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The independent reactions of Ph_3Al with $E(SiMe_3)_3$ (E = P or As) in 1:1 mole ratios afforded the adducts $Ph_3Al{\bullet}E(SiMe_3)_3$ [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 $Ph_2(Cl)Al{\bullet}E(SiMe_3)_3$ [E = P (**III**) and As (**IV**)]. The adduct $Ph(Cl)_2Al{\bullet}P(SiMe_3)_3$ (**V**) was isolated from the reaction of equimolar amounts of $PhAlCl_2$ and $P(SiMe_3)_3$. 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 $P\,2_1/n$ (C_{2h}^5), while **II** crystallizes in the triclinic space group $P\,{-1}(C_i^1)$, each with two discrete molecules per asymmetric unit. Crystals of compound **III** belong to the orthorhombic space group $P\,2_12_12_1(D_2^4)$. Compounds **I-III** are the first structurally-characterized compounds to contain phenyl-substituted Al centres bonded to heavier pnicogen atoms.

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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 $Ph_3Al{\bullet}E(SiMe_3)_3$ [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 $Ph_2(Cl)Al{\bullet}E(SiMe_3)_3$ [E = P (**III**) and As (**IV**)]. The adduct $Ph(Cl)_2Al{\bullet}P(SiMe_3)_3$ (**V**) was isolated from the reaction of equimolar amounts of $PhAlCl_2$ and $P(SiMe_3)_3$. 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.

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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 thirty 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 ten years later that Robinson and co-workers reopened this area of organoaluminium chemistry with their synthesis and characterization of the aminophenylalane compounds, $Ph_3Al{\bullet}N(H)_2{}^tBu$[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] $Mes_3Al{\bullet}(4\text{-picoline})(C_7H_8)_{0.5}$,[5] $Et(Mes)_2Al{\bullet}THF$,[5] $Mes_2(Cl)Al{\bullet}THF$,[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 $Trip_2AlP(1\text{-}Ad)SiPh_3{\bullet}0.5$ hexane (Trip = 2,4,6-${}^iPr_3C_6H_2$, 1-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, $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Cl}$.[9] The Ga-P analog, $Ph_2\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl}$, 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 $Ph_3Ga{\bullet}P(SiMe_3)_3$[11] and $Ph_3Ga{\bullet}As(SiMe_3)_3$[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, $Ph_3Al{\bullet}E(SiMe_3)_3$ [E = P (**I**) or As (**II**)], $Ph_2(Cl)Al{\bullet}E(SiMe_3)_3$ [E = P (**III**) or As (**IV**)], and $Ph(Cl)_2Al{\bullet}P(SiMe_3)_3$ (**V**).

EXPERIMENTAL

Synthesis

All reactions and manipulations were carried out under vacuum, in a Vacuum Atmospheres HE-493 Dri-Lab under an argon atmosphere, and 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 ppm 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.

$Ph_3Al{\bullet}P(SiMe_3)_3$ (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 d 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, were determined to be **I** (0.64 g, 82% yield), mp 184-204 °C (gradually melts to a yellow liquid). Anal. Calcd. (Found) for $C_{27}H_{42}AlPSi_3$: C 63.73 (63.95), H 8.32 (8.37). ^1H NMR: δ 0.11 [d, $Si(CH_3)_3$, 27H, ($J_{P\text{-}H}$ = 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, $Si(CH_3)_3$, ($J_{P\text{-}C}$ = 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).

$Ph_3Al{\bullet}As(SiMe_3)_3$ (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 d, resulting in 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 colorless crystals of **II**, suitable for X-ray crystallographic analysis, were isolated (0.51 g, 78.0% yield), mp 192 - 195 °C (slight decomposition to an orange solid was observed). Anal. Calcd. (Found) for $C_{27}H_{42}AlAsSi_3$: C 58.66 (58.43), H 7.66 (7.92). ^{1}H NMR: 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).

$Ph_2(Cl)Al\bullet P(SiMe_3)_3$ (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 d 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), mp 141-155 °C (decomposes to a glassy yellow solid before melting). Anal. Calcd. (Found) for $C_{21}H_{37}AlPClSi_3$: C 53.99 (53.87), H 7.98 (7.89), Al 5.78 (5.62), P 6.63 (6.38), Cl 7.59 (7.48). ^{1}H NMR: δ 0.17 [d, Si(CH_3)$_3$, 27H, ($J_{P\text{-}H}$ = 5.10 Hz)], 7.31 (m, C_6H_5, 9H), 8.23 (m, C_6H_5, 6H). $^{13}C\{^1H\}$ NMR: δ 2.71 [d, Si(CH_3)$_3$, ($J_{P\text{-}C} \doteq$ 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).

$Ph_2(Cl)Al{\bullet}As(SiMe_3)_3$ (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 d, 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, mp 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. Anal. Calcd. (Found) for $C_{21}H_{37}AlAsClSi_3$: C 49.35 (49.27), H 7.29 (7.18). ^{1}H NMR: δ 0.19 [s, $Si(CH_3)_3$, 27H], 7.31 (m, C_6H_5, 9H), 8.18 (m, C_6H_5, 6H). $^{13}C\{^1H\}$ NMR: δ 3.00 [s, $Si(CH_3)_3$], 123.8, 127.6, 137.7, 138.4 and 139.7 (s,C_6H_5).

$Ph(Cl)_2Al{\bullet}P(SiMe_3)_3$ (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 d 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 mp observed: 140-145 °C, colorless liquid condensed at the top of the capillary; 145-300 °C, decomposed to a yellow solid. Anal. Calcd. (Found) for $C_{15}H_{32}AlPCl_2Si_3$: C 42.34 (42.58), H 7.58 (7.30). ^{1}H NMR: δ 0.26 [d, Si(CH_3)$_3$, 27H, ($J_{\text{P-H}}$ = 5.07 Hz)], 7.25 (m, C_6H_5, 9H), 7.76 (br. s, C_6H_5), and 8.06 (m, C_6H_5, 6H). ^{13}C{^{1}H} NMR: δ 2.02 and 2.38 [d, Si(CH$_3$)$_3$, ($J_{\text{P-C}}$ = 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**, **II**, and **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-Kα radiation (λ = 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° < θ < 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 calculated positions using a riding model, with parameter refinement converging at R = 0.048 (Rw = 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 reference 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-Kα 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 was 0.0501 while R_w was 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 reference 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 $Ph_3Al{\bullet}P(SiMe_3)_3$ (**I**) and $Ph_3Al{\bullet}As(SiMe_3)_3$ (**II**), respectively (Eqn. 1).

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

E = P (**I**), Toluene, 110 °C
E = As (**II**), Benzene, 65 °C

Adduct **I** is the aluminium analogue of the gallium-phosphorus adduct $Ph_3Ga{\bullet}P(SiMe_3)_3$,[11] and it is only the second triarylaluminium-phosphorus compound to be structurally characterized. Compound **II**, the Al analogue of $Ph_3Ga{\bullet}As(SiMe_3)_3$,[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 $Ph_3Al{\bullet}P(SiMe_3)_3$ (**I**) and $Ph_3Al{\bullet}As(SiMe_3)_3$ (**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. $Ph_3Ga{\bullet}P(SiMe_3)_3$[11] and $Ph_3Ga{\bullet}As(SiMe_3)_3$.[13] Crystals of the arylaluminium monophosphide, $Trip_2AlP(1\text{-}Ad)SiPh_3.0.5$ 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 the monoclinic system, space group $P2_1/n$, and they are isomorphous with those of the gallium analogue, $Ph_3Ga{\bullet}P(SiMe_3)_3$.[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 $Ph_3Ga{\bullet}P(SiMe_3)_3$[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 that those found in other alkylhaloaluminium-silylphosphine adducts: $Et(Cl)_2Al{\bullet}P(SiMe_3)_3$ [2.435(3) Å],[29] $^{i}Bu_2(Cl)Al{\bullet}P(SiMe3)_3$ [2.504(3) Å],[29] $Cl_3Al{\bullet}P(SiMe_3)_3$.Toluene [2.392(4) Å],[30] and $Br_3Al{\bullet}P(SiMe_3)_3$.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 $Trip_2AlP(1\text{-}Ad)SiPh_3.0.5$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 isostructural with the Ga-As analogue $Ph_3Ga{\bullet}As(SiMe_3)_3$,[13] the crystals are not isomorphous. In common with the metal and pnicogen atoms in **I**, $Ph_3Ga{\bullet}P(SiMe_3)_3$, and $Ph_3Ga{\bullet}As(SiMe_3)_3$, the coordination geometry about the Al and As centres in both molecules of **II** is pseudotetrahedral. 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 $Ph_3Ga{\bullet}P(SiMe_3)_3$ [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 $Ph_3Ga{\bullet}As(SiMe_3)_3$ [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) Å and 2.613(1) Å are significantly longer than those in the only other structurally-characterized Al-As adducts, $^{i}Bu_2(Cl)Al{\bullet}As(SiMe_3)_3$[31] [2.573(1) Å] and $Cl_3Al{\bullet}As(SiMe_3)_2{\cdot}(C_7H_8)$[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 $\overline{\text{Al-E-Al-E}}$ or $\overline{\text{Al-E-Al-Cl}}$ (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 reactions yielded adducts $Ph_2(Cl)Al{\bullet}P(SiMe_3)_3$ (**III**) and $Ph_2(Cl)Al{\bullet}As(SiMe_3)_3$ (**IV**), rather than the condensation products of dehalosilylation (Eqn. 2).

$$Ph_2AlCl + E(SiMe_3)_3 \xrightarrow{\text{Toluene}} Ph_2(Cl)Al{\bullet}E(SiMe_3)_3 \qquad (2)$$

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 $Ph_2(Cl)Al{\bullet}As(SiMe_3)_3$ (**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, $Ph_2(Cl)Ga{\bullet}P(SiMe_3)_3$.[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 aluminium-phosphorus monodenatate adducts wherein the corresponding distances range from 2.391(6) to 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 (Eqn. 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, $Ph(Cl)_2Al{\bullet}P(SiMe_3)_3$ (**V**), as shown in Eqn. 3.

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

Analogous reaction of $PhAlCl_2$ and $As(SiMe_3)_3$ under similar conditions (Eqn. 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 mono-substituted phenyl rings. The observed phenyl proton signals for **I-V** have undergone the expected 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 ($^3J_{P\text{-}H}$ = 4.8 Hz), indicative of an adduct structure. A doublet is also present in the $^{13}C\{^1H\}$ solution NMR spectrum of **I** at δ = 3.15 ppm ($^3J_{P\text{-}C}$ = 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 ($^3J_{P\text{-}H}$ = 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 $J_{P\text{-}H}$ = 5.07 Hz similar to that for **III** ($J_{P\text{-}H}$ = 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) of four coordinated aluminium centre.[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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Table 1. Crystallographic Data and Data Collection Parameters for $Ph_3Al{\bullet}P(SiMe_3)_3$ (I), $Ph_3Al{\bullet}P(SiMe_3)_3$ (II), and $Ph_2(Cl)Al{\bullet}P(SiMe_3)_3$ (III).

	I	II
molecular formula	$C_{27}H_{42}AlPSi_3$	$C_{27}H_{42}AlAsSi_3$
formula weight	508.83	552.80
crystal system	monoclinic	triclinic
space group	$P2_1/n$ (C_{2h}^5) - No. 14	$P\bar{1}$ (C_i^1) - No. 2
a, Å	18.678(4)	16.097(2)
b, Å	19.010(7)	16.254(2)
c, Å	18.776(4)	12.488(2)
α, deg	90.0(-)	92.03(1)
β, deg	112.49(2)	97.70(1)
γ, deg	90.0(-)	86.85(1)
V, $Å^3$	6159(3)	3232(1)
Z	8	4
D_{calcd}, g cm^{-3}	1.097	1.136
μ, mm^{-1}	0.24	.29
temp, °C	-130	25
crystal dimension, mm	0.42 x 0.30 x 0.25	0.20 x 0.24 x 0.50
T_{max},T_{min}	0.94,0.90	T_{max}:T_{min} (relative)1.00:0.83
scan type	ω-2θ	ω-2θ
θ_{max}, deg	2θ:45	75
Total no of reflections recorded	10240$(+h,+k,\pm l)$	13784$(+h,\pm k,\pm l)$
no of non-equiv. reflections	8048	13288
R_{merge}, on I	0.041	0.022
no of reflections retained	4834 $(I > 2.5\sigma I)$	7880 $(I > 3.0\sigma I)$
no of parameters refined	578	578
R, R_w[a]	0.048 (0.051)	0.040 (0.053)
goodness-of-fit[b]	1.30	1.44
max shift; esd in final least-squares cycle	0.001	0.03
final $\Delta\rho$(e/$Å^3$) max;min	0.29; -0.30	0.30; -0.74

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[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $\Sigma w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized. [b] Goodness-of-fit = $[\Sigma w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

Table 1 (continued).

	III
molecular formula	$C_{21}H_{37}AlClPSi_3$
formula weight	467.20
crystal system	orthorhombic
space group	$P2_12_12_1(D_2^4)$-No.19
a, Å	9.759(1)
b, Å	30.463(6)
c, Å	9.343(1)
α, deg	90.0(-)
β, deg	90.0(-)
γ, deg	90.0(-)
V, Å^3	2778(1)
Z	4
D_{calcd}, g cm^{-3}	1.117
μ, cm^{-1}	34.0
temp, °C	25
crystal dimension, mm	0.16 x 0.34 x 0.70
T_{max},T_{min}	T_{max}:T_{min} (relative)1.00:0.59
scan type	ω-2θ
θ_{max}, deg	75
Total no of reflections recorded	3250$(+h,+k,+l)$
no of non-equiv. reflections	3250
R_{merge}, on I	-
no of reflections retained	2485$(I > 3.0\sigma I)$
no of parameters refined	244
R, R_w[a]	0.046 (0.064)
goodness-of-fit[b]	1.68
max shift; esd in final least-squares cycle	0.03
final $\Delta\rho$(e/Å^3) max;min	0.27; -0.32

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[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $\Sigma w\Delta^2$ $[w = 1/\sigma^2(|F_o|), \Delta = (|F_o| - |F_c|)]$ was minimized. [b] Goodness-of-fit = $[\Sigma w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Ph_3Al{\bullet}P(SiMe_3)_3$ (**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)		

Table 2 (continued).

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)		

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[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 (deg) for $Ph_3Al{\bullet}As(SiMe_3)_3$ (**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-(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)

Table 3 (continued).

(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)		

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[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 4. Selected Bond Distances (Å) and Angles (deg) 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)

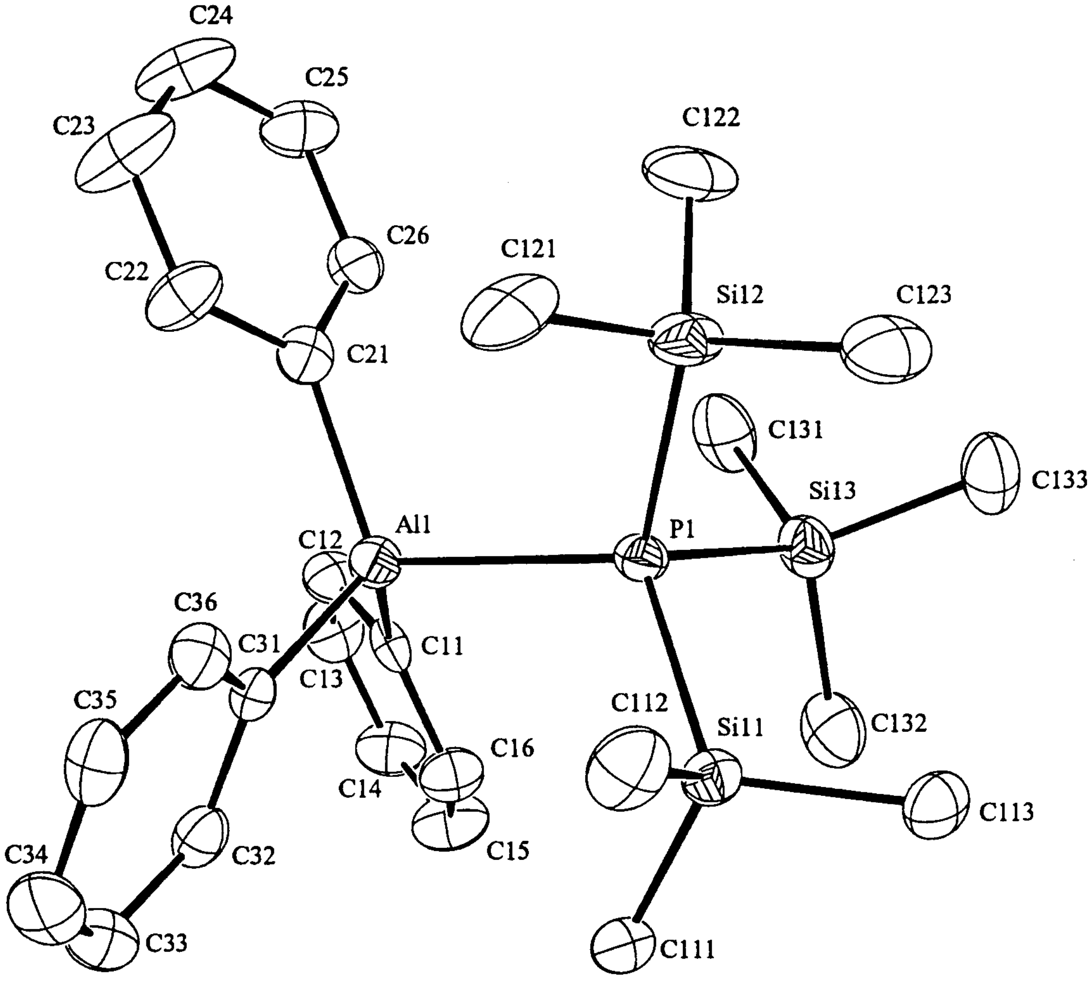
[a] The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

CAPTIONS TO FIGURES

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

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

Figure 3. A thermal ellipsoid diagram (40% probability) showing the solid state conformation and atom numbering scheme of $Ph_2(Cl)Al{\bullet}P(SiMe_3)_3$ (**III**); small circles represent hydrogen atoms.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C36
C31
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C113
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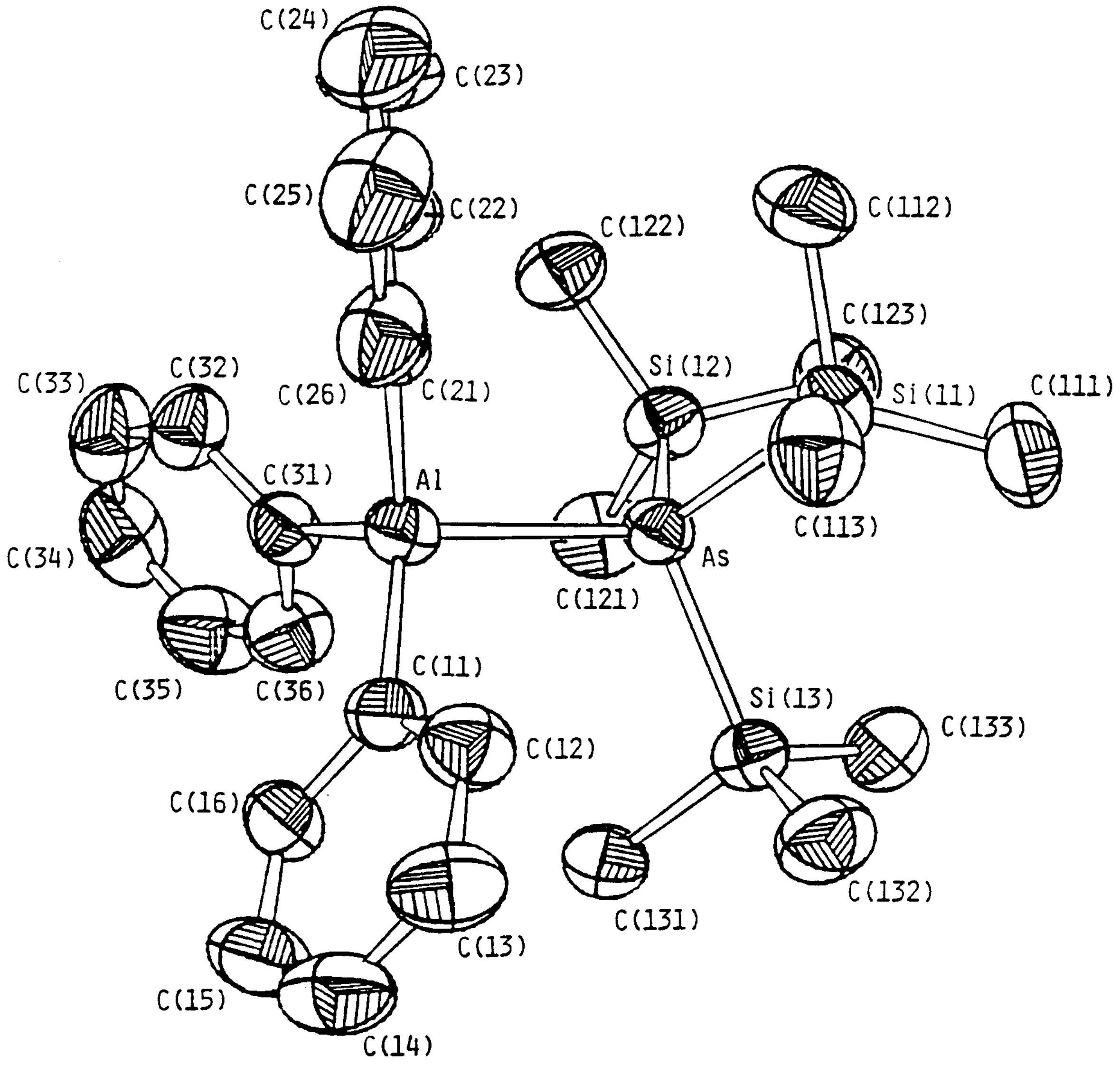
C34
C32
C33
C111

Figure 1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C(11)
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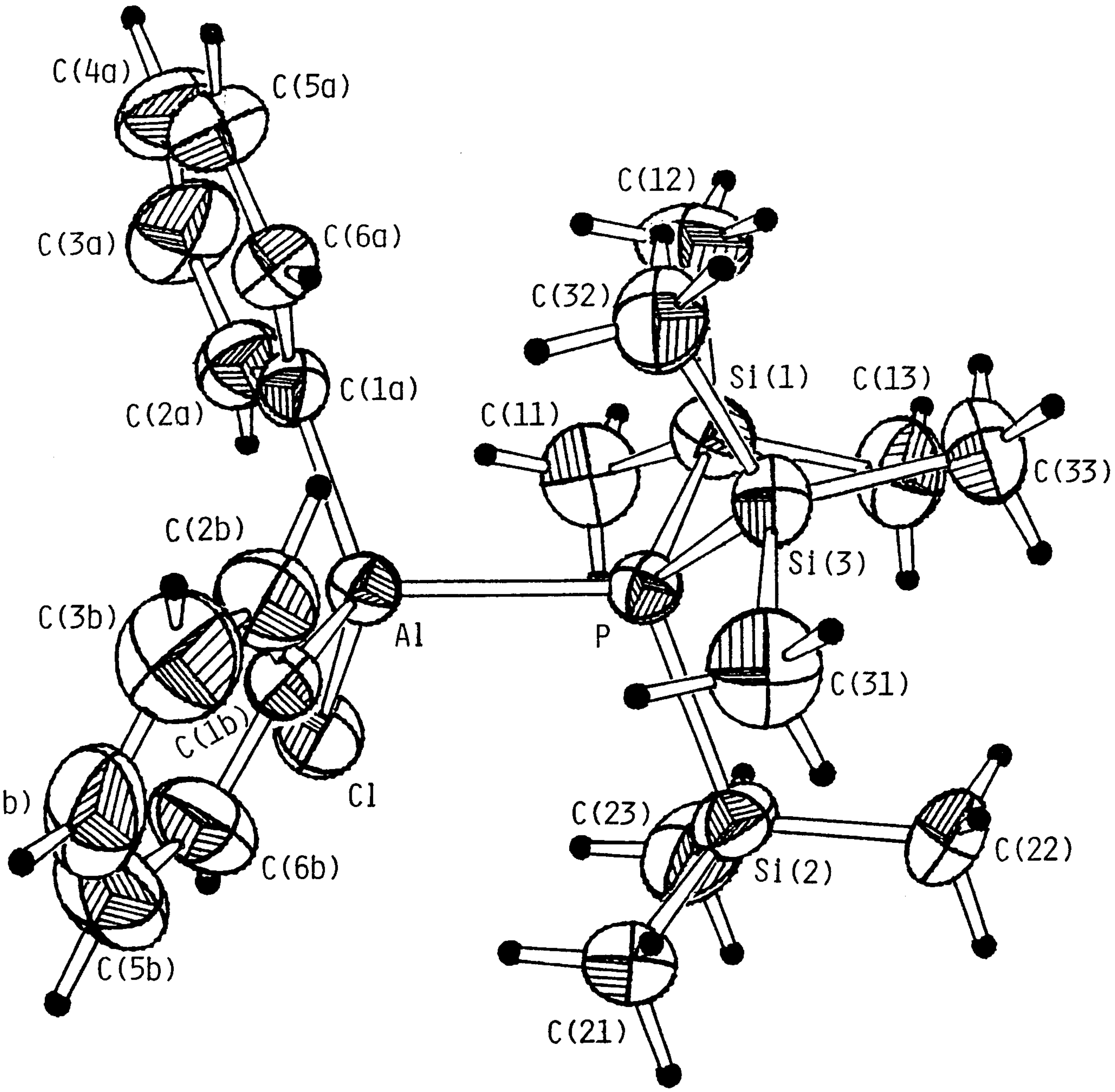
Figure 2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C(31)
C(1b)
Cl
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C(22)
C(6b)
Si(2)
C(5b)
C(21)

Figure 3

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