Reactions of Aluminopolyhydride Complexes of Tungsten. X-Ray Crystal Structures of [(Me₃P)₃H₃W(μ-H)₂AlCl(μ-N=CHEt)]₂, {[(Me₃P)₃WH₅]Li}₄, WH₂I(PMe₃)₃(SiMe₃), and (Me₃P)₃H₂W(μ-H)₃AlCl₂(NMe₃)†

Andrew R. Barron and Geoffrey Wilkinson*
Chemistry Department, Imperial College, London SW7 2AY
Majid Motevalli and Michael B. Hursthouse*
Chemistry Department, Queen Mary College, London E1 4NS

The aluminopolyhydride complex [(Me₃P)₃H₃W(μ-H)₂AlH(μ-H)]₂ reacts with RCN (R = Me or Et) to give the μ-amido complexes [(Me₃P)₃H₃W(μ-H)₂AlH(μ-N=CHR)]₂; the structure of [(Me₃P)₃H₃W(μ-H)₂AlCl(μ-N=CHEt)]₂ obtained from chloride-containing solutions has been determined. Reaction of the aluminopolyhydride with lithium alkyls gives {[(Me₃P)₃WH₅]Li}₄, and this compound reacts with Me₃SiCH₂I to give WH₂I(PMe₃)₃(SiMe₃); the structures of both products have been determined. Interaction of the polyhydride with NMe₃HCl gives (Me₃P)₃H₂W(μ-H)₃AlCl₂(NMe₃) which also has been structurally characterised. Cyclohexanone gives the monomer (Me₃P)₄W(μ-H)₂AlH₃. Proton, ³¹P, and ²⁷Al n.m.r. and i.r. spectra of the compounds have been recorded.

In previous papers we have described the synthesis and structures of various transition-metal aluminopolyhydride complexes,[1-3] as well as their reactions with tetramethylethylenediamine[1,2] and protic solvents.[1,3] Some reactions of [(Me₃P)₃H₃W(μ-H)₂AlH(μ-H)]₂ with organic nitriles, organolithium reagents, trimethylammonium chloride, and cyclohexanone are now described. The X-ray structures of certain of the products have been determined. The various reactions are shown in Scheme 1.

Results and Discussion

Organic Nitriles.—The reduction of organic nitriles[4] by LiAlH₄ and (AlH₃)ₙ proceeds as in Schemes 2 and 3.

The addition of MeCN to an Et₂O solution of [(Me₃P)₃H₃W(μ-H)₂AlH(μ-H)]₂ yields the orange, air-sensitive complex [(Me₃P)₃H₃W(μ-H)₂AlH(μ-N=CHMe)]₂ (A) which contains an imine bridge (1) between two aluminium atoms. There is no evidence for hydride migration to give the amide, as is observed with AlH₃ (Scheme 3). It appears that the bridging Al(μ-H)₂Al hydrides are transferred to form the imines since no reaction is observed between MeCN and the complex with only one aluminohydride bridge, [(Me₃P)₃H₃W(μ-H)]₂AlH₃,[1] although a band shift in the ²⁷Al-{¹H} n.m.r. spectrum (δ 70 to 82 p.p.m. on addition of MeCN) suggests that a weakly bound adduct with six-co-ordinate Al, (2), is formed. In addition to the trimethylphosphine bands the i.r. spectrum of compound (A) contains broad bands between 1 800 and 1 560 cm⁻¹, assignable to bridging and terminal hydrides, as well as a sharp peak at 1 670 cm⁻¹ due to the N=C stretch.

The terminal W–H and bridging W(μ-H)Al hydrides readily
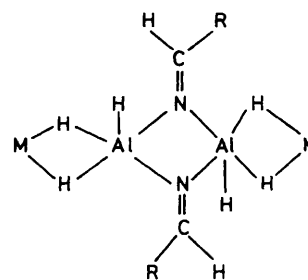
(1)
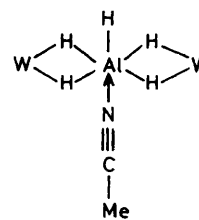
(2)

exchange[1,2] at room temperature resulting in a broad quartet [δ −5.50 p.p.m., J(P–H) = 26.8 Hz] in the ¹H n.m.r. spectrum (Table 1). However, on cooling the exchange ceases, as had been observed previously (T_c = −55 °C, ΔG_av.‡ = 11.2 kJ mol⁻¹).‡ The terminal Al–H hydride signal (δ 4.0 p.p.m.) is unaffected by changes in temperature. The methylimine protons give rise to a doublet [δ 2.30 p.p.m., J(H–H) = 7.0 Hz] due to the methyl and a broad quartet [δ 8.45 p.p.m., J(H–H) ca. 7 Hz] due to the methine proton. The ³¹P-{¹H} n.m.r. spectrum is a singlet, with tungsten satellites [δ −23.04 p.p.m., J(P–W) = 225.0 Hz]; selective decoupling of the P–CH₃ protons results in a binomial sextet [J(P–H) = 26.9 Hz]. The ²⁷Al-{¹H} n.m.r. spectrum confirms that the aluminium is five-co-ordinate.

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‡ Where there is an imbalance in the population of the hydride sites, *i.e.*, M–H/M(μ-H) ≠ 1, two values of ΔG‡ are found: for convenience the numerical average is quoted.

$$\text{M–H} \underset{\Delta G_B^{\ddagger}}{\overset{\Delta G_A^{\ddagger}}{\rightleftharpoons}} \text{M(μ-H)Al}$$

$(Me_3P)_4W(\mu\text{-}H)_2AlH_3$ $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}N{=}CHR)]_2$ $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlCl(\mu\text{-}N{=}CHEt)]_2$

(vii)   *(i)*   *(i)*

$\rightarrow [(Me_3P)_3H_3W(AlH_3Cl)]_2$
yellow oil

(ii)

$[(Me_3P)_3H_3W(AlH_4)]_2$

(vi)

$(Me_3P)_3H_2W(\mu\text{-}H)_3AlCl_2(NMe_3)$

(iii)

$\{[(Me_3P)_3WH_5]Li\}_4 \xrightarrow{\ (iv)\ } (Me_3P)_3H_3W(\mu\text{-}H)_2Li(tmen)$

(v)

$WH_2I(PMe_3)_3(SiMe_3)$
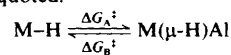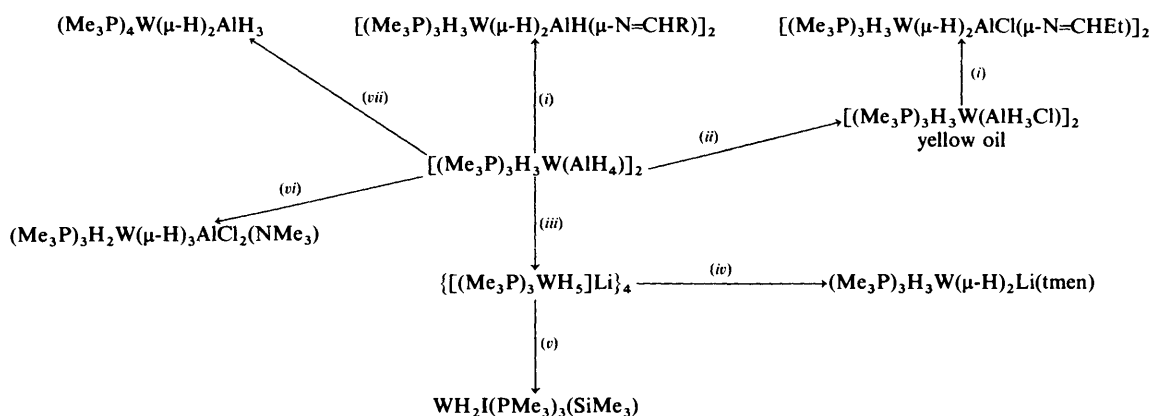
Scheme 1. (*i*) RCN, R = Me or Et; (*ii*) AlCl$_3$; (*iii*) LiR, R = Me, CH$_2$SiMe$_3$, or Bu^n; (*iv*) Me$_2$N(CH$_2$)$_2$NMe$_2$; (*v*) Me$_3$SiCH$_2$I; (*vi*) NMe$_3$HCl; (*vii*) cyclohexanone

$RC{\equiv}N \xrightarrow{\ (i)\ } [RC(H){=}N\text{-}AlH_3]^- \xrightarrow{\ (i)\ } [RCH_2\text{-}N(AlH_3)_2]^{2-}$

(ii)   *(ii)*

RCHO   RCH$_2$NH$_2$

$H_3AlN{\equiv}CR \xrightarrow{\ (i)\ } H_2Al\text{-}N{=}CRH \xrightarrow{\ (i),\,(ii)\ } \tfrac{1}{n}[\text{-}HAl\text{-}N(CH_2R)\text{-}]_n$
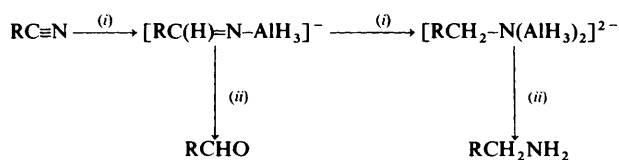
Scheme 2. (*i*) LiAlH$_4$, diethyl ether; (*ii*) water   **Scheme 3.** (*i*) Hydride migration; (*ii*) polymerisation

Table 1. Proton, ^{31}P-$\{^1H\}$, and ^{27}Al-$\{^1H\}$ n.m.r. data (298 K) for new complexes; *J* values in Hz

Compound	^1H		Assignment	$^{31}P\text{-}\{^1H\}$	$^{27}Al\text{-}\{^1H\}$
(A) $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}N{=}CHMe)]_2$	8.45 [q, J(H–H) 7.0]	2 H	N=C*H*–CH$_3$	-23.04	$+47.5$
	4.00 (br s)	2 H	Al–H		
	2.30 [d, J(H–H) 7.0]	6 H	N=CH–C*H*$_3$		
	1.50 [d, J(P–H) 6.0]	54 H	P–CH$_3$		
	-5.50 [q, J(P–H) 26.8]	10 H	W–H, W(μ-H)Al		
(B) $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}N{=}CHEt)]_2$	8.49 (br t)	2 H	N=C*H*–CH$_2$CH$_3$	-23.94	$+49.7$
	4.00 (br s)	2 H	Al–H		
	2.85 (m)	4 H	N=CH–C*H*$_2$CH$_3$		
	1.49 [d, J(P–H) 6.0]	54 H	P–CH$_3$		
	0.93 (m)	6 H	N=CH–CH$_2$C*H*$_3$		
	-5.40 [q, J(P–H) 24.9]	10 H	W–H, W(μ-H)Al		
(C) $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlCl(\mu\text{-}N{=}CHEt)]_2$	8.50 (br t)	2 H	N=C*H*–CH$_2$CH$_3$	-23.92	$+52.3$
	2.85 (m)	4 H	N=CH–C*H*$_2$CH$_3$		
	1.49 [d, J(P–H) 6.0]	54 H	P–CH$_3$		
	0.93 (m)	6 H	N=CH–CH$_2$C*H*$_3$		
	-5.42 [q, J(P–H) 24.8]				
(E) $\{[(Me_3P)_3WH_5]Li\}_4$	1.62 (m)	108 H	PCH$_3$	-24.78	
	-3.83[dt,J(P^1–H) = J(P^2–H) 25]	4 H	W–H		
	-5.02 [br t, J(P–H) 41]	4 H	W–H		
	-6.35 (br s)	12 H	W(μ-H)Li, W(μ_3-H)Li$_2$		
(F) $(Me_3P)_3H_3W(\mu\text{-}H)_2Li(tmen)$	2.10 (s)	12 H	N–CH$_3$	-24.06	
	1.89 (br s)	4 H	N–CH$_2$		
	1.50 [d, J(P–H) 6]	27 H	P–CH$_3$		
	-5.50 [q, J(P–H) 27.8]	5 H	W–H, W(μ-H)Li		
(G) $WH_2I(PMe_3)_3(SiMe_3)$	1.43 (s)	27 H	P–CH$_3$	-21.07 [d, J(P–P) 17.72]	
	0.04 (s)	9 H	Si–CH$_3$	-52.63 [t, J(P–P) 17.72]	
	-6.01 (m)	2 H	W–H		
(H) $(Me_3P)_3H_2W(\mu\text{-}H)_3AlCl_2(NMe_3)$	2.39	9 H	N–CH$_3$	-25.04	$+84.5$ (s)
	1.53 [d, J(P–H) 8.0]	27 H	P–CH$_3$		
	-5.56 [br q, J(P–H) *ca.* 20]	5 H	W–H, W(μ-H)Al		
(I) $(Me_3P)_4W(\mu\text{-}H)_2AlH_3$	1.60 (m)	36 H	P–CH$_3$	-22.11 [t, J(P–P) 15.5] -28.64 (t)	$+52.7$
	-3.48 (m)	2 H	W–H		

Figure 1. The structure of $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlCl(\mu\text{-}N{=}CHEt)]_2$ (C). Metal-bound H atoms were not located with certainty and are not shown, and the $(\mu\text{-}H)_2$ bridge system is represented by the dashed lines

Table 2. Selected bond lengths (Å) and angles (°) for $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlCl(\mu\text{-}N{=}CHEt)]_2$ (C)*

P(1)–W(1)	2.410(4)	P(2)–W(1)	2.432(3)
P(3)–W(1)	2.428(4)	C(11)–P(1)	1.816(9)
C(12)–P(1)	1.825(9)	C(13)–P(1)	1.827(9)
C(21)–P(2)	1.798(10)	C(22)–P(2)	1.826(9)
C(23)–P(2)	1.808(9)	C(31)–P(3)	1.828(9)
C(32)–P(3)	1.810(9)	C(33)–P(3)	1.812(10)
Cl(1)–Al(1)	2.208(4)	N(1)–Al(1)	1.941(6)
C(1)–N(1)	1.260(8)	C(2)–C(1)	1.501(10)
C(3)–C(2)	1.496(11)	Al(1) $\cdots$ W(1)	2.619
P(2)–W(1)–P(1)	103.2(2)	P(3)–W(1)–P(1)	95.1(2)
P(3)–W(1)–P(2)	141.0(1)	C(11)–P(1)–W(1)	115.6(3)
C(12)–P(1)–W(1)	118.4(3)	C(12)–P(1)–C(11)	98.9(5)
C(13)–P(1)–W(1)	120.7(4)	C(13)–P(1)–C(11)	100.7(5)
C(13)–P(1)–C(12)	98.7(4)	C(21)–P(2)–W(1)	115.6(4)
C(22)–P(2)–W(1)	118.4(3)	C(22)–P(2)–C(21)	99.6(5)
C(23)–P(2)–W(1)	118.3(3)	C(23)–P(2)–C(21)	100.7(5)
C(23)–P(2)–C(22)	100.9(5)	C(31)–P(3)–W(1)	117.6(3)
C(32)–P(3)–W(1)	117.7(4)	C(32)–P(3)–C(31)	100.8(5)
C(33)–P(3)–W(1)	116.7(4)	C(33)–P(3)–C(31)	101.7(5)
C(33)–P(3)–C(32)	99.3(5)	N(1)–Al(1)–Cl(1)	98.9(2)
Al(1)–N(1)–Al(1')	98.6(4)	C(1)–N(1)–Al(1)	134.4(4)
N(1)–Al(1)–N(1')	81.4(3)	C(2)–C(1)–N(1)	126.1(6)
C(3)–C(2)–C(1)	114.8(8)		

* Primed atoms are related to unprimed atoms by a centre of symmetry.

Interaction with propionitrile leads to a similar product, $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}N{=}CHEt)]_2$ (**B**), which is spectroscopically similar to (**A**) (see Experimental section and Table 1). Both (**A**) and (**B**) are moisture sensitive; hydrolysis yields $WH_6(PMe_3)_3$[5] and the corresponding aldehyde. No crystals of (**A**) or (**B**) suitable for X-ray study were obtained.

The interaction of EtCN with a yellow uncharacterised oil has also been studied. This oil is obtained on reaction of $WCl_4(PMe_3)_3$ with less than the 4 equivalents of $LiAlH_4$ that lead to $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the oil contains two singlets, one at δ -23.50 p.p.m. {due to $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$} and the other at δ -24.60 p.p.m. On selective decoupling of the P–CH$_3$ protons both peaks appear to be split into sextets with similar coupling constants (ca. 25 Hz). However, the hydride region appears to be no different from that observed for pure $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$.[1] It appears that the oil contains chloride and is a partially substituted material.

Addition of EtCN to a hexane solution of the oil results in a bright orange solution, which on cooling to $-20\,^\circ C$ gives crystals of $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlCl(\mu\text{-}N{=}CHEt)]_2$ (**C**), whose structure has been determined by X-ray diffraction (see below). Reduction in volume of the supernatant yields a mixture of (**B**) and (**C**).

The structure of compound (**C**), which is a centrosymmetric dimer, is shown in Figure 1; selected molecular geometry parameters are given in Table 2. Failure to locate the hydrogens bridging aluminium and tungsten does not allow us to define with certainty the geometry at Al, but spectroscopic evidence points to a trigonal-bipyramidal geometry analogous to that found in the compound $[Mn(dmpe)_2(AlH_4)]_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane].[6] However, the near equivalence of the two Al–N distances suggests that square pyramidal (with Cl axial) cannot be ruled out.

In view of the difficulty in locating the hydrogens bound to tungsten, it is not possible to comment on the co-ordination geometry of this atom. However, it is worth noting that the distribution of W–P bond lengths (one short and two long) and the P–W–P angles are extremely similar to those found for the complex $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}OBu^n)]_2$, for which a dodecahedral WP_3H_5 geometry was tentatively suggested.[1]
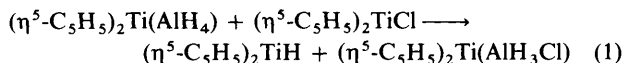
The isolation of (**C**) suggests that the second species present in the oil is $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlCl(\mu\text{-}H)]_2$ (**D**). Bulychev et al.[7] obtained, but did not isolate, a similar complex as an intermediate in the formation of $Ti(\eta^5\text{-}C_5H_5)_2(AlH_4)$; they

suggested that a chloride on titanium was exchanged with a hydride from the AlH_4^- group [equation (1)]. In the present

$$(\eta^5\text{-}C_5H_5)_2Ti(AlH_4) + (\eta^5\text{-}C_5H_5)_2TiCl \longrightarrow$$
$$(\eta^5\text{-}C_5H_5)_2TiH + (\eta^5\text{-}C_5H_5)_2Ti(AlH_3Cl) \quad (1)$$

case, the reaction sequence may be as follows. Interaction of WCl_4 with 3 equivalents of $LiAlH_4$ yields the co-ordinatively unsaturated hydride [equation (2)]. Subsequent reaction with

$$WCl_4(PMe_3)_3 \xrightarrow{3LiAlH_4}$$
$$(Me_3P)_3H_3WCl + 3LiCl + 3(AlH_3)_n \quad (2)$$

another equivalent of $LiAlH_4$ then yields $WH_4(PMe_3)_3$ which reacts with AlH_3 to yield $[(Me_3P)_3H_3W(AlH_4)]_2$ [equation (3)]. However, when the concentration of the latter is relatively

$$(Me_3P)_3H_3WCl \xrightarrow{LiAlH_4} (Me_3P)_3WH_4 \xrightarrow{AlH_3}$$
$$\tfrac{1}{2}[(Me_3P)_3H_3W(AlH_4)]_2 \quad (3)$$
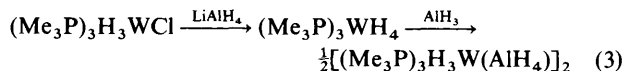
low compared to the chloride, hydride transfer may result [equation (4)]. The resulting aluminohydride may then react

$$(Me_3P)H_3WCl + \tfrac{1}{2}[(Me_3P)_3H_3W(AlH_4)]_2 \longrightarrow$$
$$(Me_3P)_3WH_4 + \tfrac{1}{2}[(Me_3P)_3H_3W(AlH_3Cl)]_2 \quad (4)$$
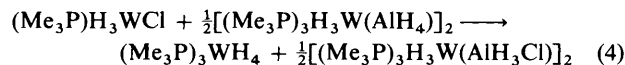
with another equivalent of $LiAlH_4$ as in equation (5) while the

$$\tfrac{1}{2}[(Me_3P)_3H_3W(AlH_3Cl)]_2 \xrightarrow{LiAlH_4}$$
$$\tfrac{1}{2}[(Me_3P)_3H_3W(AlH_4)]_2 \quad (5)$$
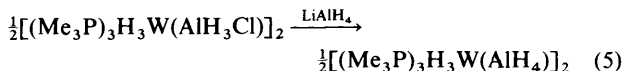
hydride reacts further as in (3). This scheme is in accord with the observation that if excess of PMe_3 is added to the reaction mixture the major product is $WH_4(PMe_3)_3$.[8] Thus the phosphine competes with AlH_3 for the vacant co-ordination site on the unsaturated hydride intermediate $WH_4(PMe_3)_3$.

Although we have been unable to isolate the complex (**D**) the addition of anhydrous $AlCl_3$ to an Et_2O solution of $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$ yields a yellow intractable oil

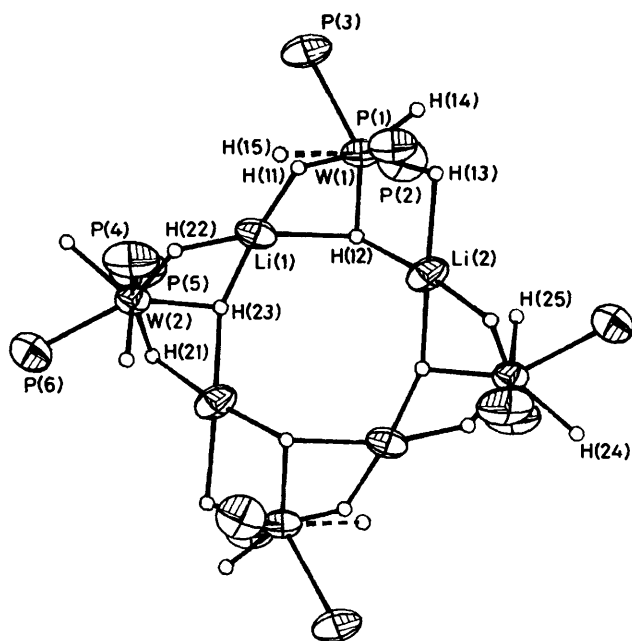**Figure 2.** The structure of $\{[(Me_3P)_3WH_5]Li\}_4$ (E). The methyl groups have been omitted for clarity and one terminal hydrogen on W(1) (shown bonded via a dashed line) was not identified experimentally

Figure 3. Variable-temperature ^1H n.m.r. (250-MHz) spectra for compound (E) over the region -3 to -7 p.p.m. vs. $SiMe_4$ in $[^2H_8]$toluene

whose ^{31}P-$\{^1H\}$ n.m.r. spectrum resembles that discussed above.

Organolithium Reagents.—Treatment of $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$ with 2 equivalents of LiR (R = Me, CH_2SiMe_3, or Bu^n) in diethyl ether at $-80\,°C$ results in $>70\%$ yield of the yellow crystalline complex[9] $\{[(Me_3P)_3WH_5]Li\}_4$ (E) which is soluble in and can be crystallised from hexane. Low yields of this complex have also been obtained from the interaction of $WH_6(PMe_3)_3$ with $LiBu^n$.

The structure of the centrosymmetric tetramer is shown in Figure 2; selected bond lengths and angles are given in Table 3. The tungsten atoms are each connected to two neighbouring Li atoms by two normal $W(\mu\text{-}H)Li$ bridges and then by one $W(\mu_3\text{-}H)Li_2$ bridge. The Li atoms are four-co-ordinate, with a strongly distorted tetrahedral geometry, due most probably to the constraints imposed by the bridge systems. On the other hand, the tungsten atoms have a geometry which approaches very closely to dodecahedral. The two mutually orthogonal trapezia which can be identified in this geometry are formed by P(1), H(15), H(11), P(2) and P(3), H(14), H(13), H(12) for W(1) and P(4), H(25), H(21), P(5) and P(6), H(24), H(22), H(23) for W(2). In each case, the three P atoms occupy equatorial B sites in the dodecahedral geometry, although there is one feature which is difficult to correlate with the apparent and assumed symmetry and equivalence of the two independent W atoms. The three W–P bonds in each molecule are grouped as two long [2.424(5)—2.434(4) Å] and one short [2.411(4), 2.406(5) Å], and the unique, short bond in each case is in a different position in a (PH$_3$) trapezium for W(2) and a (P$_2$H$_2$) group for W(1). The same results were obtained by Green and co-workers[10] in their structure determination of this compound. It is now quite likely that our assignments of the WP_3H_5 geometry for the complex $[(Me_3P)_3H_3W(AlH_3OBu^n)]_2$ and thus complex (C) are correct.

The i.r. spectrum of the lithium complex contains broad bands between 1 800 and 1 500 cm^{-1} due to terminal and bridging hydrides. N.m.r. spectra show that the complex is
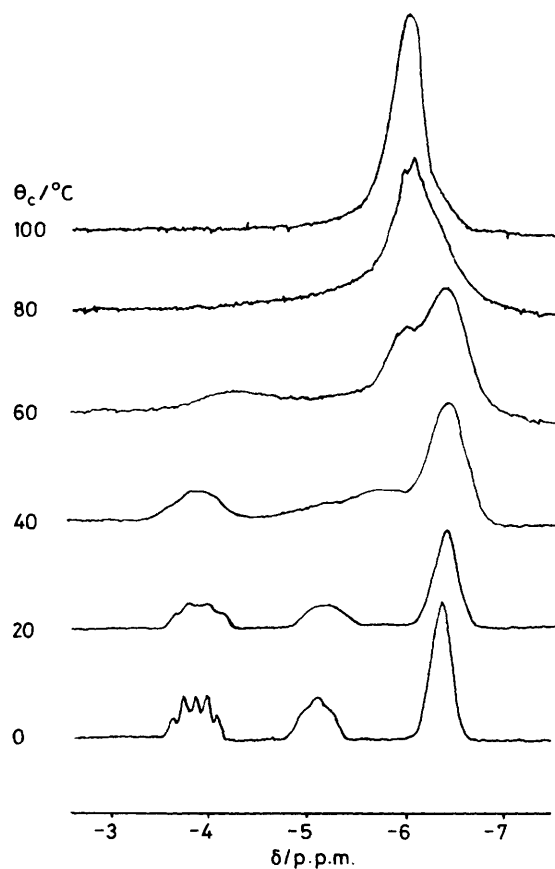
fluxional in solution at $+90\,°C$ where the ^{31}P-$\{^1H\}$ spectrum shows a singlet with tungsten satellites [δ -24.78 p.p.m., $J(P\text{-}W) = 166.0$ Hz]; selective decoupling of the phosphine protons gives a binomial sextet [$J(P\text{-}H) = 25.1$ Hz]. The ^1H n.m.r. spectrum ($90\,°C$) gives a broad singlet (δ -5.52 p.p.m.) due to terminal and bridging hydrides. As the temperature is lowered (Figure 3) the hydride region de-coalesces to give one signal due to the bridging hydrides (δ -6.35 p.p.m.) and two due to the terminal hydrides (δ -3.83 and -5.02 p.p.m.). The n.m.r. data suggest that in solution the bridging hydrides remain fluxional down to $-90\,°C$.

Addition of tetramethylethylenediamine (tmen) to a toluene solution of the complex yields the monomeric adduct $(Me_3P)_3H_3W(\mu\text{-}H)_2Li(tmen)$ (F). The ^1H n.m.r. spectrum shows this compound also to be fluxional at room temperature with the hydrides giving a quartet [δ -5.50 p.p.m., $J(P\text{-}H) = 27.8$ Hz], which de-coalesces on cooling to give a broad quartet [δ -4.35 p.p.m., $J(P\text{-}H) = 27.0$ Hz] due to the terminal W–H hydrides, and a broad singlet (δ -6.39 p.p.m.) due to bridging $W(\mu\text{-}H)Li$ hydrides. The activation energy of this process ($T_c = -50\,°C$, $\Delta G_{av.}^{\ddagger} = 10.7$ kJ mol^{-1}) is similar to that observed for the aluminohydride $[(Me_3P)_3H_3W(AlH_4)]_2$.[1]

Although suitable crystals of (F) could not be obtained, the geometry around the tungsten is undoubtedly similar to that found for other complexes with the $P_3H_3W(\mu\text{-}H)_2$ core,[1] while the lithium is most likely tetrahedral.

The compounds (E) and (F) are both air and moisture sensitive, but are stable in ethers for several days; addition of protic solvents yields $WH_6(PMe_3)_3$.[5]

Addition of 2 equivalents of Me_3SiCH_2I to a hexane solution

Table 3. Selected bond lengths (Å) and angles (°) for $\{[(Me_3P)_3WH_5]Li\}_4$ (E)

P(1)–W(1)	2.411(4)	P(2)–W(1)	2.434(4)	H(11)–W(1)	1.768(48)	H(12)–W(1)	1.958(44)
P(3)–W(1)	2.430(5)	P(4)–W(2)	2.433(5)	H(13)–W(1)	1.877(43)	H(14)–W(1)	2.219(41)
P(5)–W(2)	2.424(5)	P(6)–W(2)	2.406(5)	H(21)–W(2)	1.889(45)	H(22)–W(2)	1.759(40)
C(11)–P(1)	1.832(12)	C(12)–P(1)	1.816(12)	H(23)–W(2)	1.841(42)	H(24)–W(2)	1.838(44)
C(13)–P(1)	1.812(13)	C(21)–P(2)	1.802(14)	H(25)–W(2)	1.841(52)		
C(22)–P(2)	1.804(16)	C(23)–P(2)	1.846(16)				
C(31)–P(3)	1.807(13)	C(32)–P(3)	1.865(15)	H(11)–Li(1)	1.884(55)	H(12)–Li(1)	1.966(52)
C(33)–P(3)	1.807(16)	C(41)–P(4)	1.825(14)	H(22)–Li(1)	1.744(51)	H(23)–Li(1)	1.744(48)
C(42)–P(4)	1.824(13)	C(43)–P(4)	1.809(14)	H(12)–Li(2)	1.825(55)	H(13)–Li(2)	1.732(56)
C(51)–P(5)	1.827(14)	C(52)–P(5)	1.814(15)	H(21a)–Li(2)	2.025(52)	H(23a)–Li(2)	1.998(46)
C(53)–P(5)	1.837(14)	C(61)–P(6)	1.819(18)				
C(62)–P(6)	1.816(15)	C(63)–P(6)	1.820(16)				

P(2)–W(1)–P(1)	143.2(1)	P(3)–W(1)–P(1)	96.5(2)	H(11)–W(1)–P(1)	71.6(24)	H(11)–W(1)–P(2)	144.1(22)
P(3)–W(1)–P(2)	100.3(2)	P(5)–W(2)–P(1)	144.5(1)	H(11)–W(1)–P(3)	77.2(23)	H(12)–W(1)–P(1)	81.8(17)
P(6)–W(2)–P(4)	100.7(2)	P(6)–W(2)–P(5)	97.0(2)	H(12)–W(1)–P(2)	103.1(16)	H(12)–W(1)–P(3)	142.5(14)
C(11)–P(11)–W(1)	121.8(5)	C(12)–P(1)–W(1)	116.5(5)	H(12)–W(1)–H(11)	66.7(25)	H(13)–W(1)–P(1)	73.8(17)
C(12)–P(1)–C(11)	100.1(6)	C(13)–P(1)–W(1)	118.1(5)	H(13)–W(1)–P(2)	73.9(18)	H(13)–W(1)–P(3)	145.5(17)
C(13)–P(1)–C(11)	97.5(6)	C(13)–P(1)–C(12)	98.5(7)	H(13)–W(1)–H(11)	127.3(28)	H(13)–W(1)–H(12)	70.2(22)
C(21)–P(2)–W(1)	115.8(5)	C(22)–P(2)–W(1)	123.5(7)	H(14)–W(1)–P(1)	85.4(20)	H(14)–W(1)–P(2)	63.7(18)
C(22)–P(2)–C(21)	103.1(10)	C(23)–P(2)–W(1)	115.7(6)	H(14)–W(1)–P(3)	85.7(18)	H(14)–W(1)–H(11)	149.2(24)
C(23)–P(2)–C(21)	95.5(8)	C(23)–P(2)–C(22)	98.7(10)	H(14)–W(1)–H(12)	131.1(21)	H(14)–W(1)–H(13)	60.9(22)
C(31)–P(3)–W(1)	119.8(5)	C(32)–P(3)–W(1)	115.1(5)	H(21)–W(2)–P(4)	143.3(22)	H(21)–W(2)–P(5)	71.9(24)
C(32)–P(3)–C(31)	99.7(7)	C(33)–P(3)–W(1)	121.0(6)	H(21)–W(2)–P(6)	70.8(19)	H(22)–W(2)–P(4)	67.1(17)
C(33)–P(3)–C(31)	100.0(9)	C(33)–P(3)–C(32)	96.9(10)	H(22)–W(2)–P(5)	81.4(18)	H(22)–W(2)–P(6)	146.8(15)
C(41)–P(4)–W(2)	116.0(5)	C(42)–P(4)–W(2)	122.8(5)	H(22)–W(2)–H(21)	137.3(25)	H(23)–W(2)–P(4)	92.7(15)
C(42)–P(4)–C(41)	97.6(7)	C(43)–P(4)–W(2)	116.6(6)	H(23)–W(2)–P(5)	88.6(18)	H(23)–W(2)–P(6)	147.2(16)
C(43)–P(4)–C(41)	98.5(8)	C(43)–P(4)–C(42)	101.1(8)	H(23)–W(2)–H(21)	80.6(22)	H(23)–W(2)–H(22)	65.9(22)
C(51)–P(5)–W(2)	121.6(6)	C(52)–P(5)–W(2)	115.4(6)	H(24)–W(2)–P(4)	75.3(15)	H(24)–W(2)–P(5)	79.0(16)
C(52)–P(5)–C(51)	102.5(8)	C(53)–P(5)–W(2)	116.4(5)	H(24)–W(2)–P(6)	77.1(15)	H(24)–W(2)–H(21)	132.8(22)
C(53)–P(5)–C(51)	95.9(7)	C(53)–P(5)–C(52)	101.5(8)	H(24)–W(2)–H(22)	70.1(22)	H(24)–W(2)–H(23)	135.5(21)
C(61)–P(6)–W(2)	120.6(6)	C(62)–P(6)–W(2)	116.0(5)	H(25)–W(2)–P(4)	71.4(13)	H(25)–W(2)–P(5)	144.1(12)
C(62)–P(6)–C(61)	100.3(9)	C(63)–P(6)–W(2)	121.5(6)	H(25)–W(2)–P(6)	66.3(13)	H(25)–W(2)–H(21)	72.6(26)
C(63)–P(6)–C(61)	95.8(9)	C(63)–P(6)–C(62)	98.0(8)	H(25)–W(2)–H(22)	130.3(22)	H(25)–W(2)–H(23)	90.6(22)
				H(25)–W(2)–H(24)	123.6(21)		
				H(11)–Li(1)–H(12)	64.4(30)	H(11)–Li(1)–H(22)	105.4(32)
				H(11)–Li(1)–H(23)	147.2(32)	H(12)–Li(1)–H(22)	158.7(34)
				H(12)–Li(1)–H(23)	109.3(3)	H(22)–Li(1)–H(23)	68.3(29)
				H(12)–Li(2)–H(13)	76.6(29)	H(12)–Li(2)–H(21a)	136.6(30)
				H(12)–Li(2)–H(23a)	108.5(31)	H(13)–Li(2)–H(21a)	101.7(36)
				H(13)–Li(2)–H(23a)	174.7(38)	H(21a)–Li(2)–H(23a)	73.7(30)

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z): a $2.0 - x$, $1.0 - y$, $-z$.

Table 4. Selected bond lengths (Å) and angles (°) for $WH_2I(PMe_3)_3$-$(SiMe_3)$ (G)

I–W	2.913(4)	P(1)–W	2.481(4)
P(2)–W	2.524(6)	Si–W	2.388(6)
C(11)–P(1)	1.865(14)	C(12)–P(1)	1.839(14)
C(13)–P(1)	1.846(15)	C(31)–P(2)	1.832(14)
C(32)–P(2)	1.783(20)	C(21)–Si	1.827(15)
C(22)–Si	1.820(20)	H(1)–W	1.561(55)
H(2)–W	1.898(58)		

P(1)–W–I	79.9(2)	P(2)–W–I	89.0(2)
P(2)–W–P(1)	93.2(2)	Si(1)–W–I	135.4(1)
Si–W–P(1)	94.8(2)	Si(1)–W–P(2)	135.6(1)
C(11)–P(1)–W	119.8(5)	C(12)–P(1)–W	119.1(6)
C(12)–P(1)–C(11)	97.1(7)	C(13)–P(1)–W	115.7(5)
C(13)–P(1)–C(11)	100.7(7)	C(13)–P(1)–C(12)	100.7(7)
C(31)–P(2)–W	115.9(5)	C(32)–P(2)–W	123.5(7)
C(32)–P(2)–C(31)	99.5(7)	C(21)–Si–W	119.2(5)
C(22)–Si–W	117.0(7)	C(22)–Si–C(21)	100.8(8)
C(21)–Si–C(21)	95.8(11)	C(31)–P(2)–C(31)	98.5(10)
H(1)–W–I	157.0(21)	H(1)–W–P(1)	100.6(2)
H(1)–W–P(2)	68.0(22)	H(1)–W–Si	67.6(22)
H(2)–W–I	74.6(17)	H(2)–W–P(1)	84.0(4)
H(2)–W–P(2)	163.6(16)	H(2)–W–Si	60.8(17)
H(2)–W–H(1)	128.4(27)		

of the lithium complex (E) results in the evolution of gas and a moderate yield of $WH_2I(PMe_3)_3(SiMe_3)$ (G). The i.r. spectrum of (G) contains broad bands between 1 800 and 1 650 cm^{-1} due to the metal hydrides; similar bands are observed for the complex $WH_2(PMe_3)_5$.[8] In addition to peaks due to the phosphine and the Me_3Si group, the ^1H n.m.r. spectrum contains a multiplet (δ -5.60 p.p.m.) due to the two terminal W–H hydrides.

The molecular structure of compound (G) is shown in Figure 4; selected bond lengths and angles are given in Table 4. Both hydrogens bound to tungsten were located with some confidence, and the W geometry is pentagonal bipyramidal, with the pentagonal girdle containing W, I, P(2), Si, and the two hydrogens coincident with the crystallographic mirror plane. One hydride is located between the Si–W and W–I bonds [Si–W–I 135.4(1)°] and the other lies between the Si–W and W–P(2) bonds [Si–W–P(2) 135.6(1)°]. This structure is therefore similar to that found for $MoH_2(PMe_3)_5$,[11] in which the pentagonal girdle contained three phosphines and the two hydrogens.

The distribution of W–P and W–Si bond lengths in the present compound is interesting. The positioning of the $SiMe_3$ group in the molecule was based initially on differences in thermal parameters at the isotropic refinement stage, and the

final anisotropic coefficients are consistent with this. However, the W–P and W–Si bond lengths found are not consistent with expected values. Thus, on simple covalent-radius comparisons, $\gamma_{cov.}(P)$ would be expected to be less than $\gamma_{cov.}(Si)$ since $\gamma_{cov.}$ normally decreases on going from left to right along a row of the Periodic Table; in terms of π-back bonding, we would expect P to be stronger than Si. In spite of these differences, the bond to the atom assigned as Si is the shortest of the group for the four Si/P possibilities. Furthermore, the bond distances to methyl carbons are not helpful since the spread of values is so great. Nevertheless, we are prepared to accept the assignment made for the following reasons. The complex contains a tungsten(IV) centre with a d^2 configuration; π-back bonding is therefore unlikely to be strong. With the structures as presented we can identify two types of phosphorus atoms, axial [P(1) and P(1′)] and equatorial. The latter are longer than the former and this result parallels that found for the molybdenum complex,[11] which was explained in terms of a 'nearly-*trans*' influence, *i.e.* the equatorial W–P bond is more nearly *trans* to a W–H bond than the W–Si bond, and may thus be weakened. Finally, however, one must also presume that the σ bonding in the W–Si interaction is much stronger than in the W–P interaction, leading to a much shorter W–Si bond.

Sakurai *et al.*[12] have proposed a mechanism for the thermal decomposition of allyltrimethylsilane, involving the abstraction of a methylene group [equation (6)]. It is likely that a similar process is involved in the formation of the tungsten complex as follows. The interaction of [(Me$_3$P)$_3$WH$_5$]Li with 1 equivalent of Me$_3$SiCH$_2$I yields a tungsten(VI) alkylhydride complex [equation (7)]. Reductive elimination of Me$_4$Si then yields the co-ordinatively unsaturated hydride WH$_4$(PMe$_3$)$_3$ which may react with a further equivalent of Me$_3$SiCH$_2$I [equation (8)]. Methylene abstracted from the Me$_3$SiCH$_2$ group could be 'trapped' by one of the hydrides [equation (9)]. Final reductive elimination of CH$_4$ would then result in the complex [equation (10)].

Trimethylammonium Chloride.—The addition of 2 equivalents of trimethylammonium chloride to an Et$_2$O solution of [(Me$_3$P)$_3$H$_3$W(μ-H)$_2$AlH(μ-H)]$_2$ yields the monomeric amine complex (Me$_3$P)$_3$H$_2$W(μ-H)$_3$AlCl$_2$(NMe$_3$) (H). The molecular structure of the compound is shown in Figure 5; selected bond lengths and angles are given in Table 5. In this structure all hydride hydrogens were located and refined with some confidence and show quite clearly a (μ-H)$_3$ bridge, leading to six-fold co-ordination for aluminium. As far as we are aware, this
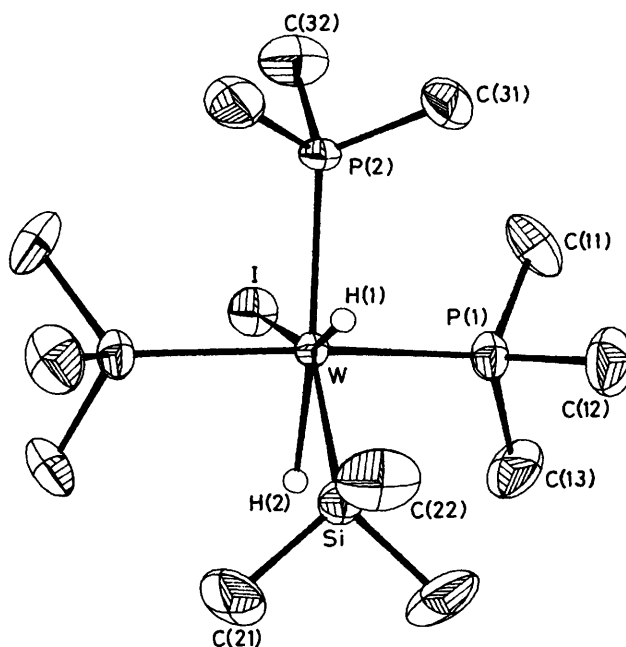

Figure 4. The structure of WH$_2$I(PMe$_3$)$_3$(SiMe$_3$) (G). Only the hydrogens bound to tungsten are shown

is the first example of such co-ordination in aluminohydride complexes. The geometry is that of a distorted octahedron with the H$_3$Al face closed down [H–Al–H 64.6(3)—69.3(2)°] and the Cl$_2$NAl face slightly opened up [angles of 95.1—101.8(1)°]. The Al–Cl bonds in this complex are very similar to that in the chloroimine complex described earlier, but the Al–N bond here is longer than those in the imine, even though these latter bonds are involved in bridging. This presumably is a reflection of the higher co-ordination here and/or a weaker interaction. The tungsten geometry is once more dodecahedral with one trapezium formed by P(1), H(3), H(5), P(2) and the other by P(3), H(1), H(2), H(4). In this case the W–P bond lengths are equally spread over the range 2.420(4)—2.439(4) Å.

The i.r. spectrum of the complex contains bands between 1 800 and 1 650 cm^{-1} due to bridging and terminal hydrides

$$Me_3SiCH_2CH{=}CH_2 \xrightarrow{500\ °C} [Me_3Si\cdots\cdots CH{\cdots}CH_2] \longrightarrow Me_3SiCH{=}CH_2 + H_2C$$

$$\underset{H_2}{C}$$

(6)

$$[(Me_3P)_3WH_5]Li + Me_3SiCH_2I \longrightarrow (Me_3P)_3WH_5(CH_2SiMe_3) + LiI \tag{7}$$

$$(Me_3P)_3WH_5(CH_2SiMe_3) \xrightarrow{-Me_4Si} (Me_3P)_3WH_4 \xrightarrow{Me_3SiCH_2I} (Me_3P)_3WH_4I(CH_2SiMe_3) \tag{8}$$

$$(Me_3P)_3WH_4I(CH_2SiMe_3) \longrightarrow (Me_3P)_3IH_4W\cdots\cdots SiMe_3 \longrightarrow (Me_3P)_3WH_3IMe(SiMe_3)$$

$$\underset{H_2}{C}$$

(9)

$$(Me_3P)_3WH_3IMe(SiMe_3) \xrightarrow{-CH_4} (Me_3P)_3WH_2I(SiMe_3) \tag{10}$$
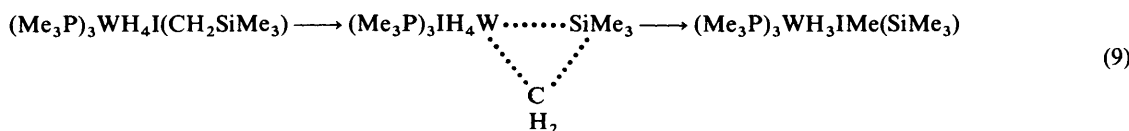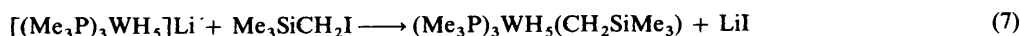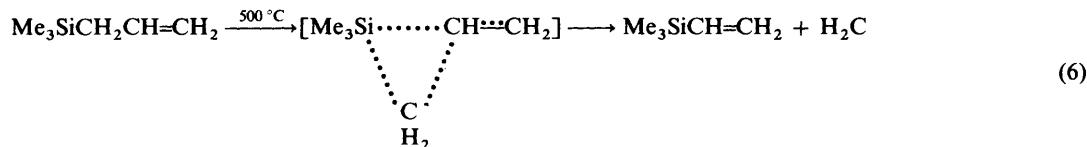
Table 5. Selected bond lengths (Å) and angles (°) for $(Me_3P)_3H_2W(\mu\text{-}H)_3AlCl_2(NMe_3)$ (H)

P(1)–W	2.439(4)	P(2)–W	2.429(4)	H(1)–W	1.611(59)	H(2)–W	1.641(59)
P(3)–W	2.420(4)	Cl(1)–Al	2.204(5)	H(3)–W	1.679(54)	H(4)–W	1.691(57)
Cl(2)–Al	2.190(5)	N–Al	2.067(8)	H(5)–W	1.671(68)	H(3)–Al	1.908(52)
C(11)–P(1)	1.811(12)	C(12)–P(1)	1.820(12)	H(4)–Al	1.684(57)	H(5)–Al	1.892(69)
C(13)–P(1)	1.836(12)	C(21)–P(2)	1.809(12)				
C(22)–P(2)	1.811(12)	C(23)–P(2)	1.826(13)				
C(31)–P(3)	1.858(13)	C(32)–P(3)	1.808(11)				
C(33)–P(3)	1.826(15)	C(1)–N	1.478(12)				
C(2)–N	1.484(12)	C(3)–N	1.492(10)				

P(2)–W–P	142.8(1)	P(3)–W–P(1)	98.9(2)	H(1)–W–P(2)	77.2(20)	H(1)–W–P(1)	77.9(20)
P(3)–W–P(2)	96.2(2)	Cl(2)–Al–Cl(1)	102.8(2)	H(2)–W–P(1)	75.2(21)	H(1)–W–P(3)	66.9(21)
N–Al–Cl(1)	95.1(3)	N–Al–Cl(2)	95.8(3)	H(2)–W–P(3)	130.1(20)	H(2)–W–P(2)	69.1(21)
C(11)–P(1)–W	116.4(4)	C(12)–P(1)–W	117.0(5)	H(3)–W–P(1)	70.6(18)	H(2)–W–H(1)	63.5(27)
C(12)–P(1)–C(11)	99.7(6)	C(13)–P(1)–W	119.0(5)	H(3)–W–P(3)	89.1(18)	H(3)–W–P(2)	143.6(17)
C(13)–P(1)–C(11)	97.3(6)	C(13)–P(1)–C(12)	103.9(6)	H(3)–W–H(2)	131.3(27)	H(3)–W–H(1)	136.3(27)
C(21)–P(2)–W	118.2(4)	C(22)–P(2)–W	117.6(5)	H(4)–W–P(2)	87.7(20)	H(4)–W–P(1)	91.3(19)
C(22)–P(2)–C(21)	101.9(6)	C(23)–P(2)–W	115.3(4)	H(4)–W–H(1)	135.7(27)	H(4)–W–P(3)	157.1(19)
C(23)–P(2)–C(21)	100.8(6)	C(23)–P(2)–C(22)	100.2(6)	H(4)–W–H(3)	74.9(26)	H(4)–W–H(2)	72.2(27)
C(31)–P(3)–W	118.0(5)	C(32)–P(3)–W	119.2(4)	H(5)–W–P(2)	67.5(24)	H(5)–W–P(1)	145.3(23)
C(32)–P(3)–C(31)	99.4(7)	C(33)–P(3)–W	118.8(6)	H(5)–W–H(1)	135.9(30)	H(5)–W–P(3)	91.0(23)
C(33)–P(3)–C(31)	98.3(8)	C(33)–P(3)–C(32)	99.1(7)	H(5)–W–H(3)	76.4(29)	H(5)–W–H(2)	122.1(31)
C(1)–N–Al	111.0(6)	C(2)–N–Al	110.8(6)	H(3)–Al–Cl(1)	95.7(17)	H(5)–W–H(4)	69.6(28)
C(2)–N–C(1)	107.1(8)	C(3)–N–Al	111.9(6)	H(3)–Al–N	92.8(16)	H(3)–Al–Cl(2)	158.8(16)
C(3)–N–C(1)	107.7(8)	C(3)–N–C(2)	108.3(8)	H(4)–Al–Cl(2)	97.6(19)	H(4)–Al–Cl(1)	97.9(20)
Al–H(3)–W	93.7(25)	Al–H(4)–W	102.0(30)	H(4)–Al–H(3)	69.3(24)	H(4)–Al–N	158.7(19)
Al–H(5)–W	94.6(33)			H(5)–Al–Cl(2)	93.4(21)	H(5)–Al–Cl(1)	157.8(20)
				H(5)–Al–H(3)	66.1(26)	H(5)–Al–N	98.2(21)
						H(5)–Al–H(4)	64.6(27)
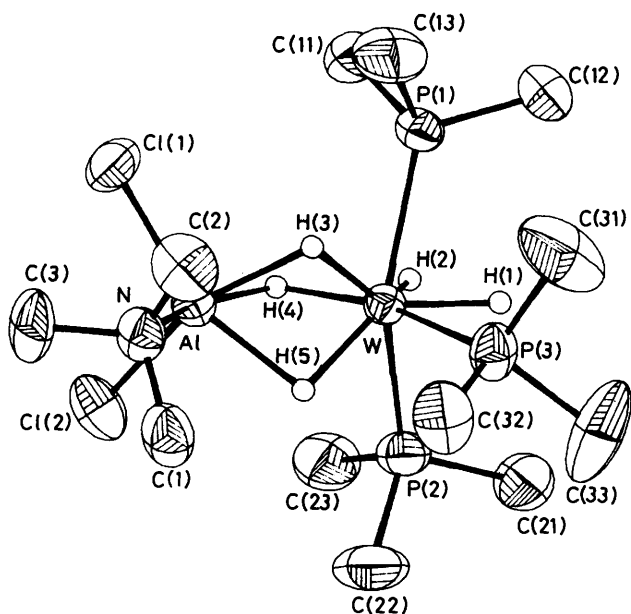
Figure 5. The structure of $(Me_3P)_3H_2W(\mu\text{-}H)_3AlCl_2(NMe_3)$ (H). Only the hydrogens bound to tungsten are shown

along with a sharp band at 520 cm⁻¹ due to terminal Al–Cl stretch. As with other aluminopolyhydrides, the complex is fluxional in solution at room temperature. The ¹H n.m.r. spectrum contains a very broad quartet [δ −5.56 p.p.m., J(P–H) ca. 20 Hz] due to the terminal W–H and bridging $W(\mu\text{-}H)Al$ hydrides. On cooling to −50 °C this signal becomes better resolved [J(P–H) = 26.8 Hz], whilst on further cooling (−80 °C) it de-coalesces to give two very broad signals at δ −3.46 and 7.28 p.p.m. due to terminal W–H and bridging

$W(\mu\text{-}H)Al$ hydrides respectively. The activation energy for this process (T_c = −78 °C, $\Delta G_{av.}^{\ddagger}$ = 9.2 kJ mol⁻¹) is slightly, although not significantly, lower than that observed for similar complexes.[1] The ²⁷Al-{¹H} n.m.r. spectrum contains a sharp singlet (δ 84.5 p.p.m., $W_{\frac{1}{2}}$ = 325 Hz) that is in agreement with the X-ray data, confirming that the aluminium is six-co-ordinate unlike the majority of aluminohydrides where a five-co-ordinate geometry is found.

The complex is moisture and air sensitive yielding $WH_6(PMe_3)_3$[5] on hydrolysis.

Cyclohexanone.—Addition of excess of cyclohexanone to an Et_2O solution of $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$ containing excess of PMe_3 produces an orange solution. Evaporation followed by extraction and crystallisation from hexane yields yellow crystals of $(Me_3P)_4W(\mu\text{-}H)_2AlH_3$ (I), which is monomeric in solution according to molecular weight determination. We have not ascertained the fate of the cyclohexanone. The i.r. spectrum of (I) contains broad bands between 1 940 and 1 600 cm⁻¹ du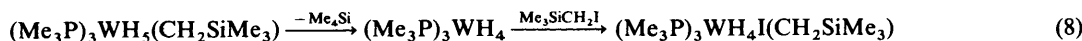e to bridging $W(\mu\text{-}H)Al$ and terminal Al–H hydrides. The ³¹P-{¹H} n.m.r. spectrum consists of two triplets [δ −22.11 (A), −28.64 (B) p.p.m., J(P_A–P_B) = 15.5 Hz] each of which is further split into triplets on selective decoupling of the P–CH₃ protons [J(P_A–H) = 55.4, J(P_B–H) = 15.5 Hz]. This is consistent with a *cis*-octahedral geometry around the tungsten, (3). A complex multiplet ($AA'XX'Y_2$) in the high-field ¹H n.m.r. spectrum (δ −3.48 p.p.m.) is in
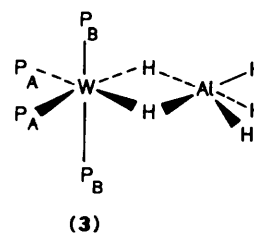

(3)

Table 6. Analytical data (%) for new complexes[a]

	C	H	P	N	Cl
(A) [(Me₃P)₃H₃W(μ-H)₂AlH(μ-N=CHMe)]₂	26.5	6.9	18.8	2.8	
	(27.0)	(7.7)	(19.0)	(2.8)	
(B) [(Me₃P)₃H₃W(μ-H)₂AlH(μ-N=CHEt)]₂	28.5	7.8	17.9	2.8	
	(28.7)	(7.9)	(18.5)	(2.8)	
(C) [(Me₃P)₃H₃W(μ-H)₂AlCl(μ-N=CHEt)]₂	26.1	6.9	16.8	2.6	6.5
	(26.8)	(7.3)	(17.3)	(2.6)	(6.6)
(E) {[(Me₃P)₃WH₅]Li}₄	26.0	7.6	20.3		
	(25.5)	(7.6)	(21.9)		
(F) (Me₃P)₃H₃W(μ-H)₂Li(tmen)	34.6	8.9	17.0	5.3	
	(33.3)	(8.9)	(17.2)	(5.2)	
(H) (Me₃P)₃H₂W(μ-H)₃AlCl₂(NMe₃)	25.0	7.8	16.0	2.4	12.3
	(25.1)	(7.1)	(16.2)	(2.4)	(12.4)
(I) (Me₃P)₄W(μ-H)₂AlH₃[b]	27.2	7.8	24.0		
	(27.7)	(7.9)	(23.8)		

[a] Required values in parentheses. [b] M (cryoscopic in benzene) 590 (calc. 520).

Table 7. Crystal data, intensity data, collection parameters, and details of refinement

Crystal data	(C)	(E)	(G)	(H)
M	1 073.36	1 696.388	614.224	574.148
a/Å	10.447(5)	14.011(2)	14.066(2)	19.563(2)
b/Å	9.118(4)	14.577(1)	13.404(2)	17.319(2)
c/Å	14.077(5)	10.818(2)	12.284(1)	14.446(5)
α/°	71.52(3)	75.64(2)	90	90
β/°	113.73(4)	109.94(2)	90	90
γ/°	103.43(4)	114.65(1)	90	90
U/Å³	1 155.66	1 873.20	2 316.03	4 894.47
System	Triclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$Cmc2_1$	$Pbca$
D_c/g cm⁻³	1.54	1.50	1.76	1.56
Z	1	1	4	8
$F(000)$	534	832	1 184	2 288
μ/mm⁻¹	54.56	65.27	66.59	52.64
Data collection				
θ (min., max.)/°	1.5, 25	1.5, 25	1.5, 25	1.5, 25
Total data measured	4 250	5 396	1 220	5 124
Unique	4 068	5 199	1 124	4 294
Observed	3 427	4 018	1 065	2 730
Significance test	$F_o > 4\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 4\sigma(F_o)$
Refinement				
No. of parameters	304	505	170	345
Absorption correction	psi-scan	psi-scan/DIFABS	psi-scan/DIFABS	psi-scan/DIFABS
Weighting scheme parameter, g*	0.000 01	0.000 01	Unit weights	0.000 01
R†	0.024 8	0.031 1	0.0207	0.031 5
R'‡	0.026 8	0.027 1	0.0237	0.025 1

* $w = 1/[\sigma^2(F_o) + gF_o]$. † $\Sigma|\Delta F|/\Sigma|F_o|$. ‡ $[\Sigma w(\Delta F)^2/\Sigma w|F_o^2|]^{\frac{1}{2}}$.

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agreement with this. The ²⁷Al-{¹H} n.m.r. spectrum (δ 52.7 p.p.m., $W_{\frac{1}{2}}$ = 5 280 Hz) indicates five-co-ordinate aluminium.

Similar complexes (η⁵-C₅H₅)₂M(μ-H)₂AlH₃, M = Mo or W, have been reported as being thermally unstable and unisolable.[13] However, Caulton and co-workers[14] have reported the synthesis and crystal structure of (η⁵-C₅H₅)₂W(μ-H)₂AlMe₃. By analogy with this complex we suggest that the present compound is an alane adduct of (Me₃P)₄WH₂. The same product is also obtained by the reaction of WCl₄(PMe₃)₃ with excess of Li[AlH(OMe)₃] in the presence of PMe₃.

Experimental

Microanalyses were by Pascher Laboratories. Melting points were determined in sealed capillaries and are uncorrected. I.r. spectra (cm⁻¹) were recorded on a Perkin-Elmer 683 grating

spectrometer in Nujol mulls. N.m.r. spectra (Table 1) were recorded on JEOL X90Q (¹H and ³¹P unless otherwise stated) or Bruker WM-250 (²⁷Al) spectrometers, δ in p.p.m. being relative to SiMe₄ (¹H), external 85% H₃PO₄ (³¹P), or external [Al(H₂O)₆]³⁺ (²⁷Al). All manipulations were carried out under argon. Solvents were dried, distilled, and degassed before use.

Analytical data are given in Table 6. The compounds MeCN and EtCN were distilled from P₂O₅ under argon, and NMe₃HCl (Aldrich) was dried under vacuum prior to use.

2,3:2,3-*Bis*-μ-*ethylideneamido*-1,2;1,2;3,4;3,4-*tetra*-μ-*hydrido*-1,1,1,2,3,4,4,4-*octahydrido*-1,1,1,4,4,4-*hexakis*(*trimethylphos-phine*)-2,3-*dialuminium*-1,4-*ditungsten*(IV), (A).—To a diethyl ether solution (50 cm³) of [(Me₃P)₃H₃W(AlH₄)]₂ [1] (0.97 g, 1.09 mmol) at 0 °C was added MeCN (2 cm³). The colour changes instantly from yellow to bright orange. After stirring for 2 h the

Table 8. Fractional atomic co-ordinates ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
(a) [(Me₃P)₃H₃W(μ-H)₂AlCl(μ-N=CHEt)]₂							
W(1)	7 555(0.5)	8 178(0.5)	7 730(0.5)	C(11)	6 174(8)	5 176(8)	6 308(6)
P(1)	7 111(2)	5 502(2)	7 639(1)	C(12)	5 992(9)	4 132(8)	8 327(6)
P(2)	6 845(2)	8 060(2)	9 202(1)	C(13)	8 565(8)	4 344(9)	8 126(7)
P(3)	9 623(2)	8 809(2)	7 226(1)	C(21)	6 957(11)	9 900(9)	9 465(7)
Al(1)	5 540(2)	9 695(2)	6 175(1)	C(22)	5 029(8)	7 301(9)	9 103(6)
Cl(1)	4 146(2)	10 768(2)	6 529(1)	C(23)	7 801(9)	6 957(11)	10 528(5)
N(1)	4 130(4)	8 782(5)	5 049(3)	C(31)	9 481(8)	8 252(10)	6 046(6)
C(1)	3 154(6)	7 666(7)	5 022(5)	C(32)	11 215(7)	8 005(11)	8 199(6)
C(2)	2 773(7)	6 641(8)	5 963(5)	C(33)	10 321(8)	10 848(9)	6 936(7)
C(3)	2 068(10)	5 047(11)	5 845(7)				
(b) {[(Me₃P)₃WH₅]Li}₄							
W(1)	10 863(0.5)	2 553(0.5)	1 347(0.5)	C(31)	12 099(10)	805(9)	3 737(13)
W(2)	12 911(0.5)	6 732(0.5)	2 117(0.5)	C(32)	13 196(12)	2 838(10)	4 248(15)
P(1)	9 688(2)	1 825(2)	2 806(2)	C(33)	13 495(14)	2 196(19)	2 272(16)
P(2)	11 018(3)	2 439(2)	−779(3)	C(41)	11 169(11)	4 935(8)	4 153(12)
P(3)	12 369(2)	2 070(2)	2 839(3)	C(42)	12 219(15)	6 765(9)	5 157(13)
P(4)	12 441(3)	6 031(2)	4 212(3)	C(43)	13 348(13)	5 481(12)	5 493(12)
P(5)	13 846(3)	6 633(2)	666(3)	C(51)	14 472(13)	7 746(10)	−416(15)
P(6)	13 981(3)	8 477(2)	2 486(3)	C(52)	14 929(13)	6 136(14)	1 470(15)
C(11)	10 233(10)	1 796(9)	4 608(9)	C(53)	13 008(12)	5 811(9)	−651(12)
C(12)	8 782(10)	505(8)	2 697(11)	C(61)	14 065(18)	8 942(11)	3 947(16)
C(13)	8 682(10)	2 366(9)	2 603(11)	C(62)	13 602(13)	9 428(9)	1 198(14)
C(21)	10 006(14)	1 354(10)	−1 588(13)	C(63)	15 440(11)	9 014(10)	2 650(17)
C(22)	12 262(14)	2 525(20)	−1 031(17)	Li(1)	11 706(12)	4 612(10)	1 558(14)
C(23)	10 695(15)	3 399(11)	−2 152(11)	Li(2)	8 994(12)	3 098(11)	−379(14)
(c) WH₂I(PMe₃)₃(SiMe₃)							
W	0*	2 211(0.5)	6 070*	C(13)	2 150(9)	1 188(10)	4 779(12)
I	0*	2 762(1)	3 776(1)	C(21)	−964(11)	−213(9)	6 846(13)
P(1)	1 733(2)	2 187(2)	5 696(2)	C(22)	0*	766(15)	8 540(14)
P(2)	0*	4 040(3)	6 557(4)	C(31)	986(9)	4 461(9)	7 415(13)
Si	0*	678(3)	7 062(3)	C(32)	0*	5 015(14)	5 571(15)
C(11)	2 313(8)	3 296(10)	5 065(10)	H(1)	0*	2 378(43)	7 327(44)
C(12)	2 567(10)	2 040(10)	6 839(10)	H(2)	0*	986(43)	5 295(44)
(d) (Me₃P)₃H₂W(μ-H)₃AlCl₂(NMe₃)							
W	1 715(0.5)	973(0.5)	1 682(0.5)	C(3)	148(5)	3 258(6)	347(7)
Al	961(1)	2 221(1)	1 554(2)	C(11)	480(5)	300(6)	3 373(8)
P(1)	889(1)	48(1)	2 289(1)	C(12)	1 207(6)	−908(6)	2 584(8)
P(2)	2 834(1)	1 530(1)	1 971(2)	C(13)	106(5)	−146(6)	1 628(8)
P(3)	2 027(1)	304(1)	273(1)	C(21)	3 536(5)	882(6)	2 217(8)
Cl(1)	−46(1)	2 228(1)	2 238(2)	C(22)	3 196(5)	2 143(7)	1 081(8)
Cl(2)	1 386(1)	3 347(1)	1 938(2)	C(23)	2 883(5)	2 180(6)	2 965(8)
N	596(3)	2 563(4)	276(4)	C(31)	1 563(9)	−601(6)	−16(9)
C(1)	1 165(6)	2 755(5)	−358(7)	C(32)	1 948(6)	801(6)	−823(6)
C(2)	198(5)	1 934(6)	−166(7)	C(33)	2 898(8)	−59(9)	150(9)

* Invariant parameter.

solvent was removed and the resulting solid extracted with toluene (30 cm³); reduction in volume and cooling to −20 °C yielded an orange powder (0.66 g, 62%), m.p. 152 °C (decomp.). I.r.: 1 800m, 1 710m, 1 670s, 1 600m, 1 410m, 1 290m, 1 270s, 1 115br,m, 935s, 895m, 850m, 715s, 655s, and 450s cm⁻¹.

1,2;1,2;3,4;3,4-Tetra-μ-hydrido-1,1,1,2,3,4,4,4-octahydrido-2,3;2,3-bis-μ-propylideneamido-1,1,1,4,4,4-hexakis(trimethyl-phosphine)-2,3-dialuminium-1,4-ditungsten(IV), (**B**).—This complex was prepared as for (**A**) but using EtCN to give orange microcrystals (73%), m.p. 149 °C (decomp.). I.r.: 1 780m, 1 700s, 1 660s, 1 630m, 1 580m, 1 295m, 1 270s, 1 145m, 940vs, 850m, 715s, 670s, and 450m cm⁻¹.

2,3-Dichloro-1,2;1,2;3,4;3,4-tetra-μ-hydrido-1,1,1,4,4,4-hexa-hydrido-2,3;2,3-bis(μ-propylideneamido)-1,1,1,4,4,4-hexakis-(trimethylphosphine)-2,3-dialuminium-1,4-ditungsten(IV), (**C**).—To a suspension of LiAlH₄ (0.82 g, 21.7 mmol) in Et₂O (60 cm³) at −78 °C was added WCl₄(PMe₃)₃ (4.01 g, 7.24 mmol). The solution was stirred and warmed to room temperature over 3 h then stirred for a further 16 h. The filtered solution was evaporated to give a yellow oil. Dissolution of the oil in hexane (30 cm³) followed by addition of EtCN (2 cm³) resulted in a bright orange solution, cooling of which gave orange crystals (1.12 g, 29%), m.p. 131 °C (decomp.). I.r.: 1 780m, 1 700s, 1 660s, 1 580m, 1 295m, 1 270s, 1 145m, 940vs, 850m, 715s, 670s, 525m, and 450m cm⁻¹.

{[(Me₃P)₃WH₅]Li}₄ (E).—To an Et₂O (80 cm³) solution of [(Me₃P)₃H₃W(AlH₄)]₂ (0.31 g, 0.34 mmol) was added LiCH₂SiMe₃ (0.7 cm³, 0.95 mol dm⁻³). The colour rapidly changed from yellow to orange and a flocculent white precipitate formed. After stirring for 3 h the solvent was removed and the residue extracted with hexane (2 × 50 cm³); reduction in volume and cooling (−20 °C) gave yellow crystals. Further product can be obtained by reduction in volume of the mother-liquor. Yield: 0.21 g, 76%. M.p. 115 °C (decomp.). I.r.: 1 750s, 1 680br,s, 1 555s, 1 420m, 1 295m, 1 275s, 1 145m, 1 020w, 945s, 855s, 720m, 710m, and 660m cm⁻¹.

Di-μ-hydrido-1,1,1-*trihydrido*-2-(NNN′N′-*tetramethylethyl-enediamine*)-1,1,1-*tris*(*trimethylphosphine*)-1-*tungsten*(IV)-2-*lithium*, (F).—Excess of tmen (1.0 cm³) was added to a toluene solution (50 cm³) of {[(Me₃P)₃WH₅]Li}₄ (0.35 g, 0.21 mmol). After 2 h the volume was reduced to *ca.* 10 cm³; cooling of the solution gave a yellow microcrystalline solid (0.36 g, 80%), m.p. 98 °C (decomp.). I.r.: 2 800m, 2 750w, 1 790s, 1 720s, 1 680s, 1 560m, 1 420m, 1 300s, 1 200vs, 1 150m, 1 130m, 1 030s, 945s, 855s, 720m, 710m, and 650m cm⁻¹.

Dihydridoiodotris(*trimethylphosphine*)(*trimethylsilyl*)-*tungsten*(IV), (G).—To a solution of {[(Me₃P)₃WH₅]Li}₄ (1.01 g, 0.60 mmol) in hexane (60 cm³), was added Me₃SiCH₂I (1.3 cm³). The solution was stirred until all gas evolution had ceased (*ca.* 12 h). The dark yellow solution was filtered, the volume reduced under vacuum to *ca.* 20 cm³, and cooled to −20 °C to give small yellow crystals which were collected and dried under vacuum. A further batch can be obtained on further cooling to −78 °C. Yield: 0.98 g, 41%. M.p. 145 °C (decomp.). I.r.: 1 950w, 1 860w, 1 750w, 1 620w, 1 400m, 1 290m, 1 270m, 1 250s, 1 145m, 1 095s, 1 020br,m, 945vs, 850s, 825m, 705s, and 660m cm⁻¹.

2,2-*Dichloro*-1,2;1,2;1,2-*tri*-μ-*hydrido*-1,1-*dihydrido*-2-*tri-methylamine*-1,1,1-*tris*(*trimethylphosphine*)-2-*aluminium*-1-*tungsten*(IV), (H).—To a stirred solution of [(Me₃P)₃H₃W-(AlH₄)]₂ (3.34 g, 3.74 mmol) in Et₂O (100 cm³) was added NMe₃HCl (1.43 g, 14.9 mmol) at −78 °C. As the mixture warmed to room temperature gas was evolved. After *ca.* 4 h the solvent was removed under vacuum and the pale yellow residue extracted into toluene (80 cm³); reduction in volume and cooling to −20 °C yielded pale yellow needles (3.52 g, 87%), m.p. 82 °C. I.r.: 1 805s, 1 700s, 1 660s, 1 402m, 1 290m, 1 280s, 1 235m, 1 095m, 1 025w, 982s, 938vs, 863s, 855m, 816s, 725s, 715s, 665s, 520m, 440m, and 415m cm⁻¹.

1,2;1,2-*Di*-μ-*hydrido*-2,2,2-*trihydrido*-1,1,1,1-*tetrakis*(*tri-methylphosphine*)-2-*aluminium*-1-*tungsten*(II), (I).—To a solution of [(Me₃P)₃H₃W(AlH₄)]₂ (0.50 g, 0.56 mmol) in Et₂O (75 cm³) containing PMe₃ (0.5 cm³) was added cyclohexanone (0.3 cm³). On stirring overnight the solvent was removed under vacuum and the orange residue extracted with hexane (2 × 20 cm³); reduction in the volume yielded small yellow crystals (0.16 g, 28%), m.p. 72 °C (decomp.). I.r.: 1 940m, 1 750br,m, 1 600br,m, 1 420m, 1 295s, 1 275s, 1 255m, 1 140 (sh), 1 100s, 1 025w, 940s, 855m, 845m, 800w, 720s, and 660m cm⁻¹.

X-Ray Crystallography.—Crystals of all compounds were sealed under argon in thin-walled glass capillaries. Orientation matrices and associated cell dimensions and intensity data were obtained following previously described procedures,[15] using an Enraf–Nonius CAD4 diffractometer and graphite-monochrom-

atised Mo-$K_α$ radiation [λ(Mo-$K_α$) = 0.710 69 Å] at 293 K. The structures were solved *via* standard heavy-atom methods and refined by using full-matrix least squares,[16] with scattering factors based on parameters in ref. 17. Details of the crystal data and structure analysis are given in Table 7. The refinements were mostly straightforward with only the location of hydrogen atoms in some cases causing difficulties. All non-hydrogen atoms were refined anisotropically. For compound (C) it was not possible to locate and refine the hydrogen atoms attached to W or Al, although the methyl hydrogens were located and successfully refined isotropically. For compound (E) all hydrogens bonded to tungsten and bridging to lithium were located and refined isotropically except for one, a terminal hydrogen attached to W(1). This was not included in the refinement, although for the purposes of discussion and representation of the structure a position was calculated so as to make the two tungsten co-ordinations compatible. Methyl hydrogens could not be located and were included in idealised positions and refined using the AFIX facility in SHELX. For compounds (G) and (H) all hydrogens were located and freely refined isotropically.

Final atomic positional parameters are given in Table 8.

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