Synthesis and Crystal Structure of Hydrido(tetrahydroborato)tetrakis(trimethylphosphine)molybdenum(II) †

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The interaction of trichlorotris(tetrahydrofuran)molybdenum(III), $MoCl_3(C_4H_8O)_3$, with trimethylphosphine in ether or tetrahydrofuran gives trichlorotris(trimethylphosphine)molybdenum(III). This has been shown to react with sodium borohydride to yield $MoH(BH_4)(PMe_3)_4$, whose structure has been determined by *X*-ray crystallography. The compound crystallizes in the orthorhombic space group *Cmcm* with a = 12.572(5), b = 12.405(5), c = 14.433(6) Å, and Z = 4 for D_c = 1.23 g cm^{-3}. The final R factor was 0.048 based on 1 078 independent observed reflections. In the crystal the molecule lies at the intersection of two mirror planes, with the hydride, the molybdenum atom, and the boron atom of the bidentate BH_4 group lying precisely on the intersection. Hydrogen-1 and ^{31}P n.m.r. spectra for the complex are also briefly reported.

In transition-metal complexes the BH_4^- ligand may be unidentate, bidentate, or tridentate. Compounds of the last two types are well documented [1] although structural evidence for unidentate BH_4 groups has only recently been presented.[2] Compounds containing both tetrahydroborate and hydride ligands are known for a number of metals where bulky phosphine or other ligands are present.[3] We now describe the preparation and *X*-ray crystal structure of a new hydridoborohydridotetrakis(trimethylphosphine)molybdenum(II) complex of the non-bulky trimethylphosphine.

RESULTS AND DISCUSSION

The slow addition of solid trichlorotris(trimethylphosphine)molybdenum(III), obtained by interaction of $MoCl_3(thf)_3$ with PMe_3 in tetrahydrofuran (thf), to a suspension of sodium tetrahydridoborate in ethanol containing PMe_3 gives a purple solution from which $MoH(BH_4)(PMe_3)_4$ can be isolated as a purple crystalline solid. This compound is very air and moisture sensitive, particularly in solution, and although insoluble in petroleum is moderately soluble in benzene, toluene, thf, *etc.* Analytical, molecular weight, and spectroscopic data indicate that the complex is $MoH(BH_4)(PMe_3)_4$ and this is confirmed by an *X*-ray diffraction study.

The molecular structure and atom-numbering scheme are shown in Figure 1. The molecule lies at the intersection of two mirror planes: the hydride, the molybdenum atom, and the boron atom lie precisely on the intersection. The overall geometry about the molybdenum atom is distorted octahedral. Important bond lengths and angles are shown in Table 1.

The molybdenum–hydrogen distance for the hydride ligand, 1.63 Å, agrees well with the sum of covalent radii, 1.60 Å.[4] It was not possible to refine the hydrogen-atom position, and therefore no standard deviation can be ascribed to the bond distance. In efforts to refine the hydrogen-atom position, it was found to move irrevocably toward the molybdenum atom and convergence was not obtained.

The borohydride ligand is clearly bidentate. The molybdenum–hydrogen (bridge) distance, 1.96 Å, is in good agreement with the molybdenum–hydrogen (bridge) distances of 1.99(9) and 2.04(8) Å found in $[N(PPh_3)_2][Mo(CO)_4(BH_4)]$.[5] The boron–hydrogen distance for the bridging atom, 1.12 Å, and the boron–hydrogen (terminal) distance, 1.08 Å, are also comparable to those found by Kirtley *et al.*[5] The H–Mo–H angle, 53°, is not significantly smaller than the 59(4)° value found in the $[Mo(CO)_4(BH_4)]^-$ structure.

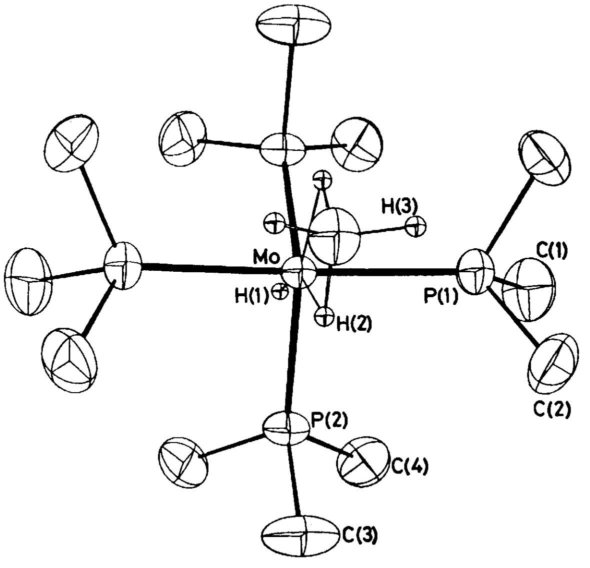

FIGURE 1 The molecular structure of hydrido(tetrahydroborato)tetrakis(trimethylphosphine)molybdenum(II) and atom-numbering scheme

Even in the absence of hydrogen-atom locations, the Mo · · · B separation unequivocally demonstrates the bidentate attachment of the BH_4^- ligand. The molybdenum–boron distance, 2.468(12) Å, is only slightly larger than the 2.41(2) Å value found for the bidentate BH_4^- in $[N(PPh_3)_2][Mo(CO)_4(BH_4)]$.[5] (From covalent radii [4] one would predict a Mo · · · B approach of 2.71 Å for a single hydrogen bridge attachment of BH_4^-.) The Mo · · · B length is, however, considerably greater than

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† No reprints available.

the 2.18 Å value which one would normally ascribe for a molybdenum–boron bond.[4] We therefore conclude that the molybdenum–boron interaction in this compound is minimal.

The two independent molybdenum–phosphorus distances, 2.381(2) and 2.435(2) Å, agree with the sum of the covalent radii, 2.40 Å,[4] but are below the normal range, 2.46—2.51 Å, tabulated for molybdenum(II) complexes.[6]

TABLE 1

Interatomic bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Mo–H(1)	1.63	B–H(2)	1.12
Mo–H(2)	1.96	B–H(3)	1.08
Mo–P(1)	2.435(2)	P(1)–C(1)	1.857(9)
Mo–P(2)	2.381(2)	P(1)–C(2)	1.839(6)
Mo $\cdots$ B	2.468(12)	P(2)–C(3)	1.858(9)
		P(2)–C(4)	1.828(6)
H(1)–Mo–P(1)	95.7	Mo–P(1)–C(1)	125.8(4)
H(1)–Mo–P(2)	59.3	Mo–P(1)–C(2)	115.7(2)
B–Mo–P(1)	84.3(1)	C(1)–P(1)–C(2)	98.6(3)
B–Mo–P(2)	120.7(1)	C(2)–P(1)–C(2′)	97.4(5)
P(1)–Mo–P(2)	92.93(2)	Mo–P(2)–C(3)	113.5(4)
P(1)–Mo–P(1′) *	168.4(1)	Mo–P(2)–C(4)	121.1(2)
P(2)–Mo–P(2′)	118.6(1)	C(3)–P(2)–C(4)	100.2(3)
H(2)–Mo–H(2′)	52.8	C(4)–P(2)–C(4′)	96.9(5)
H(2)–B–H(2′)	101.2	H(3)–B–H(3′)	100.6
		H(2)–B–H(3)	113.9

*Atoms designated by a prime are related to those given in Table 2 by a mirror plane.

The unit-cell packing shown in Figure 2 is typical for a molecular substance of this type.

Spectroscopic studies are generally in accord with the structure as determined, and the spectra are similar to those for other related complexes.[3] Thus the solid-state i.r. spectrum of this compound shows bridging and terminal B–H stretching modes which are in good agreement with a bidentate structure having approximately C_{2v} local symmetry.[1,7] The symmetric and antisymmetric B–H$_t$ stretching absorptions (A_1, B_1) are observed at 2 290 and 2 340 cm^{-1}. These values are somewhat low since the normal range extends from 2 400 to 2 600 cm^{-1}. The splitting of this strong doublet is within the usual range of 50—80 cm^{-1} generally found for these complexes. The B–H$_b$ stretching modes also appear as a strong doublet at 1 885 and 1 935 cm^{-1} and their separation is again *ca.* 50 cm^{-1}. Finally the bridge stretch (A_1) and the bridge deformation (B_2) appear as strong bands at 1 360 and 1 165 cm^{-1} respectively. The former is also somewhat low since the normal range extends to 1 500 cm^{-1}. These values are in good agreement with those for other highly covalent bidentate transition-metal tetrahydroborates.[1] Apart from these bands and others characteristic of the PMe$_3$ groups, there is a medium intensity absorption at 1 725 cm^{-1} that can be tentatively assigned to the Mo–H stretch.

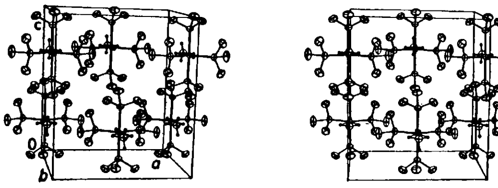

FIGURE 2 Stereoscopic view of the unit-cell packing

The ^{1}H and ^{31}P n.m.r. spectra of MoH(BH$_4$)(PMe$_3$)$_4$ are very complicated. Apart from the difficulties inherent to the spin system for this compound and those due to the presence of a BH$_4$ group, there is also evidence for the existence of isomers in solution. The ^{1}H n.m.r. spectrum of MoH(BH$_4$)(PMe$_3$)$_4$ at room temperature shows a somewhat broad resonance centred at δ 1.4 due to the methylphosphine protons and some broader ones which can be distinguished only with difficulty, extending from *ca.* δ −3.5 to −7.5. The latter are best observed in the ^{1}H (100 MHz, F.T.) n.m.r. spectrum which also displays some very broad resonances in the region δ 7—4. On cooling to 0 °C some changes are observed. Thus in the region δ −3.5 to −7.5 a broad resonance at δ −4.2 and three triplets centred at δ −15.0, −5.8, and −6.6 could be distinguished, but there were some broad bands underneath and therefore their relative intensities could not be determined. The broad bands in the region δ 7—4 collapsed into a single broad resonance centred at *ca.* δ 5.5. Although extensive crystallization occurred upon cooling to −80 °C, the same features could be noted with the three triplets now well separated from the broad resonance at δ −4.5 and their intensities approximately in the ratio 1 : 2 : 1. At this temperature, the bands at δ 5.5 and −4.5 had half-line widths of *ca.* 66 and 42 Hz respectively. We merely suggest that the resonances at δ 5.5 and −4.5 are due to the bridging and terminal BH$_2$ hydrogens respectively and the triplet of triplets at δ −15.0, −5.8, and −6.6 to the hydride ligand. However, as found for many bidentate tetrahydroborate complexes of transition metals, and due to rapid interchange on the n.m.r. time scale, the bridge and terminal hydrogen atoms may be magnetically equivalent in the temperature range studied. In this case the broad resonance at δ −4.5 could be due to the existence in solution of another isomer. This seems to be supported by the ^{31}P{^{1}H} n.m.r. spectrum which at room temperature shows two rather broad bands centred at 34.6 and 4 p.p.m.* While the former remains broad and unresolved in the temperature range 60 to −80 °C, the latter splits upon cooling giving three triplets centred at 5.6, 4.0, and 2.4 p.p.m., with the central triplet being much more intense than the outer ones. The resonances can be ascribed to the presence of isomers in solution, but little can be said of their structures or the reason for the large chemical-shift differences.

EXPERIMENTAL

Microanalyses were by the Pascher Microanalytical Laboratory (Bonn). Molecular weights were measured cryoscopically in benzene under nitrogen and the results were averages of two determinations which gave values within ±5% of the expected molecular weight. The

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* ^{31}P chemical shifts are to high frequency of external 85% H$_3$PO$_4$.

spectroscopic instruments used were a Perkin-Elmer model **456** for i.r. spectra, and a Perkin-Elmer R12A (^{1}H) and Varian XL–100–12 (^{1}H, ^{31}P, F.T.) for n.m.r. spectra.

Solvents were dried using conventional procedures. All preparations and other operations were carried out under oxygen-free nitrogen following standard Schlenk-tube techniques.

Trichlorotris(*trimethylphosphine*)*molybdenum*(III).— To trichlorotris(tetrahydrofuran)molybdenum(III) [8] (4.2 g, *ca.* 10 mmol) suspended in diethyl ether (750 cm^3) was added trimethylphosphine (6 cm^3, *ca.* 60 mmol) and the mixture stirred for 36 h at room temperature. The grey solid was removed by filtration and the red-brown solution evaporated until crystallization began. Cooling to -30 °C with addition of light petroleum (b.p. 30—40 °C) gave yellow crystals. Yield, *ca.* 80%; m.p. 50—55 °C (decomp.). It can be recrystallized from toluene–light petroleum (Found: C, 25.3; H, 6.4; Cl, 24.5; P, 21.2; *M*, 462. $C_9H_{27}Cl_3MoP_3$ requires C, 25.1; H, 6.3; Cl, 24.7; P, 21.6%; *M*, 430). The preparation can also be carried out in tetrahydrofuran (thf) ($MoCl_3$·3thf, 0.84 g, *ca.* 2 mmol), PMe_3, 1.2 cm^3, *ca.* 12 mmol in 35 cm^3 thf) when the reaction time is only 3—5 h at room temperature and the yield is *ca.* 80%.

The compound is air and moisture sensitive. It is soluble in benzene, toluene, dichloromethane, thf, *etc.*, but is less soluble in diethyl ether and almost insoluble in saturated hydrocarbons.

Hydrido(*tetrahydroborato*)*tetrakis*(*trimethylphosphine*)-*molybdenum*(II).—$MoCl_3(PMe_3)_3$ (0.47 g, *ca.* 1 mmol) was slowly added to a suspension of $NaBH_4$ (0.4 g, *ca.* 10 mmol) in ethanol (30 cm^3) in the presence of PMe_3 (0.2 cm^3, *ca.* 2 mmol). A deep purple solution was obtained, from which purple crystals precipitated after stirring at room temperature for *ca.* 3 h. The solvent was then removed *in vacuo* and the residue extracted with benzene (60 cm^3) and filtered. The resulting solution was again evaporated *in vacuo*, the residue dissolved in diethyl ether, and the solution filtered and cooled overnight at -20 °C to give microcrystals of the compound. Yield, *ca.* 60% after recrystallization from toluene (10—15 cm^3) (Found: C, 34.8; H, 10.0; P, 30.6; *M*, 410. $C_{12}H_{41}BMoP_4$ requires C, 34.6; H, 9.9; P, 29.8%; *M*, 416).

Infrared (Nujol mull and KBr disc) bands at: 2 985, 2 955, 2 895, 2 340, 2 290, 1 935, 1 885, 1 725, 1 420, 1 360, 1 290, 1 275, 1 165, 930, 850, 740, 700, 650, 515, 375, 340, and 295 cm^{-1}.

X-*Ray Data Collection, Structure Determination and Refinement*.—*Crystal data*. $C_{12}H_{41}BMoP_4$, $M = 416.1$, Orthorhombic, $a = 12.572(5)$, $b = 12.405(5)$, $c = 14.333(6)$ Å, $U = 2\,250.9$ Å^3, $Z = 4$, $D_c = 1.23$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 8.44$ cm^{-1}, space group *Cmcm*. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta \geqslant 34°$) accurately centred on an Enraf–Nonius CAD-4 diffractometer.

A crystal of dimensions 0.35 × 0.35 × 0.45 mm was sealed in a thin-walled capillary under a nitrogen atmosphere. Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were measured by the w—2θ scan technique in a manner similar to that described previously.[9] All reflections in one independent octant out to $2\theta \leqslant 50°$ were measured; 1 078 were considered observed $[I \geqslant 3\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects, but not for absorption (the minimum and maximum transmission factors differ by less than 5%).

Full-matrix least-squares refinement was carried out using the Busing and Levy ORFLS program.* The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Mo, P, C, and B were taken from Cromer and Waber; [10] those for H were taken from ref. 11. The scattering for molybdenum was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[12]

Systematic absences indicated that the space group was *C2cm*, *Cmc2$_1$*, or *Cmcm*. Subsequent structure solution and refinement showed that the proper choice was *Cmcm*. The molybdenum atom was deduced by the inspection of a Patterson map, to reside on a site of *mm* symmetry.

TABLE 2

Final fractional co-ordinates with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Mo	0	0.247 46(7)	0.250 00
P(1)	0	0.247 1(2)	0.082 1(1)
P(2)	0.162 8(1)	0.149 5(2)	0.250 0
C(1)	0	0.155 1(8)	−0.033 3(6)
C(2)	0.109 9(5)	0.347 0(6)	0.033 5(4)
C(3)	0.282 7(6)	0.237 2(8)	0.250 0
C(4)	0.196 4(5)	0.057 9(6)	0.344 8(4)
B	0	0.446 4(10)	1.250 0
H(1)	0	0.116	0.250
H(2)	0.069	0.389	0.250
H(3)	0	0.502	0.308

Subsequent calculation of Fourier maps afforded the location of the remaining non-hydrogen atoms. Refinement with isotropic temperature factors led to $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.105$. Conversion to anisotropic thermal parameters and further refinement led to $R = 0.064$. The hydrogen atoms of the hydride and borohydride ligands were located on a difference-Fourier map, and their contribution to the scattering was included. (Those on the phosphine ligands could not be found.) Additional cycles of refinement of the non-hydrogen atoms led to final values of $R = 0.048$ and $R' = \{\Sigma(|F_o| - |F_c|)^2/\Sigma(F_o)^2\}^{\frac{1}{2}} = 0.052$. The largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. A final difference-Fourier showed no feature greater than 0.4 e Å^{-3}. The standard deviation of an observation of unit weight was 2.96. Unit weights were used at all stages and unobserved reflections were not included. No systematic variation of $w(|F_o| - |F_c|)$ *vs.* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 2. The thermal parameters and the observed and calculated structure factor amplitudes are given in Supplementary Publication No. SUP 22677 (11 pp.).†

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* Other crystallographic programs used on a UNIVAC 1110 include ORFFE (distance and angle with estimated standard deviations by W. R. Busing, K. O. Martin, and H. A. Levy), ORABS (absorption correction, by D. J. Wehe, W. R. Busing, and H. A. Levy), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), BPL (least-squares planes, by W. E. Hunter), and FOURIER (D. J. Hodgson's version of Dellaca and Robinson's program).

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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