

# Synthesis and Characterisation of Tungsten and Rhenium Aluminopolyhydrides: X-Ray Crystal Structures of $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-OBU}^n)_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$ and $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$ †

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The reaction of  $\text{WCl}_4(\text{PMe}_3)_3$  with  $\text{LiAlH}_4$  in refluxing tetrahydrofuran leads to the aluminopolyhydride,  $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-OBU}^n)_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$  (1), whereas in diethyl ether the product is  $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$  (2). Addition of *NNN'*-tetramethylethylenediamine to a toluene solution of (2) results in the formation of  $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$  (3). The rhenium analogues of (1) and (2), namely compounds  $(\text{Me}_2\text{PhP})_3\text{H}_2\text{Re}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-OBU}^n)_2\text{Al}(\text{H})(\mu\text{-H})_2\text{ReH}_2(\text{PMe}_2\text{Ph})_3$  (4) and  $(\text{Me}_2\text{PhP})_3\text{H}_2\text{Re}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{ReH}_2(\text{PMe}_2\text{Ph})_3$  (5) have been obtained from  $\text{ReCl}_3(\text{PMe}_2\text{Ph})_3$ . The heavy-atom structures of (1) and (3) have been confirmed by X-ray crystallography. Hydrogen-1,  $^{31}\text{P}$ , and  $^{27}\text{Al}$  n.m.r. spectra are reported and the fluxional behaviour of the compounds discussed.

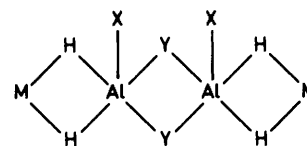
Transition metal aluminohydrides containing the  $\text{AlH}_4^-$  group are rare in contrast to the large number of borohydrides that are known.<sup>1</sup> Titanium,<sup>2a</sup> zirconium,<sup>2b</sup> and niobium<sup>2c</sup> compounds of stoichiometry  $(\eta^5\text{-C}_5\text{H}_5)_2\text{MAlH}_4$ , believed to be monomers, containing the  $\eta^2\text{-AlH}_4$  group have long been known. The first transition metal compound containing a  $\mu\text{-}\eta^2\text{-AlH}_2$  moiety to be crystallographically characterised<sup>3</sup> was  $(\text{dmpe})_2\text{Ta}(\mu\text{-H})_2\text{Al}(\text{OC}_2\text{H}_4\text{OMe})(\mu\text{-OC}_2\text{H}_4\text{OMe})_2\text{Al}(\text{OC}_2\text{H}_4\text{OMe})(\mu\text{-H})_2\text{Ta}(\text{dmpe})_2$  [dmpe = 1,2-bis(dimethylphosphino)ethane], which had both terminal (on Al) and bridging alkoxo as well as bridging Ta( $\mu\text{-H}$ )<sub>2</sub>Al groups. The first transition metal  $\mu\text{-}\eta^2\text{-AlH}_4$  complex to be structurally determined<sup>4</sup> was  $[(\text{dmpe})_2\text{MnAlH}_4]_2$ .

These compounds and the compounds reported herein have cores consisting of the moieties  $\text{M}(\mu\text{-H})_2\text{Al}(\text{OR})(\mu\text{-OR})_2\text{Al}(\text{OR})(\mu\text{-H})_2\text{M}$ ,<sup>3</sup>  $\text{M}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-OR})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{M}$ , or  $\text{M}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{M}$ <sup>4</sup> (structure I). The exception is the unique  $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$ ,<sup>5</sup> which has the core of the type II. Other aluminohydrides with the cores of types I and II such as  $(\text{Me}_3\text{P})_3\text{HRu}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{RuH}(\text{PMe}_3)_3$  are described in the following paper.

Russian workers have recently reported the structure of the complex formulated as  $\{[(\eta\text{-C}_5\text{H}_5)_2\text{Y}(\mu_3\text{-H})(\mu\text{-HAlH}_2)]_2$  and some solvent adducts thereof,<sup>6a</sup> while a different type,<sup>6b</sup>  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)\text{Al}(\text{H})(\mu\text{-H})_2\text{-Ti}(\eta^5\text{-C}_5\text{H}_5)_2$ , has tetramethylethylenediamine bridging and co-ordinated to two aluminium atoms.

## Results and Discussion

**Tungsten Aluminopolyhydrides.**—The interaction of  $\text{WCl}_4(\text{PMe}_3)_3$ <sup>7</sup> with  $\text{LiAlH}_4$  in refluxing tetrahydrofuran (thf) followed by crystallisation from toluene affords a moderate



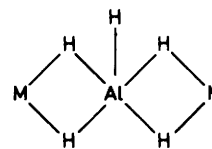
(I)

M = Ta, X = Y = OR

M = Mn, X = Y = H

M = W or Re, X = H, Y = OBU<sup>n</sup>

M = W or Re, X = Y = H



(II)

yield of the yellow  $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-OBU}^n)_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$  (1). However, if the reaction is carried out in diethyl ether at room temperature the product is  $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$  (2) in high yield.

The molecular structure of the butoxo compound (1), which has crystallographic  $C_2$  symmetry, is shown in Figure 1; selected bond lengths and angles are given in Table 1. Although the number of metal-bonded hydrogens in the structure is known with some confidence, their location in the X-ray structure was difficult. Peaks occurred in the difference synthesis at suitably distant positions but attempts to refine hydrogen atoms at these sites were generally unsuccessful. Accordingly, for the final refinement, no metal-bonded hydrogens were included.

Nevertheless, the indications were quite strong that the aluminium atom was bridged to tungsten by two hydrogens and was bonded to a third, terminal hydrogen, giving, together with the two oxygen atoms, five-co-ordination. This would be analogous to the structure found for the complex  $[(\text{dmpe})_2\text{MnAlH}_4]_2$ ,<sup>4</sup> although in the present compound the implied Al co-

† 2,3; 2,3-Di- $\mu$ -n-butoxo-1,2; 1,2; 3,4; 3,4-tetra- $\mu$ -hydrido-1,1,1,2,3,4,4,4-octahydrido-1,1,1,4,4,4-hexakis(trimethylphosphine)-2,3-dialuminium-1,4-ditungsten(IV) and 1,2; 1,2; 2,3; 2,3-tetra- $\mu$ -hydrido-1,1,1,2,3,3,3,3-heptahydrido-1,1,1,3,3,3-hexakis(trimethylphosphine)-2-aluminium-1,3-ditungsten(IV).

Supplementary data available (No. SUP 56432, 6 pp.): H-atom coordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

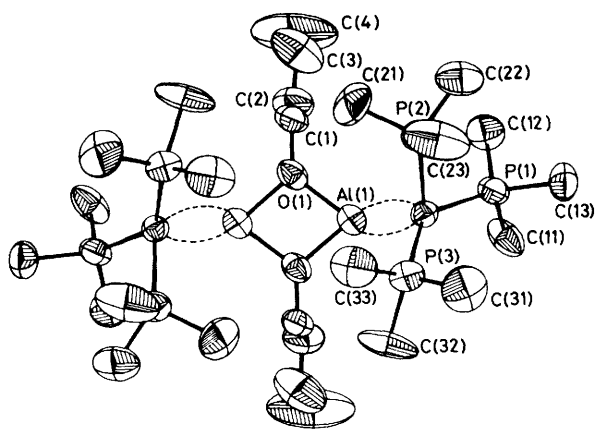


Figure 1. The molecular structure of  $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-OBu})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$  (1)

ordination was not definable as either of the two idealised five-co-ordinate geometries. It is also possible that the difficulties in locating hydrogens in this compound are due, in part, to the fluxional nature of the structure indicated by the n.m.r. data (see below) and it is not improbable that intermediate interactions of the kind found in  $\text{ReH}_4\text{AlMe}_2(\text{PPh}_2\text{Me})_3$ <sup>8</sup> are present. The tungsten geometry is difficult to define, in view of the uncertainties in the hydrogen positions, but the co-ordination number is most likely to be eight. The three W-P distances appear to fall into two groups with one [W-P(2) 2.409(6) Å] slightly shorter than the other two [2.420(6), 2.425(6) Å]. Detailed analysis of the P-W-P angles and the likely positions of the hydrogens did not suggest that the structure might correspond to either of the two standard eight-co-ordination geometries, dodecahedral or square antiprismatic, although the arrangement of the phosphines alone is consistent with their positioning at three of the four B sites of a dodecahedral structure [i.e., with P(1) and P(3) belonging to the same trapezium].

We were unable to obtain crystals of the aluminohydride (2) suitable for X-ray study due to twinning.

The i.r. spectra of (1) and (2) are similar both having broad bands in the range 1800–1600  $\text{cm}^{-1}$  due to terminal and bridging hydrides. No definitive assignment of these bands has been possible due to the poorly resolved nature of the hydride region. The synthesis of the deuterated analogue of (2) does not help in their assignment. The remaining bands can be assigned to co-ordinated ligand vibrations.

At room temperature, n.m.r. spectra indicate that both (1) and (2) are non-rigid in solution. The  $^1\text{H}$  spectrum has a broad quartet [for (1),  $\delta$  -5.28 p.p.m.,  $J(\text{P-H}) = 27.1$  Hz; for (2),  $\delta$  -5.26 p.p.m.,  $J(\text{P-H}) = 25.4$  Hz] due to terminal W-H and bridging  $\text{W}(\mu\text{-H})_2\text{Al}$  hydrides, and a very broad singlet (ca.  $\delta$  5.0 p.p.m.) due to bridging  $\text{Al}(\mu\text{-H})_2\text{Al}$  hydrides [in (2)] and terminal Al-H hydrides [in (1) and (2)]. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectra are singlets with tungsten satellites [for (1),  $\delta$  -23.56 p.p.m.,  $J(\text{P-W}) = 195.0$  Hz; for (2),  $\delta$  -23.19 p.p.m.,  $J(\text{P-W}) = 199.4$  Hz] which split into binomial sextets when the phosphine  $\text{CH}_3$  groups are selectively decoupled. The appearance of a sextet in the selectively decoupled  $^{31}\text{P}$  spectrum indicates that rapid exchange is taking place between terminal W-H and bridging  $\text{W}(\mu\text{-H})_2\text{Al}$  hydrides.

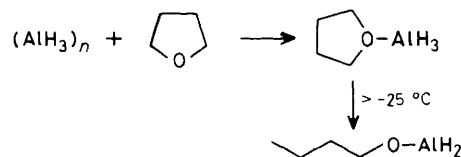
The bridging n-butoxide groups in (1) evidently arise from the well known<sup>9a</sup> cleavage of thf by aluminium hydride (above).

The complex (2) can be converted into (1) on refluxing for a few hours in thf; this implies that (2) is an intermediate in the formation of (1) in thf solution.

Table 1. Bond lengths (Å) and angles (°) for (1)\*

P(1)-W(1)	2.420(6)	P(2)-W(1)	2.409(6)
P(3)-W(1)	2.425(6)	Al(1)-W(1)	2.662(7)
C(11)-P(1)	1.821(16)	C(12)-P(1)	1.820(16)
C(13)-P(1)	1.874(18)	C(21)-P(2)	1.840(19)
C(22)-P(2)	1.877(19)	C(23)-P(2)	1.831(19)
C(31)-P(3)	1.871(19)	C(32)-P(3)	1.869(17)
C(33)-P(3)	1.778(18)		
O(1)-Al(1)	1.843(12)	Al(1)-Al(1a)	2.864(11)
Al(1)-O(1a)	1.854(12)	C(1)-O(1)	1.423(17)
C(2)-C(1)	1.524(25)	C(3)-C(2)	1.384(26)
C(4)-C(3)	1.380(27)		
P(2)-W(1)-P(1)	102.8(2)	P(3)-W(1)-P(1)	141.3(1)
P(3)-W(1)-P(2)	95.8(2)		
C(11)-P(1)-W(1)	116.6(6)	C(12)-P(1)-W(1)	120.4(6)
C(12)-P(1)-C(11)	97.9(9)	C(13)-P(1)-W(1)	116.8(8)
C(13)-P(1)-C(11)	100.8(9)	C(13)-P(1)-C(12)	100.8(8)
C(21)-P(2)-W(1)	115.7(8)	C(22)-P(2)-W(1)	116.8(6)
C(22)-P(2)-C(21)	99.1(11)	C(23)-P(2)-W(1)	119.0(9)
C(23)-P(2)-C(21)	101.5(12)	C(23)-P(2)-C(22)	101.7(11)
C(31)-P(3)-W(1)	115.8(8)	C(32)-P(3)-W(1)	115.2(7)
C(32)-P(3)-C(31)	101.7(11)	C(33)-P(3)-W(1)	121.4(8)
C(33)-P(3)-C(31)	99.0(10)	C(33)-P(3)-C(32)	100.5(10)
O(1)-Al(1)-O(1a)	78.21(4)		
Al(1)-O(1)-Al(1a)	101.5(4)	C(1)-O(1)-Al(1)	128.6(10)
C(2)-C(1)-O(1)	106.5(16)	C(3)-C(2)-C(1)	109.3(21)
C(4)-C(3)-C(2)	114.0(26)		

\* Key to symmetry operations relating designated atoms to reference atoms at (x, y, z): (a) -x, -y, z.



Both tungsten aluminopolyhydride complexes are moisture sensitive and are rapidly converted to  $\text{WH}_6(\text{PMe}_3)_3$ <sup>10</sup> by addition of  $\text{H}_2\text{O}$  or  $\text{MeOH}$  to an  $\text{Et}_2\text{O}$  solution. If  $\text{D}_2\text{O}$  is used the product obtained on work-up is entirely  $\text{WH}_4\text{D}_2(\text{PMe}_3)_3$ . This suggests that the  $\text{W}(\mu\text{-H})_2\text{Al}$  unit is cleaved symmetrically on hydrolysis to leave one of the bridging hydrides on each metal centre. This is in contrast to the asymmetric cleavage observed<sup>2c</sup> in the hydrolysis of  $(\eta\text{-C}_5\text{H}_5)_2\text{NbAlH}_4$  by  $\text{D}_2\text{O}$ .

The original synthesis<sup>10</sup> of  $\text{WH}_6(\text{PMe}_3)_3$  involved the interaction of  $\text{WCl}_4(\text{PMe}_3)_3$  with  $\text{LiAlH}_4$  in diethyl ether at room temperature followed by work-up with methanol at  $-78^\circ\text{C}$ . It now seems certain that (2) is the species present in solution before methanolysis.

Reaction of  $\text{WCl}_4$  with  $\text{LiAlH}_4$  results in an insoluble dark red product, this could not be isolated and addition of  $\text{PMe}_3$  did not afford complex (2). If excess  $\text{PMe}_3$  is present when  $\text{WCl}_4(\text{PMe}_3)_3$  is reacted with  $\text{LiAlH}_4$  then the major product is the polyhydride  $\text{WH}_4(\text{PMe}_3)_4$ .<sup>11</sup>

Treatment of complex (2) with *NNN'*-tetramethylethylenediamine (tmen) in toluene followed by extraction and crystallisation from hexane yields the bright yellow crystalline complex  $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$  (3). A white precipitate of  $\text{AlH}_3\text{-tmen}$  is also formed and the amine

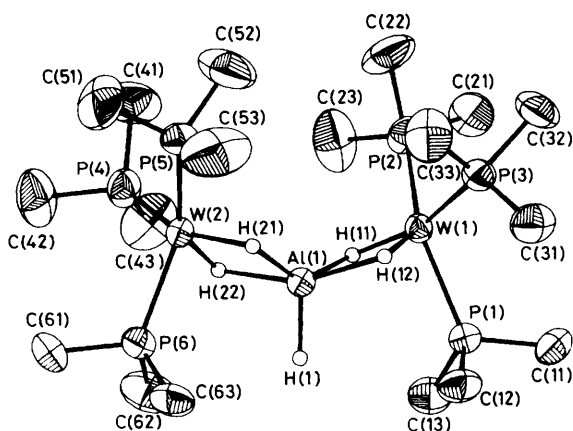


Figure 2. The molecular structure of  $(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$  (3)

therefore removes  $\text{AlH}_3$  from the bridged species (2). The cleavage of the  $\text{Al}(\mu\text{-H})_2\text{Al}$  unit with tmen has been reported for simple alanes.<sup>9b</sup> No reaction was observed between compound (2) and  $\text{NEt}_3$ .

The structure of a molecule of (3), which has no crystallographic symmetry, is shown in Figure 2. Selected bond lengths and angles are given in Table 2. For this compound, the hydrogen atoms attached to the aluminium (both terminal and bridging) were located and acceptably refined without much difficulty, but the terminal hydrogens attached to the tungsten atoms were again difficult to identify and none was included.

The co-ordination geometry at the aluminium atom approximates quite well to trigonal bipyramidal, with H(12) and H(22) defining the axial sites, and H(1), H(11), and H(21) the equator. The bridging to each tungsten then involves one axial and one equatorial hydrogen. Although the differences are hardly significant, it is intriguing to note that the axial Al-H bond lengths are the longest [av. 1.98(6) Å] the two bridging equatorial distances intermediate [av. 1.82(7) Å] and the one terminal distance shortest [1.57(6) Å]. Trigonal bipyramidal  $\text{AlH}_5$  geometry was also reliably found<sup>4</sup> in  $[(\text{dmpe})_2\text{MnAlH}_4]_2$ . The tungsten geometry is more difficult to define, partly because of the uncertainties in the hydrogen positions, and partly because of inconsistencies in the W-P distances. Whereas the three bonds to W(1) show one long [W(1)-P(1) 2.448(4) Å] and two short [W(1)-P(2) 2.408(4), W(1)-P(3), 2.400(4) Å], the bonds around W(2) are closer together at 2.410(4) [to P(4)], 2.422(4) [to P(5)], and 2.428(4) Å [to P(6)]. Nevertheless, the geometries at each tungsten as defined by the three phosphines and two bridging hydrogens, probably the most reliable set of ligand atoms, are quite similar, as can be seen in Figure 3(a) and (b), which shows views down the two Al-W vectors, and in the spread of P-W-P angles (Table 2). It is noteworthy that very similar P-W-P angles were found for the butoxo complex described above (although in that compound the three W-P bonds separate into one short and two long), and the tungsten geometry may be very similar to that found in compound (1).

**Rhenium Aluminopolyhydrides.**—Interaction of  $\text{ReCl}_3(\text{PMe}_2\text{-Ph})_3$ <sup>12</sup> with  $\text{LiAlH}_4$  in refluxing thf followed by crystallisation from toluene affords a moderate yield of the pale yellow  $(\text{Me}_2\text{PhP})_3\text{H}_2\text{Re}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-O}^n\text{Bu})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{ReH}_2(\text{PMe}_2\text{Ph})_3$  (4). Unlike the tungsten case the use of diethyl ether leads to little reaction and no aluminohydride complex could be isolated; however, if the reaction is carried out in thf at ambient temperature the product is the pale yellow

Table 2. Bond lengths (Å) and angles (°) for (3)

Al(1)-W(1)	2.694(5)	P(1)-W(1)	2.448(4)
P(2)-W(1)	2.408(4)	P(3)-W(1)	2.400(4)
H(11)-W(1)	1.653(82)	H(12)-W(1)	1.771(61)
Al(1)-W(2)	2.692(5)	P(4)-W(2)	2.410(4)
P(5)-W(2)	2.422(4)	P(6)-W(2)	2.428(4)
H(21)-W(2)	1.785(64)	H(22)-W(2)	1.761(61)
H(11)-Al(1)	1.802(80)	H(12)-Al(1)	2.020(61)
H(21)-Al(1)	1.848(67)	H(22)-Al(1)	1.937(62)
H(1)-Al(1)	1.573(60)		
C(11)-P(1)	1.837(11)	C(12)-P(1)	1.837(10)
C(13)-P(1)	1.826(10)	C(21)-P(2)	1.826(11)
C(22)-P(2)	1.832(12)	C(23)-P(2)	1.828(13)
C(31)-P(3)	1.823(10)	C(32)-P(3)	1.845(10)
C(33)-P(3)	1.831(13)	C(41)-P(4)	1.815(12)
C(42)-P(4)	1.801(12)	C(43)-P(4)	1.849(13)
C(51)-P(5)	1.821(14)	C(52)-P(5)	1.798(12)
C(53)-P(5)	1.841(15)	C(61)-P(6)	1.843(12)
C(62)-P(6)	1.831(12)	C(63)-P(6)	1.820(11)
P(2)-W(1)-P(1)	143.7(1)	P(3)-W(1)-P(1)	101.5(2)
P(3)-W(1)-P(2)	97.0(2)	H(11)-W(1)-P(1)	91.6(27)
H(11)-W(1)-P(2)	83.7(27)	H(11)-W(1)-P(3)	155.7(28)
H(12)-W(1)-P(1)	79.2(20)	H(12)-W(1)-P(2)	136.4(19)
H(12)-W(1)-P(3)	73.4(20)	H(12)-W(1)-H(11)	89.2(34)
P(5)-W(2)-P(4)	100.2(2)	P(6)-W(2)-P(4)	100.3(2)
P(6)-W(2)-P(5)	139.2(1)	H(21)-W(2)-P(4)	151.4(19)
H(21)-W(2)-P(5)	78.3(21)	H(21)-W(2)-P(6)	98.9(19)
H(22)-W(2)-P(4)	76.3(20)	H(22)-W(2)-P(5)	145.5(18)
H(22)-W(2)-P(6)	74.0(18)	H(22)-W(2)-H(21)	88.9(29)
H(12)-Al(1)-H(11)	77.8(32)	H(21)-Al(1)-H(11)	137.5(30)
H(21)-Al(1)-H(12)	89.2(27)	H(22)-Al(1)-H(11)	95.1(32)
H(22)-Al(1)-H(12)	157.9(22)	H(22)-Al(1)-H(21)	82.0(27)
H(1)-Al(1)-H(11)	110.7(36)	H(1)-Al(1)-H(12)	105.5(30)
H(1)-Al(1)-H(21)	111.8(31)	H(1)-Al(1)-H(22)	96.6(29)
C(11)-P(1)-W(1)	116.4(4)	C(12)-P(1)-W(1)	120.3(4)
C(12)-P(1)-C(11)	101.0(6)	C(13)-P(1)-W(1)	114.9(4)
C(13)-P(1)-C(11)	100.5(6)	C(13)-P(1)-C(12)	100.6(5)
C(21)-P(2)-W(1)	118.9(4)	C(22)-P(2)-W(1)	119.9(5)
C(22)-P(2)-C(21)	101.2(6)	C(23)-P(2)-W(1)	113.4(5)
C(23)-P(2)-C(21)	100.9(7)	C(23)-P(2)-C(22)	99.2(8)
C(31)-P(3)-W(1)	118.9(4)	C(32)-P(3)-W(1)	120.0(5)
C(32)-P(3)-C(31)	98.4(6)	C(33)-P(3)-W(1)	116.2(5)
C(33)-P(3)-C(31)	99.1(7)	C(33)-P(3)-C(32)	100.4(6)
C(41)-P(4)-W(2)	119.7(5)	C(42)-P(4)-W(2)	119.9(5)
C(42)-P(4)-C(41)	100.5(7)	C(43)-P(4)-W(2)	116.2(5)
C(43)-P(4)-C(41)	98.4(8)	C(43)-P(4)-C(42)	97.9(7)
C(51)-P(5)-W(2)	119.2(5)	C(52)-P(5)-W(2)	118.6(5)
C(52)-P(5)-C(51)	102.7(8)	C(53)-P(5)-W(2)	114.9(5)
C(53)-P(5)-C(51)	99.6(9)	C(53)-P(5)-C(52)	98.2(8)
C(61)-P(6)-W(2)	116.2(4)	C(62)-P(6)-W(2)	119.2(5)
C(62)-P(6)-C(61)	101.4(7)	C(63)-P(6)-W(2)	117.6(4)
C(63)-P(6)-C(61)	100.1(6)	C(63)-P(6)-C(62)	99.0(6)
Al(1)-H(11)-W(1)	102.4(43)	Al(1)-H(12)-W(1)	90.3(27)
Al(1)-H(21)-W(2)	95.6(30)	Al(1)-H(22)-W(2)	93.3(28)

complex  $(\text{Me}_2\text{PhP})_3\text{H}_2\text{Re}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{ReH}_2(\text{PMe}_2\text{Ph})_3$  (5).

The i.r. spectra of the complexes have broad bands between 1 925 and 1 740  $\text{cm}^{-1}$  due to terminal and bridging hydrides. Like the tungsten compounds they are non-rigid in solution at room temperature. The <sup>1</sup>H n.m.r. spectra have a broad quartet [(4),  $\delta$  - 8.68 p.p.m.,  $J(\text{P-H}) = 17.8$  Hz; (5),  $\delta$  - 8.67 p.p.m.,  $J(\text{P-H}) = 16.5$  Hz] due to terminal Re-H and bridging  $\text{Re}(\mu\text{-H})_2\text{Al}$  hydrides, together with a very broad singlet (*ca.*  $\delta$  5 p.p.m.) due to the bridging  $\text{Al}(\mu\text{-H})_2\text{Al}$ , in (5), and terminal Al-H, in (4) and

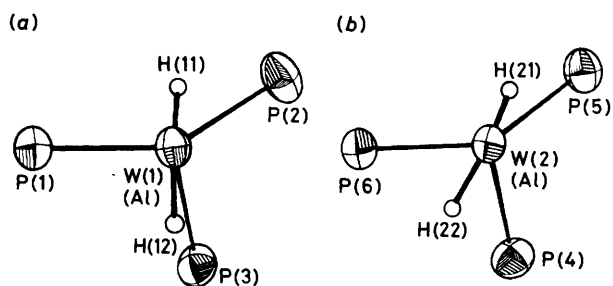


Figure 3. The partial co-ordination spheres of atoms W(1) and W(2) in compound (3), viewed down the W-Al vector

(5). The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectra are singlets [(4),  $\delta - 11.65$ ; (5),  $\delta - 11.60$ ]; attempts selectively to decouple the phosphine ( $\text{CH}_3$  and  $\text{C}_6\text{H}_5$ ) protons were unsuccessful. The structures were deduced from the integration of the hydrides in the  $^1\text{H}$  n.m.r., the variable-temperature n.m.r. (see below) and by comparison with the tungsten species.

The rhenium compounds (4) and (5) are also moisture sensitive, being converted to  $\text{ReH}_5(\text{PMe}_2\text{Ph})_3$ <sup>13</sup> by the addition of  $\text{H}_2\text{O}$  or  $\text{MeOH}$ . Deuteriation studies indicate that as in the tungsten compounds the  $\text{Re}(\mu\text{-H})_2\text{Al}$  unit is cleaved symmetrically, resulting in the formation of  $\text{ReH}_3\text{D}_2(\text{PMe}_2\text{-Ph})_3$ .

*Variable-temperature and  $^{27}\text{Al}$  Nuclear Magnetic Resonance Studies.*—The hydride region of the  $^1\text{H}$  n.m.r. spectrum of (1) from  $-10$  to  $-70^\circ\text{C}$  is shown in Figure 4. The quartet at  $-10^\circ\text{C}$  is unchanged on warming to room temperature; the broadness (observed in all complexes) can be attributed to the effect of the  $^{27}\text{Al}$  quadrupole moment. This quartet is due to terminal W-H and bridging  $\text{W}(\mu\text{-H})_2\text{Al}$  hydrides which are exchanging rapidly on the n.m.r. time-scale. This exchange is slowed on cooling and between  $-10$  and  $-40^\circ\text{C}$  the resonance broadens and the phosphorus coupling is lost. Cooling to  $-50^\circ\text{C}$  causes further broadening and between  $-50$  and  $-60^\circ\text{C}$  the signals de-coalesce. Further cooling to  $-70^\circ\text{C}$  stops the exchange between terminal and bridging hydrides and two resonances are observed, a quartet [ $\delta - 3.2$  p.p.m.,  $J(\text{P-H}) = 36.1$  Hz, terminal W-H] and a broad singlet [ $\delta - 7.2$  p.p.m., bridging  $\text{W}(\mu\text{-H})_2\text{Al}$ ].

Compounds (2), (4), and (5) show similar n.m.r. behaviour. The hydride signal for complex (2) de-coalesces between  $-50$  and  $-55^\circ\text{C}$ ; further cooling to  $-80^\circ\text{C}$  results in a broad quartet [ $\delta - 3.0$  p.p.m.,  $J(\text{P-H}) = 30.4$  Hz] and a broad singlet ( $\delta - 7.1$  p.p.m.). An interesting feature is that at room temperature there are two distinct and separate exchange processes taking place: (a) the exchange between (see structure III for labelling) terminal  $\text{W-H}_a$  and bridging  $\text{W}(\mu\text{-H}_b)_2\text{Al}$  hydrides, and (b) the exchange between terminal  $\text{Al-H}_c$  and bridging  $\text{Al}(\mu\text{-H}_d)_2\text{Al}$  hydrides. Thus  $\text{H}_a$  and  $\text{H}_b$  exchange with each other, but not with  $\text{H}_c$  or  $\text{H}_d$ ;  $\text{H}_c$  and  $\text{H}_d$  exchange with each other. The signal due to  $\text{H}_c$  and  $\text{H}_d$  in the  $^1\text{H}$  n.m.r. spectrum is a broad singlet at room temperature (*ca.*  $\delta$  5 p.p.m.) but on cooling to  $-20^\circ\text{C}$  it splits into two quite sharp singlets ( $\delta$  5.2 p.p.m. and  $\delta$  4.8 p.p.m.), indicating that exchange between the two has been stopped.

The hydride signals for compounds (4) and (5) de-coalesce between  $-60$  and  $-70^\circ\text{C}$  and further cooling to  $-90^\circ\text{C}$  results in two very broad resonances (*ca.*  $\delta - 8.0$  and  $\delta - 10.5$  p.p.m.). The exchange between the terminal  $\text{Al-H}$  and bridging  $\text{Al}(\mu\text{-H})_2\text{Al}$  hydrides in (5) is similar to that in complex (2).

From the n.m.r. data the activation energies,  $\Delta G^\ddagger$ , of these exchange processes can be calculated<sup>14</sup> (Table 3). The exchange

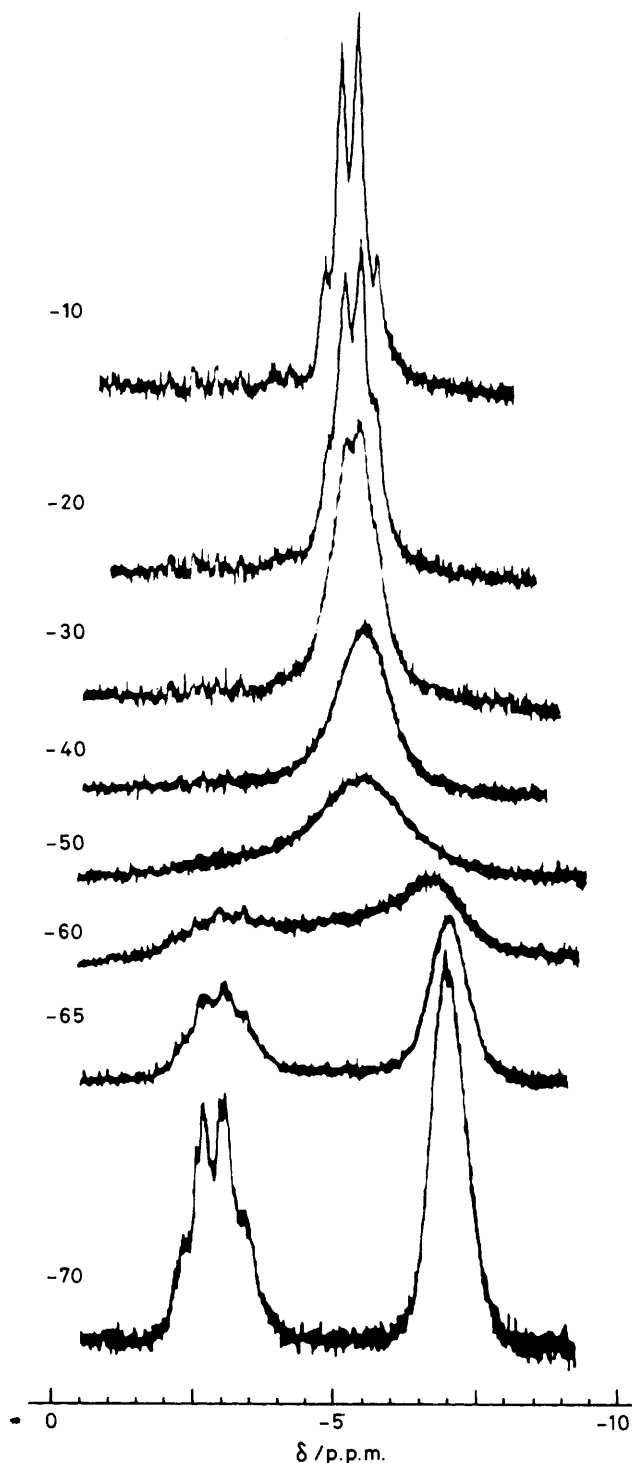
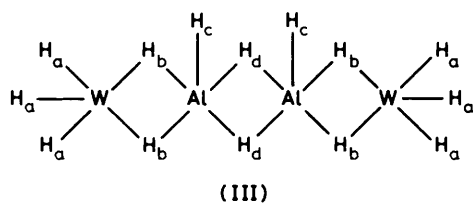


Figure 4. Variable-temperature ( $^\circ\text{C}$ )  $^1\text{H}$  n.m.r. spectra for compound (1) over the region 0 to  $-10$  p.p.m. vs.  $\text{SiMe}_4$  in  $[\text{}^2\text{H}_8]\text{toluene}$  solvent

between terminal  $\text{Al-H}$  and bridging  $\text{Al}(\mu\text{-H})_2\text{Al}$  hydrides in complexes (2) and (5) has a similar activation energy to that in other aluminohydride complexes<sup>5,15</sup> {such as  $[(\text{R}_3\text{P})_3(\text{H})\text{-M}(\text{AlH}_4)_2]$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ,  $\text{R} = \text{Me}$  or  $\text{Ph}$ )} implying that the exchange is essentially independent of the environment around the transition metal. Exchanges between terminal  $\text{M-H}$  and bridging  $\text{M}(\mu\text{-H})_2\text{Al}$  hydrides have a lower energy barrier and again are independent of other exchange processes present, but



in this case are dependent on the environment around the metal centre.<sup>14</sup>

Exchange between Re-H and Re( $\mu$ -H)<sub>2</sub>Al hydrogens has also been observed recently<sup>8</sup> in the complex ReH<sub>4</sub>AlMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> which has been proposed to have a Re( $\mu$ -H)<sub>3</sub>Al bridge and a five-co-ordinate aluminium in a H<sub>3</sub>AlMe<sub>2</sub><sup>2-</sup> unit.

Aluminium-27 n.m.r. spectra<sup>16</sup> have been mainly used for the study of the co-ordination (four or six) of aluminium complexes in aqueous solution and their pH dependence. The present hydride species are rare in having five-co-ordinate aluminium. The only reasonable analogous five-co-ordinate compounds for which <sup>27</sup>Al n.m.r. spectra are available<sup>17</sup> are various organo species such as [Me<sub>2</sub>AlO(CH<sub>2</sub>)<sub>2</sub>(OMe)]<sub>2</sub> that have broad bands and  $\delta$  values in the region 112–121 p.p.m. Both the present OBU<sup>n</sup>-bridged species show a single peak at *ca.*  $\delta$  120 p.p.m. with a linewidth of 1 740 Hz for (1) and 1 800 Hz for (4). The AlH<sub>4</sub> complexes give much broader peaks at  $\delta$  *ca.* 70 p.p.m.,  $w_{1/2}$  = 5 400 Hz for (2), 5 700 Hz for (3), and 5 850 Hz for (5), comparable to those of other AlH<sub>4</sub> compounds [*e.g.*, (dmpe)<sub>2</sub>Mn( $\mu$ -H)<sub>2</sub>Al(H)( $\mu$ -H)<sub>2</sub>Al(H)( $\mu$ -H)<sub>2</sub>Mn(dmpe)<sub>2</sub>,  $\delta$  65 p.p.m.,  $w_{1/2}$  4 888 Hz]. As the <sup>27</sup>Al n.m.r. signal of complex (3) is comparable to those of the dimeric aluminohydrides, it appears that there is no appreciable broadening of one Al signal by the quadrupole moment of the other Al atom. The large linewidths are hence a reflection of the low symmetry. Additional <sup>27</sup>Al n.m.r. data may in due course provide a useful probe in determining the structure of aluminohydride complexes.

## Experimental

Microanalyses were by Pascher Laboratories, Bonn. Melting points were determined in sealed capillaries and are uncorrected. Infrared spectra were recorded in the region 4 000–200 cm<sup>-1</sup> on a Perkin-Elmer 683 grating spectrometer in Nujol mulls. N.m.r. spectra (in C<sub>7</sub>D<sub>8</sub>) were recorded on JEOL FX90Q or Bruker WM-250 spectrometers ( $\delta$  in p.p.m. relative to SiMe<sub>4</sub> (<sup>1</sup>H), 85% H<sub>3</sub>PO<sub>4</sub> external (<sup>31</sup>P), and [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> external (<sup>27</sup>Al)). All manipulations were carried out under argon. Solvents were dried, distilled, and degassed before use.

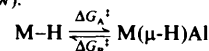
Analytical data are given in Table 4.

2,3; 2,3-Di- $\mu$ -butoxo-1,2; 1,2; 3,4; 3,4-tetra- $\mu$ -hydrido-1,1,1,2,2,3,4,4,4-octahydrido-1,1,1,4,4,4-hexakis(trimethylphosphine)-2,3-dialuminium-1,4-ditungsten(IV), (1).—To a stirred suspension of WCl<sub>4</sub>(PMe<sub>3</sub>)<sub>3</sub><sup>7</sup> (5 g, 9.03 mmol) in thf (80 cm<sup>3</sup>) was added LiAlH<sub>4</sub> (2.5 g, 65.87 mmol). The colour of the mixture quickly changed from red to orange-brown and gas was evolved. After stirring at room temperature for 10 min the mixture was heated and after refluxing for 48 h was allowed to cool to room temperature and the solvent removed under vacuum. The residue was extracted with boiling hexane (4  $\times$  100 cm<sup>3</sup>), the yellow solution evaporated and the residue extracted again with toluene (2  $\times$  50 cm<sup>3</sup>). The extracts were reduced to *ca.* 20 cm<sup>3</sup> and cooled to -20 °C affording several crops of bright yellow crystals. Yield: 1.5 g, 32%. I.r.: 1 770s, 1 700s, 1 610s, 1 450m, 1 435m, 1 420s, 1 300s, 1 280s, 1 240s, 1 130w, 1 110w, 1 090s, 1 040m, 1 010m, 950s, 865s, 820s, 775s, 740s, 730s, 715s, 685s,

**Table 3.** Activation energies ( $\Delta G^\ddagger$ /kJ mol<sup>-1</sup>) for hydride exchange processes

Compound	M-H $\rightleftharpoons$ M( $\mu$ -H)Al		Al-H $\rightleftharpoons$ Al( $\mu$ -H)Al	
	<i>T<sub>c</sub></i> /°C <sup>a</sup>	$\Delta G^\ddagger$ <sup>b</sup>	<i>T<sub>c</sub></i> /°C <sup>a</sup>	$\Delta G^\ddagger$
(1) [(Me <sub>3</sub> P) <sub>3</sub> H <sub>3</sub> W(AlH <sub>3</sub> OBU <sup>n</sup> )] <sub>2</sub>	-55	10.3, 11.1		
(2) [(Me <sub>3</sub> P) <sub>3</sub> H <sub>3</sub> W(AlH <sub>4</sub> )] <sub>2</sub>	-52	10.1, 10.9	-5	52.6
(3) [(Me <sub>3</sub> P) <sub>3</sub> H <sub>3</sub> W] <sub>2</sub> (AlH <sub>3</sub> )	-40	11.0, 11.9		
(4) [(Me <sub>2</sub> PhP) <sub>3</sub> H <sub>2</sub> Re(AlH <sub>3</sub> OBU <sup>n</sup> )] <sub>2</sub>	-65	28.0		
(5) [(Me <sub>2</sub> PhP) <sub>3</sub> H <sub>2</sub> Re(AlH <sub>4</sub> )] <sub>2</sub>	-59	30.1	-6	51.3

<sup>a</sup> Coalescence temperature. <sup>b</sup> Where there is an imbalance in the population of the hydride sites, *i.e.*, M-H/M( $\mu$ -H)Al  $\neq$  1, two values for  $\Delta G^\ddagger$  are given (see below).



**Table 4.** Analytical data for new compounds

Compound	M.p. (°C)	Analysis (%) <sup>a</sup>		
		C	H <sup>b</sup>	P
[(Me <sub>3</sub> P) <sub>3</sub> H <sub>3</sub> W(AlH <sub>3</sub> OBU <sup>n</sup> )] <sub>2</sub>	152	30.0 (30.1)	8.1 (8.1)	18.0 (18.0)
[(Me <sub>3</sub> P) <sub>3</sub> H <sub>3</sub> W(AlH <sub>4</sub> )] <sub>2</sub>	176	23.3 (24.2)	7.6 (7.6)	20.5 (20.8)
[(Me <sub>3</sub> P) <sub>3</sub> D <sub>3</sub> W(AlD <sub>4</sub> )] <sub>2</sub>	183	23.5 (23.8)	9.0 (9.0)	20.4 (20.5)
[(Me <sub>3</sub> P) <sub>3</sub> H <sub>3</sub> W] <sub>2</sub> (AlH <sub>3</sub> )	118	25.0 (25.0)	7.7 (7.5)	21.4 (21.6)
(Me <sub>3</sub> P) <sub>3</sub> WH <sub>4</sub> D <sub>2</sub>		25.8 (25.7)	8.0 (8.3)	22.1 (22.1)
[(Me <sub>2</sub> PhP) <sub>3</sub> H <sub>2</sub> Re(AlH <sub>3</sub> OBU <sup>n</sup> )] <sub>2</sub>	156	47.7 (47.7)	6.8 (6.7)	12.7 (13.2)
[(Me <sub>2</sub> PhP) <sub>3</sub> H <sub>2</sub> Re(AlH <sub>4</sub> )] <sub>2</sub>	169	45.4 (45.5)	6.0 (6.2)	14.5 (14.7)
(Me <sub>2</sub> PhP) <sub>3</sub> ReH <sub>3</sub> D <sub>2</sub>		47.0 (47.5)	6.5 (6.6)	15.0 (15.3)

<sup>a</sup> Required values are given in parentheses. <sup>b</sup> Deuterium was analysed as hydrogen.

**Table 5.** Crystal data, details of intensity measurement and structure refinement for [(Me<sub>3</sub>P)<sub>3</sub>H<sub>3</sub>W(AlH<sub>3</sub>OBU<sup>n</sup>)]<sub>2</sub> (1) and [(Me<sub>3</sub>P)<sub>3</sub>H<sub>3</sub>W]<sub>2</sub>(AlH<sub>3</sub>) (3)

Complex	(1)	(3)
Formula	C <sub>26</sub> H <sub>84</sub> Al <sub>2</sub> O <sub>2</sub> P <sub>6</sub> W <sub>2</sub>	C <sub>18</sub> H <sub>65</sub> AlP <sub>6</sub> W <sub>2</sub>
<i>M</i>	1 036.52	862.30
Crystal system	Orthorhombic	Monoclinic
<i>a</i> /Å	21.995(5)	10.204(1)
<i>b</i> /Å	11.277(3)	21.523(5)
<i>c</i> /Å	9.617(2)	16.540(2)
$\beta$ /°		93.52(2)
<i>U</i> /Å <sup>3</sup>	2 381.2	3 625.9
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.44	1.58
<i>Z</i>	2	4
$\mu$ /cm <sup>-1</sup>	51.86	63.5
$\theta_{\text{min-max}}$ /°	1.5, 25.0	1.5, 25.0
<i>T</i> /K	275	255
Total data	2 419	6 808
Total unique data	2 400	6 602
Total observed data	1 992	4 356
Significance test	$F_o > 3\sigma(F_o)$	$F_o > 4\sigma(F_o)$
No. parameters	209	336
Weighting scheme parameter		
<i>g</i> in $w = 1/[\sigma(F_o)^2 + gF_o^2]$	0.000 01	0.000 01
Final <i>R</i>	0.0393	0.0288
Final <i>R'</i>	0.0338	0.0271

**Table 6.** Fractional atomic co-ordinates ( $\times 10^4$ ) for (1)

Atom	x	y	z	Atom	x	y	z
W(1)	1 383(5)	1 265(1)	2 197(1)	C(23)	1 289(12)	2 975(19)	5 432(17)
P(1)	1 960(2)	2 274(3)	408(4)	C(31)	2 195(9)	83(20)	5 207(22)
P(2)	1 027(2)	2 876(4)	3 628(4)	C(32)	1 599(11)	-1 721(12)	3 541(19)
P(3)	1 508(2)	-139(4)	4 085(4)	C(33)	949(9)	-291(17)	5 410(19)
Al(1)	596(2)	513(4)	284(4)	O(1)	-212(4)	948(8)	372(9)
C(11)	2 254(8)	1 359(15)	-1 001(15)	C(1)	-470(8)	2 104(13)	293(20)
C(12)	1 604(7)	3 418(13)	-651(15)	C(2)	-537(10)	2 389(17)	-1 249(22)
C(13)	2 671(7)	3 056(16)	974(22)	C(3)	-758(11)	3 531(21)	-1 397(22)
C(21)	196(8)	2 974(20)	3 849(24)	C(4)	-874(16)	3 851(28)	-2 756(25)
C(22)	1 179(9)	4 418(14)	2 978(19)				

**Table 7.** Fractional atomic co-ordinates ( $\times 10^4$ ) for (3)

Atom	x	y	z	Atom	x	y	z
W(1)	6 975(0.5)	2 772(0.5)	9 183(0.5)	C(23)	8 994(12)	2 981(7)	7 528(7)
W(2)	5 759(0.5)	4 755(0.5)	7 826(0.5)	C(31)	6 768(9)	2 689(6)	11 375(5)
Al(1)	5 362(2)	3 622(1)	8 456(1)	C(32)	9 347(8)	2 598(6)	10 941(7)
P(1)	5 010(2)	2 147(1)	9 364(1)	C(33)	8 028(12)	3 752(5)	10 867(7)
P(2)	9 080(2)	2 771(1)	8 600(2)	C(41)	8 657(9)	4 879(8)	6 633(8)
P(3)	7 770(2)	2 942(1)	10 561(1)	C(42)	6 413(12)	5 361(6)	5 824(6)
P(4)	6 885(2)	4 794(1)	6 588(1)	C(43)	6 747(12)	4 094(6)	5 939(7)
P(5)	7 194(2)	5 404(1)	8 686(2)	C(51)	7 471(15)	6 207(6)	8 393(10)
P(6)	3 493(2)	4 733(1)	7 283(1)	C(52)	8 827(10)	5 132(6)	8 962(10)
C(11)	5 275(8)	1 378(4)	9 828(7)	C(53)	6 647(14)	5 531(9)	9 713(8)
C(12)	3 687(7)	2 451(5)	9 958(6)	C(61)	2 895(9)	5 438(5)	6 746(8)
C(13)	4 081(9)	1 933(5)	8 427(6)	C(62)	2 971(10)	4 125(6)	6 558(7)
C(21)	10 007(9)	2 046(5)	8 583(7)	C(63)	2 221(7)	4 639(5)	7 998(6)
C(22)	10 357(9)	3 316(5)	8 973(9)				

600s  $\text{cm}^{-1}$ . N.m.r.:  $^1\text{H}$ , 5.0 (2 H, br s, Al-H), 4.18 [4 H, t,  $J(\text{H-H}) = 6.7$ , Al-OCH<sub>2</sub>], 1.65 [54 H, d,  $J(\text{P-H}) = 7.7$ , P-CH<sub>3</sub>], 1.13 (8 H, m, Al-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.98 [6 H, t,  $J(\text{H-H}) = 7.1$ , Al-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>], -5.28 [10 H, br q,  $J(\text{P-H}) = 27.1$  Hz, W-H and W-H-Al];  $^{31}\text{P}$ -{ $^1\text{H}$ }, -23.56 [s, with  $^{183}\text{W}$  satellites,  $J(\text{P-W}) = 195.0$  Hz];  $^{27}\text{Al}$ -{ $^1\text{H}$ }, 120 ( $w_{1/2} = 1 740$  Hz).

1,2; 1,2,2,3; 2,3;3,4; 3,4-Hexa- $\mu$ -hydrido-1,1,1,2,3,4,4,4-octa-hydrido-1,1,1,4,4,4-hexakis(trimethylphosphine)-2,3-dialuminium-1,4-ditungsten(IV), (2).—To a stirred suspension of LiAlH<sub>4</sub> (1 g, 26.4 mmol) in Et<sub>2</sub>O (60 cm<sup>3</sup>) was added WCl<sub>4</sub>(PMe<sub>3</sub>)<sub>3</sub> (3.6 g, 6.5 mmol). The colour of the mixture quickly changed from red to bright yellow and gas was evolved. After 2 h at room temperature the solution was orange and gas evolution had ceased. The mixture was evaporated and the residue extracted with boiling hexane (4  $\times$  100 cm<sup>3</sup>). The resulting yellow solution was evaporated and the residue extracted with toluene (60 cm<sup>3</sup>). On reducing the volume of the solution and cooling to -20 °C several crops of bright yellow crystals were obtained. Yield: 2.5 g, 86%. I.r.: 1 785s, 1 765s, 1 700—1 650s, 1 600s, 1 415s, 1 405s, 1 360s, 1 350s, 1 295s, 1 290s, 1 275s, 1 190—1 100s, 940s, 830s, 715s, 665s, 625s, 600m, 565s, 510w, 450s, 425m  $\text{cm}^{-1}$ . N.m.r.:  $^1\text{H}$ , 5.1 (4 H, br s, Al-H and Al-H-Al), 1.56 [54 H, d,  $J(\text{P-H}) = 7.9$ , P-CH<sub>3</sub>], -5.26 [10 H, br q,  $J(\text{P-H}) = 25.4$  Hz, W-H and W-H-Al];  $^{31}\text{P}$ -{ $^1\text{H}$ }, -23.19 [s with  $^{183}\text{W}$  satellites  $J(\text{P-W}) = 199.4$  Hz];  $^{27}\text{Al}$ -{ $^1\text{H}$ }, 70 ( $w_{1/2} = 5 400$  Hz).

The deuterated analogue can be made by the above method using LiAlD<sub>4</sub>. Yield 67%. I.r.: 1 417m, 1 292m, 1 280m, 1 278s, 1 270s, 1 260m, 1 232w, 1 193w, 1 150m, 1 096m, 1 016m, 995m, 940vs, 850w, 800m, 725m, 716s, 704m, 673s, 600s, 550w, 521w, 440m, 416m  $\text{cm}^{-1}$ . N.m.r.:  $^1\text{H}$ , 1.52 [d,  $J(\text{P-H}) = 8.0$  Hz, P-CH<sub>3</sub>];  $^{31}\text{P}$ -{ $^1\text{H}$ }, -23.56 [br m,  $J(\text{P-D})$  not measurable,  $^{183}\text{W}$  satellites,  $J(\text{P-H}) = 199.2$  Hz].

1,2; 1,2; 2,3; 2,3-Tetra- $\mu$ -hydrido-1,1,1,2,3,3,3-heptahydrido-1,1,1,3,3,3-hexakis(trimethylphosphine)-2-aluminium-1,3-ditungsten(IV), (3).—To a toluene (50 cm<sup>3</sup>) solution of (2) (0.74 g, 0.83 mmol) was added tmen (0.2 cm<sup>3</sup>). After stirring for several hours the colour darkened slightly. Removal of the solvent followed by extraction into hexane (2  $\times$  20 cm<sup>3</sup>), and cooling gave bright yellow crystals. Yield: 0.51 g, 70%. I.r.: 1 750s, 1 720m, 1 625br m, 1 550s, 1 410m, 1 290m, 1 270s, 1 260s, 1 090br s, 1 015s, 940vs, 855m, 800s, 770m, 720m, 670w  $\text{cm}^{-1}$ . N.m.r.:  $^1\text{H}$ , 5.0 (1 H, br s, Al-H), 1.64 [54 H, d,  $J(\text{P-H}) = 7.0$ , P-CH<sub>3</sub>], -4.08 [10 H, br q,  $J(\text{P-H}) = 27.0$  Hz, W-H and W(H)<sub>2</sub>Al],  $^{31}\text{P}$ -{ $^1\text{H}$ }, -20.40 [s with  $^{183}\text{W}$  satellites,  $J(\text{W-P}) = 194.0$  Hz];  $^{27}\text{Al}$ -{ $^1\text{H}$ }, 70 ( $w_{1/2} = 5 700$  Hz).

2,3; 2,3-Di- $\mu$ -butoxo-1,1,1,4,4,4-hexakis(dimethylphenylphosphine)-1,2; 1,2; 3,4; 3,4-tetra- $\mu$ -hydrido-1,1,2,3,4,4-hexahydrido-2,3-dialuminium-1,4-dirhenium(III), (4).—To a stirred suspension of LiAlH<sub>4</sub> (1.5 g, 39.5 mmol) in thf (60 cm<sup>3</sup>) was added ReCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub><sup>12</sup> (4 g, 5.7 mmol). The colour of the mixture slowly changed from orange to pale yellow and gas was evolved. After stirring for 30 min the mixture was heated and after refluxing for 48 h the mixture was allowed to cool to room temperature and the solvent removed. The pale yellow residue was evacuated for 48 h, then extracted with hexane and the extract evaporated. The residue was extracted with toluene (2  $\times$  50 cm<sup>3</sup>), which was reduced in volume and cooled to -78 °C to give pale yellow crystals. Yield: 1.2 g, 30%. I.r.: 3 080m, 3 060s, 3 015m, 2 970s, 1 925m, 1 880m, 1 800s, 1 740s, 1 575m, 1 495m, 1 475s, 1 445s, 1 415m, 1 400m, 1 330m, 1 315m, 1 290s, 1 280s, 1 240w, 1 185w, 1 170w, 1 160w, 1 125m, 1 100s, 1 075s, 1 030m, 1 000s, 970m, 945s, 920s, 905s, 870s, 860m, 845s, 835m, 805w, 780s, 750s, 725s, 700s, 670s, 635s, 605s, 530s, 505s, 450s, 425s, 415s  $\text{cm}^{-1}$ . N.m.r.:  $^1\text{H}$ , 7.65, 7.15, 7.08 (30 H, m, Ph), 5.0 (2 H, br s, Al-H), 4.13 [4 H, t,  $J(\text{H-H}) = 7.5$ ,

Al-O-CH<sub>2</sub>], 1.74 [36 H, d,  $J(\text{P-H}) = 7.1$ , P-CH<sub>3</sub>], 1.35 (8 H, m, Al-O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.01 [6 H, t,  $J(\text{H-H}) = 6.7$ , Al-O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>], -8.68 [8 H, br q,  $J(\text{P-H}) = 17.8$  Hz, Re-H and Re-H-Al]; <sup>31</sup>P-{<sup>1</sup>H}, -11.65 (s); <sup>27</sup>Al-{<sup>1</sup>H}, 120 ( $\nu_{\frac{1}{2}} = 1800$  Hz).

1,1,1,4,4,4-Hexakis(dimethylphenylphosphine)-1,2; 1,2; 2,3; 2,3; 3,4; 3,4-hexa- $\mu$ -hydrido-1,1,2,3,4,4-hexahydrido-2,3-dialuminium-1,4-dirhenium(III), (5).—To a stirred suspension of LiAlH<sub>4</sub> (1.0 g, 26.3 mmol) in thf (50 cm<sup>3</sup>) was added ReCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> (3.6 g, 5.1 mmol) at -78 °C. On warming to room temperature the solution became lighter in colour and gas was evolved. After stirring at room temperature for 12 h the solvent was removed and the yellow residue extracted with toluene (2 × 20 cm<sup>3</sup>), reduction in volume and cooling to -78 °C yielded a pale crystalline solid. Yield: 0.9 g, 30%. I.r.: 3080m, 3065s, 3015m, 2960s, 1920m, 1880m, 1800s, 1765m, 1745s, 1575m, 1500m, 1470m, 1445m, 1415m, 1400m, 1310m, 1290s, 1285s, 1170w, 1160w, 1100s, 1070s, 1030m, 1000s, 965m, 945m, 920s, 905s, 870s, 840s, 830m, 750s, 675s, 635s, 600s, 530m, 500m, 450m, 425s cm<sup>-1</sup>. N.m.r.: <sup>1</sup>H, 7.65, 7.17, 7.08 (30 H, m, P-Ph), 5.0 [4 H, br s, Al-H and Al( $\mu$ -H)<sub>2</sub>Al], 1.76 [36 H, d,  $J(\text{P-H}) = 7.0$ , P-CH<sub>3</sub>], -8.67 [8 H, br q,  $J(\text{P-H}) = 16.5$  Hz, Re-H and Re( $\mu$ -H)<sub>2</sub>Al]; <sup>31</sup>P-{<sup>1</sup>H}, -11.60(s); <sup>27</sup>Al-{<sup>1</sup>H}, 60 ( $\nu_{\frac{1}{2}} = 5850$  Hz).

*Reaction of Aluminopolyhydrides with D<sub>2</sub>O.*—To an ether solution of either (1), (2), or (3) at -78 °C was added D<sub>2</sub>O in excess. After warming to room temperature the solvent was removed and the orange solid extracted with hexane. The volume was reduced and on cooling (-20 °C) white crystals of WH<sub>4</sub>D<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> [cf. WH<sub>6</sub>(PMe<sub>3</sub>)<sub>3</sub><sup>9</sup>] were obtained. I.r.: 1740br s, 1420s, 1300m, 1280s, 1260, 950vs, 860m, 725s, 680s cm<sup>-1</sup>. N.m.r.: <sup>1</sup>H, 1.57 (27 H, br d, P-CH<sub>3</sub>), -2.79 [6 H, q of quin,  $J(\text{P-H}) = 36.6$ ,  $J(\text{D-H}) = 3.4$ , with <sup>183</sup>W satellites,  $J(\text{W-H}) = 26.8$  Hz]; <sup>31</sup>P-{<sup>1</sup>H}, -18.25 [quin,  $J(\text{P-D}) = 5.7$ , with <sup>183</sup>W satellites,  $J(\text{P-W}) = 73$  Hz].

Under the same conditions the reaction of (4) or (5) with D<sub>2</sub>O on work-up yields white crystals of ReH<sub>3</sub>D<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> [cf. ReH<sub>5</sub>(PMe<sub>2</sub>Ph)<sub>3</sub><sup>13</sup>]. I.r.: 3080w, 1950w, 1930w, 1905m, 1850m, 1440s, 1330w, 1310m, 1290w, 1270s, 1090vs, 1075m, 1030s, 850m, 800s, 750vs, 700vs, 600w, 535s, 510m, 450m cm<sup>-1</sup>. N.m.r.: <sup>1</sup>H, 7.10 (15 H, br m, Ph), 1.67 [18 H, d,  $J(\text{P-H}) = 7.0$ , P-CH<sub>3</sub>], -6.20 [3 H, q,  $J(\text{P-H}) = 19.0$  Hz, Re-H]; <sup>31</sup>P-{<sup>1</sup>H}, -5.60 (br m).

*Crystallography.*—Crystals of both compounds were mounted under argon in glass capillaries. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,<sup>18</sup> using a CAD4 diffractometer operating in the  $\omega$ - $2\theta$  scan mode with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å). Semi-empirical absorption corrections using azimuthal scan data for three reflections in each case. Further experimental data are given in Table 5.

The structures were solved *via* routine heavy-atom procedures and refined by full-matrix least-squares methods. Non-hydrogen atoms were all assigned anisotropic thermal parameters. Location and attempted refinement of the hydrogen atoms caused some difficulties in both structures, but especially for compound (1). In this case a number of peaks occurred in the difference map which gave reasonable W-H and Al-H distances, and which refined acceptably in terms of isotropic thermal parameters, but which were very unstable in positioning. Various choices could be made to satisfy the required number of hydrogens giving either five-co-ordination (both trigonal bipyramidal and square pyramidal) and ( $\mu$ -H)<sub>2</sub> bridging, or very distorted six-co-ordination and ( $\mu$ -H)<sub>3</sub> bridging, for the aluminium atom.

However, in view of the uncertainties in the H positions in this structure we have not included any of the metal-bonded hydrogens in the final refinement. For compound (3), it was possible to identify and successfully refine (*i.e.* with sensible  $U_{\text{iso}}$  parameters and reasonable bond distances) five hydrogens attached to the central aluminium, one terminal and two in each of the two Al...W bridges. Difficulties were again met in defining hydrogens terminal to tungsten and none was included in the final refinement. In both structures, methyl hydrogens were included in idealised positions and the CH<sub>3</sub> groups subjected to constrained refinement (AFIX 35 in SHELX 76<sup>19</sup>). Details of the refinements are given in Table 5. Final atomic co-ordinates are given in Tables 6 and 7. Atomic scattering factors and anomalous scattering parameters are as given in ref. 18.

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