Trimethylphosphine Complexes of Molybdenum, Tungsten, Niobium, and Tantalum. *X*-Ray Crystal Structures of Di-μ-hydrido-dihydridohexakis(trimethylphosphine)dimolybdenum(II)(*Mo–Mo*) and of μ-Dimethylphosphido-μ-hydrido-tetrahydridopentakis(trimethylphosphine)ditungsten(II, IV)(*W–W*)

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The reduction of $Mo_2[O_2CMe]_4$ by sodium amalgam in tetrahydrofuran (thf) in the presence of excess of PMe_3 under hydrogen (3 atm) yields the dimeric complex $Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6$ (1), whose structure has been determined by *X*-ray crystallography. The compound is orthorhombic, space group *Pbca*, with $a = 12.133(6)$, $b = 14.892(4)$, $c = 17.692(5)$ Å, and $Z = 4$. The structure has been refined to an *R* of 0.0362 for 2 388 observed $[I > 1.5\sigma(I)]$ diffractometer data. The centrosymmetric molecule has an edge-shared (H, H) bioctahedral structure with a Mo–Mo distance of 2.194(3) Å. Of the three phosphine ligands on each metal, one is approximately perpendicular to the Mo_2H_2 plane and *trans* to the terminal hydride with Mo–P 2.430(3) Å, and two lie in the Mo_2H_2 plane; differences in the Mo–P distances to these phosphines [2.430, 2.417(3) Å] suggest possible asymmetry in the Mo–H–Mo bridges, although the low precision with which the H-atom positions are located does not allow an unequivocal decision. Reduction of the complex $W_2Cl_4(PMe_3)_4$ in thf by sodium amalgam under hydrogen leads to a species best formulated as $W_2H_4(\mu\text{-}H)(\mu\text{-}PMe_2)(PMe_3)_5$ (2). This complex is monoclinic, space group $P2_1/c$, with $a = 9.931(5)$, $b = 12.023(3)$, $c = 26.605(4)$ Å, $\beta = 91.66(3)°$, and $Z = 4$. The structure was refined to an *R* value of 0.0525 for 4 218 observed reflections. The molecule appears to be a pentahydride of the binuclear unit $(Me_3P)_2\overline{W(\mu\text{-}PMe_2)W}(PMe_3)_3$ although it has not been possible to locate the metal-bonded hydrogen atoms. The two metal atoms give two sets of W–P bond lengths, with those for the metal carrying three terminal phosphines slightly shorter [2.355—2.464(5) Å] than those to the metal carrying two phosphines [2.433—2.502(6) Å]. Interaction of MMe_5 (M = Nb or Ta) and PMe_3 gives $MMe_5(PMe_3)_2$; the niobium compound reacts with hydrogen to give $NbH_5(PMe_3)_4$.

THE synthesis and crystal structure of the dimeric phosphine hydride $Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6$ was recently noted,[1] and full details are now provided. We have also described reactions of WMe_6 and PMe_3 and the synthesis, by hydrogenolysis, of $WH_2(PMe_3)_5$ and $WH_4(PMe_3)_4$ [2] and now report similar studies on the permethyls of niobium and tantalum.

Hydrogen-1 and ^{31}P n.m.r. data for the compounds are collected in Table 1; ^{13}C data are in the Experimental section.

RESULTS AND DISCUSSION

Di-μ-hydrido-dihydridohexakis(trimethylphosphine)-dimolybdenum(II)(Mo–Mo).—The reduction of dimolybdenum tetra-acetate by sodium amalgam in tetrahydrofuran (thf) in the presence of an excess of trimethylphosphine under hydrogen (3 atm †) produces $Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6$, (1), in high yield. The compound can be crystallised with some difficulty from the deep red-brown concentrated light petroleum solutions at −20 °C; large crystals of this dark yellow compound often appear almost black.

TABLE 1

Hydrogen-1 and ^{31}P n.m.r. spectral data

Compound	^1H [a] (δ/p.p.m.)	Assignment	$^{31}P\text{-}\{^1H\}$ [b] (δ/p.p.m.)
(1) $Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6$	1.80 (m) [54]	P*Me*$_3$	12.26 (s)
	−5.5 (q) [2], ^2J(P–H) = 6	Mo–*H*	
	−6.7 (q) [2], ^2J(P–H) = 18	Mo–*H*	
(2) $W_2H_4(\mu\text{-}H)(\mu\text{-}PMe_2)(PMe_3)_5$	1.52 (m) [18]	P*Me*$_3$	−24.4 (m) [c]
	1.84 (m) [27]	P*Me*$_3$	−21.4 (m)
	−2.26 (t) [5], ^2J(P–H) = 25.2	W–*H*	67.0 (m)
	2.51 (d) [6], ^2J(P–H) = 9	μ-P*Me*$_2$	−14.7 (m)
$NbMe_5(PMe_3)_2$ [d]	1.10 (d) [18], ^2J(P–H) = 2.5	P*Me*$_3$	−10.47 (s) [e]
	1.15 (s) [15]	Nb–*Me*	
$TaMe_5(PMe_3)_2$ [f]	1.02 (d) [18], ^2J(P–H) = 6 [e]	P*Me*$_3$	−27.46 (s) [e]
	1.25 (s) [15]	Ta*Me*	
$NbH_5(PMe_3)_4$ [g]	1.30 (d) [36], ^2J(P–H) = 32.4	P*Me*$_3$	−2.60 (s)
	−0.67 (q) [5], ^2J(P–H) = 43.2	Nb–*H*	

[a] In C_6D_6 solvent referenced to $SiMe_4$ (δ 0.0) at 90 MHz and 35 °C unless otherwise stated; q = quintet. Relative intensities are given in square brackets, *J* values in Hz. [b] In C_6D_6 (10%)–C_6H_6 referenced to external 85% H_3PO_4 (δ 0.0) at 40.5 MHz, 28 °C. Peaks to high frequency (low field) of reference are positive. [c] See text. [d] At −70 °C. [e] In $[^2H_8]$toluene. [f] At −50 °C. [g] At −40 °C.

The compound appears to be the only binuclear molybdenum phosphine hydride so far known, although binuclear hydrides containing $\eta\text{-}C_5H_5$,[3] CO,[4] or Cl[5] ligands are known, as well as mononuclear species with

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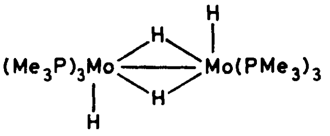
† Throughout this paper: 1 atm = 101 325 Pa.

tertiary phosphine such as $MoH_4(PMePh_2)_4$.[2] Unlike the moderately stable molybdenum(IV) hydrides, the compound is pyrophoric in the solid state and stable in solution at room temperature for only *ca.* 0.5 h. The ^{31}P-{^1H} spectrum initially shows a sharp singlet at δ 12.26 p.p.m., but after *ca.* 1 h an additional resonance at δ 6.44 p.p.m. and free PMe_3 are observed while the solution darkens and deposits insoluble brown matter.



$$[(Me_3P)_3HMo(\mu\text{-}H)_2MoH(PMe_3)_3]$$

(1)

Two high-field Mo–H resonances of approximately equal area are also observed; both can be described as quintets although they have quite different coupling constants [δ −5.5 p.p.m., $^2J(^{31}P-^1H) = 6$ Hz; δ −6.7 p.p.m., $^2J(^{31}P-^1H) = 18$ Hz]. On warming to 80 °C (in deuteriotoluene), the δ −6.7 p.p.m. multiplet sharpens considerably [now $^2J(^{31}P-^1H) = 12$ Hz], while the other remains unchanged. There is no exchange between Mo–H groups and deuterium (1 atm, 10 min).

The compound reacts readily with alkyl halides, CO, alkenes, acetylene, and H_2S although no well defined products could be isolated. The compound does not act as a catalyst for hydrogenation of hexene (3 atm, 40 °C) in benzene and there is no isomerisation of the alkene.

A molecule of this molybdenum compound is shown in Figure 1 and some of the more important bond lengths and angles are given in Table 2. In the dimeric molecule, formally a molybdenum(II) species, each metal atom is bonded to three PMe_3 groups and one terminal and two bridging hydride atoms. The hydride atoms are defined with low precision only and the apparent asymmetry and exceptionally short Mo–H distances in the Mo–H–Mo bridges cannot be regarded with any certainty and only a neutron-diffraction study would provide a clear-cut confirmation of this feature. However, there may be some asymmetry in this bridge since the two equatorial Mo–P bonds [to P(2) and P(3)] are significantly different, although if the Mo–H–Mo asymmetry is as indicated, we must attach some kind of inverse *trans* influence to the bridging Mo–H bond since the shortest Mo–P distance is *trans* to the shortest Mo–H distance.

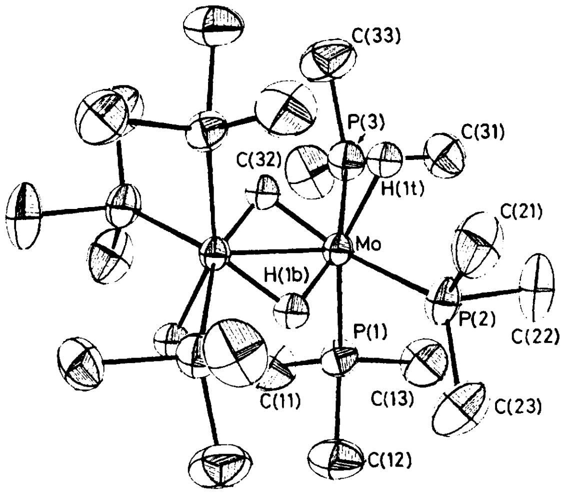


FIGURE 1 Structure of $Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6$, (1)

TABLE 2

Bond lengths and angles for $Mo_2H_4(PMe_3)_6$ (1) with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

Mo–Mo	2.194(3)	C(21)–P(2)	1.816(8)
P(1)–Mo	2.430(3)	C(22)–P(2)	1.838(8)
P(2)–Mo	2.430(3)	C(23)–P(2)	1.836(9)
P(3)–Mo	2.413(3)	C(31)–P(3)	1.828(7)
C(11)–P(1)	1.826(8)	C(32)–P(3)	1.822(8)
C(12)–P(1)	1.845(8)	C(33)–P(3)	1.825(8)
C(13)–P(1)	1.839(8)		

(*b*) Bond angles (°)

P(2)–Mo–P(1)	95.4	C(21)–P(2)–Mo	121.5(3)
P(3)–Mo–P(1)	95.1	C(22)–P(2)–Mo	104.6(3)
P(3)–Mo–P(2)	131.2	C(23)–P(2)–Mo	129.0(4)
P(1)–Mo–Mo′	101.8	C(31)–P(3)–Mo	106.0(3)
P(2)–Mo–Mo′	113.2	C(32)–P(3)–Mo	128.0(3)
P(3)–Mo–Mo′	110.8	C(33)–P(3)–Mo	120.9(3)
H(1b)–Mo–P(1)	71.1(10)	C(12)–P(1)–C(11)	95.3(4)
H(1b)–Mo–P(2)	81.2(11)	C(13)–P(1)–C(11)	100.1(5)
H(1b)–Mo–P(3)	146.7(10)	C(13)–P(1)–C(12)	98.2(4)
H(1t)–Mo–Mo′	106.3(14)	C(22)–P(2)–C(21)	99.0(4)
H(1t)–Mo–P(1)	151.8(13)	C(23)–P(2)–C(21)	97.3(5)
H(1t)–Mo–P(2)	75.1(13)	C(23)–P(2)–C(22)	100.0(5)
H(1t)–Mo–P(3)	73.5(14)	C(32)–P(3)–C(31)	98.4(4)
C(11)–P(1)–Mo	121.3(3)	C(33)–P(3)–C(31)	98.9(4)
C(12)–P(1)–Mo	123.6(3)	C(33)–P(3)–C(32)	99.0(5)
C(13)–P(1)–Mo	113.6(3)		

The molecular structure is also of interest in terms of the relationship between the hydride bridging and the metal–metal bonding assumed to be present. Since the molecule is formally a molybdenum(II) species, we might have expected a structure of the type found for most species in this class, four equatorial ligands (two hydrogens and two phosphines) and one weakly bound axial ligand (phosphine) on each metal, and a quadruple bond. In this form, both metals would have an 18-electron configuration, and initially it is difficult to see why hydride bridging is invoked, since this is formally a means by which electron counts on the metals could be increased. Of course, the 18-electron count would be satisfied by considering the two hydride bridges to replace two of the Mo–Mo bonds, the Mo–Mo interaction thus formally being reduced to a double bond. Alternatively, we can consider the ' bridging ' hydrides to be acting in a different manner and consider the structure to arise in the following manner. Each metal is considered to be sp^3d^2 hybridised, and to carry three phosphines and one hydride in the ' equatorial position ' (the M–M bond is axial). Addition of one electron to each metal gives rise to 14-electron systems and then the formation of a quadruple bond in the usual way using one axial octahedral orbital on each metal for the Mo–Mo σ bond gives 18-electron configurations and the species $[(Me_3P)_3$-HM≡oMoH$(PMe_3)_3]^{2-}$. The second axial octahedral orbital is filled and non-bonding. The two remaining protons can then be considered to interact with and stabilise one of the M–M π bonds to produce effectively two three-centre two-electron bent bonds of the B_2H_6 type. This type of interaction relates directly to the suggestion of Bau *et al.*[4] of a significant amount of M–M bonding in M–H–M bridges in general.

Of further interest is the comparison of this dimolybdenum molecule and the corresponding ruthenium(II) species.[6] The molecular structures are very similar although not unnaturally the bonding parameters (especially the M–M distance) are a little different. The change from the Mo to the Ru species involves adding two electrons to each metal. With our suggested model, these could be used to cancel out the remaining M–M π bond and the δ bond, leaving the metal atom linked by the σ bond and the diprotonated π bond.

μ-Dimethylphosphido-μ-hydrido-tetrahydridopentakis(trimethylphosphine)ditungsten(II, IV)(W–W).—Since there is no tungsten analogue of $Mo_2[O_2CMe]_4$, we attempted to prepare the analogue of the above complex by interaction of $W_2Cl_4(PMe_3)_4$ [7] with hydrogen (3 atm) and sodium amalgam in thf at 75 °C. High yields of a dark green diamagnetic light petroleum-soluble complex, considered to be $W_2H_4(\mu\text{-}H)(\mu\text{-}PMe_2)(PMe_3)_5$, (2), were obtained. The i.r. spectrum shows four broad peaks at 1 827, 1 780, 1 743, and 1 643 cm^{-1} while the ^1H n.m.r. spectrum at 25 °C shows a broad, poorly resolved triplet at δ −2.26 p.p.m. [$^2J(^{31}P-^1H)$ = 25.2 Hz]. In addition to two PMe_3 multiplets there is a sharp doublet at δ 2.51 p.p.m. [$J(^{31}P-^1H)$ = 9 Hz] that can be ascribed to the μ-PMe_2 group. The spectrum is unchanged from −100 to +90 °C.

In the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, the peak at δ 67.0 p.p.m. of μ-PMe_2 is in a similar position to that in $Co_2(\mu\text{-}PMe_2)(\mu\text{-}CH_2PMe_2)(PMe_3)_2(CO)_2$,[8] ($\delta$ 68.4 p.p.m.). The $^{31}P\text{-}\{^1H\}$ spectrum also shows a broad hump at *ca.* δ −24.4 p.p.m. and two other unresolved resonances at δ −21.4 and −14.7 p.p.m. There is also a weak line due to free PMe_3 so that although the molecular weight in benzene is normal, some phosphine evidently dissociates and there could be isomers in solution.

The W and PMe_3 skeleton of this molecule, as found from the *X*-ray study, is shown in Figure 2; some of the more important bond lengths and angles are given in Table 3. In view of our inability to locate and therefore define the number of hydride atoms, we are unable to make a definite assignment of full identity and structure for this compound.

Since the compound is diamagnetic an odd number of hydrogen atoms must be present; considering the spectroscopic data and the basic geometry, (which requires a minimum of four), five seems the most likely. We may also assume a strong bonding force between the two metal atoms not only on account of the W–W separation of 2.588(1) Å, but the very small angle [65.2(1)°] at the bridging phosphido-group. The bonding force could arise from metal–metal bonding alone or more likely, supported by M–H–M bridges.

There are several possibilities for a pentahydride with one or two bridging hydrides and differing numbers of terminal hydrides on W(1) and W(2). On the assumption that covalent radii vary as a function of oxidation state, then the differing W–P bond lengths for W(1) and W(2) imply different oxidation states for the two

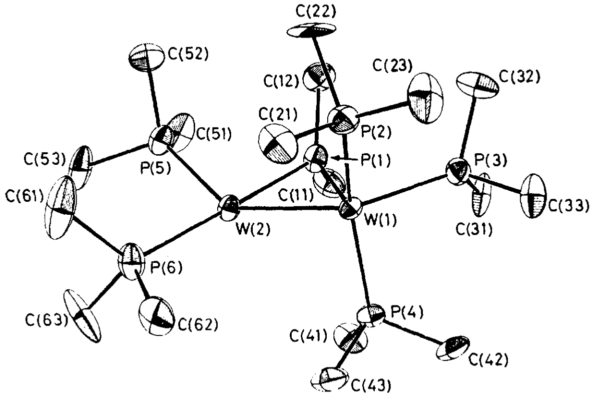


FIGURE 2 Structure of $W_2H_5(\mu\text{-}PMe_2)(PMe_3)_5$, (2), with the hydrogen atoms omitted

TABLE 3

Interatomic distances and interbond angles for $W_2H_5(\mu\text{-}PMe_2)(PMe_3)_5$ (2) with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

W(2)–W(1)	2.588(4)	C(31)–P(3)	1.840(16)
P(1)–W(1)	2.352(5)	C(32)–P(3)	1.850(16)
P(1)–W(2)	2.446(5)	C(33)–P(3)	1.801(17)
P(2)–W(1)	2.433(6)	C(41)–P(4)	1.849(18)
P(3)–W(1)	2.473(5)	C(42)–P(4)	1.846(17)
P(4)–W(1)	2.425(5)	C(43)–P(4)	1.796(17)
P(5)–W(2)	2.477(6)	C(51)–P(5)	1.823(15)
P(6)–W(2)	2.503(7)	C(52)–P(5)	1.826(19)
C(11)–P(1)	1.886(17)	C(53)–P(5)	1.835(19)
C(12)–P(1)	1.845(18)	C(61)–P(6)	1.826(19)
C(21)–P(2)	1.844(18)	C(62)–P(6)	1.831(19)
C(22)–P(2)	1.843(18)	C(63)–P(6)	1.817(23)
C(23)–P(2)	1.832(19)		

(*b*) Bond angles (°)

P(1)–W(1)–W(2)	59.1(2)	C(23)–P(2)–C(21)	98.4(8)
P(2)–W(1)–W(2)	97.6(2)	C(23)–P(2)–C(22)	98.8(9)
P(3)–W(1)–W(2)	143.2(1)	C(31)–P(3)–W(1)	120.8(6)
P(4)–W(1)–W(2)	95.6(2)	C(32)–P(3)–W(1)	121.2(7)
P(1)–W(2)–W(1)	55.6(2)	C(33)–P(3)–W(1)	117.3(7)
P(5)–W(2)–W(1)	137.1(1)	C(32)–P(3)–C(31)	95.8(9)
P(6)–W(2)–W(1)	123.6(2)	C(33)–P(3)–C(31)	98.8(8)
P(2)–W(1)–P(1)	105.6(2)	C(33)–P(3)–C(32)	98.0(9)
P(3)–W(1)–P(1)	84.0(2)	C(41)–P(4)–W(1)	122.7(6)
P(3)–W(1)–P(2)	92.6(2)	C(42)–P(4)–W(1)	120.2(7)
P(4)–W(1)–P(1)	104.3(2)	C(43)–P(4)–W(1)	113.3(6)
P(4)–W(1)–P(2)	149.9(1)	C(42)–P(4)–C(41)	97.6(9)
P(4)–W(1)–P(3)	92.9(2)	C(43)–P(4)–C(41)	99.8(8)
P(5)–W(2)–P(1)	85.5(2)	C(43)–P(4)–C(42)	98.8(9)
P(6)–W(2)–P(1)	178.5(1)	C(51)–P(5)–W(2)	121.2(6)
P(6)–W(2)–P(5)	94.8(2)	C(52)–P(5)–W(2)	117.5(7)
W(2)–P(1)–W(1)	65.3(2)	C(53)–P(5)–W(2)	115.8(7)
C(11)–P(1)–W(1)	128.1(6)	C(52)–P(5)–C(51)	101.8(9)
C(11)–P(1)–W(2)	118.9(7)	C(53)–P(5)–C(51)	96.0(9)
C(12)–P(1)–W(1)	126.9(6)	C(53)–P(5)–C(52)	100.7(9)
C(12)–P(1)–W(2)	123.8(6)	C(61)–P(6)–W(2)	120.8(9)
C(12)–P(1)–C(11)	95.1(9)	C(62)–P(6)–W(2)	111.3(7)
C(21)–P(2)–W(1)	112.2(6)	C(63)–P(6)–W(2)	118.8(8)
C(22)–P(2)–W(1)	123.1(8)	C(62)–P(6)–C(61)	100.1(9)
C(23)–P(2)–W(1)	119.6(6)	C(63)–P(6)–C(61)	101.6(11)
C(22)–P(2)–C(21)	100.4(9)	C(63)–P(6)–C(62)	101.1(10)

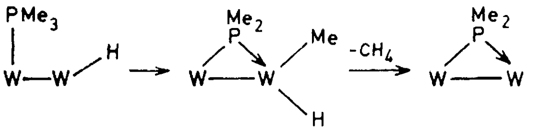
metals with that for W(1) (*i.e.* with shorter W–P distances) greater than that for W(2). However, this approach is complicated by the fact that W–P bond lengths may also be affected by W–P d_π–d_π back bonding, subject of course to the availability of *d* electrons on the metals. Indeed, it is possible to argue that the shorter W–P bonds are indicative of either a high oxidation state (leading to a smaller covalent radius for W) or a low oxidation state (with *d* electrons available for, and involved in π bonding).

It is thus very difficult to devise a model which would help to predict the possible location of the hydrides. However, all considerations lead to the probability that the tungsten atoms are linked by a W–W bond of order two which is consistent with the observed geometry. A definitive solution will have to await neutron-diffraction study, but tentatively we formulate the compound with only one bridging hydride and formal oxidation states of II and IV for tungsten.

In an attempt to explore the hydride problem still further, we have used the program HYDEX [9] to locate acceptable hydrogen positions but the results are inconclusive and suggest that any of many possibilities is feasible on the basis of steric potentials. The only positive result is that the proposed structure is one of those for which an acceptable energy minimum is obtained. Further details of this approach to the elucidation of the structure of the present compound and of other hydrides studied in our laboratories will be presented separately.

Although hydrogen transfer from the methyl group in PMe_3 in transition-metal complexes to give metallocycle groups $\overline{\mathrm{M{-}CH_2{-}P}}\mathrm{Me_2}$ is well established [10] there appears to be only one case of P–C bond cleavage for PMe_3 leading to a μ-PMe_2 group although such cleavages are well known for arylphosphines where benzene is formed.[11]

The tungsten complex could arise *via* initial oxidative addition of PMe_3 followed by loss of CH_4 (see below).



Other starting materials were used in attempts to obtain tungsten hydrido-complexes such as the product from the interaction of acetic acid and $W(CO)_6$,[12] but no pure compounds were isolated. The action of PMe_3 and sodium amalgam under hydrogen on $W_2(CH_2SiMe_3)_6$ gives only the complex $WH_4(PMe_3)_4$ reported earlier.[2]

Pentamethylbis(trimethylphosphine)-niobium(V) *and -tantalum*(V).—Since WMe_6 forms a stable PMe_3 adduct [2] which is converted into hydrides on hydrogenolysis, similar reactions of $NbMe_5$ and $TaMe_5$ [13] were studied. Both permethyls react with PMe_3 in diethyl ether to form crystalline, volatile, pyrophoric adducts, $MMe_5(PMe_3)_2$, similar to the chelating phosphine adducts MMe_5(dmpe) [dmpe = 1,2-bis(dimethylphosphino)ethane].[14] The tantalum complex decomposes only slightly in toluene at 25 °C over *ca.* 24 h, while the niobium analogue decomposes in *ca.* 1 h although it is stable at −30 °C. In pure PMe_3 both compounds decompose both thermally and under u.v. light.

Since conventional microanalyses could not be obtained due to the thermal instability, the stoicheiometry is based on integration of peak areas in the ^1H n.m.r. spectrum. At 30 °C, $TaMe_5(PMe_3)_2$ shows overlapping P*Me*$_3$ and Ta–*Me* resonances but on cooling they separate into a Ta–*Me* singlet, δ 1.25 p.p.m., and a P*Me*$_3$ doublet, δ 1.02 p.p.m., $^2J(^{31}P{-}^1H) = 6$ Hz. The spectrum of $NbMe_5(PMe_3)_2$ at −70 °C shows two singlets but no P–C coupling was observed,

Pentahydridotetrakis(trimethylphosphine)niobium(V).—Interaction of $NbMe_5(PMe_3)_2$ in the presence of an excess of PMe_3 and hydrogen (3 atm) leads to the dark red crystalline hydride in high yields. The solid compound is violently pyrophoric although it can be handled and stored readily at room temperature under argon or *in vacuo*. It decomposes quite rapidly in hydrocarbons above *ca.* −30 °C.

In [$^2H_8$]toluene at −40 °C the ^1H n.m.r. spectrum shows a broad PMe_3 doublet [δ 1.30 p.p.m., $^2J(^{31}P{-}^1H) = 32.4$ Hz] close to a symmetrical quintet [Nb–*H*, δ −0.67 p.p.m., $^2J(^{31}P{-}^1H) = 43.2$ Hz]. The ^{31}P selective decoupling n.m.r. experiments showed a poorly resolved sextet, $^2J(^{31}P{-}^1H)$ *ca.* 40 Hz, confirming the pentahydride formation as found in $NbH_5(dmpe)_2$.[14]

The tantalum compound also reacts with hydrogen but we have been unable to isolate a pure material from the dark orange-brown solutions.

EXPERIMENTAL

Microanalyses were by Pascher, Bonn. The spectrometers used were the Perkin-Elmer R32 (^1H), Varian XL-100 (^1H, ^{13}C, ^{31}P), Bruker WM-250 (Fourier-transform, ^{13}C, ^{31}P), and Perkin-Elmer 597 (i.r.). All operations were performed under oxygen-free nitrogen or argon or *in vacuo* and all solvents were dried over sodium and distilled from sodium–benzophenone under nitrogen immediately before use. Light petroleum had b.p. 40—60 °C. Melting points were determined in sealed tubes under nitrogen (uncorrected). Molecular weights were determined cryoscopically in benzene.

Di-μ-hydrido-dihydridohexakis(trimethylphosphine)-dimolybdenum(II)(Mo–Mo).—Trimethylphosphine (4.0 cm^3, 40 mmol) was added to a suspension of $Mo_2[O_2CMe]_4$ (2.0 g, 4.67 mmol) and sodium amalgam [0.9 g, Na (39 mmol) in 100 g Hg] in thf (60 cm^3) and the solution stirred under hydrogen (3 atm, 24 h). The deep red-brown homogeneous solution was filtered and volatile materials removed under vacuum. The residue was extracted into light petroleum (2 × 40 cm^3, *ca.* 40 °C), the solution filtered and reduced to *ca.* 20 cm^3, and cooled (−20 °C, 24 h). The solution was then filtered at −20 °C and the volume further reduced to *ca.* 10 cm^3. Cooling at −20 °C yielded dark yellow *prisms* after several days. These were collected at −20 °C and dried under vacuum at room temperature. A further batch was obtained from the supernatant after reduction in volume and cooling. Yield 2.4 g, 80%, m.p. 161—163 °C (decomp.) (Found: C, 33.5; H, 8.7; P, 28.5%; *M* 700. $C_{18}H_{58}Mo_2P_6$ requires C, 33.1; H, 8.9; P, 28.5%; *M* 652).

I.r. (Nujol) bands at 1 563m, 1 550s,br, 1 535m, 1 529m, 1 420s, 1 410m, 1 284s, 1 264s, 948s,br, 932m, 839m, 700m, 689m, 653s, and 645s cm^{-1}.

μ-Dimethylphosphido-μ-hydrido-tetrahydridopentakis(trimethylphosphine)ditungsten.—Sodium amalgam [0.5 g Na (21.7 mmol) in 50 g Hg] was added to $W_2Cl_4(PMe_3)_4$ (1.0 g, 1.2 mmol) in thf (60 cm^3) and the solution stirred under hydrogen (3 atm) at 75 °C (12 h). The dark solution was filtered, volatile materials removed in vacuum, and the residue extracted into light petroleum (60 cm^3). The solution was filtered, evaporated to *ca.* 10 cm^3, filtered again, and reduced to *ca.* 5 cm^3. Cooling (−20 °C) yielded dark green *crystals* which were collected and dried under vacuum. Yield 0.4 g, 40%, m.p. 85—90 °C (Found: C, 25.2; H, 6.9; P, 22.8%; *M* 790. $C_{17}H_{56}P_6W_2$ requires C, 25.2; H, 6.3; P, 23.0%; *M* 814).

I.r. (Nujol) bands at 1 827m, 1 780m, 1 742s, 1 643s,br, 1 458s, 1 435m, 1 425m, 1 415m, 1 295m, 1 288m, 1 279m, 1 275m, 1 267m, 942s,br, 860m, 849m, 719m, 710m, 700m, 667m, 658m, and 650w cm^{-1}.

Pentamethylbis(trimethylphosphine)-niobium(V) *and -tantalum*(V).—Trimethylphosphine (3.0 cm^3, 30 mmol) was added to a solution of MMe_5 (M = Nb or Ta, 2.0 g, 11.9 and 7.9 mmol respectively), prepared as described [13,14] in diethyl ether at −78 °C. The solution was warmed to *ca.* −10 °C, filtered, and recooled to −78 °C. The pale yellow (Nb) or fawn (Ta) crystals were collected and dried under vacuum at −50 °C. Evaporation and cooling of the supernatant yielded a further batch of crystals. The yields were quantitative. Melting point and i.r. data were not obtained due to the thermal instability of the compounds. N.m.r. $^{13}C-\{^1H\}$ in [$^2H_8$]toluene at 38 °C and at 25.2 MHz (using Varian XL-100) in p.p.m. relative to $SiMe_4$ (δ 0.0): for $TaMe_5(PMe_3)_2$ δ 73.56 (s), 14.70 (d), $^1J(P-C) = 5.9$ Hz; at −40 °C 66.59 (s), 14.68 (d), $^1J(P-C) = 13.4$ Hz; for $NbMe_5(PMe_3)_2$ δ 66.4 (s), 16.0 (s) (at −70 °C in [$^2H_8$]toluene at 62.9 MHz, using Bruker WM 250).

Pentahydridotetrakis(trimethylphosphine)niobium(V).—Trimethylphosphine (3.0 cm^3, 30 mmol) was added to a solution of $NbMe_5(PMe_3)_2$ (2.0 g, 6.3 mmol) in diethyl ether (15 cm^3) at −78 °C. The solution was stirred under hydrogen (3 atm), then allowed to warm slowly to room temperature (6 h), during which time the hydrogen above the solution was replaced regularly (*ca.* every 0.5 h). Volatile materials were removed under vacuum at room temperature and the residue extracted into light petroleum (50 cm^3). The solution was filtered and evaporated to *ca.* 10 cm^3 at −10 °C. Cooling (−20 °C or −78 °C) yielded dark red *crystals* which were collected and dried under vacuum at −20 °C (0.5 h) and then at room temperature (2 h). Yield: 15 g, 60%, m.p. 105—110 °C (decomp.) (Found: C, 36.6; H, 10.2; P, 31.1%; *M* 370. $C_{12}H_{41}NbP_4$ requires C, 35.8; H, 10.2; P, 30.8%; *M* 402).

Crystallographic Studies.—Crystal Data. $Mo_2H_4(PMe_3)_6$, (1), $C_{18}H_{58}Mo_2P_6$, $M = 652.39$, Orthorhombic, $a = 12.133(6)$, $b = 14.892(4)$, $c = 17.692(5)$ Å, $U = 3\,196.7$ Å^3, space group *Pbca*, $Z = 4$, $D_c = 1.36$ g cm^{-3}, $F(000) = 1\,360$, $\mu(Mo\text{-}K_\alpha) = 9.9$ cm^{-1}.

$W_2H_5(PMe_2)(PMe_3)_5$ (2), $C_{17}H_{56}P_6W_2$, $M = 813.69$, Monoclinic, $a = 9.931(5)$, $b = 12.023(3)$, $c = 26.605(4)$ Å, $\beta = 91.66(3)°$, $U = 3\,175.3$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.70$ g cm^{-3}, $F(000) = 1\,564$, $\mu(Mo\text{-}K_\alpha) = 72.2$ cm^{-1}.

Data collection. For both structures, unit-cell parameters and data were collected on a CAD4 diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å). Reflections were measured in the θ—2θ scan mode.

Compound (1). 3 129 Data ($1.5 \leqslant \theta \leqslant 26°$) were measured of which 3 129 were unique. 2 388 Reflections were considered observed [$I > 1.5\sigma(I)$]. No absorption corrections were applied.

Compound (2). 6 367 Data ($1.5 \leqslant \theta \leqslant 25°$) were measured of which 5 521 were unique. There were 4 218 observed reflections [$I > 1.5\sigma(I)$]. Correction was made for absorption.

Structure solution and refinement. The heavy-atom method was used for both compounds and all non-hydrogen atoms were refined anisotropically. For compound (1) all hydrogen atoms were located experimentally and refined with isotropic temperature factors, although the bridging hydride H(1b) consistently adopted a negative temperature factor. For compound (2), many of the methyl hydrogens were located experimentally and the remainder were inserted in suitable positions; all were refined with an overall isotropic $U_{iso.}$ value and a fixed C–H distance of 1.0 Å. The

TABLE 4

Fractional atomic co-ordinates for $Mo_2H_4(PMe_3)_6$ (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mo	7 074(2)	−801(2)	3 800(2)
P(1)	618(1)	1 291(1)	1 122(1)
P(2)	2 459(1)	269(1)	−217(1)
P(3)	256(1)	−1 064(1)	1 419(1)
C(11)	−638(6)	1 613(5)	1 622(4)
C(12)	890(6)	2 417(4)	730(4)
C(13)	1 612(7)	1 323(5)	1 906(4)
C(21)	3 029(5)	−440(6)	−956(4)
C(22)	3 493(5)	63(6)	522(4)
C(23)	2 958(6)	1 347(6)	−586(6)
C(31)	1 544(5)	−1 249(4)	1 932(3)
C(32)	−634(6)	−832(6)	2 225(4)
C(33)	−126(7)	−2 233(4)	1 252(4)

TABLE 5

Fractional atomic co-ordinates (×10^5 for W; ×10^4 for other atoms) for $W_2H_5(\mu\text{-}PMe_2)(PMe_3)_5$ (2) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W(1)	21 507(5)	17 878(4)	14 052(2)
W(2)	14 017(5)	37 686(4)	11 383(2)
P(1)	2 860(4)	2 572(3)	647(1)
P(2)	3 841(4)	2 326(3)	2 039(1)
P(3)	3 480(3)	162(3)	1 139(1)
P(4)	24(3)	899(3)	1 182(1)
P(5)	2 312(4)	5 315(3)	635(1)
P(6)	−46(4)	4 991(3)	1 659(1)
C(11)	2 312(19)	2 188(13)	−25(6)
C(12)	4 598(15)	2 939(13)	487(6)
C(21)	3 120(17)	3 153(13)	2 549(6)
C(22)	5 326(15)	3 178(15)	1 898(8)
C(23)	4 677(18)	1 255(13)	2 425(7)
C(31)	3 145(17)	−500(11)	525(5)
C(32)	5 327(14)	253(15)	1 077(7)
C(33)	3 438(18)	−1 060(11)	1 530(7)
C(41)	−801(17)	1 040(14)	554(6)
C(42)	−167(18)	−620(12)	1 248(7)
C(43)	−1 334(14)	1 335(13)	1 568(6)
C(51)	2 479(19)	5 191(12)	−43(5)
C(52)	3 955(17)	5 877(14)	830(7)
C(53)	1 297(22)	6 591(12)	614(7)
C(61)	664(26)	6 199(12)	1 988(6)
C(62)	−722(19)	4 226(14)	2 192(6)
C(63)	−1 578(21)	5 570(20)	1 376(7)

metal hydride positions could not be located with any certainty, for although peaks occurred in difference and F_o maps in sensible positions, no acceptable refinement of these could be achieved. These atoms were therefore not included in the calculation of F_c. The final R values were 0.0362 for (1) and 0.0525 for (2).

Final atomic co-ordinates are given in Tables 4 (1) and 5 (2). Methyl hydrogen-atom parameters, all thermal parameters, and structure factor tables, have been deposited as Supplementary Publication No. SUP 23082 (32 pp.).*

All computations were carried out on the ICL 2980 computer at Queen Mary College, using programs listed in ref. 15 which also gives the sources of the scattering factor data used.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.