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Unusual Products in the Reactions of Hexachlorocyclotriphosphazatriene with Sodium Aryloxides

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ABSTRACT

Reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ **1**, *with sodium aryloxides have been studied. Compound* **1** *was found to react by the nucleophilic substitution pathway to yield monocyclophosphazenes [$N_3P_3Cl_5(OC_6H_2Bu^t_3$-2,4,6)* **5** *and $N_3P_3Cl_4(OC_6H_2$ Me-4-Bu^t_2-2,6)$_2$* **6***] and bi(cyclophosphazenes) [[$Cl_5N_3P_3$-$P_3N_3Cl_4(OC_6H_3Bu^t_2$-2,6)]* **7** *and [N_3P_3 ($OC_6H_3Bu^t_2$-2,6)$_5$]$_2$* **8***]. The unusual bi(cyclophosphazenes)* **7** *and* **8** *are the first examples of two cyclotriphosphazene rings linked by a P–P bond [2.193 (2)Å], which have been obtained by reacting* **1** *with ArONa. The structures of compounds* **5–8** *are ascertained by elemental analyses, ^{1}H-, ^{31}P-^{13}C-NMR, IR, and MS spectra. The molecular structure of monocyclic-phosphazene* **5** *was determined by X-ray diffraction techniques for further structural assignment. It crystallizes in the monoclinic space group $P2_1/m$ with $a = 6.144(2)$, $b = 17.079(9)$, $c = 13.181(9)$ Å, $\beta = 92.79(7)$, and $Z = 2$, $R = 0.074$. Compound* **5** *is on a crystallographic mirror plane, and there is only a half molecule in the asymmetric unit.* © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

Although a large number of reactions of amines and alcohols with hexachlorocyclotriphosphazatriene $N_3P_3Cl_6$ **1** have been investigated [2–8], studies of the reactions of **1** with aryloxide anions are very limited [9–13]. The partial or complete series of derivatives of $N_3P_3Cl_{(6-n)}(OC_6H_4$-p-$R)_n$ (n = 1 – 6; R = H, Me, Br, or NO_2) produced in such reactions have been examined [12–14] and the major product in each case was reported to be nongeminal. The *cis*-product was preferentially formed at the stage of disubstitution. Use of a bulky steroidal sodium oxide also gives nongeminal products, i.e., equal amounts of *cis*- and *trans*-products [15]. Recently, two significant articles in this regard have appeared in the literature [16,17]. In these articles, *o*-dichloro and *o*-dimethyl-phenoxyphosphazene derivatives have been reported and it was proved that, despite the bulkiness of the *o*-dichloro and *o*-dimethyl-phenoxy

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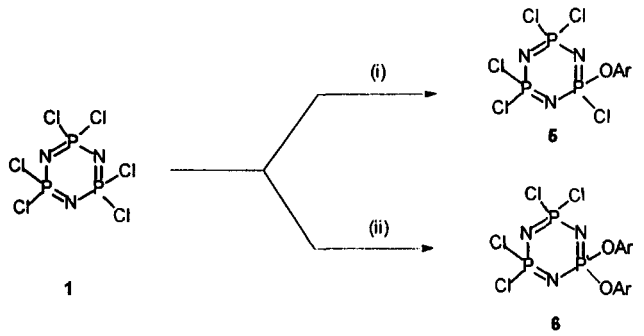
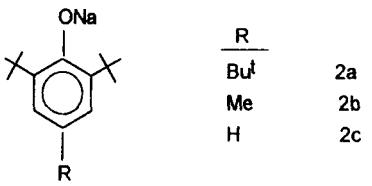


SCHEME 1 (i) ArONa **2a**; (ii) ArONa **2b** Ar = 2,4,6-tri-tert-butylphenyl Ar = 2,6-di-tert-butyl-4-methylphenyl (Ar = 2,6-di-tert-butylphenyl)

groups, their introduction into the phosphazene structure followed a geminal substitution pathway during the early stages of the reaction. In the present study, the sodium salts of representative bulky phenols of type 2 were chosen as nucleophiles. The sodium salts of bulky phenols are soluble in hydrocarbon solvents and readily available [18–21].



R	
Bu^t	2a
Me	2b
H	2c

Bulky phenols are widely used as antioxidants. Butylated hydroxytoluene (BHT) is well known for its antioxidant properties, and it is a potent inactivator of lipid-containing viruses [22]. In this article, we report the syntheses of two monocyclophosphazenes [$N_3P_3Cl_5(OC_6H_2Bu^t_2$-2,4,6) **5** and $N_3P_3Cl_4(OC_6H_2Me$-4-Bu^t_2-2,6)$_2$**6**] and two bi(cyclophosphazenes) [[$Cl_5N_3P_3$-$P_3N_3Cl_4(OC_6H_3Bu^t_2$-2,6) **7** and [$N_3P_3(OC_6H_3Bu^t_2$-2,6)$_5$]$_2$ **8**] by the reactions of **1** with the sodium salts of the corresponding phenols (Schemes 1 and 2), together with the physical and spectroscopic properties of compounds **5–8** and the crystal structure of **5**. We previously determined the solid-state structure of **7** by single-crystal X-ray diffraction analysis [23].

RESULTS AND DISCUSSION

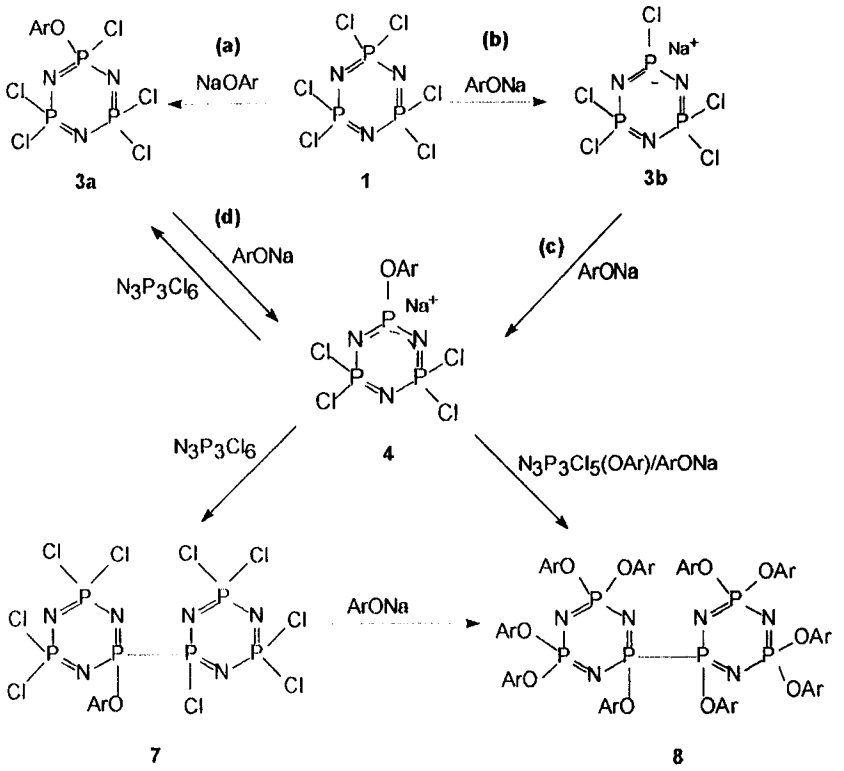
The reaction of **1** with an equimolar amount of **2a** in THF gave the monosubstituted product **5**, but **2b** gave the disubstituted geminal product **6** as shown in Scheme 1. The nongeminal *cis*- or *trans*-product could not be isolated from this nucleophilic substitution reaction.

The reaction of **1** with **2c** (Ar = 2,6-di-tert-butylphenyl) gives bi(cyclophosphazenes) **7** and **8**, in which two cyclotriphosphazene rings are linked by a P–P bond, as shown in Scheme 2. No simple nucleophilic substitution products of types **5** and **6** have been isolated from this reaction. It is apparent that, while compound **7** arises from the reaction of equimolar amounts of **1** and **2c**, compound **8** is formed by the reaction of one mole of **1** and several moles of **2c**. The results obtained in this work imply Cl^+ abstraction by the oxygen atom of the aryloxide. Formation of bi(cyclophosphazenes) **7** and **8** can be explained by a Cl^+ abstraction (metal-halogen exchange) reaction leading to the intermediates **3** and **4** (Scheme 2). These types of intermediates have been observed when Grignard, organocopper reagents, or dilithiometallocenes were employed [24–32].

Although Scheme 2 appears to provide a reasonable rationale, further work will be necessary to establish the mechanism firmly. Scheme 2 illustrates two possible alternative pathways. If the reaction follows the pathway (**a**), which involves an $S_N(P)$ reaction, then the formation of **3a** must be observed. In the next step, a Cl^+ abstraction reaction of the geminal chlorine atom in **3a** leads to the formation of the intermediate **4**, which can accommodate the subsequent formation of products **7** and **8**. On the other hand, if the first step (**b**) involves Cl^+ abstraction reaction, the ionic intermediate **3b** could then form between **1** and ArONa. The reactions of chlorophosphazenes are very complex, and it is difficult to distinguish these two pathways, **a** + **d** or **b** + **c**. The role played by the intermediate **4** is compatible with the evidence obtained for other systems in which chlorophosphazenes are extremely prone to Cl^+ abstraction reactions [25,27,29–32].

SPECTROSCOPIC STUDIES

The structures of compounds **5–8** were determined by using elemental analyses; IR, ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy. These results are given in the Experimental section. The structure of compound **5** was also determined by the single-crystal X-ray diffraction method and compared with the values obtained from the structure of compound **7** [23]. The aryl and alkyl C–H stretching frequencies of compounds **5–8** were observed to occur at 3010–3060 cm^{-1} and 2830–2890 cm^{-1}, respectively. P–N bonds have strong infrared absorbances at 1100–1300 cm^{-1} [1,4,6]. We found that compounds **5–8** have absorbance bands at 1170–1215 cm^{-1} for ν(P=N) and compounds **5–7** showed absorbance at 590 cm^{-1} ν(P–Cl), as was previously shown [10]. The latter band was



SCHEME 2 (a) Nucleophilic substitution pathway; (b) Cl^+ abstraction pathway Ar: $C_6H_3Bu^t_2$-2,6)

not observed for **8**, as expected from its structure. ^{1}H-, ^{13}C-, and ^{31}P-NMR data provided strong evidence for the structures of **5–8**. ^{1}H-NMR spectra of compounds **5–8** are relatively simple, but informative. All the CH_3 protons are singlets. The methyl protons resonate at δ = 1.3 (4-Bu^t,-CH_3) and 1.5 (2-Bu^t,-CH_3) in a 2:1 ratio and phenyl protons at δ = 7.3 for **5**. In the low-field region of the ^{1}H-NMR spectra, the singlets appearing at δ = 1.4 (**6**), 1.4 (**7**), and 1.4 (**8**) were attributed to the proton resonances of Bu^t groups. The protons of the methyl group at the para-position in **6** also gave a singlet at δ = 2.8. Low-field proton resonances of phenyl protons have been observed at δ = 7.0 for **6**, comparable with the values obtained from **7** and **8**, at δ = 7.7 and 7.7, respectively. The ^{13}C-NMR spectrum of **6**, $\underline{C}(CH_3)_3$, $C(\underline{C}H_3)_3$, and $\underline{C}H_3$ (para position) signals are observed at δ = 38.0, 30.4, and 34.3, respectively. The ^{13}C-NMR spectra of bi(cyclophosphazenes) **7** and **8** also confirm the presence of Bu^t (ortho) carbons in the same region. It is possible to distinguish the C-ipso signals from other carbon signals of phenyl groups in compounds **5–8**. We analyzed the ^{31}P-NMR spectra of **5**, **6**, and **8** (see Experimental). The proton-decoupled ^{31}P-NMR spectra of compounds **5** and **6** were interpreted as the result of a simple AB_2 spin system. According to the proton-coupled ^{31}P-NMR spectrum and data of Refs. [16] and [17], it can be concluded that compound **6** may have the geminal structure. The spin systems of compounds **7** and **8** were assigned as M_2ABN_2 and $M_2AA'M_2$ (possibly $\approx M_2A$), respectively, and were classified as deceptively simple systems [10,27]. Chemical shifts, δ [P(OAr)Cl][in **5**, δ = 6.8] or δ P(OAr)$_2$ [in **8**, δ = 8.7], were more shielded than those of the δPCl_2 [in **5**, δ = 20.9] or δ P(P)(OAr) [in **8**, δ = 23.0]. These values are in good agreement with literature values [10]. Two bond-coupling constants $^2J_{PNP}$ for **5**, **7**, and **8** are between ca. 33 and 66 Hz. The mass spectrum of **5** showed a well-defined parent ion at *m/z* 573 (32%) with the expected isotope pattern and the peaks at *m/z* 558, 516, 502, and 312, corresponding to the loss of CH_3, Bu^t, 2Cl, or Bu^t + CH_3 and OAr, respectively. From $[M]^+$, the N_3P_3 ring appears to be stable during fragmentation of the bulky substituent, OAr, and the dominant ion (*m/z* 558, 100%) indicates first the loss of a CH_3 fragment. Compound **6** also showed the parent ion at *m/z* 715 (45%) and a dominant ion at *m/z* 57 ($[Bu^t]^+$, 100%) in the mass spectrum. The fragmentation pattern was very similar to that of **5**. A parent ion was not observed in the mass spectrum of bi(cyclophosphazene) **7**; a cluster of peaks with *m/z* 721 (11%) corresponds to the effective loss of 2Cl upon ionization. The dominant ions,

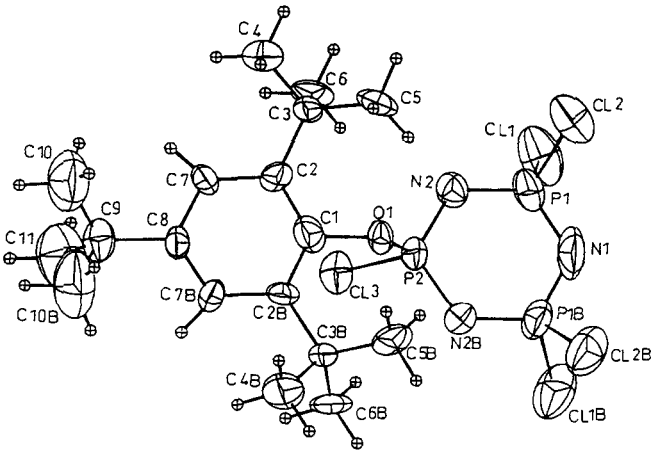


FIGURE 1 A SNOOPI [37] drawing of the title molecule with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

$[H_3N_6P_6Cl(OH)]^+$ (*m/z* 502, 100%) and $[Bu^t]^+$ (*m/z* 57, 100%), observed in the mass spectrum are important ions for identification of the molecule. A molecular ion peak was not observed in the MS spectrum of compound 8.

Crystallographic Studies

The molecular structure of compound 5, along with the atomic labeling scheme, is illustrated in Figure 1. It is on a crystallographic mirror plane, and there is only a half molecule in the asymmetric unit. The methods employed to solve the structure and other related parameters and procedures are given in Table 1. Nonhydrogen atoms were included with anisotropic thermal parameters. Difference syntheses did not show clearly the electron density for H atoms. Therefore, H atoms were geometrically positioned 1.00 Å from the corresponding atoms, and a riding model was used in the refinement process. There was disordering in the structure and therefore, some constraints are applied on some of the parameters during refinement. The final atomic coordinates and isotropic displacement parameters are listed in Table 2. Selected bond distances and angles with torsion angles are given in Table 3. As can be seen from Table 3, the P_2–N_2[1.60(1) Å] bond length is the longest one among the P–N bonds and the P_2–Cl_3[1.976(9) Å] bond length is the shortest one among the P–Cl bonds in the structure. The exocyclic Cl_3–P_2–O_1 (α')[104.5(6)°] angle is larger than that of the exocyclic Cl_1–P_1–Cl_2(α')[100.6(3)°] one due to the replacement of the bulky tri-*t*-butylphenoxy group by chlorine. The endocyclic N_2–P_2–N_2B (α) [115.8(1)°] angle decreases, while the exocyclic Cl_3–P_2–O_1 angle

TABLE 1 Experimental Details

Experimental	
Crystal data	
C18H29ON3P3CL5	Mo K_α radiation
Mr = 573.634	X = 0.71069 Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/m$	θ = 5–11°
a = 6.144(2) Å	μ = 14.3 cm^{-1}
b = 17.079(9) Å	T = 293 K
c = 13.181(9) Å	Rod shaped
β = 92.79(7)	0.06 × 0.12 × 0.20 mm
V = 1381.42(9)Å^3	Colorless
Z = 2	Crystal source: as described in comment
Dx = 1.734 $g.cm^{-3}$	
Data collection	
Enraf-Nonius CAD-4 diffractometer	θ_{max} = 24°
w/2θ scans	h = −6 → 6
Absorption correction: semiempirical [33]	k = 0 → 17
	l = 0 → 14
	Rint = 0.00
T_{min} = 0.89, T_{max} = 0.94	3 standard reflections
3107 reflections measured	frequency: 180 min
2160 independent reflections	intensity variation 1%
916 observed reflections, [F ≥ 3σ(F)]	
Refinement	
Refinement on F	$(\Delta/\delta)_{max}$ = 0.134
R = 0.074	$\Delta\delta_{max}$ = +0.18 eÅ^{-3}
wR = 0.081	$\Delta\delta_{min}$ = −1.35 eÅ^{-3}
734 reflections	Atomic scattering factors from International Tables for X-ray Crystallography [34]
133 parameters	
S not calculated	
Weighting scheme: unit weights	Extinction correction: none

The programs used were CRYSTALS [35], SHELXS86 [36], and SNOOPI [37].

increases. Hence the endocyclic P_1–N_2–P_2B (β) [122.5(1)°] angle shows an increase. The α and α' angles remain largely unchanged (Figure 2). In the benzene ring, Cl–C_2–C_7 [116.8(2)°] is the smallest and C_2–C_1–C_2B [123.8(2)°] is the largest endocyclic angle. The largest exocyclic angle is Cl–C_2–C_3 [125.8(1)°]. In Table 4, the characteristic bond lengths and angles of several monosubstituted and disubstituted cyclophosphazene derivatives are compared with the values obtained for compounds 5 and 7. In a given $N_3P_3R_6$ structure, the length of ring P–N bonds are generally equal, provided all the substituents, R, are the same. If R is a difunctional bulky substituent [38] or contains different substituents having different electron affinities, the ring P–N bonds may show significant variations in bond lengths [39,40]. Basicity measurements have demonstrated the electron re-

TABLE 2 Fractional Atomic Coordinates and Isotropic Thermal Parameters (Å²)

Atom	*x/a*	*y/b*	*z/c*	*U(iso)*
P_1	0.0911(9)	0.6701(3)	−0.0606(3)	0.0560
P_2	0.282(1)	0.7500	0.243(5)	0.0412
Cl_1	0.2555(9)	0.6046(4)	−0.1552(4)	0.0900
Cl_2	−0.1777(9)	0.6067(4)	−0.0507(4)	0.0881
Cl_3	0.599(1)	0.7500	0.1366(5)	0.0575
O_1	0.176(2)	0.7500	0.211(1)	0.0381
N_1	0.026(4)	0.7500	−0.115(2)	0.0687
N_2	0.216(2)	0.6708(9)	0.0462(9)	0.0496
C_1	0.282(3)	0.7500	0.312(2)	0.0310
C_2	0.324(3)	0.6782(9)	0.359(1)	0.0365
C_3	0.233(3)	0.5987(9)	0.322(1)	0.0368
C_4	0.218(3)	0.543(1)	0.413(1)	0.0653
C_5	0.008(3)	0.604(1)	0.271(1)	0.0514
C_6	0.387(3)	0.5585(9)	0.250(1)	0.0480
C_7	0.461(2)	0.679(1)	0.448(1)	0.0373
C_8	0.532(3)	0.7500	0.489(1)	0.0291
C_9	0.6706	0.7500	0.5857	0.0492
C_{10}	0.643(4)	0.686(1)	0.654(2)	0.1233
C_{11}	0.898(3)	0.7500	0.578(2)	0.1311

TABLE 3 Bond Lengths (Å) and Bond Angles (deg) with esd's in Parentheses

P_1–Cl_1	1.988(7)	P_2–Cl_3	1.976(9)
P_1–N_1	1.58(1)	C_2–C_3	1.54(2)
C_9–C_{11}	1.41(2)	C_2–C_7	1.41(2)
P_1–Cl_2	1.985(8)	C_3–C_4	1.53(2)
P_1–N_2	1.57(1)	C_3–C_5	1.51(2)
O_1–C_1	1.45(2)	C_3–C_6	1.54(2)
O_1–P_2	1.58(1)	C_7–C_8	1.39(2)
C_1–C_2	1.39(2)	C_8–C_9	1.50(2)
P_2–N_2	1.60(1)	C_9–C_{10}	1.42(2)
N_1–P_1–Cl_1	109.1(9)	C_3–C_2–C_1	125.8(1)
N_1–P_1–Cl_2	108.0(9)	C_7–C_2–C_1	116.8(2)
N_2–P_1–Cl_1	109.0(6)	C_7–C_2–C_3	117.4(1)
N_2–P_1–N_1	119.9(9)	P_2–N_2–P_1	122.5(1)
N_2–P_1–Cl_2	108.4(6)	C_4–C_3–C_2	109.6(1)
Cl_1–P_1–Cl_2	100.6(3)	C_5–C_3–C_2	113.3(1)
C_2–C_1–O_1	118.0(9)	C_5–C_3–C_4	107.3(2)
C_2–C_1–C_2B	123.8(2)	C_6–C_3–C_2	111.5(1)
P_1–N_1–P_1B	119.3(1)	C_6–C_3–C_4	105.8(1)
P_2–O_1–C_1	129.1(1)	C_6–C_3–C_5	109.0(1)
N_2–P_2–N_2B	115.8(1)	C_8–C_7–C_2	119.4(2)
N_2–P_2–O_1	108.8(6)	C_7–C_8–C_7B	121.8(2)
Cl_3–P_2–N_2	109.2(6)	C_9–C_8–C_7	118.9(9)
Cl_3–P_2–O_1	104.5(6)	C_{10}–C_9–C_8	117.3(9)
Cl_3–P_2–N_2	109.2(6)	C_{10}–C_9–C_{10}B	99.5(2)
C_{11}–C_9–C_8	117.5(1)	C_{11}–C_9–C_{10}	101.1(1)

leasing capacity of Ph and $NPPh_3$ groups relative to Cl atoms ($N_3P_3Cl_6$ is a standard in phosphazene chemistry) [41]. All the mono and geminal bis-substituted phosphazenes given in Table 4 showed a longer P–N bond adjacent to the P atom carrying the substituents and shorter bonds for the neighboring ones relative to the P–N [1.581(3) Å] bond in $N_3P_3Cl_6$ 1 [42]. As in the benzene ring, the changes in bond angles were more reliable guides to electronic shifts than the changes in bond lengths [39,40]. According to Figure 2 and Table 4, the changes are most pronounced in the phosphazene ring for the angles nearest the bulky substituent, viz., α(NPN) and

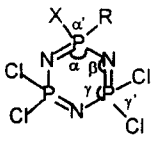


FIGURE 2 Generalized bond-angle diagram of monosubstituted pentachlorocyclotriphosphazatrienes, $N_3P_3Cl_4XR$.

TABLE 4 Selected Bond Lengths and Angles for Some Phosphazene Compounds

Compound		*Bond length Å*				*Angles, deg.*			
		(R)(X)P–N	*N–PCl_2*	*Cl_2P–N*	*NPN(α)*	*XPR(α')*	*PNP(β)*	*NPN(γ)*	*Ref.*
$N_3P_3Cl_6$	**(1)**	—	1.581(3)	—	118.3(2)	101.2(1)	121.4(3)	118.3(2)	[42]
$N_3P_3Cl_5$(OAr)	**(5)**	1.60(1)	1.57(1)	1.58(1)	115.8(1)	104.5(6)	122.5(1)	119.9(9)	This work
$N_3P_3Cl_5Ph$	**(9)**	1.590(4)	1.554(3)	1.575(4)	117.3(2)	103.5(2)	121.6(2)	118.8(2)	[43]
$N_3P_3Cl_5(OC_{14}H_9)$	**(10)**[a]	1.586(3)	1.569(3)	1.580(3)	116.6(2)	105.2(9)	121.3(2)	118.6(2)	[17]
$N_3P_3Cl_5(NPPh_3)$	**(11)**	1.604(2)	1.556(2)	1.578(2)	114.4(1)	107.2(1)	122.1(1)	119.6(1)	[39]
$N_3P_3Cl_5(OC_6H_3Cl_2$-o)	**(12)**	1.580(3)	1.571(4)	1.575(3)	118.0(2)	101.1(1)	121.3(2)	119.3(2)	[16]
$N_3P_3Cl_4(OC_6H_3Cl_2$-o)$_2$	**(13)**	1.579(3)	1.565(3)	1.576(4)	117.5(2)	99.4(1)	121.8(3)	118.9(2)	[16]
$N_3P_3Cl_4(OC_6H_3Me_2$-O)$_2$	**(14)**	1.594(3)	1.559(2)	1.579(3)	116.4(1)	101.4(1)	122.2(2)	119.2(1)	[16]
$N_3P_3Cl_4Ph(PPh_2)$	**(15)**	1.611(5)	1.548(3)	1.561(5)	114.5(2)	106.7(1)	123.0(3)	119.7(2)	[43]
$N_3P_3Cl_4(NPPh_3)_2$	**(16)**	1.64(5)	1.54(5)	1.57(5)	109.2(4)	110.9(4)	119.0(4)	120.8(3)	[39]
$Cl_5N_3P_3P_3N_3Cl_4O$(Ar)	**(7)**								[23]
$Cl_5N_3P_3$-;(ring A)		1.576(5)	1.578(5)	1.559(6)	118.0(3)	98.1(1)	121.2(3)	118.6(3)	
(ArO)$Cl_4N_3P_3$-;(ring B)		1.591(4)	1.576(4)	1.569(5)	116.7(2)	98.7(1)	122.1(3)	118.6(2)	

[a]$OC_{14}H_9$ is 9-anthryloxy unit.

α'(XPR), the former decreasing, and the latter increasing, with increasing electron supply and repulsions of the substituents relative to $N_3P_3Cl_6$. The β values are seen to change considerably and seem to increase with increasing electron supply to the N_3P_3 ring. In compound **5**, the α[115.8(1)°] angle is larger and the α'[104.5(6)°] angle is smaller than the corresponding ones in $N_3P_3Cl_5(NPPh_3)$ **11** [39], $N_3P_3Cl_4Ph(PPh_2)$ **15** [43], and $N_3P_3Cl_4(NPPh_3)_2$ **16** [39], which implies lesser electron donation to the N_3P_3 ring. In the bi(cyclophosphazene)$Cl_5N_3P_3$–$P_3N_3Cl_4(OAr)$ **7** [23], the P–P bond length [2.193(2) Å] is comparable with the P–P bond length [2.199(2) Å] of **15** [43], but bond angles α, α', and β are very different, indicating that there are no electron releasing effects to the $Cl_5N_3P_3$-ring (**A**) and the $(ArO)Cl_4N_3P_3$-ring (**B**). On the other hand, Cl is a strong electron acceptor, and some of the electron density of the ring (**A**) is transferred to the bridgehead P–Cl bond [2.016(2) Å]. Some of the electron density of bulky substituents, OAr, appears to be transferred to the ring (**B**), and as a result, the α[116.7(2)°] angle decreases. The picture that emerges is not similar to that of compound **5**. Although electronic effects seem to explain all the differences, further work on trimeric-phosphazene compounds with bulky substituents will be necessary to understand the effects of the steric factors, since they vary tremendously.

EXPERIMENTAL

The ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded on a Bruker AC-200 FT-NMR spectrometer operating at 200.05, 50.30, and 80.984 MHz, respectively. The ^{1}H and ^{13}C chemical shifts were measured using $SiMe_4$ as an internal standard; the ^{31}P chemical shifts, using 85% H_3PO_4 as an external standard. Chemical shifts downfield from the standard are assigned positive δ values. Infrared spectra were recorded on a Perkin Elmer model 377 spectrophotometer as KBr discs. Electron impact (70 eV, ca. 1.12×10^{-17} J) mass spectra were obtained on a VG-ZAPSPEC spectrometer with an ion source temperature of 240°C. Microanalyses were carried out by the microanalytical service of TÜBİTAK-MAE, Gebze-Kocaeli (Türkiye). All manipulations were carried out under an argon atmosphere using standard vacuum-line techniques $N_3P_3Cl_6$ **1** (Shin Nisso Kako Co. Ltd.), 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, and 2,4,6-tri-tert-butylphenol (Aldrich Chemical Co. Ltd.) were used as supplied. Light petroleum ether (bp 60–80°C), dichloromethane, and tetrahydrofuran (THF) were dried by conventional procedures. Silica gel used for column chromatography was 70–230 mesh (Merck), and all reactions were monitored by using Kieselgel 60 F254 (silica gel) precoated TLC plates. Compound **5** was recrystallized from toluene/light-petroleum ether (1:1) by slow evaporation in order to prepare X-ray–quality crystals.

Synthetic Procedures

Synthesis of $N_3P_3Cl_5(OC_6H_2Bu^t_3\text{-}2,4,6)$ **5**. 2,4,6-Tri-tert-butylphenol (2.26 g, 8.63 mmol) in 50 cm^3 of THF was slowly added, during 0.5 hours to small pieces of Na (0.50 g, 21.73 mmol) in 10 cm^3 of THF with vigorous stirring at 20°C, with argon being passed over the reaction mixture. Excess Na was removed by filtration, and the remaining solution of sodium-2,4,6-tri-tert-butylphenoxide was cooled and then frozen with use of a liquid nitrogen-acetone mixture. To this mixture, $N_3P_3Cl_6$ **1** (3.00 g, 8.63 mmol) in 40 cm^3 THF was slowly added, and the resulting mixture was allowed to come to ambient temperature with constant stirring. After the mixture had been vigorously stirred (72 hours) at room temperature, the precipitated salt (NaCl) was filtered off and the solvent removed under reduced pressure. The residue, after filtration on a short column of silica gel to remove traces of salts, was chromatographed (silica gel: 120 g, eluent: $CHCl_3$ light-petroleum ether 1:1) and crystallized from CH_2Cl_2 light-petroleum ether (1:1). 2-(2,4,6-tri-tert-butylphenoxo)-2,4,4,6,6-pentachlorocyclo-λ^5-triphosphazatriene **5** was obtained in 3.96 g (80%) yield, mp 155°C (found: C, 37.60; H, 5.08; N, 7.27; $C_{18}H_{29}Cl_5N_3P_3O$ requires C, 37.69; H, 5.10; N, 7.33%). IR (KBr): ν (CH aryl) 3949, ν (CH) 2967, *gn* (CO aryl) 1250, ν (P = N) 1215, 1185, ν (PCl) 590 cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 1.3 (s, 9H, 4-Bu^t CH_3), 1.5 (s, 18H, 2-Bu^t CH_3), 7.3 (s, 2H, Ar–H); ^{13}C, δ 32.1 (s, 3C, CH_3-para), 35.2 (s, 1C, $\underline{C}(CH_3)_3$-para), 32.9 (s, 6C, CH_3-ortho), 37.0 (s, 2C, $\underline{C}(CH_3)_3$-ortho), 125.1 (s, 2C, 3-phenyl), 142.8 (s, 2C, 2-phenyl), 147.9 (s, 1C, C-ipso); ^{31}P, AB_2 pattern, δA = 6.8, δB = 20.9, $^2J_{AB}$ = 62.8 Hz. MS (highest peak in multiplet): *m/z* 573 ([M]$^+$, 32), 558 ([M-CH_3]$^+$, 100), 516 ([M-Bu^t, 13]$^+$, 502 ([M-Bu^t + CH_3]$^+$ or [M-2Cl]$^+$, 44), 312 ([$N_3P_3Cl_5$]$^+$, 18), 57 ([Bu^t]$^+$, 78%).

Synthesis of $N_3P_3Cl_4(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_2$ **6**. 2,6-Di-tert-butyl-4-methylphenol (1.90 g, 8.63 mmol), Na (0.50 g, 21.73 mmol), and $N_3P_3Cl_6$ **1** (3.00 g, 8.63 mmol) were used for the preparation of **6** as for **5**. The residue was chromatographed (silica gel: 100 g, eluent: CH_2Cl_2-hexane 1:1) and 2,2-bis(2,6-di-tert-butyl-4-methylphenoxo)-4,4,6,6-tetrachlorocyclo-λ^5-triphosphazatriene **6** was crystallized from benzene light-petroleum ether (1:3), mp 166°C, 1.45

g (47%) yield (found: C, 50.63; H, 6.61; N, 5.67; $C_{30}H_{46}Cl_4N_3P_3O_2$ requires C, 50.37; H, 6.48; N, 5.87%). IR (KBr): ν (CH aryl) 3040, ν (CH) 2940, ν (CO aryl) 1235, ν (P = N) 1190, ν (PCl) 590 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 1.4 (s, 18H, $C(CH_3)_3$), 2.8 (s, 3H, CH_3-para), 7.0 (s, 2H, Ar–H); ^{13}C, δ 30.4 (s, 6C, $C(\underline{C}H_3)_3$), 34.3 (s, 1C, $\underline{C}H_3$-para), 38.0 (s, 2C, $\underline{C}(CH_3)_3$), 124.9 (s, 2C, 3-phenyl), 132.1 (s, 1C, 4-phenyl), 135.7 (s, 2C, 2-phenyl), 151.8 (s, 1C, C-ipso); ^{31}P, AB_2 pattern, δA = 27.3, δB = 19.9, $^2J_{AB}$ = 12.8 Hz. MS (highest peak in multiplet): *m/z* 715 ([M + 2]$^+$, 45), 700 ([M + 2)-CH_3]$^+$, 16), 659 ([(M + 2) + H–Bu^t]$^+$, 66), 602 ([(M + 2) + H-2Bu^t]$^+$, 26), 502 ([(M + 2) + 3H-(3Bu + 3CH_3)]$^+$], 78), 311 ([$N_3P_3Cl_4$ $(OH)_2$]$^+$, 18), 294 ([$N_3P_3Cl_4(OH)$]$^+$, 25), 57 ([Bu^t]$^+$, 100%).

Synthesis of [$Cl_5N_3P_3$–$P_3N_3Cl_4(OC_6H_3Bu^t_2$-2,6)] 7. The reactants 2,6-di-tert-butylphenol (1.78 g, 8.63 mmol), Na (0.25 g, 10.87 mmol), and $N_3P_3Cl_6$ 1 (3.00 g, 8.63 mmol) were allowed to react as in the preparation of 5. After column chromatography (silica gel: 120 g, eluent: CH_2Cl_2 light-petroleum ether 1:6); the bicyclic compound 2-(2,6-di-tert-butylphenoxo)-4,4,6,6,2′,4′,6′,6′-nonachloro bi(cyclo-λ^5-triphosphazatriene) 7 was obtained and crystallized from chloroform, mp 171°C, 1.84 g (28%) yield (found: C, 21.41; H, 2.66; N, 10.40; $C_{14}H_{21}Cl_9N_6P_6O$ requires C, 21.17; H, 2.67; N, 10.58%). IR (KBr): ν (CH aryl) 3060, ν (CH) 2970, ν (P = N) 1215, 1190, 1170, ν (PCl) 590 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 1.4 (s, 18H, $C(CH_3)_3$), 7.7 (s, 3H, Ar–H); ^{13}C, δ 32.1 (s, 6C, $C(\underline{C}H_3)_3$), 36.2 (s, 2C, $C(CH_3)_3$, 125.2 (s, 1C, 4-phenyl), 127.4 (s, 2C, 3-phenyl), 128.2 (s, 2C, 2-phenyl), 143.4 (s, 1C, C-ipso); ^{31}P, M_2ABN_2 pattern (deceptively simple, partly resolved), δ P(P)(OAr) = 6.6, δ PCl_2 = 20.9, δ P(P)Cl = 21.1, the average coupling N = $|^2J_{PNP} + {}^3J_{PPNP}|$ = 66.0 Hz and $|^2J_{PNP} + {}^3J_{PPNP}|$ = 66.3 Hz (from $N_3P_3Cl_4$(OAr) fragment). MS (highest peak in multiplet): *m/z* 721 ([M–2Cl]$^+$, 11), 687 ([M–3Cl]$^+$, 17), 672 ([M-(3Cl + CH_3)]$^+$, 8), 630 ([M-(Bu^t + 3Cl)]$^+$, 18), 502 ([$H_3N_6P_6Cl(OH)$]$^+$, 98), 294 ([$N_3P_3Cl_4(OH)$]$^+$, 32), 57 ([Bu^t]$^+$, 100%).

Synthesis of [$N_3P_3(OC_6H_3Bu^t_2$-2,6)$_5$]$_2$ 8. 2,6-Di-tert-butylphenol (5.34 g, 25.88 mmol) in 100 cm^3 of THF was allowed to react with Na (1.00 g, 43.47 mmol) at 20°C and stirred until the H_2(g) evolution had been completed $N_3P_3Cl_6$ 1 (3.00 g, 8.63 mmol) was added to this mixture, and the same procedure as in the preparation of 5 was followed. After column chromatography (silica gel: 100 g, eluent: CH_2Cl_2 light-petroleum ether 1:5), the bicyclic compound 2,4,4,6,6,2′,4′,4′,6′,6′,-deka(2,6-di-tert-butylphenoxo)-bi(cyclo-λ^5-triphosphazatriene) 8 was obtained and crystallized from CH_2Cl_2 light-petroleum ether (1:); mp 236 C, 1.68 g (28%) yield (found: C, 72.33; H, 8.99; N, 3.57; $C_{140}H_{210}O_{10}N_6P_6$ requires C, 72.39; H, 9.11; N, 3.62%). IR (KBr): ν (CH aryl) 3010, ν (CH) 2960, ν (C = C) 1610, ν (CO) 1265, ν (P = N) 1205, 1170 cm^{-1}. NMR ($CDCl_3$): ^1H, δ 1.4 (s, 3H, Ar–H); ^{13}C, δ 29.6 (s, 6C, $C(\underline{C}H_3)_3$), 36.0 (s, 2C, $C(CH_3)_3$), 125.4 (s, 1C, 4-phenyl), 126.1 (s, 2C, 3-phenyl), 136.2 (s, 2C, 2-phenyl), 150.5 (s, 1C, C-ipso); ^{31}P, $M_2AA'M_2$($\approx M_2A$) pattern, δ P(OAr)$_2$ = 8.7, δ P (P)(OAr) = 23.0, $|^2J_{PNP} + {}^3J_{PPNP}|$ = 65.6 Hz. MS: (no molecular ion peak has been observed in the mass spectrum of this compound by recording both FAB or EI techniques) *m/z* 667 ([$H_3N_3P_3(OAr)_2$-CH_4]$^+$, 575, 410, 369; 185([$C_6H_3Bu^t_2$-4H]$^+$, 100%).

SUPPLEMENTARY TABLES. Tables of (1) Atomic Coordinates and Isotropic Parameters of Hydrogen Atoms, (2) Bond Angles, and (3) Anisotropic thermal Parameters may be obtained by writing to Professor Zeynel Kılıç.

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