0 mol dm^3 solution, 15 mmol) was added slowly. After stirring for 18 h the reaction mixture was hydrolysed with EtOH (5 cm^3) and then the solvent removed *in vacuo* to yield a deep red oil. To remove any stickiness the oil was washed with methanol (25 cm^3). If after 1 h the residue remained oily, the methanol was decanted and fresh methanol (25 cm^3) was added. This procedure was repeated until a solid was obtained that could be collected by filtration. This solid was dried *in vacuo* and recrystallised from diethyl ether–methanol as waxy, off-white needles. Yield 0.4 g, 0.44 mmol, 17%.

Tetrahydridotetrakis(triethylphosphine)molybdenum and Tetrahydridotetrakis(methyldiphenylphosphine)molybdenum.—The literature procedure for the synthesis of $[MoH_4(PMePh_2)_4]$ was followed[3] with the slight modification of using only a six-fold excess (rather than 12-fold) of $Li[BHEt_3]$. The preparation of $[MoH_4(PEt_3)_4]$ was accomplished by an analogous method. The use of super hydride in the preparation of $[MoH_4(PEt_3)_4]$ gave a better yield (33%) of the product than the previous method using $NaBH_4$.[11]

Tetradeuteriotetrakis(triethylphosphine)molybdenum.—The method described above for $[MoH_4(PEt_3)_4]$ was used to prepare $[MoD_4(PEt_3)_4]$ with the following modifications. First, $Li[BDEt_3]$ was used in the place of $Li[BHEt_3]$ and secondly, MeOD was used in the place of both MeOH and EtOH during the hydrolysis and work-up stages of the preparation.

Tributylphosphonium Tetrachlorohydridobis(tributylphosphine)molybdenum.—To a solution of $[MoH_4(PBu_3)_4]$ (0.15 g, 0.16 mmol) in thf (*ca.* 10 cm^3) was added anhydrous HCl [generated *in situ* by the reaction of MeOH (0.05 cm^3, 1.6 mmol) and $SiMe_3Cl$ (0.21 cm^3, 1.6 mmol)] causing the solution to become a cloudy orange colour, with concomitant evolution of a gas (dihydrogen). The solution was stirred for about 5 min, and then the solvent was removed *in vacuo*. The residue was redissolved in diethyl ether (10 cm^3) and filtered through Celite. Storage of this solution at −20 °C resulted in the growth of chunky orange crystals. These crystals were collected by filtration, washed sparingly with hexane (2 × 2 cm^3 aliquots) and dried *in vacuo*. Yield 0.04 g, 0.05 mmol, 35%.

The other complexes, derived from reactions of acid with $[MoH_4(PEt_3)_4]$ or $[MoH_4(PMePh_2)_4]$, were prepared by analogous methods.

Crystal Structure Analysis of $[PHBu_3][MoHCl_4(PBu_3)_2]$.—*Crystal data.* $C_{36}H_{83}Cl_4MoP_3$, $M = 846.7$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 13.451(1)$, $b = 15.010(1)$, $c = 24.589(2)$ Å, $U = 4964.6$ Å^3, $Z = 4$, D_c 1.133 g cm^{-3}, $F(000) = 1816$, μ(Mo-Kα) = 5.9 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å. Crystals

Table 3 Dimensions (lengths in Å, angles in °) about the Mo atom in $[PHBu_3][MoHCl_4(PBu_3)_2]$, with e.s.d.s in parentheses

Mo–Cl(1)	2.486(2)	Mo–P(5)	2.506(2)
Mo–Cl(2)	2.433(2)	Mo–P(6)	2.515(2)
Mo–Cl(3)	2.485(2)	Mo–H(7)	1.83(4)
Mo–Cl(4)	2.413(2)		
Cl(1)–Mo–Cl(2)	88.7(1)	Cl(2)–Mo–P(6)	93.9(1)
Cl(1)–Mo–Cl(3)	82.5(1)	Cl(3)–Mo–P(6)	162.4(1)
Cl(2)–Mo–Cl(3)	88.9(1)	Cl(4)–Mo–P(6)	84.8(1)
Cl(1)–Mo–Cl(4)	95.2(1)	P(5)–Mo–P(6)	115.8(1)
Cl(2)–Mo–Cl(4)	175.7(1)	Cl(1)–Mo–H(7)	130.3(18)
Cl(3)–Mo–Cl(4)	93.6(1)	Cl(2)–Mo–H(7)	85.4(17)
Cl(1)–Mo–P(5)	163.9(1)	Cl(3)–Mo–H(7)	146.5(17)
Cl(2)–Mo–P(5)	92.5(1)	Cl(4)–Mo–H(7)	90.5(17)
Cl(3)–Mo–P(5)	81.4(1)	P(5)–Mo–H(7)	65.9(17)
Cl(4)–Mo–P(5)	84.3(1)	P(6)–Mo–H(7)	51.2(17)
Cl(1)–Mo–P(6)	80.2(1)		

of the compound are long, yellow prisms, one of which was cut into several fragments which were mounted on glass fibres. Whilst one fragment was being photographed, another, size 0.33 × 0.55 × 0.57 mm was put on to our Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for the determination of accurate cell dimensions (from the goniometer settings of 25 reflections having θ *ca.* 10.5°, each centred in four orientations) and measurement of diffraction intensities (to $\theta_{max} = 23°$).

During processing, data were corrected for Lorentz-polarisation effects, slight deterioration (*ca.* 7.8% overall), absorption (by semi-empirical, ψ-scan methods) and to eliminate negative intensities (by Bayesian statistical methods). A total of 3851 independent reflections were entered into the SHELX system[12] for structure determination (by the heavy-atom method) and refinement (by full-matrix, least-squares methods[13]). Thermal parameters of some of the atoms in the butyl chains were large, and disorder was apparent in several chains. The phosphonium cation adopts one of two principal orientations (with the alternative sites for the P atom *ca.* 0.33 Å apart); in some butyl chains the disorder was fully resolved, but in others, in both cation and anion, complete resolution was not achieved. Table 2 indicates the atoms where disorder was not resolved, having s.o.f. < 1.0; in the 'ordered' chains, C(543), C(632) and C(642) show the largest thermal motion, with $U_{eq} > 0.30$ Å^2. Hydrogen atoms in the organic ligands were not included. The hydride ligand was identified in a difference map calculated towards the end of the refinement process using only the reflections with $\sin\theta < 0.26$; this atom, on refinement, tended to move away from the Mo atom and was restrained in later cycles. Refinement of 404 atomic parameters was terminated with $R = 0.057$, $R' = 0.070$[12] for the 3766 reflections having $I > \sigma_I$, weighted $w = (\sigma_F^2 + 0.001\ 24F^2)^{-1}$. Refinement of the inverted structure (atoms at $\bar{x}$, $\bar{y}$, $\bar{z}$) gave results not significantly different from those described above. In the final difference map there were few features of significance but considerable noise around some butyl chains in both cation and anion. Scattering-factor curves for neutral atoms were from ref. 14. Computer programs used in this analysis have been noted above and in Table 4 of ref. 15, and were run on the MicroVAX II computer in this laboratory.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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