

## Tertiary Phosphine Aluminohydride Complexes of Chromium-, Molybdenum-, and Tungsten-(II)

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The syntheses of the aluminohydride complexes  $[(\text{dmpe})_2\text{HCr}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2]_2$  [ $\text{dmpe}$  = 1,2-bis(dimethylphosphino)ethane],  $[(\text{Me}_3\text{P})_4\text{HM}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2]_2$  ( $\text{M}$  = Mo or W), and  $[(\text{Me}_3\text{P})_4\text{CIW}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2]_2$  are reported. The  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{27}\text{Al}$  n.m.r. spectra are reported; all the molecules are non-rigid undergoing metal-hydride exchanges; the Al atoms are five-co-ordinate. The hydrolysis of aluminohydrides to give polyhydrides is discussed.

Until recently the structures of transition metal aluminohydrides were thought to be comparable to those of the analogous borohydrides.<sup>1,2</sup> However, X-ray crystallographic studies have indicated that aluminohydrides are dimeric,<sup>3,4</sup> involving a core  $\text{M}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{M}$  (1). Degradation of this core, either thermally<sup>4</sup> or through abstraction of  $\text{AlH}_3$  via the addition of *NNN'*-tetramethylethylenediamine (tmen),<sup>5</sup> yields complexes containing the core  $\text{M}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{M}$  (2). Bulychev and co-workers<sup>6</sup> have also reported the structure of the complexes formulated as  $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Y}(\mu_3\text{-H})][\mu\text{-HAlH}_2(\text{L})]\}_2$  (3). However, these are best considered as alane ( $\text{AlH}_3$ ) adducts of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})_2\text{Y}(\eta^5\text{-C}_5\text{H}_5)_2$ . By contrast with analogous borohydrides the aluminohydrides may show a different stereochemistry around the metal, an example being *fac*- $[(\text{Me}_3\text{P})_3\text{HRu}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2]_2$ <sup>7</sup> but *mer*- $(\text{Me}_3\text{P})_3\text{HRu}(\text{BH}_4)$ .<sup>8</sup>

Differences in the type of fluxional behaviour, between borohydrides and aluminohydrides, has also been observed. Thus in borohydrides the bridging  $\text{M}(\mu\text{-H})\text{B}$  and terminal  $\text{B-H}$  hydrides commonly undergo rapid intramolecular exchange,<sup>9</sup> a process not observed in aluminohydrides. On the other hand, the exchange between bridging  $\text{M}(\mu\text{-H})\text{Al}$  and terminal  $\text{M-H}$  hydrides<sup>3,5,7</sup> is facile whereas the similar exchanges in borohydrides are seldom observed and then only at elevated temperatures.<sup>10</sup>

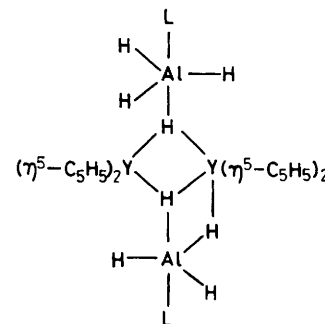
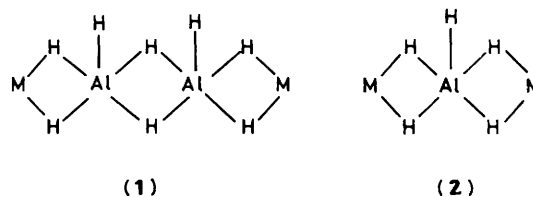
We have recently reported<sup>7</sup> the synthesis and characterisation of a series of complexes with the general formula  $\text{L}_3\text{HM}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{MHL}_3$  ( $\text{M}$  = Ru,  $\text{L}$  =  $\text{PMe}_3$ ,  $\text{PEtPh}_2$ , or  $\text{PPh}_3$ ;  $\text{M}$  = Os,  $\text{L}$  =  $\text{PMe}_3$  or  $\text{PPh}_3$ ). The exchange process between  $\text{M-H}$  and  $\text{M}(\mu\text{-H})_2\text{Al}$  proceeds even at  $-90^\circ\text{C}$  evidently allowed by the *fac* octahedral configuration about the metal atom.

We now report the synthesis and characterisation of seven-co-ordinate chromium(II), molybdenum(II), and tungsten(II) aluminohydrides.

### Results and Discussion

**Chromium.**—Treatment of  $\text{CrCl}_2(\text{dmpe})_2$  [ $\text{dmpe}$  = 1,2-bis(dimethylphosphino)ethane] with  $\text{LiAlH}_4$  in diethyl ether affords the orange-yellow complex  $(\text{dmpe})_2\text{HCr}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{CrH}(\text{dmpe})_2$  (A). The i.r. spectrum of the complex shows sharp bands between  $1680$  and  $1690\text{ cm}^{-1}$ , as well as a broad band at  $1600\text{ cm}^{-1}$ . No attempt at assigning these bands has been made although they are probably due to a mixture of bridging and terminal hydride stretches.

At room temperature the complex is fluxional in solution. The  $^1\text{H}$  n.m.r. spectrum has a broad quintet [ $\delta -9.39$  p.p.m.,  $J(\text{P-H}) = 42.0$  Hz] due to terminal  $\text{Cr-H}$  and bridging  $\text{Cr}(\mu\text{-H})\text{Al}$  hydrides, and a very broad signal (*ca.*  $\delta 4.8$  p.p.m.) due to



bridging  $\text{Al}(\mu\text{-H})\text{Al}$  and terminal  $\text{Al-H}$  hydrides. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum consists of a singlet ( $\delta 76.28$  p.p.m.), which is split into a binomial quartet when the phosphine protons are decoupled [ $J(\text{P-H}) = 42.0$  Hz]. The presence of a quartet indicates that rapid exchange is taking place between the terminal  $\text{Cr-H}$  and the two bridging  $\text{Cr}(\mu\text{-H})\text{Al}$  hydrides. This process is evidently also occurring at  $-90^\circ\text{C}$  suggesting that no rearrangement around the chromium centre is required for the exchange to take place. As found for other aluminohydrides<sup>3b,7</sup> the exchange between terminal  $\text{Al-H}$  and bridging  $\text{Al}(\mu\text{-H})\text{Al}$  hydride does indeed cease at low temperature [ $\delta 4.6$  ( $\text{Al-H}$ ),  $5.2$  p.p.m. [ $\text{Al}(\mu\text{-H})\text{Al}$ ],  $T_c = -22^\circ\text{C}$ ,  $\Delta G^\ddagger = 48.2\text{ kJ mol}^{-1}$ ]. The  $^{27}\text{Al}\{-^1\text{H}\}$  n.m.r. spectrum is similar to that of other aluminohydrides<sup>3b,7</sup> ( $\delta 54$  p.p.m.,  $w_{\frac{1}{2}} = 5540$  Hz) confirming the aluminium to be five-co-ordinate. The geometry around the chromium is uncertain as in general seven-co-ordinate complexes are fluxional even at low temperature; the co-ordination number of 7 for chromium(II) is established.<sup>12</sup>

**Molybdenum(II) and Tungsten(II).**—The complexes  $(\text{Me}_3\text{P})_4\text{HMo}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{MoH}(\text{PMe}_3)_4$  (B) and  $(\text{Me}_3\text{P})_4\text{HW}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{WH}(\text{PMe}_3)_4$  (C) are formed on the addition of  $\text{LiAlH}_4$  to  $\text{MoCl}_2(\text{PMe}_3)_4$  and  $\text{WCl}_2(\text{PMe}_3)_4$  respectively. The tungsten(IV) complex  $(\text{Me}_3\text{P})_3\text{-H}_3\text{W}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3$  was character-

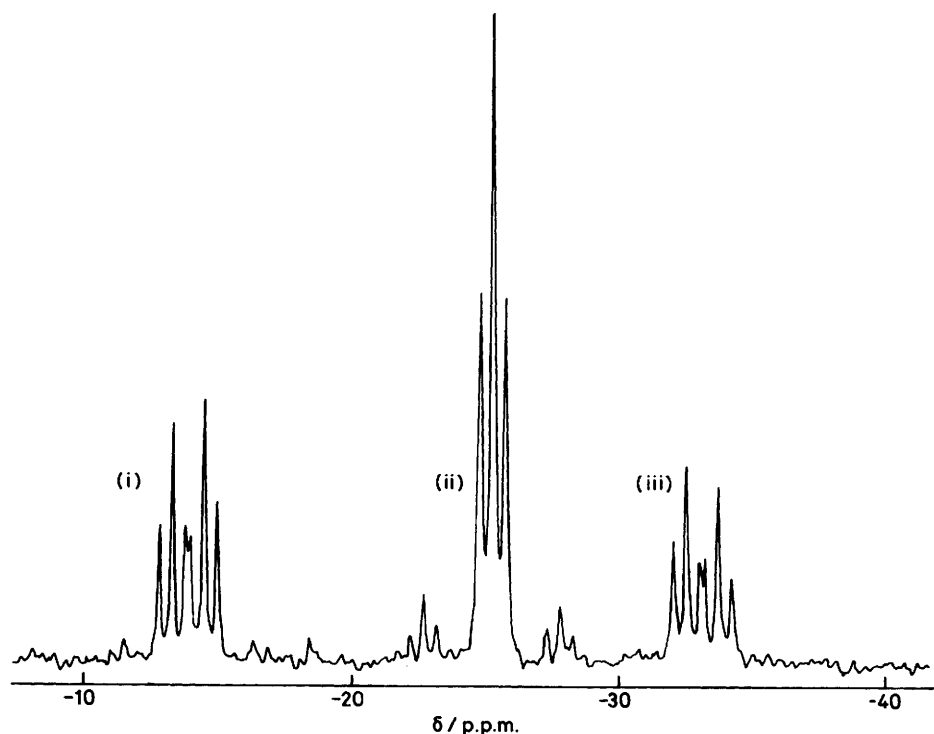


Figure.  $^{31}\text{P}\{-^1\text{H}\}$  N.m.r. spectrum of  $[(\text{Me}_3\text{P})_4\text{ClW}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2]$ . The numbering is only for convenience; the central signal (ii) is an overlapping doublet of doublets.  $J(\text{P}_{(i)}\text{-P}_{(iii)}) = 17.7$ ,  $J(\text{P}_{(i)}\text{-P}_{(ii)}) = 44.3$ , and  $J(\text{P}_{(iii)}\text{-P}_{(ii)}) = 17.7$  Hz

ised previously.<sup>3c</sup> Both (B) and (C) are bright yellow in colour, and are soluble in non-polar organic solvents.

The i.r. spectra of the compounds are similar, having broad bands between 1900 and 1600  $\text{cm}^{-1}$  due to terminal and bridging hydrides. The remaining bands can be assigned to co-ordinated  $\text{PMe}_3$  vibrations. Like the other aluminohydrides (B) and (C) are non-rigid in solution at room temperature. The  $^1\text{H}$  n.m.r. spectra have broad quintets [(B),  $\delta -7.03$  p.p.m.,  $J(\text{P-H}) = 19.0$  Hz; (C),  $\delta -6.42$  p.p.m.,  $J(\text{P-H}) = 23.4$  Hz] due to terminal M-H and bridging  $\text{M}(\mu\text{-H})\text{Al}$  hydrides, together with a very broad singlet at  $\delta 4.5\text{--}5.0$  p.p.m. due to the bridging  $\text{Al}(\mu\text{-H})\text{Al}$  and terminal  $\text{Al-H}$  hydrides. The  $^{31}\text{P}$  n.m.r. spectra are singlets [(B),  $\delta 3.05$  p.p.m.; (C),  $\delta -33.95$  p.p.m.,  $J(\text{P-W}) = 232.6$  Hz]. Selective decoupling of the phosphine  $\text{CH}_3$  groups results in binomial quartets [(B),  $J(\text{P-H}) = 18.9$  Hz; (C),  $J(\text{P-H}) = 22.9$  Hz]. The presence of this quartet indicates that rapid exchange is taking place between the bridging  $\text{M}(\mu\text{-H})\text{Al}$  and terminal M-H hydrides. Although this exchange proceeds even at  $-90^\circ\text{C}$  the exchange between terminal  $\text{Al-H}$  and bridging  $\text{Al}(\mu\text{-H})\text{Al}$  ceases on cooling [(B), 4.7, 4.3 p.p.m.,  $T_c = -22^\circ\text{C}$ ,  $\Delta G^\ddagger = 49.1$   $\text{kJ mol}^{-1}$ ; (C), 5.3, 4.7 p.p.m.,  $T_c = -40^\circ\text{C}$ ,  $\Delta G^\ddagger = 42.7$   $\text{kJ mol}^{-1}$ ]. The  $^{27}\text{Al}\{-^1\text{H}\}$  n.m.r. contains broad peaks [(B),  $\delta 53$  p.p.m.,  $w_{\frac{1}{2}} = 5540$  Hz; (C),  $\delta 49$  p.p.m.,  $w_{\frac{1}{2}} = 5590$  Hz] consistent with the proposed structure.

The reaction of  $\text{WCl}_4(\text{PMe}_3)_3$  with  $\text{Li}_3\text{AlH}_6$  in diethyl ether yields, on recrystallisation from hexane, the compound  $(\text{Me}_3\text{P})_4\text{ClW}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{WCl}(\text{PMe}_3)_4$  (D). Besides bands due to trimethylphosphine the i.r. spectrum contains three broad bands due to bridging and terminal hydrides.

The  $\text{Li}_3\text{AlH}_6$  appears to act as a two-electron reductant, reducing  $\text{W}^{\text{IV}}$  to  $\text{W}^{\text{II}}$ , and as a source of  $\text{AlH}_4^-$  yielding the tungsten(II) aluminohydride. Replacement of the remaining halide does not occur even when excess of  $\text{Li}_3\text{AlH}_6$  is added.

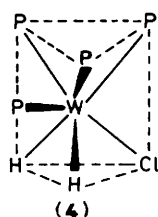
In solution the exchange between terminal  $\text{Al-H}$  and

bridging  $\text{Al}(\mu\text{-H})\text{Al}$  hydrides is again observed. The  $^{31}\text{P}$  n.m.r. spectrum (Figure) indicates the presence of three different phosphine environments. Selective decoupling of the phosphine  $\text{CH}_3$  groups splits each signal into a triplet [(i)  $J(\text{P-H}) = 20.1$  Hz, (ii)  $J(\text{P-H}) = 17.8$  Hz, and (iii)  $J(\text{P-H}) = 15.0$  Hz]. No change in the  $^{31}\text{P}$  n.m.r. spectrum is observed at low temperature; however, when the temperature is raised ( $+90^\circ\text{C}$ ) the signals (ii) and (iii) coalesce to form a doublet [ $\delta = -28.28$  p.p.m.,  $J(\text{P-P}) = 26.59$  Hz], whilst signal (i) becomes a quartet [ $\delta = 14.78$  p.p.m.,  $J(\text{P-P}) = 26.59$  Hz].

Unlike the previously studied transition metal aluminohydrides the high field signal in the  $^1\text{H}$  n.m.r. ( $\delta -3.68$  p.p.m., m) appears to be unaffected by the quadrupole moment of the aluminium nucleus. The hydride signal is split into a complex multiplet suggesting a  $\text{AA}'\text{XX}'\text{YZ}$  spin system. Irradiation of the phosphine signal at  $\delta -25.4$  p.p.m. (ii) results in the simplification of the hydride region giving a double doublet. However the close proximity of the other phosphine signals resulted in their partial decoupling, and finite values for the coupling constants could not be obtained.<sup>13</sup> The  $^{27}\text{Al}\{-^1\text{H}\}$  n.m.r. spectrum is again a broad singlet ( $\delta 52$  p.p.m.,  $w_{\frac{1}{2}} = 5400$  Hz), consistent with five-co-ordination.

We were unable to obtain crystals of (D) suitable for X-ray crystallography due to twinning. However, the  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. data suggest that the structure is probably a rigid capped trigonal prism where one triangular face is occupied by the two hydrides and one chloride, whilst the remaining sites are occupied by phosphines, as in (4). Compounds (A), (B), and (C) are probably similar in structure having a hydrido ligand in place of the chloride in (D). The exchange between bridging  $\text{M}(\mu\text{-H})\text{Al}$  and terminal M-H hydrides would thus be facile.

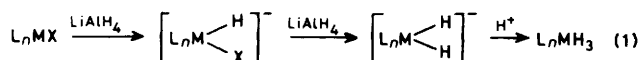
The comparison of the ruthenium aluminohydride and borohydrides has been mentioned earlier. The complex  $\text{trans-CrH}(\text{BH}_4)(\text{dmpe})_2$  has now been synthesised and a crystal structure determination<sup>14</sup> shows the *trans*-octahedral structure similar



to that in *trans*-MoH(BH<sub>4</sub>)(PMe<sub>3</sub>)<sub>4</sub>.<sup>15</sup> This configuration would restrict any fluxionality which is observed in the aluminohydrides. As noted earlier the *fac* structure around the transition metal centre enabling hydride exchange seems to be a general feature of aluminohydrides containing terminal M-H groups.<sup>7</sup>

All the above compounds are air and moisture sensitive yielding on hydrolysis the appropriate polyhydride. Addition of MeOH or water to a diethyl ether solution of complexes (A), (B), and (C) yields the polyhydrides CrH<sub>4</sub>(dmpe)<sub>2</sub>,<sup>16</sup> MoH<sub>4</sub>(PMe<sub>3</sub>)<sub>4</sub>,<sup>17</sup> and WH<sub>4</sub>(PMe<sub>3</sub>)<sub>4</sub>,<sup>18</sup> respectively in high yield. Addition of D<sub>2</sub>O to (C) gives WH<sub>2</sub>D<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>, which was characterised by n.m.r. and elemental analysis [*cf.* hydrolysis giving WH<sub>4</sub>D<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>].<sup>7</sup>

Lithium aluminium hydride has been widely used in the synthesis of transition metal polyhydrides.<sup>19</sup> Often the formal oxidation state of the metal in the product is higher than in the starting material, usually a chloride. That is, there is an apparent oxidation by what is usually regarded as a reducing agent. Davies *et al.*<sup>20</sup> attempted to explain this by the mechanism in equation (1) for the synthesis of Ru<sup>IV</sup>(η<sup>5</sup>-



C<sub>5</sub>H<sub>5</sub>H<sub>3</sub>(PPh<sub>3</sub>) from Ru(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Cl(PPh<sub>3</sub>)<sub>2</sub> by interaction of the latter with LiAlH<sub>4</sub>.<sup>\*</sup>

Our present and previous<sup>3c</sup> studies indicate that aluminohydride complexes are intermediates in the synthesis of tertiary phosphine polyhydrides, *i.e.*, as in equation (2). The formation,



prior to hydrolysis of yellow solutions in the synthesis of IrH<sub>5</sub>(PR<sub>3</sub>)<sub>3</sub><sup>22</sup> and of orange solutions in the synthesis of Ta(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>H<sub>3</sub><sup>23</sup> have been noted but without comment on the possibility of intermediate aluminohydride complexes. In some cases (*e.g.* the tantalum one<sup>23</sup>) the oxidation state of the metal is the same both in the starting material and the product. Two possibilities can be considered: (a) direct attack of H<sup>-</sup> on L<sub>n</sub>MCl<sub>m</sub> with no formation of an aluminohydride,<sup>21</sup> or (b) reduction of the metal halide complex to give an aluminohydride followed by hydrolysis. We have shown<sup>24</sup> that the reaction of TaCl<sub>5</sub> with 2 equivalents of Li(C<sub>5</sub>H<sub>4</sub>Me) followed by addition of 3 equivalents of LiAlH<sub>4</sub> yields [(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>-Ta<sup>III</sup>(μ-H)<sub>2</sub>AlH(μ-H)]<sub>2</sub> and that hydrolysis of this complex gives the trihydride.<sup>23</sup>

The actual mechanism for the hydrolysis of the aluminohydrides is as yet not certain. The deuteration studies here and in ref. 3c indicate that the M(μ-H)<sub>2</sub>Al bridge is cleaved either symmetrically,<sup>3c</sup> *i.e.* one hydride is retained on the transition metal and one on the aluminium, or asymmetrically, *i.e.* both hydrides are retained on the transition metal. The latter occurs

in the tantalum case noted above and also in the hydrolysis of an unisolated niobium aluminohydride, (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NbAlH<sub>4</sub>, characterised only by <sup>1</sup>H n.m.r. in solution and believed to be of the formula given.<sup>25</sup>

The asymmetric cleavage may result from initial nucleophilic attack on the five-co-ordinate aluminium atom followed by protonation of the resulting hydrido anion. This is supported by our studies<sup>24</sup> on the reaction of lithium alkyls with the aluminohydrides and the isolation of a stable hydrido lithium compound (Me<sub>3</sub>P)<sub>3</sub>WH<sub>5</sub>Li. Some hydrido anions, *e.g.* [RuH<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>-</sup>,<sup>26</sup> [Ir(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)H<sub>3</sub>]<sup>-</sup>, and [Ir(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)H(PMe<sub>3</sub>)]<sup>-</sup><sup>27</sup> are known. Further studies on these hydrolyses are in progress.

## Experimental

Microanalyses were by Pascher Laboratories. Melting points were determined in sealed capillaries and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 683 grating spectrometer in Nujol mulls. N.m.r. spectra were recorded on JEOL FX90Q (<sup>1</sup>H, <sup>31</sup>P) or Bruker WM-250 (<sup>27</sup>Al) spectrometers {[δ 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)]}. Spectra were taken in C<sub>7</sub>D<sub>8</sub> solutions. All manipulations were carried out under argon. Solvents were dried, distilled, and degassed before use.

Analytical data are given in the Table. The compound MoCl<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> was prepared by an improved modification of the previous procedure<sup>28</sup> by direct reduction of MoCl<sub>4</sub>(thf)<sub>2</sub> [instead of zinc reduction of MoCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>] with 2 equivalents of Na/Hg in the presence of excess of PMe<sub>3</sub> in tetrahydrofuran (thf); recrystallisation from Et<sub>2</sub>O gives 80% yield. The compounds CrCl<sub>2</sub>(dmpe)<sub>2</sub>,<sup>29</sup> WCl<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>,<sup>30</sup> WCl<sub>4</sub>(PMe<sub>3</sub>)<sub>3</sub>,<sup>30</sup> and Li<sub>3</sub>AlH<sub>6</sub><sup>31</sup> were prepared by published methods.

1,1,4,4-Tetrakis[1',2'-bis(dimethylphosphino)ethane]-1,2; 2,3; 2,3; 3,4; 3,4-hexa-μ-hydrido-1,2,3,4-tetrahydrido-1,4-dichromium(II)-2,3-dialuminium (A).—The compound CrCl<sub>2</sub>(dmpe)<sub>2</sub> (0.43 g, 1.02 mmol) was added to a suspension of LiAlH<sub>4</sub> (0.1 g, 2.64 mmol) in Et<sub>2</sub>O (100 cm<sup>3</sup>) at -78 °C and the solution stirred at room temperature until effervescence ceased. Removal of the solvent under vacuum followed by extraction with hexane (3 × 100 cm<sup>3</sup>), re-evaporation, and recrystallisation from toluene (30 cm<sup>3</sup>) yielded orange-yellow crystals (0.39 g, 70%). I.r.: 1 680br,s, 1 600br,m, 1 420m, 1 275m, 1 120w, 930s, 880m, 825s, 715ms, 680s, 630s, 600w, 535m, and 465m cm<sup>-1</sup>. N.m.r.: <sup>1</sup>H, 4.8 [4 H, br s, Al-H and Al(μ-H)Al], 1.52 [16 H, s, P-CH<sub>2</sub>], 1.20 [48 H, s, P-CH<sub>3</sub>], and -9.39 [6 H, quin, J(P-H) 42.0 Hz, Cr-H and Cr(μ-H)Al]; <sup>31</sup>P-{<sup>1</sup>H}, 76.28 (s); <sup>27</sup>Al-{<sup>1</sup>H}, 54 (br s).

1,2; 1,2; 2,3; 2,3; 3,4; 3,4-Hexa-μ-hydrido-1,2,3,4-tetrahydrido-1,1,1,1,4,4,4,4-octakis(trimethylphosphine)-1,4-dimolybdenum(II)-2,3-dialuminium (B).—Lithium aluminium hydride (0.50 g, 13.18 mmol) was suspended in Et<sub>2</sub>O (50 cm<sup>3</sup>) at -78 °C and MoCl<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (2.00 g, 4.25 mmol) added in diethyl ether solution. After stirring for 20 min the mixture was warmed to room temperature and stirred for a further 18 h. Removal of the solvent under vacuum followed by extraction and crystallisation from toluene (50 cm<sup>3</sup>) gave a fine yellow powder (1.30 g, 71%). I.r.: 1 870m, 1 800s, 1 675m, 1 600s, 1 300s, 1 285, 1 150w, 1 110w, 940vs, 850m, 720s, 705s, and 655s cm<sup>-1</sup>. N.m.r.: <sup>1</sup>H, 5.0 [4 H, br s, Al-H and Al(μ-H)Al], 1.48 [72 H, d, J(P-H) = 6, P-CH<sub>3</sub>], -7.03 [6 H, br quin, J(P-H) = 19.0 Hz, MoH and Mo(μ-H)Al]; <sup>31</sup>P-{<sup>1</sup>H}, 3.05 (s); <sup>27</sup>Al-{<sup>1</sup>H}, 53 (br s).

1,2; 1,2; 2,3; 2,3; 3,4; 3,4-Hexa-μ-hydrido-1,2,3,4-tetrahydrido-1,1,1,1,4,4,4,4-octakis(trimethylphosphine)-1,4-ditungsten(II)-2,3-

\* Despite the claim<sup>20</sup> of poor yields of Ru(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)H(PPh<sub>3</sub>)<sub>2</sub> in the interactions of the chloride with LiAlH<sub>4</sub> using the original preparation (see ref. 21), in our hands this preparation does in fact give yields of 80–90% of the monohydride.

**Table.** Analytical data for aluminohydrides with required values in parentheses

Compound	M.p. (°C)	Analysis (%)			
		C	H	P	Al
(A) [(dmpe) <sub>2</sub> HCr(μ-H) <sub>2</sub> AlH(μ-H)] <sub>2</sub>	110 (decomp.)	36.7 (37.6)	9.85 (9.5)	31.9 (32.3)	8.45 (7.1)
(B) [(Me <sub>3</sub> P) <sub>4</sub> HMo(μ-H) <sub>2</sub> AlH(μ-H)] <sub>2</sub>	163 (decomp.)	32.6 (33.3)	10.0 (9.5)	29.0 (28.7)	6.05 (6.2)
(C) [(Me <sub>3</sub> P) <sub>4</sub> HW(μ-H) <sub>2</sub> AlH(μ-H)] <sub>2</sub>	143 (decomp.)	27.9 (27.7)	7.4 (7.1)	24.0 (23.8)	6.3 (6.2)
(D) [(Me <sub>3</sub> P) <sub>4</sub> ClW(μ-H) <sub>2</sub> AlH(μ-H)] <sub>2</sub> *	148 (decomp.)	26.2 (26.5)	7.2 (7.6)	22.3 (22.5)	4.85 (4.7)

\* Cl 6.45 (5.9%).

*dialuminium* (C).—Lithium aluminium hydride (0.3 g, 7.90 mmol) was suspended in Et<sub>2</sub>O (100 cm<sup>3</sup>) at -78 °C and solid WCl<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (1.79 g, 3.20 mmol) added. After stirring for 10 min at -78 °C the mixture was warmed to room temperature and stirring continued for a further 18 h. The solvent was removed, the residue extracted with hexane (2 × 100 cm<sup>3</sup>), the yellow solution evaporated, and the residue re-extracted with toluene (50 cm<sup>3</sup>). The extracts were reduced to ca. 25 cm<sup>3</sup> and cooled to -20 °C affording several crops of bright yellow crystals (1.38 g, 83%). I.r.: 1800m, 1740s, 1665s, 1610s, 1295m, 1275m, 1255m, 1145m, 1080br,m, 1015m, 940vs, 845s, 800m, 715m, 655w, and 590w cm<sup>-1</sup>. N.m.r.: <sup>1</sup>H, 5.0 [4 H, br s, Al-H and Al(μ-H)Al], 1.52 [72 H, d, J(P-H) = 6, P-CH<sub>3</sub>], and -6.42 [6 H, br quin, J(P-H) = 23.4 Hz]; <sup>31</sup>P-{<sup>1</sup>H}, -33.95 [s, with <sup>183</sup>W satellites, J(P-W) = 232.6 Hz]; <sup>27</sup>Al-{<sup>1</sup>H}, 49 (br s).

1,4-Dichloro-1,2; 1,2; 2,3; 2,3; 3,4; 3,4-hexa-μ-hydrido-2,3-dihydrido-1,1,1,1,4,4,4,4-octakis(trimethylphosphine)-1,4-ditungsten(II)-2,3-dialuminium (D).—To a stirred suspension of Li<sub>3</sub>AlH<sub>6</sub> (0.98 g, 18.1 mmol) in thf (50 cm<sup>3</sup>) at -78 °C was added WCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> (2.5 g, 4.51 mmol); on warming to room temperature the solution became dark red. The solvent was removed under vacuum and the residue extracted with hexane; reduction in volume and cooling (-20 °C) yielded several crops of yellow crystals (0.99 g, 46%). I.r.: 1850w, 1735m, 1650w, 1410m, 1290m, 1275m, 1145m, 1080br,m, 940s, 855m, 715s, 700m, 670m, and 530w cm<sup>-1</sup>. N.m.r.: <sup>1</sup>H, 5.0 [4 H, vbr s, Al-H, Al(μ-H)Al], 1.30 [72 H, m, P-CH<sub>3</sub>], and -3.68 [4 H, m, W(μ-H)Al]; <sup>31</sup>P-{<sup>1</sup>H}, -13.91 [1 P, d(t), J(P-P) = 44.3, 17.7], -25.47 [2 P, d(d), J(P-P) = 17.7, 17.7], and -33.61 [1 P, d(t), J(P-P) = 44.3, 17.7 Hz]; <sup>27</sup>Al-{<sup>1</sup>H}, 52 (br s).

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### References

- 1 G. Henrici-Olive and S. Olive, *J. Organomet. Chem.*, 1970, **23**, 155; B. M. Bulychev, S. E. Tokareva, G. L. Soloveichik, and E. V. Evdokimova, *ibid.*, 1979, **179**, 273.
- 2 J. A. Labinger and K. S. Wong, *J. Organomet. Chem.*, 1979, **170**, 373.
- 3 (a) G. S. Girolami, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1983, **105**, 6752; (b) C. G. Howard, G. S. Girolami, G. Wilkinson, M. Thornton-Pett, M. Motevalli, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 921; (c) A. R. Barron, D. Lyons, G. Wilkinson, M. Motevalli, A. J. Howes, and M. B. Hursthouse, *ibid.*, 1986, 279.
- 4 V. K. Belsky, A. I. Suzov, B. M. Bulychev, and G. L. Soloveichik, *J. Organomet. Chem.*, 1985, **280**, 67.
- 5 A. R. Barron, M. B. Hursthouse, M. Motevalli, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1985, 664.
- 6 V. K. Belsky, A. B. Erofeev, B. M. Bulychev, and G. L. Soloveichik, *J. Organomet. Chem.*, 1984, **265**, 123; **268**, 107.
- 7 A. R. Barron and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1986, 287.
- 8 J. A. Statler, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1984, 1731.
- 9 J. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.
- 10 P. W. Frost, J. A. K. Howard, and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, 1984, 1362.
- 11 For calculation, see J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 223.
- 12 See, for example, A. M. Bond, R. Colton, and J. J. Jackowski, *Inorg. Chem.*, 1975, **14**, 2526.
- 13 W. McFarlane, City of London Polytechnic, personal communication.
- 14 A. R. Barron, J. E. Salt, G. Wilkinson, M. Motevalli, and M. B. Hursthouse, *Polyhedron*, 1986, **5**, in the press.
- 15 J. L. Atwood, W. E. Hunter, E. Carmona-Guzman, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1980, 467.
- 16 J. E. Salt, G. S. Girolami, G. Wilkinson, M. Motevalli, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 685.
- 17 D. Lyons and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1985, 587.
- 18 K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, and K. M. Abdul-Malik, *J. Chem. Soc., Dalton Trans.*, 1981, 1204.
- 19 G. G. Hlatky and R. H. Crabtree, *Coord. Chem. Rev.*, 1985, **65**, 1.
- 20 S. G. Davies, S. D. Moon, and S. J. Simpson, *J. Chem. Soc., Chem. Commun.*, 1983, 1278; G. J. Baird, S. G. Davies, S. D. Moon, S. J. Simpson, and R. H. Jones, *J. Chem. Soc., Dalton Trans.*, 1985, 1479.
- 21 T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 1971, 2376.
- 22 J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 1965, 7391.
- 23 G. W. Parshall and U. Klabunde, *J. Am. Chem. Soc.*, 1972, **94**, 9081.
- 24 A. R. Barron, Ph.D. Thesis, University of London, 1986.
- 25 J. A. Labinger and K. S. Wong, *J. Organomet. Chem.*, 1979, **170**, 373.
- 26 R. Wilczynski, W. A. Fordyce, and J. Halpern, *J. Am. Chem. Soc.*, 1983, **105**, 2066.
- 27 W. D. McGhee and R. G. Bergman, *J. Am. Chem. Soc.*, 1985, **107**, 3388; T. M. Gilbert, F. J. Hollander, and R. G. Bergman, *ibid.*, p. 3508.
- 28 E. Carmona, J. M. Marin, M. L. Poveda, J. L. Atwood, and R. D. Rogers, *Polyhedron*, 1983, **3**, 185.
- 29 G. S. Girolami, G. Wilkinson, A. M. R. Galas, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 1339.
- 30 P. R. Sharp, *Organometallics*, 1984, 1217.
- 31 R. Ehrlich, A. R. Young, G. Rice, J. Dvorak, P. Shapiro, and H. F. Smith, *J. Am. Chem. Soc.*, 1966, **88**, 858.

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