

Interaction of the bulky alane ($\text{H}_2\text{AlC}_6\text{H}_3\text{-2,6-Mes}_2$) ($\text{Mes} = \text{-C}_6\text{H}_3\text{-2,4,6-Me}_3$) with H_2EPh ($\text{E} = \text{N, P or As}$)

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The reactions of the bulky primary alane ($\text{H}_2\text{AlC}_6\text{H}_3\text{-2,6-Mes}_2$) ($\text{Mes} = \text{-C}_6\text{H}_3\text{-2,4,6-Me}_3$) with H_2EPh ($\text{E} = \text{N, P or As}$) are described. With aniline, H_2NPh , the dimeric products $2,6\text{-Mes}_2\text{H}_3\text{C}_6\{\text{Ph(H)N}\}\text{Al}\{\mu\text{-N(H)Ph}\}_2\text{Al(H)C}_6\text{H}_3\text{-2,6-Mes}_2$ (**1**) and $[2,6\text{-Mes}_2\text{H}_3\text{C}_6\{\text{H}\}\text{Al}\{\mu\text{-N(H)Ph}\}]_2$ (**2**) are obtained. The structures of both **1** and **2** feature two $\text{-C}_6\text{H}_3\text{-2,6-Mes}_2$ 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 $[2,6\text{-Mes}_2\text{H}_3\text{C}_6\{\text{H}\}\text{Al}\{\mu\text{-P(H)Ph}\}]_2$ (**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 $2,6\text{-Mes}_2\text{H}_3\text{C}_6\{\text{H}\}\text{Al}\{\text{As(H)Ph}\}(\text{OEt}_2)$ for which a partial X-ray structure was determined. Thermolysis of **2**, **3** and **4** led to decomposition. However, heating ($\text{H}_2\text{AlC}_6\text{H}_3\text{-2,6-Mes}_2$) with excess H_2AsPh led to the unique cluster ($2,6\text{-Mes}_2\text{H}_3\text{C}_6\text{Al}\})_2\{\mu\text{-As(H)Ph}\}_2\{\mu\text{-PhAsPh}\}$ 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 -NR_2 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 H_2GaMes^* ($\text{Mes}^* = \text{-C}_6\text{H}_2\text{-2,4,6-tert-Bu}_3$), HMMes_2^* ($\text{M} = \text{Al}^6$ or Ga^7) and $\text{HAL}(\text{Mes}^*)\text{N}(\text{SiMe}_3)_2$.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):



The stability of a primary metallane such as $(\text{H}_2\text{AlMes}^*)_2$ 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 ($\text{H}_2\text{AlC}_6\text{H}_3\text{-2,6-Mes}_2$)¹⁰ ($\text{Mes} = \text{-C}_6\text{H}_3\text{-2,4,6-Me}_3$) and a range of reactions of this compound with H_2EPh , ($\text{E} = \text{N, P or As}$) are described. It is shown that they are quite different from the corresponding reactions of $(\text{H}_2\text{AlMes}^*)_2$ 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 sodium-potassium alloy and degassed twice before use. ($\text{H}_2\text{AlC}_6\text{H}_3\text{-2,6-Mes}_2$)₂,¹⁰ H_2PPh ¹¹ and H_2AsPh ¹² were synthesized by literature methods. Aniline was obtained from a commercial supplier and dried by standard procedures. ^1H , ^{13}C and ^{31}P NMR spectra were recorded in C_6D_6 or C_7D_8 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-Mes₂H₃C₆{Ph(H)N}Al{μ-N(H)Ph}₂Al(H)C₆H₃-2,6-Mes₂ (1**) and [2,6-Mes₂H₃C₆{H}Al{μ-N(H)Ph}]₂ (**2**).** Aniline (0.137 mL, 1.5 mmol, 0.14 g) was added slowly *via* syringe to a solution of ($\text{H}_2\text{AlC}_6\text{H}_3\text{-2,6-Mes}_2$)₂ [prepared *in situ* by heating $(\text{Et}_2\text{O})\text{H}_2\text{AlC}_6\text{H}_3\text{-2,6-Mes}_2$ (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 (H_2) 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 $2 \cdot 0.5 \text{ PhMe}$. 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: $\nu_{\text{NH}} = 3275(\text{w})$, $3260(\text{w})$, $\nu_{\text{AlH}} = 1902(\text{st})$, $1859(\text{st}) \text{ cm}^{-1}$. ^1H NMR (C_6D_6): 7.16 (t, *p*-H, 2H, $^3J_{\text{HH}} = 7.5 \text{ Hz}$), 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 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**).** H_2PPh (0.22 mL, 2.0 mmol, 0.22 g) was added *via* syringe to finely ground $(\text{H}_2\text{AlC}_6\text{H}_3\text{-2,6-Mes}_2)_2$ (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** · 0.25 hexane, **2** · 0.5 toluene, **3** and **6** · 2Et₂O

	1 · 0.25 hexane	2 · 0.5 toluene	3	6 · 2Et ₂ O
Formula	C _{67.5} H _{72.5} Al ₂ N ₃	C _{63.5} H ₆₈ Al ₂ N ₂	C ₆₀ H ₆₄ Al ₂ P ₂	C ₈₀ H ₉₂ Al ₂ As ₄ O ₂
FW	979.75	913.16	901.01	1439.18
Space group	<i>P2₁/n</i>	<i>C2/c</i>	<i>Pbca</i>	<i>P2₁/c</i>
<i>a</i> /Å	13.873(6)	21.996(6)	13.718(4)	13.880(8)
<i>b</i> /Å	23.343(5)	13.089(3)	20.923(10)	45.59(2)
<i>c</i> /Å	18.733(6)	36.376(6)	35.886(7)	12.100(5)
β/°	107.48(3)	96.38(2)	—	112.20(3)
<i>U</i> /Å ³	5786(3)	10408(4)	10300(6)	7089(6)
<i>Z</i>	4	8	8	4
<i>T</i> /K	130(2)	130(2)	130(2)	130(2)
λ/Å	1.54178	1.54178	1.54178	1.54178
δ _{calcd} /g cm ^{−3}	1.125	1.166	1.162	1.349
μ/mm ^{−1}	0.766	0.810	1.370	2.791
<i>R</i> ₁ /%	8.49	6.14	7.35	7.13
<i>wR</i> ₂ /%	23.98	12.51	16.58	17.33
<i>R</i> ₁ = Σ <i>F</i> _o − <i>F</i> _c /Σ <i>F</i> _o ; <i>wR</i> ₂ = {Σ[<i>w</i> (<i>F</i> _o ² − <i>F</i> _c ²)]/Σ[<i>w</i> (<i>F</i> _o ²)]} ^{1/2}				

H₂PPh distills 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. The remaining colorless solid was dissolved in warm toluene (20 mL) and crystallized at −20 °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: ν_{PH} = 2355(w), ν_{AlH} = 1812(st), 1797(st) cm^{−1}. ¹H NMR (C₆D₆): 7.23 (t, *p*-H, 2H, ³*J*_{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). ¹³C{¹H} NMR (C₆D₆): 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), Δ*v* = 5.6 Hz], 129.7 (*p*-C), 128.7 [*m*-C(Mes)], 128.0 [^t' (AA'X), *o*- or *m*-C(PPh), Δ*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} ≈ 17 Hz). ³¹P NMR (C₆D₆): −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-Mes₂H₃C₆(H)Al{μ-As(H)Ph}]₂ (4**).** Finely ground (H₂AlC₆H₃-2,6-Mes₂)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: ν_{AsH} 2175(w), ν_{AlH} 1812(st), 1797(sh) cm^{−1}. ¹H NMR (C₆D₆): 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). ¹³C{¹H} 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-Mes₂C₆H₃(H)Al{As(H)Ph}(OEt₂) (5**).** H₂AsPh (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 · (OEt₂)₂] 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: ν_{AsH} 2088(m), ν_{AlH} 1805(m, br) cm^{−1}. The ¹H NMR spectrum (C₆D₆) 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 C₆D₆ solution of **4** to which 1 equiv. Et₂O per aluminum was added.

(2,6-Mes₂H₃C₆Al)₂[μ-As(H)Ph]₂(μ-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 (H₂AlC₆H₃-2,6-Mes₂)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** · 2Et₂O. Concentration of the supernatant to *ca.* 4 mL and crystallization in a −20 °C freezer for 2 weeks gave **6** · hexane (0.32 g) in the form of pale

Table 2 Selected bond distances (Å) and angles (°) for **1–3** and **6**

1			
Al(1)—N(1)	1.833(6)	Al(2)—N(3)	1.983(5)
Al(1)—N(2)	1.969(5)	Al(1)—C(1)	2.001(5)
Al(1)—N(3)	1.963(5)	Al(2)—C(37)	1.998(6)
Al(2)—N(2)	1.975(5)	Al(2)—H(2)	1.516(10)
N(2)—Al(2)—N(3)	86.3(2)	N(1)—Al(1)—C(1)	122.4(2)
N(2)—Al(2)—C(37)	115.4(2)	N(2)—Al(1)—C(1)	108.5(2)
N(3)—Al(2)—C(37)	110.1(2)	N(3)—Al(1)—C(1)	113.6(2)
N(1)—Al(1)—N(2)	107.8(2)	Al(1)—N(2)—Al(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)
Al(1)—N(2)	1.987(2)	Al(2)—N(2)	1.978(2)
Al(1)—C(1)	1.985(3)	Al(2)—C(25)	1.991(3)
Al(1)—H(1)	1.51(3)	Al(2)—H(2)	1.47(3)
C(1)—Al(1)—N(1)	118.89(10)	C(25)—Al(2)—N(2)	122.17(10)
C(1)—Al(1)—N(2)	117.31(10)	C(25)—Al(2)—H(2)	116.7(11)
C(1)—Al(1)—H(1)	115.6(10)	N(2)—Al(2)—N(1)	84.35(9)
N(1)—Al(1)—N(2)	83.83(9)	N(2)—Al(2)—H(2)	101.6(11)
N(1)—Al(1)—H(1)	109.7(11)	N(1)—Al(2)—H(2)	104.9(11)
N(2)—Al(1)—H(1)	107.2(10)	Al(1)—N(1)—Al(2)	89.36(10)
C(25)—Al(2)—N(1)	121.34(11)	Al(1)—N(2)—Al(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)
6			
Al(1)—C(1)	1.985(8)	Al(1)—Al(2)—C(25)	120.0(3)
Al(1)—As(2)	2.455(3)	Al(2)—As(1)	2.463(3)
Al(1)—As(3)	2.516(3)	Al(2)—As(3)	2.541(3)
Al(1)—As(4)	2.539(3)	Al(2)—As(4)	2.512(3)
Al(2)—C(25)	1.983(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)	76.53(7)	As(4)—Al(2)—C(25)	125.0(3)
As(3)—Al(1)—C(1)	123.5(2)	Al(1)—As(3)—Al(2)	88.25(8)
As(2)—Al(1)—C(1)	120.3(2)	Al(1)—As(4)—Al(2)	88.39(9)
As(2)—Al(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 (**6**·2Et₂O): turns red at 160 °C, melts with gas evolution at 185–7 °C to form a dark red liquid. Spectroscopic data for **6**·2Et₂O: IR: $\nu_{\text{AsH}} = 2148(\text{w}) \text{ cm}^{-1}$. 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, *J* = 7.5 Hz), 6.53 (d, AsPh, 4H, *J* = 7.8 Hz), 6.37 (br, s, 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 °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 °C for 20 min, **6** was isolated in only 4% yield.

X-ray structure determinations

Crystals of **1**·0.25 hexane, **2**·0.5 toluene, **3** and **6**·2Et₂O 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**·0.25 hexane were collected at 130 K with a Siemens P4-RA diffractometer (nickel foil monochromator) and the data for **2**·0.5 toluene, **3** and **6**·2Et₂O at 130 K with a Syntex P2₁ diffractometer (graphite monochromator) using CuKα ($\lambda = 1.54178 \text{ Å}$) 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**·0.25 hexane and **6**·2Et₂O (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**·0.25 hexane whose Al(2)—H(2) and N(1)—H(1N) distances were also restrained.

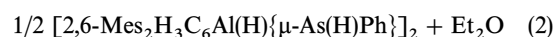
Results

Syntheses

The reaction of (H₂AlC₆H₃-2,6-Mes₂)₂ with H₂NPh (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 H₂. 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 H₂PPh with decomposition. Heating of an NMR sample of **3** to 85 °C did not change the coupling pattern in the ³¹P 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)]:



5



4

Addition of *ca.* one equiv. Et₂O to a solution of **4** in C₆D₆ gave an NMR spectrum very similar to that of **5** in C₆D₆. 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.

Structures

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 $-\text{N}(\text{H})\text{Ph}$ groups to form an almost perfectly planar Al_2N_2 core. Each aluminum is also bound to a $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$ substituent. However, the aluminum coordination is completed by bonding to terminal hydride for Al(2) and to terminal amide $-\text{N}(\text{H})\text{Ph}$ 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)° and 86.3(2)° 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 $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$ 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 $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$ and Ph substituents each have mutually *cis* orientations but are *trans* with respect to each other. The Al_2P_2 unit, like its Al_2N_2 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 $[\text{Al}(\text{C}_6\text{H}_3\text{-2,6-Mes}_2)\text{As}(\text{H})\text{Ph}]_2$ unit is quite similar to the overall structure of **3** since there is the same *cis-trans* relationship involving the $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$ and Ph substituents. Moreover, the Al_2As_2

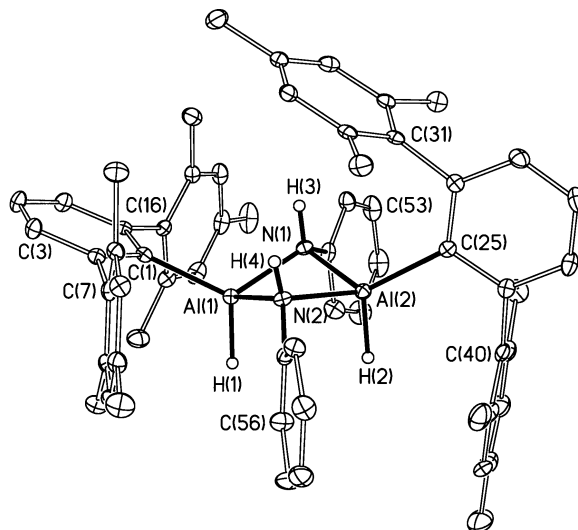


Fig. 2 Computer generated drawing of **2**. Important bond distances and angles are given in Table 2

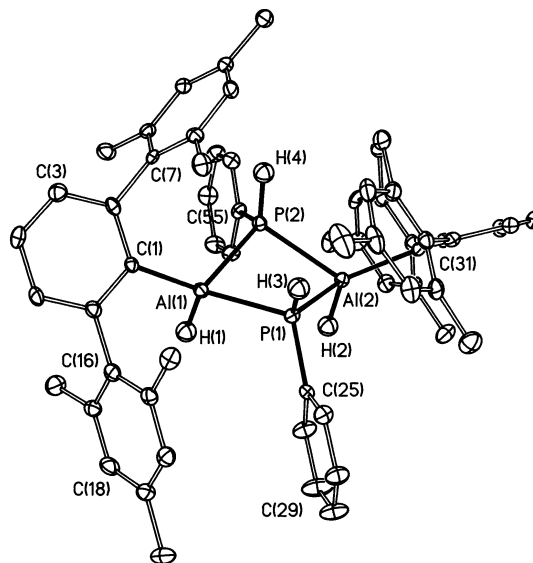


Fig. 3 Computer generated drawing of **3**. Important bond distances and angles are given in Table 2

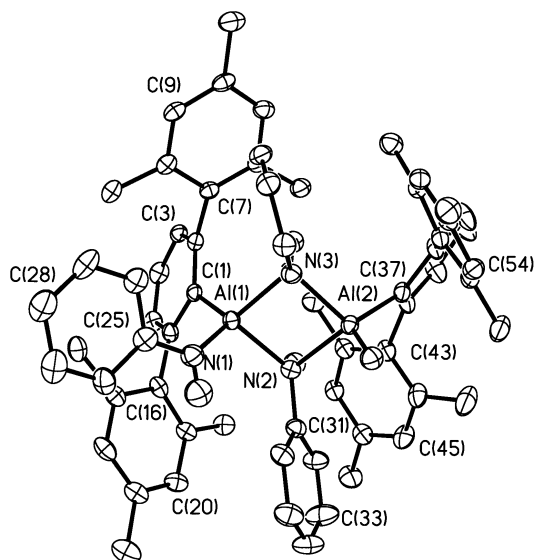


Fig. 1 Computer generated drawing of **1**. Important bond distances and angles are given in Table 2

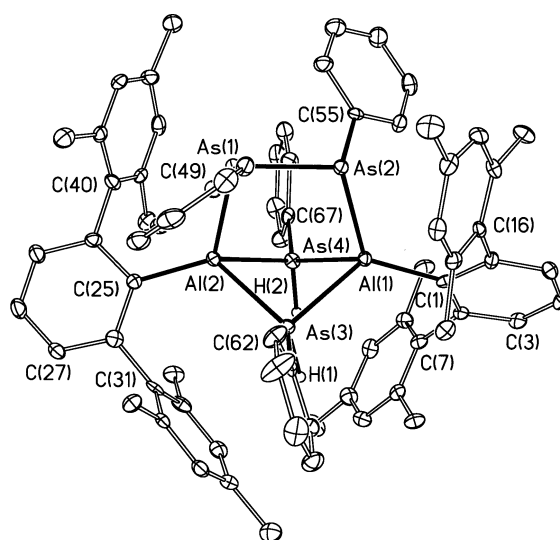


Fig. 4 Computer generated drawing of **6**. Important bond distances and angles are given in Table 2

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-Mes₂H₃C₆{Ph(H)N}Al{μ-N(H)Ph}₂Al(H)C₆H₃-2,6-Mes₂ (**1**), [2,6-Mes₂H₃C₆(H)Al{μ-N(H)Ph}₂]₂ (**2**), [2,6-Mes₂H₃C₆(H)Al{μ-P(H)Ph}₂]₂ (**3**), [2,6-Mes₂H₃C₆(H)Al{μ-As(H)Ph}₂]₂ (**4**), 2,6-Mes₂H₃C₆(H)Al{As(H)Ph}(OEt₂) (**5**) and (2,6-Mes₂H₃C₆Al)₂{μ-As(H)Ph}₂(μ-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 InC₆H₃-2,6-Trip₂ (Trip = —C₆H₃-2,4,6-*iso*-Pr₃),¹⁶ which features a one-coordinate metal in the solid, whereas the corresponding —C(SiMe₃)₃ derivative [In{C(SiMe₃)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 (H₂AlMes*)₂¹⁸ with H₂EPh (E = N, P or As) led to the monomer {Ph(H)N}₂AlMes* 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, —C₆H₃-2,6-Mes₂ or —C₆H₃-2,6-Trip₂¹⁰ have different structures and reactivity. We now extend these investigations to the interaction of these terphenyl alanes with H₂EPh (E = N, P or As) species.

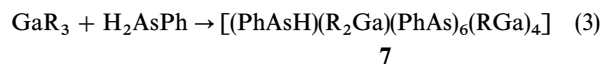
Interaction of H₂NPh with (H₂AlC₆H₃-2,6-Mes₂)₂ in an approximate 2 : 1 ratio led to the products **1** and **2**. Only small amounts of **1** were observed, however, and the major product of the reaction is the symmetrical amide-hydride dimer **2**. The stability of **2** may be contrasted with the corresponding Mes* derivative.⁹ When H₂NPh is reacted with (H₂AlMes*)₂ in a 2 : 1 ratio the only product isolated was the bisamide {Ph(H)N}₂AlMes*, in addition to some unreacted (H₂AlMes*)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 + (H₂AlMes*)₂ or hydrogen elimination reactions.⁹ Apparently, the —C₆H₃-2,6-Mes₂ substituent has the appropriate steric requirements to stabilize the compounds against these reaction pathways. Moreover, since previous work has indicated that a single —C₆H₃-2,6-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 —C₆H₃-2,6-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 (Me₂AlNMe₂)₂²⁰ or the 1.97 Å in {Al(NMe₂)₃}₂.²¹ The Al—C and Al—H distances are also very similar to those previously reported for (H₂AlC₆H₃-2,6-Mes₂)₂.¹⁰ Both **1** and **2** have the same arrangement of (bridging) amide phenyl and aluminum —C₆H₃-2,6-Mes₂ substituents whereby the two amide phenyls are on one side of the Al₂N₂ core and the two —C₆H₃-2,6-Mes₂ are on the opposite side. Their relative orientation is seen to best advantage in Fig. 2. It is apparent that the —C₆H₃-2,6-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 *ortho*-mesityl 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°.

The phosphido complex **3** has a structure very similar to that of **2** in that the —Ph and —C₆H₃-2,6-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 (Me₂AlPMe₂)₃,²² (2.43 Å) or {(Me₃Si)₂AlPPh₂}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 H₂AsPh with (H₂AlC₆H₃-2,6-Mes₂)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 OEt₂ (Al—O = 1.89 Å), —As(H)Ph (Al—As = 2.48 Å) and —C₆H₃-2,6-Mes₂ (Al—C = 2.01 Å) with the remaining tetrahedral site occupied by a hydrogen that was not located.

Heating the reaction mixture of (H₂AlC₆H₃-2,6-Mes₂)₂ and excess H₂AsPh 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):



where R is —CH₂SiMe₃. It has a Ga₅As₇ core composed of two differing, nonplanar, five-membered rings linked by three Ga—As bonds. In contrast, the As₄Al₂ 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 (H₂AlC₆H₃-2,6-Mes₂)₂ and H₂EPh (E = N, P or As) differ from the corresponding reactions with the bulky primary alane (H₂AlMes*)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 H₂EPh is observed. The stability of the compounds toward elimination of the second equivalent of H₂ is attributed to the dimerization of the amide, phosphide and arsenide derivatives, which gives four-coordinate metal species that are especially stable.

Acknowledgements

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