Articles

Novel Organo-Substituted Cyclophosphazenes via Reaction of a Monohydro Cyclophosphazene and Acetyl Chloride

G. Bosscher, A. Meetsma, and J. C. van de Grampel*

Department of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received April 29, 1996[⊗]

A new olefin-substituted tetrachlorocyclotri-λ^5-phosphazene $(NPCl_2)_2NP^iPr\{C[OC(O)Me]{=}CH_2\}$ (**4**) and an unique bicyclo-λ^5-triphosphazene $[(NPCl_2)_2NP^iPr]_2C(OH)Me$ (**5**) have been prepared from the reaction of MeC(O)Cl and $(NPCl_2)_2NP^iPrH$ in the presence of Et_3N. Exclusive formation of **4** could be achieved by using an excess of both Et_3N and MeC(O)Cl. The phosphazene rings in **5** are bridged by one carbon atom. The presence of this C(OH)Me bridge induces an asymmetric environment which renders the isopropyl ligands no longer equivalent under NMR conditions. Crystals of **4** are monoclinic, space group $P2_1/n$, with $a = 13.158(1)$ Å, $b = 9.555(1)$ Å, $c = 14.859(1)$ Å, $\beta = 115.502(6)°$, $V = 1686.1(3)$ Å^3, and $Z = 4$. Crystals of **5** are monoclinic, space group $P2_1/c$, with $a = 13.255(2)$ Å, $b = 12.050(2)$ Å, $c = 16.280(2)$ Å, $\beta = 98.91(1)°$, $V = 2568.8(7)$ Å^3, and $Z = 4$.

Introduction

Olefin-substituted chlorophosphazene rings have proven to be very suitable for radical (co)polymerization reactions resulting in hybrid inorganic−organic polymers.[1−4] In contrast to the well-known polyphosphazenes in which the backbone consists of alternating phosphorus and nitrogen atoms, these polymers have a carbon chain backbone with the cyclophosphazene rings as side groups. Due to their special architecture these systems exhibit interesting thermal properties.[1] Moreover PCl_2 groups can be used in further substitution reactions.[5]

From the literature it is known that hydro phosphazenes act as nucleophiles in addition reactions due to their polar phosphorus−hydrogen bond. By utilizing this route, it is possible to link phosphazene rings to a wide variety of functional groups as olefins, thiocyanates, ketones, and aldehydes.[6] In all cases the phosphorus attacks at the electron deficient carbon center. Alternatively, hydro phosphazenes can react with alkyllithium reagents to generate phosphazeno anions.[7]

In search of novel routes for the synthesis of chlorocyclotriphosphazene precursors with polymerizable groups linked to the inorganic ring by a phosphorus−carbon bond, we have investigated the use of hydro cyclotriphosphazenes. In our approach we allowed a monohydro phosphazene, $(NPCl_2)_2NP^iPrH$ (**1**), to react with MeC(O)Cl. This resulted in the formation of a new 1,1-disubstituted alkene $(NPCl_2)_2NP^iPr\{C[OC(O)Me]{=}CH_2\}$ (**4**). In addition a compound with formula $[(NPCl_2)_2NP^iPr]_2C(OH)Me$ (**5**) could be isolated, which is the first representative of a new class of compounds in which two cyclophosphazene rings are bridged by one carbon atom.

In this paper the synthesis and crystal structures of **4** and **5** will be discussed. The polymerization and thermal behavior of **4** will be described elsewhere.

Experimental Section

Materials and Instrumentation. All reactions were carried out in an atmosphere of dry oxygen-free nitrogen using standard Schlenck techniques. Hexachlorocyclotri-λ^5-phosphazene was kindly provided by Shin Nisso Kako Co. and purified by recrystallization from *n*-hexane (Merck). 1-Isopropyltetrachlorocyclotri-λ^5-phosphazene (**1**) was synthesized according to the literature.[8] Triethylamine (Merck) was dried on KOH and distilled from KOH under nitrogen. Acetyl chloride (98%, Janssen) was used as received. Tetrahydrofuran (THF, Janssen) was distilled from sodium/benzophenone prior to use. All other solvents were purified and dried by conventional methods.

NMR spectra were recorded on a Varian Gemini-200 spectrometer operating at 199.98 (^{1}H), 50.29 (^{13}C) and 80.95 (^{31}P) MHz. $CDCl_3$ (^{1}H and ^{13}C) was used as internal standard. $(NPCl_2)_3$ in $CDCl_3$ was applied as external reference for ^{31}P spectra. High temperature ^{1}H NMR experiments were performed on a Varian Unity 500 spectrometer operating at 499.862 MHz. Elemental analyses were carried out at the Microanalytical Department of the University of Groningen.

Preparation of $N_3P_3Cl_4(i\text{-}C_3H_7)C(OC(O)CH_3){=}CH_2$ (4). Acetyl chloride (0.9 mL, 12 mmol) was added slowly to a stirred solution of 1.0 g (3 mmol) of **1** and 1.7 mL (12 mmol) of Et_3N in 50 mL of diethyl ether, cooled to 0 °C. The reaction mixture was then stirred for 18 h and the temperature was allowed to rise to room temperature. The precipitated salts were removed by filtration. The yellow ether solution was washed with 25 mL of demineralized water, dried on $MgSO_4$, and stirred with activated carbon. The ether was evaporated under reduced pressure and the crude product was distilled (bp 140 °C/0.1 mmHg) to yield 0.75 g (1.85 mmol, 59%) of a colorless oil, which became a solid upon standing with mp 34.0−36.0 °C. Anal. Calcd for $C_7H_{12}Cl_4N_3O_2P_3$: C, 20.76; H, 2.99; Cl, 35.02. Found: C, 21.01; H, 3.07;

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

(1) Allen, C. W. *Trends Polym. Sci.* **1994**, *2*, 342.
(2) Allen, C. W.; Brown, D. E.; Hayes, R. F.; Tooze, R.; Poyser, G. L. In *Inorganic and Organometallic Polymers II*; Wisian-Neilson, P., Allcock H. R., Wynne, K. J., Eds.; ACS Symposium Series 572; American Chemical Society: Washington, DC, 1994, p 389.
(3) Inoue, K.; Kaneyuki, S.; Tanigaki, T. *J. Polym. Sci. Part A: Polym. Chem.* **1992**, *30*, 145.
(4) Inoue, K.; Nakahara, H.; Tanigaki, T. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 61.
(5) Allcock, H. R. *Phosphorus-Nitrogen Compounds, Cyclic, Linear, and High Polymeric Systems*; Academic Press: New York and London, 1972.
(6) Schmidpeter, A.; Blanck, K.; Smetana, H.; Weinand, C. *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 1.
(7) Schmidpeter, A.; Högel, J.; Ahmed, F. R. *Chem. Ber.* **1976**, *109*, 1911.
(8) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.

S0020-1669(96)00466-1 CCC: $12.00

Cl, 34.85. ^{1}H NMR ($CDCl_3$): 1.19 (dd, 6 H, Me, $^3J_{PH}$ = 20.7 Hz, $^3J_{HH}$ = 7.1 Hz), 2.07 (m, 1 H, CH), 2.23 (s, 3 H, C(O)Me), 5.81 (dd, 1 H, =CH_2, $^2J_{HH}$ = 2.4 Hz, $^3J_{PH}$ = 31.7 Hz), 5.99 (dd, 1 H, =CH_2, $^2J_{HH}$ = 2.4 Hz, $^3J_{PH}$ = 10.5 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): 14.0 (Me), 20.8 (C(O)Me), 28.4 (dt, CH, $^1J_{PC}$ = 97.7 Hz, $^3J_{PC}$ = 4.0 Hz), 119.2 (d, =CH_2, $^2J_{PC}$ = 20.4 Hz), 148.2 (d, C=, $^1J_{PC}$ = 146.5 Hz), 167.7 (C(O)). ^{31}P{^{1}H} NMR ($CDCl_3$): A_2B type, 19.4 (PCl_2), 30.5 ($POrg_2$), $^2J_{PP}$ unresolved.

Preparation of $[N_3P_3Cl_4(i\text{-}C_3H_7)]_2CCH_3OH$ (5). A solution of 0.16 g (0.5 mmol) of **1** and 50 μL (0.36 mmol) of Et_3N in 10 mL of THF was cooled to −40 °C. Acetyl chloride (40 μL, 0.56 mmol) was added quickly to the stirred solution, and the temperature was allowed to rise slowly to room temperature. After the mixture was stirred for 18 h at that temperature, the solvent was evaporated, and diethyl ether was added to precipitate the salts. After filtration the ether was removed in vacuo, and the crude product, which consisted of **1**, **4**, and **5**, was further purified by flash chromatography (silica gel 60 mesh 230−400; eluant hexane/THF 85:15; elution order **1**, **5**, and **4**). Yield: 0.05 g (0.07 mmol, 29%) of a white solid with mp 174−176 °C. Anal. Calcd for $C_8H_{18}Cl_8N_6OP_6$: C, 14.05; H, 2.65; Cl, 41.48. Found: C, 13.91; H, 2.74; Cl, 41.47. ^{1}H NMR ($CDCl_3$): 1.27 (dd, 6 H, Me, $^3J_{PH}$ = 20.0 Hz, $^3J_{HH}$ = 7.1 Hz), 1.33 (dd, 6 H, Me, $^3J_{PH}$ = 19.3 Hz, $^3J_{HH}$ = 7.1 Hz), 1.80 (t, 3 H, Me, $^3J_{PH}$ = 15.1 Hz), 2.50 (b, 1 H, COH), 2.65 (m, 2 H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$): 16.2 (CHMe), 16.6 (CHMe), 20.6 (C(OH)Me), 29.3 (dt, CHMe , $^1J_{PC}$ = 83.6 Hz, $^3J_{PC}$ = 3.0 Hz), 29.3 (t, COHMe , $^1J_{PC}$ = 64.5 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): A_2B type, 19.0 (PCl_2), 48.2 ($POrg_2$), $^2J_{PP}$ unresolved.

X-ray Structure Analysis. Transparent colorless crystals of **4** (0.07 × 0.38 × 0.52 mm) and **5** (0.10 × 0.12 × 0.15 mm) were used for characterization and data collection. The crystals were glued on a top of a glass fiber and cooled to 130 K by using an on-line liquid nitrogen cooling system[9] mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a MicroVAX-2000 computer. Unit cell dimensions and the orientation matrix were determined from a least-squares treatment of the setting angles of 22 centered high-order reflections from various parts of reciprocal space in the range $16.6 < \theta < 24.3°$ for **4** and of 22 reflections in the range $14.4 < \theta < 15.4°$ for **5** in four alternative settings,[10] respectively. The spacegroup was derived from the observed systematic absences. Reduced cell calculations did not indicate any higher metric lattice symmetry,[11] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[12,13] Crystal and/or instrumental instability was monitored by measurement of the intensities of three reference reflections that were collected after every 3 h of X-ray exposure time; there was no indication of crystal decomposition. Intensity data were corrected for Lorentz and polarization effects and scale variation, but not for absorption. Variances $\sigma^2(I)$ were calculated based on counting statistics and the term (P^2I^2) where P (=0.020 and 0.030, respectively) is the instability constant as derived from the excess variance in the reference reflections.[14] Equivalent reflections were averaged and stated observed if satisfying the $I \geq 2.5\,\sigma(I)$ criterion of observability. Pertinent numerical data on the structure determinations are given in Table 1.

The structure was solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[15] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (CRYLSQ),[16] minimizing the function $Q = \sum_h[w(|F_o| - k|F_c|)^2]$. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, which coordinates and isotropic thermal displacement parameters were refined. For **4** three strong, low-order reflections were excluded from the data set in the final refinement. The crystal of **5** exhibited some secondary extinction for which the F values were corrected by refinement of an empirical isotropic extinction parameter.[17] Final refinements on F were carried out by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms. Final difference Fourier maps did not show any significant residual features. Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for the non-hydrogen atoms are given in Table 2. Selected molecular geometry data are collected in Table 3. Scattering factors were taken from Cromer and Mann.[18] Anomalous dispersion factors were taken from Cromer and Liberman[19] and included in F_c. All calculations were carried out on the HP9000/735 computer (**4**) and on the CDC-Cyber 962-31 computer (**5**) at the University of Groningen with the program packages XTAL,[20] PLATON,[21] (calculation of geometric data), and a locally modified version of the program PLUTO[22] (preparation of illustrations).

Table 1. Crystallographic Data for **4** and **5** and Details of the Structure Determination

	4	**5**
chem formula	$C_7H_{12}Cl_4N_3O_2P_3$	$C_8H_{18}Cl_8N_6OP_6$
fw	404.92	683.74
space group	$P2_1/n$	$P2_1/c$
a, Å	13.158(1)	13.255(2)
b, Å	9.555(1)	12.050(2)
c, Å	14.859(1)	16.280(2)
β, deg	115.502(6)	98.91(1)
V, Å^3	1686.1(3)	2568.8(7)
Z	4	4
λ, Å	0.71073	0.71073
ρ_{calcd}, gcm^{-3}	1.595	1.768
$F(000)$, electrons	816	1368
μ(Mo Kα), cm^{-1}	9.9	12.7
no. of data: tot., unique	7460, 3669	6204, 5236
no. of data obsd ($I \geq 2.5\sigma(I)$)	3283	4427
no. of refined params	210	335
R, R_w[a]	0.048, 0.055	0.040, 0.055

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum(w|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

Results and Discussion

Reaction Mechanism. The reaction of *gem*-isopropyltetrachlorocyclo-λ^5-triphosphazene (**1**) with an excess of acetyl chloride and Et_3N in diethyl ether at ambient temperature yields *gem*-isopropyl-2-(α-acetoxyvinyl)tetrachlorocyclotri-λ^5-phosphazene (**4**) as the only product. This could be determined from ^{31}P NMR spectra of crude reaction mixtures. Compound **4**, which is sensitive to hydrolysis (formation of acetic acid), could be fully characterized by NMR methods and an X-ray structure determination (Figure 1).

To explain the formation of **4**, two points should be considered. First, the presence of the α-acetoxyvinyl group directly bonded to the organo-substituted phosphorus atom suggests that two acid chloride molecules are involved in the reaction with **1**. Second, it is known that hydro cyclophos-

(9) van Bolhuis, F. *J. Appl. Crystallogr*. **1971**, *4*, 263.
(10) Boer, J. L. de; Duisenberg, A. J. *Acta Crystallogr*. **1984**, *A40*, C410.
(11) Spek, A. L. *J. Appl. Crystallogr*. **1988**, *21*, 578.
(12) Le Page, Y. *J. Appl. Crystallogr*. **1987**, *20*, 264.
(13) Le Page, Y. *J. Appl. Crystallogr*. **1988**, *21*, 983.
(14) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr*. **1975**, *A31*, 245.
(15) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.
(16) Olthof-Hazekamp, R. In *CRYLSQ, XTAL3.0 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds., Universities of Western Australia, Geneva and Maryland: Nedlands, Australia, Geneva, and College Park, MD, 1992.
(17) Zachariasen, W. H. *Acta Crystallogr*. **1967**, *23*, 558.
(18) Cromer, D. T.; Mann, J. B. *Acta Crystallogr*. **1968**, *A24*, 321.
(19) Cromer, D. T.; Liberman, D. *J. Chem. Phys*. **1970**, *53*, 1891.
(20) *XTAL3.0 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland: Nedlands, Australia, Geneva, and College Park, MD, 1992.
(21) Spek, A. L. *Acta Crystallogr*. **1990**, *A46*, C34.
(22) Meetsma, A. Extended version of the program PLUTO. University of Groningen, The Netherlands. (unpublished), 1992.
(23) Johnson, C. K. ORTEP. Report ORNL-3794; Oak Ridge National Laboratory: TN, 1965.

Table 2. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Displacement Parameters for Non-H Atoms with Esd's in Parentheses

	x	*y*	*z*	U_{eq} (Å^2)[a]
		a. Compound **4**		
Cl(1)	0.04227(10)	0.50376(14)	0.21940(8)	0.0437(4)
Cl(2)	−0.07048(9)	0.53572(14)	0.36081(9)	0.0422(4)
Cl(3)	0.2369(1)	0.17789(12)	0.58203(9)	0.0415(3)
Cl(4)	0.3075(1)	0.18611(12)	0.40898(9)	0.0401(3)
P(1)	0.08018(8)	0.49808(11)	0.36579(7)	0.0237(3)
P(2)	0.24046(8)	0.30983(10)	0.47937(8)	0.0244(3)
P(3)	0.28848(8)	0.59341(10)	0.50292(7)	0.0214(2)
O(1)	0.4099(2)	0.6579(3)	0.6935(2)	0.0283(8)
O(2)	0.3371(3)	0.5023(4)	0.7631(3)	0.0508(11)
N(1)	0.1147(3)	0.3429(4)	0.4044(3)	0.0312(11)
N(2)	0.3239(3)	0.4322(3)	0.5301(2)	0.0263(9)
N(3)	0.1623(3)	0.6203(3)	0.4188(2)	0.0267(10)
C(1)	0.3883(3)	0.6753(5)	0.4673(3)	0.0283(11)
C(2)	0.3814(4)	0.6120(6)	0.3704(4)	0.0390(14)
C(3)	0.3710(5)	0.8341(5)	0.4592(4)	0.0408(16)
C(4)	0.3021(3)	0.6786(4)	0.6151(3)	0.0257(11)
C(5)	0.2249(4)	0.7569(5)	0.6240(4)	0.0388(14)
C(6)	0.4175(4)	0.5611(4)	0.7637(3)	0.0299(12)
C(7)	0.5373(4)	0.5412(6)	0.8377(4)	0.0399(14)
		b. Compound **5**		
Cl(1)	0.18384(9)	0.11955(9)	0.15765(8)	0.0349(3)
Cl(2)	0.37362(9)	0.10476(9)	0.29228(7)	0.0332(3)
Cl(3)	0.57397(8)	0.33030(9)	0.15004(6)	0.0276(3)
Cl(4)	0.40452(9)	0.36518(9)	−0.00072(6)	0.0312(3)
Cl(5)	−0.01909(8)	0.90854(8)	0.07406(6)	0.0248(3)
Cl(6)	−0.13873(8)	0.69550(8)	0.09876(6)	0.0233(3)
Cl(7)	0.07016(8)	0.70610(8)	0.39875(5)	0.0216(3)
Cl(8)	0.15515(8)	0.92481(7)	0.33909(6)	0.0245(3)
P(1)	0.30201(8)	0.43898(7)	0.23029(6)	0.0154(3)
P(2)	0.30388(8)	0.21020(8)	0.20659(6)	0.0185(3)
P(3)	0.42120(8)	0.34205(8)	0.12260(6)	0.0186(3)
P(4)	0.18587(7)	0.66160(8)	0.17165(6)	0.0142(3)
P(5)	−0.00355(7)	0.76466(7)	0.13805(6)	0.0142(3)
P(6)	0.10571(8)	0.77543(7)	0.29541(6)	0.0144(3)
O(1)	0.1098(2)	0.4969(2)	0.23919(18)	0.0220(9)
N(1)	0.2679(3)	0.3145(2)	0.2506(2)	0.0202(10)
N(2)	0.3754(3)	0.2240(3)	0.1378(2)	0.0255(10)
N(3)	0.3829(2)	0.4471(2)	0.16512(19)	0.0189(10)
N(4)	0.0834(2)	0.6945(2)	0.10969(18)	0.0177(9)
N(5)	0.0021(2)	0.7946(2)	0.23418(18)	0.0172(9)
N(6)	0.1957(2)	0.7134(2)	0.26418(18)	0.0160(9)
C(1)	0.3565(3)	0.5055(3)	0.3265(2)	0.0198(11)
C(2)	0.4623(4)	0.4559(4)	0.3554(3)	0.0288(16)
C(3)	0.2898(4)	0.4964(4)	0.3943(3)	0.0291(16)
C(4)	0.1818(3)	0.5077(3)	0.1826(2)	0.0176(11)
C(5)	0.1427(4)	0.4528(4)	0.0997(3)	0.0264(14)
C(6)	0.2950(3)	0.7109(3)	0.1277(2)	0.0216(12)
C(7)	0.2865(4)	0.8386(4)	0.1240(3)	0.0265(14)
C(8)	0.3020(4)	0.6636(4)	0.0418(3)	0.0281(14)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j \mathbf{U}_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table 3. Selected Data on the Geometry of **4** and **5**, with Standard Deviations in the Last Decimal Place Given in Parentheses

a. Compound **4**

Bond Lengths (Å)

Cl(1)−P(1)	2.012(2)	P(3)−C(1)	1.793(5)
Cl(2)−P(1)	1.985(2)	P(3)−C(4)	1.793(4)
Cl(3)−P(2)	1.995(2)		
Cl(4)−P(2)	2.016(2)		
P(1)−N(1)	1.584(4)	P(3)−N(2)	1.610(3)
P(1)−N(3)	1.555(3)	P(3)−N(3)	1.612(4)
P(2)−N(1)	1.579(4)		
P(2)−N(2)	1.558(3)		
O(1)−C(4)	1.409(5)	O(1)−C(6)	1.365(5)
C(4)−C(5)	1.313(7)		
O(2)−C(6)	1.194(7)	C(6)−C(7)	1.496(8)
C(1)−C(2)	1.528(7)	C(1)−C(3)	1.531(7)

Bond Angles (deg)

Cl(1)−P(1)−Cl(2)	100.14(7)	C(1)−P(3)−C(4)	106.5(2)
Cl(3)−P(2)−Cl(4)	100.70(7)		
N(1)−P(1)−N(3)	119.4(2))	N(2)−P(3)−N(3)	115.9(2)
N(1)−P(2)−N(2)	119.8(2)		
P(1)−N(1)−P(2)	119.5(3)	P(1)−N(3)−P(3)	122.2(2)
P(2)−N(2)−P(3)	121.9(2)		
O(1)−C(6)−O(2)	122.7(4)	O(2)−C(6)−C(7)	126.5(4)
O(1)−C(6)−C(7)	110.8(4)		

b. Compound **5**

Bond Lengths (Å)

P(1)−C(1)	1.807(4)	P(4)−C(4)	1.865(4)
P(1)−C(4)	1.856(4)	P(4)−C(6)	1.811(4)
Cl(1)−P(2)	1.992(2)	Cl(5)−P(5)	2.017(1)
Cl(2)−P(2)	2.004(2)	Cl(6)−P(5)	1.990(1)
Cl(3)−P(3)	2.010(2)	Cl(7)−P(6)	1.999(1)
Cl(4)−P(3)	2.005(1)	Cl(8)−P(6)	2.008(1)
P(1)−N(1)	1.616(3)	P(4)−N(4)	1.611(3)
P(1)−N(3)	1.624(3)	P(4)−N(6)	1.617(3)
P(2)−N(1)	1.558(3)	P(5)−N(4)	1.556(3)
P(2)−N(2)	1.584(4)	P(5)−N(5)	1.596(3)
P(3)−N(2)	1.581(4)	P(6)−N(5)	1.584(3)
P(3)−N(3)	1.565(3)	P(6)−N(6)	1.558(3)
O(1)−C(4)	1.431(5)	C(4)−C(5)	1.520(6)
C(1)−C(2)	1.530(7)	C(6)−C(7)	1.543(6)
C(1)−C(3)	1.521(6)	C(6)−C(8)	1.526(6)

Bond Angles (deg)

C(1)−P(1)−C(4)	111.5(2)	C(4)−P(4)−C(6)	113.6(2)
Cl(1)−P(2)−Cl(2)	100.63(6)	Cl(5)−P(5)−Cl(6)	100.33(6)
Cl(3)−P(3)−Cl(4)	100.56(6)	Cl(7)−P(6)−Cl(8)	100.56(6)
N(1)−P(1)−N(3)	115.1(2)	N(4)−P(4)−N(6)	115.3(2)
N(1)−P(2)−N(2)	120.0(2)	N(4)−P(5)−N(5)	119.3(2)
N(2)−P(3)−N(3)	120.0(2)	N(5)−P(6)−N(6)	119.8(2)
P(1)−N(1)−P(2)	122.7(2)	P(4)−N(4)−P(5)	122.6(2)
P(2)−N(2)−P(3)	119.4(2)	P(5)−N(5)−P(6)	119.2(2)
P(1)−N(3)−P(3)	122.2(2)	P(4)−N(6)−P(6)	122.3(2)
P(1)−C(4)−P(4)	116.6(2)	O(1)−C(4)−C(5)	111.2(3)

phazenes can act as nucleophiles,[6,7] which implies that these compounds are capable to nucleophilic addition reactions at carbonyl functionalities.[24] For that reason it is very probably that the formation of an acetyl derivative (**2,** see Scheme 1) can be considered as the first step of the reaction sequence.

Due to the presence of the strong electron-withdrawing phosphazene ring in combination with the electronegative carbonyl group, the methyl protons in **2** are slightly acidic. Abstraction of hydrogen with a base results in the formation of the enolate intermediate **3.** Subsequent reaction of **3** with a second molecule of acetyl chloride leads to the formation of **4**.

To obtain some evidence for the reaction scheme proposed, **1** was allowed to react with 1.1 equiv of acetyl chloride and 0.7 equiv of Et_3N in THF at −40 °C. Under these reaction conditions the ^{31}P NMR spectrum of the crude reaction mixture showed that only a small quantity of **4** was formed together with a relatively large amount of another product with resonance signals at 48.2 and 19.0 ppm. These resonances could be assigned to the novel compound **5** in which two cyclophosphazene rings are bridged by one carbon atom. The bicyclo-λ^5-phosphazene was fully characterized by means of NMR (^{1}H, ^{13}C, and ^{31}P) and elemental analyses. Furthermore the structure of $N_6P_6Cl_8(i\text{-}C_3H_7)_2CCH_3OH$ was confirmed by an X-ray structure determination (Figure 2).

The formation of **5** follows the proposed mechanism and explains the influence of the amount of base and acetyl chloride on the reaction pathways. When excess Et_3N and acetyl chloride are used, the equilibrium between **2** and **3** is shifted to the right, and any **3** that is formed will react directly with acetyl chloride to give **4**. Moreover, the excess acetyl chloride will convert

(24) March, J. *Advanced Organic Chemistry; Reactions, Mechanism, and Structure*; 4th ed.; John Wiley and Sons: New York, Chichester, England, Brisbane, Australia, Toronto, Canada, and Singapore, 1992; p 879.

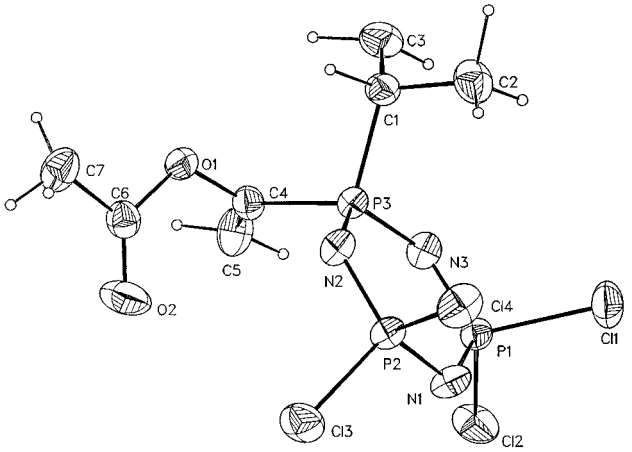
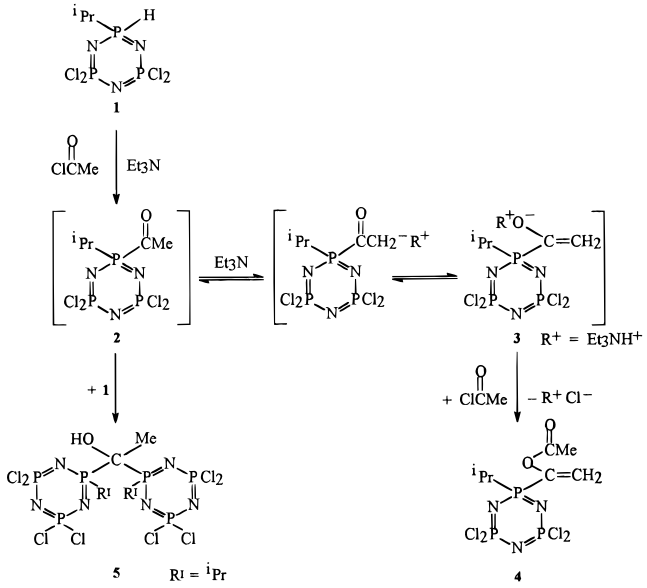


Figure 1. Perspective ORTEP[23] drawing of the non-hydrogen atoms of **4** with the atom labeling scheme for the non-hydrogen atoms. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids drawn to encompass 50% of the electron density; the hydrogen atoms are drawn with an arbitrary radius.

Scheme 1



all hydro phosphazene immediately into **2**. Consequently, there is no or very little **1** available for side reactions. This is in agreement with the observation that under these circumstances only resonance signals of **4** are found in the ^{31}P NMR spectrum of the crude reaction mixture and no traces of **5** can be detected. When an excess of **1** is present, an alternative pathway is possible during which **2** reacts with a second molecule **1** to give the bicyclic compound **5**.

NMR Spectra. In the proton decoupled ^{13}C NMR spectrum of the bicyclo-λ^5-phosphazene derivative (**5**) two singlet resonances (16.2 and 16.6 ppm) are observed in the methyl carbon region of the isopropyl group. For similar phosphazene derivatives with an isopropyl group, like **4**, only one resonance signal is found. As this phenomenon can not be the result of a P−C coupling, two magnetically inequivalent isopropyl groups must be present in the molecule. This inequivalence is only possible, when the two phosphazene rings can not rotate freely around the carbon atom that connects the two rings. Assuming a free rotation of the isopropyl groups, two pairs of methyl groups can be discerned, one facing the OH group of the bridge, the other facing the methyl group. The asymmetric influence of the bridge is also seen in ^{1}H NMR spectra. Where for **4** the methyl resonances (1.19 ppm) appear as a double doublet ($^3J_{PH}$ = 20.7 Hz, $^3J_{HH}$ = 7.1 Hz), for **5** two separate double doublets are observed. Temperature dependent ^{1}H NMR experiments in $C_2D_2Cl_4$ and $C_6D_5NO_2$ showed the two separate double doublets to remain below 125 °C. Above that temperature extensive decomposition of **5** took place.

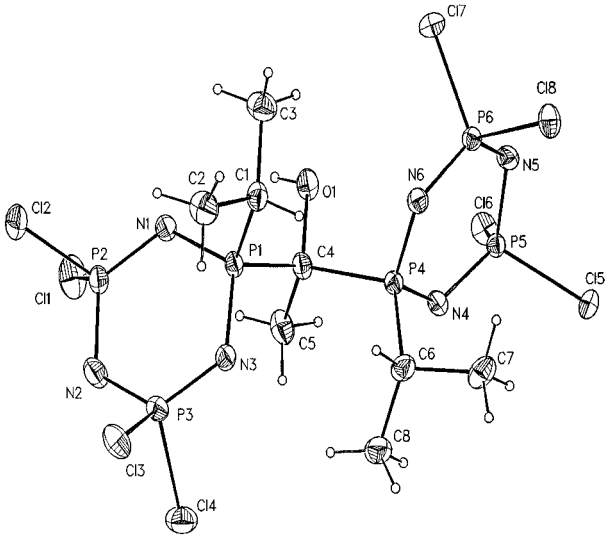


Figure 2. Perspective ORTEP[23] drawing of the non-hydrogen atoms of **5** with the atom labeling scheme for the non-hydrogen atoms. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids drawn to encompass 50% of the electron density; the hydrogen atoms are drawn with an arbitrary radius.

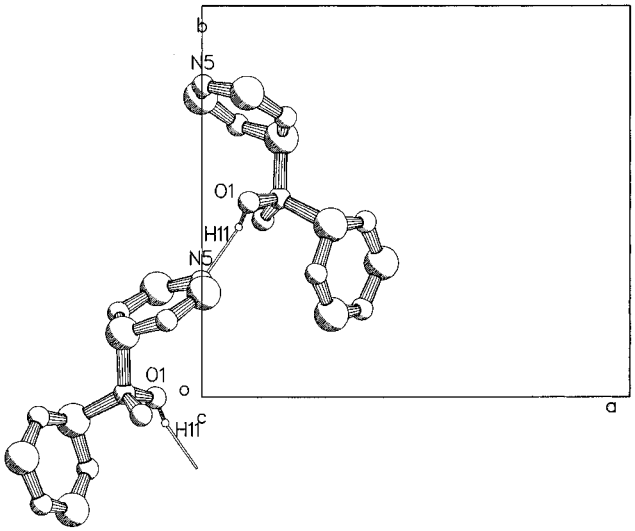


Figure 3. Projection of the unit cell of **5** along [001]. For sake of clarity only a limited set of atoms are shown. Hydrogen bridges H(11)···N(5) create infinite chains along [010].

X-ray Crystal Structures. Both in **4** and **5** the phosphazene rings are nearly planar with small deviations from planarity. For the six-membered ring in **4** the atoms P(1), P(2), P(3), N(2), and N(3) form a plane, with largest deviation being 0.011(1) Å. Atom N(1) is located at a distance of 0.148(4) Å from that plane. An almost similar situation has been found for one of the phosphazene rings in **5**: the atoms P(1), P(2), P(3), N(1) and N(3) are situated in one plane within the experimental error. Atom N(2) lies outside that plane at a distance of 0.118(6) Å. The other phosphazene ring in **5** approaches a twisted boat conformation.

Very weak hydrogen bond interactions, bordering to significance, are present in the crystal of **4**. Distinct interactions, however, can be observed between the molecules of **5**. Hydrogen bonds between H(11) and N(5) ($-x$, $-1/2 + y$, $1/2$

$-z$) with a length of 2.14(4) Å (sum of the van der Waals radii is 2.75 Å[25]) link the molecules together into infinite chains along [010] (Figure 3).

The sequence of N−P bond lengths in the molecules of **4** and **5** is for both molecules identical. In the ring segments $PCl_2-N-PCl_2$ the $N-P(Cl_2)$ bond lengths are equal (σ-weighted average for both molecules 1.586(3) Å), but longer than those in the segment $POrg_2-N-PCl_2$ (σ-weighted average for both molecules 1.558(1) Å). The largest values are found for $N-POrg_2$ bonds with an average length equal to 1.615(2) Å. These differences can be explained from the difference in electronegativity (χ) of the phosphorus centers, *viz.* the larger the electronegativity, the larger the ability for π-bonding.[26] This means that in the segment $POrg_2-N-PCl_2$, where $\chi(PCl_2) > \chi(POrg_2)$,[27] the $N-P(Cl_2)$ bond is shortened, whereas the other is lengthened. From the same reasoning equal bond lengths can be expected in the segment $PCl_2-N-PCl_2$. The same pattern holds for the endocyclic bonds in the starting material $(NPCl_2)_2NPH^iPr$.[28]

Not only the endocyclic bond lengths but also the corresponding endocyclic bond angles in the molecules of **4** and **5** are equal within the experimental error with σ-weighted averages 115.4(2)° [$N-POrg_2-N$], 119.7(1)° [$N-PCl_2-N$], 122.3(1)° [$POrg_2-N-PCl_2$], and 119.3(1)° [$PCl_2-N-PCl_2$]. Comparable values are found for $(NPCl_2)_2NPH^iPr$.[28] The exocyclic C−P−C angles in **5** are larger than in **4**, which may be explained from sterical considerations. The Cl−P−Cl angles are equal with a σ-weighted average amounting to 100.49(8)°.

Polymerization. The presence of an olefin functionality offers the possibility to use **4** in radical polymerization reactions. However it will be clear that homopolymerization of a 1,1-disubstituted alkene, such as **4**, will suffer from steric hindrance caused by the bulky acetoxy and phosphazene ring, rendering the α-carbon atom (C4) quite inaccessible for the addition of another alkene. Therefore this novel phosphazene monomer is expected not to be suitable for radical homopolymerization as in that case two sterically hindered species are involved in a propagation reaction. Preliminary polymerization experiments indeed show that homopolymerization does not proceed. Copolymerization leads to successful results. A detailed study of the polymerization behavior of **4** will be the subject of a forthcoming paper.

Supporting Information Available: Tables listing crystal data, atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles and an ORTEP plot[23] for **4** and **5** (15 pages). Ordering information is given on any current masthead paper.

IC960466B

(25) Bondi, A. *J. Phys. Chem* **1964**, *68*, 441.
(26) Craig, D. P.; Paddock, N. L. In *Nonbenzenoid Aromatics*; Snijder, J. P., Ed., Academic Press: New York, London, 1971; Vol. II, p 273.
(27) Hinze, J.; Jaffe, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540. Hinze, J.; Jaffe, H. H. *J. Phys. Chem.* **1963**, *67*, 1501. Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284. Huheey, J. E. *J. Phys. Chem.* **1966**, *70*, 2086.
(28) Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Inorg. Chem.* **1980**, *19*, 2483.