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Reactions of $(H_2AlMes^*)_2$ ($Mes^* = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$) with H_2EAr ($E = N$, P, or As; Ar = aryl): Characterization of the Ring Compounds $(Mes^*AlNPh)_2$ and $(Mes^*AlEPh)_3$ ($E = P$ or As)

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Abstract: The reaction between sterically crowded, dimeric, arylalane $(H_2AlMes^*)_2$ and some aryl amines, phosphines, or arsines are described. Treatment of $(H_2AlMes^*)_2$ ($Mes^* = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$) with the amines H_2NPh and H_2NDipp ($Dipp = 2,6\text{-}(i\text{-}Pr)_2C_6H_3$) affords the monomeric bis(amino)alane products $Mes^*Al(NHPh)_2\cdot Et_2O$ (**1**·Et_2O) and $Mes^*Al(NHDipp)_2$ (**2**) which feature three-coordinate aluminum and nitrogen centers and short Al−N bonds. Heating of a 1:1 mixture of H_2AlMes^* and aniline under carefully controlled conditions affords the dimer $(Mes^*AlNPh)_2$, **3**. Reaction of $(Mes^*AlH_2)_2$ with H_2PPh or H_2AsPh at *ca.* 160 °C gives the trimeric, six-membered-ring compounds $(Mes^*AlPPh)_3\cdot Et_2O$ (**4**·Et_2O) and $(Mes^*AlAsPh)_3\cdot Et_2O$ (**5**·Et_2O) which are formal valence analogues of borazine. The structure of **3** features a planar Al_2N_2 core, which also extends to the ipso carbons of the aryl rings; the Al−N distance is 1.824(2) Å. The structures of **4** and **5** have six-membered rings of alternating aluminum and phosphorus or arsenic atoms arranged in a nonplanar boat conformation. Little or no delocalization of the phosphorus or arsenic lone pairs is evident since the average Al−P and Al−As distances are consistent with single bond lengths. Moreover, pyramidal coordination is observed at all the pnictide centers. The structures of **5** and **4** represent respectively the first and second examples of bonding between three-coordinate aluminum and arsenic or phosphorus, whereas **3** represents a unique instance of an Al_2N_2 ring with organic substituents. The compounds were characterized by ^1H, ^{13}C, and ^{31}P (**4**, only) NMR spectroscopy and by X-ray crystallography in the case of **1**, **3**, **4**, and **5**. Crystal data with Cu Kα ($\lambda = 1.54178$ Å) radiation at 130 K: **1**, $a = 10.255(3)$ Å, $b = 16.733(5)$ Å, $c = 19.267(8)$ Å, $\beta = 95.09(3)°$, $V = 3293(2)$ Å^3, $Z = 4$, space group $P2_1/c$, 3070 ($I > 2\sigma(I)$) data, $R = 0.061$; **3**, $a = 8.750(1)$ Å, $b = 9.326(2)$ Å, $c = 14.025(3)$ Å, $\alpha = 101.04(2)°$, $\beta = 92.90(1)°$, $\gamma = 113.11(1)°$, $V = 1088.7(4)$ Å^3, $Z = 1$, space group $P\bar{1}$, 2629 ($I > 2\sigma(I)$) data, $R = 0.053$; **4**, $a = 9.383(5)$ Å, $b = 17.719(7)$ Å, $c = 23.603(14)$ Å, $\alpha = 80.86(4)°$, $\beta = 82.50(5)°$, $\gamma = 75.61°(4)$, $V = 3736(3)$ Å^3, $Z = 2$, space group $P\bar{1}$, 5626 ($I > 2\sigma(I)$) data, $R = 0.084$; **5**, $a = 9.404(7)$ Å, $b = 17.79(2)$ Å, $c = 23.643(10)$ Å, $\alpha = 81.01(6)°$, $\beta = 83.04(5)°$, $\gamma = 75.68(7)°$, $V = 3771(5)$ Å^3, $Z = 2$, space group $P\bar{1}$, 6363 ($I > 2\sigma(I)$) data, $R = 0.063$.

Introduction

The recent synthesis of well-characterized, sterically hindered, uncomplexed, primary alanes or gallanes such as $(Mes^*MH_2)_n$ ($M = Al^1$ ($n = 2$) or Ga,^{2} ($n = 1$)) and related species has provided a new, potentially important, source of starting materials from which new examples of main group III−V compounds (including main group III−V ring species) may be derived. Currently, inorganic main group III−V rings that are analogous to benzene are limited to relatively few types of molecules.[3] The best known example is borazine which was first reported in 1926.[4] Other main group III-V analogues were not reported until recently and the currently known range includes only the B−P (e.g. $(MesBPPh)_3$),[5] Al−N (the unique compound $\{MeAlN(2,6\text{-}(i\text{-}Pr)_2C_6H_3)\}_3$[6]), and Ga−P (the unique compound$\{2,4,6\text{-}Ph_3C_6H_2GaPC_6H_{11}\}_3$[7]) ring systems. Both the isoelectronic B−P and Al−N rings display planar geometries that extend to the carbon atoms bound directly to the ring. Recent calculations[8,9] on the hypothetical molecules $(HBPH)_3$ and $(HAlNH)_3$ and related species have indicated that in the ground state, at least, only the B−P system (which is not quite planar but has flattened pyramidal phosphorus coordination) has a significant resonance energy, which is slightly greater than that found in borazine.[8] In contrast, the six-membered Ga−P ring in $\{2,4,6\text{-}Ph_3C_6H_2GaPC_6H_{11}\}_3$[7] is not planar, instead it assumes a twist-boat geometry with normal single Ga−P bond lengths and pyramidal coordination at the phosphorus centers. In addition to the six-membered borazine analogues there are the related four-membered gallium−phosphorus ring species $(t\text{-}BuGaPMes^*)_2$[10] (Ga−P = 2.274(4) Å) and the compound $Cp^*\{(Me_3Si)_2N\}AlN(\mu\text{-}AlCp^*)(\mu\text{-}Al\{N(SiMe_3)_2\})NAlCp^*_2$[11] ($Cp^* = \eta^1\text{-}C_5Me_5$) that features a central Al_2N_2 ring with an

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average Al−N distance of 1.811(7) Å. There is no evidence for significant delocalization in these "antiaromatic' species.

The synthesis of further examples of unsaturated main group III−V ring systems has been slowed by limitations of previously known routes, which, to date, have proved inapplicable to other rings. From a wider perspective, there are relatively few compounds of any kind that have the low-coordination numbers that are expected in the title novel ring systems. For example, there are no well-characterized molecular compounds that feature bonding between three-coordinate aluminum and arsenic. Furthermore, there is only a single example of a structurally characterized compound with bonding between three-coordinate aluminum and phosphorus[12] and three-coordinate aluminum−nitrogen species are limited to a handful of compounds.[13]

In this paper the results of the interaction of the recently synthesized primary arylalane $(Mes^*AlH_2)_2$ with the primary pnictide derivatives H_2NPh, H_2NDipp (Dipp = 2,6-(*i*-Pr)$_2C_6H_3$), H_2PPh, and H_2AsPh are described. The most important result of these investigations is that the new ring compounds $(Mes^*AlNPh)_2$, $(Mes^*AlPPh)_3$, and $(Mes^*AlAsPh)_3$ (Mes* = 2,4,6-(*t*-Bu)$_3C_6H_2$) can be relatively easily isolated and characterized.

Experimental Section

General Procedures. All experiments were performed under a nitrogen atmosphere either by using modified Schlenk techniques or in a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled from a sodium−potassium alloy and degassed twice prior to use. ^{13}C, ^{1}H, and ^{31}P NMR spectra were recorded in C_6D_6 or C_7D_8 solutions by using a General Electric QE-300 spectrometer. The compounds $(Mes^*AlH_2)_2$,[1] H_2PPh,[14] and H_2AsPh[15] were synthesized by literature methods. The amines H_2NPh and H_2NDipp were obtained from commercial suppliers and dried by standard procedures.

Synthesis. (a) Mes*Al(NHPh)$_2$ (1). A solution of 0.69 g (1.25 mmol) of $(Mes^*AlH_2)_2$ in toluene (40 mL) was treated with H_2NPh (0.23 mL, 2.5 mmol) at room temperature. The H_2 evolution commenced immediately and ceased after *ca.* 15 min. The mixture was stirred for another 45 min, filtered, concentrated to *ca.* 5 mL, and cooled in a −20 °C freezer for 24 h to yield **1** as a colorless solid. Recrystallization from *ca.* 15 mL of Et_2O in a −20 °C freezer for 1 week results in colorless, X-ray quality plates of $Mes^*Al(NHPh)_2\cdot Et_2O$ (**1**·Et_2O) which lose solvent relatively easy. Yield: 0.11 g, 17%. Mp: softens at 85 °C, melts at 180−184 °C. ^1H NMR (C_6D_6): 7.57 (s, *m*-H (Mes*), 2H), 6.94 (t, 4H, J_{HH} = 7.8 Hz), 6.64 (partially obscured by signal at 6.61), 6.61 (d, 6H, J_{HH} = 7.8 Hz), 3.19 (s, NH, 2H), 1.55 (s, *o*-CH_3, 18H), 1.28 (s, *p*-CH_3, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): 158.6 (*o*-C (Mes*)), 151.9 (*p*-C (Mes*)), 150.1 (*i*-C (Ph)), 129.8 (*m*-C (Ph)), 122.0 (*m*-C (Mes*)), 117.4 (*p*-C (Ph)), 117.0 (*o*-C (Ph)), 37.9 (*o-C* $(CH_3)_3$), 34.9 (*p-C* $(CH_3)_3$), 32.3 (*o*-CH_3), 31.4 (*p*-CH_3). IR: ν_{NH} = 3361 cm^{-1}.

(b) Mes*Al(NHDipp)$_2$ (2). H_2NDipp (0.18 mL, 0.91 mmol, 0.16 g) was added via syringe to finely ground $(Mes^*AlH_2)_2$ (0.25 g, 0.46 mmol) at room temperature. After a few minutes a slight gas evolution was observed, whereupon the mixture became viscous. The flask was placed in a 100 °C oil bath to give a more intense gas evolution and a clear liquid. After 10 min the mixture had become viscous and gas evolution had ceased. After being cooled to room temperature, the glass-like solid was dissolved in n-hexane (20 mL), filtered, concentrated to *ca.* 3 mL, and cooled in a −20 °C freezer for 1 week to yield 0.26 g of a colorless microcrystalline solid which still contains some Mes*H. Recrystallization from *n*-hexane (5 mL) at *ca.* 5 °C for 1 week results in large colorless plates of $Mes^*Al(NHDipp)_2$. Yield: 0.08 g (28%). Mp: softens at 80 °C, melts at 95−104 °C. Anal. Calcd for $C_{42}H_{65}N_2Al$: C, 80.71; H, 10.48; N, 4.48. Found: C, 80.30; H, 10.63; H, 4.69. ^1H NMR (C_6D_6): 7.48 (s, *m*-H (Mes*), 2H), 7.08 (d, *m*-H (Dipp), 4H, $^3J_{HH}$ = 7.7 Hz), 6.97 (t, *p*-H (Dipp), 2H), 3.29 (sept, *H*-C $(CH_3)_2$, 4H, $^3J_{HH}$ = 6.9 Hz), 3.00 (s, NH, 2H), 1.59 (s, *o*-CH_3 (Mes*), 18H), 1.30 (s, *p*-CH_3 (Mes*), 9H), 1.08 (d, *o*-CH_3 (Dipp), 24H). $^{13}C\{^1H\}$ NMR (C_6D_6): 158.5 (*o*-C(Mes*)), 151.1 (*p*-C(Mes*)), 143.4 (*i*-C (Dipp)), 140.6 (*o*-C (Dipp)), 123.5 (*m*-C (Dipp)), 121.9, 121.5 (*m*-C (Mes*), *p*-C (Dipp)), 37.7 (*o-C* $(CH_3)_3$), 34.8 (*p-C* $(CH_3)_3$), 32.5 (*o*-CH_3 (Mes*)), 31.3 (*p*-CH_3 (Mes*)), 28.8 (*o*-CH), 23.5 (*o*-CH_3 (Dipp)). IR: ν_{NH} = 3348, 3363 cm^{-1}.

(c) (Mes*AlNPh)$_2$ (3). H_2NPh (0.17 mL, 1.9 mmol), 0.177 g) was added via syringe to a solution of 0.57 g (1.04 mmol) of $(Mes^*AlH_2)_2$ in 20 mL of ethylbenzene at 0 °C. Gas evolution (H_2) commenced immediately and ceased after *ca.* 5 min. The colorless solution was warmed to room temperature and stirred for 2 h. The flask was then placed in a preheated (125 °C) oil bath, without stirring. After a few minutes a smooth gas evolution occurred which was followed by the gradual formation of colorless needle-shaped crystals. The gas evolution appeared to cease after about 1 h. The mixture was maintained at 125 °C for an additional hour and slowly cooled to room temperature. The resultant crystals which reached lengths of up to 2 mm were of X-ray quality. Isolation of the crystals, followed by washing twice with 20 mL of *n*-pentane, resulted in 0.27 g of **3**. Yield: 39.1%. Mp: >300 °C. Anal. Calcd for $C_{48}H_{68}Al_2N_2$: C, 79.30; H, 9.43; N, 3.86. Found: C, 79.15; H, 9.26; N, 3.78. ^1H NMR (C_7D_8, 110 °C): 7.58 (s, *m*-H, 4H), 6.76 (t, *m*-H(Ph), 4H, J = 7.8 Hz), 6.54 ("t" *o*-H(Ph), 4H), $\Delta\nu$ = 6.0 Hz), 6.42 (t, *p*-H(Ph), 2H, *J* = 7.1 Hz), 1.71 (s, *o*-CH_3, 36H), 1.33 (s, *p*-CH_3, 18H).

(d) (Mes*AlPPh)$_3$·OEt$_2$ (4·Et$_2$O). H_2PPh (0.40 mL, 0.40 g, 3.6 mmol) was added via syringe to 0.50 g (0.9 mmol) of finely ground $(Mes^*AlH_2)_2$ at room temperature. The almost clear, slightly viscous, mixture was then placed in a preheated oil bath at 160 °C. Intense frothing commenced after *ca.* 1−2 min and continued for *ca.* 3 min after which time the mixture solidified. After cooling to room temperature, and removal of volatile fractions under reduced pressure (3 h), the pale yellow solid was dissolved in Et_2O (30 mL), filtered, and cooled to −20 °C overnight to afford colorless X-ray quality crystals, which easily lose solvent of crystallization. Yield: 0.38 g (52.1%). Mp: softens at 193 °C, melts at 241−2 °C. ^1H-NMR (C_6D_6): 7.53 (s, *m*-H, 6H), 7.14 (s, broad, *o*-H, PhP, 6H), 6.61 (m, *p*-H, PhP, 3H), 6.56 (m, *m*-H, PhP, 6H), 3.25 (q, OCH_2, trace, $^3J_{HH}$ = 6.9 Hz), 1.79 (s, *o*-CH_3, 54H), 1.32 (s, *p*-CH_3, 27H), 1.10 (t, CH_3, trace). $^{13}C\{^1H\}$ NMR (C_6D_6, 60 °C): 158.5 (*o*-C), 151.4 (*p*-C), 134.9 (*o*-C, PhP), 128.2 (*m*-C, PhP), 124.9 (*p*-C, PhP), 122.3 (*m*-C), 39.0 (*o*-*C*$(CH_3)_3$), 33.9 (*o*-CH_3), 31.4 (*p*-CH_3). ^{31}P NMR (C_6D_6): −144.2 (s).

(e) (Mes*AlAsPh)$_3$ (5). $PhAsH_2$ (7.6 mmol, 0.86 mL, 1.17 g) was added via syringe to finely ground $(Mes^*AlH_2)_2$ (1.9 mmol, 1.04 g) at room temperature. The Schlenk tube containing the resultant, slightly viscous, slurry was then placed in a preheated oil bath at 140 °C. After *ca.* 2 min the slurry became a clear liquid. The temperature was slowly raised and at 145 °C slight gas evolution was observed. This intensified when the temperature was raised to *ca.* 155−160 °C. After 2 min at this temperature the frothing liquid became yellow and then solidified. Gas evolution essentially ceased, indicating that the reaction process was essentially complete. After being cooled to room temperature the solid was placed under reduced pressure for *ca* 1 h, then for an additional hour at 100 °C. The yellow solid was dissolved in toluene (25 mL), and the small amount of insoluble material was filtered off. The pale yellow filtrate was concentrated to *ca.* 15−20 mL and cooled in a −20 °C freezer overnight to yield 0.58 g of fine colorless needles which lose co-crystallized solvent (PhMe) upon isolation. A second crop of *ca.* 0.1 g was isolated from the concentrated mother liquor upon further cooling for 3 days at −30 °C. X-ray quality crystals of **5**·Et_2O were grown from ether. Yield: 0.68 g (42%). Mp: turns orange at 208 °C, melts with a color change to red at 212−216 °C. The compound loses ether of crystallization when isolated. ^1H-NMR (C_6D_6, 60 °C): 7.53 (s, *m*-H, 6H), 7.15 (d, 6H, Ph, As, *J* = 7.5 Hz), 6.72 (t, 3H, Ph, As, *J* = 7.2 Hz), 6.61 (t, 6H, Ph, As, *J* =7.2 Hz), 3.33 (q, 2.5H, OCH_2, *J* = 6.9 Hz), 1.78 (s, *o*-CH_3, 54H), 1.36 (s, *p*-CH_3, 27H), 1.11 (t, CH_3CH_2, 3.7 H). $^{13}C\{^1H\}$-NMR, (60 °C): 158.5 (*o*-C), 151.3 (*p*-C), 137.9 (*i*-C, Mes* or Ph, As), 136.2 (*o*- or *m*-C, Ph, As), 132.3 (*i*-C, Mes* or Ph, As), 128.5 (*o*-or *m*-C, Ph, As), 125.3 (*p*-C,

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Table 1. Crystallographic Data for **1**·Et$_2$O, **3**, **4**·Et$_2$O, and **5**·Et$_2$O[a]

compound	**1**·Et$_2$O	**3**	**4**·Et$_2$O	**5**·Et$_2$O
formula	$C_{34}H_{51}AlN_2O$	$C_{48}H_{68}Al_2N_2$	$C_{76}H_{112}Al_3OP_3$	$C_{76}H_{112}Al_3As_3O$
fw	530.7	727.0	1215.51	1347.36
crystal description	colorless block	colorless plate	colorless needle	colorless needle
crystal dimens, mm	0.28 × 0.30 × 0.42	0.10 × 0.48 × 0.67	0.15 × 0.18 × 0.70	0.12 × 0.20 × 1.00
a, Å	10.255(3)	8.750(1)	9.383(5)	9.404(7)
b, Å	16.733(5)	9.326(2)	17.719(7)	17.79(2)
c, Å	19.267(8)	14.025(3)	23.603(14)	23.643(10)
α, deg		101.04(2)	80.86(4)	81.01(6)
β deg	95.09(3)	92.90(1)	82.50(5)	83.04(5)
γ, deg		103.11(1)	75.61(4)	75.68(7)
V, Å^3	3293(2)	1088.7(4)	3736(3)	3771(5)
Z	4	1	2	2
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
d(calc), g/cm^3	1.070	1.109	1.081	1.186
linear abs coeff, mm^{-1}	0.724	0.840	1.366	2.214
2θ range, deg	0−114	0−114	0−114	0−110
no. of obsd reflcns	3070 ($I > 2\sigma(I)$)	2629 ($I > 2\sigma(I)$)	5626 ($I > 2\sigma(I)$)	6363 ($I > 2\sigma(I)$)
no. of variables	343	244	744	779
R_1, R_w	0.061, 0.070	0.053, 0.144[b]	0.084, 0.185[b]	0.063, 0.134[b]

[a] The intensity data sets were collected at 130 K using a Syntex P2$_1$ diffractometer with Cu Kα (λ = 1.54178 Å) radiation. [b] R_w based on $F_o^2 - F_c^2$.

Ph, As), 122.0 (m-C), 39.1 (o-$C(CH_3)_3$), 34.9 (p-$C(CH_3)_3$), 33.9 (o-CH_3), 31.4 (p-CH_3).

X-ray Data Collection, the Solution and Refinement of the Structures

Crystals of **1** and **3**−**5** were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. Suitable crystals were selected, attached to a glass fiber by silicon grease, and immediately placed in the low-temperature N$_2$ stream.[16] X-ray data were collected with a Syntex P2$_1$ diffractometer equipped with a graphite monochromator and a locally modified LT apparatus. Calculations were carried out in a MicroVax 3200 computer using the SHELXTL-Plus program system (**1**) and on an IBM compatible 486 PC using the SHELXTL-94 program system for **3**, **4**, and **5**. Neutral atom scattering factors and the correction for anomalous dispersion were those supplied by SHELXTL-Plus or SHELXTL-94. Some details of the data collections and the refinements are provided in Table 1. Further details are in the supporting information. Structures of **1**, **3**, and **5** were solved by direct methods. The structure of **4** was solved by using the data set of **5** without the hydrogen atoms. The compounds were refined by full-matrix least-squares procedures. Hydrogen atoms were included by the use of a riding model with C−H distances of 0.96 Å and fixed isotropic thermal parameters. Important atom coordinates and bond distances and angles are given in Tables 2 and 3.

Results

Synthesis. A major objective of the work described here was the synthesis of the new ring compounds involving aluminum. It was felt that the use of $(Mes^*AlH_2)_2$[1] would prove a suitable starting material owing to the fact that, in reactions with primary amines, phosphines, or arsines, hydrogen would be the sole byproduct of the reaction thereby simplifying purification as depicted in eq 1.

$$(Mes^*AlH_2)_2 + 2H_2EPh \rightarrow (Mes^*AlEPh)_n + 4H_2 \quad (1)$$

$$(E = N, P, \text{ or } As)$$

For E = P or As the reactions between $(Mes^*AlH_2)_2$ and H_2PPh or H_2AsPh were relatively straightforward and **4** and **5** were readily obtained. The reactions proceeded under milder conditions ($ca.$ 125 °C for **3**, cf. 170 °C for $(MeAlNDipp)_3$[6]) than similar eliminations involving alkanes, which makes the possibility of side reactions less likely (vide infra for details). No attempts were made to isolate intermediates in the case of the

Table 2. Atom Coordinates (×10^4) for Important Atoms in **1**·Et$_2$O, **3**, **4**·Et$_2$O, and **5**·Et$_2$O

	x	y	z
	1·Et$_2$O		
Al(1)	1284(1)	1702(1)	6644(1)
O(1)	4372(3)	569(2)	7456(2)
N(1)	1474(3)	1250(2)	7491(2)
N(2)	2713(3)	1471(2)	6209(2)
C(1)	−259(4)	2329(2)	6297(2)
C(19)	829(4)	1352(3)	8090(2)
C(25)	2968(4)	1490(2)	5510(2)
	3		
Al(1)	4594(1)	9669(1)	5828(1)
N(1)	3855(2)	8944(2)	4546(1)
C(1)	3973(3)	9056(3)	7043(2)
C(2)	2912(3)	9719(3)	7596(2)
C(6)	4510(3)	7902(3)	7389(2)
C(19)	2602(3)	7803(3)	4056(2)
C(20)	1379(3)	7096(3)	4547(2)
C(24)	2480(3)	7297(3)	3038(2)
	4·Et$_2$O		
P(1)	4991(2)	1559(1)	1676(1)
Al(1)	4831(2)	1265(1)	2675(1)
P(2)	7536(2)	2906(1)	1922(1)
Al(2)	6900(2)	2174(1)	1299(1)
P(3)	5577(2)	2066(1)	3211(1)
Al(3)	5617(2)	3255(1)	2637(1)
C(1)	4037(8)	409(4)	3166(3)
C(19)	5203(7)	640(4)	1370(3)
C(25)	7874(8)	2161(4)	498(3)
C(43)	7973(8)	3782(4)	1474(3)
C(49)	4506(9)	4267(4)	2900(3)
C(67)	4183(8)	2159(4)	3838(3)
	5·Et$_2$O		
As(1)	4832(1)	1613(1)	1641(1)
Al(1)	4814(3)	1272(1)	2678(1)
As(2)	7722(1)	2887(1)	1945(1)
Al(2)	6922(3)	2183(1)	1285(1)
As(3)	5714(1)	2038(1)	3261(1)
Al(3)	5687(3)	3271(1)	2657(1)
C(1)	4036(8)	420(4)	3166(3)
C(19)	5138(8)	609(4)	1350(3)
C(25)	7888(8)	2157(4)	491(3)
C(43)	8095(9)	3841(4)	1465(3)
C(49)	4555(8)	4278(4)	2916(3)
C(67)	4131(8)	2174(4)	3883(3)

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(16) This method is described by: Hope, H. A Practicum in Synthesis and Characterization. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 375; American Chemical Society: Washington, DC, 1987; Chapter 10.

Table 3. Important Bond Distances (Å) and Angles (deg) in **1**·Et$_2$O, **3**, **4**·Et$_2$O, and **5**·Et$_2$O

	1·Et$_2$O		
Al(1)−N(1)	1.795(3)	O(1)−C(33)	1.415(6)
Al(1)−N(2)	1.794(4)	N(1)−C(19)	1.391(5)
Al(1)−C(1)	1.966(4)	N(2)−C(25)	1.394(5)
O(1)−C(31)	1.432(6)		
N(1)−Al(1)−N(2)	107.9(2)	C(31)−O(1)−C(33)	113.2(3)
N(1)−Al(1)−C(1)	123.7(2)	Al(1)−N(1)−C(19)	133.0(3)
N(2)−Al(1)−C(1)	128.5(2)	Al(1)−N(2)−C(25)	132.7(3)
	3		
Al(1)−N(1)	1.824(2)	Al(1)−Al(1a)	2.607(1)
Al(1)−N(1a)	1.824(2)	N(1)−C(19)	1.386(3)
Al(1)−C(1)	1.962(2)	N(1)−Al(1a)	1.824(2)
N(1)−Al(1)−N(1a)	88.75(9)	C(19)−N(1)−Al(1)	134.2(2)
N(1)−Al(1)−C(1)	133.5(1)	C(19)−N(1)−Al(1a)	134.6(2)
N(1a)−Al(1)−C(1)	137.7(1)	Al(1)−N(1)−Al(1a)	91.25(9)
C(1)−Al(1)−Al(1a)	176.91(8)		
	4·Et$_2$O		
P(1)−C(19)	1.840(7)	P(2)−Al(2)	2.328(3)
P(1)−Al(1)	2.325(3)	P(2)−Al(3)	2.336(3)
P(1)−Al(2)	2.332(3)	Al(2)−C(25)	1.990(7)
Al(1)−C(1)	1.994(6)	P(3)−C(67)	1.842(7)
Al(1)−P(3)	2.324(3)	P(3)−Al(3)	2.323(3)
P(2)−C(43)	1.838(7)	Al(3)−C(49)	1.985(8)
C(19)−P(1)−Al(1)	108.1(2)	C(25)−Al(2)−P(2)	120.3(2)
C(19)−P(1)−Al(2)	110.9(2)	C(25)−Al(2)−P(1)	125.0(2)
Al(1)−P(1)−Al(2)	113.4(1)	P(2)−Al(2)−P(1)	114.6(1)
C(1)−Al(1)−P(3)	112.8(2)	C(67)−P(3)−Al(3)	113.3(2)
C(1)−Al(1)−P(1)	128.2(2)	C(67)−P(3)−Al(1)	104.1(2)
P(3)−Al(1)−P(1)	118.9(1)	Al(3)−P(3)−Al(1)	108.1(1)
C(43)−P(2)−Al(2)	106.4(2)	C(49)−Al(3)−P(3)	121.0(2)
C(43)−P(2)−Al(3)	111.0(3)	C(49)−Al(3)−P(2)	134.3(2)
Al(2)−P(2)−Al(3)	111.6(1)	P(3)−Al(3)−P(2)	103.1(1)
	5·Et$_2$O		
As(1)−C(19)	1.957(8)	As(2)−Al(3)	2.428(3)
As(1)−Al(1)	2.432(3)	As(2)−Al(2)	2.435(3)
As(1)−Al(2)	2.433(3)	Al(2)−C(25)	1.985(7)
Al(1)−C(1)	1.990(7)	As(3)−C(67)	1.959(7)
Al(1)−As(3)	2.433(3)	As(3)−Al(3)	2.418(3)
As(2)−C(43)	1.971(7)	Al(3)−C(49)	1.990(8)
C(19)−As(1)−Al(1)	104.3(2)	C(25)−Al(2)−As(1)	123.9(2)
C(19)−As(1)−Al(2)	108.7(2)	C(25)−Al(2)−As(2)	119.9(2)
Al(1)−As(1)−Al(2)	109.4(1)	As(1)−Al(2)−As(2)	116.1(1)
C(1)−Al(1)−As(1)	127.8(2)	C(67)−As(3)−Al(3)	110.2(2)
C(1)−Al(1)−As(3)	111.1(2)	C(67)−As(3)−Al(1)	101.0(2)
As(1)−Al(1)−As(3)	121.0(1)	Al(3)−As(3)−Al(1)	104.5(1)
C(43)−As(2)−Al(3)	108.4(2)	C(49)−Al(3)−As(3)	121.1(2)
C(43)−As(2)−Al(2)	104.4(2)	C(49)−Al(3)−As(2)	135.4(2)
Al(3)−As(2)−Al(2)	108.4(1)	As(3)−Al(3)−As(2)	101.3(1)

reactions with these phosphines or arsines. In the case of H$_2$NPh or H$_2$NDipp, however, the first products to be isolated were the bis(amido)alane compounds Mes*Al(NHPh)$_2$ (**1**) or Mes*Al(NHDipp)$_2$ (**2**), suggesting that **3** is produced in a stepwise manner through amido intermediates.

Structural Descriptions. (a) Mes*Al(NHPh)$_2$·Et$_2$O (1·Et$_2$O). The molecular structure of **1**, which is illustrated in Figure 1, contains monomeric Mes*Al(NHPh)$_2$ and one ether molecule in each of the asymmetric units. The closest interactions between the two molecules involve the nitrogen hydrogens and oxygen with the distances H(1)- - -O(1) = 2.29 Å and H(2)- - -O(1) = 2.34 Å (N(1)- - -O(1) = 3.188(5) Å, N(2)- - -O(1) = 3.196(5) Å) being observed. The aluminum has a planar coordination that almost includes the phenyl groups at the nitrogens. The torsion angles between the perpendiculars to the coordination plane at aluminum and those at N(1) and N(2) are 14.7 and 18.0°. The Al−N and Al−C distances are 1.795(4) Å (av) and 1.966(4) Å and the N−Al−N angle is 107.9(2)°. There are also close approaches between the aluminum and hydrogens from *o*-*t*-Bu groups that involve the atoms H8c (Al- - -H = 2.37 Å) and H18a (Al- - -H = 2.35 Å).

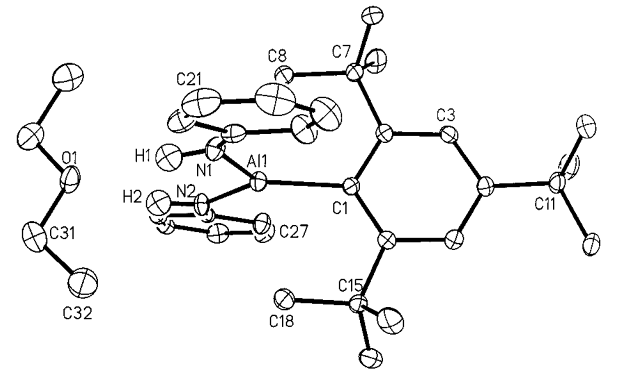

Figure 1. Thermal ellipsoid plot (30%) of **1**·Et$_2$O. H atoms (except N−H's) are not shown for clarity.

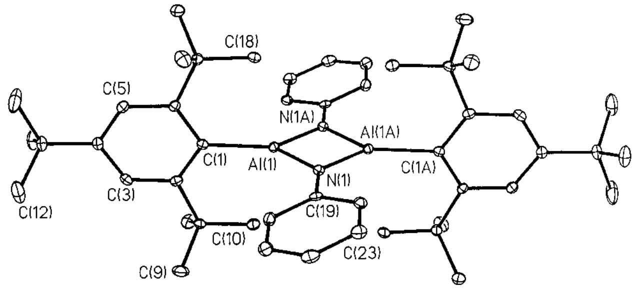

Figure 2. Thermal ellipsoid plot (30%) of **3**. H atoms are not shown for clarity.

(b) (Mes*AlNPh)$_2$ (3). Molecules of **3** consist of centrosymmetric dimers that feature a central, almost perfectly square, Al$_2$N$_2$ ring. The ipso carbon atoms of the Ph and Mes* substituents are coplanar with the Al$_2$N$_2$ array. Thus, the coordination at the aluminum and nitrogen centers is distorted trigonal planar. The internal ring angles at Al(1) and N(1) are 88.75(9)° and 91.25(9)° with equivalent Al−N distances of 1.824(2) Å. The Al−C(1) distance is 1.962(2) Å and the Al- - -Al separation is 2.607(1) Å. The shortest Al- - -H contacts, which involve the C(10) and C(18) methyl groups, are near 2.23 Å. The angle between perpendiculars to the Al$_2$N$_2$ and Mes* planes is 86.8° while the corresponding angle involving the Ph plane is 13.2°.

(c) (Mes*AlEPh)$_3$·Et$_2$O (E = P (4·Et$_2$O), As (5·Et$_2$O)). The crystals of **4**·Et$_2$O and **5**·Et$_2$O are isomorphous and are formed with a molecule of solvent ether in each asymmetric unit. There appears to be no significant interactions between the ether and the (Mes*AlEPh)$_3$ species. The latter are composed of a six-membered ring of alternating aluminum and phosphorus or arsenic atoms arranged in a nonplanar boat conformation. The aluminums have planar coordination whereas the phosphorus and arsenic atoms are pyramidally coordinated. The average Al−P and Al−As distances are 2.328(3) and 2.430(5) Å and the average sums of angles (Σ°) at phosphorus and arsenic are 329.1(3.0) and 319.7(3.0)°. In addition, there are relatively short Al- - -H contacts with some of the *o*-*t*-Bu hydrogens as exemplified by Al(1)- - -H(17c) = 2.21 Å, Al(2)- - -H(2b) = 2.06 Å, and Al(3)- - -H(57a) = 1.95 Å in **4** and Al(1)- - -H(17a) = 2.15 Å, Al(2)- - -H(32b) = 2.14 Å, and Al(3)- - -H(57d) = 2.20 Å in **5**. The Mes*C(ipso)- - -C(para) vectors subtend angles of as much as 15° with the corresponding Al−C bonds. Furthermore, the rings are oriented almost perpendicularly to the coordination planes at the aluminums. Further structural details are provided in Table 3.

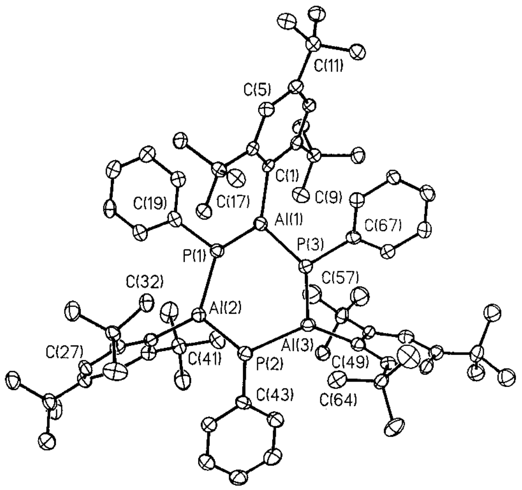

Figure 3. Thermal ellipsoid plot (30%) of $\mathbf{4}\cdot Et_2O$. Et_2O and H atoms are not shown for clarity.

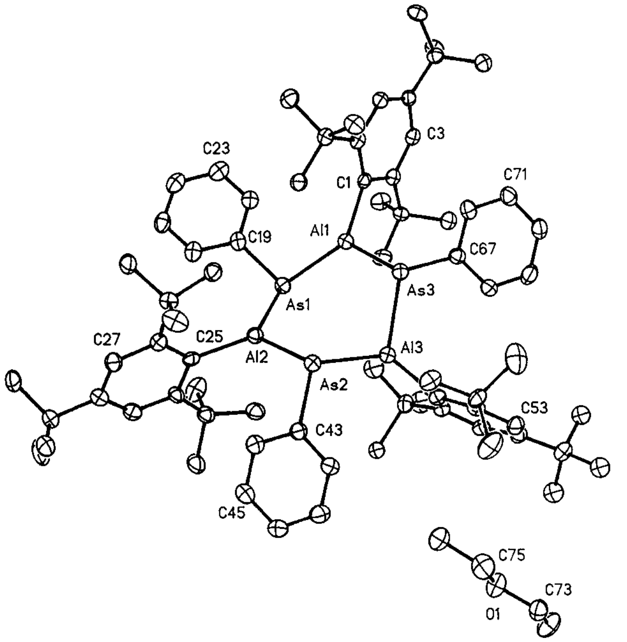

Figure 4. Thermal ellipsoid plot (30%) of $\mathbf{5}\cdot Et_2O$. H atoms are not shown for clarity.

Discussion

The synthesis of the new ring compounds **3**, **4**, and **5** proceeds through the reaction of 1 equiv of Mes*AlH_2 with H_2NPh, H_2PPh, or H_2AsPh with concomitant elimination of dihydrogen. This route is a new one for unsaturated, quasiaromatic, main group III−V rings as the previous routes involved phosphine,[5] methane,[6] or salt eliminations.[7] Hydrogen elimination reactions between phosphines, arsines, and alanes are quite rare and calculations have shown that the model species H_3AlPH_3, representing the initial step of the interaction between phosphines and alanes, is energetically less favored than dialane $H_2Al(\mu\text{-}H)_2AlH_2$ and PH_3.[17] Reactions between AlH_3 and amines, however, have been used to synthesize higher poly(imino)alanes of formula $(HAlNR)_n$ ($n \geq 4$).[18]

The mechanism of the reaction that results in the isolation of the diamides **1** or **2** is not fully understood at present although the Mes*AlH_2/H_2NPh reaction system has been examined in some detail. An initial product can be obtained by the addition of 1 equiv of aniline to a toluene solution of Mes*AlH_2 at 0 °C, followed by concentration and crystallization at −20 °C. Alternatively, addition of 1 equiv of H_2NPh to an Et_2O solution of Mes*AlH_2 at 0 °C followed by evaporation of volatile materials under reduced pressure gives a spectroscopically similar product. Its IR spectrum shows two absorptions in the ν_{N-H} region (3365 (br) and 3300 cm^{-1} (sharp), relative intensity = 1:1) and two bands in the ν_{Al-H} region (1866 and 1836 cm^{-1}, relative intensity = 1:1.3). No absorptions indicating Al−H−Al bridges are observed in the range of 1400−1000 cm^{-1}. Comparison with the IR spectra of **1** and (Mes*AlH_2)$_2$ shows the presence of traces of **1** but no (Mes*AlH_2)$_2$.

The ^1H NMR spectrum of the initial product at room temperature in the aromatic region shows the presence of **1** (*ca.* 24%), Mes*H (*ca.* 8%), and a broad signal at 7.49 ppm ($\Delta\nu_{1/2}$ = 15 Hz; *ca.* 68%). Heating of this sample to 85 °C causes a slight broadening of the *m*-H signal of **1** and a more pronounced broadening of the *o*-t-Bu and *p*-t-Bu signals of **1** which appear to coalesce with the signals of the remaining "68% fraction". A similar observation is made when a 1:1 mixture of Mes*AlH_2 and **1** in C_6D_6 is heated to 80 °C. This leads to the conclusion that an exchange of hydride and amide ligands occurs between these two species with **1** being either the most stable or the species that crystallizes first. This conclusion is supported by the isolation of $[\{2,6\text{-}Mes_2C_6H_3AlH(\mu\text{-}NHPh)\}_2]$[19] and $[2,6\text{-}Mes_2C_6H_3Al(H)(\mu\text{-}NHPh)_2(NHPh)AlC_6H_3\text{-}2,6\text{-}Mes_2]$[19] from the reaction of $[2,6\text{-}Mes_2C_6H_3AlH_2]_2$ with H_2NPh (Al:N = 1:1) (Mes = $2,4,6\text{-}Me_3C_6H_2$). Further heating of the initial product to *ca.* 120−130 °C results in a melt which shows a smooth gas evolution for a few minutes and then solidifies to a colorless solid.

This solid proved to be insoluble in refluxing Et_2O, THF, or benzene. Only small amounts of **1** and Mes*H could be found in the supernatant liquid. The IR spectrum of this solid does not contain bands attributable to N−H or Al−H vibrations but shows the presence of the Mes* and N−Ph groups. Thus, this solid is tentatively identified as (Mes*AlNPh)$_2$. Heating of this solid to 200−210 °C under reduced pressure causes it to partially melt and colorless crystals of Mes*H sublime. Crystals of (Mes*AlNPh)$_2$ (**3**) were eventually obtained in *ca.* 40% yield by treatment of (Mes*AlH_2)$_2$ with 2 equiv of H_2NPh in hot (*ca.* 125 °C) ethylbenzene. The employment of the Mes* in the synthesis and stabilization of the Al_2N_2 species may be contrasted with the reaction of Mes*NH_2 and $AlMe_3$ which affords the ortho-metallated species $(MeAlN(H)C_6H_3\text{-}2,4\text{-}(t\text{-}Bu)_2\text{-}6\text{-}CMe_2CH_2)_2$.[20] As already mentioned the hydrogen elimination route to **3** proceeds under sufficiently mild conditions that the ortho-metallation and C−H activation found with some alkane eliminations[20a,b] are not observed.

The bisamide compounds **1** and **2** are rare instances of unassociated aluminum bisamides. The only previously structurally characterized example for aluminum is $MesAl\{N(SiMe_3)_2\}_2$[13] which has an average Al−N distance of 1.807(3) Å with rather large torsion angles (*ca.* 45−50 °) between the aluminum and nitrogen planes. The average Al−N distance in **1** is 1.795(4) Å and the torsion angles, 14.7 and 18.0°, are much smaller. It could be argued that these parameters are evidence for Al−N π-bonding. However, it is probable that such differences are mainly a result of a change in the steric crowding

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and the electronic properties of the amide ligands. The structure of **1** may also be compared with that of the recently reported gallium analogue Mes*Ga(NHPh)$_2$[13] which was synthesized in a different manner from **1** by the reaction of Mes*GaCl$_2$ with 2 equiv of LiNHPh. In this compound the Ga−N distance is 1.837(8) Å with a torsion angle of 7.3° between the coordination planes at gallium and nitrogen. The longer metal−nitrogen distance in the case of the gallium species can be traced in part to the lower ionic character of the Ga−N bond. However, it is also possible that the presence of hydrogen-bonded ether in the unit cell of **1** plays a role. The weak O- - -H interaction in **1** may increase the electron density in the amido nitrogens thereby increasing the ionic component in the Al−N bond which should result in a shorter bond length being observed.

The structure (Mes*AlNPh)$_2$ (**3**) may be compared with the closely related molecules (MeAlNDipp)$_3$[6] and Cp*{(Me$_3$Si)$_2$N}-AlN(μ-AlCp*)(μ-Al{N(SiMe$_3$)$_2$})NAlCp*$_2$[11] (**6**). The latter compound also features a planar Al$_2$N$_2$ core which has an average Al−N distance of 1.811(7) Å. However, the ring nitrogens are substituted by the three-coordinate aluminum moieties Cp*{(Me$_3$Si)$_2$N}Al− or Cp*$_2$Al−, and one of the ring aluminums is substituted by an amido (−N(SiMe$_3$)$_2$) ligand. This makes possible Al−N π-interactions within the Al$_2$N$_2$ ring in **6** more difficult to assess owing to roughly equally probable Al−N π-interactions exo to the ring. In **3**, however, all the ligands are aryl groups which display no evidence of π-interaction with the Al$_2$N$_2$ core.

The Al−N distance observed in **3**, 1.824(2) Å, is slightly longer than the 1.811(7) Å observed in **6**. However, both values are well within the currently known range (1.78(2)−1.879(4) Å)[13] for compounds that involve bonding between three-coordinate nitrogen and aluminum. It is also significantly longer than the Al−N distance of 1.782(4) Å observed in the quasiaromatic trimer (MeAlNDipp)$_3$.[6] The shorter Al−N bond lengths observed in (MeAlNDipp)$_3$ tended to suggest greater delocalization and Al−N π-bonding in the Al$_3$N$_3$ array. Furthermore, the longer Al−N bonds in **3** are consistent with antiaromatic character for the Al$_2$N$_2$ array.[8,9] Calculations have shown, however, that the amount of delocalization in the six-membered Al$_3$N$_3$ ring is minimal and that any differences between the two structures are more than likely due to steric factors or to changes in σ-hybridization. With regard to the latter, it is notable that in **3** the Al−N bonds are approximately at right angles to each other indicating that the Al−N bonds have almost pure p-character while the Al−C(Mes*) bond has increased s-character. In (MeAlNDipp)$_3$ the aluminum has approximately trigonal planar coordination with interligand angles at aluminum all within 5° of 120°. Thus, Al−N σ-bonding in (MeAlNDipp)$_3$ involves approximate sp^2 hybridization at aluminum whereas in **3** the aluminum orbitals used in σ-bonding have almost pure p-character. This suggests that the Al−N bonds in **3** should be longer than those in (MeAlNDipp)$_3$ which is what is observed. It is also notable that the Al−C bond length in **3**, 1.962(2) Å, is nominally shorter than the 1.978(15) Å Al−C distance in (MeAlNDipp)$_3$. This is in spite of the large size of the Mes* substituent and is consistent with increased s-character for the Al−C bond in **3**. An interesting aspect of the structure of **3** is that the Al- - -Al separation across the Al$_2$N$_2$ ring is just 2.6074(14) Å. This distance is significantly shorter than the Al−Al single bond length in R$_2$Al−AlR$_2$ (R = −CH(SiMe$_3$)$_2$ (2.660(1) Å),[21] −C$_6$H$_2$-2,4,6-(i-Pr)$_3$ (2.647(3) Å)[22]) compounds and other Al−Al species[23] but it does not necessarily indicate the presence of any significant Al−Al bonding. Finally, it should be mentioned that the planar geometry of the nitrogens in **3** or (MeAlNDipp)$_3$ can be accounted for in terms of the low or zero inversion barrier at nitrogen caused by the electropositive Al substituents.[24]

The compounds **4** and **5** crystallize as trimers from ether solution with one non-interactive Et$_2$O molecule included in each asymmetric unit. The higher aggregation in **4** and **5** compared to **3** is presumably due to the relaxed steric requirements as a consequence of the larger size of P or As in comparison to N. The central, isostructural, six-membered rings are composed of alternating Al and P or As atoms. The phosphorus and arsenic centers are quite pyramidal with average sums of angles at P and As of 329.1(3.0)° and 319.7(3.0)°. The average Al−P distance, 2.328(3) Å, is very close to that (2.342(2) Å) observed in (2,4,6-(i-Pr)$_3$C$_6$H$_2$)$_2$AlP(1-adamantanyl)SiPh$_3$ (Σ°P = 330.0°) which is the only previously known structure of a molecule with bonding between three-coordinate Al and P.[12] In this molecule there is thought to be essentially no Al−P π-interaction.

Although there are no molecular structures with bonding between three-coordinate Al and As the average Al−As bond length, 2.430(5) Å, is consistent with single bonding, being almost identical to the sum of the covalent radii of Al and As when corrected for ionic effects.[25] This, together with the observation of pyramidal geometry at each arsenic, is consistent with negligible π-delocalization in the Al$_3$As$_3$ array. The major reasons for the lack of delocalization in either **4** or **5** are the high inversion barriers[24] at P or As and the relatively large sizes of Al, P, or As which diminish side-on p−p π-overlap. This view of the structures is in harmony with recent calculations[9] which indicated essentially no π-delocalization and which favored a chair over a boat configuration in such molecules by 3.3−6.8 kcal mol^{-1}.

The Al−As distance in **5** is *ca.* 0.1 Å shorter than the average lengths of 2.535 and 2.567 Å found in the dimers {Et$_2$AlAs(t-Bu)$_2$}$_2$[26] and {Et$_2$AlAs(SiMe$_3$)$_2$}$_2$.[27] The longer distances in the latter species are presumably a consequence of the four-coordinate nature of the Al and As centers. However, an Al−As distance of 2.463(2) Å has been reported for the adduct (Me$_3$Si)$_3$AsAlCl$_3$[28] and this may be a result of the enhanced Lewis acidity for the aluminum center owing to halide substitution. The average Al−As length in **5** may also be contrasted with the value of 2.342(5) Å found for the terminal Al−As bond in the Zintl species [Al$_2$As$_4$]$^{6-}$ which is thought to involve significant Al−As multiple bonding.[29]

The ^{31}P NMR spectrum of **4** displays a single resonance at −144.2 ppm. The relatively high upfield value is consistent with the fact that two of the substituents at phosphorus are electropositive aluminum centered groups. The shift is similar to that observed for (2,4,6-(i-Pr)$_3$C$_6$H$_2$)$_2$AlPMes(SiPh$_3$) (−157.1 ppm)[12] or PhP(SiMe$_3$)$_2$ (−132.8 ppm).[30] The high value of the shift of **4** signifies considerable electron density at phosphorus

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and is consistent with the absence of delocalization in the Al_3P_3 ring.

Conclusion

Use of the sterically encumbered alane $(Mes^*AlH_2)_2$ allows the ready isolation of previously unknown dimeric aluminum imide and trimeric phosphinidine and arsinidine derivatives. The reactions proceed at temperatures that are lower than alkane eliminations involving comparably crowded group III−V precursors. The absence of a significant tendency to activate substituent C−H bonds in the presence of low-coordinate aluminum at H_2 elimination temperatures suggests that this method may be used to generate other interesting main group III−V compounds.

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Supporting Information Available: Tables giving full data collection parameters and further details of refinement, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (45 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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