The Synthesis and Structure of a New Type of Bridged Hydrido-aluminate Complex: 1,2;1,2;2,3;2,3-Tetra-μ-hydrido-1,1,1,2,3,3,3-heptahydrido-1,1,1,3,3,3-hexakis(trimethylphosphine)-1,3-ditungsten(IV)-2-aluminium

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The reaction of $WCl_4(PMe_3)_3$ with $LiAlH_4$ in diethyl ether followed by subsequent addition of $Me_2N(CH_2)_2NMe_2$ yields the bright yellow complex $(Me_3P)_3H_3W(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2WH_3(PMe_3)_3$ whose structure has been determined by *X*-ray crystallography and nuclear magnetic resonance spectroscopy; the complex is the first alumino polyhydride with a formally AlH_5^{2-} bridge.

Although transition metal borohydride complexes have long been structurally established[1] only recently have aluminohydride species been reported.[2,3]

We have synthesised a series of tertiary phosphine alumino-polyhydrides of tungsten, rhenium, ruthenium, and osmium,[4] *e.g.* $(Me_3P)_3HRu(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2RuH(PMe_3)_3$, all of which, like the structurally characterised aluminohydrides $[TaH_2Al(OC_2H_4OMe)_2dmpe_2]_2$[2] and $[Mn(AlH_4)dmpe_2]_2$,[3] are dimers having $M(\mu\text{-}H)_2Al(OR)(\mu\text{-}OR)_2Al(OR)(\mu\text{-}H)_2M$[2,4] or $M(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2M$[3,4] cores (dmpe = $Me_2PCH_2CH_2PMe_2$).

Russian workers have also recently reported[5] the bis(η^5-cyclopentadienyl)yttrium aluminohydrides $\{[(\eta^5\text{-}C_5H_5)_2Y(\mu_3\text{-}H)][(\mu_2\text{-}H)AlH_2]\}_2$ and some solvent adducts thereof. A different type is the aluminohydride adduct, of tetramethylethylenediamine (tmeda) $(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}H)_2Al(H)_2(\mu\text{-}tmeda)Al(H)_2(\mu\text{-}H)_2Ti(\eta^5\text{-}C_5H_5)_2$[6] in which the amine bridges two aluminium atoms.

We now report the first alumino-polyhydride with a $M(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2M$ core.

The interaction of $WCl_4(PMe_3)_3$[7] with $LiAlH_4$ in diethyl ether at −80 °C followed by addition at room temperature of an excess of $Me_2N(CH_2)_2NMe_2$ yields the insoluble adduct $(tmeda)AlH_3$ and a yellow solution from which may be obtained in high yield the yellow crystalline complex (**1**). In the absence of tmeda only (**2**)[4] is obtained.

$$(Me_3P)_3H_3W(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2WH_3(PMe_3)_3$$

(**1**)

$$(Me_3P)_3H_3W(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2Al(H)(\mu\text{-}H)_2WH_3(PMe_3)_3$$

(**2**)

The i.r. spectrum of (**1**) contains broad bands between 1760 and 1550 cm^{-1} due to bridging and terminal hydrides. The complex is fluxional in solution at room temperature where the ^1H n.m.r. spectrum gives a broad quartet [δ −4.08,

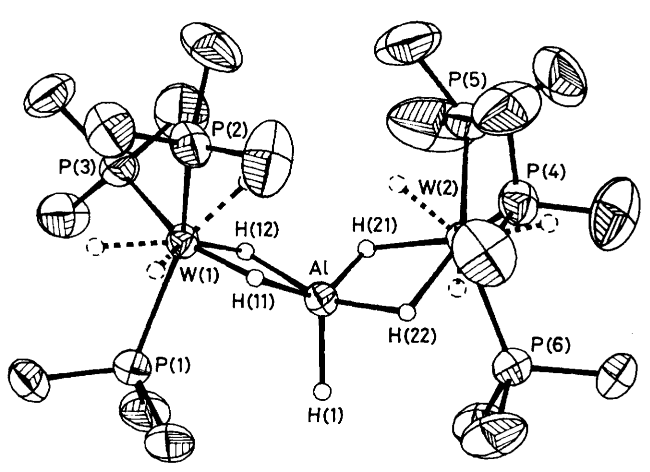

Figure 1. The structure of $\{[(Me_3P)_3WH_4]_2AlH_3\}$, (**1**). Only the hydrogen atoms attached to Al (terminal and bridging) have been located with reasonable certainty. Those attached only to W have still to be confirmed. Selected bond lengths (Å) and angles (degrees) are: W(1)–P(1) 2.449(4), W(1)–P(2) 2.408(4), W(1)–P(3) 2.399, W(1)–H(11) 1.63(7), W(1)–H(12) 1.67(6), W(1) · · · Al 2.694(5), W(2)–P(4) 2.410(4), W(2)–P(5) 2.420(4), W(2)–P(6) 2.427(4), W(2)–H(21) 1.70(7), W(2)–H(22) 1.72(6), W(2) · · · Al 2.690(5), Al–H(11) 1.80(7), Al–H(12) 1.99(6), Al–H(21) 1.81(8), Al–H(22) 1.95(6), Al–H(1) 1.65(6); P(1)–W(1)–P(2) 143.7(1), P(1)–W(1)–P(3) 101.5(1), P(2)–W(1)–P(3) 97.0(1), P(4)–W(2)–P(5) 100.1(1), P(4)–W(2)–P(6) 100.4(1), P(5)–W(2)–P(6) 139.2(1).

J(P–H) 27 Hz] due to the terminal W–H and bridging W(μ-H)$_2$Al hydrides. The terminal Al–H gives a broad single resonance (*ca.* δ 5). At −90 °C the exchange process is stopped, the hydrides then giving rise to a broad quartet [δ −2.70, *J*(P–H) 27 Hz] due to the terminal W–H and a broad singlet (δ −4.60) due to the bridging W(μ-H)$_2$Al hydrides. The $^{31}P\{^1H\}$ spectrum shows a singlet (δ −20.4 p.p.m.); selective decoupling of the P–CH_3 protons gives a binomial sextet [*J*(P–H) 27 Hz]. These spectroscopic data are in full accord with the structure determined by *X*-ray diffraction (Figure 1).† Although the complex could be considered as a bis adduct of the Lewis acid AlH_3 with $WH_4(PMe_3)_3$ it is equally valid to regard it as containing AlH_5^{2-} bridging two $WH_3(PMe_3)_3^+$ units. It may be noted that the AlH_6^{3-} anion is known.[8]

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† *Crystal data:* $C_{18}H_{65}P_6AlW_2$, $M = 862.3$, monoclinic, space group $P2_1/n$, $a = 10.204(1)$, $b = 21.523(5)$, $c = 16.540(2)$ Å, $\beta = 93.52(1)°$, $U = 3625.9$ Å^3, $Z = 4$, $D_c = 1.58$ g cm^{-3}, μ(Mo-K_α) = 63.5 cm^{-1}, λ(Mo-K_α) = 0.71069 Å. 6602 Unique intensity data, 4356 observed [$I > 2\sigma(I)$], $R = 0.0288$. Non-hydrogen atoms anisotropic, methyl hydrogens inserted in idealised positions and refined as part of rigid CH_3 groups, metal-bound hydrogens incompletely located as yet. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.