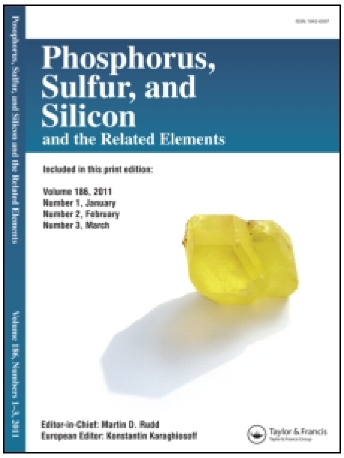

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SILYL NITROGEN COMPOUNDS[1], V: REACTIONS OF PENTASILA-PHOSPHA-PENTAZENE WITH METAL CHLORIDES

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SILYL NITROGEN COMPOUNDS[1], V: REACTIONS OF PENTASILA-PHOSPHA-PENTAZENE WITH METAL CHLORIDES

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Pentakis(trimethylsilyl)-3-phospha-2-pentazene $(Me_3Si)_2N\text{-}N(SiMe_3)\text{-}P=N\text{-}N(SiMe_3)_2$ (**1**) reacts with $AlCl_3$ and $TiCl_4$ (MX_n) to form an iminophosphorane, $(Me_3Si)_2N\text{-}N(SiMe_3)\text{-}P(X)(MX_{n-1})=N\text{-}N(SiMe_3)_2$. The latter decomposes to form 3,5,5-trichloro-1,2-bis(trimethylsilyl)-4-bis(trimethylsilyl)amino-1,2-diaza-3-phospha-4-amino-5-titanacyclo-pentane. $SbCl_3$ forms a similar cyclic product 3,5-dichloro-1,2-bis (trimethylsilyl)-4-bis(trimethylsilyl)amino-1,2-diaza-3-phospha-4-amino-5-stibacyclopentane. Lewis acids $SnCl_4$ and $SbCl_5$ act as oxidants to yield $Me_3Si\text{-}N=N\text{-}P=N\text{-}N(SiMe_3)_2$.

Keywords: Pentasila-phospha-pentazene; reactivity; Lewis acids; phosphoranes; cyclic derivatives

INTRODUCTION

Silylated cyclic pentazene is known in the literature,[2] whereas, the corresponding acyclic derivative has not been previously reported. Silylated cyclic phosphapentazene is not known but a silylated acyclic phosphapentazene has been synthesised recently.[1] Unlike silylated cyclic pentazene the acyclic silylated phosphapentazene has been found to be quite reactive and undergoes a variety of reactions.[1,3]

RESULTS AND DISCUSSION

Pentasilaphosphapentazene $(Me_3Si)_2N\text{-}N(SiMe_3)\text{-}P=N\text{-}N(SiMe_3)_2$, (**1**), isolated recently in our laboratory,[1] has been found to be quite reactive towards protonating agents.[3] Reaction of (**1**) with some representative Lewis acids are reported here.

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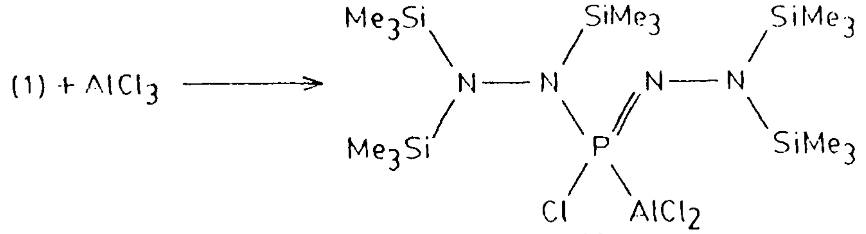
*Corresponding author.



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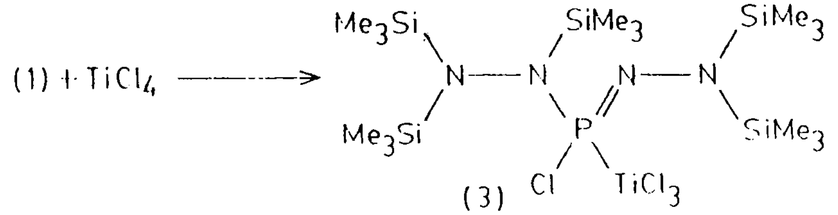


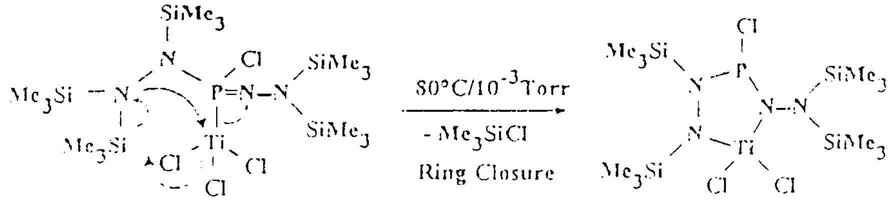
(3)

Aluminium(III)chloride and titanium(IV)chloride MCl_n react with phosphinimine (**1**) at low temperatures to form the oxidative addition products, [tris(trimethylsilyl)hydrazino] [bis(trimethylsilyl)hydrazono](dichloroalumino)-(chloro)phosphorane (**2**) (M = Al; n = 3) and [tris(trimethylsilyl)hydrazino]-[bis(trimethylsilyl)hydrazono](trichlorotitana)(chloro)phosphorane (**3**) (M = Ti; n = 4). As already suggested,[13] the reaction may first involve addition at the -P = N- linkage initiated by donor acceptor complex formation with the metal chloride. This is followed by intramolecular rearrangement of the intermediate phosphine to provide more stable iminophosphoranes.

The ^{1}H-NMR of (**2**) in benzene shows resonances at δ 0.26, 0.17 and 0.39 in the expected intensity ratio 2:2:1. The ^{31}P-NMR in C_6D_6 shows a resonance signal at δ 20.63 typical of tetracoordinated phosphorus(V)[4,5,6] and imino-chlorophosphoranes.[8] The ^{29}Si-NMR shows signals at δ 5.64, 6.58 and 7.12 with appropriate relative intensity 2:2:1. The infrared spectrum shows a strong band at 1255 cm^{-1} due to $\nu(P=N)$ to support structure (**2**). The mass spectrum of compound (**2**) shows the molecular ion at m/Z 586.

Spectral data of (**3**) is similar to that of (**2**) and is given in the Experimental section.

Compound (**3**) is stable at room temperature but decomposes on heating to lose Me_3SiCl and forms a cyclic derivative 3,5,5-trichloro-1,2-bis(trimethylsilyl)-4-bis(trimethylsilyl) amino-1,2-diaza-3-phospha-4-amino-5-titanacyclopentane (**4**) which shows ^{1}H-NMR resonance signals in benzene at δ 0.36, 0.23 and 0.19 in the intensity ratio 2:1:1.



(3) (4)

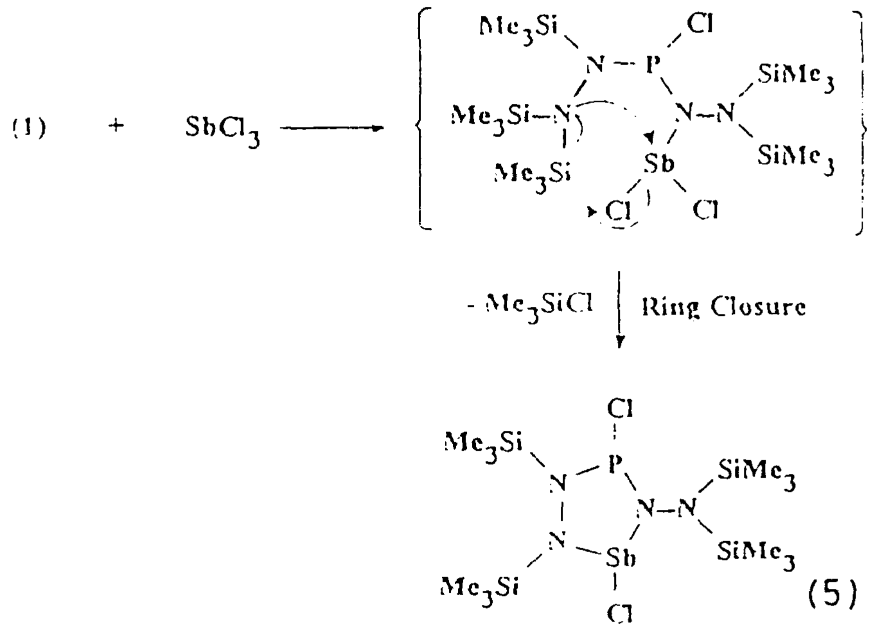
The ^{31}P-NMR in C_6D_6 shows a resonance signal at δ184.42 ppm. corresponding to tricoordinated phosphorus(III).[7] The infrared band for v(P = N) is missing in (**4**) which shows strong bands at 1050, 850 and 390 cm^{-1} attributed to ν(P-N), ν(Si_2N) and ν(Ti-Cl) groups. A mass spectral analysis of (**4**) shows molecular ion peak at m/Z 534.

Antimony(III)chloride reacts with (**1**) at lower temperatures but unlike $AlCl_3$ and $TiCl_4$, it does not appear to stabilise a phosphorane derivative. The intermediate undergoes loss of Me_3SiCl below room temperature to form a cyclic derivative, 3,5-dichloro-1,2-bis(trimethylsilyl)-4-bis(trimethylsilyl)amino-1,2-diaza-3-phospha-4-amino-5-stibacyclopentane, (**5**). Compound (**5**) resembles (**4**) and the spectral data of (**5**) is similar to that of (**4**) and is given in experimental section.

The Lewis acids $SnCl_4$ and $SbCl_5$ react differently and behave as oxidants towards (**1**). Both form the same 2-coordinated phosphorus(III) derivative, [(trimethylsilyl)azeno] [bis(trimethylsilyl)amino]phosphazene (**6**). In the process, lower metal chlorides are lost.

Phosphinimine (**6**) is a yellow liquid showing ^{1}H-NMR resonance signals in benzene at δ 0.22 d with $^5J_{H\text{-}P} = 0.9$ Hz and 0.46 with relative area 2:1. The ^{31}P-NMR shows a resonance signal at 282.10 ppm in C_6D_6. This region is characteristic of two coordinated P(III) compounds.[1,7] The ^{29}Si-NMR spectrum in C_6D_6 shows resonances at 7.33 and 5.70 ppm with relative area 2:1. The infrared spectrum shows characteristic bands (cm^{-1}) at 1445 ν(N = N), 1260 ν(P = N), 1050 ν(P-N) and 850 ν(Si_2N). Mass spectral analysis of (**6**) shows a molecular ion peak at m/Z 306. Compound (**6**) is an interesting molecule and its chemistry will be discussed separately.

It appears that the lower valent metal chlorides react with (**1**) to form phosphoranes,[3] whereas, higher valent metal chlorides behave as oxidants and in the process lose lower valent metal chlorides.



(5)

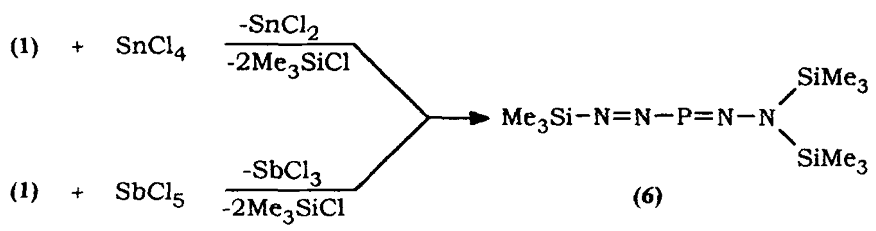
EXPERIMENTAL

General Comments

All investigations were carried out as already detailed.[1] Pentasila-3-phospha-2-pentazene was prepared as reported.[1] ^{1}H-NMR of Me_3Si protons, δ (ppm) in benzene (Et_2O/CCl_4/n-hexane):$(Me_3Si)_5N_4P$ (**1**), 0.28 d, 0.21, 0.43 (0.14 d, 0.22, 0.34), (2:2:1); Me_3SiCl, 0.21(0.40).

General Procedure

Pentasila-3-phospha-2-pentazene (**1**) (40 mmol, 18.0 g), dissolved in 50 ml diethyl ether or n-hexane, was maintained at − 50°C to 0°C and equivalent amount (40 mmol) of Lewis acid dissolved in Et_2O or n-hexane was added dropwise



(6)

and the reaction mixture was allowed to warm slowly to room temperature with stirring. The rest of the procedure remains the same as stated before[3] or is given independently.

Reaction of (1) with $AlCl_3/TiCl_4$

Phosphapentazene (**1**) was reacted with $AlCl_3$ ($TiCl_4$) at 0°C (−50°C) in ether (n-hexane). The color of reaction mixture changed to light yellow (orange) as temperature slowly rose to room temperature. The ^1H-NMR of the reaction mixture showed prominent signals at δ 0.30, 0.24 and 0.09 (δ 0.57, 0.45 and 0.35). It was evacuated to remove the solvent and the residue left behind was crystallised out of n-hexane at low temperatures. The light yellow solid from the reaction of (**1**) with $AlCl_3$ sublimed at 100°C/10^{-3} torr and was characterised as [tris(trimethylsilyl)hydrazino][bis(trimethylsilyl)hydrazono](dichloroalumino)-(chloro)phosphorane, $(Me_3Si)_2N$-$N(SiMe_3)$-$P(Cl)$ $(AlCl_2)=N$-$N(SiMe_3)_2$, (**2**), (Yield = 70%).

Found: C, 30.57; H, 7.50; N, 9.40; P, 5.10; Al, 4.52; Cl, 18.00. Calc. for $C_{15}H_{45}N_4PAlCl_3Si_5$: C, 30.79; H, 7.70; N, 9.58; P, 5.30; Al, 4.62; Cl, 18.05%.

^1H-NMR in Et_2O or n-hexane; δ (ppm) 0.28b [s, 18H, $(Me_3Si)_2N$-$N=$], 0.08 [s, 18H, $(Me_3Si)_2N$], 0.36 [s, 9H, Me_3SiN].

Mass Spectrum (70 eV) m/Z (assignment, relative intensity %) 586 [(m^+), 20], 571 [$(m\text{-}Me)^+$, 12], 556 [$(m\text{-}2Me)^+$, 11], 551 [$(m\text{-}Cl)^+$, 17], 513 [$(m\text{-}Me_3Si)^+$, 29], 499 [$(m\text{-}Me_3SiN)^+$, 15], 431[$(m\text{-}Me_2SiAlCl_2)^+$, 18], 416 [$(m\text{-}Me_3SiAlCl_2)^+$, 25], 370 [$(m\text{-}2Me_3SiCl)^+$, 31], 247 [$(Me_3Si)_3N_2{}^+$, 18], 147 [$(Me_2SiPSiMe_2)^+$, 100], 108 [$(Me_3SiCl)^+$, 14], 77 [$(MeAlCl)^+$, 25].

The reaction of (1) with $TiCl_4$ resulted in the formation of a light yellow solid [tris(trimethylsilyl)hydrazino] [bis(trimethylsilyl)hydrazono](trichlorotitana)-(chloro)phosphorane, $(Me_3Si)_2N$-$N(SiMe_3)$-$P(Cl)(TiCl_3)=N$-$N(SiMe_3)_2$, (**3**), (Yield = 67%) which decomposes on heating before its s.pt.

Found: C, 27.49; H, 6.89; N, 8.50; P, 4.57; Cl, 21.09; Ti, 7.42. $C_{15}H_{45}N_4PTiCl_4Si_5$. Calc.: C, 28.03; H, 7.00; N, 8.72; P, 4.83; Cl, 22.12; Ti, 7.47 %.

^1H-NMR in benzene (n-hexane); δ (ppm) 0.49 (0.45) (s, 18H, $(Me_3Si)_2N$-$N=$], 0.21 (0.35) [s, 18H, $(Me_3Si)_2N$], 0.47 (0.57) [s, 9H, Me_3SiN].

^{31}P-NMR in C_6D_6 (H_3PO_4 external standard) 0.83 ppm.

^{29}Si-NMR in C_6D_6 (TMS external standard) δ (ppm) 14.35 [s, 3Si, $(Me_3Si)_2N$, Me_3SiN], 4.32 [s, 2Si, $(Me_3Si)_2N$-$N=$].

IR-bands (cm^{-1}) 1260 v ($P=N$), 850 v(Si_2N), 525 ν(P-Cl), 390 v(Ti-Cl).

Mass Spectrum (70 eV) m/Z (assignment, relative intensity %) 642 [$(m)^+$, 7], 612 [$(m\text{-}2Me)^+$, 20], 592 [$(m\text{-}MeCl)^+$, 18], 534 [$(m\text{-}3Cl)^+$, 17], 487 [(m-

$TiCl_3)^+$, 14], 468 [$(m\text{-}Me_3Si)_2N_2)^+$, 20], 378 [$(m\text{-}(Me_3Si)_2TiCl_2)^+$, 21], 147 [$(Me_2SiPSiMe_2)^+$, 100], 118 [$(TiCl_2)^+$, 20], 108 [$(Me_3SiCl)^+$, 32].

Compound (**3**) (5 mmol, 3.210 g) was taken in a flask fitted with a glass boat. The apparatus was evacuated and the flask was placed in a hot temperature bath. The temperature was slowly raised to 80°C/10^{-3} torr and allowed to remain constant for 2h. The gaseous product Me_3SiCl (5 mmol) was trapped in the liquid nitrogen trap and a yellowish liquid 3,5,5-trichloro-1,2-bis(trimethylsilyl)-4-bis(trimethylsilyl)amino-1,2-diaza-3-phospha-4-amino-5-titanacyclopentane, (**4**), (Yield = 80%) was distilled into the boat kept at −78°C.

Found: C, 27.04; H, 6.76; N, 10.52; Cl, 19.81; Ti, 9.01. $C_{12}H_{36}Cl_3N_4PSi_4Ti$. Calc.: C, 26.96; H, 6.74; N, 10.48; Cl, 19.66; Ti, 8.98.

^1H-NMR in n-hexane; δ (ppm) 0.44 [s, 18H, $(Me_3Si)_2N$], 0.33 [s, 9H, Me_3SiN], 0.28 [s, 9H, Me_3SiN].

Mass Spectrum (70 eV) m/Z (assignment, relative intensity %) 534 [$(m)^+$, 15], 499 [$(m\text{-}Cl)^+$, 11], 461 [$(m\text{-}Me_3Si)^+$, 12], 427 [$(m\text{-}3Cl)^+$, 15], 357 [$(m\text{-}(Me_3Si)_2P)^+$, 27], 271 [$(Me_4Si_2TiCl_3)^+$, 17], 236 [$(Me_3SiNPTiCl_2)^+$, 20], 147 [$(Me_2SiPSiMe_2)^+$, 100], 118 [$(TiCl_2)^+$, 21], 73 [$(Me_3Si)^+$, 25].

Reaction of (1) with $SbCl_3$

The reaction of (**1**) with $SbCl_3$ was carried out in ether at −20°C and the color of the reaction mixture became reddish brown. The ^1H-NMR of the reaction mixture at room temperature showed major resonance signals at δ 0.40, 0.30, 0.24 and 0.18. The amount of Me_3SiCl (δ 0.40) was found to be one equivalent. The reaction mixture was evacuated thoroughly and the residue was heated to obtain a colorless distillate at 100°C/10^{-3} torr which was characterised as 3,5-dichloro-1,2-bis(trimethylsilyl)-4-bis(trimethylsilyl)-amino-1,2-diaza-3-phospha-4-amino-5-stiba-cyclopentane $(Me_3Si)_4N_4PSbCl_2$, (**5**).

Found: C, 25.05; H, 6.23; N, 9.67; Cl, 12.20; Sb, 21.32. $C_{12}H_{36}Cl_2N_4PSbSi_4$, Calc.: C, 25.17; H, 6.29; N, 9.79; Cl, 12.23; Sb, 21.50%.

^1H-NMR in Et_2O or n-hexane 0.26 [s, 18H, $(Me_3Si)_2N$], 0.21 [s, 9H, Me_3SiN], 0.13 [s, 9H, Me_3SiN].

^{31}P-NMR in C_6D_6 (H_3PO_4 external standard) 115.67 ppm.

IR-bands (cm^{-1}) 1050 ν(P-N), 945 ν(Sb-N), 525 ν(P-Cl), 390 ν(Sb-Cl). Mass Spectrum (70 eV) m/Z (assignment, relative intensity %) 572 [$(m)^+$, 6], 557 [$(m\text{-}Me)^+$, 18], 537 [$(m\text{-}Cl)^+$, 11], 499 [$(m\text{-}Me_3Si)^+$, 20], 485 [$(m\text{-}Me_3SiN)^+$, 15], 471 [$(m\text{-}Me_3SiN_2)^+$, 12], 365 [$(Me_3Si)_4N_3P^+$, 25], 309 [$m\text{-}(Me_3Si)_2N_2PSiMe_2{}^+$, 100], 247 [$(Me_3Si_3N)_2{}^+$, 35], 157 [$(SbCl)^+$, 18], 108 [$(Me_3SiCl)^+$, 18].

Reaction of (1) with $SnCl_4/SbCl_5$

The reaction of (**1**) with $SnCl_4$ ($SbCl_5$) was carried out in n-hexane at −50°C. The reaction mixture was protected from light. Immediately after addition, the reaction mixture became orange with a white precipitate at the bottom. Filtration of the mixture allowed isolation of the orange filtrate from the white solid which was found to be tin(II)chloride (antimony(III)chloride (39.5 mmol). The ^1H-NMR of the filtrate showed resonances at δ 0.48, 0.40 and 0.31. The signal at δ 0.40 was found to be two equivalents of Me_3SiCl. It was further confirmed from chloride estimation of the trapped Me_3SiCl. The residual orange thick liquid left behind on evacuation was further heated in vacuo to obtain a yellow liquid distilling at 70°C/10^{-3} torr, [(trimethylsilyl)azeno][bis(trimethylsilyl)-amino]phosphazene, $Me_3SiN{=}N\text{-}P{=}N\text{-}N(SiMe_3)_2$, (**6**) (Yield = 60%).

It is a yellow liquid, b.p. = 65°C/10^{-3} torr and is soluble in common organic solvents.

Found: C, 34.98; H, 8.70; N, 18.24; $C_9H_{27}N_4PSi_3$. Calc.: C, 35.29; H, 8.82; N, 18.30 %.

^1H-NMR in n-hexane, CCl_4 δ (ppm), 0.30 [d, $^5J_{H\text{-}P}$ = 0.9 Hz, 18H, $(Me_3Si)_2N$], 0.50 [s, 9H, Me_3SiN].

Mass Spectrum (70 eV) m/Z (assignment, relative intensity %) 306 [$(m)^+$, 7], 261 [$(m\text{-}3Me)^+$, 10], 247 [$(Me_3Si)_3N_2{}^+$, 61], 233 [$(m\text{-}Me_3Si)^+$, 15], 175 [$(m\text{-}Me_3SiSiMe_2)^+$, 7], 132 [$(m\text{-}(Me_3Si)_2N_2)^+$, 12], 87 [$(Me_3SiN)^+$, 10], 73 [$(Me_3Si)^+$, 100].

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