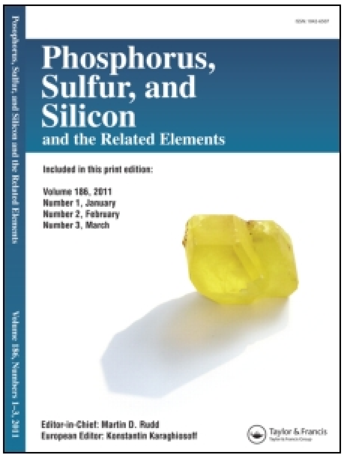

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The Reactions of Hexachlorocyclotriphosphazatriene with Ligands Including Mercapto Groups

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The Reactions of Hexachlorocyclotriphosphazatriene with Ligands Including Mercapto Groups

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In this work, the reactions of hexachlorocyclotriphosphazatriene (trimer), $N_3P_3Cl_6$ ***1****, with 2-mercapto-1-methylimidazole (methimazole)* ***2****, 2-mercaptopyrimidine* ***3****, and 2-mercaptopyridine* ***4*** *were discussed. Mono- (****5****) and pentasubstituted (****6****) phosphazenes were obtained from the reaction of* ***1*** *with 2-mercapto-1-methylimidazole. Both mono- (****7****) and disubstituted geminal (****8****) phosphazenes were obtained from the reaction of* ***1*** *with 2-mercaptopyrimidine. But phoshazene or any phosphorus compound could not be isolated from the reaction of* ***1*** *with 2-mercaptopyridine.*

Keywords Hexachlorocyclotriphosphazatriene; imidazole; methimazole; pyridine; pyrimidine

INTRODUCTION

In previous articles,[1–4] we reported on the reactions of phenols derivatives with hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, **1**. Here we report the reactions of **1** with ligands, including mercapto groups (**2**, **3**, **4**).

The reactions of **1** with different nucleofiles had been investigated in detail. Although a large number of reactions of amines[5,6] and alcohols[7,8] with phosphazenes have been investigated, studies of the reactions of **1** with thiolate derivatives are very limited.[9–13]

Replacement reactions in cyclophosphazenes have been classified as geminal or non-geminal.[14] The replacement of chlorine atoms by thiolate groups rose to products with geminal structures,[9,10] while the replacement of chlorine atoms with alcohols and amines were usually geminal or nongeminal. Consequently, the geminal pathway must result from the low π-donor ability of the sulfur atom.[5]

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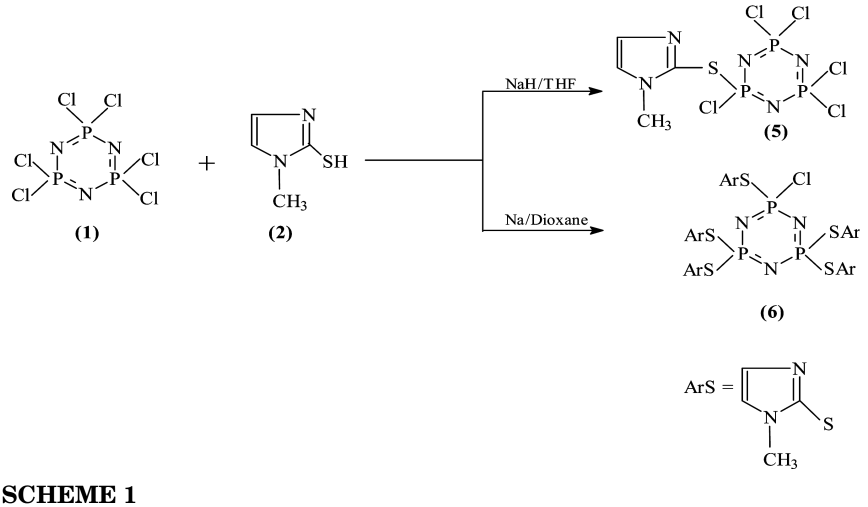
In this work, four novel phosphazene-thiolate derivatives (**5–8**) were synthesized. These derivatives are two mono **5**,**7**, one disubstituted geminal **8**, and one pentasubstituted **6** phosphazenes. Since these compounds contain S and N donor atoms, novel metal complexes could be prepared from them.

RESULTS AND DISCUSSIONS

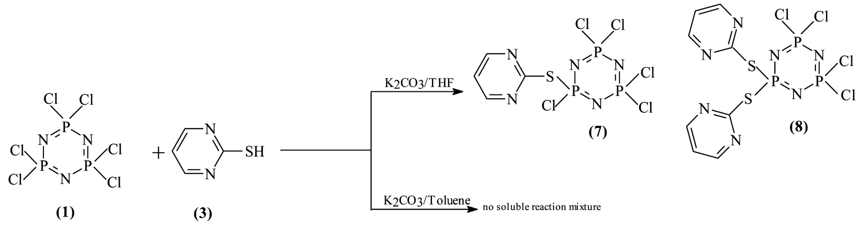
All compounds (**5–8**) were synthesized as described in the Experimental section. Compound **1** was reacted with the 1:1 and 1:6 mole ratios of sodium salts of 2-mercapto-1-methylimidazole (**2**) in THF and dioxane, respectively. Monosubstituted phosphazene (**5**) was obtained from the reaction of **1** with **2** in THF while, pentasubstitutedphosphazene (**6**) was obtained from reaction in dioxane (Scheme 1).



SCHEME 1

The reaction of 1 mole of $N_3P_3Cl_6$ with 1 mole of 2-mercaptopyrimidine in the presence of K_2CO_3 in THF lead to the formation of the mono- (**7**) and disubstituted geminal (**8**) pyrimidine derivatives. One mole of $N_3P_3Cl_6$ was reacted with 6 mole of 2-mercaptopyrimidine in the presence of K_2CO_3, also in toluene. In recent, a solid was obtained that was resin. This solid was not soluble nearly in any solvent, so no product could be isolated from this reaction (Scheme 2). The new white solid compounds (**5–8**) are air and moisture stable.

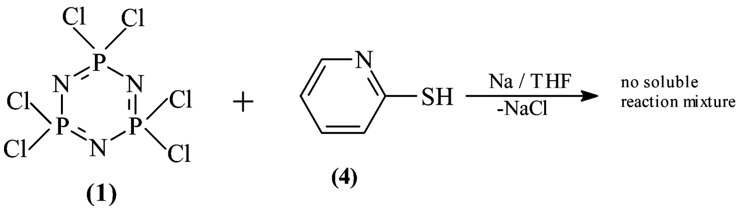
Hexachlorocyclotriphosphazatriene was reacted with the sodium salt of 2-mercaptopyridine in THF (tetrahydrofuran). Similarly, no



SCHEME 2

phosphazene or phosphorus compound also could be isolated from the reaction of phosphazene with 2-mercaptopyridine in THF (Scheme 3).

In all these reactions, major products were isolated from the reaction mixture by column chromatography. Minor products were neither isolated nor obtained in a sufficient amount. All these newly synthesized phosphazene derivatives are white solids. These compounds except for **6** are soluble in common organic solvents, such as chloroform, acetone, and dichloromethane, but compound **6** is not soluble nearly in any solvent except for THF.



SCHEME 3

The structures of the synthesized compounds have been characterized by elemental analysis, ^{1}H and ^{31}P NMR, and FTIR. All the analytical and spectroscopic data (mentioned in the Experimental section) were in accord with the proposed structure.

EXPERİMENTAL

General

All reactions were carried out under an argon atmosphere by using Schlenk Techniques.[15] K_2CO_3 was dried at 140°C prior to use. The tetrahydrofuran, dioxane, and toluene were purchased from Merck and dried by conventional methods (THF from Na-K, toluene, and dioxane, and *n*-hexane from Na-benzophenone) and distilled under nitrogen prior to use. Sodium hydride (60% dispersion in mineral oil, Merck) was washed with dry hexane, followed by decantation, to remove the oil prior to use. Melting points were measured on a Gallenkamp apparatus using a capillary tube and are uncorrected. The purity of the compounds **(5–8)** was checked by TLC and characterized by elemental analysis, ^{1}H and ^{31}P NMR spectrometry, and FTIR. ^{1}H and ^{31}P NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solutions on a Bruker DRX 500 or US 300 MHz spectrometer using TMS as an internal reference for ^{1}H and 85% H_3PO_4 as an external reference for ^{31}P. Elemental analysis was done using an LECO 932 CHNS instrument, and FTIR spectra were recorded on an ATI Unicam Mattson 1000 FTIR spectrophotometer in KBr disks and were reported in cm^{-1} units.

2-mercapto-1-methylimidazole, 2-mercaptopyrimidine, and 2-mercaptopyridine (Aldrich) were used as supplied without further purification. Hexachlorocyclotriphosphazatriene supplied by Aldrich and purified by recrystallization from hexane.

Analytical TLC was performed on Merck silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with the F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g crude mixture, 100 g silica gel was used in a column of 3 cm in diameter and 60 cm in length).

Synthetic Procedures

The new phosphazene derivatives (**5–8**) were synthesized as follows.

The Synthesis of 2,4,4,6,6-Pentachloro-2-(2-mercapto-1-methylimidazolyl)cyclo-2λ^5, 4λ^5, 6λ^5 Triphosphazatriene (5)

To a solution of 2-mercapto-1-methylimidazole (0.98 g, 8.62 mmol) in THF (25 mL) was added NaH (0.41 g, 17.24 mmol). The solution was stirred until the end of the hydrogen gas evolution while argon passed over the reaction mixture. The solution was cooled in a N_2/acetone slush bath. Compound **1** (3.00 g, 8.62 mmol) in 20 mL of THF was slowly added dropwise to this reaction vessel by stirring during 0.5 h, and the mixture was allowed to stand at ambient temperature and then stirred for 8 h at r.t. The reaction mixture was filtered to remove the sodium chloride formed; the solvent was removed under reduced pressure, and the resulting white solid was subjected to column chromatography. The starting material **1** (0.5 g, 17%) was eluted using dichloromethane:*n*-hexane (1:1), and the product **(5)** eluted using dichloromethane. Compound **5** was isolated as a white solid. Yield: 2.63 g; (72%), m.p. 160–161°C,$R_f = 0.578$ (Dichloromethane).

$N_5P_3Cl_5C_4H_5S$ (425.16): calcd: C, 11.28; H, 1.17;N16.46; found: C, 11.44; H, 1.28; N, 15.84. Compound **5** IR (cm^{-1} in KBr): 2975 (C—H), 1610 (C=C), 1215 (P=N), 590 (P—Cl), 523(P—S). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.55(3H, s, CH_3), 6.73–7.27 (2H, m, imidazole), ^{31}P NMR (202 MHz, $CDCl_3$), δ (ppm): AX_2 pattern, δ PCl_2 = 24.82 (d, 2P, $^2J_{PNP}$ = 58.7 Hz.), δ PCl(SAr) = 6.68, (t, 1P, $^2J_{PNP}$ = 58.7 Hz).

Synthesis of 2,4,4,6,6-(2-Mercapto-1-methylimidazolyl)-cyclo-2λ^5,4λ^5,6λ^5 Triphosphazatriene (6)

To a solution of **2** (5.90 g, 51.72 mmol) in dioxane (35 mL) was added small pieces of Na (2.73 g, 103 mmol). The solution was stirred until the end of the hydrogen gas evolution while argon passed over the reaction mixture. Later, excess Na was remowed by filtration. To this solution, **1** (3.00 g, 8.62 mmol) in dioxane (15 mL) was slowly added. The reaction mixture was stirred for 24 h at r.t. It was refluxed for 9 h. The solvent was removed under vacuum. The solid residue was dissolved in ethylacetate. The precipitated NaCl was filtered off, and the solvent was removed. The resulting white powder was subjected to column chromatography. The starting material **(2)** was eluted using ethylacetate, and the product eluted using THF. Compound **6** was isolated as a white powder. Yield: 0.75 g; (12%), $R_f = 0.424$ (tetrahydrofuran), m.p. >300°C (decomp. The color of the compound changed from white to brown.). $N_{13}P_3C_{20}H_{25}S_5Cl$ (735.50): calcd: C, 32.64; H, 3.40; N, 24.75; found: C, 33.27; H, 3.79; N, 23.57. Compound **6** IR (cm^{-1} in KBr): 3044 (C—H), 1620 (C=C), 1329 (P=N), 640 (P—Cl), 525(P—S).

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 3.32–3.93 (3H, m, CH_3), 6.82–7.48 (2H, m, imidazole), ^{31} P-NMR (121 MHz, DMSO-d_6), AX_2 pattern, δ PCl(SAr) = 21.99 (t, 1P), $P(SAr)_2 = -5.86$ (d, 2P) $^2J_{PNP}$ = 42.5 Hz.

The Synthesis of 2,4,4,6,6-Pentachloro-2-(2-mercaptopyrimidinyl-)cyclo-2λ^5,4λ^5,6λ^5 Triphosphazatriene (7)

A mixture of $N_3P_3Cl_6$ (3.00 g, 8.62 mmol), 2-mercaptopyrimidine (2.39 g, 8.63 mmol), and K_2CO_3 (2.39 g, 17.31 mmol) in THF (30 mL) was stirred at r.t. for 48 h. Later, it was refluxed (6 h). The reaction mixture was followed on TLC silica gel plates using $CHCl_3$/*n*-hexane 4:1, which showed 2 products, and the starting material was not detectable anymore. The reaction mixture was cooled at r.t. The solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (25 mL), the precipitated solid was filtered, and the solvent was removed. The crude product was chromatographed (silica gel; 100 g;

eluent:chloroform: *n*-hexane (4:1). Two fractions were obtained and isolated as white powders; the first is the monosubstituted compound **7** (yield 0.2 g; 5.5%, m.p. 151–152°C; $R_f = 0.467$ acetone: *n*-hexane (1:5), and the second fraction is the disubstituted derivative **8** (yield 0.64 g, 15% m.p. >208°C (decomp. The color of the compound changed from white to black.) $R_f = 0.205$ (acetone: *n*-Hexane, 1:5). Both compounds **7** and **8** were isolated as a white solid. Compound **7** $N_5P_3Cl_5C_4H_3S$ (423.31): calcd.: C, 11.33: H, 0.78; N, 16.50; found: C, 11.93; H, 0.90; N, 16.11. IR (cm^{-1} in KBr): 2965 (C—H), 1556 (C=C), 1197 (P=N), 592 (P—Cl), 523 (P—S). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.73 (2H, d, $J = 4.9$ Hz, pyrimidine-$C_{4,6}$ -H), 7.33 (1H, t, $J = 4.9$ Hz, pyrimidine-C_5 -H); ^{31}P NMR (121 MHz, $CDCl_3$), δ (ppm): AB_2 pattern, δ $PCl_2 = 22.89$ (d, 2P, $^2J_{PNP} = 26.2$), δ PCl(SAr) = 30.36 (t, 1P, $^2J_{PNP} = 26.2$). Compound **8** $N_7P_3Cl_4C_8H_6S_2$ (499.04): calcd: C, 19.24; H, 1.20; N, 19.64; found: C, 20.11; H, 1.48; N 19.03.

IR (cm^{-1} in KBr): 2961 (C—H), 1552 (C=C), 1205 (P=N), 583 (P—Cl), 525 (P—S). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm): 8.44 (2H, d, $J =$ 3.64 Hz, pyrimidine-$C_{4,6}$-H), 7.12 (1H, t, $J = 3.64$ Hz, pyrimidine-C_5-H); ^{31}P NMR (202 MHz, $CDCl_3$) AB_2 pattern, δ $PCl_2 = 25.77$ (s, 2P), δ $P(SAr)_2 = 38.98$ (s, 1P) (Two signals are pseudosinglets. No J was measurable.).

Phosphazene was reacted also with an excess of 2-mercaptopyrimidine. So compound **1** (3.00 g, 8.62 mmol), 2-mercaptopyrimidine (5.79 g, 51.78 mmol), and K_2CO_3 (14.29 g, 103.56 mmol) in toluene (35 mL) were stirred at r.t. for 24 h. Then it was refluxed for 18 h. The resulting white solid was not soluble nearly in any solvent except for tetrahydrofuran. So no phosphazene or phosphorus compound could be isolated.

SPECTROSCOPIC STUDIES

The structures of compounds (**5–8**) were characterized by ^{31}P and ^{1}H NMR, FTIR, and elemental analysis. These results are given in the Experimental section.

Infrared Spectra

IR spectra of all these newly synthesized compounds have been recorded as a KBr disc in the range 400–4000 cm^{-1}, and tentative assignments of important characteristic bands have been made with the help of earlier publications.[10,11] In the IR spectra of substituted phosphazene derivatives (**5–8**), the characteristic $\nu_{P=N}$ vibrations occur between 1197–1329 cm^{-1}. These derivatives also show medium to strong intensity absorption bands in the region 523–525 owing to (P—S) streching vibrations. The indication of the partial substitutions for compounds (**5–8**) in the $\nu_{\text{P-Cl}}$ streching bands were observed between 583–640 cm^{-1}.

NMR Spectra

The ^{1}H NMR spectra of substituted phosphazenes (**5**, **6**, and **7**) have been recorded in $CDCl_3$ or DMSO-d_6 solutions using TMS as an internal standard for ^{1}H and 85% H_3 PO_4 as an external standard for ^{31}P. The methyl protons resonate at $\delta = 3.55$ as a singlet, and the ring protons resonate at between $\delta = 6.73$–7.27 as multiplet for compound **5**. Methyl protons resonate at $\delta = 3.32$–3.93 (multiplet), and ring protons resonate at $\delta = 6.82$–7.48 (multiplet) for compound **6**. The pyrimidine protons resonate at $\delta = 8.73$ (doublet), $\delta = 7.33$ (triplet), and $\delta = 8.44$ (doublet), $\delta = 7.12$ (triplet), respectively, for compounds **7** and **8**.

^{31}P NMR spectra of compounds **5–7** gave either an AB_2 or AX_2 spin pattern due to the different phosphorus environments in the molecule. The ^{31} P NMR spectra of **5** and **6** gave an AX_2 spin pattern with $J_{\text{PNP}} =$ 58.7 and 42.5 Hz, respectively. ^{31}P NMR spectra of compound **7** were interpreted as a result of a simple AB_2 spin system. Two bond coupling constants J_{PNP} are ca. 26.2 Hz for **7**. ^{31}P NMR spectra of **8** gave two psedosinglet peaks at 28.77 and 39 88 Hz. According to the ^{31}P NMR spectrum and data ref.,[13] it can be concluded that compound **8** may have the geminal structure. The ^{31}P NMR chemical shifts were δ PCl(SAr) $= 6.68$ and δ $PCl_2 = 24.82$ in **5**, δ $P(SAr)_2 = -5.86$, δ PCl(SAr) $= 21.99$ in **6**, δ PCl(SAr) $= 30.36$, δ $PCl_2 = 22.89$ in **7**, and δ $P(SAr)_2 = 38.98$, δ $PCl_2 = 25.77$ in **8**.

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