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exhibiting an $a(^{93}\mathrm{Nb})$ value of ca. 103–106 G. These data agree with those of the intermediate species observed by method A and were thus attributed to 4. Like methods A and B, this route did not lead to isolable 4.

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Supplementary Material Available: Listings of bond lengths, bond angles, temperature factors, and derived hydrogen coordinates for 7 and 5 and a table giving a comparison of atom coordinates for 7 and 8 (10 pages). Ordering information is given on any current masthead page.

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"Genuine Heterocycles" from the Acid-Induced Cyclization of (Silylamino)(imino)(chalcogeno)phosphoranes and as a Result of Chloride Ion Abstraction from Bis[bis(trimethylsilyl)amino]thiophosphoryl Chloride

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The thio and seleno derivatives of the tricoordinate phosphorane $\mathrm{P[N^tBu(SiMe_3)](N^tBu)E}$ 1 (E = S, Se) undergo a novel cyclization upon reaction with Lewis acids. A number of derivatives of the $\overline{\mathrm{NSiEP}}$ framework have been isolated and characterized, including X-ray crystal structures of three derivatives, the neutral complexes $\mathrm{\overline{N^tBuSiMe_2SP}(Me)N^tBu{\cdot}AlCl_3}$ (**2a**) and $\mathrm{\overline{N^tBuSiMe_2SeP}(Me)N^tBu{\cdot}GaCl_3}$ (**3**), and the triflate salt of the protonated complex $\mathrm{[\overline{N^tBuSiMe_2SP}(Me)N^tBu{\cdot}H^+]}$ (**2c**). The new compounds are rare examples of ring systems which contain only one atom of each element in the heterocyclic framework, systems for which we introduce the terminology "genuine heterocycles". A similar cyclization process is observed for the new thiophosphoryl chloride $\mathrm{P[N(SiMe_3)_2]_2(S)Cl}$ (**4**) in the presence of chloride ion acceptors to give salts of the cation $\mathrm{[\overline{N(SiMe_3)SiMe_2SP}(Me)N(SiMe_3)_2]^+}$ (**5**), a direct analog of genuine heterocycles **2**. Two salts of **5** have been structurally characterized. Both cyclization reactions have been examined by variable-temperature ^{31}P and ^{1}H NMR spectroscopy, and speculations are made as to the nature of the observed intermediates. The $\mathrm{\overline{NSiSP}(N)}$ genuine heterocyclic unit is shown to be thermodynamically unstable with respect to the isomeric $\mathrm{\overline{NSiNP}(S)}$ 1,3-diazasilaphosphetidine framework **6**. The isomerization process is initiated by reaction with a base and can also be promoted thermally for salts of **5**.

Introduction

We have recently introduced the term "genuine heterocycles"[1] to describe ring systems which contain only one atom of each element in the cyclic skeleton and to distinguish them from multielement heterocycles which are derivatives of a homocyclic, or heterocatenate form.[2–5] Considering the 12 elements most commonly observed in cyclic environments (B, C, N, O, Al, Si, P, S, Ga, Ge, As, Se), one can envisage as many as 220 different three-membered *genuine heterocycles* and 1485 possible four-membered systems.[6] Interestingly, fewer than 40 examples of genuine heterocyclic frameworks (containing these elements) have been isolated and spectroscopically identified,[7–11] and only 10 examples have been characterized by X-ray crystallography.[10–12] Most recently, the first example of a five-membered genuine heterocycle con-

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(1) Preliminary communication: Burford, N.; Spence, R. E. v. H; Whalen, J. M.; Rogers, R. D.; Richardson, J. F. *Organometallics* **1990**, *9*, 2854.

(2) See, for example: Gilchrist, T. L. *Heterocyclic Chemistry*; Pitman Publishing: London, 1985. Katritzky, A. R. *Handbook of Heterocyclic Chemistry*; Pergamon Press: Oxford, U.K., 1985.

(3) See, for example: Haiduc, I.; Sowerby, D. B. *The Chemistry of Inorganic Homo- and Heterocycles*; Academic Press: New York, 1987; Vol. 1 and 2.

(4) See also, for example: Woollins, J. D. *Non-Metal Rings, Cages and Clusters*; Wiley: Chichester, U.K., 1988. Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 449. Power, P. P. *J. Organomet. Chem.* **1990**, *400*, 49. Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1209.

(5) See, for example: *Rings, Clusters, and Polymers of Main Group and Transition Elements*; Roesky, H. W., Ed.; Elsevier: Amsterdam, 1989.

(6) $n!/2m(n-m)!$, where n is the number of different elements (12) and m is the number of atoms in the ring (3 or 4).

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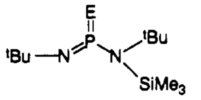
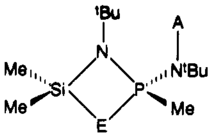
taining lithium and chlorine was reported.[13]

Here we illustrate the versatility of the acid-induced cyclization of (silylamino)(imino)(chalcogeno)phosphoranes 1, with the synthesis and isolation of the first examples of NiSiSP ($2a^1$–c) and NSiSeP (3) genuine heterocycles. The generality of the cyclization reaction is demonstrated by formation of the same heterocyclic framework from an alternative starting material, bis[bis(trimethylsilyl)-amino]thiophosphoryl chloride (4), in the form of the cation 5. The cyclization process is examined by variable-temperature ^{31}P and ^1H NMR spectroscopy in some detail. In addition, the new heterocyclic frameworks are found to be thermodynamically unstable with respect to the more familiar 1,3-diazaphosphetidine (6).



1 a: E = S

b: E = Se

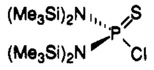


2 (E = S) a: A = $AlCl_3$,

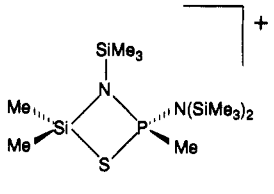
b: A = $GaCl_3$

c: A = H^+

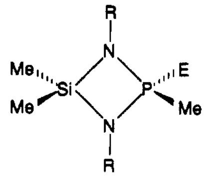
3 (E = Se, A = $GaCl_3$)



4



5



6 R = tBu, SiMe3

E = S, Se

Experimental Section

General Procedures. 1,1,1,3,3,3-Hexamethyldisilazane, thiophosphoryl chloride, *n*-butyllithium (1.6 M hexane solution), tri-*n*-butylphosphine oxide and triphenylphosphine oxide were obtained commercially (Aldrich) and used without purification. Trifluoromethanesulfonic acid (Aldrich) was distilled, and aluminum chloride and gallium chloride (Aldrich) were sublimed under vacuum before use. *tert*-Butyltrimethylsilylamine,[14] [(trimethylsilyl)(*tert*-butyl)amino](*tert*-butylimino)(thio)-phosphorane,[15] and -(seleno)phosphorane[16] were prepared by literature procedures. Methylene chloride and hexane were dried over P_2O_5 and CaH_2 and stored in evacuated bulbs. Anhydrous ether (99%) was obtained from Aldrich and used without further purification. Deuteriochloroform was dried over P_2O_5. Solids were manipulated in a Vacuum/Atmospheres nitrogen-filled glovebox. Glass equipment was flame dried before use. Reactions were performed in an evacuated (10^{-3} Torr) dual-compartment vessel,[17] unless otherwise indicated. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Gottingen, Germany. IR spectra were recorded as Nujol mulls on CsI plates using a Perkin-Elmer 283B spectrophotometer. NMR spectra were recorded on a Nicolet NT-360 spectrometer in 5- or 10-mm flame-sealed Pyrex tubes. Chemical shifts are reported in ppm relative to external 85% H_3PO_4 for $^{31}P\{^1H\}$ and relative to the internal solvent signal for ^1H and ^{13}C. The NMR data are presented in Table I.

Isolation of $N^tBuSiMe_2SP(Me)N^tBu{\cdot}AlCl_3$ (2a). A solution of $P[N^tBu(SiMe_3)](N^tBu)S$ (1a; 1.47 g, 5.28 mmol) in CH_2Cl_2 (26 g) was added to $AlCl_3$ (0.70 g, 5.3 mmol). The $AlCl_3$ dissolved within minutes to give a clear solution. Slow solvent removal under vacuum resulted in the precipitation of a white crystalline solid. The supernatant liquid was decanted, and the solid was washed by local cooling back-distillation and was characterized as 2,2-dimethyl-3-*tert*-butyl-4-methyl-4-(*tert*-butylimino)-*cyclo*-thiasilazaphosphetidine–trichloroaluminum complex, $C_{11}H_{27}$Al-

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Table I. ^1H, ^{13}C, and ^{31}P NMR Data[a]

		^{13}C			^1H		
compd	^{31}P	N^tBu[b]	$SiMe_2$	PMe	N^tBu[b]	$SiMe_2$	PMe
2a	49	60.7, 32.5 (7)	5.5	31.6 (83)	1.80	0.78	2.87 (14)
		58.5, 31.8 (6)	5.3		1.45	0.77	
2b	49	*e*			1.76	0.82	2.83 (14)
					1.45	0.79	
2c[c]	45	59.1, 31.7	5.5	24.3 (82)	1.43	0.84	2.30 (15)
		56.2, 38.6	5.4		1.39	0.82	
3	34[f]	61.4 (7), 32.1 (7)	6.5	31.6 (76)	1.80	0.80	2.86 (14)
		60.6 (6), 31.9 (6)	6.0		1.45	0.77	

		^{13}C				^1H			
compd	^{31}P	$NSiMe_3$	$N(SiMe_3)_2$	$SiMe_2$	PMe	$NSiMe_3$	$N(SiMe_3)_2$	$SiMe_2$	PMe
5[d]	56	1.7	5.3	6.0	31.2 (80)	0.39	0.56	0.91	2.57 (13)
				5.7				0.94	
6·$GaCl_3$	74	1.1		4.2	29.1 (72)	0.3		0.68	2.40 (14)
				4.0				0.56	

[a] Chemical shifts in ppm, coupling constants, in parentheses, in hertz. [b] Not possible to conclusively assign ^{13}C and ^1H signals to the two types of ^tBu. [c] H-N^tBu: ^1H, 6.02 (18); $CF_3SO_3^-$: ^{13}C, 120.3 ($^1J_{CF}$ = 320 Hz). [d] $AlCl_4^-$ and $GaCl_4^-$ salts give identical data. [e] Not recorded. [f] $^1J_{PSe}$ = 319.

Cl_3N_2PSSi. Yield: 0.95 g, 2.3 mmol, 44%. Mp: 174–176 °C. Anal. Calcd: C, 32.08; H, 6.61; N, 6.80; S, 7.79; Cl, 25.83; P, 7.52; Al, 6.55. Found: C, 32.29; H, 6.62; N, 6.81; S, 7.80; Cl, 25.76; P, 7.46; Al, 6.65. IR: 1260 m, 1225 w, 1190 m, 1170 w, 1070 s, 1045 m, 995 s, 935 m, 905 m, 880 m, 845 m, 820 w, 805 m, 775 m, 685 m, 585 m, 570 w, 525 w, 480 s, 430 m, 410 s cm^{-1}.

Isolation of $[\overline{N^tBuSiMe_2SP}(Me)N^tBu{\cdot}H]$ (2c) (SO_3CF_3). A suspension of triflic acid (0.94 g, 6.3 mmol) in CH_2Cl_2 (6 g) was added over a 5-min period to a solution of $P[N^tBu(SiMe_3)](N^tBu)S$ (**1a**; 1.69 g, 6.07 mmol) in CH_2Cl_2 (14 g). After shaking for 10 min, hexane (5 mL) was introduced and the solvent was slowly removed from the mixed-solvent system under vacuum. A white solid precipitated and was recrystallized from the warm residual solvent to give block-shaped white crystals of 2,2-dimethyl-3-*tert*-butyl-4-methyl-4-(*tert*-butylamino)-*cyclo*-thiasilazaphosphetidinium triflate, $C_{12}H_{28}F_3N_2O_3PS_2Si$. Yield 0.41 g, 0.95 mmol, 16%. Mp: 130 °C. An additional 1.26 g of crystalline material was obtained from the residual reaction mixture for a total yield of 1.67 g, 63%. Anal. Calcd: C, 33.63; H, 6.59; N, 6.54; P, 7.23; S, 14.96. Found: C, 33.91; H, 6.57; N, 6.59; P, 7.00; S, 14.99. IR: 3170 s, 1250 br, 1155, 1095, 1055, 1025, 940, 925, 910, 880 w, 850 m, 800 s, 770 w, 760 w, 685 m, 630 s, 590 w, 570 w, 515 s, 485 w, 445 m, 415 m cm^{-1}.

Isolation of $\overline{N^tBuSiMe_2SeP}(Me)N^tBu{\cdot}GaCl_3$ (3). A solution of $P[N^tBu(SiMe_3)](N^tBu)Se$ (**1b**; 0.69 g, 2.1 mmol) in CH_2Cl_2 (23 g) was added to a solution of $GaCl_3$ (0.35 g, 2.1 mmol; CH_2Cl_2, 16 g). A small amount of hexane (3 g) was introduced, and slow evaporation under vacuum gave a colorless crystalline solid which was washed by local cooling back-distillation and was characterized as 2,2-dimethyl-3-*tert*-butyl-4-methyl-4-(*tert*-butylimino)-*cyclo*-selenasilazaphosphetidine–trichlorogallium complex, $C_{11}H_{27}Cl_3GaN_2PSeSi$. Yield: 0.17 g, 0.34 mmol, 16%. Mp: 178–180 °C. Anal. Calcd: C, 26.35; H, 5.43; N, 5.49. Found: C, 26.23; H, 5.32; N, 5.65. IR: 1305 m, 1265 m, 1090 m, 1175 m, 1075 m, 1065 s, 1030 m, 1000 m, 940 m, 910 m, 765 m, 685 m, 575 m, 500 m, 370 s, 350 s cm^{-1}.

NMR Studies of Reactions of $P[N^tBu(SiMe_3)](N^tBu)S$. (a) Equimolar reaction mixtures of **1a** with $AlCl_3$, $GaCl_3$, or HSO_3CF_3 and **1b** with $GaCl_3$ were prepared in a manner similar to those described above and examined by ^1H and ^{31}P NMR spectroscopy, which showed the complexes **2a–c** and **3** as the principal components (>90%) in each case.

(b) Reaction mixtures were prepared in NMR tubes by adding solutions of **1a** or **1b** to the acid at −196 °C and were then monitored by ^{31}P and ^1H NMR spectroscopy between −90 and +20 °C. The starting material **1a** (^{31}P NMR: 142 ppm)[15] was observed as the only species in solution at −90 °C in all cases (^{31}P NMR for **1b**: 118 ppm).[16]

A = $AlCl_3$. ^{31}P signals at 177 and 53 ppm were observed prior to the signal corresponding to **2a** (49 ppm). The ^1H NMR spectrum of the reaction mixture showing three components, the starting material, the product, and the intermediate (^{31}P NMR: 53 ppm), is presented in Figure 5 and illustrates the presence of P–Me substitution in the intermediate: δ 0.91 ($SiMe_2$), 0.95 ($SiMe_2$), 1.40 (^tBu), 1.74 (^tBu), 2.54 ppm ($^2J_{PH}$ = 14 Hz). Below 0 °C an additional small signal is observed at 0.6 ppm ($SiMe_3$).

A = $GaCl_3$. A single intermediate was observed in the ^{31}P NMR spectra at 61 ppm from **1a** (49 ppm from **1b**) prior to the signal corresponding to **2b** (49 ppm) (**3**, 34 ppm). ^1H NMR spectrum of the intermediate responsible for the signal at 61 ppm: δ 0.82 ($SiMe_2$), 0.95 ($SiMe_2$), 1.30 (^tBu), 1.67 (^tBu), 2.50 ppm ($^2J_{PH}$ = 14 Hz).

A = H^+ (SO_3CF_3). Several (>10) signals were observed by ^{31}P NMR spectroscopy during the reaction prior to the formation of **2c** (SO_3CF_3) (45 ppm).

Isolation of $P[N(SiMe_3)_2]_2(S)Cl$ (4).[18] ^nBuLi (1.6 M, 78 mL, 125 mmol) was added dropwise to a stirred solution of $(Me_3Si)_2NH$ (20 g, 124 mmol) in Et_2O (100 mL), and the mixture was set to reflux for 30 min. After cooling to −10 °C, a solution of $PSCl_3$ (10.5 g, 61.9 mmol) in Et_2O (50 mL) was added rapidly, dropwise. The solution was stirred overnight and filtered through Celite, and the volatiles were then removed under vacuum. Vacuum distillation (short path, bath temperature 120–160 °C) of the resulting orange oil gave a colorless clear liquid, which was characterized as bis[bis(trimethylsilyl)amino]thiophosphoryl chloride, $C_{12}H_{36}ClN_2PSSi_4$. Yield: 10.31 g, 24.6 mmol, 40%. Bp: 90–96 °C (<1 mmHg). Anal. Calcd: C, 34.40; H, 8.59; N, 6.68; S, 7.65. Found: C, 35.26; H, 8.81; N, 6.74; S, 7.35. (N.B. This compound is thermally unstable.) IR (neat liquid): 1255 s, 925 s, 900 s, br, 760 s, 685 s, 645 m, 620 m, 490 m, 435 s, 375 w, 365 m, 320 w, 270 m cm^{-1}. ^{13}C NMR: 3.8, 2.7 ppm; ^1H NMR: 0.35 (doublet, 18 H, $^4J_{HP}$ = 15 Hz), 0.23 ppm (18 H). ^{31}P NMR: 205 ppm. Mass spectrum: *m/e* 418 (3%, $M^{\cdot+}$), 226 (100%, $[N(SiMe_3)_2]PCl^{\cdot+}$), 118 (26%, $N(SiMe_3)P^{\cdot+}$).

Isolation of $[\overline{N(SiMe_3)SiMe_2SP}(Me)N(SiMe_3)_2]$ (5) (MCl_4) (M = Al, Ga). A solution of $P[(N(SiMe_3)_2]_2(S)Cl$ (4) (M = Al, 1.43 g, 3.41 mmol; M = Ga, 1.57 g, 3.75 mmol) in CH_2Cl_2 (M = Al, 38 g; E = Ga, 11 g) was added to solid MCl_3 (M = Al, 0.46 g, 3.4 mmol; M = Ga, 0.66 g, 3.8 mmol). Immediate reaction gave an intense purple solution which became pale yellow/orange on stirring overnight. Some of the solvent was removed under vacuum and hexane (3 mL) was introduced. Clear block-shaped crystals were obtained on cooling to −10 °C and were characterized as 2,2-dimethyl-3-(trimethylsilyl)-4-methylbis[(trimethylsilyl)-amino]-*cyclo*-thiasilazaphosphetidinium tetrachloroaluminate (-gallate). **Aluminate complex**, $C_{12}H_{36}AlCl_4N_2PSSi_4$. Yield: 0.37 g, 0.68 mmol, 20%. Mp: 129 °C. Anal. Calcd: C, 25.71; H, 6.65; N, 5.42; P, 5.89; S, 6.05. Found: C, 26.10; H, 6.52; N, 5.07; P, 5.61; S, 5.81. IR: 1275 m, 1260 s, 1025 s, 995 s, 920 m, 895 m, 840 s, 795 s, 690 w, 675 w, 640 w, 630 w, 560 m, 480 s, 400 m, 360 w cm^{-1}. **Gallate complex**, $C_{12}H_{36}GaCl_4N_2PSSi_4$. Yield: 0.88 g,

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[18] A modification of a procedure described by: Kling, L., III; Colburn, C. B.; Hill, W. E. *J. Inorg. Nucl. Chem., Suppl.* **1976**, 5.

1.48 mmol, 39%. Chemical analysis not obtained. Mp: 130 °C. IR: 1275 m, 1260 s, 1025 s, 995 s, 920 m, 900 m, 840 s, 795 s, 690 w, 675 w, 645 w, 635 w, 560 m, 460 m, 410 m, 375 s, 360 w cm^{-1}.

Isolation of $N(SiMe_3)SiMe_2N(SiMe_3)P(Me)S{\cdot}GaCl_3$ (6·$GaCl_3$). A solution of $GaCl_3$ (0.45 g, 2.5 mmol) in CH_2Cl_2 (21 g) was added dropwise over 3–5 h to a stirred solution of $P[N(SiMe_3)_2]_2(S)Cl$ (4; 1.06 g, 2.53 mmol) in CH_2Cl_2 (4 g). The reaction mixture was then heated to 80 °C for 30 h to give an orange solution. A portion (21 g) of the solvent was removed, and hexane (2 g) was added. Large clear crystals were obtained on cooling to −10 °C and were characterized as 1,3-bis(trimethylsilyl)-2,2-dimethyl-4-thiodiazasilaphosphetidine-*S*-trichlorogallium, $C_9H_{27}Cl_3GaN_2PSSi_3$. Yield: 0.27 g, 0.54 mmol, 21%. Mp: 147–148 °C. Anal. Calcd: C, 22.21; H, 5.59; N, 5.76. Found: C, 21.19; H, 5.27; N, 5.77. IR: 1300 m, 1260 s, 1125 m, 1035 s, 915 w, 890 w, 840 s, 805 w, 760 w, 690 w, 635 m, 565 s, 460 s, 425 m, 380 s, 360 s, 325 m cm^{-1}.

NMR Studies of Reaction Mixtures of $P[N(SiMe_3)_2]_2(S)Cl$ (4). (a) Solutions of 4 were added at different rates to equimolar quantities of MCl_3 (M = Al, Ga), and the reaction mixtures consistently showed ^{31}P NMR signals at 56 (compound 5) and 74 ppm (compound 6·MCl_3) with an integration ratio of approximately 4:1, respectively. The corresponding compounds have been isolated as described above. Similar spectra were obtained with up to 3 times excess MCl_3.

(b) Equimolar reaction mixtures were prepared in NMR tubes by adding solutions of 4 to $GaCl_3$ at −196 °C and were then monitored by ^{31}P and ^1H NMR spectroscopy between −90 and +20 °C. The starting material 4 was observed at 205 ppm at −90 °C by ^{31}P NMR together with a signal at 206 ppm. Three further intermediate signals were observed in order at 73, 61, and 177 ppm before observation of the signals corresponding to the product. A variable-temperature ^1H NMR study of the reaction mixture shows two integral equivalent signals for each of the initially formed intermediates of similar chemical shift (0.1–0.7 ppm), and then at −30 °C the spectrum contains a single signal at 0.6 ppm only (all signals are assigned to $SiMe_3$). There is no evidence of P–Me substitution until the signals for the products appear.

NMR Studies of the Isomerism of 2 and 5. (a) Solutions of **2a** or 3 in CH_2Cl_2 were added to solutions of R_3PO (R = Ph or ^{n}Bu) in an NMR tube at −196 °C, and the reaction mixtures were monitored between −90 and 20 °C by ^{31}P NMR spectroscopy. In addition to the signals expected for $(Ph_3PO)_nAlCl_3$ or $(^nBu_3PO)_nAlCl_3$,[19] a signal was observed at 74 ppm and is assigned to the phosphetidine 6. A signal at −7 ppm was observed prior to the formation of the product.

(b) Solutions of $[N(SiMe_3)SiMe_2SP(Me)N(SiMe_3)_2]^+$ (5) ($AlCl_4^-$ and $GaCl_4^-$) in CH_2Cl_2 warmed to 80 °C for 1 week exhibited ^{31}P NMR signals at 74 ppm (>90%), assigned to $N(SiMe_3)SiMe_2N(SiMe_3)P(Me)S{\cdot}MCl_3$ (6·MCl_3) and 72 ppm, tentatively assigned to the corresponding salts of $N(SiMe_3)SiMe_2N(SiMe_3)P(Me)[SCH_2Cl]^+$.[20]

(c) Solutions of $[N(SiMe_3)SiMe_2SP(Me)N(SiMe_3)_2]$ (5) (MCl_4) (M = Al, Ga) were prepared in situ (as described above) and the solutions added to equimolar solutions of Ph_3PO (CH_2Cl_2). Signals were observed in the ^{31}P NMR spectrum for $Ph_3PO{\cdot}AlCl_3$), $N(SiMe_3)SiMe_2N(SiMe_3)P(Me)S$ (6) (R = $SiMe_3$, E = S) (74 ppm), as well as an unknown signal at 60 ppm (relative intensity, 5%).

X-ray Data Collection, Solution, and Refinement. Suitable crystals of **2a**, **2c** (SO_3CF_3), 3, 5 ($AlCl_4$),[21] 5 ($GaCl_4$), and 6·$GaCl_3$ were obtained as described in the text and mounted in thin-walled Pyrex capillaries under N_2. Enraf-Nonius CAD-4 diffractometers (Mo Kα, λ = 0.7093 Å, graphite monochromator) were used to determine the cell dimensions and to collect the data. Unit cell parameters were obtained from the setting angles of 25 accurately centered reflections. The unit cells and space groups were confirmed by the program TRACER[22] and the successful solution and refinement of the structures. The presence of two molecules in the asymmetric unit for **2c**$^+$(SO_3CF_3) was also verified by photographic study, significant differences in torsion angles in the ^{t}BuN groups, and the difference in disorder patterns for the triflate anions. All pertinent crystallographic data are summarized in Table II. Data were collected at room temperature using an $\omega/2\theta$ technique (width 0.80 + 0.35 tan θ). The stability of the crystals were monitored every 60 min using three standard reflections; no significant decay was observed. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied based on a series of ψ scans or the program DIFABS.[23] Scattering factors[24] were corrected for anomalous dispersion.[25]

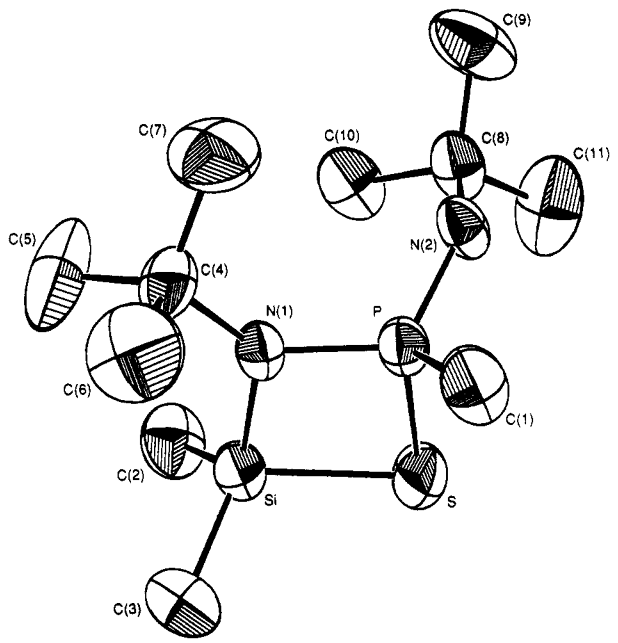

Figure 1. Crystallographic view of the cationic unit of **2c** (SO_3CF_3).

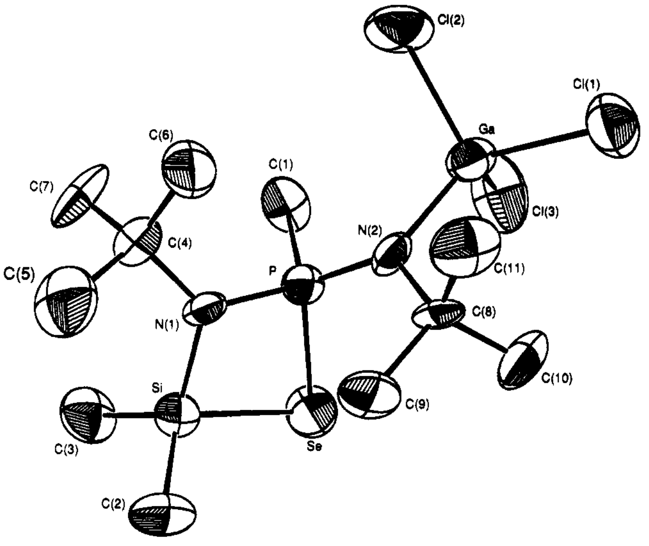

Figure 2. Crystallographic view of 3.

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(19) Burford, N.; Royan, B. W.; Spence, R. E. v. H.; Cameron, T. S.; Linden, A.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1990**, 1521. Burford, N.; Mason, S., unpublished results.

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(21) The structure of the $AlCl_4^-$ salt is disordered, but the features are essentially identical to those of the $GaCl_4^-$ salt.

(22) Lawson, S. L.; Jacobsen, R. A. Ames Laboratory Report IS-1141. USABC, Iowa State University: Ames, IA, 1965.

(23) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

(24) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B. (Present distributor: Kluwer Academic Publishers, Dordrecht and Boston.)

Table II. Crystal Data Collection[a] and Refinement Parameters

	2a	**2c** (SO_3CF_3)	**3**	**5** ($GaCl_4$)	**6**·$GaCl_3$
formula	$C_{11}H_{27}AlCl_3N_2PSSi$	$C_{12}H_{28}F_3N_2O_3PS_2Si$	$C_{11}H_{27}Cl_3GaN_2SeSi$	$C_{12}H_{36}Cl_4GaN_2PSSi_4$	$C_9H_{27}Cl_3GaN_2PSSi_3$
MW	411.82	428.55	501.45	595.35	486.70
space group	$P2_12_12_1$	$P\bar{1}$	$Pna2_1$	$P2_12_12_1$	$P2_1/n$
a, Å	10.640 (2)	13.206 (3)	15.535 (3)	8.703 (3)	10.980 (1)
b, Å	11.843 (3)	13.211 (3)	8.284 (2)	17.271 (4)	17.744 (2)
c, Å	16.217 (4)	12.662 (3)	16.432 (3)	19.645 (4)	12.170 (2)
α, deg	90	99.04 (2)	90	90	90
β, deg	90	91.18 (2)	90	90	101.24 (2)
γ, deg	90	80.54 (2)	90	90	90
V, Å^3	2043.5	2152.1	2114.7	2952.8	2325.5
D_{calcd}, g cm^{-3}	1.34	1.32	1.57	1.34	1.39
μ_{calcd}, cm^{-1}	7.2	4.0	35.1	15.8	18.27
max 2θ, deg	50	47	50	50	50
F(000)	864	904	1008	1232	1451
crystal size, mm	0.25 × 0.43 × 0.50	0.24 × 0.31 × 0.32	0.32 × 0.44 × 0.54	0.28 × 0.33 × 0.45	0.40 × 0.55 × 0.55
octants colltd	$-h,-k,-l$	$\pm h,\pm k,+l$	$-h,-k,-l$	h,k,l	$\pm h,k,-l$
no. of obsd reflns	1642	3977	1484	2091	3039
no. of variables	181	483	181	226	182
abs corrc	DIFABS	ψ scans	DIFABS	ψ scans	DIFABS
min/max abs	0.83/1.08	0.97/1.00	0.49/1.34	0.95/1.00	0.73/1.40
GOF	1.11	1.07	1.11	1.17	1.07
R_f	0.037	0.065	0.044	0.065	0.037
R_w	0.038	0.067	0.036	0.043	0.038

[a] $Z = 4$; temp 22 (1) °C; Mo Kα (λ = 0.709 30 Å) with graphite monochromator.

Table III. Positional and Isotropic Thermal Parameters for 2a

atom	x	y	z	B, Å^2
Cl(1)	−0.1431 (2)	−0.0164 (2)	0.29803 (9)	5.29 (4)
Cl(2)	−0.2440 (2)	0.1346 (2)	0.1219 (1)	5.84 (4)
Cl(3)	−0.2909 (2)	−0.1479 (1)	0.1452 (1)	5.84 (4)
S	0.1504 (2)	0.1715 (1)	0.03026 (9)	3.84 (3)
P	0.1061 (1)	0.0696 (1)	0.13019 (8)	2.63 (2)
Si	0.3335 (2)	0.1284 (1)	0.07973 (8)	3.22 (3)
Al	−0.1578 (2)	−0.0161 (1)	0.1670 (1)	3.33 (3)
N(1)	0.2549 (4)	0.0380 (3)	0.1489 (2)	2.78 (8)
N(2)	0.0029 (4)	−0.0286 (3)	0.1163 (2)	2.69 (8)
C(1)	0.0492 (5)	0.1655 (5)	0.2077 (3)	4.0 (1)
C(2)	0.4388 (6)	0.0582 (6)	0.0057 (4)	4.7 (1)
C(3)	0.4072 (6)	0.2547 (5)	0.1252 (4)	4.6 (1)
C(4)	0.3092 (5)	−0.0326 (5)	0.2179 (3)	4.0 (1)
C(5)	0.3480 (9)	−0.1470 (6)	0.1839 (4)	7.7 (2)
C(6)	0.4272 (7)	0.0271 (7)	0.2492 (4)	7.1 (2)
C(7)	0.2181 (7)	−0.0460 (8)	0.2877 (4)	8.2 (2)
C(8)	0.0170 (6)	−0.1158 (5)	0.0447 (3)	3.6 (1)
C(9)	−0.0827 (7)	−0.0904 (6)	−0.0188 (3)	5.5 (2)
C(10)	0.1459 (6)	−0.1118 (5)	0.0021 (3)	4.7 (1)
C(11)	0.0010 (6)	−0.2333 (5)	0.0821 (4)	4.7 (1)

Structures were solved using direct methods[26] to find the heavier elements, and the remaining non-hydrogen atoms were located from a series of difference Fourier maps.[27] H atoms were included in ideal positions as fixed contributions (C–H = 0.95 Å, B_{iso} = 1.3B of the bonded atom) to the structure factors. The final choices of enantiomers for **2a**, **3**, and **5** ($GaCl_4$) were based on slightly lower R factors (0.037 vs 0.038, 0.037 vs 0.043, and 0.052 vs 0.053, respectively). The models were refined using full-matrix least-squares techniques based on F, minimizing the function $\sum w(||F_o| - |F_c||)^2$, where the weight was defined as $w = [\sigma(F)^2 + (p_{wt}F)^2 + q_{wt}]^{-1}$ in all structures (p_{wt} and q_{wt} are listed in the supplementary material).[28] Atomic positional parameters are given in Tables III–VII, and selected bond distances and angles are provided in Table VIII. Representative ORTEP[29] views for the structures of **2c** (SO_3CF_3), **3**, **5** ($GaCl_4$), and **6**·$GaCl_3$ are given in Figures 1–4, respectively. A view of **2a** has been previously reported.[1]

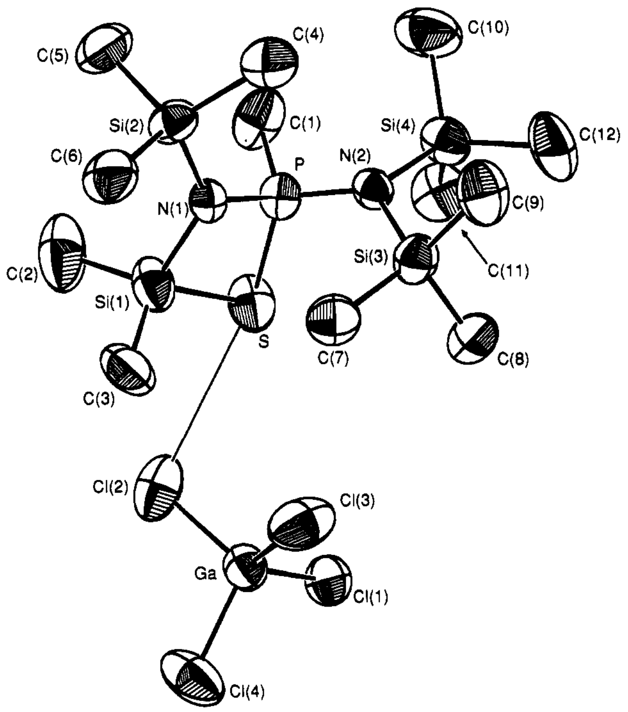

Figure 3. Crystallographic view of **5** ($GaCl_4$).

Results and Discussion

The chemistry of tricoordinate phosphorane derivatives is proving to be diverse.[30] For instance, coordination to a metal center can involve both σ^3 and π complexation.[31]

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[25] Cromer, D. T. in ref 24, Tables 2.3.1.

[26] MULTAN: A computer program for the automatic solution of crystal structures from X-ray data. Main, P; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J.-P.; Woolfson, M. M. University of York, York, England, 1982.

[27] All computations were performed using SDP/VAX: Frenz, B. A. The Enraf-Nonius CAD 4 SDP—A Real-time System for Concurrent X-ray Data Collection and Crystal Structure Determination. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C. Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

[28] Killean, R. C. G.; Lawrence, J. L. *Acta Crystallogr.* **1973**, *B25*, 1750.

[29] Johnson, C. K. *Oak Ridge Natl. Lab.*, [*Rep.*] *ORNL* (*U.S.*) **1965**, ORNL-3794.

[30] For a review, see: Germa, H.; Navech, J. *Phosphorus Sulfur* **1986**, *26*, 327.

[31] Scherer, O. J.; Jungmann, H.; Kruger, C.; Wolmershauser, G. *Chem. Ber.* **1984**, *117*, 2382.

Table IV. Positional and Isotropic Thermal Parameters for 2c (SO_3CF_3)[a]

atom	*x*	*y*	*z*	*B*, Å^2
SA	0.7829 (2)	0.0278 (2)	0.9904 (2)	5.36 (5)
PA	0.7567 (1)	0.1847 (1)	0.9896 (1)	3.40 (4)
SiA	0.8008 (2)	0.0892 (2)	1.1572 (2)	4.07 (4)
N(1)A	0.6530 (4)	0.2322 (4)	0.9339 (4)	3.7 (1)
N(2)A	0.7646 (4)	0.2139 (4)	1.1201 (4)	3.2 (1)
C(1)A	0.8558 (5)	0.2201 (7)	0.9171 (6)	5.3 (2)
C(2)A	0.5429 (5)	0.2205 (6)	0.9452 (5)	4.4 (2)
C(3)A	0.4815 (6)	0.3227 (7)	0.9234 (7)	7.2 (2)
C(4)A	0.5203 (5)	0.2017 (6)	1.0566 (6)	5.5 (2)
C(5)A	0.5213 (6)	0.1303 (8)	0.8630 (7)	8.0 (3)
C(6)A	0.7680 (5)	0.3194 (5)	1.1860 (5)	4.2 (2)
C(7)A	0.7269 (9)	0.3156 (7)	1.2972 (7)	8.7 (3)
C(8)A	0.8778 (7)	0.3410 (7)	1.1931 (8)	7.8 (3)
C(9)A	0.6991 (7)	0.4048 (6)	1.1371 (8)	7.3 (3)
C(10)A	0.7109 (7)	0.0503 (6)	1.2457 (6)	5.8 (2)
C(11)A	0.9359 (6)	0.0613 (7)	1.1987 (7)	6.6 (2)
SB	0.4569 (1)	0.2333 (2)	0.3686 (2)	5.03 (5)
PB	0.3041 (1)	0.2554 (1)	0.3285 (1)	3.73 (4)
SiB	0.3823 (2)	0.2398 (2)	0.5204 (2)	4.09 (5)
N(1)B	0.2636 (4)	0.3501 (4)	0.2647 (4)	4.2 (1)
N(2)B	0.2662 (4)	0.2655 (4)	0.4520 (4)	3.6 (1)
C(1)B	0.2756 (7)	0.1444 (5)	0.2407 (6)	5.3 (2)
C(2)B	0.2749 (6)	0.4622 (5)	0.2812 (6)	4.9 (2)
C(3)B	0.3571 (8)	0.4743 (7)	0.2065 (8)	8.7 (3)
C(4)B	0.1723 (8)	0.5230 (6)	0.2539 (8)	7.6 (3)
C(5)B	0.3039 (8)	0.4995 (6)	0.3963 (6)	6.8 (2)
C(6)B	0.1586 (5)	0.2743 (7)	0.4940 (7)	6.0 (2)
C(7)B	0.0827 (7)	0.294 (2)	0.4125 (9)	21.3 (7)
C(8)B	0.1393 (9)	0.358 (2)	0.578 (1)	21.4 (6)
C(9)B	0.151 (1)	0.185 (1)	0.542 (1)	17.9 (6)*
C(10)B	0.4065 (6)	0.1154 (6)	0.5692 (6)	6.0 (2)
C(11)B	0.4113 (7)	0.3476 (6)	0.6200 (6)	6.5 (2)

atom	*x*	*y*	*z*	*B*, Å^2	occup
S(1)	0.7081 (1)	0.1662 (2)	0.6178 (2)	4.58 (4)	1.0
C(1)	0.8381 (6)	0.1592 (7)	0.5722 (6)	5.8 (2)	1.0
F(1)*A*	0.8619 (4)	0.0891 (5)	0.4877 (4)	9.3 (2)	1.0
F(2)*A*	0.9049 (6)	0.1308 (8)	0.6462 (6)	9.0 (3)	0.6
F(3)*A*	0.8527 (5)	0.2469 (6)	0.5392 (6)	6.7 (2)	0.6
F(2)*B*	0.899 (1)	0.193 (1)	0.652 (2)	4.9 (4)*	0.2
F(3)*B*	0.810 (2)	0.257 (2)	0.517 (2)	9.2 (7)*	0.2
F(2)*C*	0.903 (2)	0.096 (2)	0.618 (2)	10.2 (8)*	0.2
F(3)*C*	0.879 (1)	0.234 (1)	0.589 (2)	4.8 (4)*	0.2
O(1)	0.6969 (4)	0.2477 (4)	0.7069 (4)	5.0 (1)	1.0
O(2)*A*	0.6488 (6)	0.2034 (6)	0.5263 (5)	6.2 (2)	0.7
O(3)*A*	0.6954 (6)	0.0668 (5)	0.6307 (7)	6.5 (2)	0.7
O(2)*B*	0.652 (2)	0.146 (2)	0.538 (2)	8.6 (6)*	0.3
O(3)*B*	0.742 (2)	0.076 (2)	0.682 (2)	7.4 (5)*	0.3
S(2)	0.1689 (2)	0.2449 (2)	−0.0330 (2)	6.38 (6)	1.0
C(2)	0.1076 (8)	0.3574 (7)	−0.0866 (8)	10.1 (3)	1.0
F(4)*A*	0.0371 (7)	0.3720 (7)	−0.1288 (8)	11.9 (3)	0.6
F(5)*A*	0.1913 (8)	0.3622 (8)	−0.1638 (7)	11.6 (3)	0.6
F(6)*A*	0.134 (1)	0.4475 (6)	−0.0270 (9)	13.1 (4)	0.6
F(4)*B*	0.044 (1)	0.316 (1)	−0.170 (1)	8.5 (3)*	0.4
F(5)*B*	0.041 (1)	0.398 (1)	0.003 (1)	10.8 (4)*	0.4
F(6)*B*	0.154 (1)	0.406 (1)	−0.101 (1)	12.4 (5)*	0.4
O(4)*A*	0.2431 (6)	0.2815 (7)	0.0391 (6)	6.0 (2)	0.6
O(5)*A*	0.0886 (7)	0.2067 (8)	0.010 (1)	13.3 (3)	0.6
O(6)*A*	0.222 (1)	0.188 (1)	−0.130 (1)	15.4 (4)	0.6
O(4)*B*	0.130 (1)	0.170 (1)	−0.093 (1)	5.8 (3)*	0.4
O(5)*B*	0.107 (2)	0.285 (2)	0.071 (2)	16.3 (9)*	0.4
O(6)*B*	0.257 (1)	0.236 (1)	0.004 (1)	9.5 (5)*	0.4

[a] The asterisk indicates that the atoms were refined isotropically.

Table V. Positional and Isotropic Thermal Parameters for 3

atom	*x*	*y*	*z*	*B*, Å^2
Se	0.26902 (6)	0.1892 (1)	0.501[a]	5.08 (2)
Ga	0.26221 (6)	0.0169 (1)	0.77073 (7)	3.79 (2)
Cl(1)	0.2337 (2)	0.1294 (3)	0.8873 (2)	6.25 (7)
Cl(2)	0.3315 (2)	−0.2013 (3)	0.8059 (2)	6.45 (7)
Cl(3)	0.1350 (2)	−0.0318 (5)	0.7218 (2)	8.09 (9)
P	0.3376 (1)	0.0560 (3)	0.5979 (1)	2.93 (4)
Si	0.4080 (2)	0.1581 (3)	0.4569 (2)	3.75 (5)
N(1)	0.4301 (4)	0.0623 (8)	0.5489 (4)	2.7 (1)
N(2)	0.3311 (4)	0.1258 (7)	0.6899 (4)	3.0 (1)
C(1)	0.2965 (6)	−0.149 (1)	0.5990 (6)	4.7 (2)
C(2)	0.4669 (7)	0.351 (1)	0.4380 (7)	6.1 (3)
C(3)	0.4134 (7)	0.030 (1)	0.3649 (6)	5.9 (3)
C(4)	0.5112 (5)	−0.033 (1)	0.5702 (6)	4.0 (2)
C(5)	0.5861 (6)	0.054 (1)	0.5317 (7)	5.9 (3)
C(6)	0.5245 (6)	−0.045 (1)	0.6592 (6)	6.0 (3)
C(7)	0.5043 (7)	−0.204 (1)	0.5328 (8)	6.6 (3)
C(8)	0.3538 (6)	0.3026 (9)	0.7116 (6)	3.7 (2)
C(9)	0.4094 (6)	0.387 (1)	0.6472 (7)	5.2 (2)
C(10)	0.2689 (7)	0.390 (1)	0.7186 (7)	5.7 (3)
C(11)	0.4055 (7)	0.302 (1)	0.7906 (6)	5.4 (2)

[a] Coordinate fixed to define the origin.

Table VI. Positional and Isotropic Thermal Parameters for 5 ($GaCl_4$)

atom	*x*	*y*	*z*	*B*, Å^2
Ga	0.2078 (1)	0.05909 (6)	0.35835 (5)	4.97 (2)
Cl(1)	0.3324 (3)	−0.0483 (1)	0.3416 (1)	6.54 (6)
Cl(2)	0.2735 (3)	0.1110 (2)	0.4545 (2)	7.64 (7)
Cl(3)	−0.0360 (3)	0.0366 (2)	0.3601 (1)	8.19 (8)
Cl(4)	0.2573 (4)	0.1384 (2)	0.2763 (2)	8.51 (8)
S	−0.0247 (2)	0.5038 (1)	0.9280 (1)	5.94 (6)
P	0.1640 (2)	0.4809 (1)	0.8680 (1)	3.95 (4)
Si(1)	0.0792 (3)	0.6170 (2)	0.9112 (2)	5.51 (6)
Si(2)	0.3927 (3)	0.6104 (1)	0.8278 (1)	4.17 (5)
Si(3)	0.3635 (3)	0.4138 (1)	0.9771 (1)	4.46 (5)
Si(4)	0.2446 (3)	0.3135 (1)	0.8582 (1)	4.98 (5)
N(1)	0.2351 (6)	0.5688 (3)	0.8728 (3)	3.4 (1)
N(2)	0.2689 (7)	0.4097 (3)	0.8941 (3)	3.6 (1)
C(1)	0.104 (1)	0.4640 (5)	0.7826 (5)	6.6 (2)
C(2)	−0.035 (1)	0.6757 (6)	0.8497 (7)	9.3 (4)
C(3)	0.117 (1)	0.6739 (5)	0.9866 (5)	7.6 (3)
C(4)	0.550 (1)	0.5374 (6)	0.8224 (5)	6.0 (2)
C(5)	0.329 (1)	0.6405 (6)	0.7421 (4)	6.2 (2)
C(6)	0.453 (1)	0.6956 (5)	0.8771 (5)	5.6 (2)
C(7)	0.362 (1)	0.5123 (5)	1.0146 (4)	5.4 (2)
C(8)	0.248 (1)	0.3547 (5)	1.0377 (5)	6.0 (2)
C(9)	0.570 (1)	0.3817 (6)	0.9653 (5)	6.1 (2)
C(10)	0.299 (2)	0.3081 (6)	0.7677 (5)	8.4 (3)
C(11)	0.042 (1)	0.2849 (5)	0.8694 (5)	6.7 (3)
C(12)	0.371 (1)	0.2419 (5)	0.9024 (6)	8.3 (3)

Table VII. Positional and Isotropic Thermal Parameters for 6•$GaCl_3$

atom	*x*	*y*	*z*	*B*, Å^2
Ga	0.43492 (4)	0.15010 (3)	0.77484 (4)	3.74 (1)
Cl(1)	0.3625 (1)	0.08114 (8)	0.6301 (1)	6.47 (3)
Cl(2)	0.2878 (1)	0.21184 (8)	0.8280 (1)	6.63 (3)
Cl(3)	0.5296 (2)	0.08278 (9)	0.9110 (1)	7.35 (4)
S	0.5674 (1)	0.22569 (7)	0.70219 (9)	4.25 (2)
P	0.63144 (9)	0.31035 (6)	0.80996 (8)	2.90 (2)
Si(1)	0.7115 (1)	0.42756 (7)	0.74607 (9)	3.44 (2)
Si(2)	0.9098 (1)	0.28992 (8)	0.7965 (1)	4.33 (3)
Si(3)	0.4235 (1)	0.43460 (7)	0.7712 91)	3.72 (2)
N(1)	0.7680 (3)	0.3371 (2)	0.7909 (3)	3.16 (7)
N(2)	0.5705 (3)	0.3935 (2)	0.7775 (3)	3.41 (7)
C(1)	0.6268 (4)	0.2833 (3)	0.9501 (3)	3.94 (9)
C(2)	0.7041 (5)	0.4435 (3)	0.5951 (4)	6.1 (1)
C(3)	0.7829 (4)	0.5057 (3)	0.8335 (4)	4.9 (1)
C(4)	0.9181 (5)	0.2102 (3)	0.8933 (5)	6.5 (1)
C(5)	0.9188 (6)	0.2550 (4)	0.6562 (5)	9.8 (2)
C(6)	1.0324 (5)	0.3595 (4)	0.8485 (8)	11.6 (3)
C(7)	0.4458 (5)	0.5354 (3)	0.7432 (5)	6.5 (1)
C(8)	0.3753 (4)	0.4202 (3)	0.9072 (4)	5.4 (1)
C(9)	0.3088 (5)	0.3931 (3)	0.6559 (4)	6.2 (1)

More structurally disruptive are the numerous cyclization processes that have been reported. Although individually unique, most involve an increase in the coordination number at phosphorus,[9,32-34] and some have been ration-

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(32) See, for example: Markovski, L. N.; Romanenko, V. D.; Ruban, A. V. *Pure Appl. Chem.* **1987**, *59*, 1047. Scherer, O. J.; Kulbach, N.-T.; Glassel, W. *Z. Naturforsch.* **1978**, *33B*, 652. Neicke, E.; Flick, W. *J. Organomet. Chem.* **1976**, *104*, C23.

(33) Scherer, O. J.; Kerth, J. *J. Organomet. Chem.* **1983**, *243*, C33. Scherer, O. J.; Kerth, J.; Anselmann, R. *Phosphorus Sulfur* **1983**, *18*, 271.

Table VIII. Selected Bond Lengths (Å) and Angles (deg)

	2a	2c (SO_3CF_3)[a]		3	5 ($GaCl_4$)	6·$GaCl_3$
P–N(1)	1.654 (4)	A	1.642 (5)	1.649 (6)	1.642 (6)	1.632 (3)
		B	1.631 (5)			
P–N(2)	1.615 (4)	A	1.608 (6)	1.622 (8)	1.615 (7)	1.637 (3)
		B	1.606 (6)			
P–C(1)	1.799 (6)	A	1.777 (8)	1.818 (9)	1.779 (9)	1.782 (4)
		B	1.783 (8)			
P–E	2.075 (2)	A	2.045 (3)	2.214 (2)	2.060 (3)	2.028 (1)
		B	2.056 (3)			
E–Si(1)	2.169 (3)	A	2.163 (3)	2.290 (3)	2.179 (3)	
		B	2.162 (3)			
Si(1)–N(1)	1.762 (4)	A	1.771 (5)	1.742 (7)	1.762 (7)	1.769 (3)
		B	1.756 (5)			
Si(1)–N(2)						1.771 (4)
A–N(2)	1.903 (4)			1.931 (7)		
Ga–S						2.280 (1)
P–E–Si(1)	77.71 (7)	A	77.71 (9)	73.57 (9)	75.8 (1)	
		B	77.7 (1)			
N(1)–P–N(2)						92.7 (2)
E–P–N(1)	93.4 (2)	A	94.0 (3)	93.0 (2)	95.1 (2)	
		B	93.2 (2)			
P–N(1)–Si(1)	101.6 (3)	A	101.4 (3)	105.4 (3)	99.9 (3)	91.7 (2)
		B	102.7 (3)			
P–N(2)–Si(1)						91.6 (2)
N(1)–Si(1)–N(2)						83.9 (2)
E–Si(1)–N(1)	87.2 (1)	A	86.5 (2)	88.0 (2)	87.8 (2)	
		B	86.2 (2)			
Ga–S–P						110.4 (2)

[a] Molecules A and B.

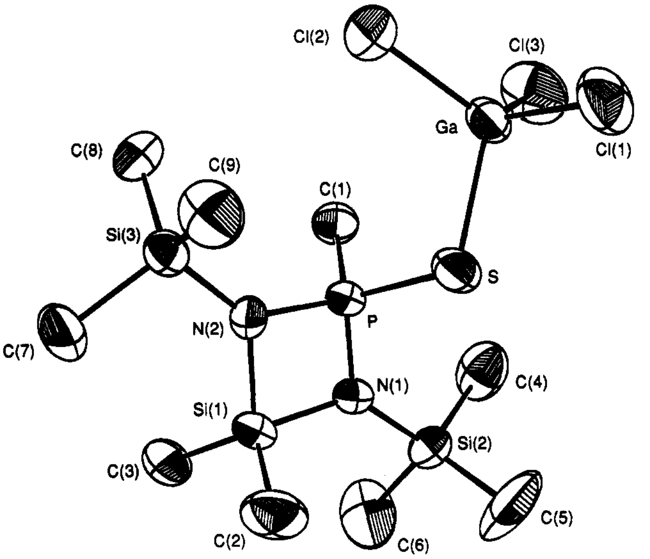

Figure 4. Crystallographic view of **6**·$GaCl_3$.

alized in terms of a cycloaddition intermediate.[34] The results presented here describe a new cyclization process in terms of the product and the proposed mechanism.

The thiophosphorane $P[N^tBu(SiMe_3)](N^tBu)S$ (**1a**) reacts with $AlCl_3$, $GaCl_3$, or H^+ ($SO_3CF_3^-$), to give *imino*-bound Lewis complexes of the form $\overline{N^tBuSiMe_2SP}$(Me)N^tBu·A **2** (A = $AlCl_3$ (**2a**), $GaCl_3$ (**2b**), or H^+ (**2c**)) in essentially quantitative yield. The compounds have been spectroscopically and crystallographically characterized and shown to contain the novel $\overline{\mathrm{NSiSP}}$ heterocycle, Figure 1. The selenium derivative **1b** behaves in an identical fashion, providing the first $\overline{\mathrm{NSiSeP}}$ heterocycle **3**, Figure 2. Formation of a tetracoordinate phosphorus center is consistent with previous reports on the chemistry of derivatives of **1**.[32,33] However, in the reactions described here, coordination expansion is the result of a 1,3 methyl migration from silicon to phosphorus and the cyclic products do not incorporate the activating reagent. In fact, induction of the cyclization process has some generality in that an identical heterocyclization occurs with both group 13 acids and a proton.

Another derivative of the $\overline{\mathrm{NSiSP}}$ heterocycle is also formed from reactions of the tetrasilyldiaminothiophosphoryl chloride $P[N(SiMe_3)_2]_2(S)Cl$ (**4**) with equimolar or excess MCl_3 (M = Al or Ga). These reactions are not quantitative (see below), but the principal components (80%) have been isolated and identified as the MCl_4^- (M = Al, Ga) salts of the cation $[\overline{N(SiMe_3)SiMe_2SP}(Me)N(SiMe_3)_2]^+$ (**5**), Figure 3 (**5** ($GaCl_4$)). Cation **5** is an isomer of the cation that would result from chloride ion abstraction from compound **4**.

The $\overline{\mathrm{NSiEP}}$ Heterocyclic Framework (E = S, Se).

Table VIII shows that bond lengths within the $\overline{\mathrm{NSiSP}}$ heterocyclic frameworks (**2a**, **2c**, and **5**) and around the phosphorus center are crystallographically indistinguishable despite differences in molecular charge. In this context **2a** is best viewed in terms of a zwitterionic model, possessing a phosphonium center and an aluminate center (a typical model for phosphorylic–Lewis acid complexes,[35] which is supported by the ^{31}P NMR chemical shifts of all derivatives of **2**, Table I). Compound **3** can be viewed in a similar manner.

The P–N(1), P–N(2), P–S, and P–Se bond lengths are shorter than the corresponding single bonds (cf. P–N, 1.77 Å;[36] P–S, 2.112 (1) Å;[37] P–Se, 2.24 Å[36]), indicating the presence of $d\pi$–$p\pi$ interaction throughout the EPN_2 moiety. The Si(1)–N(1) bond lengths are longer than

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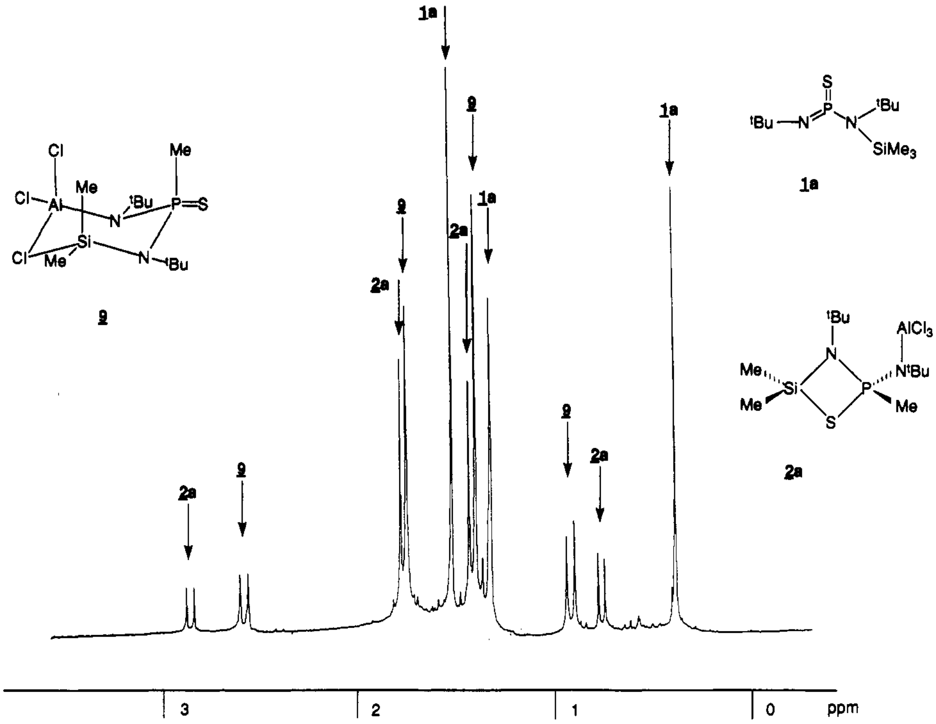
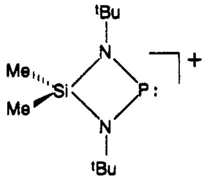


Figure 5. ^{1}H NMR spectrum of a reaction mixture containing P[N^{t}Bu(SiMe$_3$)](N^{t}Bu)S (**1a**) and AlCl$_3$ in CH$_2$Cl$_2$ at 0 °C, showing signals for **1a**, the product $\overline{\mathrm{N^tBuSiMe_2SP}}$(Me)N^{t}Bu·AlCl$_3$ (**2a**), and an intermediate **9** (^{31}P NMR: 53 ppm).

observed (1.72–1.73 Å)[3] for compounds in which a high degree of dπ–pπ bonding exists between the silicon and nitrogen atoms. A similar observation is made for the *cyclo*-1,3-diaza-2-sila-4-phosphenium cations **7**.[38] The



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S–Si(1) bond lengths are typical of those observed in silathianes (cf. 2.143 (3) Å in [MePhSiS]$_3$)[3] and are considered single.

The endocyclic bond angles are indistinguishable for the *tert*-butyl derivatives **2** and **3** and exhibit only minor differences from those of the cation **5**, presumably imposed by the differing steric requirements of the *tert*-butyl and trimethylsilyl groups. The heterocycles are only slightly distorted from planarity (fold angles NPE to NSiE: **2a**, 9.10°; **2c**, 6.36°, 5.41°; **3**, 2.87°; **5** (GaCl$_4$), 12.89°). Very narrow angles at sulfur and selenium are compensated by wide angles at the planar N(1).

The salt structures consist of discrete cations and anions, although in **5** (GaCl$_4$), the distance between the sulfur center of the cation and a chlorine atom Cl(2) of the tetrachlorogallate unit (3.666 (4) Å) is within the sum of the van der Waals radii (3.7 Å),[39] Figure 3. Interactions of this type are common for salts of nonmetal cations and are generally referred to as cation–anion contacts.[40] They have been interpreted as donations from the anion to the electrophilic centers of the cation;[41] however, their structural significance has not been fully evaluated. In contrast to **5** (GaCl$_4$), the triflate salt of **2c** exhibits no intermolecular interactions within 3.8 Å, and as the structural features of the heterocyclic unit are identical in these two compounds, it is tempting to conclude that the cation–anion contact has little effect. It is interesting to note that the neutral complex **2a** adopts a Cl(2)–S intermolecular contact of 3.552 (2) Å, which is significantly shorter than the cation–anion contact observed for **5** (GaCl$_4$) (3.666 (4) Å).

The ^{1}H and ^{13}C NMR spectra (Table I) are consistent with the solid-state structures, clearly indicating nonequivalence of the endocyclic silicon methyl groups, and methylation of the phosphorus center.

Cyclization of [(Trimethylsilyl)-*tert*-butylamino](*tert*-butylimino)(chalcogeno)phosphoranes. Cyclization of the Si–N–P–E unit of the tricoordinate phosphoranes **1** is evidently induced by coordination of the *imino* nitrogen center to the Lewis acid, which attains an exocyclic position in the product. 1,3 methyl migration from the silicon center to the phosphorus center, and the formation of a silicon–chalcogen bond, are the ultimate structural adjustments. Consequently, the process can be viewed as an isomerization of the imino-bound complex of **1**. Interestingly, coordination of the heterocycle to the acid via the imino nitrogen center is a stabilizing influence for the genuine heterocycles **2** and **3** (see below).

The course of each reaction of **1a** and **1b** has been monitored by variable-temperature ^{31}P and ^{1}H NMR spectroscopy. Reaction with HSO$_3$CF$_3$ is complex and involves a number of metastable intermediates. However, only two consecutive intermediates (^{31}P NMR: 177 and 53 ppm) are observed in the reaction with AlCl$_3$ and a single intermediate (^{31}P NMR: **1a**, 61 ppm; **1b**, 49 ppm)

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(40) See, for example: Cardinal, G.; Gillespie, R. J.; Sawyer, J. F.; Verkis, J. E. *J. Chem. Soc., Dalton Trans.* **1982**, 765. McMullan, R. K.; Prince, D. J.; Corbett, J. D. *Inorg. Chem.* **1971**, *10*, 1749. Couch, T. W.; Lokken, D. A.; Corbett, J. D. *Inorg. Chem.* **1971**, *10*, 2319. Burford, N.; Dipchand, A. I.; Royan, B. W.; White, P. S. *Inorg. Chem.* **1990**, *29*, 4938.

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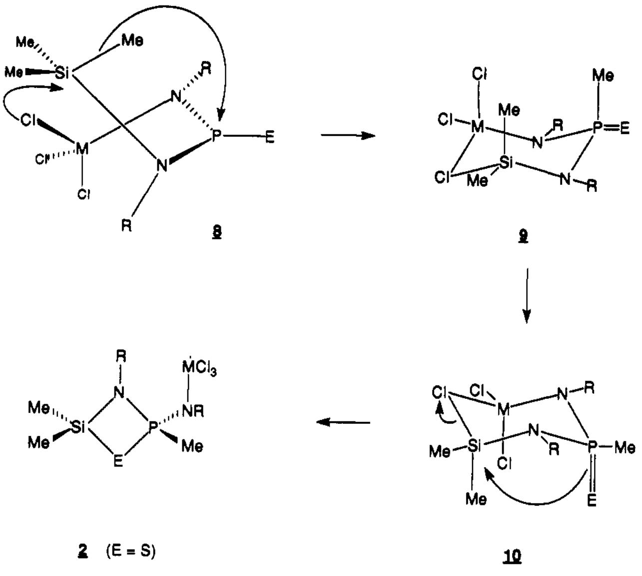
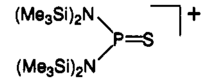
Scheme I. Proposed Intermediates for Reactions of 1 with MCl_3 (M = Al and Ga, E = S and Se, R = ^tBu)



is evident in the reactions with $GaCl_3$. ^1H NMR spectra for reactions of **1a** conclusively show that the 177 ppm resonance in the ^{31}P spectrum of the $AlCl_3$ reaction mixture contains a $SiMe_3$ group (0.56 ppm) and that the signals at 53 ppm for the reaction with $AlCl_3$ and 61 ppm for the reaction with $GaCl_3$ correspond to compounds possessing a methyl group at the phosphorus center. Moreover, these compounds (^{31}P NMR: 53 and 61 ppm) are analogous ($AlCl_3$ and $GaCl_3$ derivatives, respectively). A representative ^1H NMR spectrum of an $AlCl_3$ reaction mixture is shown in Figure 5 and contains signals for the starting material **1a**, the intermediate (^{31}P NMR: 53 ppm), and the product **2a**. On the basis of the spectroscopic data, we envisage (Scheme I) complexation of the imino nitrogen center to induce migration of a methyl group from silicon to phosphorus, and silicon–chlorine bond formation to give a six-membered heterocyclic intermediate **9**. The process can best be viewed in terms of an S_N2 displacement of the methyl group from silicon by the nucleophilic chlorine of MCl_3. As illustrated in Scheme I, the conformation most suited for this displacement renders the chalcogen and silicon centers remote. In addition, a chair conformation is most likely for the resulting six-membered ring **9** with the chalcogen forced into an equatorial position. A chair "ring-flip" brings the chalcogen into an axial position and in proximity for Si–E bond formation **10**, with consequential Si–Cl bond cleavage, and ultimate formation of the genuine heterocycle **2** (or **3**). The ^1H NMR signals observed for the intermediates (^{31}P NMR: 53 and 61 ppm) are consistent with the proposed six-membered heterocycle **9**, and the energy barrier (5–25 kJ mol^{-1})[42] associated with a ring-flip would account for their transient existence. The nature of species corresponding to the signal at 177 ppm is interpreted by comparison with reactions of **4** and is discussed in the next section.

Cyclization of Bis[bis(trimethylsilyl)amino]thiophosphoryl Chloride. In contrast to the reactions of **1**, four metastable intermediates are observed by variable-temperature ^{31}P NMR spectroscopy during the cyclization of **4**, and the process is further complicated by the existence of the minor (20%) coproduct **6**·MCl_3. The initial acid–base interaction likely produces a simple complex (assigned to the signal at 206 ppm, observed just downfield of the signal for the starting material **4**, 205 ppm), probably thio bound.[35] Subsequently, signals at 73, 60, and 177 ppm are observed prior to the signals at 56 and 74 ppm, which correspond to the products. It is tempting to correlate the proposed intermediate **9** (^{31}P NMR: $AlCl_3$, 53 ppm; $GaCl_3$, 61 ppm), formed from **1a**, with the transient signal observed at 60 ppm from **4**, especially in light of the common product. However, the intermediates formed from **4** show no sign of P–Me substitution (i.e., methyl migration is not observed until formation of the final products) in the ^1H NMR spectra. Two integral equivalent signals of similar chemical shift are observed for the first two intermediates, and a single signal is then observed as the only feature in the spectrum prior to the formation of the products. Few structures can be envisaged for the intermediates, but most obvious are **11** and **12** (E = S, R = $SiMe_3$).

The relationship between the intermediates observed at 177 ppm in the ^{31}P spectra in cyclizations of both **1a** and **4** prompts us to tentatively assign these signals to the corresponding tricoordinate phosphonium centers in **8** and **11**, respectively. The temperatures at which **11** and **8** are observed indicates a substantially greater stability for **11**, possibly due to an inability to adopt the six-membered cyclic structure **9** (no nucleophilic centers available for donation to silicon; cf. chlorine centers in **8**). On this basis, we assume that the absence of the corresponding signal (177 ppm) in the reaction of **1a** with $GaCl_3$ is a function of either the relative size of the acid or the greater nucleophilicity of the chlorine center of $GaCl_3$ with respect to that of $AlCl_3$.



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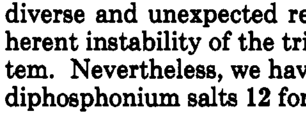
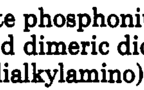
Authentic examples of tricoordinate phosphonium centers such as **8** and **11** are rare. The sterically protected methylenephosphonium cations **13** represent the only confirmed derivatives.[43] Our studies of potential routes to the corresponding *imino*[44] phosphonium salts have given diverse and unexpected results, consistent with the inherent instability of the tricoordinate phosphonium system. Nevertheless, we have observed dimeric dicationic diphosphonium salts **12** for the bis(dialkylamino)*thio*[20,45] and bis(dialkylamino)*seleno*[45] derivatives and consider





12 R = Me, Et, $SiMe_3$ **13** R = $^iPr_2N$, ^tBu

E = S, Se R'/R" = $SiMe_3$/$SiMe_3$, $SiMe_3$/H

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(42) Riddell, F. *Conformational Analysis of Heterocyclic Compounds*; Academic Press: London, 1980.

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(45) Burford, N.; Spence, R. E. v. H.; Rogers, R. D. *J. Am. Chem. Soc.* 1989, *111*, 5006.

such a structure (**12**; R = $SiMe_3$, E = S) as a viable candidate for one of the intermediate signals (60 ppm) in the cyclization of **4**. The signal at 73 ppm is as yet unassigned.

Isomerization or Rearrangement of the $\overline{\mathrm{NSiSP}}$ Heterocycle. Solution thermolyses of **5** (MCl_4) salts (M = Al or Ga) result in elimination of Me_3SiCl, heterocyclic isomerism, and coordination of MCl_3 (released from the anion) to the exocyclic sulfur center to give derivatives of **6**·MCl_3 (E = S, R = $SiMe_3$).[46] The thermodynamic preference for heterocycle **6** over the heterocyclic frameworks of **2**, **3**, and **5** is further demonstrated by the isomerism of the heterocyclic $\overline{\mathrm{NSiEP}}$(N) units of **2** and **3** in the presence of a base (R_3PO, R = Ph or ^{n}Bu). The reactions of derivatives of **2** are observed to proceed via a single metastable intermediate (^{31}P NMR: −7 ppm), which we speculate to be the free base of **2**. While derivatives of **2** are thermally stable (in contrast to salts of **5**), formation of heterocycle **6** (E = S, R = ^{t}Bu) is facilitated by cleavage of the coordinate bond, implying that the free base of **2** is stabilized by the presence of A ($AlCl_3$, $GaCl_3$, H^+, or $SiMe_3^+$). Consequently, we view the thermolytic release of Me_3SiCl from **5** (MCl_4) in terms of the Cl^- (base) abstracting $SiMe_3^+$.

Summary and Conclusion. Two types of reaction provide alternative high-yield routes to the first $\overline{\mathrm{NSiEP}}$ genuine heterocyclic systems. While a common pathway or mechanism is implied for the two heterocyclization processes, the metastable intermediates observed during the progress of the two reactions have very different spectroscopic, chemical, and structural features. It is possible that certain observed intermediates are not essential for the formation of the genuine heterocycle. For example, heterocycle **9**, formed from **1**, cannot be formed during the cyclization of **1a** with triflic acid, or during the cyclization of **4**. Nevertheless, the similarity of the 177 ppm signal in the low-temperature ^{31}P NMR spectra of both systems implies a related intermediate (assigned to **8** and **11**).

Acknowledgment. This work has been supported by grants from the Natural Sciences and Engineering Research Council of Canada (N.B.), the donors of the Petroleum Research Fund, administered by the American Chemical Society (N.B.), and Dalhousie University. We thank Dr. Don Hooper and the Atlantic Region Magnetic Resonance Centre and the Institute for Marine Biology for the use of NMR facilities, Mr. Dan Drummond and the University of New Brunswick Mass Spectroscopy facility, Dr. Peter Kusalik for helpful discussions, and Mr. Jürgen Müller for construction of custom glass apparatus.

Supplementary Material Available: Crystallographic data for **2a**, **3**, **2c** (SO_3CF_3), **5**, and **6**·$GaCl_3$ including tables of bond lengths, bond angles, positional parameters, and thermal parameters (25 pages). Ordering information is given on any current masthead page.

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(46) Compound **6**·$GaCl_3$ has been isolated and spectroscopically and crystallographically characterized, Figure 4. Selected bond lengths and angles are given in Table VIII. In general, the structural features are typical of a phosphetidine framework, and a standard coordinate linkage; see ref 35.