Synthesis and Characterization of Phosphinosilylalanes from [(CH₃)₃Si]₃Al. Crystal and Molecular Structure Determinations of {[(CH₃)₃Si]₂AlP(C₆H₅)₂}₂, {[(CH₃)₃Si]₂AlP(C₆H₅)[Si(CH₃)₃]}₂, {[(CH₃)₃Si]₂AlP(H)(c-C₆H₁₁)}₃, and [{[(CH₃)₃Si]₂N}(C₆H₅)P]₂

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The reactions of [(CH₃)₃Si]₃Al·O(C₂H₅)₂ with phosphines (C₆H₅)₂PCl, PCl₃, {[(CH₃)₃Si]₂N}(C₆H₅)PCl, (C₆H₅)₂PH, [(CH₃)₃Si](C₆H₅)PH, (C₆H₅){[(CH₃)₃Si]₂N}PH, (c-C₆H₁₁)PH₂, and PH₃ were surveyed. Reactions of the chlorophosphines led to formation of di- or polyphosphines, and the molecular structure of [{[(CH₃)₃Si]₂N}(C₆H₅)P]₂ was determined by single-crystal X-ray diffraction analysis. The compound crystallized in the tetragonal space group $I4_1/a$ with $a = 24.379$ (9) Å, $c = 10.778$ (3) Å, $Z = 8$, $V = 6405.8(4)$ Å, and $\rho_{calcd} = 1.11$ g cm⁻³. Least-squares refinement gave $R_F = 6.3\%$ and $R_{wF} = 5.3\%$ on 1613 reflections with $F \geq 4\sigma(F)$. The diphosphine has C_i symmetry, and each phosphorus atom has pseudotetrahedral geometry: P-P = 2.270 (3) Å and P-N = 1.724 (4) Å. The remaining phosphines form Lewis acid-base complexes with [(CH₃)₃Si]₃Al and/or undergo elimination/condensation chemistry resulting in production of phosphinoalane ring compounds or polymers. The molecular structures of three additional compounds have been determined by single-crystal X-ray diffraction analysis. The compound {[(CH₃)₃Si]₂AlP(C₆H₅)₂}₂ crystallized in the triclinic space group $P\bar{1}$ (No. 2) with $a = 10.989$ (3) Å, $b = 20.576$ (5) Å, $c = 21.000$ (5) Å, $\alpha = 101.52$ (2)°, $\beta = 102.17$ (2)°, $\gamma = 100.86$ (2)°, $Z = 4$, $V = 4414$ (2) Å³, and $\rho_{calcd} = 1.08$ g cm⁻³. Least-squares refinement gave $R_F = 11.3\%$ and $R_{wF} = 9.6\%$ on 7466 reflections with $F > 3\sigma(F)$. The compound {[(CH₃)₃Si]₂AlP(C₆H₅)[Si(CH₃)₃]}₂ crystallized in the monoclinic space group $P2_1/n$ with $a = 11.360$ (8) Å, $b = 12.215$ (7) Å, $c = 16.673$ (12) Å, $\beta = 102.13$ (5)°, $Z = 2$, $V = 2261$ (2) Å³, and $\rho_{calcd} = 1.04$ g cm⁻³. Least-squares refinement gave $R_F = 9.9\%$ and $R_{wF} = 7.7\%$ on 2718 reflections with $F \geq 3\sigma(F)$. The compound {[(CH₃)₃Si]₂AlP(H)(c-C₆H₁₁)}₃ crystallized in the triclinic space group $P\bar{1}$ (No. 2) with $a = 12.564$ (2) Å, $b = 12.935$ (3) Å, $c = 19.149$ (4) Å, $\alpha = 83.66$ (2)°, $\beta = 88.64$ (2)°, $\gamma = 66.65$ (1)°, $Z = 2$, $V = 2839$ (1) Å³, and $\rho_{calcd} = 1.01$ g cm⁻³. Least-squares refinement gave $R_F = 11.3\%$ and $R_{wF} = 8.6\%$ and 5213 reflections with $F \geq 3\sigma(F)$. The first two compounds contain planar four-membered (AlP)₂ rings with C_i symmetry and average Al-P distances of 2.455 and 2.466 Å, respectively. The third compound forms a six-membered skew-boat cyclohexane-like (AlP)₃ ring with an E, E, A conformation and an average Al-P distance of 2.444 Å. Pyrolysis of a polymeric product obtained from reactions involving PH₃ and [(CH₃)₃Si]₃Al·O(C₂H₅)₂ resulted in formation of aluminum phosphide, AlP.

Introduction

Although the reactions between amines and alanes have been extensively studied,[1] the parallel chemistry with phosphine bases and alanes has been sparsely developed. Trialkylaluminum reagents form a number of 1:1 Lewis acid-base complexes with phosphines, and the complexation is generally exothermic by 15-25 kcal/mol. Limited NMR data suggest that these complexes are stable in many organic solvents; however, they appear to engage in rapid self-exchange processes in the presence of excess base.[2-5] With the proper combinations of substituent groups, alanes and phosphines also undergo 1,2-elimination chemistry with the formation of cyclic phosphinoalanes, [X₂AlPY₂]ₙ, where n is typically 2 or 3. Elimination chemistry is particularly favored by small alkyl, hydride, or chloride substituents on aluminum and by hydrogen on phosphorus, R₂PH, or by use of saline organophosphides, MPR₂.[1,6-14] The degree of association for the phosphi-

noalanes appears to be sterically controlled with small substituent groups (H, CH₃, C₂H₅, Cl) favoring trimeric rings while larger groups dictate a dimeric structure.[1] Electronic effects may also help determine ring size, but these factors have not been systematically examined. Indeed, there have been very few attempts to elucidate the mechanism of the 1,2-elimination process and the subsequent condensation reactions in these systems.[7,15-17] Beachley and co-workers have studied the elimination chemistry between alkylalanes and -amines, and they have drawn interesting parallels between the alane-amine and alane-phosphine elimination processes.[7] For example, it has been tentatively concluded that elimination does not originate from an acid-base adduct as is often suggested but rather from a separated acid-base pair. In fact, it has been suggested that stable acid-base adducts represent a "dead end" for elimination chemistry.

(1) Mole, T.; Jeffery, E. A. *Organoaluminum Chemistry*; Elsevier: New York, 1972.

(2) Vriezen, W. H. N.; Jellinek, F. *Chem. Phys. Lett.* 1967, *1*, 284.

(3) Cullingworth, A. R.; Pidcock, A.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* 1966, 89.

(4) Cohen, B. M.; Cullingworth, A. R.; Smith, J. D. *J. Chem. Soc. A* 1969, 2193.

(5) Schmidbaur, H.; Lauteschlager, S.; Muller, G. *J. Organomet. Chem.* 1985, *281*, 25.

(6) Fritz, G. *Angew. Chem., Int. Ed. Engl.* 1966, *5*, 53.

(7) Beachley, O. T.; Victoriano, L. *Inorg. Chem.* 1986, *25*, 1948.

(8) Beachley, O. T.; Tessier-Youngs, C. *Organometallics* 1983, *2*, 796.

(9) Davidson, N.; Brown, H. C. *J. Am. Chem. Soc.* 1942, *64*, 316.

(10) Beachley, O. T.; Coates, G. E. *J. Chem. Soc. A* 1965, 3241.

(11) Johnson, A. W.; Larson, W. D.; Dahl, G. H. *Can. J. Chem.* 1964, *43*, 1338.

(12) Issleib, K.; Krech, F. *Z. Anorg. Allg. Chem.* 1964, *328*, 21.

(13) Issleib, K.; Deylig, H. J. *Z. Naturforsch.* 1962, *17B*, 198.

(14) Fritz, G.; Trenczek, G. *Angew. Chem., Int. Ed. Engl.* 1963, *2*, 482.

(15) Schlyer, D. J.; Ring, M. A. *J. Organometal. Chem.* 1976, *114*, 9; *J. Electrochem. Soc.* 1977, *124*, 569.

(16) Beachley, O. T. *Inorg. Chem.* 1981, *20*, 2815.

(17) Beachley, O. T.; Tessier-Youngs, C. *Inorg. Chem.* 1979, *18*, 3188.

Our own interest in phosphinoalane chemistry originates from efforts to develop new classes of main-group element ring and cage compounds as well as define new routes to the little studied electronic ceramic AlP[18] and its composites. Utilizing the background developed in our studies of the reactions of NH_3 with $[(CH_3)_3Si]_3Al$, we have examined reactions of several phosphines and $[(CH_3)_3Si]_3\cdot Al\cdot O(C_2H_5)_2$ in an effort to prepare new ring compounds and AlP. Prior to this work, Rösch[19] had briefly reported on the formation of $[(CH_3)_3Si]_3PAl[Si(CH_3)_3]_3$; however, reactions with other phosphines and $[(CH_3)_3Si]_3Al$ had not been described.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulations of all reagents and products. Infrared spectra were recorded on a Nicolet 6000 FT-IR spectrometer, and ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on FT-80A, GE-NT360, and JEOL GSX-400 spectrometers. Spectral standards were $(CH_3)_4Si$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). Downfield shifts from the standard were assigned positive δ's.

Materials. $[(CH_3)_3Si]_3Al\cdot Et_2O$,[20] $\{[(CH_3)_3Si]_2N\}(C_6H_5)PCl$,[21] and $[(CH_3)_3Si](c\text{-}C_6H_{11})PH$[22] were prepared as described in the literature. PCl_3, $(C_6H_5)_2PCl$, $(C_6H_5)_2PH$, $(C_6H_5)PH_2$, and $(c\text{-}C_6H_{11})PH_2$ were purchased from Aldrich Chemical Co., and PH_3 was obtained from Matheson. $\{[(CH_3)_3Si]_2N\}(C_6H_5)PH$ was prepared by reduction of the chloride with $LiAlH_4$.[23] All solvents were rigorously dried under dry nitrogen with appropriate drying agents and then distilled. Individual solvent transfers were accomplished by vacuum distillation.

Reactions of $[(CH_3)_3Si]_3Al\cdot Et_2O$ and Chlorophosphines. (a) $(C_6H_5)_2PCl$. $[(CH_3)_3Si]_3Al\cdot Et_2O$ (3 g, 9.4 mmol) in 20 mL of toluene was combined at −78 °C with $(C_6H_5)_2PCl$ (3.2 g, 14.4 mmol) in 20 mL of toluene, and the mixture was stirred and warmed to 25 °C overnight. The resulting mixture was evaporated, leaving a damp solid. NMR (22 °C, C_6D_6): $^{31}P\{^1H\}$ δ −44.6, −38.1, −14.4; ^1H δ 7.6–7.0 (phenyl), 0.4 ($(CH_3)_3Si$). Infrared spectroscopy and mass spectrometry identified $(CH_3)_3SiCl$ in the volatiles evaporated from the reaction mixture.

(b) $\{[(CH_3)_3Si]_2N\}(C_6H_5)PCl$. $[(CH_3)_3Si]_3Al\cdot Et_2O$ (0.54 g, 1.7 mmol) in 15 mL of hexane was combined with $\{[(CH_3)_3Si]_2N\}(C_6H_5)PCl$ (0.53 g, 1.7 mmol) in 15 mL of hexane at −78 °C. The mixture was warmed to 25 °C and stirred for 4 h. The volatiles were removed, leaving a damp solid. NMR (22 °C, C_6D_6): $^{31}P\{^1H\}$ δ 4.0, 50.4, 65.7, 220.0. Infrared spectroscopy and mass spectrometry identified $(CH_3)_3SiCl$ in the volatiles evaporated from the reaction mixture.

(c) PCl_3. $[(CH_3)_3Si]_3Al\cdot Et_2O$ (1.07 g, 3.3 mmol) in 20 mL of hexane was combined with PCl_3 (0.46 g, 3.3 mmol) in 10 mL of hexane at −78 °C, and the mixture was warmed to 25 °C. Stirring overnight resulted in the deposition of a large amount of insoluble orange solid. The volatiles were removed, and $(CH_3)_3SiCl$ was identified. The solid was found to be completely insoluble in common solvents.

Reduction of $\{[(CH_3)_3Si]_2N\}(C_6H_5)PCl$ with Mg. The chlorophosphine (3.04 g, 10 mmol) was combined with Mg chips (0.48 g, 20 mmol) in 75 mL of THF in a 250-mL Schlenk vessel, and the mixture was refluxed under nitrogen for 24 h. The resulting mixture was filtered to remove excess Mg, and then the filtrate volume was reduced in half by vacuum evaporation. Benzene (100 mL) was condensed into the flask, and the cloudy mixture was filtered to remove a portion of the $MgCl_2$. The

collected filtrate was evaporated to dryness, and the remaining solid was extracted with 100 mL of benzene.[24] The solution was filtered, and the filtrate was evaporated, leaving a microcrystalline pale yellow solid: yield 95%; mp 152–154 °C; soluble in THF, CH_2Cl_2, benzene; mass spectrum (70 eV),[25] m/e (ion) 536 (M^+), 268 $[(Me_3Si)_2N](Ph)P^+$], 146; $^{31}P\{^1H\}$ NMR (22 °C, C_6H_6/C_6D_6) δ 66, 51; $^{13}C\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2) δ 132–126 (m, phenyl), 5.2 (CH_3, J_{PC} = 5.6 Hz); ^1H NMR (C_6D_6) δ 7.6–7.2 (m, phenyl), 0.38 (J_{PH} = 0.9 Hz, CH_3), 0.33 (J_{PH} = 0.9 Hz, CH_3). Anal. Calcd for $Si_4P_2N_2C_{24}H_{46}$: C, 53.69; H, 8.64; N, 5.22. Found: C, 53.58; H, 8.49; N, 5.32.

Reactions of $[(CH_3)_3Si]_3Al\cdot Et_2O$ with Phosphines. (a) $(C_6H_5)_2PH$. $[(CH_3)_3Si]_3Al\cdot Et_2O$ (1.27 g, 4 mmol) in 5 mL of hexane was combined with $(C_6H_5)_2PH$ (0.75 g, 4 mmol) in 5 mL of hexane at −78 °C, and the mixture was stirred and warmed to 25 °C. After several hours, the hexane was evaporated, leaving a colorless oil: $^{31}P\{^1H\}$ NMR (22 °C, C_6D_6) δ −26.1 (d, J_{PH} = 339 Hz), $^{13}C\{^1H\}$ NMR (22 °C, C_6D_6) δ 134.4–129.2 (m, phenyl), 3.9 (CH_3); ^1H NMR (22 °C, C_6D_6) δ 7.8–7.0 (m, phenyl), 5.89 (d, J_{PH} = 330 Hz), 0.34 (CH_3). The oil was redissolved in hexane and refluxed for 48 h. The mixture was cooled, the supernatant liquid decanted, the solid residue washed with hexane (2 × 10 mL) to remove any unreacted phosphine, and a crystalline colorless solid was isolated; yield $\{[(CH_3)_3Si]_2AlP(C_6H_5)_2\}_2$ 65%;[26] mp ~260 °C dec; soluble in Et_2O, THF, benzene, hot hexane; IR (C_6D_6, cm^{-1}) 3058 (w), 2953 (s), 2888 (m), 1585 (w), 1480 (m), 1252 (m), 1238 (s), 1068 (w), 1048 (w), 1026 (m), 998 (w), 904 (m), 836 (s), 742 (s), 696 (s), 677 (m), 618 (w), 508 (w), 427 (w); mass spectrum (70 eV), m/e (ion) 716 (M^+), 643 (M − $SiMe_3^+$), 570 (M − $2SiMe_3^+$); $^{31}P\{^1H\}$ NMR (22 °C, C_6D_6) δ −39.1; $^{13}C\{^1H\}$ NMR (22 °C, C_6D_6) δ 135.5–128.9 (m, phenyl), 3.0 (CH_3); ^1H NMR (22 °C, C_6D_6) δ 7.6–7.1 (m, phenyl), 0.27 (CH_3). Anal.[27] Calcd for $Si_4P_2Al_2C_{36}H_{56}$: C, 60.29; H, 7.87; P, 8.64; Al, 7.51. Found: C, 57.32; H, 7.51; P, 8.84; Al, 7.53.

(b) $[(CH_3)_3Si](C_6H_5)PH$. $[(CH_3)_3Si]_3Al\cdot Et_2O$ (1.46 g, 4.6 mmol) in 20 mL of hexane was combined with $[(CH_3)_3Si](C_6H_5)PH$ (0.82 g, 4.6 mmol) in 20 mL of hexane at −78 °C. The mixture was warmed to 25 °C and stirred for 4 h. The solvent was evaporated, leaving a colorless oil which was indefinitely stable at 25 °C. $^{31}P\{^1H\}$ NMR (22 °C, C_6D_6): δ −95.9 (d, J_{PH} = 309 Hz). The oil was redissolved in 20 mL of hexane, and the mixture was refluxed for 48 h. After 4–5 h, white crystalline solid appeared on the flask walls. The liquid phase was concentrated to 5 mL, and it was decanted from the solid. The solid was washed with 5 mL of cold hexane, and the isolated solid was dried by vacuum evaporation: yield $\{[(CH_3)_3Si]_2AlP(C_6H_5)[(CH_3)_3Si]\}_2$ 50%;[26] mp 225 °C dec; soluble in Et_2O, THF, benzene, hot hexane; IR (KBr, cm^{-1}) 3072 (w), 3049 (w), 2955 (s), 2941 (s), 2886 (s), 2795 (sh), 1582 (w), 1480 (w), 1469 (w), 1433 (m), 1386 (sh), 1243 (s), 1155 (w), 1067 (w), 1026 (w), 1001 (w), 837 (s), 752 (m), 735 (s), 696 (s), 671 (s), 629 (s), 616 (s), 488 (w), 432 (s), 395 (w); mass spectrum (70 eV),[25] m/e (ion) 693 (M − CH_3^+), 635 (M − Me_3Si^+), 563 (M − $2Me_3Si^+$); $^{31}P\{^1H\}$ NMR (22 °C, C_6D_6) δ −121.8, −123.6; $^{13}C\{^1H\}$ NMR (22 °C, C_6D_6) δ 137.4–128.4 (m, phenyl), 4.3 (CH_3SiAl), 1.5–0.6 (CH_3SiP); ^1H NMR (22 °C, C_6D_6) 7.7–7.1 (m, phenyl), 0.56–0.42 (CH_3SiAl), 0.31–0.20 (CH_3SiP).

(c) $(C_6H_5)PH_2$. $[(CH_3)_3Si]_3Al\cdot Et_2O$ (0.97 g, 3.0 mmol) in 5 mL of pentane was mixed with $(C_6H_5)PH_2$ (0.33 g, 3.0 mmol) in 5 mL at −78 °C. The mixture was subsequently warmed to 25 °C and stirred for 48 h. The volatile components were evaporated, leaving a white crystalline solid which was recrystallized from a minimum of pentane: yield $\{[(CH_3)_3Si]_2AlP(C_6H_5)(H)\}_3$ 93%; mp 250–251 °C dec; soluble in Et_2O, pentane, THF, benzene. IR (C_6D_6, cm^{-1}) 3072 (w), 3059 (w), 3017 (w), 2943 (s), 2887 (m), 2810 (sh), 2114

(18) Wang, C. C.; Zaheeruddin, M.; Spinar, L. H. *J. Inorg. Nucl. Chem.* **1963**, *25*, 326. Sonomura, H.; Miyauchi, T. *Jpn. J. Appl. Phys.* **1969**, *8*, 1263. Beer, S. Z. *J. Electrochem. Soc.* **1969**, *116*, 263. Lorenz, M. R.; Chicotka, R.; Pettit, G. D. *Solid State Commun.* **1970**, *8*, 693.

(19) Rösch, L. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 480.

(20) Rösch, L.; Altman, G. *J. Organomet. Chem.* **1980**, *195*, 47.

(21) McNamara, W. F.; Duesler, E. N.; Paine, R. T.; Ortiz, J. V.; Kölle, P.; Nöth, H. *Organometallics* **1986**, *5*, 360.

(22) Becker, G.; Mundt, O.; Rossler, M.; Schneider, E. *Z. Anorg. Allg. Chem.* **1978**, *443*, 43.

(23) O'Neal, H. R.; Nielson, R. H. *Inorg. Chem.* **1983**, *22*, 814.

(24) If the initial THF solution is evaporated to dryness without treatment with benzene, the subsequent extraction of the massive residue containing the product and $MgCl_2$ is difficult to manage, and the yield of diphosphine is reduced.

(25) For the most part, only important high mass ions are listed.

(26) The yields of these products can be improved by collecting the decanted liquids and filtrates and then growing second crops of crystals from saturated hexane solution at −20 °C.

(27) Several compounds studied gave variable elemental analysis, and uncombusted residues were often observed after C/H analysis. A variety of methods were evaluated to overcome this problem, but no satisfactory solution was found.

Table I. Crystal and Diffraction Data for 2–5

	2	3	4	5
cryst dimen, mm	0.16 × 0.16 × 0.42	0.35 × 0.46 × 0.62	0.34 × 0.28 × 0.23	0.2 × 0.2 × 0.4
formula	[PSi$_2$NC$_{12}$H$_{23}$]$_2$	[PSi$_2$AlC$_{18}$H$_{28}$]$_2$	[PSi$_3$AlC$_{15}$H$_{32}$]$_2$	[PSi$_2$AlC$_{12}$H$_{30}$]$_3$
mol wt	536.9	717.2	709.3	865.5
space group	$I4_1/a$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
temp, °C	19 (2)	20 (2)	20 (2)	20 (2)
a, Å	24.379 (9)	10.989 (3)	11.360 (8)	12.564 (2)
b, Å		20.576 (5)	12.215 (7)	12.935 (3)
c, Å	10.778 (3)	21.000 (5)	16.673 (12)	19.149 (4)
α, deg		101.52 (2)		83.66 (2)
β, deg		102.17 (2)	102.13 (5)	88.64 (2)
γ, deg		100.86 (2)		66.65 (1)
Z	8	4	2	2
V, Å^3	6405.8 (4)	4414.2 (2)	2261 (2)	2839
d_{calcd}, g cm^{-3}	1.11	1.08	1.04	1.01
μ, cm^{-1}	2.93	2.64	3.1	2.95
abs corr	Ψ scans	Ψ scans	Ψ scans	Ψ scans
scan type	ω	ω	ω	θ–2θ
scan rate, deg min^{-1}	variable, 6–30	variable, 6–30	variable, 4–30	variable, 6–30
scan width, deg	0.8	0.6	1.3	1.1
2θ min, deg	1	2	2	2
2θ max, deg	50	50	50	50
octant collected	$-h,\pm k,l$	$\pm h,\pm k,l$	$\pm h,\pm k,\pm l$	$\pm h,\pm k,+l$
no. of reflctns measd	7119	16013	8936	12873
no. of unique reflctns	2835	15516	3985	9753
no. of reflctns with $I \geq (n)\sigma(E)$	1613,4	7466,3	2718,3	5213,3
no. of variables ref	145	697	181	439
final R_F	6.3	11.3	9.9	11.3
final R_{wF}	5.3	9.6	7.7	8.6

(w), 1585 (w), 1483 (m), 1437 (m), 1388 (sh), 1252 (m) 1238 (s), 1146 (w), 1069 (w), 1026 (w), 1000 (w), 904 (w), 835 (s), 738 (s), 693 (s), 681 (s), 618 (s), 419 (m); mass spectrum (20 eV),[25] m/e (ion) 831 (M – CH$_3$$^+$), 774 (M – Si(CH$_3$)$_3$$^+$), 699 (M – 2Si(CH$_3$)$_3$ – H$^+$), 563 ([(Me$_3$Si)$_2$AlP(C$_6$H$_5$)]$_2$$^+$); ^{31}P{^{1}H} NMR (22 °C, C$_6$D$_6$) δ –125.7, –125.1; ^{1}H NMR (22 °C, C$_6$D$_6$) δ 7.6–7.1 (m, phenyl), 4.68 (d, J_{PH} = 282 Hz), 4.48 (d, J_{PH} = 291 Hz), 0.32, 0.24, 0.21, 0.15 (CH$_3$Si); ^{13}C{^{1}H} NMR (22 °C, C$_6$D$_6$) δ 134–128 (m, phenyl), 3.1, 2.8, 2.5, 2.2 (CH$_3$S i). Samples of the compound {[(CH$_3$)$_3$-Si]$_2$AlP(C$_6$H$_5$)(H)} were refluxed in cyclohexane for 24 h. ^{31}P NMR spectra of the reaction mixture showed δ –123.0, –124.6, –125.1, and –126.8. The mixture was distilled and fractions containing C$_6$H$_5$PH$_2$, δ –126.8, and [(CH$_3$)$_3$Si]P(C$_6$H$_5$)(H), δ –123.0, were isolated.

(d) (c-C$_6$H$_{11}$)PH$_2$ (2:1 Ratio). [(CH$_3$)$_3$Si]$_3$Al·Et$_2$O (0.97 g, 3.0 mmol) in 10 mL of pentane was combined with (c-C$_6$H$_{11}$)PH$_2$ (0.7 g, 6.0 mmol) in 10 mL of pentane at –78 °C, and the mixture was warmed to 25 °C. After 4 h, the mixture was cooled to –20 °C and colorless crystals were separated. The solution over the crystals was decanted, and the crystals were washed with cold pentane: yield {[(CH$_3$)$_3$Si]$_2$AlP(c-C$_6$H$_{11}$)(H)]$_3$ 68%;[26] mp 160–170 °C dec; soluble in Et$_2$O, THF, benzene, hexane; IR (C$_6$D$_6$, cm^{-1}) 2936 (s), 2890 (m), 2854 (m), 2813 (sh), 2114 (w), 1445 (m), 1252 (w), 1237 (m), 1001 (w), 840 (s), 677 (m), 619 (w), 453 (w), 413 (w); mass spectrum (70 eV),[25] m/e (ion) 717 (M – 2Me$_3$Si – H$^+$); ^{31}P{^{1}H} NMR (22 °C, C$_6$D$_6$) δ –123.0, –122.2, –121.7, –120.9 (J_{PH} = 270–300 Hz); ^{1}H NMR (22 °C, C$_6$D$_6$) δ 3.0–1.0 (c-C$_6$H$_{11}$), 0.42, 0.41; ^{13}C{^{1}H} NMR (22 °C, C$_6$D$_6$) δ 35.6, 30.4, 27.5, 25.4 (c-C$_6$H$_{11}$), 3.5 (CH$_3$). Anal.[27] Calcd for Si$_6$Al$_3$P$_3$C$_{36}$H$_{90}$: C, 49.95; H, 10.48. Found: C, 46.02; H, 9.99.

(e) {[(CH$_3$)$_3$Si]$_2$N}(C$_6$H$_5$)PH. [(CH$_3$)$_3$Si]$_3$Al·Et$_2$O (0.92 g, 2.9 mmol) in 5 mL of hexane was added to {[(CH$_3$)$_3$Si]$_2$N}(C$_6$H$_5$)PH (0.77 g, 2.9 mmol) in 5 mL of hexane; the mixture was stirred at 25 °C for several hours and then refluxed for 20 h. The volatiles were evaporated, leaving a white crystalline solid: yield [(C-H$_3$)$_3$Si]$_3$Al·P(H)(C$_6$H$_5$){N[Si(CH$_3$)$_3$]$_2$} 95%; soluble in hydrocarbons, C$_6$H$_6$ and Et$_2$O; IR (oil, cm^{-1}) 3076 (w), 3063 (w), 2950 (s), 2890 (m), 2815 (sh), 2275 (w), 1483 (w), 1437 (m), 1407 (w), 1257 (s), 1198 (w), 1101 (w), 1026 (m), 989 (w), 923 (s), 844 (s), 832 (s), 788 (m), 763 (sh), 731 (m), 691 (m), 652 (sh), 617 (w), 504 (w), 484 (w), 471 (w), 463 (w), 447 (w), 436 (w); mass spectrum (70 eV),[25] m/e (ion) 412 (M – Me$_3$Si – 2Me$^+$), 269 ((Me$_3$Si)$_2$N-(Ph)PH$^+$), 246 ((Me$_3$Si)$_3$Al$^+$); ^{31}P NMR (C$_6$D$_6$, 22 °C) δ 10.9 (d, J_{PH} = 335); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C) δ 132.7–128.7 (m, phenyl), 4.1 (CH$_3$SiAl), 3.7 (d, $^3J_{PC}$ = 3.8 Hz, CH$_3$SiN); ^{1}H NMR (22 °C,

C$_6$D$_6$) δ 7.6–7.1 (m, phenyl) 6.9 (d, $^1J_{PH}$ = 335 Hz, PH), 0.3 (CH$_3$Al), 0.24 (d, $^4J_{PH}$ = 0.7 Hz, CH$_3$SiN).

(f) PH$_3$. [(CH$_3$)$_3$Si]$_3$Al·Et$_2$O (1.7 g, 5.4 mmol) in 15 mL of hexane was combined 16.3 mmol of PH$_3$, and the mixture was stirred at –78 °C for 30 min and then warmed to 25 °C. The resulting solution was stirred for 10 days. An amorphous white solid precipitated during this time, and it was collected by filtration and washed with 10 mL of hexane. The solid was insoluble in common solvents, and it gave unreliable elemental analyses:[27] IR (KBr, cm^{-1}) 2949 (m), 2888 (w), 2116 (w), 1432 (w), 1392 (w), 1251 (m), 1063 (m), 904 (m), 836 (s), 752 (m), 680 (m), 617 (m), 440 (m), 405 (m). The amorphous solid was pyrolyzed in a quartz tube first at 210 °C for 20 h and then at 700 °C for 20 h. A black solid remained in the tube, and this solid was characterized by X-ray powder diffraction: 2θ = 3.10 (111), 2.69, 1.98 (220), 1.63 (311), 1.41, and 0.84.

Crystal Structure Determinations. Each compound was recrystallized from saturated hydrocarbon solutions at –20 °C, and suitable crystals were selected and sealed in glass capillaries under dry nitrogen. Crystals were centered on a P3/F automated diffractometer, and determinations of the crystal class, orientation matrix, and accurate unit cell parameters were performed in a standard manner.[28] Data were collected by using graphite-monochromated Mo Kα radiation, a scintillation counter, and pulse height analyzer. Details of the data collection are summarized in Table I.

All calculations were performed on a SHELXTL structure determination system.[29] Neutral atom scattering factors and anomalous dispersion factors were used for all non-hydrogen atoms during refinements. The function minimized during the least-squares refinements[30] was $\sum w(|F_o| - |F_c|)^2$. The room-temperature structures of 3–5 suffer from a high degree of thermal motion in

(28) Programs used for centering reflections, auto indexing, refinement of cell parameters, and axial photographs are those described in: *Nicolet P3/R3 Operations Manual*; Sparks, R. A., Ed.; Syntex Analytical Instruments: Cupertino, CA, 1978.

(29) The SHELXTL package of programs for calculations and plots is described in: *SHELXTL Users Manual, Revision 3*, Sheldrick, G. M., July 1981, Nicolet XRD Corp. SHELXTL uses scattering factors and anomalous dispersion terms taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1968; Vol. IV.

(30) Discrepancy indices are defined as follows: $R_F = [\sum ||F_o| - |F_c||/\sum |F_o|$, $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and the goodness of fit GOF = $[w(|F_o| - |F_c|)_2/(\text{NO} - \text{NV})]^{1/2}$, where NO is the number of observations, and NV is the number of variables.
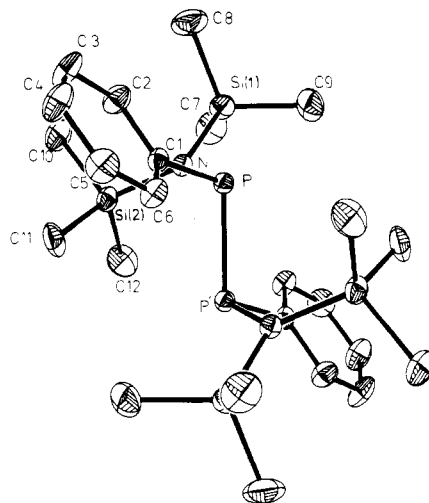
Table II. Non-Hydrogen Atom Positional Parameters and Their Esd's for [{[(CH₃)₃Si]₂N}(C₆H₅)P]₂

atom	x/a	y/b	z/c
P	0.54189 (5)	0.50314 (5)	−0.04545 (11)
Si(1)	0.56302 (7)	0.55304 (7)	−0.28657 (13)
Si(2)	0.51414 (7)	0.62657 (6)	−0.08139 (14)
N	0.5381 (2)	0.5619 (2)	−0.1341 (3)
C(1)	0.5863 (2)	0.5236 (2)	0.0852 (4)
C(2)	0.6303 (2)	0.5575 (2)	0.0617 (5)
C(3)	0.6690 (3)	0.5698 (3)	0.1514 (6)
C(4)	0.6644 (3)	0.5478 (3)	0.2676 (6)
C(5)	0.6215 (2)	0.5133 (2)	0.2913 (5)
C(6)	0.5831 (2)	0.5001 (2)	0.2028 (5)
C(7)	0.5225 (3)	0.5950 (3)	−0.3982 (5)
C(8)	0.6363 (2)	0.5734 (3)	−0.2972 (6)
C(9)	0.5574 (3)	0.4803 (3)	−0.3385 (5)
C(10)	0.5601 (3)	0.6816 (2)	−0.1397 (6)
C(11)	0.5128 (3)	0.6337 (2)	0.0905 (5)
C(12)	0.4429 (3)	0.6403 (3)	−0.1374 (7)

several trimethyl silyl carbon atoms and in one cyclohexyl group of 5. Details of the refinements are given in the supplementary material. Tables of observed and calculated structure factors, anisotropic thermal parameters, hydrogen atom positional parameters, and full listings of bond distances and angles are given in the supplementary material. Tables II–V give listings of non-hydrogen atom positional parameters for the compounds.

Results and Discussion

A. Synthesis of Phosphinoalanes. In our initial

Figure 1. Molecular structure and atom labeling scheme for [{[(CH₃)₃Si]₂N}(C₆H₅)P]₂ (2) (25% thermal ellipsoids).

search for chemistry that would produce phosphinoalane ring compounds and aluminum phosphide precursors under mild conditions, we explored potential elimination reactions between [(CH₃)₃Si]₃Al·O(C₂H₅)]₂ and several chlorophosphines. Limited average bond energy data suggested that these reactions should be exothermic,[31]

Table III. Non-Hydrogen Atom Positional Parameters and Their Esd's for {[(CH₃)₃Si]₂AlP(C₆H₅)₂}₂

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
P(1)	0.1471 (2)	0.04191 (13)	0.50011 (12)	P(3)	−0.0425 (3)	0.43120 (13)	−0.06496 (13)
C(1a)	0.2080 (6)	0.0670 (4)	0.4319 (3)	C(3a)	−0.2014 (6)	0.3788 (3)	−0.1126 (4)
C(1b)	0.1945 (6)	0.1282 (4)	0.4154 (3)	C(3b)	−0.2228 (6)	0.3449 (3)	−0.1799 (4)
C(1c)	0.2480 (6)	0.1485 (4)	0.3658 (3)	C(3c)	−0.3455 (6)	0.3069 (3)	−0.2166 (4)
C(1d)	0.3149 (6)	0.1077 (4)	0.3326 (3)	C(3d)	−0.4467 (6)	0.3030 (3)	−0.1860 (4)
C(1e)	0.3284 (6)	0.0466 (4)	0.3491 (3)	C(3e)	−0.4253 (6)	0.3370 (3)	−0.1187 (4)
C(1f)	0.2749 (6)	0.0262 (4)	0.3987 (3)	C(3f)	−0.3026 (6)	0.3749 (3)	−0.0820 (4)
C(1g)	0.2894 (6)	0.0719 (4)	0.5714 (3)	C(3g)	0.0594 (8)	0.3869 (5)	−0.1052 (4)
C(1h)	0.2883 (6)	0.0459 (4)	0.6278 (3)	C(3h)	0.1340 (8)	0.4192 (5)	−0.1413 (4)
C(1i)	0.3935 (6)	0.0690 (4)	0.6839 (3)	C(3i)	0.2138 (8)	0.3856 (5)	−0.1718 (4)
C(1j)	0.4999 (6)	0.1180 (4)	0.6836 (3)	C(3j)	0.2190 (8)	0.3197 (5)	−0.1662 (4)
C(1k)	0.5010 (6)	0.1440 (4)	0.6272 (3)	C(3k)	0.1444 (8)	0.2874 (5)	−0.1301 (4)
C(1l)	0.3958 (6)	0.1209 (4)	0.5711 (3)	C(3l)	0.0646 (8)	0.3210 (5)	0.0996 (4)
Al(1)	0.0416 (3)	−0.07912 (15)	0.47488 (14)	Al(3)	0.0197 (3)	0.44664 (16)	0.05720 (15)
Si(1)	−0.0113 (3)	−0.13320 (15)	0.35290 (14)	Si(5)	0.2352 (3)	0.42610 (19)	0.09241 (17)
C(1)	0.1224 (11)	−0.1747 (6)	0.3336 (6)	C(13)	0.3505 (11)	0.4452 (7)	0.0406 (7)
C(2)	−0.0369 (11)	−0.0789 (5)	0.2906 (5)	C(14)	0.2173 (13)	0.3331 (6)	0.0945 (7)
C(3)	−0.1600 (11)	−0.2043 (5)	0.3314 (5)	C(15)	0.3115 (12)	0.4762 (7)	0.1808 (6)
Si(2)	0.1537 (3)	−0.14457 (15)	0.54473 (15)	Si(6)	−0.1358 (3)	0.38129 (17)	0.10470 (16)
C(4)	0.3267 (10)	−0.1281 (6)	0.5397 (6)	C(16)	−0.2983 (11)	0.4001 (6)	0.1026 (6)
C(5)	0.0819 (11)	−0.2372 (5)	0.5073 (6)	C(17)	−0.0554 (12)	0.3901 (7)	0.1967 (5)
C(6)	0.1555 (12)	−0.1301 (6)	0.6367 (5)	C(18)	−0.1657 (13)	0.2908 (6)	0.0552 (7)
P(2)	0.3672 (3)	0.48258 (13)	0.43682 (13)	P(4)	0.3519 (2)	−0.04096 (13)	0.00057 (12)
C(2a)	0.2658 (6)	0.4011 (3)	0.3846 (3)	C(4a)	0.2085 (6)	−0.0652 (3)	−0.0704 (3)
C(2b)	0.2962 (6)	0.3689 (3)	0.3271 (3)	C(4b)	0.2132 (6)	−0.0362 (3)	−0.1247 (3)
C(2c)	0.2134 (6)	0.3088 (3)	0.2846 (3)	C(4c)	0.1072 (6)	−0.0541 (3)	−0.1802 (3)
C(2d)	0.1001 (6)	0.2809 (3)	0.2997 (3)	C(4d)	−0.0035 (6)	−0.1010 (3)	−0.1814 (3)
C(2e)	0.0698 (6)	0.3132 (3)	0.3572 (3)	C(4e)	−0.0082 (6)	−0.1300 (3)	−0.1271 (3)
C(2f)	0.1526 (6)	0.3733 (3)	0.3997 (3)	C(4f)	0.0978 (6)	−0.1121 (3)	−0.0716 (3)
C(2g)	0.2927 (7)	0.5452 (4)	0.4034 (4)	C(4g)	0.2921 (6)	−0.0707 (4)	0.0671 (3)
C(2h)	0.3487 (4)	0.6142 (4)	0.4338 (4)	C(4h)	0.3146 (6)	−0.1311 (4)	0.0824 (3)
C(2i)	0.2963 (7)	0.6641 (4)	0.4100 (4)	C(4i)	0.2648 (6)	−0.1551 (4)	0.1314 (3)
C(2j)	0.1878 (7)	0.6450 (4)	0.3557 (4)	C(4j)	0.1924 (6)	−0.1188 (4)	0.1653 (3)
C(2k)	0.1318 (7)	0.5760 (4)	0.3253 (4)	C(4k)	0.1699 (6)	−0.0584 (4)	0.1501 (3)
C(2l)	0.1842 (7)	0.5261 (4)	0.3491 (4)	C(4l)	0.2198 (6)	−0.0344 (4)	0.1010 (3)
Al(2)	0.5950 (3)	0.50093 (15)	0.44054 (15)	Al(4)	0.4656 (3)	0.07997 (15)	0.03103 (14)
Si(3)	0.6776 (3)	0.60548 (17)	0.40645 (16)	Si(7)	0.5187 (3)	0.12974 (16)	0.15437 (14)
C(7)	0.5758 (12)	0.6035 (7)	0.3216 (5)	C(19)	0.5333 (10)	0.0679 (5)	0.2084 (5)
C(8)	0.8414 (10)	0.6038 (6)	0.3946 (6)	C(20)	0.3881 (11)	0.1716 (6)	0.1737 (5)
C(9)	0.6885 (11)	0.6910 (5)	0.4648 (5)	C(21)	0.6706 (11)	0.1968 (6)	0.1837 (5)
Si(4)	0.6682 (3)	0.40226 (18)	0.38724 (18)	Si(8)	0.3546 (3)	0.14858 (15)	−0.03523 (15)
C(10)	0.5851 (13)	0.3125 (5)	0.3857 (6)	C(22)	0.3474 (11)	0.1374 (6)	−0.1267 (5)
C(11)	0.6535 (14)	0.4009 (7)	0.2958 (6)	C(23)	0.1849 (9)	0.1339 (6)	−0.0268 (6)
C(12)	0.8432 (11)	0.4166 (7)	0.4300 (8)	C(24)	0.4348 (10)	0.2408 (5)	0.0033 (5)

Table IV. Non-Hydrogen Atom Positional Parameters and Their Esd's for {[(CH$_3$)$_3$Si]$_2$AlP(C$_6$H$_5$)[Si(CH$_3$)$_3$]}$_2$

atom	x/a	y/b	z/c
P	0.13971 (13)	0.04829 (13)	0.04293 (9)
C(1)	0.2116 (5)	0.1728 (5)	0.0174 (4)
C(2)	0.2824 (6)	0.1724 (6)	−0.0429 (4)
C(3)	0.3428 (7)	0.2634 (7)	−0.0568 (5)
C(4)	0.3391 (8)	0.3576 (7)	−0.0127 (7)
C(5)	0.2693 (8)	0.3588 (7)	0.0482 (6)
C(6)	0.2080 (6)	0.2693 (5)	0.0620 (4)
Si(1)	0.29384 (15)	−0.01290 (15)	0.14258 (11)
C(7)	0.4258 (5)	−0.0373 (7)	0.0945 (5)
C(8)	0.2461 (6)	−0.1388 (6)	0.1865 (4)
C(9)	0.3392 (7)	0.0934 (6)	0.2217 (4)
Al	0.06207 (15)	−0.07649 (14)	−0.07232 (10)
Si(2)	0.13042 (19)	−0.26989 (17)	−0.05109 (13)
C(10)	0.2970 (7)	−0.2850 (7)	−0.0341 (5)
C(11)	0.0848 (8)	−0.3482 (6)	0.0365 (5)
C(12)	0.0702 (7)	−0.3503 (6)	−0.1467 (5)
Si(3)	0.08653 (17)	−0.01273 (19)	−0.20919 (11)
C(13)	−0.0242 (6)	−0.0845 (7)	−0.2911 (4)
C(14)	0.2398 (6)	−0.0587 (7)	−0.2241 (5)
C(15)	0.0751 (7)	0.1358 (7)	−0.2338 (5)

Table V. Non-Hydrogen Atom Positional Parameters and Their Esd's for {[(CH$_3$)$_3$Si]$_2$AlP(H)(c-C$_6$H$_{11}$)}$_3$

atom	x/a	y/b	z/c
P(1)	0.89436 (17)	1.03218 (18)	0.18062 (11)
C(1)	1.0218 (6)	0.9065 (7)	0.1551 (4)
C(2)	0.9881 (7)	0.8303 (8)	0.1151 (5)
C(3)	1.0945 (8)	0.7247 (8)	0.0994 (6)
C(4)	1.1792 (8)	0.7593 (9)	0.0587 (6)
C(5)	1.2159 (7)	0.8356 (8)	0.0976 (5)
C(6)	1.1097 (7)	0.9409 (7)	0.1152 (5)
P(2)	0.58292 (17)	1.15433 (17)	0.23152 (11)
C(7)	0.5085 (6)	1.2154 (6)	0.1458 (4)
C(8)	0.5769 (7)	1.2623 (7)	0.0966 (4)
C(9)	0.5172 (7)	1.3126 (8)	0.0262 (5)
C(10)	0.3971 (7)	1.3991 (8)	0.0318 (5)
C(11)	0.3278 (7)	1.3534 (9)	0.0802 (6)
C(12)	0.3866 (7)	1.3022 (7)	0.1513 (5)
P(3)	0.79792 (20)	1.22124 (22)	0.32519 (13)
C(13)	0.8334 (11)	1.2968 (11)	0.3885 (7)
C(14)	0.7797 (14)	1.3145 (16)	0.4473 (7)
C(15)	0.8226 (13)	1.3551 (16)	0.5081 (7)
C(16)	0.8768 (17)	1.4314 (14)	0.4812 (9)
C(17)	0.9447 (17)	1.4059 (15)	0.4267 (8)
C(18)	0.8995 (13)	1.3541 (12)	0.3711 (6)
Al(1)	0.7390 (2)	0.9717 (2)	0.21714 (13)
Si(1)	0.6653 (2)	0.8892 (2)	0.12824 (14)
C(19)	0.6641 (7)	0.9494 (7)	0.0359 (4)
C(20)	0.5113 (7)	0.9083 (8)	0.1501 (5)
C(21)	0.7483 (8)	0.7310 (7)	0.1295 (5)
Si(2)	0.8020 (3)	0.8419 (2)	0.32597 (15)
C(22)	0.6821 (11)	0.8031 (11)	0.3584 (6)
C(23)	0.8517 (11)	0.8915 (9)	0.4014 (5)
C(24)	0.9278 (10)	0.7089 (8)	0.3063 (6)
Al(2)	0.5889 (2)	1.2951 (2)	0.30580 (13)
Si(3)	0.4967 (2)	1.5004 (2)	0.26361 (15)
C(25)	0.5149 (9)	1.5577 (8)	0.1741 (6)
C(26)	0.3339 (8)	1.5500 (9)	0.2717 (6)
C(27)	0.5364 (12)	1.5814 (8)	0.3237 (7)
Si(4)	0.4926 (3)	1.2557 (3)	0.41361 (15)
C(28)	0.3413 (10)	1.2867 (12)	0.3904 (6)
C(29)	0.4840 (11)	1.3450 (12)	0.4829 (6)
C(30)	0.5530 (14)	1.1120 (11)	0.4546 (8)
Al(3)	0.9626 (2)	1.1461 (2)	0.24752 (14)
Si(5)	0.9783 (2)	1.2986 (2)	0.16261 (15)
C(31)	1.0819 (8)	1.2391 (8)	0.0903 (5)
C(32)	0.8364 (8)	1.3900 (8)	0.1168 (6)
C(33)	1.0322 (8)	1.3969 (8)	0.2012 (5)
Si(6)	1.1410 (2)	1.0257 (3)	0.31745 (16)
C(34)	1.2057 (12)	0.8764 (10)	0.3104 (9)
C(35)	1.2599 (10)	1.0657 (14)	0.2810 (9)
C(36)	1.1429 (11)	1.0437 (16)	0.4061 (7)

although it was not clear if the products would be [R$_2$AlPR$_2$]$_n$ and (CH$_3$)$_3$SiCl or R$_2$AlCl and R$_2$PSi(CH$_3$)$_3$.

Table VI. Selected Structural Parameters for {[(CH$_3$)$_3$Si]$_2$N(C$_6$H$_5$)P}$_2$

Bond Distances (Å)			
P–N	1.724 (4)	P–C(1)	1.845 (5)
P–P′	2.270 (3)	Si(1)–N	1.765 (4)
Si(1)–C(7)	1.864 (6)	Si(1)–C(8)	1.858 (6)
Si(1)–C(9)	1.865 (6)	Si(2)–N	1.775 (4)
Si(2)–C(10)	1.858 (6)	Si(2)–C(11)	1.861 (5)
Si(2)–C(12)	1.869 (6)	C(1)–C(2)	1.377 (7)
C(1)–C(6)	1.394 (7)	C(2)–C(3)	1.384 (8)
C(3)–C(4)	1.367 (9)	C(4)–C(5)	1.364 (8)
C(5)–C(6)	1.376 (8)		

Bond Angles (deg)			
N–P–C(1)	103.2 (2)	N–P–P′	104.3 (2)
C(1)–P–P′	102.5 (2)	N–Si(1)–C(7)	110.6 (2)
N–Si(1)–C(8)	110.8 (2)	C(7)–Si(1)–C(8)	108.9 (3)
N–Si(1)–C(9)	111.7 (2)	C(7)–Si(1)–C(9)	106.8 (3)
C(8)–Si(1)–C(9)	107.8 (3)	N–Si(2)–C(10)	109.5 (2)
N–Si(2)–C(11)	114.0 (2)	C(10)–Si(2)–C(11)	106.3 (3)
N–Si(2)–C(12)	111.2 (2)	C(10)–Si(2)–C(12)	108.8 (3)
C(11)–Si(2)–C(12)	106.7 (3)	P–N–Si(1)	113.3 (2)
P–N–Si(2)	125.3 (2)	Si(1)–N–Si(2)	121.3 (2)
P–C(1)–C(2)	118.6 (4)	P–C(1)–C(6)	123.4 (4)
C(2)–C(1)–C(6)	117.3 (5)	C(1)–C(2)–C(3)	122.1 (5)
C(2)–C(3)–C(4)	120.0 (6)	C(3)–C(4)–C(5)	118.4 (6)
C(4)–C(5)–C(6)	122.5 (5)	C(1)–C(6)–C(5)	119.7 (5)

The high lattice energy for AlCl$_3$ and the outcome of the reactions of BCl$_3$ and o-$\overline{\text{OC}_6\text{H}_4\text{OBCl}}$ with [(CH$_3$)$_3$Si]$_3$Al·O(C$_2$H$_5$)$_2$ which produce AlCl$_3$[32] suggested that silylphosphines might be obtained from these reactions. In fact, examination of the reaction products showed that the majority of the [(CH$_3$)$_3$Si]$_3$Al was consumed, (CH$_3$)$_3$SiCl was formed in large amounts, and high yields of two diphosphines, (C$_6$H$_5$)$_2$PP(C$_6$H$_5$)$_2$ (1) and {[(CH$_3$)$_3$Si]$_2$N}(C$_6$-H$_5$)P–P(C$_6$H$_5$){N[Si(CH$_3$)$_3$]$_2$} (2),[33] were obtained along with several other unidentified minor products as indicated by ^{31}P NMR spectra. The formation of the diphosphines and [(CH$_3$)$_3$Si]Cl is consistent with the chemistry outlined in eq 1 and 2. Transient formation of the silylphosphines

$$[(\text{CH}_3)_3\text{Si}]_3\text{Al·O(C}_2\text{H}_5)_2 + (\text{C}_6\text{H}_5)(\text{R})\text{PCl} \rightarrow$$
$$[(\text{CH}_3)_3\text{Si}]_2\text{AlCl} + [(\text{CH}_3)_3\text{Si}](\text{C}_6\text{H}_5)\text{P(R)} + \text{Et}_2\text{O} \quad (1)$$

$$[(\text{CH}_3)_3\text{Si}](\text{C}_6\text{H}_5)\text{P(R)} + (\text{C}_6\text{H}_5)(\text{R})\text{PCl} \rightarrow$$
$$(\text{C}_6\text{H}_5)(\text{R})\text{P–P(R)}(\text{C}_6\text{H}_5) + (\text{CH}_3)_3\text{SiCl} \quad (2)$$

$$\text{R} = \text{C}_6\text{H}_5 \text{ and } [(\text{CH}_3)_3\text{Si}]_2\text{N}$$
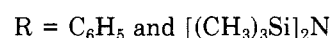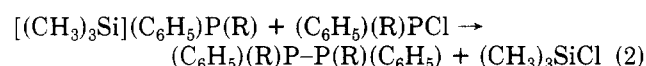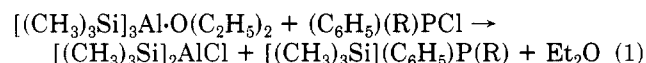
[(CH$_3$)$_3$Si](C$_6$H$_5$)P(R) was indicated by ^{31}P NMR spectra from reaction mixtures. Further, the subsequent elimination chemistry to form diphosphines has precedent in chemistry described by Schumann and Fischer.[36] The reaction of [(CH$_3$)$_3$Si]$_3$Al·O(C$_2$H$_5$)$_2$ with PCl$_3$ produced (CH$_3$)$_3$SiCl and an uncharacterized insoluble orange polymer which is ubiquitous in many reducing systems involving PCl$_3$. Attempts to trap the intermediate chlo-

(31) Huheey, J. E. *Inorganic Chemistry, Principles of Structure and Reactivity*; 2nd ed.; Harper and Row: New York, 1978. Wade, K.; Banister, A. J. *Comprehensive Inorganic Chemistry*; Pergamon Press: Oxford, 1973, Vol. 1, p 993.

(32) Janik, J. F.; Narula, C. K.; unpublished results.

(33) The ^{31}P NMR spectra for the diphosphines show resonances at δ −14.4, 50.4, and 65.7, respectively. The value for [(C$_6$H$_5$)$_2$P]$_2$ agrees closely with the value in the literature,[34] δ −15.2. Solutions of {[(CH$_3$)$_3$-Si]$_2$N(C$_6$H$_5$)P}$_2$ display two resonances which have been assigned to two isomers: meso, trans δ 65.7 (∼70%) and (R,R)(S,S), trans δ 50.4 (∼30%).[35]

(34) Mark, V.; Dungan, C. H.; Crutchfield, M. M.; VanWazer, J. R. *Top. Phosphorus* 1967, 5, 231.

(35) Similar isomer mixtures for diphosphines (RR′P)$_2$ have been detected by ^{31}P NMR spectroscopy: Lamberg, J. B.; Jackson, G. F.; Mueller, D. C. *J. Am. Chem. Soc.* 1970, 92, 3093. Appel, R.; Geisler, K.; Schöler, H. *Chem. Ber.* 1977, 110, 376. Hinke, A.; Kuchen, W. *Chem. Ber.* 1983, 116, 3003.

(36) Schumann, H.; Fischer, R. *J. Organomet. Chem.* 1975, 88, C13.

ropolyphosphines, e.g. $Cl_2P(PCl)_nPCl_2$, by substitution chemistry have not yet been successful. The chiral diphosphine $\{[(CH_3)_3Si]_2N(C_6H_5)P\}_2$ was alternatively prepared in good yield from reductive coupling of the chlorophosphine with Mg.

Since two isomers were detected in the NMR spectra of solutions of **2**,[33] it was appropriate to determine the molecular structure of crystalline **2** by single-crystal X-ray diffraction techniques. A view of the molecule is shown in Figure 1, and selected bond distances and angles are listed in Table VI. The molecule has a *meso*, trans structure (C_i symmetry), and the phosphorus and silicon atoms have local pseudotetrahedral symmetry. The nitrogen atoms are trigonal planar. The P–P bond distance 2.270 (3) Å is longer than this distance in most diphosphines: $[(t\text{-BuOC})(Ph)P]_2$, 2.211 (2) Å,[37] and $[(c\text{-}C_6H_{11})_2P]_2$, 2.215 (3) Å.[38] The long P–P bond in **2** may be a manifestation of the large steric requirements of the two substituent groups, $N(SiMe_3)_2$ and C_6H_5, and this parallels the similarly long distance in $\{[(CH_3)_3C_6H_2]_2P\}_2$, 2.260 (1) Å.[39] The P–N distance, 1.724 (4) Å, is shorter than the P–N single bond distance (1.77–1.80 Å) and intermediate between the P–N distances in $(C_5H_5)Mo(C\text{-}O)_2\{P(C_6H_5)N[Si(CH_3)_3]_2\}$, 1.698 (2) Å,[40] and in $(C_5H_5)\text{-}Fe(CO)_2\{P(C_6H_5)N[Si(CH_3)_3]_2\}$, 1.734 (4) Å.[41] The Si–N distances 1.765 (4) and 1.775 (4) Å are comparable to those found in the Mo and Fe complexes, as is the average Si–C distance, 1.863 Å. The P–C_{ipso}(phenyl) distance in **2**, 1.845 (5) Å, is considerably longer than the related distances in the metal complexes,[40,41] but it is comparable to the distance in $[(t\text{-BuOC})(Ph)P]_2$, 1.841 Å.

Although the reactions of the chlorophosphines with $[(CH_3)_3Si]_3Al\cdot O(C_2H_5)_2$ are interesting, they clearly did not provide routes to ring compounds of interest, and no further reactions of this type were explored. In the second phase of this study, the reactions of $[(CH_3)_3Si]_3Al\cdot O(C_2H_5)_2$ and several phosphines with P–H bonds were examined. The reactions were expected to be exothermic, and formation of the desired phosphinoalanes $[R_2AlPR_2]_n$ and $(CH_3)_3SiH$ by elimination chemistry appeared likely.

Combination of $[(CH_3)_3Si]_3Al\cdot O(C_2H_5)_2$ and $(C_6H_5)_2PH$ in a 1:1 ratio at 25 °C showed no evidence for release of $(CH_3)_3SiH$. Instead, ^{31}P NMR spectra of the resulting oil displayed a resonance at δ −26.1 (d, J_{PH} = 339 Hz) shifted upfield of the ligand $(C_6H_5)_2PH$, δ −41.4 (d, J_{PH} = 218 Hz). This resonance was assigned to the Lewis acid–base adduct $[(CH_3)_3Si]_3Al\cdot P(C_6H_5)_2(H)$. The large P–H coupling constant is consistent with the values found for other phosphine alane adducts.[8] ^{1}H and ^{13}C{^{1}H} NMR spectra displayed resonances for free $(C_2H_5)_2O$ in the original reaction solution, and these resonances were not present in solutions of the isolated complex when it was redissolved in C_6D_6. In the presence of excess phosphine, only one [31]P{[1]H} resonance was observed for the mixture of the complex and free phosphine, and this resonance moved progressively upfield with increasing phosphine concentration. This suggests that free and complexed phosphine undergo rapid exchange at 22 °C. Sealed NMR samples, stored for a month at 25 °C, gave very little decomposition of the complex.

The complex $[(CH_3)_3Si]_3Al\cdot P(C_6H_5)_2(H)$ was subsequently refluxed for 48 h in hexane. During this time, $(CH_3)_3SiH$ was collected and identified by infrared spectroscopy and mass spectrometry. In addition, a colorless, crystalline, air-sensitive solid, shown to be $\{[(CH_3)_3Si]_2\text{-}AlP(C_6H_5)_2\}_2$ (**3**), was isolated in good yield. The mass spectrum of **3** showed a parent ion at m/e 716 consistent with the dimeric formulation and a number of expected fragment ions. The infrared spectra showed no evidence for ν_{PH}. The ^{31}P and ^{31}P{^{1}H} NMR spectra both displayed a single resonance centered at δ −39.1. The resonance for **3** was upfield of the resonance reported for $[(C_2H_5)_2AlP\text{-}(C_6H_5)_2]_2$, δ 42.3.[8] The ^{1}H NMR spectrum showed a singlet for the $(CH_3)_3Si$ groups, δ 0.27, and two broad, poorly resolved multiplets for the phenyl groups centered at δ 7.6 and 7.1. The integrated area ratio for the silyl and phenyl groups was ∼1.7. The resonance for the $(CH_3)_3Si$ groups is comparable to the resonance found for $[(CH_3)_3Si]_3Al\cdot O(C_2H_5)_2$.[42] The ^{13}C{^{1}H} NMR spectrum revealed a single high-field peak, δ 3.0, which was assigned to the $(CH_3)_3Si$ groups and a complex pattern of low-field peaks, δ 135–128, assigned to the phenyl groups. In the latter region, virtual coupling by the two equivalent phosphorus atoms was evident in a triplet pattern centered at δ 135.2 (J_{CP} = 6 Hz). These data are consistent with the dimeric structure revealed by single-crystal X-ray analysis discussed below.

In a similar fashion, combination of $[(CH_3)_3Si]_3Al\cdot O(C_2H_5)_2$ and $[(CH_3)_3Si](C_6H_5)PH$ in a 1:1 ratio at 25 °C showed no evidence for formation of $(CH_3)_3SiH$. An adduct, $[(CH_3)_3Si]_3Al\cdot P(H)(C_6H_5)[Si(CH_3)_3]$, was isolated in high yield as a colorless oil, and it was indefinitely stable at 25 °C. The adduct gave a single peak in the ^{31}P{^{1}H} NMR spectrum, δ −95.9, which was downfield of the resonance in $[(CH_3)_3Si](C_6H_5)(H)P$, δ −122.1. Restoration of proton coupling resulted in a coupling constant, J_{PH} = 309 Hz, which was significantly larger than the coupling in the free ligand, J_{PH} = 199 Hz. Addition of excess base to the complex resulted in rapid base exchange as indicated by the position of a single resonance in [31]P{[1]H} spectra, and the position of the peaks varied with phosphine concentration.

The adduct was then heated to reflux in hexane for 48 h, and $(CH_3)_3SiH$ and a colorless crystalline air-sensitive solid were isolated as products. The crystalline solid was shown to be $\{[(CH_3)_3Si]_2AlP(C_6H_5)[(CH_3)_3Si]\}_2$ (**4**) by single-crystal X-ray diffraction analysis, and spectroscopic characterization data for solutions of **4** are consistent with this structure. The mass spectrum of **4** did not display a parent ion; however, the highest mass ion observed, m/e 693, corresponded to $[M - CH_3^+]$. The infrared spectrum for **4** displayed no evidence for the presence of a P–H stretching vibration. The ^{31}P{^{1}H} NMR spectrum of **4** contained two peaks, δ −121.8 and −123.6, in an area ratio ∼3:1. These resonances were assigned to trans and cis isomers, respectively.[43] The isomer assignment was confirmed by details of the ^{1}H and ^{13}C{^{1}H} NMR spectra.

The ^{1}H NMR spectrum contained a single sharp, intense resonance, δ 0.42, which is assigned to the $[(CH_3)_3Si]_2Al$ group protons and a virtual triplet centered at δ 0.22 (J_{PH} = 2.9 Hz) for the $[(CH_3)_3Si]P$ unit. These resonances are assigned to the trans isomer. In addition, the spectrum

(37) Becker, G.; Mundt, O.; Rössler, M. *Z. Anorg. Allg. Chem.* **1980**, *468*, 55.

(38) Rechter, R.; Kaiser, J.; Sieler, J.; Hartung, H.; Peter, C. *Acta Crystallogr.* **1977**, *B33*, 1884.

(39) Baxter, S. G.; Cowley, A. H.; Davis, R. E.; Riley, P. E. *J. Am. Chem. Soc.* **1981**, *103*, 1699.

(40) McNamara, W. F. Ph.D. Thesis, University of New Mexico, 1987.

(41) McNamara, W. F.; Reisacher, H. U.; Duesler, E. N.; Paine, R. T. *Organometallics* **1988**, *7*, 1313.

(42) The ^{1}H NMR spectrum for $[(CH_3)_3Si]_3Al\cdot Et_2O$ was quite concentration dependent in C_6D_6 with δ range 0.06–0.38. The ^{13}C{^{1}H} NMR spectrum shows a singlet for the $(CH_3)_3Si$ groups at δ 2.9.

(43) An alternate assignment would involve the formation of the trans four-membered ring and a six-membered ring, $\{[(CH_3)_3Si]_2AlP(C_6H_5)\text{-}[Si(CH_3)_3]\}_3$. This possibility seems less likely because of the combination of two bulky substituents on phosphorus. Further, there is no evidence in mass spectra for the higher molecular weight ring.

displayed two equal intensity, weak resonances assigned to inequivalent trimethylsilyl groups on aluminum, δ 0.56 and 0.45 and a virtual triplet at δ 0.30 (J_{PH} = 2.9 Hz) for the [(CH$_3$)$_3$Si]P group. These resonances are assigned to the cis isomer. The trans isomer resonances are more intense than the respective cis isomer resonances by a ratio of ~2.8:1. The phenyl region of the spectrum showed a broad set of resonances δ 7.8–7.1, and no attempt was made to assign resonances to cis or trans isomers. The ^{13}C{^{1}H} NMR spectrum shows a series of peaks in the phenyl region, δ 138–128, which also could not be clearly assigned to specific isomers. A single peak at δ 4.3 was assigned to the [(CH$_3$)$_3$Si]$_2$Al groups of both isomers. An intense virtual triplet centered at δ 0.9 ($^2J_{PC}$ = 4.9 Hz) was observed for the trans isomer [(CH$_3$)$_3$Si]P group and a weak virtual triplet at δ 1.2 ($^2J_{PC}$ = 4.0 Hz) was found for the cis isomer [(CH$_3$)$_3$Si]P group. The expected second virtual triplet for the cis isomer could not be resolved.

The primary phosphine C$_6$H$_5$PH$_2$ was allowed to react for 48 h in a 1:1 ratio with [(CH$_3$)$_3$Si]$_3$Al·O(C$_2$H$_5$)$_2$ at 25 °C in pentane. Unlike the two secondary phosphine systems described above, ^{31}P NMR spectra provided no evidence for the formation of an adduct. After 2 h, the only ^{31}P resonance present was that for the free phosphine, δ –124 ($^1J_{PH}$ = 199 Hz). Subsequently, two resonances at δ –125.1 and –125.7 slowly grew in. At the end of the reaction period, a white crystalline solid was isolated in high yield, and this compound was indefinitely stable at 25 °C. Infrared spectra for the product reveal a weak P–H stretch at 2114 cm^{-1}. The mass spectrum did not reveal a parent ion at m/e 846; however, several fragment ions were seen which would be consistent with a trimeric, six-membered ring composition, {[(CH$_3$)$_3$Si]$_2$AlP(C$_6$H$_5$)(H)}$_3$. Further support for the trimeric formulation was gained from determination of the molecular weight by cryoscopic freezing point depression in C$_6$H$_6$: calcd, 847.3; found, 820.8. If the compound has an Al$_3$P$_3$ core ring, it would be expected to have a cyclohexane-like structure related to those found in several cyclic boron–phosphorus compounds,[44] and because of the two different substituents on phosphorus, more than one isomer may be found. The ^{31}P{^{1}H} NMR spectrum of the isolated solid showed two closely spaced resonances, δ –125.1 and –125.7 in a 5:1 ratio with J_{PH} = 291 and 282 Hz, respectively. On the basis of the crystal structure determination for the closely related {[(CH$_3$)$_3$Si]$_2$AlP(C$_6$H$_{11}$)(H)}$_3$ described below, it is proposed that the more intense resonance may be assigned to an E, E, A isomer, while the small resonance may be ascribed to an E, E, E isomer.

^{1}H and ^{13}C{^{1}H} NMR spectra support the structural conclusion deduced from the ^{31}P{^{1}H} spectra. The proton NMR spectra provided a four-line pattern, δ 0.34, 0.24, 0.21, and 0.15, in an area ratio of 2:1:1:2. Further, the ^{13}C{^{1}H} NMR spectrum showed four resonances, δ 3.1, 2.8, 2.5, and 2.2 in a 1:2:2:1 ratio. These resonances are assigned to the four different trimethylsilyl group environments on the aluminum atoms in an E, E, A isomer. Only one of the expected two proton resonances, δ 0.12, was found for the E, E, E isomer. In addition, two weak doublets, δ 4.48 and 4.68, in an area ratio of 2:1, were resolved that correspond to the two different P–H environments in an E, E, A isomer. The P–H resonance for the E, E, E isomer was not confidently identified. Although the spectroscopic data are not unambiguous, they

strongly point to the trimeric cyclohexane-like structure for {[(CH$_3$)$_3$Si]$_2$AlP(C$_6$H$_5$)(H)}$_3$ with a preponderance of E, E, A isomer. Suitable single crystals for X-ray analysis were not obtained.

During the course of the above studies, samples of {[(CH$_3$)$_3$Si]$_2$AlP(C$_6$H$_5$)(H)]}$_3$ were refluxed for 24 h in cyclohexane in an effort to form larger rings or clusters. About 50% of the trimer decomposed in this time period with the formation of C$_6$H$_5$PH$_2$ and [(CH$_3$)$_3$Si][(C$_6$H$_5$)PH. The course of the decomposition to give these two phosphines is not understood at this time, but the interesting silyl migration from aluminum to phosphorus may have some synthetic utility.

The combination of [(CH$_3$)$_3$Si]$_3$Al·O(C$_2$H$_5$)$_2$ and a second primary phosphine, (c-C$_6$H$_{11}$)PH$_2$, in several stoichiometric ratios revealed very complex reaction pathways which have been only partially elucidated. Reagents were mixed in 2:1, 1:1, and 0.5:1 ratios at –78 °C and the mixtures warmed to 25 °C. Samples for NMR analysis were taken after 2 h and after 1 week. At the early stage of the reactions, the 1:1 and 2:1 ratios showed the presence of a compound which was assumed to be the adduct [(CH$_3$)$_3$Si]$_3$Al·P(c-Hex)(H)$_2$, δ –77.4 (J_{PH} = 311 Hz), on the basis of the large P–H coupling constant.[45] These data can be compared to the parameters for the free ligand, δ –122.8 (J_{PH} = 187 Hz). The 2:1 reactant ratio also showed a resonance which could be assigned to a silylation reaction adduct, [(CH$_3$)$_3$Si]$_3$Al·P(c-C$_6$H$_{11}$)(H)[Si(CH$_3$)$_3$] (6), δ –96.4 (J_{PH} = 310 Hz). Upon standing, ^{31}P NMR spectra for 1:1 and 0.5:1 reactant mixtures indicated the formation of a new product shown to be {[(CH$_3$)$_3$Si]$_2$AlP(c-C$_6$H$_{11}$)(H)}$_3$ (5). The 2:1 reactant ratio produced another final product with a ^{31}P resonance at δ –116.6 (J_{PH} = 270 Hz), which was not identified. On the basis of the results of this chemistry, it was clear that (c-C$_6$H$_{11}$)PH$_2$ was inclined toward elimination chemistry since elevated temperatures were not required to affect the reaction. Attempts to isolate and fully characterize the adduct were also frustrated by the elimination chemistry.

The 1:1 and 0.5:1 reactant ratios were studied in greater detail in an effort to obtain good yields of the elimination product. Typically, the 1:1 reaction mixture, when refluxed in pentane, gave a solid product which, when redissolved, showed five to seven different resonances in the ^{31}P{^{1}H} NMR spectrum from δ –95 to δ –130. Attempts to purify this solid by recrystallization were unsuccessful. The best reactant system for obtaining significant yields of 5 was the 0.5:1 combination. The mixture was stirred at 25 °C for only 4 h and then cooled in the refrigerator. The resulting crystallized product was collected and washed with cold pentane. A mass spectrum did not show a parent ion for the trimeric species, but several ions expected for a trimer were detected. The NMR spectra for 5 were complicated, suggesting that more than one isomer was present in solution. For example, the ^{31}P{^{1}H} spectrum showed resonances at δ –120.9, –121.7, –122.2, and –123.0 in ratios 1:5:5:2. The ^{13}C{^{1}H} and ^{1}H NMR spectra were sufficiently complex to be of little help in elucidating the structures of the isomeric products. A single crystal of an E, E, A isomer, however, was obtained from pentane solution, and the molecular structure determination is described below.

The silylation reaction adduct [(CH$_3$)$_3$Si]$_3$Al·P(c-C$_6$H$_{11}$)(H)[(CH$_3$)$_3$Si] (6) mentioned above was prepared independently from the phosphine [(CH$_3$)$_3$Si](c-C$_6$H$_{11}$)P-

(44) Burg, A. B. *Inorg. Chem.* **1978**, *17*, 593. Sens, M. A.; Odom, J. D.; Goodrow, M. H. *Inorg. Chem.* **1976**, *15*, 2825. Goodrow, M. H.; Wagner, R. I. *Inorg. Chem.* **1976**, *15*, 2830. Hamilton, W. C. *Acta Crystallogr.* **1955**, *8*, 199. Burg, A. B.; Wagner, R. I. *J. Am. Chem. Soc.* **1953**, *75*, 3872.

(45) The ^{31}P resonance for the adduct is highly dependent upon the concentration of phosphine in solution, and it appears that the adduct undergoes rapid exchange with excess phosphine.
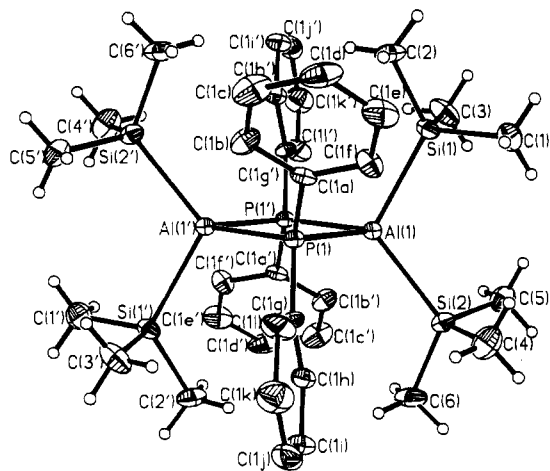
Figure 2. Molecular structure and atom labeling scheme for {[(CH₃)₃Si]₂AlP(C₆H₅)₂}₂ (3) (20% thermal ellipsoids).
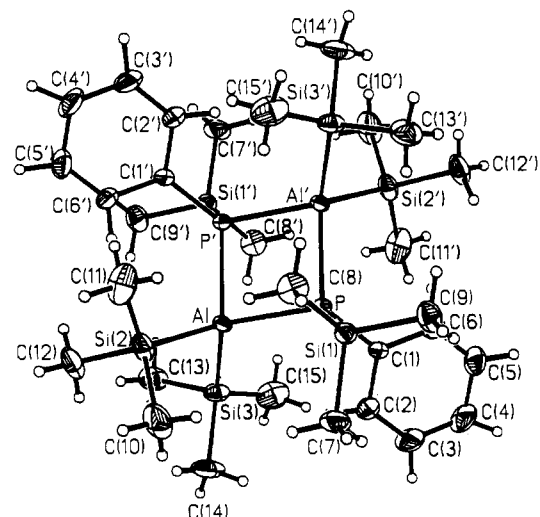
Table VII. Average Bond Distances (Å) and Angles (deg) for Phosphinoalanes

	3	4	5
	A. Distances		
Al–P	2.446 (4)	2.466 (2)	2.444 (4)
	2.458 (4)	2.467 (2)	
Al–Si	2.475 (5)	2.489 (3)	2.475 (4)
		2.482 (3)	
Al···Al	3.573	3.567	
P···P	3.360	3.407	
P–C$_{phenyl}$	1.824 (6)	1.818 (6)	
P–Si		2.272 (2)	
P–C$_{c-Hex}$			1.841 (16)
	B. Angles		
Al–P–Al′	93.5 (1)	92.6 (1)	127.8 (1)
P–Al–P′	86.5 (1)	87.4 (1)	99.6 (1)
Si–Al–Si′	112.3 (2)	109.7 (1)	112.2 (1)
C–P–C′	102.6 (3)		
Si–P–C		97.6	

(H) and [(CH₃)₃Si]₃Al·O(C₂H₅)₂. The adduct displayed the same ³¹P NMR parameters as listed above, and these can be compared to the data for the free ligand, δ –126.2 (J$_{PH}$ = 188 Hz). It is important to note that solutions of the adduct, in the presence of excess phosphine, showed ³¹P NMR resonances for both species, suggesting that base exchange is slow. Further, the complex did not eliminate (CH₃)SiH when refluxed in hexane or benzene. Prolonged reflux in toluene slowly produced an insoluble polymeric compound. Similarly, combination of {[(CH₃)₃Si]₂N}(C₆-H₅)PH with [(CH₃)₃Si]₃Al·O(C₂H₅)₂ in hexane led to the formation of an adduct which displayed a doublet in the ³¹P NMR spectrum, δ 10.9 (J$_{PH}$ = 335 Hz). In the presence of excess phosphine, resonances for both the adduct and free phosphine, δ 9.7 (J$_P$ = 211 Hz), appeared in the ³¹P NMR spectrum. Like 6, this adduct is stable toward (CH₃)₃SiH elimination when refluxed in cyclohexane or heated as a neat oil to 100 °C. Reflux in toluene for 24 h produced apparent decomposition of the adduct to free phosphine and [(CH₃)₃Si]₃Al degradation products. In agreement with Beachley's observations, the behavior of the last two compounds suggests that stable adducts represent a dead end for elimination chemistry which could lead to formation of cyclic phosphinoalane compounds.

B. Structures of Molecular Phosphinoalanes. The molecular structures of {[(CH₃)₃Si]₂AlP(C₆H₅)₂}₂ (3), {[(C-H₃)₃Si]₂AlP(C₆H₅)[(CH₃)₃Si]}₂ (4), and {[(CH₃)₃Si]₂AlP(c-C₆H₁₁)(H)}₃ (5) have been determined by single-crystal X-ray diffraction techniques, and views of the molecules are shown in Figures 2–5. Selected bond distances and
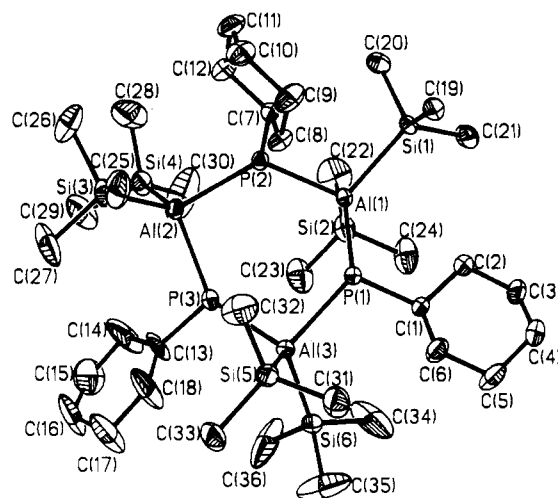

Figure 3. Molecular structure and atom labeling scheme for {[(CH₃)₃Si]₂AlP(C₆H₅)[Si(CH₃)₃]}₂ (4) (20% thermal ellipsoids).

Figure 4. Molecular structure and atom labeling scheme for {[(CH₃)₃Si]₂AlP(H)(c-C₆H₁₁)}₃ (5) (20% thermal ellipsoids).
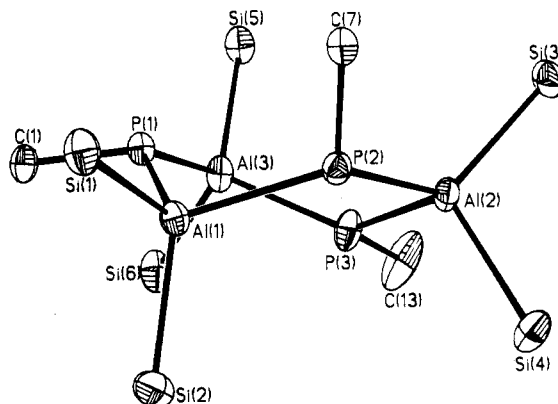
Figure 5. View of the conformation of the ring core for {[(CH₃)₃Si]₂AlP(H)(c-C₆H₁₁)}₃.

angles are summarized in Table VII. The molecular structures of 3 and 4 are very similar, and they confirm the dimeric formulations for these compounds. They display C$_i$ symmetry with planar Al₂P₂ rings. It is important to note that 3 has four unique molecules per asymmetric unit, and all four rings show dissimilar Al–P distances. The ring in 3 is more rhombic with average distances for the unequal sides being 2.446 Å (range 2.440 (4)–2.453 (4) Å) and 2.459 Å (range 2.450 (4)–2.463 (4) Å).

The ring in 4 has equivalent sides, 2.466 (2) and 2.467 (2) Å. These distances can be compared with the distances in six-membered ring compounds [(CH$_3$)$_2$AlP(CH$_3$)$_2$]$_3$, 2.434 (4) Å,[46] [(CH$_3$)$_2$AlCH$_2$P(CH$_3$)$_2$]$_2$, 2.451 (2) Å,[47] and [(CH$_3$)$_2$AlNP(C$_6$H$_5$)$_2$]$_2$, 2.526 (3) and 2.543 (3) Å.[48] The longer bond distance found in the adduct (CH$_3$)$_3$Al·P(C-H$_2$)$_3$, 2.53 (4) Å,[49] and in [(CH$_3$)$_2$AlNP(C$_6$H$_5$)$_2$]$_2$ may indicate a higher degree of dative bonding in these Al–P interactions. The average Al–Si bond distances in 3 and 4 are comparable with the distances in {[(CH$_3$)$_3$Si]$_2$AlNH$_2$}$_2$, Al–Si = 2.478 (1) and 2.467 (1) Å,[50] {[(CH$_3$)$_3$Si]$_2$Al}$_2$·[(C-H$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)$_2$], 2.472 (3) Å, and [(CH$_3$)$_3$Si]$_3$Al·O(C$_2$H$_5$)$_2$, 2.47 Å.[51] The bond angles in 3 and 4 would be anticipated to mirror the steric and electronic effects of the substituent groups. For example, on the basis of cone angle arguments, it might be assumed that steric congestion at phosphorus is slightly greater in 4 than in 3. Indeed, the Al–P–Al' angle in 4 is slightly smaller than in 3 as expected, but the Si–P–C angle of 97.6° is smaller than the C–P–C angle of 102.6°. Interestingly, the comparable angles in the aminoalane {[(CH$_3$)$_3$Si]$_2$AlNH$_2$}$_2$[50] are intermediate between those of 3 and 4: Al–N–Al' = 93.1° and N–Al–N' = 86.9°.

The structure determination for 5 reveals that this compound is trimeric with a six-membered skew-boat Al$_3$P$_3$ ring geometry. The ring conformation is depicted in Figure 5. The internal ring angles vary considerably: range Al–P–Al 124.4 (1)–132.8 (1)°; range P–Al–P 98.3 (1)–100.5 (1)°. The Al–P–Al angles span the value of the Al–P–Al angle reported for [(CH$_3$)$_2$AlP(CH$_3$)$_2$]$_3$, 131.7 (8)°;[47] however, the P–Al–P angle in that molecule, 96.4 (7)°, is smaller than the smallest of the angles in 5. Whether this results from steric/electronic effects in the molecular species or crystal packing forces in 5 or from the assumption of the gas phase idealized C_{3v} geometry for [(CH$_3$)$_2$AlP(CH$_3$)$_2$]$_3$[47] is not clear. The cyclohexyl substituent groups occupy E, E, A positions on the skew-boat Al$_3$P$_3$ ring, and it is assumed that this arrangement minimizes the steric interactions of the c-C$_6$H$_{11}$ rings (chair conformation) with the (CH$_3$)$_3$Si groups on the aluminum atoms. The average Al–P distance, 2.444 Å (range 2.433 (4)–2.454 (4) Å), and Al–Si distance, 2.475 Å (range 2.455 (3)–2.483 (3) Å), are similar to those observed for 3 and 4.

The solid-state structural data for 3 and 4 are consistent with the solution-state structures deduced from the spectroscopic data. It is often proposed that main-group ring sizes depend, in part, on substituent group size and that four-membered rings are favored over six-membered rings when the substituent groups are large. These assumptions seem sound with 3 and 4. Compound 5 exists with a six-membered ring structure, and this apparently results from the presence of the very small proton substituent group. It is more ambiguous to draw conclusions with respect to the solution-state structure of 5. It would be expected that if the E, E, A isomer found in the solid

state also dominates in solution, then the ^{31}P NMR should display two peaks with similar chemical shifts in a 2:1 area ratio. Unfortunately, the spectra showed four resonances in the region δ –120.9 to –123.0 and each displayed P–H coupling. This observation suggests that several isomers are formed.

C. Formation of Aluminum Phosphide. Reactions of [(CH$_3$)$_3$Si]$_3$Al·O(C$_2$H$_5$)$_2$ and PH$_3$ were examined in order to determine if this system might provide a pyrolysis precursor for AlP. This proposal was plausible since the related system with NH$_3$ gave AlN. Combination of the reagents in a 1:1 ratio in hexane at 25 °C for 5 days left a mixture of an oil and solid. Attempts to purify this mixture and isolate pure intermediate products were unsuccessful. A reaction with a 1:3 ratio was also examined in a similar fashion, and this produced an insoluble polymeric solid which could not be characterized. The pyrolysis of the polymeric solid was studied in stages: 320, 600, and 900 °C. The final solid product, obtained in about 50% ceramic yield, was a shiny blue-black solid. This material was characterized by powder X-ray diffraction. The pattern showed sharp reflections 2θ = 3.10 (111), 1.98 (210), and 1.63 (311) which are closely comparable to the 2θ values for cubic AlP with a = 5.45 Å.[18,52] Several additional weak, diffuse lines at 2θ ~ 2.69, 1.41, and 0.84 likely correspond to α-SiC. An X-ray elemental analysis further showed the presence of Al and Si in about a 4:1 ratio.

In conclusion, it has been found that the reactions of [(CH$_3$)$_3$Si]$_3$Al·O(C$_2$H$_5$)$_2$ with chlorophosphines do not lead to phosphinoalanes; however, reactions with secondary and primary phosphines do provide a route to form four- and six-membered (AlP)$_n$ ring compounds. Further, reactions with PH$_3$ produce a preceramic polymer which has been pyrolyzed to form mixtures of AlP and SiC. Additional studies of the reactions of phosphines and silylalanes are in progress as well as chemical vapor deposition studies of the PH$_3$ system.

Supplementary Material Available: Details of structure refinements and tables of anisotropic thermal parameters, hydrogen atom positional parameters, and full listings of bond distances and angles (34 pages); listings of observed and calculated structure factors (95 pages). Ordering information is given on any current masthead page.

(46) Haaland, A.; Haugen, J.; Volden, H. V.; Hanika, G.; Karsch, H. H. *J. Organomet. Chem.* **1987**, *322*, C24.

(47) Karsch, H. H.; Appelt, A.; Köhler, F. H.; Müller, G. *Organometallics* **1985**, *4*, 231.

(48) Schmidbaur, H.; Lauteschlager, S.; Milewski-Mohrla, B. *Chem. Ber.* **1983**, *116*, 1403.

(49) Almenningen, A.; Fernholt, L.; Hoaland, A.; Weidlein, J. *J. Organomet. Chem.* **1978**, *145*, 109.

(50) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1987**, *26*, 4341.

(51) Goebel, D. W.; Hencher, J. L.; Oliver, J. P. *Organometallics* **1983**, *2*, 746.

(52) Wang, C. C.; Spinar, L. H. *J. Phys. Chem. Solids* **1963**, *24*, 953. Addamiano, A. *J. Am. Chem. Soc.* **1960**, *82*, 1537.