Notes

Unique Intramolecular Interaction in Cyclotriphosphazene Molecule. Synthesis, Structure, and Properties of 1,1-Bis(pyridyl-2-thio)-3,3,5,5-tetrachloro-cyclotriphosphazene

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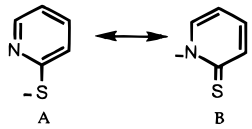
Introduction

The substitution reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with a number of nucleophiles such as amines, alcohols, and organometallic reagents have been widely studied.[1−3] Sometimes, however, the isolation of the products tends to be somewhat intricate due to the formation of several isomers and the degree of chlorine replacement. Recent research in this field has largely involved substitution mechanisms, the isolation of isomers, and the pattern of chlorine replacement (*geminal* or *nongeminal*, and *cis* or *trans*).[4−7] For aminolysis, alcoholysis, and phenolysis of $N_3P_3Cl_6$, fully substituted products have been predominantly obtained even at or below room temperature.[1,8] However, the degree of replacement can be governed by several factors such as the steric requirements of nucleophiles, the control of reaction time, and the choice of solvent.[8−11] For instance, the reaction of hexachlorocyclotriphosphazene with sodium phenylthiolate in boiling diethyl ether or benzene solution yielded a mixture of $N_3P_3(SPh)_2Cl_4$ and $N_3P_3(SPh)_6$; the yield of the latter increased with the prolongation of the reaction time.[8,12,13]

The reactions of the phosphazene trimer with thiolates are surprisingly less well evaluated compared with aminolysis or alcoholysis. Moreover, to our knowledge, no studies on the X-ray structure of thiolatocyclotriphosphazenes were carried out yet. In order to clarify the substitutions with thiolates, we report the reaction of $N_3P_3Cl_6$ with an attracting ligand, pyridine-2-thiolate[14,15] and a relationship between reactivities and structure. The bulkiness of the pyridine-2-thiol is very similar to that of phenylthiol whereas the coordination mode of the pyridine-2-thiol is versatile via tautomerization (**A** and **B**) in contrast to benzenethiol.[16,17]



A B

Experimental Section

Chemicals and Measurements. Pyridine-2-thiol (2-HSPy) and hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) were purchased from Aldrich. Potassium pyridine-2-thiolate (KSPy) was prepared by the reaction of 2-HSPy with potassium hydroxide in 95% ethanol. Chemical analyses were carried out by the Advanced Analysis Center at KIST. IR spectra were recorded on a Perkin-Elmer 16F PC model FT-IR spectrometer as KBr pellets. NMR spectra were measured on a Varian Gemini 300 NMR spectrometer operating at 300.00 MHz (^{1}H), 75.48 MHz (^{13}C), and 121.44 MHz (^{31}P) in pulse mode with Fourier transform. The chemical shifts were relative to internal Me_4Si (^{1}H and ^{13}C) and external $(C_6H_5O)_3PO$ (^{31}P)[18] for the indicated nuclei.

Preparation of $N_3P_3(2\text{-}SPy)_2Cl_4$. $N_3P_3Cl_6$ (3.48 g, 10.0 mmol) and triethylamine (10.12 g, 100 mmol) were combined in 150 mL of dried tetrahydrofuran. The mixture was stirred for 5 min at room temperature, and 2-HSPy (11.12 g, 100.0 mmol) was added. The reaction solution was refluxed for 3 days. The triethylamine hydrochloride formed was filtered off. The filtrate was concentrated to 20 mL, and excess distilled water was added to precipitate the thin yellow product in 92% yield. Recrystallization from a mixture of chloroform and hexane (1:1) gave colorless crystals suitable for X-ray crystallography. Mp: 130−133 °C. Anal. Found (Calcd for $C_{10}H_8N_5Cl_4P_3S_2$): C, 24.10 (24.16); H, 1.59 (1.62); N, 13.96 (14.09). IR (KBr, cm^{-1}): ν(P═N), 1194. ^{1}H NMR (Me_2SO-d_6, ppm): 8.47 (1H, d, 5.0 Hz), 7.80 (1H, t, 8.0 Hz), 7.61 (1H, d, 8.0 Hz), 7.27 (1H, t, 5.0 Hz). ^{13}C NMR (Me_2SO-d_6, ppm): 146.7, 139.0, 127.5, 111.1, 108.9. ^{31}P NMR (Me_2SO-d_6, ppm): 59.4, 39.0.

X-ray Crystallography. All the crystallographic data were obtained on an Enraf-Nonius CAD 4 automatic diffractometer with graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.709\,30$ Å, $\lambda(K\alpha_2) = 0.713\,59$ Å) at an ambient temperature of 23(2) °C. Preliminary diffractometric investigation indicated a monoclinic system. Accurate cell dimensions were obtained from the setting angles of 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections monitored after every hour did not reveal any systematic variation in intensity. The structure was solved by direct methods, followed by successive difference Fourier synthesis. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. All calculations were carried out on

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Table 1. Crystallographic Data for $N_3P_3(2\text{-SPy})_2Cl_4$

formula	$C_{10}H_8N_5Cl_4P_3S_2$
fw	497.04
T, °C	23(2)
λ, Å	0.710 73
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	8.672(4)
b, Å	15.276(5)
c, Å	14.221(2)
β, deg	98.80(2)
V, Å^3	1862(1)
Z	4
d_{calcd}, Mg/m^3	1.773
abs coeff, mm^{-1}	1.122
F(000)	992
cryst size, mm	0.24 × 0.82 × 0.32
θ_{max}, deg	25
index ranges	$0 \le h \le 10$, $0 \le k \le 18$, $-16 \le l \le 16$
no. of reflcns collcd	2978
no. of indepnt reflcns [$I > 2\sigma(I)$]	2742
no. of params refined	217
goodness of fit	1.380
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0634, wR2 = 0.2102
R indices (all data)	R1 = 0.0736, wR2 = 0.2215
largest diff peak and hole, e A^{-3}	+0.480 and −0.660

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum(F_o^2 - F_c^2)^2/\sum wF_o^4\}^{1/2}$, where $w = 1/\{\sigma^2F_o^2 + (0.0197P)^2 + 0.00P\}$ and where $P = \{\text{Max}(F_o^2, 0) + 2F_c^2\}/3$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $N_3P_3(2\text{-SPy})_2Cl_4$

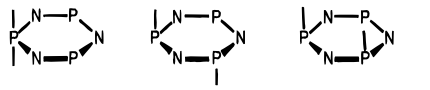
	x	y	z	U(eq)[a]
P(1)	1064(1)	8592(1)	7852(1)	35(1)
P(2)	−157(2)	6936(1)	7573(1)	43(1)
P(3)	−2121(2)	8341(1)	7478(1)	41(1)
N(1)	1290(5)	7557(3)	7757(3)	42(1)
N(2)	−1869(5)	7321(3)	7430(3)	51(1)
N(3)	−673(4)	8965(2)	7715(3)	40(1)
N(4)	247(6)	8388(3)	5767(3)	55(1)
N(5)	61(6)	8063(3)	9688(3)	50(1)
S(1)	2384(2)	9269(1)	6984(1)	49(1)
S(2)	2306(2)	9061(1)	9127(1)	45(1)
Cl(1)	70(2)	6154(1)	6474(1)	86(1)
Cl(2)	−2(2)	6040(1)	8619(1)	69(1)
Cl(3)	−3427(2)	8742(1)	6268(1)	65(1)
Cl(4)	−3614(2)	8574(1)	8389(1)	65(1)
C(1)	1363(6)	8979(3)	5833(3)	43(1)
C(2)	−474(8)	8199(4)	4889(4)	60(2)
C(3)	−108(7)	8577(4)	4086(4)	58(2)
C(4)	1053(7)	9188(4)	4175(4)	58(1)
C(5)	1824(7)	9400(4)	5064(4)	52(1)
C(6)	977(6)	8741(3)	9913(3)	41(1)
C(7)	−891(7)	7822(4)	10269(4)	56(1)
C(8)	−939(8)	8241(4)	11125(4)	59(2)
C(9)	−12(7)	8943(4)	11349(4)	57(2)
C(10)	977(7)	9220(4)	10738(3)	52(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

a personal computer with use of SHELXS 86 or SHELXL 93.[19] Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1. Atomic positions and equivalent isotropic thermal parameters are reported in Table 2.

Results and Discussion

Synthesis. The reaction of $N_3P_3Cl_6$ with 2-HSPy in the presence of triethylamine in boiling tetrahydrofuran (THF) solution afforded a bis-substituted cyclotriphosphazene. Among the following possible three isomers,



1,1-isomer *trans*-1,3-isomer *cis*-1,3-isomer

geminal *nongeminal*

only a *geminal* isomer, 1,1-bis(pyridyl-2-thio)-3,3,5,5-tetrachlorocyclotriphosphazene was selectively obtained as established by the two ^{31}P chemical shifts (59.4 and 39.0 ppm) in a ratio of 1:2. The same isomer was obtained in a similar yield by the reaction of $N_3P_3Cl_6$ with potassium salt of pyridine-2-thiolate, 2-KSPy, under the same conditions. The fully substituted compound, $[NP(2\text{-SPy})_2]_3$, was not produced by the change of the reaction conditions such as the mole ratio of the reactants and extension of the reaction time in contrast to $[NP(2\text{-OPy})_2]_3$[20] and $[NP(SPh)_2]_3$,[8,12,13] (2-OPy, 2-pyridinolate; SPh: thiophenolate) which were easily prepared by the reaction of $N_3P_3Cl_6$ with HOPy and HSPh, respectively. Interestingly, the reaction with the cognate ligand, 4-HSPy, predominantly produces a hexasubstituted compound, $[NP(4\text{-SPy})_2]_3$ ($^{31}P(\delta$, Me_2SO-$d_6) = 59.5$ ppm) under the same conditions. Thus, the formation of only a *geminal* bis-substituted product, $N_3P_3(2\text{-SPy})_2Cl_4$, irrespective of the reaction conditions seems to be ascribed to its intrinsic properties, which will be explained later. NMR studies indicate that the structure of the title compound is retained even in solution. The compound exists as thin yellow crystals with melting point in the range 130−133 °C, which are soluble in polar organic solvents such as THF, dimethyl sulfoxide, and dimethylformamide, *etc*. The compound was easily melt-polymerized to produce its corresponding polymer at about 180 °C, which report will be published separately.

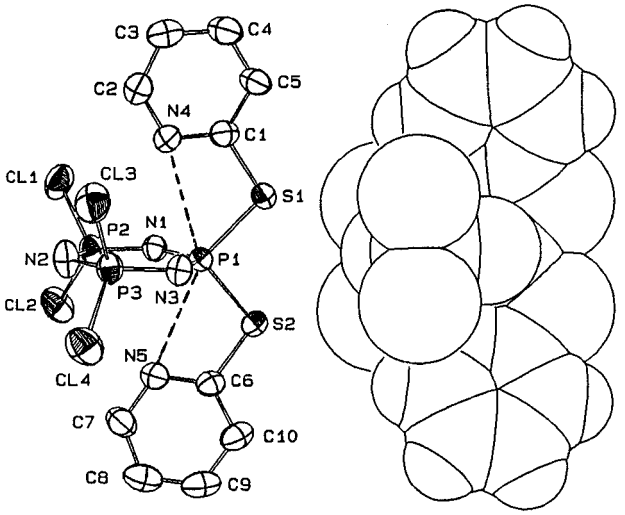


Figure 1. ORTEP shown at 50% probability level (left) and space-filling (right) views of 1,1-bis(pyridyl-2-thio)-3,3,5,5-tetrachlorocyclotriphosphazene.

Crystal Structure. The ORTEP and space-filling views of the present compound is depicted in Figure 1, and selected bond lengths and bond angles are listed in Table 3. For the *geminal* isomer, the bond lengths of the pyridyl group disclose that the pyridine-2-thiolate group exists as the thiol tautomer **A** in contrast to the thione tautomer **B**, which is often seen as a ligand

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $N_3P_3(2\text{-}SPy)_2Cl_4$

P(1)−N(3)	1.594(4)	P(1)−N(1)	1.601(4)
P(1)−S(1)	2.082(2)	P(1)−S(2)	2.089(2)
P(2)−N(1)	1.563(4)	P(2)−N(2)	1.581(4)
P(2)−Cl(1)	2.000(2)	P(2)−Cl(2)	2.011(2)
P(3)−N(3)	1.571(4)	P(3)−N(2)	1.576(4)
P(3)−Cl(4)	1.998(2)	P(3)−Cl(3)	2.006(2)
N(3)−P(1)−N(1)	117.9(2)	N(3)−P(1)−S(1)	110.2(2)
N(1)−P(1)−S(1)	110.8(2)	N(3)−P(1)−S(2)	109.6(2)
N(1)−P(1)−S(2)	111.0(2)	S(1)−P(1)−S(2)	94.95(7)
N(1)−P(2)−N(2)	120.6(2)	N(1)−P(2)−Cl(1)	108.7(2)
N(2)−P(2)−Cl(1)	109.0(2)	N(1)−P(2)−Cl(2)	109.1(2)
N(2)−P(2)−Cl(2)	107.7(2)	Cl(1)−P(2)−Cl(2)	99.74(9)
N(3)−P(3)−N(2)	119.8(2)	N(3)−P(3)−Cl(4)	109.2(2)
N(2)−P(3)−Cl(4)	108.2(2)	N(3)−P(3)−Cl(3)	109.1(2)
N(2)−P(3)−Cl(3)	109.2(2)	Cl(4)−P(3)−Cl(3)	99.47(9)
C(1)−S(1)−P(1)	100.3(2)	C(6)−S(2)−P(1)	98.8(2)

to a soft metal.[21,22] The six-membered ring of "N_3P_3" (P−N bond lengths: 1.563(5)−1.601(4) Å) approximates to a plane, the N_3P_3 atoms deviate from the resonance plane by less than 0.024(3) Å. The most striking feature is that the nitrogen atom of the pyridine-2-thiolate group significantly interacts with P(1) (P(1)−N(4), 2.96 Å, and P(1)−N(5), 2.96 Å), within the sum of the van der Waals radii (3.40 Å).[23] However, the distance of N···P is too long to indicate a normal covalent bond, and thus the interaction is best described to be the host−guest type reminiscent of molecular recognition. Such an interaction in the molecule is easily visualized by examining a space-filling view drawn with the crystallographic coordinates shown in Figure 1. The nitrogen atom of the pyridine group is validly embedded between two chlorine atoms. As a proof of the interaction, the angle of S(1)−P(1)−S(2) (94.95(7)°) is noticeably pinched from a tetrahedral arrangement. Moreover, the angles of P(1)−S(1)−C(1) (100.3(2)°) and P(1)−S(2)−C(6) (98.8(2)°) are much smaller than the corresponding angles of simply S-coordinated pyridine-2-thiol compounds of [AuCl(2-C_5H_5NS)] (110.5(5)°)[22] and [Cu(totp)(tzdth)] (112.8(2)°).[21] However, the angles of P−S−C are splayed out compared with that (77.4(1)°) of a normal N,S-bidentate compound, [$V(pyr)_2$(tmeda)].[15] Thus, the pyridine-2-thiolate group is bonded to a phosphorus atom in a pseudobidendate fashion in the molecule.

Nucleophilic Substitution. Why does the present reaction so selectively produce only a *geminal* 1,1-isomer? In contrast, the cognate reaction with HSPh predominantly affords the fully substituted product, $(NP(SPh)_2)_3$, under the same reaction conditions even though 2-SPy and SPh are very similar in bulkiness.[8,12,13] The question about further attack can be framed thus: will the second attack of nucleophile (2-HSPy) take place at the P(2-SPy)Cl center, or will it go for another, untouched PCl_2 center on the ring? Even though the P(2-SPy)Cl center is sterically unfavorable compared with the PCl_2 center, formation of the *geminal* 1,1-isomer implies that P(2-SPy)Cl center is more reactive than untouched PCl_2. Thus, the second nucleophilic attack of 2-HSPy seems to proceed via the S_N1 type. On the other hand, the absence of any further reaction in the present system suggests that the first pyridine-2-thiolate substitution of untouched PCl_2 is performed via an S_N2 mechanism. For the title molecule, the P···N intramolecular interaction causes difficulty in further substitution at other untouched phosphorus atoms via S_N2 mechanism involving a pentacoordinate phosphorus intermediate. The easy production of fully substituted $(NP(4\text{-}SPy)_2)_3$ under the same conditions may be another piece of conclusive evidence, where the nitrogen atom of 4-SPy cannot structurally interact with the phosphorus atom of the phosphazene ring. Thus, it seems that the first and second nucleophilic substitution reactions of two pyridine-2-thiolate groups proceed successively via S_N2 and S_N1 mechanisms, respectively.

In conclusion, the present compound is the first crystal structure of pseudohexacoordinate cyclotriphosphazenes. The formation of only a *geminal* isomer and its prominent structural feature imply the mechanism of the nucleophilic substitution of the pyridine-2-thioate with hexachlorocyclotriphosphazene.

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Supporting Information Available: Tables of crystallographic details, positional parameters, bond distances and angles, anisotropic and isotropic thermal parameters of atoms, and least-squares planes (7 pages). Ordering information is given on any current masthead page.

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