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Crystal and Molecular Structure of 1-Hydrido-1-isopropyltetrachlorocyclotriphosphazene[1]

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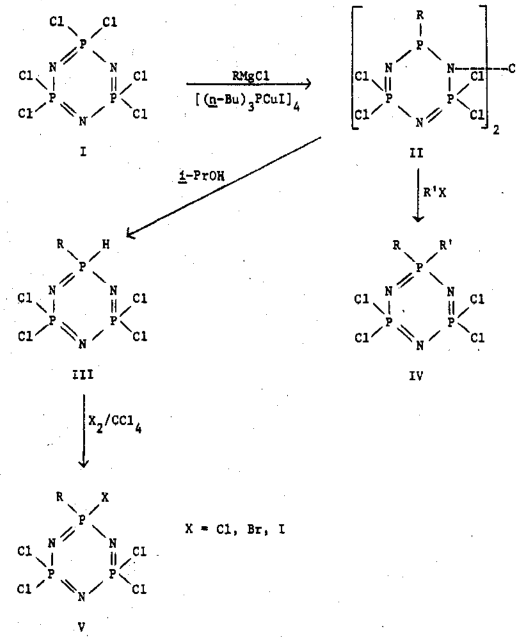
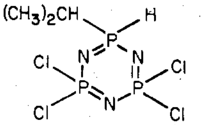
The first structural determination is described of a cyclic phosphazene, $N_3P_3Cl_4(i\text{-Pr})H$ (VI), which contains both a hydrogen atom and an alkyl group as substituents attached to phosphorus. Compound VI contains a planar phosphazene ring with a curious alternation of P–N bond lengths at progressively greater distances from the P(i-Pr)H unit and with corresponding distortions in the bond angles within the ring. The longest P–N bonds are those connected to the P(i-Pr)H unit. The phosphorus–hydrogen bond length is 1.26 (7) Å, the phosphorus–carbon bond distance is 1.765 (1) Å, and the H–P–C bond angle is 109 (3)°. The structural features of the molecule can be understood in terms of crystal-packing forces and π-bonding hypotheses. Crystals of VI were orthorhombic of the space group $P2_12_12_1$ with a = 6.128 (4) Å, b = 11.485 (2) Å, c = 17.467 (3) Å, and Z = 4. The final R_1 and R_2 factors were 0.043 and 0.045, respectively.

Introduction

In earlier papers we described the synthesis of a new class of phosphazene compounds that contain a hydrogen atom as a side group bonded directly to phosphorus. These hydridoalkylphosphazenes (III) are synthesized readily via the reaction of hexachlorocyclotriphosphazene (I) with alkyl Grignard reagents in the presence of $[(n\text{-Bu})_3PCuI]_4$, followed by treatment of the resultant metallophosphazene intermediate (II) with 2-propanol[2,3] (Scheme I). Such hydridophosphazene compounds (III) have since proved to be important intermediates for the synthesis of a variety of 1-halo-1-alkyltetrachlorocyclotriphosphazenes (V),[4-6] including those which contain phosphorus–iodine bonds. This approach to phosphazene synthesis via II has also yielded numerous 1,1-dialkylcyclotriphosphazenes (IV) including a number with unsaturated alkyl units.[7,8]

Scheme I





VI

We describe here the first X-ray structural determination of a hydridocyclophosphazene (VI). This particular compound was chosen as a prototype for structural studies because it is less sensitive to air and moisture than other hydridophosphazenes of this type.[2,3] The structural determination was carried out in an attempt to answer the following questions. (1) Is the hydrogen atom linked directly to a phosphorus atom? (Earlier infrared and NMR evidence had provided a strong indication of the presence of a direct P–H bond,[2,3] but confirmatory evidence was needed.) (2) Does the small steric size of a hydrogen atom compared to, say, chlorine or alkyl induce unusual changes in the geometry of the groups attached to phosphorus? (3) What effect, if any, does the hydrogen atom exert on the lengths of the phosphorus–nitrogen bonds, or on the overall geometry of the molecule? (4) Is the hydrogen

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0020-1669/80/1319-2483$01.00/0

Table I. Positional and Thermal Parameters for All Nonhydrogen Atoms

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Cl(1)	0.0766 (5)	−0.1797 (2)	0.1412 (2)	5.53 (15)	4.64 (11)	5.49 (12)	−1.63 (14)	1.47 (15)	−0.20 (12)
Cl(2)	0.5231 (5)	−0.2387 (2)	0.0732 (1)	5.53 (15)	3.62 (11)	5.04 (12)	0.58 (14)	0.06 (15)	0.25 (12)
Cl(3)	0.8339 (6)	0.1180 (3)	0.1683 (2)	5.48 (15)	4.88 (16)	8.70 (12)	−0.97 (14)	−1.67 (17)	0.41 (16)
Cl(4)	0.3921 (6)	0.2038 (3)	0.2258 (1)	8.75 (30)	5.46 (16)	5.05 (12)	−0.54 (14)	0.94 (17)	−2.22 (14)
P(1)	0.3446 (5)	0.0888 (2)	−0.0014 (1)	5.07 (15)	2.43 (11)	3.60 (11)	0.37 (14)	−0.32 (15)	0.265 (14)
P(3)	0.3354 (5)	−0.1013 (2)	0.0958 (1)	4.22 (14)	2.56 (11)	2.93 (10)	−0.50 (14)	−0.14 (13)	0.017 (14)
P(5)	0.5168 (5)	0.1022 (2)	0.1444 (1)	5.29 (15)	2.74 (11)	3.07 (10)	−1.04 (14)	−0.40 (15)	−0.41 (14)
N(2)	0.268 (1)	−0.0419 (6)	0.0195 (4)	5.54 (45)	2.25 (32)	3.07 (37)	−0.71 (42)	−1.41 (43)	0.23 (28)
N(4)	0.445 (2)	−0.0275 (6)	0.1612 (4)	7.52 (60)	3.15 (32)	2.84 (37)	−2.30 (42)	−0.21 (40)	0.44 (32)
N(6)	0.470 (2)	0.1574 (6)	0.0653 (4)	9.21 (60)	2.00 (32)	3.36 (37)	−1.12 (42)	−1.05 (43)	−0.18 (28)
C(1)	0.504 (2)	0.0888 (8)	−0.0858 (5)	7.36 (75)	2.85 (37)	4.58 (49)	−1.77 (56)	0.19 (64)	0.59 (40)
C(2)	0.719 (2)	0.0216 (11)	−0.0757 (7)	6.62 (75)	6.26 (63)	7.24 (61)	0.56 (70)	2.90 (64)	0.29 (80)
C(3)	0.368 (3)	0.0418 (11)	−0.1529 (6)	10.65 (1.05)	7.88 (69)	4.22 (49)	−0.14 (84)	−0.25 (85)	−0.38 (40)

Table II. Hydrogen Atom Positions and Isotropic Thermal Parameters

atom	x	y	z	B, Å^2
H(1)	0.16 (1)	0.137 (7)	−0.015 (4)	4.5000 (0)
H(11)	0.56 (1)	0.159 (7)	−0.087 (4)	6.0000 (0)
H(21)	0.78 (1)	0.037 (7)	−0.024 (4)	6.0000 (0)
H(22)	0.65 (1)	−0.060 (7)	−0.061 (4)	6.0000 (0)
H(23)	0.83 (2)	0.041 (7)	−0.125 (4)	6.0000 (0)
H(31)	0.23 (1)	0.075 (7)	−0.155 (4)	6.0000 (0)
H(32)	0.43 (2)	0.054 (7)	−0.198 (4)	6.0000 (0)
H(33)	0.35 (2)	−0.050 (7)	−0.127 (4)	6.0000 (0)

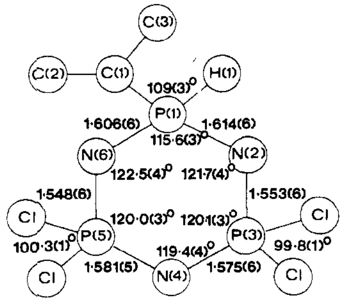

Figure 1. Atom designations, selected bond angles, and interatomic distances for 1,1-$N_3P_3Cl_4$(*i*-Pr)H (VI).

atom in VI especially sterically shielded in a way that would explain its higher than expected stability to air and moisture?

Experimental Section

Synthesis of 1-Hydrido-1-isopropyltetrachlorocyclotriphosphazene (VI). This compound was prepared by the reaction of hexachlorocyclotriphosphazene (I) with *i*-PrMgCl, in tetrahydrofuran, in the presence of $[(n\text{-Bu})_3PCuI]_4$, followed by treatment of the intermediate II (R = *i*-Pr) with *i*-PrOH, as reported earlier.[2,3] Crystals of VI suitable for single-crystal X-ray diffraction were grown slowly from a saturated solution in hexane at −10 °C.

Crystallographic Data Collection. A clear fragment of VI, with dimensions ca. 0.4 × 0.4 × 0.5 mm, was mounted on a glass fiber and placed in a glass capillary tube under an atmosphere of dry nitrogen. Precession photographs were obtained with the use of zirconium-filtered molybdenum Kα radiation (λ = 0.710 69 Å). These photographs indicated that the crystal possessed an orthorhombic cell (Laue symmetry *mmm*), and the observed systematic presences $h00$, $h = 2n$; $0k0$, $k = 2n$; and $00l$, $l = 2n$, uniquely determined the space group as $P2_12_12_1$ (No. 19). A second crystal was mounted as before, in a random orientation, and was placed on an Enraf-Nonius CAD-4 diffractometer. The unit cell dimensions, determined from 25 reflections at moderate 2θ angles, were a = 6.128 (4) Å, b = 11.485 (2) Å, c = 17.467 (3) Å, and V = 1229.3 Å^3. The measured density was 1.710 g/cm^3 (determined in tribromomethane/tetrachloromethane), and this value was consistent with a calculated value of 1.734 g/cm^3 based on Z = 4 (molecular weight 320.92). A graphite-crystal incident-beam monochromater was used with Mo Kα radiation [λ(Mo Kα_1) = 0.709 30 Å]. Data were collected at a takeoff angle of 2.80°. The crystal to incident beam collimator distance was 48 mm, and the crystal to aperture distance was 173 mm. A θ–2θ scan method was used with a variable scan rate, which ranged from 20°/min for the most intense reflections to 1°/min for the weakest reflections. The angular scan width (ω) was variable and amounted to 0.65° before 2θ(Mo Kα_1) and $(0.65 + 0.347 \tan \theta)°$ after 2θ(Mo Kα_2). Right and left backgrounds were each scanned for 25% of the total scan time. Three "check" reflections, measured after every 1 h of actual X-ray exposure time, showed no significant change in intensity throughout the entire data collection. A total of 3089 unique reflections were collected out to a value for 2θ of 70°; of these reflections 784 had intensities with $I \geq 3\sigma(I)$ and were considered as observed. (Here, $\sigma(I) = [S^2(C + R^2B) + (\rho I)^2]^{1/2}$ and $I = S(C - RB)$, where S = scan rate, C = total integrated peak count, R = ratio of scan time to background count time, B = total background count, and ρ = 0.05.) These data were corrected for Lorentz and polarization factors and were used in the refinement of the structure. (No correction was made for absorption; μ = 13.04 cm^{-1} for Mo Kα.)

Solution and Refinement of the Structure. The structure was solved through conventional heavy-atom techniques. An initial three-dimensional Patterson synthesis was used to locate the position of one of the phosphorus atoms. Three cycles of full-matrix least-squares refinement of the positional and isotropic thermal parameter of this atom gave R_1 = 0.46. A difference Fourier revealed the location of the other two phosphorus atoms. Refinement of the positional and thermal parameters for these three atoms lowered R_1 to 0.44, and a difference Fourier disclosed the positions of two of the chlorine atoms. Three cycles of refinement with these five atoms gave R_1 = 0.34, and a difference Fourier allowed the location of the remaining two chlorine atoms and the three ring nitrogen atoms. Refinement at this stage resulted in R_1 = 0.16, and the subsequent difference Fourier allowed the location of the remaining nonhydrogen atoms. Three cycles of isotopic refinement lowered R_1 to 0.10, and a difference Fourier based on these values located all of the hydrogen atoms. At this stage the hydrogen atoms were added to the model, and three cycles of full-matrix least-squares refinement of positional and anistropic thermal parameters for all nonhydrogen atoms and positional parameters for all hydrogen atoms (hydrogen atom anistropic temperature factors were set at 1 more than that of the atom to which they were bonded) led to convergence. Final values were R_1 = 0.043 and R_2 = 0.045; the esd of an observation of unit weight equals 2.031 (convergence was considered complete when all the shifts were less than one-tenth of their standard deviations). Here, $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $\sigma = 1/\sigma^2(F_o)$, and $\sigma(F_o)^2 = [\sigma(I)^2 + (0.02F^2)^2]^{1/2}/(Lp)$ where $F_o^2 = F^2/(Lp)$. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. Atomic scattering factors for all atoms were taken from the compilation of Cromer and Waber[9] and were corrected for anomalous dispersion (both real and imaginery parts).[10] The highest peak on the final difference Fourier map had a value of 0.492 e/Å^3. The coordinates were inverted and the structure was again refined to convergence to determine the correct chirality of the structure. This refinement gave R_1 and R_2 as 0.044 and 0.051, respectively, and this result confirmed that the original chirality was correct.

The refined positional and anistropic thermal parameters for all nonhydrogen atoms are given in Table I. The hydrogen atom positions

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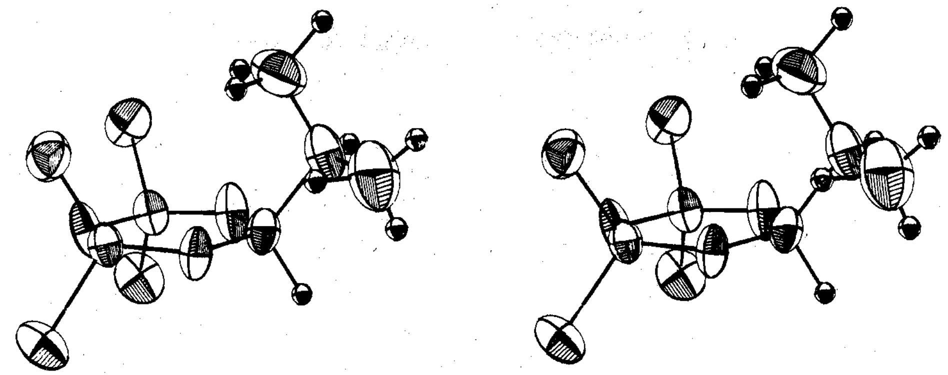

Figure 2. A stereoview of 1,1-$N_3P_3Cl_4$(*i*-Pr)H (VI).

Table IV. Distances and Angles in 1,1-$N_3P_3Cl_4$(*i*-Pr)H (VI)

dist, Å		angle, deg	
P(1)–H(1)	1.26 (7)	H(1)–P(1)–C(1)	109 (3)
P(1)–C(1)	1.765 (1)	P(1)–C(1)–C(2)	112.0 (7)
P(1)–N(2)	1.614 (6)	P(1)–C(1)–C(3)	109.8 (8)
P(1)–N(6)	1.606 (6)	C(2)–C(1)–C(3)	112.2 (9)
P(3)–N(1)	1.553 (6)	H(1)–P(1)–N(2)	101 (3)
P(3)–N(4)	1.575 (6)	H(1)–P(1)–N(6)	110 (3)
P(3)–Cl(1)	1.988 (3)	C(1)–P(1)–N(2)	110.4 (4)
P(3)–Cl(2)	1.992 (3)	C(1)–P(1)–N(6)	110.0 (4)
P(5)–N(4)	1.581 (5)	N(2)–P(1)–N(6)	115.6 (3)
P(5)–N(6)	1.548 (6)	P(1)–N(2)–P(3)	121.7 (4)
P(5)–Cl(3)	1.997 (4)	N(2)–P(3)–N(4)	120.1 (3)
P(5)–Cl(4)	1.989 (3)	P(3)–N(4)–P(5)	119.4 (4)
C(1)–H(11)	0.87 (7)	N(4)–P(5)–N(6)	120.0 (3)
C(1)–C(2)	1.540 (1)	P(5)–N(6)–P(1)	122.5 (4)
C(1)–C(3)	1.537 (1)	Cl(1)–P(3)–Cl(2)	99.8 (1)
C(2)–H(21)	1.00 (8)	Cl(3)–P(5)–Cl(4)	100.3 (1)
C(2)–H(22)	1.04 (7)	Cl(1)–P(3)–N(2)	109.2 (3)
C(2)–H(23)	1.10 (9)	Cl(2)–P(3)–N(2)	109.4 (2)
C(3)–H(31)	0.91 (8)	Cl(1)–P(3)–N(4)	107.2 (2)
C(3)–H(32)	0.90 (7)	Cl(2)–P(3)–N(4)	108.8 (3)
C(3)–H(33)	1.15 (7)	Cl(3)–P(5)–N(4)	108.5 (3)
		Cl(4)–P(5)–N(4)	108.3 (3)
		Cl(3)–P(5)–N(6)	109.4 (3)
		Cl(4)–P(5)–N(6)	109.0 (3)

and their isotropic parameters are shown in Table II. A listing of the observed and calculated structure factor amplitudes for the 784 reflections used in the refinement appears in Table III (supplementary material).

All the programs used in this study were part of the Enraf-Nonius structure determination package (SDP), Enraf-Nonius, Delft, Holland, 1975, revised 1977, and were implemented on a PDP 11/34 computer. The perspective and stereo drawings were obtained with the use of a Versatec plotter.

Results and Discussion

General Structural Features of the Molecule. The X-ray structure determination of VI indicated that the phosphazene ring in this molecule is planar ($\chi^2 = 177$). The hydrogen atom and isopropyl group are bound to one phosphorus atom, P(1), and two chlorine atoms are linked to each of the remaining two phosphorus atoms. The mean P–Cl bond lengths of 1.944 Å and the Cl–P–Cl bond angle of 100.05° are similar to the lengths and angles reported for hexachlorocyclotriphosphazene.[11-13] The general structure of the molecule, together with the numbering system used for all nonhydrogen atoms, is shown in Figure 1. A stereoscopic view is shown in Figure 2. The bond distances and angles are listed in Table IV.

Bonding about Phosphorus Atom P(1). The skeletal phosphorus atoms in cyclic phosphazenes usually display a distorted tetrahedral geometry, with a ring angle near 120° and an exocyclic angle near 100°.[14] As shown in Figure 1, the bond angles at P(1) in VI are appreciably distorted from this normal arrangement. Specifically, the N–P–N ring angle is narrowed to 115.6 (3)°, and the exocyclic C–P–H angle is widened to 109 (3)°. This cannot be a result of a steric interaction between the side groups because of the small size of the hydrogen linked to P(1) and the particular orientation adopted by the isopropyl group. Hence, as will be discussed later, the wide exocyclic C–P–H angle is probably a response (scissoring effect) to the narrow N–P(1)–N ring angle which, in turn, may depend on unusual electronic effects within the phosphazene ring.

The P(1)–H(1) bond length is 1.26 (7) Å. This distance is shorter than phosphorus–hydrogen bond lengths reported for phosphines. For example, the P–H bond distance in PH_3 was reported[15] to be 1.44 Å. However, this difference is not considered to be significant because of the shortened X–H bond distances determined by the X-ray method.[16] A neutron diffraction study[17] has been used to show that the P–H bond distance in PH_4^+ is 1.414 Å.

Orientation of the Isopropyl Group. The isopropyl group bonded to P(1) occupied an unusual orientation. The group was positioned in such a way that carbon atom C(2) was located *over* the phosphazene ring and C(3) was displaced to the side of an imaginary plane through P(1), C(1), C(2), and N(4). Hydrogen atoms H(21) and H(22) lie adjacent to nitrogen atoms N(6) and N(2), respectively. The distances N(6)···H(21) and N(2)···H(22) are almost exactly the sum of the van der Waals radii for these atoms (2.75 Å). Thus, the orientation of the isopropyl group could be a response to these van der Waals interactions, or even a consequence of weak hydrogen bonding.

However, it was concluded that crystal-packing forces are probably responsible for this conformation. A variable-temperature ^{13}C NMR study[18] showed that no particular conformation for the isopropyl group was preferred in solution, even at temperatures as low as −60 °C. The spectrum—a doublet of triplets [P–CH$(CH_3)_2$] centered at 29.53 ppm (J_{PC} = 90.1 Hz, J_{PNPC} = 3.2 Hz) and a singlet [P–CH$(\mathit{C}H_3)_2$] at 12.93 ppm—did not change over the temperature range of +40

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(18) The ^{13}C NMR data were recorded on a Varian Associates CFT-20 NMR spectrometer. The sample of VI was dissolved in dry, deoxygenated CD_2Cl_2. The spectra were recorded at 20 °C intervals between +40 and −60 °C. Chemical shifts are related to internal tetramethylsilane at 0 ppm.

Table V. Comparison of Structural Data for Compound VI and Related Organocyclophosphazenes

compd	P–C bond, Å	C–P–C, deg	X–P–X,[a] deg	N–P–N,[b] deg	ref
1,1-$N_3P_3Cl_4$(*i*-Pr)H	1.765 (1)	109 (3)	100.3 (1)	115.6 (3)	this work
1,1-$N_3P_3Cl_4(C_6H_5)_2$	1.792 (6)	104.4 (3)	100.3 (1)	115.2 (2)	19
1,1,3,3-$N_3P_3Cl_2(C_6H_5)_4$	1.802 (8)	104.3 (5)	98.6 (2)	115.0 (4), 116.1 (4)	20
1,1-$N_4P_4F_6(CH_3)_2$	1.794 (8)	105.7 (6)	94.1 (5)	116.9 (5)	21, 22
1,1,5,5-$N_4P_4F_4(CH_3)_4$	1.81 (1)	106.9 (7)	96.7 (1)	117.5 (5)	21, 23

[a] X = chlorine or fluorine; exocyclic bond angle is at halogenated phosphorus atoms. [b] Endocyclic bond angle is at the alkylated phosphorus atom.

to −60 °C. Thus the unusual orientation found for the isopropyl group is a phenomenon of the solid-state system and is not an intrinsic characteristic of VI in the solution state. In solution, the isopropyl group may exert some steric shielding effect on the reactivity of the hydrido function.

The P(1)–C(1) bond length was found to be 1.765 (1) Å. This distance is similar to phosphorus–carbon bond lengths that have been determined for other alkylhalocyclophosphazenes (Table V).[19–23] The C(1)–C(2) and C(1)–C(3) bond lengths, of 1.540 (1) and 1.537 (1) Å, respectively, are typical for carbon–carbon single bonds.[24]

Bonding within the Phosphazene Ring. Three different P–N bond lengths were found in the skeletal ring of VI. The two P–N bonds connected to P(1) (the phosphorus atom bearing the hydrogen and isopropyl group) were longer (average 1.61 Å) than the other P–N bonds. In fact, an alternation in longer and shorter bonds existed for the P–N bonds located at increasing distances from P(1). Thus, P(1)–N(2) and P(1)–N(6) were 1.61 Å (average), N(6)–P(5) and N(2)–P(3) were 1.55 Å (average), and P(3)–N(4) and P(5)–N(4) were 1.58 Å (average). (This last distance is considered to be significant.) The lengths of the P–N bonds furthest from P(1) are very similar to those determined for hexachlorocyclotriphosphazene.[12–14] The variation in P–N bond lengths found in compound VI has been observed for other partially alkylated cyclophosphazenes,[19–23] and it has been ascribed to the influence by the less electronegative substituents at P(1) on the π bonding in the ring.[21–23,25,26] We agree with this interpretation.

The unequal bond lengths within the six-membered ring led to corresponding distortions in the endocyclic bond angles away from 120°. The decrease in the N(6)–P(1)–N(2) bond angle (to 115.6°) has already been mentioned. However, the N(2)–P(3)–N(4) and N(4)–P(5)–N(6) angles (mean value 120.0°) are close to those found in $(NPCl_2)_3$[12–14] and in $(NPF_2)_3$.[27] The exocyclic Cl–P(3)–Cl and Cl–P(5)–Cl angles (100.0°) are similar to those found in $(NPCl_2)_3$.[12–14] Comparisons between the structural parameters for VI and for closely related phosphazenes are listed in Table V.

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Registry No. VI, 71982-86-0.

Supplementary Material Available: Table III, a complete listing of the observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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