Insertion of Zinc into the Cyclophosphazene Skeleton: Synthesis and Structure of Six-Membered-Ring Complexes of Zinc

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Cyclozincaphosphazenes have been synthesized by the reaction of the bis-silylated ligand $HN[P(NMe_2)_2NSiMe_3]_2$ (**1**) with ZnR_2 (**2**) ($R = N(SiMe_3)_2$, Me, Et). These complexes have been characterized by IR, NMR, and mass spectroscopy and by X-ray crystal structural analysis. X-ray analysis of $[N\{P(NMe_2)_2NSiMe_3\}_2ZnN(SiMe_3)_2]$ (**3**) revealed that it crystallizes as a monomer in the solid state.

Introduction

In the last two decades transition metal complexes of acyclic phosphazenes have been investigated.[1-5] However, in recent years the syntheses of cyclometallaphosphazenes having transition metals as building blocks in ring skeletons have created an interesting new field of organometallic chemistry.[6-8] The studies on cyclic zinc amides have been quite limited.[9] In contrast, the syntheses of Zn–O and Zn–S heterocycles are known.[10] Recently, the synthesis and structure of a dimeric species, cyclozincdisilatriazene, were reported by our laboratory.[11] So, in view of these findings, it was considered worthwhile to synthesize the cyclophosphazene derivatives of zinc. Herein we report the synthesis of cyclophosphazenes containing zinc in the phosphazene ring and the X-ray structure of $[N\{P(NMe_2)_2NSiMe_3\}_2ZnN(SiMe_3)_2]$ (**3**).

Results and Discussion

The acyclic bis-silylated phosphazene moiety $HN[P(NMe_2)_2NSiMe_3]_2$ (**1**) reacts with $Zn[N(SiMe_3)_2]_2$, $ZnMe_2$, and $ZnEt_2$ in 1:1 molar ratios resulting in the formation of cyclic derivatives **3**–**5**, respectively. The pathways for the reaction can be depicted as follows:

$$\underset{\mathbf{1}}{HN[P(NMe_2)_2NSiMe_3]_2} + \underset{\substack{\mathbf{2}\\ R = N(SiMe_3)_2,\\ Me,\ Et}}{ZnR_2} \xrightarrow[-RH]{n\text{-hexane}} \underset{\substack{R = N(SiMe_3)_2\ (\mathbf{3}),\\ Me\ (\mathbf{4}),\ Et\ (\mathbf{5})}}{[N\{P(NMe_2)_2NSiMe_3\}_2ZnR]}$$

It is found that monocyclic complexes are the final products, even when the reactions are carried out in a 2:1 molar ratios and forcing conditions such as higher boiling solvents and long refluxing times are used. The versatility of the bonding mode of the ligand is noteworthy here; in complexes **3**–**5**, bidentate modes of attachment are observed, while in case of an alkaline earth metal, e.g. Ba, the mode of bonding is tridentate.[12]

Table I. Crystallographic Data for **3**

chem formula	$C_{20}H_{60}N_8P_2Si_4Zn$
space group	$C2/c$
fw	652.43
T (K)	153(1)
a (pm)	2023.3(4)
b (pm)	1173.2(3)
c (pm)	1695.3(4)
β (deg)	117.56(1)
V (nm^3)	3.568(1)
Z	4
crystal size	0.5 × 0.3 × 0.3
ρ_{calc} (g cm^{-3})	1.215
μ(Mo Kα) (cm^{-1})	0.936
F(000)	1408
2θ range (deg)	8–55
no. of reflns measd	4295
no. of unique reflns	4119
no. of reflns used	4118
R_{w2} (all data)[a]	0.109
R_1 ($F > 4\sigma(F)$)[a]	0.041
g_1	0.0685
g_2	2.556
no. of refined params	170
ρ (e nm^{-3})	896

[a] $R_1 = \sum|F_o - F_c|/\sum F_o$ and $R_{w2} = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

The electron impact mass spectra indicate the monomeric species in the gas phase; for **3** the ion at m/z 489 (62%, M – N(SiMe$_3$)$_2$) and for **5** the peak at m/z 490 (100%, M – Me) are found. The characteristic absorptions for P–N bonds were found between 1135 and 1289 cm^{-1} in the IR spectra of these compounds, indicating the formation of a phosphazene ring. ^{1}H NMR gives the characteristic resonance pattern, the signal for the methyl protons of NMe$_2$ appearing as a doublet (δ 2.6 ppm with J = 10.5 Hz), which is in accordance with the symmetry of the ring system. In the ^{31}P NMR spectra, one singlet is observed in each case with a downfield chemical shift, showing the equivalence of phosphorus nuclei in the molecule.

X-ray Structure of 3

Important bond lengths and angles are listed in Table III. Compound **3** crystallizes as a monomer in the solid state (Figure

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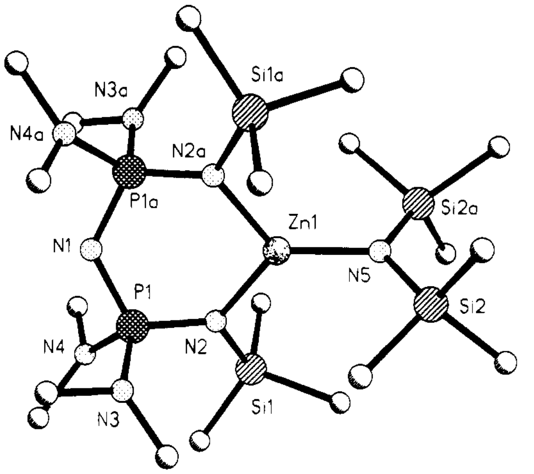

Figure 1. Molecular structure of $[N\{P(NMe_2)_2NSiMe_3\}_2ZnN(SiMe_3)_2]$ (3), giving the numbering scheme used in Tables II and III.

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **3**[a]

	x	*y*	*z*	*U*(eq)
Zn(1)	5000	1908.0(3)	2500	16.8(2)
P(1)	4226.3(3)	−333.1(5)	1820.7(3)	17.3(2)
Si(1)	3244.7(3)	1529.1(6)	1880.2(4)	23.3(3)
Si(2)	4957.2(4)	4201.9(6)	1578.7(5)	32.2(4)
N(1)	5000	−859(2)	2500	22.1(12)
N(2)	4083.6(9)	961(2)	2012.9(11)	18.2(8)
N(3)	4162.4(10)	−397(2)	813.0(12)	24.1(9)
N(4)	3566.8(10)	−1178(2)	1812.4(13)	26.6(9)
N(5)	5000	3545(2)	2500	24.6(14)
C(1)	4444(2)	−1381(2)	533(2)	35.4(14)
C(2)	3642(2)	297(2)	75(2)	34.1(14)
C(3)	3088(2)	−1907(2)	1084(2)	39.8(13)
C(4)	3593(2)	−1480(3)	2659(2)	39.0(14)
C(5)	2389.5(13)	702(3)	1158(2)	41.2(11)
C(6)	3278(2)	1664(3)	2995(2)	42.5(15)
C(7)	3092.7(14)	2960(2)	1350(2)	32.2(12)
C(8)	4287(2)	5420(3)	1177(2)	53(2)
C(9)	5865(2)	4826(3)	1744(2)	56(2)
C(10)	4661(2)	3136(3)	653(2)	40(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (pm) and Angles (deg) for **3**

Zn(1)–N(5)	192.1(3)	Zn(1)–N(2)	198.4(2)
P(1)–N(1)	157.78(13)	P(1)–N(2)	160.7(2)
P(1)–N(3)	165.4(2)	P(1)–N(4)	165.7(2)
Si(1)–N(2)	173.8(2)	Si(2)–N(5)	170.75(15)

N(2)–Zn(1)–N(2a)	111.91(10)	N(5)–Zn(1)–N(2)	124.04(5)
N(1)–P(1)–N(2)	115.62(11)	N(1)–P(1)–N(3)	108.25(8)
N(2)–P(1)–N(3)	108.47(10)	N(1)–P(1)–N(4)	107.16(11)
N(2)–P(1)–N(4)	110.34(10)	N(3)–P(1)–N(4)	106.63(10)
P(1)–N(1)–P(1a)	133.9(2)	P(1)–N(2)–Si(1)	126.32(11)
P(1)–N(2)–Zn(1)	113.10(9)	Si(1)–N(2)–Zn(1)	120.51(10)
Si(2)–N(5)–Si(2a)	126.4(2)	Si(2)–N(5)–Zn(1)	116.82(8)

1) with a crystallographic 2-fold axis through N(1), Zn(1), and N(5). A side view perpendicular to this axis (Figure 2) shows that the six-membered cyclozincadiphosphatriazene ring system is slightly twisted. The coordination at the zinc atom is trigonal planar, with a shorter Zn–N distance to N(5) [192.1(3) pm] and two equal distances to the phosphazene nitrogen atoms [N(2), N(2a): 198.4(2) pm]. For comparison the Zn–N distance in $O\{O[Me_2SiN(t\text{-}Bu)]_2Zn\}_2$ is 184.3 pm (mean).[13]

Experimental Section

All experiments were carried out strictly under a moisture- and oxygen-free nitrogen atmosphere or in vacuo by using Schlenk methods. All solvents were dried and distilled prior to use and stored under dry nitrogen. $ZnCl_2$, $ZnMe_2$, and $ZnEt_2$ were obtained from Strem Chemicals and Schering AG. $Zn[N(SiMe_3)_2]_2$ was prepared by the method described in the literature.[14]

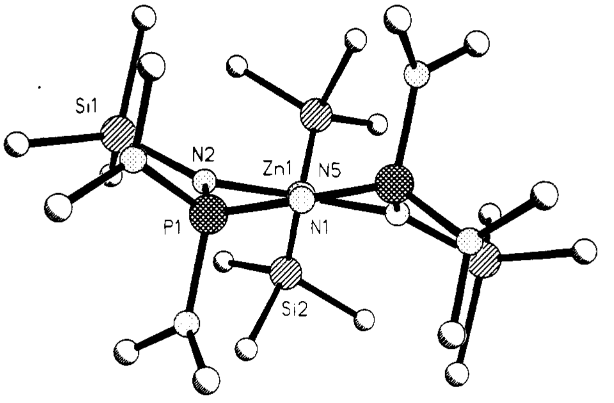

Figure 2. Side view showing the slightly twisted phosphazene ring system in **3**.

^1H, ^{29}Si, and ^{31}P NMR spectra were recorded by means of a Bruker AM 250 instrument using TMS (^1H, ^{29}Si) and 85% H_3PO_4 (^{31}P) as external standards. Infrared spectra were recorded on a Bio-Rad FTS 7 spectrophotometer. Mass spectrometric analyses were performed with a Finnigan MAT 8230 instrument.

Preparations. $[N\{P(NMe_2)_2NSiMe_3\}_2ZnN(SiMe_3)_2]$ (3). A solution of **1** (2.0 g, 4.7 mmol) in *n*-hexane (20 mL) was added dropwise to an *n*-hexane solution of $Zn[N(SiMe_3)_2]_2$ (1.8 g, 4.7 mmol), and the contents were heated just below reflux and stirred overnight. The evaporation of all volatiles under reduced pressure resulted in a spectroscopically pure white solid in quantitative yield. Mp: 115–120 °C. MS (EI, *m/z*): 489 (M − $N(SiMe_3)_2$, 62%). ^1H NMR ($CDCl_3$): δ 0.10 (s, 18H, $SiMe_3$), 0.20 (s, 18H, $NSiMe_3$), 2.50 ppm (d, 24H, NMe_2, *J* = 10.5 Hz). ^{31}P NMR ($CDCl_3$): δ 20.8 ppm (s). ^{29}Si NMR ($CDCl_3$ + toluene): δ −4.8, 2.3 ppm (s). IR (Nujol): 1287 b, 1244 s, 1196 s, 1145 m, 1104 s, 1064 m, 981 vs, 839 vs, 773 m, 724 s, 675 m, 627 s, 536 vs, 506 s cm^{-1}.

$[N\{P(NMe_2)_2NSiMe_3\}_2ZnMe]$ (4). A 2.0-g (4.7-mmol) sample of **1** was dissolved in *n*-hexane (20 mL). This solution was cooled by liquid air (−193 °C), and $ZnMe_2$ (0.45 g, 4.7 mmol) was added by condensation through a vacuum line. Finally the flask was allowed to warm to room temperature, and the mixture was stirred for about 18 h. All volatiles were evaporated under reduced pressure, giving a white solid product in quantitative yield. Mp: 103–105 °C. MS (EI, *m/z*): 490 (M − Me, 100%). ^1H NMR ($CDCl_3$): δ 0.1 (s, 18 H, $SiMe_3$), 0.3 (s, 3H, Me), 2.6 ppm (d, 24H, NMe_2, *J* = 10.5 Hz). ^{29}Si NMR ($CDCl_3$ + toluene): δ −4.5 ppm (s). ^{31}P NMR ($CDCl_3$): δ 22.3 ppm (s). IR (Nujol): 1287 m, 1245 s, 1170 s, 1135 m, 1101 m, 981 vs, 852 s, 835 s, 780 m, 726 s, 679 m, 637 m, 536 s, 505 m cm^{-1}. Anal. Calcd for $C_{15}H_{45}N_7P_2Si_2Zn$ (M_r 507.01): C, 35.5; H, 8.9; N, 19.3. Found: C, 34.8; H, 8.6; N, 18.5.

$[N\{P(NMe_2)_2NSiMe_3\}_2ZnEt]$ (5). A 2.0-g (4.7-mmol) sample of **1** and 0.58 g of $ZnEt_2$ (4.7 mmol) were used for the reaction. The experimental details were the same as for compound **4**. **5** was obtained as a white semisolid. MS (EI, *m/z*): 517 (M − 2H, 4%), 427 (M − ZnEt, 20%), 75 (−$PNMe_2$, 100%). ^1H NMR ($CDCl_3$): δ 0.05 (s, 18H, $SiMe_3$), 0.20 (m, 3H, CH_3), 1.20 (t, 2H, CH_2), 2.60 ppm (d, 24H, NMe_2, *J* = 10.5 Hz). ^{31}P NMR ($CDCl_3$): δ 22.0 ppm (s). IR (Nujol): 1289 m, 1245 vs, 1180 s, 1135 m, 1097 m, 981 vs, 851 m, 835 s, 781 m, 727 s, 679 m, 628 m, 537 s, 505 s cm^{-1}.

X-ray Measurements of 3. The intensities for the structure were collected on a Stoe-Siemens AED instrument with graphite-monochromated Mo Kα radiation (λ = 71.073 pm). Data were collected from an oil-coated rapidly-cooled crystal at −120 °C with a profile-fitted method.[15] The structure was solved by Direct Methods[16] and refined by full-matrix least-squares procedures against F^2.[17] All non-hydrogen atoms were refined anisotropically, and the hydrogen positions were set geometrically.

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A weighting scheme of the form $w^{-1} = \sigma(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$ was introduced.

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Supplementary Material Available: Tables of crystallographic parameters, hydrogen atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles for **3** (4 pages). Ordering information is given on any current masthead page.