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REACTIONS OF PHENYLALUMINIUM COMPOUNDS WITH $E(SiMe_3)_3$ (E = P or As): X-RAY CRYSTAL STRUCTURES OF $Ph_3Al \cdot E(SiMe_3)_3$ (E = P or As) AND $Ph_2(Cl)Al \cdot P(SiMe_3)_3$

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Abstract—The independent reactions of Ph_3Al with $E(SiMe_3)_3$ (E = P or As) in 1 : 1 mole ratios afforded the adducts $Ph_3Al \cdot E(SiMe_3)_3$ [E = P (**I**) and As (**II**), respectively]. The attempted dehalosilylation reactions between Ph_2AlCl and $E(SiMe_3)_3$ (E = P or As) in 1 : 1 mole ratios yielded only the adducts $Ph_2(Cl)Al \cdot E(SiMe_3)_3$ [E = P (**III**) and As (**IV**)]. The adduct $Ph(Cl)_2Al \cdot P(SiMe_3)_3$ (**V**) was isolated from the reaction of equimolar amounts of $PhAlCl_2$ and $P(SiMe)_3$. Compounds **I**–**V** were characterized by NMR spectroscopy and partial elemental analysis. In addition, the solid-state structures of **I**–**III** were determined by single-crystal X-ray analysis. Compound **I** crystallizes in the monoclinic space group $P2_1/n$ (C_{2h}^5), while **II** crystallizes in the triclinic space group $P\bar{1}$(C_i^1), each with two discrete molecules per asymmetric unit. Crystals of compound **III** belong to the orthorhombic space group $P2_12_12_1$(D_2^4). Compounds **I**–**III** are the first structurally-characterized compounds to contain phenyl-substituted Al centres bonded to heavier pnicogen atoms. Copyright © 1996 Elsevier Science Ltd

In contrast to the significant collection of literature concerning reactions of aluminium alkyls and alkylaluminium halides with pnicogen compounds, there is a dearth of analogous studies with arylaluminium derivatives. Although the solid-state dimeric structure of triphenylaluminium, Ph_3Al, was reported nearly 30 years ago by Malone and McDonald,[1] the first structurally-characterized triarylaluminium-based complex did not appear in the literature until 1979 when Burlitch *et al.*[2] reported the triphenyl[(η^5-cyclopentadienyl)dicarbonyliron] aluminate anion, $[Ph_3Al\text{-}Fe(CO)_2Cp]^-$. It was more than 10 years later that Robinson and co-workers reopened this area of organoaluminium chemistry with their synthesis and characterization of the aminophenylalane compounds, $Ph_3Al \cdot N(H)_2{}^tBu$[3] and $[Ph_2AlN(H)Ph']_2$ (Ph′ = biphenyl).[4] The Oliver group has also recently reported an extensive series of mesitylaluminium compounds, including $[Mes_2Al(\mu\text{-}Cl)]_2$,[5] $Mes_3Al \cdot (4\text{-picoline})(C_7H_8)_{0.5}$,[5] $Et(Mes)_2Al \cdot THF$,[5] $Mes_2(Cl)Al \cdot THF$,[5] $[Mes_2Al(\mu\text{-}SR)]_2$ (R = phenyl, benzyl)[6] and $[Mes_2Al(\mu\text{-}SeMe)]_2$[7] (Mes = 2,4,6-$Me_3C_6H_2$). To date, only one compound containing an arylaluminium moiety bonded to a heavier group 15 atom has been characterized by X-ray diffraction techniques, and it is the unassociated aluminium monophosphide $Trip_2AlP(1\text{-}Ad)SiPh_3 \cdot 0.5$hexane (Trip = 2,4,6-${}^iPr_3C_6H_2$, 1-

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Ad = adamantyl), which was reported by Power and co-workers in 1994.[8]

The limited research into the arylaluminium chemistry of pnicogen compounds led us to investigate the reactions of phenylaluminium species with silylpnictines. Previously, researchers in our laboratory studied dehalosilylation and salt-elimination reactions between silylpnicogen compounds and heavier group 13 phenyl-substituted reagents, which led to the isolation of several novel 13–15 compounds.[9–12] For example, the 2 : 1 reaction of Ph_2GaCl and $As(SiMe_3)_3$ afforded the first gallium–arsenic mixed-bridge compound $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl$.[9] The Ga—P analog, $Ph_2GaP(SiMe_3)_2Ga(Ph)_2Cl$, was synthesized from a similar reaction of Ph_2GaCl and $P(SiMe_3)_3$.[11] Lithium salt-elimination reactions between equimolar amounts of Ph_2MCl (M = Ga or In) and $LiE(SiMe_3)_2$ (E = As or P) yielded dimeric compounds of the type $[Ph_2ME(SiMe_3)_2]_2$ (M = Ga, E = As;[9] M = In, E = As;[12] and M = In, E = P[12]). The triphenylgallium Lewis acid–base adducts $Ph_3Ga \cdot P(SiMe_3)_3$[11] and $Ph_3Ga \cdot As(SiMe_3)_3$[13] have been prepared by the direct combination of Ph_3Ga and $E(SiMe_3)_3$ (E = P and As, respectively) and also by unique rearrangement reactions involving the monolithium salts, $LiE(SiMe_3)_2$ (E = P and As, respectively). Herein, we report the synthesis and characterization of the phenylaluminium-pnictine compounds, $Ph_3Al \cdot E(SiMe_3)_3$ [E = P (**I**) or As (**II**)], $Ph_2(Cl)Al \cdot E(SiMe_3)_3$ [E = P (**III**) or As (**IV**)], and $Ph(Cl)_2Al \cdot P(SiMe_3)_3$ (**V**).

EXPERIMENTAL

Synthesis

All reactions and manipulations were carried out either in a Vacuum Atmospheres HE-493 Dri-Lab under argon or under argon using standard Schlenk apparatus.[14] The ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer at 300.0 and 75.4 MHz, respectively. ^{27}Al NMR spectra were acquired on a Varian Unity 500 spectrometer at 130.3 MHz. ^{31}P NMR spectra were obtained on either a Varian XL-300 (121.4 and 300.0 MHz, respectively) or a Varian Unity 500 (202.4 and 500.1 MHz, respectively) spectrometer. ^1H and $^{13}C\{^1H\}$ spectra were referenced to TMS *via* the residual protons or carbons of deuterated benzene (δ 7.15 and 128.0 ppm, respectively). ^{27}Al and ^{31}P NMR spectra were externally referenced to $Al(NO_3)_3$ and 80% H_3PO_4, respectively, at δ 0.00 ppm. All solvents were appropriately dried and distilled under dry nitrogen. The compounds $P(SiMe_3)_3$,[15] and $As(SiMe_3)_3$[16,17] were prepared by literature methods. Triphenylaluminium, Ph_3Al, was prepared by the literature procedure.[1] $AlCl_3$ was purchased from Strem Chemical, Inc. and purified by sublimation prior to use. Ph_2AlCl and $PhAlCl_2$ were prepared by the stoichiometric equilibration of $AlCl_3$ and Ph_3Al[1] in toluene. Melting points (uncorrected) were obtained with a Thomas-Hoover Uni-melt apparatus in flame-sealed capillaries. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, New York.

$Ph_3Al \cdot P(SiMe_3)_3$ (**I**)

Triphenylaluminium, Ph_3Al (0.39 g, 1.53 mmol), was placed in a 300 cm^3 round-bottomed screw-top flask, along with 30 cm^3 of toluene and a stir-bar. A toluene (30 cm^3) solution of $P(SiMe_3)_3$ (0.38 g, 1.53 mmol) was added to the Ph_3Al solution. No immediate reaction was observed. The flask was immersed in a preheated oil bath (110°C) and heated for 2 days to give a clear, colourless solution. Solvent was removed *in vacuo*, resulting in an off-white crystalline solid, which was recrystallized from toluene at $-30°C$. After several days, colourless, X-ray-quality crystals were isolated from the toluene solution, and determined to be **I** (0.64 g, 82% yield), m.p. 184–204°C (gradually melts to a yellow liquid). Calc. (Found) for $C_{27}H_{42}AlPSi_3$: C, 63.7 (63.9); H, 8.3 (8.4)%. ^1H NMR: δ 0.11 [d, $Si(CH_3)_3$, 27H (J_P—H = 4.85 Hz)], 7.33 (m, C_6H_5, 9H), 8.18 (m, C_6H_5, 6H). $^{13}C\{^1H\}$ NMR: δ 3.15 (d, $Si(CH_3)_3$, (J_P—C = 7.3 Hz)], 127.6, 128.0, 128.4, and 140.0 (s, C_6H_5). ^{27}Al NMR: δ 189.5 (br s). ^{31}P NMR: δ -232.5 (s).

$Ph_3Al \cdot As(SiMe_3)_3$ (**II**)

In a manner similar to the preparation of **I**, Ph_3Al (0.31 g, 1.20 mmol) and benzene (30 cm^3) were added to a 200 cm^3 round-bottomed screw-top flask, equipped with a stir-bar. A solution of $As(SiMe_3)_3$ (0.36 g, 1.21 mmol) in benzene (30 cm^3) was added to the flask, resulting in partial dissolution of the Ph_3Al. The flask was immersed in an oil bath preheated to 65°C, and heated for 2 days, resulting in a homogeneous yellow solution. The volatiles were removed *in vacuo*, leaving a yellowish semi-solid in the flask. The flask was taken into the dry box, where the product was recrystallized from toluene at $-30°C$. After several days, long, rectangular colourless crystals of **II**, suitable for X-ray crystallographic analysis, were isolated (0.51 g, 78.0% yield), m.p. 192–195°C (slight decomposition to an orange solid was observed).

Calc. (Found) for $C_{27}H_{42}AlAsSi_3$: C, 58.7 (58.4); H, 7.7 (7.9)%. ^1H HMR: δ 0.15 [s, $Si(CH_3)_3$, 27H], 7.34 (m, C_6H_5, 9H), 8.15 (m, C_6H_5, 6H). $^{13}C\{^1H\}$ NMR: δ 3.22 [s, $Si(CH_3)_3$], 127.5, 127.9, 128.5, and 139.7 (s, C_6H_5).

$Ph_2(Cl)Al \cdot P(SiMe_3)_3$ (III)

Diphenylaluminium chloride, Ph_2AlCl (0.22 g, 1.01 mmol), $P(SiMe_3)_3$ (0.25 g, 1.01 mmol), and hexane (75 cm^3) were combined in a 250 cm^3 round-bottomed screw-top flask, equipped with a stir-bar. The resultant solution was turbid at room temperature, due to the limited solubility of Ph_2AlCl in hexane. The flask was then immersed in an oil bath, preheated to 65°C, and heated for 2 days, during which time the solution became clear and colourless. The volatiles were then removed *in vacuo*, yielding an off-white solid product. The flask was taken into the dry-box, where the solid was recrystallized from pentane at −30°C. Needle-like, colourless, X-ray quality crystals were isolated and determined to be **III** (0.37 g, 78% yield), m.p. 141–155°C (decomposes to a glassy yellow solid before melting). Calc. (Found) for $C_{21}H_{37}AlClPSi_3$: C, 54.0 (53.9); H, 8.0 (7.9); Al, 5.8 (5.6); P, 6.6 (6.4); Cl, 7.6 (7.5)%. ^1H NMR: δ 0.17 [d, $Si(CH_3)_3$, 27H, (J_P—H = 5.10 Hz)], 7.31 (m, C_6H_5, 6H), 8.23 (m, C_6H_5, 4H). $^{13}C\{^1H\}$ NMR: δ 2.71 [d, $Si(CH_3)_3$, (J_P—C = 7.9 Hz)], 127.5, 128.5, 129.0, and 138.6 (s, C_6H_5). ^{27}Al NMR: δ 181.6 (br s). ^{31}P NMR: δ −225.2 (s).

$Ph_2(Cl)Al \cdot As(SiMe_3)_3$ (IV)

Inside a dry-box, a 250 cm^3 round-bottomed screw-top flask, equipped with a stir-bar, was charged with Ph_2AlCl (0.26 g, 1.20 mmol) and 25 cm^3 of toluene, resulting in a colourless solution. A solution of $As(SiMe_3)_3$ (0.35 g, 1.20 mmol) in toluene (30 cm^3) was then added to the flask. The solution was immersed in a preheated oil bath (75°C) and warmed for 1 day, during which time the solution remained clear and colourless. After 24 h, the flask was removed from the oil bath and cooled to room temperature for 8 h, but no crystallization or precipitation of a solid product occurred. Volatiles were then stripped *in vacuo*, leaving an off-white crystalline solid, **IV** (0.49 g, 81% yield), which was washed with pentane, then dried, m.p. 131–135°C (becomes a cloudy liquid), 138–140°C (melts to a yellow liquid). X-ray quality single crystals of **IV** were unobtainable from repeated attempts at recrystallization. Calc. (Found) for $C_{21}H_{37}Al AsClSi_3$: C, 49.3 (49.3); H, 7.3 (7.2)%. ^1H NMR: δ 0.19 [s, $Si(CH_3)_3$, 27H], 7.31 (m, C_6H_5, 6H), 8.18 (m, C_6H_5, 4H). $^{13}C\{^1H\}$ NMR: δ 3.00 [s, $Si(CH_3)_3$], 123.8, 127.6, 137.7, 138.4 and 139.7 (s, C_6H_5).

$Ph(Cl)_2Al \cdot P(SiMe_3)_3$ (V)

In the dry-box, a mixture of $PhAlCl_2$ (0.48 g, 2.74 mmol) and benzene (40 cm^3) was added to a 250 cm^3 round-bottomed screw-top flask, equipped with a stir-bar. To this was added a colourless solution of $P(SiMe_3)_3$ (0.69 g, 2.74 mmol) in benzene (30 cm^3). The resultant solution was turbid at room temperature, and a white solid began to precipitate. The reaction solution was immersed in an oil bath, preheated to 60°C, and heated for 2 days, during which time, the solution remained colourless with a white precipitate. The volatiles were then removed *in vacuo*, yielding a white solid product. The wash solution was decanted and transferred to a vial, then refrigerated at −30°C. The solid was recrystallized from hexane and pentane to give a white crystalline solid, **V** (1.03 g, 88% yield), no m.p. observed: 140–145°C colourless liquid condensed at the top of the capillary; 145–300°C decomposed to a yellow solid. Calc. (Found) for $C_{15}H_{32}AlCl_2PSi_3$: C, 42.3 (42.6); H, 7.6 (7.3)%. ^1H NMR: δ 0.26 [d, $Si(CH_3)_3$, 27H, (J_P—H = 5.07 Hz)], 7.25 [(m, C_6H_5, 3H), 7.76 (br s, C_6H_5)], and 8.06 (m, C_6H_5, 2H). $^{13}C\{^1H\}$ NMR: δ 2.02 and 2.38 [d, $Si(CH_3)_3$, (J_P—C = 8.4 and 8.2 Hz, respectively)], 128.5, 129.0, 130.3, 130.6 and 138.1 (s, C_6H_5). ^{31}P NMR: δ −220.1 (s).

X-ray structural solution and refinement

Crystallographic data for **I**–**III** are summarized in Table 1. The X-ray crystal structure analysis of **I** was performed at the University of North Carolina-Chapel Hill Single-Crystal X-Ray Facility. A crystal of **I** was affixed to the end of a glass fibre using a viscous oil under a flow of nitrogen. Intensity data were recorded at −130°C using the ω scan mode on a Rigaku AFC6/S diffractometer [graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å)]. Intensity data were corrected for absorption using ψ-scans. Refined unit-cell parameters were obtained from the diffractometer setting angles for 84 reflections ($15 < \theta < 20°$) widely separated in reciprocal space. The space group $P2_1/n$ was established uniquely from the Laue symmetry and systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $h+l \neq 2n$. The asymmetric unit consists of two crystallographically-independent formula units. The crystal structure was solved by direct methods. Non-hydrogen atom positional and thermal parameters were refined using full-matrix least-squares adjustment techniques. In the final iterations, hydrogen atoms were incorporated at their cal-

Table 1. Crystallographic data and data collection parameters for $Ph_3Al \cdot P(SiMe_3)_3$ (**I**), $Ph_3Al \cdot P(SiMe_3)_3$ (**II**), and $Ph_2(Cl)Al \cdot P(SiMe_3)_3$ (**III**)

	I	**II**	**III**
Molecular formula	$C_{27}H_{42}AlPSi_3$	$C_{27}H_{42}AlAsSi_3$	$C_{21}H_{37}AlClPSi_3$
Formula weight	508.83	552.80	467.20
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/n(C^5_{2h})$–No. 14	$P\bar{1}$ (C^1_i)–No. 2	$P2_12_12_1(D^4_2)$–No. 19
a (Å)	18.678(4)	16.097(2)	9.759(1)
b (Å)	19.010(7)	16.254(2)	30.463(6)
c (Å)	18.776(4)	12.488(2)	9.343(1)
α (°)	90.0(–)	92.03(1)	90.0(–)
β (°)	112.49(2)	97.70(1)	90.0(–)
γ (°)	90.0(–)	86.85(1)	90.0(–)
V (Å^3)	6160(6)	3232(1)	2778(1)
Z	8	4	4
$D_{calc.}$ (g cm^{-3})	1.097	1.136	1.117
μ (mm^{-1})	0.24	2.9	3.4
Temp. (°C)	−130	25	25
Crystal dimension (mm)	0.42 × 0.30 × 0.25	0.20 × 0.24 × 0.50	0.16 × 0.34 × 0.70
T_{max}, T_{min}	0.94, 0.90	$T_{max}:T_{min}$ (relative) 1.00:0.83	$T_{max}:T_{min}$ (relative) 1.00:0.59
Scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
θ_{max} (°)	2θ:45	75	75
Total no. of reflections recorded	10240 $(+h, +k, \pm l)$	13784 $(+h, \pm k, \pm l)$	3250$(+h, +k, +l)$
No. of non-equiv. reflections	8048	13288	3250
R_{merge}, on I	0.041	0.022	—
No. of reflections retained	4834 $(I > 2.5\sigma I)$	7880 $(I > 3.0\sigma I)$	2485 $(I > 3.0\sigma I)$
No. of parameters refined	578	578	244
R, $R_w{}^a$	0.048 (0.051)	0.040 (0.053)	0.046 (0.064)
Goodness-of-fit^b	1.30	1.44	1.68
Max shift; esd in final least-squares cycle	0.001	0.03	0.03
Final $\Delta\rho$ (e Å) max; min	0.29; −0.30	0.30; −0.74	0.27; −0.32

[a] $R = \Sigma\|F_0|-|F_c\|/\Sigma|F_0|$; $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_0|^2]^{1/2}$; $\Sigma w\Delta^2$ $[w = 1/\sigma^2(|F_o|),\ \Delta = (|F_o|-|F_c|)]$ was minimized.

[b] Goodness-of-fit $= [\Sigma w\Delta^2/(N_{observations}-N_{parameters})]^{1/2}$.

culated positions using a riding model, with parameter refinement converging at $R = 0.048$ ($R_w = 0.051$). Crystallographic calculations were performed on a DEC 3000/400 computer using the NRCVAX suite of structure-determination programs.[18] Neutral atom scattering factors and their anomalous dispersion corrections were taken from Ref. 19.

X-ray crystallographic analyses of **II** and **III** were performed at the Duke University Structure Centre. For X-ray measurements, crystals were mounted inside thin-walled glass capillaries, temporarily sealed with grease and then flame-sealed. Intensity data were collected at ambient temperature on an Enraf–Nonius CAD-4 diffractometer [graphite-monochromated Cu-K_α radiation ($\lambda = 1.5418$ Å)]. Refined unit-cell parameters for each were derived from the diffractometer setting angles for 25 reflections ($36 < \theta < 40°$) widely separated in reciprocal space. Intensity data were corrected for the usual Lorentz and polarization effects; empirical absorption corrections, based on the ϕ-dependency of the intensities of several reflections with χ *ca* 90°, were also applied.

Laue symmetry indicated that crystals of **II** were triclinic, space group $P1$ or $P\bar{1}$; the latter was assumed at the outset and shown to be correct by the structure solution and refinement. The asymmetric unit consists of two crystallographically-independent formula units. The crystal structure was solved by direct methods (MULTAN11/82). Initial coordinates for the Al, As, and Si atoms were obtained from an E-map. A series of weighted F_o and difference Fourier syntheses yielded positions for the other non-hydrogen atoms. Positional and thermal parameters of the non-hydrogen atoms (at first isotropic, then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculations. Hydrogen atoms were incorporated at their calculated positions and an extinction correction was included as a variable in the final least-squares iterations which converged at $R = 0.040$ ($R_w = 0.053$). A final difference Fourier synthesis contained no unusual features.

The space group for **III** was established uniquely as $P2_12_12_1$ by the systematic absences: $h00$ when $h \neq 2n$, $0k0$ when $k \neq 2n$, $00l$ when $l \neq 2n$. Coordinates for the isomorphous Ga analogue[11] were used as initial input to the structure-factor calculations. Several rounds of full-matrix least-squares refinement of positional and anisotropic thermal parameters of these atoms, with hydrogen atoms incorporated at their calculated positions in the later iterations, converged at $R = 0.0473$ ($R_w = 0.0661$). The polarity of the crystal used for data collection was then established by introduction of the imaginary contributions to the anomalous dispersion corrections into the structure-factor calculations. For the parameters corresponding to those of the Ga analogue, $R = 0.0501$ while $R_w = 0.0703$, whereas values of $R = 0.0464$ and $R_w = 0.0648$ were obtained for those of the mirror image. The differences[20] indicated that the polarity had to be reversed. Continuation of the least-squares refinement led to convergence at $R = 0.046$ ($R_w = 0.064$). No unusual features were present in a final difference Fourier synthesis.

Crystallographic calculations for **II** and **III** were performed on PDP11/44 and MicroVAX computers by use of the Enraf–Nonius Structure Determination Package (SDP). For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from Ref. 19.

RESULTS AND DISCUSSION

The independent reactions of Ph_3Al with $P(SiMe_3)_3$ and $As(SiMe_3)_3$ in 1:1 mole ratios afforded the Lewis acid–base adducts $Ph_3Al \cdot P(SiMe_3)_3$ (**I**) and $Ph_3Al \cdot As(SiMe_3)_3$ (**II**), respectively [eq. (1)].

$$Ph_3Al + E(SiMe_3)_3 \xrightarrow[\Delta]{} Ph_3Al \cdot E(SiMe_3)_3 \quad (1)$$

E = P (**I**), Toluene, 110°C

E = As (**II**), Benzene, 65°C

Adduct **I** is the aluminium analogue of the gallium-phosphorus adduct $Ph_3Ga \cdot P(SiMe_3)_3$,[11] and it is only the second triarylaluminium-phosphorus compound to be structurally characterized. Compound **II**, the Al analogue of $Ph_3Ga \cdot As(SiMe_3)_3$,[13] is only the third example of an Al—As adduct to be reported and it is the first arylaluminium-arsenic compound to be characterized by X-ray crystallographic analysis.

Both of the isostructural triphenylaluminium-pnicogen adducts $Ph_3Al \cdot P(SiMe_3)_3$ (**I**) and $Ph_3Al \cdot As(SiMe_3)_3$ (**II**) have unit cells that contain two crystallographically-independent, but virtually structurally identical, molecules in the asymmetric crystal unit. The same phenomenon was previously encountered in the crystal structures of the respective Ga analogues of **I** and **II**, *viz* $Ph_3Ga \cdot P(SiMe_3)_3$[11] and $Ph_3Ga \cdot As(SiMe_3)_3$.[13] Crystals of the arylaluminium monophosphide, $Trip_2AlP(1\text{-}Ad)SiPh_3 \cdot 0.5$ hexane, were also found to contain two discrete monomers in the asymmetric unit.[8] ORTEP[21] diagrams showing the solid-state conformations and atom numbering schemes of one of the unique molecules of **I** and **II** are given in Figs 1 and 2, respectively; selected bond distances and angles are listed in Tables 2 and 3.

Crystals of **I** belong to the monoclinic system, space group $P2_1/n$, and they are isomorphous with those of the gallium analogue, $Ph_3Ga \cdot P(SiMe_3)_3$.[11] The Al and P atoms in the pair of crystallographically-independent molecules have similar pseudotetrahedral coordination geometries. There are small, but significant, differences between corresponding pairs of angles (see Table 3). The Al—C and P—Si bonds are rotated by slightly different amounts from an eclipsed orientation about the Al—P bonds (mean 26.5° and 24.7°) in each of the molecules; corresponding values in $Ph_3Ga \cdot P(SiMe_3)_3$[11] are 25.5° and 23.2°). The Al—P bond lengths at 2.514(2) and 2.521(2) Å in the independent molecules of **I** lie well within the observed range for other monodentate Al—P adducts [2.391(6)–2.585(2) Å].[22–30] The distances in **I** are longer than those found in other alkylhaloaluminium-silylphosphine adducts: $Et(Cl)_2Al \cdot P(SiMe_3)_3$ [2.435(3) Å],[29] $^iBu_2(Cl)Al \cdot P(SiMe_3)_3$ [2.504(3) Å],[29] $Cl_3Al \cdot P(SiMe_3)_3 \cdot$toluene [2.392(4) Å],[30] and $Br_3Al \cdot P(SiMe_3)_3 \cdot$toluene [2.391(6) Å].[30] The bond lengthening in **I** can be attributed to a decrease in the Lewis acidity of the Ph_3Al moiety *versus* the other Al-containing species. The only reported, shorter Al—P bond length in an arylaluminium-phosphorus compound is that at 2.342(2) Å in $Trip_2\ AlP(1\text{-}Ad)SiPh_3 \cdot 0.5$ hexane where the Al centre has a three-coordinate trigonal planar geometry.[8]

The novel triphenylaluminium-arsenic adduct **II** crystallizes in the triclinic system, space group $P\bar{1}$ with two crystallographically-independent molecules in the asymmetric unit. Although it is iso-

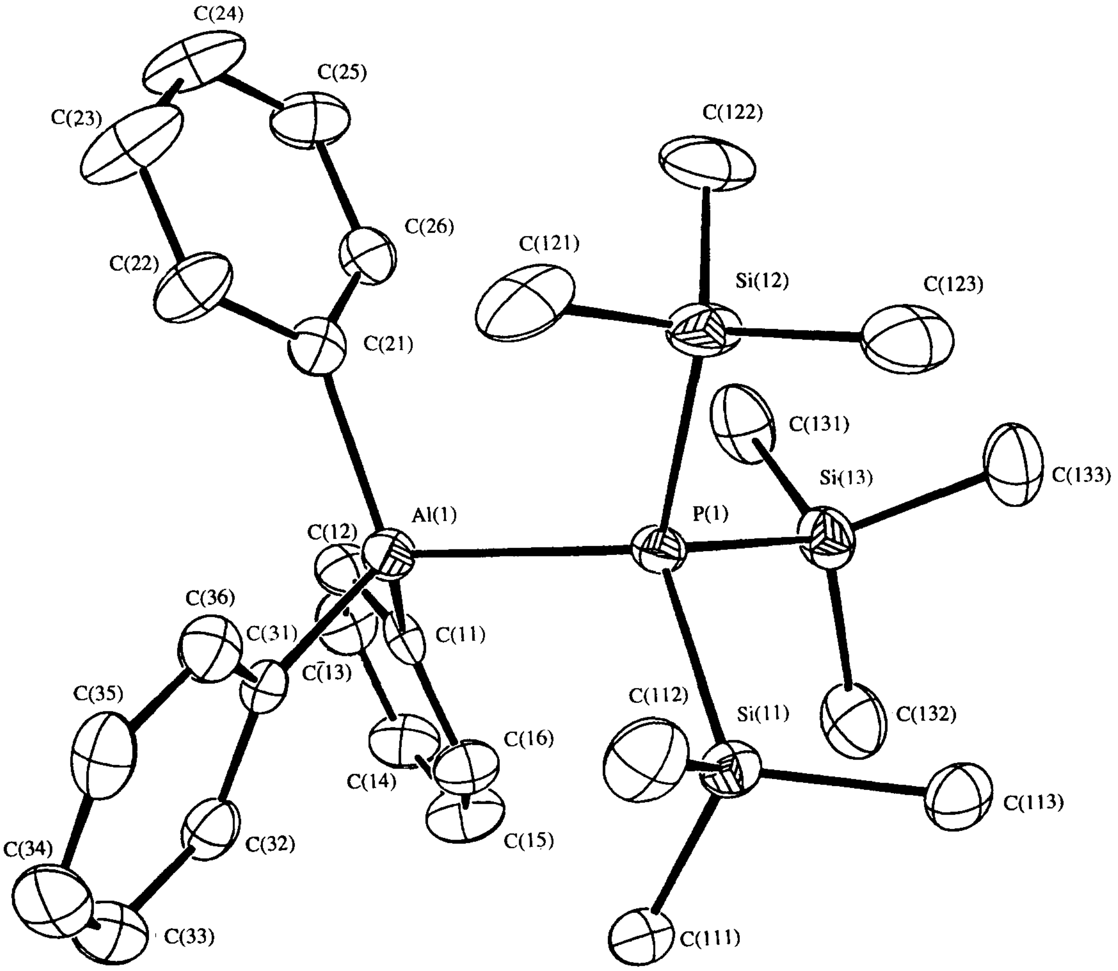

Fig. 1. Thermal ellipsoid diagrams (40% probability) showing the solid-state conformation and atom numbering scheme of $Ph_3Al \cdot P(SiMe_3)_3$ (**I**) (molecule 1) in the asymmetric crystal unit; hydrogen atoms have been omitted for clarity.

structural with the Ga—As analogue $Ph_3Ga \cdot As(SiMe_3)_3$,[13] the crystals are not isomorphous. In common with the metal and pnicogen atoms in **I**, $Ph_3Ga \cdot P(SiMe_3)_3$, and $Ph_3Ga \cdot As(SiMe_3)_3$, the coordination geometry about the Al and As centres in both molecules of **II** is pseudo-tetrahedral. The C—Al—C angles in **II** [112.4(2)°–115.0(2)°] are consistently larger than the C—Al—As angles [102.9(1)°–105.5(1)°] whereas the Si—As—Si angles [104.77(4)°–106.78(4)°] are smaller than the Al—As—Si angles [111.88(4)°–113.37(5)°]. This pattern is similar to that in the Al—P analogue **I** [C—Al—C, 110.5(2)°–114.5(2)° > C—Al—P, 104.6(2)°–107.2(2)°; Si—P—Si, 105.7(1)°–107.0(1)° > Al—P—Si, 110.1(1)°–114.1(1)°] as well as in $Ph_3Ga \cdot P(SiMe_3)_3$ [C—Ga—C, 111.8(8)°–116.2(8)° > C—Ga—P, 103.7(6)°–107.3(6)°; Si—P—Si, 104.9(3)°–107.0(3)° > Ga—P—Si, 110.7(2)°–114.3(2)°] and $Ph_3Ga \cdot As(SiMe_3)_3$ [C—Ga—C, 111.2(8)°–115.7(4)° > C—Ga—As, 103.3(2)°–106.0(2)°; Si—As—Si, 104.9(1)°–106.6(1)° > Ga—As—Si, 110.74(7)°–114.45(7)°]. The Al—C and As—Si bonds are rotated by different amounts from an eclipsed orientation about the Al—As bonds in each of the molecules (mean 29.0° and 23.3°). The corresponding Al—As bond lengths at 2.598(1) and 2.613(1) Å are significantly longer than those in the only other structurally-characterized Al—As adducts, $^{i}Bu_2(Cl)Al \cdot As(SiMe_3)_3$[31] [2.573(1) Å] and $Cl_3Al \cdot As(SiMe_3)_2 \cdot (C_7H_8)$[32] [2.463(2) Å] with the longer distance in **II** being associated with the more nearly eclipsed conformer.

In an effort to prepare aluminium-pnicogen compounds containing either Al—E—Al—E or Al—E—Al—Cl (E = P or As) core rings by the elimination of Me_3SiCl, Ph_2AlCl was allowed to react with $E(SiMe_3)_3$ in a 1 : 1 mole ratio. The

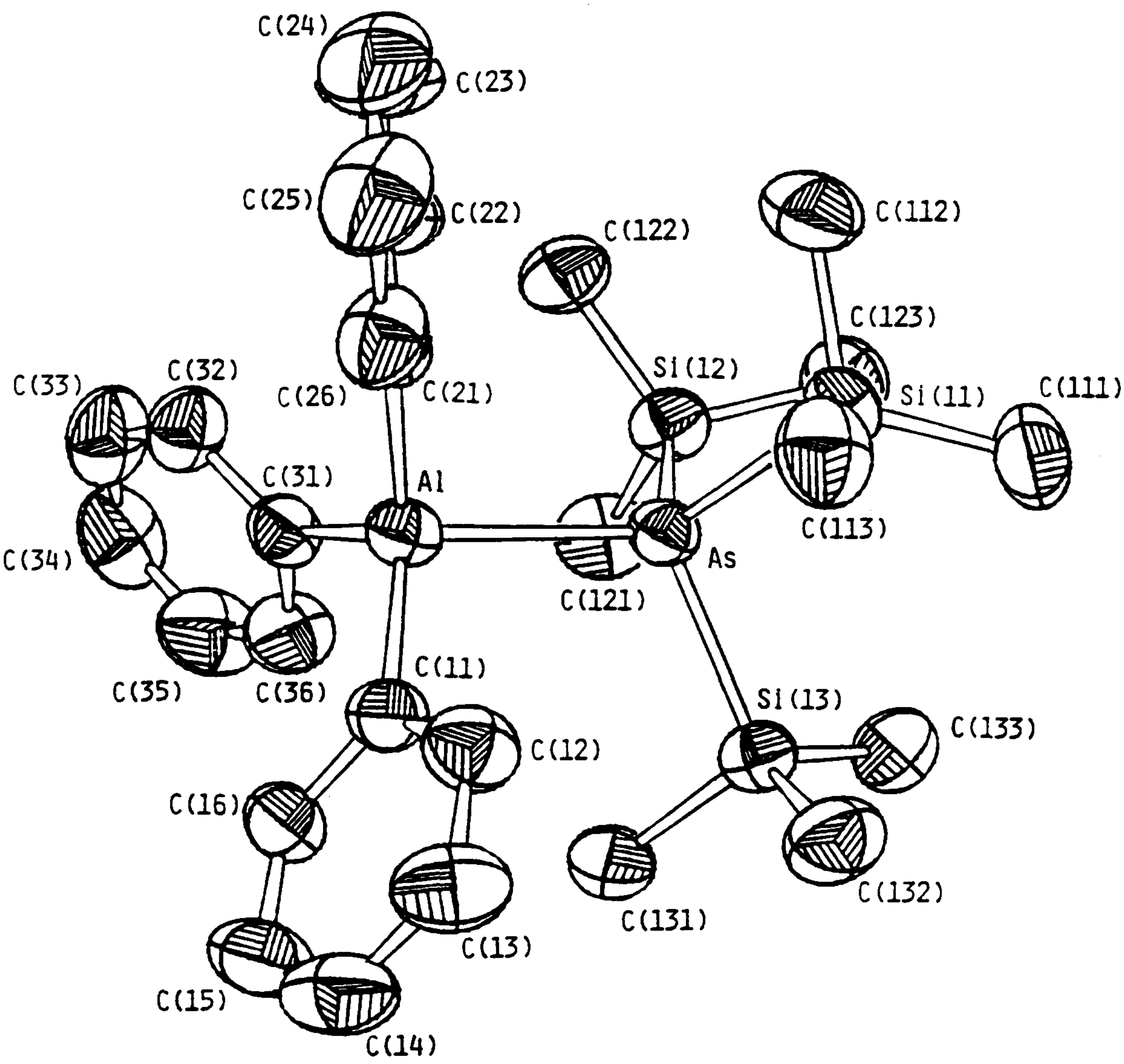

Fig. 2. Thermal ellipsoid diagram (40% probability) showing the solid-state conformation and atom numbering scheme of $Ph_3Al \cdot As(SiMe_3)_3$ (**II**) (molecule 1) in the asymmetric crystal unit; hydrogen atoms have been omitted for clarity.

reactions yielded adducts $Ph_2(Cl)Al \cdot P(SiMe_3)_3$ (**III**) and $Ph_2(Cl)Al \cdot As(SiMe_3)_3$ (**IV**), rather than the condensation products of dehalosilylation [eq. (2)].

$$Ph_2AlCl + E(SiMe_3)_3 \xrightarrow{\text{Toluene}} Ph_2(Cl) \cdot E(SiMe_3)_3 \quad (2)$$

E = P (**III**), 110°C

E = As (**IV**), 75°C

Several attempts were made to recrystallize **IV**, but X-ray quality single crystals were not obtained. ^1H, $^{13}C\{^1H\}$ NMR spectra and partial elemental analysis (*vide supra*) are consistent with an adduct having the formula $Ph_2(Cl)Al \cdot As(SiMe_3)_3$ (**IV**), which is the arsenic analogue of compound **III**.

An ORTEP[21] diagram showing the solid-state conformation and atom numbering scheme of **III** is presented in Fig. 3; selected bond distances and angles are listed in Table 4. In contrast to the triphenylaluminium-pnicogen adducts **I** and **II**, compound **III** crystallizes with only one molecule in the asymmetric unit of an orthorhombic unit cell (space group $P2_12_12_1$). Crystals of **III** are isomorphous with those of the Ga analogue, $Ph_2(Cl)Ga \cdot P(SiMe_3)_3$.[11] The Al and P atoms in **III** have the expected four-coordinate, distorted tetrahedral coordination geometries. the Al—P bond length at 2.467(2) Å lies well within the range of other

Table 2. Selected bond distances (Å) and angles (°) for $Ph_3Al \cdot P(SiMe_3)_3$ (**I**) with estimated standard deviations in parentheses

Molecule 1			
(a) Bond lengths			
Al(1)—P(1)	2.514(2)	P(1)—Si(11)	2.282(2)
Al(1)—C(11)	1.988(5)	P(1)—Si(12)	2.282(2)
Al(1)—C(21)	1.990(5)	P(1)—Si(13)	2.281(2)
Al(1)—C(31)	1.985(6)	Si—C	1.846(7)–1.864(7)
(b) Bond angles			
P(1)—Al(1)—C(11)	107.1(2)	Al(1)—P(1)—Si(11)	113.8(1)
P(1)—Al(1)—C(21)	107.2(2)	Al(1)—P(1)—Si(12)	110.4(1)
P(1)—Al(1)—C(31)	104.6(1)	Al(1)—P(1)—Si(13)	113.2(1)
C(11)—Al(1)—C(21)	110.5(2)	Si(11)—P(1)—Si(12)	106.7(1)
C(11)—Al(1)—C(31)	113.0(2)	Si(11)—P(1)—Si(13)	105.9(1)
C(21)—Al(1)—C(31)	113.9(2)	Si(12)—P(1)—Si(13)	106.4(1)
(c) Torsion angles[a]			
Si(11)—P(1)—Al(1)—C(11)	−94.4(2)	Si(13)—P(1)—Al(1)—C(31)	146.7(2)
Si(11)—P(1)—Al(1)—C(21)	147.0(2)	P(1)—Al(1)—C(11)—C(12)	−129.8(4)
Si(11)—P(1)—Al(1)—C(31)	25.8(2)	P(1)—Al(1)—C(21)—C(22)	−112.3(5)
Si(12)—P(1)—Al(1)—C(11)	145.7(2)	P(1)—Al(1)—C(31)—C(32)	−112.2(3)
Si(12)—P(1)—Al(1)—C(21)	27.1(2)	Al(1)—P(1)—Si(11)—C(111)	41.7(2)
Si(12)—P(1)—Al(1)—C(31)	−92.1(2)	Al(1)—P(1)—Si(12)—C(121)	45.3(2)
Si(13)—P(1)—Al(1)—C(11)	26.6(2)	Al(1)—P(1)—Si(13)—C(131)	37.4(2)
Si(13)—P(1)—Al(1)—C(21)	−94.1(2)		
Molecule 2			
(a) Bond lengths			
Al(2)—P(2)	2.521(2)	P(2)—Si(21)	2.285(2)
Al(2)—C(41)	1.990(5)	P(2)—Si(22)	2.288(2)
Al(2)—C(51)	1.989(6)	P(2)—Si(23)	2.283(2)
Al(2)—C(61)	1.991(6)	Si—C	1.847(7)–1.863(6)
(b) Bond angles			
P(2)—Al(2)—C(41)	105.5(2)	Al(2)—P(2)—Si(21)	114.1(1)
P(2)—Al(2)—C(51)	106.2(2)	Al(2)—P(2)—Si(22)	110.1(1)
P(2)—Al(2)—C(61)	104.9(2)	Al(2)—P(2)—Si(23)	113.5(1)
C(41)—Al(1)—C(51)	111.2(2)	Si(21)—P(2)—Si(22)	107.0(1)
C(41)—Al(1)—C(61)	114.5(2)	Si(21)—P(2)—Si(23)	105.7(1)
C(51)—Al(1)—C(61)	113.6(3)	Si(22)—P(2)—Si(23)	106.0(1)
(c) Torsion angles[a]			
Si(21)—P(2)—Al(2)—C(41)	−96.6(2)	Si(23)—P(2)—Al(2)—C(61)	145.8(2)
Si(21)—P(2)—Al(2)—C(51)	145.3(2)	P(2)—Al(2)—C(41)—C(42)	−122.6(4)
Si(21)—P(2)—Al(2)—C(61)	24.7(2)	P(2)—Al(2)—C(51)—C(52)	−114.0(4)
Si(22)—P(2)—Al(2)—C(41)	143.1(2)	P(2)—Al(2)—C(61)—C(62)	−114.3(4)
Si(22)—P(2)—Al(2)—C(51)	24.9(2)	Al(2)—P(2)—Si(21)—C(211)	42.2(2)
Si(22)—P(2)—Al(2)—C(61)	−95.7(2)	Al(2)—P(2)—Si(22)—C(221)	43.5(2)
Si(23)—P(2)—Al(2)—C(41)	24.5(2)	Al(2)—P(2)—Si(23)—C(231)	38.8(2)
Si(23)—P(2)—Al(2)—C(51)	−93.6(2)		

[a] The torsion angle A—B—C—D is defined as positive if, when viewed along the B—C bond, atom A must be rotated clockwise to eclipse atom D.

Table 3. Selected bond distances (Å) and angles (°) for $Ph_3Al\cdot As(SiMe_3)_3$ (**II**), with estimated standard deviations in parentheses

Molecule 1			
(a) Bond lengths			
As—Al	2.598(1)	Al—C(11)	1.989(4)
As—Si(11)	2.382(1)	Al—C(21)	1.979(4)
As—Si(12)	2.376(1)	Al—C(31)	1.987(3)
As—Si(13)	2.379(1)	Si—C	1.851(6)–1.863(5)
(b) Bond angles			
Al—As—Si(11)	112.53(4)	As—Al—C(11)	105.2(1)
Al—As—Si(12)	113.18(4)	As—Al—C(21)	102.9(1)
Al—As—Si(13)	112.91(4)	As—Al—C(31)	105.3(1)
Si(11)—As—Si(12)	104.77(4)	C(11)—Al—C(21)	114.1(2)
Si(11)—As—Si(13)	106.78(4)	C(11)—Al—C(31)	114.0(2)
Si(12)—As—Si(13)	106.04(5)	C(21)—Al—C(31)	113.9(2)
(c) Torsion angles[a]			
Si(11)—As—Al—C(11)	−91.5(1)	Si(13)—As—Al—C(31)	−91.2(1)
Si(11)—As—Al—C(21)	28.2(1)	As—Al—C(11)—C(12)	65.5(3)
Si(11)—As—Al—C(31)	147.8(1)	As—Al—C(21)—C(22)	72.8(3)
Si(12)—As—Al—C(11)	150.0(1)	As—Al—C(31)—C(36)	62.9(4)
Si(12)—As—Al—C(21)	−90.3(1)	Al—As—Si(11)—C(113)	42.4(2)
Si(12)—As—Al—C(31)	29.2(1)	Al—As—Si(12)—C(122)	41.7(2)
Si(13)—As—Al—C(11)	29.5(1)	Al—As—Si(13)—C(131)	39.2(2)
Si(13)—As—Al—C(21)	149.2(1)		
Molecule 2			
(a) Bond lengths			
As′—Al′	2.613(1)	Al′—C(11′)	1.985(5)
As′—Si(11′)	2.371(1)	Al′—C(21′)	1.994(4)
As′—Si(12′)	2.382(1)	Al′—C(31′)	1.980(3)
As′—Si(13′)	2.372(1)	Si—C	1.846(6)–1.865(6)
(b) Bond angles			
Al′—As′—Si(11′)	111.88(4)	As′—Al′—C(11′)	103.4(1)
Al′—As′—Si(12′)	112.91(4)	As′—Al′—C(21′)	105.5(1)
Al′—As′—Si(13′)	113.37(5)	As′—Al′—C(31′)	104.9(1)
Si(11′)—As′—Si(12′)	106.23(5)	C(11′)—Al′—C(21′)	115.0(2)
Si(11′)—As′—Si(13′)	105.40(5)	C(11′)—Al′—C(31′)	114.3(2)
Si(12′)—As′—Si(13′)	106.46(5)	C(21′)—Al′—C(31′)	112.4(2)
(c) Torsion angles[a]			
Si(11′)—As′—Al′—C(11′)	−96.8(2)	Si(13′)—As′—Al′—C(31′)	−97.9(1)
Si(11′)—As′—Al′—C(21′)	24.2(1)	As′—Al′—C(11′)—C(12′)	73.8(4)
Si(11′)—As′—Al′—C(31′)	143.1(1)	As′—Al′—C(21′)—C(22′)	66.3(3)
Si(12′)—As′—Al′—C(11′)	143.4(1)	As′—Al′—C(31′)—C(36′)	61.4(4)
Si(12′)—As′—Al′—C(21′)	−95.6(1)	Al′—As′—Si(11′)—C(113′)	38.6(2)
Si(12′)—As′—Al′—C(31′)	23.3(1)	Al′—As′—Si(12′)—C(122′)	38.4(2)
Si(13′)—As′—Al′—C(11′)	22.2(1)	Al′—As′—Si(13′)—C(131′)	46.1(2)
Si(13′)—As′—Al′—C(21′)	143.2(1)		

[a] The torsion angle A—B—C—D is defined as positive if, when viewed along the B—C bond, atom A must be rotated clockwise to eclipse atom D.

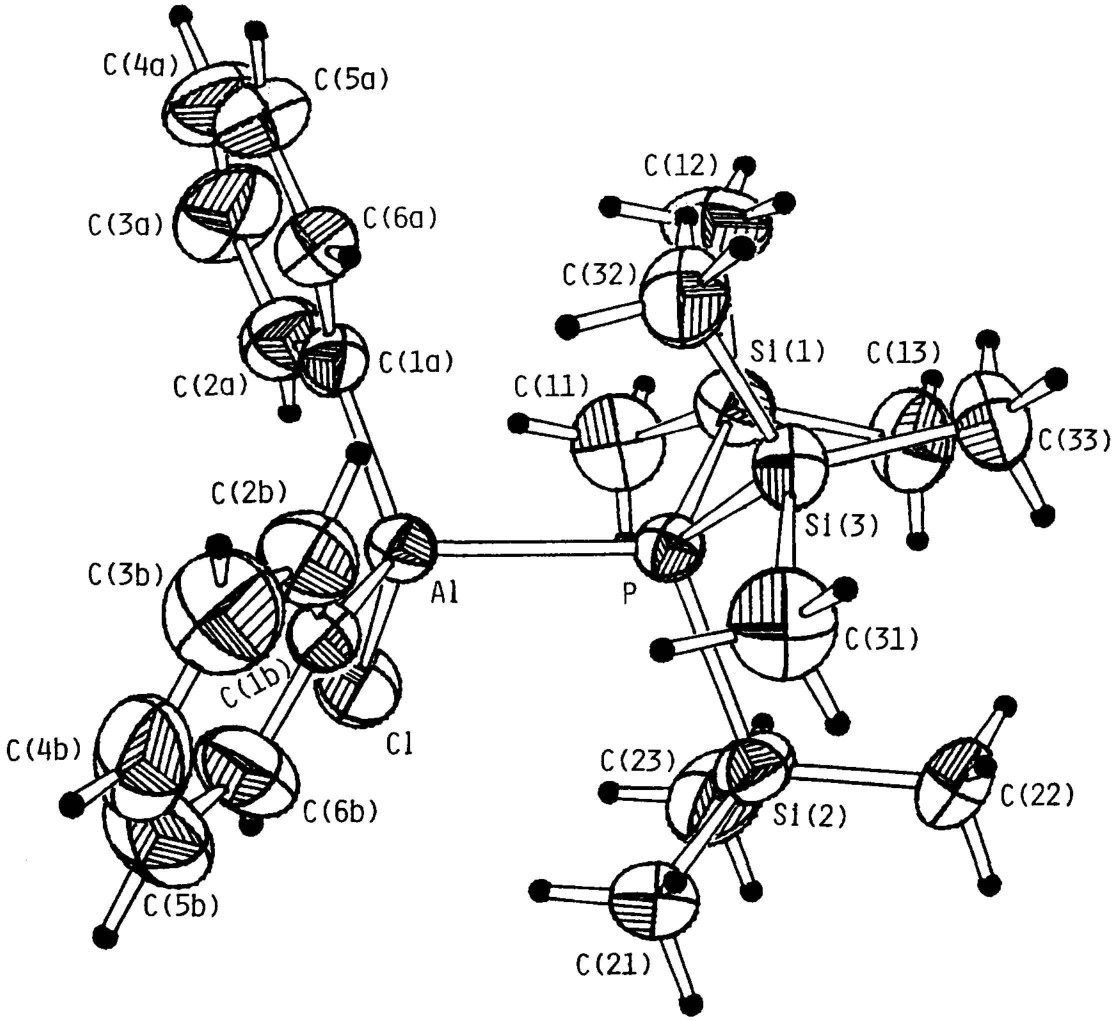

Fig. 3. A thermal ellipsoid diagram (40% probability) showing the solid-state conformation and atom numbering scheme of $Ph_2(Cl)Al \cdot P(SiMe_3)_3$ (**III**); small circles represent hydrogen atoms.

aluminium–phosphorus monodentate adducts wherein the corresponding distances range 2.391(6)–2.585(2) Å.[22–29] Consistent with the increased Lewis acidity of Ph_2AlCl over the Ph_3Al moiety as a consequence of replacement of a phenyl substituent by a more electronegative Cl atom as well as the greater degree of rotation from an eclipsed conformation, the Al—P bond in **III** is noticeably shorter than those in **I** [2.514(2), 2.521(2) Å].

When equimolar amounts of $PhAlCl_2$ and $P(SiMe_3)_3$ were allowed to react in benzene at 60°C, a white solid immediately precipitated out of solution [eq. (3)]. Titration of the volatiles collected from the reaction flask revealed that no Me_3SiCl was eliminated during the course of the reaction. Several attempts at recrystallization of the white solid product were made; however, X-ray quality single crystals were unobtainable. ^1H, $^{13}C\{^1H\}$ NMR spectra and partial elemental analysis of the product are consistent with a 1 : 1 Lewis acid–base adduct structure, $Ph(Cl)_2Al \cdot P(SiMe_3)_3$ (**V**), as shown in eq. (3).

$$PhAlCl_2 + P(SiMe_3)_3 \xrightarrow[60^\circ C]{\text{Toluene}} \underset{(\mathbf{V})}{Ph(Cl_2)Al \cdot P(SiMe_3)_3} \quad (3)$$

Analogous reaction of $PhAlCl_2$ and $As(SiMe_3)_3$ under similar conditions [eq. (3)] gave a brown intractable solid which was insoluble in aromatic solvents and THF, and was not further investigated.

^1H, $^{13}C\{^1H\}$ NMR spectra for compounds **I**–**V** are consistent with their formulation as adducts. The ^1H NMR spectra for **I**–**V** contain two multiplets in the phenyl region, consistent with monosubstituted phenyl rings. The observed phenyl proton signals for **I**–**V** have undergone the expected

Table 4. Selected bond distances (Å) and angles (°) for $Ph_2(Cl)Al \cdot P(SiMe_3)_3$ (**III**), with estimated standard deviations in parentheses

(a) Bond lengths			
Al—Cl	2.173(2)	P—Si(1)	2.284(2)
Al—P	2.467(2)	P—Si(2)	2.285(1)
Al—C(1a)	1.968(5)	P—Si(3)	2.283(2)
Al—C(1b)	1.989(6)	Si—C	1.841(8)–1.879(6)
(b) Bond angles			
Cl—Al—P	102.1(1)	Al—P—Si(1)	108.6(1)
Cl—Al—C(1a)	109.7(2)	Al—P—Si(2)	110.7(1)
Cl—Al—C(1b)	110.1(2)	Al—P—Si(3)	114.4(1)
P—Al—C(1a)	109.0(2)	Si(1)—P—Si(2)	108.4(1)
P—Al—C(1b)	109.3(2)	Si(1)—P—Si(3)	107.5(1)
C(1a)—Al—C(1b)	115.7(2)	Si(2)—P—Si(3)	107.1(1)
(c) Torsion angles[a]			
Si(1)—P—Al—Cl	79.0(1)	Si(3)—P—Al—C(1b)	−44.4(2)
Si(1)—P—Al—C(1a)	−37.1(2)	P—Al—C(1a)—C(2a)	104.8(4)
Si(1)—P—Al—C(1b)	−164.5(2)	P—Al—C(1b)—C(2b)	82.0(4)
Si(2)—P—Al—Cl	−39.9(1)	Al—P—Si(1)—C(11)	−42.4(3)
Si(2)—P—Al—C(1a)	−155.9(2)	Al—P—Si(2)—C(21)	−45.5(3)
Si(2)—P—Al—C(1b)	76.7(2)	Al—P—Si(3)—C(32)	−42.7(2)
Si(3)—P—Al—Cl	−161.0(2)	Cl—Al—C(1a)—C(2a)	−6.3(5)
Si(3)—P—Al—C(1a)	83.0(2)	Cl—Al—C(1b)—C(6b)	−2.2(5)

[a] The torsion angle A—B—C—D is defined as positive if, when viewed along the B—C bond, atom A must be rotated clockwise to eclipse atom D.

downfield shift from those of base-free Ph_3Al. The ^1H NMR spectrum of **I** contains a doublet at δ 0.11 ppm, arising from the coupling of a single ^{31}P atom with the $SiMe_3$ protons (^3J_P—H = 4.8 Hz), indicative of an adduct structure. A doublet is also present in the $^{13}C\{^1H\}$ solution NMR spectrum of **I** at $\delta = 3.15$ ppm (^3J_P—C = 7.31 Hz), which is due to the coupling of the $SiMe_3$ carbons with the phosphorus atom. The ^1H NMR spectrum of **III** contains a doublet at δ 0.17 ppm (^3J_P—H = 5.10 Hz), due to the coupling of the P atom with the Me_3Si protons, and that of compounds **IV** and **V** contain a singlet at δ 0.19 ppm and a doublet at δ 0.26 ppm, respectively. The ^{31}P NMR spectra of **I**, **III**, and **V** contain only a singlet at δ −232.5, −225.2, and −220.1 ppm respectively, which are within the range typically observed for Al—P adduct compounds.[22 30,33] The chemical shifts for $SiMe_3$ protons in **II** and **IV** are in accordance with those previously observed for other Al—As Lewis acid–base adducts.[31,34] Compound **V** has a coupling constant J_P—H = 5.07 Hz similar to that for **III** (J_P—H = 5.10 Hz). The chemical shifts observed for ^{27}Al NMR spectra of **I** (δ 189.5 ppm) and **III** (δ 181.6 ppm) are well within the range (120–220 ppm) for four-coordinated aluminium centres.[35]

CONCLUSIONS

The adducts **I**–**V** are the first examples of triphenylaluminium compounds containing heavier pnicogen atoms. The syntheses and characterization of these species reiterates the tendency for phenylaluminium derivatives to form 1 : 1 Lewis acid–base adducts with silylpnictines rather than elimination–condensation products.

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Supplementary material

Atomic coordinates, thermal parameters, complete bond lengths and angles, and crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

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