Aluminum–Phosphorus Chemistry: Preparation and Structural Characterization of $[Et_2AlP(SiMe_3)_2]_2$, $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$, and *i*-$Bu_2(Cl)Al{\cdot}P(SiMe_3)_3$

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Reactions of R_2AlCl (R = Et, *i*-Bu) and $EtAlCl_2$ with $P(SiMe_3)_3$ and $LiP(SiMe_3)_2$ were studied to investigate the potential use of dehalosilylation and lithium chloride elimination reactions for the preparation of compounds containing either Al–P–Al–P or Al–P–Al–Cl core rings. The dimeric compound $[Et_2AlP(SiMe_3)_2]_2$ (1) was isolated from the 1:1 reaction of Et_2AlCl and $LiP(SiMe_3)_2$ at −78 °C, as a result of LiCl elimination. The 1:1 reaction of $EtAlCl_2$ and $P(SiMe_3)_3$ yields $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (2). Interestingly, a similar reaction between Et_2AlCl and $P(SiMe_3)_3$ in a 2:1 mole ratio also affords **2**, in moderate yield, suggesting a rearrangement of the original aluminum alkyl halide. However, when Et_2AlCl was reacted with $P(SiMe_3)_3$ in a 1:1 mole ratio, the expected adduct $Et_2(Cl)AlP(SiMe_3)_3$ (3) results. Unlike the Et_2AlCl reaction, the analogous 2:1 mole reaction of *i*-Bu_2AlCl and $P(SiMe_3)_3$ forms the monochloro adduct, *i*-$Bu_2AlCl{\cdot}P(SiMe_3)_3$ (4), rather than a rearrangement product. Compounds 1–4 were characterized by partial elemental analysis, melting point data, as well as ^1H, ^{13}C, ^{31}P, and ^{27}Al NMR spectroscopy. Compounds 1, 2, and 4 were also characterized by single-crystal X-ray crystallography. Dimer 1 crystallizes in the monoclinic system, space group $C2/c$ (C_{2h}^6), with unit cell dimensions of a = 18.085(2) Å, b = 9.452(1) Å, c = 20.233(2) Å, and β = 100.30(1)° for Z = 4. Crystals of adduct 2 have unit cell parameters of a = 13.234(2) Å, b = 13.147(2) Å, and c = 13.043(2) Å for Z = 4 and belong to the orthorhombic system, space group $Pca2_1$ (C_{2v}^5), while adduct 4 crystallizes in the monoclinic system, space group $P2_1/c$ (C_{2h}^5), with cell dimensions of a = 14.986(3) Å, b = 11.489(2) Å, c = 18.570(4) Å, and β = 119.57 (2)° for Z = 4.

Introduction

The renewed activity in the development of group 13–15 single-source precursors to semiconductor[1–6] materials has prompted our laboratory to undertake the synthesis of novel organoaluminum–phosphorus compounds which might serve as sources of AlP.[7,8] Much of the early work in this area involved the use of alkane elimination reactions between R_3Al (R = alkyl) and Ph_2EH (E = P, As) to prepare dimers of the type $[R_2AlEPh_2]_2$.[9,10] As alternatives to such an approach, we have employed two additional routes to generate compounds containing either Al–P–Al–P or Al–P–Al–Cl (mixed-bridge) core rings: (1) coupling reactions between alkylaluminum halides and $LiP(SiMe_3)_2$ or (2) dehalosilylation between alkylaluminum halides and $P(SiMe_3)_3$. These two methods have been successfully applied to heavier group 13–15 systems to yield compounds with Al–As, Ga–P, Ga–As, In–As, and In–P dimeric and mixed-bridge core structures,[3–6,11–13] but their utility for the synthesis of analogous Al-P compounds remained to be explored. We describe herein synthesis of the dimer $[Et_2AlP(SiMe_3)_2]_2$ (1) by the lithium coupling method and preparation of the Lewis base adducts $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (2), $Et_2(Cl)Al{\cdot}P(SiMe_3)_3$ (3), and *i*-$Bu_2(Cl)Al{\cdot}P(SiMe_3)_3$ (4) by attempted dehalosilylation reactions.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk vacuum techniques or in a Vacuum Atmospheres HE-493 Dri-Lab under an argon atmosphere. Pentane was dried over $LiAlH_4$, while all other solvents were distilled from sodium/benzophenone ketyl under dry nitrogen. Et_2AlCl and *i*-Bu_2AlCl were purchased from Strem Chemicals, Inc. and used without further purification. $P(SiMe_3)_3$ was prepared *via* procedures by Becker *et al.*[14] $LiP(SiMe_3)_2$[15] was prepared *via* the reaction of 1 equiv of MeLi with 1 equiv of

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$P(SiMe_3)_3$. ^1H, $^{13}C\{^1H\}$, ^{31}P, and ^{27}Al NMR spectra were obtained on a Varian XL-300 spectrometer (300.0, 75.4, 121.4, and 78.2 MHz, respectively) in sealed 5-mm tubes. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to TMS using the residual protons or carbons of benzene-d_6 at δ 7.15 ppm and δ 128 ppm, respectively. ^{31}P and ^{27}Al spectra were referenced externally to H_3PO_4 and $Al(NO_3)_3$, respectively, at δ 0.00 ppm. Melting points were obtained on a Thomas Hoover Uni-melt apparatus in sealed capillaries. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Crystals used in X-ray analyses were flame-sealed under argon in 0.7-mm thin-walled glass capillaries. The Me_3SiCl content of volatile reaction products was determined by hydrolysis, followed by standardized NaOH titration to a phenolphthalein endpoint.

Preparation of $[Et_2AlP(SiMe_3)_2]_2$ (1). $LiP(SiMe_3)_2$ (0.138 g, 0.749 mmol) was dissolved in 15 mL of pentane and 5 mL of THF in a small glass vial, and the solution was transferred into the top bulb of a two-bulb reaction flask. Et_2AlCl (0.901 g, 0.749 mmol) was washed into the bottom bulb of the flask using 20 mL of pentane, followed by the addition of a stir bar. The lower bulb was evacuated and cooled to −78 °C in an acetone/dry ice bath, while the top bulb was cooled with a liquid nitrogen wand. The $LiP(SiMe_3)_2$ solution was added dropwise to Et_2AlCl over a 10-min period. Upon mixing, the solution turned yellow with a white precipitate (presumably LiCl, 0.0283 g, 89% yield). After stirring at −78 °C for 18 h, the reaction mixture was allowed to warm to room temperature, and the volatiles were removed *in vacuo* to leave a beige semisolid which was recrystallized from pentane at −15 °C to give 1 (0.137 g, 69.5% yield), mp 280–282.5 °C. Anal. Calcd (Found) for $C_{20}H_{56}Al_2P_2Si_4$: C, 45.70 (45.51); H, 10.77 (10.85); P, 11.80 (11.87). ^1H NMR: δ 1.37 (t, CH_3, 12H), 0.48 (q, CH_2, 8H), 0.38 [(t, $Si(CH_3)_3$, 36H, J_{P-H} = 2.5 Hz]. $^{13}C\{^1H\}$ NMR: δ 9.55 (s, CH_3), 4.48 [t, $Si(CH_3)_3$, J_{P-C} = 5.0 Hz], CH_2 not observed. ^{27}Al NMR: δ 164.3 (br s). ^{31}P NMR: δ −246.9 (s).

Preparation of $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (2). $P(SiMe_3)_3$ (0.251 g, 1.00 mmol) was dissolved in 15 mL of pentane, and the solution was placed in a high-pressure screw-top reaction tube. $EtAlCl_2$ (0.125 g, 1.00 mmol) was dissolved in 15 mL of pentane, and the resulting solution was added to the $P(SiMe_3)_3$ solution. A white solid immediately precipitated out of the reaction solution. Upon stirring at room temperature for 24 h, the white solid became crystalline in appearance. Inside the drybox, the solvent was decanted from the solid. Evaporation of the residual solvent from the solid resulted in 2 (0.3685 g, 97.6% yield), mp 221.5–223 °C. Anal. Calcd (Found) for $C_{11}H_{32}AlCl_2PSi_3$: C, 34.97 (34.73); H, 8.56 (8.57); Cl, 18.78 (18.66); P, 8.21 (7.97); Al, 7.15 (7.45). ^1H NMR: δ 1.51 (t, CH_3, 3H), 0.47 (q, CH_2, 2H), 0.25 [d, $Si(CH_3)_3$, 27H]. $^{13}C\{^1H\}$ NMR: 2.98 (s, CH_3), 2.37 [d, $Si(CH_3)_3$], CH_2 not observed. ^{27}Al NMR: δ 177. 6 (br s). ^{31}P NMR: δ −229.4 (s).

Isolation of $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (2) from the 2:1 Mole Reaction of Et_2AlCl and $P(SiMe_3)_3$. $P(SiMe_3)_3$ (0.386 g, 1.54 mmol) was dissolved in 20 mL of pentane, and the solution was placed in a high-pressure screw-top reaction tube. Et_2AlCl (0.371 g, 3.08 mmol) was dissolved in 10 mL of pentane, and the resulting solution was added to the $P(SiMe_3)_3$ solution. The clear, colorless reaction mixture was allowed to stir at room temperature for 3 days. The solution was transferred *via* cannula into a 100-mL Schlenk flask, and volatiles were removed *in vacuo* to yield an off-white semisolid along with a viscous yellow liquid. Isolated from this mixture were colorless X-ray quality crystals of 2 (0.280 g, 48.3% yield), as confirmed by comparison to an authentic sample, ^1H, ^{13}C, and ^{31}P NMR, (*vide infra*).

Preparation of $Et_2(Cl)Al{\cdot}P(SiMe_3)_3$ (3). Et_2AlCl (0.121 g, 1.00 mmol) was dissolved in 20 mL of pentane, and the solution was added to a high-pressure reaction tube equipped with a stir bar. $P(SiMe_3)_3$ (0.251 g, 1.00 mmol) was dissolved in 20 mL of pentane, and the resulting solution was combined with the Et_2AlCl solution. The reaction was allowed to stir at room temperature for 24 h. Inside the drybox, the clear, colorless solution was allowed to evaporate, yielding a white crystalline solid, 3 (0.3643 g, 98.2% yield), mp 185.7–188.5 °C. X-ray quality crystals were unobtainable. Anal. Calcd (Found) for $C_{17}H_{45}AlClPSi_3$: C, 42.04 (41.82); H, 10.07 (10.09); Cl, 9.55 (9.34); P, 8.35 (8.08); Al 7.27 (7.60). ^1H NMR: δ 1.54 (t, CH_3, 6H), 0.43 (q, CH_2, 4H), 0.24 [d, $Si(CH_3)_3$, 27H]. $^{13}C\{^1H\}$ NMR: δ 9.89 (s, CH_3), 2.72 [d, $Si(CH_3)_3$], CH_2 not observed. ^{27}Al NMR: δ 177.6 (br s). ^{31}P NMR: δ −227.6 (s).

Preparation of i-$Bu_2(Cl)Al{\cdot}P(SiMe_3)_3$ (4). $P(SiMe_3)_3$ (0.394 g, 1.57 mmol) was dissolved in 20 mL of pentane, and the solution was placed in a high-pressure screw-top reaction tube. This was added to i-Bu_2AlCl (0.556 g, 3.15 mmol) dissolved in 10 mL of pentane. This clear, colorless solution was stirred for 3 days at room temperature and then transferred *via* cannula into a 100-mL Schlenk flask. The volatiles were removed *in vacuo*, leaving an off-white crystalline solid 4 (0.577 g, 86.1% yield), mp 145.2 °C, of which some X-ray quality crystals were isolated. Anal. Calcd (Found) for $C_{17}H_{45}AlClPSi_3$: C, 47.76 (43.95); H, 10.64 (9.55); Cl, 8.29 (7.83); P, 7.26 (7.02); Al, 6.32 (6.52). ^1H NMR: δ 1.31 [d, $(CH_3)_2CH$, 12H], 2.35 (m, CH, 2H), 0.48 (d, CH_2, 4H), 0.27 [d, $Si(CH_3)_3$, 27H]. $^{13}C\{^1H\}$ NMR: δ 28.60 [s, $(CH_3)_2CH$], 28.11 (d, CH_2), 26.94 (s, CH), 2.73 [d, $Si(CH_3)_3$]. ^{27}Al NMR: d 183.1 (br s). ^{31}P NMR: δ −222.23 (s).

X-ray Structural Analyses of 1, 2, and 4. Crystallographic data and data collection parameters are summarized in Table I. Refined unit-cell parameters were derived from the diffractometer setting angles for 25 reflections (35° < θ < 40° for 1 and 2, 30° < θ < 35° for 4) widely separated in reciprocal space. Intensity data for all three compounds were corrected for the usual Lorentz and polarization effects. Empirical absorption corrections, based on the ϕ dependency of the intensities of several reflections with ψ ca. 90°, were also applied. Crystallographic calculations were performed on PDP11/44 and Micro-VAX 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 16.

Crystals of compounds 1 and 4 are isomorphous with those of the isostructural As analogs reported in refs 3 and 4, respectively. Accordingly, final coordinates for the As analogs were used as initial input to the structure-factor calculations with substitution of P for As. The crystal structure of 2 was solved by direct methods (MULTAN11/82). Systematic absences for 2 ($0kl$ when $l \neq 2n$, $h0l$ when $h \neq 2n$) are consistent with space groups $Pca2_1$ and $Pbcm$ (with a and b axes interchanged). With four formula units per unit cell the space group $Pbcm$ requires that the molecules lie on an inversion center, a 2-fold axis, or a mirror plane of symmetry; the constitution of 2 allows only the possibility that the molecules lie on a mirror plane. The space group $Pca2_1$ was assumed at the outset. Approximate coordinates for the aluminum, chlorine, silicon, and phosphorus atoms were obtained from an E-map. The remaining non-hydrogen atoms were located in a weighted F_o Fourier synthesis phased by the heavier atoms. That the molecule did not possess a mirror plane of symmetry was indicated by the disposition of the atoms, thus confirming the choice of space group. Non-hydrogen atom positional and thermal parameters (at first isotropic, then anisotropic) for 1, 2, and 4 were adjusted by means of several rounds of full-matrix least-squares calculations. For 2, parameter refinement with omission of the imaginary contributions to the anomalous scattering converged at R = 0.0458 (R_w = 0.0593). Introduction of the imaginary contributions into the structure-factor calculations then yielded R = 0.0460 (R_w = 0.0603) for the (hkl) data set and R = 0.0476 (R_w = 0.0616) when their Friedel pairs ($\bar{h}\bar{k}\bar{l}$) were used. These differences are significant[17] and established the polarity of the crystal employed; all further refinement was performed using the (hkl) data. In the subsequent least-squares iterations, hydrogen atoms for 1, 2, and 4, were incorporated at their calculated positions (C–H = 1.05 Å). Final difference Fourier syntheses contained no unusual features.

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Table I. Crystallographic Data and Data Collection Parameters[a] for $[Et_2AlP(SiMe_3)_2]_2$ (1), $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (2), and $i\text{-}Bu_2(Cl)Al{\cdot}P(SiMe_3)_3$ (4)

	1	2	4
molecular formula	$C_{20}H_{56}Al_2P_2Si_4$	$C_{11}H_{32}AlCl_2PSi_3$	$C_{17}H_{45}AlClPSi_3$
fw	524.92	377.50	427.21
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$C2/c$ (C_{2h}^6)—No. 15	$Pca2_1$(C_{2v}^5)—No. 29	$P2_1/c$(C_{2h}^5)—No. 14
a, Å	18.085(2)	13.234(2)	14.986(3)
b, Å	9.452(1)	13.147(2)	11.489(2)
c, Å	20.233(2)	13.043(2)	18.570(4)
β, deg	100.30(1)	90.0(–)	119.57(2)
V, Å^3	3403(1)	2269(1)	2781(2)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.025	1.105	1.020
μ, cm^{-1}	31.0	51.4	33.4
temp, °C	25	25	25
cryst dimens, mm	0.12 × 0.28 × 0.36	0.20 × 0.20 × 0.30	0.15 × 0.40 × 0.40
T_{max}:T_{min}	1.00:0.65	1.00:0.63	1.00:0.42
scan type	ω–2θ	ω–2θ	ω–2θ
scan width, deg	0.80 + 0.14 tan θ	1.00 + 0.14 tan θ	1.20 + 0.14 tan θ
θ_{max}, deg	75	75	60
intensity control refls	222, 1$3\bar{4}$, 1$1\bar{4}$, 153	331, 222, 643, 124	1$1\bar{2}$, 4$2\bar{4}$, 023, 3$1\bar{1}$
variation; repeat time, h	<1%; 2	<2%; 2	<2%; 2
Total no. of refls recorded	3595 (+h,+k,±l)	2448 (+h,+k,+l)	4281 (+h,+k,±l)
no. of nonequiv refls	3484	2448	4105
R_{merge}, on I	0.019		0.041
no. of refls retained, $I > 3.0\ \sigma(I)$	1959	1426	1574
no. of params refined	127	162	208
R, R_w[b]	0.041 (0.059)	0.045 (0.059)	0.059 (0.070)
goodness-of-fit[c]	1.35	1.37	1.29
max shift; esd in final least-squares cycle	0.02	0.03	0.01
final $\Delta\rho$ max; min, e/Å^3	0.23; –0.19	0.28; –0.28	0.47; –0.24

[a] An Enraf-Nonius CAD-4 diffractometer (Cu Kα radiation, graphite monochromator) was used for all measurements. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $\sum w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized. [c] Goodness-of-fit = $[\sum w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

Table II. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $[Et_2AlP(SiMe_3)_2]_2$ (1), with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}, Å^2
P	0.18819(5)	0.2528(1)	–0.07618(4)	4.04(1)
Al	0.18284(5)	0.3319(1)	0.03869(5)	4.17(2)
Si(1)	0.10749(6)	0.0760(1)	–0.11420(5)	5.27(2)
Si(2)	0.17182(6)	0.4276(1)	–0.15354(5)	5.55(2)
C(1)	0.1060(2)	0.2305(4)	0.0781(2)	5.7(1)
C(2)	0.1052(3)	0.2675(5)	0.1514(2)	8.0(1)
C(3)	0.1785(2)	0.5397(4)	0.0467(2)	6.5(1)
C(4)	0.1047(3)	0.5978(6)	0.0476(3)	12.0(2)
C(11)	0.1109(3)	–0.0630(5)	–0.0494(2)	7.6(1)
C(12)	0.1328(3)	–0.0087(5)	–0.1905(2)	8.5(1)
C(13)	0.0103(2)	0.1463(6)	–0.1347(3)	9.3(2)
C(21)	0.2466(3)	0.5616(5)	–0.1321(3)	8.4(1)
C(22)	0.0798(3)	0.5171(6)	–0.1559(3)	10.1(2)
C(23)	0.1758(3)	0.3550(6)	–0.2387(2)	8.7(1)

Table III. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (2), with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}, Å^2
P	0.4686(1)	0.2509(1)	0.0000(–)[a]	3.48(3)
Al	0.5979(2)	0.2403(2)	–0.1324(2)	5.07(5)
Si(1)	0.5386(2)	0.2371(2)	0.1597(2)	4.72(4)
Si(2)	0.3900(2)	0.4050(2)	–0.0139(2)	5.04(4)
Si(3)	0.3530(2)	0.1239(2)	–0.0254(2)	5.02(4)
Cl(1)	0.6242(2)	0.0801(2)	–0.1480(3)	7.42(6)
Cl(2)	0.7306(2)	0.3069(2)	–0.0640(3)	9.87(8)
C(11)	0.4388(8)	0.2116(8)	0.2579(7)	7.2(3)
C(12)	0.6332(7)	0.1337(7)	0.1563(8)	7.5(2)
C(13)	0.5995(7)	0.3621(7)	0.1903(8)	6.6(2)
C(21)	0.3027(7)	0.4005(6)	–0.1257(8)	7.1(2)
C(22)	0.3159(8)	0.4345(7)	0.1037(10)	8.0(3)
C(23)	0.4908(8)	0.5015(7)	–0.0370(9)	7.1(2)
C(31)	0.3334(7)	0.1123(6)	–0.1640(8)	6.3(2)
C(32)	0.4032(9)	0.0047(7)	0.0289(10)	8.6(3)
C(33)	0.2308(8)	0.1568(8)	0.0365(9)	8.1(3)
C(1)	0.5592(11)	0.3042(8)	–0.2601(8)	9.5(3)
C(2)	0.5403(19)	0.2583(9)	–0.3473(11)	16.1(7)

[a] The z-coordinate of the P atom was held constant throughout the least-squares parameter refinement to define the space group origin in this direction.

Results and Discussion

Reaction of Et_2AlCl with $LiP(SiMe_3)_2$ in a 1:1 mole ratio at –78 °C yielded $[Et_2AlP(SiMe_3)_2]_2$ (1), eliminating LiCl in 89% yield (eq 1). Solution ^1H, ^{31}P, and ^{27}Al NMR

$$2Et_2AlCl + 2LiP(SiMe_3)_2 \rightarrow \underset{\mathbf{1}}{[Et_2AlP(SiMe_3)_2]_2} \quad (1)$$

spectral data are consistent with the solid-state structure of 1 as revealed by a single-crystal X-ray analysis. The solution ^1H NMR spectrum contains a triplet which is consistent with the virtual coupling between the ring phosphorus atoms and the $SiMe_3$ protons, indicating the dimeric nature of the product in solution. An ORTEP drawing of 1 is shown in Figure 1; selected bond lengths and bond angles are listed in Table V. Dimer 1, which is isostructural and isomorphous with its As analog $[Et_2AlAs(SiMe_3)_2]_2$ (5),[3] lies on a crystallographic center of symmetry and thus contains a planar $\overline{\text{Al–P–Al–P}}$ core. The approximately equal Al–P bond lengths in 1 [2.460(1), 2.454(1) Å] lie well within the 2.446–2.476-Å range of those found in other Al–P dimers,[18–20] and the associated Al–P–Al′ and P–Al–P′ bond angles of 90.17(4) and 89.83(4), respectively, indicate that the four-membered core ring departs only slightly from an exactly square geometry. The C(1)–Al–C(3) and Si(1)–P–Si(2) bond angles of 114.2(2) and 107.95(5)°, respectively, are similar to the corresponding values of 115.0(3) and 107.59(6) in the As analog 5.

To date $[Et_2AlP(SiMe_3)_2]_2$ (1) is only the fifth dimeric

Table IV. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for i-$Bu_2(Cl)Al{\cdot}P(SiMe_3)_3$ (4), with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}, Å^2
P	0.2516(1)	0.1843(2)	0.2655(1)	4.07(5)
Al	0.2880(2)	0.3980(2)	0.2729(1)	5.08(6)
Si(1)	0.2753(2)	0.1178(2)	0.3896(1)	5.84(7)
Si(2)	0.3576(2)	0.0805(2)	0.2339(1)	5.59(6)
Si(3)	0.0865(2)	0.1475(2)	0.1690(2)	5.80(7)
Cl	0.4544(2)	0.3912(3)	0.3284(2)	7.80(7)
C(1)	0.2474(6)	0.4635(7)	0.3508(5)	5.7(2)
C(2)	0.3071(8)	0.5532(11)	0.4107(6)	10.5(4)
C(3)	0.2707(9)	0.5870(11)	0.4696(6)	11.3(4)
C(4)	0.3566(10)	0.6433(11)	0.3904(9)	14.4(6)
C(5)	0.2288(6)	0.4516(7)	0.1586(5)	6.6(3)
C(6)	0.2061(7)	0.5817(9)	0.1403(6)	8.1(3)
C(7)	0.1160(9)	0.6214(13)	0.1431(7)	13.6(5)
C(8)	0.1973(10)	0.6155(11)	0.0585(6)	12.5(4)
C(11)	0.1653(7)	0.1631(10)	0.4039(5)	8.3(3)
C(12)	0.3959(7)	0.1824(9)	0.4730(5)	7.7(3)
C(13)	0.2858(7)	−0.0454(8)	0.3937(5)	8.0(3)
C(21)	0.4841(6)	0.0674(9)	0.3281(6)	8.0(3)
C(22)	0.3696(6)	0.1634(9)	0.1535(5)	7.5(3)
C(23)	0.3027(6)	−0.0672(8)	0.1948(5)	7.4(3)
C(31)	0.0054(6)	0.2641(9)	0.1789(6)	7.4(3)
C(32)	0.0725(7)	0.1541(9)	0.0637(5)	7.6(3)
C(33)	0.0438(7)	0.0026(9)	0.1846(6)	8.3(3)

Table V. Bond Distances (Å) and Angles (deg) for $[Et_2AlP(SiMe_3)_2]_2$ (1), with Estimated Standard Deviations in Parentheses

	Bond Lengths		
P–Al	2.460(1)	Si(1)–C(12)	1.867(5)
P–Si(1)	2.261(1)	Si(1)–C(13)	1.855(4)
P–Si(2)	2.259(1)	Si(2)–C(21)	1.847(5)
P–Al′	2.454(1)	Si(2)–C(22)	1.860(6)
Al–C(1)	1.970(4)	Si(2)–C(23)	1.868(5)
Al–C(3)	1.974(4)	C(1)–C(2)	1.526(6)
Si(1)–C(11)	1.849(5)	C(3)–C(4)	1.446(7)
	Bond Angles		
Al–P–Si(1)	114.46(5)	P–Si(1)–C(12)	111.1(2)
Al–P–Si(2)	114.21(5)	P–Si(1)–C(13)	109.8(2)
Al–P–Al′	90.17(4)	C(11)–Si(1)–C(12)	107.4(2)
Si(1)–P–Si(2)	107.95(5)	C(11)–Si(1)–C(13)	108.9(3)
Si(1)–P–Al′	112.58(5)	C(12)–Si(1)–C(13)	109.3(2)
Si(2)–P–Al′	116.89(5)	P–Si(2)–C(21)	109.8(2)
P–Al–C(1)	112.6(1)	P–Si(2)–C(22)	110.9(2)
P–Al–C(3)	112.9(1)	P–Si(2)–C(23)	110.4(2)
P–Al–P′	89.83(4)	C(21)–Si(2)–C(22)	108.0(2)
C(1)–Al–C(3)	114.2(2)	C(21)–Si(2)–C(23)	108.7(3)
C(1)–Al–P′	114.6(1)	C(22)–Si(2)–C(23)	109.0(3)
C(3)–Al–P′	110.4(1)	Al–C(1)–C(2)	114.3(3)
P–Si(1)–C(11)	110.3(2)	Al–C(3)–C(4)	115.4(3)

Al–P compound to be reported[18–20] and the first to be produced by a lithium coupling reaction. Previously, Lappert and co-workers isolated the methyl analog of 1, $[Me_2AlP(SiMe_3)_2]_2$,[18] but it resulted from a rearrangement reaction between $\{Zr(cp)_2Cl[P(SiMe_3)_2]\}$ (cp = C_5H_4) and $AlMe_3$, rather than a LiCl elimination or dehalosilylation reaction. Interestingly, Paine *et al.* reported two aluminum–phosphorus dimers, $[(Me_3Si)_2AlP(Ph)_2]_2$ and $[(Me_3Si)_2AlP(Ph)(SiMe_3)]_2$, which were actually prepared through dehalosilylation, but the source of Me_3SiCl elimination was the reverse of that employed in our laboratory, as the Me_3Si groups were bonded to the Al atom while the halide atoms were located on the P atom.[20]

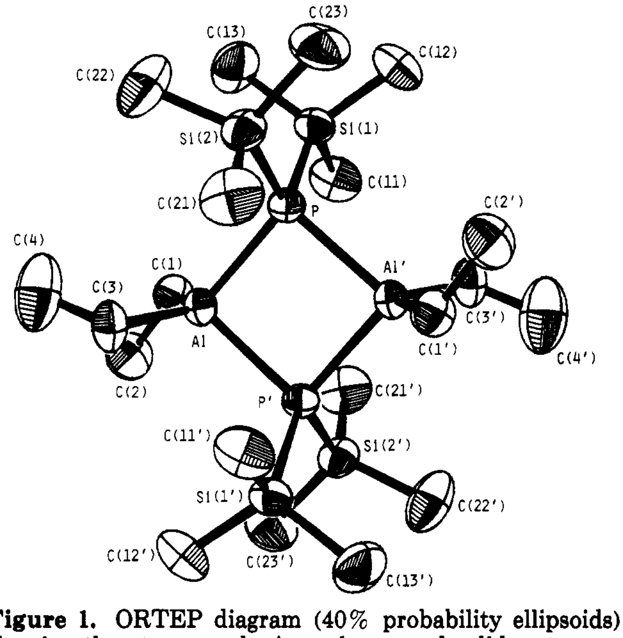

Figure 1. ORTEP diagram (40% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of $[Et_2AlP(SiMe_3)_2]_2$ (1). Hydrogen atoms have been omittted for clarity. Primed atoms are related to the unprimed atoms by a crystallographic center of symmetry.

The synthesis of the only other known Al–P dimer, $[(i\text{-}Bu)_2AlPPh_2]_2$, also differed from that of 1 in that it was the product of an H_2 elimination reaction between an alkylaluminum hydride and a secondary phosphine.[19] The isolation of compound 1 further emphasizes that the lithium coupling reaction may be successfully utilized with most group 13–15 combinations, as well as a wide range of alkyl groups.[2–5,13]

Considering that dehalosilylation reactions have also been used successfully to isolate oligomeric compounds from many combinations of group 13–15 elements,[2,5–6,11–13] this preparative method was also applied to the aluminum–phosphorus system. When $EtAlCl_2$ was reacted with $P(SiMe_3)_3$ in a 1:1 mole ratio in pentane, the adduct $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (2) was isolated in quantitative yield. Compound 2 is a white crystalline solid that immediately precipitates out of solution upon the addition of $EtAlCl_2$ to $P(SiMe_3)_3$. Compound 2 is quite stable under an inert atmosphere but rapidly decomposes in air. The solution ^1H NMR spectrum of 2 is consistent with its solid-state structure as it contains a doublet at $\delta = 0.253$ ppm, arising from the coupling of the $SiMe_3$ protons and the phosphorus atom of the adduct.

Interestingly, the reaction of Et_2AlCl and $P(SiMe_3)_3$ in a 2:1 mole ratio also afforded the adduct $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (2) (eq 2) in moderate yield. The presence of

$$2Et_2AlCl + P(SiMe_3)_3 \rightarrow \underset{\mathbf{2}}{Et(Cl)_2Al{\cdot}P(SiMe_3)_3} + Et_3Al \quad (2)$$

the $EtAlCl_2$ moiety in 2 rather than Et_2AlCl is noteworthy, as it suggests that a redistribution of the latter occurred. Although alkylaluminum halides have been shown to exist normally as dihalo-bridged dimers,[21–24] Ziegler has sug-

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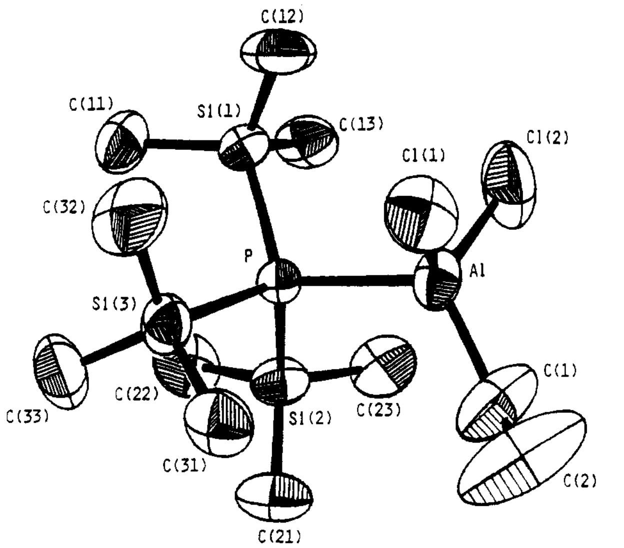
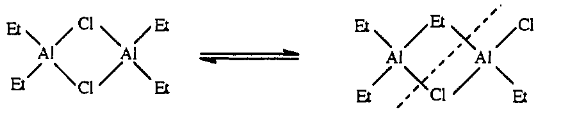


Figure 2. ORTEP diagram (50% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (**2**). Hydrogen atoms have been omitted for clarity.

gested that, under appropriate conditions (in the presence of a sufficiently strong Lewis base), alkyl–halo-bridged dimers may participate in an equilibrium (eq 3) involving



(3)

transient alkyl–halo-bridged species that readily dissociate to form stronger Lewis acids than those available from the original dimer.[25] This is most often true when the mole ratio of organoaluminum monomer to donor base is 2:1, as in the preparation of **2**.[26] Additionally, there have been several reports by Robinson and co-workers of similarly modified constitutions of alkylaluminum halides with group 15 species.[27–30] In the case of Et_2AlCl, reaction with $P(SiMe_3)_3$ in a 2:1 mole ratio results in redistribution of the dialkylaluminum chloride dimer to give $EtAlCl_2$, the strongest available Lewis acid from the transient alkyl–halo-bridged species. Et_3Al which, though not isolated, is indicated by mass balance.

The molecular structure of $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (**2**) is illustrated in Figure 2; selected bond lengths and angles are provided in Table VI. The bonds emanating from the Al and P atoms in **2** are rotated by a mean angle of 36.3° from an eclipsed orientation, and thus the conformation is similar to that around the Al–As bond in $i\text{-}Bu_2(Cl)Al{\cdot}As(SiMe_3)_3$ (**6**)[4] where the value is 36.9°. The Al–P bond distance of 2.435(3) Å in **2** is, to our knowledge, the shortest found to date in monodentate adducts, the

Table VI. Bond Distances (Å) and Angles (deg) for $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (2), with Estimated Standard Deviations in Parentheses

Bond Lengths

P–Al	2.435(3)	Si(1)–C(13)	1.87(1)
P–Si(1)	2.287(3)	Si(2)–C(21)	1.86(1)
P–Si(2)	2.285(3)	Si(2)–C(22)	1.86(1)
P–Si(3)	2.289(3)	Si(2)–C(23)	1.87(1)
Al–Cl(1)	2.144(4)	Si(3)–C(31)	1.83(1)
Al–Cl(2)	2.156(4)	Si(3)–C(32)	1.84(1)
Al–C(1)	1.93(1)	Si(3)–C(33)	1.86(1)
Si(1)–C(11)	1.87(1)	C(1)–C(2)	1.31(2)
Si(1)–C(12)	1.85(1)		

Bond Angles

Si(1)–P–Al	110.9(1)	C(21)–Si(2)–C(23)	109.8(5)
Si(2)–P–Al	108.3(1)	C(22)–Si(2)–C(23)	111.6(5)
Si(3)–P–Al	109.0(1)	P–Si(3)–C(31)	107.3(3)
Si(1)–P–Si(2)	109.1(1)	P–Si(3)–C(32)	108.9(4)
Si(1)–P–Si(3)	110.2(1)	P–Si(3)–C(33)	110.4(4)
Si(2)–P–Si(3)	109.3(1)	C(31)–Si(3)–C(32)	111.1(5)
P–Si(1)–C(11)	110.6(3)	C(31)–Si(3)–C(33)	108.9(5)
P–Si(1)–C(12)	108.1(3)	C(32)–Si(3)–C(33)	110.2(5)
P–Si(1)–C(13)	107.4(3)	P–Al–Cl(1)	103.7(1)
C(11)–Si(1)–C(12)	111.3(5)	P–Al–Cl(2)	104.8(1)
C(11)–Si(1)–C(13)	108.4(5)	P–Al–C(1)	113.6(4)
C(12)–Si(1)–C(13)	111.0(4)	Cl(1)–Al–Cl(2)	107.8(2)
P–Si(2)–C(21)	108.5(3)	Cl(1)–Al–C(1)	112.8(4)
P–Si(2)–C(22)	111.1(3)	Cl(2)–Al–C(1)	113.3(4)
P–Si(2)–C(23)	106.9(3)	Al–C(1)–C(2)	126.7(9)
C(21)–Si(2)–C(22)	109.0(5)		

Torsion Angles about the P–Al Bond[a]

Si(1)–P–Al–Cl(1)	81.0(2)	Si(2)–P–Al–C(1)	−36.5(4)
Si(1)–P–Al–Cl(2)	−32.0(2)	Si(3)–P–Al–Cl(1)	−40.4(2)
Si(1)–P–Al–C(1)	−156.2(4)	Si(3)–P–Al–Cl(2)	−153.4(1)
Si(2)–P–Al–Cl(1)	−159.3(1)	Si(3)–P–Al–Cl(1)	82.4(4)
Si(2)–P–Al–Cl(2)	87.7(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.

corresponding lengths in previously reported Al–P adducts ranging from 2.451(2) to 2.585(2) Å.[30–37] The shortness of the distance in **2** can be attributed in part to the electron-withdrawing character of the Cl atoms bonded to the Al atom, which greatly increases the Lewis acidity of the aluminum moiety, and to the modest steric demands of the Al substituents. Interestingly, in the diadduct $Cl_3Al{\cdot}P(Ph)_2CH_2P(Ph)_2{\cdot}AlCl_2(Me)$,[30] the Al–P bond lengths of 2.451(2) and 2.497(2) Å associated with the $AlCl_3$ and $AlCl_2(Me)$ moieties, respectively, are both longer than that in **2**, presumably due to the fact that the bond-shortening effect of the halogens is counteracted by the steric demands of the phenyl rings located on the P atoms. A similar case can be made for the Al–P bond length of 2.489(2) Å in $Me_2(Cl)Al{\cdot}P(Ph)_2CH_2P(Ph)_2$.[37]

In order to examine the effect of molar ratios on disproportionation, Et_2AlCl was reacted in a 1:1 mole ratio with $P(SiMe_3)_3$ under conditions identical to those of the 2:1 mole ratio reaction. With the aluminum alkyl halide and the phosphine present in equimolar amounts, the 1:1 reaction afforded the expected adduct $Et_2(Cl)Al{\cdot}P(SiMe_3)_3$

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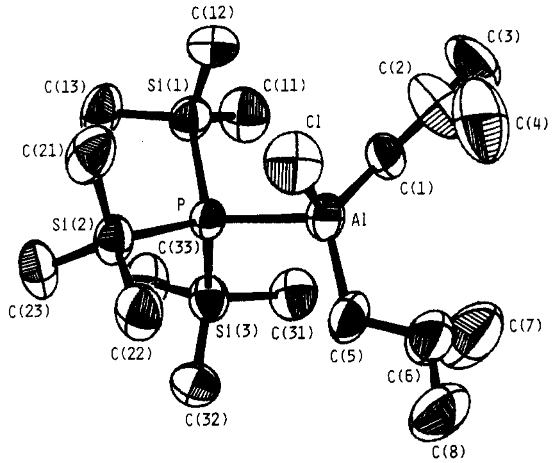

Figure 3. ORTEP diagram (50% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of i-$Bu_2(Cl)Al{\cdot}P(SiMe_3)_3$ (4). Hydrogen atoms have been omitted for clarity.

(3) in quantitative yield. No rearrangement products were observed. Although no suitable X-ray quality crystals of 3 could be isolated, the solution ^1H NMR spectrum is consistent with an adduct, as indicated by coupling between the P atom and the $SiMe_3$ protons giving a doublet signal at $\delta = 0.243$ ppm. Integration of spectra of 2 and 3 shows a 1:2 ratio between the ethyl groups of 2 and 3, respectively: the $SiMe_3$ proton signal of 2 is approximately 9:1 with the ethyl proton signal, while the ratio for 3 is 9:2. An upfield shift of the CH_2 signal ($\Delta = 0.04$ ppm) in the ^1H NMR spectrum of $Et_2(Cl)Al{\cdot}P(SiMe_3)_3$ (3) from that of 2, can be attributed to the presence of only one Cl atom in the adduct. The dichloro and monochloro structures of 2 and 3, respectively, are also evidenced in the partial elemental analyses of these compounds (*vide infra*).

The adduct i-$Bu_2(Cl)Al{\cdot}P(SiMe_3)_3$ (4) was prepared using reaction conditions identical to those resulting in the formation of 2. In contrast to the situation with Et_2AlCl, i-$Bu_2(Cl)Al$ did not undergo redistribution. This observed difference is likely due to the fact that the bulkier isobutyl groups cannot readily form the transient alkyl–halo-bridged dimer as easily as the ethyl groups. Therefore, 4 results from the expected Lewis acid/base adduct formation (eq 4). All solution NMR spectral data are in

$$2i\text{-}Bu_2AlCl + P(SiMe_3)_3 \rightarrow i\text{-}Bu_2(Cl)Al{\cdot}P(SiMe_3)_3 + i\text{-}Bu_2AlCl \quad (4)$$

4

agreement with the solid-state structure of 4 as determined by X-ray crystallographic analysis. An ORTEP diagram of 4 is provided in Figure 3; selected bond distances and bond angles are listed in Table VII. Bond angles in 3 characterizing the distorted tetrahedral geometries about the P and Al atoms range from 107.5(1) to 111.5(1)° and 99.1(1) to 122.5(4)°, respectively, and corresponding values are not significantly different from those in the As analog i-$Bu_2(Cl)Al{\cdot}As(SiMe_3)_3$ (6).[4] The smaller than tetrahedral P–Al–Cl and mean P–Al–C bond angles of 99.1(1) and 106.1(1)°, respectively, in 4 are associated with overcrowding involving the geminal isobutyl groups at the Al atoms [C–Al–Cl(mean) = 110.1°, C–Al–C = 122.5(4)°]; corresponding values in 6 follow: 99.07(7), 105.2, 110.6, 123.2(3)°. The Al–P bond length of 2.504(3) Å is consistent with those in previously reported Al-P adducts (*vide supra*).[30-37] The lengthening of the Al–P bond length in 4 over that in 2 [2.435(3) Å] can be ascribed to a combination of the decreased Lewis acidity of the Al moiety in 4 (due to the presence of only one Cl on the Al atom in contrast to two in 2) and the increased steric overcrowding between the $SiMe_3$ groups on P (mean Al–P–Si = 110.9° < mean Si–P–Si = 108.1) and the bulky pair of isobutyl groups on the Al atom in 4 (versus the ethyl substituents in 2; mean Al–P–Si = 109.4, mean Si–P–Si = 109.5°).

Table VII. Selected Bond Distances (Å) and Angles (deg) for i-$Bu_2(Cl)Al{\cdot}P(SiMe_3)_3$ (4), with Estimated Standard Deviations in Parentheses

Bond Lengths			
P–Al	2.504(3)	Si(2)–C(22)	1.85(1)
P–Si(1)	2.283(3)	Si(2)–C(23)	1.87(1)
P–Si(2)	2.283(4)	Si(3)–C(31)	1.88(1)
P–Si(3)	2.266(3)	Si(3)–C(32)	1.86(1)
Al–Cl	2.179(4)	Si(3)–C(33)	1.86(1)
Al–C(1)	1.97(1)	C(1)–C(2)	1.46(1)
Al–C(5)	1.95(1)	C(2)–C(3)	1.49(2)
Si(1)–C(11)	1.87(1)	C(2)–C(4)	1.43(2)
Si(1)–C(12)	1.86(1)	C(5)–C(6)	1.53(1)
Si(1)–C(13)	1.88(1)	C(6)–C(7)	1.45(2)
Si(2)–C(21)	1.85(1)	C(6)–C(8)	1.51(2)
Bond Angles			
Al–P–Si(1)	110.6(1)	P–Si(2)–C(22)	107.2(3)
Al–P–Si(2)	111.5(1)	P–Si(2)–C(23)	110.2(4)
Al–P–Si(3)	110.5(1)	C(21)–Si(2)–C(22)	110.1(5)
Si(1)–P–Si(2)	107.7(1)	C(21)–Si(2)–C(23)	110.1(4)
Si(1)–P–Si(3)	107.5(1)	C(22)–Si(2)–C(23)	110.7(4)
Si(2)–P–Si(3)	109.0(1)	P–Si(3)–C(31)	107.2(3)
P–Al–Cl	99.1(1)	P–Si(3)–C(32)	109.6(3)
P–Al–C(1)	106.0(3)	P–Si(3)–C(33)	111.7(3)
P–Al–C(5)	106.2(2)	C(31)–Si(3)–C(32)	109.3(5)
Cl–Al–C(1)	111.2(2)	C(31)–Si(3)–C(33)	109.6(5)
Cl–P–C(5)	109.0(3)	C(32)–Si(3)–C(33)	109.4(5)
C(1)–Al–C(5)	122.5(4)	Al–C(1)–C(2)	122.3(8)
P–Si(1)–C(11)	110.0(3)	C(1)–C(2)–C(3)	115.8(11)
P–Si(1)–C(12)	108.1(4)	C(1)–C(2)–C(4)	121.0(11)
P–Si(1)–C(13)	110.0(4)	C(3)–C(2)–C(4)	115.4(11)
C(11)–Si(1)–C(12)	109.5(4)	Al–C(5)–C(6)	118.7(6)
C(11)–Si(1)–C(13)	109.5(5)	C(5)–C(6)–C(7)	114.0(11)
C(12)–Si(1)–C(13)	109.7(3)	C(5)–C(6)–C(8)	111.9(10)
P–Si(12)–C(21)	108.6(3)	C(7)–C(6)–C(8)	109.6(9)
Torsion Angles about the P–Al Bond[a]			
Si(1)–P–Al–Cl	82.8(2)	Si(2)–P–Al–C(5)	−152.3(3)
Si(1)–P–Al–C(1)	−32.5(3)	Si(3)–P–Al–Cl	−158.4(1)
Si(1)–P–Al–C(5)	−164.3(3)	Si(3)–P–Al–C(1)	−86.4(3)
Si(2)–P–Al–Cl	−37.0(1)	Si(3)–P–Al–C(5)	−45.4(4)
Si(2)–P–Al–C(1)	−152.3(3)		

[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.

Conclusions

In systems of the heavier group 13–15 elements, dimeric and mixed-bridge species were obtained from LiCl elimination and dehalosilylation reactions. Indeed, elimination of LiCl resulted in $[Et_2AlP(SiMe_3)_2]_2$ (1). In contrast, similar dehalosilylation reactions between R_2AlCl (R = Et, i-Bu) and $EtAlCl_2$ with $P(SiMe_3)_3$ afforded the Lewis base adducts $Et(Cl)_2Al{\cdot}P(SiMe_3)_3$ (2), $Et_2(Cl)Al{\cdot}P(SiMe_3)_3$ (3), and i-$Bu_2(Cl)Al{\cdot}P(SiMe_3)_3$ (4), rather than the anticipated elimination products. This effect may be unique to Al systems, as analogous adducts were isolated when alkylaluminum chlorides were reacted with $As(SiMe_3)_3$, and may be a consequence of the increased Lewis acidity of Al versus the heavier group 13 elements which have been shown to readily undergo such dehalosilylation reactions.[3,4] However, such Al adducts have demonstrated the ability to undergo internal dehalosilylation to form dimeric compounds in the aluminum–arsenic system.[3] The four Al–P compounds reported herein may likely show promise as single-source precursors to the material AlP, and future studies will address this potential.

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Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, and interatomic distances and angles, including torsion angles, for **1**, **2**, and **4** and equations of least-squares planes for **1** (14 pages). Ordering information is given on any current masthead page.