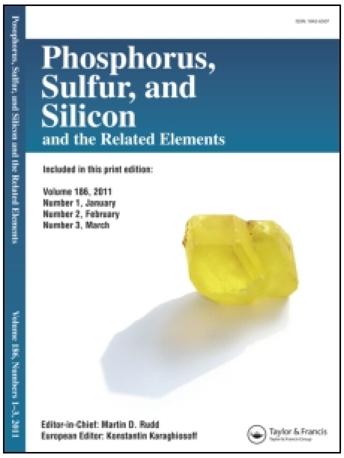


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SILYL-NITROGEN COMPOUNDS,[1] III: SYNTHESIS AND CHARACTERISATION OF PENTASILA-PHOSPHA AND PENTASILA-ARSA PENTAZENES

S. K. Vasisht[a]; Tripat P. Kaur[a]; K. Usha[a]; Jyotsna Kaushal[a]; Kavita Bandhu[a]
[a] Department of Chemistry, Panjab University, Chandigarh, India

To cite this Article Vasisht, S. K. , Kaur, Tripat P. , Usha, K. , Kaushal, Jyotsna and Bandhu, Kavita(1995) 'SILYL-NITROGEN COMPOUNDS,[1] III: SYNTHESIS AND CHARACTERISATION OF PENTASILA-PHOSPHA AND PENTASILA-ARSA PENTAZENES', Phosphorus, Sulfur, and Silicon and the Related Elements, 107: 1, 189 — 195

To link to this Article: DOI: 10.1080/10426509508027934

URL: http://dx.doi.org/10.1080/10426509508027934

Phosphorus, Sulfur, and Silicon, 1995, Vol. 107, pp. 189-195
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

SILYL-NITROGEN COMPOUNDS,[1] III: SYNTHESIS AND CHARACTERISATION OF PENTASILA-PHOSPHA AND PENTASILA-ARSA PENTAZENES

S. K. VASISHT,* TRIPAT P. KAUR, K. USHA, JYOTSNA KAUSHAL and KAVITA BANDHU

Department of Chemistry, Panjab University, Chandigarh-160014, India

(Received July 22, 1995)

Heteroatom incorporated pentazenes, pentakis(trimethylsilyl)-3-phospha-2-pentazene $(Me_3Si)_2N—N(SiMe_3)—P{=}N—N(SiMe_3)_2$ and pentakis(trimethylsilyl)-3-arsa-2-pentazene $(Me_3Si)_2N—N(SiMe_3)—As{=}N—N(SiMe_3)_2$ have been isolated by the reaction of [tris(trimethylsilyl)hydrazino]-dichlorophosphine $(Me_3Si)_2N—N(SiMe_3)—PCl_2$ with dilithium-bis(trimethylsilyl)hydrazine $Li(SiMe_3)N—N(SiMe_3)Li$ and of [tris(trimethylsilyl)hydrazino]dichloroarsine $(SiMe_3)_2N—N(SiMe_3)—AsCl_2$ with $Li_2N_2(SiMe_3)_2$, respectively. Both the compounds are reactive solids. The former thermolyses slowly at 120°C ($\tau_{1/2}$ = 25 h) whereas the latter decomposes rapidly at 100°C and is sensitive to light. Phosphapentazene reacts with methanol both with addition at —P=N— as well as desilylation, whereas, arsapentazene undergoes cleavage reaction.

Key words: Pentasila-phospha-pentazene, pentasila-arsa-pentazene, synthesis, characterisation, reactivity.

INTRODUCTION

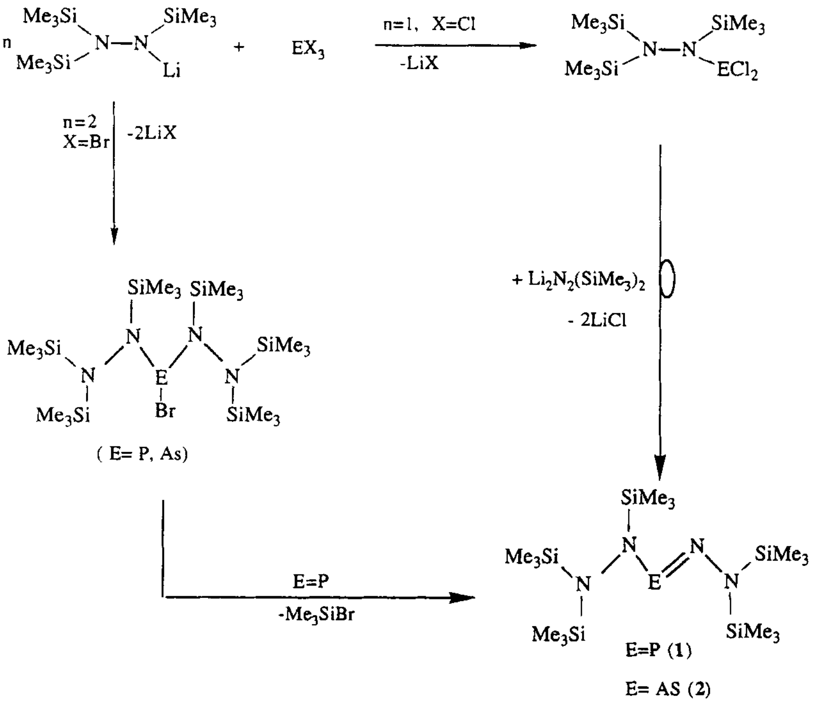
Acyclic inorganic tetrazene N_4H_4 and its silylated, germylated and stannylated derivatives are well known[2-7] but the same is not true for an analogous pentazene N_5H_5.[7] Tetrasila-2-phospha-1-tetrazene $(Me_3Si)_2—N(SiMe_3)—P{=}N—SiMe_3$ and tetrasila-2-arsa-2-tetrazene $(Me_3Si)_2N—As{=}N—N(SiMe_3)_2$ were isolated in our laboratory.[1] In continuation of this, we report the synthesis of the first heteroatom incorporated inorganic pentazenes: 1,1,5,5,4-pentakis(trimethylsilyl)-3-phospha-2-pentazene $(Me_3Si)_2N—N(SiMe_3)—P{=}N—N(SiMe_3)_2$ and 1,1,5,5,4-pentakis-(trimethylsilyl)-3-arsa-2-pentazene $(Me_3Si)_2N—N(SiMe_3)—As{=}N—N(SiMe_3)_2$.

RESULTS AND DISCUSSION

Lithium-tris(trimethylsilyl)hydrazine $Li(SiMe_3)N{-}N(SiMe_3)_2$ reacts with phosphorus (III) chloride to form a white crystalline solid [tris(trimethylsilyl)hydrazino]-dichlorophosphine $(Me_3Si)_2N—N(SiMe_3)PCl_2$ which when treated with an equivalent amount of dilithium-bis(trimethylsilyl)hydrazine $Li(SiMe_3)N—N(SiMe_3)Li$ gives a yellowish colored solution. The solution provides yellow crystalline solid, 1,1,5,5,4-pentakis(trimethylsilyl)-3-phospha-2-pentazene (**1**) either by crystallization from ether at low temperatures or by sublimation at 80°C/10^{-3} Torr. Compound

---

*Author to whom correspondence should be addressed.



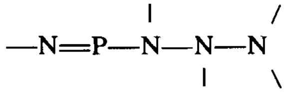
SCHEME I

(**1**) is also formed by the reaction of PBr_3 with two equivalents of lithium-tris(trimethylsilyl)hydrazine. Bis[tris(trimethylsilyl)hydrazino]-bromophosphine $[(Me_3Si)_3N_2]_2PBr$, thus formed, undergoes elimination of Me_3SiBr at higher temperatures to form (**1**). Compound (**1**), so obtained, is contaminated with $[(Me_3Si)_3N_2]_2PBr$ and needs repeated crystallization for the required purity. Similarly a 1:1 reaction of $LiN_2(SiMe_3)_3$ with $AsCl_3$ forms a white crystalline solid, $(Me_3Si)_2N—N(SiMe_3)AsCl_2$ which reacts with $Li_2N_2(SiMe_3)_2$ to give a red colored solution that provides 1,1,5,5,4-pentakis(trimethylsilyl)-3-arsa-2-pentazene (**2**). In the reaction of $AsBr_3$ with two equivalents of $LiN_2(SiMe_3)_3$, the product dihydrazinoarsine$[(Me_3Si)_3N_2]_2AsBr$ is resistant to the elimination of Me_3SiBr. The reactions are summarized in Scheme I.

The reaction of $(Me_3Si)_3N_2ECl_2$ with 1,2-dilithiumdisilylhydrazine involves a 1,2-anionic rearrangement observed frequently in silylhydrazines.[1,9,10]

Compound (**1**) is a yellow crystalline solid melting at 55°C. It is soluble in common organic solvents. When pure, it is stable in closed vessels. Compound (**2**) is a waxy red solid but is an oil when impure. It is also soluble in common organic solvents. It is sensitive to light and moisture.

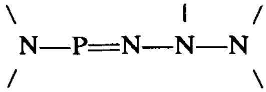
Heteroatom incorporated acyclic pentazenes can exhibit position isomerism



$-N{=}P{-}N{-}N{-}N$

(A)

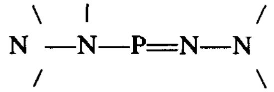
2-phospha-1-pentazene



$N{-}P{=}N{-}N{-}N$

(B)

2-phospha-2-pentazene



$N{-}N{-}P{=}N{-}N$

(C)

3-phospha-2-pentazene

Structure (**A**) is not supported by NMR studies. Structures (**B**) and (**C**) are difficult to distinguish from NMR but the methods of preparation of (**1**) from hydrazino derivatives do not support structure (**B**).

^{1}H-NMR of (**1**) in benzene shows signals at 0.24 (d; $J_{H-P} = 0.8$ Hz), 0.20 (d; $J_{H-P} = 0.4$ Hz) and 0.40 (s) ppm in the expected ratio 2:2:1. ^{31}P-NMR spectrum of (**1**) in C_6D_6 shows a low field absorption at 310.86 ppm which is characteristic of 2-coordinated phosphorus(III)azenes.[1,8] ^{29}Si-NMR of (**1**) in C_6D_6 shows signals at 14.05 [d, $^3J_{Si-P} = 4.34$ Hz), 11.76 (s) and 4.08 (d, $^2J_{Si-P} = 6.57$ Hz) with relative area 2:2:1.

Mass spectral analysis of (**1**) shows a molecular ion peak at m/Z 452 and the isotopic pattern agrees with that calculated for $C_{15}H_{45}N_4PSi_5$. A prominent fragment at 205 $[m\text{-}Me_3SiN{-}N(SiMe_3)_2]^+$ is supported by the appropriate metastable ion at m* = 93.

$$452 \xrightarrow[\text{calc.} = 93]{m^* = 93} 205[(Me_3Si)_2N_2P]$$

Compound (**1**) thermolyses by a free radical process mostly as:

$$(\mathbf{1}) \xrightarrow[\text{Benzene}]{120°\text{C},\ \tau_{1/2} = 25\ \text{h}} (Me_3Si)_2N^{\cdot} + (Me_3Si)_2N{-}N(SiMe_3){-}P{=}N^{\cdot}$$

Bis(silyl)amino radicals abstract proton from the solvent to form $(Me_3Si)_2NH$, whereas, the phosphazene radicals, besides proton abstraction, undergo intramolecular migrations to form phosphatetrazene $(Me_3Si)_2N{-}NH{-}P{=}NSiMe_3$.

About 20% of (**1**) thermolyses as follows:

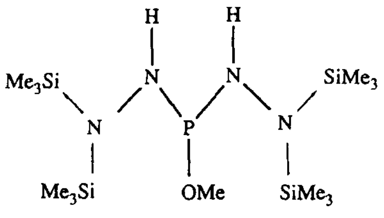
$$(\mathbf{1}) \rightarrow (Me_3Si)_3N_2^{\cdot} + (Me_3Si)_2N{-}N{=}P^{\cdot}$$

Hydrazyl radicals form tris(trimethylsilyl)hydrazine but the termination product of phosphazene could not be established exclusively. Probably, it ends up in $(Me_3Si)_2NH$ and a polymeric solid $(PNH_2)_n$.

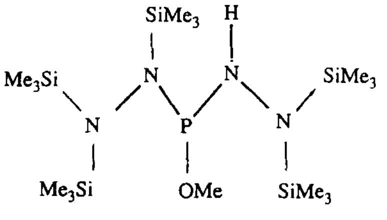
^{1}H-NMR of pentasila-arsa-pentazene (**2**) in benzene shows three kinds of silyl protons with relative area 2:2:1 at 0.26, 0.29 and 0.48 ppm. ^{1}H-decoupled ^{29}Si-NMR in C_6D_6 shows three bands at 12.10, 9.86 and 4.36 ppm with relative area 2:1:2. Mass spectral analysis of (**2**) shows a molecular ion peak at m/Z 496.

As with tetrasila-arsa-tentrazene,[1] compound (**2**) is also sensitive to light. A short exposure to sun light leads to the disappearance of the red color. The exposed mixture contains bis(trimethylsilyl)amine and tris(trimethylsilyl)hydrazine. The formation of $(Me_3Si)_2NH$ and $(Me_3Si)_2N{-}NH(SiMe_3)$ is also observed in the thermolysis of (**2**) at 100°C.

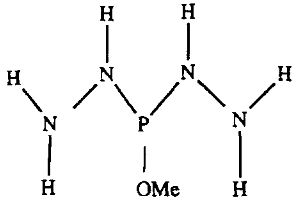
Compound (**1**) is quite reactive.[14] Phospha-tetrazene is already reported[1] to combine with methanol in an oxidative addition at P(III) to form four coordinated phosphoranes (V), whereas, a similar reaction with phospha-pentazene (**1**) provides addition at —P═N— only to form phosphines. For example, a 1:3 reaction of (1) with MeOH forms phosphines (3), (4) and (5). Absence of phosphoranes and the formation of phosphine is supported by NMR as well as IR of (3), (4) and (5) (Experimental Section).



(3)



(4)



(5)

EXPERIMENTAL

General Comments

All investigations were carried out in the absence of air and moisture on a vacuum line connected to a dry nitrogen supply system. Bis(trimethylsilyl)hydrazine,[11] tris(trimethylsilyl)hydrazine,[11] dilithium-bis(trimethylsilyl)hydrazine,[12] lithiumtris(trimethylsilyl)hydrazine[12] and butyl lithium[13] were prepared as reported in the literature. NMR measurements were recorded on Varian EM 390 and Bruker FT NMR 300 Mhz, IR spectra on Perkin Elmer 621 and Mass spectrum on GC Mass Spectrometer Model 705-250 + (VG). ^{1}H-NMR of Me_3Si protons, δ(ppm) in benzene (Et_2O): $(Me_3Si)_2N_2H_2$, 0.12(0.07); $(Me_3Si)_3HN_2$, 0.13, 0.11(2:1) (0.09); $Li_2N_2(SiMe_3)_2$, 0.21(0.00); $Li(SiMe_3)N—N(SiMe_3)_2$, 0.25(0.19); $(Me_3Si)_2NH$, 0.09(0.05); $(Me_3Si)_3N_2PCl_2$, 0.38, 0.20 d (0.44, 0.28 d) (1:2); $(Me_3Si)_3N_2AsCl_2$, 0.15, 0.37 (0.28, 0.43) (2:1).

Preparation of 1,1,5,5,4-pentakis(trimethylsilyl)-3-phospha-2-pentazene (**1**): Dilithium-1,2-bis(trimethylsilyl)-hydrazine, 200 mmol (37.50 g), suspended in 200 ml of Et_2O (or *n*-hexane), was cooled to −20°C and an equivalent amount of bis(trimethylsilyl)-hydrazinodichlorophosphine, solution in 200 ml of *n*-hexane-Et_2O (1:1) mixture, was added to it dropwise with constant stirring. A yellow colour appeared at −20°C which then changed slowly to reddish brown as the temperature rose gradually to 0°C. Reaction mixture was then stirred at room temperature overnight and then filtered to get 398 mmol (9.34 g) of LiCl. ^{1}H-NMR of the reddish brown filtrate showed major signals at 0.34, 0.20 and 0.13 d ppm in the intensity ratio 1:2:2. Solvents and other volatile impurities were removed under vacuum at room temperature. The residual reddish brown thick liquid was quickly sublimed under vacuum. Yellow crystals subliming at 80°C/10^{-3} Torr were collected to obtain 100 mmol (50% yield) of pure 1,1,5,5,4-pentakis(trimethylsilyl)-3-phospha-2-pentazene (1).

Compound (1) was also prepared by the addition of 100 mmol of PBr_3 (10 ml) solution in 100 ml Et_2O to lithiumtris(trimethylsilyl)hydrazine 200 mmol (50.80 g) suspended in 200 ml of *n*-hexane. The reaction was done at −40°C and the reaction mixture was allowed to come to the room temperature slowly over a period of 2 h. Lithium bromide (17.00 g) was filtered out and the filtrate was evacuated at room temperature to isolate bis[tris(trimethylsilyl)hydrazino]bromophosphine $[(Me_3Si)_3N_2]_2PBr$. It was heated at 80–100°C/100^{-3} Torr, to eliminate Me_3SiBr and isolate (1). However, the distillate cum sublimate contained a mixture of (1) and the dihydrazino-phosphine $[(Me_3Si)_3N_2]_2PBr$. Compound (**1**) could not be purified by sublimation but could be isolated in pure form by repeated crystallisation from ether at low temperatures. Compound (**1**) is a yellow crystalline solid (mp = 55°C) soluble in common organic solvents. It is stable at room temperature if protected from air and moisture.

Found: C, 39.62; H, 9.82; N, 12.29. $C_{15}H_{45}N_4PSi_5$ Calcd: C, 39.82; H, 9.95, N, 12.38%.
^{1}H-NMR in benzene (Et_2O): δ(ppm) 0.24 (0.13) [d, 18 H, $(Me_3Si)_2N$, $J_{H—P} = 0.8$ Hz]; 0.20 (0.20) [d, 18 H, $(Me_3Si)_2N—N$, $J_{H—P} = 0.4$ Hz] and 0.40 (0.33) [s, 9 H, Me_3SiN].
^{31}P-NMR in C_6D_6 (H_3PO_4, external standard): δ(ppm) 310.86.
^{29}Si-NMR (^{1}H-decoupled) in C_6D_6 (TMS external standard): δ(ppm) 14.05 [d, 2Si, $(Me_3Si)_2N$, $^3J_{Si—P} = 4.34$ Hz], 11.76 [s, 2Si, $(Me_3Si)_2N$] and 4.08 [d, 1Si, Me_3SiN, $^2J_{Si—P} = 6.57$ Hz].
UV-Vis (*n*-hexane solution): λmax in nm (log ε); 315 (4.96) $\pi \rightarrow \pi^*$; 375 (4.04) $n \rightarrow \pi^*$.
Important IR bands (thin film, cm^{-1}): 1255$_s$[ν(P═N)], 1060 [ν(N—N)], 970 [νas (Si_2N)]. Mass spectrum (70 eV) m/Z (assignment; relative intensity %): 452 [$(m)^+$; 20], 437 [$(m\text{-}Me)^+$; 36], 407 [$(m\text{-}3Me)^+$; 22], 398 [$(m\text{-}C_4H_6)^+$; 10], 365 [$(m\text{-}NSiMe_3)^+$ - m′; 22], 350 [$(m'\text{-}Me)^+$; 13], 278 [$m\text{-}(Me_3Si)_2N_2^+ = (Me_3Si)_3N_2P^+ = m''$; 16], 205 [$(Me_3Si)_2N—N{=}P^+$; 96], 191 [$(Me_3SiN{=}PSiMe_3)^+ = m'''$; 10], 176 [$(m'''\text{-}Me)^+$ 17], 174 [$(Me_3SiN{=}NSiMe_3)^+$; 15], 132 [$(Me_3SiN_2P)^+ = (m''\text{-}Me_6Si_2)^+$; 7], 131 [$(Me_5Si_2)^+$; 67], 130 [$(m''\text{-}Me_3Si\text{-}NPMe_2)^+$; 16] and 73 [$(Me_3Si)^+$; 100]. Metastable fragment is observed at m/Z 205.

Isotopic pattern (calcd.) of $C_{15}H_{45}N_4PSi_5$:

Mass	452	453	454	455	456
Imax = 100	100	62.06	37.93	17.24	14.40

Preparation of 1,1,5,5,4-pentakis(trimethylsilyl)-3-arsa-2-pentazene (**2**): Tris(trimethylsilyl)hydrazino-dichloroarsine, 100 mmol (18.77 g) in 100 ml *n*-hexane, was added dropwise with constant stirring to dilithium-1,2-bis(trimethylsilyl)hydrazine 100 mmol (19.80 g) in 100 ml Et_2O at −70°C. The yellowish orange solution containing a white precipitate changed to dark red as temperature was allowed to come to room temperature over a period of 4 h. The reaction mixture was filtered to remove LiCl, 198 mmol (8.4 g). ^{1}H-NMR of the red filtrate showed major signals at 0.21, 0.22, 0.32 ppm and very small signals at 0.05 and 0.09 ppm. Solvents and other volatile impurities were removed under vacuum at room temperature to get a dark red liquid. Its ^{1}H NMR in benzene (Et_2O) showed signals at 0.26 (0.22), 0.29 (0.23) and 0.48 (0.34) ppm with relative area 2:2:1. The dark red liquid was fractionated at 90°C /10^{-3} Torr to get an orange distillate. The distilled product was contaminated with tris(trimethylsilyl)hydrazine indicating partial decomposition at 90°C/10^{-3} Torr. Bis(trimethylsilyl)amine was found to be present in the liquid nitrogen cooled trap. Tris(trimethylsilyl)hydrazine was then removed by long evacuation at 30°C/10^{-3} Torr to get a residual waxy orange red solid. It was further purified by crystallization from diethyl ether or *n*-hexane at low temperatures. The compound was protected from bright day light due to its tendency to decompose into tris(trimethylsilyl)hydrazine and bis(trimethylsilyl)amine.

Found: C, 36.18; H, 9.62; N, 11.28. $C_{15}H_{45}N_4AsSi_5$ calcd. C, 36.29; H, 9.72; N, 11.29%.
^{1}H-NMR in benzene (Et_2O): δ(ppm) 0.26 (0.22) [s, 18 H, $(Me_3Si)_2N$], 0.29 (0.23) [s, 18 H, $(Me_3Si)_2N$], 0.48 (0.34) [s, 9 H, Me_3SiN].
^{29}Si-NMR (^{1}H-decoupled) in C_6D_6 (TMS external) δ(ppm) 4.36 [s, 2 Si, $(Me_3Si)_2N$], 9.86 [s, 1 Si, Me_3SiN], 12.10 [s, 2 Si, $(Me_3Si)_2N$].
Mass spectrum (70 eV), m/Z (assignment, relative intensity %): 496 [$(m)^+$; 3], 481 [$(m\text{-}Me)^+$; 20], 409 [$(m\text{-}Me_3SiN)^+$; 35], 336 [$m\text{-}(Me_3Si)_2N^+$; 10], 322 [$m\text{-}(Me_3Si)_2N_2^+$; 50], 248 [$(Me_3Si)_3N_2H^+$; 33], 247 [$(Me_3Si)_3N_2$, 100], 233 [$(Me_3Si)_3N^+$; 4], 221 [$(Me_3Si)_2As^+$; 3], 174 [$(Me_3SiN{=}NSiMe_3)^+$; 6], 146 [$(Me_5Si_2NH)^+$; 70} and 73 [$(Me_3Si)^+$, 45].

Thermolysis of 1,1,5,5,4-pentakis(trimethylsilyl)-3-phospha-2-pentazene (**2**): Pentasila-3-phospha-2-pentazene (**1**), (4.50 g, 10 mmol) was dissolved in 10 ml benzene and the solution was sealed in an evacuated glass ampule. The sealed tube was heated at 120°C for 150 h and then opened. ^{1}H-NMR of the thermolysed mixture showed signals at 0.13, 0.11 (2:1) [$(Me_3Si)_3N_2H$], 0.09 [$(Me_3Si)_2NH$] and 0.31, 0.28 (2:1) [$(Me_3Si)_2N—N(H)—P{=}NSiMe_3$]. The mixture was first evacuated at room temperature/50 Torr to remove benzene and then carefully to a vacuum of 0.1 Torr to trap bis(trimethylsilyl)amine (1.60 g). The residual mixture was fractionated to obtain tris(trimethylsilyl)hydrazine (0.5 g) at 40°C/10^{-2} Torr and tris(trimethylsilyl)-2-phospha-1-tetrazene (2.0 g) at 60°C/10^{-3} Torr. Its mass spectrum shows a molecular ion peak at m/Z 293. A similar thermolysis at 120°C in a sealed NMR tube was monitored by ^{1}H-NMR to determine tentative half life of thermolysis ($\tau_{1/2}$ = 25 h).

Thermolysis of 1,1,5,5,4-pentakis(trimethylsilyl)-3-arsa-2-pentazene (**2**): Pentasila-3-arsa-2-pentazene, (**2**) (0.50 g, 1 mmol) in 0.4 ml benzene and 2 drops of TMS were taken together and sealed in an NMR tube. The NMR tube was placed in a bath at 100°C for 4 h. ^{1}H-NMR of the thermolysed mixture showed NMR signals at 0.09 [$(Me_3Si)_2NH$] and 0.13, 0.11 (2:1) [$(Me_3Si)_3N_2H$]. The formation of bis(trimethylsilyl)-amine and tris(trimethylsilyl)hydrazine was confirmed by their actual isolation.

Reaction of (**1**) *with MeOH*: Compound (**1**) (18.00 g, 40 mmol) was taken in 50 ml ether and methanol (4.8 ml, 120 mmol), taken in 20 ml ether, was added dropwise with constant stirring at room temperature. The yellow solution developed turbidity. The reaction mixture was stirred overnight at room temperature and then filtered to isolate a white solid (**5**). ^1H-NMR of the filtrate showed major signals at 0.31, 0.25, 0.20, 0.14 and 0.06 ppm. This solution was evacuated to remove ether and other volatile product Me_3SiOMe (0.06 ppm). The residual liquid was then distilled in vacuum and the first fraction distilling at 100°C/10^{-3} Torr was collected as bis[bis(trimethylsilyl)hydrazino]methoxyphosphine $(Me_3Si)_2N—NH—P(OMe)—NH—N(SiMe_3)_2$ (**3**) (1.20 g) and the second fraction distilling between 120–130°C/10^{-3} Torr was redistilled at 120°C/10^{-3} Torr to get tris(trimethylsilyl)-hydrazinobis(trimethylsilyl)hydrazino-methoxyphosphine $(Me_3Si)_2N—N(SiMe_3)—P(OMe)—NH—N(SiMe_3)_2$, (**4**), (1.80 g). The white solid (**5**) was washed with *n*-hexane and dried in vacuo. It was found to be a desilylated product, dihydrazino-methoxyphosphine, $H_2N—NH—P(OMe)—NH—NH_2$ (**5**), (0.37 g).

Characterisation of bis[bis(trimethylsilyl)hydrazino]methoxyphosphine (**3**): Compound (**3**) is a colourless liquid, bp = 100°C/10^{-3} Torr. It is soluble in common organic solvents.

Found: C, 37.52; H, 9.90; N, 13.48. $C_{13}H_{41}N_4OPSi_4$ Calcd: C, 37.86; H, 9.95; N, 13.59%.
^1H-NMR in benzene (Et_2O/*n*-hexane); δ(ppm) 0.21 (0.14)[s, 36 H, 2 $(Me_3Si)_2N$], 3.50 (3.64) [d, 3 H, OCH_3; $^3J_{P-H}$ = 12.0 Hz].
^{31}P-NMR in C_6D_6 (H_3PO_4 external standard) 150.04 ppm. This is indicative of three coordinated P(III) and does not support a four coordinated phosphorane (V) entity.[1] The absence of phosphorane structure is also supported by infrared which shows prominent band at 3290 cm^{-1} (νNH) and absence of any bands due to ν (P—H) and ν(P=N).[1]
^{29}Si-NMR (^1H-decoupled in C_6D_6 (TMS external standard) 20.13 ppm [s, 4 Si, 2 $(Me_3Si)_2N$].
Mass spectrum (70 eV) m/Z (assignment, relative intensity %) 412 [$(m)^+$, 5], 398 [$(m\text{-}CH_2)^+$, 6], 397 [$(m\text{-}Me)^+$, 20], 339 [$(m\text{-}Me_3Si)^+$, 30], 252 [$m\text{-}(Me_3Si)_2N^+$, 20], 237 [$m\text{-}(Me_3Si)_2N_2H^+$, 18], 205 [$(Me_3Si)_2N_2P^+$, 22], 176 [$(Me_3Si)_2N_2H_2^+$, 100], 162 [$(Me_3Si)_2O^+$, 14], 146 [$(Me_3Si\text{-}SiMe_3)^+$, 10], 90 [$(Me_3SiOH)^+$, 22], 73 [$(Me_3Si)^+$, 93].

$C_{13}H_{41}N_4OPSi_4$; Isotopic pattern (calcd.):

Mass	412	413	414	415	416
Imax = 100	100	37.18	19.96	5.04	1.39

Characterisation of tris(trimethylsilyl)hydrazino-bis(trimethylsilyl)hydrazino-methoxyphosphine (**4**): It is a colourless liquid, bp = 120°C/10^{-3} Torr. It is soluble in common organic solvents.

Found: C, 38.99; H 10.01; N, 11.43. $C_{16}H_{49}N_4OPSi_5$ calcd: C, 39.67; H, 10.12; N, 11.57%.
^1H-NMR in benzene (Et_2O/*n*-hexane) δ(ppm) 0.36 (0.32) [s, 18 H, $(Me_3Si)_2N$], 0.33 (0.20) [s, 18 H, $(Me_3Si)_2N$], 0.30 (0.25) [s, 9 H, Me_3SiN], 3.50 (3.64) [d, 3 H, OCH_3; $^3J_{P-H}$ = 12.0 Hz].
^{31}P NMR in C_6D_6 (H_3PO_4, external standard) 145.80 ppm. This indicates the presence of three coordinated P(III). Prominent IR bands supporting phospine structure (**4**) is observed at 3270 cm-1 ν(N—H). Like in (**3**), IR bands due to ν(P—H) and ν(P=N) are absent.
^{29}Si-NMR (^1H-decoupled) in C_6D_6 (TMS external standard) 32.40 [d, 2 Si, $(Me_3Si)_2N$], 29.80 [d, 2Si, $(Me_3Si)_2N$] and 28.98 [s, 1 Si, Me_3SiN]. The bis(silyl)amino signals appear as doublets with $^3J_{Si-P}$ = 10.0 Hz.
Mass spectrum (70 eV), m/Z (assignment, relative intensity %) 484 [$(m)^+$, 10], 469 [$(m\text{-}Me)^+$, 30], 453 [$(m\text{-}OMe)^+$, 20], 309 [$(Me_3Si)_3N_2POMe^+$, 100], 277 [$(Me_3Si)_3N_2P^+$, 10], 237 [$(Me_3Si)_2N_3HPOMe^+$, 8], 207 [$(Me_3Si)_2N_2PH_2^+$, 11], 205 [$(Me_3Si)_2N_2P^+$, 22], 174 [$(Me_3SiN{=}NSiMe_3)^+$, 20], 162 [$(Me_3Si)_2O^+$, 20], 160 [$(Me_3Si)_2N^+$, 12], 132 [$(Me_3SiN_2P)^+$, 14], 89 [$(Me_3SiNH_2)^+$, 5], 73 [$(Me_3Si)^+$, 90].

Characterisation of dihydrazino-methoxyphosphine (**5**): It is a white solid insoluble in common organic solvents.

Found: C, 9.59; H, 7.12; N, 45.22. CH_9N_4OP calcd: C, 9.67; H, 7.25; N, 45.16%.
^{31}P-NMR in D_2O (H_3PO_4 external standard) 168.40 ppm. This is indicative of P(III).
IR (thin film, cm^{-1}) 3250, 3100 (νNH_2), 1070 (νN—N), 859 (νP—N).
Mass spectrum (70 eV), m/Z (assignment, relative intensity %) 124 [$(m)^+$ 12], 123 [$(m\text{-}H)^+$, 23], 120 [$(m\text{-}4H)^+$, 25], 109 [$(m\text{-}Me)^+$, 34], 107 [$(m\text{-}OH)^+$, 14], 96 [$(m\text{-}N_2)^+$, 19], 93 [$(m\text{-}OMe)^+$, 24], 92 [$(m\text{-}MeOH)^+$, 8], 74 [$(PN_3H)^+$, 31], 73 [$(PN_3)^+$, 100], 62 [$(H_2NP{=}NH)^+$, 12], 59[$(PN_2)^+$; 18].

Reaction of (**2**) *with methanol*: Compound (**2**) (4.96 g, 10 mmol) was dissolved in 20 ml ether and methanol (0.40 ml, 10 mmol) in 10 ml ether was added to it with constant stirring at room temperature. The orange coloured reaction mixture turned colourless in a few minutes. ^{1}H-NMR of the mixture showed resonance signals at 0.09 and 0.05 ppm due to tris(trimethylsilyl)hydrazine and bis(trimethylsilyl)amine, respectively. The mixture was first evacuated carefully to remove ether. Then it was evacuated further to trap volatiles coming at room temperature/0.1 Torr. It was found to be $(Me_3Si)_2NH$. Residual mixture was fractionated to obtain$(Me_3Si)_2N$—$NH(SiME_3)$ at 80°C/10 Torr. This indicates cleavage of (**2**) to form silylated amine and hydrazine.

ACKNOWLEDGEMENTS

The authors are thankful to DST as well as CSIR, New Delhi for financial support.

REFERENCES

1. S. K. Vasisht, M. Sood, P. K. Verma, T. Kaur and K. Usha, *Phosphorous, Sulphur and Silicon*, **47**, 349 (1990).
2. N. Wiberg, H. Bayer and H. Bacchuber, *Agnew. Chem. Int. Ed. Engl.*, **14**, 177 (1975).
3. N. Wiberg, H. W. Haering and S. K. Vasisht, *Z. Naturforsch.*, **34**, 356 (1979).
4. N. Wiberg, S. K. Vasisht, H. Bayer and R. Meyers, *Chem. Ber.*, **112**, 2718 (1979).
5. N. Wiberg, H. Bayer, S. K. Vasisht and R. Meyers, *Chem. Ber.*, **113**, 2916 (1980).
6. N. Wiberg, R. Meyers, S. K. Vasisht and H. Bayer, *Chem. Ber.*, **117**, 2886 (1984).
7. N. Wiberg, *Adv. Organomet. Chem.*, **24**, 179 (1985).
8. O. J. Scherer and W. Glaessel, *Chem. Ber.*, **110**, 3874 (1977).
9. R. West, *Adv. Organomet. Chem.*, **16**, 1 (1977).
10. S. K. Vasisht, M. Sood, N. Sood and Gursharan Singh, *J. Organomet. Chem.*, **301**, 15 (1986).
11. U. Wannagat and H. Niederprum, *Z. Anorg. Allg. Chem.*, **310**, 32 (1961).
12. N. Wiberg, E. Weinberg and W, Ch. Joo, *Chem. Ber.*, **107**, 1764 (1974).
13. U. Wannagat, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).
14. Cycloaddition, ring closure, complexation, oxidative addition and desilylation reactions have been observed.