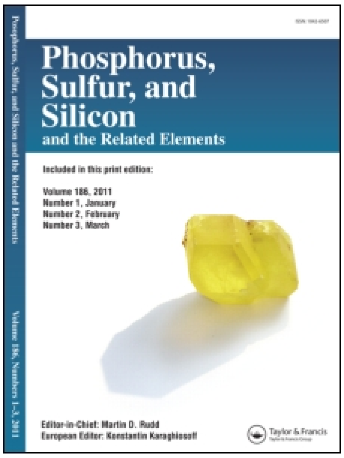

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FUNCTIONALIZATION OF THE CLASSICAL OXOANION VO^{3-}_4 BY BIS-SILYLATED PHOSPHAZENE LIGAND: SYNTHESES AND X-RAY STRUCTURE

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FUNCTIONALIZATION OF THE CLASSICAL OXOANION VO_4^{3-} BY BIS-SILYLATED PHOSPHAZENE LIGAND: SYNTHESES AND X-RAY STRUCTURE

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The reaction of the acyclic phosphazene ligand, $HN\{P(NMe_2)_2NSiMe_3\}_2$ (**1**) with NH_4VO_3 in 1:1 molar ratio resulted in the formation of an ionic species $N\{P(NMe_2)_2NH_2\}_2^+\{VO_4(SiMe_3)_2\}^-$ (**2**) in quantitative yield. The reaction shows the migration of silyl group from the terminal nitrogen atoms of the phosphazene ligand **1** to the oxygen of the vanadyl group. Compound **2** crystallizes as monomer in the solid state. The X-ray structure of the phosphazenium salt, $N\{P(NMe_2)_2NH_2\}_2^+Cl^-$ (**3**) has also been described which crystallizes as a polymeric zig-zag chain in the solid state.

Key words: Silylated phosphazene; X-ray.

INTRODUCTION

In the last two decades a substantial amount of work has been carried out on phosphazene derivatives.[1] We have started our investigation in this field in 1986 and synthesized cyclometallaphosphazene complexes by reacting the linear phosphazenium salt, $N\{PPh_2NH_2\}_2^+Cl^-$, with transition metal halides.[2] These complexes have transition metals as part of the ring skeleton.[3] Recently, we have reported on the syntheses of mono-, bis- and tris-silylated phosphazene ligands. These compounds have proven to be an important synthetic tool for cyclization reactions.[4] In recent years many complexes have been synthesized from our laboratory giving interesting precursors for the preparation of polymeric and "high tech" materials.[5] Herein, we report on the synthesis and X-ray structure of an ionic phosphazene derivative of vanadium and also the X-ray structure of a phosphazenium salt, $N\{P(NMe_2)_2NH_2\}_2^+Cl^-$ (**3**) which has been synthesized previously.[6]

RESULTS AND DISCUSSION

It is found that migration of a trimethylsilyl group takes place when the bis-silylated acyclic phosphazene ligand **1** is reacted with NH_4VO_3 in 1:1 molar ratio at room

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TABLE I
Crystal data and structure refinement for **2** and **3**

Compound	**2**	**3**
Colour	yellow-green	colourless
Formula	$C_{14}H_{46}N_7P_2Si_2V$	$C_8H_{28}ClN_7P_2$
Formula weight	545.64	319.77
Space group	$P\bar{1}$	C2/c
a / pm	1093.7(2)	1121.9(1)
b / pm	1145.8(2)	1798.3(3)
c / pm	1374.8(2)	955.0(1)
α / °	89.17(3)	90
β / °	72.09(3)	121.008(7)
γ / °	69.99(3)	90
U / nm^3	1.5324(5)	1.6517(3)
Z	2	4
F (000)	584	688
D_c / g cm^{-3}	1.182	1.286
Crystal size / mm	0.8 x 0.6 x 0.4	0.6 x 0.5 x 0.4
μ / mm^{-1}	0.535	0.423
No. data measured	4004	3273
No. unique data	3464	1083
2 θ range / °	8 - 45	8 - 45
Refined parameter	271	95
$R1$ ($I > 2\sigma(I)$) *	0.074	0.031
$wR2$ *	0.217	0.086
$g1$	0.1325	0.0163
$g2$	3.9771	2.4623
ρ / e nm^{-3}	1014	203

* $R1 = \Sigma \mid F_o - F_c \mid / \Sigma F_o$ and
$wR2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$

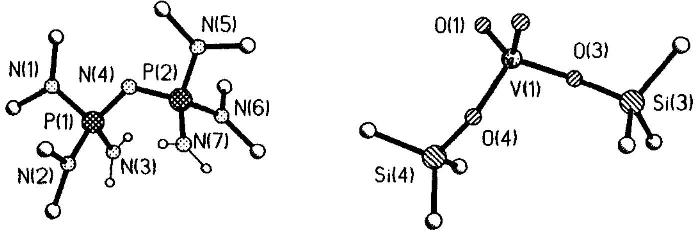

FIGURE 1 Molecular structure of **2**.

temperature resulting in a soluble ionic species. The reaction can be depicted as below.

$$\underset{\mathbf{1}}{HN\{P(NMe_2)_2NSiMe_3\}_2} + NH_4VO_3 \xrightarrow{\text{toluene}} \underset{\mathbf{2}}{N\{P(NMe_2)_2NH_2\}_2^+\{VO_4(SiMe_3)_2\}^-}$$

Compound **2** obtained as a yellow-green solid is fairly soluble in hydrocarbon solvents. **2** can be crystallized as needles by cooling its *n*-hexane solution at 0°C for two days.

In the IR spectra of compound **2**, the stretching frequencies for P—N have been found in the region 1114–1293 cm^{-1}. The band for V—O has been found at 948 cm^{-1}. The ^1H NMR spectra shows a multiplet for —NMe_2 protons (2.5–2.7 ppm) and a singlet for —$SiMe_3$ observed at 0.01 ppm. The signal for the —NH proton could not be found in the ^1H NMR. However, in the IR spectra, the NH stretching frequency has been found at 3301 cm^{-1}. ^{31}P NMR gives a singlet (20.9 ppm) with a small low field shift in comparison to the ligand. The occurrence of the singlet demonstrates the presence of one type of phosphorus nuclei in the molecule.

X-ray Structure of **2**

Suitable crystals of **2** were obtained by cooling its *n*-hexane solution to 0°C for ten days. The crystal data are given in Table I. Two $[N\{P(NMe_2)_2NH_2\}_2]^+$ cations and two $[(Me_3SiO)_2VO_2]^-$ anions (Figure 1) are connected by hydrogen-bridges i.e. NH——) functions. The polymeric structure pattern can be described as a ladder within alternating anions and cations (Figure 2). The bond lengths of V——O are short [V(1)—O(1): 163.6(3) pm, V(1)—O(2): 163.4(4) pm] compared to V——$OSiMe_3$ bond lengths [V(1)—O(3): 180.7(4) V(1)—O(4): 179.4 pm]. The

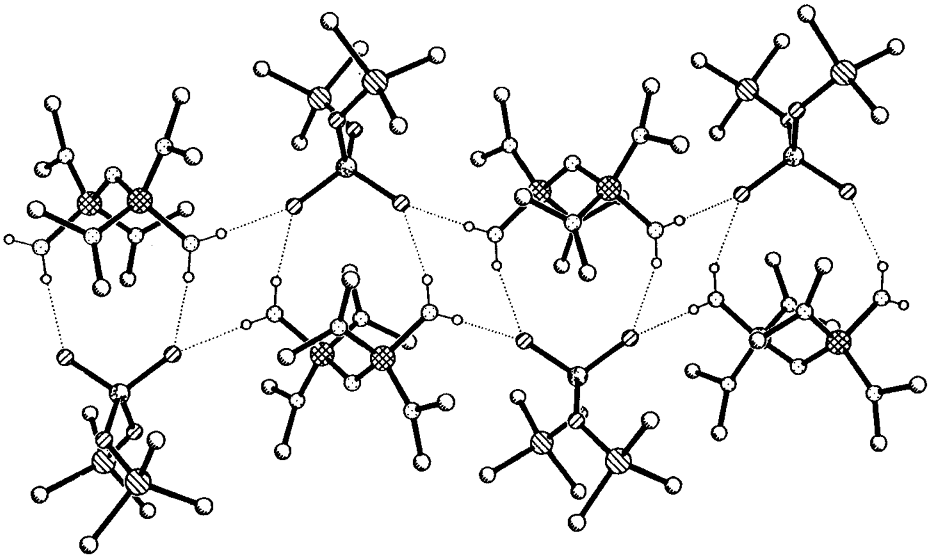

FIGURE 2 Ladder type formation in the crystal structure of **2**.

TABLE II

Bond lengths [pm] and angles [°] for **2**

V(1)-O(2)	163.4(4)	V(1)-O(1)	163.6(3)
V(1)-O(4)	179.4(4)	V(1)-O(3)	180.7(4)
O(3)-Si(3)	162.5(4)	O(4)-Si(4)	163.6(4)
P(1)-N(4)	158.4(4)	P(1)-N(3)	161.7(4)
P(1)-N(1)	163.6(5)	P(1)-N(2)	164.4(4)
N(4)-P(2)	157.4(4)	P(2)-N(7)	162.4(4)
P(2)-N(5)	163.8(4)	P(2)-N(6)	164.7(5)
O(2)-V(1)-O(1)	109.7(2)	O(2)-V(1)-O(4)	108.0(2)
O(1)-V(1)-O(4)	111.3(2)	O(2)-V(1)-O(3)	111.1(2)
O(1)-V(1)-O(3)	107.6(2)	O(4)-V(1)-O(3)	109.1(2)
Si(3)-O(3)-V(1)	139.4(2)	Si(4)-O(4)-V(1)	139.2(2)
N(4)-P(1)-N(3)	119.6(2)	N(4)-P(1)-N(1)	104.6(2)
N(3)-P(1)-N(1)	106.8(2)	N(4)-P(1)-N(2)	111.5(2)
N(3)-P(1)-N(2)	102.6(2)	N(1)-P(1)-N(2)	111.7(3)
P(2)-N(4)-P(1)	129.4(3)	N(4)-P(2)-N(7)	119.8(2)
N(4)-P(2)-N(5)	104.6(2)	N(7)-P(2)-N(5)	107.0(2)
N(4)-P(2)-N(6)	112.2(2)	N(7)-P(2)-N(6)	102.8(2)
N(5)-P(2)-N(6)	110.2(3)		

TABLE III

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **2**. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
V(1)	54(1)	7432(1)	1983(1)	26(1)
O(1)	279(4)	8522(3)	1242(3)	38(1)
O(2)	-152(4)	6356(3)	1351(3)	42(1)
O(3)	-1444(4)	8162(4)	3089(3)	46(1)
Si(3)	-2525(2)	7775(1)	4020(1)	39(1)
C(31)	-4025(7)	7841(7)	3612(6)	61(2)
C(32)	-3104(8)	8933(6)	5146(5)	57(2)
C(33)	-1689(9)	6185(6)	4347(6)	70(2)
O(4)	1510(4)	6701(4)	2405(3)	44(1)
Si(4)	2672(2)	7066(1)	2717(1)	37(1)
C(41)	4101(6)	6988(6)	1527(5)	53(2)
C(42)	3320(7)	5900(7)	3565(5)	58(2)
C(43)	1896(9)	8671(7)	3410(6)	65(2)
P(1)	11201(1)	7753(1)	-1781(1)	28(1)
N(1)	12043(5)	8047(5)	-2907(4)	43(1)
C(11)	11510(8)	8460(9)	-3719(5)	72(2)
C(12)	13366(7)	8218(8)	-3036(5)	64(2)
N(2)	12132(4)	6485(4)	-1405(3)	33(1)
C(21)	12441(6)	5280(5)	-1961(5)	45(2)
C(22)	12994(6)	6424(5)	-790(5)	46(2)
N(3)	11018(5)	8839(4)	-952(3)	33(1)
N(4)	9885(5)	7599(4)	-1933(3)	35(1)

TABLE III (Continued)

	x	y	z	U(eq)
P(2)	8625(1)	7392(1)	-1117(1)	28(1)
N(5)	7725(5)	7140(4)	-1794(3)	38(1)
C(51)	6440(7)	6949(7)	-1247(5)	60(2)
C(52)	8305(7)	6612(7)	-2846(5)	59(2)
N(6)	7686(5)	8618(4)	-269(3)	40(1)
C(61)	7337(7)	9837(5)	-663(5)	49(2)
C(62)	7009(6)	8625(5)	795(4)	45(1)
N(7)	8885(5)	6253(4)	-400(3)	33(1)

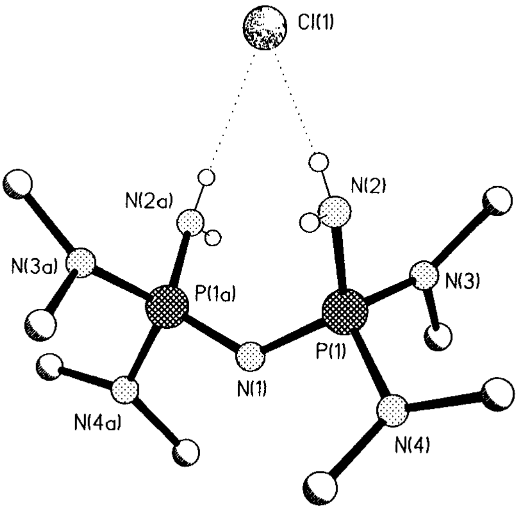

FIGURE 3 Molecular structure of **3**.

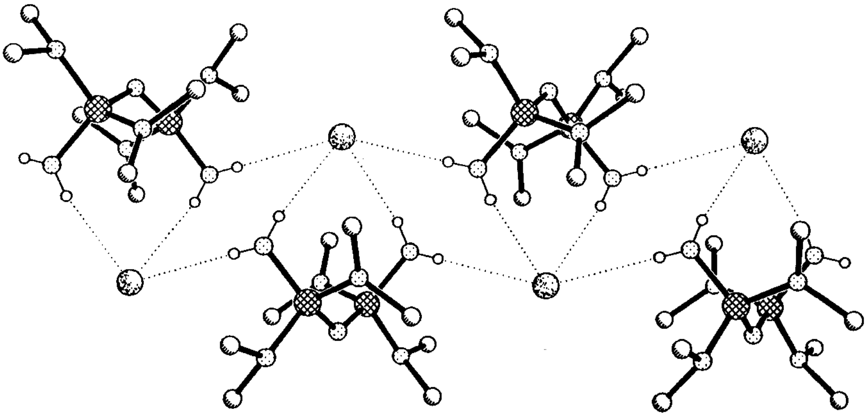

FIGURE 4 Plot showing polymeric zig-zag chain in **3**.

TABLE IV

Selected bond lengths [pm] and angles [°] for **3**

P(1)-N(1)	157.47(13)	P(1)-N(2)	161.7(2)
P(1)-N(3)	163.1(2)	P(1)-N(4)	164.3(2)
N(1)-P(1)#1	157.47(13)		
N(1)-P(1)-N(2)	120.27(11)	N(1)-P(1)-N(3)	111.16(7)
N(2)-P(1)-N(3)	103.40(12)	N(1)-P(1)-N(4)	104.34(12)
N(2)-P(1)-N(4)	107.29(12)	N(3)-P(1)-N(4)	110.24(10)
P(1)-N(1)-P(1)#1	131.7(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+1/2

TABLE V

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **3**. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Cl(1)	10000	-956(1)	2500	35(1)
P(1)	8647(1)	1205(1)	2319(1)	22(1)
N(1)	10000	1563(2)	2500	26(1)
N(2)	8761(2)	505(2)	3445(3)	28(1)
N(3)	7614(2)	903(1)	464(2)	26(1)
N(4)	7905(2)	1887(1)	2735(2)	29(1)
C(1)	6606(2)	309(2)	-11(3)	39(1)
C(2)	7391(3)	1372(2)	-903(3)	34(1)
C(3)	8747(3)	2405(2)	4063(3)	36(1)
C(4)	6558(2)	1732(2)	2578(3)	40(1)

important bond lengths and angles are given in Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters for **2** are given in Table III.

X-ray Structure of $N\{P(NMe_2)_2NH_2\}_2^+Cl^-$ (**3**)

Suitable crystals of **3** for X-ray measurements were obtained from its toluene solution at 0°C. The crystal data are given in Table I. The structure can be described as a polymeric zig-zag chain in which chloride anions are connected by hydrogen bridges to —NH functions of $[N\{P(NMe_2)_2NH_2\}_2]^+$ cations (Figures 3 and 4). A crystallographic two-fold axis is going through each chloride anion and the central nitrogen atom of each cation which results in the symmetric bonding pattern. The important bond lengths and angles for **3** are given in Table IV. Atomic coordinates and equivalent isotropic displacement parameters for **3** are given in Table V.

EXPERIMENTAL

All experiments were carried out strictly under moisture and oxygen-free nitrogen atmosphere. Solvents were dried and distilled prior to use. NH_4VO_3 was obtained from Aldrich and phosphazenium salt, $N\{P(NMe_2)_2NH_2\}_2^+Cl^-$ (**3**) was prepared as described in the literature.[6]

^1H and ^{31}P NMR spectra were recorded by means of a Bruker AM 250 instrument using TMS and 85% H_3PO_4 as an external standard, respectively. Infrared spectra were recorded on Bio-Rad FTS 7 spectrophotometer. Mass spectrometric analyses were performed with a Finnigan MAT 8230 instrument.

X-Ray Measurements. The intensities for both structures were collected on a Stoe-Siemens AED instrument with graphite-monochromated MoKα radiation ($\lambda = 71.073$ pm). Data were collected from oil coated rapidly-cooled crystals at $-120°C$ with a profile-fitted method.[7] The structures were solved by direct methods[8] and refined by Full-matrix-least-squares procedures against F^2.[9] All non-hydrogen atoms were refined anisotropically and the hydrogen positions were set geometrically with the exception of the N-bonded hydrogen in **3**, which were refined free. A weighting scheme of the form $w^{-1} = \sigma^2(F_0^2) + (g1 \cdot P)^2 + g2 \cdot P$ with $P = (F_0^2 + 2F_c^2)/3$ was introduced.[10]

Synthesis of $N\{P(NMe_2)_2NH_2\}_2^+\{VO_4(SiMe_3)_2\}^-$ (**2**). 1.0 g (0.24 mmol) of **1** and 0.3 g (0.24 mmol) of NH_4VO_3 were mixed in a flask with 50 ml of toluene. The contents were heated below the refluxing temperature for 2 h. A clear yellow-green solution was obtained. After evaporation of all the volatiles in vacuo, a yellow-green solid remained, mp 75°C. Anal. Calcd. for $C_{14}H_{46}N_7O_4P_2Si_2V$ (545.64): C, 30.78; H, 8.43; N, 17.96. Found: C, 30.5; H, 8.4; N, 17.8. MS (EI): m/z(%) = 541 (2) ($M^+ - 4H$), 509 (44) ($M^+ - 2O$). ^1H NMR ($CDCl_3$) δ 2.5–2.7 (m, —NMe_2), 0.09 (d, —$SiMe_3$) ppm; ^{31}P NMR ($CDCl_3$) δ 20.9 (s) ppm. IR (nujol): 1293 m, 1245 s, 1178 s, 1114 m, 1064 m, 986 vs, 948 vs, 839 s, 747 s, 638 s and 485 m cm^{-1}.

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10. Further details of the X-ray structural investigation can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, under quotation of the deposit number (CSD-57368), the authors and publication.