Silyl-nitrogen compounds\(^1\) : Part IX - Reactions of pentasila-phosphapentazene with group VI and VII compounds

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Pentakis(trimethylsilyl)-3-phospha-2-pentazene (\(\text{Me}_3\text{Si})_5\text{N}(\text{SiMe}_3)_2\), \((1)\) reacts with sulphur as well as DMSO to form \([2+1]\)-cycloadducts, 3-tris(trimethylsilyl)hydrazino-2-bis(trimethylsilyl)-amino-1-thia-2-amo-3-phosphacyclopropane and 1,1-dimethyl-3-tris(trimethylsilyl)-hydrazino-3-bis(trimethylsilyl)hydrazono-1-thia-2-oxa-3-phosphacyclopropane, respectively. Thionyl chloride and chlorine provide the oxidative addition product, [tris(trimethylsilyl) hydrazino][bis(trimethylsilyl)] (dichloro)-phosphorane. Bromine and iodine undergo insertion reaction to form a P(III) derivative, [tris (trimethylsilyl) hydrazino] [bis(trimethylsilyl)] (bromo-iodo)hydrazono (bromo-iodo) phosphine.

Acyclic pentasilaphosphapentazene and pentasilarsapentazene have been synthesised recently.\(^2\) The former has been found to be quite stable and still reasonably reactive whereas the latter is quite sensitive to light as well as air and moisture. The former has been found to show reactivity at P(III) as well as -P=N\(^{14}\). In continuation of that, its reactions with derivatives of group VI and VII are reported here.

Materials and Methods
All investigations and measurements were carried out as reported\(^1\).

General procedure
Pentasil-3-phospha-2-pentazene \((1)\) (40 mmol, 18.0 g), dissolved in 50 ml of diethyl ether/n-hexane/toluene, was maintained at temperatures mentioned in each case and an equivalent amount (40 mmol) of thionyl chloride, dimethyl sulphoxide, chlorine, bromine, iodine and sulphur diluted/dissolved/suspended in \(\text{Et}_2\text{O}/\text{n-hexane}/\text{toluene}\) was added dropwise and the reaction mixture was allowed to come to room temperature slowly with stirring. \(^1\)H-NMR spectrum of a part of the filtrate was studied. The main filtrate was evacuated up to 30 torr/room temperature to remove solvent and other volatile compounds and the residue was characterised by NMR. It was then fractionated (sublimed) in vacuum to isolate various products. The products were refractionated/crystallised to isolate pure fractions which were characterised by methods described subsequently in each case.

Reaction of \((1)\) with sulphur: It was done at 50°C for 12 h. Reddish brown solid was crystallized from \(\text{n-hexane}\) at -78°C to get a pale yellow solid 3-[tris(trimethylsilyl) hydrazino]-2-[bis(trimethylsilyl)] amino]-1-thia-2-amino-3-phosphacyclopropane \((2)\) which decomposes before its m.p. Found: C, 36.95; H, 9.01; N, 11.20; S, 6.47. Calc. for \(\text{C}_{24}\text{H}_{35}\text{N}_4\text{PS}\): C, 37.19; H, 9.29; N, 11.57; S, 6.66%.

\(^1\)H-NMR in benzene/toluene (\(\text{n-hexane}/\text{Et}_2\text{O}\)): \(\delta\) (ppm) 0.27 (0.27) [s, 36H, \((\text{Me}_3\text{Si})_2\text{N}\)], 0.35 (0.31) [s, 9H, \(\text{Me}_3\text{SiN}\)]. \(^3\)P-NMR in \(\text{C}_6\text{D}_6\) (H\(_3\)PO\(_4\) external standard): 205.51 ppm.

\(^3\)Si-NMR in \(\text{C}_6\text{D}_6\) (TMS external standard) : 14.15 [s, 4Si, \((\text{Me}_3\text{Si})_2\text{N}\)], 24.70 [s, 1Si, \(\text{Me}_2\text{SiN}\)]. IR bands (cm\(^{-1}\)) : 1055 v(P-N), 850 v(Si,N).

Mass spectrum (70 eV) : (assignment, relative intensity %): 484 [(m)+, 15], 452 [(m-S)-, 20], 411 [(m-Me, Si)+, 25], 369 [(m-Me, SiN)+, 11], 251 [(Me, Si), N, PS, 17]+, 206 [(Me, Si), N, S]+, 150 [(Me, SiNPS)+, 20], 136 [(Me, SiPS)+, 12], 105[(Me, Si)+, 19], 75 [(MeSi)+, 100], 73 [(Me, Si)+, 25].

Reaction of \((1)\) with DMSO: The reactants were mixed at 0°C, stirred at room temperature for 4 days and then warmed to 40°C for 2 days. A colourless fraction of \([1+2]\)-cycloadduct, 1,1-dimethyl-3-tris-(trimethylsilyl) hydrazino-3-bis (tris-
methyilsilyl)-hydrazono-1-thia-2-oxa-3-phosphacyclopropane (3) was distilled at 110°C/10⁻³ torr. Found: C, 38.41; H, 9.58; N, 10.45; S, 5.98. Calc. for C₁₉H₂₅N₄OPSSi₅: C, 38.49; H, 9.62; N, 10.56; S, 6.03%.

1H-NMR in benzene (n-hexane/Et₂O): δ (ppm) 2.05 (0.16) [s, 18H, (Me₃Si)N], 2.00 (0.10) [s, 18H, Me₃SiNSiMe₃], 0.29 (0.19) [s, 9H, Me₃SiN], 2.60d (2.60d) JHH=2.4 Hz [s, 6H, 2Me].

3¹P-NMR in C₆D₆ (H₃PO₄ external standard): 13.84 ppm.

3²Si-NMR in C₆D₆ (cTMS): 23.70 [s, 1Si, Me₃SiN], 14.04 [s, 2Si, Me₃Si₂N], 7.61 [s, 2Si, (Me₃Si)₂N-N=].

Infrared spectrum: 1250 v(P=O), 1055 v(P-N), 1020 v(P-O), 1200 v(P-Si), 1350 v(P=O), 1500 v(P-N), 1650 v(P=O), 1750 v(P-Si), 2100 v(P=O), 2450 v(P-Si), 2920 v(P-Si), 2980 v(P-Si), 3080 v(P-Si).

1H-NMR in benzene (n-hexane): δ (ppm) 0.21 [s, 18H, (Me₃Si)N], 0.11 (0.27) [s, 18H, (Me₃Si)N], 0.28 (0.08) [s, 9H, Me₃SiN].

3¹P-NMR in C₆D₆ (H₃PO₄ external standard): 16.92 ppm.

3²Si-NMR in C₆D₆ (TMS external standard): δ (ppm) 14.09 [s, 4Si, 2(Me₃Si)²N], 16.31 [s, 1Si, Me₃SiN].

IR spectrum (cm⁻¹): 1050 v(P=O) and 490 v(P-Br).

Mass spectrum (70 eV) m/z (assignment, relative intensity %): 612 [(m+), 10], 539 [(m+), 20], 533 [(m+), 25], 525 [(m+), 28], 460 [(m+), 32], 278 [(m+), 12], 152 [(m+), 28], 147 [(m+), 100].

Analyses of (5): Found: C, 25.28; H, 6.10; N, 7.59; I, 35.01. Calc. for C₁₅H₄₅N₄PSi₂I₂: C, 25.48; H, 6.37; N, 7.93; I, 35.97%.

1H-NMR in benzene (n-hexane): δ (ppm) 0.20 [s, 18H, (Me₃Si)N], 0.11 (0.27) [s, 18H, (Me₃Si)N], 0.28 (0.08) [s, 9H, Me₃SiN].

3¹P-NMR in C₆D₆ (H₃PO₄ external standard): 155.77 ppm.

3²Si-NMR in C₆D₆ (TMS external standard): δ (ppm) 12.89 [s, 4Si, 2(Me₃Si)²N], 15.34 [s, 1Si, Me₃SiN].

Mass spectrum (70 eV) m/z (assignment, relative intensity %): 706 [(m+), 5], 506 [(m+), 25], 405 [(m+), 10], 363 [(m+), 18], 200 [(m+), 12].

Results and Discussion

Trisilaphosphatriazene is reported to react with elemental sulphur to form a tricoordinated
phosphorane (A), whereas phosphapentazene (1) 
\((\text{Me}_3\text{Si})_2\text{N-N(SiMe}_3)\text{-P=}\text{N-N(SiMe}_3)\text{)}_2\) provides a 
[2+1]-cycloadduct, 3-tris(trimethylsilyl)-hydrazino-
2-bis(trimethylsilyl)amino-1-thia-2-amino-3-
phosphacyclopropane (2).

Compound (2) is not very stable and tends to 
decompose on heating as well as on keeping at 
room temperatures for longer periods. The $^{31}$P-
NMR spectrum in $\text{C}_6\text{D}_6$ shows a signal at 205.51 
ppm which is characteristic of 3-coordinated phosphorus(III) compound$^{8,9}$. This supports structure (2) in preference to 3-coordinated P(V) arrangement reported in (A)$^{8,9}$. The $^1\text{H}$- and $^{29}\text{Si}$-NMR spectra show two characteristic signals with relative area 4:1 (Experimental). Structure (2) is also supported by the absence of infrared bands due to $\nu(\text{P=N})$ and $\nu(\text{P=S})$. Mass spectrum of compound (2) shows molecular ion peak at $m/z$ 484. The observed isotopic pattern agrees with that calculated for $\text{C}_4\text{H}_9\text{N}_2\text{OS}_{\text{Si}}$.

Dimethyl sulfoxide, DMSO with a polar sul-
phur-oxygen bond is expected to combine with (1) 
either with addition at $-\text{P=N}$- to form a [2+2]-
cycloadduct (3B) or with [1+2]-cycloaddition at 
P(III) to provide a phosphorane (3A).

It is a colourless liquid. Its $^{31}$P-NMR spectrum 
has a resonance at 13.84 ppm which is characteristic of tetracoordinated phosphorus(V)$^{11,12}$. This rules out (3B) and supports [1+2]-cycloadduct (3A). This is further supported by the $^1\text{H}$-NMR of Me$\text{SO}$ protons at $\delta$ 2.60d with $^{3}J_{\text{HP}}=2.4$ Hz$^{16}$. The infrared spectrum showing a strong band ($\text{cm}^{-1}$) at 1250 
$v(\text{P=N})$ also favours (3A). Mass spectral analysis of 
(3) shows a molecular ion peak at $m/z$ 530 and the 
observed isotopic pattern agrees with that calculated for $\text{C}_5\text{H}_{14}\text{N}_2\text{OPSSi}$.

Thionyl chloride oxidises (1) to give an oxidative 
addition product, [tris(trimethylsilyl) hydrazino] 
[bis(trimethylsilyl) hydrazono](dichloro) phosphorane (4).

It is a colourless liquid. Its $^{31}$P-NMR spectrum in 
$\text{C}_6\text{D}_6$ shows a peak at -4.99 ppm characteristic of 
P(V) compounds$^{11,12}$. The $^1\text{H}$- and $^{29}\text{Si}$-NMR spectra shows three signals in the expected ratio 2:2:1
(experimental). The infrared spectrum shows a prominent band (cm⁻¹) at 1260 v(P=N) to support (4). Mass spectrum of compound (4) shows a molecular ion peak at m/z 522 with the observed isotopic pattern agreeing with that calculated for C₁₅H₄₅C₁₂N₄PSi₅.

Unlike chlorine which oxidises (1) in an oxidative addition reaction to form phosphorane (4), bromine and iodine react with (1) with addition at -P=N- to form phosphine derivatives (5) and (6), respectively. This behaviour may be attributed to a stronger oxidising character of Cl₂ compared to Br₂ or I₂ and bulkier sizes of the latter which may not favour two sterically heavier halogen atoms on the same phosphorus atom.

Bromine forms a pale yellow solid [tris(trimethylsilyl)hydrazino]-[bis(trimethylsilyl)(bromo)hydrazino]-(bromo)phosphine, (Me₃Si)₂N-P(Br)-P(Br)-N(SiMe₃)₂, (5) but iodine provides a reddish brown solid, [tris(trimethylsilyl)hydrazino]-[bis(trimethylsilyl)(iodo)hydrazino]-(iodo)phosphine, (Me₃Si)₂N-P(SiMe₃)₂-P(I)-N(SiMe₃)₂, (6). The ¹H-decoupled $^{31}$P-NMR spectra of (5) and (6) show singlets at δ 169.22 and 155.77, respectively. This region is characteristic of tricoordinated P(III)⁶ and supports structures (5) and (6). Their ¹H- and $^{29}$Si-NMR spectral data are characteristic and are given in experimental section along with their mass spectral fragments.

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References