Interaction of the bulky alane $(H_2AlC_6H_3-2,6-Mes_2)_2$ (Mes = $-C_6H_3-2,4,6-Me_3$) with H_2EPh (E = N, P or As)

Rudolf J. Wehmschulte and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616, USA

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The reactions of the bulky primary alane $(H_2AlC_6H_3-2,6-Mes_2)_2$ (Mes = $-C_6H_2-2,4,6-Me_3$) with H_2EPh (E = N, P or As) are described. With aniline, H_2NPh , the dimeric products 2,6-Mes_2 H_3C_6 {Ph(H)N}Al{ μ -N(H)Ph}_2Al(H)C_6H_3-2,6-Mes_2 (1) and [2,6-Mes_2H_3C_6(H)Al{ μ -N(H)Ph}]_2 (2) are obtained. The structures of both 1 and 2 feature two $-C_6H_3-2,6$ -Mes_2 substituted aluminums bridged by two -N(H)Ph groups. In 2 each aluminum is also bound to a terminal hydrogen whereas in 1 one of these hydrogens is replaced by a terminal -N(H)Ph substituent. The structure of the -P(H)Ph derivative [2,6-Mes_2H_3C_6(H)Al{ μ -P(H)Ph}]_2 (3) is very similar to that of 2 (and presumably the arsenido derivative 4) and features bridging phosphido groups and four-coordinate aluminums. The arsenido dimer 4 is cleaved by ether to give the ether adduct 2,6-Mes_2H_3C_6(H)Al{As(H)Ph}(OEt_2) for which a partial X-ray structure was determined. Thermolysis of 2, 3 and 4 led to decomposition. However, heating ($H_2AlC_6H_3-2,6$ -Mes_2) with excess H_2AsPh led to the unique cluster (2, 6-Mes_2H_3C_6Al)_{ μ -As(H)Ph}_2(\mu-PhAsAsPh) which has a basket-type Al_2As_4 core.

Interest in neutral hydride derivatives of heavier main group 13 elements has undergone rapid growth over the last decade.¹ The variety of such compounds is large and it includes numerous types of Lewis base stabilized² and uncomplexed metallanes.³ The latter are characterized by strong hydride bridging unless other strongly bridging ligands such as -OR or -NR₂ are present.⁴ Hydride bridging can also be prevented by the use of bulky substituent groups, and a number of unassociated alanes and gallanes featuring only terminally bound hydrogens have been synthesized. Examples of stable compounds include the monomeric species H₂GaMes^{*5} $(Mes^* = -C_6H_2 - 2, 4, 6 - tert - Bu_3), HMMes_2^* (M = Al^6 \text{ or } Ga^7)$ and HAl(Mes*)N(SiMe₃)₂.⁸ A further advantage of the use of sterically crowding groups is that it stabilizes primary metallane derivatives toward rearrangement reactions of the type described by eqn. (1):

$$2 H_2 A l R \rightarrow H A l R_2 + H_3 A l \tag{1}$$

The stability of a primary metallane such as $(H_2AlMes^*)_2$ has permitted its use in the synthesis of a variety of compounds that are often not readily accessible by other routes.⁹ This work is now extended to the reactions of the primary alane $(H_2AlC_6H_3-2,6-Mes_2)_2^{10}$ (Mes = $-C_6H_2-2,4,6-Me_3$) and a range of reactions of this compound with H_2EPh , (E = N, P or As) are described. It is shown that they are quite different from the corresponding reactions of $(H_2AlMes^*)_2$ with the same substrates.

Experimental

General procedures

All reactions were performed under N_2 by using either modified Schlenk techniques or a Vacuum Atmospheres HE43-2 dry box. Solvents were freshly distilled from sodiumpotassium alloy and degassed twice before use. $(H_2AlC_6H_3-$ 2,6-Mes₂)₂,¹⁰ H₂PPh¹¹ and H₂AsPh¹² were synthesized by literature methods. Aniline was obtained from a commercial supplier and dried by standard procedures. ¹H, ¹³C and ³¹P NMR spectra were recorded in C₆D₆ or C₇D₈ solutions by using a General Electric QE-300 spectrometer. IR spectra were recorded as a Nujol mull between CsI plates using a Perkin–Elmer PE-1430 spectrometer.

Syntheses

 $2,6-Mes_{2}H_{3}C_{6}{Ph(H)N}Al{\mu-N(H)Ph}_{2}Al(H)C_{6}H_{3}-2,6-$ Mes₂ (1) and $[2,6-Mes_2H_3C_6(H)Al\{\mu-N(H)Ph\}]_2$ (2). Aniline (0.137 mL, 1.5 mmol, 0.14 g) was added slowly via syringe to a solution of (H2AlC6H3-2,6-Mes2)2 [prepared in situ by heating (Et₂O)H₂AlC₆H₃-2,6-Mes₂ (0.62 g, 1.5 mmol) to 115 °C under reduced pressure for 30 min] in toluene (30 mL) at room temperature. Intensive gas evolution (H₂) commenced immediately and ceased a few minutes after the addition was completed. After 1 h at room temperature the colorless, clear solution was concentrated to 5 mL and cooled to -20 °C overnight. As no crystals had formed, the solution was concentrated further to ca. 3 mL and 2 mL of n-hexane were added; cooling to +6 °C for 3 days gave a few, small crystals. The solution was then cooled in a -20 °C freezer for a week to give ca. 60 mg of small colorless crystals of a mixture of 1 and 2 and some unidentified products. From this batch the crystal used for the X-ray structure determination of 1 was chosen. Further concentration of the mother liquor and cooling to -20 °C for 3 days gave 0.37 g of small colorless crystals, which consisted mostly of 2. Recrystallization from toluene-n-hexane (2 mL : 4 mL) at -20 °C afforded 0.21 g of 2 in the form of large colorless blocks (≈ 1 mm on a side). It crystallizes as a toluene solvate of formula $2 \cdot 0.5$ PhMe. The toluene may be removed by prolonged pumping at room temperature. Yield: 30.6%. Mp: softens at 160 °C, melts with gas evolution at 165–170 °C. IR: $v_{\rm NH} = 3275(w)$, 3260(w), $v_{\rm AIH} = 1902(st)$, 1859(st) cm⁻¹. ¹H NMR (C₆D₆): 7.16 (t, *p*-H, 2H, ³J_{HH} = 7.5 Hz), 6.82 [m, *m*-H(NPh), 4H], 6.76 (d, *m*-H, 4H), 6.60 [s, m-H(Mes), 8H], 6.58 [m, o-, p-H(NPh), 6H], 4.09 (br, s, Al–H, 2H), 2.50 (s, N–H, 2H), 2.10 (s, *p*-CH₃, 12H), 1.93 (s, *o*-CH₃, 24H). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆): 151.1 (*o*-C), 142.7 [i-C(NPh)], 141.6 [i-C(Mes)], 136.1 [p-C(Mes)], 135.7 [o-C(Mes)], 129.3 (p-C), 129.1 [m-C(Mes)], 127.9 [m-C or m-C(NPh)], 122.8 [o-C(NPh)], 122.5 [p-C(NPh)], 21.7 (o-CH₃), 21.2 (p-CH₃).

[2,6-Mes₂H₃C₆(H)Al{ μ -P(H)Ph}]₂ (3). H₂PPh (0.22 mL, 2.0 mmol, 0.22 g) was added *via* syringe to finely ground [H₂AlC₆H₃-2,6-Mes₂]₂ (0.48 g, 0.7 mmol) at room temperature to give a paste. After 5 min the flask was placed into a 150 °C oil bath for 5 min during which time the excess

Table 1	Crystallographic	data for $1 \cdot 0.25$	hexane, $2 \cdot 0.5$	toluene, 3 and 6	$5 \cdot 2Et_2O$
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	$1 \cdot 0.25$ hexane	$2 \cdot 0.5$ toluene	3	$6 \cdot 2 \mathrm{Et}_2 \mathrm{O}$			
Formula	$C_{67.5}H_{72.5}Al_2N_3$	$C_{63} {}_{5}H_{68}Al_{2}N_{2}$	$C_{60}H_{64}Al_2P_2$	C ₈₀ H ₉₂ Al ₂ As ₄ O ₂			
FW	979.75	913.16	901.01	1439.18			
Space group	$P2_1/n$	C2/c	Pbca	$P2_1/c$			
a/Å	13.873(6)	21.996(6)	13.718(4)	13.880(8)			
b/Å	23.343(5)	13.089(3)	20.923(10)	45.59(2)			
c/Å	18.733(6)	36.376(6)	35.886(7)	12.100(5)			
β/°	107.48(3)	96.38(2)		112.20(3)			
$U/Å^3$	5786(3)	10408(4)	10300(6)	7089(6)			
Z	4	8	8	4			
T/K	130(2)	130(2)	130(2)	130(2)			
λ/Å	1.54178	1.54178	1.54178	1.54178			
$\delta_{calcd}/g \ cm^{-3}$	1.125	1.166	1.162	1.349			
μ/mm^{-1}	0.766	0.810	1.370	2.791			
$R_{1}/\%$	8.49	6.14	7.35	7.13			
$w R_2 / \%$	23.98	12.51	16.58	17.33			
$R_{1} = \Sigma F_{o} - F_{c} \Sigma F_{o} ; wR_{2} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}] \}^{1/2}$							

H₂PPh distils to the cooler part of the flask. After being held at room temperature for ca. 30 min the sticky, colorless solid was heated to 160 °C for 15 min, cooled to room temperature and the excess H₂PPh was removed under reduced pressure. No gas evolution was apparent during the reaction. The remaining colorless solid was dissolved in warm toluene (20 mL) and crystallized at $-20\ ^\circ C$ for 2 days to afford 0.40 g of small colorless crystals. Concentration of the supernatant liquid to 2–3 mL followed by cooling to -20 °C overnight gave another 0.08 g of product. Total yield: 76%. X-ray quality crystals were grown from benzene (0.2 g in 10 mL) at 6 °C for one week. Mp: turns yellow at ca. 230 °C, melts with gas evolution at 235–6 °C. IR: $v_{PH} = 2355(w)$, $v_{AIH} = 1812(st)$, 1797(st) cm⁻¹. ¹H NMR (C₆D₆): 7.23 (t, *p*-H, 2H, ³J_{HH} = 7.5 Hz), 7.23 [br, s, m-H(PPh), 4H], 6.95 [br, s, o-, p-H(PPh), 6H], 6.86 (d, m-H, 4H), 6.62 [s, m-H(Mes), 8H], 4.03 (br, s, Al-H 2H), 2.61 (center of AA'XX' multiplet, P-H, 2H, 3 of 10 possible lines observed: 3.07, 2.74, 2.29; absorption at 3.07 split into three lines due to coupling to Al—H, ${}^{3}J_{HH} = 7.5$ Hz), 2.15 (s, *p*-CH₃, 12 H), 1.92 (s, *o*-CH₃, 24H). ${}^{13}C{}^{1}H{}$ NMR (C_6D_6) : 151.3 (*o*-C), 142.4 [*i*-C(Mes)], 136.0 [*o*-C(Mes)], 135.9 [p-C(Mes)], 132.8 ['t' (AA'X), o- or m-C(PPh), $\Delta v = 5.6$ Hz], 129.7 (p-C), 128.7 [m-C(Mes)], 128.0 ['t' (AA'X), o- or *m*-C(PPh), $\Delta v = 5.5$ Hz], 127.5 [*p*-C(PPh)], 126.6 (*m*-C), 22.2 (p- and m-CH₃). ³¹P{¹H} NMR (C₆D₆): -116 (s, w_{1/2} \approx 17 Hz). ³¹P NMR (C_6D_6): -116 [six-line multiplet (AA'XX'): -113.1, -115.3, -116.1, -117.2, -118.0, -120.2, rel. intensity: 1:5:4.3:4.3:5:1].

 $[2,6-Mes_2H_3C_6(H)Al\{\mu-As(H)Ph\}]_2$ (4). Finely ground $(H_2AlC_6H_3-2,6-Mes_2)_2$ (0.48 g, 0.7 mmol) was treated with H₂AsPh (0.23 mL, 2.0 mmol, 0.31 g) at room temperature to form a paste. After ca. 2-3 min a weak gas evolution commenced and within ca. 10 min the paste solidified and 10 min later excess H₂AsPh was removed under reduced pressure. Crystallization from toluene (5–7 mL) at -20 °C for one week afforded 0.11 g of colorless, microcrystalline 4. Concentration of the mother liquor to 2 mL and subsequent cooling to -20°C for one week afforded another 0.03 g of 4. Total yield: 20%. Mp: turns yellow at 140 °C, orange at 160 °C and melts with gas evolution and color change to red-orange at 175-178 °C. IR: v_{AsH} 2175(w), v_{A1H} 1812(st), 1797(sh) cm⁻¹. ¹H NMR (C_6D_6) : 7.24 [m, *m*-H(AsPh), 4H], 7.23 (t, *p*-H, 2H, ³ $J_{HH} = 7.5$ Hz), 6.97 [m, o-, p-H(AsPh), 6H], 6.86 (d, m-H, 4H), 6.62 [s, m-H(Mes), 8H], 4.13 (br, s, Al-H, 2H), 2.13 (s, p-CH₃, 12H), 1.96 (s, o-CH₃, 24H). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆): 151.3 (o-C), 142.2 [i-C(Mes)], 136.2 [o- and p-C(Mes)], 133.3 [o- or m-C(AsPh)], 131.2 [i-C(AsPh)], 129.8 (p-C), 128.7 [m-C(Mes)], 128.4 [o- or m-C(AsPh)], 127.4 [p-C(AsPh)], 126.7 (m-C), 21.2 (o- and p-CH₃).

 $2,6-Mes_2C_6H_3(H)Al\{As(H)Ph\}(OEt_2)$ (5). H_2AsPh (0.34 mL, 3.0 mmol, 0.46 g) was added via syringe to 1.5 mmol of finely ground (H₂AlC₆H₃-2,6-Mes₂)₂ [prepared in situ from 0.64 g of 2,6-Mes₂H₃C₆AlH₂ \cdot (OEt₂)] at room temperature to form a colorless paste. After ca. 5 min a smooth gas evolution commenced and after a further 10 min the paste solidified and the gas evolution ceased. The volatile material was removed 30 min later under reduced pressure (1.5 h) and the remaining colorless solid was dissolved into Et₂O (30 mL). Concentration to ca. 5 mL and subsequent cooling to -20 °C for 5 days afforded 0.53 g of colorless needles. Recrystallization from Et₂O-hexane (25 mL : 5 mL) at -20 °C for 2 days gave X-ray quality crystals of 5. An X-ray data set of 5 was collected and could be solved. Subsequent refinement showed disorder that could not be modeled successfully to give a R_1 value of <0.2. Nevertheless, the identity of 5 was confirmed. Mp: turns opaque at 119-122 °C (desolvation), gradually changes color to orange, melts with gas evolution and color change to red at 168–175 °C. IR: v_{AsH} 2088(m), v_{AlH} 1805(m, br) cm⁻¹. The ¹H NMR spectrum (C_6D_6) displayed a mixture of compounds indicating an equilibrium between 5 and 4 and free Et₂O in solution. Heating to 80 °C drives the equilibrium almost completely to 4 and free Et₂O. The room temperature spectrum of 5 was identical with a spectrum of a C_6D_6 solution of 4 to which 1 equiv. Et₂O per aluminum was added.

 $(2,6-Mes_2H_3C_6Al)_2[\mu-As(H)Ph]_2(\mu-PhAsAsPh)(6)$. H₂AsPh (0.48 mL, 4.2 mmol, 0.65 g) was added via syringe to 0.71 g (2.1 mmol) of finely ground $(H_2AlC_6H_3-2,6-Mes_2)_2$ at room temperature. After ca. 10 min the colorless paste solidified into a sticky solid. After 1 h, the flask was placed into a 100-110 °C oil bath for 10 min, after which the solid turned pale yellow. The flask was then heated to 150-160 °C for about 5 min to complete the reaction. The orange solid was cooled to room temperature and then placed under reduced pressure at 60 °C for 1 h to remove all volatile materials. Upon cooling, Et₂O (20 mL) was added. Concentration to ca. 5 mL and cooling in a -20 °C freezer for 10 days gave a small amount (<100 mg) of colorless needles of 5, which were separated. A mixture of Et₂O-hexane (20 mL : 20 mL) was added to the pale yellow supernatant, insoluble material was separated and the remaining solution was concentrated to 15 mL and cooled in a -20 °C freezer for 5 days to give *ca*. 20 mg of X-ray quality crystals (yellow plates) of $6 \cdot 2Et_2O$. Concentration of the supernatant to ca. 4 mL and crystallization in a -20 °C freezer for 2 weeks gave $\mathbf{6} \cdot \mathbf{hexane} (0.32 \text{ g})$ in the form of pale Table 2 Selected bond distances (Å) and angles (°) for 1-3 and 6

1			
$A_{1(1)} = N(1)$	1 833(6)	A1(2) - N(3)	1 983(5)
$A_1(1) = N(2)$	1.055(0)	$A_1(1) - C(1)$	2.001(5)
$A_1(1) = N(2)$	1.909(5) 1.062(5)	$A_1(1) = C(1)$ $A_1(2) = C(27)$	2.001(5)
AI(1) = IN(3) AI(2) = IN(3)	1.903(3) 1.075(5)	$A_1(2) - U(3)$	1.556(0)
AI(2) = IN(2) N(2) = AI(2) = N(2)	1.973(3)	AI(2) - H(2) N(1) - AI(1) - C(1)	1.310(10)
N(2) - AI(2) - N(3)	86.3(2)	N(1) - AI(1) - C(1)	122.4(2)
N(2) - AI(2) - C(37)	115.4(2)	N(2) - AI(1) - C(1)	108.5(2)
N(3) - Al(2) - C(37)	110.1(2)	N(3) - AI(1) - C(1)	113.6(2)
N(1) - AI(1) - N(2)	107.8(2)	AI(1) - N(2) - AI(2)	93.0(2)
N(1) - Al(1) - N(3)	111.5(2)	Al(1) - N(3) - Al(2)	93.0(2)
N(2) - Al(1) - N(3)	87.0(2)		
2			
Al(1) - N(1)	1.973(2)	Al(2) - N(1)	1.961(2)
AI(1) - N(2)	1.987(2)	A1(2) - N(2)	1.978(2)
$A_{1}(1) - C(1)$	1 985(3)	$A_1(2) - C(25)$	1 991(3)
$A_{1}(1) - H(1)$	1 51(3)	$A_1(2) - H(2)$	147(3)
C(1) - A(1) - N(1)	118 89(10)	C(25) - A1(2) - N(2)	122 17(10)
C(1) - AI(1) - N(2)	117 31(10)	C(25) - A1(2) - H(2)	1167(11)
C(1) = A1(1) = H(2) C(1) = A1(1) = H(1)	117.51(10) 115.6(10)	N(2) - A(2) - N(1)	84 35(0)
N(1) = A1(1) = N(2)	22 82(0)	N(2) = A1(2) = H(2)	101.6(11)
N(1) - AI(1) - IN(2) N(1) - AI(1) - II(1)	100.7(11)	N(2) = AI(2) = H(2) N(1) = AI(2) = H(2)	101.0(11) 104.0(11)
N(1) - AI(1) - H(1) N(2) - AI(1) - H(1)	109.7(11) 107.2(10)	N(1) - AI(2) - H(2)	104.9(11)
N(2) = AI(1) = H(1)	107.2(10)	AI(1) = N(1) = AI(2)	89.30(10)
C(25) - AI(2) - N(1)	121.34(11)	AI(1) - N(2) - AI(2)	88.48(9)
3			
Al(1) - P(1)	2.428(2)	Al(2) - P(1)	2.436(2)
Al(1) - P(2)	2.442(2)	Al(2) - P(2)	2.425(2)
Al(1) - H(1)	1.43(6)	Al(2) - H(2)	1.49(6)
Al(1)-C(1)	1.980(5)	Al(2) - C(31)	1.981(5)
P(1) - Al(1) - P(2)	82.93(7)	P(1) - Al(2) - C(31)	120.1(2)
P(1) - Al(1) - H(1)	110(2)	P(1) - Al(2) - H(2)	97(2)
P(1) - Al(1) - C(1)	122.1(2)	P(2) - Al(2) - C(31)	123.8(2)
P(2) - Al(1) - H(1)	106(2)	P(2) - Al(2) - H(2)	100(2)
P(2) - Al(1) - C(1)	121.0(2)	C(31) - Al(2) - H(2)	123(2)
C(1) - Al(1) - H(1)	111(2)	Al(1) - P(1) - Al(2)	91.44(8)
P(1) - Al(2) - P(2)	83.13(7)	Al(1) - P(2) - Al(2)	91.38(8)
<i>c</i>			
$O_{A1(1)-C(1)}$	1 085(8)	$\Lambda_{2}(1) = \Lambda_{1}(2) = C(25)$	120.0(3)
$A_1(1) = A_2(2)$	1.905(0)	$A_1(2) = A_2(1)$	120.0(3)
AI(1) = AS(2) AI(1) = AS(2)	2.433(3)	A1(2) - As(1)	2.403(3)
AI(1) - AS(3)	2.510(5)	A1(2) - As(3)	2.341(3)
AI(1) - AS(4)	2.539(3)	AI(2) = AS(4)	2.512(5)
AI(2) = C(25)	1.985(8)	As(1) - As(2)	2.4453(14)
As(3) - Al(1) - As(2)	101.35(10)	As(1) - Al(2) - As(4)	101.01(9)
As(3) - Al(1) - As(4)	/6.53(/)	As(4) - Al(2) - C(25)	125.0(3)
As(3) - Al(1) - C(1)	123.5(2)	AI(1) - As(3) - AI(2)	88.25(8)
As(2) - Al(1) - C(1)	120.3(2)	AI(1) - As(4) - AI(2)	88.39(9)
As(2) - AI(1) - As(4)	102.18(10)	C(49) - As(1) - As(2)	96.2(2)
As(4) - Al(1) - C(1)	123.5(3)	C(49) - As(1) - Al(2)	98.1(2)
As(3) - Al(2) - As(1)	101.70(9)	C(55) - As(2) - As(1)	97.1(2)
As(3) - Al(2) - As(4)	76.58(7)	C(55) - As(2) - Al(1)	100.4(2)
As(3) - Al(2) - C(25)	123.0(3)	As(1) - As(2) - Al(1)	102.39(7)

yellow microcrystals. The hexane or ether solvents of crystallization may be removed completely by pumping under reduced pressure (*ca.* 0.01 mm Hg for *ca.* 4 h). Yield: 21%. Mp ($\mathbf{6} \cdot 2\text{Et}_2\text{O}$): turns red at 160 °C, melts with gas evolution at 185–7 °C to form a dark red liquid. Spectroscopic data for $\mathbf{6} \cdot 2\text{Et}_2\text{O}$: IR: $v_{\text{AsH}} = 2148(\text{w}) \text{ cm}^{-1}$. ¹H NMR (C₆D₆): 7.85 (m, AsPh, 4H), 7.21 (t, *p*-H, 2H, ³J_{HH} = 7.5 Hz), 6.95, 6.94 [s, *m*-H(Mes), 4H each], 6.95 (m, AsPh, 4H), 6.88 (d, *m*-H, 4H), 6.78 (t, AsPh, 4H), 3.25 (q, CH₂O, 8H, ³J_{HH} = 6.6 Hz), 2.29, 2.15, 1.59 [s, CH₃(Mes), 12H each], 1.11 (t, OCH₂CH₃, 12H). ¹³C{¹H} NMR: 152.0, 144.7, 142.7, 136.4, 136.2, 130.4 (quaternary carbons), 136.8, 134.9, 130.2, 129.7, 129.3, 128.0, 127.9, 127.8, 127.4, 126.0 (aromatic C—H), 65.9 (OCH₂), 21.8, 21.2, 21.1 [CH₃(Mes)], 15.6 (OCH₂CH₃).

Heating of the mixture to $160 \degree C$ for 3-5 min until it begins to turn orange appears to be essential for the formation of **6**. In a separate experiment, in which the reaction mixture was heated to only $110-120 \degree C$ for 20 min, **6** was isolated in only 4% yield.

X-ray structure determinations

Crystals of $1 \cdot 0.25$ hexane, $2 \cdot 0.5$ toluene, 3 and $6 \cdot 2Et_2O$ were removed from the Schlenk tube under a stream of N₂ and immediately covered with a layer of hydrocarbon oil.¹³ A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low temperature nitrogen stream as described in ref. 13. The data for $1 \cdot 0.25$ hexane were collected at 130 K with a Siemens P4-RA diffractometer (nickel foil monochromator) and the data for $2 \cdot 0.5$ toluene, 3 and $6 \cdot 2Et_2O$ at 130 K with a Syntex P2₁ diffractometer (graphite monochromator) using CuK α ($\lambda = 1.54178$ Å) radiation.

Crystallographic programs used for the structure solutions were those of the SHELXTL Version 5.03 (Siemens, 1994) program package. Scattering factors were obtained from ref. 14. Absorption corrections were applied by using the method described in ref. 15. Some details of the data collections and refinements are given in Table 1 and selected bond distances and angles are given in Table 2. Further details are provided in the supplementary material, CCDC reference number 440/ 061. The structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically except for the disordered solvent molecules in $1 \cdot 0.25$ hexane and $6 \cdot 2Et_2O$ (for details see supplementary material). Hydrogen-atoms attached to the carbons were included in the refinement at calculated positions using a riding model. Heteroatom-bound hydrogen atoms were generally located in the Fourier maps and refined freely with fixed thermal isotropic parameters except for H(2) and H(1N) in $1 \cdot 0.25$ hexane whose Al(2)-H(2) and N(1)—H(1N) distances were also restrained.

Results

Syntheses

The reaction of $(H_2AlC_6H_3-2,6-Mes_2)_2$ with H_2NPh (aniline) at room temperature in toluene afforded a small amount of the asymmetric product 1 in addition to the expected product 2. The formation of 1 may be rationalized by the presence of a small excess of aniline. In contrast, reaction of (H₂AlC₆H₃-2,6-Mes₂)₂ with excess H₂PPh at 150 °C gave only the mixed aluminum hydride-phosphide 3 with elimination of H_2 . Significantly, no reaction was observed at room temperature. Heating of 3 to its melting point (235-6 °C) did not lead to the elimination of a further equivalent of H₂ but to the loss of H_2 PPh with decomposition. Heating of an NMR sample of 3 to 85 °C did not change the coupling pattern in the ${}^{31}P$ spectrum, indicating little or no dissociation in solution at this temperature. In contrast to H₂PPh, H₂AsPh reacts with the alane at room temperature to give 4, which was identified by IR and NMR spectroscopy. In the presence of Et₂O the adduct 5 is formed, for which only a relatively low quality X-ray data set could be obtained. A ¹H NMR spectrum of 5 indicates loss of Et₂O in solution and formation of 4 [eqn. (2)]:

2,6-Mes₂H₃C₆(H)AlAs(H)Ph · OEt₂
$$\rightleftharpoons$$

5
1/2 [2,6-Mes₂H₃C₆Al(H){ μ -As(H)Ph}]₂ + Et₂O (2)

4

Addition of *ca.* one equiv. Et₂O to a solution of **4** in C_6D_6 gave an NMR spectrum very similar to that of **5** in C_6D_6 . Attempted elimination of a further equivalent of H₂, by heating the reaction mixture of (H₂AlC₆H₃-2,6-Mes₂)₂ and excess H₂AsPh to 150–160 °C, gave the unusual cage compound **6** · 2Et₂O, featuring an As—As bond in the As₄Al₂ core in which all the aluminum hydrogens have been eliminated.

1.0.25 hexane. The structure of 1 (Fig. 1) is composed of dimeric molecules in which the four-coordinate aluminum centers are bridged by two -N(H)Ph groups to form an almost perfectly planar $\mathrm{Al}_2\mathrm{N}_2$ core. Each aluminum is also bound to a $-C_6H_3$ -2,6-Mes₂ substituent. However, the aluminum coordination is completed by bonding to terminal hydride for Al(2) and to terminal amide -N(H)Ph for Al(1). The coordination of the metals is thus distorted tetrahedral in each case. Within the Al_2N_2 core the Al-N distances are in the range 1.963(5)-1.983(5) Å. The internal angles at Al(1) and Al(2) are $87.0(2)^{\circ}$ and $86.3(2)^{\circ}$ and those at N(2) and N(3) are both 93.0(2)°. The Al-C distances are essentially identical and average 2.000(5) Å; the Al(2)-H(2) distance is 1.52(1) Å. The terminal Al(1)-N(1) distance is 1.833(6) Å and there is approximately planar coordination at N(1). Other selected bond distances and angles may be found in Table 2.

2.0.5 PhMe. The structure of **2** (Fig. 2) has many similarities to that of **1**. The major differences are that in **2** both aluminums are bound to a terminal hydride ligand and the Al_2N_2 core is folded with a fold angle along the Al(1)-Al(2) axis of 139.5°. The Al-N bond lengths [range 1.961(2)-1.987(2) Å] within the Al_2N_2 unit are almost identical to those in **1**. The Al-C and Al-H distances average 1.988(4) and 1.49(3) Å, respectively. The $-C_6H_3$ -2,6-Mes₂ aluminum substituents adopt a *cis* orientation across the Al_2N_2 core, as do the two nitrogen phenyl substituents.

3. The structure of the bridged phosphido derivative 3 (Fig. 3) is very similar in its overall configuration to that of 2 in that the two pairs of $-C_6H_3$ -2,6-Mes₂ and Ph substituents each have mutually *cis* orientations but are *trans* with respect to each other. The Al₂P₂ unit, like its Al₂N₂ counterpart in 2, also is folded in a similar manner with a fold angle of 143.3° along the Al(1)-Al(2) vector. The internal ring angles at aluminum and phosphorus average 83.03(10) and 91.41(3)°. The Al-P and Al-C distances average 2.433(5) and 1.981(5) Å. The Al-H distances of 1.43(6) and 1.49(6) Å are comparable to those in 1 and 2 and the P-H distances are both 1.31(6) Å.

6.2Et₂O. The structure of **6** (Fig. 4) has a number of features in common with that of **3**. First, the cyclic $[Al(C_6H_3-2,6-Mes_2)As(H)Ph]_2$ unit is quite similar to the overall structure of **3** since there is the same *cis-trans* relationship involving the $-C_6H_3-2,6-Mes_2$ and Ph substituents. Moreover, the Al₂As₂



Fig. 1 Computer generated drawing of 1. Important bond distances and angles are given in Table 2



Fig. 2 Computer generated drawing of 2. Important bond distances and angles are given in Table 2



Fig. 3 Computer generated drawing of 3. Important bond distances and angles are given in Table 2



Fig. 4 Computer generated drawing of **6**. Important bond distances and angles are given in Table 2

core is folded in a similar manner although the amount of folding (fold angle of 119.4°) is substantially more than that in **3**. The structure of **6** is completed by the 'diarsene' PhAs(1)As(2)Ph unit in which each arsenic is bound to a single aluminum atom. The internal angles within the Al(1)Al(2)As(3)As(4) ring may average 76.55(8)° at aluminum and 88.32(9)° at arsenic and the Al—As distances average 2.53(1) Å. The Al—As bonds to the PhAsAsPh moiety average slightly shorter than 2.459(5) Å. These arsenics possess distorted trigonal pyramidal coordination with Σ° As(1) = 297.1° and Σ° As(2) = 299.9°. The As—As bond length is 2.4453(14) Å.

Discussion

The following compounds are the focus of this discussion: $2,6-Mes_{2}H_{3}C_{6}\{Ph(H)N\}Al\{\mu-N(H)Ph\}_{2}Al(H)C_{6}H_{3}-2,6-Mes_{2}$ $[2,6-Mes_2H_3C_6(H)Al{\mu-N(H)Ph}]_2$ [2,6-(1). (2). $Mes_{2}H_{3}C_{6}(H)Al\{\mu-P(H)Ph\}]_{2}$ (3), [2,6- $Mes_{2}H_{3}C_{6}(H)Al(\mu-H)Ph\}]_{2}$ $As(H)Ph]_{2}$ (4), 2,6-Mes₂H₃C₆(H)Al{As(H)Ph}(OEt_{2}) (5) and $(2,6-\text{Mes}_2\text{H}_3\text{C}_6\text{Al})_2\{\mu-\text{As}(\text{H})\text{Ph}\}_2(\mu-\text{PhAsAsPh})$ (6). Previous work in a number of areas has shown that large terphenyl groups can often stabilize compounds with coordination numbers or bonding that are not known with other currently available ligands. A recent example is provided by the group 13 metal derivative InC_6H_3 -2,6- $Trip_2$ ($Trip = -C_6H_3$ -2,4,6iso-Pr₃),¹⁶ which features a one-coordinate metal in the solid, whereas the corresponding $-C(SiMe_3)_3$ derivative $[In{C(SiMe_3)_3}]_4$ is tetrameric with an In₄ tetrahedrane structure.¹⁷ In the context of group 13 metal hydride chemistry it has been shown that the reaction of $(H_2AlMes^*)_2$ ¹⁸ with H_2EPh (E = N, P or As) led to the monomer ${Ph(H)N}_{2}AlMes^{*}$ and the ring compounds ${PhNAlMes^{*}}_{2}$, (PhPAlMes*)₃ and (PhAsAlMes*)₃.⁹ It has also been demonstrated that the aluminum halide or hydride derivatives of the Mes* ligand and those of terphenyl ligands such as -C₆H₂-2,4,6-Ph₃, $-C_6H_3$ -2,6-Mes₂ or $-C_6H_3$ -2,6-Trip₂ ¹⁰ have different structures and reactivity. We now extend these investigations to the interaction of these terphenyl alanes with $H_2EPh (E = N, P \text{ or } As)$ species.

Interaction of H_2NPh with $(H_2AlC_6H_3-2,6-Mes_2)_2$ in an approximate 2:1 ratio led to the products 1 and 2. Only small amounts of 1 were observed, however, and the major product of the reaction is the symmetrical amide-hydride dimer 2. The stability of 2 may be contrasted with the corresponding Mes* derivative.⁹ When H_2NPh is reacted with $(H_2AlMes^*)_2$ in a 2:1 ratio the only product isolated was the bisamide ${Ph(H)N}_{2}$ AlMes*, in addition to some unreacted $(H_2AlMes^*)_2$. The structures of both 1 and 2 thus provide unique instances of stable group 13 compounds with geminal hydrido and primary amide groups. Such compounds are prone to a rearrangement reaction as seen in the H₂NPh + $(H_2AlMes^*_2)_2$ or hydrogen elimination reactions.⁹ Apparently, the $-C_6H_3$ -2,6-Mes₂ substituent has the appropriate steric requirements to stabilize the compounds against these reaction pathways. Moreover, since previous work has indicated that a single $-C_6H_3$ -2,6-Mes₂ substituent is not as effective as -Mes* at preventing further coordination at aluminum,¹⁰ it seems probable that the stability of 1 and 2 is a result of their dimerized configurations in which the metals are four-coordinate and less prone to further reaction than a putatively monomeric species such as HAl{N(H)Ph}Mes*. The symmetric dimer 2 readily undergoes hydrogen elimination at its melting point of 162 °C. This process eventually results in pale yellow glassy material, which dissolves in hydrocarbon solvent. The ¹H NMR revealed a 1:1 ratio of Ph and $-C_6H_3$ -2,6-Mes₂ with no Al-H resonances being observed. The IR spectrum also shows no Al-H stretching absorptions. Possibly, the glassy material contains an imide of formula (PhNAlC₆H₃-2,6-Mes₂)_n.

The structural parameters for 1 and 2 are within normal ranges. For instance, the terminal Al(1)-N(1) distance in 1, 1.833(6) Å, is very close to the reference value (1.81 Å) for a normal Al-N bond to four-coordinate aluminum.¹⁹ The bridging Al-N distances in both 1 and 2 are close to the 1.96 Å observed in the dimers $(Me_2AINMe_2)_2^{20}$ or the 1.97 Å in ${Al(NMe_2)_3}_2$ ²¹ The Al-C and Al-H distances are also very similar to those previously reported for (H2AlC6H3-2,6- Mes_2 ₂.¹⁰ Both 1 and 2 have the same arrangement of (bridging) amide phenyl and aluminum $-C_6H_3$ -2,6-Mes₂ substituents whereby the two amide phenyls are on one side of the Al₂N₂ core and the two $-C_6H_3$ -2,6-Mes₂ are on the opposite side. Their relative orientation is seen to best advantage in Fig. 2. It is apparent that the $-C_6H_3$ -2,6-Mes₂ groups are oriented essentially perpendicular to each other. The folding of the Al₂N₂ unit is also readily apparent as is the orientation of the -N(H)Ph phenyls perpendicular to the core. It can be seen in Fig. 2 that the -N(H)Ph phenyl rings to some extent eclipse and sterically interact with the orthomesityl groups of the C(1)-C₆H₃-2,6-Mes₂ ligand. This is reflected in the asymmetry of the Al(1)-N-C and Al(2)—N—C angles, which differ by $ca. 14^{\circ}$.

The phosphido complex 3 has a structure very similar to that of 2 in that the -Ph and $-C_6H_3$ -2,6-Mes₂ substituents have similar orientations with respect to the dimeric core unit. The average Al-P distance of 2.433(5) Å is very close to the predicted value, 2.43 Å,¹⁹ for these type of bonds and to the average Al-P distances in complexes such as $(Me_2AlPMe_2)_3$,²² (2.43 Å) or $\{(Me_3Si)_2AlPPh_2\}_2$ (2.452 Å).²³ The length of the Al-P bonds in comparison to the Al-N bond lengths in 2 allows a more sterically relaxed structure and this is reflected in the almost equal Al-P-C angles, which differ only by 4.8° for P(1) and by 1.6° for P(2).

The arsenido complex 4 could be isolated in poor yield from the reaction of H_2AsPh with $(H_2AlC_6H_3-2,6-Mes_2)_2$. This reaction takes place at room temperature in contrast to the corresponding reaction with H₂PPh which requires heating to ca. 150 °C to obtain 3. Unfortunately, crystals of 4 of sufficient size for an X-ray structure determination have not been obtained. If 4 is synthesized in the presence of Et₂O, however, the adduct 5 is produced, which may also be synthesized by the simple addition of Et₂O to 4. ¹H NMR studies of 5 indicate an equilibrium in accordance with eqn. (2) in which the ether is lost to afford 4. A good quality X-ray data diffraction set was not obtained for 5 owing to deterioration of crystal quality, which is probably a result of desolvation and disorder problems. However, sufficient data were obtained to confirm that the aluminum was bound to OEt_2 (Al-O = 1.89 Å), $-As(H)Ph_{1}$ (Al-As = 2.48 Å) and $-C_{6}H_{3}$ -2,6-Mes₂ $(A1-C = 2.01 \text{ \AA})$ with the remaining tetrahedral site occupied by a hydrogen that was not located.

Heating the reaction mixture of $(H_2AlC_6H_3-2,6-Mes_2)_2$ and excess H_2AsPh to 150–160 °C gives the cage species 6. This unique compound, which is the first structurally characterized aluminum arsenic cluster, is related to the gallium–arsenic cluster 7,²⁴ which also features an As—As bond. The latter is formed by the reaction in eqn. (3):

$$GaR_{3} + H_{2}AsPh \rightarrow [(PhAsH)(R_{2}Ga)(PhAs)_{6}(RGa)_{4}] \quad (3)$$
7

where R is $-CH_2SiMe_3$. It has a Ga_5As_7 core composed of two differing, nonplanar, five-membered rings linked by three Ga—As bonds. In contrast, the As_4Al_2 basket-like core in **6** has a less complicated structure with the As—As moiety acting as the 'handle' for the Al(1)Al(2)As(3)As(4) 'basket'. Within the 'basket' the Al—Al distances of 2.53(1) Å are very similar to those in other compounds involving arsenide ligands bridging four-coordinate aluminum centers.²⁵ The shorter (by *ca.* 0.07 Å) aluminum–arsenic bonds to the As(1) and As(2) atoms are attributable to their lower (*i.e.*, three) coordination number. The As—As distance of 2.4453(14) Å is normal for an As—As single bond.²⁶

Conclusions

The reactions between $(H_2AlC_6H_3-2,6-Mes_2)_2$ and H_2EPh (E = N, P or As) differ from the corresponding reactions with the bulky primary alane $(H_2AlMes^*)_2$. Essentially, elimination of the second equivalent of hydrogen to give rings featuring three-coordinate metals is not observed for the terphenyl substituted compounds. Instead, either thermal decomposition or the substitution of some or all of the remaining hydrogens (*e.g.*, in 1 or 6) in the presence of an excess of H_2EPh is observed. The stability of the compounds toward elimination of the second equivalent of H_2 is attributed to the dimerization of the amide, phosphide and arsenide derivatives, which gives four-coordinate metal species that are especially stable.

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