© 1997 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 70, 2125—2130 (1997)

# Synthesis, Structure, and Properties of 2,2-Bis(2-pyrimidinylthio)-4,4,6,6-tetrachlorocyclotri($\lambda^5$-phosphazene)s. Insight into Bonding Mode

**Ok-Sang Jung,* Yong Tae Kim, Hyun Lee, Kwan Mook Kim, Hee Kwon Chae,† and Youn Soo Sohn**

Inorganic Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Korea

†Department of Chemistry, Hankuk University of Foreign Studies, Yongin 449-791, Korea

(Received February 14, 1997)

The reaction of hexachlorocyclotri($\lambda^5$-phosphazene), $N_3P_3Cl_6$, with a series of pyrimidine-2-thiol in the presence of triethylamine in boiling tetrahydrofuran solution affords only a *geminal* isomer, $N_3P_3(N\text{–}S)_2Cl_4$ (N–S = 2-pyrimidinylthio (pms), 4,6-dimethyl-2-pyrimidinylthio (dmpms), and trifluoromethyl-2-pyrimidinylthio (fmpms)) in high yield. The molecular structures of $N_3P_3(pms)_2Cl_4$ (monoclinic $P2_1/n$, $a = 7.686(2)$, $b = 28.236(7)$, $c = 8.760(2)$ Å, $\beta = 99.87(2)°$, $V = 1873.2(8)$ Å$^3$, $Z = 4$, $R = 0.052$) and $N_3P_3(dmpms)_2Cl_4$ (triclinic $P\bar{1}$, $a = 8.698(3)$, $b = 9.630(3)$, $c = 14.179(6)$ Å, $\alpha = 100.88(3)$, $\beta = 92.83(3)$, $\gamma = 103.84(3)°$, $V = 1126.9(7)$ Å$^3$, $Z = 2$, $R = 0.049$) have been solved. The crystal structures disclose that the nitrogen atom of the 2-pyrimidinylthiol group significantly interacts with the phosphorus atom of the cyclotri(phosphazene) ring within the sum of the van der Waals radii (3.40 Å). The P···N intramolecular interaction of $N_3P_3(dmpms)_2Cl_4$ (P(1)–N(5), 3.109(4); P(1)–N(7), 3.126(4) Å) is considerably longer than that of $N_3P_3(pms)_2Cl_4$ (2.965(7), 2.986(7) Å). Although such a unique intramolecular interaction does not seem to be exactly retained in solution, the steric effects of the geminal bis-substituted ligands seem to hinder further substitution at other untouched phosphorus atoms. The formation of only a *geminal* isomer and its structure seem to be involved in the mechanism of the substitution reaction.

The reactions of hexachlorocyclotri($\lambda^5$-phosphazene), $N_3P_3Cl_6$, with a number of nucleophiles such as amines, alcohols, and organometallic reagents have been widely studied, since its substituted analogs are excellent models for exploratory reactions that can be applied subsequently at its linear polymer level.[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.[4—7] For the 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 the reaction time, and the choice of solvent.[8—11] For instance, the reaction of hexachlorocyclotri($\lambda^5$-phosphazene) with sodium benzenethiolate in a 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 prolongation of the reaction time.[8,12,13] In particular, according to our previous paper,[14] the reaction of $N_3P_3Cl_6$ with pyridine-2-thiol produced only a *gem*-2,2-bis(2-pyridinylthio)-4,4,6,6-tetrachlorocyclotri($\lambda^5$-phosphazene). Furthermore, the nitrogen atom of the 2-pyridinylthio group significantly interacts with the phosphorus atom of the cyclotri($\lambda^5$-phosphazene) ring (P···N, 2.96 Å). Such a fascinating bonding mode has stimulated our interest in understanding the structure and reaction of cyclotri($\lambda^5$-phosphazene) molecules. The crucial factor on the intramolecular interaction and its related chemistry could not be clearly explained by simple studies of only the molecular structure. Moreover, the asymmetric 2-pyridinylthio groups have left a question about its behavior in solution.

In order to expand the chemistry on the substituent effects and solution-behavior, we report on a series of $N_3P_3(N\text{–}S)_2Cl_4$ (N–S = pms, dmpms, fmpms) obtained from the reaction of $N_3P_3Cl_6$ with 2-pyrimidinethiol or its analogs. The ligands are capable of chelating to metals as either 2-pyrimidinethiol (A, thiol) or pyrimidine-2(1*H*)-thione (B, thione) (Chart 1). The coordination modes of the ligands are directed by various factors, such as the basicity of the central metal, the overall charge of the complex, and medium effects.[15—19]

## Experimental

**Chemicals and Measurements.** 2-Pyrimidinethiol (pms), 4,6-dimethyl-2-pyrimidinethiol (dmpms), 3-trifluoromethyl-2-

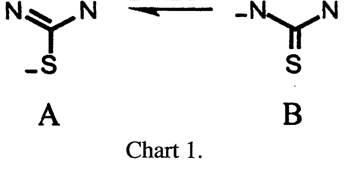


Chart 1.

pyrimidinethiol (fmpms), and hexachlorocyclotri($\lambda$-phosphazene) ($N_3P_3Cl_6$) were purchased from Aldrich. 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 in chloroform on a Varian Gemini 300 NMR spectrometer for $^{31}$P (121.44 MHz) and on a Varian Gemini 200 spectrometer for $^1$H (200.00 MHz) and $^{13}$C (50.32 MHz). The chemical shifts were relative to internal $Me_4Si$ ($^1$H and $^{13}$C) and external $(C_6H_5O)_3$ PO ($^{31}$P)[20] for the indicated nuclei.

**Preparation of $N_3P_3(pms)_2Cl_4$.** $N_3P_3Cl_6$ (3.48 g, 10.0 mmol) and triethylamine (10.12 g, 100.0 mmol) were combined in 150 mL of dried tetrahydrofuran. The mixture was stirred for 5 min at room temperature, and pmsH (11.22 g, 100.0 mmol) was added. The reaction solution was refluxed for 24 h. 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 84% yield. Recrystallization from a mixture of chloroform and hexane (1 : 1) gave colorless crystals suitable for X-ray crystallography. Mp 170 °C (decomp). Found: C, 19.10; H, 1.19; N, 19.50%. Calcd for $C_8H_6N_7Cl_4P_3S_2$: C, 19.25; H, 1.21; N, 19.65%. IR (KBr) 1556 (s), 1380 (s), 1206 (s, P=N), 1163 (s, C–S), 580 (s), 520 (s). $^1$H NMR ($CDCl_3$) $\delta = 8.68$ (4H, N–CH, d, $J = 5.0$ Hz), 7.21 (2H, CH, t, $J = 5.0$ Hz). $^{13}$C NMR ($CDCl_3$) $\delta = 167.44$ (C=S), 167.36 (C=S), 158.58 (N–CH), 158.53 (N–CH), 119.40 (CH). $^{31}$P NMR ($CDCl_3$) $\delta = 55.6$, 42.4.

**$N_3P_3(dmpms)_2Cl_4$.** This compound was synthesized in 80 % yield by the same procedure as mentioned above. The crude product was recrystallized from toluene to obtain colorless crystals. Mp 160 °C (decomp). Found: C, 25.20; H, 2.59; N, 17.53%. Calcd for $C_{12}H_{14}N_7Cl_4P_3S_2$: C, 25.96; H, 2.54; N, 17.66%. IR (KBr) 1580 (s), 1512 (m), 1247 (s, P=N), 1190 (s, C–S), 580 (s), 521 (s). $^1$H NMR ($CDCl_3$) $\delta = 6.90$ (2H, CH, s), 2.50 (12H, $-CH_3$, s). $^{13}$C NMR ($CDCl_3$) $\delta = 168.78$ (C=S), 168.75 (C=S), 165.64 (N–C), 165.54 (N–C), 119.02 (–CH), 23.96 ($-CH_3$). $^{31}$P NMR ($CDCl_3$) $\delta = 55.8$, 40.9.

**$N_3P_3(fmpms)_2Cl_4$.** This compound was prepared in 75% yield using the same procedure for $N_3P_3(pms)_2Cl_4$. Thin needle colorless crystals were obtained in a mixture of toluene and hexane. Mp 155 °C (decomp). IR (KBr) 1560 (m), 1338 (s), 1220 (s, P=N), 1195 (s, C–S), 1158 (s), 1123 (m), 590 (s), 522 (s) cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta = 8.96$ (2H, $CF_3$–C–*CH*, d, $J = 5.0$ Hz), 7.55 (2H, –CH, d, $J$=5.0Hz). $^{13}$C NMR ($CDCl_3$) $\delta$=168.21 (C=S), 168.13 (C–S), 160.4 (–CH), 157.33, 157.25 (q, $CF_3$–*C*, $^2J_{C-F}$=35.4 Hz), 119.4 (q, $-CF_3$, $^1J_{C-F}$=276.6Hz), 114.99 ($CF_3$–C–*CH*), 114.93 ($CF_3$–C–*CH*). $^{31}$P NMR ($CDCl_3$) $\delta = 54.2$, 41.9.

**X-Ray Crystallography.** All of the crystallographic data were obtained on an Enraf–Nonius CAD 4 automatic diffractometer with graphite-monochromated molybdenum radiation ($\lambda (K\alpha_1) = 0.70930$ Å, $\lambda (K\alpha_2) = 0.71359$ Å) at ambient temperature of 23(2) °C. A preliminary diffractometric investigation indicated a crystal 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 the intensity. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical $\phi$-scan method. The structures were solved by a direct method, followed by a successive difference Fourier synthesis. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions with the isotropic thermal factors. All of calculations were carried out on a personal computer with use of SHELXS 86 or SHELXL 93.[21] The crystal parameters and procedural information corresponding to the data collection and structure refinement are given in Table 1. The atomic positions and equivalent isotropic thermal parameters are reported in Table 2 for $N_3P_3(pms)_2Cl_4$, and Table 3 for $N_3P_3(dmpms)_2Cl_4$.

Further details of the crystal structure investigation for $N_3P_3(pms)_2Cl_4$, and for $N_3P_3(dmpms)_2Cl_4$ are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ, (U.K.). The complete $F_o - F_c$ data have been deposited as Document No. 70031 at the Office of the Editor of Bull. Chem. Soc. Jpn.

## Results

**Synthesis.** The reaction of $N_3P_3Cl_6$ with a series of 2-pyrimidinethiol in the presence of triethylamine in a boiling tetrahydrofuran (THF) solution afforded only a bis-substituted cyclotri($\lambda^5$-phosphazene). The two $^{31}$P chemical shifts in the ratio of 1 : 2 explain the formation of the bis-substitute (Fig. 1). Although the chemical shift at around 40 ppm corresponds to untouched $PCl_2$, a paucity of structural information still remains. Thus, single-crystal X-ray

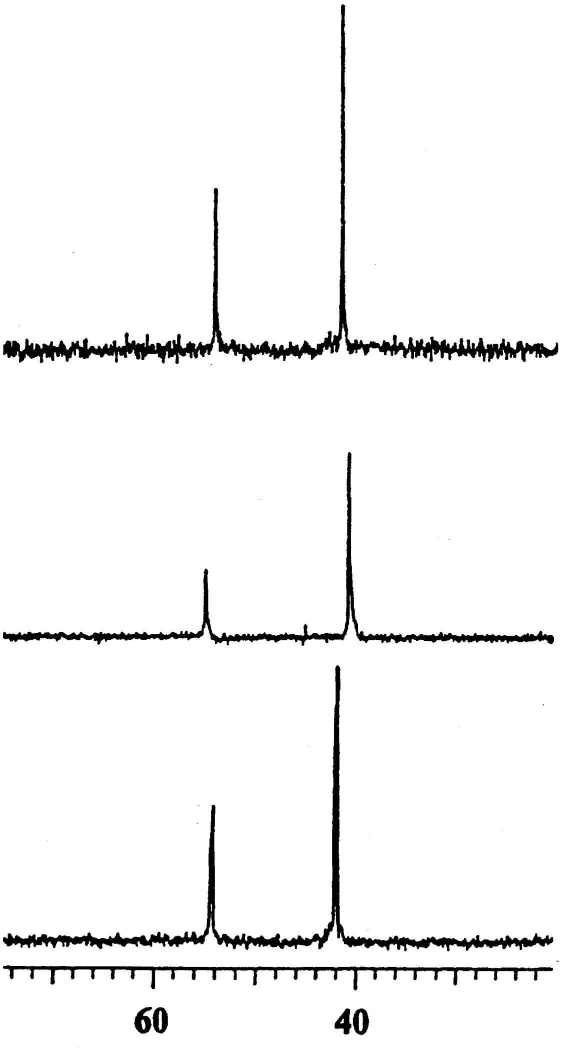


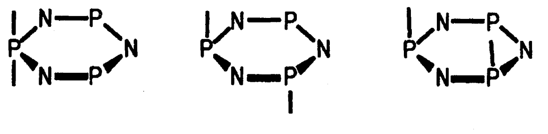
Fig. 1. $^{31}$P NMR spectra of $N_3P_3(pms)Cl_4$ (55.6, 42.4; top), $N_3P_3(dmpms)_2Cl_4$ (55.8, 40.9; middle), and $N_3P_3(fmpms)_2Cl_4$ (54.2, 41.9; bottom) in $CDCl_3$.

Table 1. Crystallographic Data

| Compounds | $N_3P_3(pms)_2Cl_4$ | $N_3P_3(dmpms)_2Cl_4$ |
|---|---|---|
| Formula | $C_8H_6N_7Cl_4P_3S_2$ | $C_{11}H_{14}N_7Cl_4P_3S_2$ |
| Formula weight | 499.03 | 555.13 |
| $T/°C$ | 23(2) | 23(2) |
| $\lambda/Å$ | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/n$ (No.14) | $P\bar{1}$ (No.2) |
| $a/Å$ | 7.686(2) | 8.698(3) |
| $b/Å$ | 28.236(7) | 9.630(3) |
| $c/Å$ | 8.760(2) | 14.179(6) |
| $\alpha$/deg | | 100.88(3) |
| $\beta$/deg | 99.87(2) | 92.83(3) |
| $\gamma$/deg | | 103.84(3) |
| $V/Å^3$ | 1873.2(8) | 1126.9(7) |
| $Z$ | 4 | 2 |
| $d_{cal}$/Mg m$^{-3}$ | 1.770 | 1.636 |
| Absorption coefficient/mm$^{-1}$ | 1.119 | 0.939 |
| $F(000)$ | 992 | 560 |
| Crystal size/mm | $0.15 \times 0.25 \times 0.50$ | $0.35 \times 0.40 \times 0.60$ |
| $\theta_{max}$/deg | 25 | 25 |
| Index ranges | $h, k, \pm l$ | $h, \pm k, \pm l$ |
| Reflections collected | 2193 | 3522 |
| Independent refns $[I > 2\sigma(I)]$ | 2045 | 3288 |
| Parameters refined | 217 | 253 |
| Goodness of fit | 0.977 | 1.113 |
| Final $R$ indices $[I > 2\sigma(I)]$[a] | $R1 = 0.0516$, $wR2 = 0.1304$ | $R1 = 0.0492$, $wR2 = 0.1296$ |
| $R$ indices (all data) | $R1 = 0.0567$, $wR2 = 0.1357$ | $R1 = 0.0498$, $wR2 = 0.1304$ |
| Largest diff. peak and hole/Å$^3$ | 0.409 and −0.380 | 0.792 and −0.346 |

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 $w = 1/\{\sigma^2 F_o^2 + (0.0197P)^2 + 0.00P\}$, and where $P = \{\mathrm{Max}(F_o^2, 0) + 2F_c^2\}/3$.

studies were undertaken for the title compounds. Among the following possible three isomers for the bis-substitute, only a *geminal*-1, 1-isomer was selectively obtained in high yields (75—84%) (Chart 2). When excess ligands were used in the reaction, the dimerization of the ligand occurred, in particular, for dmpms ligand. Only the same isomer was obtained in a similar yield by the reaction of $N_3P_3Cl_6$ with potassium salt of the free ligands under the same conditions. Fully substituted compounds, $[NP(N–S)_2]_3$, were not produced by changing the reaction conditions, such as the mole ratio of the reactants and an extension of the reaction time (3 days), in contrast to $[NP(2\text{-}OPy)_2]_3$[22] and $[NP(SPh)_2]_3$,[8,12,13] (2-OPy: 2-pyridinoxy; SPh: phenylthio), which were easily prepared by the reaction of $N_3P_3Cl_6$ with HOPy and HSPh, respectively. Thus, the formation of only a *geminal* bis-substituted product, $N_3P_3(N–S)_2Cl_4$, irrespective of the reaction conditions, seems to be ascribed to its intrinsic molecular properties, which are explained later. The title compounds are stable colorless crystals, which are soluble in polar organic solvents such as THF, dimethyl sulfoxide, and dimethylformamide, etc. but are insoluble in water.



**2,2-isomer** ***trans*-2,4-isomer** ***cis*-2,4-isomer**

***geminal*** ***nongeminal***

Chart 2.

**Crystal Structures of $N_3P_3(pms)_2Cl_4$ and $N_3P_3$-**

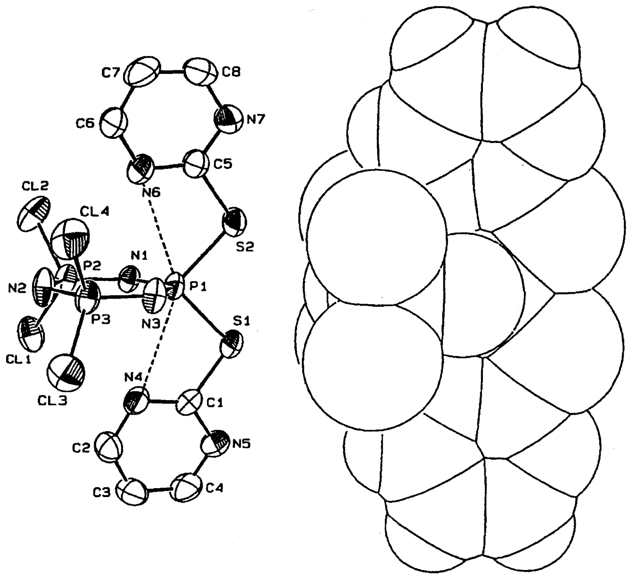


Fig. 2. ORTEP shown at 50% probability level (left) and space-filling (right) views of $N_3P_3(pms)_2Cl_4$.

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

| Atom | *x* | *y* | *z* | $U$(eq)[a] |
|---|---|---|---|---|
| S(1) | 8561(3) | 694(1) | 658 (2) | 50(1) |
| S(2) | 9335(3) | 1725(1) | 1291(2) | 52(1) |
| P(1) | 8115(2) | 1179(1) | 2335(2) | 36(1) |
| P(2) | 5184(2) | 1263(1) | 3746(2) | 41(1) |
| P(3) | 8371(2) | 1033(1) | 5476(2) | 43(1) |
| Cl(1) | 3166(2) | 809(1) | 3396(2) | 63(1) |
| Cl(2) | 3909(3) | 1869(1) | 3913(3) | 71(1) |
| Cl(3) | 8837(3) | 401(1) | 6480(2) | 68(1) |
| Cl(4) | 9731(3) | 1449(1) | 7106(2) | 72(1) |
| N(1) | 6069(7) | 1276(2) | 2241(6) | 36(1) |
| N(2) | 6363(7) | 1150(2) | 5365(6) | 52(2) |
| N(3) | 9249(7) | 1054(2) | 3980(6) | 47(2) |
| N(4) | 6812(7) | 196(2) | 2537(6) | 48(2) |
| N(5) | 7497(8) | −172(2) | 259(7) | 50(2) |
| N(6) | 8319(9) | 2146(2) | 3734(7) | 61(2) |
| N(7) | 10272(9) | 2553(2) | 2368(7) | 56(2) |
| C(1) | 7506(9) | 186(3) | 1235(7) | 42(2) |
| C(2) | 6069(10) | −206(3) | 2879(9) | 57(2) |
| C(3) | 6003(11) | −598(3) | 1974(9) | 59(2) |
| C(4) | 6739(12) | −562(3) | 659(9) | 63(2) |
| C(5) | 9281(10) | 2195(3) | 2630(8) | 47(2) |
| C(6) | 8319(13) | 2517(3) | 4675(9) | 70(2) |
| C(7) | 9277(14) | 2914(3) | 4509(10) | 78(3) |
| C(8) | 10204(12) | 2922(3) | 3322(11) | 72(3) |

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

**(dmpms)$_2$Cl$_4$.** ORTEP and space-filling views of the $N_3P_3(pms)_2Cl_4$ are depicted in Fig. 2, and selected bond lengths and bond angles are listed in Table 4. As expected from the $^{31}P$ chemical shifts, the molecular structure was confirmed to be a *geminal* 2,2-isomer. The C–S bond lengths (C(1)–S(1), 1.763(8) Å; C(5)–S(2), 1.778(7) Å) of the 2-pyrimidinylthio group disclose that the ligand exists as a thio tautomer (A) in contrast to the corresponding bond (1.692(2) Å) of the PySH ligand[23] (the crystal structure of PymSH is not available) that exists as a thion tautomer (B) in the solid state. The six-membered ring of "$N_3P_3$" (P–N bond lengths: 1.565(6)—1.590(5) Å) approximates to a plane, the $N_3P_3$ atoms deviate from the resonance plane by less than 0.012 Å. The most fascinating feature is that the nitrogen atom of the 2-pyrimidinylthio group significantly interacts with P(1) (P(1)–N(4), 2.965(7) Å and P(1)–N(6), 2.986(7) Å), within the sum of the van der Waals radii (3.40 Å).[24] The distances of N···P are very similar to those of $Co(SPy)_3$ (2.96 Å),[14] but are too long to indicate a normal covalent bond. Thus, the interaction is best described to be the van der Waals-type host–guest reminiscent of molecular recognition. Such an intramolecular interaction in the molecule is easily visualized by examining a space-filling view drawn with the crystallographic coordinates shown in Fig. 2. The nitrogen atom (N(4) and N(6)) of the pyrimidine group is validly embedded between two chlorine atoms. As proof of the interaction, the angle of S(1)–P(1)–S(2) (92.0(1)°) is noticeably pinched from a tetrahedral arrangement. Moreover, the angles of P(1)–S(1)–C(1) (101.2(2)°) and P(1)–S(2)–C-(5) (101.5(3)°) are much smaller than the corresponding an-

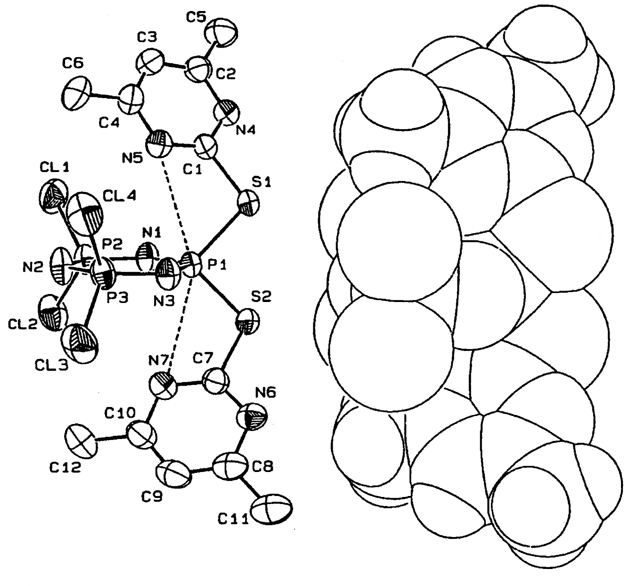


Fig. 3. ORTEP shown at 50% probability level (left) and space-filling (right) views of $N_3P_3(dmpms)_2Cl_4$.

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

| Atom | *x* | *y* | *z* | $U$(eq)[a] |
|---|---|---|---|---|
| P(1) | −1719(1) | 7673(1) | 2212(1) | 37(1) |
| P(2) | −4731(1) | 8091(1) | 2424(1) | 43(1) |
| P(3) | −3441(1) | 6729(1) | 3653(1) | 46(1) |
| N(1) | −3174(3) | 8277(3) | 1899(2) | 44(1) |
| N(2) | −4849(3) | 7332(4) | 3317(2) | 54(1) |
| N(3) | −1934(3) | 6861(3) | 3092(2) | 46(1) |
| S(1) | 376(1) | 9312(1) | 2389(1) | 48(1) |
| S(2) | −952(1) | 6410(1) | 1071(1) | 52(1) |
| Cl(1) | −5203(1) | 10044(1) | 2822(1) | 75(1) |
| Cl(2) | −6604(1) | 7071(2) | 1484(1) | 71(1) |
| Cl(3) | −4326(2) | 4635(1) | 3708(1) | 83(1) |
| Cl(4) | −2822(2) | 7585(2) | 5049(1) | 79(1) |
| N(4) | 489(4) | 12072(3) | 2849(2) | 48(1) |
| N(5) | −1210(4) | 10568(4) | 3734(2) | 58(1) |
| N(6) | −1477(4) | 3602(3) | 823(2) | 50(1) |
| N(7) | −3719(4) | 4548(4) | 1195(3) | 62(1) |
| C(1) | −215(4) | 10826(4) | 3068(3) | 45(1) |
| C(2) | 137(5) | 13267(4) | 3365(3) | 53(1) |
| C(3) | −894(5) | 13121(5) | 4065(3) | 61(1) |
| C(4) | −1543(5) | 11767(5) | 4240(3) | 63(1) |
| C(5) | 918(6) | 14689(5) | 3129(4) | 70(1) |
| C(6) | −2615(7) | 11520(6) | 5031(4) | 93(2) |
| C(7) | −2220(5) | 4643(4) | 1045(3) | 49(1) |
| C(8) | −2390(6) | 2223(4) | 733(3) | 56(1) |
| C(9) | −3969(6) | 2017(5) | 896(3) | 65(1) |
| C(10) | −4618(5) | 3161(5) | 1114(3) | 66(1) |
| C(11) | −1588(7) | 1031(5) | 467(3) | 74(1) |
| C(12) | −6346(6) | 3023(6) | 1257(5) | 96(2) |

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

Table 4. Selected Bond Lengths (Å) and Angles (deg)

| $N_3P_3(pms)_2Cl_4$ | | $N_3P_3(dmpms)_2Cl_4$ | |
|---|---|---|---|
| P(1)–N(1) | 1.584(5) | P(1)–N(1) | 1.590(3) |
| P(1)–N(3) | 1.590(5) | P(1)–N(3) | 1.588(3) |
| P(2)–N(1) | 1.584(5) | P(2)–N(1) | 1.567(3) |
| P(2)–N(2) | 1.579(5) | P(2)–N(2) | 1.573(3) |
| P(3)–N(2) | 1.565(6) | P(3)–N(2) | 1.565(3) |
| P(3)–N(3) | 1.575(6) | P(3)–N(3) | 1.558(3) |
| P(2)–Cl(1) | 1.994(3) | P(2)–Cl(1) | 2.004(2) |
| P(2)–Cl(2) | 1.989(3) | P(2)–Cl(2) | 1.981(2) |
| P(3)–Cl(3) | 1.994(3) | P(3)–Cl(3) | 1.997(2) |
| P(3)–Cl(4) | 1.999(3) | P(3)–Cl(4) | 1.989(2) |
| P(1)–S(1) | 2.080(2) | P(1)–S(1) | 2.074(2) |
| P(1)–S(2) | 2.094(3) | P(1)–S(2) | 2.072(2) |
| S(1)–C(1) | 1.763(8) | S(1)–C(1) | 1.788(4) |
| S(2)–C(5) | 1.778(7) | S(2)–C(5) | 1.785(4) |
| P(1)···N(4) | 2.965(7) | P(1)···N(5) | 3.109(4) |
| P(1)···N(6) | 2.986(7) | P(1)···N(7) | 3.126(4) |
| | | | |
| S(1)–P(1)–S(2) | 94.95(7) | S(1)–P(1)–S(2) | 92.06(6) |
| C(1)–S(1)–P(1) | 101.2(2) | C(1)–S(1)–P(1) | 101.3(1) |
| C(5)–S(2)–P(1) | 101.5(3) | C(7)–S(2)–P(1) | 101.4(1) |
| N(1)–P(1)–S(2) | 111.4(2) | N(1)–P(1)–S(1) | 109.8(1) |
| N(3)–P(1)–S(1) | 111.1(2) | N(3)–P(1)–S(1) | 113.1(1) |
| N(4)–C(1)–S(1) | 119.7(5) | N(5)–C(1)–S(1) | 117.9(3) |
| N(6)–C(5)–S(2) | 118.9(6) | N(7)–C(7)–S(2) | 118.1(3) |

gles of simply S-coordinated pyridine-2-thiol compounds of [AuCl(2-$C_5H_5NS$)] (110.5(5)°)[25] and [Cu(totp)(tzdth)I] (112.8(2)°).[26] 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)].[27] In particular, each 2-pyrimidinylthio group is almost perpendicular to the six-membered phosphazene plane (dihedral angle: 81.0(2)°; 85.6(2)°), indicating the presence of the van der Waals intramolecular interaction. Thus, the 2-pyrimidinylthio group is bonded to a phosphorus atom of cyclotri($\lambda^5$-phosphazene) in a pseudo-bidendate fashion in the solid state.

The molecular structure and space-filling views of $N_3P_3(dmpms)_2Cl_4$ are shown in Fig. 3, and the relevant bond lengths and angles are tabulated in Table 3. The molecule was also elucidated as a *gem*-bis-substituted cyclotri($\lambda^5$-phosphazene). Among the two possible tautomeric forms, the dmpms ligand predominantly acts as a thiol character in the molecule (C(1)–S(1), 1.788(4) Å; (C(7)–S(2), 1.785(4) Å). Thus, its overall structure is similar to the above $N_3P_3(pms)_2Cl_4$, including both the bond angles of N–C–S, C–S–P, and S–P–S and the bond lengths of C–N, C–S, and S–P. In striking contrast, the dihedral angles (58.9(1)°; 58.6(1)°) between the pyrimidine group and the phosphazene ring in $N_3P_3(dmpms)_2Cl_4$ are severely deviated from 90°, in contrast to those (81.0(2)°; 85.6(2)°) of the $N_3P_3(pms)_2Cl_4$. The torsion angles of P(1)–S(1)–C(1)–N(5) (37.5(3)°) and P(1)–S(2)–C(7)–N(7) (39.8(3)°) of the $N_3P_3$ $(dmpms)_2Cl_4$ are significantly different from those (11.1(7)°; 4.1(6)°) of the $N_3P_3(pms)_2Cl_4$. Such deviations of the dihedral angles and the torsion angles can be seen from the space-filling diagram in Fig. 3. Thus, the intramolecular P···N distances (P(1)–N(5), 3.109(4) Å; P(1)–N(7), 3.126(4) Å) are considerably longer than those of $N_3P_3(pms)_2Cl_4$ (2.965(7) Å; 2.986(7) Å), presumably owing to the presence of the methyl group substituted to the pyrimidine ring.

## Discussion

Though the reaction of $N_3P_3Cl_6$ with a series of pyrimidine-2-thiol ligands can lead to the formation of several isomers and various degrees of chloride replacement, only a *geminal* 2,2-isomer was obtained in a boiling THF solution. Why does the present reaction so selectively produce only a *gem*-2,2-isomer? In contrast, the cognate reaction with HSPh predominantly affords a fully substituted product, $(NP(SPh)_2)_3$, under the same reaction conditions, even though pms and SPh are very similar in bulkiness.[8,12,13] Thus, for the present system, the pseudo-coordination of the nitrogen atom may play an important role in the formation of the final product. Such a unique structure seems to hinder a further reaction, resulting in the formation of only a *gem*-isomer, even though the conformation and the van der Waals interaction of the title compounds are not exactly retained in solution. That is, the restricted freedom of the substituted ligand may cause difficulty in a further substitution at other untouched phosphorus atoms. As proof of the limited freedom of the substituted ligand, the $^{13}C$ resonances around N atom in $N_3P_3(pms)_2Cl_4$ (C(1), C(2), C(4)), $N_3P_3(dmpms)_2Cl_4$ (C(1), C(2), C(4)), and $N_3P_3(fmpms)_2Cl_4$ consist of two sets. The characteristic chemical shifts demonstrate that the present molecules are less fluxional in solution. However, such a nonrigidity was not observed by the $^1H$ NMR spectra in solution at room temperature. Thus, NMR studies on the present system containing symmetric ligands, such as pms and dmpms, clearly visualize the solution-behavior in contrast to the 2-pyridinylthio analog, $N_3P_3(SPy)_2Cl_4$. Besides the pseudo-coordination via the nitrogen atom, the size and bond angle of the sulfur atom of the molecule may be in part responsible for the molecular rigidity induced by the unique intramolecular interaction. For instance, in the case of an oxygen analog instead of a sulfur-containing ligand, the fully substituted $(NP(OPy)_2)_3$ (OPy = 2-pyridyloxy) was easily obtained instead of a bis-substitute, $N_3P_3(OPy)_2Cl_4$.[22]

Even though the present ligands have an additional nitrogen atom in the aromatic ring relative to the 2-pyridinylthio ligand, a significant structural difference between the $N_3P_3(pms)_2Cl_4$ and the $N_3P_3(SPy)_2Cl_4$ was not observed. A comparison of the two compounds indicates that the additional nitrogen atom prominently does not affect the molecular structure, including the strength of the unique intramolecular interaction. In contrast, the P···N interaction of the $N_3P_3(pms)_2Cl_4$ is fairly shorter than that of the $N_3P_3(dmpms)_2Cl_4$. The methyl group of the dmpms ligand may induce a deviation of the dihedral angle between the pyrimidine group and the phosphazene plane, and thus the distance of the P···N interaction significantly increases. This fact is direct evidence that the bonding mode of the pseudo-bidentate ligand is dependent on steric effects rather than electronic effects.

In conclusion, the reaction of $N_3P_3Cl_6$ with a series of 2-pyrimidinelthiol in boiling tetrahydrofuran solution afforded only a geminal bis-substituted cyclotri($\lambda^5$-phosphazene) as the main product. The 2-pyrimidinethiol acts as a unique pseudo-bidentate to a phosphorus atom in cyclotri($\lambda^5$-phosphazene) analogs. The bonding mode of the ligand is sensitive to the steric effects rather than the electronic effects. The formation of only a *geminal* isomer can be explained in terms of its prominent structural feature, which seems to be involved in nucleophilic substitution.[28]

This research was financially supported by the Ministry of Science and Technology in Korea. OSJ thanks to Dr. B. R. Yoo for helpful discussion.

## References

1) S. S. Krishnamurthy, A. C. Sau, and M. Woods, *Adv. Inorg. Chem. Rad. Chem.*, **21**, 41 (1978).

2) H. R. Allcock, J. L. Desorcie, and G. H. Riding, *Polyhedron*, **6**, 119 (1987).

3) V. Chandrasekhar, M. G. R. Muralidhara, and I. I. Selvaraj, *Heterocycles*, **31**, 2231 (1990).

4) J. Jaud, F. Sournies, and J.-F. Labarre, *J. Mol. Struct.*, **212**, 305 (1989).

5) K. Brandt, *J. Mol. Struct.*, **243**, 163 (1991).

6) M. Veith, M. Kross, and J.-F. Labarre, *J. Mol. Struct.*, **243**, 189 (1991).

7) A. Chandrasekaran, S. S. Krishnamurthy, and M. Nethaji, *Inorg. Chem.*, **32**, 6102 (1993).

8) A. P. Carroll and R. A. Shaw, *J. Chem. Soc. A*, **1966**, 914.

9) H. R. Allcock, P. R. Suszko, L. J. Wagner, R. R. Whittle, and B. Boso, *J. Am. Chem. Soc.*, **106**, 4966 (1984).

10) H. R. Allcock, D. J. Brennen, B. S. Dunn, and M. Parvez, *Inorg. Chem.*, **27**, 3226 (1988).

11) H. R. Allcock, I. Manners, M. N. Maug, and M. Parvez, *Inorg. Chem.*, **29**, 522 (1990).

12) A. P. Carroll and R. A. Shaw, *Chem. Ind. (London)*, **1962**, 1908.

13) N. Boden, J. W. Emsely, J. Feeney, and L. H. Sutcliffe, *Chem. Ind. (London)*, **1962**, 1909.

14) O.-S. Jung, S. H. Park, Y.-A. Lee, K. M. Kim, S. Lee, H. K. Chae, and Y. S. Sohn, *Inorg. Chem.*, **35**, 6899 (1996).

15) B. A. Cartwright, D. M. L. Goodgame, I. Jeeves, and P. O. Langguth, Jr., *Inorg. Chim. Acta*, **24**, L45 (1977).

16) S. G. Rosenfield, H. P. Berends, L. Gelmini, D. W. Stephan, and P. K. Mascharak, *Inorg. Chem.*, **26**, 2792 (1987).

17) G. P. A. Yap and C. M. Jensen, *Inorg. Chem.*, **31**, 4823 (1992).

18) P. D. Cookson and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, **1993**, 259.

19) K. Yamanari, S. Dogi, K. Okusaka, T. Fujihara, A. Fuyuhira, and S. Kaizaki, *Bull. Chem. Soc. Jpn.*, **67**, 3004 (1994).

20) $\delta$($^{31}$P, $(PhO)_3PO$) = $-18$ ppm relative to $H_3PO_4$; J. Mason, "Multinuclear NMR," 3rd ed, Plenum Press, New York (1987), p. 375.

21) a) G. M. Sheldrick, "SHELXS-86: A Program for Structure Determination," University of Göttingen, Germany (1986); b) G. M. Sheldrick, "SHELXL-93: A Program for Structure Refinement," University of Göttingen, Germany (1993).

22) G. A. Carriedo, P. G. Elipe, F. J. Garcia Alonso, L. Fernandez-Catuxo, M. R. Diaz, and S. G. Granda, *Inorg. Chim. Acta*, **498**, 207 (1995).

23) J. J. Perez-Torrente, M. A. Casado, M. A. Ciriano, F. J. Lahoz, and L. A. Oro, *Inorg. Chem.*, **35**, 1782 (1996).

24) J. E. Huheey, "Inorganic Chemistry : Principle of Structure and Reactivity," 3rd ed, Harper & Row, New York (1983), p. 256.

25) G. Jia, R. J. Puddephatt, and J. J. Vittal, *Polyhedron*, **11**, 2009 (1992).

26) S. K. Hadjikakou, P. Aslanidis, P. Karagiannidis, A. Aubry, and S. Skoulika, *Inorg. Chim. Acta*, **193**, 129 (1992).

27) J. G. Reynolds, S. C. Sendlinger, A. M. Murray, J. C. Huffman, and G. Christou, *Inorg. Chem.*, **34**, 5745 (1995).

28) The possible reaction mechanism on $N_3P_3(SPy)_2Cl_4$ was already reported in our previous paper, Ref. 14.