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Synthesis and Characterization of Sterically Hindered Alkylaluminum−Phosphorus and −Arsenic Compounds. X-ray Crystal Structures of $(Me_3ECH_2)_3Al\cdot E'(SiMe_3)_3$ (E = Si, E′ = As; E = C, E′ = P, As), $(Me_3SiCH_2)_2(Br)Al\cdot P(SiMe_3)_3$, and $[(Me_3SiCH_2)(X)AlE(SiMe_3)_2]_2$ (X = Br, E = P, As; X = Me_3SiCH_2, E = As)

Richard L. Wells* and Edward E. Foos

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27708

Arnold L. Rheingold, Glenn P. A. Yap, and Louise M. Liable-Sands

Department of Chemistry, Drake Hall, University of Delaware, Newark, Delaware 19716

Peter S. White

Department of Chemistry, Venable Hall, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514

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Reaction of $(Me_3SiCH_2)_3Al$ with $E(SiMe_3)_3$ (E = P, As) in a 1:1 mole ratio affords the Lewis acid−base adducts $(Me_3SiCH_2)_3Al\cdot P(SiMe_3)_3$ (**1**) and $(Me_3SiCH_2)_3Al\cdot As(SiMe_3)_3$ (**2**). Similarly, the 1:1 mole ratio reaction of $(Me_3CCH_2)_3Al$ with $E(SiMe_3)_3$ (E = P, As) leads to the isolation of $(Me_3CCH_2)_3Al\cdot P(SiMe_3)_3$ (**3**) and $(Me_3CCH_2)_3Al\cdot As(SiMe_3)_3$ (**4**). The adduct $(Me_3SiCH_2)_2(Br)Al\cdot P(SiMe_3)_3$ (**5**) was obtained from the 1:1 mole ratio reaction of $(Me_3SiCH_2)_2AlBr$ with $P(SiMe_3)_3$. The dimers $[(Me_3SiCH_2)(Br)AlP(SiMe_3)_2]_2$ (**6**) and $[(Me_3SiCH_2)(Br)AlAs(SiMe_3)_2]_2$ (**7**) were isolated as products of the lithium halide elimination reactions of $(Me_3SiCH_2)AlBr_2$ (**10**) with $LiE(SiMe_3)_2$ (E = P, As), while reaction of $(Me_3SiCH_2)_2AlBr$ with these same lithium pnictide salts leads to the isolation of $[(Me_3SiCH_2)_2AlP(SiMe_3)_2]_2$ (**8**) and $[(Me_3SiCH_2)_2AlAs(SiMe_3)_2]_2$ (**9**). Various physical and spectroscopic data, including a variable-temperature NMR study of the dimeric compounds **6**−**9**, are presented for the above compounds, as are the single-crystal X-ray structures of **2**−**7** and **9**.

Introduction

The bulk of research in our laboratory over the past decade has focused on the synthesis and characterization of potential single-source precursor compounds to group 13−group 15 materials, obtained predominately through dehalosilylation and lithium halide elimination reactions. In an attempt to prepare compounds which may serve as precursors to aluminum phosphides and arsenides, we have become interested in the synthesis of novel compounds containing this 13−15 linkage. For example, we have recently reported the isolation of the Lewis acid−base adducts $X_3Al\cdot E(SiMe_3)_3$ (X = Cl and Br, E = P;[1] X = Cl, E = As[2]) and $Ph_3Al\cdot E(SiMe_3)_3$ (E = P and As[3]), as well as the ring-compounds $[Et_2AlE(SiMe_3)_2]_2$ (E = P[4] and As[5]). In the present study, we undertook the synthesis of a series of aluminum compounds containing the bulkier (trimethylsilyl)methyl and neopentyl ligands. While these starting materials have been known for some time, relatively little chemistry has been performed with them, especially in the area of 13−15 precursor compounds. A comparison of these results with a similar series of reactions involving the heavier metals gallium and indium[6] would be of interest. Additionally, we wished to probe the feasibility of trimethylsilyl bromide elimination in the synthesis of aluminum−phosphorus and −arsenic compounds.

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Experimental Section

General Considerations. All manipulations of air- and moisture-sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere or by standard Schlenk techniques. Pentane, hexane, toluene, and THF were distilled over sodium/potassium alloy under dry dinitrogen. $(Me_3SiCH_2)_3Al$,[7] $(Me_3SiCH_2)_2AlBr$,[8] $(Me_3CCH_2)_3Al$,[9] $P(SiMe_3)_3$,[10] and $As(SiMe_3)_3$[11] were prepared from literature procedures. $LiP(SiMe_3)_2$[12] and $LiAs(SiMe_3)_2$[11] were prepared from the 1:1 reaction of $P(SiMe_3)_3$ or $As(SiMe_3)_3$ with $LiCH_3$ in THF. $AlBr_3$ was purchased from Strem Chemicals, Inc., and purified through sublimation. The integrity of all starting materials was confirmed using ^1H NMR spectroscopy. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Unity XL-400 spectrometer operating at 400, 100.6, and 161.9 MHz, respectively. ^1H and $^{13}C\{^1H\}$ spectra were referenced to TMS using the residual protons or carbons of deuterated benzene at δ 7.15 or 128.0, respectively. $^{31}P\{^1H\}$ spectra were referenced externally to 80% H_3PO_4 at δ 0.00. All NMR samples were prepared in 5-mm tubes which were septum-sealed under argon or flame-sealed under vacuum (in the case of the variable-temperature experiments). Melting points (uncorrected) were obtained with a Thomas-Hoover Unimelt apparatus, using capillaries that were flame-sealed under argon. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

Preparation of $(Me_3SiCH_2)_3Al\cdot P(SiMe_3)_3$ (1). $(Me_3SiCH_2)_3Al$ (0.288 g; 1.00 mmol) was added with 20 mL of hexane to a 250 mL flask equipped with a stir bar and Teflon valve. $P(SiMe_3)_3$ (0.250 g; 1.00 mmol) in 30 mL of hexane was added slowly via pipet, and the clear colorless solution was stirred for 6 h at room temperature. The volatiles were removed in vacuo, yielding a white solid which was extracted with warm pentane and allowed to evaporate at −30 °C, producing colorless crystals of **1** (0.468 g, 86% yield). Mp: 95−99 °C. Anal. Calcd (found) for $C_{21}H_{60}AlPSi_6$: C, 46.78 (46.46); H, 11.22 (11.41). ^1H NMR: δ −0.46 (s, 6H, $Me_3Si\mathit{CH_2}-$), δ 0.27 [d, 27H, $-SiMe_3$ (J_{P-H} = 4.4 Hz)], δ 0.31 (s, 27H, $\mathit{Me_3}SiCH_2-$). $^{13}C\{^1H\}$ NMR: δ 3.33 (s, $Me_3Si\mathit{CH_2}-$), δ 3.45 (s, $\mathit{Me_3}SiCH_2-$), δ 3.66 [d, $-SiMe_3$ (J_{P-C} = 9.1 Hz)]. $^{31}P\{^1H\}$ NMR: δ −240.86 (s).

Preparation of $(Me_3SiCH_2)_3Al\cdot As(SiMe_3)_3$ (2). The procedure used was identical to that described for **1**, with $(Me_3SiCH_2)_3Al$ (0.288 g; 1.00 mmol) and $As(SiMe_3)_3$ (0.294 g; 1.00 mmol). $(Me_3SiCH_2)_3Al\cdot As(SiMe_3)_3$ (**2**) was isolated (0.554 g, 95% yield). Mp: 89−95 °C. Anal. Calcd (found) for $C_{21}H_{60}AlAsSi_6$: C, 43.25 (42.88); H, 10.37 (10.11). ^1H NMR: δ −0.42 (s, 6H, $Me_3Si\mathit{CH_2}-$), δ 0.29 (s, 27H, $\mathit{Me_3}SiCH_2-$), δ 0.32 (s, 27H, $-SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 3.37 (s, $\mathit{Me_3}SiCH_2-$), δ 3.97 (s, $-SiMe_3$).

Preparation of $(Me_3CCH_2)_3Al\cdot P(SiMe_3)_3$ (3). $(Me_3CCH_2)_3Al$ (0.240 g; 1.00 mmol) was added with 20 mL of hexane to a 250 mL flask equipped with a stir bar and Teflon valve. $P(SiMe_3)_3$ (0.250 g; 1.00 mmol) in 30 mL of hexane was added slowly via pipet, and the clear colorless solution was stirred for 12 h at room temperature. The solvent level was reduced in vacuo and allowed to evaporate at −30 °C, producing colorless crystals of **3** (0.431 g, 88% yield). Mp: 115−117 °C. Anal. Calcd (found) for $C_{24}H_{60}AlPSi_3$: C, 58.72 (58.63); H, 12.32 (12.16). ^1H NMR: δ 0.31 [d, 27H, $-SiMe_3$ (J_{P-H} = 4.4 Hz)], δ 0.66 (s, 6H, $Me_3C\mathit{CH_2}-$), δ 1.28 (s, 27H, $\mathit{Me_3}CCH_2-$). $^{13}C\{^1H\}$ NMR: δ 32.64 (s, $Me_3C\mathit{CH_2}-$), δ 35.51 (s, $\mathit{Me_3}CCH_2-$), δ 3.82 [d, $-SiMe_3$ (J_{P-C} = 9.1 Hz)]. $^{31}P\{^1H\}$ NMR: δ −241.34 (s).

Preparation of $(Me_3CCH_2)_3Al\cdot As(SiMe_3)_3$ (4). The procedure used was identical to that described for **3**, with $(Me_3CCH_2)_3Al$ (0.240 g; 1.00 mmol) and $As(SiMe_3)_3$ (0.294 g; 1.00 mmol). $(Me_3CCH_2)_3Al\cdot As(SiMe_3)_3$ (**4**) was isolated (0.422 g, 79% yield). Mp: 114−117 °C. Anal. Calcd (found) for $C_{24}H_{60}AlAsSi_3$: C, 53.89 (53.66); H, 11.31 (11.27). ^1H NMR: δ 0.34 (d, 27H, $-SiMe_3$), δ 0.64 (s, 6H, $Me_3C\mathit{CH_2}-$), δ 1.20 (s, 27H, $\mathit{Me_3}CCH_2-$). $^{13}C\{^1H\}$ NMR: δ 4.15 (s, $-SiMe_3$), δ 32.19 (s, $Me_3C\mathit{CH_2}-$), δ 35.33 (s, $\mathit{Me_3}CCH_2-$).

Preparation of $(Me_3SiCH_2)_2(Br)Al\cdot P(SiMe_3)_3$ (5). The procedure used was identical to that described for **3**, with $(Me_3SiCH_2)_2AlBr$ (0.281 g; 1.00 mmol) and $P(SiMe_3)_3$ (0.250 g; 1.00 mmol). $(Me_3SiCH_2)_2(Br)Al\cdot P(SiMe_3)_3$ (**5**) was isolated (0.301 g, 57% yield). Mp: 94−100 °C. Anal. Calcd (found) for $C_{17}H_{49}AlPBrSi_5$: C, 38.39 (38.47); H, 9.29 (9.26). ^1H NMR: δ −0.45 (s, 4H, $Me_3Si\mathit{CH_2}-$), δ 0.28 [d, 27H, $-SiMe_3$ (J_{P-H} = 4.8 Hz)], δ 0.31 (s, 18H, $\mathit{Me_3}SiCH_2-$). $^{13}C\{^1H\}$ NMR: δ 3.33 (s, $Me_3Si\mathit{CH_2}-$), δ 3.44 (s, $\mathit{Me_3}SiCH_2-$), δ 3.65 [d, $-SiMe_3$ (J_{P-C} = 10.3 Hz)]. $^{31}P\{^1H\}$ NMR: δ −225.28 (s).

Preparation of $[(Me_3SiCH_2)(Br)AlP(SiMe_3)_2]_2$ (6). $(Me_3SiCH_2)AlBr_2$ (0.411 g; 1.50 mmol) was added with 20 mL of hexane to a 250 mL flask equipped with a stir bar and Teflon valve. To this stirred room-temperature solution was added $LiP(SiMe_3)_2\cdot 0.6THF$ (0.340 g; 1.50 mmol). Within minutes, a hazy red color developed, and stirring was continued for 12 h. At the end of this time, the LiCl was allowed to settle, and the red solution was transferred to a second flask via cannula. The solvent volume was reduced in vacuo and allowed to evaporate at −30 °C. Within 24 h, clear, colorless crystals of **6** (0.265 g, 71% yield) had formed. Mp: 187−192 °C. Anal. Calcd (found) for $C_{20}H_{58}Al_2P_2Br_2Si_6$: C, 32.33 (32.45); H, 7.87 (7.93). ^1H NMR: δ −0.06 (bs, 4H, $Me_3Si\mathit{CH_2}-$), δ 0.36 (s, 18H, $\mathit{Me_3}SiCH_2-$), δ 0.49 [t, 36H, $-SiMe_3$ (J_{P-H} = 2.8 Hz)]. $^{13}C\{^1H\}$ NMR: δ 2.95 (s, $\mathit{Me_3}SiCH_2-$), δ 4.13 [t, $-SiMe_3$ (J_{P-C} = 4.9 Hz)]. $^{31}P\{^1H\}$ NMR: δ −215.15 (s).

Preparation of $[(Me_3SiCH_2)(Br)AlAs(SiMe_3)_2]_2$ (7). The procedure used was identical to that described for **6**, with $(Me_3SiCH_2)_2AlBr$ (0.274 g; 1.00 mmol) and $LiAs(SiMe_3)_2\cdot 0.6THF$ (0.270 g; 1.00 mmol). $[(Me_3SiCH_2)(Br)AlAs(SiMe_3)_2]_2$ (**7**) was isolated (0.310 g, 75% yield). Mp: 189−191 °C (decomposed to an orange liquid). Anal. Calcd (found) for $C_{20}H_{58}Al_2As_2Br_2Si_6$: C, 28.91 (28.73); H, 7.04 (6.72). ^1H NMR: δ −0.01 (s, 4H, $Me_3Si\mathit{CH_2}-$), δ 0.37 (s, 18H, $\mathit{Me_3}SiCH_2-$), δ 0.52 (s, 36H, $-SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 2.87 (s, $\mathit{Me_3}SiCH_2-$), δ 4.13 (s, $-SiMe_3$).

Preparation of $[(Me_3SiCH_2)_2AlP(SiMe_3)_2]_2$ (8). The procedure used was identical to that described for **6**, with $(Me_3SiCH_2)_2AlBr$ (0.281 g; 1.00 mmol) and $LiP(SiMe_3)_2\cdot 0.6THF$ (0.227 g; 1.00 mmol). $[(Me_3SiCH_2)_2AlP(SiMe_3)_2]_2$ (**8**) was isolated (0.266 g, 70% yield). Mp: 190−198 °C. Anal. Calcd (found) for $C_{28}H_{80}Al_2P_2Si_8$: C, 44.39 (44.19); H, 10.64 (10.79). ^1H NMR: δ −0.18 (bs, 8H, $Me_3Si\mathit{CH_2}-$), δ 0.35 (s, 36H, $\mathit{Me_3}SiCH_2-$), δ 0.48 [t, 36H, $-SiMe_3$ (J_{P-H} = 2.4 Hz)]. $^{13}C\{^1H\}$ NMR: δ 2.48 (bs, $Me_3Si\mathit{CH_2}-$), δ 4.11 (s, $\mathit{Me_3}SiCH_2-$), δ 5.28 [t, $-SiMe_3$ (J_{P-C} = 4.1 Hz)]. $^{31}P\{^1H\}$ NMR: δ −234.97 (s).

Preparation of $[(Me_3SiCH_2)_2AlAs(SiMe_3)_2]_2$ (9). The procedure used was identical to that described for **6**, with $(Me_3SiCH_2)_2AlBr$ (0.281 g; 1.00 mmol) and $LiAs(SiMe_3)_2\cdot 0.6THF$ (0.270 g; 1.00 mmol). $[(Me_3SiCH_2)_2AlAs(SiMe_3)_2]_2$ (**9**) was isolated (0.326 g, 77% yield). Mp: 201−212 °C (decomposed to a yellow liquid). Anal. Calcd (found) for $C_{28}H_{80}Al_2As_2Si_8$: C, 39.78 (39.77); H, 9.54 (9.79). ^1H NMR: δ −0.13 (s, 8H, $Me_3Si\mathit{CH_2}-$), δ 0.35 (s, 36H, $\mathit{Me_3}SiCH_2-$), δ 0.51 (s, 36H, $-SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 2.89 (s, $Me_3Si\mathit{CH_2}-$), δ 3.39 (s, $\mathit{Me_3}SiCH_2-$), δ 5.19 (s, $-SiMe_3$).

Preparation of $(Me_3SiCH_2)AlBr_2$ (10). $(Me_3SiCH_2)_3Al$ (1.00 g; 3.5 mmol) in 30 mL of hexane was added to a 250 mL

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Table 1. Crystallographic Data for $(Me_3SiCH_2)_3Al{\cdot}As(SiMe_3)_3$ (2), $(Me_3CCH_2)_3Al{\cdot}P(SiMe_3)_3$ (3), $(Me_3CCH_2)_3Al{\cdot}As(SiMe_3)_3$ (4), $(Me_3SiCH_2)_2(Br)Al{\cdot}P(SiMe_3)_3$ (5), $[(Me_3SiCH_2)(Br)AlP(SiMe_3)_2]_2$ (6), $[(Me_3SiCH_2)(Br)AlAs(SiMe_3)_2]_2$ (7), and $[(Me_3SiCH_2)_2AlAs(SiMe_3)_2]_2$ (9)

	2	3	4	5	6	7	9
formula	$C_{21}H_{60}AlAsSi_6$	$C_{24}H_{60}AlPSi_3$	$C_{24}H_{60}AlAsSi_3$	$C_{17}H_{49}AlBrPSi_5$	$C_{20}H_{58}Al_2Br_2P_2Si_6$	$C_{20}H_{58}Al_2As_2Br_2Si_6$	$C_{28}H_{80}Al_2As_2Si_8$
fw	583.11	490.94	534.89	531.87	742.92	830.82	845.44
space group	$P3_1$	$P3$	$P3$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pbcn$
a, Å	16.1093(25)	16.1189(12)	16.182(2)	12.847(1)	9.791(1)	9.850(1)	12.852(3)
b, Å				12.671(2)	19.392(3)	16.627(3)	21.095(2)
c, Å	12.0895(12)	11.285(2)	11.415(1)	20.573(3)	11.415(1)	11.452(1)	18.580(1)
β, deg				103.07(1)	111.782(9)	112.057(9)	
V, Å^3	2717.0(5)	2539.1(4)	2589.4(7)	3262.8(8)	2012.6(3)	2051.9(4)	5038(1)
Z	3	3	3	4	2	2	4
crystal color, habit	colorless block	colorless block	colorless block	colorless block	colorless block	colorless block	colorless block
D(calc), g cm^3	1.069	0.963	1.029	1.083	1.226	1.345	1.115
μ(Mo Kα), cm^{-1}	11.6	2.22	11.23	15.22	23.26	38.04	15.68
temp, K	138	233(2)	233(2)	298(2)	298(2)	298(2)	251(2)
radiation	Mo Kα (λ = 0.710 73 Å)						
$R(F)$, %[a]	4.4	4.99	7.88	9.38	4.92	5.79	3.41
$R(wF^2)$, %[a]	5.6	12.00	15.98	17.98	10.02	14.17	6.94

[a] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

flask equipped with a stir bar and Teflon valve. $AlBr_3$ (1.80 g; 7.00 mmol) in 50 mL of hexane was added to the clear colorless solution, and stirring was continued at room temperature for 48 h. The solvent was removed in vacuo, and **10** was isolated as a clear, colorless liquid (1.60 g, 93% yield). ^1H NMR: δ −0.29 (s, 2H, Me_3SiCH_2-), δ 0.09 (s, 9H, Me_3SiCH_2-). $^{13}C\{^1H\}$ NMR: δ 1.75 (s, Me_3SiCH_2-).

^{1}H NMR Equilibration of 6 and 7. In a drybox, **6** (9.8 mg, 0.03 mmol) and **7** (11.0 mg, 0.03 mmol) were each dissolved separately in 0.37 mL of toluene-d_8. The two solutions were then added to the same NMR tube via pipet, and the tube was flame-sealed. An initial spectrum was taken, after which the sealed tube was placed in an oil bath at 70 °C. Spectra were recorded every 24 h for a period of 7 d. ^1H NMR (initial): δ −0.09 (bs, 4H, Me_3SiCH_2-, **6**), δ −0.03 (s, 4H, Me_3SiCH_2-, **7**), δ 0.33 (s, 36H, Me_3SiCH_2-, **6** and **7**), δ 0.50 [t, 36H, $-SiMe_3$ (J_{P-H} = 2.6 Hz), **6**], δ 0.52 (s, 36H, $-SiMe_3$, **7**). $^{31}P\{^1H\}$ NMR (initial): δ −214.20 (s, **6**). ^1H NMR (final): δ −0.09 (bs, Me_3SiCH_2-, **6**), δ −0.07 (bs), δ −0.03 (s, Me_3SiCH_2-, **7**), δ 0.33 (s, Me_3SiCH_2-, **6** and **7**), δ 0.49 (d, J_{P-H} = 5.2 Hz), δ 0.50 [t, $-SiMe_3$ (J_{P-H} = 2.6 Hz), **6**], δ 0.52 (s, $-SiMe_3$, **7**), δ 0.53 (s). $^{31}P\{^1H\}$ NMR (final): δ −214.23 (s, **6**), δ −209.73 (s).

^{1}H NMR Equilibration of 8 and 9. The procedure used was identical to that described for **6** and **7**. ^1H NMR (initial): δ −0.20 (bs, 8H, Me_3SiCH_2-, **8**), δ −0.15 (s, 8H, Me_3SiCH_2-, **9**), δ 0.34 (s, 72H, Me_3SiCH_2-, **8** and **9**), δ 0.48 [t, 36H, $-SiMe_3$ (J_{P-H} = 2.4 Hz), **8**], δ 0.52 (s, 36H, $-SiMe_3$, **9**). $^{31}P\{^1H\}$ NMR (initial): δ −234.97 (s). ^1H NMR (final): δ −0.15 (s, Me_3SiCH_2-, **9**), δ 0.23 (d, J_{P-H} = 4.4 Hz), δ 0.34 (s, Me_3SiCH_2-, **8** and **9**), δ 0.48 (d, J_{P-H} = 4.8 Hz), δ 0.48 [t, $-SiMe_3$ (J_{P-H} = 2.4 Hz), **8**], δ 0.52 (s, $-SiMe_3$, **9**). $^{31}P\{^1H\}$ NMR (final): δ −234.18 (s), δ −230.19 (s), δ −226.25 (s).

High-Temperature ^{1}H NMR Study of 6. In a drybox, a NMR sample was prepared by dissolving a small amount of the crystalline solid (approximately 20.0 mg) in 0.75 mL of toluene-d_8 and adding the solution to the NMR tube via pipet. The tube was then flame-sealed. ^1H NMR spectra were recorded at 25, 40, 60, 80, and 95 °C, allowing 5 min for equilibration at each temperature. The sample was then cooled, and spectra were recorded at 60 and 25 °C. ^1H NMR (95 °C): δ −0.13 (bs, 4H, Me_3SiCH_2-), δ 0.28 (s, 18H, Me_3SiCH_2-), δ 0.50 [t, 36H, $-SiMe_3$ (J_{P-H} = 4.0 Hz)].

High-Temperature ^{1}H NMR Study of 7. The procedure used was similar to that described for **6**. ^1H NMR (90 °C): δ −0.07 (s, 4H, Me_3SiCH_2-), δ 0.28 (s, 18H, Me_3SiCH_2-), δ 0.53 (s, 36H, $-SiMe_3$).

X-ray Structural Solution and Refinement. Crystallographic data are summarized in Table 1, while Table 2 lists selected bond lengths and bond angles. The structural analyses were performed as follows:

Compound 2. A single crystal of **2** was mounted on a glass fiber with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at −135 °C on a Rigaku AFC6/S diffractometer utilizing graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), and the structure was solved by direct methods. Full-matrix least-squares refinement with weights based upon counting-statistics was performed. Hydrogen atoms were incorporated at their calculated positions using a riding model in the later iterations of refinement which converged at $R = 0.044$ ($R_w = 0.056$). A final difference Fourier synthesis revealed no unusual features. Crystallographic calculations were performed using the NRCVAX[13] suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 14. An ORTEP[15] diagram showing the solid-state confirmation and atom numbering scheme for **2** is shown in Figure 1.

Compounds 3−7 and 9. Suitable crystals were selected and mounted in nitrogen-flushed glass capillaries and flame-sealed. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° ≤ 2θ ≤ 24°). The systematic absences in the diffraction data are consistent with the trigonal space groups $P\bar{3}$ and $P3$ for **3** and **4**, uniquely consistent for the space group $P2_1/c$ for **5**−**7**, and uniquely consistent for the space group $Pbcn$ for **9**. Solution in both the centrosymmetric and the chiral option were pursued for **3** and **4**, but only solution in the chiral space group, $P3$, afforded chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semiempirical ellipsoid absorption corrections were not necessary because there was less than 10% intensity variation in the ψ-scan data. There are three independent, but chemically equivalent, molecules in the asymmetric unit for **3** and **4**. The molecule in **6** and **7** lies on a crystallographic inversion center, and the molecule in **9** is located on a 2-fold axis. The absolute

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[13] Gabe, E. J.; Page, Y. L.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

[14] *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

[15] Johnson, C. K. *ORTEP-A Fortran Thermal Ellipisoid Plot Program*; Technical Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2−7 and 9, with Estimated Standard Deviations in Parentheses

Bond Lengths for **2**			
Al(1)−As(1)	2.671(3)	As(1)−Si(1)	2.377(3)
Al(1)−C(41)	1.985(9)	As(1)−Si(2)	2.367(3)
Al(1)−C(51)	2.009(10)	As(1)−Si(3)	2.371(3)
Al(1)−C(61)	1.989(10)		
Bond Angles for **2**			
Al(1)−As(1)−Si(1)	111.15(10)	As(1)−Al(1)−C(41)	101.2(3)
Al(1)−As(1)−Si(2)	116.15(10)	As(1)−Al(1)−C(51)	99.2(3)
Al(1)−As(1)−Si(3)	114.17(10)	As(1)−Al(1)−C(61)	102.5(3)
Si(1)−As(1)−Si(2)	104.34(11)	C(41)−Al(1)−C(51)	115.7(4)
Si(1)−As(1)−Si(3)	105.57(10)	C(41)−Al(1)−C(61)	116.2(4)
Si(2)−As(1)−Si(3)	104.45(10)	C(51)−Al(1)−C(61)	117.4(4)
Bond Lengths for **3**			
Al−P	2.681(4)	P−Si	2.278(2)
Al−C(4)	1.996(4)		
Bond Angles for **3**			
Al−P−Si	112.93(7)	P−Al−C(4)	95.3(2)
Si−P−SiA	105.80(8)	C(4)−Al−C(4A)	119.17(5)
Bond Lengths for **4**			
Al−As	2.72(2)	As−Si	2.363(7)
Al−C(4)	1.97(2)		
Bond Angles for **4**			
Al−As−Si	114.3(2)	As−Al−C(4)	97.0(9)
Si−As−SiA	104.3(3)	C(4)−Al−C(4A)	118.5(3)
Bond Lengths for **5**			
Al−P	2.498(7)	P−Si(3)	2.271(6)
Al−Br	2.351(5)	P−Si(4)	2.306(6)
Al−C(1)	1.97(2)	P−Si(5)	2.286(7)
Al−C(5)	1.96(2)		
Bond Angles for **5**			
Al−P−Si(3)	110.5(2)	P−Al−Br	100.7(2)
Al−P−Si(4)	113.2(3)	P−Al−C(1)	104.4(6)
Al−P−Si(5)	111.7(2)	P−Al−C(5)	107.0(5)
Si(3)−P−Si(4)	107.4(2)	Br−Al−C(1)	109.2(5)
Si(3)−P−Si(5)	107.7(3)	Br−Al−C(5)	113.4(6)
Si(4)−P−Si(5)	106.1(3)	C(1)−Al−C(5)	119.9(7)
Bond Lengths for **6**			
Al(1)−P(1)	2.436(2)	Al(1)−P(1A)	2.435(3)
Al(1)−Br(1)	2.312(2)	Al(1)−C(7)	1.941(7)
P(1)−Si(1)	2.276(3)	P(1)−Si(2)	2.273(3)
Bond Angles for **6**			
Al(1)−P(1)−Al(1A)	89.42(8)	P(1)−Al(1)−P(1A)	90.58(8)
Br(1)−Al(1)−P(1)	105.55(9)	C(7)−Al(1)−P(1)	121.9(2)
Br(1)−Al(1)−P(1A)	108.55(10)	C(7)−Al(1)−P(1A)	114.1(2)
Br(1)−Al(1)−C(7)	113.5(2)	Si(1)−P(1)−Si(2)	107.58(10)
Si(1)−P(1)−Al(1)	113.18(10)	Si(2)−P(1)−Al(1)	119.65(10)
Si(1)−P(1)−Al(1A)	114.79(10)	Si(2)−P(1)−Al(1A)	111.59(10)
Bond Lengths for **7**			
Al−As	2.505(3)	Al−AsA	2.515(3)
Al−Br	2.316(3)	Al−C(4)	1.955(10)
As−Si(2)	2.364(3)	As−Si(3)	2.362(3)
Bond Angles for **7**			
Al−As−AlA	90.15(9)	As−Al−AsA	89.85(9)
Br−Al−As	105.52(11)	C(4)−Al−As	122.3(3)
Br−Al−AsA	107.99(12)	C(4)−Al−AsA	113.9(3)
Br−Al−C(4)	114.2(3)	Si(2)−As−Si(3)	107.23(11)
Si(2)−As−Al	119.65(10)	Si(3)−As−Al	113.05(10)
Si(2)−As−AlA	111.45(10)	Si(3)−As−AlA	114.85(10)
Bond Lengths for **9**			
Al(1)−As	2.567(2)	Al(2)−As	2.560(2)
Al(1)−C(4)	1.962(4)	Al(2)−C(8)	1.965(4)
As−Si(3)	2.358(2)	As−Si(4)	2.357(2)
Bond Angles for **9**			
Al(1)−As−Al(2)	92.85(4)	As−Al(1)−AsA	86.99(7)
As−Al(2)−AsA	87.31(6)	C(4)−Al(1)−C(4A)	122.1(3)
C(4)−Al(1)−As	115.7(2)	C(4)−Al(1)−AsA	105.54(13)
C(8)−Al(2)−C(8A)	122.2(3)	C(8)−Al(2)−As	113.7(2)
C(8)−Al(2)−AsA	107.29(14)	Si(3)−As−Si(4)	104.04(6)
Si(3)−As−Al(1)	111.40(5)	Si(3)−As−Al(2)	116.03(5)
Si(4)−As−Al(1)	121.42(5)	Si(4)−As−Al(2)	111.61(5)

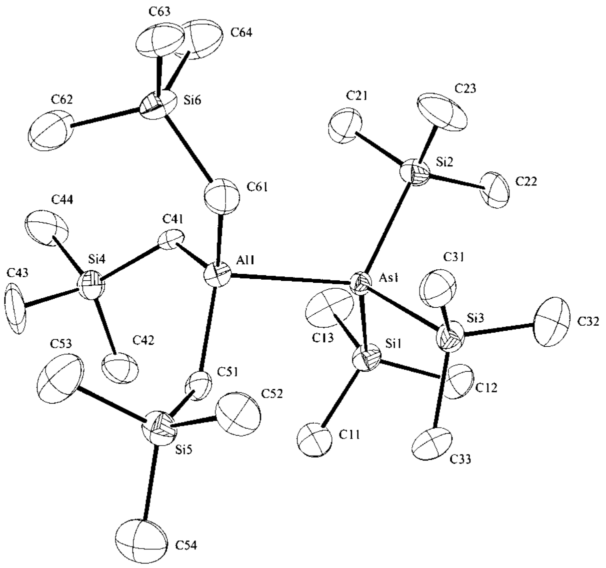

Figure 1. ORTEP diagram (30% probability ellipsoids), showing the solid-state structure and atom-numbering scheme for $(Me_3SiCH_2)_3Al{\cdot}As(SiMe_3)_3$ (**2**). Hydrogen atoms are omitted for clarity.

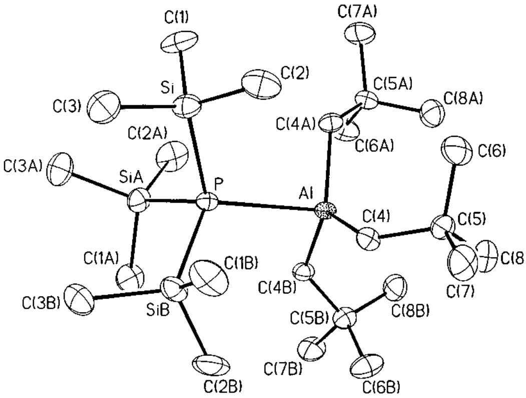

Figure 2. ORTEP diagram of $(Me_3CCH_2)_3Al{\cdot}P(SiMe_3)_3$ (**3**), showing the atom-labeling scheme. Only one of the three independent, but chemically equivalent, molecules are shown. Thermal ellipsoids are at 30% probability, and hydrogen atoms are omitted for clarity.

configuration of **3** was determined (Flack = 0.2(2)), and **4** was refined as a 70/30 racemic twin. All non-hydrogen atoms were refined with anisotropic displacement coefficients, except for the carbon atoms of **4** and carbon atoms on the trimethysilyl groups of **5** which were refined isotropically to conserve data. Hydrogen atoms were treated as idealized contributions. Structures **3** and **4** are isomorphous, as are structures **6** and **7**. ORTEP diagrams are found in Figures 2−7.

All software and sources of the scattering factors are contained in the SHELXTL (version 5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

The room-temperature, 1:1 reactions of $(Me_3SiCH_2)_3$-Al with $P(SiMe_3)_3$ and $As(SiMe_3)_3$ yield the expected Lewis acid−base adducts $(Me_3SiCH_2)_3Al{\cdot}P(SiMe_3)_3$ (**1**) and $(Me_3SiCH_2)_3Al{\cdot}As(SiMe_3)_3$ (**2**), respectively. These adducts have been characterized through multinuclear NMR, partial elemental analysis, and, in the case of **2**, single-crystal X-ray analysis. Repeated attempts to

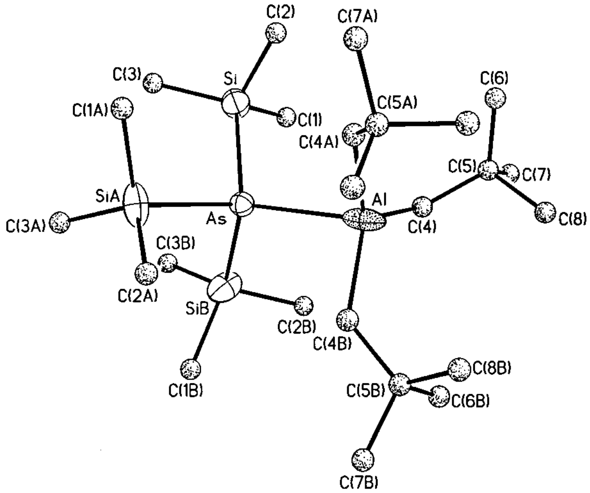

Figure 3. ORTEP diagram of $(Me_3CCH_2)_3Al{\cdot}As(SiMe_3)_3$ (**4**), showing the atom-labeling scheme. Only one of the three independent, but chemically equivalent, molecules are shown. Thermal ellipsoids are at 30% probability, and hydrogen atoms are omitted for clarity.

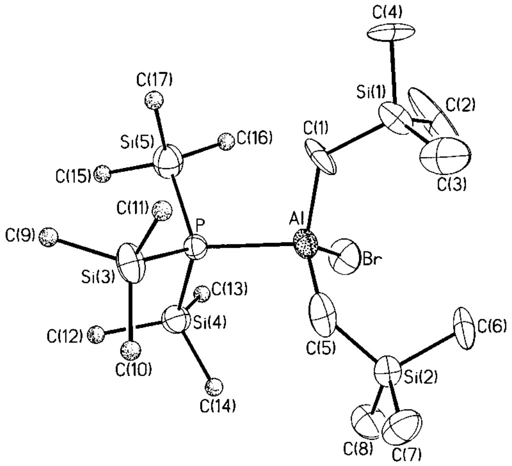

Figure 4. ORTEP diagram of $(Me_3SiCH_2)_2(Br)Al{\cdot}P(SiMe_3)_3$ (**5**), showing the atom-labeling scheme. Thermal ellipsoids are at 30% probability, and hydrogen atoms are omitted for clarity.

recrystallize **1** failed to yield X-ray-quality crystals. These reactions are analogous to those used previously to form $(Me_3SiCH_2)_3M{\cdot}P(SiMe_3)_3$ and $(Me_3SiCH_2)_3M{\cdot}As(SiMe_3)_3$, where M = Ga[6e] or In.[16] The (trimethylsilyl)methyl− groups on the aluminum and the trimethylsilyl− groups on the arsenic of **2** adopt a staggered conformation to one another, and both the aluminum and arsenic reside in distorted tetrahedral environments. The Al−As bond length of 2.671(3) Å is well within the expected range and compares favorably with the average Al−As distance of 2.60 Å reported for the adduct $Ph_3Al{\cdot}As(SiMe_3)_3$.[3] The slightly longer bond length in **2** can be attributed to the greater steric bulk of the alkyl− groups around the aluminum when compared to the phenyl− groups. These phenyl− groups are also electron withdrawing, serving to increase the Lewis acidity of the aluminum and decrease the bond length. The average As−Al−C bond angle of 101.0° in **2** is also smaller than the corresponding average angle of 104.5° seen in $Ph_3Al{\cdot}As(SiMe_3)_3$.

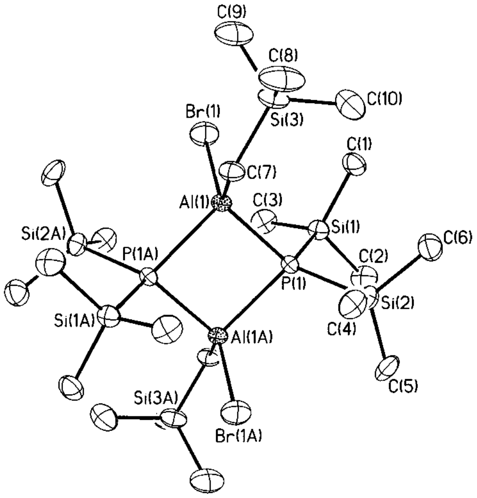

Figure 5. ORTEP diagram of $[(Me_3SiCH_2)(Br)AlP(SiMe_3)_2]_2$ (**6**), showing the atom-labeling scheme. Thermal ellipsoids are at 30% probability, and hydrogen atoms are omitted for clarity.

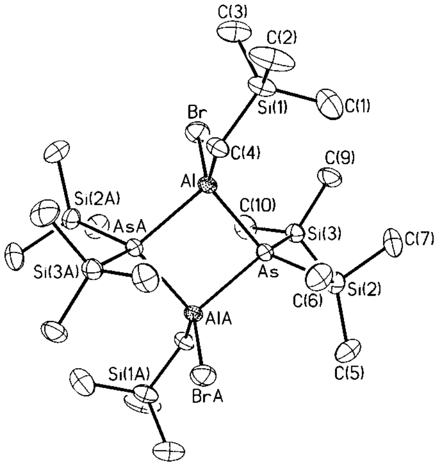

Figure 6. ORTEP diagram of $[(Me_3SiCH_2)(Br)AlAs(SiMe_3)_2]_2$ (**7**), showing the atom-labeling scheme. Thermal ellipsoids are at 30% probability, and hydrogen atoms are omitted for clarity.

Similarly, the independent 1:1 reactions of $(Me_3CCH_2)_3Al$ with $P(SiMe_3)_3$ and $As(SiMe_3)_3$ at room temperature in hexane solution result in a high yield of the Lewis acid−base adducts $(Me_3CCH_2)_3Al{\cdot}P(SiMe_3)_3$ (**3**) and $(Me_3CCH_2)_3Al{\cdot}As(SiMe_3)_3$ (**4**). Again, the (trimethylsilyl)methyl− and trimethylsilyl− groups adopt a staggered conformation with respect to one another, and the aluminum and pnicogen atoms reside in distorted tetrahedral environments. The average Al−P bond length of 2.67 Å found in **3** is longer than the analogous Al−P distance of 2.52 Å found in $Ph_3Al{\cdot}P(SiMe_3)_3$,[3] again due to the decreased steric bulk and electron withdrawing nature of the phenyl− group. The average Al−As bond length of 2.72 Å found in **4** is comparable to the Al−As bond length of 2.671(3) Å in **2**, due to the similarity of the ligands attached to the aluminum atoms.

The 1:1 mixture of $(Me_3SiCH_2)_2AlBr$ and $P(SiMe_3)_3$ fails to undergo intermolecular dehalosilylation at room temperature and instead affords the Lewis acid−base adduct $(Me_3SiCH_2)_2(Br)Al{\cdot}P(SiMe_3)_3$ (**5**). This result is not surprising, and the failure of aluminum to partici-

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(16) Wells, R. L.; McPhail, A. T.; Jones, L. J.; Self, M. F.; Butcher, R. J. *Organometallics* **1992**, *11*, 2694.

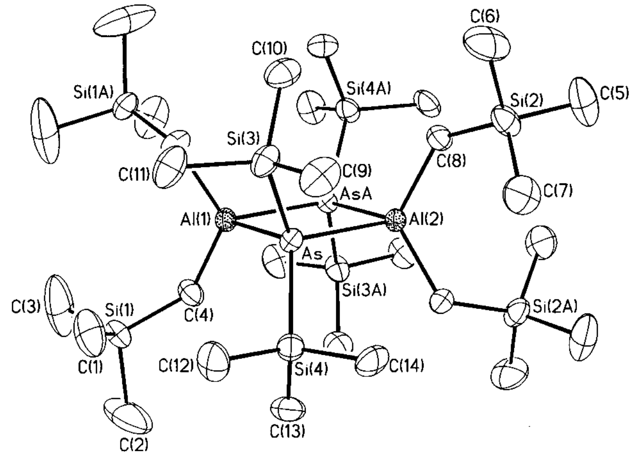

Figure 7. ORTEP diagram of $[(Me_3SiCH_2)_2AlAs(SiMe_3)_2]_2$ (**9**), showing the atom-labeling scheme. Thermal ellipsoids are at 30% probability, and hydrogen atoms are omitted for clarity.

pate in dehalosilylation reactions has been well documented,[3,17] especially in the case of aluminum−phosphorus linkages. The isolation of **5** shows that the trend holds for this system as well. The Al−P bond length of 2.498(7) Å is very close to the analogous length in a similar structure, $Ph_2ClAl \cdot P(SiMe_3)_3$,[3] found to be 2.467(2) Å. Another interesting comparison between these structures is the P−Al−halogen bond angle of 100.7(2)° in **5** and 102.1(1)° in $Ph_2ClAl \cdot P(SiMe_3)_3$, where the increased size of the bromine atom combined with the increased steric bulk of the (trimethylsilyl)methyl− groups appears to have a small effect. The aluminum and phosphorus atoms in **5**, as expected, reside in distorted tetrahedral environments with the attached groups adopting a staggered conformation.

The 1:1 salt-elimination reactions between $(Me_3SiCH_2)AlBr_2$ (**10**) and $LiP(SiMe_3)_2$ and $LiAs(SiMe_3)_2$ yield the anticipated dimers $[(Me_3SiCH_2)(Br)AlP(SiMe_3)_2]_2$ (**6**) and $[(Me_3SiCH_2)(Br)AlAs(SiMe_3)_2]_2$ (**7**), respectively. The synthesis of **10** was effected by comproportionation between $(Me_3SiCH_2)_3Al$ and $AlBr_3$. Similarly, reaction of $(Me_3SiCH_2)_2AlBr$ with $LiP(SiMe_3)_2$ and $LiAs(SiMe_3)_2$ yielded the dimers $[(Me_3SiCH_2)_2AlP(SiMe_3)_2]_2$ (**8**) and $[(Me_3SiCH_2)_2AlAs(SiMe_3)_2]_2$ (**9**), respectively. Their structures were determined by single-crystal X-ray diffraction, except for **8**. The suggested dimer structure of **8** is based solely on the triplet present in the ^1H NMR spectrum, which appears as a result of virtual coupling of the trimethylsilyl− protons to the two phosphorus atoms in the central ring. Attempts to isolate X-ray-quality crystals of this compound were unsuccessful. The average Al−P bond length of 2.44 Å in **6** is very close to the average Al−P bond length of 2.46 Å found in the dimer $[Et_2AlP(SiMe_3)_2]_2$.[4] The average endocyclic ring angles in **6** are 89.4° for Al−P−Al and 90.6° for P−Al−P, and the central Al−P−Al−P ring is planar as evidenced by the inversion center present in the molecule. The (trimethylsilyl)methyl− groups and bromine atoms also adopt a trans conformation in relation to one another. In **7**, the average Al−As bond length of 2.51 Å also compares well with the average length of 2.53 Å reported for the dimer $[Et_2AlAs(SiMe_3)_2]_2$.[5] The exocyclic bromine atoms are again in a trans conformation, and the endocyclic ring angles are 90.15(9)° for Al−As−Al and 89.85(9)° for As−Al−As. Again, the inversion center present in the molecule demonstrates the planarity of this central ring. The average Al−As bond length of 2.57 Å and the average Al−As−Al and As−Al−As endocyclic ring angles of 92.9 and 87.2°, respectively, of **9** compare well with the analogous lengths and angles reported for **7** and the dimer $[Et_2AlAs(SiMe_3)_2]_2$ (vide supra).

In an attempt to study the solution behavior of these dimeric compounds, and judge the utility of equilibrating them to form a mixed-pnicogen type structure as in $Et_2\overline{AlP(SiMe_3)_2Al(Et)_2A}s(SiMe_3)_2$,[18] two independent NMR tube equilibration reactions were attempted, the first between **6** and **7** and the second between **8** and **9**. Repeated scans of the samples at room temperature revealed no change in the peak multiplicities, positions, or integrations. However, heating the samples to 70 °C for 7 days resulted in a significant change in both samples. In the case of **6** and **7**, the triplet assigned to the $-SiMe_3$ protons of **6** lost intensity, and a new doublet appeared in this same region at δ 0.49 (J_{P-H} = 5.2 Hz), superimposed on the triplet. Two new singlets also appeared in the ^1H spectra, at δ −0.07 and 0.53. In addition, a new peak was observed in the $^{31}P\{^1H\}$ NMR spectra, at δ −209.72. Presumably, these new peaks arise from and are consistent with the formation of the desired mixed-pnicogen structure. However, the compound seems to be in equilibrium with the starting dimers, since there was no noticeable change in the spectra after 4 days, and all three compounds still were present. In the equilibration of dimers **8** and **9**, no mixed-pnicogen structure was observed on heating, but **8** decomposed. This is shown most clearly by the rapid reduction in intensity of the triplet assigned to the $-SiMe_3$ protons of **8** in comparison to the $-SiMe_3$ protons of **9**. This triplet was replaced with a doublet centered at δ 0.48 (J_{P-H} = 4.8 Hz), apparently due to the decomposition product.

In the only recorded cases of internal dehalosilylation by aluminum−arsenic compounds, trimethylsilyl chloride elimination was induced by heating a sample of $Cl_3Al \cdot As(SiMe_3)_3$ in a cool flame[19] or by heating $Et_2(Cl)Al \cdot As(SiMe_3)_3$ at 87 °C in an NMR tube.[5] Both a bromine atom and a trimethylsilyl− group are present in **6** and **7**, allowing for the potential loss of trimethylsilyl bromide to form a cubane or rearrange to another novel structure. To explore this possibility, a high-temperature ^1H NMR study of **6** and **7** was undertaken. Since it was of interest to isolate an intermediate compound as opposed to the aluminum pnictide, these studies were done at the same temperature used to initiate elimination in $Et_2(Cl)Al \cdot As(SiMe_3)_3$ (vide supra). In both cases, no trimethylsilyl bromide elimination occurred. Both dimers maintained their integrity, as there was no change in the spectra up to 95 °C (for **6**) or 90 °C (for **7**). In fact, the triplet in the spectra of **6** due to the trimethylsilyl− protons was still present, indicating the dimeric structure of this compound is maintained at the

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(18) Laske Cooke, J. A.; Wells, R. L.; White, P. S. *Organometallics* **1995**, *14*, 3562.

(19) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 45.

higher temperature. A notable difference between **6** and **7** and $Et_2(Cl)Al{\cdot}As(SiMe_3)_3$ is that, in the present study, the attempted intramolecular dehalosilylation involves loss of the "second" trimethylsilyl− group from the phosphorus or arsenic atom. While $P(SiMe_3)_3$ and $As(SiMe_3)_3$ readily participate in room temperature dehalosilylation reactions, it has been seen in our laboratory that loss of a second or third trimethylsilyl− group is often difficult, requiring progressively higher temperatures.[20] Considering this, as well as the unwillingness of aluminum to participate in dehalosilylation reactions in general, the stability of **6** and **7** at increased temperatures can be understood.

Acknowledgment. We wish to thank the Office of Naval Research and the ONR AASERT Program for their financial support of this work.

Supporting Information Available: Tables of X-ray parameters, bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates and *U* values for **2**−**7** and **9** (42 pages). Ordering information is given on any current masthead page.

OM980097M

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[20] (a) Wells, R. L.; Aubuchon, S. R.; Kher, S. S.; Lube, M. S.; White, P. S. *Chem. Mater.* **1995**, *7*, 793. (b) Janik, J. F.; Baldwin, R. A.; Wells, R. L.; Pennington, W. T.; Schimek, G. L.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1996**, *15*, 5385.