Syntheses and Crystal Structures for the First Two Examples of the Four-Membered PNSiS Heterocycle

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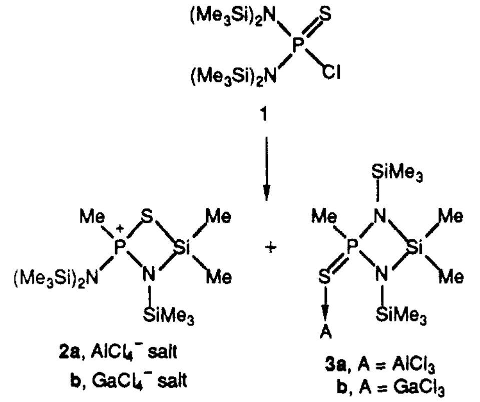
Summary: **The first two examples of PNSiS heterocycles are obtained by halide ion abstraction from $[(Me_3Si)_2N]_2P(S)Cl$ and by isomerization of $[(Me_3Si)^tBuN](^tBuN{=})P{=}S$ and are structurally characterized.**

Diverse and novel synthetic pathways are responsible for the now extensive series of stable nonmetal heterocycles.[1] However, examples of "genuine" heterocycles (that is, ring systems containing only one atom of each element) are rare. Here we report the syntheses and characterization data for the first two examples of the PNSiS four-membered heterocycle. An unexpected cyclization process is common for both phosphoryl and phosphorane precursors, illustrating important electronic relationships between the two systems.

Reaction of bis(bis(trimethylsilyl)amino)thiophosphoryl chloride (1)[2] with equimolar quantities of the Lewis acid $AlCl_3$ (3.41 mmol) or $GaCl_3$ (2.53 mmol) in CH_2Cl_2 proceeds rapidly at room temperature to give 4:1 mixtures of 2 and 3, respectively (^{31}P NMR spectroscopy). Compounds **2a** (20%) and **2b** (40%) were isolated as crystalline solids from the respective reaction mixtures. When solutions of 2 were heated (80 °C), loss of Me_3SiCl resulted in near-quantitative formation of compounds **3**. Spectroscopic characterization[3] and X-ray crystallographic analysis[4] of **2a**, **2b**,[5] and **3b** confirmed their structures. A view of the cation of **2b** is shown in Figure 1.



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2a, $AlCl_4^-$ salt
b, $GaCl_4^-$ salt

3a, A = $AlCl_3$
b, A = $GaCl_3$

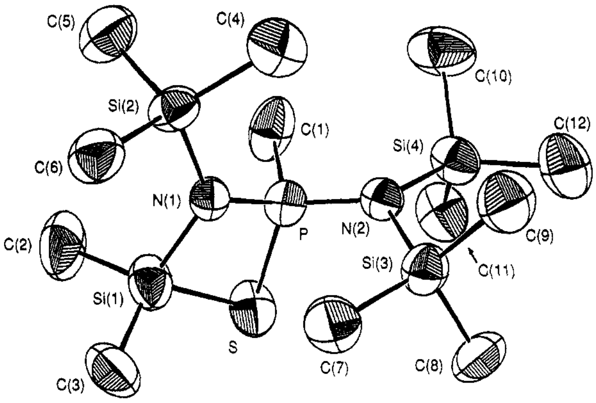

Figure 1. View of the cation of **2b**.

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

(2) Reaction of lithium bis(trimethylsilyl)amide (125 mmol) with thiophosphoryl chloride (61.9 mmol) in ether produced the new sterically crowded bis(bis(trimethylsilyl)amino)thiophosphoryl chloride (1; 51%), in a modification of the procedure described by: Kling, L., III; Colburn, C. B.; Hill, W. E. *J. Inorg. Nucl. Chem., Suppl.* **1976**, 5. Characterization data for compound 1: bp 120 °C at 1 mm; 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}; ^{31}P NMR (146 MHz, $CDCl_3$, 85% H_3PO_4 external) 204 ppm; ^1H NMR (360 MHz, $CDCl_3$) 0.35 (doublet, 18 H, $^4J_{HP}$ = 1.5 Hz), 0.23 ppm (18 H); ^{13}C NMR (91 MHz, $CDCl_3$) 3.8, 2.7 ppm (inequivalence of Me_3Si groups likely due to steric hindrance of rotation about P–N bonds). 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. Silicon-containing compounds can give difficulties with chemical analysis.)

(3) Characterization data for compound **2a**: mp 129 °C; IR (Nujol mull) 1275 (m), 1260 (s), 1025 (s), 995 (s), 920 (m), 895 (m), 840 (s), 795 (s), 690 (w), 674 (w), 640 (w), 630 (w), 560 (m), 480 (s), 400 (m), 360 (w) cm^{-1}; ^{31}P NMR (146 MHz, CH_2Cl_2, 85% H_3PO_4 external) 56 ppm; ^{27}Al NMR (94 MHz, CH_2Cl_2, $[Al(H_2O)_6]^{3+}$ external) 104 ppm ($AlCl_4^-$); ^1H NMR (360 MHz, $CDCl_3$) 2.57 (doublet, 3 H, $^2J_{HP}$ = 13.2 Hz), 0.92 (doublet, 6 H, $^4J_{HP}$ = 8.5 Hz), 0.56 (18 H), 0.39 ppm (9 H); ^{13}C NMR (91 MHz, $CDCl_3$) 31.2 (doublet, $^1J_{CP}$ = 80.3 Hz), 5.9, 5.3, 1.7 ppm. 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. Characterization data for compound **2b**: mp 130 °C; IR (Nujol mull) 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}; NMR data identical with those of **2a**, except for ^{71}Ga (110 MHz, $Ga(H_2O)_6^{3+}$ external) 249 ppm ($GaCl_4^-$). Characterization data for compound **3b**: mp 147–148 °C; IR (Nujol mull) 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}; ^{31}P NMR (146 MHz, 85% H_3PO_4) 75 ppm; ^{71}Ga NMR ($Ga(H_2O)_6^{3+}$ external) 260 (broad), 249 ppm (shoulder, $GaCl_4^-$): ^1H NMR (360 MHz, $CDCl_3$) 2.4 (doublet, 3 H, $^2J_{HP}$ = 13.8 Hz), 0.62 (doublet, 6 H, $^4J_{HP}$ = 40.5 Hz), 0.3 ppm (18 H); ^{13}C NMR (91 MHz, $CDCl_3$) 29.1 (doublet, $^1J_{CP}$ = 71.7 Hz), 4.1, 1.1. ppm. Anal. Calcd: C, 22.21; H, 5.59; N, 5.76. Found: C, 21.19; H, 5.27; N, 5.77.[2]

(4) The crystal structure of **2b** is reported here. The structure of compound **2a** is similar to that of **2b**. The heterocyclic diazaphosphasiletidine framework of compound **3b** has been previously observed for P(III) derivatives (Veith, M.; Bertsch, B.; Huch, V. *Z. Anorg. Allg. Chem.* **1988**, *559*, 73. Scherer, O. J.; Puttmann, M.; Kruger, C.; Wolmershauser, G. *Chem. Ber.* **1982**, *115*, 2076), and the structural details will be presented in a full paper.

(5) Crystal data for **2b**: $C_{12}H_{36}Cl_4GaSi_4N_2PS$, M_r = 595.35, orthorhombic, space group $P2_12_12_1$, a = 8.703 (3) Å, b = 17.271 (4) Å, c = 19.645 (4) Å, V = 2952.8 Å^3, Z = 4, D_c = 1.34 g cm^{-3}, μ = 15.8 cm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.709 30 Å). An absorption correction was applied with use of ψ scans, and the structure was solved by direct methods and refined by full-matrix least squares to residuals of R = 0.044 and R_w = 0.043 for 2091 observed reflections with $I > 3\sigma(I)$ and with 226 variables. All calculations were performed on a VAX computer using SDP/VAX: Frenz, B. A. The Enraf-Nonius CAD-4 SDP-A realtime 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.

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Table I. Selected Bond Lengths (Å) and Angles (deg) for the Cation of 2b and Compound 5

	2b	5
P-N(1)	1.642 (6)	1.654 (4)
P-N(2)	1.615 (7)	1.615 (4)
P-C(1)	1.779 (9)	1.799 (6)
P-S	2.060 (3)	2.075 (2)
N(1)-Si(1)	1.762 (7)	1.762 (4)
S-Si(1)	2.179 (3)	2.169 (2)
N(2)-Si(3)	1.828 (6)	1.903 (4)[a]
N(2)-Si(4)	1.817 (7)	
N(1)-P-N(2)	118.2 (4)	120.9 (3)
N(1)-P-S	95.1 (2)	93.4 (2)
N(2)-P-S	114.5 (2)	117.7 (2)
N(1)-P-C(1)	108.4 (4)	109.7 (2)
N(2)-P-C(1)	109.9 (4)	108.8 (2)
P-N(1)-Si(1)	99.9 (3)	101.6 (3)
N(1)-Si(1)-S	87.8 (2)	87.2 (1)
Si(1)-S-P	75.8 (1)	77.17 (7)

[a] N(2)-Al.

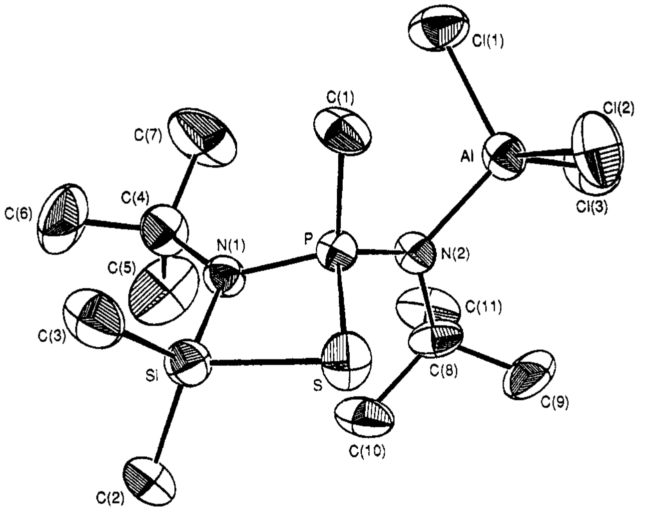
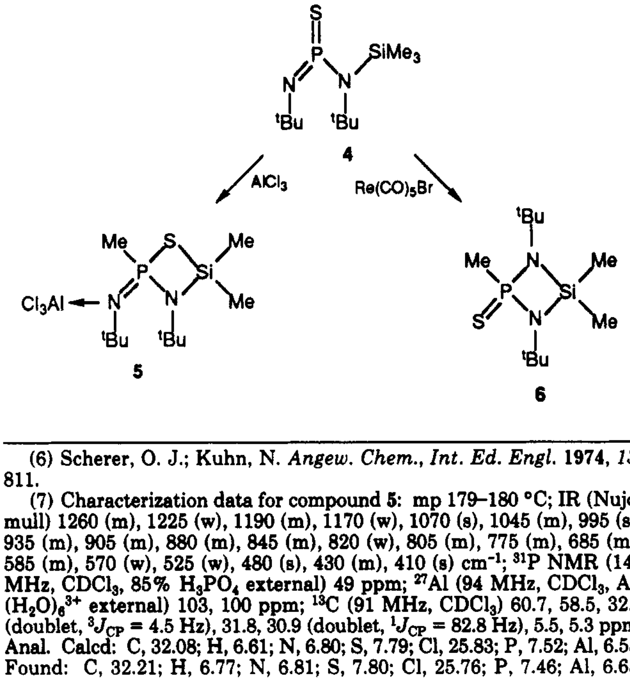


Figure 2. View of compound 5.

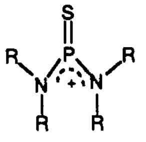
The reaction of (*tert*-butyl(trimethylsilylamino))(*tert*-butylimino)thiophosphorane[6] (4; 5.3 mmol) with $AlCl_3$ (5.3 mmol) gave compound 5 (44%), which is thermally stable (80 °C). Spectroscopic[7] and crystallographic[8] characterization revealed compound 5 to consist of a PNSiS heterocyclic isomer of 4 coordinatively bound to $AlCl_3$ via the exocyclic imine center (Figure 2).



Compounds 2 and 5 represent the first examples of systems containing a monocyclic four-membered PNSiS heterocycle. Consistent with their isovalent relationship, the cation of **2b** and the neutral compound **5** exhibit remarkably similar structural features. The Si–S bond lengths (**2b**, 2.179 (3) Å; **5**, 2.169 (2) Å) are typical for single bonds.[9] However, the Si(1)–N(1) bonds (1.762 (7) Å; 1.762 (4) Å) are long (cf. Si–N typically 1.72 Å),[9] and the P–S (**2b**, 2.060 (3) Å; **5**, 2.075 (2) Å) and P–N bonds (**2b**, P–N(1), 1.642 (6), P–N(2), 1.615 (7) Å; **5**, P–N(1), 1.654 (4), P–N(2), 1.615 (4) Å) are short (cf. single bonds P–S = 2.112 (1) Å[10] and P–N = 1.77 Å[11]), indicating substantial π-bonding over the N_2PS moiety, which is common for aminophosphonium centers.[12] Moreover, the nitrogen centers N(1) are almost planar (**2b**, N(1) angles total 357.1°; **5**, N(1) angles total 359°). Therefore, by comparison with 2, compound 5 is best viewed as a zwitterion possessing a phosphonium center and an aluminate center.

The formation of heterocycles 2 and 5 involves identical sulfur to silicon cyclizations coupled with 1,3-methyl migrations from silicon to phosphorus. Interestingly, an alternative isomerization of 4 is reported for the reaction with $Re(CO)_5Br$, which involves the 1,3-methyl migration coupled with an imino to silicon cyclization (6).[13] The alternative isomerization pathways available to 4 are likely a function of coordinative capacities of the acid initiators. In other words, preference for cyclization through sulfur may be the result of imino–$AlCl_3$ coordination, while rhenium is observed to form an adduct with the sulfur center.

The cyclization of 1 is a further[14] demonstration of the novel synthetic potential offered by the thiophosphoryl unit. In addition, the related reactivity of 1 and 4 illustrates the phosphoryl character of 4 and the potential for tricoordinate phosphonium character in 1 (1a).[14]



1a

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[7] Characterization data for compound **5**: mp 179–180 °C; IR (Nujol mull) 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}; ^{31}P NMR (146 MHz, $CDCl_3$, 85% H_3PO_4 external) 49 ppm; ^{27}Al (94 MHz, $CDCl_3$, $Al(H_2O)_6^{3+}$ external) 103, 100 ppm; ^{13}C (91 MHz, $CDCl_3$) 60.7, 58.5, 32.5 (doublet, $^3J_{CP}$ = 4.5 Hz), 31.8, 30.9 (doublet, $^1J_{CP}$ = 82.8 Hz), 5.5, 5.3 ppm. 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, 32.21; H, 6.77; N, 6.81; S, 7.80; Cl, 25.76; P, 7.46; Al, 6.65.

[8] Crystal data for **5**: $C_{11}H_{27}AlCl_3N_2PSSi$, M_r = 411.82, orthorhombic, space group $P2_12_12_1$, a = 10.640 (2) Å, b = 11.843 (3) Å, c = 16.217 (4) Å, V = 2043.5 Å^3, Z = 4, D_c = 1.34 g cm^{-3}, μ = 7.2 cm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.70930 Å). An absorption correction was applied with use of DIFABS, and the structure was solved by direct methods and refined by full-matrix least squares to residuals of R = 0.037 and R_w = 0.038 for 1642 observed reflections with $I > 3\sigma(I)$ and with 181 variables. See ref 5 for computer programs. DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

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Foundation's Instrument Program for financial support, Dr. Don Hooper and the Atlantic Region Magnetic Resonance Centre for the use of the instrument, and Beller for performing the chemical analyses.

Supplementary Material Available: Crystal structure tables of experimental parameters, atomic positional parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, and planes for $C_{12}H_{36}Cl_4GaN_2PSSi_4$ (**2b**) and $C_{11}H_{27}AlCl_3N_2PSSi$ (**5**) (17 pages); tables of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

Quadratic Hyperpolarizabilities of Group 6A Metal Carbonyl Complexes

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Summary: The molecular hyperpolarizabilities of $M(CO)_5$(pyridine), $M(CO)_4$(1,10-phenanthroline), and $M(CO)_5$(styrylpyridine) complexes (M = Cr, Mo, W) have been measured. The relationships between molecular hyperpolarizabilities and molecular modifications on the structures are discussed.

Organometallic molecules should offer the same attributes as organic molecules for nonlinear optics,[1] but interest in organometallic compounds for nonlinear optics (NLO) has been limited to using the second-harmonic generation (SHG) test on powdered materials.[2-7] Results obtained in this way are almost entirely determined by crystallographic and dispersive factors and provide limited information on the inherent molecular hyperpolarizabilities of molecules. Since molecular structure modification is often accompanied by crystallographic changes, powder testing cannot be reliably used to probe structure–property relations. Solution-phase dc electric-field-induced second-harmonic (EFISH) generation is a more appropriate method to extract hyperpolarizability. It allows extraction of a vectorial projection (β) of the quadratic hyperpolarizability tensor along the molecular dipole (μ) direction. When experiments are carried out with radiation of sufficiently long wavelength, EFISH results provide direct information on the intrinsic optical nonlinearity of a molecule.[8] In this paper, we describe EFISH results on group 6A metal carbonyl complexes and draw some conclusions concerning the hyperpolarizabilities of these organometallics.[9]

Table I. EFISH Results for $W(CO)_5$(4-X-pyridine) Complexes

X	solvent[a]	λ_{max}[b]	μ[c]	β[d]
H	toluene	332	6.0	−4.4
phenyl	$CHCl_3$	330–340	6.0	−4.5
n-butyl	*p*-dioxane	328	7.3	−3.4
NH_2	DMSO	290	8 (±1)	−2.1 (±0.3)
COMe	$CHCl_3$	420–440	4.5	−9.3
CHO	$CHCl_3$	420–440	4.6	−12

[a] Solvent in which EFISH experiments were run. [b] Absorption maximum (nm) in *p*-dioxane. [c] Dipole moment (×10^{-18} esu). [d] Units are 10^{-30} esu. Error bars represent experimental precision.

Table II. EFISH Results for $W(CO)_5$(4-X-styrylpyridine) Complexes[a]

X	λ_{max}	μ	β
H (1)	302, 390	6.4	−5.7
COH (2)	320–420	3.8	−17
NO_2 (3)	322, 425	2.5	−20

[a] See footnotes for Table I. The solvent is $CHCl_3$.

Metal pyridine complexes are capable of SHG.[2,6] EFISH is ideal for probing the effect of ligand and metal modifications on β in $M(CO)_5$(pyridine) complexes because these complexes are known to have their CT axis along the dipole direction. The low-energy metal to ligand charge-transfer (MLCT) excited states have been extensively studied and involve the low-lying π^*-acceptor orbitals of the pyridine ligands.[10] All measurements reported here have been performed at 1907 nm to minimize dispersive enhancement due to low-energy electronic excitations. EFISH results for a series of simple substituted tungsten pyridines are shown in Table I. The negative sign of β indicates a reduction of the dipole moment upon electronic excitation, which is consistent with the negative solvatochromism observed in this class of compounds.[11] The influence of coordination to the pyridines is clearly significant: pyridine has a β value of only 0.3 × 10^{-30} esu

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(8) Interpretation of EFISH results may be hampered if the molecule lacks a clear charge-transfer (CT) axis along the dipole direction; other tensorial components inaccessible by EFISH may contribute to the bulk properties for such compounds. The EFISH response is comprised of a dipolar part derived from the $\mu\beta$ product and an electronic part that originates in the molecular second hyperpolarizability (γ). The electronic component must be determined and substracted from the EFISH response to determine β. The electronic component is determined from third-harmonic generation experiments and can only be obtained on materials that are transparent at the third harmonic (633 nm when a 1.9-μm laser is used).

(9) The details of our EFISH methodology and data analysis are described in: Cheng, L. T.; Tam, W.; Meredith, G. R.; Rikken, G.; Meijer, E. W. *Proc. SPIE-Int. Soc. Opt. Eng.* **1989**, *1147*, 61.

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